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A Specialist Periodical Report

Inorganic Reaction Mechanisms
Volume 5

A Review of the Literature Published between January 1975 and June 1976

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Foreword

In this volume, the format, coverage, and approach in dealing with various aspects of Inorganic Reaction Mechanisms are similar to those adopted for the previous volumes of the series. Once again, rather than make an attempt at cataloguing all the articles in which mention is made of mechanism, we have chosen (with an eye on volume size and cost!) to concentrate on papers in which kinetics and mechanisms in solution form the principal interest. This policy inevitably leads to mention of some papers being cursory with a consequent loss of subtlety. It is our hope, however, that any resultant oversimplification or misrepresentation is minimal. Review articles cited are those which should be accessible to the great majority of readers.

The period of literature coverage extends from January 1975 to June 1976. The boundaries at both ends are somewhat vague since not all libraries have issues available at the same time. Care has been taken to ensure that an overlap with Volume 4 has been maintained in all areas. Material which is derived from *Chemical Abstracts* rather than from the original source is indicated by inclusion of a *Chem. Abs.* citation in the reference quoted. References to the Russian literature derived from this source quote the page number of the original article whereas those giving the title of the English translation quote the page number of the translation.

As in previous volumes, kinetic data are reported in the form (E_a or $\log A$ or $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) or units (SI or other) used in the original article, although some conversions have been made both in the text and in the tables where comparisons are required.

The Reporters are grateful to many of their colleagues for helpful comments. We are particularly indebted to Drs R. W. D. Kemmitt and A. G. Sykes for their critical reading of sections of the manuscript.

A. McAuley

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Abbreviations for Ligands and Solvents

Abbreviations which appear only once in the text are generally defined at their point of use; those which appear more than once are defined below.

General

R	alkyl, aryl
L	unidentate ligand
LL	bidentate ligand
LLL	terdentate ligand
LLLL	quadridentate ligand
X	halide (except where otherwise stated)

Specific

acac	acetylacetonate
ADP	adenosine-5′-diphosphate
2′-AMP	adenosine-2′-monophosphate
3′-AMP	adenosine-3′-monophosphate
5′-AMP	adenosine-5′-monophosphate
AN	acetonitrile
asp	aspartate
ATP	adenosine-5′-triphosphate
big	biguanide
bipy	2,2′-bipyridyl
bzac	benzoylacetonate (1-phenylbutane-1,3-dionate)
bzbz	1,3-diphenylpropane-1,3-dionate
cal	calmagite [1-(1-hydroxy-4-methyl-2-phenylazo)-2-naphthol-4-sulphonate]
CDP	cytosine-5′-diphosphate
cod	cyclo-octadiene
Cp	cyclopentadienyl
CTP	cytosine-5′-triphosphate
cyclam	1,4,8,11-tetra-azacyclotetradecane
cydta	cyclohexane-1,2-diaminetetra-acetate
dacoda	1,5-diazacyclo-octane-*NN′*-diacetate
diars	*o*-phenylenebisdimethylarsine
dien	diethylenetriamine
dien−H	diethylenetriamine minus one nitrogen proton
dimetn	*NN′*-dimethylpropane-1,3-diamine
diphos	1,2-bisdiphenylphosphinoethane
DMF	dimethylformamide
dmg	dimethylglyoximate

dmp	2,9-dimethyl-1,10-phenanthroline
DMSO	dimethyl sulphoxide
dmtu	*NN'*-dimethylthiourea
DNA	deoxyribonucleic acid
dpt	dipropylenetriamine
dtc	dithiocarbamate
dto	dithio-oxalate
dtp	diethyldithiophosphate
dtpa	diethylenetriaminepenta-acetate
edda	ethylenediaminediacetate
eddda	ethylenediaminediacetatedipropionate
edds	*NN'*-ethylenediaminedisuccinate
edma	ethylenediaminemonoacetate
edta	ethylenediaminetetra-acetate
egta	ethylene glycol bis-(2-aminoethyl ether)-tetra-acetate
en	ethylenediamine
Et_4dien	*NNN"N"*-tetraethyldiethylenetriamine
ete	4,8-dithia-1,11-diazaundecane
gedta	2,2'-ethylenedioxybis(ethyleneiminodiacetate)
glu	glutamate
gly	glycinate
Hb	Haemoglobin
hedta	*N*-(2-hydroxyethyl)ethylenediaminetriacetate
hfac	hexafluoroacetylacetonate
himda	hydroxymethyliminodiacetate
his	histidine
hm	histamine
ida	iminodiacetate
ind	indenyl
isn	isonicotinamide
mal	malonate
Me_4dien – H	*NNN"N"*-tetramethyldiethylenetriamine minus the nitrogen proton
Me mal	methylmalonate anion
Me_6tren	2,2',2"-tris-(*NN*-dimethylamino)triethylamine
metu	*N*-methylthiourea
mida	*N*-methyliminodiacetate
mnt	maleonitriledithiolate
mq	2-methyl-8-quinolinate
NADH	nicotinamide adenine dinucleotide (reduced form)
niox	nioxime
nta	nitrilotriacetate
ox	oxalate
pada	pyridine-2-azo-*p*-dimethylaniline
pdta	propylenediaminetetra-acetate
phen	1,10-phenanthroline
pn	propylenediamine
py	pyridine

salen	*NN'*-bis(salicylaldehydo)ethylenediamine
tar	tartrate
tcne	tetracyanoethylene
tea	triethanolamine
terpy	2,2′,2″-terpyridyl
2,3,2-tet	1,4,8,11-tetra-azaundecane
tet-*a*, tet-*b*	5,7,7,12,14,14-hexamethyl-1,4,8,11-cyclotetra-azatetradecane
tetren	tetraethylenepentamine
tfac	1,1,1-trifluoroacetylacetonate
thiox	monothio-oxalate
tmd	trimethylenediamine
tmeda	*NNN'N'*-tetramethylethylenediamine
TP	tripolyphosphate
trans-14-diene	5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene
tren	triaminotriethylamine
trien	triethylenetetramine
trigly	triglycine
ttha	triethylenetetraminehexa-acetate
tu	thiourea
xyl	xylenol orange

Part I

ELECTRON TRANSFER PROCESSES

By
R. D. CANNON
A. G. LAPPIN
A. McAULEY

1

Reactions Between Two Metal Complexes

BY R. D. CANNON

1 General and Theoretical

Theory of the Electron Transfer Process.—A lengthy review of electron-transfer theory has appeared in a companion publication to this series,[1] and a further review is promised in the next volume.* New studies have also appeared of outer-sphere electron transfer in solution,[2] covering the intermediate range between adiabatic and non-adiabatic conditions, and of inner-sphere transfer in the solid state.[3] The relationship between electron transfer and magnetic exchange interactions has been pointed out. Antiferromagnetic coupling has been demonstrated in copper(II)–copper(II) dimers with no direct inner-sphere bridging ligands, and it is suggested that further work on such systems will lead to a better understanding of outer-sphere electron transfer in solution.[4] There is continuing discussion of the possibility of electron transfer over long distances, but the evidence for such a process in solution still seems inconclusive.[5–7]

Of more direct interest to kineticists is a reconsideration[8] by Marcus and Sutin of the basis for the well known equation (1) relating activation free energies $\Delta G^{\ddagger}$ to

$$\Delta G^{\ddagger} = A(1 + \Delta G^{\ominus}/4A)^2 \qquad (1)$$

standard free-energy changes $\Delta G^{\ominus}$. Equation (1) is commonly illustrated by diagrams of the type of Figure 1 (*cf.* Figures 2 and 3, pp. 9 and 10). For restricted ranges of $\Delta G^{\ominus}$, it predicts an approximate linear correlation of $\Delta G^{\ddagger}$ with $\Delta G^{\ominus}$, with slope α [equation (2)], such that when $\Delta G^{\ominus}$ is close to zero, α is *ca.* 0.5, and this has been verified in several cases:[9]

$$\alpha = \frac{\partial \Delta G^{\ddagger}}{\partial \Delta G^{\ominus}} = \tfrac{1}{2}(1 + \Delta G^{\ominus}/4A) \qquad (2)$$

However, equation (2) also predicts that as $\Delta G^{\ominus}$ becomes more negative α decreases, until when $\Delta G < -4A$ further decrease in $\Delta G^{\ominus}$ leads to an increase in $\Delta G^{\ddagger}$. Marcus

* Two other reviews are inaccessible at the time of writing (see refs. 114 and 115).

[1] P. P. Schmidt, in 'Electrochemistry', ed. H. R. Thirsk (Specialist Periodical Reports), The Chemical Society, London, 1975, Vol. 5, p. 21.
[2] S. G. Christov, *Ber. Bunsengesellschaft phys. Chem.*, 1975, **79**, 357.
[3] J. Mulak and K. W. H. Stevens, *Z. phys.* (*B*), 1975, **20**, 21.
[4] E. J. Laskowski, D. M. Duggan, and D. N. Hendrickson, *Inorg. Chem.*, 1975, **14**, 2449.
[5] K. I. Zamaraev and R. F. Khairutdinov, *Chem. Phys.*, 1974, **4**, 181.
[6] A. G. Rykov and N. B. Blokhin, *Russ. J. Phys. Chem.*, 1975, **49**, 737 (*Zhur. fiz. Khim.*, 1975, **49**, 1262).
[7] R. F. Khairutdinov and K. I. Zamaraev, *Doklady Phys. Chem.*, 1975, **222**, 521 (*Doklady Akad. Nauk S.S.S.R.*, 1975, **222**, 654).
[8] R A. Marcus and N. Sutin, *Inorg. Chem.*, 1975, **14**, 213.
[9] J. E. Earley, *Progr. Inorg. Chem.*, 1970, **13**, 243.

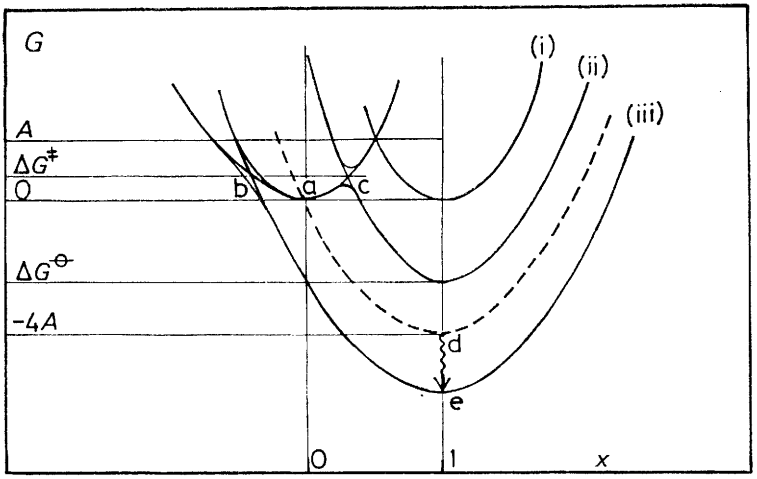


Figure 1 *Reaction profiles for electron-transfer reactions* (x = *reaction co-ordinate*, G = *free energy*), *showing the cases* (i) $\Delta G^{\ominus} = 0$, (ii) $0 > \Delta G^{\ominus} > -4A$, (iii) $\Delta G^{\ominus} < -4A$ [cf. *equation* (1) *of text*]. *The dotted curve represents a possible electronically excited state of* (iii)

and Sutin now point out that this is not to be expected. The region $\Delta G^{\ominus} < -4A$ corresponds to intersection of reactants' and products' curves on the left-hand side of the diagram ($x < 0$, point b, Figure 1), in contrast to 'normal' intersections at $x > 0$ (point c), and this requires a non-adiabatic transition. It is suggested that for these transitions nuclear tunnelling may become important, and that as a result $\Delta G^{\ddagger}$ will not increase with decreasing $\Delta G^{\ominus}$ but will remain constant, with the specific rate at the diffusion-controlled limit. An analogous situation has indeed already been recognized for electron transfer between organic molecules. Over a range of $\Delta G^{\ominus}$ from -5 to $+5$ kcal mol^{-1}, Rehm and Weller obtained[10] a parabolic plot of $\Delta G^{\ddagger}$ against $\Delta G^{\ominus}$, but from $\Delta G^{\ominus} = -5$ to -62 kcal mol^{-1} $\Delta G^{\ominus}$ remained constant. Another theory based on the non-adiabatic description leads to a linear dependence of $\Delta G^{\ominus}$ on $\Delta G^{\ddagger}$ in this region,[11] but constancy of $\Delta G^{\ddagger}$ can also be explained in a different way:[12] it has been suggested that when the ground-state products' curve passes the minimum on the reactants' curve (point d), other curves for higher electronic levels become available, as for example the dotted curve (iii) in Figure 1; hence the reaction may still proceed with zero thermal activation energy along the route a→d→e. More sophisticated quantum mechanical models involving multiple energy states have also been discussed.[13,14]

The minimum value of $\Delta G^{\ddagger}$ (on the old theory) or the limiting value (on the new) is expected to be zero only if the work terms are negligible, and if there are no rapid

[10] D. Rehm and A. Weller, *Israel J. Chem.*, 1970, **8**, 259.
[11] R. P. Van Duyne and S. F. Fischer, *Chem. Phys.*, 1974, **5**, 183.
[12] S. Efrima and M. Bixon, *Chem. Phys. Letters*, 1974, **25**, 34.
[13] J. Ulstrup and J. Jortner, *J. Chem. Phys.*, 1975, **63**, 4358.
[14] W. Schmickler, *J.C.S. Faraday II*, 1976, **72**, 307.

equilibrium steps preceding the electron-transfer process. Previously, Hyde *et al.*[15] had found a non-linear correlation of $\Delta G^{\ddagger}$ with ΔG°, for a reaction of a series of reductants with the common oxidant $[Co(H_2O)_6]^{3+}$. The limiting value of $\Delta G^{\ddagger}$ was found to be *ca.* 9 kcal mol^{-1}. Ekstrom *et al.*[17] have now added an additional point for the reaction $Co^{3+} + U^{3+}$, which fits well on to the curve, but they point out that data for a large number of cation–cation reactions involving oxidants other than $[Co(H_2O)_6]^{3+}$ also cluster quite well round the same curve and Falcinella *et al.*[18] have produced an analogous correlation for reactions of Tl^{2+}, acting alternatively as oxidant and reductant.

The limiting value, $\Delta G^{\ddagger} \approx 9$ kcal mol^{-1}, had previously been felt to be rather high, and one possible explanation considered was a rapid equilibrium between the two spin states of cobalt(III) ($t_{2g}^6 \rightleftharpoons t_{2g}^5 e_g$) prior to the electron transfer. The data from other oxidants have weakened if not altogether removed the necessity for this. It has moreover been argued from ligand-field considerations that for the hexa-aquo-cobalt(III) ion the spin-change free energy may in any case be quite small.[19]

It is accordingly now argued that the high limiting value is sufficiently accounted for by the work terms, *i.e.* the limiting rate constant does represent the diffusion-controlled value for the reactants in equation. The specific collision rate calculated by the Debye equation[17] for the reaction $U^{3+} + Co^{3+}$ is 1.7×10^4 l mol^{-1} s^{-1} (at 25 °C, zero ionic strength), to be compared with the experimental 7.1×10^3 l mol^{-1} s^{-1}. In theory there should be different limiting rates depending on the ionic charges, and it is perhaps a cause for concern that reactions as diverse as $Co^{3+} + NpO_2^{+}$, $UO_2^{2+} + Eu^{2+}$, and $Fe^{3+} + U^{3+}$ all fall near the same curve.

Activation Parameters.—Negative heats of activation have previously been reported for some outer-sphere reactions,[20,21] and it has been suggested that some special factor, not covered by the simple Marcus theory, might need to be invoked to explain them. (It will be recalled that negative heats of activation of some inner-sphere reactions have been rationalized in terms of the energetics of formation of precursor complexes.)[22] Marcus and Sutin point out,[8] however, that negative $\Delta H^{\ddagger}$ values are theoretically predicted, under certain conditions. On differentiating equation (1) with respect to temperature, they obtain

$$\Delta H^{\ddagger} = -\partial(\Delta G^{\ddagger}/T)/\partial(1/T) = \Delta H_A(1 - 4\beta^2) + \tfrac{1}{2}\Delta H^{\circ}(1 + 2\beta) \quad (3a)$$

$$\Delta S^{\ddagger} = -\partial(\Delta G^{\ddagger})/\partial T = \Delta S_A(1 - 4\beta^2) + \tfrac{1}{2}\Delta S^{\circ}(1 + 2\beta) \quad (3b)$$

where ΔH_A and ΔS_A are activation parameters corresponding to the intrinsic free-energy barrier A [equation (1)] and $\beta = 2\Delta G^{\circ}/A$. The term β may be positive or negative, but is usually small; hence if the overall enthalpy change is sufficiently negative $\Delta H_{12}^{\ddagger}$ may be negative even when ΔH_A is positive. A complete calculation requires a knowledge of ΔH_A and ΔS_A, from the appropriate cross-reactions, as well

[15] M. R. Hyde, R. Davies, and A. G. Sykes, *J.C.S. Dalton*, 1972, 1838.
[16] A. Ekstrom, A. B. McLaren, and L. E. Smythe, *Inorg. Chem.*, 1975, **14**, 1035.
[17] A. Ekstrom, A. B. McLaren, and L. E. Smythe, *Inorg. Chem.*, 1975, **14**, 2899.
[18] B. Falcinella, P. D. Felgate, and G. S. Laurence, *J.C.S. Dalton*, 1975, 1.
[19] I. Bodek and G. Davies, *Coordination Chem. Rev.*, 1974, **14**, 269.
[20] J. N. Braddock and T. J. Meyer, *J. Amer. Chem. Soc.*, 1973, **95**, 3158.
[21] J. L. Cramer and T. J. Meyer, *Inorg. Chem.*, 1974, **13**, 1250.
[22] R. C. Patel, R. E. Ball, J. F. Endicott, and R. G. Hughes, *Inorg. Chem.*, 1970, **9**, 23.

as of $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$. For two reactions, $[Fe(bipy)_3]^{3+}$ and $[Ru(bipy)_3]^{3+}$ with Fe^{2+}, the calculated parameters agree with experiment at least as regards the negative sign, *i.e.* $\Delta H^{\ddagger} = -3.2$ and -2.9 kcal mol^{-1} respectively by calculation, -0.8 and -0.3 kcal mol^{-1} by experiment. Further confirmation is provided by new measurements[23] on related systems such as $[Ru(bipy)(NH_3)_4]^{2+} + [Fe(H_2O)_6]^{3+}$: a graph of $(\Delta H^{\ddagger} - \frac{1}{2}\Delta H_A^{\ddagger})$ against $\frac{1}{2}\Delta H^{\ominus}(1+2\beta)$ conforms reasonably well to the expected straight line of unit slope for seven systems over a range of *ca.* 25 kcal mol^{-1}. The actual rate data have not yet been reported.

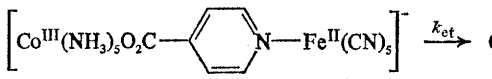
Stereoselectivity.—An earlier report[24] that reactions between chiral oxidants and reductants could show stereoselectivity, *e.g.* that $(+)_D$-$[Co(phen)_3]^{3+}$ reacted at different rates with the two optical isomers of $[Cr(phen)_3]^{2+}$, has been shown to be in error.[25]

2 Intramolecular Electron Transfer

The Precursor Complex.—Interest in intramolecular electron-transfer processes continues to grow, and the search continues for additional long-lived dinuclear complexes preceding the electron-transfer reaction proper.

Jwo and Haim[26] have reported reactions of $[Fe^{II}(CN)_5(H_2O)]^{3-}$ with the isomeric oxygen-bonded pyridinecarboxylatopenta-amminecobalt(III) complexes. With the 2-isomer there is no reaction, presumably for steric reasons; with the 3-isomer a dinuclear complex is produced which shows no tendency to react further ($k_{et} \leqslant 3 \times 10^{-5}$ s^{-1}), but with the 4-isomer the reaction sequence is as shown in equation (4), all steps proceeding at measurable rate ($k_f = 1.5 \times 10^3$ l mol^{-1} s^{-1}, $k_d = 2.5 \times 10^{-3}$ s^{-1}, $k_{et} = 1.75 \times 10^{-4}$ s^{-1}).

$$[Co(NH_3)_5L]^{2+} + [Fe(CN)_5(H_2O)]^{3-} \underset{k_d}{\overset{k_f}{\rightleftharpoons}}$$



(4)

The reactions of $[Co(NH_3)_5X]^{2+}$ (X = F, Cl, or Br) with iron(II) in DMF conform[27] to the Michaelis–Menten rate law (5) where the value of K_3 is interpreted as the

$$\frac{-\mathrm{d}[Co^{III}]}{\mathrm{d}t} = \frac{k_4 K_3 [Fe^{II}]}{1 + K_3[Fe^{II}]} \qquad (5)$$

equilibrium constant of formation of dinuclear complexes $[Co(NH_3)_5XFe]^{4+}$. This is the first report of such complexes involving like-charged reactants. It should be noted, however, that the values of K_3 are quite small (*e.g.* $K_3 = 19$ l mol^{-1} for X = Cl) and although the ionic strength was maintained constant with $KClO_4$ the range of iron concentrations was such as to require complete replacement of K^+ *ion* by Fe^{2+} at the highest concentrations used.

[23] J. N. Braddock, J. L. Cramer, and T. J. Meyer, *J. Amer. Chem. Soc.*, 1975, **97**, 1972.
[24] J. H. Sutter and J. B. Hunt, *J. Amer. Chem. Soc.*, 1969, **91**, 3107.
[25] N. A. P. Kane-Maguire, R. M. Tollison, and D. E. Richardson, *Inorg. Chem.*, 1976, **15**, 499.
[26] J.-J. Jwo and A. Haim, *J. Amer. Chem. Soc.*, 1976, **98**, 1172.
[27] B. A. Matthews, J. V. Turner, and D. W. Watts, *Austral. J. Chem.*, 1976, **29**, 551.

Haim and Sutin[28] have studied the rapid reversible reaction (6). Although both the

$$[Fe(CN)_6]^{3-} + [Co(phen)_3]^{2+} \rightleftharpoons [Fe(CN)_6]^{4-} + [Co(phen)_3]^{3+} \quad (6)$$

precursor and the successor complexes are formed of oppositely charged ions, they could not be detected, and only upper limits could be placed on their stability constants, of 20 and 100 l mol^{-1} respectively. This contrasts with the earlier results on the reaction $[Co(NH_3)_5(OH_2)]^{3+}+[Fe(CN)_6]^{4-}$, where a precursor ion pair was observed, with formation constant 1500 l mol^{-1}. The difference between the two systems underlines the importance of specific, short-range interactions, as opposed to overall Coulombic attraction, in determining the stabilities of ion pairs. Nevertheless, the limiting values cited above are close to the actual values predicted by the Fuoss equation, and an argument based on the Marcus theory has been invoked to show that these are in fact the correct orders of magnitude. A rate constant k for reaction (6) can be predicted from the rate constants of the appropriate cross-reactions together with the measured equilibrium constant. The experimental value of k is *ca.* 3000 times higher than predicted, and this may be explained by the fact that the Coulombic effect in equation (6) is favourable to electron transfer, but the Coulombic effects in the cross-reactions are unfavourable. By choosing reasonable values for the stabilities of all three precursor complexes, based on electrostatic effects, it is possible to recalculate the predicted k and obtain close agreement with experiment. Thus the role of the precursor complexes in determining rates is demonstrated even though the complexes themselves cannot be detected. The argument is similar to that previously put forward by Fay and Sutin to rationalize the relative rates of electron-transfer reactions with NCS^-, NNN^-, and SCN^- bridging groups.[29]

An example of *reversible* intramolecular electron transfer has now been reported though not for a metal–metal system. It had previously[30,31] been shown that the complexes $[Ni^{II}(TPP)]$ (TPP^{2-} = tetraphenylporphinate) when electrochemically oxidized in benzonitrile solution yield first the brown-coloured[30] nickel(III) complex, which then decays at a measurable rate by a process of ligand-to-metal electron transfer [reaction (7), forward step; $(TPP^{\bullet})^-$ = radical-ion]:

$$[Ni^{III}(TPP)]^+ \rightleftharpoons [Ni^{II}(TPP^{\bullet})]^+ \quad (7)$$

When the solvent is changed to methylene dichloride this process is apparently more rapid since electrolysis of $[Ni^{II}(TPP)]$ leads directly to the green $[Ni^{II}(TPP^{\bullet})]^+$ with no detectable intermediate.[32] On cooling to 77 K, however, the green solution changes to an orange solid, and e.p.r. data are consistent with the reverse of reaction (7).[33] The optical spectra of the two complexes are reported.[33]

Another example has been reported of a direct comparison of rates of intramolecular and intermolecular electron transfer between the same or very similar pairs of oxidizing and reducing centres. Previously, Hofmann and Simic[34] had generated

[28] A. Haim and N. Sutin, *Inorg. Chem.*, 1976, **15**, 476.
[29] D. P. Fay and N. Sutin, *Inorg. Chem.*, 1970, **9**, 1291.
[30] A. Wolberg and J. Manassen, *J. Amer. Chem. Soc.*, 1970, **92**, 298.
[31] A. Wolberg and J. Manassen, *Inorg. Chem.*, 1970, **9**, 2365.
[32] D. Dolphin, Z. Muljiani, K. Rousseau, D. C. Borg, J. Fajer, and R. H. Felton, *Ann. New York Acad. Sci.*, 1973, **206**, 177 (*Chem. Abs.*, 1974, **80**, 92042).
[33] D. Dolphin, T. Niem, R. H. Felton, and I. Fujita, *J. Amer. Chem. Soc.*, 1975, **97**, 5288.
[34] M. Z. Hofmann and M. Simic, *J. Amer. Chem. Soc.*, 1972, **94**, 1757; Proceedings of the 14th International Conference on Coordination Chemistry, Toronto, 1972, p. 501.

the complex $[Co^{III}(NH_3)_5(O_2CC_6H_4NO_2\text{-}p)]^+$, containing the *p*-nitrophenylbenzoate radical-ion, and had measured the rate of reaction (8). Cohen and Meyerstein [35] have

$$[Co^{III}(NH_3)_5(O_2CC_6H_4NO_2\text{-}p)]^+ \longrightarrow Co^{2+} + 5NH_3 + p\text{-}NO_2C_6H_4CO_2^- \quad (8)$$

now obtained rate constants of reaction (9) (X = NH_3, *p*-$NO_2C_6H_4CO_2^-$, or various

$$[Co^{III}(NH_3)_5X] + p\text{-}NO_2C_6H_4CO_2^{2-} \xrightarrow{k_2} Co^{2+} + 5NH_3 + X + p\text{-}NO_2C_6H_4CO_2^- \quad (9)$$

other ligands). Interpreting their rate constant k_2 as Kk_1, where K is the stability constant of the outer-sphere precursor complex and k_1 the specific rate of electron transfer within the precursor complex, and assuming maximum values of K consistent with the observed rate law, they conclude that the intramolecular reaction (8) is not significantly faster than any of the intermolecular outer-sphere reactions. These results confirm that the carboxylate group is a poor mediator of electrons, and this is borne out by the previous observation [34] that intramolecular transfer in $[Co^{III}(NH_3)_5(O_2CC_6H_4NO_2\text{-}o)]^+$ is more than 10^2 times faster than in the *para*-isomer. It seems likely that the electron transfer is a 'through-space' interaction, not directly involving the carboxylate bridge, as has also been suggested in other cases.[36, 37]

Optical Electron Transfer.—The reaction of electron transfer is closely paralleled by the spectroscopic charge-transfer process, and energy curve diagrams such as Figure 2 are now familiar. The intervalence charge-transfer transition a→b may be followed by decay along the products' curve to yield the valence isomer, b→c→d. Vogler and Kunkely[38,39] now claim to have detected such processes [reactions (10)—(12)] in a group of bridged dinuclear complexes. The complex $[(NC)_5Co^{III}NCFe^{II}(CN)_5]^{6-}$ has absorption maxima at 326 and 385 nm, assigned to Co^{III} ligand-field

$$[(NC)_5Co^{III}NCFe^{II}(CN)_5]^{6-} \overset{h\nu}{\rightleftharpoons} [Co^{II}(CN)_5]^{3-} + [Fe^{III}(CN)_6]^{3-} \quad (10)$$

$$2[Co^{II}(CN)_5]^{3-} + O_2 \longrightarrow [(NC)_5Co^{III}O_2Co^{III}(CN)_5]^{6-} \quad (11)$$

$$[(NC)_5Co^{III}O_2Co^{III}(CN)_5]^{6-} + [Fe(CN)_6]^{3-} \longrightarrow [(NC)_5Co^{III}O_2Co^{III}(CN)_5]^{5-} + [Fe(CN)_6]^{4-} \quad (12)$$

and intervalence transfer respectively.[38] Irradiation into either of these has little effect, presumably because the primary photolysis product quickly falls back to the ground state, but in the presence of oxygen, overall reactions are seen consistent with the formation of the highly reducing $[Co(CN)_5]^{3-}$ ion. In alkaline solution, for example, the dinuclear superoxo-complex is formed *via* reactions (11) and (12). The maximum quantum yields were found on irradiation in the IT band. Analogous results have been obtained[39] with the complex $[(NH_3)_5Co^{III}NCRu^{II}(CN)_5]^-$: irradiation at 375 nm leads to the redox reaction (13).

$$[(NH_3)_5Co^{III}NCRu^{II}(CN)_5]^- \xrightarrow{h\nu} 5NH_3 + Co^{2+} + [Ru(CN)_6]^{3-} \quad (13)$$

[35] H. Cohen and D. Meyerstein, *J.C.S. Dalton*, 1975, 2477.
[36] S. S. Isied and H. Taube, *J. Amer. Chem. Soc.*, 1973, **95**, 8198.
[37] K. Wieghardt and A. G. Sykes, personal communications.
[38] A. Vogler and H. Kunkely, *Ber. Bunsengesellschaft phys. Chem.*, 1975, **79**, 301.
[39] A. Vogler and H. Kunkely, *Ber. Bunsengesellschaft phys. Chem.*, 1975, **79**, 83.

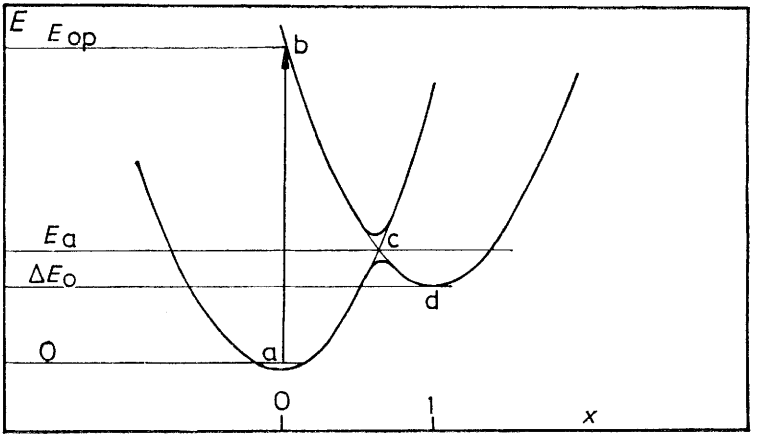
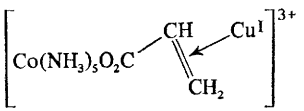


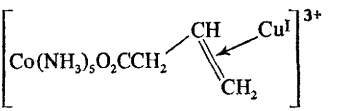
Figure 2 *Electronic energies E in a mixed-valence complex as functions of nuclear geometry, expressed as one-dimensional reaction co-ordinate x; unsymmetrical case with* $\Delta E_0 = 0$. *The pathway* a→c→d *denotes a thermal electron transfer reaction in which the electronic wavefunction transforms smoothly from the reactants' to the products' configuration, as the nuclear configuration changes along the reaction co-ordinate. The vertical transition* a→b *represents an intervalence charge transfer in which the electronic configuration changes from reactants' to products' while the nuclei remain fixed*

Some new examples of dinuclear (Fe^{II}–Co^{III})[40,41] and trinuclear (Fe^{II}–Co^{III}–Fe^{II})[42] bridged mixed-metal complexes may conveniently be mentioned here, though they have not been found to undergo thermal electron-transfer reactions.

Photochemically induced electron transfer has also been reported[43] in a series of Co^{III}–Cu^{I} complexes with organic bridging ligands. A typical complex (1) has an absorption at 318 nm[44] attributable to a Cu(*d*)→ligand(π^*) transition, and irradiation into this band produces Co^{II} and Cu^{II} whereas the corresponding thermal electron transfer is almost immeasurably slow.[44] It is interesting to note that complexes with π-electron systems not conjugated with the carboxy-group react about equally well: in fact the quantum yield is greater for complex (2) than for (1). Irradiation in the cobalt(III) ligand-field region is much less effective. Intermolecular electron transfer is also promoted in this way, as for example the reaction $[Co(NH_3)_5OAc]^{2+}$ + $[Cu(CH_2{=}CHCH_2OH)]^{+}$. It is proposed that the primary excitation product is the



(1)



(2)

[40] K. L. Scott, R. S. Murray, and W. C. E. Higginson, *J.C.S. Dalton*, 1975, 1339.
[41] S. Bagger and K. Gibson, *Acta Chem. Scand.*, 1973, **27**, 3227.
[42] S. Bagger and A. Németh, *Acta Chem. Scand.*, 1975, **A29**, 269.
[43] J. K. Farr, L. G. Hulett, R. H. Lane, and J. K. Hurst, *J. Amer. Chem. Soc.*, 1975, **97**, 2654.
[44] J. K. Hurst and R. H. Lane, *J. Amer. Chem. Soc.*, 1973, **95**, 1703.

singlet state Cu(d^9)·L(π^*), and that this reacts directly and rapidly in a thermal intramolecular process to give the observed products. This is an example of photon-excited 'chemical' transfer, as distinct from the photoexcited 'resonance' transfer proposed by Vogler and Kunkely.[38,39]

Symmetrical Exchange Processes.—Symmetrical mixed-valence complexes are important prototypes for electron-transfer studies. A complex of the Robin and Day Class II,[45] with trapped valencies, is a model precursor complex, and a complex of Class III with a symmetrical charge distribution in the electronic ground state is, in some respects, a model for the adiabatic electron-transfer transition state. (These

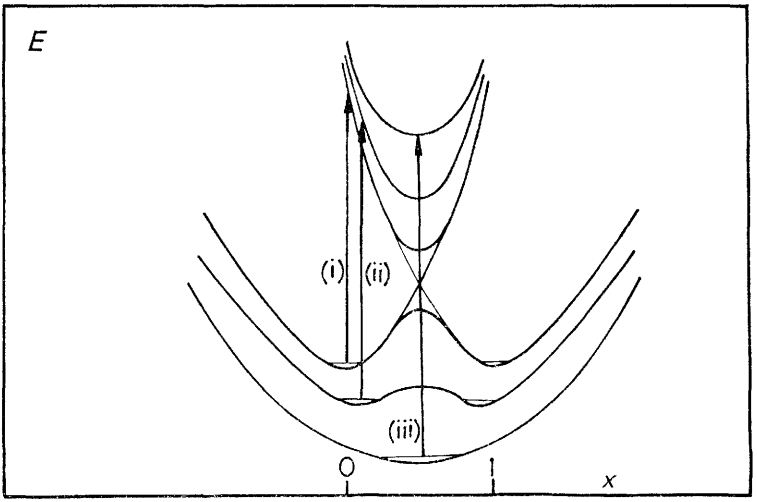


Figure 3 *Electronic energy levels for mixed-valence complexes (x = reaction co-ordinate, E = electronic energy); symmetrical cases, showing different degrees of interaction between reactants' and products' wavefunctions. The vertical transitions are all characteristic of the respective mixed-valence systems, and not of the isolated ions, but they lose their intervalence charge-transfer character as the resonance interaction increases in the sequence* (i)→(ii)→(iii)

relationships are illustrated in Figure 3.) The complex (3; L=NCCN) has been

$$[(H_3N)_5RuLRu(NH_3)_5]^{5+}$$

(3)

characterized,[46] and on various lines of evidence is classed as a fully delocalized species. It shows only a single i.r. frequency for CN stretching, at 2210 cm^{-1}, intermediate between those of cyanogen bound to Ru^{II} or Ru^{III}, and the kinetic behaviour leads to the same conclusion: the rate of hydration of the cyanogen ligand in aqueous media is *ca.* 10^2 times lower than that expected of a Ru^{III} complex. The complex does show a near-i.r. electronic transition, at *ca.* 1450 nm, but the lack of solvent depen-

[45] M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 247.
[46] G. M. Tom and H. Taube, *J. Amer. Chem. Soc.*, 1975, **97**, 5310.

dence and the narrow bandwidth are inconsistent with an internuclear charge transfer.[47] It may be assigned as in Figure 3, transition (iii).

The classification of the original Creutz and Taube ion (3; L = pyrazine) is also undergoing reassessment, following new experimental and theoretical work. In this complex the near-i.r. band formerly attributed to an intervalence $Ru^{II}Ru^{III} \rightarrow (Ru^{III}Ru^{II})^*$ transition has been shown to be largely independent of solvent,[48] and this, together with the bandwidth, also suggests valence delocalization. A new theoretical study[49] indicates that the photoelectron spectrum, formerly cited in favour of localized valences, is actually consistent with delocalization. It had already been reported[50] that some i.r. frequencies are averaged, and the latest i.r. work by Beattie *et al.*[51] gives evidence of averaging of frequencies for the NH_3 rocking (500 cm^{-1}) and Ru—NH_3 stretching (449 cm^{-1}) vibrations. On the other hand the latest Raman investigation by Strekas and Spiro[52] is interpreted on the basis of trapped valences, particular evidence being a band at 1070 cm^{-1} attributable to the Ru^{III} centre and several bands attributable to Ru^{II} and showing a strong resonance enhancement when excited in the range of the near-i.r. electron absorption. The most recent suggestion of Taube is that, in the pyrazine-bridged complex, electron exchange is more rapid than solvent reorganization, but delocalization is still not as complete as in the cyanogen-bridged complex. The latter point seems to be firmly supported by measurements of the conproportionation equilibrium constants $K_c = [RuRu^{5+}]^2/[RuRu^{4+}][RuRu^{6+}]$. As the bridging ligand is changed from 4,4′-bipy to pyrazine to cyanogen, log K_c increases from *ca.* 1.0[53] to 6.2[48] to > 13.[46]

It is worth stressing here that the mere fact that a series of complexes in a formally mixed oxidation state shows a band at low energy characteristic of the mixed valencies does not prove localization in the ground state. As the resonance energy increases, the electronic transition does not disappear but merely loses its charge-transfer character, as shown in the sequence (i)–(ii)–(iii) in Figure 3.

In recent years there have been several attempts to correlate rates of electron transfer, energies of intervalence charge transfer, and ground-state energy differences, using equations (14) and taking $E_a = \Delta G^{\ddagger}$, $E_{op} = Lh\nu$, $\Delta E_0 = \Delta G^{\ominus}$ (*cf.* Figures 1 and 3). Most calculations have been performed on molecules for which $\Delta E_0 = 0$, [equation (14c); *cf.* Figures 2 and 3). An unsymmetrical case has been considered by

$$E_a = E_{op}^2/16A \tag{14a}$$

$$= E_{op}^2/4(E_{op} - \Delta E_0) \tag{14b}$$

$$= E_{op}/4 \quad \text{when} \quad \Delta E_0 = 0 \tag{14c}$$

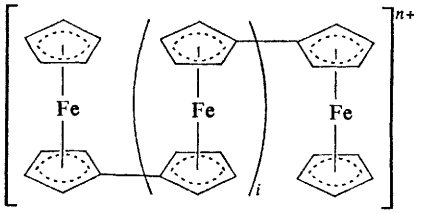
Brown *et al.*[54] who have made a series of electrochemical and spectroscopic measurements on compounds of the general type (4) where $0 \leqslant i \leqslant 2, 0 \leqslant n \leqslant 2$. By a series of comparisons of oxidation potentials which need not be detailed here, they have estimated

[47] N. S. Hush, *Progr. Inorg. Chem.*, 1967, **8**, 391.
[48] C. Creutz and H. Taube, *J. Amer. Chem. Soc.*, 1973, **95**, 1086.
[49] N. S. Hush, *Chem. Phys.*, 1975, **10**, 361.
[50] C. Creutz, I. M. Treitel, Ph.D. Theses cited in ref. 46.
[51] J. K. Beattie, N. S. Hush, and P. R. Taylor, *Inorg. Chem.*, 1976, **15**, 993.
[52] T. C. Strekas and T. G. Spiro, *Inorg. Chem.*, 1976, **15**, 974.
[53] G. M. Tom, C. Creutz, and H. Taube, *J. Amer. Chem. Soc.*, 1974, **96**, 7827.
[54] G. M. Brown, T. J. Meyer, D. O. Cowan, C. Le Vanda, F. Kaufman, P. V. Roling, and M. D. Rausch, *Inorg. Chem.*, 1975, **14**, 506.

the energy differences ΔE_0 in two pairs of valence isomers [equations (15)], where FcFcFc denotes the molecular framework (4; $n=1$), and the signs indicate localiza-

$$FcFc^+Fc \longrightarrow Fc^+FcFc \quad (15a)$$

$$Fc^+FcFc^+ \longrightarrow Fc^+Fc^+Fc \quad (15b)$$



(4)

tion of the iron(III) oxidation states. They also observed electronic spectral bands at low energies as shown in equations (16):

$$FcFc^+ \longrightarrow (Fc^+Fc)^* \quad (16a)$$

$$FcFc^+Fc \longrightarrow (Fc^+FcFc)^* \quad (16b)$$

$$Fc^+FcFc^+ \longrightarrow (Fc^+Fc^+Fc)^* \quad (16c)$$

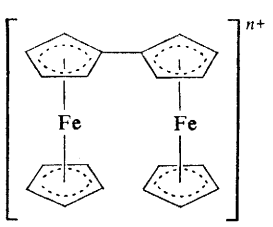
Taking the first of these three as a measure of $4A$ (since $\Delta E_0 = 0$), and taking this to apply also to the other two complexes, values of E_{op} are calculated as $E_{op} = \Delta E_0 + 4A$, *i.e.* 5.3×10^3 and 6.3×10^3 cm^{-1}, for comparison with the actual values, 5.0×10^3 and 6.0×10^3 cm^{-1}. Finally, thermal activation energies are estimated, leading to calculated rate constants, *e.g.* $k \approx 3 \times 10^{10}$ s^{-1} for reaction (17).

$$Fc^+Fc \rightleftharpoons FcFc^+ \quad (17)$$

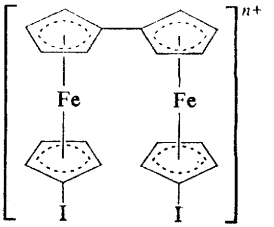
Measurements and calculations of this sort are of interest in providing a check on the validity of equations (14) and of diagrams such as Figures 2 and 3. Already, however, there are indications that the calculations of E_a from optical data may not be generally valid. Morrison and Hendrickson[55] have published a detailed study of the electron-transfer process in the partially oxidized dinuclear ferrocene-type complexes (5)—(8) ($n=1$) based on new magnetic resonance, susceptibility, electronic, and Mössbauer spectra and have reviewed earlier work from their own and other laboratories. Only the main conclusions relevant to optical and thermal electron transfer can be summarized here.

Mössbauer spectra of salts of (5) in the solid state showed clearly the two doublets for Fe^{II} and Fe^{III}, implying that the thermal exchange rate constant k_{ex} is less than 10^7 s^{-1}, even at room temperature. There is, however, some change in the spectrum with temperature and this may be due to the presence at the higher temperature of a second form of the cation, in a different crystal structure, with delocalized valencies. The band in the near i.r., which is not shown by either the fully reduced $Fe^{II}Fe^{II}$ or fully oxidized $Fe^{III}Fe^{III}$ complex, is attributed to the intervalence transition. The

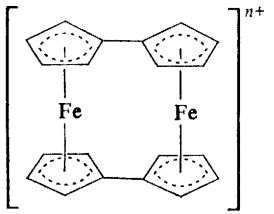
[55] W. H. Morrison and D. N. Hendrickson, *Inorg. Chem.*, 1975, **14**, 2331.



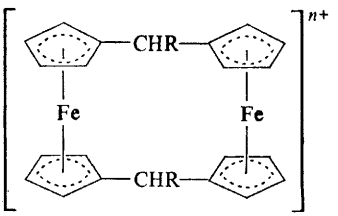
(5)



(6)



(7)



(8)

energy of this band varies slightly in MeCN solution, and more substantially on going to the solid state at 77 K.

In contrast, the di-iodo-substituted cation (6) shows the characteristics of valence delocalization not only on the Mössbauer but also (at 77 K) on the e.s.r. time-scale. Again it is possible that structural considerations are important: if, for example, the salts of (6) had the *cis* configuration and (5) the *trans* or if (6) were *trans* and (5) had a structure twisted about the central C—C bond by some angle other than 180°, the electronic coupling in (6) would be stronger than in (5), in agreement with the observations. It may be significant that in solution the two ions show rather similar properties: the near-i.r. bands are at practically the same energy, and the successive oxidation potentials (in acetonitrile) are quite similar [equations (18)]. Presumably in

$$(5;\ n = 0) \xrightarrow{0.42\ \text{V}} (n = 1) \xrightarrow{0.70\ \text{V}} (n = 2) \qquad (18a)$$

$$(6;\ n = 0) \xrightarrow{0.31\ \text{V}} (n = 1) \xrightarrow{0.72\ \text{V}} (n = 2) \qquad (18b)$$

solution there is free rotation about the central C—C bond, and the distribution of conformations is similar for the two complexes.

The bisferrocenylium complex (7) would be expected to show much stronger metal–metal coupling and certainly the electron transfer is rapid on the Mössbauer time-scale. However, it is apparently not yet possible to place any higher limit on the rate. *X*-Ray photoelectron spectra imply complete localization ($k_{ex} > 10^{17}\ s^{-1}$) but the i.r. spectra show bands in the regions 1200—1300 and 1600—1800 cm^{-1} reminiscent of the reduced Fe^{II}–Fe^{II} form of the complex, which could indicate $k_{ex} < 10^{13}\ s^{-1}$. Again there is a low-energy electronic transition (*ca.* $6.5 \times 10^3\ cm^{-1}$) but it is not necessarily to be interpreted as intervalence charge transfer.

The two [1,1]-ferrocenophane systems (8) show marked differences, again illustrating the importance of seemingly small structural variations in the particular salts used. Complex (8b) (I_3^- salt) has localized valences ($k_{ex} < 10^7\ s^{-1}$) but complex (8a)

behaves like a mixture of two forms, one localized and one delocalized on the Mössbauer time-scale, the proportions varying with temperature. (*X*-Ray data on the corresponding unoxidized complex have shown two crystallographically different forms of the molecule, with different Fe—Fe distances.) In solution, the two complexes differ again, (8a) having a band at 13.3×10^3 cm^{-1} which is not shown by (8b); this has been tentatively assigned as intervalence charge transfer.

These results are discussed in relation to equation (14c), and it is found that where the comparison is possible the experimental values of the thermal transfer energy are greater than $E_{op}/4$. The authors add serious reservations which are relevant to any attempt to correlate thermal and optical transfer energies: (i) the low-energy band in complex (7) has a shoulder even at room temperature, and at 77 K is clearly resolved into two bands; hence the electronic structure is more complicated than is assumed in drawing Figure 3; (ii) there is no clear basis for using the same 'reaction co-ordinate' for both thermal and optical processes.

3 Intermolecular Electron Transfer

In this section we review* most of the new experimental data on metal–metal electron transfer reactions in solution, in which the rate law for the primary process (19) can be expressed in the second-order form (20), or in related forms explicable in terms of

$$\text{Ox} + \text{Red} \longrightarrow \text{Products} \quad (19)$$

$$\text{Rate} = k[\text{Ox}][\text{Red}] \quad (20)$$

equilibria, stepwise processes, *etc.* Space forbids detailed discussion of every paper, but those not mentioned in the text will be found in the Tables, some with additional comment in the Footnotes.

Methods of Measurement.—Spectrophotometric methods, both conventional and stopped-flow, continue to dominate the scene. An interesting variation is being pursued by Tockstein and Skopal,[56] who have used stopped-flow mixing methods with electrode-potential measurements to follow the rate of reaction. Data for the $Fe^{III} + V^{III}$ and $V^{IV} + V^{II}$ reactions are in satisfactory agreement with earlier work.[57] Temperature-jump methods continue to be used in the rather rare cases where the overall equilibrium constant is close to unity.[28]

Scott *et al.*[58] have developed a technique for obtaining rate constants and activation enthalpies directly by a calorimetric method, measuring the change of temperature with time after the reagents are mixed in a reactor immersed in a constant-temperature environment. Their new data on the Fe^{III}–Sn^{II} reaction in chloride media agree well with earlier work.[59]

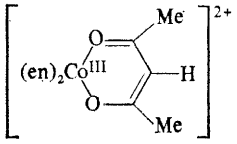
Complementary Reactions.—Kinetic data for reductions by Cr^{II}, V^{II}, Ti^{III}, and U^{III} are summarized in Table 1, beginning on p. 26. Data for other reductants are in Table 2, beginning on p. 35.

* Reviews on electron-transfer reactions of noble metal complexes (ref. 116) and of actinides (ref. 117) are inaccessible at the time of writing.

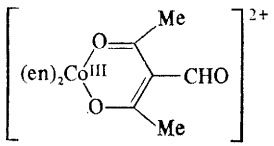
[56] A. Tockstein and F. Skopal, *Coll. Czech. Chem. Comm.*, 1974, **39**, 3430.
[57] J. W. Olver and J. W. Ross, *J. Phys. Chem.*, 1962, **66**, 1699; see also other references cited in ref. 56.
[58] P. D. Scott, D. Glasser, and M. J. Nicol, *J.C.S. Faraday I*, 1975, **71**, 1413.
[59] F. R. Duke and R. C. Pinkerton, *J. Amer. Chem. Soc.*, 1951, **73**, 3045.

Chromium(II). Studies with chromium(II) as reductant continue to yield detailed information on the structures of transition states and on the effects of functional groups in the ligands in determining reactivity.

Reduction of the cobalt complex (10) is much faster than reduction of (9) and leads to a chelate chromium(III) product, identified as (11) on the basis of its visible–u.v. spectrum.[60] It is presumed that the reaction involves attack of chromium(II) at the formyl group of (10), followed by rapid ring closure.



(9)



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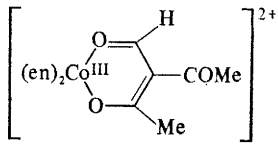
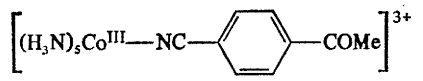


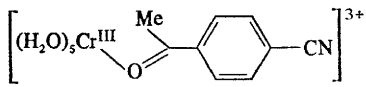
(11)

Reduction of malonatotetra-amminecobalt(III) yields the chelate product[61] tetra-aquomalonatochromium(III), and separate experiments on the ring closure of unidentate penta-aquomalonatochromium(III) ion show that the latter complex cannot be an intermediate. On the other hand, chromium(II) reduction of trismalonato-cobaltate(III) ion yields both chelate and unidentate products, the ratio of chelate to unidentate decreasing with increased acidity of the medium. This is consistent with a mechanism in which chromium(II) is attached to two carboxy-groups (of the same malonate) at low acidities, but to only one carboxy-group at high activities. The fact that only one malonate group is transferred from cobalt to chromium is in striking contrast to the chromium(II) reductions of $[Co(C_2O_4)_3]^{3-}$,[62] $[Cr(C_2O_4)_3]^{3-}$,[63] and *cis*- or *trans*-$[Cr(H_2O)_2(C_2O_4)_2]^-$,[63] where in each case two oxalate ions are transferred.

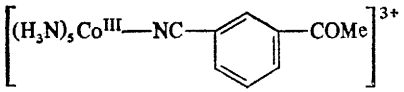
Reduction of the *p*-acetylbenzonitrile complex (12) apparently proceeds by remote attack, the immediate chromium(III) product being the complex (13). Chromium(II)



(12)



(13)



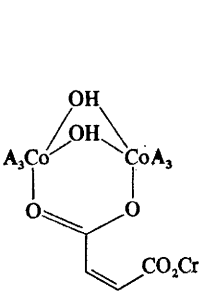
(14)

reduction of the corresponding *meta*-isomer (14) is much slower; the only chromium(III) product detected was the hexa-aquo-ion, though kinetically it is possible that an intermediate might be involved.[64]

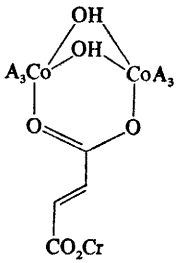
Reactions with μ-carboxylato-cobalt(III) dimers have yielded further evidence of

[60] R. J. Balahura and N. A. Lewis, *Canad. J. Chem.*, 1975, **53**, 1154.
[61] J. D. Edwards, Y. Sulfab, and A. G. Sykes, *Inorg. Chem.*, 1975, **14**, 1474.
[62] P. B. Wood and W. C. E. Higginson, *J. Chem. Soc.* (*A*), 1966, 1645.
[63] K. R. Ashley and R. E. Hamm, *Inorg. Chem.*, 1965, **4**, 1120.
[64] R. J. Balahura and W. L. Purcell, *Inorg. Chem.*, 1975, **14**, 1469.

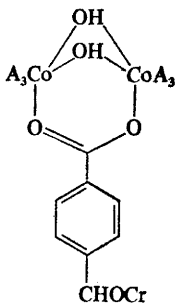
remote attack.[65,66] Some examples of the transition states [inferred from chromium-(III) product composition] are shown [(15)—(19) (A = NH_3, ionic charges omitted)].



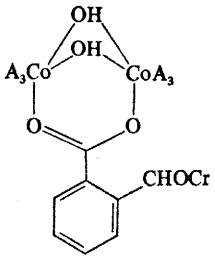
(15)



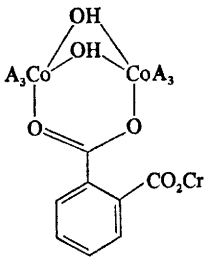
(16)



(17)



(18)



(19)

Comparison with penta-amminecobalt(III) complexes with the same carboxylato-ligands confirms that the bridging carboxy-group is not available for adjacent attack. The μ-phthalato-complex is believed to react *via* the precursor complex (19), but electron transfer *via* the aromatic ring system is not invoked. An outer-sphere type of electron transfer is suggested, on the basis of the value of $\Delta H^{\ddagger}$ and the ratio of rates of chromium(II) and vanadium(II) reductions.[67]

Another example of remote attack is the chromium(II) reduction of the tetra-(γ-sulphonatophenyl)porphinatocobalt(III) complex. The product is a dinuclear species with cobalt(II) still *in situ* and chromium(III) attached to one of the sulphonate groups.[68]

The reaction of $[Co(dmg)_2(NH_3)]_2^+$ with Cr^{2+} is confirmed to be of the inner-sphere type, product analysis experiments having demonstrated transfer of one or both of the dimethylglyoxime ligands from cobalt to chromium.[69]

A hitherto unstudied bridging group is the chlorate ion. The complex $[(H_2O)_5Cr(ClO_3)]^{2+}$ has been produced[70] by the reaction of chromium(VI) with $HClO_2$.

[65] M. R. Hyde, K. L. Scott, K. Wieghardt, and A. G. Sykes, *J.C.S. Dalton*, 1976, 153.
[66] M. R. Hyde, K. Wieghardt, and A. G. Sykes, *J.C.S. Dalton*, 1976, 690.
[67] A. T. Thornton, K. Wieghardt, and A. G. Sykes, *J.C.S. Dalton*, 1976, 147.
[68] E. B. Fleischer, M. Krishnamurthy, and S. K. Cheung, *J. Amer. Chem. Soc.*, 1975, **97**, 3873.
[69] R. H. Prince and M. G. Segal, *J.C.S. Dalton*, 1975, 1245; (*cf. Nature*, 1974, **249**, 246).
[70] R. C. Thompson, *Inorg. Chem.*, 1975, **14**, 1279.

Kinetics are reported for aquation and for reduction by chromium(II). The stoicheiometry is

$$6Cr^{2+} + [CrClO_3]^+ \longrightarrow CrCl^{2+} + 1.4Cr^{3+} + 2.3[Cr_2(OH)_2]^{4+} \qquad (21)$$

Isotopic trace studies show that the chromium in the two monomeric species originates in the chromium(II). The rate law for the redox reaction is comparatively simple, giving a transition state with the composition $[CrClO_3Cr^{4+}]^{\ddagger}$.

The reaction of $[Cr^{II}(edta)]^-$ with penta-amminenitrosylchromium(III), $[Cr(NH_3)_5NO]^{2+}$, yields mainly $[Cr(NH_3)_6]^{3+}$ and a reddish-violet species, probably containing the $Cr(NH_3)_5$ group linked to a Cr^{III}–(edta) group.[71] There is thus no evidence of chromium–chromium electron transfer.

The concepts of 'chemical' electron transfer, in which the electron spends significant time on the bridging ligand in a free-radical-type intermediate, and 'resonance transfer', in which the electron passes directly from oxidant to reductant, have been discussed extensively in the past. Itzkowitz and Nordmeyer[72] have used the kinetic isotope effect in a further effort to distinguish these mechanisms. In general, for reduction of $[Co(NH_3)_5L]$ complexes, deuteriation of the ammonia molecules leads to a lowering of the rate. The ratio k_H/k_D has now been found to be smaller in three cases where chemical transfer is believed to occur (L = isonicotinamide, 4-carboxylatopyridine, or fumarate) than for the acetato-complex for which only a resonance mechanism seems possible. A high ratio is also observed for the nicotinamide complex, and on this basis a resonance transfer mechanism is suggested.

Gould and co-workers have reported acid dependence of the rates of reduction of acetato- and propionato-penta-amminecobalt(III) by chromium(II), vanadium(II), and europium(II).[73] In all cases they note a decrease in rate with increasing acidity, which in the case of the acetatopenta-ammine + chromium(II) system confirms earlier work.[74,75] Assuming the protonation equilibria (22; R = Me or Et) they have fitted

$$[Co(NH_3)_5(O_2CR)]^{2+} + H^+ \overset{K_{HA}}{\rightleftharpoons} [Co(NH_3)_5(HO_2CR)]^{3+} \qquad (22)$$

their data to the general equation (23), where k_A and k_{HA} are specific rates of reduction of the free and protonated complexes. It should be noted that in no case were

$$-\frac{d\,[Co^{III}]}{dt} = \frac{k_A K_{HA} + k_{HA}[H^+]}{K_{HA} + [H^+]}[Co^{III}][Cr^{II}] \qquad (23)$$

there more than eight experimental points to be fitted to this three-parameter equation. The need for caution in interpreting data of this kind is illustrated by another paper from the same laboratory.[76] Previously,[77] the chromium(II) reductions of carboxylatopenta-amminecobalt(III) complexes with conjugatively unsaturated sidechains, *e.g.* $[Co(NH_3)_5(O_2CCH{=}CH_2)]^{2+}$, were reported to have complicated hydrogen-ion dependence, and the suggestion was made that these complexes were partially protonated under the conditions of the experiments ($[H^+]$ up to 1.0 mol l^{-1})

[71] H. Ogino, K. Tsukahara, and N. K. Tanaka, *Bull. Chem. Soc. Japan*, 1975, **48**, 3401.
[72] M. M. Itzkowitz and F. R. Nordmeyer, *Inorg. Chem.*, 1975, **14**, 2124.
[73] J. C. Thomas, J. W. Reed, and E. S. Gould, *Inorg. Chem.*, 1975, **14**, 1696.
[74] M. B. Barrett, J. H. Swinehart, and H. Taube, *Inorg. Chem.*, 1971, **10**, 1983.
[75] E. A. Deutsch, Ph.D. Thesis, Stanford University, 1967.
[76] P. K. Thamburaj and E. S. Gould, *Inorg. Chem.*, 1975, **14**, 15.
[77] A. Liang and E. S. Gould, *Inorg. Chem.*, 1973, **12**, 12.

and that the protonated and non-protonated forms were reduced at different rates. It is now[76] reported that the reductions of the same complexes with Eu^{2+} and V^{2+} show much less pronounced hydrogen-ion dependence than those with Cr^{2+} under the same conditions. Thus the protonation hypothesis seems unlikely, and the authors now prefer to invoke a non-specific medium effect which is greater for Cr^{2+} than for the other two reductants.

The rates of reactions (24) and (25) (M = Cr) have been measured[78] and compared

$$[Co(NH_3)_5(O_2CCH_2N(CH_2CO_2)_2] + M^{2+} \longrightarrow Co^{II} + M^{III} \quad (24)$$

$$[Co(NH_3)_5(O_2CMe)]^{2+} + MeN(CH_2CO_2)_2M^{II} \longrightarrow Co^{II} + M^{III} \quad (25)$$

with the previously reported[79] rates for M = Fe. The change from Fe^{2+} to Cr^{2+} produces a smaller increase in rate than in the case of the reaction $[Co(NH_3)_5(O_2CMe)]^{2+} + M^{2+}$, and this is consistent with the non-linear dependence of $\log k$ upon $\log K$ implied by equation (1) above. On the assumption that the chromium(II) reductions have the same mechanism as the iron(II) reduction, the specific rate of reaction of the precursor complex $[Co(NH_3)_5(O_2CCH_2N(CH_2CO_2)_2Cr]^{2+}$ is estimated to be 600 s^{-1}.

The chromium(II) acetate dimer has again been used as a reductant. Cannon and Stillman found two forms of kinetic behaviour, depending on the nature of the oxidant X, but consistent with a single mechanism[80] [equation (26)]. This involves dissociation into mononuclear chromium(II) complexes which are the effective reductants:

$$Cr_2(O_2CMe)_4 \underset{-1}{\overset{1}{\rightleftharpoons}} 2Cr(O_2CMe)_2 \quad (26a)$$

$$Cr(O_2CMe)_2 + X \xrightarrow{2} \text{products} \quad (26b)$$

With highly reactive oxidants such as $[Co(NH_3)_5Cl]^{2+}$, $[Co(C_2O_4)_3]^{3-}$, and I_2, step 1 is rate determining and the rate law is

$$-d[X]/dt = k_1[Cr_2(OAc)_4] \quad (27)$$

whereas with mild oxidants X, such as $[Cr(NH_3)_5Cl]^{2+}$, $[Cr(NH_3)_5Br]^{2+}$, $[Co(edta)]^-$, or $[Co(NH_3)_5(OH_2)]^{3+}$, step 2 is rate determining and the rate law is

$$-d[X]/dt = k_2K_1^{1/2}[Cr_2(OAc)_4]^{1/2}[X] \quad (28)$$

When the total chromium(II) concentration is sufficiently small, equilibrium is appreciably displaced to the right and (28) is replaced by (29)

$$-d[X]/dt = \tfrac{1}{4}k_2K_1\{-1 + (1 + 8[Cr^{II}]_T/K_1)^{1/2}\}[X] \quad (29)$$

from which it has been possible to determine the equilibrium constant K_1.[81]

Przystas and Sutin[82] have published a further study of the reduction of ferricytochrome *c* by chromium(II) with new data on the effects of chloride and thiocyanate. The authors propose a three-fold classification of anion effects on electron transfer to

[78] R. D. Cannon and J. Gardiner, *J.C.S. Dalton*, 1976, 622.
[79] R. D. Cannon and J. Gardiner, (*a*) *Inorg. Chem.*, 1974, **13**, 390; (*b*) *J.C.S. Dalton*, 1972, 887.
[80] R. D. Cannon and J. S. Stillman, *Inorg. Chem.*, 1975, **14**, 2207.
[81] R. D. Cannon and J. S. Stillman, *Inorg. Chem.*, 1975, **14**, 2202.
[82] T. J. Przystas and N. Sutin, *Inorg. Chem.*, 1975, **14**, 2103.

the ferricytochrome molecule: bulk effects in which the anion interacts mainly with the structure of the protein or the water; peripheral effects in which the anion interacts mainly with the porphyrin; and inner-sphere effects in which the anion interacts mainly with the iron atom. Rate enhancement by chloride is thought to be of the inner-sphere type. The effects of thiocyanate ion are thought to be mainly peripheral, but there is also an inner-sphere pathway.

Vanadium(II). Studies of the V^{2+} reaction with azido-chromium(III) complexes have produced evidence[83] of the inner-sphere processes (30a) and (31a) with subsequent

$$CrN_3^{2+} + V^{2+} \rightleftharpoons VN_3^{2+} + Cr^{2+} \quad (30a)$$

$$VN_3^{2+} + H^+ \longrightarrow V^{3+} + NH_3 \quad (30b)$$

$$cis\text{-}Cr(N_3)_2^+ + V^{2+} \longrightarrow Cr^{2+} + VN_3^+ + N_3^- \quad (31a)$$

$$VN_3^{2+} + Cr^{2+} \rightleftharpoons V^{2+} + CrN_3^{2+} \quad (31b)$$

$$VN_3^{2+} + H^+ \longrightarrow V^{3+} + HN_3 \quad (31c)$$

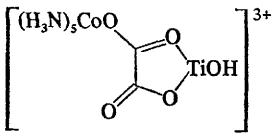
steps as shown. Reaction (30a) is thermodynamically unfavourable but is driven to completion by reaction (30b). In reaction (31a), single bridging is postulated, in contrast to the corresponding reduction by Cr^{2+}.[84, 85]

The reaction $[Co(dmgH)_2(NH_3)_2]^+ + V^{2+}$ is diagnosed as inner-sphere on the basis of the activation parameters.[86] The lack of acid catalysis in contrast with the corresponding reaction with Cr^{2+} [69] is consistent with a substitution-controlled mechanism. The reactions of $[Co(dmgH)_2(NH_3)X]$ (X = Cl or Br) with V^{2+} do show acid catalysis and have very similar rate parameters, suggesting outer-sphere mechanisms.[86] Along a series of cobaloximes, with varying axial ligands, there appears to be a progression from inner-sphere to outer-sphere reactions as the cobalt becomes more strongly oxidizing.[69]

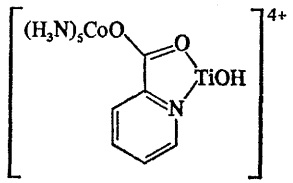
Titanium(III). In a further attempt to establish inner- and outer-sphere mechanisms, Birk[87] has compared rates of reduction of $[Co(NH_3)_5NCS]^{2+}$ and $[Co(NH_3)_5N_3]^{2+}$. The azide complex reacts the faster by a factor of at least 3.6×10^4, strongly indicating a bridged mechanism. Rates have been reported[88] for reduction of a number of other penta-amminecobalt(III) complexes with organic side-chains potentially capable of forming electron-mediating bridges. Although there is no direct evidence of bridging, indirect evidence is provided by hydrogen-ion dependences in two cases, which show the unusual feature of an inverse second-order term. This suggests chelation of $TiOH^{2+}$ in transition states such as (20) and (21).

Orhanovic and Earley[89] and Thompson and Sykes[90] have measured rates of reduction of various ammine-cobalt(III) complexes. They find strong base catalysis, according to equation (32) for the dichlorobisethylenediamine complexes,[89] or otherwise equation (33),[89, 90] with equation (34) as a limiting form at high acidities.[90]

[83] R. C. Thompson, *Inorg. Chem.*, 1976, **15**, 1080.
[84] R. Snellgrove and E. L. King, *J. Amer. Chem. Soc.*, 1962, **84**, 4609.
[85] A. Haim, *J. Amer. Chem. Soc.*, 1966, **88**, 2324.
[86] R. H. Prince and M. G. Segal, *J.C.S. Dalton*, 1975, 330.
[87] J. P. Birk, *Inorg. Chem.*, 1975, **14**, 1724.
[88] A. H. Martin and E. S. Gould, *Inorg. Chem.*, 1975, **14**, 873.
[89] M. Orhanovic and J. E. Earley, *Inorg. Chem.*, 1975, **14**, 1478.
[90] G. A. K. Thompson and A. G. Sykes, *Inorg. Chem.*, 1976, **15**, 638.



(20)



(21)

$$-\frac{d\,[Co^{III}]_T}{dt} = \frac{a + b[H^+]^{-1}}{1 + c[H^+]^{-1}}[Co^{III}]_T[Ti^{III}]_T \quad (32)$$

$$-\frac{d\,[Co^{III}]_T}{dt} = \frac{b[H^+]^{-1}}{1 + c[H^+]^{-1}}[Co^{III}]_T[Ti^{III}]_T \quad (33)$$

$$-\frac{d\,[Co^{III}]_T}{dt} = b[H^+]^{-1}[Co^{III}]_T[Ti^{III}]_T \quad (34)$$

These are interpreted in terms of partial acid hydrolysis of titanium ion,

$$Ti^{3+} \overset{K_a}{\rightleftharpoons} TiOH^{2+} + H^+ \quad (35a)$$

$$Co^{III} + Ti^{3+} \xrightarrow{k_0} \text{products} \quad (35b)$$

$$Co^{III} + TiOH^{2+} \xrightarrow{k_{OH}} \text{products} \quad (35c)$$

giving $a = k_0$, $b = k_{OH}K_a$, $c = K_a$ [equation (35)].

Thompson and Sykes have discussed the relative rates in terms of hardness and softness of the metal ions and bridging groups. With the aid of free-energy correlations with rates of V^{2+} and $[Ru(NH_3)_6]^{2+}$ they have assigned outer-sphere mechanisms for the oxidants $[Co(NH_3)_5Cl]^{2+}$, $[Co(NH_3)_5Br]^{2+}$, $[Co(NH_3)_5I]^{2+}$, and *cis*- and *trans*-$[Co(en)_2Cl_2]^+$ and inner-sphere mechanisms for $[Co(NH_3)_5SO_4]^{2+}$, $[Co(NH_3)_5(O_2CMe)]^{2+}$, $[Co(NH_3)_5F]^{2+}$, and $[\{Co(NH_3)_5\}_2O_2]^{5+}$.[90]

In the cases of $[Co(NH_3)_5N_3]^{2+}$[87] and $[Co(NH_3)_5F]^{2+}$,[90] inner-sphere mechanisms are implied by the rate law. The hydrogen-ion dependences are of the same form as (33) but the term c is too large to be interpreted as K_a. Although it is still necessary to allow for the partial hydrolysis of Ti^{3+} according to equation (35a), two alternative mechanisms may be written with a dinuclear intermediate at steady-state concentrations [*e.g.* equations (36) and (37), $Ro = Co(NH_3)_5$].

$$RoN_3^{2+} + Ti^{3+} \underset{-1}{\overset{1}{\rightleftharpoons}} [RoN_3TiOH]^{4+} + H^+ \quad (36a)$$

$$[RoN_3TiOH]^{4+} \xrightarrow{2} \text{Products} \quad (36b)$$

$$Ti^{3+} \overset{K_a}{\rightleftharpoons} TiOH^{2+} + H^+ \quad (37a)$$

$$RoN_3^{2+} + TiOH^{2+} \underset{-3}{\overset{3}{\rightleftharpoons}} [RoN_3TiOH]^{4+} \quad (37b)$$

$$[RoN_3TiOH]^{4+} + H^+ \xrightarrow{4} \text{Products} \quad (37c)$$

The net activation rate constants corresponding to transition states $[RoN_3Ti]^{8+}$ and $[RoN_3TiOH]^{7+}$ are $b = K_1k_2 = K_ak_3$ and $b/c = k_1 = K_aK_3k_4$.

Uranium(III). New data reported by Ekstrom *et al.*[16,17] are shown in Table 1. The lack of an acid dependence in most cases is remarkable, particularly so for the cases of Fe^{3+} and Co^{3+} which show base catalysis in many electron-transfer reactions. It is paralleled, however, in the reductions by V^{2+} which from their high rate must be outer-sphere, and the U^{3+} reduction may therefore be outer-sphere as well. The reaction $V^{3+}+U^{3+}$ is strongly base catalysed, as also is the reaction $V^{3+}+V^{2+}$.

Neptunium(VII). The reaction $Np^{VII}+Co^{2+}$ is acid catalysed[123] but with the non-integral-order rate law (38), and a recalculation of earlier data[91] on the $Np^{VII}+Tl^{+}$

$$-\frac{d}{dt}[Np^{VII}] = \frac{\beta c[H^+]}{1 + c[H^+]}[Np^{VII}][Co^{II}] \qquad (38)$$

reaction shows that the same equation applies. A mechanism consistent with the rate law is the following (here shown for the case of Co^{2+}):

$$NpO_2^{3+} + Co^{2+} \underset{-1}{\overset{1}{\rightleftharpoons}} NpO_2Co^{5+} \qquad (39a)$$

$$NpO_2Co^{5+} + H^+ \overset{K_2}{\rightleftharpoons} NpO_2CoH^{6+} \qquad (39b)$$

$$NpO_2CoH^{6+} \xrightarrow{k_3} \text{products} \qquad (39c)$$

giving rate constants $\beta=k_1$ and $\beta c=K_1K_2k_3$ corresponding to transition states NpO_2Co^{5+} and NpO_2CoH^{6+} respectively. A possible structure for the latter is $HONpOCo^{6+}$ and, by analogy, structures are now suggested for the transition states in the reactions previously studied, $NpO_2^{2+}+VO^{2+}$ [92] and $NpO_2^{2+}+Hg^{2+}$,[93] *i.e.* $HONpO(VO)OH^{6+}$ and $HONpOHg_2OH^{6+}$.

Excited $[*Ru(bipy)_3]^{2+}$. The redox potential of the $[Ru(bipy)_3]^{3+}/[*Ru(bipy)]^{2+}$ couple has been estimated to be -0.83 V in water at 25 °C.[94] Further emission-quenching experiments have been reported[94,95] supporting the view that quenching can occur by outer-sphere *reduction* [equation (40)] when Q is a reagent such as $[Fe(CN)_6]^{4-}$,

$$[*Ru(bipy)_3]^{2+} + Q \xrightarrow{k_q} [Ru(bipy)_3]^{+} + Q^{+} \qquad (40)$$

$S_2O_4^{2-}$, or $[Ru(NH_3)]_6^{2+}$, as well as by oxidation [equation (41)] when Q is an ion

$$[*Ru(bipy)_3]^{2+} + Q \xrightarrow{k_q} [Ru(bipy)_3]^{3+} + Q^{-} \qquad (41)$$

such as Fe^{3+} or $[Co(phen)_3]^{3+}$. Other reagents such as $[Cr(CN)_6]^{3-}$ appear to quench by energy transfer rather than electron transfer, and $[Co(CN)_6]^{3-}$ is not an effective quencher at all.[95] A detailed study of the $[Ru(bipy_3)]^{2+}+Fe^{3+}$ system has led to the mechanism shown in equation[96] (42). Irradiation of $[Ru(bipy)_3]^{2+}$ gives the triplet state with a characteristic phosphorescent emission which is quenched by Fe^{3+} in two ways, energy transfer (k_{en}) and electron transfer (k_{el}). The latter gives rise to steady-state concentrations of $[Ru(bipy)_3]^{3+}$ and Fe^{2+}. The measurements yield the total

[91] R. C. Thompson and J. C. Sullivan, *J. Amer. Chem. Soc.*, 1970, **92**, 3028.
[92] K. O. Watkins, J. C. Sullivan, and E. Deutsch, *Inorg. Chem.*, 1974, **13**, 1712.
[93] M. A. Thompson, J. C. Sullivan, and E. Deutsch, *J. Amer. Chem. Soc.*, 1971, **93**, 5667.
[94] C. Creutz and N. Sutin, *Inorg. Chem.*, 1976, **15**, 496.
[95] A. Juris, M. I. Gandolfi, M. F. Manfrin, and V. Balzani, *J. Amer. Chem. Soc.*, 1976, **98**, 1047.
[96] C.-t. Lin and N. Sutin, *J. Amer. Chem. Soc.*, 1975, **97**, 3543.

$$\begin{array}{lcccl} [Ru(bipy)_3]^{2+} & & & & [Ru(bipy)_3]^{3+} \\ + & \xleftarrow{k_{en}} & [^*Ru(bipy)_3]^{2+} + Fe^{3+} \xrightarrow{k_{el}} & [Ru(bipy)_3]^{3+}\cdot Fe^{2+} \underset{-2}{\overset{2}{\rightleftharpoons}} & + \\ Fe^{3+*} & & \Big\| h\nu \quad k_0 & \Big\downarrow k_1 & Fe^{2+} \end{array}$$

$$[Ru(bipy)_3]^{2+} + Fe^{3+} \longleftrightarrow [Ru(bipy)_3]^{2+}\cdot Fe^{3+} \qquad (42)$$

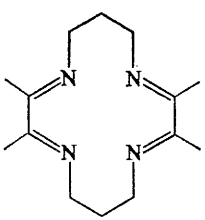
quenching rate constant ($k_{el}+k_{en}$) and the ratio $k_{el}k_2/k_1k_{-2}$; from previous studies of the reaction $[Ru(bipy)_3]^{3+}+Fe^{2+}$ the constant k_1k_{-2}/k_2 is already known, whence $k_{en}=0.4\times10^9$ l mol^{-1} s^{-1}, $k_{el}=1.9\times10^9$ l mol^{-1} s^{-1}.

Europium(II). Evidence of the prevalence of inner-sphere mechanisms with Eu^{2+} continues to accumulate. Reduction of the *S*-bonded isomer of $[Co(NH_3)_5(SCN)]^{2+}$ is much more rapid than reduction of the *N*-bonded isomer.[97] Thamburaj and Gould[98] have compared the reductants Cr^{2+} and Eu^{2+}, reacting with a variety of substituted benzoatopenta-amminecobalt(III) ions, and confirmed the relation (43).[99]

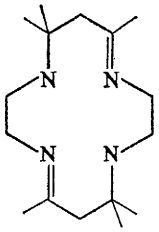
$$\log k_{Eu} = 0.67 \log k_{Cr} + 0.54 \qquad (43)$$

Detailed comparisons are also consistent with inner-sphere assignments (*cf.* Table 1). Rates vary little with substitution in the benzene ring but diminish when the carboxylate function is removed as in the *NN*-dimethylnicotinamide complex. They increase when there is the possibility of chelation in the transition state, notably in the case of the sulphoacetato-complex.

Other Reagents. Cobalt(I) complexes have been proposed as intermediates in the chromium(II) reduction of macrocyclic cobalt(III) complexes.[100] The reaction $[CoLd(NH_3)_2]^{3+}+Cr^{2+}$ [Ld = (22)] is autocatalytic,[101] and it is also strongly catalysed by the addition of $[CoLt(H_2O)_2]^{2+}$ [Lt = ligand (23)]. In the proposed mechanism (44)



(22)



(23)

step 3 is rate determining, and from the fact that the known reaction (45) does not compete, the lower limit of k_4 is obtained.

$$CoLt^{2+} + Cr^{2+} \underset{-3}{\overset{3}{\rightleftharpoons}} CoLt^{+} + Cr^{3+} \qquad (44a)$$

$$CoLt^{+} + [CoLd(NH_3)_2]^{3+} \xrightarrow{4} CoLt^{2+} + CoLd^{2+} + 2NH_3 \qquad (44b)$$

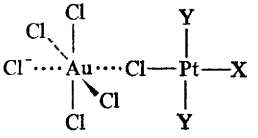
$$CoLt^{+} + H^{+} \longrightarrow HCo^{III}Lt^{2+} \qquad (45)$$

[97] A. Adegite and T. A. Kuku, *J.C.S. Dalton*, 1976, 158.
[98] P. K. Thamburaj and E. S. Gould, *Inorg. Chem.*, 1975, **14**, 15.
[99] F.-R. F. Fan and E. S. Gould, *Inorg. Chem.*, 1973, **13**, 2639, 2647.
[100] D. P. Rillema and J. F. Endicott, *Inorg. Chem.*, 1976, **15**, 1459.
[101] D. P. Rillema and J. F. Endicott, *Inorg. Chem.*, 1972, **11**, 2361.

Oxidation of a series of monochloroplatinum(II) complexes by $[AuCl_4]^-$ has been reported [equation (46)].[102] Presumably the two chloride ions added to the platinum

$$[AuCl_4]^- + [Pt^{II}Y_2XCl] \longrightarrow [AuCl_2]^- + [Pt^{IV}Y_2XCl_3] \quad (46)$$

come from the bulk medium and are not directly transferred. Rate terms of the form $[Pt^{II}][Au^{III}][Cl^-]$ are consistent with chloride-assisted bridged transition states of the type (24). An additional term in the rate law, tending to zero-order in gold(III), is



(24)

interpreted in terms of a prior solvolysis step, followed by electron transfer [equation (47); S = MeCN].

$$[PtXY_2Cl] + S \rightleftharpoons [PtXY_2S]^+ + Cl^- \quad (47a)$$

$$[PtXY_2S]^+ + [AuCl_4]^- + Cl^- \longrightarrow [PtXY_2Cl_3]^+ + [AuCl_2]^- + S \quad (47b)$$

The first kinetic data have been reported[103] for a rhodium(II) species with 'innocent' ligands, namely $[Rh(NH_3)_4]^{2+}$. This short-lived species is produced by interaction of hydrated electrons with penta-amminerhodium(III) complexes [equation (48)]. The

$$[Rh(NH_3)_5Cl]^{2+} + e^-(aq) \longrightarrow [Rh(NH_3)_5Cl]^+ \longrightarrow [Rh(NH_3)_4]^{2+} + Cl^- + NH_4^+ \quad (48)$$

complex is identified as the tetra-ammine by the use of rapid conductimetric measurements to determine the amount of ammonia liberated in the initial rapid reactions. Two subsequent electron-transfer processes have been detected, *i.e.* disproportionation according to reaction (49) ($k_2 = 1.4 \times 10^7$ l mol^{-1} s^{-1}) and a chain reaction involving rhodium(II)–rhodium(III) electron transfer [reaction (50); $k_3 = 1.4 \times 10^6$ l mol^{-1} s^{-1}).

$$[Rh(NH_3)_4]^{2+} + [Rh(NH_3)_4]^{2+} \xrightarrow{k_2} [Rh(NH_3)_4]^+ + [Rh(NH_3)_4]^{3+} \quad (49)$$

$$[Rh(NH_3)_4Br_2]^+ + [Rh(NH_3)_4]^{2+} \xrightarrow{k_3} [Rh(NH_3)_4Br_2] + [Rh(NH_3)_4(OH_2)]^{3+} \quad (50)$$

Non-complementary Reactions.—Reactions in which the valence changes of oxidant and reductant differ can yield interesting new information on intermediates of unusual oxidation state. They also include some of the best known oxidants and reductants, with a long history of study and mechanistic speculation. Kinetic data for these reactions are summarized in Table 3, on p. 40.

New data[104] on the oxidation of VO^{2+} by permanganate ion show that in acidic solution with reductant in excess, the stoicheiometry conforms to equation (51). The kinetics when followed spectrophotometrically at $\lambda = 526$ nm lead to the rate law

[102] A. Peloso, *Coordination Chem. Rev.*, 1975, **16**, 95.
[103] J. Lilie, M. G. Simic, and J. F. Endicott, *Inorg. Chem.*, 1975, **14**, 2129.
[104] F. M. Moore and K. W. Hicks, *Inorg. Chem.*, 1975, **14**, 413.

(52), but the immediate product decays in a second, slower step, and from its

$$MnO_4^- + 5VO^{2+} + H_2O = Mn^{2+} + 5VO_2^+ + 2H^+ \quad (51)$$

$$-d[Mn^{VII}]/dt = k[MnO_4^-][VO^{2+}] \quad (52)$$

spectrum is thought to be a manganese(v) species. A possible mechanism is

$$Mn^{VII} + V^{IV} \xrightarrow{k_1} Mn^{VI} + V^V \quad (53a)$$

$$Mn^{VI} + V^{IV} \longrightarrow\longrightarrow Mn^V + V^V \quad (53b)$$

$$Mn^V + 3V^{IV} \longrightarrow Mn^{II} + 3V^V \quad (53c)$$

The rate constant k contains a positive hydrogen-ion dependence. The reaction $MnO_4^- + Pu^{4+}$ has the analogous overall stoicheiometry and rate law, but requires a two-term negative hydrogen-ion dependence (Table 3). The possibility of a manganese(v) intermediate in this case as well is discussed, but apparently without any positive experimental evidence.[105]

The reaction $U^{IV} + Fe^{III}$ in 8M-HCl is retarded[106] by Fe^{II}, implying the mechanism (54). It was also shown[106] that iron(III) catalyses the exchange of radioactivity

$$U^{IV} + Fe^{III} \underset{-1}{\overset{1}{\rightleftharpoons}} U^V + Fe^{II} \quad (54a)$$

$$U^V + Fe^{III} \xrightarrow{2} U^{VI} + Fe^{II} \quad (54b)$$

between U^{VI} and U^{IV}, the rates being consistent with formation of a U^V intermediate.

This reduction of chromium(VI) by plutonium(III) is closely analogous to the reduction by iron(II) [equation (55)]. The kinetics[107] and the observation of induced

$$Cr^{VI} + Pu^{III} \underset{-1}{\overset{1}{\rightleftharpoons}} Cr^V + Pu^{IV} \quad (55a)$$

$$Cr^V + Pu^{III} \xrightarrow{2} Cr^{IV} + Pu^{IV} \quad (55b)$$

$$Cr^{IV} + Pu^{III} \longrightarrow Cr^{III} + Pu^{IV} \quad (55c)$$

oxidation of I^- ions are consistent with the mechanism shown. Step 1 is nearly rate determining, but some retardation by Pu^{IV} implies competition between steps -1 and 2. Other complications are participation of $[Cr_2O_7]^{2-}$ and formation of a stable complex $[Pu^{IV}Cr^{VI}O_4]^{2+}$ analogous to the $[NpCrO_4]^{2+}$ and $[ThCrO_4]^{2+}$ already known.[108] The principal rate term implies a transition state of composition $[PuCrO_4H_3]^{4+}$.

Oxidation of the molybdenum(v) dimer $[Mo_2O_4(edta)]^{2-}$ by one-electron reagents such as $[IrCl_6]^{2-}$ or $[Fe(phen)_3]^{3+}$ leads ultimately to monomeric molybdenum(VI), but the kinetics[109] are characteristic of a non-complementary reaction, with retardation by added $[IrCl_6]^{3-}$ or $[Fe(phen)_3]^{2+}$ respectively. The mechanism proposed [*e.g.* equation (56)] contains a mixed-valence Mo^VMo^{VI} complex, presumably

[105] V. S. Koltunov, G. I. Zhuravleva, and V. I. Marchenko, *Soviet Radiochem.*, 1975, **17**, 305.
[106] H. Tomiyasu and H. Fukutomi, *Bull. Chem. Soc. Japan*, 1975, **48**, 13.
[107] T. W. Newton, *Inorg. Chem.*, 1975, **14**, 2394.
[108] M. J. Burkhart and R. C. Thompson, *J. Amer. Chem. Soc.*, 1972, **94**, 2999.
[109] R. K. Wharton, J. F. Ojo, and A. G. Sykes, *J.C.S. Dalton*, 1975, 1526.

$$Mo^{V}{}_2 + Ir^{IV} \underset{-1}{\overset{1}{\rightleftharpoons}} Mo^{V}Mo^{VI} + Ir^{III} \quad (56a)$$

$$Mo^{V}Mo^{VI} \xrightarrow{k_2} Mo^{V} + Mo^{VI} \quad (56b)$$

$$Mo^{V} + Ir^{IV} \xrightarrow{3} Mo^{VI} + Ir^{III} \quad (56c)$$

similar in structure to the starting material. Other possible mechanisms could involve oxidation of $Mo^{V}Mo^{VI}$ to a further dimer $Mo^{VI}{}_2$ in place of step 2 or, alternatively, recombination of Mo^{V} to give $Mo^{V}{}_2$, in place of step 3.

The reactions of $[PtCl_6]^{2-}$ and $[Pt(NH_3)_5Cl]^{2+}$ with V^{2+} proceed[110] with the stoicheiometry (57). Of the alternative mechanisms, (*a*) $Pt^{IV}+2V^{II}\rightarrow Pt^{III}+V^{III}+V^{II}\rightarrow Pt^{II}+2V^{III}$ and (*b*) $Pt^{IV}+2V^{II}\rightarrow Pt^{II}+V^{IV}+V^{II}\rightarrow Pt^{II}+2V^{III}$, mechanism (*b*) is ruled out by the known rate of $V^{IV}+V^{II}$ reaction. Hence a platinum(III) intermediate is proposed, but it must be short-lived since there is no retardation by vanadium(III). Both of the rate-determining reactions, $[PtCl_6]^{2-}+V^{2+}$ and $[Pt(NH_3)_5Cl]^{3+}+V^{2+}$, are classed as outer-sphere, the former on the basis of its specific rate being too high to allow substitution at V^{2+}(aq), the latter on the basis of a linear free-energy correlation between reduction by V^{2+} and by $[Ru(NH_3)_6]^{2+}$.[111]

$$Pt^{IV} + 2V^{II} \longrightarrow Pt^{II} + 2V^{III} \quad (57)$$

The reaction $Fe^{3+}+Sn^{2+}$ is catalysed by the addition of $[Ta_6Cl_{12}]^{2+}$, and the proposed mechanism involves the three cluster ions $[Ta_6C_{12}I]^{n+}$ ($n=2$, 3, or 4), with rapid reaction between Sn^{2+} and $[Ta_6Cl_{12}]^{4+}$ which is either a two-electron transfer or a rapid sequence of one-electron transfers *via* the Sn^{III} state.[112] Reactions (58a—c) are the principal steps at low iron(II) concentrations, reactions (58d and e) becoming significant at higher iron(II) concentrations.

$$Fe^{3+} + [Ta_6Cl_{12}]^{3+} \rightleftharpoons Fe^{2+} + [Ta_6Cl_{12}]^{4+} \quad (58a)$$

$$[Ta_6Cl_{12}]^{4+} + Sn^{2+} \longrightarrow\!\!\!\rightarrow [Ta_6Cl_{12}]^{2+} + Sn^{IV} \quad (58b)$$

$$Fe^{3+} \text{ (or } [Ta_6Cl_{12}]^{4+}) + [Ta_6Cl_{12}]^{2+} \longrightarrow Fe^{2+} \text{ (or } [Ta_6Cl_{12}]^{3+}) + [Ta_6Cl_{12}]^{3+} \quad (58c)$$

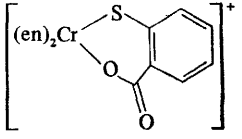
$$[Ta_6Cl_{12}]^{3+} + Sn^{2+} \longrightarrow [Ta_6Cl_{12}]^{2+} + Sn^{III} \quad (58d)$$

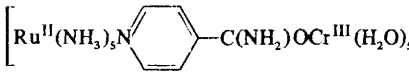
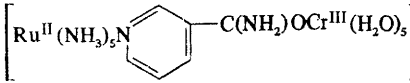
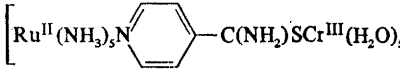
$$Fe^{3+} \text{ (or } [Ta_6Cl_{12}]^{4+}) + Sn^{III} \longrightarrow\!\!\!\rightarrow Fe^{2+} \text{ (or } [Ta_6Cl_{12}]^{3+}) + Sn^{IV} \quad (58e)$$

The reaction $Co^{3+}+Sn^{2+}$ shows no retardation by either product, Co^{II} or Sn^{IV}.[113] There is evidence of an intermediate since on adding Fe^{III} to the mixture some is reduced to Fe^{II}, but the alternatives of two-electron transfer leading to a Co^{I} intermediate or one-electron transfer leading to Sn^{III} cannot be distinguished experimentally.

[110] A. Bakac, T. D. Hand, and A. G. Sykes, *Inorg. Chem.*, 1975, **14**, 2540.
[111] M. R. Hyde, R. S. Taylor, and A. G. Sykes, *J.C.S. Dalton*, 1973, 2730.
[112] D. M. Haynes and W. C. E. Higginson, *J.C.S. Dalton*, 1976, 308.
[113] N. A. Daugherty and J. K. Erbacher, *Inorg. Chem.*, 1975, **14**, 683.
[114] E. D. German, A. V. Gorodynskii, and V. G. Dvali, *Izvest. Akad. Nauk gruz. S.S.R., Ser. khim.*, 1975, **1**, 259 (*Chem. Abs.*, 1976, **84**, 65695).
[115] A. V. Gorodynskii and V. G. Dvali, *V. Sb., XI Mendeleevsk. S'ezd po Obshch. i Prikl. Khimii. Ref. Dokl. i Soobshch.*, 1975, **3**, 252 (*Chem. Abs.*, 1976, **84**, 156061).
[116] P. I. Novoselov, Z. A. Muzykantova, and I. P. Sokolovskaya, *Koord. Khim.*, 1975, **1**, 544 (*Chem. Abs.*, 1975, **83**, 16261).
[117] V. S. Koltunov, V. I. Marchenko, G. I. Zhuravleva, and M. F. Tikhonov, *V. Sb., XI Mendeleevsk. S'ezd po Obshch. i Prikl. Khimii, Ref. Dokl. i Soobshch.*, 1975, **1**, 204 (*Chem. Abs.*, 1976, **84**, 156233).

Table 1 *Rate constants* and activation parameters for electron-transfer reactions involving two metal-ion complexes*

Oxidant	*Rate law*	*Medium*	*Rate constant* (25 °C)	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
Reductant = Cr^{2+}						
VN_3^{2+}	k	0.97 ($LiClO_4$)		3.85	−27.3	83[a]
$[Cr(H_2O)_5\{OC(Me)C_6H_4CN\text{-}p\}]^{3+}$	$k+k'[H^+]^{-1}$	0.5 ($LiClO_4$)	k 420 k' 6.8			64
$[Cr(H_2O)_5(OClO_2)]^+$	k	2.1 ($LiClO_4$)	0.41	8.1	−31	70[b]
$[Cr(H_2O)_3(N_3)_3]$	k	0.97 ($LiClO_4$)	98			83[c,d]
$[Cr(NH_3)_5Cl]^{2+}$	k	1 $HClO_4$	5.41×10^{-2}			81
	k	1 (Na)ClO_4	3.25×10^{-2}			81
	k	1 ($NaClO_4$)	5.0×10^{-2}			9
	k	acetate buffer, 1 ($NaClO_4$)	0.60			81[e]
	k	acetate buffer, 1 ($NaClO_4$)	0.5			81[e,f]
$Cr(en)_2(SCH_2CO_2)]^+$	$k+k'[H^+]^{-1}$	1 ($LiClO_4$)	k 1.2×10^{-3} k' 2.17×10^{-2}	18.4 9.4	−10.5 −34.8	121[g,h,a]
$[Cr(en)_2(SCH_2CH_2NH_2)]^{2+}$	k	1 ($LiClO_4$)	11.2×10^{-5}			121[g-i]
	$k+k'[H^+]$	1 ($LiClO_4$)	k 0.25×10^{-3} k' 1.6×10^{-3}			121
$[Cr(en)_2(O_2CCO_2)]^+$	k		2.63×10^{-3}			121[h]
Ferricytochrome *c*	$k+k'[H^+]^{-1}+k''[H^+]+k_x[NCS^-]$	1 (Na)Cl	k 3.6×10^2 k' 40 k'' 4.7×10^3 k_x 1.1×10^6			82[j,k]
	$k+k'[H^+]^{-1}+k_x[NCS^-]$	0.1 (Na)ClO_4	k 10 k' 3.2 k_x 2.3×10^6			82[l,k]
Ferricytochrome *c*	$k'[H^+]^{-1}$	0.1 (Na)Cl	k' 18			82
$[Fe^{III}\{tetrakis(4\text{-}pyridyl)porphine\}]^+$		0.1 ClO_4				82[k]

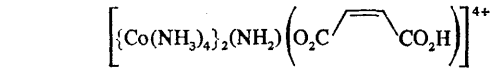
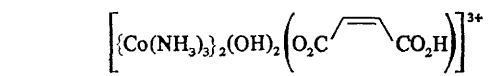
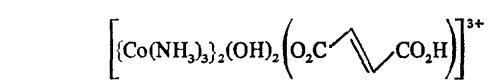
	$k[H^+]^{-1}$	1 ($HClO_4$) 0.4 ($HClO_4$)	4.74×10^{-4} 3.41×10^{-4}	122 122
	$k[H^+]^{-1}$	0.1 ($HClO_4$)	4.05×10^{-5}	122
	$k[H^+]^{-1}$	0.01 ($HClO_4$)	0.27	122
$[Co(NH_3)_5(OH_2)]^{3+}$	$k+k'[H^+]^{-1}$	acetate buffer, 1 ($NaClO_4$)	k 4.9×10^3 k' 0.23	80[e]
$[Co(NH_3)_5(OH_2)]^{3+}$	$k[H^+]^{-1}$	1 ($LiClO_4$)	2.48	72[m]
$[Co(NH_3)_5CN]^{2+}$	k	1 ($LiClO_4$)	71.3	72[m]
$[Co(NH_3)_5(NCS)]^{2+}$	k	1 ($LiClO_4$)	15.0	72[m]
$[Co(NH_3)_5(O_2CMe)]^{2+}$	k	1 ($LiClO_4$)	0.29	72[m]
$[Co(NH_3)_5(O_2CMe)]^{2+}$	$\frac{k_0K+k_1[H^+]}{K+[H^+]}$	4 ($LiClO_4$)	k_0 0.46 k_1 0.024 K 0.35	73
$[Co(NH_3)_5(O_2CEt)]^{2+}$	$\frac{k_0K+k_1[H^+]}{K+[H^+]}$	4 ($LiClO_4$)	k_0 0.33 k_1 0.025 K 0.24	73

* Rate constants are quoted in $(dm^3\ mol^{-1})^n\ s^{-1}$ where n is defined by the rate law; ΔH^* and ΔS^* in kcal mol^{-1} and cal $K^{-1}\ mol^{-1}$ respectively (cal = 4.184 J). Unless otherwise specified, all reactions are first-order in oxidant and reductant, and the expression in the column headed *Rate law* is the second-order rate coefficient. For example, the first entry implies $-d[V^{III}]/dt = k[VN_3^{2+}][Cr^{2+}]$. Media are specified according to the conventions of L. G. Sillén and A. E. Martell, 'Stability Constants', Chemical Society Special Publication No. 17, London, 1964. For example, 1.0 denotes an ionic strength of 1.0 mol l^{-1}, salts unspecified; 1.0 ($LiClO_4$) denotes an ionic strength 1.0 mol l^{-1} maintained by the addition of $LiClO_4$; 1.0 $LiClO_4$ denotes a concentration 1.0M-$LiClO_4$ in addition to the reacting species; 1.0 (Li)ClO_4 denotes a constant concentration 1.0 mol l^{-1} of ClO_4^- ion maintained by the addition of $LiClO_4$.

[a] Inner-sphere mechanism. [b] For stoicheiometry see text. [c] At 0 °C. [d] Inner-sphere mechanism; double bridging. [e] Reductant is chromium(II) monomer in acetate buffer, average composition $Cr(OAc)_2$. [f] At 30 °C. [g] Data at $I=4.0$ mol l^{-1} are also reported. [h] There is also a Cr^{2+}-independent aquation term in the rate law. [i] The only detectable Cr^{III} product is $[Cr(H_2O)_6]^{3+}$; however, an inner-sphere mechanism is suggested, the primary product undergoing rapid aquation. [j] When $[H^+]>0.2$ mol l^{-1} the order in chromium(II) decreases. [k] Chromium(III) product contains *S*-bonded thiocyanate. [l] When $[H^+]>0.02$ mol l^{-1} the order in chromium(II) decreases. [m] The $Co(ND_3)_5$ complex was also studied.

Table 1—*continued*

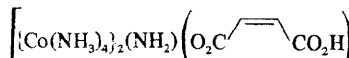
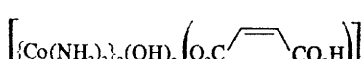
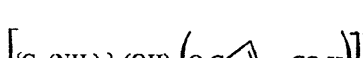
Oxidant	*Rate law*	*Medium*	*Rate constant* (25 °C)	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
$[Co(NH_3)_5O_2C\diagup\!\!\diagdown Me)]^{2+}$	$k_0+k_1[H^+]$	1 ($LiClO_4$)	k_0 1.69 k_1 3.40			72[m]
$[Co(NH_3)_5$(DL-alanine)$]^{3+}$	k	0.1 H^+, 1 ($NaClO_4$)	0.049	8.0	−37	118[n]
$[Co(NH_3)_5$(DL-valine)$]^{3+}$	k	0.1 H^+, 1 ($NaClO_4$)	0.042	8.2	−38	118[n]
$[Co(NH_3)_5$(DL-isoleucine)$]^{3+}$	k	0.1 H^+, 1 ($NaClO_4$)	0.039	8.6	−40	118[n]
$[Co(NH_3)_5$(DL-leucine)$]^{3+}$	k	0.1 H^+, 1 ($NaClO_4$)	0.055	7.6	−37	118[n]
$[Co(NH_3)_5$(DL-serine)$]^{3+}$	k	0.1 H^+, 1 ($NaClO_4$)	0.060	7.55	−37	118[n]
$[Co(NH_3)_5$(DL-threonine)$]^{3+}$	k	0.1 H^+, 1 ($NaClO_4$)	0.033	9.2	−43	118[n]
$[Co(NH_3)_5$(L-arginine)$]^{3+}$	k	0.1 H^+, 1 ($NaClO_4$)	0.115	6.7	−33	118[n]
$[Co(NH_3)_5(O_2CC_6F_5)]^{2+}$	k	1 ($LiClO_4$)?	0.08			98[o]
$[Co(NH_3)_5(O_2CC_6H_4CO_2H$-*o*$)]^{2+}$	$k+k'[H^+]^{-1}$	1 ($LiClO_4$)	k 0.12 k' 6.15×10^{-3}			119[p]
$[Co(NH_3)_5\{O_2CCH_2N(CH_2CO_2)_2H_2\}]^{2+}$	$k[H^+]^{-2}$	1 ($NaClO_4$)	2.45			78
$[Co(NH_3)_5(O_2CMe)]^{3+}$	k[Hmida$^-$]$[H^+]^{-1}$	1 ($NaClO_4$)	0.24			78[q]
$[Co(NH_3)_5py]^{3+}$	k	1 ($LiClO_4$)	3.80×10^{-3}			72[m]
$[Co(NH_3)_5$(nicotinamide$)]^{3+}$	k	1 ($LiClO_4$)	4.76×10^{-2}			72[m,r]
$[Co(NH_3)_5$(isonicotinamide$)]^{3+}$	k	1 ($LiClO_4$)	16.4, 18.8			72[m,r]
$[Co(NH_3)_5$(isonicotinic acid$)]^{3+}$	$k+k'[H^+]^{-1}$	1 ($LiClO_4$)	k 1.00 k' 1.06×10^{-2}			72[m,r]
$[Co(NH_3)_5(NCC_6H_4COMe$-*p*$)]^{3+}$	k	0.5 ($LiClO_4$)	6×10^3	−2.0	−48	64
$[Co(NH_3)_5(NCC_6H_4COMe$-*m*$)]^{3+}$	k	0.5 ($LiClO_4$)	0.28	3.2	−50	64
(10)	k	1 ($LiClO_4$)	0.0863	9.9	−30	60
(9)	k	1 ($LiClO_4$)	10^{-4}—10^{-6}			60
$[Co(NH_3)_4$(malonate$)]^+$	k	1 ($LiClO_4$)	26.4	7.2	−28	61
$[Co$(malonate$)_3]^{3-}$	k	1 ($LiClO_4$)	$>10^6$			61
$[Co^{III}$(tetra-*p*-sulphonatophenyl-porphinate$)]^{5-}$	$k'[H^+]^{-1}+k_{Cl}[Cl^-]+k_{NCS}[NCS^-]$	0.25 ($NaClO_4$)	k' 4.9 k_{Cl} 2.9×10^4 k_{NCS} 1.3×10^6			68
$[Co$(edta$)]^-$	k	acetate buffer, 1 ($NaClO_4$)	1.5×10^4			80
$[Co(Hdmg)_2(tu)_2]^+$	k	0.1 ($NaClO_4$)	1.22×10^4			120[a]
$[Co(Hdmg)_2(dmtu)_2]^+$	—	—	—			120[a]
$[\{Co(NH_3)_3\}_2(OH)_2(O_2CC_6H_4CO_2H$-*o*$)]^{3+}$	$k+k'[H^+]^{-1}$	1 ($LiClO_4$)	k 2.34×10^{-3} k' 0.36×10^{-3}	7.44 11.2	−45.5 −36.5	119[s]

	$k[H^+]^0$	1 ($LiClO_4$)	0.59	5.5	−41.3	65[t]
	$k[H^+]^0$	1 ($LiClO_4$)	1.87	4.3	−43.0	65[t]
	$k[H^+]^0$	1 ($LiClO_4$)	2.64	2.8	−47.1	65[t]
$[\{Co(NH_3)_3\}_2(OH)_2(O_2CC_6H_4CHO\text{-}p)]^{3+}$	k	1 ($LiClO_4$)	1.23×10^2	1.4	−44.2	66[t]
$[\{Co(NH_3)_3\}_2(OH)_2(O_2CC_6H_4CHO\text{-}o)]^{3+}$	k	1 ($LiClO_4$)	31.6	−3.6	−63.7	66[t]
Reductant = V^{2+}						
$[Cr(H_2O)_5N_3]^{2+}$	k	0.97 ($LiClO_4$)		12.9	−13.0	83[a]
cis-$[Cr(H_2O)_4(N_3)_2]^+$	k	0.97 ($LiClO_4$)		12.4	−12.9	83[a]
$[Cr(H_2O)_3(N_3)_3]$	k	0.97 ($LiClO_4$)		14.1	−6.5	83[a]
$[Co(NH_3)_5(O_2CMe)]^{2+}$	$\frac{k_0K+k_1[H^+]}{K+[H^+]}$	4 ($LiClO_4$)	k_0 3.15 k_1 1.22 K 0.35			73
$[Co(NH_3)_5(O_2CEt)]^{2+}$	$\frac{k_0K+k_1[H^+]}{K+[H^+]}$	4 ($LiClO_4$)	k_0 2.66 k_1 1.30 K 0.24			73
$[Co(NH_3)_5Co(OH_2)]^{3+}$	k	1 ($LiClO_4$)	0.55			72
$[Co(NH_3)_5CoN_3]^{2+}$	k	1 ($LiClO_4$)	11.6			72

[n] Co complexes are *O*-bonded and protonated, $[Co(NH_3)_5(O_2CHRNH_3)]^{3+}$. [o] Quoting A. Liang, Ph.D. Thesis, Kent State University, 1972. [p] The k pathway yields the unidentate complex $[Cr(H_2O)_5(O_2CC_6H_4CO_2H)]^{2+}$; the k' pathway yields the chelate $[Cr(H_2O)_4\{(O_2C)_2C_6H_4\}]^+$. [q] $mida^{2-} = MeN(CH_2CO_2)_2^{2-}$. [r] Co complex is the *N*-bonded isomer. [s] The k pathway is outer-sphere; the k' pathway involves remote attack by Cr^{2+}. [t] Inner-sphere mechanism with remote attack.

118 R. Bembi and W. V. Malik, *J. Inorg. Nuclear Chem.*, 1975, **37**, 570.
119 A. T. Thornton, K. Wieghardt, and A. G. Sykes, *J.C.S. Dalton*, 1976, 147.
120 R. H. Prince and M. G. Segal, *J.C.S. Chem. Comm.*, 1976, 100.
121 C. J. Weschler and E. Deutsch, *Inorg. Chem.*, 1976, **15**, 139.
122 R. W. Craft and R. G. Gaunder, *Inorg. Chem.*, 1975, **14**, 1283.

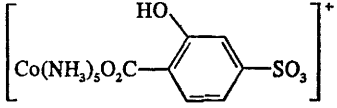
Table 1—*continued*

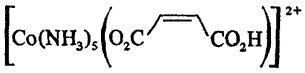
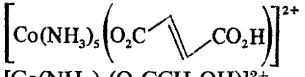
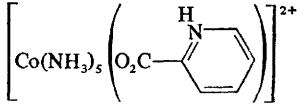
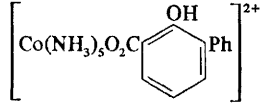
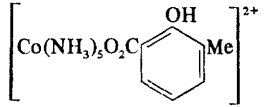
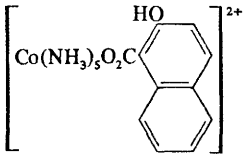
Oxidant	*Rate law*	*Medium*	*Rate constant* (25 °C)	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
$[Co(NH_3)_5Co(NCS)]^{2+}$	k	1 ($LiClO_4$)	0.253			72
$[\{Co(NH_3)_3\}_2(OH)_2(O_2CC_6H_4CO_2H\text{-}o)]^{3+}$	$k+k'[H^+]^{-1}$	1 ($LiClO_4$)	k 0.11 k' 2.72×10^{-2}	8.3 9.9	−35.1 −32.6	119
	k	1 ($LiClO_4$)	1.46	9.8	−24.9	65
	$k+k'[H^+]^{-1}$	1 ($LiClO_4$)	k 0.164 k' 0.045	5.8 10.6	−42.3 −29.3	65
	k	1 ($LiClO_4$)	0.099	7.5	−38.0	65
$[\{Co(NH_3)_3\}_2(OH)_2(O_2CC_6H_4CHO\text{-}p)]^{3+}$	k	1 ($LiClO_4$)	0.148	7.8	−36.4	66
$[\{Co(NH_3)_2\}_2(OH)_2(O_2CC_6H_4CHO\text{-}o)]^{3+}$	k	1 ($LiClO_4$)	0.235	6.1	−41.0	66
$[Co(NH_3)_5py]^{3+}$	k	1 ($LiClO_4$)	0.253			72
$[Co(NH_3)_5(nicotinamide)]^{3+}$	k	1 ($LiClO_4$)	2.18			72
$[Co(NH_3)_5(isonicotinamide)]^{3+}$	k	1 ($LiClO_4$)	3.98			72
$[Co(NH_3)_5(O_2CC_6F_5)]^{2+}$	k	1 ($LiClO_4$)	0.72			98
$[Co(NH_3)_5(O_2CC_6H_4SMe\text{-}o)]^{2+}$	k	1 ($LiClO_4$)	0.75			98
$[Co(NH_3)_5(O_2CC_6H_4OMe\text{-}o)]^{2+}$	k	1 ($LiClO_4$)	0.60			98
$[Co(NH_3)_5(O_2CCH_2SO_3)]^{+}$	k	1 ($LiClO_4$)	6.8			98
$[Co(NH_3)_5(O_2CCH{=}CH_2)]^{2+}$	k	1 ($HClO_4$)	0.82			76[u]
$[Co(NH_3)_5(O_2CCH{=}CHC_6H_4OMe\text{-}m)]^{2+}$	k	1 ($HClO_4$)	0.91			76[u]
$[Co(NH_3)_5(O_2CCH{=}CHC_6H_4OH\text{-}o)]^{2+}$	k	1 ($HClO_4$)	0.85			76[u]
$[Co(NH_3)_5(O_2CCH{=}CHC_6H_4OH\text{-}p)]^{2+}$	k	1 ($HClO_4$)	0.78			76[u]
$[Co(NH_3)_5(O_2CCH{=}CHCH{=}CHPh)]^{2+}$	k	1 ($HClO_4$)	0.89			76[u]
$[Co(Hdmg)_2(NH_3)_2]^{+}$	k	0.1 ($NaClO_4$) 0.99 HCl 0.012 H^+, 1.0 (NaCl)	0.55 1.57 1.02	14.5	−11.0	69, 86

$[Co(Hdmg)_2(NH_2Et)_2]^+$	k	0.1 ($NaClO_4$)		14.7	−11	69
$[Co(Hdmg)_2(3,5\text{-}Me_2py)_2]^+$	k	0.1 ($NaClO_4$)		9.9	−26	69
$[Co(Hdmg)_2(py)_2]^+$	k	0.1 ($NaClO_4$)		7.5	−31	69
$[Co(Hdmg)_2(NH_2Ph)_2]^+$	k	0.1 ($NaClO_4$)		7.0	−32	69
$[Co(Hdmg)_2(NH_3)Br]$	$k+k'[H^+]$	1 ($NaClO_4$)	k 76 k' 64	5.7	−31	86[v]
$[Co(Hdmg)_2(NH_3)Cl]$	$k+k'[H^+]$	1 ($NaClO_4$)	k 44 k' 29	5.4	−33	86
$[Co(Hdmg)_2(tu)_2]^+$	k	0.1 ($NaClO_4$)	2.56×10^2	5.0	−30.7	120
Reductant = Eu^{2+}						
$[Co(NH_3)_5(O_2CMe)]^{2+}$	$\frac{k_0K+k_1[H^+]}{K+[H^+]}$	4 ($LiClO_4$)	k_0 2.43 k_1 0.31 K 0.35			73
	k	4 ($LiClO_4$)	1.97			98[w]
$[Co(NH_3)_5(O_2CEt)]^{2+}$	$\frac{k_0K+k_1[H^+]}{K+[H^+]}$	4 ($LiClO_4$)	k_0 1.39 k_1 0.33 K 0.24			73
$[Co(NH_3)_5(NCS)]^{2+}$	k	0.1 H^+, 1 ($LiClO_4$)	4.95×10^{-2}	7.5	−39.7	97
$[Co(NH_3)_5(SCN)]^{2+}$	k	0.1 H^+, 1 ($LiClO_4$)	3.1×10^3	2.7	−33.4	97
$[Co(NH_3)_5(O_2CCH_2SO_3)]^+$	k	1 ($LiClO_4$)	36			98
$[Co(NH_3)_5(O_2CPh)]^{2+}$	k	1 ($LiClO_4$)	0.83			98
$[Co(NH_3)_5(O_2CC_6F_5)]^{2+}$	k	1 ($LiClO_4$)	1.10			98
$[Co(NH_3)_6(O_2CC_6H_4I\text{-}o)]^{2+}$	k	1 ($LiClO_4$)	0.78			98
$[Co(NH_3)_5(O_2CC_6H_4Br\text{-}o)]^{2+}$	k	1 ($LiClO_4$)	1.03			98
$[Co(NH_3)_5(O_2CC_6H_4Cl\text{-}o)]^{2+}$	k	1 ($LiClO_4$)	1.15			98
$[Co(NH_3)_5(O_2CC_6H_4F\text{-}o)]^{2+}$	k	1 ($LiClO_4$)	2.0			98
$[Co(NH_3)_5(O_2CC_6H_4Me\text{-}o)]^{2+}$	k	1 ($LiClO_4$)	0.80			98
$[Co(NH_3)_5(O_2CC_6H_4SMe\text{-}o)]^{2+}$	k	1 ($LiClO_4$)	1.20			98
$[Co(NH_3)_5(O_2CC_6H_4OMe\text{-}o)]^{2+}$	k	1 ($LiClO_4$)	2.20			98
$[Co(NH_3)_5(O_2CC_6H_4OMe\text{-}p)]^{2+}$	k	1 ($LiClO_4$)	0.78			98

[u] Slightly higher rates are found when $[H^+]=0.1$ mol l^{-1} at $I=1.0$ mol l^{-1} ($LiClO_4$). [v] Similar results also in 1.0M-$LiClO_4$. [w] Limiting specific rate at low acidities. Experiments of J. Thomas – but *cf.* the data quoted from ref. 73.

Table 1—*continued*

Oxidant	*Rate law*	*Medium*	*Rate constant* (25 °C)	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
	k	1 ($LiClO_4$)	0.88			98
$[Co(NH_3)_5(O_2CC_6H_4SO_3\text{-}p)]^+$	k	1 ($LiClO_4$)	1.16			98
$[Co(NH_3)_5(O_2CC_6H_4SO_3\text{-}m)]^+$	k	1 ($LiClO_4$)	1.43			98
$[Co(NH_3)_5(O_2CC_6H_4SO_3\text{-}o)]^+$	k	1 ($LiClO_4$)	7.40			98
$[Co(NH_3)_5(O_2CCH_2C_6H_4F\text{-}o)]^{2+}$	k	1 ($LiClO_4$)	1.67			98
$[Co(NH_3)_5(O_2CCH_2C_6H_4F\text{-}p)]^{2+}$	k	1 ($LiClO_4$)	1.10			98
$[Co(NH_3)_5(O_2CCH{=}CH_2)]^{2+}$	k	1 ($HClO_4$)	1.60			76[u]
$[Co(NH_3)_5(O_2CCH{=}CHC_6H_4OMe\text{-}m)]^{2+}$	k	1 ($HClO_4$)	1.85			76[u]
$[Co(NH_3)_5(O_2CCH{=}CHC_6H_4OH\text{-}o)]^{2+}$	k	1 ($HClO_4$)	1.92			76[u]
$[Co(NH_3)_5(O_2CCH{=}CHC_6H_4OH\text{-}p)]^{2+}$	k	1 ($HClO_4$)	2.24			76[u]
$[Co(NH_3)_5(O_2CCH{=}CHCH{=}CHPh)]^{2+}$	k	1 ($HClO_4$)	2.00			76[u]
Reductant = Ti^{3+}						
$[Co(NH_3)_5(SO_4)]^+$	$k[H^+]^{-1}$	0.5 (LiCl)	1.98×10^{-2}			90
$[Co(NH_3)_5(OH_2)]^{3+}$	$k[H^+]^{-1}$	0.5 (LiCl)	2.49×10^{-4}			90
$[Co(NH_3)_6]^{3+}$	$k[H^+]^{-1}$	0.5 (LiCl)	3.0×10^{5}			90
$[Co(NH_3)_5Cl]^{2+}$	$k[H^+]^{-1}$	0.5 (LiCl)	1.89×10^{-3}			90[x]
	$k[H^+]^{-1}$	1 (CF_3SO_3Li)	2.2×10^{-3}			89[y,z]
$[Co(NH_3)_5I]^{2+}$	$k[H^+]^{-1}$	0.5 (LiCl)	1.3×10^{-3}			90
$[Co(NH_3)_5I]^{2+}$	$k+k'[H^+]^{-1}$	0.5 (LiCl)	k 0.050; k' 2.11×10^{-3}			90
$[Co(NH_3)_5N_3]^{2+}$	$k[H^+]^{-1}$	0.5 (LiCl)	2.21			87[y]
$[Co(NH_3)_5F]^{2+}$	$k[H^+]^{-1}$	0.5 (LiCl)	6.29			90[y]
$[Co(bipy)_3]^{3+}$	$k[H^+]^{-1}$	0.5 (LiCl)	4.4×10^{-2}			90
$[\{Co(NH_3)_5\}_2O_2]^{5+}$	$k+k'[H^+]^{-1}$	0.5 (LiCl)	k 2.8×10^{2}; k' 1.86×10^{2}			90
cis-$[Co(en)_2Cl_2]^+$	$k[H^+]^{-1}$	1 (CF_3SO_3Li)	3.45×10^{-3}			89[y,aa]
trans-$[Co(en)_2Cl_2]^+$	$k[H^+]^{-1}$	1 (CF_3SO_3Li)	1.29×10^{-2}			89[y,aa]
$[Co(NH_3)_5(O_2CH)]^{2+}$	$k[H^+]^{-1}$	1 (NaOTs)	7.0×10^{-3}			88

	$k[H^+]^{-1}$	1 (NaOTs)	3.3×10^{-3}	88
	$k[H^+]^{-1}$	1 (NaOTs)	5.5×10^{-3}	88
$[Co(NH_3)_5(O_2CCH_2OH)]^{2+}$	$k[H^+]^{-1}$	1 (NaOTs)	3.1	88
$[Co(NH_3)_5\{O_2CCH(OH)Me\}]^{2+}$	$k[H^+]^{-1}$	1 (NaOTs)	6.7	88
	$k[H^+]^{-1}+k'[H^+]^{-2}$	1 (NaOTs)	k 1.8×10^{-3} k' 4.4×10^{-3}	88
$[Co(NH_3)_5(O_2CCO_2H)]^{2+}$	$k[H^+]^{-2}$	1 (NaOTs)	1.20	88
	$k[H^+]^0$	1 (NaOTs)	1.40	88
	$k[H^+]^0$	1 (NaOTs)	2.5	88
	$k[H^+]^0$	1 (NaOTs)	2.6	88
$[Co(NH_3)_5(O_2CMe)]^{2+}$	k	1 H^+, 1.7 (NaOTs)	4.9×10^{-3}	88
$[Co(NH_3)_5(O_2CCF_3)]^{2+}$	k	1 H^+, 1.7 (NaOTs)	3.9×10^{-3}	88

[x] Same results in 0.5 (ClO_4^-) medium. [y] The result quoted refers to the net activation process represented by $Co^{III}+Ti^{3+}-H^+ \rightleftharpoons [Co^{III}Ti^{3+}OH^-]^{\ddagger}$. For the actual rate law in terms of total concentrations of reagents; see text. Similar results in 1.0M-LiCl and 1.0M-NaCl media. [aa] A small contribution from an acid-independent term was also reported.

Table 1—*continued*

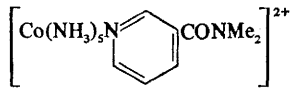
Oxidant	*Rate law*	*Medium*	*Rate constant* (25 °C)	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
$[Co(NH_3)_5(O_2CC_6H_4OH\text{-}p)]^{2+}$	k	1 H^+, 1.7 (NaOTs)	4.2×10^{-3}			88
$[Co(NH_3)_5(O_2CC_6H_4OMe\text{-}o)]^{2+}$	k	1 H^+, 1.7 (NaOTs)	1.5×10^{-3}			88
$[Co(NH_3)_5(O_2CC_6H_4CHO\text{-}o)]^{2+}$	k	1 H^+, 1.7 (NaOTs)	1.7×10^{-3}			88
$[Co(NH_3)_5(O_2CC_6H_4CHO\text{-}p)]^{2+}$	k	1 H^+, 1.7 (NaOTs)	2.2×10^{-3}			88
	k	1 H^+, 1.7 (NaOTs)	$<6\times10^{-4}$			88
Reductant = U^{3+}						
UO_2^{2+}	k	2 ($NaClO_4$)	1.2×10^{4}	4.15	−26.1	16
VO^{2+}	k	2 ($NaClO_4$)	3.7×10^{5}	6.04	−12.3	16
V^{3+}	$k+k'[H^+]^{-1}$	2 ($NaClO_4$)	k 54.2	9.77	−17.1	16
			k' 2.78×10^{2}	9.48	−15.0	
Fe^{3+}	k	2 ($NaClO_4$)	3.9×10^{5}	1.53	−27.7	16
Co^{3+}	k	2 ($NaClO_4$)	1.12×10^{6}	2.0	−25.6	17

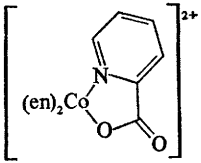
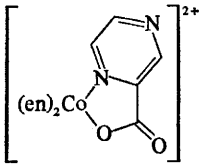
Table 2 *Rate constants and activation parameters for various electron transfer reactions involving two metal ion complexes. For explanation of conventions used, see Table 1*

Oxidant	*Reductant*	*Rate law*	*Medium*	*Rate constant* (25 °C)	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
Np^{VII}	Co^{2+}	$\frac{\beta c[H^+]}{1+c[H^+]}$	1 ($LiClO_4$)	β 5.4×10⁴ c 1.83	9.5 −13.1	−5.0 −42.9	123[a]
Np^{VII}	Ag^+	$k[H^+]$	1 ($LiClO_4$)	3.54×10^3	0.81	−41	123
Np^{VII}	Tl^+	$\frac{\beta c[H^+]}{1+c[H^+]}$	1 ($LiClO_4$)	β 26.1 c 0.204	7.6 −0.6	−2.6 −5	123[a,b]
Np^{V}	Np^{V}	k	4 H_2SO_4, 4 H_3PO_4	3.0×10^{-4}			135[c]
NpO_2^+	NpO_2^+	k	4 H^+, 5 ($NaClO_4$)	2.03×10^{-2}	17.6	−24	105[d]
		$k[H^+]^2$	5 ($NaClO_4$)	1.4×10^{-5}			105[d,e]
$[(H_2O)_5Cr^{III}O\text{-}Np^{V}O]^{4+}$	Np^{3+}	$k[H^+]^0$	0.5 ($LiClO_4$)	1.6×10^3	2.6	−35	133[f]
UO_2^{2+}	U^{4+}	$k[H^+]^{-3}$	2.3 ($NaClO_4$)	6.3×10^{-6}			134[g]
U^{VI}	Sn^{II}	k	Me_2NCOMe–H_2O mixtures				127[h]
$Ce(SO_4)_2$	$[Fe(phen)_3]^{2+}$	k	0.6	4.56×10^5	10.1	1.3	132[i]
$[Ce(SO_4)_3]^{2-}$	$[Fe(phen)_3]^{2+}$	k	0.6	4.18×10^4	7.3	−13	132[i]
$Ce(SO_4)_2$	Fe^{2+}	k	0.6	1.12×10^6	2	−23	132[i]
$[Ce(SO_4)_3]^{2-}$	Fe^{2+}	k	0.6	7.3×10^5	6.1	−9.5	132[i]
V^{V}	Sb^{III}	k	$4H_2SO_4$	2.4×10^{-2}	11.3	−32.7	128[j]
			$4HClO_4$	0.72×10^{-2}	8.5	−43.6	
V^{IV}	V^{II}	k	1 H_2SO_4	5.6	16.4		56[k]
$[Cr(NH_3)_5Cl]^{2+}$	$[Cr\{C_2H_4[N(CH_2CO_2)\text{-}(C_2H_4CO_2)]_2\}]^{2-}$	k	1 ($NaClO_4$)	7.12×10^4	7.7	−10.4	9

[a] The terms β and βc correspond to net activation processes $[Np^{VII}+(\text{reductant})]$ and $[Np^{VII}+(\text{reductant})+H^+]$ respectively. [b] Recalculation in ref. 123 of data originally given in ref. 91. [c] Also data for other mixtures of H_2SO_4 and H_3PO_4. [d] At 92 °C. [e] Only studied over the range $[H^+]=3$—5 mol l^{-1}. [f] Stoicheiometry is $Cr^{III}-Np^{V}+Np^{III}\rightarrow Cr^{III}+2Np^{IV}$. [g] At 35 °C; rate constant estimated from graph in the original paper. Rate also increased by SO_4^{2-} ion, and decreased by F^- (data in paper). [h] Rate constants tabulated for mixed solvents varying from 20% to 80% *N*-methylacetamide–water, at temperatures 30—50 °C. [i] Temperature 45 °C; higher rates at higher H_2SO_4 or $HClO_4$ concentrations. Also higher rates when HOAc is added to mixture. [j] The authors also report catalytic effects of various bases such as pyrazine and substituted pyridines. [k] At 20 °C.

[123] E. Deutsch, J. C. Sullivan, and K. O. Watkins, *Inorg. Chem.*, 1975, **14**, 550.

Table 2—*continued*

Oxidant	*Reductant*	*Rate law*	*Medium*	*Rate constant* (25 °C)	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
$[Cr(NH_3)_5Cl]^{2+}$	$[Cr(hedta)]^{2-}$	k	1 ($NaClO_4$)	3.42×10^3			9
$[Cr(NH_3)_5Cl]^{2+}$	$[Cr(edta)]^{2-}$	k	1 ($NaClO_4$)	1.24×10^3	12.9	−1.4	9[l]
$[Cr(NH_3)_5Cl]^{2+}$	[Cr(mida)]	k	1 ($NaClO_4$)	3.15			9
Fe^{III}	U^{IV}	k	1.6 H^+, 3 ($NaNO_3$)	10.1			
		$k'[H^+]^{-1.15}$	3 ($NaNO_3$)	16.8	17.6	5	105[m]
Fe^{III}	V^{III}	k	1 H_2SO_4	1.5	21.5		56[k]
$[Fe(CN)_6]^{3-}$	$[Fe(CN)_5py]^{3-}$	k	0.05 (KNO_3)	3.4×10^4	5.5	−19	125
			0	1.2×10^4			
$[Fe(CN)_5py]^{2-}$	$[Fe(CN)_6]^{4-}$	k	0.05 (KNO_3)	8.8×10^4	4.6	−21	125
			0	0.5×10^4			
$[Fe(CN)_5py]^{2-}$	$[Fe(CN)_5py]^{3-}$	k	0.05 (KNO_3)	7×10^5			125[n]
			0	2.5×10^6			
Co^{3+}	Tl^{2+}	k	0.5 H^+, 0.55 ($NaClO_4$)	9.5×10^6			17
	$[Co(CN)_5]^{3-}$	$k+k'[CN^-]$	0.1 ($LiClO_4$)	k 1.6×10^3	6	−24	126
				k' 8.3×10^4	3	−26	
	$[Co(CN)_5]^{3-}$	$k[CN^-]^0$	0.1 ($LiClO_4$)	3.1×10^7	5	−7	129[o]
$[Co^{III}(P)(H_2O)_2]^{5+}$	$[Ru(NH_3)_6]^{2+}$	$k_0+k_{Cl}[Cl^-]+k_{NCS}[NCS^-]$	0.5 Cl^-	k_0 1.2×10^5	4.8	−17	137[p]
				k_{Cl} 3.3×10^5			
				k_{NCS} 6.6×10^5			

$[Co^{III}(P)(H_2O)(NCS)]^{4+}$	$[Ru(NH_3)_6]^{2+}$	k	0.5 Cl^-	k 3.6×10^6			137[p]
$[Co^{III}(P)(H_2O)N_3]^{4+}$	$[Ru(NH_3)_6]^{2+}$	k	0.5 Cl^-	k 1.5×10^4			137[p]
$[\{Co(NH_3)_5\}_2O_2]^{5+}$	$[Ru(NH_3)_6]^{2+}$	k	0.1 ($LiClO_4$)	3.7×10^6	0.8	−26	124
$[Co(NH_3)_5F]^{2+}$	Fe^{2+}	k	0.34 ($NaClO_4$)	3.3×10^{-3}	13.4	−25.4	129[q]
		k	DMSO, 0.34 ($NaClO_4$–$KClO_4$)	4.7	8.9	−25.8	129[q,r]
		kK	DMF, 0.34 ($KClO_4$)	k 3.20; K 10.6			130[s]
$[Co(NH_3)_5Cl]^{2+}$	Fe^{2+}	k	0.34 ($NaClO_4$)	0.71×10^{-3}	15.1	23.0	129[q]
		k	DMSO, 0.34 ($NaClO_4$–$KClO_4$)	9.7×10^{-3}	21.5	3.8	129[q,r]
		kK	DMF, 0.34 ($KClO_4$)	k 1.61×10^{-3}; K 19.1			130[s]
$[Co(NH_3)_5Br]^{2+}$	Fe^{2+}	k	0.34 ($NaClO_4$)	0.46×10^{-3}	14.1	−23.9	129[q]
		k	DMSO, 0.34 ($NaClO_4$–$KClO_4$)	2.51×10^{-3}	21.8	1.9	129[q,r]
		kK	DMF, 0.34 ($KClO_4$)	k 0.34×10^{-3}; K 12.4			130[s]
$[Co(C_2O_4)_3]^{3-}$	Fe^{2+}	$k+k'[Co(C_2O_4)_3^{3-}]$	3 ($NaClO_4$)	k 6.9; k' 1.50×10^3			131

[l] Inner-sphere mechanism. [m] Catalytic step in the oxidation of U^{IV} by HNO_2; rates vary with NO_3^- concentration. [n] Estimated from data on $[Fe(CN)_6]^{3-}+[Fe(CN)_6]^{4-}$, and on cross-reaction, using the Marcus equation. [o] Inner-sphere mechanism with attack of $[Co(CN)_5]^{3-}$ at the remote heteronitrogen atom. [p] (P) = tetrakis-(4-*N*-methylpyridyl)porphine. [q] At 25.8 °C. [r] Also data for various DMSO–H_2O mixtures. [s] The composite rate constant kK is for the rate term in the form $kK[Co^{III}][Fe^{2+}]$. The stoicheiometric rate term is $kK[Co^{III}][Fe^{II}]_T(1+K[Fe^{II}]_T)^{-1}$, where k and K are as shown. Values tabulated are for 25.8 °C. The temperature dependence of kK is reported for certain Fe^{II} concentrations.

124 T. D. Hand, M. R. Hyde, and A. G. Sykes, *Inorg. Chem.*, 1975, **14**, 1720.
125 H. E. Toma and J. M. Malin, *J. Amer. Chem. Soc.*, 1975, **97**, 288.
126 H. E. Toma, *J. Inorg. Nuclear Chem.*, 1975, **37**, 785.
127 R. T. Mayhew and E. S. Amis, *J. Phys. Chem.*, 1975, **79**, 862.
128 B. B. Pal and K. K. Sengupta, *Inorg. Chem.*, 1975, **14**, 2268.
129 B. A. Matthews and D. W. Watts, *Austral. J. Chem.*, 1976, **29**, 97.
130 B. A. Matthews, J. V. Turner, and D. W. Watts, *Austral. J. Chem.*, 1976, **29**, 551.

Table 2—*continued*

Oxidant	*Reductant*	*Rate law*	*Medium*	*Rate constant* (25 °C)	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
$[Co(C_2O_4)_3]^{3-}$	Fe^{2+}	k	1 ($NaClO_4$)	23.0			131[t]
	Fe^{2+}	k	1 $HClO_4$	33.7			131[t]
	Fe^{2+}	k	3 ($NaClO_4$)	4.4			131[t,u]
	Fe^{2+}	k	3 [$Mg(ClO_4)_2$]	5.8			131[t,v]
$[Co(O_2CCH_2CO_2)_3]^{3-}$	$[Fe(CN)_6]^{4-}$	k	2.77 $K_2C_4H_2O_4$	140	13.2		136
			3.38 $Na_2C_4H_2O_4$	4.80	26.1		
		$k[Na^+]+k'[Na^+]^2$	$Na_2C_4H_2O_4$ var.	k 0.42			136
				k' 0.043			136
		$k[K^+]$	$K_2C_4H_2O_4$ var.	k 0.25			136
$[Rh(NH_3)_4]^{2+}$	$[Rh(NH_3)_4]^{2+}$	k	~0	1.4×10^7			103
$[Rh(NH_3)_4Br_2]^+$	$[Rh(NH_3)_4]^{2+}$	k	~0	1.4×10^6			103
$[AuCl_4]^-$	$[Pt(bipy)Cl_2]$	$k[Cl^-]$	MeCN	3.30	7.8	−32	102
$[AuCl_4]^-$	*trans*-$[Pt(AsEt_3)_2Cl_2]$	$k[Cl^-]$	MeCN	2.64	8.6	−30	102[w]
$[AuCl_4]^-$	*trans*-$[Pt(PEt_3)_2Cl_2]$	$k[Cl^-]$	MeCN	~0.1			102
$[AuCl_4]^-$	*trans*-$[Pt(PEt_3)_2(Ph)Cl]$	$k[Cl^-]$	MeCN	0.76	8.5	−33	102[w]
$[AuCl_4]^-$	*trans*-$[Pt(PEt_3)_2(p\text{-}MeOC_6H_4)Cl]$	$k[Cl^-]$	MeCN	1.06	9.7	−30	102[w]
$[AuCl_4]^-$	*trans*-$[Pt(PEt_3)_2(p\text{-}ClC_6H_4)Cl]$	$k[Cl^-]$	MeCN	1.32	8.5	−32	102[w]
$[AuCl_4]^-$	*trans*-$[Pt(PEt_3)_2(p\text{-}FC_6H_4)Cl]$	$k[Cl^-]$	MeCN	1.27	8.3	−33	102
$[AuCl_4]^-$	*trans*-$[Pt(PEt_3)_2(m\text{-}FC_6H_4)Cl]$	$k[Cl^-]$	MeCN	1.07	8.5	−33	102[w]
Tl^{2+}	Mn^{2+}	k	0.5 H^+, 0.75 ($NaClO_4$)	1.9×10^4			18[x]
Tl^{2+}	Fe^{2+}	k	0.25 H^+, 0.3 ($NaClO_4$)	2.6×10^6			18[x]

[t] Experiments with Fe^{III} in excess over Co^{III}. The specific rate includes a small contribution (*ca.* 10%) from the k' term. [u] At 5.2 °C. [v] At 5.8 °C. [w] There is an additional rate term of the form $k_3'k_s[Pt^{II}][AuCl_4^-]/(k_{-s}+k_3'[AuCl_4^-])$, where k_s is interpreted as the displacement of Cl^- from the Pt^{II} complex by the solvent MeCN. [x] At 22±3 °C.

[131] R. D. Cannon and J. S. Stillman, *J.C.S. Dalton*, 1976, 428.
[132] J. Ulstrup, *J.C.S. Faraday I*, 1975, **71**, 435.
[133] E. J. Hinderberger and R. C. Thompson, *Inorg. Chem.*, 1975, **14**, 784.
[134] A. Ekstrom, G. E. Batley, T. M. Florence, and Y. J. Farrar, *J. Inorg. Nuclear Chem.*, 1974, **36**, 2355.
[135] I. V. Moiseev, A. Ya. Kuperman, and N. N. Borodina, *Soviet Radiochem.*, 1975, **17**, 192.
[136] Y. Sulfab, M. S. Al-Obadie, and N. A. Al-Salem, *Z. phys. Chem. (Frankfurt)*, 1975, **94**, 77.
[137] R. F. Pasternack, *Inorg. Chem.*, 1976, **15**, 643.

Table 3 *Rate constants and activation parameters for non-complementary redox reactions involving two metal ion complexes. The expression in the column headed* Rate *is defined so that for a reaction of stoicheiometry* $aA+bB+\ldots\rightarrow$products, *the rate is given by* $R=-(1/a)\,d[A]/dt=-(1/b)\,d[B]/dt$, etc. *For other conventions, see Table* 1

Reaction	*Rate* (25 °C)	*Medium*	*Rate constants*	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
$U^{IV}+2Fe^{III}\rightarrow U^{VI}+2Fe^{II}$	$\frac{k_3k_2[U^{IV}][Fe^{III}]^2}{k_{-2}[Fe^{II}]+k_3[Fe^{III}]}$	8 HCl	k_2 0.32 k_3/k_{-2} 5.83			106[a]
$Cr^{VI}+3Pu^{III}\rightarrow Cr^{III}+3Pu^{IV}$	$k[HCrO_4^-][Pu^{3+}][H^+]+k'[HCrO_4^-][Pu^{3+}][H^+]^2$	1 ($LiClO_4$)	k 8.6×10^3 k' 0.23×10^3	−0.75	−42	107[b]
$2MnO_4^-+5Pu^{4+}+2H_2O\rightarrow 2Mn^{2+}+5PuO_2^{2+}+4H^+$	$k[MnO_4^-][Pu^{4+}][H^+]^{-2}$	3 ($NaClO_4$)	68	21.7	21	105
$8MnO_4^-+5RuNO^{3+}+5H^+\rightarrow 8Mn^{2+}+5RuO_4+5NO_3^-+2H_2O$	$k[MnO_4^-][RuNO^{3+}]$	2 H^+	k 1.98×10^{-3}			138[c]
$2Fe^{3+}+Sn^{2+}\rightarrow 2Fe^{2+}+Sn^{IV}$	$\{k_1k_2[Fe^{3+}]+k_{-1}k_3[Fe^{2+}]+(2)k_2k_3[Sn^{2+}]\}\times[Ta_6Cl_{12}][Sn^{2+}]/\{k_1[Fe^{3+}]+k_{-1}[Fe^{2+}]+(2)k_2[Sn^{2+}]\}$	1.1 ($NaClO_4$)	k_1 28.5 k_{-1} 830 k_2 18.7 k_3 6.3×10^{-3}			112[d]
$2Mn^{3+}+Pu^{4+}+2H_2O\rightarrow 2Mn^{2+}+PuO_2^{2+}$	$k[Mn^{3+}][Pu^{4+}][H^+]^{-2}+k'[Mn^{3+}][Pu^{4+}][H^+]^{-3}$	3.05 ($NaClO_4$)	k 22 k' 106			105
$2Mn^{III}+Pu^{IV}\rightarrow 2Mn^{II}+Pu^{VI}$	$k[Mn^{III}][Pu^{IV}]$	3 $HClO_4$	5.25	15.7	4	105[e]
$2Fe^{III}+Sn^{II}\rightarrow 2Fe^{II}+Sn^{IV}$	$\sum_{i=3}^{6} k_i[Fe^{3+}][Sn^{2+}][Cl^-]^i$	2 ($H(ClO_4)$)	k_3 75 k_4 8.3×10^2 k_5 4.0×10^3 k_6 4.0×10^3	25.0 25.0 25.0 25.0	34.0 38.8 42.1 42.1	58
$2[Fe(phen)_3]^{3+}+[Mo_2O_4(edta)]^{2-}\rightarrow 2[Fe(phen)_3]^{3+}+2Mo^V$	$\frac{k_1k_2[Fe(phen)_3^{3+}][Mo_2O_4(edta)^{2-}]}{k_2+k_{-1}[Fe(phen)_3^{2+}]}$	1 ($LiClO_4$)	k_1 1.9×10^3 k_{-1}/k_2 1.17×10^4	16.6 −4.0	12.3 5.2	109
$2Co^{3+}+Sn^{2+}\rightarrow 2Co^{2+}+Sn^{4+}$	$k[Co^{3+}][Sn^{2+}][H^+]^{-1}+k'[Co^{3+}][Sn^{2+}][H^+]^{-2}$	2 ($LiClO_4$)	k k'	13.2 17.4	5.2 17	113 113
$2[IrCl_6]^{2-}+[Mo_2O_4(edta)]^{2-}\rightarrow 2[IrCl_6]^{3-}+2Mo^V$	$\frac{k_1k_2[IrCl_6^{2-}][Mo_2O_4(edta)^{2-}]}{k_2+k_{-1}[IrCl_6^{2-}]}$	1 ($LiClO_4$)	k_1 6.61 k_{-1}/k_2 1.74×10^3	13.3 −2.9	−10.0 5.1	109
$[PtCl_6]^{2-}+2V^{2+}\rightarrow[PtCl_4]^{2-}+2V^{3+}+2Cl^-$	$k[PtCl_6^{2-}][V^{2+}][H^+]^0$	1 ($LiClO_4$)	3.36×10^4	4.6	−22.4	110

$[Pt(NH_3)_5Cl]^{2+}+H^++2V^{2+}\rightarrow$ $[Pt(NH_3)_4]^{2+}+2V^{3+}+NH_4^++Cl^-$	$k[Pt(NH_3)_5Cl^{2+}][V^{2+}][H^+]^0$	1 ($LiClO_4$)	1.15	9.9	−25.1	110
$[Pt(NH_3)_5Cl]^{3+}+2[Ru(NH_3)_6]^{2+}+$ $H^+\rightarrow[Pt(NH_3)_4]^{2+}+$ $2[Ru(NH_3)_6]^{3+}+NH_4^++Cl^-$	$k[Pt(NH_3)_5Cl^{2+}][Ru(NH_3)_6^{2+}]$	1 ($LiClO_4$)	110			110[f]
$MnO_4^-+5VO^{2+}+H_2O\rightarrow$ $Mn^{2+}+5VO_2^++2H^+$	$k[MnO_4^-][VO^{2+}]$	1 $HClO_4$	105	10.8	−12.9	104
	$(k_0+k_1[H^+])[MnO_4^-][VO^{2+}]$	1 ($NaClO_4$)	$\begin{cases} k_0\ 73 \\ k_1\ 29 \end{cases}$			104

[a] Also measurements of equilibrium constant $[U^{VI}]^{1/2}[Fe^{II}]/[U^{IV}]^{1/2}[Fe^{III}]=31$. [b] Rate law cited in the limiting case, in the absence of $[Pu^{4+}]$. For details see text. [c] At 50 °C. [d] The term $[Ta_6Cl_{12}]$ denotes the total concentration of $[Ta_6Cl_{12}]^{n+}$ ions present in the reacting mixture; they mainly consist of $[Ta_6Cl_{12}]^{3+}$. The rate constants correspond to the following elementary steps: k_1, $Fe^{3+}+[TaCl_{12}]^{3+}\rightarrow Fe^{2+}+[Ta_6Cl_{12}]^{4+}$; k_{-1}, reverse of k_1; k_2, $[Ta_6Cl_{12}]^{4+}+Sn^{2+}\rightarrow[Ta_6Cl_{12}]^{3+}+Sn^{III}$ *or* $[Ta_6Cl_{12}]^{2+}+Sn^{IV}$; k_3, $[Ta_6Cl_{12}]^{3+}+Sn^{2+}\rightarrow[Ta_6Cl_{12}]^{2+}+Sn^{III}$. The factors (2) in parentheses are included or omitted depending on which of certain alternative rapid reactions follow after these rate-determining ones. [e] No experiments to test inhibition by products. [f] Temperature dependence data also tabulated.

[138] V. S. Koltunov and R. G. Denotkina, *Jad. Energ.*, 1974, **20**, 380 (*Chem. Abs.*, 1975, **82**, 77579).

2
Metal Ion–Ligand Redox Reactions

BY A. G. LAPPIN

The format used in this chapter is similar to that in previous volumes. An attempt has been made to cover the area of reactions of metal ions in high oxidation states with inorganic and organic substrates as comprehensively as possible although some selectivity has been imposed. Where possible compilations of data have been assembled to allow for comparison of rate data.

In the period covered by this volume, a book chapter[1] and a whole book[2] dealing with aspects of metal ion–ligand redox reactions have been published.

1 Chromium (VI)

The kinetics of the oxidation of hydrazine by $[HCrO_4]^-$ have been reported.[3] Only molecular nitrogen is formed in the overall reaction, indicating a simultaneous two-electron-transfer process:

$$4[HCrO_4]^- + 3N_2H_5^+ + 13H^+ + 8H_2O \longrightarrow 4[Cr(H_2O)_6]^{3+} + 3N_2$$

The rate is first-order in both oxidant and substrate and the proposed mechanism involves rate-determining formation of a weak complex:

$$[HCrO_4]^- + N_2H_5^+ \overset{\text{slow}}{\rightleftharpoons} {}^-O_3CrNHN\overset{+}{H}H_3 + H_2O$$

$${}^-O_3CrNHN\overset{+}{H}H_3 \overset{\text{fast}}{\longrightarrow} [HCrO_3]^- + NHNH_2^+$$

A number of subsequent reactions steps are possible.

In a second paper on the same reaction,[4] kinetic evidence for complex formation was obtained. The rate law in sulphate media,

$$-d[Cr^{VI}]/dt = k_2[N_2H_4,H_2SO_4][Cr^{VI}][H^+]$$

becomes zero-order in hydrazine sulphate at high concentrations. Sulphate and bisulphate affect the reaction by adjusting the acidity *via* the equilibrium

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$$

Chloride has an inhibiting effect and the formation of a less reactive $[ClCrO_3]^-$

[1] R. A. Shelden and J. K. Kochi, *Adv. Catalysis*, 1976, **25**, 274.
[2] D. Benson, 'Mechanisms of Oxidation by Metal Ions', Reaction Mechanisms in Organic Chemistry, Vol. 10, Elsevier, New York, 1976.
[3] K. K. S. Gupta, S. S. Gupta, and H. R. Chatterjee, *J. Inorg. Nuclear Chem.*, 1976, **38**, 549.
[4] V. M. S. Ramanujam, S. Sundaram, and N. Venkatasubramanian, *Inorg. Chim. Acta*, 1975, **13**, 133.

species is proposed. As in the previous paper, the only substrate product was nitrogen and the proposed mechanism involves two-electron oxidation steps:

$$^{-}O_3CrNH_2\overset{+}{N}H_3 \longrightarrow Cr^{IV} + N_2H_2$$

$$Cr^{IV} + Cr^{VI} \longrightarrow 2Cr^{V}$$

$$Cr^{V} + N_2H_2 \longrightarrow Cr^{III}$$

Added edta has an accelerative effect on the reaction with local rate maxima at edta:Cr^{VI} ratios of 1:2 and 1:1. The proposed mechanism involves stable Cr^{VI}–edta complexes and ternary complex formation with hydrazine:

$$2Cr^{VI} + \text{edta} \rightleftharpoons [Cr^{VI}_2(\text{edta})] \overset{\text{edta}}{\rightleftharpoons} 2[Cr^{VI}(\text{edta})]$$

$$[Cr^{VI}(\text{edta})] + N_2H_4 \rightleftharpoons [Cr^{VI},N_2H_4,\text{edta}] \overset{\text{slow}}{\longrightarrow} [Cr^{IV}(\text{edta})] + N_2H_2$$

$$[Cr^{IV}(\text{edta})] \overset{\text{fast}}{\longrightarrow} [Cr^{III}(\text{edta})]$$

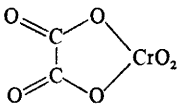
The purple $[Cr^{III}(\text{edta})]$ complex was shown to be a reaction product.

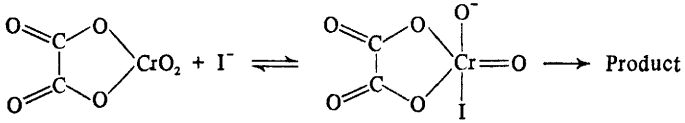
The effect of edta on the reaction was reinvestigated in another paper.[5] Though the above experimental results were verified, the reaction with added edta was found to be pH-dependent and the local rate maxima resulted from a combination of a monotonic edta acceleration and a rate decrease due to change in pH. When the pH was maintained constant, no maxima were observed. Spectroscopic evidence for Cr^{VI}–edta complexes was attributed to experimental error in the measurements.

In the oxalic acid-catalysed oxidation of iodide,[6] the complex rate-law dependence of iodide ion, changing from first-order at low reagent concentrations to zero-order at high concentrations, suggests a mechanism involving reaction of a Cr^{VI}–oxalate chelate. The decomposition of the intermediate complex (1) probably proceeds in a one-electron step producing I· and a Cr^{V}–oxalate complex. Oxalate catalysis is explained by the stabilization of the Cr^{V} intermediate enhancing the oxidizing power of Cr^{VI}.

$$[HCrO_4]^- + (CO_2H)_2 \rightleftharpoons [HO_2CCO_2CrO_3]^-$$

$$[HO_2CCO_2CrO_3]^- + H^+ \rightleftharpoons$$





(1)

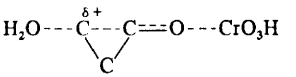
Relief of ring strain in the oxidation of cyclopropanols causes an acceleration in their rates of reaction with Cr^{VI} compared with other secondary alcohols.[7] The same

[5] M. T. Beck, D. Durham, and G. Rabai, *Inorg. Chim. Acta*, 1976, **18**, L17.
[6] G. F. Vandegrift and J. Roček, *J. Amer. Chem. Soc.*, 1976, **98**, 1371.
[7] A. M. Martinez, G. E. Cushmac, and J. Roček, *J. Amer. Chem. Soc.*, 1975, **97**, 6502.

effect also causes a change in mechanism from the normal C—H bond cleavage to ring-opening, C—C bond cleavage. Free hydroxyl is a prerequisite for the enhanced reactivity and the rate law,

$$-\mathrm{d}[Cr^{VI}]/\mathrm{d}t = (k'[H^+] + k''[H^+]^2)[Cr^{VI}][\text{cyclopropanol}]$$

suggests two pathways *via* the chromate esters $ROCrO_3H$ and $ROCrO_3H_2^+$. The values for k' and k'' are 1.8 l^2 mol^{-2} s^{-1} and 30 l^3 mol^{-3} s^{-1} for cyclopropanol (T = 20 °C, I = 0.01 mol l^{-1}) while those for the tertiary 1-methylcyclopropanol are 7.9 l^2 mol^{-2} s^{-1} and 160 l^3 mol^{-3} s^{-1}, contrary to the trend expected with aliphatic alcohols. A study[7] of the relative rates of oxidation of a number of alkyl- and aryl-substituted cyclopropanols indicates that the rate increases with steric strain, β-substituents having a larger effect than α-substituents, and with electron-donating power of the substituents. The proposed mechanism involves formation of a chromate ester followed by two-electron transfers. A transition state of the type (2) might be formulated.



(2)

Steric effects were also noted[8] in the oxidation of β-substituted cyclopentanols by Cr^{VI}. The rates show only a small increase relative to cyclohexanol and, since 1,3-non-bonded interactions in five-membered rings may be relieved by pseudorotation, steric acceleration by torsional strain is indicated. Similarities in the activation parameters suggest a common mechanistic path involving chromate esters.

Force-field calculations have been used to correlate the rates of oxidation of secondary alcohols with steric strain.[9] The results indicate that the chromate ester transition state is substantially like the ketone product but suggest that the steric effect of the ketone is not fully developed. The temperature dependence of the kinetic isotope criterion has been applied to studies of the Cr^{VI} oxidation of a variety of alcohols in an attempt to distinguish between three possible mechanisms:[10]

(i) hydrogen transfer to external base without specification of the timing of bond-breaking and -making;
(ii) cyclic hydrogen transfer with concerted bond-making and -breaking;
(iii) cyclic hydrogen transfer with formation of a radical intermediate.

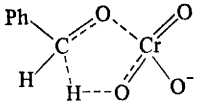
Alcohols which are regarded as being normal in their behaviour display parameters which are fully consistent with a pericyclic transition state (ii). Alcohols which are highly hindered or have electron-withdrawing substituents require a transition-state structure which allows hydrogen transfer through the solvent (i). This latter mechanism resembles the transfer of electrons through a bridging structure of water molecules.

These conclusions are substantiated by a study of the temperature dependence of

[8] P. S. Weschler and B. Fuchs, *J.C.S. Perkin II*, 1976, 943.
[9] P. Müller and J.-C. Perlberger, *J. Amer. Chem. Soc.*, 1975, **97**, 6862.
[10] H. Kwart and J. H. Nickle, *J. Amer. Chem. Soc.*, 1976, **98**, 2881.

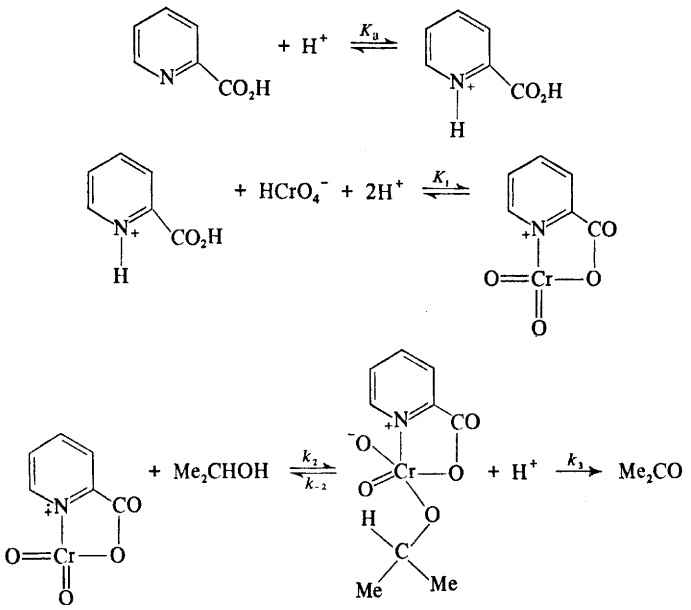
the kinetic isotope criterion in the oxidation of benzhydrol and fluoren-9-ol.[11] These normal alcohols show behaviour consistent with a pericyclic transition state.

In neutral aqueous solution at elevated temperatures, sodium dichromate oxidizes benzyl alcohol to benzaldehyde.[12] The mechanism involves formation of a chromate ester and the unfavourable entropy of activation may be due to formation of a cyclic transition state (3) in which the carbonyl group is developed, while a substantial isotope effect ($k_H/k_D = 9.4 \pm 0.9$) indicates transfer of a proton. The oxidation of benzaldehyde to benzoic acid is substantially slower and involves a pre-equilibrium step in which the carbonyl is hydrated.[12] A similar cyclic transition state is proposed, however.



(3)

Picolinic acid has been found[13] to act as a catalyst in the oxidation of isopropyl alcohol by chromic acid. The rate, at constant acidity, is first-order in picolinic acid, hydrogen chromate, and isopropyl alcohol concentrations and the acidity dependence



Scheme 1

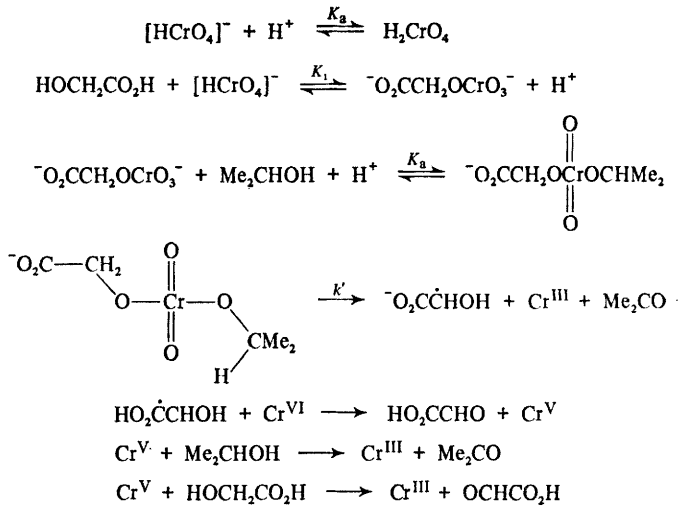
may be explained by the proposed mechanism (Scheme 1) with the rate equation

$$\frac{-d[HCrO_4^-]}{dt} = \frac{K_a K_1 k_2 k_3 [PA]_T [ROH][HCrO_4^-][H^+]^2}{k_3 K_a + (k_{-2} K_a + k_3)[H^+] + k_{-2}[H^+]^2}$$

[11] V. M. S. Ramanujan and N. Venkatasubramanian, *Indian J. Chem.*, 1975, **13**, 285.
[12] D. G. Lee and V. A. Spitzer, *Canad. J. Chem.*, 1975, **53**, 3709.
[13] T.-Y. Peng and J. Roček, *J. Amer. Chem. Soc.*, 1976, **98**, 1026.

where $[PA]_T$ represents the total picolinic acid concentration. The catalytic effect is related to the proximity of the nitrogen and the carboxy-group of picolinic acid and depends on its ability to stabilize intermediate chromium valence states, probably chromium(IV).

The rate of oxidation of isopropyl alcohol is also enhanced by the presence of glycolic acid (GA) as a co-oxidant.[14] The rate law is complex but a kinetic term, first-order in $[HCrO_4^-]$, [GA], and [ROH], indicates that the reduction of chromium(VI) through a termolecular complex must be more feasible than through either Cr^{IV}–glycolic acid or Cr^{IV}–alcohol complexes themselves. The reason for this preference is considered to be the avoidance of unstable intermediates, particularly Cr^{IV}. This is accomplished by a one-step three-electron reduction of chromium(VI) to chromium(III) (Scheme 2). Two of the electrons are provided by the alcohol and the third by



Scheme 2

glycolic acid. The mechanism differs from that found with the co-oxidation of oxalic acid and isopropyl alcohol[15] in that two C—H bonds are simultaneously broken rather than a single C—C bond. This results in isotope effects of equal magnitude exhibited by both the alcohol and glycolic acid.[14]

A number of reports of the oxidation of 2-hydroxy-carboxylic acids have appeared. In one paper[16] the rates and mechanisms of six substituted glycolic acid derivatives are compared. Chromate(VI)–substrate complexes could be detected kinetically with glycolic and benzilic acids and could not be ruled out with the others. The proposed mechanism for glycolic acid involves a series of one- and two-electron changes:

[14] F. Hasan and J. Roček, *J. Amer. Chem. Soc.*, 1975, **97**, 3762.
[15] F. Hasan and J. Roček, *J. Amer. Chem. Soc.*, 1972, **94**, 3181.
[16] K. K. S. Gupta, A. K. Chatterjee, T. Sarkar, and S. S. Gupta, *Indian J. Chem.*, 1975, **13**, 1024.

$$HO_2CCH_2OH + H^+ + [HCrO_4]^- \rightleftharpoons HO_2CCH_2OCrO_2OH + H_2O$$

$$HO_2CCH_2OCrO_2OH \longrightarrow HOO\dot{C}CHO + H_2CrO_3$$

$$Cr^{IV} + Cr^{VI} \longrightarrow 2Cr^{V}$$

$$HOO\dot{C}CH_2OH + Cr^{V} \longrightarrow HO_2C\overset{+}{C}HOH + Cr^{III} + H^+$$

$$HO_2C\overset{+}{C}HOH \longrightarrow HO_2CCHO + H^+$$

$$HO_2CCH(OH)_2 + Cr^{V} \longrightarrow H\overset{+}{C}(OH)_2 + CO_2 + Cr^{III} + H^+$$

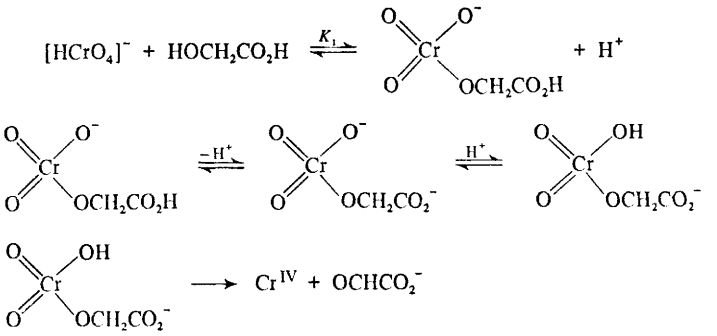
$$H\overset{+}{C}(OH)_2 \longrightarrow HCO_2H + H^+$$

Although the major product is glyoxylic acid, the last two reaction steps are required to explain the observation that formic acid is produced in conditions of excess substrate. The oxidation of benzilic acid is similar but proceeds only to the ketone stage.

An alternative mechanism incorporating simultaneous three-electron oxidation of glycolic acid is proposed in a second paper.[17] The rate law,

$$-d[Cr^{VI}]/dt = K_1[HCrO_4^-][GA](k_2 + k_3[GA])$$

indicates two reaction pathways. The products of the first pathway (k_2) are glyoxylic acid, formaldehyde, and carbon dioxide. Glyoxylic acid is formed in a two-electron step involving either Cr^{VI} or Cr^{V} as oxidant. The Cr^{IV} product of the former process favours C—C bond cleavage producing formaldehyde and $CO_2^{-\bullet}$ radicals, as shown in Scheme 3. Formic acid is produced only by oxidation of glyoxylic acid. The second



$$Cr^{IV} + HOCH_2CO_2H \longrightarrow Cr^{III} + CH_2O + \cdot CO_2H$$

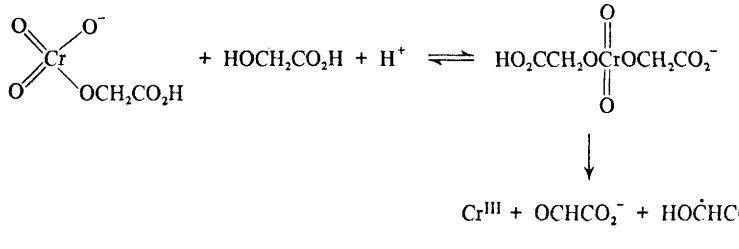
$$\cdot CO_2H + Cr^{VI} \longrightarrow CO_2 + Cr^{V}$$

$$HOCH_2CO_2H + Cr^{V} \longrightarrow OCHCO_2H + Cr^{III}$$

Scheme 3

pathway (k_3) proceeds by a single three-electron-transfer process involving two moles of glycolic acid and producing Cr^{III}, glyoxylic acid, and $HO\dot{C}HCO_2H$. These latter species react with Cr^{VI} to form a detectable Cr^{V} intermediate (Scheme 4).

[17] F. Hasan and J. Roček, *J. Amer. Chem. Soc.*, 1975, **97**, 1444.

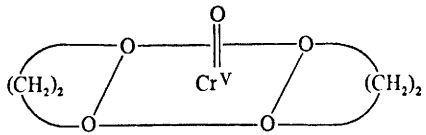


$$HOCHCO_2^- + Cr^{VI} \longrightarrow OCHCO_2H + Cr^V$$

Scheme 4

The two tertiary hydroxy-acids citric acid and 2-hydroxy-2-methylbutyric acid form Cr^V complexes of considerable stability.[18] The kinetic behaviour observed in the oxidation of these compounds by chromic acid is complex, proceeding slowly to 35—40% depletion of Cr^{VI} and then rapidly to completion. The latter reaction is synchronous with the disappearance of an intermediate which absorbs at 750 nm and is formed during the initial reaction. Consideration of the overall stoicheiometry reveals that this intermediate has two-thirds the oxidizing power of Cr^{VI} and may therefore be either Cr^{IV} or an equimolar mixture of Cr^{III} and Cr^V. The latter explanation is preferred since Cr^{IV} is known to be less stable in aqueous solution and the spectra are consistent with Cr^V.

Chromium(v) is also detected in the course of oxidation of ethylene glycol by dichromate.[19] The e.s.r. spectrum is consistent with a bis-complex (4) and its formation may be enhanced photochemically. A similar result is reported in the photochemical oxidation of pinacol by dichromate.[20]



(4)

Two papers involving the interaction of Cr^{VI} with sulphur-containing substrates have appeared. In the first,[21] thiourea and *NN'*-ethylenethiourea (L) are shown to form spectrophotometrically detectable complexes:

$$[HCrO_4]^- + H^+ + L \overset{K}{\rightleftharpoons} LCrO_3 + H_2O$$

The values of K, 380 and 256 l mol^{-1} respectively for thiourea and its *NN'*-ethylene derivative, do not change significantly with substitution on nitrogen, suggesting Cr—S bonding. This is consistent with a red shift in the charge-transfer band to 380 nm. An oxidation mechanism proceeding by three parallel pathways,

[18] M. Krumpolc and J. Roček, *J. Amer. Chem. Soc.*, 1976, **98**, 872.
[19] M. Mitewa, P. R. Bontchev, K. Kabassanov, and A. Malinovski, *Inorg. Nuclear Chem. Letters*, 1975, **11**, 793.
[20] P. R. Bontchev, M. Mitewa, K. Kabassanov, and A. Malinovski, *Inorg. Nuclear Chem. Letters*, 1975, **11**, 799.
[21] M. A. Olatunji and A. McAuley, *J.C.S. Dalton*, 1975, 682.

$$O_3CrL \xrightarrow{k_0} Cr^V + L\cdot$$

$$O_3CrL + H^+ + L \xrightarrow{k_1} Cr^{IV} + L^1{-}L^1$$

$$O_3CrL + 2H^+ + L \xrightarrow{k_2} Cr^{IV} + L^1{-}L^1$$

$$2L\cdot \longrightarrow L^1{-}L^1$$

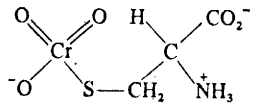
(L = thiourea, $L^1{-}L^1$ = disulphide)

is required to explain the observed rate law

$$\frac{-d[Cr^{VI}]}{dt} = \frac{(k_0 + k_1[H^+][L] + k_2[H^+]^2[L])K[L][H^+][Cr^{VI}]}{1 + K[L][H^+]}$$

Although the pathway involving Cr^V is a minor one, radicals were detected. The principal pathways allow a two-electron transfer to two moles of reductant with incipient disulphide formation in the transition state. The role of the hydrogen ions may be to doubly protonate the chromate complex and allow easier access to co-ordination of the second thiourea. Labile Cr^{IV} formed in the rate-determining step reacts with excess thiourea to form a mixture of hexa-aquochromium(III) and a chromium(III)–thiourea complex.

The second paper[22] deals with the reaction of Cr^{VI} with L-cysteine in perchlorate media. Oxidation proceeds through a similar sulphur-bonded complex (5) with an



(5)

absorption maximum at 420 nm ($\varepsilon = 1180\ l\ mol^{-1}\ cm^{-1}$) and the kinetics and mechanism of complex formation are discussed. The rate law for the redox step,

$$\frac{-d[Cr^{VI}]}{dt} = \frac{K_1(k_1[H^+] + k_2[H_3L^+])[H_3L^+][Cr^{VI}]}{1 + K_1[H_3L^+]}$$

is consistent with the mechanism

$$H_2L + [HOCrO_3]^- \overset{K_1}{\rightleftharpoons} [HLCrO_3]^- + H_2O$$

$$[HLCrO_3]^- + H^+ \xrightarrow{k_1} Cr^V$$

$$[HLCrO_3]^- + H_3L^+ \xrightarrow{k_2} Cr^{IV}$$

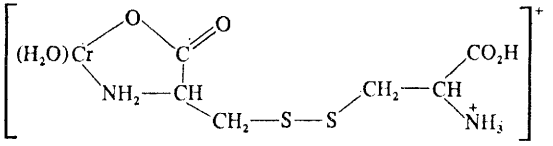
where $K_1 = 1030\ l\ mol^{-1}$, $k_1 = 9.4 \times 10^{-2}\ l^2\ mol^{-2}\ s^{-1}$, and $k_2 = 12 \times 10^{-3}\ l^2\ mol^{-2}\ s^{-1}$. The latter pathway provides a low-energy route for disulphide formation as was found with the thiourea derivates.[21] When compared with other systems which have similar pathways, second-order in substrate, the rates indicate a similar process. Although the stoicheiometry of the reaction was determined as

$$3H_2L + Cr^{VI} \longrightarrow Cr^{III} + \tfrac{3}{2}(HL^1{-}L^1H) + 3H^+$$

the chromium(III) product is not the hexa-aquo-ion. It is suggested that cysteine

[22] J. P. McCann and A. McAuley, *J.C.S. Dalton*, 1975, 783.

co-ordinates to chromium in a labile intermediate valence state which is then reduced to form (6).



(6)

Random-walk calculations have been used[23] to explain why, in the oxidation of fatty acids, C-7—C-10 methane protons are oxidized more than others in acetic acid media:

$$MeO_2C(CH_2)_nMe + CrO_3 \longrightarrow MeO_2C(CH_2)_xCO(CH_2)_yMe \quad (x + y = n - 1)$$

The model which involves intramolecular contact of the carbon chain with activated oxygen on a tetrahedral diacetylchromium(VI) dioxide agrees fairly well with the experimental results.

2 Iron(III)

Substituted derivatives of mercaptoacetic acid form five-membered chelate complexes with iron(III) in aqueous perchloric acid solution:[24]

$$[Fe(H_2O)_6]^{3+} + HORSH \overset{K_1}{\rightleftharpoons} [FeORS]^+ + H^+$$

Equilibrium constants K_1 reflect the degree of substitution, decreasing from 2.7 for mercaptoacetic acid to 1.31 for 2-mercaptopropanoic acid, and to 0.35 for 2-mercapto-2-methylpropanoic acid ($T = 20$ °C, $I = 1.0$ mol l^{-1}). The trend reflects steric interaction in the five-membered ring. These complexes decompose to yield the corresponding disulphides and iron(III) with a bimolecular rate-determining step.[25] The overall mechanism,

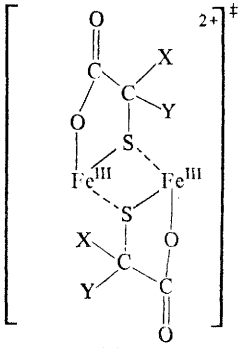
$$[Fe(H_2O)_6]^{3+} \overset{K_1}{\rightleftharpoons} [Fe(H_2O)_5OH]^{2+} + H^+$$

$$[Fe(H_2O)_5OH]^{2+} + HORSH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [FeORS]^+ + H^+$$

$$2[FeORS]^+ \xrightarrow{k_0} 2Fe^{II} + \bar{O}RSSR\bar{O}$$

yields a complex rate expression since the complex-formation rates are comparable with the redox rate k_0. Electron transfer takes place in a dinuclear transition state (7), which allows formation of the disulphide product without recourse to high-energy radical species. The rate constant k_0 decreases with increasing bulk of the substituents X and Y as shown in Table 1. This change in k_0, a factor of three, is insufficient to explain a 10^3-fold decrease in the rate of disappearance of the transient in going from

[23] M. A. Winnik and D. S. Saunders, *J.C.S. Chem. Comm.*, 1976, 156.
[24] A. G. Lappin and A. McAuley, *J.C.S. Dalton*, 1975, 1560.
[25] K. J. Ellis, A. G. Lappin, and A. McAuley, *J.C.S. Dalton*, 1975, 1930.



(7)

Table 1 *Effect of substituents* X *and* Y *on the dimerization of* $[Fe(SCXYCO_2)]^+$ ($T = 25$ °C, $I = 1.0$ l mol^{-1})[25]

X	Y	k_0/l mol^{-1} s^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
H	H	167	5.3	−31
H	Me	130	9.1	−18
Me	Me	47	13.6	−52
H	CH_2CO_2H	68	10.1	−16

mercaptoacetic acid to its dimethyl derivative. The rate-controlling factor is the magnitude of the equilibrium K_1, which on varying by a factor of ten[24] for the above substrates causes a 100-fold change in the product $k_0[FeORS^+]^2$.

The reduction of a series of substituted tris-(2,2′-bipyridyl) and tris-(1,10-phenanthroline) complexes of iron(III) and osmium(III) with hydroxide ion have been studied.[26] The overall reaction

$$4[M(LL)_3]^{3+} + 4OH^- \longrightarrow 4[M(LL)_3]^{2+} + O_2 + 2H_2O$$

obeys a simple rate law:

$$-d[Fe(LL)_3{}^{3+}]/dt = k[Fe(LL)_3{}^{3+}][OH^-]$$

Although free-energy relationships exist between the rates and the standard free-energy changes for the metal complexes, these hold only for each metal and each ligand type. The rates of reduction by Os^{III} are lower than with Fe^{III} complexes (Table 2), and phenanthroline complexes react faster than bipyridyl complexes. The activation enthalpies are consistently smaller than the standard enthalpy change for the reaction

$$[M(LL)_3]^{3+} + OH^- \longrightarrow [M(LL)_3]^{2+} + \cdot OH$$

which suggests that the mechanism may involve an intermediate complex:

$$[M(LL)_3]^{3+} + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [M(LL)_3OH]^{2+} \xrightarrow{k_2} \text{products}$$

This intermediate is depicted as a radical, explaining the greater reactivity of

[26] G. Nord and O. Wernberg, *J.C.S. Dalton*, 1975, 845.

Table 2 *Rate and thermodynamic parameters for the reactions of substituted polypyridyl complexes of* Fe^{III}, Os^{III}, *and* Ru^{III} *with non-metallic substrates* ($T = 25$ °C, $I = 1.0$ mol l^{-1})

Reaction	k/ l mol^{-1} s^{-1}	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal K^{-1} mol^{-1}	*Ref.*
$[Fe(phen)_3]^{3+}$ + OH^-	421	10.9	−10.0	26
$[Fe(5\text{-}Mephen)_3]^{3+}$ + OH^-	190			26
$[Fe(5,6\text{-}Me_2phen)_3]^{3+}$ + OH^-	117	9.1	−18.6	26
$[Fe(4,7\text{-}Me_2phen)]_3^{3+}$ + OH^-	34.8	10.3	−17.1	26
$[Fe(3,4,7,8\text{-}Me_4phen)_3]^{3+}$ + OH^-	16.9	15.1	−2.9	26
$[Fe(4,7\text{-}Me_2phen)_3]^{3+}$ + CXO[a]	0.03			28
$[Fe(5\text{-}Phphen)_3]^{3+}$ + CXO	6.65			28
$[Fe\{4,7\text{-}(PhSO_3H)_2phen\}_3]^{3+}$ + CXO	7.00			28
$[Fe(5\text{-}Clphen)_3]^{3+}$ + CXO	11.6			28
$[Fe(5\text{-}Brphen)_3]^{3+}$ + CXO	9.72			28
$[Fe(5\text{-}NO_2phen)_3]^{3+}$ + CXO	45.0			28
$[Fe(bipy)_3]^{3+}$ + OH^-	15.8	14.8	−4.1	26
$[Fe(4,4'\text{-}Me_2bipy)_3]^{3+}$ + OH^-	1.6	12.9	−14.3	26
$[Fe(bipy)_3]^{3+}$ + CXO	0.72			28
$[Os(phen)_3]^{3+}$ + OH^-	156	11.9	−8.4	26
$[Os(5\text{-}Mephen)_3]^{3+}$ + OH^-	93	8.6	−19	26
$[Os(bipy)_3]^{3+}$ + OH^-	4.7	15.6	−3.1	26
$[Os(4,4'Me_2bipy)_3]^{3+}$ + OH^-	0.3	15.3	−11.0	26
$[Ru(phen)_3]^{3+}$ + CXO	40.6			28
$[Ru(bipy)_3]^{3+}$ + CXO	12.1			28

[a] CXO = cyclohexanone.

phenanthroline complexes over bipyridyl complexes in terms of increased resonance stabilization of this species.

Thiocyanate is oxidized[27] by phenanthroline complexes of iron(III) according to the equation

$$6[Fe(phen)_3]^{3+} + SCN^- + 4H_2O \longrightarrow 6[Fe(phen)_3]^{2+} + CN^- + SO_4^{2-} + 8H^+$$

The rate expression,

$$d[Fe(phen)_3^{2+}]/dt = k_3[SCN^-]_T^2[Fe(phen)_3^{3+}]$$

has an acidity dependence which suggests that the protonated form of thiocyanate is inactive. To explain the second-order dependence on thiocyanate ion, a reactive intermediate $[Fe(phen)_3SCN]^{2+}$ is proposed:

$$[Fe(phen)_3]^{3+} + SCN^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Fe(phen)_3SCN]^{2+}$$

$$[Fe(phen)_3SCN]^{2+} + SCN^- \xrightarrow{k_3} [Fe(phen)_3]^{2+} + (SCN)_2^{-\bullet}$$

Although the nature of this intermediate is not directly established, the determination of k_1 (~ 55 l mol^{-1} s^{-1}) in acetone favours a radical-cation species rather than an ion pair whose rate of formation would be diffusion controlled. Direct reaction of $[Fe(phen)_3]^{3+}$ with SCN^- to form $^{\bullet}SCN$ is thermodynamically unfavourable and this initial complex formation probably serves to lower the potential energy for subsequent electron transfer. The overall rate constants (k_3k_1/k_{-1}) obey the Marcus free-

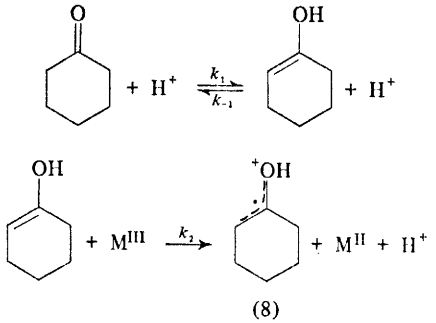
[27] F. T. T. Ng and P. M. Henry, *Canad. J. Chem.*, 1975, **53**, 3319.

energy relationship with the exception of the 4,7-phenanthroline derivative, which could provide steric hindrance to the complex formation.

The same authors also studied the polypyridyl-iron(III) and -ruthenium(III) oxidations of cyclohexanone in 1.0M-H_2SO_4.[28] Under these conditions a simple rate expression was obtained:

$$d[M^{II}]/dt = k[M^{III}][\text{cyclohexanone}]$$

At lower acidities and high oxidant concentrations, however, the rate became zero-order in oxidant and first-order in hydrogen ion, the limiting rate constant being similar to that for the acid-catalysed enolization of cyclohexanone. The mechanism



(8)

Scheme 5

(Scheme 5), in which reaction occurs only with the enol form, yields the rate expression

$$\frac{d[Fe^{II}]}{dt} = \frac{k_1k_2[\text{cyclohexanone}][H^+][Fe^{III}]}{k_{-1}[H^+] + k_2[Fe^{III}]}$$

A linear free-energy relationship between the composites $k_2' = k_1k_2/k_{-1}$ and the metal electrode potentials had a slope of 0.51 ± 0.06, close to the theoretical Marcus value. Values for both iron(III) and ruthenium(III) fall on the same line, indicating that the outer-sphere reaction is little affected by the size of the metal *d*-orbitals. It is suggested that the electron transfer takes place *via* the periphery of the polypyridyl ring. An isotope effect, $k_2'(D_2O)/k_2'(H_2O) = 2.7$, can be accounted for by the (k_1/k_{-1}) term indicative of electron transfer before loss of proton from the radical cation (8).

The oxidation of hypophosphite by $[Fe(CN)_6]^{3-}$ in basic media obeys[29] the rate law

$$-d[Fe(CN)_6^{3-}]/dt = k'[Fe(CN)_6^{3-}][H_2PO_2^-][OH^-]$$

Since no hydroxide complexes of hexacyanoferrate(III) have been reported, the hydroxide dependence is assigned to a reactive adduct with hypophosphite,

$$[H_2PO_2]^- + OH^- \overset{K_1}{\rightleftharpoons} [H_3PO_3]^{2-}$$

$$[H_3PO_3]^{2-} + [Fe(CN)_6]^{3-} \overset{k}{\rightleftharpoons} [H_3PO_3]^- + [Fe(CN)_6]^{4-}$$

$$[H_3PO_3]^- + [Fe(CN)_6]^{3-} \xrightarrow{\text{fast}} H_3PO_3 + [Fe(CN)_6]^{4-}$$

[28] F. T. T. Ng and P. M. Henry, *J. Amer. Chem. Soc.*, 1976, **98**, 3606.
[29] D. Mohan, V. K. Chhabra, and Y. K. Gupta, *J.C.S. Dalton*, 1975 1737.

with $k' = K_1k$. The effects of ionic strength on the rate suggest that ion-pairing with cations may produce more reactive species in the reaction between two negatively charged ions.

In the initial stages of the reaction between hexacyanoferrate(III) and thiosulphate, the rate is independent of oxidant:[30]

$$-\mathrm{d}[Fe(CN)_6^{3-}]/\mathrm{d}t = k_1[H^+][S_2O_3^{2-}]^2$$

The third-order rate constant $k_1 = 2.3 \times 10^3$ l^2 mol^{-2} s^{-1} is comparable in magnitude to that for the spontaneous acid decomposition of thiosulphate,

$$HS_2O_3^- + S_2O_3^{2-} \overset{k_1}{\rightleftharpoons} [HS_2O_3 \cdot S_2O_3]^{3-} \longrightarrow SO_3^{2-} + HSO_3^- + 2S$$

($k_1 = 1.9 \times 10^3$ l^2 mol^{-2} s^{-1}). The adduct $[HS_2O_3 \cdot S_2O_3]^{3-}$ presents thiosulphate in a form which facilitates electron removal by hexacyanoferrate(III) and is stabilized by anions such as acetate and tetrathionate (a reaction product). Stabilization of the intermediate also retards production of colloidal sulphur and acceleration of the rate by cations may involve attack by water and formation of a bond to sulphur in an ion-paired complex followed by rapid reaction with hexacyanoferrate(III).

Another paper[31] dealing with the same reaction reports catalysis by copper(II). In the absence of free Cu^{II} (presence of edta), the reaction is autocatalytic with an induction period, which may be reduced by the addition of tetrathionate. Production of colloidal sulphur is explained by the reactions of tetrathionate to form polythionates. It is evident that the copper catalysis is present not only in the initial reactions but also in many side reactions.

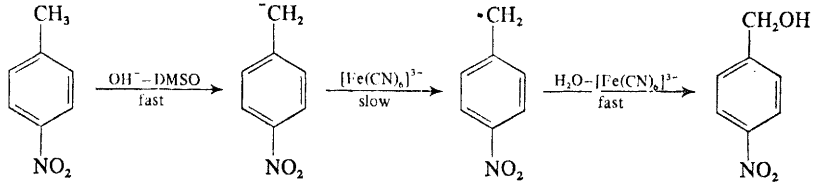
In the same paper,[31] the effects of copper catalysis on the oxidation of a number of substrates are discussed. The study is hampered by a lack of comparable quantitative data but it may be concluded that the copper-catalysis rate constant decreases with the acidity of the substrate. Three explanations are forwarded:

(i) copper may exist in three oxidation states and might therefore mediate between a one-electron oxidant and a two-electron reductant;
(ii) copper forms complexes with almost all the substrates used and these complexes may be more reactive than the substrate alone;
(iii) copper and hexacyanoferrate(III) may form a reactive mixed complex with the substrate.

The rate of oxidation of *o*- and *p*-nitrotoluenes by $[Fe(CN)_6]^{3-}$ in 50% DMSO is retarded by the presence of edta.[32] Copper catalysis is discounted on the grounds that the nitrotoluenes would not form complexes with copper(II). The retardation may be explained by a general salt effect. Base catalysis and a specific solvent effect of DMSO suggest that the reaction proceeds by an initial rapid proton abstraction (Scheme 6).

Catalysis by copper has also been observed in the oxidations of cyanide[33] and

[30] K. E. Howlett and B. L. Wedzidia, *Inorg. Chim. Acta*, 1976, **18**, 133.
[31] K. Madlo, A. Hasnedl, and J. Vepřek-Šiška, *Coll. Czech. Chem. Comm.*, 1976, **41**, 7.
[32] P. S. Radhakishnamurti and S. N. Mahapatra, *Indian J. Chem.*, 1975, **13**, 1029.
[33] F. R. Duke, *Inorg. Nuclear Chem. Letters*, 1976, **12**, 107.



Scheme 6

mercaptoacetate.[34] The former reaction was found to be heterogeneous on glassware and was studied in teflon apparatus. The experimental rate law,

$$\frac{-\mathrm{d}[\mathrm{Fe(CN)_6}^{3-}]}{\mathrm{d}t} = kK\frac{[\mathrm{Fe(CN)_6}^{3-}]^2[\mathrm{Cu}]}{[\mathrm{Fe(CN)_6}^{2-}]}$$

with a value of $kK = 40\ \mathrm{l\ mol^{-1}\ s^{-1}}$ at 30 °C suggests either of two mechanisms. The first involves disproportionation of $[Fe(CN)_6]^{3-}$ to form $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{2-}$. The latter then reacts with copper(I) to regenerate hexacyanoferrate(III) and copper(II). The second and more probable mechanism includes reaction of a dimeric copper complex:

$$[\mathrm{Fe(CN)_6}]^{3-} + [\mathrm{Cu^I_2(CN)}_x] \overset{K}{\rightleftharpoons} [\mathrm{Fe(CN)_6}]^{4-} + [\mathrm{Cu^{II}{-}Cu^{I}(CN)}_x]$$

$$[\mathrm{Fe(CN)_6}]^{3-} + [\mathrm{Cu^{II}{-}Cu^{I}(CN)}_x] \overset{k}{\longrightarrow} [\mathrm{Fe(CN)_6}]^{4-} + 2[\mathrm{Cu^{II}(CN)}_x]$$

In both cases, copper(II) rapidly oxidizes CN^- to complete the reaction. With mercaptoacetate, the proposed mechanism is similar with $Kk = 2.6 \times 10^{-5}\ \mathrm{l\ mol^{-1}\ s^{-1}}$ (30 °C),

$$[\mathrm{Fe(CN)_6}]^{3-} + \mathrm{Cu^I(SR)}_n \overset{K}{\rightleftharpoons} [\mathrm{(CN)_6FeCNCu^I(SR)}_n] \overset{k}{\longrightarrow} [\mathrm{Fe(CN)_6}]^{4-} + \mathrm{Cu^{II}(SR)}_n$$

followed by copper(II) oxidation in a non-rate-determining step. The structure of the intermediate is not surprising in view of the affinity of copper(I) for nitrogen and sulphur donors.

In the presence of piperidine or cyanide in non-aqueous media, iron(III), tetraphenylporphyrin (TPP) undergoes a one-electron redox step.[35] Piperidine is oxidized to an alkylamine radical while in DMSO the reaction rate with cyanide depends on the cyanide concentration and is inhibited by small amounts of water. Water forms a strong hydrogen bond with cyanide co-ordinated to iron(III) porphyrins, thus making the cyanide more difficult to oxidize. The intramolecular oxidation step is followed by reaction of the product with CN^-:

$$[\mathrm{(TPP)Fe^{III}(CN)_2}]^- \longrightarrow [\mathrm{(TPP)Fe^{II}(CN)}]^- + \cdot\mathrm{CN} \overset{\mathrm{CN^-}}{\longrightarrow} [\mathrm{(TPP)Fe^{II}(CN)_2}]^{2-}$$

Catechol is oxidized by ferricytochrome *c* in aqueous solution (pH 7.5—6.0).[36] The rate law,

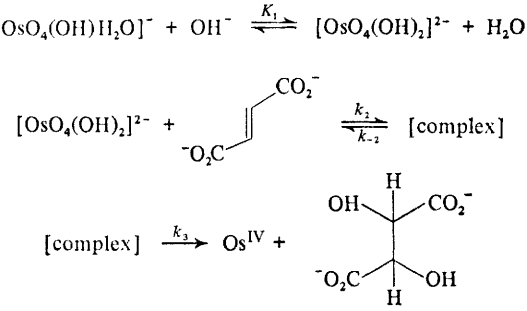
$$\mathrm{d[cyt^{II}}c]/\mathrm{d}t = k[\mathrm{cyt^{III}}c]^2[\mathrm{catechol}][\mathrm{H^+}]^{-1}$$

is second-order in oxidant and reciprocal first-order in hydrogen-ion concentration,

[34] F. R. Duke and V. C. Bulgrin, *J. Phys. Chem.*, 1975, **79**, 2323.
[35] J. D. Gandio and G. N. La Mar, *J. Amer. Chem. Soc.*, 1976, **98**, 3014.
[36] D. L. Toppen, *J. Amer. Chem. Soc.*, 1976, **98**, 4023.

which suggests reaction with the catechol anion, HC^-. Two mechanisms are proposed: either cytochrome *c* forms a reactive dimeric complex or a cytochrome *c*–catechol complex is formed and this reacts with a second cytochrome *c* molecule. In either case the complexation constant is small. The mechanism is explained by considering that cytochrome *c* may not be a strong enough oxidant to form a semiquinone radical. It is suggested that if catechol binds to one iron centre direct transfer of an electron from the second metal centre is sterically impossible and may occur through the exposed metal-porphyrin edge.

Several papers reporting the kinetics and mechanisms of the OsO_4 catalysed oxidation of organic substrates by $[Fe(CN)_6]^{3-}$ have appeared. The reactions are all zero-order in $[Fe(CN)_6]^{3-}$ and reflect oxidation by Os^{VIII}, the role of the iron(III) being to regenerate this species. Rate differences in the reactions of maleate and fumarate with OsO_4 are explained by steric factors in the complex-formation reactions.[37] The mechanisms are similar (Scheme 7) except that in the *cis* (maleate)

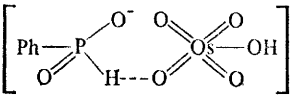


Scheme 7

case formation (k_2) is rapid and k_3 is rate determining whereas with the *trans* (fumarate) both k_2 and k_3 are involved in the rate expression; *meso*-tartaric acid is the final product in both cases. The reactions with 4-bromomandelate, benzyl alcohol,[38] propan-2-ol, and propan-1-ol[39] all follow a mechanism similar to that of the maleate reaction.

A different mechanism is proposed in the corresponding reaction with phenylphosphonous acid.[40] It is suggested that the oxidizing power of the $[Fe(CN)_6]^{3/4-}$ couple is comparable to that of the $P^{III/V}$ couple and that reaction will proceed only in the presence of a suitable complexing agent which can lower the redox potential of the $P^{III/V}$ couple. Such an agent is Os^{VIII}, which is considered to form the complex (9) which subsequently reacts with OH^- in the rate-determining step to give Os^{VI}. The reaction is completed by rapid oxidation by two moles of $[Fe(CN)_6]^{3-}$ with product phenylphosphoric acid.

[37] M. P. Singh, H. S. Singh, B. S. Arya, R. K. Singh, and A. K. Sisodia, *Indian J. Chem.*, 1975, **13**, 112.
[38] M. P. Singh, H. S. Singh, B. Singh, R. K. Singh, and A. K. Sisodia, *Indian J. Chem.*, 1975, **13**, 489.
[39] H. S. Singh, S. P. Singh, S. M. Singh, R. K. Singh, and A. K. Sisodia, *J. Phys. Chem.*, 1975, **79**, 1920.
[40] K. K. Sengupta and P. C. De, *J. Indian Chem. Soc.*, 1975, **52**, 252.



(9)

3 Manganese(III)

Evidence[41] for substitution-controlled mechanisms in redox reactions of $MnOH_{aq}^{2+}$ is obtained from a comparison of the available rate constants and activation parameters (Table 3). The rate constants for a series of structurally distinct, but formally

Table 3 *Kinetic and thermodynamic data for reactions of* Mn^{III} ($T = 25$ °C, $I = 2.0$ mol l^{-1})

	Substituent	k/ l mol^{-1} s^{-1}	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal K^{-1} mol^{-1}	*Ref.*
Mn^{3+} +	1,2-dihydroxybenzene	6.5×10^3	10	−12	43
	4-CH(OH)CH_2NHMe[a]	2.0×10^3	7	−25	44
	4-$CH_2CHNHCO_2H$[a]	2.8×10^3			44
	4-$CH_2CH_2NH_2$[a]	2.7×10^3			44
	4-Me	10.5×10^3			45
	4-Bu^t	8.3×10^3			45
Mn^{3+} +	4,4′-biphenyldiol[b]	9×10^3	10	−13	46
Mn^{3+} +	1,2-dihydroxybenzene[c]	2.9×10^4	15	10	43
	4-CH(OH)CH_2NHMe[a,c]	1.3×10^4	10	−9	44
	4-$CH_2CHNHCO_2H$[a,c]	1.1×10^4			44
	4-$CH_2CH_2NH_2$[a,c]	1.2×10^4			44
Mn^{3+} +	4,4′-biphenyldiol[b,c]	2.63×10^4	12	−2	46

[a] $T = 16$ °C. [b] $I = 4.0$ mol l^{-1}. [c] $1/[H^+]$ pathway; k has units s^{-1}.

neutral, species fall in the narrow range 2.3—8.3×10^4 l mol^{-1} s^{-1} at 25 °C and are similar to the value for complex formation with HF. The rate of reaction with uninegatively charged reductants may be predicted using criteria established for reactions of cobalt(III), *viz.* an increase in enthalpy and entropy of activation of 2.5 kcal mol^{-1} and 10 cal K^{-1} mol^{-1}. The theoretical value (1×10^5 l mol^{-1} s^{-1}) for the rate constant compares favourably with the experimental value (3×10^5 l mol^{-1} s^{-1}) for SCN^-.[42] Lack of useful thermodynamic data for reactions of the hexa-aquo-ion are lamented but a similar mechanism is considered likely.[41]

A series of papers dealing with the oxidation of catechols by Mn^{III} in perchlorate media has appeared. With catechol[43] the overall stoicheiometry requires two moles of Mn^{III} per mole of substrate (Qno = quinone):

$$2Mn^{III} + H_2cat \longrightarrow 2Mn^{II} + Qno + 2H^+$$

[41] G. Davies, *Inorg. Chim. Acta*, 1975, **14**, 213.
[42] G. Davies, *Inorg. Chem.*, 1972, **11**, 2488.
[43] E. Mentasti, E. Pelizzetti, E. Pramauro, and G. Giraudi, *Inorg. Chim. Acta*, 1975, **12**, 61.
[44] E. Mentasti, E. Pellizzetti, and E. Pramauro, *Gazzetta*, 1975, **105**, 551.
[45] E. Pelizzetti, E. Mentasti, and G. Giraudi, *Inorg. Chim. Acta*, 1975, **15**, L1.
[46] E. Pelizzetti, E. Mentasti, and C. Baiocchi, *J. Inorg. Nuclear Chem.*, 1976, **38**, 557.

The rate expression is first-order in both oxidant and substrate and reveals two reaction pathways, one independent of acidity, the other dependent on $[H^+]^{-1}$. Intermediate species of the type $[Mn^{III}(Hcat)]^{2+}$, proposed in the mechanism (Scheme 8), may be ion pairs or weak inner-sphere complexes, there being no kinetic

$$\begin{array}{ccccccc} Mn^{3+} & + & H_2cat & \overset{\beta_1}{\rightleftharpoons} & [Mn^{III}(H_2cat)]^{3+} & \xrightarrow{k} & Mn^{II} + Hcat\cdot + H^+ \\ \Big\| K_h & & & & \Big\| K_h & & \\ MnOH^{2+} & + & H_2cat & \overset{\beta_2}{\rightleftharpoons} & [Mn^{III}(Hcat)]^{2+} & \xrightarrow{k'} & Mn^{II} + Hcat\cdot \end{array}$$

$$Mn^{III} + Hcat\cdot \xrightarrow{\text{fast}} Mn^{II} + Qno + H^+$$

Scheme 8

or spectroscopic evidence for substantial complex formation. The derived rate expression,

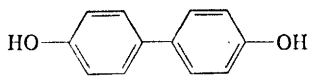
$$\frac{-d[Mn^{III}]}{dt} = \frac{2(k + k'K_h[H^+]^{-1})\beta_1[Mn^{III}]_T[H_2cat]}{1 + K_h[H^+]^{-1} + \beta_1[H_2cat](1 + K_h[H^+]^{-1})}$$

agrees with the experimental rate law if $\beta_1[H_2cat](1 + K_h[H^+]^{-1}) \ll 1$.

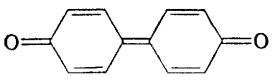
The catecholamines adrenaline, L-dopa, and dopamine, have the same oxidation stoicheiometry and show identical kinetic behaviour to catechol.[44] Again no evidence was found for complex formation and the kinetic behaviour might be explained either by outer-sphere reactions of Mn^{3+} and $MnOH^{2+}$ or by reactions of a weak complex which can exist in either of two forms differing by a proton. The ligand structure does, however, have little effect on the kinetic behaviour.

Further data are recorded from the corresponding reactions of 4-methyl- and 4-t-butylbenzene-1,2-diols.[45] Again the oxidation behaviour is similar and rate parameters are evaluated. The data with substituted benzene-1,2-diols may be summarized in a linear-free-energy relationship between the free energies of activation for the reaction with Mn^{3+} and the overall reaction free energy. The slope of a plot of $\Delta G^{\neq}$ against ΔG° is 0.25, agreeing with the Marcus predictions and implying that electron transfer and not substitution is rate determining. On the other hand, the rate constants for reaction of $MnOH^{2+}$ exhibit a narrow range of values and a substitution-controlled mechanism can be advanced.

A comparison of the oxidation of 4,4′-biphenyldiol (10) and 4,4′-biphenoquinone (11) by Mn^{III}, Ce^{IV}, and Ag^{II} has been made.[46] In the case of the first ion,



(10)



(11)

oxidation of the diol proceeds by the same mechanism as proposed for catechols, with rate constants 0.90×10^4 l mol^{-1} s^{-1} ($k\beta$) and 2.63×10^4 l mol^{-1} s^{-1} ($k'K_h\beta$) respectively for reactions with Mn^{3+} and $MnOH^{2+}$ at 25 °C. These results are consistent with the conclusions on rate-determining substitution discussed above for these ions. It is noted that the absence of a second-order term in $[Mn^{III}]$ supports the suggestion that paths involving activated complexes in which two metal ions are present for each molecule of substrate require the formation of stable 1:1 precursor

complexes. The reaction product is (11), which is in turn oxidized by Mn^{III}. No dependence on oxidant concentration was observed, implying that the rate-determining step involves hydrolysis of the ketone:

$$(11) + H^+ \overset{K_5}{\rightleftharpoons} [(11)-H]^+$$

$$[(11)-H]^+ + H_2O \overset{k_6}{\rightleftharpoons} [(11)-H_2O] + H^+$$

$$[(11)-H_2O] + Mn^{III} \xrightarrow{k_7} \text{radical} + Mn^{II}$$

The derived rate expression,

$$\frac{-d[(11)]}{dt} = \frac{k_6k_7K_5[Mn^{III}][(11)][H^+]}{k_{-6} + k_7[Mn^{III}]}$$

is consistent with this behaviour with $k_7[Mn^{III}] > k_{-6}$. A similar mechanism is found with Ce^{IV}.

A number of papers on the oxidation of non-metallic substrates by Mn^{III} in sulphuric acid media have appeared. In these cases the reactive species are sulphate complexes of the metal ion and have lower oxidizing power. A 2:1 stoicheiometry was found in the oxidation of phenylphosphonous acid ($PhPO_2H_2$) in acidic media.[47]

$$PhPO_2H_2 + 2Mn^{III} \longrightarrow PhPO_3H_2 + 2Mn^{II}$$

First-order dependences on oxidant, substrate, and the reciprocal of the hydrogen-ion concentration were observed and a mechanism, involving reaction of $MnHSO_4^{2+}$ with $PhPO_2H_2$ to produce $Ph\dot{P}O_2H$ radicals in the rate-determining step, is proposed. These radicals react subsequently with a second mole of oxidant and undergo hydrolysis. Although there is no evidence for the formation of a transient Mn^{III}–substrate complex, a mechanism in which such a species undergoes a two-electron transfer cannot be ruled out.

The oxidations of glycol and glycolic acid are oxygen-sensitive and were carried out[48] in an atmosphere of nitrogen. Stoicheiometry determinations lead to the following overall reaction formulations:

$$HOCH_2CH_2OH + 2Mn^{III} \longrightarrow 2CH_2O + 2H^+ + 2Mn^{II}$$

$$HOCH_2CO_2H + Mn^{III} \longrightarrow CH_2O + CO_2 + 2H^+ + Mn^{II}$$

In both cases the reactions followed a rate expression which was acidity-independent

$$\frac{-d[Mn^{III}]}{dt} = \frac{kK[\text{substrate}][Mn^{III}]}{1 + K[\text{substrate}]}$$

suggesting complex formation without release of a proton from the substrate followed by rate-determining redox giving Mn^{II} and an organic radical. The effect of oxygen is explained by the formation of peroxy-species. A rate increase when the substituted hydroxy-acids lactic and mandelic acid were used implies greater radical stability in these cases. The amino-acids glycine and DL-alanine are oxidized by a similar mechanism.[49] A second-order dependence on $[Mn^{III}]$ in the rate expression

$$\frac{-d[Mn^{III}]}{dt} = \frac{k'[Mn^{III}]^2[AH]}{k''[Mn^{II}][H^+]}$$

[47] K. K. Sengupta and T. Sarkar, *J. Indian Chem. Soc.*, 1975, **52**, 248.
[48] D. K. Kamrui, D. C. Mukherjee, and K. K. Sengupta, *Indian J. Chem.*, 1975, **13**, 1288.
[49] M. A. Beg and Kamaluddin, *Indian J. Chem.*, 1975, **13**, 1167.

and inhibition by $[Mn^{II}]$ suggest that the production of radicals is a reversible process:

$$Mn^{III} + HA \overset{\text{fast}}{\rightleftharpoons} Mn^{III}A + H^+$$

$$Mn^{III}A \overset{\text{slow}}{\rightleftharpoons} Mn^{II} + A\cdot$$

$$Mn^{III} + A\cdot \longrightarrow \text{products}$$

Mn^{II} inhibition in the previous paper[48] was explained by competition between Mn^{III} and Mn^{II} for the substrate.

The oxidation of nitrite ion by 1,2-diaminocyclohexanetetra-acetatomanganate-(III), $[Mn^{III}(cydta)]^-$, has been studied[50] between pH 4.5 and 7.5. The overall reaction,

$$2[Mn^{III}(cydta)]^- + NO_2^- \longrightarrow 2[Mn^{II}(cydta)]^{2-} + NO_3^- + 2H^+$$

has a rate law which is independent of pH,

$$\frac{-d[Mn^{III}(cydta)^-]}{dt} = \frac{k_a[Mn^{III}(cydta)^-]^2[NO_2^-]^2}{k_b[Mn^{II}(cydta)^{2-}]^2 + [Mn^{II}(cydta)^{2-}]}$$

with values of $k_a = 7.13 \times 10^2\ l^2\ mol^{-2}\ s^{-1}$ and $k_b = 2.72 \times 10^2\ l\ mol^{-1}\ s^{-1}$ ($T = 25$ °C, $I = 0.25$ mol l^{-1}). To explain the second-order dependences on $[Mn^{III}(cydta)^-]$ and $[NO_2^-]$, the proposed mechanism involves N_2O_4 as an intermediate,

$$[Mn^{III}(cydta)(OH_2)]^- + NO_2^- \overset{K_1}{\rightleftharpoons} [Mn^{III}(cydta)(NO_2)]^{2-} + H_2O$$

$$2[Mn^{III}(cydta)(NO_2)]^{2-} + H_2O \overset{K_2}{\rightleftharpoons} [Mn^{II}(cydta)(OH_2)]^{2-} + [Mn^{III}(cydta)(N_2O_4)]^{2-}$$

$$[Mn^{III}(cydta)(N_2O_4)]^{2-} + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [Mn^{II}(cydta)(OH_2)]^{2-} + N_2O_4$$

$$N_2O_4 + H_2O \overset{k_3}{\longrightarrow} NO_2^- + NO_3^- + 2H^+$$

giving $k_a = K_1^2K_2k_1$ and $k_b = k_2/k_3$. Using a literature value for k_3, the value of k_2 (2.7×10^5 l mol^{-1} s^{-1}) is 10^3-fold smaller than the expected rate of water exchange of $[Mn^{II}(cydta)(OH_2)]^{2-}$ and it is concluded that intermolecular electron transfer is rate determining for this step. At lower pH, the reaction is more complex and is sensitive to the presence of oxygen.

4 Manganese(VII)

The rate of electron transfer between $[MnO_4]^-$ and Br^- changes from first-order to zero-order in $[MnO_4]^-$ as the concentration of this reagent is reduced although the reaction stoicheiometry remains the same:[51]

$$[MnO_4]^- + 5Br^- + 8H^+ \longrightarrow Mn^{2+} + \tfrac{5}{2}Br_2 + 4H_2O$$

A proposed mechanism

$$2H^+ + Br^- + [MnO_4]^- \overset{K}{\rightleftharpoons} [H_2MnO_4Br]$$

$$[H_2MnO_4Br] + H^+ + Br^- \overset{k}{\longrightarrow} H_3MnO_4 + Br_2$$

[50] T. E. Jones and R. E. Hamm, *Inorg. Chem.*, 1975, **14**, 1027.
[51] S. A. Lawani, *J. Phys. Chem.*, 1976, **80**, 105.

is consistent with the experimental rate law,

$$-d[Mn^{VII}]/dt = k_0[MnO_4^-]^0[Br^-]^2[H^+]^3$$

in the initial stages of the reaction only. Although six reactant species combine in the rate step to form only two product molecules, the activation entropy $\Delta S^{\ddagger}$ (−19.9 cal K^{-1} mol^{-1}) is not as large as expected, an observation which is attributed to release of solvent.

A biphasic reaction is observed when co-ordinated DMSO reacts with permanganate in aqueous solution:[52]

$$3[(NH_3)_5CoO{=}SMe_2]^{3+} + 2MnO_4^- + 2H^+ \longrightarrow 3[(NH_3)_5CoOH_2]^{3+} + 3SO_2Me_2 + 2MnO_2 + H_2O$$

The first step is first-order in the cobalt complex and permanganate but is independent of acidity indicating that the outer-sphere formation of a radical-cation is not operative since the oxidizing power of $HMnO_4$ is greater than that of $[MnO_4]^-$. In the proposed mechanism,

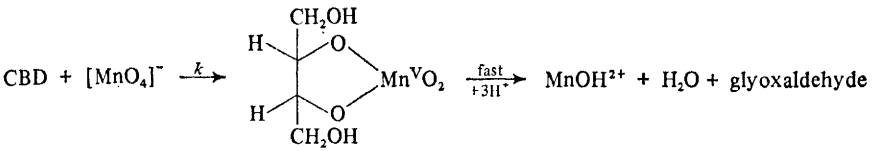
$$[(NH_3)_5Co^{III}O{=}SMe_2]^{3+} + [MnO_4]^- \overset{K}{\rightleftharpoons} [\text{intermediate}] \overset{k}{\longrightarrow} Mn^{V} \text{ or } Mn^{VI} \text{ species}$$

a lower limit of $K = 3$ l mol^{-1} is suggested and the rate constants, Kk, are 28 l mol^{-1} s^{-1} in the case of DMSO co-ordinated to cobalt(III) and 102 l mol^{-1} s^{-1} for the free substrate which reacts by a similar mechanism. Precipitation of manganese dioxide related to the disproportionation of Mn^{V} and Mn^{VI} is suggested for the second phase.

Manganese(III) was detected spectrophotometrically[53] as a short-lived intermediate in the oxidation of *cis*-but-2-ene-1,4-diol (CBD). Addition of pyrophosphate traps Mn^{III} by forming the stable pyrophosphatomanganate(III) complex. In the presence of this reagent, the rate of oxidation may be described by

$$-d[MnO_4^-]/dt = k[MnO_4^-][CBD]$$

with $k = 240$ l mol^{-1} s^{-1} at 25 °C ($I = 0.1$ mol l^{-1}). The kinetic behaviour is consistent with the formation of an undetectable cyclic hypomanganate ester (12) in the rate-determining step, followed by a rapid two-electron transfer to give Mn^{III}. Subsequent reactions of Mn^{III} involve disproportionation to Mn^{II} and Mn^{IV} since neither the organic product nor the diol itself is attacked.

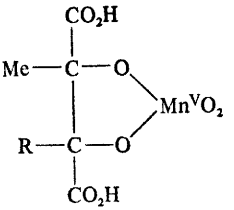


(12)

Evidence for Mn^{III} was also found in the oxidation of methylmaleic, methylfumaric, and dimethylmaleic acids.[54] The rates were found to be pH-dependent in the range 0—5.0, resulting from reaction of permanganate with different protonated

[52] L. A. deOliveria, H. E. Toma, and E. Giesbrecht, *Inorg. Nuclear Chem. Letters*, 1976, **12**, 195.
[53] N. T. Son, M. Jáky, and L. I. Simándi, *Inorg. Nuclear Chem. Letters*, 1976, **12**, 291.
[54] M. Jáky and L. I. Simándi, *J.C.S. Perkin II*, 1976, 939.

forms of the acids. Differences in the rate constants with substrate structure are consistent with a *cis* attack by $[MnO_4]^-$ on the double bond resulting in short-lived, undetected hypomanganate esters (13). Large negative activation entropies reflect the increased order in forming this chelate. Manganese(III) is produced by a two-electron C—C bond cleavage of these esters.



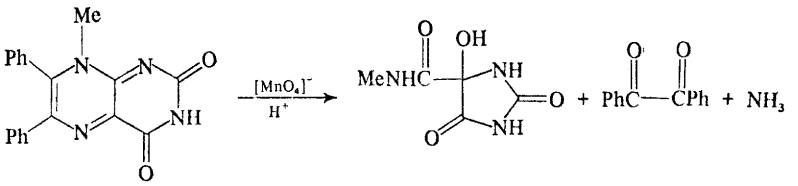
(13)

Acid catalysis was observed in the oxidation of the amino-acids glycine, DL-alanine, DL-valine, and DL-leucine by $[MnO_4]^-$ in aqueous sulphuric and perchloric acids.[55] The protonated form $HMnO_4$ is the active oxidizing species. Consideration of the acidity dependence leads to the conclusion that water acts as a proton acceptor in the rate-determining step,

$$^+NH_3CHRCO_2H + HMnO_4 + H_2O \xrightarrow{k_1} {}^+NH_3CHRCO_2^\bullet + [HMnO_4]^- + H_3O^+$$

which is followed by rapid decarboxylation and deamination of the substrate to form ammonia, carbon dioxide, and the aldehyde RCHO. The trends in rates and activation parameters reflect the observation that amino-acids with an even number of carbon atoms are more easily oxidized than those with odd numbers.

The reaction of (14) with permanganate is specific acid catalysed.[56] Two pathways,



(14)

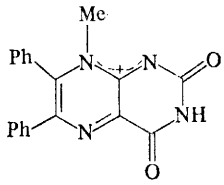
one dependent on and one independent of permanganate were observed. The former is attributed to reaction of (14) with the acid-activated form of the permanganate ion MnO_4^* or to the kinetically indistinguishable reaction of (15), the protonated form of (14), with $[MnO_4]^-$. The former explanation is preferred but the rate must be very large:

$$(14) + MnO_4^* \xrightarrow{k > 10^5\ l\ mol^{-1}\ s^{-1}}$$

Rate-determining hydrolysis of the conjugate acid (15) followed by rapid perman-

[55] R. S. Verma, M. J. Reddy, and V. R. Shastry, *J.C.S. Perkin II*, 1976, 469.
[56] R. Stewart and K. Oyama, *J. Amer. Chem. Soc.*, 1975, **97**, 6510.

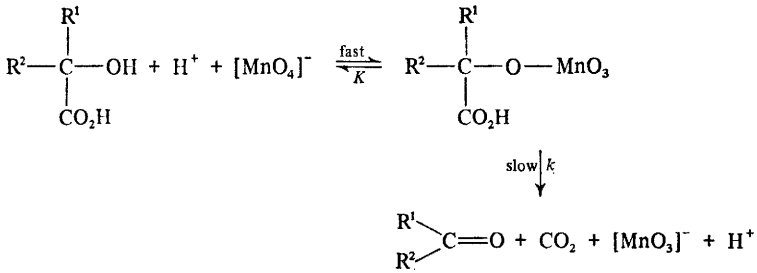
ganate oxidation is deduced to be the mechanism for the permanganate-independent pathway.



(15)

The identity of the activated form of permanganate in high acid media has been established[57] as the permanganyl cation $[MnO_3]^+$. Solutions of $[MnO_4]^-$ in trifluoroacetic acid are green and not purple as would be expected for $HMnO_4$. The spectrum is identical to that found in sulphuric acid and the equilibrium between $[MnO_4]^-$ and $[MnO_3]^+$ behaves as a protonation–dehydration process. Although the formation of trifluoroacetate esters is considered likely, the permanganyl ion is almost certainly the more reactive oxidant.

The intermediate Mn^{III} is the active oxidant in the reactions of 2-hydroxycarboxylic acids with permanganate in sulphuric acid.[58] This is consistent with acceleration of the rate by Mn^{II} and the fact that the substrates are oxidized at higher rates in the corresponding reactions with Mn^{III} alone. The mechanism (Scheme 9) in



Scheme 9

the initial stages (low $[Mn^{III}]$) explains the complex acidity dependence if the equilibrium K is enhanced by increasing acidity while the rate-determining step k, which involves liberation of a proton, is retarded.

In a further paper[59] by the same authors, dealing with the oxidation of glycol and glycolic acid, Mn^{IV}, produced by the reaction of $[MnO_4]^-$ with Mn^{II}, is considered the active oxidant in the latter stages. The reaction of this species is assumed to proceed through formation of an intermediate metal-ion complex.

Retardation by manganese(II) of the rate of oxidation of substituted toluene derivatives by $[MnO_4]^-$ in 50% acetic acid rules out intermediate valence states as reactants.[60] Electron-releasing substituents favour the oxidation, suggesting that the

[57] V. A. Spitzer, T. W. Toone, and R. Stewart, *Canad. J. Chem.*, 1976, **54**, 440.
[58] K. K. Sengupta, D. K. Khemrui, and D. C. Mukherjee, *J. Indian Chem. Soc.*, 1975, **52**, 467.
[59] K. K. Sengupta, D. K. Khemrui, and D. C. Mukherjee, *Indian J. Chem.*, 1975, **13**, 348.
[60] P. S. Radhakrishnamurti and S. N. Mahapatro, *Indian J. Chem.*, 1975, **13**, 1294.

formation of a benzylic radical with cationic character is the rate-determining step. This intermediate subsequently breaks down to yield the corresponding carboxylic acid.

In oxalate solution, the dimeric $[Mn^{IV}_2O_2(C_2O_4)_4]^{4-}$ complexes spontaneously decompose in two steps, the first yielding $[Mn^{III}(C_2O_4)_3]^{3-}$ which subsequently gives Mn^{II} complexes.[61] At a constant pH of 3.9, the rate equation

$$-d[Mn^{IV}]/dt = \alpha[Mn^{III}] + \beta[Mn^{IV}]^{\frac{1}{2}}[Mn^{III}] + \gamma[Mn^{IV}]^{\frac{1}{2}}$$

suggests the mechanism

$$ox + Mn^{IV}_2 \overset{K}{\rightleftharpoons} 2Mn^{IV}$$

$$Mn^{IV} \overset{k_\gamma}{\rightleftharpoons} Mn^{II} + 2CO_2$$

$$Mn^{IV} + Mn^{II} \xrightarrow{\text{fast}} 2Mn^{III}$$

$$Mn^{III} \xrightarrow{k_\alpha} Mn^{II} + CO_2^{-\cdot} + CO_2$$

$$Mn^{III} + Mn^{IV} \xrightarrow{k_\beta} Mn^{II} + Mn^{III} + 2CO_2$$

$$Mn^{III} + CO_2^{-\cdot} \xrightarrow{\text{fast}} Mn^{II} + CO_2$$

$$Mn^{IV} + CO_2^{-\cdot} \xrightarrow{\text{fast}} Mn^{III} + CO_2$$

where Mn^n represents the oxalate complex of manganese in oxidation state n. The pathway k_α carries only a small fraction of the reaction while, under the experimental conditions, k_γ predominates.

5 Cobalt(III)

The kinetics of oxidation of catechol (benzene-1,2-diol) derivatives by $[Co(H_2O)_6]^{3+}$ in aqueous perchloric acid have been reported.[62] A two-term rate law,

$$-d[Co^{III}]/dt = (A + B/[H^+])[Co^{III}][H_2cat]$$

is suggestive of the mechanism

$$Co^{3+} \overset{K_h}{\rightleftharpoons} [Co(OH)]^{2+} + H^+$$

$$Co^{3+} + H_2cat \xrightarrow{k_a} Co^{II} + Hcat^{\cdot} + H^+$$

$$CoOH^{2+} + H_2cat \xrightarrow{k_b} Co^{II} + Hcat^{\cdot}$$

$$Co^{III} + Hcat^{\cdot} \xrightarrow{\text{fast}} Co^{II} + H^+ + \text{quinone}$$

the derived rate expression,

$$\frac{-d[Co^{III}]}{dt} = \frac{2(k_a + k_b K_h[H^+]^{-1})[H_2cat][Co^{III}]}{1 + K_h[H^+]^{-1}}$$

reducing to that observed experimentally since $K_h[H^+]^{-1} \ll 1$ ($K_h = 2 \times 10^{-3}$ mol l^{-1}).

[61] T. Vehiro, I. Taminaga, and Y. Yoshino, *Bull. Chem. Soc. Japan*, 1975, **48**, 2809.
[62] E. Pelizzetti, E. Mentasti, and E. Pramauro, *J.C.S. Dalton*, 1976, 23.

From comparisons of the rate constants with previously recorded data for substitution-limited cobalt(III) oxidations (Table 4), it was concluded that water exchange is

Table 4 *Kinetic and thermodynamic data for reactions of* Co^{III} ($T = 25$ °C, $I = 2.0$ mol l^{-1})

Substituent	k/ l mol^{-1} s^{-1}	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal K^{-1} mol^{-1}	*Ref.*
Co^{3+} + 1,2-dihydroxybenzene				
4-$CH(OH)CH_2NHMe$	330	14.7	2.2	62
3-Me	160	15.0	2.0	62
4-Me	720	12.1	−5.0	62
3-CO_2H	880	14.8	4.7	62
4-CO_2H[a]	~40			62
4-CN	~30			62
Co^{3+} + 1,4-dihydroxybenzene	930	16	4	63
2-Me	1450	16	6	63
2-Cl	360	15	−1	63
2-SO_3H	320	14	−9	63
Co^{3+} + phenol				
4-OMe	650	19	13	63
4-OEt	630	16	4	63
$CoOH^{2+}$ + 1,2-dihydroxybenzene				
4-$CH(OH)CH_2NHMe$	2.0×10^5	17.6	12.4	62
3-Me	2.0×10^5	17.6	12.4	62
4-Me	3.4×10^5	17.9	14.4	62
3-CO_2H	3.9×10^5	16.9	9.4	62
4-CO_2H[a]	7.5×10^4	18.4	14.6	62
4-CN	1.5×10^5	11.9	−8.0	62
$CoOH^{2+}$ + 1,4-dihydroxybenzene	2.8×10^5	12	2	63
2-Me	5.6×10^5	10	−3	63
2-Cl	3.9×10^5	6	−16	63
2-SO_3H	2.5×10^5	5	−22	63
$CoOH^{2+}$ + phenol				
4-OMe	1.2×10^5	6	−21	63
4-OEt	1.7×10^5	6	−19	63

[a] $T = 18$ °C.

not rate limiting with the benzene-1,2-diols. The pathway involving Co^{3+} (k_a) obeys a linear free-energy relationship with the overall free-energy change in the reaction consistent with the outer-sphere mechanisms in which the rate-determining step is electron transfer. For $CoOH^{2+}$ the rates are similar to previously reported rate constants. Differences in k_b with substrate structure may be attributed to the ease of attaining the optimum configuration of hydroxide in bridging the reactants in the activated complex for electron transfer.

A similar mechanism was found with the corresponding benzene-1,4-diols.[63] It was concluded that reactions of both Co^{3+} and $CoOH^{2+}$ proceed by an outer-sphere mechanism since the rates are higher than the rate of water exchange on cobalt(III). The hydrolysed form again facilitates the redox and the ratio k_a/k_bK_h decreases with increasing electron-withdrawing substitution on the benzene ring.

[63] E. Mentasti, E. Pelizzetti, and G. Giraudi, *J. Inorg. Nuclear Chem.*, 1976, **38**, 795.

The preparations and reactions of diammineaquocobalt(III) complexes, which combine the strong oxidizing power and lability of hexa-aquocobalt(III) and the inertness of hexa-amminecobalt(III), have been studied.[64] Chloride ion forms a redox inert complex with *cis*-$[Co(NH_3)_2]^{3+}_{aq}$ with kinetic behaviour similar to that of the hexa-aquo-ion. $[Co(NH_3)_2OH]^{2+}$ is more reactive than $[Co(NH_3)_2]^{3+}$. With bromide ion, reduction takes place according to the rate law

$$-d[Co^{III}]/dt = (C + D/[H^+])[Co^{III}][Br^-]$$

and the similarity of the parameters C and D to the corresponding values for chloride suggests that the redox mechanism is substitution controlled,

$$[Co(NH_3)_2]^{3+} \overset{K_h}{\rightleftharpoons} [Co(NH_3)_2OH]^{2+} + H^+$$

$$[Co(NH_3)_2]^{3+} + Br^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [Co(NH_3)_2Br]^{2+}$$

$$[Co(NH_3)_2OH]^{2+} + Br^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} [Co(NH_3)_2(OH)Br]^+$$

$$[Co(NH_3)_2Br]^{2+} \xrightarrow[H^+]{k_5} Co^{II} + 2NH_4^+ + Br\cdot$$

$$[Co(NH_3)_2(OH)Br]^+ \xrightarrow[H^+]{k_6} Co^{II} + 2NH_4^+ + Br\cdot$$

$$Br\cdot + Br^- \rightleftharpoons Br_2^{-}\cdot$$

$$Co^{III} + Br_2^{-}\cdot \rightleftharpoons Co^{II} + Br_2$$

The derived ratelaw reduces to give $k_3 = C$ and $k_4K_h = D$. A value of less than 10^{-2} mol l^{-1} is estimated for K_h and it may be as low as $10^{-3.5}$ mol l^{-1}. This results in the hydroxy-form being 10^3—10^4 times more labile than the tetra-aquodiammine, both being 10^5 times less labile than $[Co(H_2O)_6]^{3+}$. In contrast to this, the oxidations of iodide ion and hydroquinone are rapid and probably outer-sphere in nature.[65] The rate law

$$-d[Co^{III}]/dt = A[Co^{III}][I^-]$$

where A is 0.38 and 0.0285 l mol^{-1} s^{-1} in the cases of I^- and hydroquinone respectively, lacks an acidity dependence and suggests a general outer-sphere pathway for both forms of the oxidant.

The dinuclear complex di-μ-hydroxo-bis[nitrilotriacetatocobaltate(III)] may be hydrolysed in acid solution[66] to give diaqua(nitrilacetato)cobalt(III). No more than two nitrogen atoms are thought to be co-ordinated, giving this complex moderate oxidative properties. The reactions with reducing substrates (S) show a two-term rate law:

$$\frac{-d[Co^{III}]}{dt} = \left\{\frac{k_a[H^+]}{K_1 + [H^+]} + \frac{k_bK_1}{K_1 + [H^+]}\right\}[Co^{III}(nta)_{aq}][S]$$

where $K_1 = 10^{-6.71}$ mol l^{-1}, is the first hydrolysis constant of the metal complex

$$[Co^{III}(nta)(OH_2)_2] \overset{K_1}{\rightleftharpoons} [Co^{III}(nta)(OH_2)OH]^- + H^+$$

[64] I. Bodek, G. Davies, and J. H. Ferguson, *Inorg. Chem.*, 1975, **14**, 1708.
[65] I. Bodek and G. Davies, *Inorg. Chem.*, 1976, **15**, 922.
[66] M. A. Thacker and W. C. E. Higginson, *J.C.S. Dalton*, 1975, 704.

Similarities in the parameters k_a and k_b with those of non-reducing substrates suggest that redox takes place with rate-determining complex formation. Only in the case of sulphite does the rate step change to the electron-transfer process. As with other cobalt(III) complexes, the conjugate base reacts more rapidly than the diaquo-form. For rate data for the reaction with hydroxylamine see Table 6 on p. 80.

A rapid intramolecular oxidation of the carbanion $[(NH_3)_5Co(N{\equiv}C\bar{C}HPh)]^{2+}$ results in dissociation and dimerization of the organic radical.[67] Generation of the carbanion by base

$$[(NH_3)_5Co(N{\equiv}CCH_2Ph)]^{3+} \xrightarrow{OH^-} [(NH_3)_5Co(N{\equiv}\bar{C}CHPh)]^{2+}$$

allows control of radical production.

Reduction of the water-soluble porphyrin tetrakis-(4-*N*-methylpyridyl)porphine-cobalt(III), Co(TMpyP), is achieved[68] with dithionite at pH 8. Addition of an excess of dithionite initially causes a reversible shift in the Soret band followed by its irreversible disappearance, implying that the first reduction step occurs at the metal site and that the metalloporphyrin remains intact but that, in a subsequent step, the porphyrin ring system itself is reduced. This is consistent with the kinetic results which have a half-order dependence on dithionite, suggesting that the reactive reductant might be the SO_2^- radical, a one-electron reducing agent. This is the sole reaction with the diaquo and bis(pyridine) complexes of Co(TMpyP), with rate constants 3.1×10^8 and 2.9×10^6 l mol^{-1} s^{-1} ($T = 25$ °C, $I = 0.5$ mol l^{-1}) respectively, whereas for the aquohydroxo-derivative direct reaction with dithionite is also observed,

$$S_2O_4^{2-} \overset{k}{\rightleftharpoons} 2SO_2^-$$

$$Co^{III}(TMpyP) + SO_2^- \xrightarrow{k_1} \text{products}$$

$$Co^{III}(TMpyP) + S_2O_4^{2-} \xrightarrow{k_2} \text{products}$$

with $k_1 = 5.5 \times 10^6$ and $k_2 = 5.2 \times 10^3$ l mol^{-1} s^{-1}. In all cases, the mechanism for the reduction reactions is outer-sphere and the rates of reduction correlate with the overall free-energy changes.

6 Vanadium(V)

Propan-2-ol is oxidized to acetone by vanadium(V) in perchloric acid media requiring a 2:1 stoicheiometry:[69]

$$2V^V + Me_2CHOH \longrightarrow 2V^{IV} + Me_2CO + 2H^+$$

The reaction is insensitive to O_2 and at 60 °C the rate law is consistent with a mechanism which does not involve intermediate complexes:

[67] I. I. Creaser and A. M. Sargeson, *J.C.S. Chem. Comm.*, 1975, 324.
[68] R. F. Pasternack, M. A. Cobb, and N. Sutin, *Inorg. Chem.*, 1975, **14**, 866.
[69] C. F. Wells and A. F. M. Nazer, *J.C.S. Faraday I*, 1976, **72**, 910

$$VO_2^+ + H^+ \overset{K_1}{\rightleftharpoons} [VO(OH)]^{2+}$$

$$ROH + H^+ \overset{K_C}{\rightleftharpoons} ROH_2^+$$

$$VO_2^+ + ROH \xrightarrow{k} V^{IV} + \text{radical} + H^+$$

$$VO_2^+ + \overset{+}{R}OH_2 \xrightarrow{k'} V^{IV} + \text{radical} + 2H^+$$

$$[VO(OH)]^{2+} + ROH \xrightarrow{k_1} V^{IV} + \text{radical} + H^+$$

$$[VO(OH)]^{2+} + \overset{+}{R}OH_2 \xrightarrow{k_1'} V^{IV} + \text{radical} + 2H^+$$

The radical reacts in a subsequent step with a second mole of V^V to yield the organic product. This mechanism, however, requires that the species $\overset{+}{R}OH_2$ be more reactive than ROH with $[VO(OH)]^{2+}$ but less reactive with VO_2^+, an unlikely situation which was resolved by invoking kinetically indistinguishable pathways involving further protonation on VO_2^+:

$$[VO(OH)]^{2+} + H^+ \overset{K_2}{\rightleftharpoons} [V(OH)_2]^{3+}$$

$$[V(OH)_2]^{3+} + ROH \xrightarrow{k_2} V^{IV} + \text{radical} + H^+$$

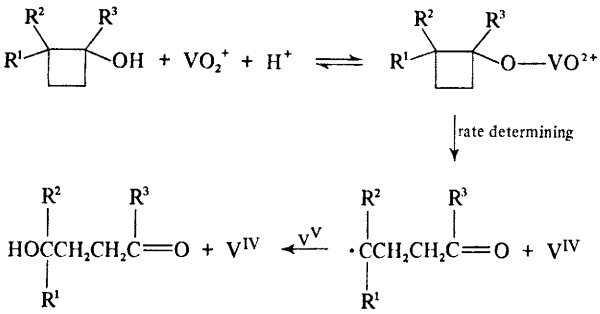
$$[V(OH)_2]^{3+} + \overset{+}{R}OH_2 \xrightarrow{k_2'} V^{IV} + \text{radical} + 2H^+$$

Analysis of the data gives values 3.25×10^{-5} l mol^{-1} s^{-1} and 6.5×10^{-6} l^3 mol^{-3} s^{-1} for k and the product $K_1K_2k_2$ respectively at 60 °C (I = 5.0 mol l^{-1}). Comparisons of the overall activation parameters with those of the corresponding reactions of other metal ions require greater steric restriction in the vanadium(IV) transition state.

Vanadium(V) reacts with cyclobutanol to give 4-hydroxybutyraldehyde almost quantitatively.[70] The experimental rate law,

$$-d[V^V]/dt = k[V^V][ROH][H^+]$$

suggests that the protonated form of the oxidant HVO_2^+ is more reactive in acid media. Methyl cyclobutyl ether is 10^4 times less reactive than cyclobutanol, implying that the O—H bond plays an important part in the oxidation process. This is considered good evidence for the formation of a vanadic ester intermediate with C—C bond cleavage in the rate-determining step (Scheme 10). Substituted cyclobutanols



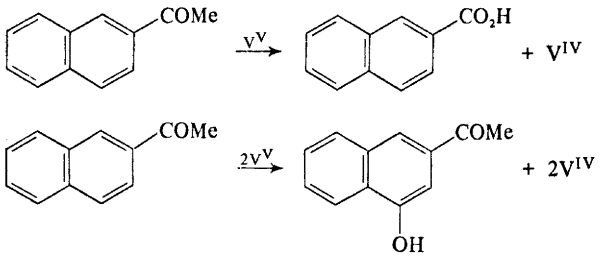
Scheme 10

[70] J. Roček and D. E. Aylward, *J. Amer. Chem. Soc.*, 1975, **97**, 5452.

cleave toward the more substituted carbon atom, consistent with a rate acceleration with increasing substitution in the 2-position. Further information on the nature of the mechanisms comes from isotopic labelling studies which show that the oxygen atom originally in the cyclobutanol is oxidized to the carbonyl group, thereby ruling out any possibility of a ring-expansion process.

Free radicals are produced in the oxidation of cyclohexanone by V^V in aqueous hydrochloric acid.[71] The reaction rate depends on the type of mineral acid used, decreasing in the order $H_2SO_4 > HCl > HNO_3 > HClO_4$. Kinetic behaviour in HCl suggests that the positively charged species $[V(OH)_3Cl]^+$ is a more powerful oxidant than $[V(OH)_3]^{2+}$ but less reactive than the bisulphate complex.

In mixed aqueous–acetic acid media, V^V oxidizes[72] acetonaphthone with a stoicheiometry V^V:ketone = 1.5. Different stages in the oxidation may be represented by Scheme 11. Both naphthoic acid and the naphthol were identified as products. The



Scheme 11

corresponding reactions with substituted derivatives of acetophenone have also been studied.[73] Increasing acidity increases the reaction rate consistent with pathways involving $[V(OH)_2]^{3+}$ and $[V(OH)_3]^{2+}$. Electron-withdrawing substituents also increase the rate of reaction which is considered to be outer-sphere in nature.

Medium effects are observed in the oxidation of cinnamic acid by V^V in aqueous acetic acid.[74] The replacement of a hydroxyl hydrogen by an acetyl group makes the vanadium ion a better electrophile, thereby enhancing the rate. No free radicals were detected but the proposed rate-determining step involves the formation of a radical benzylic carbonium ion which immediately decarboxylates and then dimerizes to form the product:

$$PhCH{=}CHCO_2H \xrightarrow[\text{slow}]{V^{(V)}} Ph\overset{+}{C}H{-}\dot{C}HCO_2H$$

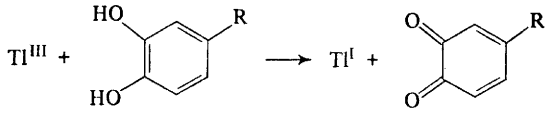
$$Ph\overset{+}{C}H{-}\dot{C}HCO_2H \xrightarrow{\text{fast}} PhCH{=}\dot{C}H + CO_2 + H^+$$

$$2PhCH{=}\dot{C}H \xrightarrow{\text{fast}} PhCH{=}CHCH{=}CHPh$$

[71] G. S. S. Murty, B. Sethuram, and T. N. Rao, *Indian J. Chem.*, 1975, **13**, 849.
[72] A. K. Sahu, B. K. Sinha, and G. B. Behera, *J. Indian Chem. Soc.*, 1975, **52**, 894.
[73] G. C. Misra, B. K. Sinha, and G. B. Behera, *J. Indian Chem. Soc.*, 1975, **52**, 1053.
[74] G. B. Behera, V. K. Nayak, K. K. Mukherjee, and M. K. Rout, *J. Indian Chem. Soc.*, 1975, **52**, 1056.

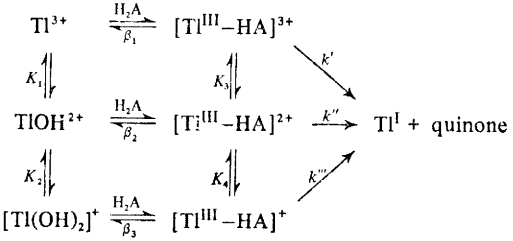
7 Thallium(III)

Studies of the oxidations of derivatives (16) of dihydroxybenzene have been extended



(16)

to Tl^{III}. Highly acidic conditions ($[H^+] > 0.1$ mol l^{-1}) prevent cyclization of adrenoquinone, the product of the kinetically irreversible oxidation of adrenaline.[75] The rate law is independent of the reagent in excess, although deviations from first-order behaviour in both reagents were observed at high adrenaline and low-hydrogen-ion concentrations, suggesting complex formation as a prerequisite to redox. The



Scheme 12

proposed mechanism (Scheme 12) yields the rate expression

$$\frac{-d[Tl^{III}]}{dt} = \frac{(k'\beta_1 + k''\beta_2K_1[H^+]^{-1} + k'''\beta_3K_1K_2[H^+]^{-2})[Tl^{III}]_T[H_2A]}{1 + K_1[H^+]^{-1} + K_1K_2[H^+]^{-2} + (\beta_1 + \beta_2K_1[H^+]^{-1} + \beta_3K_1K_2[H^+]^{-2})[H_2A]}$$

with Tl^{III} as limiting reagent. No dependence on Tl^{I} was observed. Under the prevailing conditions, only pathways for $TlOH^{2+}$ and $[Tl(OH)_2]^+$ were detected with rate constants 5×10^3 and 6.0×10^5 l mol^{-1} s^{-1} for $k''\beta_2$ and $k'''\beta_3$ respectively at 14 °C ($I = 2.0$ mol l^{-1}). A single two-electron transfer mechanism is preferred to successive steps involving Tl^{II} and the corresponding semiquinone.

Different acidity dependences observed in the reactions of Tl^{III} with organic substrates (Table 5) can either be explained by selective reactions of the various hydrolysed metal-ion species or in terms of differences in the release of protons on coordination in an inner-sphere mechanism. This observation prompted an investigation of the redox kinetics of a series of substituted derivatives of 1,2-dihydroxybenzene.[76] No spectroscopic evidence was found for precursor complexes with any of the compounds. If a general mechanism similar to that proposed above with adrenaline is operative, all the complexes studied except 3-methoxy-4-hydroxybenzylamine (17) have $k'''\beta_3$ as a major pathway. This suggests that either $[Tl(OH)_2]^+$ is highly reactive, in which case it should react with (17) or that an inner-sphere intermediate is formed with loss of two protons before the rate-determining step. The compound (17) has

[75] E. Pelizzetti, E. Mentasti, E. Pramauro, and M. E. Carlotti, *Gazzetta*, 1975, **105**, 307.
[76] E. Mentasti, E. Pelizzetti, and E. Pramauro, *J. Inorg. Nuclear Chem.*, 1975, **37**, 1733.

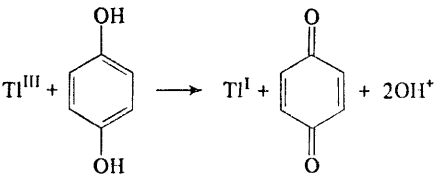
Table 5 *Kinetic parameters for reactions of* Tl^{III} *in aqueous perchlorate media* ($T = 25$ °C, $I = 2.0$ mol l^{-1})

Substituent	$10^{-2}k'\beta_1$/ l mol^{-1} s^{-1}	$10^{-3}k''\beta_2$/ l mol^{-1} s^{-1}	$10^{-5}k'''\beta_3$/ l mol^{-1} s^{-1}	*Ref.*
1,2-Dihydroxybenzene				
4-CH(OH)CH_2NHMe[a]		5.0	6.0	75
4-Bu^t		54	45	76
4-CO_2H			6.1	76
4-CN			2.9	76
3-CO_2H			30	76
3,5-Benzenedisulphonic acid			18	76
Phenol				
2-OMe, 4-NH_2	0.06	0.09		76
2-OMe	25	4.0		77
4-OMe	3.1	1.6		78
4-OEt	3.7	$\leqslant 0.4$		79
4-OBu^n	2.0	$\leqslant 0.2$		79
1,4-Dihydroxybenzene	6.8	2.1		78
2-Me	16	40		78
2-Cl	1.35	2.5		79
2-Br	2.8	4.9		79
2-SO_3H	3.5×10^3	0.27		79

[a] $T = 14$ °C.

only one available proton and is excluded from pathway $k'''\beta_3$ but reacts by pathways $k'\beta_1$ and $k''\beta_2$. Similar arguments are used to suggest the presence of unidentate and bidentate co-ordination. It is concluded that the reactions are inner-sphere and involve a two-electron transfer in the rate-determining step. Comparison of the rates for the bidentate chelate path $k'''\beta_3$ reveals that electrophilic substituents decrease the rate by lowering the electron density on the 1,2-dihydroxy-system. Reactions of 1-hydroxy-2-methoxybenzene are in agreement with the above general mechanism.[77] Only two pathways $k'\beta_1$ and $k''\beta_2$ are observed, consistent with the formation of a unidentate complex.

Derivatives of 1,4-dihydroxybenzene (18) have been oxidized by Tl^{III}.[78] In the case



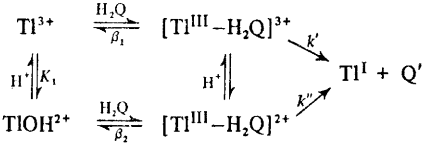
(18)

of 1-hydroxy-4-methoxybenzene, the products are the quinone and methanol. These reactions conform to the general mechanism outlined for the 1,2-dihydroxybenzene derivatives but in all cases the $k'\beta_1$ and $k''\beta_2$ paths were observed. No definite assignment on the nature of the precursor complexes can be made but the same mode of

[77] E. Mentasti, E. Pelizzetti, E. Pramauro, and G. Giraudi, *J. Inorg. Nuclear Chem.*, 1975, **37**, 537.
[78] E. Pelizzetti, E. Mentasti, M. E. Carlotti, and G. Giraudi, *J.C.S. Dalton*, 1975, 794.
[79] E. Pelizzetti, E. Mentasti, and E. Pramauro, *Gazzette*, 1975, **105**, 403.

reaction holds no matter the reagent in excess, thereby requiring precursor complex formation to a small extent. It is suggested from the ratio $k''\beta_2/k'\beta_1$ that the hydroxide ligand acts as a bridge for electron transfer.

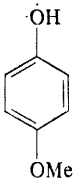
The results of the above investigation and others have been summarized in a second paper.[79] In all cases the kinetic behaviour conforms to the restricted mechanism and both pathways, $k'\beta_1$ and $k''\beta_2$, are observed (Scheme 13). Electron-releasing



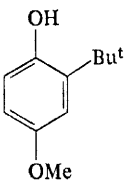
Scheme 13

groups were shown to increase the reaction rate and a trend was established between the inverse of the ligand redox potentials and the rates.

Although the kinetic behaviour does not change, ethoxy- or n-butoxy-derivatives but not methoxy-derivatives show a negligible term in $k''\beta_2$. There is also a steric effect with bulky substituents *ortho* to the probable reaction site, increasing the activation energy from 10 kcal mol^{-1} for (19) to 17 kcal mol^{-1} for (20), for $k'\beta$.



(19)



(20)

Despite this, the specific rate constants remain about the same, suggesting a balancing inductive effect of the substituent. It is apparent that a considerable contribution to the overall activation energy should be attributed to the redox process.[79]

Although the stoicheiometry of the reaction between hydroxylamine and Tl^{III} depends on the relative concentrations of the reactants, in conditions of excess hydroxylamine it can be described[80] by the equation

$$Tl^{III} + NH_3OH^+ \longrightarrow Tl^I + \tfrac{1}{2}H_2N_2O_2 + 3H^+$$

The exact form of the N^I is, however, in doubt since hyponitrous acid could not be detected as its silver(I) salt. Addition of an excess of Tl^{III} causes two-, four-, and six-electron transfers to form a variety of products. Reaction of the hydrolysed metal ion $[TlOH]^{2+}$ is considered to be the rate-determining step in the oxidation,

$$Tl^{3+} \overset{K_h}{\rightleftharpoons} [TlOH]^{2+} + H^+$$

$$[TlOH]^{2+} + NH_3OH^+ \overset{k}{\longrightarrow} Tl^+ + \tfrac{1}{2}H_2N_2O_2 + 2H^+ + H_2O$$

[80] B. M. Thakuria and Y. K. Gupta, *J.C.S. Dalton*, 1975, 77.

with values of 0.078 mol l^{-1} and 154 l mol^{-1} s^{-1} respectively for K_h and k (T = 25 °C, I = 0.5 mol l^{-1}) (see Table 6, p. 80). Subsequent steps include the isomerization and decomposition of $H_2N_2O_2$. Formation of a precursor [Tl^{III}–NH_3OH^+] complex is thought likely though no kinetic or spectrophotometric evidence was found. Such a mechanism would be consistent with the observed rate inhibition by chloride ion which was ascribed to formation of $Tl^{III}Cl_n$ complexes. Similar chloride inhibition was observed in the oxidation of hydrazine to form nitrogen,[81]

$$2Tl^{III} + N_2H_5^+ \longrightarrow 2Tl^{I} + N_2 + 5H^+$$

and the formation of chloro-complexes was again considered the explanation. The results are consistent with the mechanism

$$Tl^{3+} \overset{K_h}{\rightleftharpoons} [TlOH]^{2+} + H^+$$

$$[TlOH]^{2+} + N_2H_5^+ \overset{k}{\longrightarrow} Tl^+ + N_2H_2 + 2H^+ + H_2O$$

$$Tl^{III} + N_2H_2 \overset{\text{fast}}{\longrightarrow} Tl^{I} + N_2 + 2H^+$$

although, as in the previous paper, the possibility of complex formation cannot be ruled out. No spectrophotometric or kinetic evidence for complex formation was observed.

The effect of added chloride was investigated in detail in the oxidation of phosphite to phosphate.[82] Determination of the order in Tl^{III} at a series of chloride concentrations yielded a rate law

$$\frac{-d[Tl^{III}]}{dt} = \left\{kK\frac{[Tl^{III}]_{aq}}{[H^+]} + k_1[TlCl^{2+}] + k_2[TlCl_2^+] + k_3[TlCl_3] + k_4[TlCl_4^-]\right\}\frac{[H_3PO_3]_T[H^+]}{[H^+] + K_d}$$

which corresponds to the mechanism

$$H_3PO_3 \overset{K_d}{\rightleftharpoons} H_2PO_3^- + H^+$$

$$[TlCl_n]^{3-n} + H_3PO_3 \overset{k_n}{\longrightarrow} \text{products}$$

$$Tl^{3+} + H_3PO_3 \overset{K}{\rightleftharpoons} [TlH_2PO_3]^{2+} + H^+$$

$$H^+ \Big\Vert\, K_h$$

$$[TlOH]^{2+} + H_3PO_3 \overset{K'}{\rightleftharpoons} [TlH_2PO_3]^{2+}$$

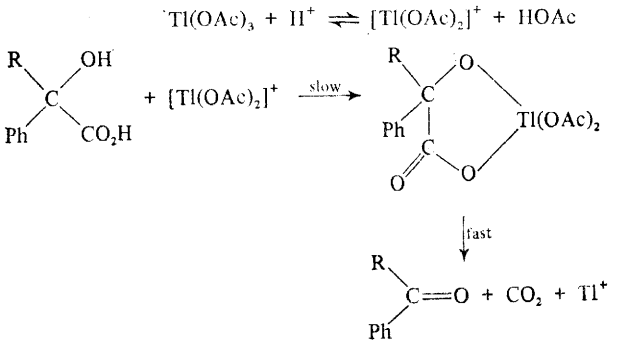
$$[TlH_2PO_3]^{2+} \overset{k}{\longrightarrow} \text{products}$$

The order of reactivity, $TlCl_4^- > TlCl_3 > TlCl_2^+ > Tl^{3+} > TlCl^{2+}$, reflects the change in mechanism from a chloride-bridged activated mechanism with the chloro-complexes to one involving intermediate complex formation with the aquo-ion.

Changing the ratio of water to acetic acid as the solvent in the oxidation of

[81] B. M. Thakuria and Y. K. Gupta, *J.C.S. Dalton*, 1975, 2541.
[82] K. S. Gupta and Y. K. Gupta, *Inorg. Chem.*, 1975, **14**, 2000.

substituted 2-hydroxycarboxylic acids reveals that $[Tl(OAc)_2]^+$ is the reactive oxidizing species.[83] The mechanism shown in Scheme 14 is considered to involve rate-



Scheme 14

determining formation of a chelate complex which subsequently decomposes by oxidative decarboxylation. As the bulk of R increases from H, Me, Ph, to $PhCH_2$ the rate increases, a fact attributed to the steric influence of these groups in the transition state.

In mixed acetic acid–sulphuric acid solvent, the oxidation of substituted benzyl alcohols involves C—H bond rupture in the rate-determining step.[84] Acceleration of the rate by electron-releasing substituents indicates that the hydrogen on the primary alcohol carbon is lost as a hydride ion.

8 Cerium(IV)

Cerium(IV) oxidizes DMSO to dimethyl sulphone in aqueous perchloric acid:[85]

$$Me_2SO + Ce^{IV} + H_2O \rightleftharpoons Me_2SO_2 + Ce^{III} + 2H^+$$

The dependence of the observed first-order rate constant on [DMSO] is consistent with the formation of a complex between the reactants and suggests the mechanism

$$CeOH^{3+} + H^+ \overset{K_1}{\rightleftharpoons} Ce^{4+}$$

$$Ce^{4+} + Me_2SO \overset{K_2}{\rightleftharpoons} [\text{complex}]$$

$$[\text{complex}] \xrightarrow{k_3} Ce^{III} + Me_2\overset{+}{S}-O\cdot$$

$$Me_2\overset{+}{S}-O\cdot + H_2O \xrightarrow{\text{rapid}} Me_2SO + H^+ + \cdot OH$$

$$Me_2\overset{+}{S}-O\cdot + \cdot OH \xrightarrow{\text{rapid}} Me_2SO_2{}^+H$$

The proposed scheme yields a rate law

$$\frac{-d[Ce^{IV}]}{dt} = \frac{K_1K_2k_3[Ce^{IV}][DMSO][H^+]}{1 + K_1K_2[H^+][DMSO] + K_1[H^+]}$$

[83] S. B. Mohanty, R. C. Acharya, C. N. Nanda, and M. K. Rout, *J. Indian Chem. Soc.*, 1976, **53**, 59.
[84] V. S. Srinivasan and N. Venkatasubramanian, *Indian J. Chem.*, 1975, **13**, 526.
[85] H. K. Pratihari, A. K. Roy, and P. L. Nayak, *J. Indian Chem. Soc.*, 1976, **53**, 4.

with values of K_1, K_2, and k_3 of 8.12 l mol^{-1}, 19.05 l mol^{-1}, and 1×10^{-3} l mol^{-1} s^{-1} respectively at 25 °C (I = 1.5 mol l^{-1}). Inhibition of the rate by the addition of sulphate reflects the formation of sulphate complexes.

In the Ce^{IV} oxidation of 4,4′-biphenyldiol (10) the rate law

$$-\tfrac{1}{2}\,d[Ce^{IV}]/dt = k_0'[Co^{IV}][10]$$

has no significant variation with acidity[46] with a value of k_0' of 13×10^6 l mol^{-1} s^{-1} at 16 °C (I = 4.0 mol l^{-1}). Under the acidic conditions used, $CeOH^{3+}$ is considered the major reactant and the proposed mechanism involves rapid complex formation followed by a one-electron transfer to yield the semiquinone, which in turn is oxidized to 4,4′-biphenoquinone (11).

$$(10) + Ce^{IV} \overset{K}{\rightleftharpoons} [(10)\text{–}Ce^{IV}] \xrightarrow{k'} (10)^{\cdot} + Ce^{III} \xrightarrow[\text{fast}]{Ce^{IV}} (11) + Ce^{III}$$

This product (11) is further oxidized by Ce^{IV} with a rate step which is independent of metal ion and similar to the corresponding oxidation by Mn^{III}. Rate-determining acid-catalysed addition of water to (11) followed by rapid electron transfer is proposed.

The rate laws observed in the oxidation of substituted mandelic acids (H_2A) by Ce^{IV} in nitrate media,

$$\frac{-d[Ce^{IV}]}{dt} = \frac{k[H_2A][Ce^{IV}]}{K^{-1} + [H_2A]}$$

are consistent with a general mechanism involving complex formation with $CeOH^{3+}$ as the active oxidizing species:[86]

$$Ce^{IV} + H_2A \overset{K}{\rightleftharpoons} [\text{complex}] \xrightarrow{k_2} Ce^{III} + \text{radical}$$

The radical product is further oxidized to give CO_2 and the corresponding substituted benzaldehyde. Although it was shown that the effect of substituents on the complex formation constant K is minor, their effect on the rate suggests a weakly electron-deficient transition state. The absence of a kinetic isotope effect shows that the α-C—H bond is not cleaved in the rate-determining step and the proposed mechanism involves oxidative decarboxylation with simultaneous production of a free radical.

Pentane-1,5-diol is oxidized to 5-hydroxypentanal (P) by Ce^{IV} in sulphate media.[87] Two competing effects explain the dependence of the reaction rate on addition of H_2SO_4: the rate is accelerated by H^+ but retarded by HSO_4^-. Inclusion of a dimeric species in the mechanism explains why, when Ce^{IV} is the rate-limiting reagent, the observed 'first-order' rate constant has a dependence on $[Ce^{IV}]$:

$$2Ce(SO_4)_2 \overset{K_1}{\rightleftharpoons} [Ce(SO_4)_2\text{–}Ce(SO_4)_2]$$

$$Ce(SO_4)_2 + HSO_4^- \overset{K}{\rightleftharpoons} [Ce(SO_4)_3]^{2-} + H^+$$

$$Ce(SO_4)_2 + \text{diol} \overset{K_2}{\rightleftharpoons} \text{complex} \xrightarrow{k} R^{\cdot} + Ce^{III} + H^+$$

$$[Ce(SO_4)_3]^{2-} + \text{diol} \xrightarrow{k'} R^{\cdot} + Ce^{III} + H^+$$

$$Ce^{IV} + R^{\cdot} \xrightarrow[\text{fast}]{k'} P + Ce^{III} + H^+$$

[86] K. K. Banerji, *J. Indian Chem. Soc.*, 1975, **52**, 573.
[87] P. S. Senkhla and R. N. Mehotra, *Indian J. Chem.*, 1975, **13**, 904.

where $R^{\cdot} = CH_2OH(CH_2)_3\dot{C}HOH$. Values of 2.53×10^{-5} and 1.03×10^{-2} l mol^{-1} s^{-1} were obtained for k' and K_2k respectively. It is of interest to note that the 1,5-diol is oxidized in a fashion similar to an alcohol with C—H bond fission rather than a 1,2-diol with C—C bond fission.

Oxygen has a marked effect on the rate of oxidation of substituted benzaldehydes by Ce^{IV} in mixed acetic acid–sulphuric acid media.[88] The reactions were studied under an atmosphere of nitrogen and the kinetics and stoicheiometry are consistent with the mechanism

$$Ce^{IV} + PhCHO \xrightarrow[\text{slow}]{k} Ce^{III} + Ph\dot{C}O + H^+$$

$$Ph\dot{C}O + Ce^{IV} \xrightarrow{\text{fast}} Ph\overset{+}{C}O + Ce^{III}$$

$$Ph\overset{+}{C}O + H_2O \xrightarrow{\text{fast}} PhCO_2H + H^+$$

in which C—H bond cleavage takes place in the rate-determining step. The presence of free radicals was confirmed by the addition of acrylamide and the effect of substituents on the rate is in accordance with formation of an electron-deficient centre.

The reactive Ce^{IV} species in sulphuric acid media is the neutral $Ce(SO_4)_2$ rather than $[CeSO_4]^{2+}$ or $[Ce(SO_4)_3]^{2-}$. This conclusion was reached in a study[89] in which the effects of changing the solvent dielectric on the rates of Ce^{IV} oxidations of a series of organic substrates were examined. In another paper,[90] the e.p.r. method was used to study the oxidation of t-butyl hydroperoxide by Ce^{IV}. In 0.1M-$HClO_4$, the second-order rate constant, 1.2×10^5 l mol^{-1} s^{-1} was larger than that in 0.4M-H_2SO_4, 1.3×10^4 l mol^{-1} s^{-1} and was explained by sulphate complex formation and changes in the degree of hydrolysis of Ce^{IV}.

The kinetics and mechanism of the iodine-catalysed Ce^{IV} oxidation of As^{III} in aqueous acidic sulphate media have been reported.[91] Under pseudo-first-order conditions (excess of $[As^{III}]$), the observed rate is accelerated by H^+ and I^- and retarded by HSO_4^-. The mechanism

$$H_3AsO_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H^+ + H_2AsO_3^-$$

$$[Ce(SO_4)_3]^{2-} + H^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Ce(SO_4)_2 + HSO_4^-$$

$$Ce(SO_4)_2 + I^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [Ce(SO_4)_2I]$$

$$[Ce(SO_4)_2I] + H_3AsO_3 \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} [Ce(SO_4)_2\cdots I\cdots As(OH)_3]$$

$$[Ce(SO_4)_2\cdots I\cdots As(OH)_3] + [Ce(SO_4)_3]^{2-} \xrightarrow{k_5} Ce^{III} + As^V + I^-$$

[88] P. K. Saiprakash, B. Sethuram, and T. N. Rao, *J. Indian Chem. Soc.*, 1975, **52**, 973.
[89] P. K. Saiprakash, B. Sethuram, and T. N. Rao, *J. Inorg. Nuclear Chem.*, 1976, **38**, 880.
[90] G. P. Voskerchya, V. G. Shuvalov, V. V. Konovalenko, S. S. Ivanchev, and Y. S. Lekedev, *Zhur. fiz. Khim.*, 1975, **49**, 3021.
[91] Y. A. El-Tantawy, A. I. Abu-Shady, *Z. phys. Chem.* (*Frankfurt*), 1975, **96**, 189.

explains the sulphate retardation with $Ce(SO_4)_2$ as the reactive oxidant and it is considered that the role of iodide centres around formation of the transient $[Ce(SO_4)_2\cdots I\cdots As(OH)_3]$, which facilitates electron exchange and is consistent with the low activation energy of 12.4 kcal mol^{-1} compared with that for the uncatalysed reaction (20.6 kcal mol^{-1}).[92]

In a further study of the Ce^{IV} oxidizing system by e.p.r. methods, the rate of production of thiyl radicals was found[93] to be *ca.* 10^3 l mol^{-1} s^{-1}. Significant reactions in their subsequent oxidation were suggested to involve production of sulphinyl and sulphonyl radicals,

$$Ce^{IV} + RSH \longrightarrow RS\cdot$$
$$Ce^{IV} + RS\cdot + H_2O \longrightarrow RSOH$$
$$Ce^{IV} + RSOH \longrightarrow RSO\cdot$$
$$Ce^{IV} + RSO\cdot + H_2O \longrightarrow RSO_2H$$
$$Ce^{IV} + RSO_2H \longrightarrow RSO_2\cdot$$

all of which were detected in the case of RSH = $HO(CH_2)_2SH$. When the corresponding disulphides were subjected to the same conditions, no radicals could be detected.

9 Copper(II)

Three distinct processes were identified in the Cu^{II}-catalysed decarboxylation of oxaloacetate.[94] Although decarboxylation takes place only through the $Cu(oxac)_k$ complex, as shown in Scheme 15, where $(oxac)_k$ represents the keto-form of the

$$(oxac)_k + Cu^{2+} \rightleftharpoons Cu(oxac)_k \xrightarrow{-CO_2} Cu(pyr)_{el} \xrightarrow{H^+} \text{pyruvate}$$
$$\Downarrow \qquad\qquad \Downarrow$$
$$(oxac)_e + Cu^{2+} \rightleftharpoons Cu(oxac)_e$$

Scheme 15

substrate, various complexation and tautomeric equilibria come into play to make the kinetic behaviour complex. The important mechanistic steps which explain the triphasic behaviour are as follows.

Initial $Cu(oxac)_k$ formation is accompanied by the appearance of a transient in the u.v. region of the spectrum. Since the keto–enol equilibrium for Cu(oxac) lies closer to the enol form than for free oxac, this transient disappears at comparable rates by enolization and by decarboxylation to a steady-state concentration. The third phase of the reaction is decarboxylation through this steady-state species. Between these two phases is an intermediate process which is manifest only in pH-stat measurements and involves no decarboxylation. This is assigned to protonation of the copper pyruvate-enolate product $Cu(pyr)_{el}$:

$$Cu(pyr)_{el} + H^+ \longrightarrow Cu(\text{pyruvate})^+$$

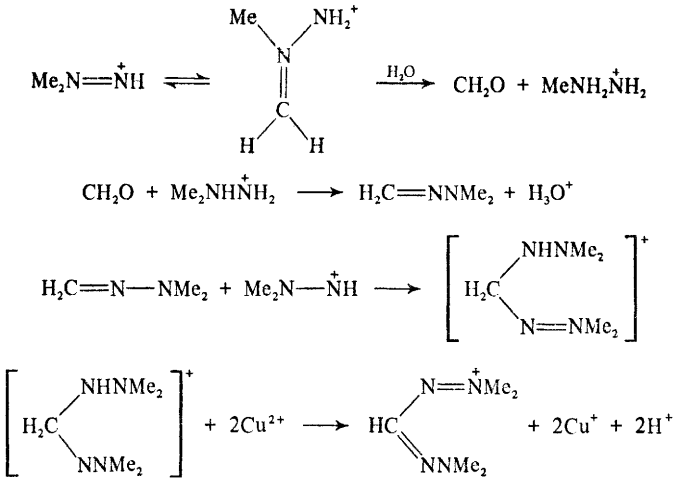
[92] K. G. Everett and D. A. Skoog, *Analyt. Chem.*, 1971, **43**, 1541.
[93] B. C. Gilbert, H. A. H. Laue, R. O. C. Norman, and R. C. Sealy, *J.C.S. Perkin II*, 1975, 892.
[94] N. V. Raghavan and D. L. Leussing, *J. Amer. Chem. Soc.*, 1976, **98**, 723.

A comparison of the rate constants with those for the uncatalysed and Zn^{II}-catalysed reactions[95] reveals that the rates of enolization reflect the keto–enol equilibria, Cu(oxac) > Zn(oxac) ≫ $oxac^{2-}$, and parallel the decarboxylation rate constants, 0.17 s^{-1}, 0.047 s^{-1}, and 1.66×10^{-4} s^{-1} respectively for $Cu(oxac)_k$, $Zn(oxac)_k$, and $oxac_k^{2-}$. This latter observation is in agreement with the weakening effect of the metal on the C—C bond.[94]

The oxidation of 1,1-dimethylhydrazine by $CuCl_2$ in dilute hydrochloric acid solution at 0 °C produces a purple complex $[(Me_2N{=}N)_2Cu_3Cl_3]$ in which the hydrazine has been converted into a diazine derivative:[96]

$$Me_2N\overset{+}{N}H_3 + 2Cu^{2+} \longrightarrow Me_2N{=}\overset{+}{N}H + 2Cu^{+} + 2H^{+}$$

Subsequent treatment with acid and then ammonia leads to the formation of a tetrazine derivative by the route proposed in Scheme 16. Release of hydrogen ions



Scheme 16

creates a pH sensitivity in the reaction and although the reaction has been written as a series of two-electron oxidation steps, radical intermediates are almost certainly involved.

Both copper(II) and copper(I) form complexes with trimethylamine.[97] The oxidation of this substrate by $CuCl_2$ involves the dimethylmethyleneammonium cation $Me_2N{=}\overset{+}{C}H_2$,

$$2CuCl + 2Me_3N \longrightarrow Me_2N{=}\overset{+}{C}HCl^{-} + 2CuCl + Me_3\overset{+}{N}HCl^{-}$$

followed by polymerization to yield a tarry product:

$$Me_3N + Me_2N{=}\overset{+}{C}H_2Cl^{-} \longrightarrow Me_3\overset{+}{N}HCl^{-} + 1/n(Me_2NCH)_n$$

[95] W. D. Carey and D. L. Leussing, *J. Amer. Chem. Soc.*, 1974, **96**, 3860.
[96] J. R. Boehm, A. L. Balch, K. F. Bizol, and J. H. Enemerk, *J. Amer. Chem. Soc.*, 1975, **97**, 501.
[97] T. A. Lane and J. T. Yoke, *Inorg. Chem.*, 1976, **15**, 484.

Variable stoicheiometry is observed owing to complexation with the metal ions and subsequent oxidation steps.

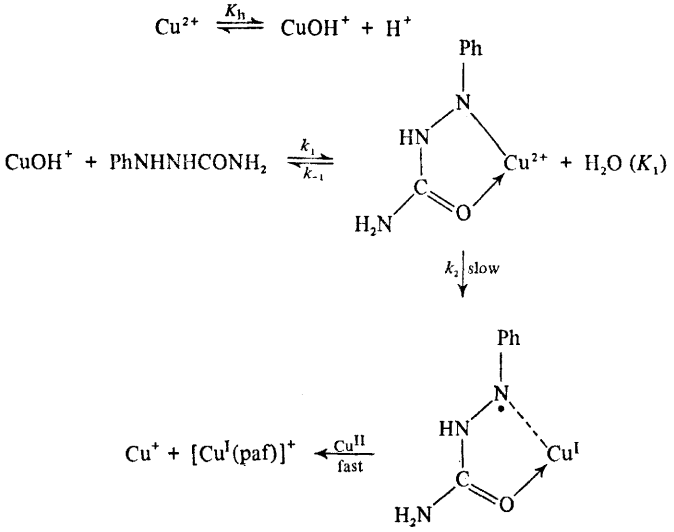
Reduction of Cu^{II} by 1-phenylsemicarbazide (PSC) produces[98] the brown copper(I) phenylazoformamide complex Cu^{I}(paf):

$$2Cu^{2+} + PhNHNHCONH_2 \longrightarrow [Cu(PhN{=}NCONH_2)]^+ + Cu^+$$

The reaction kinetics follow a rate law

$$d[Cu(paf)^+]/dt = k[Cu^{2+}][PSC][H^+]^{-1}$$

consistent with reaction of $CuOH^+$ with the protonated substrate as shown in Scheme 17, where $k = k_2K_1K_h$ has a value of 7.8×10^{-4} s^{-1} at 20 °C (I = 1.2 mol



Scheme 17

l^{-1}). It is proposed that complete intramolecular electron transfer takes place in the rate-determining step to give a co-ordinated radical which subsequently reacts with a second mole of Cu^{2+}, possibly with formation of a mixed-valence dinuclear complex. This mechanism is kinetically indistinguishable from one in which the rate step is free-radical production, though no polymer was produced on addition of acrylonitrile to the reaction mixture.

Bathocuproin disulphonate (bcds) has been used to scavenge copper(I) produced in the copper(II) oxidation of hydroxylamine.[99] The rate law in sulphate media,

$$\tfrac{1}{2}\, d[Cu^{I}(bcds)_2]/dt = k[NH_2OH][Cu^{2+}][H^+]^{-1}$$

gives a value of k of 3.1×10^{-4} s^{-1} at 25 °C (I = 0.15 mol l^{-1}) and the proposed mechanism involves rate-determining formation of a radical species from a Cu^{II}–

[98] M. A. El-Dessonuy, M. F. Amira, M. S. Abu El Amayem, and M. F. Iskander, *J. Inorg. Nuclear Chem.*, 1976, **38**, 463.
[99] T. Imamura and M. Fujimoto, *Bull. Chem. Soc. Japan*, 1975, **48**, 2971.

hydroxylamine complex (Scheme 18), equating k with the composite k_1KK_a. The low

$$\begin{array}{ccccc} Cu^{2+} & + & NH_2OH & \overset{K}{\rightleftharpoons} & Cu^{II}NH_2OH \\ H^+ \uparrow\downarrow K_h & & K_a \uparrow\downarrow H^+ & & \downarrow k_1 \\ CuOH^+ & & {}^+NH_3OH & & Cu^I + NH_2O\cdot + H^+ \end{array}$$

$$2Cu^{II} + 2NH_2O\cdot \xrightarrow{k_2} 2Cu^I + N_2O + H_2O + 2H^+$$

$$Cu^I + 2bcds \xrightarrow{\text{fast}} [Cu^I(bcds)_2]$$

Scheme 18

value for this parameter is attributed to a small formation constant K. Data for several redox reactions of hydroxylamine are collected in Table 6.

Table 6 *Rate and thermodynamic parameters for selected comparable redox reactions at* 25 °C

Reaction	k/ l mol^{-1} s^{-1}	I/ mol l^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	*Ref.*
$Cu^{2+} + NH_2OH$	6.2×10^{-3}	0.15			99
$[Co^{III}(nta)(OH_2)_2] + NH_2OH$	<0.26	1.0			66
$[Co^{III}(nta)(OH_2)_2OH]^- + NH_2OH$	0.022	1.0			66
$[Co^{III}(nta)(OH_2)_2] + \overset{+}{N}H_3OH$	4.2	1.0			66
$[Co^{III}(nta)(OH_2)OH]^- + \overset{+}{N}H_3OH$	<1.2	1.0			66
$[TlOH]^{2+} + \overset{+}{N}H_3OH$	154	1.0	10	-17	80

The sulphur-containing substrates thiocyanate and thiourea undergo[100] oxidation by 2,9-dimethyl-1,10-phenanthroline (dmp) complexes of copper(II). As with bcds, this ligand forms thermodynamically stable and brightly coloured bis-complexes with copper(I), which is otherwise unstable in aqueous perchlorate media. Under the conditions used, the oxidant is mainly in the form $[Cu(dmp)_2]^{2+}$. Oxidation of thiocyanate obeys a rate law

$$\frac{d[Cu^I(dmp)_2]}{dt} = \frac{[SCN^-][Cu^{II}(dmp)_2]}{B[H^+] + C}$$

consistent with a mechanism involving formation of a $[Cu(dmp)_2(OH)SCN]$ species in a pre-equilibrium step followed by rate-determining electron transfer. The choice between a number of equivalent, alternative mechanisms is made by considering the corresponding reaction with thiourea (RS).[100] In perchlorate media, the kinetics suggest the mechanism

$$[Cu(dmp)]^{2+} + dmp \overset{K_1}{\rightleftharpoons} [Cu(dmp)_2]^{2+}$$

$$[Cu(dmp)]^{2+} \overset{K_h'}{\rightleftharpoons} [Cu(dmp)OH]^+ + H^+$$

$$[Cu(dmp)]^{2+} + RS \overset{K_2}{\rightleftharpoons} [Cu(dmp)SR]^{2+}$$

$$[Cu(dmp)OH]^+ + RS \overset{K_3}{\rightleftharpoons} [Cu(dmp)(SR)OH]^+$$

$$[Cu(dmp)(SR)OH]^+ + SR \xrightarrow{k_4} \text{products}$$

[100] G. Davies and D. J. Loose, *Inorg. Chem.*, 1976, **15**, 694.

in which the rate-determining step is k_4, with values of 74.5 and 72 l mol^{-1} s^{-1} respectively for thiourea and thiocyanate at 25 °C (I = 0.1 mol l^{-1}). The absence of a rate dependence on [dmp] is attributed to the high thermodynamic stabilities of the complex [Cu(dmp)SR]$^{2+}$.

In methanol, the reaction with thiourea has a different mechanism,

$$[Cu(dmp)]^{2+} + dmp \overset{K_4}{\rightleftharpoons} [Cu(dmp)_2]^{2+}$$

$$[Cu(dmp)]^{2+} + RS \overset{K_5}{\rightleftharpoons} [Cu(dmp)SR]^{2+}$$

$$[Cu(dmp)SR]^{2+} + RS \overset{K_6}{\rightleftharpoons} [Cu(dmp)(SR)_2]^{2+}$$

$$[Cu(dmp)_2]^{2+} + RS \xrightarrow{k_7} [Cu(dmp)_2]^{+} + radical$$

$$2(radical) \xrightarrow{fast} product$$

in which the direct reaction, k_7 (5×10^3 l mol^{-1} s^{-1}) is much faster than the production of the mono-complex [Cu(dmp)]$^+$ in aqueous solution. This is in agreement with the increased thermodynamic stability of the bis-species and is supported by the apparent oxidative stability of [Cu(dmp)SR]$^{2+}$ and [Cu(dmp)(SR)$_2$]$^{2+}$ in methanol.

A number of papers dealing with the interaction of copper(II) with sulphur-containing substrates have appeared. Complications found in the reaction of copper(II) with penicillamine have been outlined.[101] These can be overcome substantially by using the related substrate 2-mercapto-2-methylpropanoic acid (21). The results indicate that the intensely brown complex (λ_{max} = 485 nm, ε = 1500 l mol^{-1} cm^{-1}) formed in the reaction with $CuCl_2$ has a stoicheiometry [$Cu^{I}_2Cu^{II}_2(21)_3$] and may be

$$4Cu^{II} + 5(21) \longrightarrow [Cu^{I}_2Cu^{II}_2(21)_3] + (22)$$

$$5Cu^{I} + 3(22) \longrightarrow [Cu^{I}_2Cu^{II}_2(21)_3] + Cu^{II}$$

formed from Cu^{II} or from Cu^{I} and the corresponding disulphide (22). It is suggested that the complications in the penicillamine system are due to polymerization and inhibition of the reaction by disulphide.

The crystal structure of a cluster complex, formed in the reaction with penicillamine, has been reported.[102] Eight sulphur-bonded Cu^{I} ions surround a central chloride ion and each of six Cu^{II} ions is N_2S_2-co-ordinated by two chelating penicillamine ligands (L) in the complex [$Cu^{I}_8Cu^{II}_6L_{12}Cl$]$^{5-}$.

Penicillamine also undergoes reactions with copper(II) peptide complexes which might act as models for the therapeutic effect of penicillamine in the removal of copper in Wilson's disease.[103] A number of species could be identified by e.p.r. and visible absorption techniques, including 1:1 and 1:2 penicillamine–copper(II) complexes, in the binary system although in the ternary systems there was no e.p.r.-detectable ternary complex. The results are consistent with the scheme shown, in

$$Cu^{II}G_2 + pen \rightleftharpoons \tfrac{1}{2}[Cu^{II}_2G_2(pen)_2]$$

$$\tfrac{1}{2}[Cu^{II}_2G_2(pen)_2] + pen \rightleftharpoons [Cu^{II}(pen)_2] + G_2$$

$$[Cu^{II}(pen)_2] \rightleftharpoons \frac{1}{n}[Cu^{I}(pen)]_n + disulphide$$

[101] W. K. Musker and C. H. Neagley, *Inorg. Chem.*, 1975, **14**, 1728.
[102] P. J. M. W. L. Birker and H. C. Freeman, *J.C.S. Chem. Comm.*, 1976, 312.
[103] S. H. Laurie, T. Lund, and J. B. Rayner, *J.C.S. Dalton*, 1975, 1389.

which pen represents D-penicillamine and G_2 represents diglycine. Dimeric $[Cu^{II}_2G_2(pen)_2]$ is considered to be *N,S*-bonded with the sulphur acting as a bridge between the two metal centres. The significant finding relates to the solubility of the copper(I) polymer with penicillamine compared with similar products in the reactions of other sulphur-containing substrates. This may reflect the therapeutic value of penicillamine.

10 Miscellaneous Redox Reactions

Propan-2-ol is oxidized[104] to acetone by two equivalents of Ag^{II}. The reaction is rapid and shows a first-order dependence on $[Ag^{II}]$, suggesting that direct participation of Ag^{III} in the reaction is unlikely. Disproportionation of Ag^{II} to form Ag^{I} and Ag^{III} with direct oxidation by Ag^{III} would result in a second-order dependence on Ag^{II}. Stabilization of the tervalent form by a strong complex with alcohol can also be discounted since this would result in a zero-order dependence on alcohol, and not the first-order dependence observed. It is concluded that the reaction involves direct attack of Ag^{II} on propan-2-ol. Rate retardation by the addition of Ag^{I} was shown to be inconsistent with the formation of oxidatively inert Ag^{I}–ROH complexes and was explained by the existence of a back reaction in the rate-determining steps

$$ROH + H^+ \overset{K_o}{\rightleftharpoons} \overset{+}{R}OH_2$$

$$Ag^{2+} \overset{K_h}{\rightleftharpoons} AgOH^+ + H^+$$

$$Ag^{2+} + ROH \overset{K}{\rightleftharpoons} [Ag^{I}\ \text{radical}] \xrightarrow{k_1} Ag^{I} + \text{radical}$$

$$AgOH^+ + ROH \overset{K'}{\rightleftharpoons} [Ag^{I}(OH_2)\text{radical}] \xrightarrow{k_1} Ag^{I} + \text{radical}$$

The formulation $[Ag^{I}\ \text{radical}]$ can be considered as existing in a solvent cage. Oxidation then proceeds when the radical diffuses out of the cage to be further oxidized to acetone by a second mole of Ag^{II}. The rate data show that the oxidative reactivity of $AgOH^+$ towards propan-2-ol is much less than that of Ag^{2+}. Comparison of activation parameters with those for propan-2-ol oxidations by other oxidants reveals no relation to the standard redox potential.

In the corresponding reaction of 4,4′-biphenyldiol (10), which is also very rapid and was studied[46] at 0 °C, a free-energy correlation between the rates of oxidation by Mn^{III}, Ce^{IV}, and Ag^{II} and the standard redox potentials was considered fortuitous in the light of the different mechanisms and pathways involved with different metal ions. Assuming a second-order rate law, the rate constant for the reaction with Ag^{II}

$$Ag^{II} + (10) \longrightarrow (11)$$

is greater than 5×10^7 l mol^{-1} s^{-1} in 4.0M-$HClO_4$. Reaction of the product of this oxidation, 4,4′-biphenoquinone (11), with Ag^{II} is consistent with the mechanism

$$\begin{array}{lll} Ag^{2+} + (11) & \xrightarrow{k_{10}} & \text{radical} + Ag^{I} \\ H^+ \Big\Vert K_h & & \\ AgOH^+ + (11) & \xrightarrow{k_{11}} & \text{radical} + Ag^{I} \\ Ag^{II} + \text{radical} & \xrightarrow{\text{fast}} & \text{products} \end{array}$$

[104] C. F. Wells and D. Fox, *J. Inorg. Nuclear Chem.*, 1976, **38**, 287.

and the value of k_{10} is 1.61×10^4 l mol^{-1} s^{-1} at 25 °C (I = 4.0 mol l^{-1}). The acid-catalysed pathway is small and it is suggested that the reaction consists of direct attack of the metal ion at a C=C double bond.

In the formation of CO_2 from the silver(II) oxidation of formic acid,[105] the experimental rate law at constant [H$^+$] and excess substrate is

$$-\mathrm{d[Ag^{II}]}/\mathrm{d}t = k_{\mathrm{I}}^{0}[\mathrm{Ag^{II}}][\mathrm{HCO_2H}] + k_{\mathrm{II}}^{0}[\mathrm{Ag^{II}}]^2[\mathrm{HCO_2H}][\mathrm{Ag^{I}}]^{-1}$$

To explain the dependence on [H$^+$], it was necessary to take into account the presence of the hydrolysed species $AgOH^+$ and $AgOH^{2+}$ in the mechanism:

$$\mathrm{Ag^{2+}} \overset{K_h}{\rightleftharpoons} \mathrm{AgOH^+} + \mathrm{H^+}$$

$$\mathrm{Ag^{2+}} + \mathrm{HCO_2^-} \xrightarrow{k_1} \mathrm{Ag^{I}} + \text{radical}$$

$$\mathrm{AgOH^+} + \mathrm{HCO_2H} \xrightarrow{k_2} \mathrm{Ag^{I}} + \text{radical}$$

$$\mathrm{Ag^{II}} + \text{radical} \xrightarrow{k_3} \mathrm{Ag^{I}} + \mathrm{CO_2}$$

$$\mathrm{HCO_2H} \overset{K_a}{\rightleftharpoons} \mathrm{HCO_2^-} + \mathrm{H^+}$$

It is not possible to distinguish between the pathways $K_a k_1$ and $K_h k_2$ which carry the major part of the reaction, corresponding to the k_{I}^0 term. The second-order path k_{II}^0,

$$2\mathrm{Ag^{2+}} \overset{K}{\rightleftharpoons} \mathrm{Ag^{3+}} + \mathrm{Ag^+}$$

$$\mathrm{Ag^{3+}} \overset{K_h'}{\rightleftharpoons} \mathrm{AgOH^{2+}} + \mathrm{H^+}$$

$$\mathrm{Ag^{3+}} + \mathrm{HCO_2^-} \xrightarrow{k_4} \mathrm{Ag^{I}} + \mathrm{CO_2}$$

$$\mathrm{AgOH^{2+}} + \mathrm{HCO_2H} \longrightarrow \mathrm{Ag^{I}} + \mathrm{CO_2}$$

shows a similar ambiguity involving hydrolysis of Ag^{III} which is formed by disproportionation of Ag^{II}. Although resolution of the individual rate constants was not possible, the hydrolysis constants for Ag^{2+} and Ag^{3+} were evaluated as 0.35 and 0.42 l mol^{-1} respectively (T = 22 °C, I = 4.0 mol l^{-1}).

The reaction of tetrahydroxoargentate(III) with ethylenediamine involves reduction of the metal ion to metallic silver.[106] At 25 °C and an ionic strength of 1.2 mol l^{-1}, the rate law consists of three terms with k_1 = 0.60 s^{-1}, k_2 = 32.2 l mol^{-1} s^{-1}, and k_3 = 26.6 l mol^{-1} s^{-1},

$$-\mathrm{d[Ag^{III}]}/\mathrm{d}t = (k_1 + k_2[\mathrm{en}] + k_3[\mathrm{en}][\mathrm{OH^-}])[\mathrm{Ag^{III}}]$$

and is best explained by a mechanism in which metal complexation is rate determining,

$$[\mathrm{Ag(OH)_4}]^- + \mathrm{H_2O} \xrightarrow{k_1} [\mathrm{Ag(OH)_3OH_2}] + \mathrm{OH^-}$$

$$[\mathrm{Ag(OH)_3OH_2}] + \mathrm{en} \xrightarrow{\text{fast}} [\mathrm{Ag(en)(OH)}_n] + (3-n)\mathrm{OH^-} + \mathrm{H_2O}$$

$$[\mathrm{Ag(OH)_4}]^- + \mathrm{en} \xrightarrow{k_2} [\mathrm{Ag(en)(OH)}_n] + (4-n)\mathrm{OH^-}$$

[105] E. Pelizzetti and E. Mentasti, *J.C.S. Dalton*, 1975, 2086.
[106] L. J. Kirschenbaum, *J. Inorg. Nuclear Chem.*, 1976, **38**, 881.

the number of remaining hydroxy-groups, n, depending on whether ethylenediamine acts as a unidentate ($n = 3$) or a bidentate ($n = 2$) ligand. Intramolecular electron transfer can then occur rapidly:

$$[\mathrm{Ag(en)(OH)}_n] \xrightarrow{k} \text{products}$$

The products, though not identified, are assumed to be similar to those found[107] in the corresponding reaction with copper(III). Support for the mechanism of the base-catalysed pathway $k_3 = k_9K_8$ is also obtained from the copper(III) system:

$$[\mathrm{Ag(OH)_4}]^- + \mathrm{en} \overset{K_8}{\rightleftharpoons} [\mathrm{(HO)_4Ag(en)}]^-$$

$$[\mathrm{(HO)_4Ag(en)}]^- + \mathrm{OH}^- \xrightarrow{k_9} \mathrm{Ag^I} + \mathrm{NH_3} + \mathrm{NH_2CH_2CHO}$$

Prior formation of a five-co-ordinate precursor $[\mathrm{(HO)_4Ag(en)}]^-$ is followed by reduction by hydroxide ion. Metallic silver is produced by reaction of Ag^I with the organic product glycinealdehyde.

Univalent silver catalyses the oxidation of water by peroxodiphosphate.[108] The experimental rate law ($[P_2O_8^{2-}] > 5 \times 10^{-3}$ mol l^{-1}),

$$-\mathrm{d}[\mathrm{P_2O_8^{2-}}]/\mathrm{d}t = k_a[\mathrm{P_2O_8^{2-}}][\mathrm{Ag^+}] + k_b[\mathrm{P_2O_8^{2-}}][\mathrm{Ag^+}][\mathrm{H^+}] + k_w[\mathrm{P_2O_8^{2-}}][\mathrm{H^+}]$$

reflects the formation of Ag^{III} from disproportionation of Ag^{II} produced in the oxidation of Ag^+ by $H_3P_2O_8^-$. Values for k_a and k_b are 0.62 l mol^{-1} s^{-1} and 0.86 l^2 mol^{-2} s^{-1} respectively at 40 °C ($I = 0.85$ mol l^{-1}) and the uncatalysed term k_w is negligible by comparison. Oxidation of water proceeds by hydrolysis of Ag^{3+}:

$$\mathrm{Ag^{3+}} \rightleftharpoons \mathrm{AgO^+} + 2\mathrm{H^+} \longrightarrow \mathrm{Ag^+} + \tfrac{1}{2}\mathrm{O_2}$$

Catalysis by Ag^I was also observed[109] in the peroxodiphosphate oxidation of As^{III} in perchloric acid media. The reaction rate is independent of $[As^{III}]$ and conforms to the expression

$$-\mathrm{d}[\mathrm{P_2O_8^{4-}}]/\mathrm{d}t = k_2[\mathrm{H_3P_2O_8^-}] + k_3[\mathrm{H_4P_2O_8}]$$

with values for k_2 and k_3 of 2.7×10^{-4} and 8.65×10^{-3} s^{-1} respectively at 45 °C ($I = 2.5$ mol l^{-1}). Under the conditions of the study, reactions of the diprotonated form $[H_2P_2O_8]^{2-}$ are undetected and the rate is apparently controlled by hydrolysis of the oxidant. This is followed by the rapid oxidation of As^{III} in a step which does not produce free-radical species.

The effects of allyl acetate, a radical trap, on the rates of decomposition of peroxodisulphate and oxidation of formamide by this reagent, both catalysed by Ag^+, are similar.[110] This suggests that the radical involved in both processes may be the same. The proposed mechanism,

[107] D. Meyerstein, *Inorg. Chem.*, 1971, **10**, 2244.
[108] P. Maruthamuthu and M. Santappa, *J. Inorg. Nuclear Chem.*, 1975, **37**, 1305.
[109] S. Kapoor and Y. K. Gupta, *J.C.S. Dalton*, 1976, 473.
[110] S. P. Srivastava, H. Singh, and A. Kumar, *J. Indian Chem. Soc.*, 1975, **52**, 404.

$$S_2O_8^{2-} + Ag^+ \xrightarrow{k_1} Ag^{2+} + SO_4^{2-} + SO_4^{-\cdot}$$

$$SO_4^{-\cdot} + H_2O \xrightarrow{k_2} HSO_4^- + {\cdot}OH$$

$$HCONH_2 + H_2O \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} HCO_2H + NH_3$$

$$HCO_2H + {\cdot}OH \xrightarrow{k_4} HCO_2^{\cdot} + H_2O$$

$$HCO_2H + Ag^{2+} \xrightarrow{k_5} HCO_2^{\cdot} + H^+ + Ag^+$$

$$HCO_2^{\cdot} + S_2O_8^{2-} \xrightarrow{k_6} CO_2 + HSO_4^{-\cdot} + SO_4^{-\cdot}$$

$$HCO_2^{\cdot} + SO_4^{-\cdot} \xrightarrow{k_7} HSO_4^- + CO_2$$

yields a rate law which is independent of formamide concentration.

A mechanism involving Ag^{2+} and ·OH as active oxidants is also proposed for the corresponding oxidation of 3-phenylpropionic acid.[111] Similar initiating reactions k_1 and k_2 lead to a rate law which is the main feature of the reaction,

$$-d[S_2O_8^{2-}]/dt = 3k_1[Ag^+][S_2O_8^{2-}]$$

The role of substituents on the silver(I)-catalysed oxidation of phenols by peroxydisulphate correlates better with attack at the phenol oxygen rather than at the 3-carbon atom.[112] Rate acceleration by electron-releasing groups is observed.

Peroxydisulphate is unstable in aqueous solution and the kinetics and mechanism of its decomposition in base have been reinvestigated.[113] The rate is first-order in peroxydisulphate and the observed rate constant shows a dependence on $[OH^-]$ and the ionic strength:

$$-d[S_2O_8^{2-}]/dt = (k_0 + k_1[OH^-])[S_2O_8^{2-}]$$

Rate-determining bond cleavage, proposed for the k_0 pathway, involves the separation of two negative charges, a repulsive interaction which is reduced with increasing ionic strength, thereby explaining the observed decrease in rate constant:

$$S_2O_8^{2-} \xrightarrow{k_0} 2SO_4^{-\cdot}$$

$$SO_4^{-\cdot} + H_2O \xrightarrow{\text{fast}} HSO_4^- + {\cdot}OH$$

$$2{\cdot}OH \xrightarrow{\text{fast}} H_2O + \tfrac{1}{2}O_2$$

$$S_2O_8^{2-} + OH^- \xrightarrow{k_1} HSO_4^- + SO_5^{2-}$$

$$SO_5^{2-} \xrightarrow{\text{fast}} SO_4^{2-} + \tfrac{1}{2}O_2$$

In contrast the k_1 pathway involves nucleophilic attack by ^-OH on $S_2O_8^{2-}$ and is accelerated by increasing ionic strength.

[111] G. L. Mahanshwari, S. K. Singhal, and B. D. Tyagi, *J. Indian Chem. Soc.*, 1975, **52**, 1029.
[112] L. D. Sharma, R. C. Gupta, and S. P. Srivastava, *Indian J. Chem.*, 1975, **13**, 978.
[113] V. C. Singh and K. Venkatarao, *J. Inorg. Nuclear Chem.*, 1976, **38**, 541.

Acidity dependences in the reactions of $[AuCl_4]^-$ are complicated by the hydrolysis equilibria[114]

$$[AuCl_4]^- + H_2O \overset{K_A}{\rightleftharpoons} [AuCl_3(OH_2)] + Cl^-$$

$$[AuCl_3(OH_2)] \overset{K_B}{\rightleftharpoons} [AuCl_3(OH)]^- + H^+$$

where $K_A = 9.5 \times 10^{-6}$ and $K_B = 0.25$ mol l^{-1} at 25 °C. The suggested mechanism in the oxidation of oxalate involves rate-determining formation of a complex $[AuCl_3(C_2O_4)]^{2-}$ followed by ring closure and then rapid two-electron transfer:[115]

$$[AuCl_3(C_2O_4)]^{2-} \longrightarrow [AuCl_2(C_2O_4)]^- + Cl^-$$

$$[AuCl_2(C_2O_4)]^- \longrightarrow AuCl_2^- + 2CO_2$$

While the latter is always non-rate determining, under certain conditions ring closure provides a limiting rate for the reaction. Substitutions on $[AuCl_3(OH_2)]$ and $[AuCl_3(OH)]^-$ are more rapid than those with $[AuCl_4]^-$ and reduction by oxalic acid is negligible compared with the oxalate and bioxalate ions.

Oxidation of formate was examined by the same workers.[116] The main points of the mechanism, which is similar to that observed with oxalate, are rate-determining complex formation,

$$[AuCl_4]^- + HCO_2H \xrightarrow{k_1'} [AuCl_3(HCO_2)]^- + HCl$$

$$[AuCl_4]^- + HCO_2^- \xrightarrow{k_1''} [AuCl_3(HCO_2)]^- + Cl^-$$

$$[AuCl_3(OH)]^- + HCO_2H \xrightarrow{k_2'} [AuCl_3(HCO_2)]^- + H_2O$$

$$[AuCl_3(OH)]^- + HCO_2^- \xrightarrow{k_2''} [AuCl_3(HCO_2)]^- + OH^-$$

$$[AuCl_3(HCO_2)]^- \xrightarrow{k_3} [AuCl_2]^- + CO_2 + HCl$$

followed by a rapid two-electron transfer (k_3). The absence of pathways involving $[AuCl_3(OH_2)]$ is a function of the restricted pH range ($3 \leqslant pH \leqslant 4$) used. The substitution reactivity $[AuCl_3(OH)]^- > [AuCl_4]^-$ is, however, in the expected order and while formate reacts faster than formic acid, both are slower than with the corresponding forms of oxalic acid.[115]

In 95% methanol, the oxidation of methionine to methionine sulphoxide by $[AuCl_4]^-$ is stereospecific.[117] The absorbance at 320 nm shows that the reaction is biphasic, involving formation of an intermediate species:

$$[AuCl_4]^- + RSMe \rightleftharpoons [Au^{III}Cl_3(RSMe) + Cl^-]$$

$$\qquad\qquad\qquad

On substitution of RSMe for Cl^-, the metal centre becomes more positive and thus a better oxidant. Co-ordination creates a chiral centre at sulphur, determined by the adjacent asymmetric carbon atom, and the approach of the second methionine is affected by the asymmetrically bound ligand. Participation of water in the redox step is implied by the optical purity of the product sulphoxide.

Reduction of the co-ordinated nitrosyl in pentacyanonitrosylferrate(II) (23) under nitrogen has been investigated[118] and was found to proceed in several stages, the first two of which, (23)→(24) and (24)→(25), are readily reversible while the third

$$\underset{(23)}{[(NC)_5Fe-\overset{+}{N}=O]^{2-}} \overset{e^-}{\rightleftharpoons} \underset{(24)}{[(NC)_5Fe-\dot{N}=O]^{3-}} \overset{e^-}{\rightleftharpoons} \underset{(25)}{[(NC)_5Fe-\ddot{N}=O]^{4-}}$$

$$\downarrow 2e^-$$

$$\underset{(26)}{[(NC)_5Fe(NH_2OH)]^{3-}}$$

(25)→(26) is achieved in a single two-electron transfer. Evidence to suggest that the structures of the species change with pH was obtained by e.p.r. methods. In the presence of the thiolates (RS^-) thioglycolic acid and 2-mercaptoethanol, a radical anion is produced from (23). Production of the pink product (27) is rapid and is followed by slow decomposition to give the radical anion (24) and disulphide RSSR:

$$(23) + RS^- \rightleftharpoons \underset{(27)}{\left[(NC)_5Fe^{II}-\overset{+}{N}\begin{matrix}=O\\ \diagdown SR\end{matrix}\right]^{3-}}$$

$$(27) \longrightarrow [(NC)_5Fe^{II}-\dot{N}=O]^{3-} + RS\cdot$$

$$2RS\cdot \longrightarrow RSSR$$

A second pathway involves nucleophilic attack by RS^- to give (25) and direct disulphide formation:

$$(27) + RS^- \longrightarrow [(NC)_5Fe-\ddot{N}=O]^{4-} + RSSR$$

Although the experimental results in the case of thioglycolic acid agree well with the proposed mechanism, the occurrence of secondary reactions does not merit a detailed analysis.

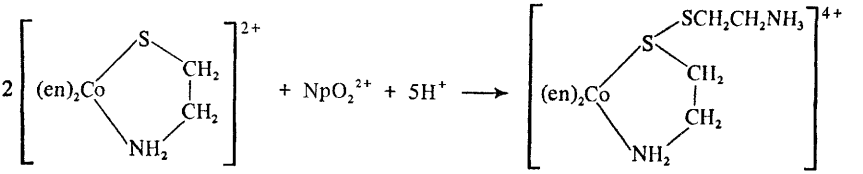
The electron-transfer properties of nitrosyl complexes of Ru^{II} are carried mainly by the nitrosyl ligand.[119] Electrochemical and chemical reduction with I^- in acetonitrile gives a product which is best formulated with a formal reduction of $\overset{+}{N}O$ to NO:

$$[Ru(bipy)_2(NO)Cl]^{2+} \xrightarrow{+e^-} [Ru(bipy)_2(NO)Cl]^{+}$$

This reinforces the idea that the nitrosyl ion can be adequately described as a chemically modified nitrosonium ion.

[118] D. Mulvey and W. A. Waters, *J.C.S. Dalton*, 1975, 951.
[119] R. W. Callahan, G. M. Brown, and T. J. Meyer, *J. Amer. Chem. Soc.*, 1975, **97**, 894.

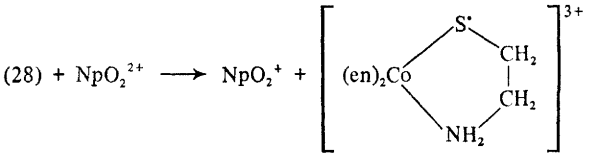
Oxidation of [(2-mercaptoethylamine)-*N*,*S*]bis(ethylenediamine)cobalt(III) (28)



(28) (29)

$$+ Co^{2+} + NpO_2^+ + 2enH_2^{2+}$$

with the one-equivalent oxidant Np^{VI} yields a cobalt(III) complex containing the corresponding disulphide (29).[120] The reaction mechanism is considered to involve formation of a cobalt(III) radical ion dimer (31) which decays by internal electron transfer.



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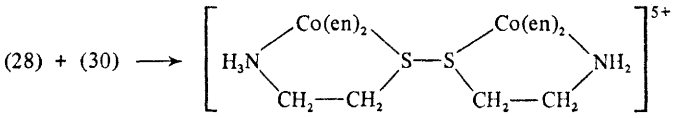
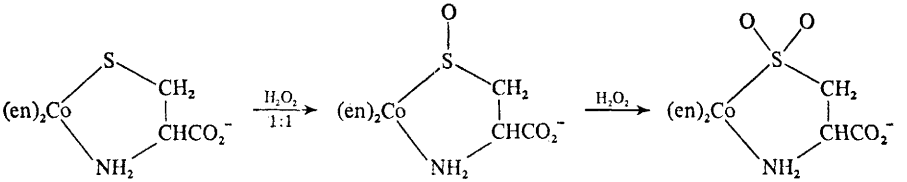


(31)

The corresponding complexes with cysteine do not follow the same oxidation mechanism.[121] In their reactions with H_2O_2, there is oxidation at the co-ordinated sulphur leading first to the highly reactive sulphenato-derivative (32) which is stabilized by the metal ion. Subsequent oxidation leads to the sulphinato-species (33).



(32) (33)

The properties and preparation of a number of ammine–ruthenium complexes of sulphur substrates have been reported.[122] Electrochemical oxidation of $[Ru(NH_3)_5$-

[120] M. Woods, J. C. Sullivan, and E. Deutsch, *J.C.S. Chem. Comm.*, 1975, 749.
[121] C. P. Sloan and J. H. Kreuger, *Inorg. Chem.*, 1975, **14**, 1481.
[122] C. C. Keuhn and H. Taube, *J. Amer. Chem. Soc.*, 1976, **98**, 689.

$SH_2]^{2+}$ proceeds through the deprotonated form $[Ru(NH_3)_5SH]^+$ and leads first to the tervalent ion $[Ru(NH_3)_5SH]^{2+}$. This species is unstable and either by disproportionation or by further oxidation produces the disulphide-bridged dimer $[(NH_3)_5RuSSRu(NH_3)_5]^{4+}$.

Azide complexes of ruthenium(III) can be prepared by oxidation of the corresponding ruthenium(II) species either electrochemically or chemically by Ce^{IV} or Br_2 in acetonitrile:[123]

$$[Ru(bipy)_2(N_3)_2] \xrightarrow{-e^-} [Ru(bipy)_2(N_3)_2]^+$$

The ensuing decomposition reactions are light-catalysed and show a first-order dependence on the ruthenium(III) complex. Although back-bonding ($d\pi$–$p\pi$) is important in metal–nitrene chemistry, the trend in rates observed with the complexes $[Ru(bipy)_2L(N_3)]^{2+}$ (L = N_3^-, MeCN, or py) does not reflect the ability of the metal centre to donate π-electron density but instead correlates with the oxidizing power of the complexed ruthenium(III). No free azide radicals were detected in solution and it is suggested that the rate-determining step involves either metal–nitrene formation,

$$[Ru(bipy)_2(N_3)_2]^+ \longrightarrow [Ru(bipy)_2(N_3)N]^+ + N_2$$

or intramolecular electron transfer,

$$[Ru^{III}(bipy)_2(N_3)N_3]^- \longrightarrow [Ru^{II}(bipy)_2(N_3)N_3]^0$$

to form an intermediate in which the radical is bound to ruthenium(II), followed by nitrene formation.

The oxidations of co-ordinated amines have also been the subjects of a number of papers. A common first step leading to the formation of an imine intermediate (34) is proposed in the oxidation of $[Ru(NH_3)_5NH_2R]$ (R = Ph, Me, or C_6H_{11}) by electrochemical methods.[124] This imine is the product in the case of cyclohexylamine and was detected with benzylamine as a transient which was subject to further oxidation,

$$[Ru^{III}(NH_2CH_2R)] \rightleftharpoons [Ru^{III}(\bar{N}H-CH_2R)] + H^+ \xrightarrow{-e^-} [Ru^{II}(NH=CHR)] + H^+$$
(34)

With methylamine, no intermediate was detected and it is inferred that further oxidation proceeds readily in this instance. Subsequent reactions involve the oxidation of Ru^{II} to Ru^{III} followed by hydrolysis (with cyclohexylimine) or dehydrogenation to form the corresponding nitrile complexes. It is noted that the chemistry of imine complexes in water is severely restricted by their ease of hydrolysis.

Oxidation of methylamine in the complex $[Ru(NH_2Me)_5OH]^{2+}$ has also been examined.[125] It is proposed that the rate-determining step in the conversion into $Ru(CN)_3$ is the replacement of a co-ordinated methylamine by water, with $k_2 = 2.83 \times 10^{-4}\ s^{-1}$ at 25 °C:

$$[Ru(NH_2Me)_5OH]^{2+} + H_2O \longrightarrow [Ru(NH_2Me)_4(OH)(H_2O)]^{2+} + MeCN$$

[123] G. M. Brown, R. W. Callahan, and T. J. Meyer, *Inorg. Chem.*, 1975, **14**, 1915.
[124] S. E. Diamond, G. M. Tom, and H. Taube, *J. Amer. Chem. Soc.*, 1975, **97**, 2661.
[125] J. D. Miller, J. B. Watts, and D. Y. Waddan, *Inorg. Chim. Acta*, 1975, **12**, 267.

As in the previous study, subsequent steps involve imine intermediates.

The oxidative dehydrogenation behaviour of $[Ru(bipy)_2(en)]$ and related compounds has been examined electrochemically in acetonitrile.[126] A net four-electron uptake observed with diamino substrates involves as its first step rapid reversible oxidation to ruthenium(III),

$$[Ru(bipy)_2(en)]^{2+} \overset{-e^-}{\rightleftharpoons} [Ru(bipy)_2(en)]^{3+}$$

followed by formation of the di-imine (dim) complex of ruthenium(II), $[Ru(bipy)_2(dim)]^{2+}$. With substrates which contain an amino and an imine group (imen), a net two-electron uptake is observed. Although in this case, the initial step may again involve formation of a ruthenium(III) complex, the electrode potential is higher and later steps are more rapid such that no reversibility is observed. The results are in accord with the general scheme, where each step involves a single electron release:

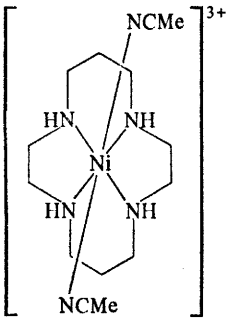
$$[Ru(bipy)_2(en)]^{2+} \longrightarrow [Ru(bipy)_2(en)]^{3+} \longrightarrow [Ru(bipy)(imen)]^{2+}$$

$$\downarrow$$

$$[Ru(bipy)_2(dim)]^{2+} \longleftarrow [Ru(bipy)_2(imen)]^{3+}$$

Where there is no possibility of conjugation in the final di-imine product, further oxidation, again *via* Ru^{III}, occurs.

The oxidation of co-ordinated amine also occurs[127] in the base-promoted reduction of the Ni^{III} macrocyclic complexes (35) and (36). Addition of water to (36) was



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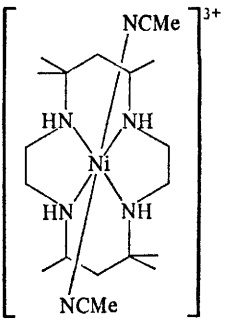


(36)

accompanied by the formation of an intense transient red colour (λ_{max} = 540 nm, $\varepsilon \sim 10^4$) with a half-life of 90 s, decaying to the corresponding square-planar nickel(II) complex. A similar observation was made on the addition of pyridine to either (35) or (36) although the transient stabilities were diminished and a mixture of macrocyclic products was obtained. Addition of water to (19) gave no transient and reverted to the Ni^{II} form much more slowly.

[126] G. M. Brown, T. R. Weaver, F. R. Keene, and T. J. Meyer, *Inorg. Chem.*, 1976, **15**, 190.
[127] E. K. Barefield and M. T. Mocella, *J. Amer. Chem. Soc.*, 1975, **97**, 4238.

It is suggested that the red transient corresponds to Ni^{II} with a co-ordinated ligand radical intermediate formed according to the equation, where B represents a base:

$$Ni^{III}N{<}\!\!\!\!\diagup\!\!\!\!\diagdown{-}H + B \longrightarrow Ni^{II}N{<}\!\!\!\!\diagup\!\!\!\!\diagdown{\cdot} + BH^+$$

Depending on the solvent, the radical may decompose with rupture of the macrocyclic ring or be converted into the Ni^{II} tetramine complex by hydrogen abstraction from ligand fragments or from a second radical species, in which case a monoimine complex is formed. Although no radical species is observed in the reaction of (35) with H_2O, product analysis studies are not inconsistent with radical formation.

Two pathways are indicated in the rate equation for the oxidation of I^- by substituted 1,10-phenanthroline and 2,2′-bipyridyl complexes of Pt^{IV} in acetonitrile:[128]

$$-d[Pt^{IV}]/dt = k_1[Pt(LL)Cl_4] + k_2[Pt(LL)Cl_4][I^-]$$

Rate-determining Pt—Cl bond cleavage followed by a fast redox process is considered to be the mechanism of the k_1 pathway:

$$Pt(LL)Cl_4 + MeCN \underset{}{\overset{k_1}{\rightleftharpoons}} [Pt(LL)Cl_3(NCMe)]^+ + Cl^-$$

$$\text{fast} \downarrow +I^-$$

$$[Pt(LL)Cl_2] + ICl + MeCN$$

Such a pathway is only slightly affected by changes in the uncharged ligand LL and may be removed by the addition of Cl^-. The k_2 path involves an inner-sphere redox mechanism with direct interaction between I^- and a metal-bound chloride in the activated complex. A linear correlation between the rate constants k_2 and the σ-donor ability of LL reflects the oxidizing power of the $Pt^{IV/II}$ couple.

In highly acidic media, ascorbic acid (H_2A) is oxidized[129] by mercury(II) chloride to produce the dehydro-derivative A^1:

$$2HgCl_2 + H_2A \longrightarrow Hg_2Cl_2 + A^1 + 2H^+ + 2Cl^-$$

The proposed mechanism involving a rapid formation of ascorbate ion and subsequent rate-determining interaction with $HgCl_2$,

$$AH_2 \overset{K}{\rightleftharpoons} AH^- + H^+$$

$$HgCl_2 + AH^- \overset{k_1}{\longrightarrow} AH\cdot + HgCl + Cl^-$$

explains the first-order rate dependences on $[AH_2]$, $[HgCl_2]$, and $[H^+]^{-1}$ and gives a value for Kk_1 of 8.06×10^{-5} s^{-1} at 25 °C. Subsequent rapid steps involve further oxidation of the AH· radical by $HgCl_2$ and dimerization of the HgCl product. An initial rapid absorbance jump in the reaction is attributed to ascorbate oxidation by equilibrium amounts of free Hg^{2+}.

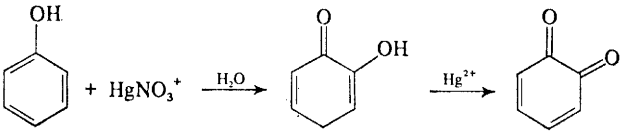
Phenol is oxidized by Hg^{2+} in nitric acid–acetate mixtures.[130] Catalysis by hydrogen

[128] A. Peloso, *J.C.S. Dalton*, 1976, 984.
[129] R. Sanehi, R. M. Mehotra, and S. P. Mushran, *J. Inorg. Nuclear Chem.*, 1975, **37**, 1753.
[130] V. S. Rao, B. Sethuram, and T. N. Rao, *Indian J. Chem.*, 1975, **13**, 1291.

ion and retardation by nitrate suggest that $HgNO_3^+$ and its hydrolysis product $HgNO_3OH$ might be the reactive oxidants. The mechanism proposed (Scheme 19) involves an outer-sphere two-electron transfer to Hg^{2+}.

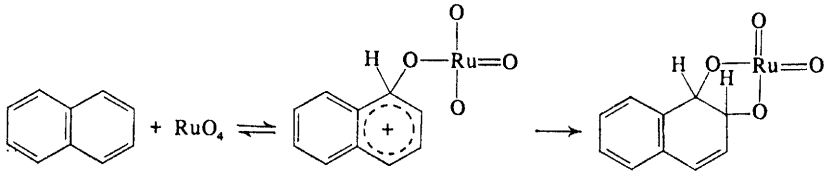
$$Hg^{2+} + NO_3^- \rightleftharpoons HgNO_3^+$$

$$HgNO_3^+ + NO_3^- \rightleftharpoons Hg(NO_3)_2$$



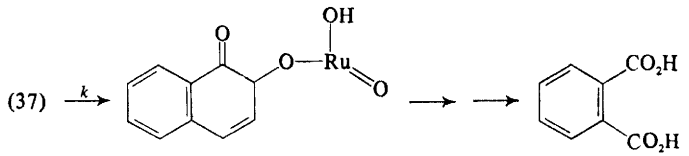
Scheme 19

The oxidation of naphthalene by RuO_4 takes place in two distinct steps.[131] The first shows an inverse hydrogen isotope effect and is accelerated by the presence of electron-releasing substituents consistent with the formation of a transient Ru^{VI}



(37)

intermediate complex (37) involving production of a positive charge. In carbon tetrachloride at 25 °C, the rate of appearance of (37), measured by the increase in absorbance at 385 nm, is 24.1 l mol^{-1} s^{-1}. A slower, first-order decomposition reaction to form phthalic acid (38) exhibits a deuterium isotope effect and the associated negative activation entropy (-20 cal K^{-1} mol^{-1}) is consistent with hydride transfer in the rate-determining step.

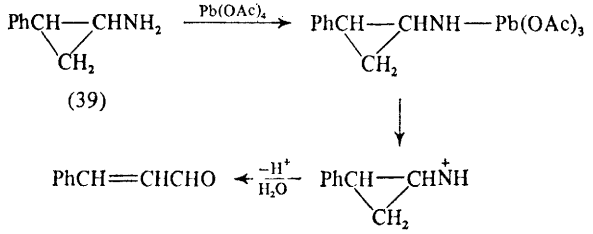


(38)

Cation-radical intermediates are not formed in the oxidation of substituted adamantane derivatives by Pb^{IV}, Co^{III}, and Mn^{III} trifluoroacetate.[132] Instead, attack by the metal salts takes place at a C—H bond.

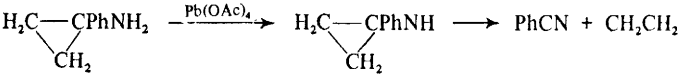
Products of the reactions of substituted cyclopropylamines and aziridines with lead(IV) tetra-acetate may be explained by assuming the common intermediacy of a nitrenium ion.[133] The substrate 2-phenylcyclopropylamine (39) reacts to give *trans*-

[131] V. A. Spitzer and D. G. Lee, *Canad. J. Chem.*, 1975, **53**, 2865.
[132] S. R. Jones and J. M. Mellor, *J.C.S. Chem. Comm.*, 1976, 385.
[133] T. Hiyama, H. Koido, and H. Nozaki, *Bull. Chem. Soc. Japan*, 1975, **48**, 2918.



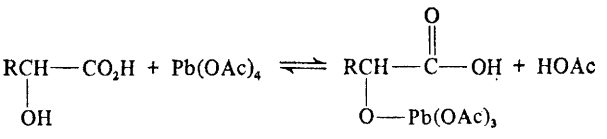
(39)

cinnamaldehyde whereas the 1-phenyl isomer (40) gives benzonitrile and ethylene. The corresponding oxidation of 2-phenylaziridine involves ring-opening to yield benzaldehyde.

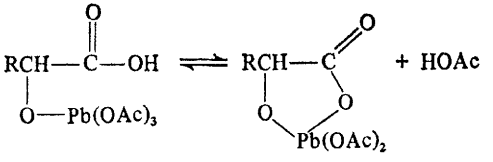


(40)

In acetic acid media, the oxidative decarboxylations of 2-hydroxy-carboxylic acids by $Pb(OAc)_4$ probably involve the formation of hydroxyl-bound complexes (41) with participation of the carboxyl either in a unimolecular decomposition step or in chelate formation (42) followed by decomposition in the rate-determining step.[134] No decarboxylation is found with 3-hydroxybutyric acid, showing the importance of both OH and CO_2H groups in the intermediate formation. The effect of substituents is consistent with a two-electron transfer with development of a carbonyl group from the hydroxy-group in the transition state. No radicals were detected.



(41)



(42)

(41) or (42) ⟶ products

Pyruvate has been shown to trap an intermediate in the Zn^{2+}-catalysed decarboxylation of oxaloacetic acid.[135] Identification of this species as parapyruvate provides evidence that both the zinc-catalysed dimerization of pyruvate and the decarboxylation of oxaloacetate proceed with formation of the pyruvate enolate. Since the rate of

[134] K. Swaminathan, S. Sundaram, and N. Venkatasubramanian, *Indian J. Chem.*, 1975, **13**, *1163*.
[135] B. J. Lillis and D. L. Leussing, *J.C.S. Chem. Comm.*, 1975, 397.

oxaloacetate decarboxylation is unaffected by the addition of pyruvate though dimerization is induced, it is implied that CO_2 is lost before condensation occurs:

$$[Zn(O_2CCOCH_2CO_2)] \underset{k_1}{\overset{-CO_2}{\rightleftharpoons}} [Zn(O_2CCOCH_2)] \begin{cases} \xrightarrow{MeCOCO_2^-} [Zn\{O_2CCOCH_2C(OH)(Me)CO_2\}] \\ \underset{k_{-3}}{\overset{k_3H^+}{\rightleftharpoons}} [Zn(O_2COMe)]^+ \end{cases}$$

It is suggested that the metal ion promotes condensation through a proximity effect with formation of a mixed pyruvate–pyruvate-enolate complex.

A number of papers dealing with aspects of models for nitrogenase enzymes have appeared. Electrochemical methods have been used to generate a monomeric Mo^{III} thiol complex which is catalytically active in the reduction of acetylene.[136] Ferredoxin model compounds of the type $[Fe_4S_4(SR)_4]^{2-}$ accelerate the reduction of similar molybdothiol catalysts[137] by BH_4^- or $S_2O_4^{2-}$. The most effective reducing system in the catalysed reduction of acetylene to ethylene contains the elements Fe^{2+}:S^{2-}:RS^- in the molar ratios 1:2:6. Reduced ferredoxin models and other strong reducing agents also reduce[138] co-ordinated CN^- to NH_3 and alkanes in the monomeric complexes of the type $[MoO_2(CN)_4]^{4-}$. The reduction of N_2 to NH_3 and N_2H_4 was also observed in these systems.

Oscillating chemical systems, observed in the mixture Ce^{IV}–BrO_3^-–malonic acid have been investigated. The sequence of intermediates formed in the oxidation of malonic acid by Ce^{IV} is apparently malonic→tartronic→glyoxylic→formic acids.[139] Though formic acid is normally inert to oxidation by Ce^{IV}, Br^- catalyses the reaction with a mechanism which involves Br_2 and HOBr as active species. In the presence of Ce^{IV}, Br^- also reacts with malonyl radicals to form bromomalonic acid which is in turn oxidized by Ce^{IV} by a complex mechanism. Oscillations of these systems only occur if between 0.25 and 0.75 bromide ions are produced for every Ce^{IV} consumed.[140] This requires that malonyl radicals preferentially attack bromomalonic acid to liberate Br^-. Inhibition of the oscillations in this system by Cl^- has been shown[141] to be of only temporary duration. The mechanism involves oxidation of chloride ion to chlorous acid which then reduces Ce^{IV} to Ce^{III}. Oscillations resume when the chlorous acid has been completely oxidized to chlorate.

Several new oscillating systems have been described.[142] Sustained oscillations with a simple ketone have been observed in H_2O_2–HIO_3–Mn^{II}–acetone mixtures.[143] Preliminary investigations indicate that the mechanism involves production of I_2 by reaction of H_2O_2 and HIO_3, catalysed by Mn^{II}. Iodide ion is formed from the reaction of iodine with acetone and is reoxidized by H_2O_2 and HIO_3 in a step which may involve Mn^{II}.

[136] D. A. Ledwith and F. A. Schultz, *J. Amer. Chem. Soc.*, 1975, **97**, 6591.
[137] K. Tano and G. N. Schrauzer, *J. Amer. Chem. Soc.*, 1975, **97**, 5404.
[138] G. N. Schrauzer, P. R. Robinson, E. L. Moorehead, and T. M. Vickrey, *J. Amer. Chem. Soc.*, 1975, **97**, 7069.
[139] J.-J. Jwo and R. M. Noyes, *J. Amer. Chem. Soc.*, 1975, **97**, 5422.
[140] R. M. Noyes and J.-J. Jwo, *J. Amer. Chem. Soc.*, 1975, **97**, 5431.
[141] S. S. Jacobs and I. R. Epstein, *J. Amer. Chem. Soc.*, 1976, **98**, 1721.
[142] P. Stroot and D. Janjic, *Helv. Chim. Acta*, 1975, **58**, 116.
[143] D. O. Cooke, *J.C.S. Chem. Comm.*, 1976, 27.

11 Halogens and Halogenate Ions

Data for some of the reactions discussed in this section are collected in Table 7.

Table 7 *Rate and thermodynamic parameters for reaction of halogen–oxygen compounds with metal ions at* 25 °C

Reaction	k/ l mol^{-1} s^{-1}	I/ mol l^{-1}	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal K^{-1} mol^{-1}	Ref.
$V^{III} + Cl_2$	$\sim 10^4$	1.5			146
$Ti^{III} + HOCl$[a]	1.02×10^4	1.0	16.0	12.2	144
$V^{IV} + HOCl$	19.6	1.0			145
$V^{III} + HOCl$	3	1.0			147
$U^{IV} + HOCl$	51.4	3.0			149
$V^{III} + HClO_2$	75	1.0			147
$V^{III} + ClO_2$	22	1.0			147
$V^{III} + ClO_3^-$	5.4	1.0	15.9	−1.9	147
$V^{III} + BrO_3^-$	3—6	1.0			148
$V^{III} + HIO_3$	360	1.0			148
$V^{II} + IO_3^-$	219	1.0			148

[a] $T = 30$ °C.

A number of studies of the oxidation of metal ions by solutions containing molecular chlorine have been reported. The rate law in the oxidation Ti^{III} in acid media is first-order in both oxidant and reductant and shows inhibition by chloride ion.[144] Consideration of the hydrogen-ion dependence leads to the proposed reaction scheme

$$[Ti(OH_2)_6]^{3+} \overset{K_h}{\rightleftharpoons} [(H_2O)_5TiOH]^{2+} + H^+$$

$$Ti^{3+} + Cl^- \overset{K_1}{\rightleftharpoons} [TiCl]^{2+}$$

$$Cl_2 + H_2O \overset{K_{OH}}{\rightleftharpoons} HOCl + H^+ + Cl^-$$

$$Cl_2 + Cl^- \overset{K_{Cl}}{\rightleftharpoons} [Cl_3]^-$$

$$[TiOH]^{2+} + Cl_2 \xrightarrow{k_1} [TiO]^{2+} + H^+ + [Cl_2]^-$$

$$[TiCl]^{2+} + HOCl \xrightarrow{k_2} [TiO]^{2+} + H^+ + [Cl_2]^-$$

$$Ti^{3+} + HOCl \xrightarrow{k_3} [Ti(OH)]^{3+} + Cl$$

$$[Ti(OH)]^{2+} + [Cl_3]^- \xrightarrow{k_4} [Ti(OH)]^{3+} + Cl^- + [Cl_2]^-$$

which yields the rate expression

$$-d[Cl_2]/dt = (k_1K_h + k_2K_1K_{OH}[Cl^-] + k_3K_{Cl} + k_4K_hK_{Cl}[Cl^-]^2)[Ti^{3+}][Cl_2][H^+]^{-1}[Cl^-]^{-1}$$

144 A. Adegite and S. Edeogu, *J.C.S. Dalton*, 1975, 1203.
145 A. Adegite, *J.C.S. Dalton*, 1975, 1199.
146 R. D. Cornelius and G. Gordon, *Inorg. Chem.*, 1976, **15**, 997.
147 R. D. Cornelius and G. Gordon, *Inorg. Chem.*, 1976, **15**, 1002.
148 A. Bakač, A. T. Thornton, and A. G. Sykes, *Inorg. Chem.*, 1976, **15**, 274.
149 R. A. Silverman and G. Gordon, *Inorg. Chem.*, 1976, **15**, 35.

The subsequent kinetic analysis allows evaluation only of k_3 ($1.02 \pm 0.01 \times 10^4$ l mol^{-1} s^{-1}) at 30 °C (I = 1.0 mol l^{-1}).

Comparison of the mechanism with the corresponding mechanism for reactions of Cl_2 with other metal-ion reductants suggests a number of generalizations. In the reactions which involve modification of the metal hydration sphere from an aquo- to a hydroxo- or an oxo-form, the direct reactions between the aquo-metal ion and Cl_2 are unimportant. Many examples show that the precursor complex contains the same number of oxygen atoms as the final products. Thus while hydrogen-ion dependences reveal little about whether the mechanism is inner-sphere or outer-sphere, it is suggested that hydroxo-complexes, which are structurally closer to the products, are formed, thereby lowering the activation energy for either an inner- or an outer-sphere electron transfer. In the reaction between Ti^{3+} and HOCl, similar reasoning suggests transfer of hydroxyl by an inner-sphere process. The rate constant k_3 is of the correct order of magnitude for a substitution process on Ti^{3+}.

For a d^1 ion such as Ti^{3+}, the probability of a two-electron transfer

$$Ti^{III} + Cl_2 \rightleftharpoons Ti^{V} + 2Cl^-$$

$$Ti^{III} + Ti^{V} \longrightarrow (Ti^{IV})_2 \longrightarrow 2Ti^{IV}$$

is low and indeed no complicated kinetic behaviour resulting from the formation of dimeric $(Ti^{IV})_2$ is observed. The suggested one-electron transfer

$$Ti^{III} + Cl_2 \rightleftharpoons Ti^{IV} + Cl_2^{-\bullet}$$

$$Ti^{III} + Cl_2 \longrightarrow Ti^{IV} + 2Cl^-$$

might explain the lack of an observed inhibition by Ti^{IV} if relative magnitudes of the $Cl_2/Cl_2^{-\bullet}$ and Ti^{IV}/Ti^{III} couples are such as to favour the initial redox process.

This is not the case in the reaction between V^{IV} and Cl_2 in which strong inhibition by V^{V} is observed[145] and, from values of the $Cl_2/Cl_2^{-\bullet}$ couple, the rate constant for the reaction between $Cl_2^{-\bullet}$ and V^{V} is estimated to be two orders of magnitude larger than for the corresponding process with V^{IV}.

In the absence of V^{V}, the rate law is first-order in $[V^{IV}]$, $[Cl_2]$, and $[H^+]^{-1}$ and shows inhibition by Cl^-, suggesting the pathways

$$[VO]^{2+} \overset{K_h}{\rightleftharpoons} [VO(OH)]^+ + H^+$$

$$Cl_2 + H_2O \overset{K_{OH}}{\rightleftharpoons} HOCl + H^+ + Cl^-$$

$$[VO(OH)]^+ + Cl_2 \overset{k_3}{\longrightarrow} [VO_2]^+ + H^+ + [Cl_2]^{-\bullet}$$

$$[VO]^{2+} + HOCl \overset{k_4}{\longrightarrow} [VO(OCl)]^+ + H^+$$

$$[VO(OH)]^+ + [Cl_2]^{-\bullet} \overset{\text{fast}}{\longrightarrow} [VO_2]^- + H^+ + 2Cl^-$$

with values for k_3 and k_4 of 1.28×10^6 and 19.6 l mol^{-1} s^{-1} respectively at 25 °C (I = 1.0 mol l^{-1}).

Vanadium(v) is also produced[146] in the oxidation of V^{III} by Cl_2. Initial rate studies, however, show that the proportion of V^{V} resulting from a two-electron transfer pathway is small compared with production of V^{IV}. At its simplest, the

experimental rate law may be written

$$\frac{-\mathrm{d}[V^{III}]}{\mathrm{d}t} = \frac{k_1[V^{III}]}{[H^+]} + \frac{k_2[V^{III}][Cl_2]}{[H^+]}$$

with values for k_1 and k_2 of 0.042 l mol^{-1} s^{-1} and 18.3 s^{-1} respectively ([H$^+$] = 1.0 mol l^{-1}, [Cl$^-$] = 0.5 mol l^{-1}) at 25 °C, although the k_1 term has a slight dependence on [Cl_2] and reaches a limiting value at high chloride-ion concentrations. It is considered that the k_1 pathway corresponds to rate-determining formation of a V^{III} oxo-species which reacts rapidly with chlorine. The chlorine-dependent term k_2 can be represented by the mechanism

$$V^{III} + Cl_2 \overset{k_2}{\rightleftharpoons} V^{IV} + Cl_2^{-\cdot} + 2H^+$$

$$V^{III} + Cl_2^{-\cdot} \xrightarrow{k_3} V^{IV} + 2Cl^- + 2H^+$$

$$V^{IV} + Cl_2^{-\cdot} \xrightarrow{k_4} V^{V} + 2Cl^- + 2H^+$$

$$Cl_2^{-\cdot} + Cl_2^{-\cdot} \xrightarrow{k_5} Cl_3^- + Cl^-$$

$$V^{III} + V^{V} \xrightarrow{k_6} 2V^{III}$$

in which the reactive species in the outer-sphere rate-determining step are hydroxyvanadium(III) (and either Cl_2 or Cl_3^-, which react at comparable rates). It was possible to detect the intermediate $Cl_2^{-\cdot}$ by its reaction with Co^{II} and by the fact that addition of V^{IV} decreases the rate, suggesting reversibility in the step k_2.

Reactions of a series of chlorine–oxygen oxidants with V^{III} have also been investigated by the same authors.[147] In contrast to reactions with V^{IV}, HOCl reacts less rapidly with V^{III} than does Cl_2. Consideration[146] of the metal-ion redox potentials suggests that the greater reactivity of V^{III} with Cl_2 is a result of the possibility of thermodynamically favourable direct one-electron oxidation.

Chloride ion, produced in the reaction of HOCl with V^{III}, reacts autocatalytically with HOCl to produce Cl_2, the better oxidant.[147] With chlorous acid, the reaction is biphasic with initial production of an intermediate chlorine(II) species in a one-electron transfer,

$$V^{III} + Cl^{III} \longrightarrow V^{IV} + Cl^{II}$$

followed by slower reduction to Cl^I which can be scavenged with phenol. An alternative explanation involves reactions of V^{III} with Cl^{III} and one of the products of its spontaneous decomposition. Reaction with ClO_2 is also complicated by interference from chlorine–oxygen products in intermediate oxidation states.

One-electron-transfer processes are indicated in the reduction of chlorate[147] by V^{III}. Although the rate constant (5.4 l mol^{-1} s^{-1}) for the reaction

$$V^{III} + ClO_3^- \xrightarrow{2H^+} V^{IV} + ClO_2 + H_2O$$

is within the range expected for a substitution-controlled mechanism, the high entropy of activation compared with known inner-sphere reductants suggests that an outer-sphere mechanism might be operative. That such a mechanism could be common to all the chlorine–oxygen oxidants discussed is supported by the small range in rate constants observed with V^{III}.

Reductions of iodate and bromate by V^{III} and V^{II} have also been reported[148] in a

study designed to distinguish between one- and two-electron processes. The rate in the vanadium(III) reduction of iodate depends on the ratio of reactants and suggests that disproportionation of an intermediate, I^{III}, is effective at low reductant concentrations. Although no VO_2^+, the primary product of a two-electron oxidation, was detected, no distinction between one- and two-electron processes can be made since the reaction

$$VO_2^+ + V^{III} \longrightarrow 2VO^{2+}$$

is more rapid than the overall reductions of iodate and bromate. The pH dependence of the rate law, however, reveals that only two kinetically indistinguishable pathways,

$$H^+ + IO_3^- \overset{K_a}{\rightleftharpoons} HIO_3$$

$$V^{3+} \overset{K_h}{\rightleftharpoons} VOH^{2+} + H^+$$

$$V^{3+} + IO_3^- \xrightarrow{k_1}$$

$$VOH^{2+} + HIO_3 \xrightarrow{k_2}$$

might be important, and if a two-equivalent process were operative, significantly greater hydrolysis of the reactants would be expected.

Bromate reduction is biphasic and complex. In the initial stage, V^{IV} is produced from the reaction of V^{III} and BrO_3^- with a rate constant in the range 3—6 l mol^{-1} s^{-1}. Subsequent oxidation of V^{III} by BrO_3^- was identified as the slower process. The rates of reaction with V^{III}, 189 and 3—6 l mol^{-1} s^{-1} for IO_3^- and BrO_3^- respectively, lie within the range of values expected for substitution on V^{III} and an inner-sphere mechanism is possible.

In the corresponding reductions by V^{II}, reaction with iodate proceeds almost entirely by one-equivalent changes and formation of the product, I_2, is biphasic consistent with the steps

$$5V^{II} + I^V \longrightarrow 5V^{III} + \tfrac{1}{2}I_2$$

$$5V^{IV} + I^V \longrightarrow 5V^V + \tfrac{1}{2}I_2$$

A positive $[H^+]$ dependence found in the former process indicates that the reaction between V^{3+} and HIO_3, with a rate constant $\geqslant 360$ l mol^{-1} s^{-1} at 25 °C is the dominant pathway. Although this rate excludes substitution of iodate on V^{2+} (10 l mol^{-1} s^{-1}), HIO_3 is a labile species with a water exchange rate of 10^4 s^{-1} and it is conceivable that reaction occurs with V^{2+} entering the inner co-ordinate sphere of HIO_3.

A small proportion of the reaction with bromate proceeds with a two-equivalent change and a V^{III}_2 dimer formed in the reaction

$$V^{IV} + V^{II} \longrightarrow V^{III}_2$$

was identified. One-equivalent reactions are, however, predominant in the reaction of oxy-halogen species with V^{2+}. No conclusion regarding the inner-sphere or outer-sphere nature of the BrO_3^- reduction could, however, be drawn.

In the U^{IV} reduction of HOCl,

$$U^{4+} + 2HOCl \longrightarrow UO_2^{2+} + Cl_2 + 2H^+$$

the suggested mechanism involves a two-electron transfer in the rate-determining step.[149] The rate law shows a reciprocal hydrogen-ion dependence,

$$-\mathrm{d[U^{IV}]}/\mathrm{d}t = k_0[\mathrm{U^{4+}}][\mathrm{HOCl}][\mathrm{H^+}]^{-1}$$

consistent with a pre-equilibrium hydrolysis of U^{4+},

$$\mathrm{U^{4+}} \overset{K_h}{\rightleftharpoons} \mathrm{UOH^{3+}} + \mathrm{H^+}$$

$$\mathrm{UOH^{3+}} + \mathrm{HOCl} \xrightarrow{k_a} \text{products}$$

giving a value of 54 l mol^{-1} s^{-1} for k_a at 25 °C (I = 3.0 mol l^{-1}). A kinetically indistinguishable pathway involving hydrolysis of hypochlorous acid leads to an unusually large activation energy (14.5 kcal mol^{-1}) for the magnitude of the rate constant. The proposed inner-sphere uranyl-like transition state [HO—U—OH—Cl^{3+}]* decomposes in a two-electron transfer to give an intermediate Cl^- ion which reacts with HOCl to form chlorine. If a one-electron process were operative, UO_2^+ catalysis of the oxygen exchange of inert UO_2^{2+} would be expected, but none was observed.

The kinetics and mechanism of the reduction of I_2 by [Fe^{II}(edta)] have been investigated.[150] Rate inhibition by iodine is explained by an equilibrium process in which the I—I bond is cleaved:

$$[\mathrm{Fe^{II}(edta)}]^{2-} + \mathrm{I_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{Fe(edta)\cdots I}]^- + \mathrm{I^-}$$

$$[\mathrm{Fe(edta)\cdots I}]^- \xrightarrow{k_2} [\mathrm{Fe^{III}(edta)}]^- + \mathrm{I}$$

$$[\mathrm{Fe^{II}(edta)}]^{2-} + \mathrm{I} \xrightarrow[\text{fast}]{k_3} [\mathrm{Fe^{III}(edta)}]^- + \mathrm{I^-}$$

The enhanced stability of the tervalent complex over the bivalent complex represses a backward reaction between Fe^{III} and I^-.

The rate law[151] in the periodic acid oxidation of a series of benzene-1,2-diols (H_2Q) in aqueous perchloric acid,

$$\mathrm{d[Q]}/\mathrm{d}t = (A + B[\mathrm{H^+}]^{-1})[\mathrm{HIO_4}][\mathrm{H_2Q}]$$

is consistent with the mechanism

$$\mathrm{HIO_4} \overset{K_a}{\rightleftharpoons} \mathrm{IO_4^-} + \mathrm{H^+}$$

$$\mathrm{H_2Q} + \mathrm{HIO_4} \xrightarrow{k_1} \mathrm{Q} + \mathrm{HIO_3} + \mathrm{H_2O}$$

$$\mathrm{H_2Q} + \mathrm{IO_4^-} \xrightarrow{k_2} \mathrm{Q} + \mathrm{IO_3^-} + \mathrm{H_2O}$$

giving $A = k_1$ and $B = k_2K_a$. Pathway k_1 has a decreased rate with increasing electron-withdrawing effect of substituents whereas path k_2 is almost independent. A correlation between the activation energy for k_1 and the overall free-energy change in the reaction has a slope of 0.2 rather than 0.5 predicted by the Marcus theory Although this is not proof of an outer-sphere process, the differences in the substitu-

[150] D. N. Sharma and Y. K. Gupta, *Indian J. Chem.*, 1975, **13**, 54.
[151] E. Mentasti, E. Pelizzetti, and G. Giraudi, *Z. phys. Chem. (Frankfurt)*, 1976, **100**, 17.

tion dependences of k_1 and k_2 are considered to reflect rate-determining electron transfer for k_1 while a strong interaction between the oxidant and substrate is suggested for k_2.

Iodate is reduced by iodide to give iodite and iodine:[152]

$$IO_3^- + 2I^- + 2H^+ \longrightarrow IO_2^- + I_2 + H_2O$$

In the presence of phenol, both IO_2^- and I_2 are scavenged, preventing the formation of tri-iodide, and the rate law suggests a mechanism in which the slow step is formation of a square-pyramidal iodate–iodide complex with values of 1.5 l mol^{-1} s^{-1} and 3.2×10^{-5} l^2 mol^{-2} respectively for k and K_1 at 35 °C (I = 0.02 mol l^{-1}). Subsequent reaction with a second iodide ion is rapid.

$$IO_3^- + 2H^+ \overset{K_1}{\rightleftharpoons} [IO_3H_2]^+$$

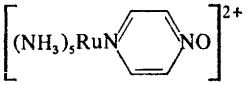
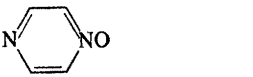
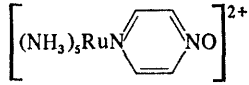
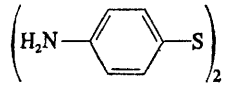
$$[IO_3H_2]^+ + I^- \overset{k}{\longrightarrow} [IO_3H_2I]$$

$$[IO_3H_2I] + I^- \overset{\text{fast}}{\longrightarrow} IO_2^- + I_2 + H_2O$$

12 Metal-ion Reductions

Data for several of the reactions discussed in this section are collected in Table 8.

Table 8 *Kinetic and thermodynamic parameters for metal-ion reductions*

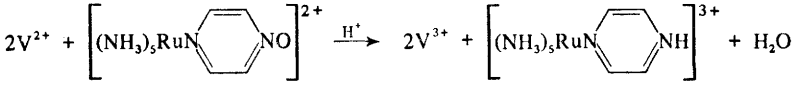
Reaction	k/ l mol^{-1} s^{-1}	I/ mol l^{-1}	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal K^{-1} mol^{-1}	*Ref.*
V^{II} + 	0.204	0.1	10.0	−17	153
V^{II} + 	2.29	0.1	8.1	−18	153
Cr^{II} + 	13.4	0.1			
Cr^{II} + Cl_3CCO_2H[a]	9.54	0.8	6.9	−29.8	154
Cr^{II} + 	0.103	2.0	9.4	−33	156

[a] T = 15 °C.

Reduction of pyrazine oxide by V^{II} is inhibited by co-ordination to ruthenium(II) (43), and an expected net two-electron transfer using the internal and external

[152] H. S. Varma, M. N. Srivastava, and B. B. L. Saxena, *Indian J. Chem.*, 1975, **13**, 56.

reductants is not observed.[153] Although the strength of the N—O bond is reduced on co-ordination, the reduction process, which involves N—O bond cleavage, is not facilitated. An important factor may be stabilization, due to back-bonding, which is lost on reduction. With both free and co-ordinated substrates, the reduction rate is low enough to suggest that, although inner-sphere complexes may be involved, electron transfer is rate determining.



(43)

The rate of oxidation of Cr^{II} by trichloroacetic acid is independent of hydrogen-ion concentration in aqueous perchloric acid and involves chlorine transfer in a bridged activated complex in the rate-determining step:[154]

$$Cr^{2+} + Cl_3CCO_2H \longrightarrow [CrClCCl_2CO_2H^{2+}]^+ \longrightarrow CrCl^{2+} + Cl_2\dot{C}CO_2H$$

Subsequent rearrangement of the organic radical,

$$Cl_2\dot{C}CO_2H \rightleftharpoons Cl_2CHCO_2\cdot$$

and reactions of both forms with Cr^{2+} are required to explain the distribution of products, $CrCl^{2+}$, $[CrO_2CCHCl_2]^{3+}$, and $[CrCCl_2CO_2H]^{3+}$.

In the reduction of salicylaldehyde (sal) by Cr^{II}, the Cr^{III} products retard the reaction rate.[155] Initial rate studies, however, reveal a rate law

$$-d[Cr^{II}]/dt = (k' + k''[H^+])[Cr^{II}][sal]$$

suggesting reactions with two differently protonated forms of salicylaldehyde. Of the two products isolated, one was identified as $[Cr_2(OH)_2]^{4+}$ formed in a side reaction with O_2 while the other, a yellow tripositively charged species, was considered to contain a Cr—C bond. Addition of Cl^- to the reaction medium did not affect the rate-determining step although chloride was incorporated into the products. It is suggested that chloride ion reacts with an intermediate after the rate-controlling process.

The rate expression in the oxidation of Cr^{II} by *p*-aminophenyl disulphide (RSSR) in aqueous perchloric acid is independent of the reagent in excess[156] with values for

$$\frac{d[(H_2O)_5Cr(SC_6H_4NH_3)^{3+}]}{dt} = \frac{a[Cr^{II}][RSSR^{2+}]}{1 + b[RSSR^{2+}]}$$

a and b of 0.103 l mol^{-1} s^{-1} and 14.5 l mol^{-1} respectively at 25 °C (I = 2.0 mol l^{-1}). The rate is dependent on the ionic strength and $[ClO_4^-]$ in a manner which may be explained by a disulphide–perchlorate complex which reacts at a lower rate with Cr^{II} than does the free disulphide.

153 M. A. Blesa and H. Taube, *Inorg. Chem.*, 1976, **15**, 1454.
154 P. Ševčik, *J. Inorg. Nuclear Chem.*, 1976, **38**, 553.
155 P. Ševčik, *Coll. Czech. Chem. Comm.*, 1975, **40**, 2935.
156 L. E. Asher and E. Deutsch, *Inorg. Chem.*, 1975, **14**, 2799.

The proposed mechanism,

$$Cr^{2+} + RSSR^{2+} \xrightarrow{k_1} [Cr(RSSR)]^{4+}$$

$$[Cr(RSSR)]^{4+} \xrightarrow{k_2} [CrSR]^{3+} + RS^{+\cdot}$$

$$Cr^{2+} + RS^{+\cdot} \xrightarrow{\text{fast}} [CrSR]^{3+}$$

$$[Cr(RSSR)]^{4+} + RSSR^{2+} \xrightarrow{k_3} [Cr(RSSR)]^{5+} + RSSR^{+}$$

$$2RSSR^{+} + 2H^{+} \xrightarrow{\text{fast}} RSSR^{2+} + 2RSH^{+}$$

involves the formation of a steady-state intermediate $[Cr(RSSR)]^{4+}$ and gives $a = 2k_1$ and $b = k_3/k_2$. The step k_3, which produces the relatively stable $RSSR^+$ radical intermediate, is required to explain differences in the reaction stoicheiometry with different reagents in excess. Stoicheiometric yields of $[CrSR]^{3+}$ are produced with excess Cr^{2+}, since the k_3 reaction, ineffective under these conditions, will be replaced by reactions of the type

$$Cr^{2+} + [Cr(RSSR)]^{4+} \xrightarrow{\text{fast}} 2[CrSR]^{3+}$$

while, with an excess of disulphide, the product $[Cr(RSSR)]^{5+}$ might undergo hydrolysis.

The benzylchromium cation $[(H_2O)_5Cr(CH_2Ph)]^{2+}$ is oxidized in aqueous perchloric acid at the same rate, 2.63×10^{-3} s^{-1} at 25 °C (I = 1.0 mol l^{-1}), by a number of reagents.[157] A rate-determining homolytic cleavage,

$$[Cr(CH_2Ph)]^{2+} \rightleftharpoons Cr^{2+} + \cdot CH_2Ph$$

$$\downarrow [ox] \qquad \downarrow [ox]$$

$$Cr^{3+} \qquad \text{products}$$

is proposed and the reactions proceed if either or both of the initial products are scavenged by the oxidizing agent. Those reagents which oxidize benzyl radicals produce benzyl alcohol whereas with others which are slow to react the product is $PhCH_2CH_2Ph$ and polymerization of acrylonitrile is initiated.

In dichloromethane solution, the monomeric Mo^V species $[MoOCl_3(OPPh_3)_2]$ is oxidized by nitrate[158] and nitrite[159] ions. Both reactions proceed in three observable stages and the proposed mechanisms are similar.

The first step in the reaction with NO_3^- is the formation[158] of a Mo^V–NO_3^- complex by an S_N1 limiting mechanism. The rate constant, 40.3 s^{-1}, is close to the values of 42.0, 41.6, and 51.8 s^{-1} for the comparable reactions with Cl^-, Br^-,[160] and NO_2^-,[159] and the activation parameters indicate a similar process. In this step, the kinetic product contains NO_3^-, oxygen bound, in a position *trans* to the M=O bond. Rearrangement of this species either by isomerization to form the thermodynamically more stable *cis*-bonded nitrate or by chelate formation and displacement of a

[157] R. S. Nohr and J. H. Espenson, *J. Amer. Chem. Soc.*, 1975, **97**, 3392.
[158] C. D. Garner, M. R. Hyde, F. E. Mabbs, and V. I. Routledge, *J.C.S. Dalton*, 1975, 1180.
[159] M. R. Hyde and C. D. Garner, *J.C.S. Dalton*, 1975, 1186.
[160] C. D. Garner, M. R. Hyde, F. E. Mabbs, and V. I. Routledge, *J.C.S. Dalton*, 1975, 1175.

chloride ion is essential for the redox process. One, and only one, *cis* position must be occupied by a nitrate oxygen to allow rapid electron transfer and formation of Mo^{VI}:

$$O_2NO-\overset{O}{\overset{\|}{Mo^{V}}} \longrightarrow O=\overset{O}{\overset{\|}{Mo^{VI}}} + NO_2$$

The rates of this rearrangement-controlled redox process are 1.0 s^{-1} and 2.58×10^{-2} s^{-1} respectively for NO_3^- and NO_2^- and it is suggested that these differences may be due to the preference to form an Mo—N bond by NO_2^- which restrains the subsequent rearrangement and hence the overall redox process, thereby modelling the ability of nitrate reductases to differentiate between the two oxidants. Subsequent reactions involve the formation of nitrate and nitrite complexes of Mo^{VI}.

A comparable reaction of $(NH_4)_2MoOCl_5$ with nitrate in anhydrous DMF has also been investigated as a model for biological nitrate reduction:[161]

$$[MoOCl_5]^{2-} + NO_3^- \longrightarrow [MoO_2Cl_2] + NO_2 + 3Cl^-$$

The proposed mechanism involves a rapid pre-equilibrium formation of $[MoOCl_4]^-$ followed by replacement of a second chloride by nitrate to explain rate inhibition by Cl^-:

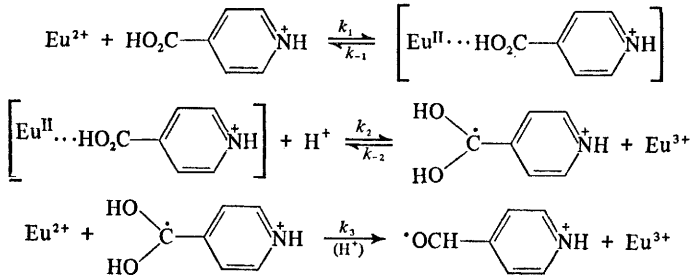
$$[MoOCl_5]^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [MoOCl_4]^- + Cl^-$$

$$[MoOCl_4]^- + NO_3^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [MoOCl_3NO_3]^- + Cl^-$$

$$[MoOCl_3NO_3]^- \xrightarrow{k_3} [MoO_2Cl_2] + Cl^- + NO_2$$

The electron-transfer rate k_3 is considered to be much larger than the observed value of the composite k_3k_2/k_{-2}, 1.7×10^{-4} s^{-1}.

Derivatives of pyridine carboxylic acids form 1:1 complexes with Eu^{2+} in strongly acidic conditions.[162] Whereas the complexes with nicotinic and picolinic acids are stable with respect to further reaction, isonicotinic acid and its *N*-methyl derivative undergo reduction with an Eu^{2+}:substrate stoicheiometry of 2:1.



Scheme 20

[161] R. D. Taylor and J. T. Spence, *Inorg. Chem.*, 1975, **14**, 2815.
[162] E. Vrachnou-Astra and D. Katakis, *J. Amer. Chem. Soc.*, 1975, **97**, 5357.

The proposed mechanism with isonicotinic acid (Scheme 20) yields a rate law

$$\frac{-\mathrm{d}[Eu^{2+}]}{\mathrm{d}t} = \frac{k_2k_3K_1[Eu^{2+}][HO_2CC_5H_4\overset{+}{N}H][H^+]}{k_{-2}[Eu^{3+}] + k_3[Eu^{2+}]}$$

in agreement with the experimentally derived expression with values of 1.9 l mol^{-1}, ~1, and ~0.03 mol^{-1} s^{-1} for K_1, K_2, and k_3 respectively at 23 °C. Although nicotinic acid has the ability to form a chelate complex, the value for K_1 is 0.15 l mol^{-1} and it is considered that the bonding in this weak complex is essentially ionic and derives from a synergic mechanism of charge transfer from the metal to the ligand.

13 Pulse Radiolysis Studies

Second-order rate constants, $k_1 \sim 10^6$ l mol^{-1} s^{-1}, for the intermolecular reduction of $[Co^{III}(NH_3)_5X]$ complexes by pulse-radiolytically generated p-$O_2NC_6H_4CO_2^-$ (L·) can be compared[163] with the value for the intramolecular electron transfer,[164] $k_2 = 2.6 \times 10^3$ s^{-1}, in carboxyl-bonded $[Co^{III}(NH_3)_5L]^+$ if a pre-equilibrium encounter complex is assumed and rate-determining electron transfer

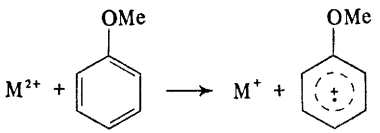
$$[Co^{III}(NH_3)_5L]^+ \xrightarrow{k_2} Co^{II} + 5NH_3 + L\cdot$$

$$[Co^{III}(NH_3)_5X]^+ + L\cdot^{2-} \overset{K}{\rightleftharpoons} [Co^{III}(NH_3)_5X,L\cdot] \xrightarrow{k} Co^{II} + L^-$$

occurs in a second step. The magnitude of K, < 100 l mol^{-1}, leads to a value for the outer-sphere constant k ($= k_2/K$) which is not significantly smaller than the inner-sphere constant k_2, and suggests that the co-ordinated carboxylate group has poor electron permeability.

The reaction of ·OH with $[(NH_3)_5Co^{III}py]$ produces[165] a reactive transient with a second-order rate constant of 6.5×10^8 l mol^{-1} s^{-1} (pH = 5.2). The absorption spectrum of this transient has a maximum at 320 nm (ε = 1800 l mol^{-1} cm^{-1}) and is similar to the spectrum obtained in the radiolysis of free pyridine. It is proposed that the hydroxyl radical adds to the pyridine ligand to form a ligand radical co-ordinated to the Co^{III} centre. This species undergoes intramolecular redox to yield Co^{II} and pyOH with a rate constant of 6.0 s^{-1}.

Pulse radiolysis of solutions of anisole produces the anisole radical cation which is characterized[166] by two intense absorption bands at λ_{max} = 280 nm (ε = 7400 l mol^{-1} cm^{-1}) and λ_{max} = 430 nm (ε = 3200 l mol^{-1} cm^{-1}). At pH 1.0, this species oxidizes iron(II) to regenerate anisole with a rate constant of 6×10^8 l mol^{-1} s^{-1}.



(44)

163 H. Cohen and D. Meyerstein, *J.C.S. Dalton*, 1975, 2477.
164 M. Z. Hoffman and M. Simic, *J. Amer. Chem. Soc.*, 1972, **94**, 1757.
165 M. Z. Hoffman and D. W. Kimmel, *J.C.S. Chem. Comm.*, 1975, 549.
166 J. Holcman and K. Sahested, *J. Phys. Chem.*, 1976, **80**, 1642.

A series of methoxylated benzene derivatives react with Tl^{2+} and Ag^{2+}, generated by the action of ·OH on Tl^+ and Ag^+ respectively, to form the radical cations (44).[167] For anisole, the rate constants for $M^{2+} = Tl^{2+}$ and Ag^{2+} are 5×10^8 and 3.8×10^7 l mol^{-1} s^{-1}, and these values depend little on further substitution on the benzene ring. Subsequent dimerizations of the radicals proceed with rate constants between 4×10^3 and 1×10^9 l mol^{-1} s^{-1} depending on the relative positions of the methoxy-groups.

Conductance and optical measurements on the reaction of ·OH with Tl^+ indicate that above pH 4 significant amounts of $TlOH^{2+}$, absorbing at 360 nm, are formed:[168]

$$Tl^+ + \cdot OH \longrightarrow TlOH^+$$

Both techniques yield similar values (2×10^{-5} mol l^{-1}) for the hydrolysis constant of Tl^{2+}.

Hyper-reduced metal ions Cd^+, Co^+, Ni^+, and Zn^+ are produced by reductions of the corresponding bivalent metal ions with solvated electrons.[169] Subsequent reactions with hydroxyl radicals regenerate the bivalent ions and in the presence of a hydroxyl radical scavenger R· the major decomposition pathway becomes

$$M^+ + R\cdot \longrightarrow MR^+$$

Similar conclusions were reached[170] in a second paper dealing with the pulse-radiolytic reduction of Cd^{2+} alone. Further reactions of these ions are the subject of another paper[171] and, besides electron-transfer processes, additions of unsaturated compounds and oxygen atom transfers from N_2O are described. The products of these latter reactions, MO^+, behave like OH in their reactions with halide ions. In the electron-transfer processes, the reactions with peroxodisulphate proceed by a second-order pathway with rate constants of *ca.* 10^9 l mol^{-1} s^{-1}:

$$M^+ + S_2O_8^{2-} \longrightarrow M^{2+} + SO_4^- + SO_4^{2-}$$

The order of reactivity of the univalent ions in electron-transfer reactions is $Co^+ \sim Zn^+ \geqslant Cd^+ \geqslant Ni^+$.

Kinetic redox potentials for M^+/M^{2+} couples of a number of metal ions have been determined from a study of the percentage efficiency of the electron-transfer reactions with various electron acceptors A:[172]

$$M^+ + A \longrightarrow M^{2+} + A^{-\cdot}$$

Rates close to the diffusion-controlled limit are found for acceptors which have a higher potential than the oxidation potentials of the M^+/M^{2+} couples. The reducing power of these metal ions decreases in the order

$$Zn^+ \geqslant Co^+ \geqslant Cd^+ > Tl^0 > Pb^+ > Ni^+ > Cr^{2+}.$$

Radical species generated by pulse radiolysis have been used[173] to produce Ni^I and Cu^I complexes of 14-membered macrocyclic ligands from the corresponding

[167] P. O'Neill, S. Steenken, and D. Schulte-Frohlinde, *J. Phys. Chem.*, 1975, **79**, 2773.
[168] P. O'Neill and D. Schulte-Frohlinde, *J.C.S. Chem. Comm.*, 1975, 387.
[169] G. V. Buxton and R. M. Sellers, *J.C.S. Faraday I*, 1975, **71**, 558.
[170] M. Kelm, J. Lilie, and A. Henglin, *J.C.S. Faraday I*, 1975, **71**, 1132.
[171] G. V. Buxton, R. M. Sellers, and D. R. McCracken, *J.C.S. Faraday I*, 1976, **72**, 1464.
[172] P. S. Rao and E. Hayon, *J. Phys. Chem.*, 1975, **79**, 865.
[173] A. M. Tait, M. Z. Hoffman, and E. Hayon, *Inorg. Chem.*, 1976, **15**, 934.

bivalent reagents with second-order rate constants between 10^8 and 10^{10} l mol^{-1} s^{-1}. The univalent complexes have intense absorption bands in the visible region ($\varepsilon > 10^4$ l mol^{-1} cm^{-1}) and behave as bases in their reactions with proton donors. As in the previous paper, values for the potential of the M^+/M^{2+} couples were derived from studies with organic electron acceptors, and oxidations by O_2, N_2O, and MeI were investigated. Superoxide ion O_2^- produced in the reaction of Ni^I with O_2 is not scavenged by the Ni^{II} product, setting an upper limit of 10^6 l mol^{-1} s^{-1} for the reaction

$$Ni^{II} + O_2^- \longrightarrow Ni^I + O_2$$

With the corresponding copper(I) complexes, no free O_2^- is detected and, since a determination of the rate of reaction between Cu^{II} and O_2^- again sets an upper limit of 10^6 l mol^{-1} s^{-1}, an addition mechanism is preferred.

The dismutation of the superoxide ion, produced pulse-radiolytically, catalysed by Cu^{II} complexes has also been investigated.[174] Two catalytic decomposition pathways are possible,

(*a*)
$$O_2^- + Cu^{II} \longrightarrow O_2 + Cu^I$$
$$Cu^I + O_2^- \xrightarrow{2H^+} Cu^{II} + H_2O_2$$

or

(*b*)
$$Cu^{II} + O_2^- \xrightarrow{2H^+} Cu^{III} + H_2O_2$$
$$Cu^{III} + O_2^- \longrightarrow Cu^{II} + O_2$$

In the presence of formate, the reactivity of Cu^{II} toward O_2^- decreases as higher HCO_2^- complexes are formed. A similar conclusion is reached for ammonia complexes and an explanation based on the change in the Cu^{II} redox potential is proposed, Cu^{II} being stabilized with respect to reduction (path *a*) on complexation. The possibility that O_2^- may tend to oxidize Cu^{II} cannot, however, be ruled out. Amino-acid complexes of copper(II) show a range of rate constants with O_2^-, increasing from Cu^{II}–proline (5×10^5 l mol^{-1} s^{-1}) through Cu^{II}–glycine (2×10^6 l mol^{-1} s^{-1}) to Cu^{II}–glycylglycine (2×10^7 l mol^{-1} s^{-1}). Further reactions of Cu^{II} complexes with superoxide ion prepared by an alternative method using KO_2 and dicyclohexyl-18-crown-6 in DMSO are also reported.[175]

Hydroxyalkyl radicals generated by the pulse radiolytic reaction

$$HO\cdot + CHRCR_2 \longrightarrow HOCHR-\dot{C}R_2$$

are oxidized[176] by copper(II) ion in aqueous solution at pH 3—6. The major pathway involves the formation of a Cu^{II}—C bond followed by epoxidation to give (45) and

$$\underset{\underset{OH}{|}}{HCR-\dot{C}R_2} + Cu^{II} \xrightarrow{k_1} \underset{\underset{OH}{|}}{HCR-\dot{C}R_2-Cu^{II}} \longrightarrow \underset{\diagdown\,O\,\diagup}{HCR-CR_2} + Cu^I + H^+$$

(45)

the rate constants 2×10^7 and 3×10^6 l mol^{-1} s^{-1} for R = H and Me respectively are consistent with steric hindrance in the k_1 step.

[174] D. Klug-Roth and J. Rabani, *J. Phys. Chem.*, 1976, **80**, 588.
[175] J. S. Valentine and A. B. Curtis, *J. Amer. Chem. Soc.*, 1975, **97**, 224.
[176] G. V. Buxton, J. C. Green, R. Higgins, and S. Kanji, *J.C.S. Chem. Comm.*, 1976, 158.

3

Reactions of Oxygen and Hydrogen Peroxide

BY A. McAULEY

The interaction of molecular oxygen with transition-metal complexes continues to attract considerable interest and several reviews have been published dealing with differing aspects of these reactions. Attempts have been made to present a unified view of the data to date.[1] The two types of interaction involving superoxo- and peroxo-co-ordination of the dioxygen are discussed together with a summary of the reactivity and structure of the complexes. Two reviews[2,3] deal with the use of inorganic oxygen carriers as models for biological systems. Treatments for both cobalt and iron systems have been developed. A more biologically oriented view of the chemistry of dioxygen has been presented by Ochiai[4] in which there is a description of dioxygenase and mono-oxygenase activity as well as an account of the storage and transport of O_2. Information has been presented on the composition and properties of mono-oxygenase enzymes.[5] An analysis of the kinetics and mechanism of their action in the hydroxylation of aliphatic and aromatic compounds is included together with an assessment of their role in biological oxidation.

1 Cobalt(II) Complexes

Many of the studies undertaken recently have centred on the reversibility of the oxygen binding and on the nature of the adducts formed. Using the isomeric diethylenetriaminemonoacetic acids (L) as ligands, stable cobalt(II) complexes are formed which on oxygenation show no measurable tendency towards irreversible oxidation to the cobalt(III) state.[6] Thermodynamic equilibrium constants may be defined by the equation

$$2Co^{2+} + 2L^- + O_2 \rightleftharpoons [Co_2L_2(O_2)OH]^+ + H^+$$

The rate scheme envisaged is similar to that proposed by Wilkins[7] for dioxygen complexes without hydroxo-bridges:

$$CoL^+ + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [CoL(O_2)]^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Co_2L_2(O_2)OH]^+ + H^+$$

Values for k_1 are in the range $3—14 \times 10^3$ l mol^{-1} s^{-1} and are closely similar to those

[1] L. Vaska, *Accounts Chem. Res.*, 1976, **9**, 175.
[2] F. Basolo, B. M. Hoffman, and J. A. Ibers, *Accounts Chem. Res.*, 1975, **8**, 384.
[3] G. McLendon and A. E. Martell, *Coordination Chem. Rev.*, 1976, **19**, 1.
[4] E. I. Ochiai, *J. Inorg. Nuclear Chem.*, 1975, **37**, 1503.
[5] A. A. Akhrem, D. I. Metelitsa, and M. E. Skurko, *Russ. Chem. Rev.*, 1975, **44**, 398.
[6] G. McLendon, D. T. MacMillan, M. Harihan, and A. E. Martell, *Inorg. Chem.*, 1975, **14**, 2322.
[7] F. Miller and R. G. Wilkins, *J. Amer. Chem. Soc.*, 1970, **92**, 2687.

derived previously for the isostructural nitrogen isomers, *e.g.* tren and trien. The mechanism involves the replacement of co-ordinated water by O_2, presumably in an octahedral intermediate in which H_2O exchange dominates. It has been widely considered that only complexes containing three nitrogen atoms in the inner co-ordination sphere would interact with oxygen.[8] Recently, however, studies with ethylenediaminediacetic acids[9] have shown this to be incorrect. Using both the symmetrical and unsymmetrical edda complexes, the reaction with O_2 is unusually slow ($k_1 \sim 10^2$—10^3 times smaller than those observed previously). One of the requirements for oxygen binding is that there must be to some degree an electron delocalization from the metal centre to the oxygen. Such a transfer would be facilitated by ligands which can donate electrons to the central metal. If this is the case then N-co-ordination may be considered to favour oxygenation to a greater extent than oxygen systems where a larger energy of activation would be required for the transfer of the electron in the activated complex. ^{59}Co and ^1H n.m.r. spectra have been used to investigate oxygenation of solutions of triethylenetetraminecobalt(II).[10] A mixture of isomeric forms of $[Co_2(trien)_2\mu\text{-}(O_2,OH)]^{3+}$ is produced in which the chelate configuration is predominantly either *α-cis* or *β-cis* in both centres of the dinuclear species.

The nature of the binding of dioxygen in these complexes has been the subject of considerable discussion. Tovrog and Drago[11] provided experimental evidence to argue against the formulation of the complexes as Co^{III}—O_2^-. Co-ordination of CO to the cobalt and an e.s.r. spectrum indistinguishable from that of the O_2 complex were presented to substantiate their claim. Two groups, however, have provided e.s.r. evidence[12,13] in which the O_2^- structure is unambiguously proved and have failed to confirm the evidence for co-ordination of carbon monoxide. A crystal structure of the tetraethylammonium salt of the pseudo-octahedral ion $[Co(CN)_5O_2]^{3-}$ indicates that it is best described as a σ-bonded cobalt(III) superoxide.[14] Comparison with other σ-bonded dioxygen complexes shows that this is the probable mode of binding of O_2 in biological oxygen-transport molecules. A kinetic study[15] of the reaction of Co^{II}-etioporphyrin II with O_2 shows that the order with respect to the metal ion is 1.25. This result is interpreted in terms of some participation of a dinuclear complex. The reaction rate, however, is markedly dependent on solvent. Reversible oxygen uptake has been observed in the reaction with electrochemically reduced tetrasulphonated cobalt phthalocyanins.[16] Using this system, polyhydric phenols such as catechol and hydroquinone are oxidized catalytically at ambient temperature. The kinetics and mechanism of the oxidation of the cobalt(II) macrocycle $[Co(OH_2)_2L]^+$ [L = 2,2-difluoro-5,6,12,13-tetramethyl-1,3-dioxa-4,7,11,14-tetra-aza-2-boracyclotetradeca-4,6,11,13-tetraene(1−)] have been investigated.[17]

[8] S. Fallab, *Angew. Chem. Internat. Edn.*, 1967, **6**, 496.
[9] G. McLendon, R. J. Motekaitis, and A. E. Martell, *Inorg. Chem.*, 1975, **14**, 1993.
[10] M. Zehnder and S. Fallab, *Helv. Chim. Acta*, 1975, **58**, 13.
[11] B. S. Tovrog and R. S. Drago, *J. Amer. Chem. Soc.*, 1974, **96**, 6765.
[12] B. M. Hoffman, T. Szymanski, and F. Basolo, *J. Amer. Chem. Soc.*, 1975, **97**, 673.
[13] D. Getz, E. Melamund, B. L. Silver, and Z. Dori, *J. Amer. Chem. Soc.*, 1975, **97**, 3846.
[14] L. D. Brown and K. N. Raymond, *Inorg. Chem.*, 1975, **14**, 2595.
[15] A. V. Savitskii, V. I. Nelyubin, and A. F. Mironov, *Doklady Akad. Nauk S.S.S.R.*, 1975, **222**, 852.
[16] S. Meshitsuka, M. Ichikawa, and K. Tamaru, *J.C.S. Chem. Comm.*, 1975, 360.
[17] R. Dreos, G. Tauzher, G. Costa, and M. Green, *J.C.S. Dalton*, 1975, 2329.

The reaction is catalysed by H^+ and by halide ions. Several reaction pathways are proposed involving an initial dissociation of one of the axial water molecules. The product is a cobalt(III) complex and the fact that H_2O_2 is not detected is interpreted in terms of a mechanism similar to that for Fe^{II}-oxygen carrying systems (see p. 110).

An unusual cobalt–dioxygen adduct is formed in the reaction of O_2 with $[Co^{II}(CN)_2(PMe_2Ph)_3]$,[18] in that during the course of reaction a dimeric complex is formed with the exclusion of only a single mole of dimethylphenylphosphine. The rate law of the form

$$-d[O_2]/dt = k_3[Co(CN)_2(PMe_2Ph)_3]^2[O_2][PMe_2Ph]^{-1}$$

is consistent with the mechanism shown in Scheme 1, in which $k_3 = Kk_1$. The

$$[Co^{II}(CN)_2(PMe_2Ph)_3] + O_2 \overset{K}{\rightleftharpoons} [Co^{II}(CN)_2(PMe_2Ph)_2O_2] + [PMe_2Ph]$$

$$\downarrow k_1 \; +[Co^{II}(CN)_2(PMe_2Ph)_3]$$

$$[(PhMe_2P)_3(NC)_2Co^{II}-N-C-Co^{II}(CN)(PMe_2Ph)_2(O_2)]$$

$$\downarrow$$

$$[(PhMe_2P)_3(NC)_2Co-N-C-Co(CN)(PMe_2Ph)_2O_2]$$

Scheme 1

product is a nearly linear Co—N—C—Co dinuclear complex in which the oxygen is co-ordinated to only one cobalt centre. The mechanism may be viewed as a CN-bridged inner-sphere electron transfer. The product is substitution-inert, which is considered consistent with the assignment of the +3 oxidation states at both cobalt atoms.

2 Iron(II) Complexes

One of the major difficulties encountered in attempts to prepare monomeric iron–oxygen adducts, particularly of iron porphyrins, is in preventing the conversion of the adduct into the μ-oxo-dimer:

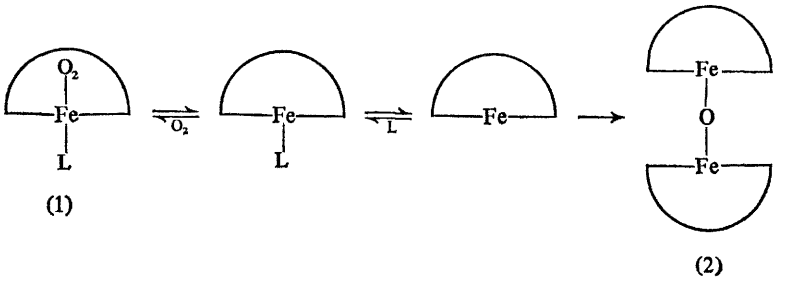
$$Fe^{III} + O_2 \rightleftharpoons FeO_2 \xrightarrow{Fe^{II}} Fe^{III}-O-Fe^{III}$$

An approach which has proved successful has been to introduce substituents into the porphyrin ring in such a manner that there is a steric hindrance to dimerization. Both 'picket fence'[19] and 'capped'[20] complexes have been identified. In the former example a model system is provided for the active site of both myoglobin and oxymyoglobin. The lifetime of the dioxygen complex of the latter type (1) is ~20 h, at which time some iron(III) is present. Rapid auto-oxidation occurs in solution unless a strongly co-ordinating base (L) is present. Kinetic studies of this reaction are consistent with

[18] J. Halpern, B. L. Goodall, G. P. Khare, H. S. Lim, and J. J. Pluth, *J. Amer. Chem. Soc.*, 1975, **97**, 2301.

[19] J. P. Collman, R. R. Gagne, C. A. Reed, T. R. Halbert, G. Lang, and W. T. Robinson, *J. Amer. Chem. Soc.*, 1975, **97**, 1427.

[20] J. Almog, J. E. Baldwin, and J. Huff, *J. Amer. Chem. Soc.*, 1975, **97**, 227.



Scheme 2

Scheme 2, in which the adduct (1) is dissociated to the auto-oxidizable species (2) which undergoes oxidation *via* the unprotected side of the molecule.[20] The effects of matrix fixation on the oxygen reactions of haemoglobin have been reviewed.[21]

In an alternative approach to the formation of stable adducts, Basolo and co-workers[22] have reported a detailed kinetic and thermodynamic study of oxygen and carbon monoxide binding. Using the complexes $[Fe^{II}(TPP)L_2]$ (TPP = *meso*-tetraphenylporphyrin, L = pyridine, piperidine, or 1-methylimidazole), the reactions with O_2 in methylene chloride at -79 °C show first-order rate dependences and for a given complex are independent of the concentration of oxygen present. The data are again consistent with a dissociative process:

$$[Fe(TPP)L_2] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Fe(TPP)L] + L$$

$$[Fe(TPP)L] + O_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Fe(TPP)L(O_2)]$$

The k_1 values are in the sequence piperidine > pyridine > 1-methyl-imidazole, which may reflect the longer axial bond lengths in the piperidine complex when compared with the imidazole species. In the oxygenation of *meso*-tetrakis-(2,4,6-alkoxyphenyl)-porphinato-complexes, however, preliminary kinetic evidence is suggestive of two distinct steps in the reaction.[23]

The rate of oxygenation of iron(II) in neutral and slightly acidic media has been investigated in the presence of several anions.[24] The overall rate law may be expressed in the form

$$-d[Fe^{II}]/dt = k[Fe^{II}][O_2][OH^-]^2$$

the rate constant k being strongly dependent on the ion present and decreasing in the order of anions ClO_4^-, NO_3^-, Cl^-, $H_3SiO_4^-$, Br^-, I^-, SO_4^{2-}. Fluoride and phosphate show considerable rate acceleration. The mechanism proposed involves the reaction of the monohydroxo-species $FeOH^+$ with a dissociated form of hydrated oxygen,

[21] A. V. Savitskii and V. I. Nelyubin, *Russ. Chem. Rev.*, 1975, **44**, 110.
[22] C. J. Weschler, D. L. Anderson, and F. Basolo, *J. Amer. Chem. Soc.*, 1975, **97**, 6707.
[23] A. R. Amundsen and L. Vaska, *Inorg. Chim. Acta*, 1975, **14**, L49.
[24] H. Tamura, K. Goto, and M. Nagayama, *J. Inorg. Nuclear Chem.*, 1976, **38**, 113.

$$FeOH^+ + O_2OH^- \longrightarrow Fe^{III} + O_2^- \quad (1)$$

$$O_2^- + H^+ \rightleftharpoons HO_2$$

$$Fe^{II} + HO_2 \longrightarrow Fe^{III} + HO_2^-$$

$$H^+ + HO_2^- \rightleftharpoons H_2O_2$$

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{III} + HO\cdot + HO^-$$

$$Fe^{II} + HO\cdot \longrightarrow Fe^{III} + HO^-$$

with rapid subsequent reaction of iron(II) with the radical species and the H_2O_2 formed. The specificity of interaction of the anions (X^-) may be accounted for by the additional reaction of the ferrous complexes FeX^+ in a step corresponding to the reaction of $FeOH^+$ above. The oxidation of $[Fe(CN)_5(H_2O)]^{3-}$ by molecular oxygen is strongly catalysed by traces of iron(II).[25] The rate data at pH > 3.8 are consistent with the rate law

$$-d[Fe(CN)_5(H_2O)^{3-}]/dt = k_3[Fe(CN)_5(H_2O)^{3-}][Fe^{II}][O_2]$$

In the presence of edta, the rate falls dramatically owing to complexing of the aquated metal ion. A complex of the type $[(NC)_5FeO_2Fe]^-$ is considered as an intermediate in preference to the radical ion mechanism,

$$[Fe(CN)_5(H_2O)]^{3-} + O_2 \longrightarrow [Fe(CN)_5(H_2O)]^{2-} + O_2^-$$

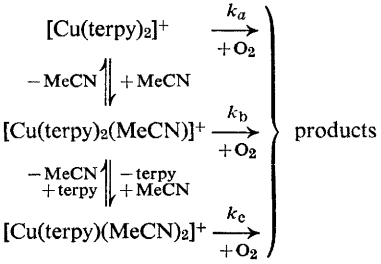
and the catalytic activity of copper(II) ions may be interpreted using a mechanism similar to that when the bridged dinuclear intermediate is formed.

3 Copper-(I) and -(II) Complexes

The oxidation of the bis-copper(I) complex $[Cu(terpy)_2]^+$ in acetonitrile[26] proceeds *via* a two-electron reduction of O_2,

$$2[Cu(terpy)_2]^+ + O_2 \xrightarrow{2H^+} 2[Cu(terpy)_2]^{2+} + H_2O_2$$

The rate is independent of pH in the region 5.3—8.0 and first-order with respect to Cu^I and O_2 at constant terpy and MeCN concentrations. From details of the rate dependence of [terpy] and [MeCN], three reaction pathways are indicated (Scheme 3).



Scheme 3

The k_a rate term may refer to either a ring-opening followed by co-ordination of the oxygen or to an electron transfer *via* the π-electron system of the ligand. Similar

[25] H. E. Toma, *Inorg. Chim. Acta*, 1975, **15**, 205.
[26] A. L. Crumblin and A. T. Poulos, *Inorg. Chem.*, 1975, **14**, 1529.

outer-sphere and inner-sphere routes are possible for the other reactions. It is noteworthy, however, that whereas $[Cu(MeCN)_4]^+$ is inert to air oxidation the mixed complex $[Cu(terpy)(MeCN)_2]^+$ is oxidized by O_2. In the corresponding reaction of $[Cu(phen)_2]^+$ in nitromethane,[27] a second-order dependence on $[Cu^I]$ has been interpreted in terms of the mechanism

$$Cu^I + O_2 \rightleftharpoons Cu^IO_2 + Cu^I \overset{k_a}{\rightleftharpoons} [Cu^{II}O_2Cu^{II}] \xrightarrow{\text{solvent}} \text{products}$$

in which the unstable copper(I) adduct reacts to yield a copper(II) peroxo-species which undergoes rapid dissociation. Again, a two-electron reduction of the oxygen is postulated.

A low-oxidation state peroxide has been characterized in the reaction of copper(I) chloride in pyridine,[28]

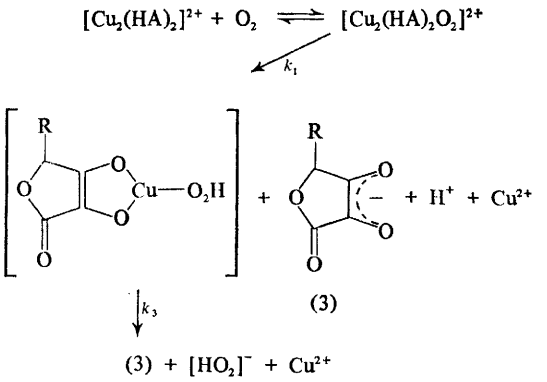
$$4Cu^I + O_2 \xrightarrow{py} 2Cu^{II} + Cu_2O_2$$

The species which is formally copper(I) is evidently strongly stabilized by electron delocalization. No solid sample was isolable so that the number of pyridine molecules associated with the metal centre is not known. The spectrum of the complex shows no maximum in the range 305—800 nm and is similar to that observed for the proposed peroxide grouping in oxyhaemocyanin.[29]

The kinetics and mechanism of the copper(II)-catalysed oxidation of ascorbic acid H_2A by dissolved oxygen have been re-investigated.[30,31] In nitrate media over the pH range 2.0—3.5, the rate law is represented as

$$-d[O_2]/dt = k_1[Cu^{II}][HA^-][O_2]^{\frac{1}{2}}$$

A detailed treatment of the ligand and copper concentration dependences shows that as well as the complex $CuHA^+$ (formed from the reaction of the bivalent metal ion with the monoprotonated ligand species) there is present a small amount of a dimeric complex $[Cu_2(HA)_2]^{2+}$. The proposed mechanism (Scheme 4) involves two-



Scheme 4

[27] J. A. Arce, E. Spodine, and W. Zamudio, *J. Inorg. Nuclear Chem.*, 1975, **37**, 1304.
[28] C. E. Kramer, G. Davies, R. B. Davis, and R. W. Slaven, *J.C.S. Chem. Comm.*, 1975, 606.
[29] T. B. Freedman, J. S. Loehr, and T. M. Loehr, *J. Amer. Chem. Soc.*, 1976, **98**, 2809.
[30] R. F. Jameson and N. J. Blackburn, *J. Inorg. Nuclear Chem.*, 1975, **37**, 809.
[31] R. F. Jameson and N. J. Blackburn, *J.C.S. Dalton*, 1976, 534.

electron transfer to oxygen (the latter binding across the dinuclear Cu—Cu site). The half-order dependence on $[O_2]$ derives from a radical chain mechanism *via* the ascorbate–copper(II)–peroxide complex which is presumed to undergo either unimolecular decomposition (k_3) or a bimolecular termination. The primary electron-transfer process can thus be considered to involve formally copper(III) intermediates and the catalytic activity of the dimers parallels that of the oxygen binding sites in a number of copper-containing oxidases. Tervalent copper has also been proposed as a probable intermediate in the reaction catalysed by galactose oxidase.[32] The addition of $[Fe(CN)_6]^{3-}$ to the galactose oxidase reaction system not only increases the reaction rate but causes an almost complete disappearance of the e.p.r. signal due to enzymic copper. Stable complexes of deprotonated amides with copper(III) have recently been identified.[33] An interesting observation has been made on the reactions of copper(II) peptide complexes with molecular oxygen. Unlike the reaction with Ni^{II}, activation of the copper species takes place only in the dark.[34] Radiation of 340—420 nm wavelength inhibits the reaction. In the reaction with deprotonated tetraglycine, an autocatalytic uptake of O_2 is accompanied by the formation of a copper(III) complex. The explanation of the inhibition effects is still not resolved but it may be that a weak copper–peptide–O_2 complex is efficiently dissociated by light of the relevant wavelength.

The reaction of superoxide anion with a copper(II) complex has been reported.[35] Pale blue solutions of $[Cu(phen)_2]^{2+}$ in DMSO react with O_2 on mixing to yield deep brown solutions of $[Cu(phen)_2]^{+}$. The copper(I) species reacts only relatively slowly with dissolved oxygen in this solvent but the reaction is dramatically accelerated by protons. The overall equilibria are

$$[Cu(phen)_2]^{2+} + O_2^- \rightleftharpoons [Cu(phen)_2]^{+} + O_2$$

and

$$[Cu(phen)_2]^{+} + O_2 + H^+ \rightleftharpoons [Cu(phen)_2]^{2+} + HO_2$$

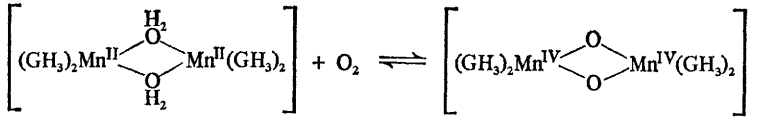
The reactions of copper(II) complexes with O_2^- have also been investigated pulse-radiolytically.[36] The reactivity decreases as the number of ligands attached to the metal centre increases, the effect being associated with change in the redox potentials relative to copper(II).

4 Other Metal Complexes

A manganese(II) porphyrin complex, Mn^{II}(TPP), has been shown to react reversibly with O_2 in the presence of pyridine at −79 °C in toluene solutions.[37] Qualitatively the affinity for O_2 of the [M(TPP)py] complexes increases in the order $Co^{II} < Fe^{II} < Mn^{II}$ and may reflect the ease of oxidation of the analogous metalloporphyrins. E.s.r. evidence is interpreted in terms of the metal(IV) oxidation state in the manganese oxygen complex. A similar oxidation state has been postulated in the reactions of manganese-

[32] G. R. Dyrkacz, R. D. Libby, and G. A. Hamilton, *J. Amer. Chem. Soc.*, 1976, **98**, 626.
[33] D. W. Margerum, *Chem. Eng. News*, 1975, **53**, No. 49, p. 26.
[34] G. L. Burce, E. B. Paniago, and D. W. Margerum, *J.C.S. Chem. Comm.*, 1975, 261.
[35] J. S. Valentine and A. B. Curtis, *J. Amer. Chem. Soc.*, 1975, **97**, 224.
[36] D. Klug-Roth and J. Rabani, *J. Phys. Chem.*, 1976, **80**, 588.
[37] C. J. Weschler, B. M. Hoffman, and F. Basolo, *J. Amer. Chem. Soc.*, 1975, **97**, 5278.

(II) gluconate, $[Mn(GH_3)_2]^{2-}$, which is considered as a redox model for the photosynthetic evolution of oxygen.[38] In solutions more concentrated than 5 mmol l^{-1}, a dimeric form is present which reversibly binds O_2:



Chromium(II) is rapidly oxidized by molecular oxygen to yield the $[Cr(OH)_2Cr]^{4+}$ dimer as product. Pulse-radiolysis studies have been made of the reaction,[39] the initial step,

$$Cr^{2+} + O_2 \xrightarrow{k} CrO_2^{2+} \qquad k = 1.6 \pm 0.2 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$$

being first-order with respect to oxygen concentration. Under the conditions employed the complex is relatively long lived. In conditions of excess reductant, however, reaction takes place with a second mole of Cr^{2+} to yield the dinuclear complex.

The kinetics of oxygenation of the nitrosyl ligands in the species $[Ir(PPh_3)_2(CO)Cl(X)(NO)]$ are dependent on the group X,[40] the rates decreasing in the order $I > Br > Cl > NCS > NCO > N_3$, which is approximately that attributable to decreasing electron release by the ligands. Evidence has been presented for a ready aerial oxidation of co-ordinated ammonia in the complex $[Ru(NH_3)_6]^{3+}$.[41] At pH 13 under ambient conditions, the ion $[Ru(NH_3)_5(NO)]^{3+}$ is obtained. Tracer experiments carried out in excess NH_3 indicate that it is the co-ordinated ammine which is oxidized. Yields of *ca.* 30% are produced, and further purging with oxygen tends not to increase the nitrosyl complex concentration but rather to promote the anation to *trans*-$[Ru(NH_3)_4(NO)(OH)]^{2+}$. On exposure of aqueous (pH ~9.3) solutions of $[Ru(NH_2Me)_6]^{2+}$ to oxygen, the species $[Ru(NH_2Me)_5(OH)]^{2+}$ is identifiable as an intermediate.[42] In this case a slow replacement of the methylamine is followed by a rapid oxidation of the ruthenium(II) aquo-complex. Further replacement of the amine ligand by water has also been reported.

The oxidation of uranium(IV) by O_2 in toluene and in trioctylamine has been shown to be second-order in $[U^{IV}]$.[43]

5 Reactions of Hydrogen Peroxide

The stoicheiometry and kinetics of reduction of Cu^{II} dmp complexes (dmp = 2,9-dimethyl-1,10-phenanthroline) by H_2O_2 have been reported[44] in borato-buffered media over the range pH = 6.6—8.6. The overall reaction may be represented as

$$4\text{dmp} + 2Cu^{II} + H_2O_2 \longrightarrow 2[Cu(\text{dmp})_2]^+ + O_2 + 2H^+$$

[38] D. T. Sawyer and M. E. Bondini, *J. Amer. Chem. Soc.*, 1975, **97**, 6588.
[39] R. M. Sellers and M. G. Simic, *J.C.S. Chem. Comm.*, 1975, 401.
[40] M. Kubota and D. A. Phillips, *J. Amer. Chem. Soc.*, 1975, **97**, 5637.
[41] S. D. Pell and J. N. Armor, *J. Amer. Chem. Soc.*, 1975, **97**, 5012.
[42] J. D. Miller, J. B. Watts, and D. Y. Waddan, *Inorg. Chim. Acta*, 1975, **12**, 267.
[43] K. Juznic and M. Senegacnik, *Inorg. Nuclear Chem. Letters*, 1975, **11**, 349.
[44] G. Davies, R. Higgins, and D. J. Loose, *Inorg. Chem.*, 1976, **15**, 700.

The rate is strictly first-order in H_2O_2 at fixed $[H^+]$ and high [dmp], indicating the absence of any stoicheiometrically important metal peroxo-complexes. The mechanism postulated may be represented by the equations

$$[Cu(dmp)_2]^{2+} \rightleftharpoons [Cu(dmp)_2(OH)]^+ + H^+$$

$$H_2O_2 \rightleftharpoons HO_2^- + H^+$$

$$[Cu(dmp)_2]^{2+} + HO_2^- \xrightarrow{k_\alpha} Cu^I + O_2^{-\cdot} + H^+$$

$$[Cu(dmp)_2(OH)]^+ + H_2O_2 \xrightarrow{k_\beta} Cu^I + O_2^{-\cdot} + H^+$$

$$Cu^{II} + O_2^{-\cdot} \xrightarrow{\text{fast}} Cu^I + O_2$$

This system is of interest in that not only does the $[Cu^{II}(dmp)_2]^{2+}$ concentration represent virtually all the copper ions present, but that no involvement of the borate buffer is detectable, in contrast to other reactions of this type. It would appear from this study that the main requirement for efficient catalytic activity is related to the rate with which the copper-(I) and -(II) co-ordination spheres can be made to resemble each other. Copper(II) ions have been shown to catalyse the oxidation of ascorbic acid by hydrogen peroxide.[45] In the corresponding reaction with hydrazine as substrate,[46] the rate law ($[Cu^{II}]_T$ = total $[Cu^{II}]$ present),

$$d[N_2]/dt = k_1K[N_2H_4][H_2O_2][Cu^{II}]_T/(1 + K[N_2H_4])$$

is consistent with the mechanism in which a copper(II) hydrazine complex is formed prior to the rate-determining electron-transfer step:

$$Cu^{II} + N_2H_4 \overset{K}{\rightleftharpoons} Cu^{II}-N_2H_4$$

$$Cu^{II}-N_2H_4 + H_2O_2 \xrightarrow{k_1} \text{Intermediate products} + 2H_2O$$

The catalytic decomposition of H_2O_2 by copper(II) ammine complexes has been described in terms of an ion-radical chain mechanism involving OH, O_2^-, and $[Cu(NH_3)_2]^+$ as intermediates.[47] In the reactions of H_2O_2 with $[Cu(bipy)_2]^+$,[48] there is no evidence for the OH· radical as an intermediate. An oxygen transfer process is postulated,

$$H_2O_2 + [Cu(bipy)_2]^+ \longrightarrow [(bipy)_2CuO]^+ + H_2O$$

with the formation of a cupryl form of copper(III).

The reaction of hydrogen peroxide with aquosilver(II) ions has been reported.[49] In the presence of excess reductant, the reaction is first-order in Ag^{II} and zero-order in H_2O_2, with no dependence on acidity in the range 2.0—4.8M-$HClO_4$. It is suggested that an Ag–H_2O_2 complex is formed, and that the mechanism is similar to one proposed by the authors for other oxidations of this substrate.[50] The interpretations presented do, however, conflict markedly with those of a variety of other workers

[45] E. V. Shtamm, Y. I. Skurlatov, and A. P. Purmal, *Russ. J. Phys. Chem.*, 1975, **49**, 1338.
[46] C. R. Wellman, J. R. Ward, and L. P. Kuhn, *J. Amer. Chem. Soc.*, 1976, **98**, 1683.
[47] T. P. Vorob'eva, V. M. Berdnikov, and Yu. N. Kozlov, *Russ. J. Phys. Chem.*, 1975, **49**, 1176.
[48] N. V. Gorbunova, A. P. Purmal, and Y. I. Skurlatov, *Russ. J. Phys. Chem.*, 1975, **49**, *1169*.
[49] C. F. Wells and D. Fox, *J. Inorg. Nuclear Chem.*, 1976, **38**, 107.
[50] C. F. Wells and M. Husain, *J. Chem. Soc.* (*A*), 1970, 1013.

whose data are quoted and it appears that further investigations may be required to clarify the situation. In contrast with the aquo ion, the reaction of $[Ag(bipy)_2]^{2+}$ with H_2O_2 exhibits a first-order dependence on the reductant and is pH-dependent in the range 1.75—3.0.[50] The origin of the latter effect is considered to derive from the protonation of two of the nitrogen atoms on the ligands rendering the reactive species as a diaquo-bis-unidentate complex which undergoes reduction,

$$[Ag(bipy)_2]^{2+} + 2H^+ \rightleftharpoons [Ag(Hbipy)_2]^{4+} \xrightarrow{+H_2O_2} [Ag(bipy)_2]^+ + 3H^+ + HO_2\cdot$$

The radical formed is then rapidly oxidized to O_2 and H^+.

A review of the chemistry and mode of reaction of Fenton's reagent has been presented.[51] Previous models for the competitive reactions of organic substrates and iron(II) with the hydroxyl radical have been modified to give kinetic rate ratios and the mechanistic implications of the reactions of metal ions with radicals have been discussed. The titrimetric technique described has also been used in a re-evaluation of the iron(III)-catalysed decomposition of hydrogen peroxide. The reaction of $[Fe(CN)_5(H_2O)]^{3-}$ (prepared by *in situ* aquation of the corresponding ammine complex) with ROOH substrates (R = H or Bu^t) have been investigated using the stopped-flow method.[52] The rates are independent of pH at values less than 10.5 and the rate law, allowing for the stoicheiometry, may be represented by the expression

$$d[Fe^{III}]\,dt = \frac{2(k_1 + k_2K_a/[H^+])}{1 + K_a/[H^+]}[ROOH]_T$$

where K_a is the acid dissociation constant of the hydroperoxide. The mechanism

$$[Fe(CN)_5(H_2O)]^{3-} + RO_2H \xrightarrow{k_1} [Fe(CN)_5H_2O]^{2-} + RO\cdot + OH^-$$

$$[Fe(CN)_5(H_2O)]^{3-} + RO_2^- \xrightarrow{k_2} [Fe(CN)_5OH]^{2-} + RO\cdot + OH^-$$

$$Fe^{II} + RO\cdot \xrightarrow{\text{fast}} Fe^{III} + RO^-$$

$$RO^- + H^+ \overset{\text{fast}}{\rightleftharpoons} Fe^{III} + RO^-$$

involves two rate-determining paths interrelated by the dissociation of the peroxide. Comparison of the rate constants and thermodynamic parameters for the two substrate reactions with the corresponding data for the complexation of a variety of ligands (CN^-, NO_2^-, pyrazine, thiourea, MeCN) strongly supports the view that the oxidation processes are limited by the substitution of the peroxide species at the iron(II) centre. There is also no kinetic or spectroscopic evidence for any intermediate peroxo-complexes. In the reaction of the *cis*-$[Co(NH_3)_2(OH)]^{2+}$ ion with H_2O_2 [53] the mechanism postulated is also inner-sphere, the parameters being closely similar to those for the complexation of Cl^- and the oxidation of Br^-. In this case a peroxo-complex is postulated but it is of interest that only the hydroxo-form of the *cis*-diammine complex shows significant reactivity. Estimates from data at the highest $[H^+]$ studied indicate that the presence of inner-sphere OH^- in $[Co(NH_3)_2]^{3+}$

[51] C. Walling, *Accounts Chem. Res.*, 1975, **8**, 125.
[52] G. Davies and A. R. Garafalo, *Inorg. Chem.*, 1976, **15**, 1101.
[53] I. Bodek and G Davies, *Inorg. Chem.*, 1975, **14**, 2580.

leads to $\sim 10^4$-fold increase in the lability of the remaining co-ordinated water molecules.

Further evidence has been provided[54] on the mechanism of the catalase-like activity of cobalt(III)-haematoporphyrin ($Co^{III}HP$). The disproportionation of H_2O_2 may be formulated as

$$Co^{III}\cdot HP + H_2O_2 \rightleftharpoons [Co^{III}\cdot HP\cdot H_2O_2]$$

$$[Co^{III}HP\cdot H_2O_2] \rightleftharpoons [Co^{III}\cdot HP\cdot HO_2^-] + H^+$$

$$[Co^{III}\cdot HP\cdot HO_2^-] + H_2O_2 \rightleftharpoons [HO_2H\cdot Co^{III}\cdot HP\cdot HO_2^-] \longrightarrow Co^{III}HP + H_2O + O_2 + OH^-$$

Comparisons of the first substitution step have been made with the reaction involving SCN^-. Unlike most cobalt(III) complexes $Co^{III}HP$ is relatively labile, it enhances the acidity of bound substrate, and can co-ordinate H_2O_2, and these factors together with its redox activity are seen to be of importance in its suitability as a model for catalase. The kinetics of the reduction of the catalase–H_2O_2 complex by ethanol have been reported.[55]

A kinetic study has been made of the intermediate formed in the reaction of Cr^{III} with H_2O_2.[56] In basic media, with the conditions in the flow experiments controlled such that only the Cr^{III} monomer is reactive, the mechanism may be written as in Scheme 5, where the peroxide complex formed initially may react in a branching

$$CrO_2^- + H_2O_2 \xrightarrow{k_1} [Cr^{III}—H_2O_2]$$

$$[Cr^{III}—H_2O_2] \xrightarrow{k_4} [Cr^{IV}]$$

$$[Cr^{III}—H_2O_2] \xrightarrow{k_2 + H_2O_2} [Cr^{V}\text{–peroxide}] \xrightarrow{k_3} Cr^{IV}(OH\cdot)$$

Scheme 5

manner to yield either Cr^{IV} or an e.s.r.-active Cr^V species which is detectable at $\lambda = 500$ nm in the flow system. Addition of ethylenediamine greatly diminishes the optical signal at 500 nm by chelating to the Cr^{IV} and Cr^V and thereby inhibiting the co-ordination of the second peroxide ligand. The Cr^{IV} formed is considered to be consumed in a two-electron exchange to the hydrogen chromate ion.

An e.s.r. study has been made of the reaction of TiF_2^+ with H_2O_2,[57] the initial reaction being the formation of a hydroxo-complex of titanium(IV):

$$TiF_2^+ + H_2O_2 \longrightarrow [TiF_2OH]^+ + HO\cdot$$

Both this species and the hydroxyl radical formed undergo further reaction with substrates present. Little effect is noted on the reaction rate in chloride media but in sulphate[58] a Ti^{III} sulphate complex leads to an increase in the decay rates involving organic radicals.

[54] H. Sigel and R. F. Pasternack, *J. Inorg. Nuclear Chem.*, 1975, **37**, 1093.
[55] M. L. Dremer, *J. Phys. Chem.*, 1975, **79**, 951.
[56] M. Knoblowitz and J. I. Morrow, *Inorg. Chem.*, 1976, **15**, 1674.
[57] H. B. Brooks and F. Silicio, *J. Phys. Chem.*, 1975, **79**, 2544.
[58] H. B. Brooks and F. Silicio, *J. Phys. Chem.*, 1975, **79**, 2547.

Triphenylstibine has been shown to reduce t-butyl hydroperoxide about as fast as triphenylphosphine, but the reaction with Ph_3As is ~ 60 times slower.[59] Rates are first-order in each component and some catalysis by vanadium and molybdenum complexes has been observed. The variation in rates may reflect the differing availability of the *d*-orbitals for π-bonding with the peroxidic oxygen.

The kinetics of the oxidation of sulphite by H_2O_2 in acid solution have been investigated[60] using the stopped-flow method. The reaction is subject to general acid catalysis. A mechanism consistent with the data may be written as

$$H^+ + SO_3^{2-} \rightleftharpoons HSO_3^-$$

$$HSO_3^- + H_2O_2 \overset{K}{\rightleftharpoons} \begin{matrix} {}^{-}O \\ \diagdown \\ S—O_2H \\ \diagup \\ O \end{matrix} + H_2O$$

$$\begin{matrix} {}^{-}O \\ \diagdown \\ S—O_2H \\ \diagup \\ O \end{matrix} + HA \xrightarrow{k} H_2SO_4 + A^-$$

where HA represents a proton donor in solution. The rate-determining step is the rearrangement of the peroxomonosulphurous acid intermediate. The data are consistent with earlier data under the same reaction conditions where the product sulphate was found to have incorporated two ^{18}O atoms originally present in the doubly labelled peroxide even though the stoicheiometry requires the net addition of only one oxygen atom.

[59] R. Hiatt, C. McColeman, and G. R. Howe, *Canad. J. Chem.*, 1975, **53**, 560.
[60] M. R. Hoffman and J. O. Edwards, *J. Phys. Chem.*, 1975, **79**, 2096.

Part II

SUBSTITUTION AND RELATED REACTIONS

By
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1
Non-metallic Elements

BY G. STEDMAN

The coverage and the style of treatment are essentially the same in this chapter as in the corresponding section of Volume 4 of these Reports.

1 Group III

Boron.—Several articles have appeared[1] in which aspects of the reaction mechanisms of boron compounds have been discussed.

Tetrahedral Anions. The hydrolysis of the $[BH_4]^-$ anion in aqueous DMSO has the kinetic form for a general-acid-catalysed reaction,[2] but with the catalytic coefficients k_{H_2O} and k_{H^+} very different to the values observed for aqueous media. This difference is ascribed to the inability of DMSO to act as a proton relay system. A series of molecular orbital calculations suggest[3] that BH_5 could be a metastable intermediate in the hydrolysis of $[BH_4]^-$. They indicate the presence of identifiable BH_3 and H_2 subunits in the structure. The authors conclude, however, that limitations in the theoretical methods used do not yet allow experimental and computational results to be reconciled (at least to within a few kcal). The acid-catalysed ammonolysis in liquid ammonia is first-order in both $[NH_4]^+$ and $[BH_4]^-$, but is appreciably slower than the corresponding reaction in water; the rate is markedly decreased by increases in ionic strength. This may be due[4] to the participation of a water molecule in the latter case. The rates of reduction of a variety of substrates by $[BH_4]^-$ have been reported,[5] and for the reduction of ketones it is suggested[6] on the basis of H/T isotope effects that a four-centre transition state is involved.

Boron–Hydrogen Compounds. Several studies of fluxional behaviour have been reported,[7] and there has been a very authoritative discussion[8] of intra molecular

[1] K. Mislow, *Accounts Chem. Res.*, 1976, **9**, 26; D. S. Matteson, *J. Organometallic Chem.*, 1975, **98**, 295; K. Niedenzu, *J. Organometallic Chem.*, 1975, **98**, 369; J. C. Lockhart, in 'Reaction Mechanisms in Inorganic Chemistry', ed. M. L. Tobe, (M.T.P. International Review of Science), Inorganic Chemistry, Series 2, Butterworths, London, 1974, Vol. 9, p. 1.

[2] L. M. Abts, J. T. Langland, and M. M. Kreevoy, *J. Amer. Chem. Soc.*, 1975, **97**, 3181.

[3] T. A. Halgren, I. M. Pepperberg, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 1976, **98**, 3442.

[4] T. S. Briggs and W. L. Jolly, *Inorg. Chem.*, 1975, **14**, 2267.

[5] G. T. Bruce, A. R. Cooksey, and K. J. Morgan, *J.C.S. Perkin II*, 1975, 551.

[6] D. J. Pasto and B.Lepeska, *J. Amer. Chem. Soc.*, 1976, **98**, 1091.

[7] J. D. Odoh, V. F. Kalasinsky, and J. R. Durig, *Inorg. Chem.*, 1975, **14**, 2837; C. H. Bushweller, H. Beau, and W. J. Dewkett, *Inorg. Chem.*, 1976, **15**, 1739; E. J. Stampf, A. R. Garber, J. D. Odom, and P. D. Ellis, *Inorg. Chem.*, 1975, **14**, 2446; R. J. Remmel, H. D. Johnson, jun., I. S. Jaworiwsky, and S. G. Shore, *J. Amer. Chem. Soc.*, 1975, **97**, 5395; D. F. Games and J. H. Morris, *J.C.S. Chem. Comm.*, 1975, 626.

[8] E. L. Muetterties, E. I. Hoel, C. G. Salentine, and M. F. Hawthorne, *Inorg. Chem.*, 1975, **14**, 950; E. L. Muetterties and B. F. Beier, *Bull. Soc. Chim. belges*, 1975, **84**, 397.

rearrangements in boron cluster compounds. Papers have appeared making predictions of the reactivity of boranes towards electrophiles and nucleophiles based on a theoretical approach.[9] In the oxidative degradation of $[2\text{-}B_{12}H_{12}]^{2-}$ with alkaline permanganate, $[B_{12}H_{11}OH]^{2-}$ and $[B_{12}H_{10}(OH)_2]^{2-}$ have been observed[10] as stable intermediates. For the carbaboranes, a computational approach to rearrangements suggests[11] the formation of a ditrigonal prism as an intermediate in the conversion of $1,2\text{-}C_2B_4H_6$ into $1,6\text{-}C_2B_4H_6$. The kinetics of formation of 1,2-dicarba-*closo*-dodecaborane(12) from $B_{10}H_{12}(Me_2S)_2$ and a range of acetylenes have been studied.[12]

Boron–Nitrogen and Boron–Phosphorus Compounds. The rates of exchange in adducts of the type $PhMe_2NBX_3$ have been measured[13] by n.m.r. methods, and there have been further studies[14] on the redistribution reactions of the adducts of BX_3 with Me_3P, Me_3PO, and Me_3PS. The presence of an intermediate in the reaction of LiH with $(Me_2NBH_2)_2$ in diethyl ether, possibly $[Me_2NBH_2NMe_2BH_3]^-$, is indicated[15] by ^{11}B n.m.r. In the decomposition of H_3PBH_3 in liquid ammonia or liquid aliphatic amines, $[H_2PBH_3]^-$ may be an intermediate.[16]

Boron–Oxygen Compounds. Work on the kinetics of complexation between phenylboronic acid and oxalic acid[17] or malonic acid[18] shows the existence of parallel pathways involving conjugate acid–base species of the ligand. Studies have also been published on the kinetics of complex formation between boric acid and benzoylacetone[19] or a substituted benzophenone.[20]

Aluminium.—A review on the organometallic chemistry of aluminium contains some mechanistic work,[21] particularly n.m.r. studies of exchange reactions. Kinetic studies of the exchange between bridging and terminal sites for alkyl aluminium dimers indicate[22] that, for the methyl compound, reaction proceeds by a dissociative mechanism but that for *meta*- and *para*-tolyl alkyls the mechanism involves only partial dissociation of the bridge. For the addition of $(Bu^i_2AlH)_3$ to oct-4-yne, the kinetic order of $\frac{1}{3}$ for the aluminium compound indicates that the monomer, Bu^i_2AlH, is the active species.[23] Further studies on the Lewis acid behaviour of a range of species, including aluminium compounds, have been published.[24]

Ligand substitution in Al^{3+} (and Be^{2+}) has been reviewed.[25] A most interesting

[9] J. H. Hall, jun., D. A. Dixon, D. A. Kleier, T. A. Halgren, L. D. Brown, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 1975, **97**, 4202; R. W. Rudolph and D. A. Thompson, *Inorg. Chem.*, 1974, **13**, 2779.
[10] A. Kaczmarczyk and M. Collins, *Inorg. Chem.*, 1975, **14**, 207.
[11] T. A. Halgren, I. M. Pepperberg, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 1975, **97**, 1248.
[12] W. E. Hill, F. A. Johnson, and R. W. Novak, *Inorg. Chem.*, 1975, **14**, 1244.
[13] J. Blackborow, *J. Magn. Resonance*, 1975, **18**, 107.
[14] M. J. Bula, J. S. Hartman, and C. V. Raman, *Canad. J. Chem.*, 1975, **53**, 326.
[15] P. C. Keller, *Inorg. Chem.*, 1975, **14**, 440.
[16] E. A. Dietz, K. W. Morse, and R. W. Parry, *Inorg. Chem.*, 1976, **15**, 1.
[17] S. Friedman and R. Pizer, *J. Amer. Chem. Soc.*, 1975, **97**, 6059.
[18] G. Lorber and R. Pizer, *Inorg. Chem.*, 1976, **15**, 978.
[19] M. Marcantonatos, *Inorg. Chim. Acta*, 1976, **16**, 17.
[20] M. Marcantonatos and C. Menzinger, *Inorg. Chim. Acta*, 1975, **14**, 227.
[21] J. D. Smith, *J. Organometallic Chem.*, 1975, **103**, 39.
[22] T. B. Stanford and K. L. Henold, *Inorg. Chem.*, 1975, **14**, 2426.
[23] J. J. Eisch and S. G. Rhee, *J. Amer. Chem. Soc.*, 1974, **96**, 7276.
[24] R. S. Satchell, K. Bukka, and C. J. Payne, *J.C.S. Perkin II*, 1975, 541.
[25] J. J. Delpuech, M. R. Khaddar, A. A. Peguy, and P. R. Rubini, *NATO Adv. Study Ser.*, (*C*), 1975, 18 (*Chem. Abs.*, 1976, **84**, 141134).

study of the formation of complexes between ligands containing phosphorus and aluminium(III) in nitromethane has been carried out[26] by ^{27}Al and ^{31}P n.m.r. methods. Octahedral solvates are observed with trialkyl phosphates, phosphonates, and dialkyl hydrogen phosphites, while a tetrahedral species was found for hexamethylphosphorotriamide. Ligand exchange occurs by a dissociative process for octahedral complexes and an associative process for tetrahedral complexes. For Al^{3+} in aqueous mixtures with acetone and DMSO there is no change in free energy for the replacement of water by DMSO in the co-ordination shell provided[27a] that the mole ratio DMSO:H_2O is less than 0.8. In these solutions acetone does not complex with the aluminium ion [equation (1)]. A direct study of the rate of solvent exchange

$$DMSO + [H_2O,Al]^{3+} \rightleftharpoons H_2O + [DMSO,Al]^{3+} \quad (1)$$

between $[Al(DMSO)_6]^{3+}$ and $[^2H_6]DMSO$ by stopped-flow n.m.r. has been reported in preliminary form. The results are in good agreement with those obtained by extrapolating results obtained at higher temperatures by the n.m.r. line-broadening method to 296 K.[27b] The Eigen–Wilkins mechanism seems to describe the reaction between aluminium(III) and the salicylate monoanion,[28] with Al^{3+} and $[AlOH]^{2+}$ as the active species. The kinetics of ligand exchange between Al^{3+} and $[MnL]^{2-}$ (L = edta) have been found[29] to be first-order in $[Al^{3+}]$ and independent of $[MnL^{2-}]$ at low concentrations of the latter species, with an activation energy of 6.9 kcal mol^{-1}. The catalysis of the hydrolysis of $[(NH_3)_5CoCO_2CH_2CO_2H]^{2+}$ by Al^{3+} (and also by Ga^{3+} and In^{3+}) has been ascribed[30] to complexation with the free carboxy-group. Studies of the rate of formation of AlF^{2+} have been reported.[31]

Gallium.—The equilibria involved in a solution of gallium(III) in concentrated solutions of lithium chloride and hydrochloric acid have been studied by ^{71}Ga n.m.r. and the rate of chloride exchange by ^{35}Cl n.m.r. The exchange reactions of chloride can be rationalized in terms of an associative mechanism[32] involving Cl^- and $[GaCl_4]^-$. This technique, ^{35}Cl nuclear relaxation, has also been used[33] to investigate the exchange of chloride with $[InCl_4(H_2O)]^-$ and $[TlCl_6]^{3-}$. N.m.r. (^1H and ^{71}Ga) has been used[34] to examine the exchange between citrate complexed to gallium(III) and the free ligand; reaction is slow on the n.m.r. time-scale. Racemization and isotopic exchange studies of the tris-β-diketonate complexes of aluminium(III), gallium(III), indium(III), silicon(IV), and germanium(IV) have been reviewed,[35] and a paper has appeared on the exchange between $[Ga(acac)_3]$ and labelled Hacac in THF. The rate law found is given in equation (2). A dissociative mechanism involving an inter-

$$\text{Rate} = [Ga(acac)_3](k_1 + k_2[H_2O] + k_3[Hacac]) \quad (2)$$

[26] J. J. Delpuech, M. R. Khaddar, A. A. Peguy, and P. R. Rubini, *J. Amer. Chem. Soc.*, 1975, **97**, 3373.

[27] (*a*) H. Chi, C. H. Ng, and N. C. Li, *J. Inorg. Nuclear Chem.*, 1976, **38**, 529; (*b*) A. J. Brown, D. A. Couch, O. W. Howarth, and P. Moore, *J. Magn. Resonance*, 1976, **21**, 503.

[28] F. Secco and M. Venturini, *Inorg. Chem.*, 1975, **14**, 1978.

[29] A. A. Popel, Z. A. Saprykoua, and S. I. Galeeva, *Kinetika i Kataliz*, 1974, **15**, 1079 (*Chem. Abs.*, 1974, **81**, 177224).

[30] A. C. Dash and R. K. Nanda, *J. Inorg. Nuclear Chem.*, 1975, **37**, 2145.

[31] V. V. Shurukhin, Yu. A. Kozlov, V. V. Blokhin, and V. E. Mironov, *Zhur. fiz. Khim.*, 1976, **50**, 250 (*Chem. Abs.*, 1976, **84**, 170223).

[32] S. F. Lincoln, A. C. Sandercock, and D. R. Stranks, *J.C.S. Dalton*, 1975, 669.

[33] S. F. Lincoln, A. C. Sandercock, and D. R. Stranks, *Austral. J. Chem.*, 1975, **28**, 1901.

[34] J. D. Glickson, T. P. Pitner, J. Webb, and R. A. Gams, *J. Amer. Chem. Soc.*, 1975, **97**, 1679.

[35] K. Saito, *Pure Appl. Chem.*, 1974, **38**, 325.

mediate containing a unidentate ligand is proposed. Comparison with the reactions of other acetylacetonate complexes leads[36] to a lability sequence titanium(IV) > indium(III) > gallium(III) > aluminium(III) > beryllium(II) > palladium(II) > cobalt(III) > silicon(IV) > germanium(IV) > chromium(III). This sequence should be interpreted with caution, because the co-ordination number is not the same in all cases, and there may be more than one mechanism involved. Another ligand-exchange process, between Me_3Ga and $Me_3Ga,AsMe_3$, is reported[37] to proceed by a slow dissociation of the complex with $\Delta H^{\ddagger} = 8.3$ kcal mol^{-1}; the corresponding antimony complex reacts very slowly.

Indium.—Ligand exchange between Me_2InL and HL, where L = $[CF_3COCHCOR]^-$ with R = Me or Bu^t, obeys kinetics that are first-order in each reactant, and is suggested[38] to involve a species with two unidentate diketonate ligands, the slow step being rotation of one of these about a partial double bond. Kinetic data on the formation of a complex between indium(III) and murexide lead to a somewhat different stability constant to that obtained by other methods. The authors speculate[39] on the possibility that more than one type of complex may be involved. Several further accounts of the formation and reactions of indium(I) species have appeared.[40]

Thallium.—The mechanisms of some organometallic reactions of thallium compounds have been reviewed,[41] and the decomposition of $MeTl(OAc)_2$ in a range of solvents has been studied.[42] The action of thallium(III) in inducing the aquation[43] of *trans*-$[Co(dmg)_2(NH_3)X]$, X = Cl or Br, and in catalysing the elimination of chloride[44] from $[(NH_3)_4Co\text{-}\mu\text{-}(NH_2,Cl)Co(NH_3)_4]^{4+}$ has been reported. Ligand exchange in $Tl(dtc)_3$ follows[45] simple first-order kinetics, and probably involves a dissociative mechanism. The rate is faster than for the analogous complexes of gallium(III) and indium(III). Variable-temperature ^{203}Tl and ^{205}Tl n.m.r. provides evidence[46] for exchange processes in $(Me_2TlOEt)_2$. For univalent thallium species, the diffusion coefficient of Tl^+ has been measured,[47] while an investigation of the kinetics of complexation between Tl^+ and I_3^- attributes[48] the unusually low rate of the reaction for a univalent cation to solvent reorganization around the thallium in the transition state.

[36] C. Chatterjee, K. Matsuzawa, H. Kidd, and K. Saito, *Bull. Chem. Soc. Japan*, 1974, **47**, 2809.
[37] G. M. Gusakov, V. I. Bregadze, B. G. Gribov, and B. I. Kozyrkin, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1974, 2116 (*Chem. Abs.*, 1975, **82**, 8020).
[38] H. L. Chung and D. G. Tuck, *Canad. J. Chem.*, 1974, **52**, 3945.
[39] Y. Kawai, T. Imamura, and M. Fujimoto, *Bull. Chem. Soc. Japan*, 1975, **48**, 3142.
[40] I. A. Sheka and V. F. Kozin, *Ukrain. khim. Zhur.*, 1975, **41**, 370 (*Chem. Abs.*, 1975, **83**, 48895); I. A. Sheka and V. F. Kozin, *Ukrain. khim. Zhur.*, 1975, **41**, 10 (*Chem. Abs.*, 1975, **82**, 116687); V. S. Dmitriev and V. A. Smirnov, *Zhur. fiz. Khim.*, 1975, **49**, 362 (*Chem. Abs.*, 1975, **82**, 145734).
[41] H. Kurosawa and R. Okawara, *J. Organometallic Chem.*, 1975, **98**, 467.
[42] U. Pohl and F. Huber, *J. Organometallic Chem.*, 1976, **116**, 141.
[43] S. F. Chan and S. L. Tan, *Inorg. Nuclear Chem. Letters*, 1975, **11**, 435.
[44] S. W. Foong, J. D. Edwards, R. S. Taylor, and A. G. Sykes, *J.C.S. Dalton*, 1975, 277.
[45] H. Abrahamson, J. R. Hetman, and L. H. Pignolet, *Inorg. Chem.*, 1975, **14**, 2070.
[46] G. M. Sheldrick and J. P. Yesinowski, *J.C.S. Dalton*, 1975, 870.
[47] P. Beran, S. Vojackova, and B. Porsch, *J.C.S. Chem. Comm.*, 1975, 908.
[48] N. Purdie, M. M. Farrow, M. Steggall, and E. M. Eyring, *J. Amer. Chem. Soc.*, 1975, **97**, 1078.

2 Group IV

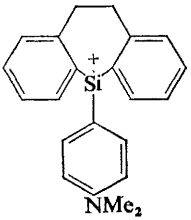
A good deal of mechanistic work for the Group IV elements can generally be described as organometallic, and is reviewed elsewhere. Only a limited number of papers are dealt with below.

Carbon.—The use of isotopes in studies of the mechanisms of reactions of carbon dioxide or carbonates has been reviewed.[49] Measurements using ^{13}C and ^{18}O give[50] a rate constant of 114 l mol^{-1} s^{-1} for the exchange reaction between carbon dioxide and carbonate ion at 25 °C; the same techniques have been applied to the bovine carbonic anhydrase-catalysed exchange between carbon dioxide, its related species, and water.[51] The decomposition rates of the alkyl monocarbonates in aqueous alkali[52] and the effect of polyelectrolytes on the conversion of ammonium cyanate into urea[53] have been reported. The application of calculations originally used for S_E2 processes to the classical S_N2 halide ion–alkyl halide exchange reaction accounts quantitatively[54] for the relative reactivities in terms of steric effects alone; it is not necessary to invoke polar effects. Some further evidence for ion-pair intermediates in S_N2 substitutions has been obtained.[55]

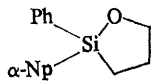
Silicon.—Reviews on reaction mechanisms in silicon chemistry,[56] on the mechanism of the solvolysis of organosilicon compounds containing silicon–oxygen, –nitrogen, or –carbon bonds,[57] and on the mechanism of the cleavage of aryl–silicon bonds by electrophiles[58] have been published. A recent paper on medium effects on the rate of alkaline cleavage of Me_3MR (M = Si or Sn) provides evidence for electrophilic assistance by the solvent for some tin compounds, whereas for the silicon substrates studied it appears[59] that carbanions are liberated in the rate-determining stage. These conclusions are in line with measurements of the solvent isotope effect.[60] A kinetic study of the reaction between I_2 and $[Me_3MMn(CO)_5]$ (M = Si, Ge, Sn, or Pb) and with $[Me_3MFe(CO)_2(\eta\text{-}C_5H_5)]$ (M = Si, Ge, or Sn) in carbon tetrachloride shows[61] a close parallelism between the rates and those observed in protodemetallation in R_3MAr. A siliconium ion (1) has been detected[62] in solution. Nucleophilic attack on an optically active oxacyclopentane (2) has been studied. Hard nucleophiles are suggested[63] to attack equatorially and give retention of configuration while soft nucleophiles attack axially, leading to inversion.

The kinetics of racemization of silicon(IV) complexes of four types of β-diketonate

[49] G. M. Harris, *Phys. Chem. Sci. Res. Rep.*, 1975, 417.
[50] C. K. Tu and D. N. Silverman, *J. Phys. Chem.*, 1975, **79**, 1647.
[51] C. K. Tu and D. N. Silverman, *J. Amer. Chem. Soc.*, 1976, **98**, 978.
[52] C. K. Sauers, W. P. Jencks, and S. Groh, *J. Amer. Chem. Soc.*, 1975, **97**, 5546.
[53] K. Mita, S. Kunugi, T. Okubo, and N. Ise, *J.C.S. Faraday I*, 1975, **71**, 936.
[54] M. H. Abraham, P. L. Grellier and M. J. Hogarth, *J.C.S. Perkin II*, 1975, 1365.
[55] F. G. Bordwell and T. G. Mecca, *J. Amer. Chem. Soc.*, 1975, **97**, 123, 127.
[56] O. W. Steward, *J. Organometallic Chem.*, 1974, **83**, 265.
[57] B. Bøe, *J. Organometallic Chem.*, 1976, **107**, 139.
[58] C. Eaborn, *J. Organometallic Chem.*, 1975, **100**, 43.
[59] C. Eaborn, J. R. Jones, and G. Seconi, *J. Organometallic Chem.*, 1976, **116**, 83.
[60] C. Eaborn and G. Seconi, *J.C.S. Perkin II*, 1976, 925.
[61] J. R. Chipperfield, A. C. Hayter, and D. E. Webster. *J.C.S. Chem. Comm.* 1975, 625.
[62] J. Y. Corey, *J. Amer. Chem. Soc.*, 1975, **97**, 3237.
[63] R. Corrin, G. Guerin, and J. Masse, *J.C.S. Chem. Comm.*, 1975, 75.



(1)



(2)

ligands are consistent with[64] a mechanism involving an intermediate with a unidentate ligand. In contrast to this, n.m.r. studies of the averaging process of the ring acac proton in *cis*-[PhClM(acac)$_2$] (M = Si or Ge) [Ph$_2$Ge(acac)$_2$], and [MeClSi(acac)$_2$] in deuteriochloroform or carbon tetrachloride are interpreted in terms of[65] a twist mechanism, though the authors cannot unequivocally exclude other possible explanations. The exchange of labelled cyanide between alkylsilicon cyanides, R$_3$SiCN (R = Me, Et, or Pr^i), and the rearrangement of the isocyanide to the cyanide complex have been studied. The first reaction is probably[66] a bimolecular process, but for dilute solutions in 1-chloronaphthalene the rearrangement is unimolecular. The kinetics of the reaction [equation (3)] have been examined, and a

$$S_8 + 8Me_3SiCN \longrightarrow 8Me_3SiNCS \qquad (3)$$

mechanism involving a small concentration of Me$_3$SiNC as an intermediate has been proposed.[67] Kinetic data on the polymerization–depolymerization of polysilicic acids in aqueous solutions have been fitted[68] to a series of equations.

Germanium.—A survey of organometallic chemistry contains some mechanistic material.[69] Activation parameters for rotation about the carbon–nitrogen bond in Me$_3$Ge, Me$_3$Pb, and Me$_3$C esters of *NN*-dimethylcarbamic acid, *NN*-dimethylmonothiocarbamic acid, and *NN*-dimethyldithiocarbamic acid have been published.[70] Studies on [MeClGe(acac)$_2$] using n.m.r. indicate that in solution the complex is *cis*; line-broadening measurements lead to a rate law that is second-order in complex. It is proposed[71] that germanium–oxygen bond fission occurs, and that two five-coordinate species form a bis-acac-bridged dimer.

Tin.—For the exchange of protons between different sites in [Ph$_2$Sn(acac)$_2$], [MeClSn(acac)$_2$], and [PhClSn(acac)$_2$] lability increases in the order Cl$_2$ < PhCl < MeCl < Ph$_2$. It is suggested[72] that rearrangement occurs by a twist mechanism,

[64] T. Indue, J. Fujita, and K. Saito, *Bull. Chem. Soc. Japan*, 1975, **48**, 1228.
[65] N. Serpone and K. A. Hersh, *J. Organometallic Chem.*, 1975, **84**, 177.
[66] J. A. Seckar and J. S. Thayer, *Inorg. Chem.*, 1976, **15**, 501.
[67] J. A. Seckar and J. S. Thayer, *Inorg. Chem.*, 1975, **14**, 573.
[68] V. I. Bogdanova and S. V. Bogdanov, *Kinetika i Kataliz*, 1975, **16**, 1386 (*Chem. Abs.*, 1976, **84**, 170206).
[69] B. C. Pant, *J. Organometallic Chem.*, 1975, **89**, 1.
[70] R. E. Lemire and J. C. Thompson, *Canad. J. Chem.*, 1975, **53**, 3732.
[71] K. A. Hersh and N. Serpone, *Canad. J. Chem.*, 1975, **53**, 448.
[72] K. A. Hersh and N. Serpone, *Inorg. Chem.*, 1974, **13**, 2901, 2908.

involving a trigonal-prismatic transition state. The hydrolysis of $[X_2Sn(acac)_2]$ (X = Cl, Br, or I) of $[Cl_2Sn(acac)_2]$, and of $[Cl_2Sn(bzbz)_2]$ in wet chloroform follows second-order kinetics [equation (4)]. However, when the excess of water

$$\text{Rate} = k_2[\text{complex}][H_2O] \qquad (4)$$

over complex was less than 100-fold, retardation was observed,[73] probably because of the formation of the product HX. The solvolysis of py_2SnCl_4 and $(Mepy)_2SnCl_4$ in acetonitrile or nitromethane seems to occur[74] by an S_N1 process (Mepy = 3-methylpyridine). An n.m.r. study of pseudorotation and geometrical isomerism in $(Me_2RPO)_2SnCl_4$ (R = Me, OMe, or SMe) has been reported;[75] kinetic parameters are given. A dissociative mechanism for halogen exchange between the trimethyltin halides in non-polar solvents has been proposed,[76] based upon n.m.r. work. These species also catalyse the decomposition of hexamethylditin. In contrast to earlier work it is found[77] that it is R_3SnX that is the electrophilic reagent, not $[R_3Sn]^+$. Electrophilic substitution of Sn_2Me_6 by $HgCl_2$ in methanol involves $Me_3SnHgCl$ as an intermediate.[78] The kinetics of the removal of R from $RSnPr^i_3$ in methanol by $Hg(OAc)_2$ reveal[79] the existence of very large steric effects, although the pattern is very different to that for S_N2 substitutions. Steric effects for the displaced group are much larger than for the other alkyl groups bonded to the tin. Halogen substitution reactions between alkyl halides and Bu_3SnX have been studied[80] by n.m.r., and the mechanism shown in equation (5) has been proposed. Evidence for tin analogues of the carbenes has been published.[81]

$$RX + Bu_3SnX \rightleftharpoons R{-}X{-}Sn(X)Bu_3 \rightleftharpoons R^+ + [X_2SnBu_3]^- \qquad (5)$$

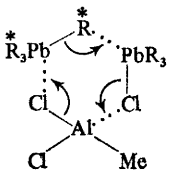
Lead.—The thermolysis of Pb_2Me_6 in toluene or benzene solution follows first-order

$$\begin{aligned} Pb_2Me_6 &\longrightarrow PbMe_4 + PbMe_2 \\ PbMe_2 + Pb_2Me_6 &\rightleftharpoons Pb_3Me_8 \\ Pb_3Me_8 &\longrightarrow 2PbMe_4 + Pb \end{aligned} \qquad (6)$$

kinetics, and a mechanism [equations (6)] has been suggested;[82] there is no evidence for a chain process. The redistribution reactions of alkyl groups in organolead compounds, $R^1{}_4Pb$, R_3PbCl, $R^2{}_2PbCl_2$, *etc.* in the presence of $MeAlCl_2$ has been suggested[83] to occur by a mechanism involving a six-membered ring (3).

The irreversible dissolution of the closed cluster ion $[Pb_4(OH)_4]^{4+}$ in perchloric

[73] M. J. Frazer and L. I. B. Haines, *J.C.S. Dalton*, 1975, 1471.
[74] S. S. Sandhu and J. C. Bhatia, *Res. J. Sci.*, 1974, **1**, 1; R. C. Paul, M. M. Mahajan, and J. C. Bhatia, *Indian J. Chem.*, 1975, **13**, 966.
[75] A. V. Aganov, A. A. Musina, I. Y. Kuramshin, E. G. Yarkova, Y. Y. Samitov, and A. A. Muratova, *Zhur. strukt. Khim.*, 1974, **15**, 779 (*Chem. Abs.*, 1975, **82**, 116659).
[76] J. A. Ladd and B. R. Glasberg, *J.C.S. Dalton*, 1975, 2378.
[77] D. C. McWilliam and P. R. Wells, *J. Organometallic Chem.*, 1975, **85**, 167.
[78] D. C. McWilliam and P. R. Wells, *J. Organometallic Chem.*, 1975, **85**, 335, 347.
[79] M. H. Abraham, D. F. Dadjour, M. Gielen, and B. de Poorter, *J. Organometallic Chem.*, 1975, **84**, 317.
[80] E. C. Friedrich, P. F. Vartanian, and R. L. Holmstead, *J. Organometallic Chem.*, 1975, **102**, 41.
[81] U. Schroer and W. P. Newmann, *Angew. Chem. Internat. Edn.*, 1975, **14**, 246.
[82] D. P. Arnold and P. R. Wells, *J.C.S. Chem. Comm.*, 1975, 642.
[83] M. Boleslawski, S. Pasynkiewicz, and K. Jaworski, *J. Organometallic Chem.*, 1975, **92**. 175.



(3)

acid[84] occurs by a rapid conversion into an open cluster ion $[Pb_4(OH)_2]^{6+}$. The open cluster disappears, following the rate law, shown in equation (7), where c is the

$$-dc/dt = (k_1 + k_2[H^+])c + (k_3 + k_4[H^+])c^{1/2} \quad (7)$$

open-cluster concentration. The k_3 and k_4 terms refer to reaction of a dimer $[Pb_2OH]^{3+}$ which is in equilibrium with the tetramer. The substitution of some lead(II) polyamine-*N*-polyacetate complexes with indium(III) usually involves a binuclear intermediate. For cydta a dissociative process is observed.[85] The reactive indium species is mainly $[InOH]^{2+}$.

3 Group V

Nitrogen.—Two reviews of reaction mechanisms of nitrogen compounds have appeared.[86] There is a brief report on the kinetics of the reaction between sulphamic acid and nitric acid, in which it is suggested[87] that an electrophilic displacement of $[SO_3H]^+$ by $[NO_2]^+$ occurs; nitroamine, NH_2NO_2, is suggested as an intermediate. There continues to be a steady flow of papers elucidating the chemistry of some of the less familiar inorganic compounds of nitrogen. The reaction between nitroamine and nitrous acid has been shown to have the stoicheiometry given in equation (8). The

$$HNO_2 + NH_2NO_2 \longrightarrow HNO_3 + N_2 + H_2O \quad (8)$$

rate law is of the form shown in equation (9), and is interpreted[88] as a reaction

$$\text{Rate} = (k + k'[H^+])[HNO_2][NH_2NO_2] \quad (9)$$

between the nitrosonium cation (or the nitrous-acidium ion, $[H_2NO_2]^+$) and nitroamine (k') and its conjugate base (k) [equation (10)]. This is followed by further fast

$$[NO]^+ + [NHNO_2]^- \longrightarrow ONNHNO_2 \longrightarrow HON{=}NNO_2 \quad (10)$$

steps leading to the final products. The solvent isotope effect on the general-base-catalysed decomposition of nitroamine has been investigated.[89] Studies of the rate of exchange of ^{15}N between nitric acid and nitrogen(II) oxide have been reported.[90] The

[84] V. Frei and H. Wendt, *Z. phys. Chem. (Frankfurt)*, 1974, **88**, 59.
[85] T. Nozaki and N. Suemitsu, *Bull. Chem. Soc. Japan*, 1976, **49**, 445.
[86] M. N. Hughes, in 'Reaction Mechanisms in Inorganic Chemistry', ed. M. L. Tobe (M.T.P. International Review of Science), Inorganic Chemistry Series 2, Butterworths, London, 1974, Vol. 9, p. 21; L. Dozsa, I. Szilassy, and M. T. Beck, *Kem. Kozl*, 1975, **43**, 5 (*Chem. Abs.*, 1975, **83**, 103859).
[87] D. Attwood and G. Stedman, *J.C.S. Dalton*, 1976, 508.
[88] M. N. Hughes and J. R. Lusty, *J.C.S. Dalton*, 1976, 1175.
[89] J. R. Jones and T. G. Rumney, *J.C.S. Chem. Comm.*, 1975, 995.
[90] D. Axente, O. Piringer, M. Abrudean, A. Baloea, and N. Palibroda, *J. Radioanalyt. Chem.*, 1976, **30**, 233.

photolysis of nitrate solutions has been interpreted[91] to show the formation of peroxonitrite by an intramolecular rearrangement of pyramidal $[NO_3]^{-*}$ in the $^3\pi\pi$ state. The mechanism of the decomposition of Angeli's salt, $Na_2N_2O_3$, has been cleared up as a result of the investigations of two groups of workers.[92] At sufficiently high pH values the rate-determining step [equation (11)] is the heterolysis of the monoanion.

$$[HN_2O_3]^- \longrightarrow [NOH] + [NO_2]^- \qquad (11)$$

The nitroxyl species, which under the conditions studied largely exists as $[NO]^-$, undergoes a rapid dimerization forming dinitrogen(I) oxide and water. There is some disagreement as to what happens at lower pH values. Nitrite is undoubtedly involved, and the most likely explanation is set out in reaction (12). A free-radical chain

$$[NO]^+ + H_2N_2O_3 \longrightarrow ONON{=}NO(OH) \longrightarrow NO_2 + N_2O + OH \qquad (12)$$

mechanism is suggested to follow this initiation step. A number of interesting parallels have been pointed out between the chemistry of Angeli's salt and that of sodium *trans*-hyponitrite, $Na_2N_2O_2$. Other nitrosation reactions investigated are those of urea,[93] *N*-alkylthioureas,[94] and aliphatic alcohols.[95] A series of papers on the Fischer–Hepp rearrangement has been published, and these lead to kinetic parameters for the nitrosation of a number of inorganic species.[96] The chloride- and bromide-catalysed hydrolysis of the nitrito-group in $[(NH_3)_5CrONO]^{2+}$ involves nucleophilic attack at the nitrogen of the protonated nitrito-ligand,[97] and seems very similar to the substitution of these nucleophiles at protonated nitrous acid. There is a report[98] of a new nitrous acid-catalysed pathway in aromatic nitration, but the details are not yet available.

The decomposition of the nitrosyldisulphonate free-radical anion, $[ON(SO_3)_2]^{\cdot -}$, in DMSO has been examined kinetically. There are two processes involved, a first-order reaction ($k \sim 10^{-5}$ s^{-1} at 25 °C) and a rapid chain reaction. The first-order process has the stoicheiometry[99] given in reaction (13) and the rate-determining step

$$4[ON(SO_3)_2]^{\cdot -} \longrightarrow [NO]^+ + [ON(SO_3)_2]^{3-} + 2[ON(SO_3)_3]^{3-} \qquad (13)$$

is the initial loss of $[SO_3]^{2-}$ from the starting material. The chain process can be inhibited, either by careful drying of the solvent or by the addition of sulphamate. Nitrous acid is probably involved in the chain propagation. The kinetics of the alkaline hydrolysis of hydroxylamine-*N*-monosulphonate are found[100] to involve the conjugate base $[ONHSO_3]^{2-}$ as an intermediate [reaction (14)]. The hydrolysis of

$$[ONHSO_3]^{2-} \longrightarrow HNO + [SO_3]^{2-} \qquad (14)$$

hydroxylamine-*O*-sulphonate is affected by trace metals. Addition of edta scavenger

[91] N. S. Bayliss and R. B. Bucat, *Austral. J. Chem.*, 1975, **28**, 1865.
[92] M. N. Hughes and P. E. Wimbledon, *Chem. Ind.*, 1975, 742; M. N. Hughes and P. E. Wimbledon, *J.C.S. Dalton*, 1976, 703; E. T. Bonner and B. Ravid, *Inorg. Chem.*, 1975, **14**, 558.
[93] I. V. Shilin and D. P. Adaev, *Kinetika i Kataliz*, 1975, **16**, 1103 (*Chem. Abs.*, 1975, **83**, 184203).
[94] P. Collings, K. Y. Al-Mallah, and G. Stedman, *J.C.S. Perkin II*, 1975, 1734.
[95] A. Dalcq and A. Bruylants, *Tetrahedron Letters*, 1975, 377.
[96] I. D. Biggs and D. L. H. Williams, *J.C.S. Perkin II*, 1976, 601.
[97] J. Victor and A. Haim, *Inorg. Chem.*, 1975, **14**, 3130.
[98] J. C. Giffney, D. J. Mills, and J. H. Ridd, *J.C.S. Chem. Comm.*, 1976, 20.
[99] B. J. Wilson, J. M. Hayes, and J. A. Durbin, *Inorg. Chem.*, 1976, **15**, 1702.
[100] F. Seel and J. Kaschuba, *Z. phys. Chem. (Frankfurt)*, 1974, **92**, 235.

removes the catalytic effect, but introduces a new term (k_A) into the rate law, equation (15), due to reaction of the substrate with edta.

$$-d[NH_2OSO_3^-]/dt = (k_A + k_B[OH^-])[NH_2OSO_3^-] \quad (15)$$

Reaction in the presence of hydrazine or hydroxylamine introduces[101] new pathways involving N_2H_4 and $[NH_2O]^-$ as nucleophiles. The latter reagent is said to lead to the formation of di-imide [reaction (16)]. Theoretical calculations have been made

$$[NH_2OSO_3]^- + [NH_2O]^- \longrightarrow HN{=}NH + [SO_4]^{2-} + 2H_2O \quad (16)$$

of the stability of the *cis*- and *trans*-isomers of di-imide,[102] and it has been calculated that the *trans*-isomer is 6.6 kcal mol^{-1} more stable than the *cis*, and that the lowest-energy pathway for isomerization should involve inversion at one nitrogen, with E_a = 47 kcal mol^{-1}. *Ab initio* calculations on X—N=N—X give activation energies for *cis–trans* isomerization by inversion at nitrogen to be[103] in the sequence F > H > Me > CN. Di-imide is known as a ligand, and a *X*-ray crystallographic study of $[N_2H_2\{Cr(CO)_5\}_2]$,2THF has shown[104] it to possess the *trans*-configuration. Another frequently postulated intermediate, tetrazene, has been isolated as *trans*-NH_2—N=N—NH_2. On thermolysis of the pure compound a 75% yield of $N_2 + N_2H_4$ and a 25% yield of $[NH_4]^+[N_3]^-$ was obtained;[105] the corresponding yields in methanol solution were 40% and 60% respectively. Activation parameters have been measured[106] for nitrogen inversion rates in bicyclohydrazines, and calculations have been made[107] of the effect of the electronegativity of X on the inversion barrier for XH_3. Finally three other papers should be mentioned, a study of proton-transfer reactions in liquid ammonia + aqueous potassium hydroxide,[108] measurements of the kinetics of the thermal decomposition of nitrogen trichloride in a range of organic solvents,[109] and an investigation of *NN*-dichloroamides and *NN*-dichlorocarbamates which suggests[110] that a chloronitrene may be formed:

$$RCONCl_2 + [R^1O]^- \longrightarrow RCOOR^1 + [NCl_2]^-$$

$$[NCl_2]^- \longrightarrow NCl + Cl^-$$

$$2NCl \longrightarrow Cl{-}N{=}N{-}Cl \longrightarrow Cl_2 + N_2$$

Phosphorus.—*Oxoanions.* Evidence for the formation of the metaphosphate anion $[PO_3]^-$ as an intermediate in acyl phosphate reactions has been reported,[111] and *ab initio* calculations on this species suggest[112] that its high electrophilicity may be due to contributions from both π^* and σ^* molecular orbitals. Its methyl ester, $MeOPO_2$, can substitute electrophilically in the aromatic ring[113] for activated aro-

[101] W. E. Steinmetz, D. H. Robinson, and M. N. Ackermann, *Inorg. Chem.*, 1975, **14**, 421.
[102] N. W. Winter and R. M. Pitzer, *J. Chem. Phys.*, 1975, **62**, 1269; E. R. Talaty, A. K. Schwartz, and G. Simons, *J. Amer. Chem. Soc.*, 1975, **97**, 972.
[103] J. M. Howell and L. J. Kirschenbaum, *J. Amer. Chem. Soc.*, 1976, **98**, 877.
[104] G. Huttner, E. W. Gartzke, and K. Allinger, *Angew. Chem. Internat. Edn.*, 1974, **13**, 822.
[105] N. Wiberg, H. Bayer, and H. Bachuber, *Angew. Chem. Internat. Edn.*, 1975, **14**, 177.
[106] S. F. Nelsen and G. R. Weisman, *J. Amer. Chem. Soc.*, 1976, **98**, 1842.
[107] C. C. Levin, *J. Amer. Chem. Soc.*, 1975, **97**, 5649.
[108] S. B. Marks and M. Karni, *J. Inorg. Nuclear Chem.*, 1976, **38**, 1027.
[109] B. A. Radbil, *Kinetika i Kataliz*, 1975, **16**, 360 (*Chem. Abs.*, 1975, **83**, 85541).
[110] R. E. White and P. Kovacic, *J. Amer. Chem. Soc.*, 1975, **97**, 1180.
[111] J. Rebek and F. Gaviña, *J. Amer. Chem. Soc.*, 1975, **97**, 3221.
[112] L. M. Loew, *J. Amer. Chem. Soc.*, 1976, **98**, 1630.
[113] C. H. Clapp, A. Satterthwait, and F. H. Westheimer, *J. Amer. Chem. Soc.*, 1975, **97**, 6873.

matic substrates. The solvent isotope effect has been used[114] as a tool to examine the mechanism of both magnesium(II)-catalysed and yeast inorganic pyrophosphatase-catalysed hydrolysis of pyrophosphate. One of the models is consistent with the formation of a metaphosphate species. Pyrophosphate degradation has also been studied[115] in molten sodium nitrate. The hydrolysis of sodium trimeta-, tetrameta-, and tripoly-phosphate has been examined[116] under both acidic and basic conditions, and several different aqueous–organic solvents have been used. This work has been extended[117] to the hydrolysis of Graham's salt. Catalytic effects due to the sodium ion are reported. The kinetics of the breakdown of hypophosphite in alkaline solution have been investigated, and $[HPO_3]^{2-}$ has been suggested as an intermediate.[118] This last species has also been proposed[119] as being involved in the oxidation of hypophosphite by alkaline hexacyanoferrate(III). The Arbuzov reaction has been shown by ^{31}P n.m.r. to involve a five-co-ordinate phosphorus intermediate (4).[120] Oxidation reactions by peroxodiphosphate, $H_4P_2O_8$, have been the

$$(R^1O)_3P + R^2X \longrightarrow (R^1O)_2\overset{\displaystyle X}{\underset{\displaystyle R^2}{P}}\!\!-\!O\!-\!R^1 \longrightarrow (R^1O)_2P(O)R^2 + R^1X$$

(4)

subject of some mechanistic work recently. The oxidation of arsenic(III) involves a rate-determining hydrolysis of $H_4P_2O_8$ and $[H_3P_2O_8]^-$ to H_3PO_5 (or its conjugate base), followed[121] by a rapid redox reaction (17). A similar result is found for the

$$\text{Rate} = k[H_4P_2O_8] + k'[H_3P_2O_8^-] \qquad (17)$$

oxidation of the bromide ion, where the hydrolysis of $[H_3P_2O_8]^-$ determines the rate.[122]

The oxidation of hexacyanoferrate(II) by $[P_2O_8]^{4-}$ is strongly inhibited by CN^-, and a substitution process is again involved[123] [reaction (18)]. Nucleophilic sub-

$$[Fe(CN)_6]^{4-} + [P_2O_8]^{4-} \rightleftharpoons [Fe(CN)_4P_2O_8]^{6-} + 2[CN]^- \qquad (18)$$

stitutions at peroxomonophosphoric acid species are involved in the oxidation of iodide, and rate constants for the reaction of the iodide ion with a variety of species have been measured.[124] The reactivity sequence is $[HSO_5]^- \approx H_3PO_5 \gg [H_2PO_5]^- \gg [HPO_5]^{2-}$. The basicity of the leaving group is considered to be one of the main factors affecting reactivity.

[114] L. M. Konsowitz and B. S. Cooperman, *J. Amer. Chem. Soc.*, 1976, **98**, 1994.
[115] J. L. Copeland, A. S. Metcalf, and B. R. Hubble, *J. Phys. Chem.*, 1976, **80**, 236.
[116] M. Watanabe, S. Sato, and H. Saito, *Bull. Chem. Soc. Japan*, 1975, **48**, 3593.
[117] M. Watanabe, S. Sato, and H. Saito, *Bull. Chem. Soc. Japan*, 1975, **48**, 896.
[118] A. Luneckas, A. Yu. Prokopchik, and J. Liaukonis, *Lietuvos T.S.R. Mokslu Akad. Darbai Ser. B*, 1975, 3 (*Chem. Abs.*, 1976, **84**, 80296).
[119] D. Mohan, V. K. Chabra, and Y. K. Gupta, *J.C.S. Dalton*, 1975, 1737.
[120] A. Skowronska, J. Mikolajczak, and J. Michalski, *J.C.S. Chem. Comm.*, 1975, 791.
[121] S. Kapoor and Y. K. Gupta, *J.C.S. Dalton*, 1976, 473.
[122] L. M. Bharadwaj, D. N. Sharma, and Y. K. Gupta, *Inorg. Chem.*, 1976, **15**, 1695.
[123] P. Maruthamuthu and M. S. Santappa, *Inorg. Chim. Acta*, 1976, **16**, 35.
[124] F. Secco and M. Venturini, *J.C.S. Dalton*, 1976, 1410.

The rates of dissociation of $MeP(OPh)_4$ and related phosphoranes have been measured by n.m.r. methods,[125] and the association reaction of $[OPh]^-$ and $[R_nP(OPh)_{4-n}]^+$ shown[126] to proceed at the encounter rate. The hydrolysis of $[MeP(OPh)_3]^+$ in aqueous acetonitrile involves a rate-determining addition of water at low acidity (k_1), but at high acidity a rate-determining loss of phenoxide ion occurs:[127]

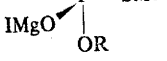
$$[MeP(OPh)_3]^+ + H_2O \rightleftharpoons [MeP(OH_2)(OPh)_3]^+ \qquad k_1, k_{-1}$$

$$[MeP(OH_2)(OPh)_3]^+ \rightleftharpoons [MePO(OPh)_3]^- + 2H^+ \qquad \text{fast}$$

$$[MePO(OPh)_3]^- \longrightarrow MePO(OPh)_2 + [OPh]^- \qquad k_2$$

The *A*2 mechanism which has been thought to describe the acid-catalysed hydrolysis of methyl methylarylphosphinate esters, ArMeP(O)OMe, has been confirmed by ^{18}O bond fission studies. However, some 10% of reaction involves[128] carbon–oxygen and not phosphorus–oxygen cleavage, so another pathway is in competition with the main process. The hydrolysis of aryl dimethylphosphinates, $Me_2P(O)OAr$, is catalysed[129] by nucleophiles.

Phosphorus–Oxygen–Sulphur Compounds. The reaction of methylmagnesium iodide with *S*-alkylphosphonthioates, Ph(SMe)P(O)OR, involves either the displacement of $[SMe]^-$ with retention of configuration, or of $[OR]^-$ with inversion. The suggested[130] intermediate is (5). The alkaline hydrolysis of Me(SR)P(O)OEt occurs with inversion



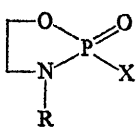
(5)

of configuration in contrast to the *S*-alkyl phosphorothioates, $(SR)P(O)(OEt)_2$. The *S*-phosphoro-compounds are hydrolysed more rapidly than the *S*-phosphono-species, a reversal of the usual pattern for phosphoro- and phosphono-compounds. The authors suggest[131] that in phosphonothioates nucleophilic displacements may occur by an $S_N2(P)$ mechanism, rather than by processes involving five-co-ordinate intermediates.

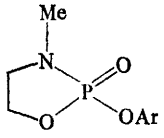
Phosphorus–Oxygen–Nitrogen Compounds. The alkaline hydrolysis of cyclic phosphoramidates (6) can be rationalized[132] in terms of trigonal-bipyramidal intermediates in which sufficiently basic nitrogens will occupy an apical position. Differences in the behaviour of aryl derivatives (7) and their acyclic analogues (8) have been discussed.[133] Square-pyramidal intermediates are preferred[134] in the alkaline

[125] D. I. Phillips, I. Szele, and F. H. Westheimer, *J. Amer. Chem. Soc.*, 1976, **98**, 184.
[126] C. L. Lerman and F. H. Westheimer, *J. Amer. Chem. Soc.*, 1976, **98**, 179.
[127] C. M. Lonzetta, S. J. Kubisen, and F. H. Westheimer, *J. Amer. Chem. Soc.*, 1976, **98**, 1632.
[128] R. A. McClelland, *J.C.S. Chem. Comm.*, 1976, 226.
[129] K. T. Douglas and A. Williams, *J.C.S. Perkin II*, 1976, 515.
[130] K. E. DeBruin and D. M. Johnson, *J.C.S. Chem. Comm.*, 1975, 753.
[131] T. D. Inch, G. J. Lewis, R. G. Wilkinson, and P. Watts, *J.C.S. Chem. Comm.*, 1975, 500.
[132] C. Brown, J. A. Boudreau, B. Hewitson, and R. F. Hudson, *J.C.S. Chem. Comm.*, 1975, 504.
[133] C. Brown, J. A. Boudreau, B. Hewitson, and R. F. Hudson, *J.C.S. Perkin II*, 1976, 888.
[134] J. A. Boudreau, C. Brown, and R. F. Hudson, *J.C.S. Chem. Comm.*, 1975, 679.

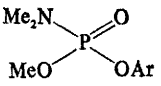
hydrolysis of (9). An *E*1cb mechanism is claimed[135] for the alkaline hydrolysis of Ph(PhNH)P(O)OAr whereas for the thio-analogue, Ph(PhNH)P(S)OAr, an addition–elimination pathway is found. This is considered to be consistent with the poorer electron-releasing ability of P—S^- than P—O^-. The acid-catalysed methanolysis of optically active PhMeP(O)NHR has been examined, and it is claimed[136] that the case for the *A*1 mechanism is not fully proven.



(6)



(7)



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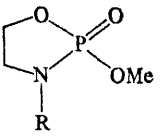


(9)

Phosphazanes. 18-Crown-6-ether can catalyse nucleophilic substitution in $P_3N_3Cl_6$ in benzene, acetonitrile, or THF as solvent.[137] Substitution reactions of $P_3N_3Cl_6$ with 1,2-, 1,3-, and 1,4-$C_6H_4(CH_2OH)_2$ have been studied,[138] and intermediates have been identified[139] in the reactions of catechol and *o*-aminophenol with the halogenocyclophosphazanes. The role of steric effects for substitution by bulky nucleophiles in $P_3N_3Cl_6$ has been discussed; they appear to be important in substitution by $[CF_3CH_2O]^-$, where a *trans*, non-geminal pattern of substitution for all of the successive substitutions is observed.[140] The mechanisms involved in the reactions of $P_3N_3(NMe_2)_6$ with HCl, HBr, and HI in xylene have been discussed.[141] A stepwise mechanism for the reaction of DMSO with $P_3N_3X_6$ and $P_4N_4X_8$ (X = Cl or F) has been reported.[142] A detailed study of the reaction of reaction of ethylamine with $P_4N_4Cl_8$ shows[143] a non-geminal pathway to be followed up to the stage when each initial PCl_2 group has been substituted, in line with earlier studies on $P_3N_3Cl_6$. The hydrolysis of $P_4N_4(NH_2)_8$ has been investigated[144] in acidic, neutral, and alkaline conditions.

Miscellaneous Compounds. The rate of the alkaline decomposition of $[PPh_4]^+Cl^-$ in aqueous acetone increases rapidly with the acetone content of the solvent,[145] a result similar to that observed previously with aqueous dioxan. Qualitatively similar results are found[146] for $[Ph_3PCH_2Ph]^+Cl^-$ in aqueous THF. A virtually identical rate was observed for the ylide Ph_3PCHPh. Media of low dielectric constant are held[147] to favour the formation of five-co-ordinate hydroxyphosphoranes from phosphonium

[135] A. Williams, K. T. Douglas, and J. S. Loran, *J.C.S. Perkin II*, 1975, 1010.
[136] M. J. Harger, *J.C.S. Chem. Comm.*, 1976, 520.
[137] E. J. Walsh, E. Derby, and J. Smegal, *Inorg. Chim. Acta*, 1976, **16**, L9.
[138] M. Kajiwara and H. Saito, *J. Inorg. Nuclear Chem.*, 1975, **37**, 29.
[139] H. R. Allcock, R. L. Kugel, and G. Y. Moore, *Inorg. Chem.*, 1975, **14**, 2831.
[140] M. ul. Hasan, R. A. Shaw, and M. Woods, *J.C.S. Dalton*, 1975, 2202; J. L. Schmutz and H. R. Allcock, *Inorg. Chem.*, 1975, **14**, 2433.
[141] S. N. Nabi, R. A. Shaw, and C. Stratton, *J.C.S. Dalton*, 1975, 588.
[142] E. J. Walsh, S. Kaluzene, and T. Jubach, *J. Inorg. Nuclear Chem.*, 1976, **38**, 397.
[143] S. S. Krishnamurthy, A. C. Sau, A. R. V. Murthy, R. Keat, R. A. Shaw, and M. Woods, *J.C.S. Dalton*, 1976, 1405.
[144] E. Kobayashi, *Chem. Letters*, 1975, 479.
[145] F. Y. Khalil and G. Aksnes, *Z. Phys. Chem. (Frankfurt)*, 1975, **97**, 179.
[146] A. Schnell and J. C. Tebby, *J.C.S. Chem. Comm.*, 1975, 134.
[147] A. Schnell, J. G. Dawber, and J. C. Tebby, *J.C.S. Perkin II*, 1976, 633.

hydroxides. A review of the role of ylides in inorganic chemistry has appeared.[148] Kinetic data on the quaternization reaction of a range of triarylphosphines has been reported.[149] Complete inversion of configuration is found[150] for the reaction of n-butyl- and t-butyl-lithium with optically active phosphines; an $S_N2(P)$ reaction seems to be involved. For the reaction of phosphines with aryl azides, an intermediate can be isolated, and n.m.r. data strongly support[151] a linear P=N—N=N structure.

Intramolecular Processes. An earlier claim to have observed intramolecular fluorine exchange in a number of compounds has been vitiated because of the discovery[152] of a reaction with the wall of the vessels used. Axial–equatorial exchange has been observed[153] in $R^1PF_3OR^2$ and in a number[154] of radicals $ROPF_3$. Pseudorotation in $MeP(OR)_4$($R = 2,6\text{-}Me_2C_6H_3$) can be observed by n.m.r. As phosphoranes with four phosphorus–oxygen bonds usually undergo pseudorotation rapidly on the n.m.r. time-scale, the relatively slow process in this case is ascribed[155] to steric crowding. A study of the Raman spectrum of gaseous phosphorus pentafluoride leads[156] to a calculated barrier of 3.9 kcal mol^{-1} for axial–equatorial fluorine exchange. It is planned to extend this work to other pentafluorides. *Ab initio* calculations on PH_5 indicate that pseudorotation by the Berry mechanism is expected[157] to be a concerted process of low activation energy, whereas pseudorotation by turnstile rotation may be a sequential process with a considerably larger activation energy. Low-temperature ^1H n.m.r. suggests[158] that the barrier to rotation around the phosphorus–nitrogen bond in $(R^1O)_3P(NR^2)$ is below 8 kcal mol^{-1}, despite its formal double-bond character. The barrier to rotation about the phosphorus–nitrogen bond in $RP(S)Cl(NPr^i_2)$ has also been measured.[159] Intramolecular exchange in fluorophosphoranes containing the —O—$C(CF_3)_2$—$C(CF_3)_2$—O— ring has been examined by ^{19}F n.m.r.,[160] while ^{31}P n.m.r. has shown the existence of exchange processes[161] in $M_2(PPh)_n$ (M = Li, Na, K, or Cs, n = 3 or 4).

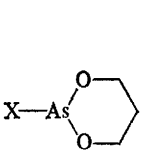
Arsenic.—Evidence of the much smaller tendency of arsenic than phosphorus to undergo valence-shell expansion to form a quinquecovalent species has been presented.[162] However, the rapid exchange of alcohol and trialkyl arsenates is ascribed[163] to a five-co-ordinate transition state. The reduction of arsenic(III) by

[148] H. Schmidbaur, *Accounts Chem. Res.*, 1975, **8**, 62.
[149] W. E. McEwen, W. I. Shiau, Y.-I. Yeh, D. N. Schulz, R. U. Pagilagan, J. B. Levy, C. Symmes, jun., G. O. Nelson, and I. Granoth, *J. Amer. Chem. Soc.*, 1975, **97**, 1787.
[150] E. P. Kyba, *J. Amer. Chem. Soc.*, 1975, **97**, 2554.
[151] H. Goldwhite, P. Gysegem, S. Schow, and C. Swyke, *J.C.S. Dalton*, 1975, 16.
[152] G. Moreland, G. O. Doak, L. B. Littlefield, N. S. Walker, J. W. Gilje, R. W. Braun, and A. H. Cowley, *J. Amer. Chem. Soc.*, 1976, **98**, 2161.
[153] J. G. Riess and D. U. Roberts, *Bull. Soc. chim. France*, 1975, 425.
[154] I. H. Elson, M. J. Parrott, and B. P. Roberts, *J.C.S. Chem. Comm.*, 1975, 586.
[155] I. Szele, S. J. Kubisen, jun., and F. H. Westheimer, *J. Amer. Chem. Soc.*, 1976, **98**, 3533.
[156] L. Bernstein, J. J. Kim, K. S. Pitzer, S. Abramowitz, and I. W. Levin, *J. Chem. Phys.*, 1975, **62**, 3671.
[157] J. A. Altman, K. Yates, and I. G. Csizmadia, *J. Amer. Chem. Soc.*, 1976, **98**, 1450.
[158] H. Goldwhite, P. Gysegen, S. Schow, and C. Swyke, *J.C.S. Dalton*, 1975, 12.
[159] J. Burdon, J. C. Hotchkiss, and W. B. Jennings, *J.C.S. Perkin II*, 1976, 1052.
[160] J. A. Gibson, G.-V. Röschenthaler, and R. Schmutzler, *J.C.S. Dalton*, 1975, 918.
[161] P. R. Hoffman and K. G. Gaulton, *J. Amer. Chem. Soc.*, 1975, **97**, 6370.
[162] D. W. Allen and G. Jackson, *J. Organometallic Chem.*, 1976, **110**, 315.
[163] P. J. White, M. J. Kaus, J. O. Edwards, and P. H. Rieger, *J.C.S. Chem. Comm.*, 1976, 429.

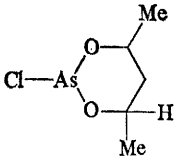
sodium borohydride in aqueous solution involves[164] $AsH(OH)_2$ and AsH_2OH as intermediates. For the reaction[165] of MPh_3 (M = P, As, or Sb) with t-butyl hydroperoxide [reaction (19)] the reactivity sequence is $Ph_3P \geqslant Ph_3Sb > Ph_3As \gg PhNH_2$.

$$Ph_3M + Bu^tOOH \longrightarrow Ph_3MO + Bu^tOH \qquad (19)$$

N.m.r. studies indicate intermolecular halide exchange processes in (10)[166] (X = Cl or Br) and (11).[167] The temperature dependence of the n.m.r. spectrum of pentakis(chloromethyl)cyclopenta-arsine, $(ClCH_2As)_5$, is interpreted[168] by means of processes involving pseudorotation and inversion at arsenic. A recent structure determination of a five-co-ordinate spiroarsane requires[169] a revised interpretation of the n.m.r. spectrum of the compound in terms of its fluxional behaviour.



(10)



(11)

Antimony.—The kinetics of ligand exchange reactions in a number of antimony(III) complexes have been measured.[170] The elimination of methyl bromide from $[Ph_3SbMe]^+Br^-$ in acetonitrile has been studied, and after allowance for salt effects and for ion-pairing the results fit[171] second-order kinetics. The solvolysis of Ph_4SbAr (Ar = *p*-tolyl, *m*-chlorophenyl- or *p*-anisyl) in octan-2-ol occurs[172] by parallel S_N1(Sb) mechanisms, with the formation of benzene and ArH. The presence of the alkoxide ion of octan-2-ol causes a marked change in the product ratio, and a bimolecular process may then be involved.

4 Group VI

Sulphur.—A theoretical study gives[173] a value of 23 kcal mol^{-1} for the barrier to the interconversion of the boat and chair forms of S_6. The mechanism of the reaction of $[N_3]^-$ with S_8 to produce $[S_4N]^-$ has been discussed.[174] Previous studies on the reaction of triphenylphosphine with aryl disulphides have been extended to symmetrical alkyl disulphides in 50% aqueous dioxan. Only a trace of Ph_3PS is found, and a two-step mechanism [reaction (20)] is proposed,[175] similar to that for the aryl

$$XCH_2SSCH_2X + Ph_3P \rightleftharpoons [Ph_3PSCH_2X]^+ + [XCH_2S]^-$$
$$[Ph_3PSCH_2X]^+ + H_2O \longrightarrow Ph_3PO + [RS]^- + 2H^+ \qquad (20)$$

[164] I. S. Kulakov and I. A. Frolov, *Kinetika i Kataliz*, 1975, **16**, 41 (*Chem. Abs.*, 1975, **82**, 160791).
[165] R. Hiatt, C. McColeman, and G. R. Howe, *Canad. J. Chem.*, 1975, **53**, 559.
[166] D. W. Aksnes, *Acta Chem. Scand.*, 1974, **A28**, 1175.
[167] D. W. Aksnes and S. Tøgersen, *Acta Chem. Scand.*, 1975, **A29**, 376.
[168] A. L. Rheingold and J. M. Bellama, *J. Organometallic Chem.*, 1975, **102**, 445.
[169] H. Goldwhite, J. Grey, and R. Teller, *J. Organometallic Chem.*, 1976, **113**, C1.
[170] S. D. Wandiga, *J.C.S. Dalton*, 1975, 1894.
[171] J. E. Parris, G. G. Long, B. C. Andrews, and R. M. Parris, *J. Org. Chem.*, 1976, **41**, 1276.
[172] G. F. Lanneau, R. J. Wikholm, C. T. Lin, and W. E. McEwen, *J. Organometallic Chem.*, 1975, **85**, 179.
[173] Z. S. Herman and K. Weiss, *Inorg. Chem.*, 1975, **14**, 1592.
[174] J. Bojes and T. Chivers, *J.C.S. Dalton*, 1975, 1715.
[175] L. E. Overman and E. M. O'Connor, *J. Amer. Chem. Soc.*, 1976, **98**, 771.

compounds. There is no evidence for any neighbouring-group participation in the mechanism. The nucleophilic activity of a range of arenethiols, $[ArS]^-Na^+$, towards *p*-nitrophenylacetate has been measured;[176] the rate constants correlate with the pK_a values, and the Brønsted plot has a slope of 0.61. Triarylsulphonium halides react with alkoxide ions in alcohol solution, a radical chain process and an aromatic nucleophilic substitution occurring in parallel.[177]

There has been a good deal of activity in the field of the thionous and thionic acids. Mechanisms for the decomposition of $Na_2S_2O_4$ have been put forward,[178,179] and ^{35}S labelling has been used to investigate[180] the reaction of $[S_2O_4]^{2-}$ with S^{2-}. Sulphur exchange between the two sites in $[S_2O_3]^{2-}$ in KSCN–$Na_2S_2O_3$ melts has been studied,[181] but at the temperatures used there is also exchange between $[S_2O_3]^{2-}$ and $[SCN]^-$. The kinetics of formation of $[S_2O_6]^{2-}$ from $[SO_3]^{2-}$ and $[S_2O_8]^{2-}$ are first-order in each reactant,[182] and at 25 °C, pH 9, $I = 3.00$ mol l^{-1} the second-order rate constant is 0.0082 l mol^{-1} s^{-1}, with $E_a = 53.0$ kJ mol^{-1}. Radiochemical investigations of the hydrolysis of $[S_3O_6]^{2-}$ and $[S_4O_6]^{2-}$ have been published,[183] and also a kinetic study of the reaction of $[S_3O_6]^{2-}$ with aqueous ammonia.[184] Work described in the previous volume of this series on nucleophilic substitution by cyanide ion at sulphur and selenium centres in acetonitrile has been extended to a range of thionic acids and related compounds. These papers are a most useful contribution in a rather complex area of chemistry. Substitution by cyanide ion in pentathionate and a seleno-derivative have been described[185] (X = S or Se):

$$[O_3S{-}S{-}X{-}S{-}SO_3]^{2-} + [CN]^- \longrightarrow [O_3S{-}S{-}XCN]^- + [S_2O_3]^{2-} \quad \text{slow}$$

$$[O_3S{-}S{-}XCN]^- + [CN]^- \longrightarrow [O_3S{-}SCN]^- + [XCN]^- \quad \text{fast}$$

With an excess of cyanide an additional, slower process (21) is observed. For

$$[O_3SSCN]^- + [CN]^- \longrightarrow [O_3SCN]^- + [SCN]^- \qquad (21)$$

X = S it is found that $\Delta H^{\ddagger} = 6.3$ kcal mol^{-1} and $\Delta S^{\ddagger} = -40$ cal K^{-1} mol^{-1}; for X = Se the reaction is very much faster, and activation parameters were not measured. Cyanide substitutions in $PhSO_2(X)_nSO_2Ph$ (X = S or Se, n = 1 or 2) and in $[O_3SSeSO_3]^{2-}$ have also been reported.[186] Other studies on related systems have appeared.[187] The reduction of *N*-tosylsulphilimines, R^1R^2SNTs, with cyanide ion to

[176] G. Guanti, C. D. Erba, F. Pero, and G. Leandri, *J.C.S. Dalton*, 1975, 212.
[177] J. W. Knapczyk, C. C. Lai, W. E. McEwen, J. L. Calderon, and J. J. Lubinkowski, *J. Amer. Chem. Soc.*, 1975, **97**, 1188.
[178] P. E. Depoy and D. M. Mason, *Faraday Symp. Chem. Soc.*, 1975, No. 9, p. 47.
[179] V. Cermak and M. Smutek, *Coll. Czech. Chem. Comm.*, 1975, **40**, 3241, 3265; V. N. Plakhotnik and A. Kh. Drabkina, *Vopr. Khimii i Khim. Tekhnol. Resp. Mezhved. Temat. Nauch—Tekhn. Sbornik*, 1975, **37**, 51 (*Chem. Abs.*, 1976, **84**, 50333).
[180] A. H. W. Aten, jun., *Radiochim. Acta*, 1975, **22**, 93.
[181] A. Seibert, *Z. phys. Chem. (Frankfurt)*, 1975, **97**, 11.
[182] L. C. Tan and D. A. House, *New Zealand J. Sci.*, 1974, **17**, 319 (*Chem. Abs.*, 1975, **82**, 116685).
[183] H. Wagner and H. Schreier, Report 1974, AED-CONF-74-08-010 (*Chem. Abs.*, 1975, **83**, 333834).
[184] K. Naito, H. Hayata, and M. Mochizuki, *J. Inorg. Nuclear Chem.*, 1975, **37**, 1453.
[185] T. Austad, *Acta Chem. Scand.*, 1974, **A28**, 935.
[186] T. Austad, *Acta Chem. Scand.*, 1975, **A29**, 241.
[187] T. Mizoguchi and T. Okabe, *Bull. Chem. Soc. Japan*, 1975, **48**, 1799; T. Mizoguchi, Y. Takei, and T. Okabe, *ibid.*, 1976, **49**, 70.

form sulphides, R^1SR^2, is also thought to occur[188] by nucleophilic attack at sulphur. Problems in studying the kinetics of the reaction between sulphide and sulphite have been discussed.[189]

The decomposition of a range of substituted benzenesulphonyl chlorides in 1% aqueous dioxan have been examined kinetically,[190] and there have been further studies of the cleavage of arylalkylsulphonates by electron donors.[191] The decomposition of trifluoromethanesulphonic acid in aqueous solution at high temperatures (571—593 K) has been examined.[192] Two pathways, reactions (22) and (23), can be

$$[CF_3SO_3]^- + 2H_2O \longrightarrow 3HF + [HSO_4]^- + CO \quad (22)$$

$$[CF_3SO_3]^- + H_2O + H^+ \longrightarrow 3HF + H_2O + SO_2 + CO_2 \quad (23)$$

$$3H_2O + 3SO_2 \longrightarrow 2[HSO_4]^- + S + H_2O + 2H^+$$

distinguished. These are thought to arise from nucleophilic attack by water at sulphur and carbon respectively. In alkaline solution there is a single pathway, with a rate law first-order in $[CF_3SO_3^-]$ and $[OH^-]$ which leads initially to carbon(II) and sulphur(VI); the formate ion under these conditions undergoes further reactions with water and carbonate ion and hydrogen are the final products. The alkaline hydrolysis of sulphinate esters $R^1S(O)OR^2$ involves bimolecular nucleophilic attack at the sulphur atom and cleavage of the sulphur–oxygen bond. No exchange of ^{18}O with the solvent was observed.[193] An n.m.r. study of the reaction between alkanesulphenyl chlorides and dialkyl sulphides in liquid sulphur dioxide in the presence of Lewis and Brønsted acids has led[194] to the characterization of a reaction intermediate, $[RS(SR)_2]^+$, that had previously been postulated. Several articles have appeared[195] on the mechanism of reactions of sulphoxides. The kinetics of the alkaline hydrolysis of phenylbenzene-thiolsulphonates show[196] the formation of a large amount of a reaction intermediate:

$$[HO]^- + Ph{-}S{-}SO_2Ph \longrightarrow [PhSO_2]^- + PhSOH$$

$$PhSOH \rightleftharpoons [PhSO]^- + H^+$$

$$[PhSO]^- + PhS{-}SO_2Ph \longrightarrow PhS{-}SOPh + [PhSO_2]^-$$

The intermediate undergoes a further reaction (24). This can occur by nucleophilic

$$3PhS{-}SOPh + 2[OH]^- \longrightarrow 2Ph{-}S{-}S{-}Ph + 2[PhSO_2]^- + H_2O \quad (24)$$

attack at either sulphur atom. The same group of workers have investigated the reactivity of RSH, $[RS]^-$, and a range of nucleophiles towards this intermediate, and the results seem to fit hard–soft acid–base theory. For hydrazine as a nucleophile, diimide appears to be formed as a transient product.

[188] S. Oae, T. Aida, and N. Furukawa, *Internat. J. Sulfur Chem.*, 1975, **8**, 401.
[189] A. Teder and A. Wilhelmsson, *Svensk Papperstidn.*, 1975, **78**, 480 (*Chem. Abs.*, 1975, **83**, 183151).
[190] A. R. Haughton, R. M. Laird, and M. J. Spence, *J.C.S. Perkin II*, 1975, 637.
[191] J. C. Carnahan, jun., W. D. Closson, J. R. Ganson, D. A. Juckett, and K. S. Quaal, *J. Amer. Chem. Soc.*, 1976, **98**, 2526.
[192] L. Fabes and T. W. Swaddle, *Canad. J. Chem.*, 1975, **53**, 3052.
[193] A. A. Najam and J. G. Tillett, *J.C.S. Perkin II*, 1975, 859.
[194] G. Capozzi, V. Lucchini, G. Modena, and F. Rivetti, *J.C.S. Perkin II*, 1975, 900.
[195] J. R. Shelton and K. E. Davies, *Internat. J. Sulfur Chem.*, 1973, **3**, 197, 205, 217.
[196] J. L. Kice and T. E. Rogers, *J. Amer. Chem. Soc.*, 1974, **96**, 8009, 8015; J. L. Kice, T. E. Rogers, and A. C. Warheit, *ibid.*, p. 8020.

Sulphur–Nitrogen Compounds. A review on the chemistry of sulphamic acid has appeared,[197] and this does deal with mechanisms. The kinetics of hydrolysis of the sulphamate ion in aqueous alkali at high temperatures have been measured.[198] Salt effects on the rate of hydrolysis of the sulphur trioxide–trimethylamine adduct have been examined.[199] The *E*1cb mechanism has been identified[200] in the hydrolysis of aryl *N*-methylaminosulphonates $MeNHS(O)_2OAr$. A careful kinetic analysis of the acid- and alkali-catalysed hydrolysis of thioacetamide has been carried out.[201] Parallel pathways involving acetamide and thioacetic acid as intermediates were characterized. Thioamides usually protonate on the sulphur but evidence for protonation on nitrogen has been obtained[202] for *N*-neopentylthioformamide. The kinetics and mechanism of the mercury(II) and copper(II) reactions with thiobenzamide have been reported,[203] and the same group has examined the metal ion-catalysed conversion of PhCSOEt into $PhCO_2Et$.[204] Here the reactivity sequence is $Hg^{2+} \gg Ag^{+} \gg H_3O^{+} > Cu^{2+} \approx Pb^{2+}$. Finally we may mention a kinetic and product study of the reactions of *N*-chloroarenesulphonamides, $[ArS(O)_2NCl]^-Na^+$, with organic sulphides that has led to the conclusion[205] that the reactive electrophiles are $ArS(O)_2NHCl$ and $ArS(O)_2NCl_2$.

Intramolecular Processes. Two studies of axial–equatorial exchange in sulphur tetrafluoride have been published. Provided that the sulphur tetrafluoride is carefully purified it is claimed[206] that the data are in good agreement with the Berry pseudorotation mechanism. The presence of impurities readily leads to intermolecular fluorine exchange. It has been claimed[207] that the rate of exchange (in the absence of hydrogen fluoride) is the same in the liquid phase (E_a = 11.2 kcal mol^{-1}) as in the gas phase (E_a = 11.7 kcal mol^{-1}).

Selenium.—Much of the work on selenium chemistry has come from the same laboratory that has investigated the cyanide substitutions at the polythionates. A ^{13}C study of nucleophilic substitution by cyanide ion at the dicyanides of sulphur and selenium in acetonitrile leads (in excess cyanide) to the di-iminosuccinonitrile dianion, $[(CN)_4]^{2-}$.

$$X(CN)_2 + [CN]^- \longrightarrow [XCN]^- + (CN)_2 \qquad \text{slow}$$

$$(CN)_2 + 2[CN]^- \longrightarrow [(CN)_4]^{2-} \qquad \text{fast}$$

For tellurium dicyanide the pattern is different[208] [reaction (25)].

$$Te(CN)_2 + [CN]^- \longrightarrow [Te(CN)_3]^- \longrightarrow Te + [CN]^- + (CN)_2 \qquad (25)$$

[197] W. J. Spillane, *Internat. J. Sulfur Chem.*, 1975, **8**, 469.
[198] V. N. Plakhotnik and A. Kh. Drabkina, *Kinetika i Kataliz*, 1975, **13**, 60 (*Chem. Abs.*, 1975, **83**, 184147).
[199] J. Burgess, M. J. Blandamer, and S. H. Morris, *J.C.S. Dalton*, 1975, 2118.
[200] A. Williams and K. T. Douglas, *J.C.S. Perkin II*, 1974, 1727.
[201] O. M. Peeters and C. J. de Ranter, *J.C.S. Perkin II*, 1974, 1831; *ibid.*, 1976, 1062.
[202] W. Walters, M. Franzen-Sieveking, and E. Schaumann, *J.C.S. Perkin II*, 1975, 528.
[203] A. J. Hall and D. P. N. Satchell, *J.C.S. Perkin II*, 1975, 778, 953.
[204] D. P. N. Satchell, M. N. Waite, and J. J. Weil, *Chem. and Ind.*, 1975, 791.
[205] F. Ruff and A. Kucsman, *J.C.S. Perkin II*, 1975, 509.
[206] W. G. Klemperer, J. K. Krieger, M. D. McCreary, E. L. Muetterties, D. D. Traficante, and G. M. Whitesides, *J. Amer. Chem. Soc.*, 1975, **97**, 7023.
[207] F. Seel and W. Gombler, *J. Fluorine Chem.*, 1974, **4**, 327.
[208] T. Austad and S. Esperas, *Acta Chem. Scand.*, 1974, **A28**, 892.

For $[O_3S—Se—SO_3]^{2-}$ nucleophilic attack occurs at selenium:[209]

$$[O_3S—Se—SO_3]^{2-} + [CN]^- \longrightarrow [O_3S—SeCN]^- + [SO_3]^{2-} \quad \text{slow}$$

$$[O_3S—SeCN]^- + [CN]^- \longrightarrow [SO_3]^{2-} + Se(CN)_2 \quad \text{fast}$$

$$Se(CN)_2 + 3[CN]^- \longrightarrow [SeCN]^- + [(CN)_4]^{2-} \quad \text{fast}$$

The reaction of $[O_3S—Se—Se—SO_3]^{2-}$ with $[CN]^-$ is more complex, the stoicheiometry varying with reaction conditions. Second-order rate constants (l mol^{-1} s^{-1}) at 25 °C are $[O_3S—Se—Se—SO_3]^{2-}$, 2500; $[O_3S—SeCN]^-$, 0.2; and $[O_3S—S—S—SO_3]^{2-}$, 0.0029. For $[O_3S—SCN]^-$ at 30 °C the rate constant is 0.0295 l mol^{-1} s^{-1}. Another system that has been investigated is $[O_3S—S—Se—S—SO_3]^{2-}$; nucleophilic attack by $[CN]^-$ occurs[210] at selenium, and is about two orders of magnitude faster than on the central sulphur in $[O_3S—S—S—S—SO_3]^{2-}$. Related species appear[211] to be involved in the selenium-catalysed disproportionation of sulphite to sulphate + sulphur. Nucleophilic substitution at *o*-nitrobenzeneseleneyl halides has also been studied.[212]

Tellurium.—Substitution of cyanide ion at $[O_3S—S—Te—S—SO_3]^{2-}$ occurs by a different mechanism to that observed for the sulphur and selenium analogues:[213]

$$[O_3S—S—Te—S—SO_3]^{2-} + [CN]^- \longrightarrow [O_3S—S—TeCN]^- + [S_2O_3]^{2-} \quad \text{slow}$$

$$[O_3S—S—TeCN]^- + [CN]^- \longrightarrow [NCS—TeCN] + [SO_3]^{2-} \quad \text{fast}$$

The interesting product proposed for the second reaction, an inter-pseudohalogen, is not isolated. The final observed stoicheiometry is given by reaction (26). The

$$[O_3S—S—Te—S—SO_3]^{2-} + 6[CN]^- \longrightarrow [TeCN]^- + [SCN]^- + [S_2O_3]^{2-} + [SO_3]^{2-} + [(CN)_4]^{2-} \quad (26)$$

reactivity sequence is $[O_3S—S—Se—S—SO_3]^{2-} \gg [O_3S—S—S—S—SO_3]^{2-} > [O_3S—S—Te—S—SO_3]^{2-}$. Studies on the reaction of telluric acid with liquid hydrogen fluoride have been carried out using ^{19}F n.m.r., and a number of the substitution products $Te(OH)_nF_{6-n}$ (n = 0—3) have been identified. For the reverse reaction, the hydrolysis of tellurium hexafluoride, products with values of n from 0 to 5 have been identified.[214] Related studies have been made[215] of $Te(OMe)_6$ in liquid hydrogen fluoride. A theoretical treatment of the *cis* effect in substituted tellurium hexafluoride complexes predicts[216] that *cis* fluorine atoms should be more labile.

5 Group VII

Fluorine.—The kinetics and mechanism of chlorine–fluorine exchange between compounds containing carbon–chlorine bonds and antimony(v) halides is suggested[217] to involve a mechanism involving the formation of fluorine bridges. The

[209] T. Austad, *Acta Chem. Scand.*, 1975, **A29**, 71.
[210] T. Austad, *Acta Chem. Scand.*, 1974, **A28**, 935.
[211] M. Schmidt and H. P. Kopp, *Angew. Chem. Internat. Edn.*, 1975, **14**, 638.
[212] T. Austad, *Acta Chem. Scand.*, 1975, **A29**, 895.
[213] T. Austad, *Acta Chem. Scand.*, 1974, **A28**, 927.
[214] U. Elgad and H. Selig, *Inorg. Chem.*, 1975, **14**, 140.
[215] I. Agranat, M. Rabinovitz, and H. Selig, *Inorg. Nuclear Chem. Letters*, 1975, **11**, 185.
[216] D. Armstrong, G. W. Fraser, and G. D. Meikle, *Inorg. Chim. Acta*, 1975, **15**, 39.
[217] L. Kolditz and S. Schultz, *J. Fluorine Chem.*, 1975, **5**, 141.

nucleophilic reactivity of the fluoride ion in glacial acetic acid is much reduced by hydrogen-bonding.[218]

Chlorine.—The neutral solvolysis of methyl perchlorate shows [219] the perchlorate ion to be an excellent leaving group. A contact ion-pair mechanism is preferred.

Bromine.—The dismutation reaction of $[Br_2]^-$ in the presence of cationic micelles can occur[220] by two diffusion processes, one a 'two-dimensional' diffusion across the surface of the micelle and the other a normal 'three-dimensional' process. The formation of bromine cyanide from bromine and hydrogen cyanide has a two-term rate law, equation (27). The k_b term, which corresponds to nucleophilic attack by

$$d[BrCN]/dt = (k_a + k_b[H^+]^{-1})[Br_2][HCN] \quad (27)$$

cyanide ion upon bromine, gives a rate very close to that found for iodine, and is close to the encounter limit[221] (7×10^9 l mol^{-1} s^{-1}). Bromine exchange between $R^{82}Br$ and $GaBr_3$ (R = Me, Et, or Pr^i) in 1,2,4-trichlorobenzene or nitrobenzene follows[222] a third-order rate law (28). The reactivity sequence is Me < Et < Pr^i. The

$$\text{Rate} = k[RBr][\text{solvent}:GaBr_3]^2 \quad (28)$$

photodecomposition of the perbromate ion has been reported.[223]

Iodine.—Kinetic data on the reactions of iodine atoms with iodide ions and with nitrite ions have been obtained[224] from flash-photolytic studies, and there has been[225] a picosecond study of the dynamics of the cage effect in the recombination of iodine atoms. Iodine has recently been used as a cyanide-ion scavenger to investigate the loss of cyanide from inert transition-metal complexes, and so it is particularly appropriate that the kinetics of the reaction between cyanide and the tri-iodide ion should have been published[226] [equation (29)]. The first term simply represents a

$$-d[I_3^-]/dt = k[HCN][I_3^-][H^+]^{-1}[I^-]^{-1} + k'[HCN][I_3^-][H^+]^{-1} \quad (29)$$

nucleophilic attack by cyanide ion upon iodine, to form, it is assumed, $[I_2CN]^-$. The bimolecular rate constant is 3×10^9 l mol^{-1} s^{-1}. The second term is interpreted as a nucleophilic displacement of iodide from the tri-iodide ion, and has a rate constant of 4×10^8 l mol^{-1} s^{-1}. The reactions of iodine in concentrated nitric acid are complex. The oxidation to iodine(v) proceeds[227] by a mechanism involving at least two steps:

$$I_2 + 3HNO_3 \rightleftharpoons 2I^+ + 2[NO_3]^- + HNO_2 + H_2O$$

$$I^+ + 6HNO_3 \rightleftharpoons I^{5+} + 4[NO_3]^- + 2HNO_2 + 2H_2O$$

In sufficiently concentrated nitric acid the nitrous acid is converted into dinitrogen

[218] J. H. Clark and J. Emsley, *J.C.S. Dalton*, 1975, 2129.
[219] R. E. Robertson, J. M. W. Scott, and A. Annesa, *Canad. J. Chem.*, 1975, **53**, 3106.
[220] A. J. Frank, M. Gratzel, and J. J. Kozak, *J. Amer. Chem. Soc.*, 1976, **98**, 3317.
[221] M. F. Nolan, J. N. Pendlebury, and R. H. Smith, *Internat. J. Chem. Kinetics*, 1975, **7**, 205.
[222] O. C. Kwon, *Hwahak Kwa Kongop Ui Chinbo*, 1974, **14**, 322 (*Chem. Abs.*, 1975, **83**, 48867).
[223] U. K. Klaening, K. J. Olsen, and E. H. Appelman, *J.C.S. Faraday I*, 1975, **71**, 473.
[224] A. Barkatt and M. Ottolenghi, *Mol. Photochem.*, 1974, **6**, 253.
[225] K. B. Eisenthal, *Ber. Bunsengesellschaft phys. Chem.*, 1974, **11**, 1105.
[226] J. O. Edwards, M. Kaus, and M. C. Sauer, *Inorg. Chem.*, 1976, **15**, 1723.
[227] J. C. Mailen and T. O. Tiffany, *J. Inorg. Nuclear Chem.*, 1975, **37**, 127; J. C. Mailen, *J. Inorg. Nuclear Chem.*, 1975, **37**, 1019.

tetroxide. In a mechanistic study of the nitration of 3-iodoanisole and 2,6-dimethyl-4-odoanisole, evidence for a species $[HNO_2I]^+$ has been found.[228]

6 Group VIII

Xenon.—The decomposition of xenon trioxide in aqueous media shows[229] a maximum at pH 4—4.5 and a minimum at pH 6—6.5. In alkaline solution XeO_3 and $[HXeO_4]^-$ are the active species, the former being some 50 times more reactive than the latter.

[228] A. R. Butler and A. P. Sanderson, *J.C.S. Perkin II*, 1974, 1784.
[229] B. L. Korsunskii, N. N. Aleinikov, E. N. Nazarenko, and F. I. Dubovitskii, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1976, 279 (*Chem. Abs.*, 1976, **84**, 141269).

2

Inert Metal Complexes: Co-ordination Numbers Four and Five

BY J. BURGESS

1 Square-planar Complexes

The reactivity of planar four-co-ordinate metal complexes has been the subject of two recent reviews, one fairly comprehensive[1] and the other very brief.[2] An exhaustive handbook running to 688 pages has been published, in Russian, on the kinetics of ligand substitution reactions in complex compounds of the platinum metals and gold.[3] Reviews dealing with specific areas include one comparing solvent effects in square-planar substitution with those operating in organic nucleophilic substitution,[4] one discussing the mutual effects of ligands (*i.e. cis* and *trans* effects),[5] one describing the effect of the nature of the incoming ligand on determining reactivity,[6] and one outlining the role of chelating ligands.[7] This last review covers multidentate ligands acting as entering groups or as leaving groups and their effects as non-reacting ligands.

Several investigations have demonstrated the possibility or probability of the existence of persistent five- or six-co-ordinate intermediates in the associative pathway for nucleophilic substitution. Examples include the reactions of $[AuCl_4]^-$ with thiocyanate[8] and with *N*-cyclohexylthiobenzamide[9] and of *cis*-$[Pt(NO_2)_2(NH_3)_2]$ with hydrogen bromide.[10] The behaviour of stable five-co-ordinate compounds has been examined with a view to treating them as models for such transient intermediates in associative substitution at four-co-ordinate complexes (see Section 3). A thorough and unusually extensively referenced molecular orbital treatment of

[1] J. S. Coe, 'Reaction Mechanisms in Inorganic Chemistry', ed. M. L. Tobe, M.T.P. International Review of Science, Inorganic Chemistry Series Two, Vol. 9, Butterworths, London, 1974, p. 45.
[2] L. Cattalini, *Pure Appl. Chem.*, 1974, **38**, 363.
[3] B. I. Peshchevitskii, A. V. Belyaev, R. L. Shchekochikhina, and G. D. Mal'chikov, 'Kinetika Reaktsii Zameshcheniya Ligandov v Kompleksnykh Soedineniyakh Platinovykh Metallov i Zolota (Spravochnik), Nauka Sib. Otd., Novosibirsk, U.S.S.R., 1974.
[4] K. M. Ibne-Rasa, J. O. Edwards, and J. L. Rogers, *J. Solution Chem.*, 1975, **4**, 609.
[5] Yu. N. Kukushkin, *Russ. Chem. Rev.*, 1974, **43**, 805.
[6] Yu. S. Varshavskii and M. I. Gel'fman, *Koord. Khim.*, 1975, **1**, 99 (*Chem. Abs.*, 1975, **83**, 52555).
[7] L. Cattalini, Proceedings of the 16th International Conference on Coordination Chemistry, Dublin, 1974, S10 (*Chem. Abs.*, 1976, **85**, 28069).
[8] A. J. Hall and D. P. N. Satchell, *J.C.S. Chem. Comm.*, 1976, 163.
[9] A. J. Hall and D. P. N. Satchell, *J.C.S. Perkin II*, 1975, 1351.
[10] G. S. Muravenskaya and I. I. Antokol'skaya, *Koord. Khim.*, 1975, **1**, 779 (*Chem. Abs.*, 1975, **83**, 125423).

five-co-ordinate species is of relevance in this connection.[11] Insertion is an alternative consequence to substitution from such five-co-ordinate intermediates.[12] An alternative mode of associative substitution is *via* attack at a co-ordinated ligand and subsequent rearrangement.[13] Details of these variants will be found in the platinum(II) section below.

Two groups of authors have suggested that there is a difference between the detailed mechanism of associative nucleophilic substitution at platinum(II) or palladium(II) and that at gold(III). It is claimed that there are indications that bond-breaking and bond-making are asynchronous (*A* mechanism) at Pt^{II} and Pd^{II}, but synchronous (I_a mechanism) at Au^{III}.[4,14] This distinction is hardly consistent with the demonstration of a persistent five-co-ordinate intermediate in the reaction of $[AuCl_4]^-$ with thiocyanate [see above and under gold(III) below], nor indeed with solvent effects on substitution rates at $[Pd(dien)X]^+$ cations [see under palladium(II) below]. However, the Pt^{II} and Pd^{II} *versus* Au^{III} distinction of *A versus* I_a substitution may be true within limits, perhaps for ligands and nucleophiles 'harder' than chloride and thiocyanate.

Platinum(II).—*General.* Activation volumes are often useful guides to the diagnosis of mechanism, frequently permitting distinction between associative and dissociative mechanisms and sometimes permitting more subtle distinctions, as between I_d and *D* or I_a and *A* alternatives. Reactions of a series of complexes $[Pt(dien)X]^+$ (X = Cl, Br, I, or N_3) with a range of incoming nucleophiles Nu (Nu = OH^-, I^-, N_3^-, NO_2^-, SCN^-, or py) follow the usual rate law (1) characteristic of substitution at square-planar species. Activation volumes have been determined, in aqueous solution, both

$$-\mathrm{d[complex]/d}t = (k_1 + k_2[\mathrm{Nu}])[\mathrm{complex}] \qquad (1)$$

for the k_1 and for the k_2[Nu] terms. The values lie between $\Delta V_1^{\ddagger} = -15$ to $-18\ \mathrm{cm^3\ mol^{-1}}$ for the former path, and $\Delta V_2^{\ddagger} = -6$ to $-12\ \mathrm{cm^3\ mol^{-1}}$ for the latter. The $\Delta V_1^{\ddagger}$ values are rather large for an I_a or *A* mechanism. The authors[15] discuss the possibility and consequences of heavy solvation of the leaving groups, which are less encumbered here than in an octahedral complex, on expected $\Delta V_1^{\ddagger}$ values for dissociative and for associative mechanisms. The $\Delta V_2^{\ddagger}$ values are within the range expected for associative activation. The observed dependence of $\Delta V_2^{\ddagger}$ on the nature of the leaving and entering groups is best accommodated by a mechanism approximating to *A* in nature, with bond-making predominant.[15]

Substitution at platinum(II) may be involved when Pt^{II} complexes are used to catalyse substitution at platinum(IV). Some new views on the role of the platinum(II) species in such reactions have been offered. The notion of direct relevance to this chapter is that the primary step is formation of a dinuclear intermediate directly from the simple hydrated platinum(II) complex and the platinum(IV) complex.[16]

Aquation, Solvolysis, and Anation. The kinetics of aquation of $[PtCl_4]^{2-}$ over the range 50—70 °C are consistent with data published earlier for aquation at lower

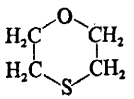
[11] A. R. Rossi and R. Hoffmann, *Inorg. Chem.*, 1975, **14**, 365.
[12] A. Albinati, A. Musco, G. Carturan, and G. Strukul, *Inorg. Chim. Acta*, 1976, **18**, 219.
[13] F. Pesa and M. Orchin, *J. Organometallic Chem.*, 1976, **108**, 135.
[14] L. Cattalini, M. Cusumano, V. Ricevuto, and M. Trozzi, *J.C.S. Dalton*, 1975, 771.
[15] D. A. Palmer and H. Kelm, *Inorg. Chim. Acta*, 1976, **19**, 117.
[16] L. I. Elding and L. Gustafson, *Inorg. Chim. Acta*, 1976, **18**, L35; 1976, **19**, 31.

temperatures. The reaction of $[PtCl_4]^{2-}$ with acetonitrile, producing $[PtCl_3(MeCN)]^-$, is about twenty times faster than the aquation of this complex anion. Rate constants and activation parameters are included in Table 1 (see p. 145).[17] Rate constants for aquation of *cis*- and of *trans*-$[PtCl(NO_2)(NH_3)_2]$ have been measured.[18] Anation of the $[PtCl_3(OH_2)]^-$ anion by thiocyanate is reported to be extremely slow.[19]

The mechanism of base hydrolysis of, as of cyanide attack at, 2,2′-bipyridyl and 1,10-phenanthroline complexes of platinum(II) and iron(II) has been a matter for discussion for some years. The original assumption of direct nucleophilic attack at the metal centre[20] has in recent years been challenged by Gillard,[21] who has presented persuasive evidence for initial attack at the co-ordinated ligand. The evidence for interaction of hydroxide ion with the ligand in $[Pt(bipy)_2]^{2+}$ is strong.[22] Nonethe less the latest kinetic study of the base hydrolysis of $[Pt(bipy)_2]^{2+}$ is interpreted in terms of the hydroxide ion removing a proton from a water molecule solvating the platinum rather than in terms of attack at the co-ordinated bipyridyl.[23] The arguments here are confused by unexpected differences in behaviour between the $[Pt(bipy)_2]^{2+}$ and $[Pt(bipy)(py)_2]^{2+}$ cations.

Aquation of *trans*-$[PtBr(gly)(NH_3)]$ is catalysed by Hg^{2+}_{aq} . The mechanism is of an equilibrium formation of a Pt—Br—Hg intermediate, followed by slow generation of the *trans*-$[Pt(gly)(NH_3)(OH_2)]^+$ product. The enthalpy and entropy of formation of the bromo-bridged dinuclear intermediate, its u.v.–visible spectrum, and its kinetics of decomposition, have been measured.[24]

Ligand Exchange. Chloride exchange in the system $[PtCl_4]^{2-}$–*cis*-$[PtCl_2(NH_3)_2]$–Cl^- occurs both *via* aquation and *via* direct exchange through a doubly bridged transition state.[25] The latter pathway is unusual for chloro-platinum(II) compounds, though direct bromide exchange by such a mechanism has been demonstrated in several systems. Examples include $[PtBr_4]^{2-}$–*cis*-$[PtBr_2(NH_3)_2]$–Br^- and the simpler *cis*-$[PtBr_2(NH_3)_2]$–Br^-.[26] Exchange of thioxan (1) with $[Pt(thioxan)_4]^{2+}$ is instantane-



(1)

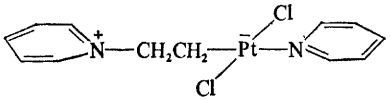
ous on a radioassay time-scale. Such exchange presumably occurs by an easy associative pathway; there is evidence for the existence of the cations $[Pt(thioxan)_n]^{2+}$

[17] A. K. Johnson and J. D. Miller, *Inorg. Chim. Acta*, 1976 **16**, 93.
[18] M. I. Gel'fman, N. M. Karpinskaya, N. A. Kustova, and V. V. Razumovskii, *Koord. Khim.*, 1975, **1**, 158 (*Chem. Abs.*, 1975, **82**, 176000).
[19] R. Mureinik, *Inorg. Chim. Acta*, 1975, **13**, 127.
[20] See, *e.g.*, D. W. Margerum and L. P. Morgenthaler, *J. Amer. Chem. Soc.*, 1962, **84**, 706; J. Burgess, *Inorg. Chim. Acta*, 1971, **5**, 133; *J.C.S. Dalton*, 1972, 1061.
[21] R. D. Gillard, *Inorg. Chim. Acta*, 1974, **11**, L21; *Coordination Chem. Rev.*, 1975, **16**, 67.
[22] R. D. Gillard and J. R. Lyons, *J.C.S. Chem. Comm.*, 1973, 585.
[23] G. Nord, *Acta Chem. Scand.*, 1975, **A29**, 270.
[24] A. B. Venediktov and A. V. Belyaev, *Izvest. sibirsk. Otdel. Akad. Nauk S.S.S.R., Ser. khim. Nauk*, 1975, 67 (*Chem. Abs.*, 1975, **83**, 121395).
[25] K. W. Lee and D. S. Martin, *Inorg. Chim. Acta*, 1976, **17**, 105.
[26] G. F. Vandegrift and D. S. Martin, *Inorg. Chim. Acta*, 1975, **12**, 179.

with $n = 5$ or 6 in solution, and nitrate and picrate salts of $[Pt(thioxan)_6]^{2+}$ have been characterized.[27]

Entering Groups. In this section we report on kinetic and mechanistic studies where the main interest lies in the nature of the entering group; the leaving group is usually chloride. This aspect of platinum(II) kinetic behaviour has been reviewed recently.[6]

Some years ago it was suggested that the first step in the reaction of *trans*-$[PtCl_2(C_2H_4)(py)]$ with pyridine was attack of the incoming pyridine at the co-ordinated ethylene, rather than directly at the platinum.[28] Now further evidence has been presented, from which the existence of the zwitterion (2), at -15 °C, has been demonstrated. Slow release of ethylene from (2) was observed.[13]



(2)

Reactions of the $[PtCl_4]^{2-}$ anion with organic sulphides and sulphoxides are second-order. Rate constants and activation parameters have been determined for 21 such reactions. Sulphides react much more rapidly than sulphoxides. Some illustrative data are included in Table 1.[29] The kinetics of the reaction between $[PtCl_4]^{2-}$

Table 1 *Kinetic parameters for associative nucleophilic attack at the* $[PtCl_4]^{2-}$ *anion*

Nucleophile	10^3k_2/l mol^{-1} s^{-1} (T/°C)	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	*Ref.*
DMSO	2.8 (25)	15.2	−23.1	29
Thioxan (1)	4.4 (25)	11.1	−34.1	29
Et_2S	120 (25)	15.2	−13.5	29
SCN^-	3.5 (25)	11.6	−31	19
	2.1 (25)			30
pn[a]	2.4 (25)	7.6	−45	31
MeCN	18.2 (50)	15.5	−19.4	17
H_2O	0.56[b] (50)	21.8	−14.7[c]	17
	0.042[b] (25)	21	−8[c]	33
	0.037[b] (25)	21.6	−6.4[c]	34, 35

[a] Propane-1,3-diamine. [b] k_{obs}/s^{-1}. [c] Based on second-order rate constants for water attack.

and thiocyanate have been re-examined. The present report states that the k_1 term [equation (1)] is zero,[19] whereas the earlier workers reported a k_1 term corresponding to the normal solvent pathway.[30] The reaction of $[PtCl_4]^{2-}$ with propane-1,3-diamine (pn) follows the usual two-term rate law of equation (1). Propane-1,3-diamine, unlike the rigid 1,10-phenanthroline, is a 'normal' entering group. Both for $[PtCl_4]^{2-}$ + pn and for the subsequent $[PtCl_2(pn)]$ + pn stage, making the first Pt—ligand bond is the rate-determining step, with subsequent ring closure rapid.[31] The mechanisms of

[27] Yu. N. Kukushkin and V. V. Golosov, *Russ. J. Inorg. Chem.*, 1975, **20**, 112.
[28] P. D. Kaplan, P. Schmidt, and M. Orchin, *J. Amer. Chem. Soc.*, 1968, **90**, 4175.
[29] Yu. N. Kukushkin and V. V. Kirillov, *Russ. J. Inorg. Chem.*, 1975, **20**, 1504.
[30] L. Cattalini, A. Orio, and M. Nicolini, *J. Amer. Chem. Soc.*, 1966, **88**, 5734.
[31] R. J. Mureinik, *J.C.S. Dalton*, 1976, 1036.

reactions of $[PtCl_4]^{2-}$ with alkenols have been examined by n.m.r. spectroscopy.[32] Kinetic parameters for substitution at the $[PtCl_4]^{2-}$ anion are collected together in Table 1.[17,19,29–31,33–35]

Second-order rate constants and activation parameters have been reported for the reactions

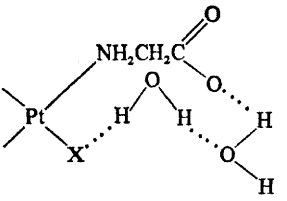
$$[PtClX(bipy)] + en \longrightarrow [Pt(bipy)(en)]^{2+} + Cl^- + X^-$$

for X = Cl, Br, SCN, N_3, or NO_2, in methanol solution. Rate constants vary little with the nature of X. From this fact, and the observation that in the reactions of [PtClX(bipy)] with unidentate amines it is the Cl^- which is displaced, it may be deduced that the mechanism of reaction with ethylenediamine involves rate-determining displacement of Cl^- followed by rapid ring closure and elimination of X^-. There may be significant hydrogen-bonding interaction between the 'free' end of the unidentate ethylenediamine and the potential leaving ligand X^-.[36] The rate of release of chloride from *cis*-$[PtCl_2(NH_3)_2]$ on reaction with oxalate is independent of oxalate concentration. Moreover, the rate constant ($k_{obs} = 5.1 \times 10^{-5}$ s^{-1} at 35 °C) and activation parameters ($\Delta H^{\ddagger} = 18.2$ kcal mol^{-1} and $\Delta S^{\ddagger} = -18.9$ cal K^{-1} mol^{-1})[37] are close to those previously reported[38] for aquation of *cis*-$[PtCl_2(NH_3)_2]$. Thus this reaction with oxalate seems to proceed by initial rate-determining aquation, a conclusion reached several years ago by a different group of investigators[39] (*cf.* Vol. 3, p. 149).

The reaction of $[PtEt_2(bipy)]$ with methyl acrylate to give $[Pt\{CH(Me)(CO_2Me)\}_2(bipy)]$ involves an unusual reaction sequence. The first step is the displacement of the bipy by methyl acrylate. Subsequent β-elimination and insertion are finally followed by return of the bipy to the platinum.[40]

Ring Closure. The kinetics of ring closure in *trans*-$[PtCl_2(NH_2CH_2CO_2H)_2]$ have been examined over a wide pH range, $0.6 < pH < 11.7$. Rate constants and activation parameters are reported for the various paths for closure of the second chelate ring; closure of the first ring is too fast for monitoring by conventional 'slow' techniques. Ring closure in this chloro-complex is about half as fast as in its bromo-analogue.[41] The dependence of rates for amino-acid chelate ring closure in *trans*-$[Pt(aa)_2X_2]^{2-}$ and $[Pt(aa)_2X]^-$ (aa = α-aminoacetate or β-aminopropionate, X = Cl or Br) on water concentration in aqueous alcohol has been rationalized in terms of hydrogen-bonding solvation interactions of the type shown in (3).[42] The complexes [bis-(2-aminoethyl)methylamine hydrochloride]dichloroplatinum(II) and dichloro[tris-(2-aminoethyl)amine bis-hydrochloride]platinum(II) contain potentially ter- and quadri-dentate ligands acting as bidentate ligands. Kinetics of ring closure to give the

[32] J. Hubert and T. Theophanides, *J. Organometallic Chem.*, 1975, **93**, 265.
[33] L. F. Grantham, T. S. Elleman, and D. S. Martin, *J. Amer. Chem. Soc.*, 1955, **77**, 2965.
[34] L. I. Elding, *Acta Chem. Scand.*, 1966, **20**, 2559.
[35] L. Drougge, L. I. Elding, and L. Gustafson, *Acta Chem. Scand.*, 1967, **21**, 1647.
[36] M. J. Hynes and S. P. Russell, *Proc. Roy. Irish Acad.*, 1975, **75B**, 339.
[37] B. K. Maji and S. K. Siddhanta, *J. Indian Chem. Soc.*, 1975, **52**, 82 (*Chem. Abs.*, 1975, **83**, 85535).
[38] J. N. Reishus and D. S. Martin, *J. Amer. Chem. Soc.*, 1961, **83**, 2457.
[39] J. E. Teggins, K. W. Lee, J. M. Baker, and E. D. Smith, *J. Coordination Chem.*, 1972, **1**, 215.
[40] N. Chaudhury and R. J. Puddephat, *J.C.S. Dalton*, 1976, 915.
[41] G. D. Mal'chikov and T. R. Lastushkina, *Russ. J. Inorg. Chem.*, 1974, **19**, 1033.
[42] L. M. Volshtein, L. F. Krylova, and L. D. Dikanskaya, *Russ. J. Inorg. Chem.*, 1975, **20**, 1526.

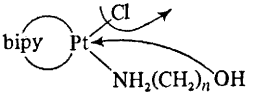


(3)

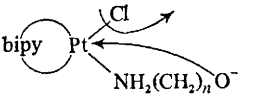
respective terdentate ligand complexes have been studied in acidic and in alkaline media. The mechanism of ring closure is presumably internal associative.[43] The observed rate constant, k_{obs}, for ring closure in the ethanolamine and propanolamine complexes $[PtCl(bipy)\{NH_2(CH_2)_nOH\}]^+$, where $n = 2$ or 3 respectively, in methanol solution is the usual combination of two terms:

$$k_{obs} = k_1 + k_2[OMe^-]$$

The k_1 term corresponds to direct ring closure in the alkanolamine complex (4), the k_2 term to ring closure in the conjugate base (5) of the complex. The differences



(4)



(5)

between rate constants for the two complexes arise from differences in $\Delta S^{\ddagger}$, as expected; $\Delta H^{\ddagger}$ values for the two complexes are the same within experimental uncertainty.[44] Ring-closure kinetics in *cis*- and *trans*-$[PtCl_2L(NH_2CH_2CH_2OH)]$ are dealt with below in relation to the *cis* and *trans* effects of dimethyl sulphoxide.[45]

Ring-opening. At a given pH, the rate law for the opening of the ethanolamine chelate ring in *cis*- and *trans*-$[Pt(LL)_2]$ and in *trans*-$[PtCl(LL)(NH_3)]$, where LL = (singly) deprotonated ethanolamine, in the presence of chloride is

$$-d[chelate]/dt = (k_1 + k_2[Cl^-])[chelate]$$

This rate law, of the form normal for nucleophilic substitution at platinum(II) [*cf.* equation (1) above], implies parallel spontaneous and chloride-promoted reaction pathways. The observed dependence of rates on pH was rationalized in terms of ligand protonation equilibria.[46] Chelate ring-opening is an important feature in the displacement of bidentate ligands, discussed in the following section.

Displacement of Bidentate Groups. A kinetic study of the reaction of the $[Pt(ox)_2]^{2-}$ anion with thiocyanate indicated the intermediacy of complexes containing unidentate oxalate ligands.[47] Now the isolation of a salt of the $[Pt(ox)_2(SCN)_2]^{4-}$ anion

[43] G. Natile, G. Albertin, E. Bordignon, and A. A. Orio, *J.C.S. Dalton*, 1976, 626.
[44] E. Rotondo, R. Pietropaolo, V. Marsala, and F. Faraone, *J. Inorg. Nuclear Chem.*, 1975, **37**, 1465.
[45] Yu. N. Kukushkin, V. F. Lobantsova, and V. B. Ukraintsev, *Russ. J. Inorg. Chem.*, 1975, **20**, 1875.
[46] Yu. N. Kukushkin, V. B. Ukraintsev, and A. I. Mokhov, *Russ. J. Inorg. Chem.*, 1974, **19**, 1028.
[47] A. Giacomelli and A. Indelli, *Inorg. Chem.*, 1972, **11**, 1033.

has been reported. An *X*-ray structure determination proves the presence of unidentate oxalate ligands.[48] This is claimed to be the first unequivocal demonstration of oxalate acting as a unidentate ligand, and so provides useful support for the numerous hypotheses of kinetic intermediates containing unidentate oxalate. The reaction of $[Pt(NO_2)_2(ox)]^{2-}$ with thiocyanate proceeds in at least three stages *en route* to the final product, $[Pt(SCN)_4]^{2-}$. Intermediates *cis*-$[Pt(NO_2)_2(ox)(SCN)]^{3-}$ and *trans*-$[Pt(NO_2)(ox)(SCN)_2]^{3-}$, which both presumably contain unidentate oxalate, were isolated. Rate constants and activation parameters are in the region expected for a ring-opening mechanism.[49]

Displacement of Alkenes. Two recent publications on the displacement of alkenes from platinum(II) provide illustrations of the importance of steric factors of general relevance to substitution at this centre. In the photochemical generation of dimers $Pt_2Cl_4L_2$ from $[PtCl_2(alkene)L]$ (L = amine) relative rates of alkene loss are determined by the bulk of the leaving alkene.[50] In the replacement of the butene in [PtCl(L-prolinato)(*S,S-trans*-but-3-ene)] by other alkenes, an important factor determining rates is steric interaction between the co-ordinated ligands and the incoming alkene.[51]

As a by-product of thermochemical studies, rate constants have been estimated for *trans*-$[PtCl_2(alkene)(py)]$, where the alkene is, for example, ethylene or cyclohexene, reacting with triphenyl phosphite. Rate constants were also estimated for the subsequent reaction of $[PtCl_2\{P(OPh)_3\}(py)]$ with a further molecule of triphenyl phosphite.[52]

Effects of Non-leaving Ligands. The kinetics of ring closure in *cis-* and in *trans*-$[PtCl_2L(NH_2CH_2CH_2OH)]$ have been used to assess the relative non-leaving ligand effects of ligands L. In particular dimethyl sulphoxide shows a large *trans* effect and a marked *cis* effect.[45] The *cis* and *trans* effects of diethyl sulphide and of iodide have been compared by establishing the kinetics of reaction of *cis-* and of *trans*-$[PtI_2(SEt_2)_2]$ with ammonia in ethanol solution. The overall impression is of diethyl sulphide exerting a large *trans* effect, iodide a moderate *trans* effect.[53] Presumably there will also be a significant *cis* effect of the diethyl sulphide (*cf.* DMSO above). Rates of aquation of the *cis-* and *trans*-isomers of $[PtCl(NO_2)(NH_3)_2]$ have been measured as part of a programme of study of the *trans* effect of the nitro-group.[18]

Qualitative deductions of *trans* effects of various ligands have been made from observations on reactions of the complexes *trans*-$[PtClL(NH_3)_2]^+$ with a range of nucleophiles,[54] and of the complexes *cis*-$[PtMe_2L_2]$ with phosphines.[55] Further information on the *trans* effect of ligands L comes from preparative observations on

[48] A. C. Villa, A. G. Manfredotti, A. Giacomelli, C. Guastini, and A. Indelli, *Inorg. Chem.*, 1975, **14**, 1654.
[49] A. Giacomelli, *Inorg. Chem.*, 1975, **14**, 1409.
[50] P. Courtot, A. Peron, R. Rumin, J. C. Chottard, and D. Mansuy, *J. Organometallic Chem.*, 1975, **99**, C59.
[51] Y. Terai, H. Kido, J. Fujita, and K. Saito, *Bull. Chem. Soc. Japan*, 1975, **48**, 1233.
[52] W. Partenheimer, *J. Amer. Chem. Soc.*, 1976, **98**, 2779.
[53] V. V. Valyaeva, *Russ. J. Inorg. Chem.*, 1975, **20**, 1507.
[54] M. I. Gel'fman, O. P. Kor'yakov, N. A. Kustova, and V. V. Razumovskii, *Russ. J. Inorg. Chem.*, 1974, **19**, 1816.
[55] A. Johnson and R. J. Puddephat, *J.C.S. Dalton*, 1975, 115.

reactions of the $[PtCl_4]^{2-}$ anion.[56] This last reference is primarily concerned with the *trans* effects of aromatic amines.

Effects of non-leaving ligands,[5] and of chelating ligands in particular,[7] on reactivities have been reviewed. The *cis* and *trans* influences, *i.e.* initial-state effects as far as kinetic phenomena are concerned, of some groups in platinum(II) complexes have been assessed by CNDO–MO calculations. The *cis* influences were found to be comparable in magnitude to *trans* influences, but the ligand orders in the two series of influences were not identical.[57]

Isomerization, Symmetrization, and Inversion. During the past year and a half reports of kinetics and mechanisms of isomerizations of platinum(II) complexes have invoked transition states in which the platinum has a co-ordination number of three, four, five, or even six.

The isomerization of *trans*-$[PtCl_2(C_2H_4)(\text{isoquinoline})]$ to its *cis*-isomer is facilitated by u.v. irradiation. The mechanism suggested involves the intermediacy of a bridged dimer $[PtCl_2(\text{isoquinoline})]_2$. The process is thus initially dissociative, but involves a four-co-ordinate intermediate.[58] Thermal isomerization of *cis*-$[PtI_2(py)_2]$ or of *cis*-$[PtI_2(NH_2Me)_2]$ to their respective *trans*-isomers in the solid state is said to go through a tetrahedral four-co-ordinate intermediate.[59] Ease of thermal isomerization of $[PtX_2(PR_3)_2]$ complexes is linked to the platinum–phosphorus bond strengths of the compounds involved.[60]

The dependence of isomerization and halide replacement and substitution rates, in methanol, on the shape and size of R in *cis*-$[PtRX(PEt_3)_2]$ (R = Me, Et, Ph, *o*-C_6H_4Y, or *p*-C_6H_4Y) strongly suggests that the isomerization is dissociative in character, perhaps with a transient three-co-ordinate intermediate.[61,62]

Isomerization of *cis*-$[PtMe(NO_3)(PMe_2Ph)_2]$ is a slow reaction which follows the symmetrization reaction

$$\textit{cis}\text{-}[PtMe_2(PMe_2Ph)_2] + \textit{cis}\text{-}[Pt(NO_3)_2(PMe_2Ph)_2] \longrightarrow 2\ \textit{cis}\text{-}[PtMe(NO_3)(PMe_2Ph)_2]$$

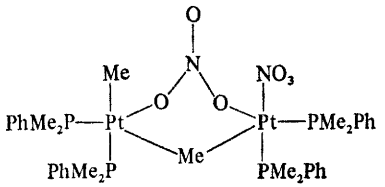
The symmetrization produces solely the *cis*-isomer, at least in dichloromethane solution. The most attractive mechanism for such stereospecific symmetrization involves a cyclic dinuclear transition state (6), in which both platinum atoms are five-co-ordinate.[63] A similar mechanism [S_E2(cyclic)] with an analogous transition state has been suggested for closely related ligand-transfer reactions of the type[64]

$$\textit{cis}\text{-}[PtMe_2(PMe_2Ph)_2] + \textit{cis}\text{-}[PdCl_2(PMe_2Ph)_2] \longrightarrow \textit{trans}\text{-}[PtClMe(PMe_2Ph)_2] + \textit{trans}\text{-}[PdClMe(PMe_2Ph)_2]$$

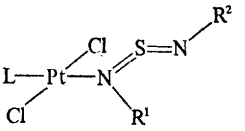
It is almost impossible to tell whether the dinuclear species such as (6) are true transition states or transient intermediates.

[56] T. O. Blyumental', L. V. Konovalov, and V. V. Razumovskii, *J. Gen. Chem. U.S.S.R.*, 1975, **45**, 1489.
[57] D. R. Armstrong, R. Fortune, P. G. Perkins, R. J. Dickinson, and R. V. Parish, *Inorg. Chim. Acta*, 1976, **17**, 73.
[58] F. Pesa and M. Orchin, *Inorg. Chem.*, 1975, **14**, 994.
[59] Yu. N. Kukushkin, L. Konovalov, and V. G. Pogareva, *Koord. Khim.*, 1975, **1**, 1635 (*Chem. Abs.*, 1976, **84**, 115287).
[60] E. A. Allen, J. del Gaudio, and W. Wilkinson, *Thermochim. Acta*, 1975, **11**, 197.
[61] R. Romeo, D. Minniti, and M. Trozzi, *Inorg. Chim. Acta*, 1975, **14**, L15; 1976, **15**, 1134.
[62] R. Romeo, D. Minniti, and S. Lanza, *Inorg. Chim. Acta*, 1976, **18**, L15.
[63] P. J. Thompson and R J. Puddephat, *J.C.S. Chem. Comm.*, 1975, 841.
[64] R. J. Puddephat and P. J. Thompson, *J.C.S. Dalton*, 1975, 1810.

The isomerization *cis*-→*trans*-$[PtX_2(TeEt_2)_2]$ is fast in solution.[65] N.m.r. coalescence temperatures have been determined, and thence Gibbs free energies of activation ($\Delta G^{\ddagger}$) estimated, for inversion at the pyramidal sulphur, selenium, or tellurium atom (M) in complexes $[PtX_2(MEt_2)_2]$. The barrier to inversion decreases in the order Te > Se > S. Experiments were conducted in deuteriochloroform, chlorobenzene, or *sym*-tetrachloroethane; no dependence of barrier on solvent nature was observed.[66] The *trans*-$[PtCl_2$(diarylsulphurdi-imine)L] complexes (7) or (8) undergo



(6)



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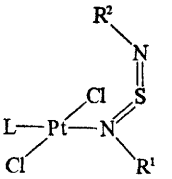


(8)

two intramolecular processes. In the low-temperature process the geometry of the diarylsulphurdi-imine ligand changes, (7)⇌(8). In the high-temperature process the platinum shifts from one ligand nitrogen to the other. The mechanism of this latter intramolecular rearrangement involves a five-co-ordinate platinum intermediate.[67]

Photochemistry. Two photochemical reactions have already been mentioned in other contexts, the isomerization of *trans*-$[PtCl_2(C_2H_4)$(isoquinoline)][59] and the generation of dinuclear compounds by alkene loss (L = amine):[50]

$$2[PtCl_2(\text{alkene})L] \xrightarrow{h\nu} Pt_2Cl_4L_2 + 2 \text{ alkene}$$

The effect of the leaving ligand on photosubstitution of $[PtX(dien)]^+$ and $[Pt(dien)L]^{2+}$ has been described for X = Br (earlier work) or I and L = py. The photochemical reactions were conducted in the presence of varying concentrations of hydroxide and of bromide. Photosubstitution of $[PtI(dien)]^+$, giving $[Pt(OH)(dien)]^+$ or $[PtBr(dien)]^+$ depending on conditions, proceeds *via* dissociative formation of an ion pair $[Pt(dien)(OH_2)]^{2+},I^-$. In photosubstitution of $[Pt(dien)(py)]^{2+}$, $[Pt(dien)(OH_2)]^{2+}$ is either the product or the primary intermediate *en route* to $[Pt(OH)(dien)]^+$ or $[PtBr(dien)]^+$.[68]

Reactions of Co-ordinated Ligands. The possibility that pyridine attacks *trans*-$[PtCl_2(C_2H_4)(py)]$ at the co-ordinated ethylene rather than directly at the platinum[13] has been mentioned above. Conversely, insertion of carbon disulphide into one of the platinum–hydrogen bonds of *trans*-$[PtH_2\{P(C_6H_{11})_3\}_2]$ is thought to proceed *via* formation of a five-co-ordinate intermediate and subsequent insertion to give *trans*-$[PtH(S_2CH)\{P(C_6H_{11})_3\}_2]$. The evidence suggesting the five-co-ordinate intermediate includes the rate law, which is first-order in complex and in carbon disulphide, and the fact that the reaction only occurs in non-co-ordinating solvents such as heptane, benzene, or diethyl ether.[12]

[65] R. J. Cross, T. H. Green, and R. Keat, *J.C.S. Dalton*, 1976, 382.
[66] R. J. Cross, T. H. Green, and R. Keat, *J.C.S. Dalton*, 1976, 1150.
[67] J. Kuyper and K. Vrieze, *J. Organometallic Chem.*, 1975, **86**, 127.
[68] C. Bartocci, F. Scandola, and V. Carassiti, *J. Phys. Chem.*, 1974, **78**, 2349.

Palladium(II).—*Aquation and Anation.* Discussion and controversy continue over the interpretation of the kinetics of the anation and aquation reactions which constitute the equilibria (2). Bekker and Robb[69] report rate constants and activation para-

$$\textit{cis}\text{- or }\textit{trans}\text{-}[PdCl_2(OH_2)_2] + Cl^- \rightleftharpoons [PdCl_3(OH_2)]^- + H_2O \qquad (2)$$

meters for all the reactions involved, and discuss at length the relation between these reactions and similar ones for platinum complexes. Subsequently Elding[70] has claimed that there are flaws in earlier discussions of this palladium system. He maintains that Bekker and Robb[69] misattributed intercepts to reverse reactions which had in fact been suppressed under their experimental conditions. Elding also states that Pearson and Hynes[71] made an invalid assumption when they took the establishment of the equilibrium

$$[PdCl_3(OH_2)]^- + Cl^- \rightleftharpoons [PdCl_4]^{2-} + H_2O$$

to be rapid compared with reaction rates in the equilibrium of equation (2) above. This is not so for the *cis*-$[PdCl_2(OH_2)_2]$ system. Elding reinterprets the earlier results in terms of a flow chart claimed to apply generally to anation at palladium(II) and platinum(II).[70] Some kinetic results on anation of $[Pd(OH_2)_4]^{2+}$ by chloride and bromide[72] have recently been brought to this Reporter's attention.

Aquation of $[PdX(LLL)]^+$ cations, where LLL = Et_4dien or its *N'*-methyl derivative and X = Cl, Br, or I, is catalysed by Hg^{2+}_{aq} or Cd^{2+}_{aq}.[73,74] The kinetic pattern observed corresponds to reversible generation of a dinuclear intermediate whose solvolysis is rate determining:

$$[PdX(LLL)]^+ + M^{2+} \overset{\text{fast}}{\rightleftharpoons} [Pd(LLL)XM]^{3+} \overset{\text{slow}}{\longrightarrow} [Pd(LLL)(OH_2)]^{2+} + MX^+$$

This appears to be the first kinetic study of catalysis by a 'soft' cation of aquation of a chloro-complex of a square-planar metal centre; many analogous examples are of course known for octahedral complexes. Interestingly, whereas Hg^{2+} is very effective both in octahedral and in square-planar systems, Cd^{2+} is a very feeble catalyst in octahedral systems (*cf.*, for example, aquation of the $[ReCl_6]^{2-}$ anion[75]). Another type of aquation catalysis well established for octahedral complexes is that of acid catalysis of aquation of nitro- and azido-complexes. Kinetics of comparable reactions have now been described for acid-catalysed aquation of $[PdX(LLL)]^+$ cations, where LLL = dien, Et_4dien, or the *N'*-methyl derivative of the latter, and X = N_3 or NO_2, in methanol. These reactions were conducted in the presence of chloride, and the complete rate law established as

$$-\text{d[complex]}/dt = (k_1 + k_2[Cl^-] + k_1'[H^+] + k_2'[H^+][Cl^-])[\text{complex}]$$

There are thus four significant pathways, both the unprotonated and protonated

[69] P. van Z. Bekker and W. Robb, *J. Inorg. Nuclear Chem.*, 1975, **37**, 829.
[70] L. I. Elding, *Inorg. Chim. Acta*, 1975, **15**, L9.
[71] R. G. Pearson and M. J. Hynes, *Kungl. Tekn. Högsk. Handl.*, 1972, **285**, 829.
[72] R. G. Pearson and M. J. Hynes, in 'Coordination Chemistry in Solution', ed. E. Högfeldt, Swedish Natural Science Research Council, Lund, 1972, p. 461.
[73] M. Cusumano, G. Guglielmo, V. Ricevuto, R. Romeo, and M. Trozzi, *Atti Soc. Peloritana Sci. fis. mat. nat.*, 1974, **54**, 109 (*Chem. Abs.*, 1976, **85**, 25789).
[74] M. Cusumano, G. Guglielmo, V. Ricevuto, R. Romeo, and M. Trozzi, *Inorg. Chim. Acta*, 1976, **17**, 45.
[75] J. Burgess and S. J. Cartwright, *J.C.S. Dalton*, 1976, 1561.

forms of the complexes reacting by parallel solvolytic and chloride-attack routes.[76,77]

Substitution. Rates of substitution in $[PdX(dien)]^+$ cations (X = Cl, Br, I, N_3, or NO_2) have been measured in DMSO and in DMF. Nucleophilic discrimination is much less marked in these dipolar aprotic solvents than in such solvents as water or methanol.[78] A detailed kinetic study of substitution at $[PdX(dien)]^+$ cations in methanol at 25 °C has been published. Leaving groups (X^-) included Cl^-, Br^-, I^-, N_3^-, and NO_2^-; entering groups included Cl^-, Br^-, I^-, N_3^-, SCN^-, and thiourea. The pattern here is similar to that established for platinum(II). Second-order rate constants for associative attack are generally around a thousand times larger for palladium(II) than for platinum(II) analogues, but the ordering of rate constants for the various entering and leaving groups is very similar for these two centres. The authors believe that bond breaking and formation are to a large extent asynchronous, in other words that the mechanism approximates to *A* rather than I_a (*cf.* Introduction to this chapter).[14] The detailed timing of bond-breaking and -making has been probed by kinetic studies of substitution at the cations $[PdX(LLL)]^+$ (LLL = dien or Et_4dien, X = Cl or I) in mixed solvents.[79] This work is also discussed in Chapter 5 of this Part; suffice it here to summarize the authors' conclusions that bond cleavage and leaving-group solvation are important in transition-state formation.[79] Thus here the mechanism suggested is I_a rather than *A* [S_N2(lim)].

In some of the reactions detailed in the previous paragraph, associative attack by the incoming nucleophile [k_2 term of equation (1)] dominates over the solvolytic or dissociative path (k_1 term). However, when the non-reacting ligand(s) is (are) exceptionally bulky, the k_2 term may become negligible as a result of the difficulty the entering nucleophile experiences in trying to approach the central metal atom closely enough to interact with it in the transition state. Such behaviour is termed 'pseudo-octahedral' and has been extensively described and documented.[80] Ligands such as Et_4dien often lead to pseudo-octahedral behaviour. A significant k_2 term had only been reported for very good nucleophiles such as thiosulphate* reacting with $[PdX(Et_4dien)]^+$ cations in aqueous solution. The k_2 pathway can become more significant in mixed aqueous media (see above), and now Palmer and Kelm have shown that a k_2 term can be detected even in aqueous solution for reaction with several nucleophiles if much higher concentrations of nucleophile than usual are employed. They report significant k_2 terms for N_3^- and SCN^- as entering groups, small k_2 terms for Br^- and I^-. The order of k_2 terms here, which is (for Cl^- leaving) $S_2O_3^{2-} > SCN^- > N_3^- > Br^- \sim I^-$, is a somewhat different order from that for a 'typical' substrate such as *trans*-$[PtCl_2(py)_2]$. The differences can be ascribed to steric factors modifying the normal nucleophilicity order.[81]

* There is also a significant k_2 term for the reaction with hydroxide, but here of course this is assigned to a conjugate-base pathway.

[76] M. Cusumano, G. Guglielmo, V. Ricevuto, R. Romeo, and M. Trozzi, *Atti Soc. Peloritana Sci. fis. mat. nat.*, 1974, **54**, 89 (*Chem. Abs.*, 1976, **85**, 25788).

[77] M. Cusumano, G. Guglielmo, V. Ricevuto, R. Romeo, and M. Trozzi, *Inorg. Chim. Acta*, 1976, **16**, 135.

[78] M. Cusumano, V. Ricevuto, R. Romeo, and M. Trozzi, *Atti Soc. Peloritana Sci. fis. mat. nat.*, 1974, **54**, 175 (*Chem. Abs.*, 1976, **84**, 185446).

[79] L. A. P. Kane-Maguire and G. Thomas, *J.C.S. Dalton*, 1975, 1890.

[80] See, *e.g.* Vol. 1, pp. 147–8.

[81] D. A. Palmer and H. Kelm, *Inorg. Chim. Acta*, 1975, **14**, L27.

Rate constants and activation parameters (Table 2) have been reported for reactions of $[PdCl_4]^{2-}$ and $[PdBr_4]^{2-}$ with thiourea and selenourea. Two steps were monitored,

$$[PdX_4]^{2-} + L \longrightarrow [PdX_3L]^- + X^-$$

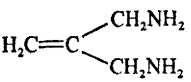
and

$$[PdX_2L_2] + L \longrightarrow [PdXL_3]^+ + X^-$$

Reactions of $[PdX_3L]^-$ and of $[PdXL_3]^+$ were too fast even for stopped-flow monitoring, owing to the very high *trans* effects of thiourea and selenourea.[82] The reactions of $[PdCl_4]^{2-}$ with 1,3-diamino-2-methylenepropane [diampr (9)] and its *NN'*-dimethyl derivative have also been studied[83] (Table 2).

Table 2 *Kinetic parameters for associative nucleophilic attack at* $[PdX_4]^{2-}$ *halogeno-anions*

Nucleophile	k_2/l mol^{-1} s^{-1} (25 °C)	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	*Ref.*
$[PdCl_4]^{2-}$				
Ammonia	33			87
Thiourea	9.1×10^3	6.0	−19.5	82
Selenourea	45×10^3	4.4	−26.0	82
diampr (9)	4.9×10^{-3}	20	+14	83
NN'-Me$_2$diampr	0.55×10^{-3}	23	+20	83
enH$^+$	296			86
Me$_2$enH$^+$	153			86
Me$_4$enH$^+$	14			86
$[PdBr_4]^{2-}$				
Thiourea	20×10^3	7.3	−19.0	82
Selenourea	90×10^3	10.7	−0.5	82



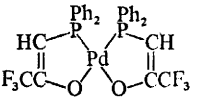
(9)

Other substitution reactions for which kinetic data have been reported include those of *cis*-$[PdCl_2(NH_3)_2]$ with ammonia,[84] of $[PdX_2\{P(OMe)_3\}_2]$ with thiourea,[85] and of $[PdCl_4]^{2-}$ and $[PdCl_2(en)_2]$ with protonated diamines.[86] From the last investigation it emerged that the discriminating power of palladium(II) is markedly less than that of platinum(II). Kinetic parameters for k_2 (associative) substitution paths at $[PdCl_4]^{2-}$ and at $[PdBr_4]^{2-}$ are collected in Table 2[82, 83, 86, 87] (*cf.* Table 1 for substitution at $[PtCl_4]^{2-}$).

Ligand exchange and ring closure are two special cases of substitution. ^{1}H N.m.r.

[82] P. van Z. Bekker and W. Robb, *Internat. J. Chem. Kinetics*, 1975, **7**, 87.
[83] H. Hennig, K. Schulze, M. Mühlstädt, E. Hoyer, R. Kirmse, and L. S. Emeljanowa, *Z. anorg. Chem.*, 1975, **413**, 10.
[84] R. G. Hibler, *Chem. Abs.*, 1975, **83**, 85574.
[85] A. D. Troitskaya, I. A. Orlova, and G. P. Sadakova, *Zhur. obshchei Khim.*, 1976, **46**, 444 (*Chem. Abs.*, 1976, **84**, 129854).
[86] R. Ernst and R. Roulet, *Chimia* (*Switz.*), 1974, **28**, 347.
[87] R. A. Reinhardt and W. W. Monk, *Inorg. Chem.*, 1970, **9**, 2026.

spectra of solutions containing *trans*-$[PdX_2(SEt_2)_2]$ and diethyl sulphide taken over a wide temperature range show two coalescence temperatures. The low-temperature coalescence is ascribed to inversion at the sulphur (see below), the high-temperature coalescence to ligand exchange by an associative mechanism. These assignments are supported by the concentration independence of the former and contrasting concentration dependence of the latter.[88] Unequivocal mechanistic assignments from n.m.r. spectroscopy are more difficult for palladium(II) than for platinum(II), since there is no equivalent in palladium systems to the persistence or otherwise of coupling to ^{195}Pt. Acidification of solutions of $[PdCl_2(histamine)_2]$ produces $[PdCl_2(histamine)]$; spectrophotometric evidence has been presented for the intermediacy of $[PdCl(histamine)(histamineH)]^{2+}$ in this reaction.[89] The mechanism of formation of the bis-chelate (10) from (11) in aqueous media under mild conditions has been discussed.[90]



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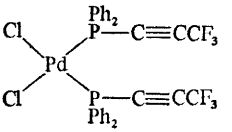
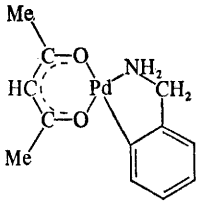


(11)

Reaction of $[Pd(acac)_2]$ with benzylamine produces (12), in which the benzylamine acts as a bidentate ligand, *via* (13) in which one acac is bonded to the metal through carbon.[91] Further information has been published about the conversion of palladium-β-diketonate complexes into *C*-bonded isomers by the action of pyridine.[92]

A co-ordinated ligand reaction whose kinetics and mechanism have been investigated is that of the generation of the carbene complex *cis*-$[PdCl_2\{C(NH\text{-}p\text{-}C_6H_4Cl)NMePh\}(PPh_3)]$ from the reaction of the isocyanide complex *cis*-$[PdCl_2(p\text{-}CNC_6H_4Cl)(PPh_3)]$ with *N*-methylaniline. Solvent, ligand, and temperature effects have been examined. Ligand variation, of other phosphines or phosphites in place of the PPh_3, has steric and electronic effects. Solvent variation affects rates through solvent–incoming amine hydrogen-bonding.[93]



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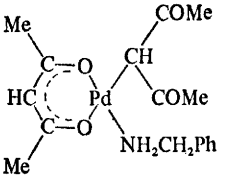


(13)

[88] R. J. Cross, T. H. Green, R. Keat, and J. F. Paterson, *Inorg. Nuclear Chem. Letters*, 1975, **11**, 145.

[89] M. Cain and S. Valladas-Dubois, *Compt. rend.*, 1975, **280**, *C*, 9.

[90] A. J. Carty, S. E. Jacobson, R. T. Simpson, and N. J. Taylor, *J. Amer. Chem. Soc.*, 1975, **97**, 7254.

[91] S. Baba and S. Kawaguchi, *Inorg. Nuclear Chem. Letters*, 1975, **11**, 415.

[92] M. Horike, Y. Kai, N. Yasuoka, and N. Kasai, *J. Organometallic Chem.*, 1975, **86**, 269.

[93] L. Calligaro, P. Uguagliati, B. Crociani, and U. Belluco, *J. Organometallic Chem.*, 1975, **92**, 399; P. Uguagliati, B. Crociani, U. Belluco, and L. Calligaro, *ibid.*, 1976, **112**, 111.

Isomerization and Inversion. The kinetics of catalysed and uncatalysed *cis* ⇌ *trans* isomerization of $[Pd(N_3)_2(PMe_2Ph)_2]$ and of $[Pd(N_3)_2(PMePh_2)_2]$ have been investigated by variable-temperature ^1H n.m.r. spectroscopy. Five-co-ordinate intermediates are indicated in the catalysed processes. Such intermediates are eminently plausible, since five- and six-co-ordinate adducts of these complexes with certain amines and phosphines are known.[94] A predominantly thermodynamic study of *cis*-⇌*trans*-$[PdX_2\{PMe_n(p\text{-}C_6H_4Y)_{3-n}\}_2]$ in nitrobenzene, 1,2-dichlorobenzene, deuteriochloroform, and 1,1,2,2-tetrachloroethane yielded the mechanistic information that these isomerizations are entropy-controlled and probably solvent-assisted.[95]

cis-$[PdCl_2(TeEt_2)_2]$ can be isolated in the solid state, but rapidly isomerizes in solution, for example in benzene.[65] The product, and analogous compounds containing $SeEt_2$ or SEt_2, or other halide ligands, invert at low temperatures. The barrier to inversion is slightly lower (*ca.* 30—40 kJ mol^{-1}) for palladium than for analogous platinum complexes.[66,88] The mechanism of rearrangement of carboxylatopalladium(II) dimers of the type $[Pd(O_2CR)_2(PR_3)]_2$ and $[Pd(O_2CR^1)(O_2CR^2)(PR_3)]_2$ involves solvent assistance of ring-opening of the $Pd(OCO)_2Pd$ bridge.[96]

Gold(III).—There has for some time been discussion as to whether the k_2[Nu] term in the two-term rate law characteristic of substitution at square-planar complexes,

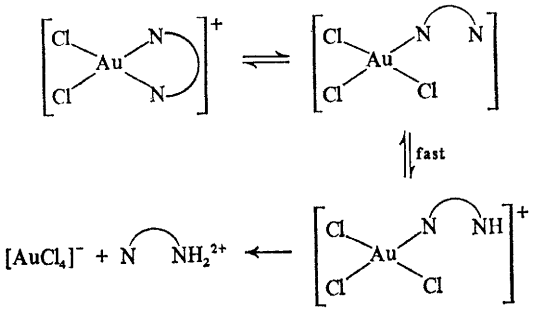
$$-\mathrm{d[complex]}/\mathrm{d}t = (k_1 + k_2[\mathrm{Nu}])[\mathrm{complex}]$$

can be assigned to an I_a or A pathway. Recently the view was expressed that this term corresponded to an A mechanism for most d^8 complexes, but to an I_a mechanism for gold(III) complexes.[4] Both before and since this, however, evidence has been presented for the intermediacy of five- and even six-co-ordinate species in substitution at gold(III). The involvement of a six-co-ordinate intermediate in the reaction of $[AuX_2(bipy)]^+$ with X^- (X = Cl or Br)[97] was mentioned in Volume 4. Subsequently a six-co-ordinate anion $[AuCl_5L]^{2-}$ has been proposed as one of the intermediates generated in the complicated reaction sequence of the $[AuCl_4]^-$ anion with *N*-cyclohexylthiobenzamide (L).[9] The most direct and convincing demonstration for an intermediate of increased co-ordination number relates to the reaction of $[AuCl_4]^-$ with thiocyanate. Here both the build-up and the decay of the intermediate can be monitored.[8] It is assumed that this intermediate contains five-co-ordinate gold(III); more information may be vouchsafed in the full paper which should follow this preliminary communication.

The displacement of bipy from the $[AuCl_2(bipy)]^+$ cation by chloride is third-order in chloride,[97] but the displacement of 5-NO_2phen from the analogous cation $[AuCl_2(5\text{-}NO_2phen)]^+$ is only second-order in chloride.[98] This difference is attributed to competition between entering chloride and chelate-ring reclosure for the complex containing the flexible bipy, but the absence of such an effect when the bidentate leaving group is rigid, *e.g.* (substituted) phen. Rate laws and rate constants have also been established for the analogous reactions of the cations $[AuCl_2(LL)]^+$ (LL = *NNN'N'*-tetramethylethylenediamine or its tetraethyl analogue) with chloride,

[94] D. A. Redfield, L. W. Cary, and J. H. Nelson, *Inorg. Chem.*, 1975, **14**, 50.
[95] A. W. Verstuyft and J. H. Nelson, *Inorg. Chem.*, 1975, **14**, 1501.
[96] T. R. Jack and J. Powell, *Canad. J. Chem.*, 1975, **53**, 2558.
[97] G. Annabile, L. Cattalini, A. A. El-Awady, and G. Natile, *J.C.S. Dalton*, 1974, 802.
[98] G. Annibale, G. Natile, and L. Cattalini, *J.C.S. Dalton*, 1976, 285.

again to give $[AuCl_4]^-$ as product.[99] These bidentate ligands are removed in two kinetically distinguishable steps (Scheme). The rate of breaking the first Au—N



Scheme

bond is similar to that for displacement of a unidentate nitrogen ligand from similar gold(III) complexes. Both steps involve associative attack by the entering chloride at the gold atom.

The kinetics of aquation of the $[Au(NH_3)_4]^{3+}$ cation, and the kinetics of its formation, have been studied in aqueous solution.[100]

Several redox reactions involving gold(III) complexes proceed by an initial substitution step, followed by the electron-transfer step(s). This was adumbrated for the oxidation of formate and of oxalate by $[AuBr_4]^-$ several years ago.[101] A similar mechanism has now been established for the oxidations of formate[102] and of oxalate[103] by $[AuCl_4]^-$. In both cases both $[AuCl_4]^-$ and $[AuCl_3(OH_2)]$ are active species. The oxalate reaction sequence is more complicated than that for formate, since reactions with H_2ox, Hox^-, and ox^{2-} have all to be considered, as does the possibility of ring-closure reactions of the type

$$[AuCl_3(\text{unidentate ox})]^{2-} \longrightarrow [AuCl_2(\text{bidentate ox})]^- + Cl^-$$

The oxidation of thiosulphate by $[Au(NH_3)_4]^{3+}$ is also thought to proceed by substitution, giving $[Au(S_2O_3)(NH_3)_3]^+$, and subsequent electron transfer. Kinetic parameters were determined for the initial substitution step.[104]

The substitution of a methyl ligand in $[AuMe_3(PR_3)]$ by a benzenethiolato-ligand goes *via* a non-redox radical route. This contrasts with analogous reactions at platinum(II), which can proceed *via* an oxidative addition path.[55] However, the reaction

$$cis\text{-}[Au^{III}IMe_2(PPh_3)] + [Au^{I}Me(PPh_3)] \longrightarrow [Au^{III}Me_3(PPh_3)] + [Au^{I}I(PPh_3)]$$

does not, on labelling, stereochemical, and solvent-effect evidence, proceed either by a radical or a redox mechanism. An intermediate containing a bridging methyl group, in other words a mechanism associative with respect to the Au^{III} and the Au^{I}, is proposed.[105]

[99] G. Annibale, L. Cattalini, and G. Natile, *J.C.S. Dalton*, 1975, 188.
[100] L. H. Skibsted and J. Bjerrum, *Acta Chem. Scand.*, 1974, **A28**, 740.
[101] V. P. Kazakov and M. N. Konovalova, *Russ. J. Inorg. Chem.*, 1968, **13**, 1226.
[102] B. S. Maritz and R. van Eldik, *J. Inorg. Nuclear Chem.*, 1976, **38**, 1545.
[103] B. S. Maritz and R. van Eldik, *Inorg. Chim. Acta*, 1976, **17**, 21.
[104] G. Nord, L. H. Skibsted, and A. S. Halonin, *Acta Chem. Scand.*, 1975, **A29**, 505.
[105] G. W. Rice and R. S. Tobias, *J. Organometallic Chem.*, 1975, **86**, C37.

Nickel(II).—A re-examination[106] of the kinetics of dissociation of the $[Ni(CN)_4]^{2-}$ anion in acidic aqueous solution indicated the rate law

$$-d[Ni(CN)_4^{2-}]/dt = k_{obs}[Ni(CN)_4^{2-}]$$

where

$$k_{obs}^{-1} = (k_{00} + k_{01}h)^{-1} + (k_{11}h + k_{12}h^2)^{-1}[HCN]$$

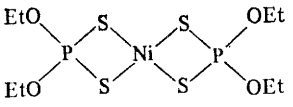
where h is the hydrogen-ion concentration. This rate law suggests that the following two equilibria are relevant to the mechanism of dissociation:

$$[Ni(CN)_4]^{2-} + H^+ \rightleftharpoons [Ni(CN)_3(CNH)]^-$$

$$[Ni(CN)_3(OH_2)]^- + H^+ \rightleftharpoons [Ni(CN)_2(CNH)(OH_2)]$$

Dissociation proceeds by parallel loss of CN^- and of HCN from the species cited in the above equilibria. The chief area of disagreement between this[106] and the earlier study of this system[107] is the extent of protonation. Reactions of macrocyclic ligand complexes of nickel(II) with cyanide go into two distinct steps, formation of a 1:1 (or sometimes 1:2) adduct and subsequent ligand displacement. Rates for the second step vary greatly with the nature of the macrocycle being displaced. Removal of 12-, 13-, and 14-membered ligands of the cyclam type covers a range of reactivities of the order of 10^5. These dramatic differences arise from differences in geometry and strain within the complexes. Methylation of the nitrogen atoms causes a marked reduction in rate.[108]

The remaining references in this section deal with processes closely related to substitution at nickel. The reaction of bis-(*OO*-diethylphosphorodithioato-*SS'*-) nickel(II) (14) with bidentate nitrogen ligands involves addition rather than substitution. Rates are controlled by steric factors, with addition of 2,9-Me_2phen much slower than that of phen, bipy, or pada. Activation entropies are within the range -20 to -93 J K^{-1} mol^{-1} (in benzene), consistent with the expected associative activation step.[109] 'Kinetic stabilization' by cyanide ligands is demonstrated by the relative slowness of proton transfer to doubly deprotonated derivatives of the



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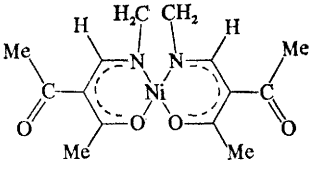


(15)

[Ni(CN)(glycylglycylglycinato)]$^+$ cation and its glycylglycinamido-analogue.[110] The activation entropy for linkage isomerization of 3,3'-ethylenebis(nitrilomethylidyne)-di-2,4-pentanedionatonickel (15), which is -21 cal K^{-1} mol^{-1} in bromoform, suggests that the mechanism involves a transition state containing five-co-ordinate nickel(II).[111]

[106] H. Persson and C. G. Ekström, *Acta Chem. Scand.*, 1976, **A30**, 31.
[107] G. B. Kolski and D. W. Margerum, *Inorg. Chem.*, 1968, **7**, 2239.
[108] L. Hertli and T. A. Kaden, *Chimia* (*Switz.*), 1975, **29**, 304.
[109] M. W. Grant and R. J. Magee, *Austral. J. Chem.*, 1976, **29**, 749.
[110] G. K. Pagenkopf and V. T. Brice, *Inorg. Chem.*, 1975, **14**, 3118.
[111] L. A. Funke and G. A. Melson, *Inorg. Chem.*, 1975, **14**, 306.

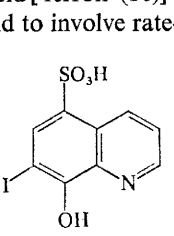
Iron(II), Rhodium(I), and Iridium(I).—Arguably iron(II) is square-planar in ferrous phthalocyanine in DMSO solution (*cf.* $[PtCl_4]^{2-}$ in water!). The reaction of this compound with imidazole has been much studied, but kinetic ambiguities have prevented the unequivocal assignment of mechanism. Now the kinetic pattern for the analogous reactions with *N*-methylimidazole and with *N*-n-butylimidazole, where there is no possibility of proton removal from nitrogen, has been shown to be very similar to that with imidazole. It is therefore now reasonable to rule out reaction of ferrous phthalocyanine with the deprotonated imidazole anion as a plausible pathway.[112]

The mechanism of displacement of ethylene from $[Rh(\eta^5\text{-}C_5H_5)(C_2H_4)_2]$ and analogous derivatives containing substituted cyclopentadienyl ligands depends on the nature of the incoming ligand and on the capacity of the (substituted) cyclopentadienyl ligand to accept electron density in transition-state formation. Strong nucleophiles, such as PBu^n_3, displace the ethylene at rates proportional to their concentration and greater than the rate of dissociation of the ethylene, and thus react by an associative mechanism.[113]

cis ⇌ *trans* Isomerization is frequently encountered in platinum(II) and palladium(II) chemistry, but is hitherto unknown for iridium(I) compounds. Now *cis*- and *trans*-isomers have been reported for the σ-(η^1-)mesityl compound $[Ir(2,4,6\text{-}Me_3C_6H_2)(CO)(PPh_3)_2]$. Interestingly, *cis* → *trans* isomerization does not take place in pure benzene or chloroform, but occurs readily if triphenylphosphine be added.[114] Kinetic data are not reported.

2 Tetrahedral Complexes

The main area of activity here has been in the examination of the kinetics of various reactions involving homo- and hetero-polyoxoanions containing transition metals of Groups V and VI. The simplest species studied has been heptamolybdate, $[Mo_7O_{24}]^{6-}$. The base hydrolysis of this anion involves parallel hydroxide-dependent and hydroxide-independent pathways. The rates of these paths vary greatly with the nature of the alkali-metal cation present; ion-pairing effects are important here. The mechanism of base hydrolysis of $[Mo_7O_{24}]^{6-}$ is thought to differ markedly from that of decavanadate, $[V_{10}O_{28}]^{6-}$.[115] Decavanadate dissociates in the presence of 7-iodo-8-hydroxyquinoline-5-sulphonic acid ['ferron' (16)] to give a mononuclear vanadium(V) product. The mechanism is said to involve rate-determining attack of the ferron



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[112] J. G. Jones and M. V. Twigg, *Inorg. Chim. Acta*, 1975, **12**, L15.
[113] R. Cramer and L. P. Seiwell, *J. Organometallic Chem.*, 1975, **92**, 245.
[114] L. Dahlenburg and R. Nast, *Angew. Chem. Internat. Edn.*, 1976, **15**, 110.
[115] D. M. Druskovich and D. L. Kepert, *Austral. J. Chem.*, 1975, **28**, 2365.

at vanadium in $[HV_{10}O_{28}]^{5-}$.[116] Decavanadate and selenite react to give an equilibrium mixture also containing a pentavanadoselenite mixed anion:

$$[HV_{10}O_{28}]^{5-} + 4[HSeO_3]^- + 5H^+ \rightleftharpoons 2[HV_5Se_2O_{18}]^{2-} + 4H_2O$$

The kinetics of the forward and reverse reactions have been studied. The forward reaction is first-order in decavanadate and in selenite; the reverse reaction is first-order in vanadoselenite. If the selenite is present in large excess, the product is $[H_3VSe_2O_{10}]^{4-}$ and the kinetic pattern more complicated. These results and observations on the production of the $[HV_5Se_2O_{18}]^{2-}$ anion from VO_2^+ and selenite have been combined into a single mechanistic scheme of considerable complexity.[117] The kinetics of formation and of dissociation of 12-molybdogermanic acid, $[H_4GeMo_{12}O_{40}]$, in strongly acid solution have been described.[118]

Whereas hydroxide encourages the decomposition of such polynuclear oxoanions as heptamolybdate (see above), it acts in a converse capacity in the reaction of hexatantalate with tungstate. Here it facilitates formation of the $[WTa_{12}O_{38}]^{10-}$ anion, perhaps by aiding the elimination of water in building up the oxide polyhedra.[119] Kinetic studies of the generation of yet more complicated heteropolynuclear oxoanions are represented by the study of the reaction of $[SiW_{11}O_{39}]^{8-}$ with cobalt(II) to give the $[SiCoW_{11}O_{39}]^{6-}$ anion.[120]

The dependence of the rate constants for the forward and reverse reactions of the equilibrium

$$[CoCl_3(solv)]^- + Cl^- \rightleftharpoons [CoCl_4]^{2-} + solv$$

on the nature of the solvent (solv) is discussed in Chapter 5 of this Part. Both reactions are likely to be associative.[121]

Alcohol (ROH) exchange with esters $VO(OR)_3$ has been monitored by ^1H n.m.r. line-broadening techniques, for R = Pr^n, Pr^i, Bu^n, and n-pentyl. Activation enthalpies vary between 21.4 and 32.7 kJ mol^{-1}, activation entropies between -129 and -150 J K^{-1} mol^{-1}. These negative ΔS^+ values are strongly suggestive of a predominantly associative reaction mechanism.[122]

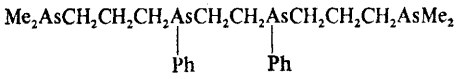
3 Five-Co-ordinate Complexes

The topics of four- and five-co-ordinate complexes are conveniently linked by a study of the kinetics of ligand dissociation and intramolecular rearrangement for a series of cations $[ML_5]^+$ (M = Co^I, Rh^I, or Ir^I) and $[HML_4]^+$ (M = Ni^{II}, Pd^{II}, or Pt^{II}), where L = PEt_3 or a trialkyl phosphite. The relevance to four-co-ordinate complexes is of course that these five-co-ordinate species can be regarded as models for transition states for associative substitution at four-co-ordinate species.[123]

Several quadridentate arsenic ligands are effective in stabilizing five-co-ordinate

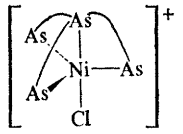
[116] B. Viossat, *Bull. Soc. chim. France*, 1975, 1111.
[117] M. Cadiot and C. Volfovsky, *Rev. Chim. minérale*, 1975, **12**, 493.
[118] M. Biquard and P. Souchay, *Ann. Chim. (France)*, 1975, **10**, 163.
[119] G. C. Bhattacharya and S. K. Roy, *J. Indian Chem. Soc.*, 1975, **52**, 1151.
[120] D. Dauzonne and M. Fournier, *Compt. rend.*, 1974, **279**, *C*, 37.
[121] U. Mayer, *Pure Appl. Chem.*, 1975, **41**, 291.
[122] P. J. White, M. J. Kaus, J. O. Edwards, and P. H. Rieger, *J.C.S. Chem. Comm.*, 1976, **429**.
[123] P. Meakin, A. D. English, and J. P. Jesson, *J. Amer. Chem. Soc.*, 1976, **98**, 414; A. D. English, P. Meakin, and J. P. Jesson, *ibid.*, p. 422; *Inorg. Chem.*, 1976, **15**, 1233.

complexes, *e.g.* of nickel, of the type $[MX(LLLL)]^+$. Complexes of this formula, with M = Ni, Pd, or Pt, LLLL = tetars (17), and X = halide, are thermodynamically



(17)

stable in non-polar solvents but are kinetically fairly labile. A variable-temperature n.m.r. study of solutions of such complexes has shown that exchange processes are complicated, with three different bimolecular mechanisms involved. The stereochemical characteristics of this ligand are important in elucidating the possible reaction pathways.[124] The kinetics of reaction of the $[NiCl(qas)]^+$ cation (18), where qas is the tripodal ligand (19), with cyanide or thiocyanate in methanol have been



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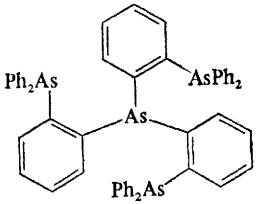


(19)

reported.[125] The discussion of these reactions is limited by the difficulty of making comparisons with distantly related systems; no firm assignment of mechanism appears possible. Complexes of the ligand 1,5-diazacyclo-octane-*NN'*-diacetate (dacoda) are five-co-ordinate since one of the ligand alkyl protons blocks the potential sixth co-ordination position.[126] The kinetics of formation and dissociation of the complexes $[M(dacoda)(OH_2)]$ (M = Co or Ni) have been studied.[127] Formation may involve an internal conjugate-base (ICB) mechanism, though perhaps here one should remind readers of a recent claim that the ICB mechanism is a superfluous postulate![128] Dissociation rates are acid-dependent, with $k_{obs} = k_1 + k_2[H^+]$. Rate constants and activation parameters have been reported.[127]

Sweigart has published three more papers on substitution kinetics of five-co-ordinate complexes of the $[M(dithio\text{-}ligand)_2L]$ type. Reactions of the tri-n-butylphosphine adducts of bis-(*O*-dialkyldithiophosphato)nickel(II) complexes with bidentate nitrogen or phosphorus nucleophiles go by the *D* $[S_N1(lim)]$ mechanism.[129] It now appears that the substitution mechanism operating for this type of complex depends on the charge on the complex, *i.e.* on the formal oxidation state of the metal. Reactions

$$[M\{S_2C_2(CF_3)_2\}_2L^1]^z + L^2 \longrightarrow [M\{S_2C_2(CF_3)_2\}_2L^2]^z + L^1$$

[124] B. Bosnich, W. G. Jackson, and S. T. D. Lo, *Inorg. Chem.*, 1975, **14**, 2998.
[125] E. Grimley, J. M. Grimley, Tsong-Dsu Li, and D. Emerich, *Inorg. Chem.*, 1976, **15**, 1716
[126] D. F. Averill, J. I. Legg, and D. L. Smith, *Inorg. Chem.*, 1972, **11**, 2344.
[127] C. Chatterjee and T. A. Kaden, *Helv. Chim. Acta*, 1975, **58**, 1881.
[128] R. B. Jordan, *Inorg. Chem.*, 1976, **15**, 748.
[129] D. A. Sweigart and P. Heidtmann, *J.C.S. Dalton*, 1975, 1686.

with M = Fe or Co and L^1 and L^2 = phosphines or phosphites go by a dissociative (*D*) mechanism when $z = -1$, but by an associative mechanism when $z = 0$.[130] It seems that substitution reactions at 14- or 16-electron systems of this type may proceed by dissociative or associative mechanisms, whereas substitution at 18-electron centres always takes place by a dissociative mechanism.[130, 131]

[130] D. A. Sweigart, *J.C.S. Chem. Comm.*, 1975, 688; *Inorg. Chim. Acta*, 1976, **18**, 179
[131] C. A. Tolman, *Chem. Soc. Rev.*, 1972, **1**, 337.

3

Inert Metal Complexes: Co-ordination Numbers Six and Higher

BY P. MOORE

1 Introduction

The layout in this chapter is essentially the same as that in previous Reports. All the studies of a particular metal ion will not be found in one section, but rather the chapter is subdivided in the first instance according to reaction type Studies of dissociation reactions are covered first, the majority of investigations of this type being of aquation or solvolysis reactions in neutral or acidic media. This is followed by sections covering base hydrolysis, formation reactions (*i.e.* replacement of a co-ordinated solvent molecule by an incoming ligand), ligand exchange and replacement (including solvent exchange and replacement or exchange of ligands other than solvent molecules), metal exchange and displacement, and finally isomerization and racemization processes. Each section is subdivided according to the central metal ion, beginning with cobalt(III) and chromium(III), which are by far the most widely studied metal ions, and followed by other metal ions in order of their increasing numbers of *d*-electrons. Most of the metal ions outside the *d*-block are excluded since they are nearly all labile, but a few references to slower reactions (*e.g.* of the lanthanides and actinides) will be found in Sections 7 and 8, which cover ligand and metal exchange processes. For the sake of completeness a few references to labile systems are included, since the usually accepted definition of lability[1] is understandably vague, and there is sometimes a need to draw comparisons between labile and inert systems. Two topics which are not covered in any depth are photochemistry and studies in mixed solvents. The only photochemical studies included are photosolvolyses or photoisomerizations, and references to mixed or non-aqueous solvent studies are kept deliberately brief to avoid too much overlap with Chapter 5. Reviews of kinetic studies in mixed aqueous–organic solvents[2] and of the photochemical quenching and sensitization processes of co-ordination compounds[3] have appeared. There is also a new book[4] entitled 'Concepts of Inorganic Photochemistry'.

In this introduction, some of the highlights of the past eighteen months will be mentioned, and references will be found to other reviews or publications of a general

[1] H. Taube, *Chem. Rev.*, 1952, **50**, 69.
[2] M. J. Blandamer and J. Burgess, *Chem. Soc. Rev.*, 1975, **4**, 55.
[3] V. Balzani, L. Moggi, M. F. Manfrin, F. Balletta, and G. S. Laurence, *Coordination Chem. Rev.*, 1975, **15**, 321.
[4] A. W. Adamson and P. D. Fleischer, 'Concepts of Inorganic Photochemistry', *Wiley, New* York, 1975.

nature. This Report covers literature available between January 1975 and June 1976.

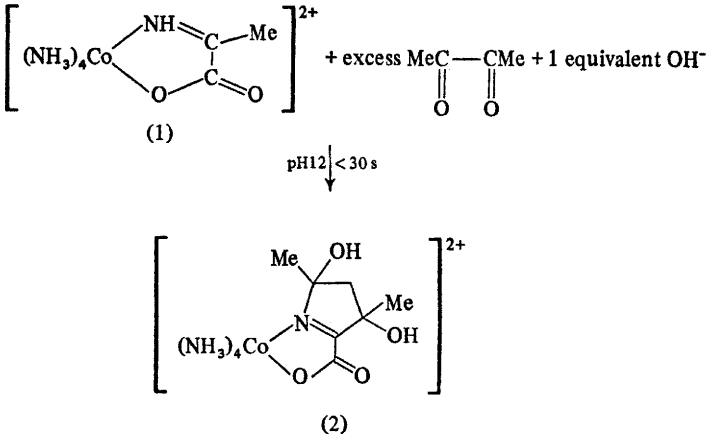
The preoccupation of most investigators with studies of cobalt(III) and chromium(III) has been remarkably consistent since the pioneering work of Alfred Werner. A review of Werner's research into geometric isomerism in co-ordination compounds has appeared recently.[5] Despite the extensive effort into an understanding of the basic mechanisms of the substitution reactions of cobalt(III) and chromium(III) complexes during the past twenty years, recent research has shown that there are subtle differences between these two metal ions which are not evident in most of the reference texts on this subject. For a long time it was thought that nucleophilic substitutions at cobalt(III), chromium(III), and many other octahedral metal complexes occurred by dissociative mechanisms [S_N1 and S_N1(lim), or I_d and D using the nomenclature of Langford and Gray [6]]. Although this picture has not been challenged for most substitution reactions of cobalt(III), work in the past few years suggests that the picture for chromium(III) is not so simple. Even in his early review Taube pointed out that associative nucleophilic substitutions were more probable for metal ions with relatively few *d*-electrons (*e.g.* d^1—d^3 systems).[1] In terms of ligand-field theory, octahedrally co-ordinated metal ions with an incomplete t_{2g} set are more susceptible to associative attack by an incoming nucleophile. In a recent review[7] a case was made for an I_a mechanism in substitution reactions of several octahedrally co-ordinated metal ions including chromium(III) ($3d^3$).

The most compelling evidence comes from measurements of volumes of activation, which are large and negative for substitution reactions of $[CrS_6]^{3+}$ and $[CrS_5X]^{n+}$ ions (*e.g.* S = H_2O or DMSO, X = anion). Two reviews have appeared outlining the use of high-pressure kinetics for determining volumes of activation and the elucidation of reaction mechanisms of co-ordination compounds in solution.[8,9] The most recent research shows that associative mechanisms do not occur for all chromium(III) substitutions. Thus I_d and D mechanisms have been reported recently for formations and solvolyses of $[Cr(NH_3)_5X]^{m+}$ and $[Cr(NCS)_5X]^{n-}$ ions (X = anion or solvent molecule) respectively.[10,11] For anations of the $[Cr(NH_3)_5OH_2]^{3+}$ ion by eight varied univalent anions, the values of the second-order formation rate constants (k_f) vary by less than an order of magnitude, and the rates are very similar to the solvent-exchange rate under the same conditions.[10] This behaviour is typical of that expected for an I_d mechanism and contrasts with that observed for anations of the $[Cr(H_2O)_6]^{3+}$ ion where values of k_f are observed to vary more markedly. For example, the ratio of k_f values for anations by NCS^- and Cl^- ions is *ca.* 60 in the case of $[Cr(H_2O)_6]^{3+}$, but only *ca.* 6 in the case of $[Cr(NH_3)_5OH_2]^{3+}$. Therefore, whereas an I_a mechanism is most probable for anations of the former ion, an I_d mechanism is much more likely for the latter. It is argued that this difference arises because the five ammonia molecules in $[Cr(NH_3)_5OH_2]^{3+}$ are better σ-donors than five water mole-

[5] G. B. Kauffman, *Coordination Chem. Rev.*, 1975, **15**, 1.
[6] C. H. Langford and H. B. Gray, 'Ligand Substitution Processes', 2nd edn., W. Banjamin, New York, 1975.
[7] T. W. Swaddle, *Coordination Chem. Rev.*, 1974, **14**, 217.
[8] D. A. Palmer and H. Kelm, 'Proceedings of the 4th International Conference on High Pressure', 1974, ed. J. Osugi, Phys. Chem. Soc. Japan, Kyoto, Japan, 1975, p. 657.
[9] D. R. Stranks, *Pure Appl. Chem.*, 1974, **38**, 303.
[10] T. Ramasami and A. G. Sykes, *J.C.S. Chem. Comm.*, 1976, 378.
[11] S. T. D. Lo and D. W. Watts, *Austral. J. Chem.*, 1975, **28**, 491, 501, 1907.

cules and, therefore, dissociative mechanisms are promoted in the ammine complexes.[10] This view is supported by the observation of the extreme S_N1(lim) or *D* mechanism in the case of formations and dissociations of the $[Cr(NCS)_5S]^{2-}$ ions (S = solvent molecule or anion),[11] the thiocyanate ions promoting a dissociative mechanism even more than ammonia molecules by virtue of their increased σ-donor properties. The substitution reactions of cobalt(III) and chromium(III) are not so very different, therefore, since I_d and *D* mechanisms have been widely accepted for reactions of $[Co(NH_3)_5X]^{2+}$ and $[Co(CN)_5X]^{3-}$ ions respectively. It is even conceivable that substitution reactions of the $[Co(H_2O)_6]^{3+}$ ion are associative like those of $[Cr(H_2O)_6]^{3+}$.[10]

One aspect of the co-ordination chemistry of inert metal ions which has not received the attention it fully deserves is the way in which the changed reactivity of co-ordinated ligands can be used to preparative advantage. Recent examples show how cobalt(III) complexes can be employed in this way.

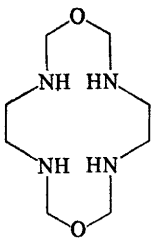


Synthesis and stabilization of a pyrroline ring system (2) has been established by means of a crystal structure.[12] The reaction proceeds by deprotonation of the imine nitrogen of (1) and attack of this deprotonated imine group at a carbonyl of the diketone, followed by deprotonation of the *C*-methyl group of (1) and ring closure by attack of this carbanion at the second carbonyl group of the diketone. Kinetic studies of the base-catalysed hydrogen–deuterium exchange reactions of (1) and the model *N*-methyl derivative of (1) help to establish this mechanism. Thus the half-life for deuteriation of the *C*-methyl group of (1) is *ca.* 10 h at pH 10 and 305 K, whereas in the *N*-methyl model compound the *C*-methyl proton exchange is much faster (half-life *ca.* 5 min at pH 10 and 303 K). This establishes that the first step in the conversion of (1) into (2) is alkylation of the N-centre, since this increases the acidity of the *C*-methyl group as shown by the model study. Furthermore, the increase in acidity of this *C*-methyl group must be sufficiently great to compete with deprotonation of an

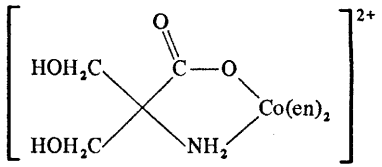
[12] J. MacB. Harrowfield, G. B. Robertson, A. M. Sargeson, and P. O. Whimp, *J.C.S. Chem. Comm.*, 1975, 109.

adjacent NH_3 group (pK_a *ca.* 16), and attack of that amide ion at the diketone carbonyl group to give a terdentate ligand as found in a related study.[13]

Other examples of template syntheses centred around cobalt(III) complexes have appeared. The macrocyclic ligand 1,4,8,11-tetra-aza-6,13-dioxacyclotetradecane [dioxacyclam (3)] can be synthesized by a template reaction between formaldehyde (1.8 mol dm^{-3}) and $[Co(en)_2gly]Cl_2$ (0.3 mol dm^{-3}) in saturated aqueous Li_2CO_3.



(3)



(4)

Condensation of two moles of formaldehyde produces the α-hydroxymethylserinebis-(1,2-diaminoethane)cobalt(III) ion (4), and a further six moles of formaldehyde condense with the two co-ordinated 1,2-diaminoethane ligands of (4) to produce the co-ordinated dioxacyclam (3) in the [Co(dioxacyclam) (α-$HOCH_2$-serine)]$^{2+}$ ion.[14]

The considerable enhancement of the rate of attack of bases at co-ordinated nitriles is well documented, and recently this has been used to preparative advantage in reactions of co-ordinated acrylonitrile with carbanions (Michael addition):

$$[(NH_3)_5CoNCCH_2{=}CH_2]^{3+} + (MeCO)_2CH^- \xrightarrow[\text{ii, } H^+]{\text{i, pH 9, 298 K, 5 s}} [(NH_3)_5CoN{\equiv}CCH_2CH_2CH(COMe)_2]^{3+}$$

In an analogous reaction with nitromethane, a 55% yield of the $[(NH_3)_5CoN{\equiv}CCH_2CH_2CH_2NO_2]^{3+}$ ion is obtained in 15 s. The reaction of unco-ordinated acrylonitrile with nitromethane under similar conditions is much slower, the half-life of the reaction being greater than 7 h.[15] Surprisingly, it was even possible to reduce acetonitrile co-ordinated to cobalt(III) by sodium borohydride (pH 9 and 298 K) without complete reduction to cobalt(II). A 50% yield of $[(NH_3)_5CoNH_2CH_2Me]^{3+}$ was obtained in this way.[15]

Two groups have reported the partial asymmetric synthesis of threonine (5) and allothreonine (6) from the reaction between acetaldehyde and either the glycine ligands of optically active (+)-$[Co(en)_2(gly)]^{2+}$, (+)-*trans*-(*O*)-, (+)-β-*cis*-(*O*)-, and (+)-α-*cis*-(*O*)-$[Co(en)(gly)_2]^+$ (pH 9.5, 298 K)[16] or the glycine fragments of optically active potassium Λ- and Δ-bis-(*N*-salicylideneglycinato)cobalt(III) and the analogous *N*-3-methyl derivative (pH 11.0—11.6, room temperature).[17]

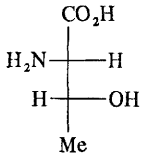
[13] B. T. Golding, J. MacB. Harrowfield, G. B. Robertson, A. M. Sargeson, and P. O. Whimp, *J. Amer. Chem. Soc.*, 1974, **96**, 3691.

[14] R. J. Geue, M. R. Snow, J. Springborg, A. J. Herlt, A. M. Sargeson, and D. Taylor, *J.C.S. Chem. Comm.*, 1976, 285.

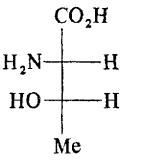
[15] I. J. Creaser and A. M. Sargeson, *J.C.S. Chem. Comm.*, 1976, 974.

[16] J. C. Dabrowiak and D. W. Cooke, *Inorg. Chem.*, 1975, **14**, 1305.

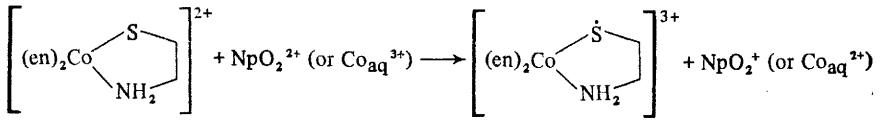
[17] Y. N. Belokon, V. M. Belikov, S. V. Vitt, M. M. Dalgaya, and T. F. Savel'eva, *J.C.S. Chem. Comm.*, 1975, 86.



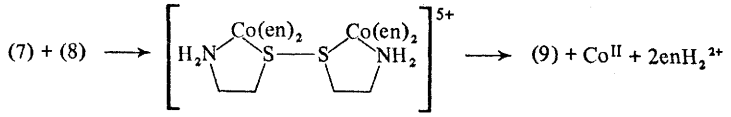
(5) (*S*)-threonine

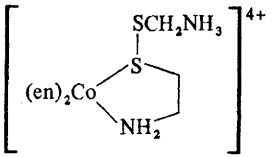


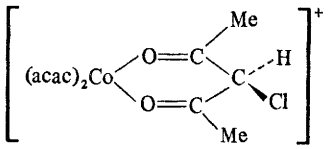
(6) (*S*)-allothreonine



(7) (8)







(9) (10)

Other interesting reports have appeared dealing with reactions of ligands co-ordinated to cobalt(III). Reaction of 2-mercaptoethylamine in (7) with one equivalent of Np^{VI} or Co^{III} in aqueous $HClO_4$ gives the radical (8) which dimerizes and finally produces the disulphide-bridged mononuclear product (9).[18]

A transient intermediate (10) has also been detected during the chlorination of $[Co(acac)_3]$ by *N*-chlorosuccinimide,[19] using a relatively new technique of stopped-flow pulse Fourier-transform ^1H n.m.r.[20] This technique should be very useful for investigating the rates of moderately rapid hydrogen–deuterium exchange reactions and for establishing the site of deprotonation in base catalysis.

In a study of the base hydrolysis of two isomers of $[Co(tren)(NH_3)Cl]^{2+}$ it was shown that deprotonation at the nitrogen-centre in a *trans* position to the chloride ion leads to the most reactive intermediate for loss of Cl^-.[21] Conjugate-base formation is now widely accepted as the initial product in the Garrick mechanism for the base hydrolysis of amine complexes, and this was very firmly established by the spectrophotometric determination of the pK_a's of the $[Co(en)_3]^{3+}$ and $[Co(NH_3)_5NO_2]^{2+}$ ions using aqueous solutions of hydroxide ion in DMSO.[22] pK_a's of 14.9

[18] M. Woods, J. C. Sullivan, and E. Deutsch, *J.C.S. Chem. Comm.*, 1975, 749.
[19] D. A. Couch, O. W. Howarth, and P. Moore, *J.C.S. Chem. Comm.*, 1975, 822.
[20] D. A. Couch, O. W. Howarth, and P. Moore, *J. Phys.* (*E*), 1975, **8**, 831.
[21] D. A. Buckingham, P. J. Cresswell, and A. M. Sargeson, *Inorg. Chem.*, 1975, **14**, 1485.
[22] D. M. Goodall and M. J. Hardy, *J.C.S. Chem. Comm.*, 1975, 919.

(extrapolated to $I=0$) and 16.8 respectively were obtained for these two ions, using an acidity function derived from the solvent dependence of the rate of base hydrolysis of $[Co(NH_3)_5Cl]^{2+}$.

A new study has extended measurements of the relative rates of deuteriation of the *cis*- and *trans*-ammonia molecules and amines in several acido-cobalt(III) complexes (Table 1).[23] Co-ordinated CN^-, NO_2^-, and possibly SO_3^{2-} ions decelerate the rate of

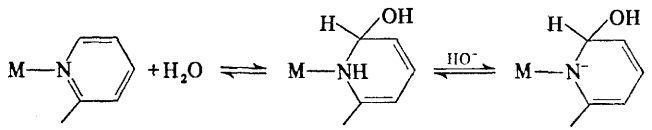
Table 1 *Rate constants for the deuteriation of* cis- *and* trans-*amine groups in several cobalt*(III) *complexes in* D_2O (*at* 303 K, *saturated aqueous solutions*)[a]

Complex	$10^6k(cis)/s^{-1}$	$10^6k(trans)/s^{-1}$
$[Co(NH_3)_5CN](ClO_4)_2$	60	6.2
$[Co(NH_3)_5NO_2](NO_3)_2$ [b]	180	17
$[Co(NH_3)_5F](NO_3)_2$	58	fast
cis-$[Co(NH_3)_4(CN)_2]Cl$	390	62
$[Co(NH_3)_4CO_3]_2SO_4$	1300	2200
cis-$[Co(NH_3)_4(OAc)_2]ClO_4$	140	680
cis-$NH_4[Co(NH_3)_4(SO_3)_2]$	fast	490
$[Co(NH_3)_4(en)](NO_3)_3$ [c]	1500	6500
cis-$[Co(en)_2(CN)_2]Cl$	680	310

[a] Data from ref. 23; rate constants statistically corrected. [b] In 90% $[^2H_6]$dmso–10% D_2O by weight. [c] Rate constant for the deuteriation of en: $10^6k = 3200\ s^{-1}$.

hydrogen–deuterium exchange for the amine protons in a *trans* position, whereas F^-, Cl^-, Br^-, H_2O, CO_3^{2-}, $NH_2CO_2^-$, N_3^-, $MeNH_2$, AcO^-, mal$^-$, ox$^-$, and fumarate ions accelerate deuteriation of the *trans*-NH_2 or -NH_3 groups.

Although base-catalysed hydrolyses of ammine, amine, and amide complexes almost certainly occur *via* conjugate-base formation, such a mechanism is not possible for complexes which lack an acidic proton. In a recent review stress was placed on the importance of attack by the OH^- ion at an alternative site, namely the 2-position of substituted pyridine complexes (*e.g.* bipy and phen):[24]



There is a growing interest in the involvement of metal ions and co-ordination compounds in biological systems, and this has been recognized in the United Kingdom by the inauguration of a new discussion group of the Dalton division of the Chemical Society. Some recent reviews are devoted to various aspects of this very broad field. Of relevance here are articles dealing with the kinetics and mechanism of metalloporphyrin formation,[25] mechanisms for the reactions of molybdenum in enzymes,[26] and a review of the chemistry of vitamin B_{12} co-enzyme.[27] A review has also appeared of the kinetics and mechanisms of substitution reactions in cobalt(III)

[23] U. Sakaguchi, K. Maeda, and H. Yoneda, *Bull. Chem. Soc. Japan*, 1976, **49**, 397.
[24] R. D. Gillard, *Coordination Chem. Rev.*, 1975, **16**, 67.
[25] W. Schneider, *Structure and Bonding*, 1975, **23**, 123.
[26] R. A. D. Wentworth, *Coordination Chem. Rev.*, 1976, **18**, 1.
[27] R. H. Abeles and D. Dolphin, *Accounts Chem. Res.*, 1976, **9**, 114.

trans-dioximes which are model compounds for cobalamins,[28] and two more reviews deal further with the chemistry of molybdenum.[29,30]

Kinetic studies of molybdenum complexes have continued, and a picture is now available for the relative labilities of molybdenum complexes with the metal ion in oxidation states +3,[31] +4,[32,33] +5,[34] and +6.[35] The nature of molybdenum(IV) species in aqueous acidic solutions is in dispute, one group having rejected a previous proposal for a dimeric species $[Mo_2O_2]^{4+}$ in favour of the mononuclear MoO^{2+} ion,[32] whilst the latest work suggests that the $[Mo_2O_2]^{4+}$ formulation is in fact correct.[33] One possible explanation of this anomaly could be the reported[33] reduction of perchlorate ions by Mo^{IV}, since one group[32] worked in perchloric acid solutions whereas the second group favoured trifluoracetic acid.[33] The latest results from cryoscopic measurements in 5.1 mol dm^{-3} CF_3CO_2H are difficult to reconcile with a mononuclear structure,[33] and so the earlier ion-exchange measurements in perchloric acid may be in error. Therefore, the kinetic data reported recently for the reaction of the MoO^{2+} ion with thiocyanate ion[32] may refer to a reaction of the $[Mo_2O_2]^{4+}$ dimer.

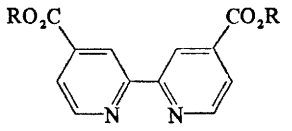
Ruthenium is another of the rarer metals whose chemistry continues to flourish. A possibly important method of storing solar energy comes from recent studies of the photochemistry of tris-(bipyridyl)ruthenium(II) complexes:[36,37]

$$[Ru^{II}(bipy)_3]^{2+} \xrightarrow[\lambda<560\text{ nm}]{h\nu} \text{C.T. excited state} + H_2O \longrightarrow H_2 + [Ru^{III}(bipy)_3]^{3+}$$

$$[Ru(bipy)_3]^{3+} + OH^- \longrightarrow [Ru(bipy)_3]^{2+} + \tfrac{1}{4}O_2 + \tfrac{1}{2}H_2O$$

In the first report based on the above reactions a design for a cell is proposed which could bring about the photochemical decomposition and separation of water into H_2 and O_2.[36] The method is based on the reduction of H_2O to H_2 by a photochemically excited charge-transfer state of the $[Ru(bipy)_3]^{2+}$, the $[Ru(bipy)_3]^{3+}$ ion produced being converted back into $[Ru(bipy)_3]^{2+}$ by reduction with hydroxide ion, and O_2 being released at the same time. In a novel extension of this idea, one of the three bipyridyl molecules was substituted by two long carboxylic acid ester side-chains in the 4- and 4′-positions (11). The resulting surfactant $[Ru(bipy)_2L]^{2+}$, which is immiscible with water, forms a monolayer film when chloroform solutions are spread on an air–water interface. When glass slides containing such monolayer assemblies are immersed in water which is irradiated through pyrex by a 100 W medium-pressure mercury lamp, a steady stream of a mixture of hydrogen and

[28] A. V. Ablov and N. M. Samus, *Coordination Chem. Rev.*, 1975, **17**, 253; N. M. Samus, A. V. Ablov, T. S. Luk'yonets, O. N. Damaskina, E. A. Konunova, and Nguyen Thanh Hong, *Chem. Abs.*, 1975, **83**, 153094.
[29] B. Spivak and Z. Dori, *Coordination Chem. Rev.*, 1975, **17**, 99.
[30] K. Saito and Y. Sasaki, *Chem. Abs.*, 1975, **83**, 20988.
[31] Y. Sasaki and A. G. Sykes, *J.C.S. Dalton*, 1975, 1048.
[32] J. F. Ojo, Y. Sasaki, R. S. Taylor, and A. G. Sykes, *Inorg. Chem.*, 1976, **15**, 1006; T. Ramasami, R. S. Taylor, and A. G. Sykes, *J. Amer. Chem. Soc.*, 1975, **97**, 5918.
[33] M. Ardon, A. Bino, and G. Yahav, *J. Amer. Chem. Soc.*, 1976, **98**, 2338; M. Ardon and A. Pernick, *J. Amer. Chem. Soc.*, 1973, **95**, 6871.
[34] Y. Sasaki, R. S. Taylor, and A. G. Sykes, *J.C.S. Dalton*, 1975, 396.
[35] J. F. Ojo, R. S. Taylor, and A. G. Sykes, *J.C.S. Dalton*, 1975, 500.
[36] C. Creutz and N. Sutin, *Proc. Nat. Acad. Sci. U.S.A.*, 1975, **12**, 2858.
[37] G. Sprintschnik, H. W. Sprintschnik, P. P. Kirsch, and D. G. Whitten, *J. Amer. Chem. Soc.*, 1976, **98**, 2337.



R = dioctadecyl (L) or bis(dihydrocholesteryl)

(11)

oxygen gases is evolved over a long period of time.[37] The effective quantum efficiency is reported to be 0.3.

Studies of the interesting thermal reactions of ruthenium complexes continue to grow, and in a major paper the reactions of $[Ru^{II}(NH_3)_5L]^{2+}$ and *trans*-$[Ru^{II}(NH_3)_4$-(isonicotinamide)$L]^{2+}$ ions (L = H_2S, Me_2S, or EtSH) have been described along with studies of their ruthenium(III) analogues.[38] These results enable a comparison to be made between H_2O, H_2S, and EtSH as ligands, and their pK_a's when co-ordinated to ruthenium(II) and ruthenium(III) are shown in Table 2. The chemistry of these ions is described in a later section dealing with the aquation of ruthenium complexes (p. 209).

Table 2 *Comparison of the* pK_a*'s of co-ordinated* H_2O, H_2S, *and* EtSH (*data from ref.* 38)

Complex	L = H_2O	H_2S	EtSH
$[Ru^{II}(NH_3)_5L]^{2+}$	13.1	4.0	9.2
trans-$[Ru^{II}(NH_3)_4$(isn)$L]^{2+}$ [a]	11.7	<3.2[b]	—
$[Ru^{III}(NH_3)_5L]^{3+}$	4.2	-10[c]	-7[c]

[a] isn = isonicotinamide. [b] At 278 K. [c] Estimated values.

A number of short reviews have appeared in addition to those already mentioned. They deal with the reactivity of dinuclear μ-peroxo-cobalt(III) chelates[39] and rhodium cyanides,[40] with metal and ligand isotopic exchange reactions of chelate complexes,[41] and the applications of isotopes to kinetic studies of carbonate systems.[42] A new book deals with the diverse applications of n.m.r. for kinetic studies in solution, including a chapter devoted to stereochemically non-rigid metal chelate complexes.[43] In a further review the dynamics of intramolecular metal-centred rearrangement reactions of *tris*-chelate complexes is described.[44]

2 Aquation: Cobalt(III) Complexes

Unidentate Leaving Groups.—Several new reports have appeared concerned with the reactions of DMSO in the $[Co(NH_3)_5DMSO]^{3+}$ ion. Activation parameters for aquation in aqueous $HClO_4$ are reported to be $\Delta H^{\ddagger} = 24.7 \pm 0.3$ kcal mol^{-1} and $\Delta S^{\ddagger} = +4.5 \pm 0.4$ cal K^{-1} mol^{-1} at 300 K and $I = 0.5$ ($NaClO_4$).[45] These results

[38] C. G. Kuehn and H. Taube, *J. Amer. Chem. Soc.*, 1976, **98**, 689.
[39] R. Caraco, D. Braun-Steinle, and S. Fallab, *Coordination Chem. Rev.*, 1975, **16**, 147.
[40] J. Halpern and R. Cozens, *Coordination Chem. Rev.*, 1975, **16**, 141.
[41] H. Elias, *J. Radioanalyt. Chem.*, 1976, **30**, 25.
[42] G. M. Harris, *Phys. Chem. Sci. Res. Report*, 1975, **1**, 417 (Nat. Seawater Rep. Dahem Workshop, 1975).
[43] R. H. Holm, 'Dynamic Nuclear Magnetic Resonance Spectroscopy', ed. L. M. Jackson and F. A. Cotton, Academic Press, New York, 1975.
[44] L. H. Pignolet, *Topics Current Chem.*, 1975, **56**, 91.
[45] N. Rodriguez, E. Kremer, C. R. Piriz Mac-Coll, and L. Beyer, *Z. anorg. Chem.*, 1975, **412**, 59.

are in good agreement with those reported by a second group who studied the reaction over a range of ionic strengths ($I = 0.007$—3.01 mol l^{-1}) and in ethanol–water mixtures.[46] Both groups report the reaction to be acid-independent, and the second group found that the reaction rate did not vary with ionic strength and with the cation concentration, but varied with $[ClO_4^-]$ and the ethanol–water ratio. Two further studies of $[Co(NH_3)_5DMSO]^{3+}$ were aimed at oxidation of the co-ordinated DMSO in the presence of anions to trap the five-co-ordinate intermediate, $[Co(NH_3)_5]^{3+}$, which might be formed.[47,48] In the first of these reports it was found that when the oxidation was carried out by permanganate ion in aqueous solutions containing HCl and $HClO_4$ the ratio of the concentrations of $[Co(NH_3)_5Cl]^{2+}$ and $[Co(NH_3)_5OH_2]^{3+}$ ions formed was the same as that observed when, under related conditions, the azido- and carbamato-penta-amminecobalt(III) ions were treated with nitrous acid. This strongly suggests that the same five-co-ordinate intermediate is formed in these reactions, but it was established that solvolysis of $[Co(NH_3)_5DMSO]^{3+}$ does not proceed *via* the same intermediate.[47] In a second study using chlorine as oxidant the reaction was found to be

$$[Co(NH_3)_5DMSO]^{3+} + Cl_2 + H_2O \xrightarrow{(X^-)} \begin{matrix}(1-x)[Co(NH_3)_5OH_2]^{3+} + Me_2SO_2 \\ + \\ x[Co(NH_3)_5X]^{2+} + 2H_2O\end{matrix}$$

In this case dimethyl sulphone was established as the only organic product, and unlike the previous study it was found that oxidation in the presence of the poorly co-ordinating anions ClO_4^- and $CF_3SO_3^-$ gave clear evidence for the formation of $[Co(NH_3)_5OClO_3]^{2+}$ and $[Co(NH_3)_5OSO_2CF_3]^{2+}$ ions. These two new species are very labile for cobalt(III) complexes; at 298.1 K, $I = 1.0$ mol l^{-1} ($NaClO_4$), the rate constants for aquation are 0.1 s^{-1} and 2.7×10^{-2} s^{-1} respectively.[48] A solid perchlorato-complex, $[Co(NH_3)_5OClO_3](ClO_4)_2$, was isolated from the nitrosation of the $[Co(NH_3)_5N_3]^{2+}$ ion in 70% $HClO_4$. It can be readily converted into solvento-complexes by dissolving in the appropriate solvent (*e.g.* DMSO or DMF). Chlorination of the $[Co(NH_3)_5DMSO]^{3+}$ ion in acids HX {where X is an anion which forms a slow aquating product, $[Co(NH_3)_5X]^{2+}$, *e.g.* Cl^-, NO_3^-, or HSO_4^-} gave a rate law which was independent of $[H^+]$,

$$-d[Co(NH_3)_5DMSO^{3+}]/dt = k[Co(NH_3)_5DMSO^{3+}][Cl_2]$$

At 298.1 K, $I = 1.0$, $k \approx 10$ dm^3 mol^{-1} s^{-1}. Chlorination of the $[Co(NH_3)_5DMSO]^{3+}$ ion in 1 mol dm^{-3} HBF_4 gave, unexpectedly, 11% $[Co(NH_3)_5F]^{2+}$, and similar results were obtained when HPF_6 was used or when the $[Co(NH_3)_5N_3]^{2+}$ ion was nitrosated in the presence of HBF_4.

The induced aquations of *cis*- and *trans*-$[Co(en)_2(N_3)Cl]^+$ and *cis*- and *trans*-$[Co(en)_2Cl_2]^+$ ions (by NO^+ and Hg^{2+} ions respectively) gave 70—79% and 27—28% *cis*-$[Co(en)_2(OH_2)Cl]^{2+}$ and the rest *trans*-product, starting from the *cis*- and *trans*-reactants respectively. D-*cis*-$[Co(en)_2Cl_2]^+$ reacted with Hg^{2+} to give *ca.* 70% D-*cis*-$[Co(en)_2(OH_2)Cl]^+$. It is concluded that a common intermediate is not involved in these reactions, and it is also argued that a common intermediate is not involved

[46] M. Glavas and W. L. Reynolds, *J.C.S. Dalton*, 1975, 1706.
[47] W. L. Reynolds, *Inorg. Chem.*, 1975, **14**, 680.
[48] J. MacB. Harrowfield, A. M. Sargeson, B. Singh, and J. C. Sullivan, *Inorg. Chem.*, 1975, **14**, 2864.

during the aquation of *cis*- and *trans*-$[Co(en)_2(X)Cl]^+$ ions ($X^- = N_3^-$, Cl^-, *etc.*). The previously held view that a trigonal-bipyramidal intermediate with an equatorial Cl^- directing ligand is produced from induced aquations of *cis*-complexes, and a square-pyramidal intermediate from those of *trans*-complexes, is rejected on the basis of several pieces of indirect evidence. It is shown that the intermediates formed are sufficiently stable to survive many collisions and to react selectively with a choice of nucleophiles.[49]

Equilibrium constants have been determined for the formation of an ion pair (K_{IP}) and for overall complex formation (K_{eq}) in mixed aqueous–organic solvents for the following reaction:[50]

$$[Co(NH_3)_5OH_2]^{3+} + Cl^- \overset{K_{IP}}{\rightleftharpoons} \text{(ion pair)} \rightleftharpoons [Co(NH_3)_5Cl]^{2+} + H_2O$$

At 318 K in 10:1 (mole ratio) of H_2O:DMSO $K_{IP} = 1.21 \pm 0.20$ and $K_{eq} = 3.74 \pm 0.25$, and in 25% (wt/wt) H_2O:EtOH $K_{IP} = 1.58 \pm 0.17$ and $K_{eq} = 6.07 \pm 0.54$. These results were used together with a study of the rates of aquation and anation at 318 K over a range of chloride-ion concentrations ($0 < [Cl^-] < 0.9$ mol dm^{-3}) to show that an I_d rather than a D mechanism applies. The aquation rate is independent of $[Cl^-]$, and the anation rate varies inversely with $[Cl^-]$.[50]

Two studies have appeared describing the effect of high pressures on the rate of aquation of cobalt(III) complexes. Hydrolysis of *trans*-$[Co(en)_2Cl_2]^+$ has been studied at pressures up to 2.5 kbar and at four temperatures in the range (292—328 K).[51] Values of $\Delta C_p^{\ddagger}$ for the acid-independent aquation pathways of the $[Co(NH_3)_5X]^{n+}$ ions ($X = Br^-$ or SO_4^{2-}) in 0.1 mol dm^{-3} $HClO_4$ are reported to be strongly temperature-dependent, a pronounced maximum occurring near 308 K, and values of $\Delta C_p^{\ddagger}$ are approximately twice as large for $X = SO_4^{2-}$ as for $X = Br^-$. These results are explained in terms of solvational changes occurring during the activation process using a modified theory due to Leung and Grunwald.[52] Reviews dealing with high-pressure studies were mentioned previously.[8,9]

Aquation of $[Co(RNH_2)_5H_2O]^{3+}$ ions (R = Me, Et, Pr^n, Bu^n, or Bu^i) is reported to proceed with loss of one amine ligand followed by spontaneous reduction to the cobalt(II) state.[53] The instability of the $[Co(RNH_2)_4(H_2O)_2]^{3+}$ ion differs from that found for the analogous ammine complexes, since reduction to cobalt(II) only occurs for the $[Co(NH_3)_n(H_2O)_{6-n}]^{3+}$ ions when $n \leqslant 3$.[54]

Hg^{2+} reacts rapidly with the $[Co(NH_3)_5SCN]^{2+}$ ion to give the dinuclear complex ion $[(H_3N)_5Co(SCN)Hg]^{4+}$, the equilibrium constant for formation being 1.2 mol dm^{-3} ($\Delta H^{\circ} = -5.2$ kcal mol^{-1} and $\Delta S^{\circ} = -17$ cal K^{-1} mol^{-1} at 298.1 K, and $I = 1.0$ mol l^{-1}).[55] This dinuclear species undergoes two parallel reactions at approximately equal rates; one pathway gives the linkage isomer $[(H_3N)_5Co(NCS)Hg]^{4+}$ and the second pathway involves aquation to the $[Co(NH_3)_5H_2O]^{3+}$ ion. The

[49] W. L. Reynolds, N. Morey, S. C. McFarlan, M. Collins, and M. Rigney, *J. Amer. Chem. Soc.*, 1975, **97**, 7165.
[50] W. L. Reynolds and E. S. Barber, *Internat. J. Chem. Kinetics*, 1975, **7**, 443.
[51] H. Lentz and S. O. Oh, *Chem. Abs.*, 1976, **84**, 35836p.
[52] A. M. Newton and T. W. Swaddle, *J. Phys. Chem.*, 1975, **79**, 795.
[53] R. Mitzner and W. Depkat, *Z. phys. Chem. (Leipzig)*, 1974, **255**, 861.
[54] See P. Moore, in 'Inorganic Reaction Mechanisms', ed. A. McAuley, Specialist Periodical Reports, The Chemical Society, London, 1976, Vol. 4, p. 133.
[55] A. Adegite, M. Orhanović, and N. Sutin, *Inorg. Chim. Acta*, 1975, **15**, 185.

rapid rate of disappearance of $[(H_3N)_5Co(SCN)Hg]^{4+}$ is characterized by $k=0.23$ s^{-1}, $\Delta H^{\ddagger}=21.4$ kcal mol^{-1}, and $\Delta S^{\ddagger}=10$ cal K^{-1} mol^{-1} at 298.1 K. A common intermediate is proposed for the aquation and isomerization processes.[55]

A study of the acid hydrolysis of complexes of the type *cis*- and *trans*-$[Co(en)_2(OCOR)_2]^+$ has been reported, and values of $\Delta H^{\ddagger}$ support the postulated 'special *cis* effect' (Przystas, Ward, and Haim, 1973). This effect explains the marked difference in reactivity between *cis*- and *trans*-complexes, the *cis*-complexes being in a position to form a hydrogen-bonded cyclic structure.[56]

Previous studies of the hydrolysis of the $[Co(NH_3)_5NO_2]^{2+}$ ion at very high and low pH have been shown to produce the $[Co(NH_3)_5OH]^{2+}$ and $[Co(NH_3)_5OH_2]^{3+}$ ions respectively. However, a recent study in ammonia–ammonium perchlorate buffer is at variance with the generally accepted picture of an inert $[Co^{III}(NH_3)_n]$ frame, there being evidence for preferential loss of the ammonia molecule in a *trans* position to the nitro-group under these conditions:

$$[Co(NH_3)_5NO_2]^{2+} \xrightarrow{k_2} [Co(NH_3)_5OH]^{2+}$$
$$\underset{k_1}{\rightleftharpoons} \qquad \uparrow$$
$$trans\text{-}[Co(NH_3)_4(NO_2)(OH)]^{+}$$

A comparison of the activation parameters for these reactions under various conditions is shown in Table 3. In an ammonia buffer $k_1 > k_2$, the nitro-group exerting a *trans* effect which is reflected in the activation parameters for the reaction.[57]

Table 3 *Comparison of activation parameters at* 298.1 K *for reactions of the* $[Co(NH_3)_5NO_2]^{2+}$ *ion under various conditions (data from ref.* 57)

Reaction	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	*Conditions*
Base hydrolysis	158.7±2	168.6±6	Ammonia buffer
Base hydrolysis	156	177	NaOH; $I=0$ (extrapolated)
Base hydrolysis[a]	153±1	149±4	$I=1.0$ (NaOH)
Aquation	135.7±6	51.0±18	Ammonia buffer
Aquation[a]	124	19	$I=0.12$ ($HClO_4$)
Redox	131	27	$I=1.0$ (HOAc)

[a] Comparable activation parameters for the hydrolysis of the $[Co(NH_3)_6]^{3+}$ ion in 0.16 mol l^{-1} $HClO_4$ and 1.4 mol l^{-1} NaOH are respectively $\Delta H^{\ddagger}=153$ kJ mol^{-1} and $\Delta S^{\ddagger}=45$ J K^{-1} mol^{-1} (aquation) and $\Delta H^{\ddagger}=144$ kJ mol^{-1} and $\Delta S^{\ddagger}=114$ J K^{-1} mol^{-1} (base hydrolysis at high pH).

A number of reports have appeared outlining the effects of ion-pairing upon the rates of hydrolysis of complex ions of the type $[Co(NH_3)_5X]^{n+}$. When X = Cl ($n=2$), ion pairs formed with maleate and phthalate ions increase the rate of aquation, and the equilibrium constants and associated thermodynamic parameters for ion-pair formation were obtained along with the rate constants at 313—323 K.[58] When X is unidentate oxalate ion (ox^{2-}), SO_4^{2-} and HSO_4^- ions accelerate the rate of acid hydrolysis through the formation of the ion pairs $[Co(NH_3)_5ox]^{3+}$,SO_4^{2-} and

[56] V. Carunchio, A. Messina, and G. Ortaggi, *Ann. Chim. (Italy)*, 1974, **64**, 111.
[57] S. Balt and C. Dekker, *J. Coordination Chem.*, 1975, **4**, 167.
[58] N. C. Naik and R. K. Nanda, *J. Indian Chem. Soc.*, 1975, **52**, 1169.

$[Co(NH_3)_5oxH]^{2+}$,SO_4^{2-}. Base hydrolysis of $[Co(NH_3)_5ox]^+$ is not affected by OAc^-, but the rate of reaction is retarded by other ions in the order $CO_3^{2-} < SO_4^{2-} < PO_4^{3-}$.[59] When X is unidentate malonate ion, the rate of aquation is accelerated by added cations M^{3+} (M = Al, Ga, or In) owing to complex formation with the unco-ordinated carboxylate group:

$$[Co(NH_3)_5O_2CCH_2CO_2H]^{2+} + M^{3+} \rightleftharpoons [Co(NH_3)_5O_2CCH_2CO_2M]^{4+} + H^+$$

Equilibrium constants are reported along with the rate constants at 333 K and $I = 0.3$ mol dm^{-3}.[60] The reactions are believed to proceed with Co—O bond fission. In a related study of the rate of aquation of the *cis*-$[Co(en)_2(NH_3)O_2CCO_2]^+$ ion, the order of catalytic effectiveness of added metal ions parallels the stability constants for complexation with the unco-ordinated carboxylate group: $Mn^{II} < Co^{II} < Ni^{II} < Cu^{II} > Zn^{II}$; $In^{III} < Al^{III} \sim Ga^{III} < Fe^{III}$; and tervalent ions are more effective than bivalent ions.[61] In a further study of the rate of acid hydrolysis of the $[Co(NH_3)_5O_2CR]^{2+}$ ions [R = CH_2CO_2H, $(CH_2)_2CO_2H$, *o*-$C_6H_4CO_2H$, or *o*-C_6H_4OMe] the observed rate constants (k) vary linearly with $[H^+]$ (5×10^{-3}—0.30 mol dm^{-3}); $k = k_1 + k_2[H^+]$ at constant ionic strength ($I = 0.30$ mol dm^{-3}). The unco-ordinated carboxylate groups do not catalytically affect the values of k_1 and k_2, and again Co—O bond fission is postulated for both pathways.[62] pK_a values were determined for the phthalate and malonate complexes. The rate of chelate ring closure for the $[Co(en)_2Cl(NH_2CH_2CO_2)]^+$ ion containing unidentate *N*-bound glycinate ion has also been studied in the presence of H^+ and Cu^{2+} ions. The formation of the $[Co(en)_2gly]^{2+}$ ion proceeds with inhibition by co-ordination of H^+ and Cu^{2+} at the unbound carboxylate group.[63] Loss of the Cl^- ion is rate determining, and the question arises whether or not a ring closure of this type proceeds *via* an aqua-intermediate of the type $[Co(en)_2(OH_2)(NH_2CH_2CO_2)]^+$. This question has been partially answered in studies of related systems of the type $[CoLX]^{2-}$, $[Co(HL)X]^-$, and $[CoL(OH_2)]^-$ (L = edta^{4-}, cydta^{4-}, or *N*-methylethylenediamine-*NN'N'*-triacetate ion, Meedta^{3-}; X = Cl or Br).[64] The rate of ring closure for the $[Co(edtaH)Cl]^-$ ion is approximately ten times as large as for the aquation of the very similar ion $[Co(Meedta)Cl]^-$ and is attended by a substantially smaller $\Delta H^{\ddagger}$ value. This strongly suggests that ring closure within the $[Co(edtaH)Cl]^-$ ion occurs directly without prior formation of $[Co(edtaH)(OH_2)]$. There is evidence for the absence of an aqua-intermediate in the ring closure of $[Co(cydta)Cl]^{2-}$ also:

$$[Co(cydta)Cl]^{2-} + H_2O \xrightarrow{k_1} [Co(cydta)(OH_2)]^- + Cl^-$$

$$[Co(cydta)(OH_2)]^- \xrightarrow{k_2} [Co(cydta)]^- + H_2O$$

At 325 K, separate experiments show that $k_1 = 10^{-3}$ s^{-1} and $k_2 = 10^{-2}$ s^{-1}, so that if this were the mechanism for ring closure at least 8% of the total cobalt(III) species would be in the form of the aqua-intermediate at some stage of the reaction. Spectral studies indicate that the maximum amount of $[Co(cydta)(OH_2)]^-$ ion formed is

[59] A. C. Dash and R. K. Nanda, *J. Indian Chem. Soc.*, 1975, **52**, 298.
[60] A. C. Dash and R. K. Nanda, *J. Inorg. Nuclear Chem.*, 1975, **37**, 2139.
[61] A. C. Dash and R. K. Nanda, *J. Indian Chem. Soc.*, 1975, **52**, 289.
[62] A. C. Dash and R. K. Nanda, *J. Inorg. Nuclear Chem.*, 1976, **38**, 119.
[63] A. C. Dash, R. K. Nanda, and S. K. Mohapatra, *J.C.S. Dalton*, 1975, 897.
[64] M. H. Evans, B. Grossman, and R. G. Wilkins, *Inorg. Chim. Acta*, 1975, **14**, 59.

substantially less than 8%, so direct ring closure is again likely.[64] Another remarkable feature of this study is the observation that the rate constant for ring closure of the cydta complex containing a protonated carboxylate group, $[Co(cydtaH)OH_2]$ ($10^4k = 160\ s^{-1}$ at 298.1 K), is substantially larger than for the unprotonated complex, $[Co(cydta)OH_2]^-$ ($10^4k = 7.0\ s^{-1}$ at 298.1 K). This is attributed to the proton of the constrained carboxylic acid group partially assisting with the departure of the co-ordinated water molecule, although in the related chloro-complexes $[Co(cydtaH)Cl]^-$ and $[Co(cydta)Cl]^{2-}$ a similar but less pronounced rate difference is observed ($10^4k = 1.5$ and $0.7\ s^{-1}$ respectively at 298.1 K). The less hindered complexes of edta and 1,2-pdta show the opposite behaviour as might be expected. Rate data for the ring closure and aquation of these and related complexes are collected in Table 4.

Table 4 *Rate data at* 298.1 K *for the aquation or ring closure of several diaminopolycarboxylate complexes of cobalt*(III) (*data from ref.* 64)

Complex[a]	*Reaction*[b]	$10^4k/s^{-1}$	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal K^{-1} mol^{-1}
$[Co(edtaH)OH_2]$	rc	2.3	25.0	+9
$[Co(edta)OH_2]^-$	rc	19	24.6	+12
$[Co(edtaH)Cl]^-$	rc	0.01	23.5	−5
$[Co(edta)Cl]^{2-}$	rc	0.03	22.9	−7
$[Co(edta)Br]^{2-}$ [c]	rc	0.30	21.8	−7
$[Co(edta)Br]^{2-}$ [d]	rc	0.030	24.6	+2
$[Co(cydtaH)OH_2]$	rc	160		
$[Co(cydta)OH_2]^-$	rc	7.0	18.8	−10
$[Co(cydtaH)Cl]^-$	rc	1.5	17.8	−3
$[Co(cydta)Cl]^{2-}$	rc	0.70	19.9	+4
$[Co(1,2\text{-}pdtaH)OH_2]$	rc	2.7	25.4	+10
$[Co(1,2\text{-}pdta)OH_2]^-$	rc	20	23.4	+7
$[Co(1,2\text{-}pdtaH)Cl]^-$	rc	0.04	20.3	−10
$[Co(1,2\text{-}pdtaH)Br]^-$	rc	0.12	16.6	−26
$[Co(Hydta)OH_2]$	rc	0.19	27.6	+13
$[Co(Hydta)Cl]^-$	rc	0.01	20.8	−16
$[Co(Hydta)Br]^-$	rc	0.05	20.6	−13
$[Co(Medta)Cl]^-$	aq	0.0028	25.7	−2
$[Co(Medta)Br]^-$ [e]	aq	0.021	23.5	−6
$[Co(Medta)Br]^-$ [e]	aq	0.0056	22.7	−11

[a] 1,2-pdta^{4-} = 1,2-diaminopropane-*NNN'N'*-tetra-acetate ion; Hydta^{3-} = *N*-(2-hydroxyethyl)ethylenediamine-*NNN'*-triacetate ion; Medta^{3-} = *N*-methylethylenediamine-*NN'N'*-triacetate ion. [b] rc = ring closure; aq = aquation. [c,d] Probably 'axial' and 'equatorial' isomers respectively; see O. W. Howarth, P. Moore, and N. Winterton, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 553. [e] Isomers of unknown structure, possibly the same as *c* and *d*.

Several other examples involving the aquation of unidentate ligands in complexes of the type $[Co(en)_2LX]^{n+}$ or $[CoA_4LX]^{n+}$ [A_4 = $(dmgH)_2$ or other planar quadridentate N-donor ligand, L and X are unidentate ligands] will be found in later sections dealing with the effects of non-leaving groups, solvent effects, and catalysed aquation by acids, bases, electrophiles such as the Hg^{2+} ion, and micellar and heterogenous catalysis.

Multidentate Leaving Groups.—Rate data are reported for the acid-catalysed

aquation of the $[Co(phen)_2(ox)]^+$ ion in aqueous HCl–KCl ($I=2.0$, $[H^+]=1$—2.0 mol dm^{-3}).[65] Only one step was observed, to give the *cis*-$[Co(phen)_2(OH_2)_2]^{3+}$ ion as product: the rate is given by $Rate=k[H^+][Co(phen)_2(ox)^+]$, and at 348 K $10^5k=1.03$ dm^3 mol^{-1} s^{-1}, $\Delta H^{\ddagger}=22.1$ kcal mol^{-1}, $\Delta S^{\ddagger}=-18.7$ cal K^{-1} mol^{-1}.

Effects of Non-leaving Ligands.—$[Co(en)_2XY]^{n+}$ *Complexes.* A number of different groups have reported rate data for the aquation of cobalt(III) complexes of the type *cis*- and *trans*-$[Co(en)_2XY]^{n+}$ (X and Y are unidentate ligands with X the leaving group). The results are collected in Table 5. When X = Cl, the ratio of the rate

Table 5 *Summary of recent rate data for the aquation of* cis- *and* trans-$[Co(en)_2XY]^{n+}$ *ions* (X *and* Y *are unidentate ligands,* X *the leaving group), at* 298.1 K *unless specified*

X	Y	*Geometry*	10^6k/s^{-1}	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal K^{-1} mol^{-1}	*Ref.*
Cl	CN	*cis*	0.62	24.6	−5	66
Cl	CN	*trans*	82	22.5	−2	66
NO_2	NO_2	*cis* or *trans*	*ca.* 0.3[a]			67
Cl	OH	*cis*	1830[b]			68
Br	aniline	*cis*	5.5[c]	22.6	10.7	69
Br	*m*-toluidine	*cis*	10.4[c]			70
Br	CB(*m*-toluidine)[d]	*cis*	13.4[c]			70
Br	*m*-xylidine	*cis*	0.95[c]	24.9	−2.1	71
Br	CB(*m*-xylidine)[d]	*cis*	2.21[c]	21.2	−7.6	71
N_3, Cl	N_3, Cl	*cis* or *trans*	[e]			49

[a] Data reported for several counterions. [b] At 283 K; data also reported in aqueous–organic solvents. [c] At 313 K. [d] Conjugate base of these amines, MeC_6H_4NH. [e] Hg^{2+}- or NO^+-induced aquation studies.

constants for aquation of the *trans*- and *cis*-complexes (k_{trans}/k_{cis}) increases dramatically with Y along the sequence $NH_3<N_3<NO_2<CN$. However, the absolute reactivities do not follow the same sequence, both *cis*- and *trans*-$[Co(en)_2(CN)Cl]^+$ ions being less labile than the corresponding $[Co(en)_2(NO_2)Cl]^+$ ions, the *cis*-species reacting more to change than the *trans*-complex. If the *trans*-labilizing effect was the dominant influence controlling reactivity, it would be necessary for the absolute reactivities and the ratio k_{trans}/k_{cis} to follow the same reactivity sequence. It is concluded, therefore, that although cyanide ion does exert a specific *trans*-labilizing effect, this is opposed by a positionally non-specific retarding effect which arises from its π-acceptor properties.[66] The spontaneous and Hg^{II}-catalysed aquations of the *cis*-$[Co(en)_2(CN)Cl]^+$ ion proceed with 100% retention of configuration, but base hydrolysis gives 90% *cis*- and 10% *trans*-$[Co(en)_2(CN)(OH)]^+$. Spectroscopic and kinetic evidence was found for an adduct with Hg^{II}.

Precise conductivity measurements have been used to study the effect of varying the counterions in complexes of the type *cis*- and *trans*-$[Co(en)_2(NO_2)_2]X$ (X^- = Cl^-, Br^-, I^-, NO_3^-, or ClO_4^-) on the extent of the ion-pairing and on the rate of the very slow aquation.[67] The effect on the rate constants is not marked except when

[65] J. Roy and D. Banerjea, *J. Inorg. Nuclear Chem.*, 1976, **38**, 1313.
[66] M. L. Tobe and C. K. Williams, *Inorg. Chem.*, 1976, **15**, 918.
[67] A. D. Pethybridge and D. J. Spiers, *J.C.S. Faraday I*, 1976, **72**, 64.

X^- = $[Co(edta)]^-$ when the rate constant increases by a factor of *ca.* 10. This is attributed to a lowering of the pH arising from the solvolysis of the $[Co(edta)]^-$ ion:

$$[Co(edta)]^- + H_2O \rightleftharpoons [Co(edta)OH_2]^- \rightleftharpoons [Co(edta)OH]^{2-} + H^+$$

Conjugate-base formation is again reported in several studies of the aquation of $[Co(en)_2(RC_6H_4NH_2)Br]^{2+}$ ions even under fairly acidic conditions (*ca.* 10^{-3}—0.1 mol dm^{-3} (H^+)). The conjugate base, $[Co(en)_2(RC_6H_4NH)Br]^+$ hydrolyses significantly faster than the parent ion as expected. For example, a rate increase of *ca.* 13 is observed at 313 K for the conjugate base of the complex containing *m*-toluidine.[70]

$[Co(LL)_2(L)X]^{n+}$ *and* $[Co(LLL)(LL)X]^{n+}$ *Complexes.* Here L, LL, and LLL are uni-, bi-, and ter-dentate ligands with X the leaving group. A possible correlation has been observed between the in-plane δ(N—Co—N) modes in the low-frequency i.r. spectra of *trans*-$[Co(amine)_4Cl_2]^+$ ions and the rate constants for aquation (see Figure). This

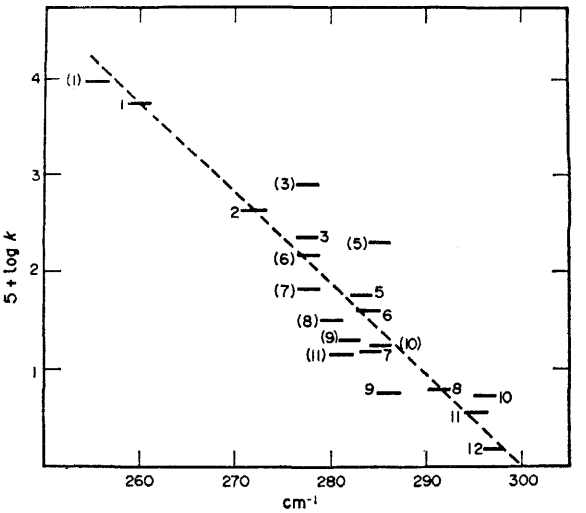


Figure *Variation of the rate constant (k) for the aquation of* trans-$[Co(amine)_4X_2]^+$ *ions with the in-plane* δ(N—Co—N) *deformation frequencies in their i.r. spectra. Figures in parentheses refer to* X = Br; *otherwise* X = Cl. $(amine)_4$ = $(tmd)_2$ (1), $(NH_2CHMeCHMeNH_2)_2$ (2), $(NH_2CMe_2CH_2NH_2)_2$ (3), $(NH_3)_4$ (4), (NH_3)(dien) (5), (en)(tmd) (6), (pn)(tmd) (7), $(pn)_2$ (8), (en)(pn) (9), 3,2,3-tet (10), $(en)_2$ (11), 2,3,2-tet (12)

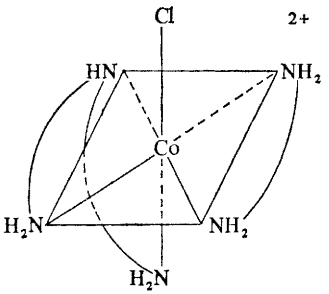
correlation may reflect the ease with which these complexes can distort *via* a deformational vibration made to a trigonal-bipyramidal structure.[72, 73]

[68] V. V. Udovenko, L. G. Reiter, and A. A. Andreiko, *Zhur. neorg. Khim.*, 1974, **19**, 2794.
[69] R. Ripan and M. Várhelyi, *Chem. Abs.*, 1975, **83**, 66093.
[70] Cs. Várhelyi, I. Zsakó, and I. Gherghel-Kiss, *Zhur. neorg. Khim.*, 1974, **19**, 1842.
[71] R. Ripan and M. Várhelyi, *Rev. Roumaine Chim.*, 1975, **20**, 523.
[72] L. M. Eade, G. A. Rodley, and D. A. House, *J. Inorg. Nuclear Chem.*, 1975, **37**, 1049.
[73] L. S. Dong and D. A. House, *Inorg. Chim. Acta*, 1976, **19**, 23.

Table 6 *Comparison of kinetic parameters at* 298.2 K *for the aquation of chloropentaaminecobalt*(III) *complexes containing polyamine ligands (data from refs.* 72 *and* 73)

Complex	*Structure*	$10^7 k/s^{-1}$	$\log(PZ/s^{-1})$	E_a/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
$[Co(dien)(en)Cl]^{2+}$	(12)	2.56	12.78	110±5	−8±10
$[Co(dien)(tmd)Cl]^{2+}$	(12)	43.0	7.40	72.8±4	−111±8
$[Co(dien)(en)Cl]^{2+}$	(13)	1.78	11.57	104±5	−31±10
$[Co(dien)(tmd)Cl]^{2+}$	(13)	56.5	11.36	94.7±3	−36±6
$[Co(dpt)(en)Cl]^{2+}$	(13)	213	11.88	94.5±2	−25±4
$[Co(dien)(en)Cl]^{2+}$	(14)	0.94	12.84	113±4	−7±8
$[Co(dien)(tmd)Cl]^{2+}$	(14)	2.15	12.69	110±3	−10±6
$[Co(dpt)(en)Cl]^{2+}$	(15)	116	12.68	105±3	−10±6
$[Co(dpt)(tmd)Cl]^{2+}$	(15)	174	10.51	87.2±6	−52±12
Racemization reactions					
$[Co(dien(tmd)OH_2]^{3+}$	(12)	9.1	16.80	130±2	68±4
$[Co(en)_2(NH_3)OH_2]^{3+}$		0.018	17.49	150	82

Rate data for the aquation of three geometric isomers of the $[Co(dien)(tmd)Cl]^{2+}$ ion and one isomer of $[Co(dpt)(tmd)Cl]^{2+}$ [dpt = $NH_2(CH_2)_3NH(CH_2)_3NH_2$], together with the rate of racemization of the product Δ-$[Co(dien)(tmd)OH_2]^{3+}$, ion are collected in Table 6. The proposed structures of the geometric isomers are (12)—(15). In all cases the six-membered ring compounds aquate much more rapidly than their five-membered ring analogues, except for configuration (14) where the rate



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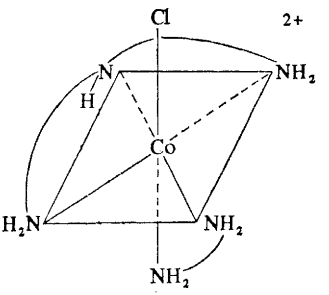

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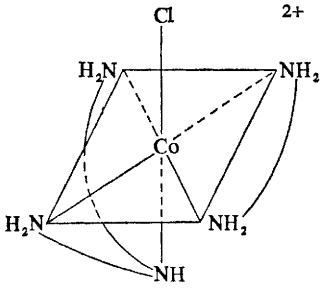

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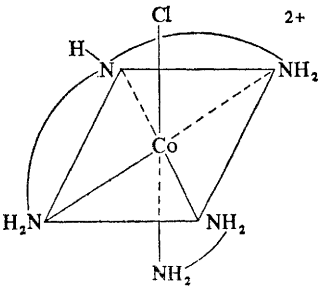


(15)

increases by only a factor of 2.4. Curiously, replacing 1,2-diaminoethane (en) by 1,3-diaminopropane (tmd) causes a 32-fold rate increase whereas for the analogous chromium(III) complexes the two rates are almost identical. The rate differences for the cobalt complexes can be explained in terms of a dissociative mechanism, with a trigonal-bipyramidal transition state which is formed more readily by the 'loose' chelating systems such as (tmd)(dien), (en)(dpt), and (tmd)(dpt), compared with the 'tight' chelating systems such as (en)(dien) which restrict this distortion.

Careful studies have shown that highly pure samples of the *cis*-$[M(N\text{–}N)_2Cl_2]^+$ ions (N–N = bipy or phen, M = Co^{III} or Cr^{III}) are much more inert than their ethylenediamine analogues.[74] For example, a solution of the $[Co(phen)_2Cl_2]^+$ ion in 10^{-3} mol dm^{-3} HCl does not show any hydrolysis after two weeks in the dark! These reactions are catalysed by traces of cobalt(II) and by light. In basic solution relatively rapid reactions occur for the cobalt complex without conjugate-base formation, and a redox mechanism is favoured. The alternative possibility of OH^- ion attacking at the aromatic rings was mentioned previously.[24] In view of these observations, the data reported recently for the aquation of the $[Co(N\text{–}N)(NO_2)Cl]^+$ and $[Co(N\text{–}N)(en)(NH_3)X]^{2+}$ ions (N–N = bipy or phen; Table 7) should be judged with some caution. In these studies the acid dissociation constants of the product aqua-ions were

Table 7 *Rate data at* 298.2 K *for the aquation of* cis-$[Co(LL)_2XY]^+$ *and* $[Co(LL)(en)(NH_3)X]^{2+}$ *ions* (LL = bipy *or* phen, X = *halide ion*, Y = *halide or nitrite ion*) (*data from refs.* 75 *and* 76)

Complex	$10^4k/s^{-1}$	E/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
$[Co(bipy)_2(NO_2)Cl]^+$	2.5	14.9±0.9	−24.9±0.05
$[Co(bipy)_2(NO_2)Br]^+$	2.4	14.1±0.6	−28.0±0.2
$[Co(bipy)_2Cl_2]^+$	1.0	21.4	3.1
$[Co(phen)_2(NO_2)Cl]^+$	0.13	16.0±0.7	−22.6±0.1
$[Co(phen)_2(NO_2)Br]^+$	1.4	19.2±0.9	−11.8±0.2
$[Co(phen)_2Cl_2]^+$	0.68	23.7	9.9
$[Co(phen)(en)(NH_3)Cl]^{2+}$	0.065	27.6±0.3	18.5±0.2
$[Co(phen)(en)(NH_3)Br]^{2+}$	0.15	29.0±0.4	24.8±0.1
$[Co(bipy)(en)(NH_3)Cl]^{2+}$	0.045	28.0±0.5	20.0±0.1
$[Co(bipy)(en)(NH_3)Br]^{2+}$	0.22	28.4±0.6	23.6±0.1

determined and used to try to establish the geometry of the $[Co(N\text{–}N)(en)(NH_3)X]^{2+}$ ions. The base hydrolysis of the $[Co(N\text{–}N)(NO_2)Cl]^+$ ion is reported to be faster for the bipy than for the phen complex.

$[Co(LLLL)(L)X]^{n+}$ *and* $[Co(LLLLL)X]^{n+}$ *Complexes.* Included in this section are studies in which the non-leaving group is an open-chain or cyclic quadridentate (LLLL) or quinquedentate (LLLLL) ligand. Excluded are the complexes of edta and related ligands discussed earlier [64] and the dioximato-complexes covered in the next section.

A study of the spontaneous and mercury(II)-catalysed aquations of the α-*cis*-

[74] M. P. Hancock, J. Josephsen, and C. E. Schäffer, *Acta Chem. Scand.*, 1976, **A30**, 79.
[75] D. M. Palade, T. N. Volokh, G. V. Chudaeva, and E. G. Saakyan, *Zhur. neorg. Khim.*, 1975, **20**, 715.
[76] D. M. Palade, E. V. Popa, A. Ablov, N. A. Breslavskaya, and G. V. Chudaeva, *Zhur. neorg. Khim.*, 1975, **20**, 2138.

$[Co(eee)LX]^{n+}$ ions [eee = $NH_2(CH_2)_2S(CH_2)_2S(CH_2)_2NH_2$, L = X = Cl, or L = H_2O, X = Cl][77] follows an earlier study of the *cis*- and *trans*-$[Co(ete)LX]^{n+}$ ions [ete = $NH_2(CH_2)_2S(CH_2)_3S(CH_2)_2NH_2$].[78] The ligands eee and ete are analogous to dien and 2,3,2-tet respectively, with sulphur atoms replacing the secondary amine groups. For aquation of *α-cis*-$[Co(eee)Cl_2]^+$, $10^4k = 1.77\ s^{-1}$ at 323 K in 0.1 mol dm^{-3} $HClO_4$, $\Delta H^{\ddagger} = 20.4$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -12.6$ cal K^{-1} mol^{-1}, and for the aquation of *α-cis*-$[Co(eee)(OH_2)Cl]^{2+}$, $10^6k = 1.1\ s^{-1}$ at 323 K. The Hg^{II}-induced aquation of the $[Co(eee)Cl_2]^+$ ion proceeds *via* a dinuclear complex:

$$-d[Co(eee)Cl_2^+]/dt = k_1K[Hg^{II}][Co^{III}]/\{1 + K[Hg^{II}]\}$$

At 288 K in 0.1 mol dm^{-3} $HClO_4$, $10^2k_1 = 2.72\ s^{-1}$ and $K = 34.4$ mol dm^{-3}. The Hg^{II}-induced aquation of the $[Co(eee)(OH_2)Cl]^{2+}$ ion proceeds with second-order kinetics, the rate constant being 8.41×10^{-2} dm^3 mol^{-1} s^{-1} at 323 K in 0.1 mol dm^{-3} $HClO_4$, with $\Delta H^{\ddagger} = 22.7$ kcal mol^{-1} and $\Delta S^{\ddagger} = 6.75$ cal K^{-1} mol^{-1}. The thioether atoms play a deactivating role when in a *trans* position to the active sites within these complex ions.[77]

A study of the acid hydrolysis [equations (1)—(3)] of the α- and β-$[Co(edda)CO_3]^-$ ons at high acidity[79] extends a previous study between pH 1 and 5.[80]

$$[Co(edda)CO_3]^- + H_2O \xrightarrow{k_0} [Co(edda)(OH)(CO_3H)]^- \quad (1)$$

$$[Co(edda)CO_3]^- + H_3O^+ \xrightarrow{k_1} [Co(edda)(OH_2)(CO_3H)] \quad (2)$$

$$[Co(edda)(OH_2)(CO_3H)] \xrightarrow{k_2} [Co(edda)(OH_2)(OH)] + CO_2 \quad (3)$$

At the higher pH values the rate-determining step is ring-opening (k_0, k_1), but as the acidity increases a limiting rate (k_2) is eventually attained. Rate constants and activation parameters associated with k_0, k_1, and k_2 are collected in Table 8. A

Table 8 *Rate parameters for the acid-catalysed aquation reactions of* α- *and* β-$[Co(edda)CO_3]^-$ *ions at* 298.1 K *and* $I = 2.0$ mol dm^{-3} (KNO_3) [*reactions* (1)—(3); *data from ref.* 79; *values in parentheses from ref.* 80 *at* $I = 1.0$ mol dm^{-3} ($NaClO_4$)]

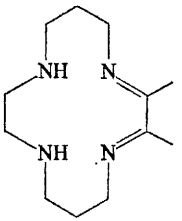
	$10^3k_0/s^{-1}$	k_1/l mol^{-1} s^{-1}	k_2/s^{-1}
α-Isomer: Rates	2.9±0.2 (2.2)	118±1 (83)	55.0
$\Delta H^{\ddagger}$/kcal mol^{-1}	17±2 (21±3)	12±1 (16±1)	11.1±0.6
$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	−14±7 (0±12)	−8±8 (5±3)	−13±2
β-Isomer: Rates	0.98±0.43 (0.38)	2.44±0.11 (3.04)	2.31
$\Delta H^{\ddagger}$/kcal mol^{-1}	21±6 (21±3)	10.8±0.3 (17±1)	16.3±1.5
$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	−2±20 (2±12)	−20±1 (2±3)	−2±5

significant amount of isomerization between the α- and β-forms was also observed to occur during the time taken to bring the solutions to constant temperature. Values of k_2 (the decarboxylation rate constant) are larger by a factor of more than 20 for

[77] J. H. Worrell, *Inorg. Chem.*, 1975, **14**, 1699.
[78] M. L. Tobe and M. L. Tucker, *Inorg. Chem.*, 1973, **12**, 2994.
[79] R. Van Eldik, T. P. Dasgupta, and G. M. Harris, *Inorg. Chem.*, 1975, **14**, 2573.
[80] P. J. Garnett and D. W. Watts, *Inorg. Chim. Acta*, 1974, **8**, 293, 313.

α-[Co(edda)(OH_2)(CO_3H)] and for [Co(nta)(OH_2)(CO_3H)] (at 298.1 K, $k_2 = 57.1$ s^{-1}, $\Delta H^{\ddagger} = 15.3$ kcal mol^{-1}, and $\Delta S^{\ddagger} = 1$ cal K^{-1} mol^{-1}) compared with the β-edda-isomer, the presence of an amido-group in a *cis* position to the bicarbonate group somewhat hindering the decarboxylation process. Values of the ring-opening rate constant, k_1, vary by a factor of more than 10^7 between the complex ion most resistant to aquation {$[Co(py)_4CO_3]^+$, $10^6 k_1 = 8.9$ s^{-1}, $\Delta H^{\ddagger}$ 24.0 kcal mol^{-1}, and $\Delta S^{\ddagger} = 1$ cal K^{-1} mol^{-1} at 298.1 K} and the α-[Co(edda)CO_3]$^-$ ion, which aquates most rapidly. No clear-cut reason for this marked difference in reactivity can be given, there being no obvious variation with the overall charge on the complex ions or with the pK_a's of the non-leaving ligands. The anionic complexes are, however, much more reactive than the cationic species.[79]

Two more studies have appeared concerned with the effects of macrocyclic ligands upon the rates of aquation of cobalt(III) complexes.[81, 82] The complexes *trans*-[Co(L)(X)N_3]$^{n+}$ have been prepared[81] [L = (16), X = Cl or Br; L = (17), X = Cl, Br, N_3, or H_2O] and the rates of aquation studied and compared with data for the analogous complexes of cyclam [L = (18)]. The rates of aquation of corresponding complexes vary in the order (18) < (16) < (17); at 298.1 K relative rates are 1:440:2400 and 1:58:260 for X = Cl and Br respectively. The relative rates of



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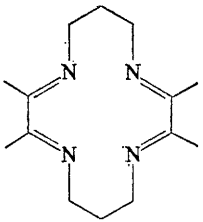

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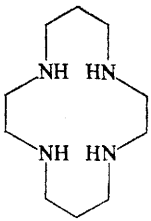

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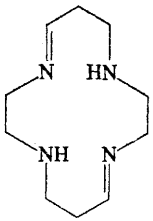

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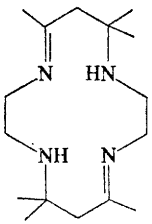


(20)

aquation of bromo- and chloro-complexes, k_B/k_{Cl}, are 11:1.4:1.1 for L = (18), (16), and (17) respectively, and these results support the view that increased lability is brought about by increasing the 'softness' of the central cobalt(III) ion by means of the increased extent of election delocalization between the metal ion and the encircling ligand. The results are collected in Table 9 together with those for the *trans*-[Co(L)(NO_2)Cl]$^+$ ions [where L is again a partially unsaturated ligand (19) or (20)].[82]

[81] C. K. Poon and C. L. Wong, *J.C.S. Dalton*, 1976, 966.
[82] R. W. Hay and G. A. Lawrance, *J.C.S. Dalton*, 1975, 1556.

Table 9 *Rate data for the aquation of* trans-$[Co(LLLL)XY]^{n+}$ *ions* (X = *leaving group*) *at* 298.1 K (*data from refs.* 81 *and* 82)

LLLL	X	Y	k_x/s^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
(16)	Cl	N_3	1.6×10^{-3}	25.8±0.5	13±4
(16)	Br	N_3	2.2×10^{-3}	20.8±0.2	0±1
(17)	Cl	N_3	8.8×10^{-3}	21.5±0.2	4±1
(17)	Br	N_3	1.0×10^{-2}	20.4±0.2	1±1
(18)	Cl	N_3	3.6×10^{-6}	23.7±0.3	−4±2
(18)	Br	N_3	3.8×10^{-5}	23.7±0.3	1±1
(19)[a]	Cl	NO_2	4.4×10^{-4}	18.5	−11.9
(18)	Cl	NO_2	4.3×10^{-5}	20.6	−8.8
(20)[b]	Cl	NO_2	5.5×10^{-4}		

[a] $k_{OH}=2.5\times10^{2}$ dm^3 mol^{-1} s^{-1}; $\Delta H^{\ddagger}=69$ kJ mol^{-1}; $\Delta S^{\ddagger}=24.5$ J K^{-1} mol^{-1}.
[b] $k_{OH}=2.2\times10^{2}$ dm^3 mol^{-1} s^{-1}.

The only report involving a complex of a quinquedentate ligand is for the α-$[Co(tetren)Cl]^{2+}$ ion. The rate constant for hydrolysis is given by $k=k_a+k_b[OH^-]$ as expected.[83]

Dioximato-complexes. References to studies of complexes of the type *trans*-$[Co(dioxime)_2(L)X]^{n+}$ are collected in Table 10. When L is an *S*-bonded sulphinato-ligand, RSO_2^- (R = Me or *p*-MeC_6H_4), the *trans* effect is greater than that of iodide

Table 10 *References to studies of dioximato-complexes of the type* trans-$[Co(dioxime)_2LX]^{n+}$ (X = *leaving group*)

Dioxime	L	X	*Reactions studied/conditions*	*Ref.*
$dmgH^-$	*S*-RSO_2^-	MeOH	R = Me or *p*-MeC_6H_4; formation studies with tu, *p*-toluidine, py, Pr_2S, Ph_3E (E = P, As, or Sb); methanol exchange	84
$dmgH^-$, diphenylglyoxime, α-benzyldioxime	NH_3, $PhNH_2$, py	Cl^-, Br^-, I^-	Solvolysis by MeOH, EtOH, DMF, or H_2O	85
$dmgH^-$	tu	tu	Solvolysis in mixed aqueous–organic solvents; rate of second step an order of magnitude slower than first step	86
	H_2O	tu		
$dmgH^-$	CN	Cl^-, Br^-, I^-	Aquation	87
$dmgH^-$	H_2O	NO_2^-	pH 3.7—8.0 and various temperatures	88
diacetyldioxime	CN^-	NO_2^-	Aquation	89
methyl-, dimethyl-, methylpropyl-, methylbutyl-, α-benzyl-, and 1,2-cyclohexanedione-dioximes	tu	tu	As ref. 86	90
	H_2O	tu		
	SO_3^{2-}	SO_3^{2-}	308—323 K; aquation and anation studies	91
$dmgH^-$	NH_3	Cl, Br	Hg^{II}- and Tl^{III}-catalysed aquations	92

[83] Z. F. Lin and C. Chen, *T'ai-wan K'o Hsueh*, 1974, **28**, 51.

ion, but much less than that of *S*-bonded sulphite ion; the relative order of the *trans*-effect is $CH_3^- > SO_3^{2-} \gg RSO_2^- > I^- \approx NO_2^-$. This *trans* effect has been shown to arise at least in part by a ground-state weakening of the cobalt–ligand bond in the *trans* position.[84] A *D* mechanism is thought to be likely for the replacement of MeOH in *trans*-[Co(dmgH)(RSO_2)(MeOH)] by a wide range of nucleophiles (tu, *p*-toluidine, py, Pr_2S, and Ph_3E, where E = P, As, or Sb).[84] The second-order formation rate constants are all in the range $(3.7—18.2) \times 10^{-2}$ dm^3 mol^{-1} s^{-1} at 298.1 K, with $\Delta H^{\ddagger}$ between 20.0 and 25.5 kcal mol^{-1}.

In a series of papers concerned with the rate of solvolysis of complexes of the type *trans*-[Co(dioxime)$_2$(amine)X], the effect of varying the dioxime (dimethyl- and diphenyl-glyoxime and α-benzyldioxime), the amine (py, NH_3, and $PhNH_2$), and the incoming solvent (MeOH, EtOH, DMF, and H_2O) was investigated for X = Cl, Br, and I.[85] For methanolysis of [Co(dmgH)$_2$(amine)X] the rates increase with the amine in the order $NH_3 < PhNH_2 <$ py, and decrease with X in the order Cl > Br > I. This behaviour is as expected for complexes which show class (*b*) behaviour. The effect of replacing dimethylglyoxime by diphenylglyoxime is to cause the rates to decrease in the order py > NH_3 > $PhNH_2$. Solvolysis by methanol is also observed to be much faster than by ethanol or DMF.[85]

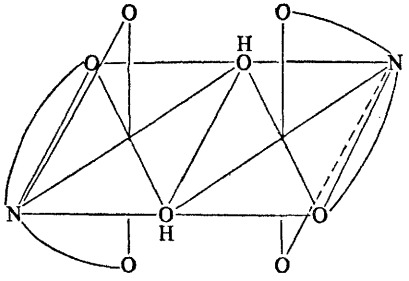
The stepwise solvolysis of the *trans*-[Co(dioxime)$_2$(tu)$_2$]$^+$ ions (dioxime = methyl-, dimethyl-, or methylpropyl-dioxime) has been studied,[86, 90] and for the methylglyoxime complexes the rate constants and activation parameters for the two steps were resolved:[90] $10^4k_1 = 10.0$ s^{-1}, $\Delta H^{\ddagger} = 23.5$ kcal mol^{-1}, and $\Delta S^{\ddagger} = +7$ cal K^{-1} mol^{-1}; $10^5k_2 = 11.0$ s^{-1}, $\Delta H^{\ddagger} = 24.2$ kcal mol^{-1}, and $\Delta S^{\ddagger} = +5$ cal K^{-1} mol^{-1}.

The Hg^{II}- and Tl^{III}-induced aquations of *trans*-[Co(dmgH)$_2$(NH_3)X] (X = Cl or Br) show that for these complexes Tl^{III} is a better electrophile than Hg^{II}; at 298.2 K and X = Cl, $10^2k = 3.91$ and 6.26 dm^3 mol^{-1} s^{-1}, $\Delta H^{\ddagger} = 121$ and 82 kJ mol^{-1}, and $\Delta S^{\ddagger} = 134$ and 8 J K^{-1} mol^{-1} for reactions with Hg^{II} and Tl^{III} respectively.[92]

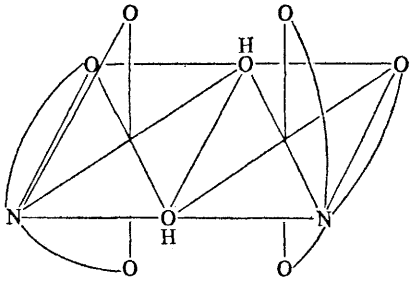
Demethylation of methylcobalamin by the electrophiles HgX_2 (X = ClO_4^-, AcO^-, Cl^-, Br^-, SCN^-, or CN^-) has also been reported.[93] Rates decrease in the order $OAc^- \gg Cl^- \geqslant SCN^- \geqslant Br^- \gg CN^-$, a sequence which correlates with the stability of the Hg—X bond. The $[HgX]^+$ ion acts as the more reactive electrophile in each case, $[HgCl_4]^{2-}$ ion is somewhat less reactive than $HgCl_2$, and HgCl(CN) is very unreactive.

Bridged Dicobalt Complexes.—A study of the acid-catalysed bridge-cleavage reactions of the [(nta)Co-μ-$(OH)_2$-Co(nta)]$^{2-}$ ion has revealed the presence of two isomers in solution [probably (21) and (22)] with differing reactivities.[94] The faster-reacting species is characterized by an observed rate constant, $k = 0.35 \pm 0.05$ s^{-1} at

[84] J. M. Palmer and E. Deutsch, *Inorg. Chem.*, 1975, **14**, 17.
[85] N. M. Samus and T. S. Luk'yanets, *Zhur. neorg. Khim.*, 1974, **19**, 2473, 2477, 2788.
[86] G. P. Syrtsova and G. I. Shpakov, *Zhur. neorg. Khim.*, 1975, **20**, 1887.
[87] Z. Finta and Cs. Várhelyi, *Acta Chim. Acad. Sci. Hung.*, 1974, **83**, 281.
[88] J. Zsakó, Cs. Várhelyi, Z. Finta, and J. Kiss-Jakab, *Z. Naturforsch.*, 1975, **30b**, 393.
[89] Cs. Várhelyi, Z. Finta, and S. Kiss, *Monatsh.*, 1975, **106**, 1325.
[90] G. P. Syrtsova and G. I. Shpakov, *Russ. J. Inorg. Chem.*, 1975, **20**, 1053.
[91] G. P. Syrtsova and N. N. Cheban, *Zhur. neorg. Khim.*, 1976, **21**, 1050; N. N. Cheban, *Chem. Abs.*, 1976, **84**, 170236.
[92] S. F. Chan and S. L. Tan, *Inorg. Nuclear Chem. Letters*, 1975, **11**, 435.
[93] H. Yamamoto, T. Yokoyama, J. L. Chen, and T. Kwan, *Bull. Chem. Soc. Japan*, 1975, **48**, 844.
[94] M. A. Thacker and W. C. E. Higginson, *J.C.S. Dalton*, 1975, 704.



(21)



(22)

2×10^{-2} mol dm^{-3} H^+ (298.1 K, $I = 1.0$ mol dm^{-3}), the reaction being first-order in $[H^+]$. The slower-reacting complex ion shows a more complex dependence on $[H^+]$ as expected for a mechanism of the following type:

$$[(\text{nta})\text{Co-}\mu\text{-}(\text{OH})_2\text{-Co(nta)}]^{2-} \underset{k_{-1}}{\overset{k_1[H^+]}{\rightleftharpoons}} [(H_2O)(\text{nta})\text{Co-}\mu\text{-(OH)-Co(nta)}(OH_2)]^-$$

$$[(H_2O)(\text{nta})\text{Co-}\mu\text{-(OH)-Co(nta)}(OH_2)]^- \xrightarrow{k_2[H^+]} 2[\text{Co(nta)}(OH_2)_2]$$

With this mechanism $k = a[H^+]^2/(b + [H^+])$, with $a = k_1 = 0.131 \pm 0.005$ dm^3 mol^{-1} s^{-1} and $b = k_{-1}/k_2 = (1.1 \pm 0.1) \times 10^{-2}$ mol dm^{-3}. An alternative $[H^+]$ dependence of the type $k = a[H^+] + b[H^+]^2$ could not be ruled out from the results obtained. At 298.1 K and 2×10^{-2} mol dm^{-3} H^+, the rate constant for the bridge-cleavage reaction of the slower-reacting isomer is $k = 1.6 \times 10^{-3}$ s^{-1}, at least 200 times less than that for the faster-reacting species. The product $[\text{Co(nta)}(OH_2)_2]$ is reduced to Co^{2+} by hydrazine, hydroquinone, hydroxylamine, iodide, and thiosulphate ions in acidic solutions. However, anation occurs with the NCS^- ion and with NO_2^- ion at pH 4.5, but at pH 5.6 NO_2^- ion again causes reduction. Similarities in the rate constants for these redox reactions suggest that the formation of an inner-sphere complex with the substrate is rate determining. Sulphite ion also causes reduction, but in this case the rate-determining step is decomposition of the rapidly formed sulphito-complex.[94]

Elimination of Cl^- ion from the $[(NH_3)_4\text{Co-}\mu\text{-}(NH_2,Cl)\text{-Co}(NH_3)_4]^{4+}$ ion (23) is catalysed by Hg^{2+} and Tl^{3+} ions. The uncatalysed reactions are[95]

$$[(NH_3)_4\text{Co-}\mu\text{-}(NH_2,Cl)\text{-Co}(NH_3)_4]^{4+} + H_2O$$
(23)

$$\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$$

$$[(H_2O)(NH_3)_4\text{Co-}\mu\text{-}(NH_2)\text{-Co}(NH_3)_4Cl]^{4+}$$
(24)

$$\downarrow k_2$$

$$[(NH_3)_4\text{Co-}\mu\text{-}(NH_2,OH)\text{-Co}(NH_3)_4]^{4+} + H^+ + Cl^-$$
(25)

Both reactions are independent of $[H^+]$ in the range 0.5—2.0 mol dm^{-3} with $I = 2.0$

[95] S. W. Foong, J. D. Edwards, R. S. Taylor, and A. G. Sykes, *J.C.S. Dalton*, 1975, 277.

mol dm^{-3} ($NaClO_4$). With Hg^{2+} there is a less than first-order dependence on $[Hg^{2+}]$ which cannot be satisfactorily accounted for in terms of a 1:1 adduct. Instead Hg^{2+} is believed to catalyse conversion of (24) into (25), with the steady-state approximation applying to (24). At 298.1 K, $k_1 = 3.02 \times 10^{-3}$ s^{-1}, $\Delta H^{\ddagger} = 19.2 \pm 0.5$ kcal mol^{-1}, $\Delta S^{\ddagger} = -5.7 \pm 1.8$ cal K^{-1} mol^{-1}, and $k_2/k_{-1} = 0.028$. The $[HgCl]^+$ ion is nearly as effective a catalyst as the Hg^{2+} ion, the relative rate constants being $k_4/k_2 = 1.3 \times 10^3$ dm^3 mol^{-1} and $k_3/k_2 = 1.57 \times 10^3$ dm^3 mol^{-1} respectively at 298.1 K. Tl^{3+}, however, produces only a small rate enhancement, $k_5/k_2 = 15$ dm^3 mol^{-1}, in contrast to the pronounced catalytic behaviour of Tl^{3+} towards mononuclear chloro-complexes.

Cleavage of the OH bridge in the $[(NH_3)_4Co\text{-}\mu\text{-}(NH_2,OH)\text{-}Co(NH_3)_4]^{4+}$ ion is brought about by excess thiocyanate ion in $HClO_4$ solution:[96]

$$[(NH_3)_4Co\text{-}\mu\text{-}(NH_2,OH)\text{-}Co(NH_3)_4]^{4+} + H^+ + NCS^- \downarrow [(NCS)(NH_3)_4Co\text{-}\mu\text{-}(NH_2)\text{-}Co(NH_3)_4(NCS)]^{3+} + H_2O$$

At low $[H^+]$ and $[NCS^-]$ the observed pseudo-first-order rate constant $k = k_1[H^+][NCS^-] + k_2[NCS^-]$, but k varies non-linearly with $[H^+]$ at concentrations above 0.5 mol dm^{-3}. At 298.1 K, $10^4 k_1 = 4.7 \pm 0.1$ dm^6 mol^{-2} s^{-1}, $\Delta H_1^{\ddagger} = 17.5 \pm 0.4$ kcal mol^{-1}, and $\Delta S_1^{\ddagger} = -14.7 \pm 1.4$ cal K^{-1} mol^{-1}.

The kinetics of the acid-catalysed decomposition of μ-peroxo-μ-hydroxo-dicobalt(III) complexes of the type $[LCo\text{-}\mu\text{-}(O_2,OH)\text{-}CoL]$ (L = trien, tren, or en_2) have been studied by the stopped-flow method.[97] The products are Co^{II} and protonated ligand L, and up to 100% of the bound O_2 is released. At 293 K and pH 2 the rate constants are in the range 10^{-3}—10^{-1} s^{-1} and depend not only on the nature of L but also on the ligand conformation and the diastereoisomeric structure of the dinuclear cation. When L = trien, eight isomers are possible, but oxygenation of $[Co(trien)]^{2+}$ in dilute solutions gives only three of them. Oxygenation of $[Co(en)_2]^{2+}$ gives approximately equal amounts of a racemate and a *meso*-form, the latter dissociating about five times faster than the former. When L = tren, only one of the three possible achiral isomers is formed.

Two groups have reported the formation of dinuclear complexes between cobalt(III) and iron(II) and iron(III) complexes. Discussion of these will be found in the sections concerned with iron complexes.

Solvent Variation.—References to the aquation of cobalt(III) complexes in mixed aqueous–organic solvents will be found in earlier sections. The aquation of the $[Co(NH_3)_5DMSO]^{3+}$ ion[46] and the equilibrium between Cl^- and $[Co(NH_3)_5OH_2]^{3+}$ ions[50] have been investigated in ethanol–water mixtures, and references to a few studies of the solvolysis of dioximato-complexes in mixed non-aqueous solvents are given in Table 10. The effect of solvent variation is the subject of Chapter 5.

Catalysed Aquation.—Electrophiles such as Hg^{2+} and Tl^{3+} are often used to catalyse the aquation of halogeno-complexes, the reactions nearly always proceeding with retention of configuration. Cases where such studies were carried out in parallel with an investigation of the uncatalysed aquation reactions will be found in previous

[96] K. L. Scott, R. S. Taylor, R. K. Wharton, and A. G. Sykes, *J.C.S. Dalton*, 1975, 2119.
[97] M. Zehnder, H. Maecke, and S. Fallab, *Helv. Chim. Acta*, 1975, **58**, 2306.

sections. Reactions of the *cis*-$[Co(en)_2(CN)Cl]^+$,[66] $[Co(NH_3)_5SCN]^{2+}$,[55] and *α-cis*-$[Co(eee)Cl_2]^+$ ions [eee = $NH_2(CH_2)_2S(CH_2)_2S(CH_2)_2NH_2$][77] with Hg^{2+} proceed with the formation of an adduct:

$$-d\{\ln[\text{Complex X}]\}/dt = kK[Hg^{2+}]/(1 + K[Hg^{2+}])$$

For the $[Co(en)_2(CN)Cl]^+$ ion, $K = 85$ dm^3 mol^{-1} and $10^2k = 1.30$ s^{-1} at 324.0 K and $I = 0.5$ mol dm^{-3}, the presence of an adduct being confirmed by spectrophotometry.[66] For the *α-cis*-$[Co(eee)Cl_2]^+$ ion at 288 K in 0.1 mol dm^{-3} $HClO_4$, $K = 34.4$ dm^3 mol^{-1} and $10^2k = 2.72$ s^{-1}.[77] Reaction of $[Co(NH_3)_5SCN]^{2+}$ with Hg^{2+} produces the $[Co(NH_3)_5(SCNHg)]^{4+}$ ion ($K = 1.2$ dm^3 mol^{-1}, $\Delta H^{\ddagger} = -5.2$ kcalmol^{-1}, and $\Delta S^{\ddagger} = 17$ cal K^{-1} mol^{-1} at 298.2 K and $I = 1.0$ mol dm^{-3}), whichundergoes parallel aquation and isomerization reactions to yield $[Co(NH_3)_5OH_2]^{3+}$ and $[Co(NH_3)_5(NCSHg)]^{4+}$ respectively.[55] The two products are formed at approximately equal rates ($k = 0.23$ s^{-1}, $\Delta H^{\ddagger} = 21.4$ kcal mol^{-1}, and $\Delta S^{\ddagger} = 10$ cal K^{-1} mol^{-1} at 298.1 K), and a common intermediate is proposed for the two reactions.

Product competition studies are reported for the Hg^{2+}- and NO^+-induced aquation reactions of *cis*- and *trans*-$[Co(en)_2(X)Cl]^+$ (X = Cl and N_3 respectively). The five-co-ordinate intermediates which are formed are sufficiently stable to survive many collisions and react selectively with a choice of nucleophiles.[49]

The Hg^{2+}-induced aquation reactions of $[Co(dmgH)_2NH_3X]$ (X = Cl or Br)[92] and methylcobalamin,[93] and the Hg^{2+}- and Tl^{3+}-induced removal of chloride ion from the $[(NH_3)_4Co\text{-}\mu\text{-}(NH_2,Cl)\text{-}Co(NH_3)_4]^{4+}$ ion[95] were referred to earlier. Studies of the Hg^{2+}-induced aquation of *cis*-$[Co(en)_2(PhNH_2)Cl]^{2+}$ in aqueous solution,[98] *trans*-$[Co(dmgH)_2(PhNH_2)Br]$ in 40% v/v EtOH–H_2O,[98] and $[Co(en)_2(L)Cl]^{2+}$ (L = unidentate 1,2-diaminoethane) in acidic solution[99] have also been reported.

Metal ions can also catalyse the aquation of complexes containing multidentate ligands in which all of the donor atoms of the multidentate ligand are not co-ordinated. This occurs because the metal ion catalyst can complex with the uncoordinated donor sites of the multidentate ligand. Two recently reported examples are the complex ions $[Co(en)_2(NH_3)(ox)]^{2+}$ (ref. 61) and $[Co(NH_3)_5O_2CCH_2CO_2H]^{2+}$ (ref. 60) containing unidentate oxalato- and malonato-ligands respectively. Labile bivalent and tervalent metal ions (M) react to form dinuclear species of the type $[L_5CoO_2C(CH_2)_nCO_2M]^{m+}$, which increases the rate of aquation, the catalytic effectiveness of M paralleling the stability of the dinuclear species formed.

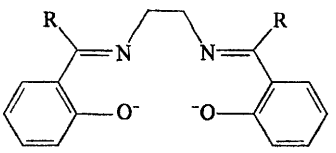
The electrophiles *trans*-$[Co^{III}(L)(H_2O)_2]^+$ [L = salen, Me_2salen (26) (R = H or Me), or L = saloph (27)], H_3O^+, and $PhHg^+$ all catalyse methyl-group transfer from the complexes *trans*-$[Co^{III}(L')Me_2]$ [L′ = (28), (29), or (17)].[100] A second-order rate law is observed in all cases.

$$\textit{trans}\text{-}[Co(L')Me_2] + \textit{trans}\text{-}[Co(L)(H_2O)_2]^+ \longrightarrow \begin{matrix}\textit{trans}\text{-}[Co(L')(Me)OH_2]^+ \\ + \\ \textit{trans}\text{-}[Co(L)(Me)OH_2]^+\end{matrix} \quad (4)$$

$$\textit{trans}\text{-}[Co(L')Me_2] + PhHg^+ \xrightarrow{(H_2O)} \textit{trans}\text{-}[Co(L')(Me)OH_2]^+ + PhHgMe \quad (5)$$

$$\textit{trans}\text{-}[Co(L')Me_2] + H_3O^+ \longrightarrow \textit{trans}\text{-}[Co(L')(Me)OH_2]^+ + CH_4 \quad (6)$$

[98] S. F. Chan and G. S. Tan, *J. Inorg. Nuclear Chem.*, 1976, **38**, 345.
[99] R. W. Hay and K. B. Nolan, *J.C.S. Dalton*, 1975, 1621.
[100] J. H. Espenson, H. L. Fritz, R. A. Heckman, and C. Nicoloni, *Inorg. Chem.*, 1976, **15**, 906.



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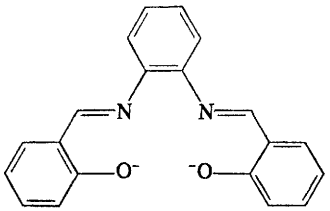

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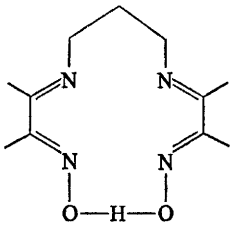

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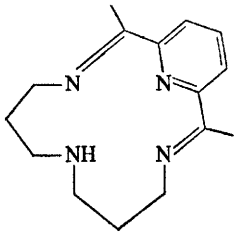


(29)

The reaction with H_3O^+ is interesting since monomethylcobalt(III) complexes do not react in this way even under forcing conditions. The second-order rate constants for the reactions with H_3O^+ were determined in 1:1 v/v THF–H_2O: at 298.2 K, I= 0.10 mol dm^{-3} ($LiClO_4$), $k_{H^+} = 4.5 \pm 0.2$ and 0.27 ± 0.01 dm^3 mol^{-1} s^{-1} for L′ = (28) and (29) respectively. The reactions with the *trans*-$[Co(L)(H_2O)_2]^+$ ions are also curious since the reaction with vitamin B_{12a} is very slow, and *trans*-$[Co(dmgH)_2(H_2O)_2]^+$ and *trans*-$[Co(28)(H_2O)_2]^{2+}$ do not react in this way at all. It might have been expected that the water exchange rate in the *trans*-$[Co(L)(H_2O)_2]^+$ ions would be too slow to permit electrophilic reactions of this type, and it is possible that these reactions are substitution controlled.[100] The relative reactivities of the three types of electrophile are $PhHg^+ > trans\text{-}[Co(L)(H_2O)_2]^+ > H_3O^+$ as shown by the results in Table 11. Direct transfer of the methyl carbanion is believed to be involved.

Table 11 *Comparison of the second-order rate constant* (k/dm^3 mol^{-1} s^{-1}) *for electrophilic attack at* trans-$[Co(L')Me_2]$, [*reactions* (4)—(6), L′ = (28), (29), *or* (17)] *at* 298.2 K *and* I=0.1 mol dm^{-3} ($LiClO_4$) (*data from ref.* 100)

Electrophile	L′ = (28)[a]	L′ = (29)[b]	L′ = (17)[b]
H_3O^+	40	4.5	0.27
trans-$[Co(saloph)(H_2O)_2]^+$ [c]	2.9×10^3	1.13×10^3	1.03×10^3
trans-$[Co(salen)(H_2O)_2]^+$ [d]		1.73×10^4	1.33×10^4
trans-$[Co(Me_2salen)(H_2O)_2]^+$ [e]		2.9×10^4	1.64×10^4
$PhHg^+$		*ca.* 2×10^6	1.3×10^5

[a] In 1:1 MeOH–H_2O. [b] In 1:1 THF–H_2O. [c] saloph = (27). [d] salen = (26; R = H). [e] Me_2salen = (26; R = Me).

The effect of binding complex ions to an ion-exchange resin (Dowex 50W) upon the rates of hydrolysis of the $[Co(NH_3)_5OReO_3]^{2+}$ and $[Cr(H_2O)_5Cl]^{2+}$ ions, or the

rate of water exchange with the $[Co(NH_3)_5OH_2]^{3+}$ and $[ReO_4]^-$ ions has been reported.[101] The aquation of $[Co(NH_3)_5OReO_3]^{2+}$ and the rate of water exchange with $[ReO_4]^-$ have modified pH dependences; the aquation of $[Cr(H_2O)_5Cl]^{2+}$ is much slower when resin bound, an effect which can be related to the known ionic-strength dependence of this reaction. The rate of water exchange with $[Co(NH_3)_5OH_2]^{3+}$ is not affected by binding to the resin. This is surprising since ion-pairing often accelerates dissociative reactions.[58,59]

Micellar catalysis has been investigated for the aquation of the *cis*- and *trans*-$[Co(en)_2Cl_2]^+$ ions in the presence of sodium dodecyl sulphate.[102] This negatively charged micelle affects the reaction rate, but non-catalytically. The positively charged micellar agent hexadecyltrimethylammonium bromide has no effect.

The use of oxidants (MnO_4^- and Cl_2) to catalyse the loss of DMSO from $[Co(NH_3)_5DMSO]^{3+}$ has been discussed previously.[47,48]

Photochemistry.—A new book entitled 'Concepts of Inorganic Photochemistry' has appeared.[4]

Three groups have reported studies of the photochemistry of cyano-cobalt(III) complexes. Unlike the corresponding $[Co(NH_3)_5X]^{2+}$ ions, the quantum yields for ligand-field excitation and photoaquation of the $[Co(CN)_5X]^{3-}$ ions (X = N_3, NCS, or SCN) are appreciable (0.03—0.2) and wavelength-independent.[103] Values of Φ are reported to be medium-dependent (*e.g.* solvent viscosity is important),[103] and this is confirmed for the photoaquation of the $[Co(CN)_6]^{3-}$ ion where Φ changes from 0.31 in H_2O to 0.10 in glycerol. A cage-recombination mechanism is proposed.[104] The importance of the solvent cage surrounding the complex is also stressed in studies of the photoaquation of $[Co(CN)_6]^{3-}$ and the photoanation of $[Co(CN)_5OH_2]^{2-}$ by N_3^- and I^- ions and by HN_3 and HCN.[105]

The value of the quantum yield for the photoaquation of cyanocobalamin (B_{12}) is very low (10^{-4}) and independent of wavelength.[106] There is no characteristic corrin phosphorescence, probably because the energy absorbed by the corrin ligand is rapidly transferred to a reactive ligand-field excited state which lies below the corrin triplet energy level. In support of this view, and unlike cyanocobalamin, the dicyanorhodium(III) corrin does not undergo photoaquation, but emits a strong phosphorescence. This is consistent with the assumption that the lowest ligand-field excited state in the rhodium(III) corrin now lies well above the energy of the lowest corrin triplet state. When both of the strong-field cyano-ligands are replaced by weak-field chloride ions, the energy of the lowest excited ligand-field state falls considerably. The behaviour of dichlororhodium(III) corrin indicates that the energy of the lowest corrin triplet is only slightly below the lowest excited ligand-field state which is responsible for its reactivity. The reactive ligand-field state can be populated from the lowest corrin triplet by thermal activation. Thus at 77 K dichlororhodium-(III) corrin shows a strong corrin phosphorescence, but at room temperature this emission is quenched and the complex undergoes photoaquation.[106]

[101] I. B. Liss and R. K. Murmann, *Inorg. Chem.*, 1975, **14**, 2314.
[102] M. J. Blandamer, J. Burgess, and J. G. Chambers, *Inorg. Chim. Acta*, 1976, **17**, L37.
[103] J. F. Endicott and G. J. Ferraudi, *J. Phys. Chem.*, 1976, **80**, 949.
[104] F. Scandola, M. A. Scandola, and C. Bartocci, *J. Amer. Chem. Soc.*, 1975, **97**, 4757.
[105] L. Viaene, J. D'Olieslager, and S. De Jaegere, *Bull. Soc. chim. belges*, 1976, **85**, 89.
[106] A. Vogler, R. Hirschmann, H. Otto, and H. Kunkely, *Ber. Bunsengesellschaft phys. Chem.*, 1976, **80**, 420.

3 Aquation: Chromium(III) Complexes

Chromium(III) continues to be the second most widely studied metal ion after cobalt(III). The question of dissociative (I_d) or associative (I_a) mechanisms for substitutions at chromium(III) has been clarified somewhat by comparing data for the formation and dissociation of the $[Cr(H_2O)_5X]^{2+}$ and $[Cr(NH_3)_5X]^{2+}$ ions (X = unidentate leaving anion).[10] Recent studies indicate that an associative mechanism is important for aqua-chromium(III) complexes,[7] but for the $[Cr(NH_3)_5X]^{2+}$ ions a dissociative-interchange mechanism is favoured.[10] A summary of kinetics and thermodynamic data for the formation and aquation of $[Cr(NH_3)_5X]^{2+}$ ions is given in Table 12.

$$[Cr(NH_3)_5OH_2]^{3+} + X^- \overset{K_{os}}{\rightleftharpoons} [Cr(NH_3)_5OH_2]^{3+},X^- \text{ (rapid)} \quad (7)$$

$$[Cr(NH_3)_5OH_2]^{3+},X^- \underset{k_{aq}}{\overset{k_{an}}{\rightleftharpoons}} [Cr(NH_3)_5X]^{2+} + H_2O \quad (8)$$

Table 12 *Kinetic and thermodynamic data for the formation and aquation of* $[Cr(NH_3)_5X]^{2+}$ *ions [reactions* (7) *and* (8)*] at* 323.2 K, $[H^+]=0.1$—0.5 mol dm^{-3}, *and* $I=1.0$ mol dm^{-3} ($LiClO_4$) *(data from ref.* 10)

X^-	10^4k_f/ $dm^3\ mol^{-1}\ s^{-1}$	10^4k_{an}/[a] s^{-1}	10^4k_{aq}/ s^{-1}	$K_{os}K_{is}$/[b] $dm^3\ mol^{-1}$	$K_{os}K_{is}$/[c] $dm^3\ mol^{-1}$	K_{os}/[d] $dm^3\ mol^{-1}$
NCS^-	4.16	6.12	0.011	310	380	0.68
$CCl_3CO_2^-$	1.81		0.37	5.3	4.9	
$CF_3CO_2^-$	1.37		0.50	2.4	2.7	
Cl^-	0.69		1.75	0.48	0.4	
Br^-	3.71		12.5	0.21	0.3	
I^-			102	0.022		
$\overset{+}{N}H_3CH_2CO_2^-$	7.82	14.2				0.55
$HC_2O_4^-$	6.45	5.86				1.16
$C_2O_4^{2-}$	29.1	6.46				4.5
H_2O		13.7				

[a] $k_{an} = k_f/K_{os}$. [b] From ion-exchange experiments; K_{os} and K_{is} are the outer-sphere and inner-sphere equilibrium constants respectively. [c] From k_f/k_{aq}. [d] Kinetically determined.

K_{os} and K_{is} represent the outer-sphere and inner-sphere equilibrium constants respectively, $K_{is} = k_{an}/k_{aq}$, and the formation rate constant $k_f = K_{os}k_{an}$. An I_d mechanism is favoured for reactions (7) and (8) because the values of k_f vary by less than an order of magnitude for ions of the same charge, and the observed rate is only slightly less than the solvent exchange rate. Also a plot of log k_{aq} *versus* log ($K_{os}K_{is}$) [$=\log(k_f/k_{aq})$] has a slope of 0.91 ± 0.05 compared with a value of 0.56 for the analogous $[Cr(H_2O)_5X]^{2+}$ ions. Furthermore, the ratio of the rate constants for the formation of thiocyanato- and chloro-complexes, k_f^{NCS}/k_f^{Cl}, is only 6 for reaction with the $[Cr(NH_3)_5OH_2]^{3+}$ ion, but for the reaction with $[Cr(H_2O)_6]^{3+}$ the ratio is 60, which is more in line with the associative behaviour for the latter reactions. Interestingly, values of k_f for the reaction of NCS^- and Cl^- ions with $[Co(H_2O)_6]^{3+}$ are 86.5 and $\leqslant 2.0$ $dm^3\ mol^{-1}\ s^{-1}$ respectively, which indicates that an I_a mechanism may also be important for this cobalt(III) ion. Since a D mechanism is well established for the aquation of $[Co(CN)_5X]^{3-}$ ions, and is likely for $[Cr(NCS)_5X]^{3-}$ ions,[11] it would appear that analogous complexes of cobalt(III) and chromium(III) react with similar

mechanisms, D, I_d, and I_a mechanisms being probable for $[ML_5X]^{3-}$ (M = Co^{III} or Cr^{III}, L = CN^- or NCS^-), $[M(NH_3)_5X]^{2+}$, and $[M(H_2O)_5X]^{2+}$ ions respectively. The tendency is towards dissociative mechanisms with the increasing σ-donor properties of the non-leaving groups.

Unidentate Leaving Groups.—*Ammonia Loss.* Previous studies of the acid hydrolysis of $[Cr(H_2O)_5(pyX)]^{3+}$ ions (pyX = pyridine or substituted pyridine) have been extended to the $[Cr(H_2O)_5NH_3]^{3+}$ ion.[107] The rate of aquation of $[Cr(H_2O)_5NH_3]^{3+}$ is significantly greater than expected on the basis of the correlation observed between log k_{aq} for the aquation of $[Cr(H_2O)_5(pyX)]^{2+}$ and the pK_a of the leaving pyridine. The observed rate constant (k_{obs}) for the aquation of $[Cr(H_2O)_5NH_3]^{2+}$ varies with acidity as expected for the normal mechanism of aquation of aquachromium(III) complexes involving conjugate-base formation: $k_{obs}=k_0+k_{-1}/[H^+]$. At 298.2 K and $I=1.0$ mol dm^{-3}, k_0(extrapolated) $=1.8\times10^{-9}$ s^{-1}, $\Delta H^{\ddagger}$ (k_0) = 27.8 kcal mol^{-1}, and $\Delta S^{\ddagger}(k_0)=-5.3$ cal K^{-1} mol^{-1}; k_{-1} (extrapolated) $=7.0\times10^{-12}$ mol dm^{-3} s^{-1}, $\Delta H^{\ddagger}(k_{-1})$ = 34.8 kcal mol^{-1}, and $\Delta S^{\ddagger}(k_{-1})=7.0$ cal K^{-1} mol^{-1}.

A previous report that the aquation of $[Cr(NH_3)_5OH_2]^{3+}$ produces *cis*- and *trans*-$[Cr(NH_3)_4(OH_2)_2]^{3+}$ ions has been disputed, and the *cis*-complex is claimed to be the only product.[108]

The relative effectiveness of co-ordinated anions (X^{n-}) upon the rate of loss of co-ordinated ammonia from $[Cr(NH_3)_5X]^{(3-n)+}$ ions has been considered for X^{n-} = $HC_2O_4^-$, $\overset{+}{N}H_3CH_2CO_2^-$, SO_4^{2-}, and IO_3^- ions.[109]

$[Cr(H_2O)_5L]^{n+}$ *Complexes.* Aquation of the $[Cr(H_2O)_5I]^{2+}$ ion has been studied at high pressures (0.1—250 MPa) as a function of $[H^+]$ (0.1—1.0 mol kg^{-1}) at 298.2 K and $I=1.0$ mol kg^{-1} ($HClO_4$–$LiClO_4$). Volumes of activation are -5.4 ± 0.5 and -1.6 ± 0.3 ml mol^{-1} for the $[H^+]$-independent and $1/[H^+]$- dependent pathways respectively. This indicates an I_a mechanism for the acid-independent pathway, and a dissociative mechanism for the conjugate-base pathway.[110]

The $[Cr(H_2O)_5SH]^{2+}$ ion has been characterized further[111] after isolation as the sulphate, $[Cr(H_2O)_5SH]SO_4$. Two kinetic studies of this ion have appeared, one concerned with its aquation and equilibrium with thiocyanate ion,[111] and a second study outlining its oxidation by iodine and ferric ions to give dinuclear species.[112] Acid hydrolysis gives the $[Cr(H_2O)_6]^{3+}$ ion and H_2S, the pseudo-first-order rate constant (k) varying with acidity (0.01—1.0 mol dm^{-3} H^+); $k=k_0+k_1[H^+]$. At 313.2 K and $I=1.0$ mol dm^{-3} ($LiClO_4$), the rate parameters are $10^5k_0=3.09\pm0.07$ s^{-1}, $\Delta H^{\ddagger}(k_0)=27.7\pm0.3$ kcal mol^{-1}, and $\Delta S^{\ddagger}(k_0)=9.4\pm0.9$ cal K^{-1} mol^{-1}; $10^5k_1=3.82\pm0.16$ dm^3 mol^{-1} s^{-1}. For the reaction with thiocyanate ion, both $[Cr(H_2O)_5SH]^{2+}$ and $[Cr(H_2O)_5SH_2]^{3+}$ ions are involved:

$$[Cr(H_2O)_5SH]^{2+} + NCS^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Cr(H_2O)_4(NCS)(SH)]^+ + H_2O$$

$$[Cr(H_2O)_5SH_2]^{3+} + NCS^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [Cr(H_2O)_4(NCS)(SH_2)]^{2+} + H_2O$$

[107] A. Bakač, V. Butković, and M. Orhanović, *Croat. Chem. Acta*, 1976, **48**, 35.
[108] L. Moensted and O. Moensted, *Acta Chem. Scand.*, 1974, A**28**, 1040.
[109] T. Ramasani, R. K. Wharton, and A. G. Sykes, *Inorg. Chem.*, 1975, **14**, 359.
[110] M. C. Weekes and T. W. Swaddle, *Canad. J. Chem.*, 1975, **53**, 3697.
[111] T. Ramasami and A. G. Sykes, *Inorg. Chem.*, 1976, **15**, 1010.
[112] T. Ramasami, R. S. Taylor, and A. G. Sykes, *J.C.S. Chem. Comm.*, 1976, 383.

$$[Cr(H_2O)_5SH]^{2+} + H^+ \overset{K_1}{\rightleftharpoons} [Cr(H_2O)_5SH_2]^{3+} \text{ (rapid)}$$

$$[Cr(H_2O)_4(NCS)(SH)]^+ + H^+ \overset{K_2}{\rightleftharpoons} [Cr(H_2O)_4(NCS)(SH_2)]^{2+} \text{ (rapid)}$$

For the reaction with excess thiocyanate ion the pseudo-first-order rate constant $k = k_2[NCS^-] + k_3K_1[H^+][NCS^-]$. At 298.2 K and $I = 1.0$ mol dm^{-3} ($NaClO_4$), $10^4k_2 = 8.57 \pm 0.015$ dm^3 mol^{-1} s^{-1}, $10^3k_3K_1 = 1.61 \pm 0.05$ dm^6 mol^{-2} s^{-1}, and the kinetically and spectroscopically determined equilibrium constants at 0.1 mol dm^{-3} H^+ are 2.8 ± 0.08 and 4.8 ± 0.1 dm^3 mol^{-1} respectively. A comparison of the relative labilities of *S*-bonded aqua-chromium(III) complexes is given in Table 13. Oxidation

Table 13 *Comparison of the acid-independent rate constants and activation parameters for the aquation of* S*-bonded aqua-chromium*(III) *complexes at* 298.2 K (*data from ref.* 111)

Complex	10^6k/s^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
$[(H_2O)_5Cr(SC_6H_4NH_3)]^{3+}$	4.0	29.8	16.7
$[(H_2O)_5Cr\{S(CH_2)_2NH_3\}]_3^+$	45	27.6	14
$[(H_2O)_5Cr(SH)]^{2+}$	4.3	27.7	9.4

of the $[Cr(H_2O)_5SH]^{2+}$ ion by I_2 and $[Fe(H_2O)_6]^{3+}$ gives the dinuclear ions $[(H_2O)_4Cr\text{-}\mu\text{-}(S_2)\text{-}Cr(OH_2)_4]^{4+}$ and $[(H_2O)_4Cr\text{-}\mu\text{-}(S_2H)\text{-}Cr(OH_2)_4]^{4+}$ respectively:[112]

$$2[Cr(H_2O)_5SH]^{2+} + I_2 \longrightarrow [(H_2O)_4Cr\text{-}\mu\text{-}(S_2)\text{-}Cr(OH_2)_4]^{4+} + 2H_3O^+ + 2I^- \quad (9)$$

$$2[Cr(H_2O)_5SH]^{2+} + 2[Fe(H_2O)_6]^{3+} \longrightarrow \begin{matrix} [(H_2O)_4Cr\text{-}\mu\text{-}(S_2H)\text{-}Fe(OH_2)_4]^{4+} + H_2O \\ + \\ [Cr(H_2O)_6]^{3+} + [Fe(H_2O)_6]^{2+} + H_3O^+ \end{matrix} \quad (10)$$

The mixed dinuclear Fe^{II}/Cr^{III} complex [reaction (10)] is also produced by treating the $[Cr(S_2)Cr]^{4+}$ species with $[Fe(H_2O)_6]^{2+}$:

$$H^+ + [Cr(S_2)Cr]^{4+} + Fe^{2+}_{aq} \longrightarrow [Cr(S_2H)Fe]^{4+} + Cr^{3+}_{aq} \quad (11)$$

The *cis*-labilizing effect of oxoanions such as nitrate or acetate when co-ordinated to chromium(III) was discussed in Volume 4 of this series.[113] This is believed to occur through the formation of transient bidentate species through chelation of the oxoanion. From studies of the nitrate substitution reactions of $[Cr(H_2O)_5ONO_2]^{2+}$ in aqueous DMSO, the rate constant at 298.2 K for water exchange with $[Cr(H_2O)_5ONO_2]^{2+}$ is reported to be *ca.* 8×10^{-2} s^{-1}, which is several orders of magnitude larger than for $[Cr(H_2O)_6]^{3+}$,[114] The rate constant for the aquation of $[Cr(H_2O)_5ONO_2]^{2+}$ is $10^6k = 8.8$ s^{-1} at 298.2 K.

A number of oxoanions are known to react rapidly with co-ordinated water molecules in cobalt(III), chromium(III), and other inert metal complexes, reactions which occur without cleavage of the metal–water oxygen bonds. Some recent examples have appeared. Relaxation studies have been used to study the rapid

[113] P. Moore, in 'Inorganic Reaction Mechanisms', ed. A. McAuley, Specialist Periodical Reports, The Chemical Society, London, 1976, Vol. 4, pp. 131 and 168.

[114] M. L. Mitchell, T. Montag, J. H. Espenson, and E. L. King, *Inorg. Chem.*, 1975, **14**, 2852.

reactions of $[Cr(H_2O)_6]^{3+}$ with IO_3^- and HSO_3^- ions,[115] and the accelerating effects of NO_2^- ion and CO_2 upon the rate of reaction of H_2O and DMSO with the $[Cr(H_2O)_n(DMSO)_{6-n}]^{3+}$ ions ($n=2$—6) has been reported.[116] The latter reactions are catalysed by NO_2^- and CO_2 provided that a co-ordinated water molecule is present. Aquation of the $[Cr(DMSO)_6]^{3+}$ ion is not affected. A value for the stability constant of the $[Cr(H_2O)_5(HCO_3)]^{2+}$ ion is estimated from the kinetic data.[116]

Inner-sphere reduction of the $[Co(NH_3)_5(p\text{-acetylbenzonitrile})]^{3+}$ ion by $[Cr(H_2O)_6]^{2+}$ is reported to give an intermediate which rapidly aquates to $[Cr(H_2O)_6]^{3+}$.[117] The observed pseudo-first-order rate constant (k) for the aquation of the intermediate is characterized by

$$k = (k_1 + k_2[H^+]^{-1})[Cr^{II}] + k_3[H^+]^{-1}$$

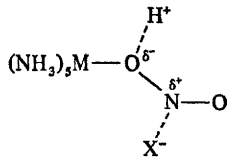
At 298.2 K, $k_1 = 420 \pm 150$ dm^3 mol^{-1} s^{-1}, $k_2 = 6.8 \pm 6.6$ s^{-1}, and $k_3 = 0.91 \pm 0.13$ mol dm^{-3} s^{-1}.

Data for the aquation of the $[Cr(H_2O)_5NH_3]^{3+}$ ion were discussed in the previous section.[107] Catalytic removal of alkyl groups (R) from $[Cr(H_2O)_5R]^{2+}$ ions by IBr is discussed in the section on catalysed aquation.

Other Complexes. Following an earlier study which showed that chloride and bromide ions (X^-) catalyse the aquation of the $[Co(NH_3)_5(ONO)]^{2+}$ ion, a similar behaviour has now been established for the analogous $[Cr(NH_3)_5(ONO)]^{2+}$ ion:[118]

$$-d[Cr(NH_3)_5(ONO)^{2+}]/dt = d[Cr(NH_3)_5OH_2^{3+}]/dt = k[Cr(NH_3)_5(ONO)^{2+}][H^+][X^-]$$

At 298.2 K and $I = 1.0$ mol dm^{-3}, $k = 3.12 \pm 0.10$ and 27.9 ± 1.3 dm^6 mol^{-2} s^{-1} for X = Cl and Br respectively. In the absence of halide ions and at $I = 1.0$ mol dm^{-3} ($LiClO_4$), the second-order rate constant is $10^2k = 6.89 \pm 0.12$ dm^3 mol^{-1} s^{-1} at 298.2 K. These reactions proceed with N—O rather than Cr—O bond cleavage and are catalysed by H^+ and X^- ions through a transition of type (30) (M = Co^{III} or Cr^{III}).



(30)

The rates of hydrolysis of the $[Cr(NCS)_5CN]^{3-}$, *trans*-$[Cr(NCS)_4(CN)_2]^{3-}$, and $[Cr(NCS)_6]^{3-}$ ions have been investigated using high-voltage ionophoresis.[119] The products are the $[Cr(NCS)_5OH_2]^{2-}$ and $[Cr(NCS)_4(OH_2)_2]^-$ ions and $[Cr(NCS)_3(OH_2)_3]$ respectively. The reactions are strongly photocatalysed, aquation being fifty times faster in the presence of light than in total darkness. The solvolysis of $[Cr(NCS)_6]^{3-}$ has also been examined in DMF, DMSO, and other non-aqueous solvents, details of which will be found in the section concerned with non-aqueous

[115] G. Bazsa and H. Diebler, *Reaction Kinetics Catalysis Letters*, 1975, **2**, 217.
[116] G. Rabai, G. Bazsa, and M. Beck, *Magyar Kém. Folyóirat*, 1976, **82**, 60.
[117] R. J. Balahura and W. L. Purcell, *Inorg. Chem.*, 1975, **14**, 1469.
[118] V. Joel and A. Haim, *Inorg. Chem.*, 1975, **14**, 3130.
[119] E. Blasius, H. Augustin, and T. Erhardt, *Z. anorg. Chem.*, 1975, **417**, 105.

solvents.[11] Rates and activation parameters are also reported for the acid hydrolysis (0·5 mol dm^{-3} $HClO_4$) of the $[Cr(NH_3)_2(H_2O)_2(NCS)_2]^+$ and $[Cr(NH_3)_2(H_2O)_3NCS]^{2+}$ ions, complexes which are derivatives of Reinecke's salt.[120] Although the first of these reactions is reversible, the second reaction is irreversible.

Separate reports have appeared of studies of the solvolysis of the $[Cr(NCS)_4(NH_2Ph)_2]^-$ ion[121] and the $[Cr(NCS)_4(NH_2CH_2Ph)_2]^-$ ion[122] in mixed aqueous–organic solvents. The $[Cr(NCS)_4(NH_2Ph)_2]^-$ ion was investigated in acetone–water mixtures containing $HClO_4$ (10^{-3}—0.1 mol dm^{-3}). Two of the thiocyanate ions are first replaced by water molecules, and this is followed by the replacement of one aniline molecule by an acetone molecule in a second-order reaction catalysed by H^+. The other two thiocyanate ions are also lost in neutral or weakly acidic solutions.[121] Solvolysis of $[Cr(NCS)_4(NH_2CH_2Ph)_2]^-$ was investigated in ethanol–water mixtures and the first stage again involves the replacement of two thiocyanate ions by H_2O. In acidic solution the reaction ceases at this stage, but the other two thiocyanate ions are reported to be lost under neutral conditions. Loss of benzylamine was not detected in this case.[122]

Studies of the loss of unidentate ligands from complexes which also contain multidentate ligands (*e.g.* en, ox^{2-}, tren, or edta) will be found in a later section dealing with the effects of non-leaving ligands.

Multidentate Leaving Groups.—Chelate ring-opening reactions for the majority of polyamine-chromium(III) complexes have been detected in recent years. A study of the hydrolysis of the $[Cr(en)_3]^{3+}$ and *cis*- and *trans*-$[Cr(en)_2(OH_2)_2]^{3+}$ ions in 1 mol dm^{-3} $HClO_4$ has revealed the existence of a large number of complexes containing unidentate monoprotonated 1,2-diaminoethane (enH^+).[123] Among the species separated and characterized were $[Cr(en)_2(enH)(H_2O)]^{4+}$, (?)-$[Cr(en)(enH)_2(H_2O)_2]^{5+}$, *fac*- and *mer*-$[Cr(en)(enH)(H_2O)_3]^{4+}$, $[Cr(en)(H_2O)_4]^{3+}$, *cis*-$[Cr(enH)_2(H_2O)_4]^{5+}$, and $[Cr(enH)(H_2O)_5]^{4+}$. Comparison with an earlier study of the acid hydrolysis of $[Cr(NH_3)_6]^{3+}$ shows that for $[Cr(en)_3]^{3+}$ *trans*-tetra-amines and -diamines are not found as reaction products. Also, *trans*-$[Cr(en)_2(H_2O)_2]^{3+}$ only gives the *mer*-$[Cr(en)(enH)(H_2O)_3]^{3+}$ ion. Racemization of *cis*-$[Cr(en)_2(H_2O)_2]^{3+}$ but not of $[Cr(en)_3]^{3+}$ was detected.[123]

The rates and activation parameters for the acid hydrolysis of the $[Cr(LL)_2(ox)]^+$ ions (LL = bipy or phen) are nearly identical to those reported for the racemization reactions (Table 14). Therefore, the racemization and hydrolysis reactions occur by a

Table 14 *Comparison of rate data for the acid-catalysed hydrolysis and racemization reactions (values in parentheses) of the* $[Cr(LL)_2(ox)]^+$ *ions* (LL = bipy *or* phen) (*data from ref.* 124)

LL	$10^7 k_{H^+}$/dm^3 mol^{-1} s^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
bipy	9.06	82.4 (79.5)	−84 (−61)
phen	5.93	88.9 (82.9)	−67 (−57)

[120] P. Kita and A. Lodzinska, *Roczniki Chem.*, 1975, **49**, 239.
[121] I. Ganescu, V. Voiculescu, and Cs. Várhelyi, *Monatsch.*, 1975, **106**, 801.
[122] J. Zsakó, Cs. Várhelyi, I. Ganescu, and D. Oprescu, *Roczniki Chem.*, 1974, **48**, 1141.
[123] L. Moensted and O. Moensted, *Acta Chem. Scand.*, 1975, **A29**, 29.

common ring-opening mechanism involving the same intermediate. Both reactions involve Cr—O bond fission.[124]

The complex $[Cr(ox)_2(enH)(OH_2)]$ has been detected as a major intermediate in the aquation of the $[Cr(ox)_2(en)]^-$ ion at pH 1.[125] Aquation of this intermediate gives *cis*-$[Cr(ox)_2(OH_2)_2]^-$, the rate constant for aquation being $10^5k = 1.9\ s^{-1}$ at 298.2 K. Loss of the oxalato-ligands is also involved, especially at low pH, and two other intermediates, the $[Cr(ox)(en)(OH_2)_2]^+$ and $[Cr(ox)(enH)(OH_2)_3]^{2+}$ ions, were separated by ion-exchange chromatography. Both of these intermediates react further to give $[Cr(ox)(OH_2)_4]^+$. The kinetics of the first step in the aquation of $[Cr(ox)_2(en)]^-$ were studied at 570 nm, an isosbestic point for the products which were formed. The pseudo-first-order rate constant, k, is given by $k = k_0 + k_1[H^+] + k_2[H^+]^2$; at 298.2 K and $I = 2.01$ mol dm^{-3} (KNO_3), $10^5k_1 = 1.7\ s^{-1}$ ($\Delta H^{\ddagger} + 20.6 \pm 0.6$ kcal mol^{-1}, $\Delta S^{\ddagger} = -11.4 \pm 1.9$ cal K^{-1} mol^{-1}), $10^5k_2 = 7.69 \pm 0.11$ dm^3 mol^{-1} s^{-1} ($\Delta H^{\ddagger} = 17.6 \pm 0.2$ kcal mol^{-1}, $\Delta S^{\ddagger} = -18.3 \pm 0.5$ cal K^{-1} mol^{-1}), and $10^5k_3 = 6.15 \pm 0.07$ dm^6 mol^{-2} s^{-1} ($\Delta H^{\ddagger} = 16.6 \pm 0.6$ kcal mol^{-1}, $\Delta S^{\ddagger} = -22.0 \pm 1.8$ cal K^{-1} mol^{-1}). k_1 is ascribed to the primary uncatalysed aquation of the 1,2-diaminoethane, and k_2 to the acid-catalysed loss of oxalate ion. k_2 is a composite rate constant which can be broken down into the rate constants for the acid-catalysed loss of en (k_2') and ox (k_2''); $10^5k_2' = 1.7 \pm 0.8$ dm^3 mol^{-1} s^{-1} and $10^5k_2'' = 6.0 \pm 0.9$ dm^3 mol^{-1} s^{-1}. A protonated half-bonded oxalato-ligand is involved.[125]

Two reports have appeared of the acid hydrolyses of the $[Cr(en)_2(ox)]^+$ ion.[126,127] In concentrated HCl at 299.7 K a two-step reaction is involved, the products being $[Cr(en)_2(OH_2)Cl]^{2+}$ and $[Cr(en)_2Cl_2]^+$. The second step is the slower and the rate depends upon both $[H^+]$ and $[Cl^-]$, which indicates a mechanism involving protonation and rate-determining chloride-ion anation. Four stages are reported for the aquation of $[Cr(en)_2(ox)]^+$ in the absence of chloride ion, stepwise loss of both en molecules being involved:

$$[Cr(en)_2(ox)]^+ + H_3O^+ \longrightarrow [Cr(en)(enH)(ox)(OH_2)]^{2+}$$

$$[Cr(en)(enH)(ox)(OH_2)]^{2+} + H_3O^+ \longrightarrow [Cr(en)(ox)(OH_2)_2]^+ + enH_2^{2+}$$

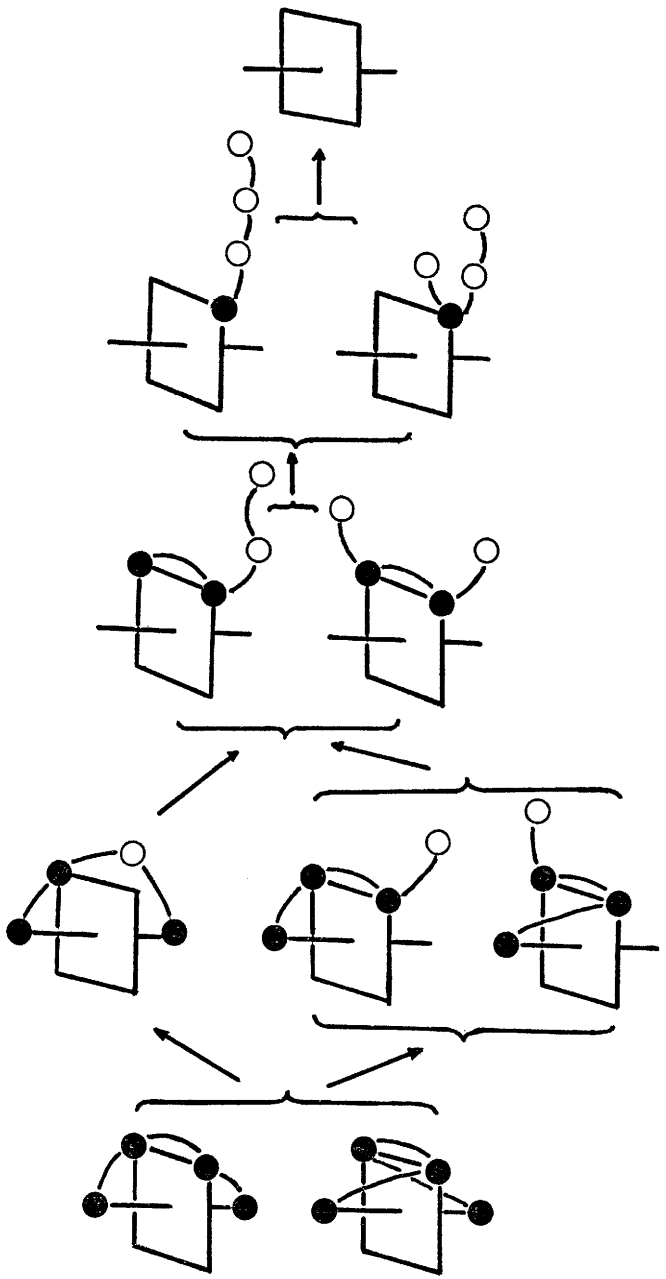
$$[Cr(en)(ox)(OH_2)_2]^+ + H_3O^+ \longrightarrow [Cr(ox)(enH)(OH_2)_3]^{2+}$$

$$[Cr(ox)(enH)(OH_2)_3]^{2+} + H_3O^+ \longrightarrow [Cr(ox)(OH_2)_4]^+ + enH_2^{2+}$$

The effects of varying the dielectric constant of the solvent and the ionic strength of the medium upon the rate of aquation of $K_3[Cr(ox)_3]$ are reported in aqueous 1,4-dioxan solutions. The rate varies inversely with the dielectric constant of the solvent, and studies in the presence of $NaClO_4$ give somewhat higher rates than in the presence of $NaNO_3$ at the same ionic strength.[128]

Potentiometric titrations indicate that the species previously reported to be the *mer*-$[Cr(trienH)(OH_2)_3]^{4+}$ ion [trienH$^+$ = $NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_3^+$] is in fact *α-cis*-$[Cr(trien)(OH_2)_2]^{3+}$.[129] The p$K_a$'s of this species are reported to be 4.47 ± 0.03 and 7.14 ± 0.05. This observation necessitates a reinterpretation of the

[124] O. Farver and G. Nord, *Acta Chem. Scand.*, 1976, **A30**, 121.
[125] T. W. Kallen, *Inorg. Chem.*, 1975, **14**, 2687.
[126] M. B. Davies and J. W. Lethridge, *J. Inorg. Nuclear Chem.*, 1975, **37**, 171.
[127] M. B. Davies, J. W. Lethridge, O. Nor, and L. Y. Goh, *J. Inorg. Nuclear Chem.*, 1975, **37**, 175.
[128] M. W. Raphael and M. A. Malati, *Inorg. Chim. Acta*, 1975, **12**, L11.
[129] L. Moensted and O. Moensted, *Acta Chem. Scand.*, 1976, **A30**, 203.



Scheme 1 *Pathways observed in the acid hydrolysis of the* α*-cis-*$[Cr(trien)(OH_2)_2]^{3+}$ *ion (from ref.* 129)

earlier kinetic study, and it is suggested that dechelation of α-*cis*-$[Cr(trien)(OH_2)_2]^{3+}$ takes place preferentially from the secondary amino-groups, the large-ring species which initially forms reacting rapidly to give *cis*-$[Cr(trienH_2)_2(H_2O)_4]^{5+}$. Scheme 1 shows the pathways so far elucidated for the acid hydrolysis of α-*cis*-$[Cr(trien)(OH_2)_2]^{3+}$.

The kinetics of the formation and acid hydrolysis of the $[Cr(bipy)(H_2O)_4]^{3+}$ ion have been reported.[130] These results are considered in the section concerned with complex formation.

Effects of Non-leaving Groups.—There have been a number of reports of the kinetics of the first step in the stepwise aquation of chloride ions from complex ions of the type *cis*-$[Cr(LL)_2Cl_2]^+$ [LL = en, iso-bn (bn = butylenediamine), *meso*-bn, *dl*-bn, or 1,2-diaminobenzene] in acidic solution.[131–133] The results are collected in Table 15. There is no marked effect of changing the nature of LL, and the reactions generally proceed with retention of configuration.

Table 15 *Kinetic parameters at* 298.2 K *for the first step in the stepwise aquation of* cis-$[Cr(LL)_2Cl_2]^+$

LL	$10^4k_{aq}/s^{-1}$	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
iso-bn	1.54 ± 0.11^a	21.3 ± 0.8^a	-4.5 ± 2.8
meso-bn	3.55 ± 0.27^a	19.6 ± 1.2^a	-8.6 ± 4.2
dl-bn	3.91 ± 0.34^a	18.4 ± 0.4^a	-12.3 ± 1.5
1,2-diaminobenzene	1.71^b	18.4	−14.0
en	2.67^c	16.5	−20.0

[a] Activation energies quoted are 0.6 kcal mol^{-1} less than the values of E_a given in the paper; data from ref. 131. [b] In 0.1 mol dm^{-3} $HClO_4$, $I=1.0$ mol dm^{-3} ($NaClO_4$); data from ref. 132. [c] Aquation in the presence of bipy, phen, and glycine; data from ref. 133. For studies in non-aqueous media see Table 19.

The complex ions *cis*-$[Cr(en)_2(CN)_2]^+$ and *cis*-$[Cr(en)_2(OH_2)CN]^{2+}$ have recently been prepared and kinetic studies are underway.[134]

Mutarotation is reported to proceed for reaction (12) without complications from racemization, *cis–trans*-isomerization, or chelate ring-opening.[135]

$$\Lambda\text{-}cis\text{-}(+)\text{-}[Cr(en)_2(N_3)_2]^+ + H_3O^+ \longrightarrow \Lambda\text{-}cis\text{-}(+)\text{-}[Cr(en)_2(N_3)(OH_2)]^{2+} + HN_3 \quad (12)$$

An I_d mechanism is proposed from studies of the aquation of the *cis*-$[Cr(ox)_2(N_3)(OH_2)]^{2-}$ ion at pH 3—10.5 and 308 K, and at pH 9—10.6 at 298 and 318 K.[136]

One isomer has been isolated for each of the complexes [Cr(dien)(LL)Cl][$ZnCl_4$],H_2O (LL = en, pn, or tmd), and the kinetics of aquation have been measured for comparison with the previously studied cobalt(III) analogues (Table 16).[137] The

[130] R. Marčec and M. Orhanović, *J.C.S. Dalton*, 1975, 319.
[131] C. P. Madhusudhan and J. A. McLean, *Inorg. Chem.*, 1975, **14**, 82; C. P. Madhusudhan, *Diss Abs. Internat.* (*B*), 1975, **35**, 4823.
[132] J. C. Chang, *J. Inorg. Nuclear Chem.*, 1976, **38**, 1390.
[133] J. Roy and D. Banerjea, *J. Indian Chem. Soc.*, 1975, **52**, 897.
[134] A. P. Sattelberger, D. D. Darsow, and W. B. Schaap, *Inorg. Chem.*, 1975, **15**, 1412.
[135] I. J. Kindred and D. A. House, *J. Inorg. Nuclear Chem.*, 1975, **37**, 1320.
[136] K. R. Ashley, and I. C. Chen, *J. Inorg. Nuclear Chem.*, 1975, **37**, 1052.
[137] D. A. House, *Inorg. Nuclear Chem. Letters*, 1976, **12**, 259.

Table 16 *Comparison of the rates of aquation of analogous cobalt*(III) *and chromium*(III) *complexes at* 323 K (*data from ref.* 137)

Complex	$10^6k/s^{-1}$ (M = Co^{III})	$10^6k/s^{-1}$ (M = Cr^{III})
$[M(NH_3)_5Cl]^{2+}$	36.2[a]	175 ± 4[b]
$[M(dien)(en)Cl]^{2+}$	3.13[c]	526 ± 20[b]
$[M(dien)(tmd)Cl]^{2+}$	6.61[c]	523 ± 20[b]
$[M(dien)(pn)Cl]^{2+}$		526 ± 20[b]
$[M(MeNH_2)_5Cl]^{2+}$	650[b]	13.8[d]

[a] 0.01 mol dm^{-3} H^+. [b] 0.10 mol dm^{-3} H^+. [c] 1.0 mol dm^{-3} H^+. [d] 0.4 mol dm^{-3} H^+, $I = 1.0$.

complexes have a geometry in which the dien is *facial* and the chloride ion is in a *trans* position to one of the primary amine groups of the dien (*a*-chloro-*bc*-diamine-*def*-diethylenetriamine). The thermal or Hg^{2+}-ion-induced aquation reactions proceed with retention of configuration. At 323 K these chromium(III) complexes aquate *ca.* 10^2 times as fast as their cobalt(III) analogues and *ca.* 3 times as fast as the $[Cr(NH_3)_5Cl]^{2+}$ ion. No clear-cut mechanism was established for the reactions, but in view of the recent studies of chromium(III) ammines[10] it seems unlikely that an I_a mechanism is operative. If the reactions have any associative character, it is suggested that the increased rates for the chromium(III) chelates compared with the $[Cr(NH_3)_5Cl]^{2+}$ ion could be explained by the 'tying-back' of the NH_2 groups by the chelate rings to allow for a more facile approach of the incoming water molecule.[137]

A series of complex ions of the type $[Cr(tren)XY]^+$ has been prepared. Stepwise aquation of the dichloro-complex (X = Y = Cl) occurs with loss of Cl^- (first step) and with Cr—N bond fission (second step) to give a complex in which tren is acting as a protonated terdentate ligand (trenH):[138]

$$[Cr(tren)Cl_2]^+ + H_2O \xrightarrow{k_1} [Cr(tren)(OH_2)Cl]^{2+} + Cl^-$$

$$[Cr(tren)(OH_2)Cl]^{2+} + H_3O^+ \xrightarrow{k_2} [Cr(trenH)(OH_2)_2Cl]^{3+}$$

At 298.2 K in 0.1 mol dm^{-3} ($HClO_4$) the rate parameters for the two steps are $10^2k_1 = 5.18 \pm 0.27$ s^{-1} ($\Delta H^{\ddagger} = 12.3 \pm 0.5$ kcal mol^{-1}, $\Delta S^{\ddagger} = -23.0 \pm 1.3$ cal K^{-1} mol^{-1}) and $10^4k_2 = 7.15 \pm 0.02$ s^{-1} ($\Delta H^{\ddagger} = 19.1 \pm 0.4$ kcal mol^{-1}, $\Delta S^{\ddagger} = -8.4 \pm 1.0$ cal K^{-1} mol^{-1}). A comparison of the rate of aquation of the $[Cr(tren)Cl_2]^+$ ion with the cobalt(III) and rhodium(III) analogues, and with analogous *cis*-$[M(en)_2Cl_2]^+$ and *α-cis*-$[M(trien)Cl_2]^+$ ions is given in Table 17. The peculiar geometry of the tren ligand is believed to favour an I_a mechanism for the chromium(III) complexes. Preference for an I_a mechanism decreases in the order $Cr^{III} > Rh^{III} > Co^{III}$.[138]

Table 17 *Rates of aquation of* $[M(tren)Cl_2]^+$ *ions at* 298.2 K *and the relative rates of aquation of* cis-$[M(en)_2Cl_2]^+$ *and* α-cis-$[M(trien)Cl_2]^+$ *ions* (*data from ref.* 138)

M	$[M(tren)Cl_2]^+$ *aquation* k/s^{-1}	*Ratio of values of k to those for the aquation of the ions* cis-$[M(en)_2Cl_2]^+$ *and* α-cis-$[M(trien)Cl_2]^+$	
Cr^{III}	5.18×10^{-2}	200	250
Co^{III}	2.96×10^{-3}	12	20
Rh^{III}	1.97×10^{-5}	50	60

[138] S. G. Zipp and S. K. Madan, *Inorg. Chem.*, 1976, **15**, 587.

The effect of polyaminocarboxylates (Y^{n-}) upon the rates of formation and dissociation and the stability of acetato-complexes of the type $[Cr(Y)OAc]^{(n-2)-}$ has been investigated for Y^{n-} = edta^{4-}, *N*-hydroxyethylenediamine-*NN'N'*-triacetate^{3-} (hedta^{3-}), ethylenediamine-*NN'N'*-triacetate^{3-} (edtra^{3-}), and *N*-methylethylenediamine-*NN'N'*-triacetate^{3-} (medtra^{3-}):[139]

$$[Cr(Y)(H_2O)]^{(n-3)-} + AcO^- \underset{k_d}{\overset{k_f}{\rightleftharpoons}} [Cr(Y)(OAc)]^{(n-2)-} + H_2O \qquad (13)$$

The results are collected in Table 18.

Table 18 *Rates of formation* (k_f) *and dissociation* (k_d) *and the stability constants* (K) *of* $[Cr(Y)(OAc)]^{(n-2)-}$ *ions at* 298.2 K *and* I = 1.0 mol dm^{-3} ($NaClO_4$) [*reaction* (13); *data from ref.* 139]

Y^{n-}	k_f/dm^3 mol^{-1} s^{-1}	k_d/s^{-1}	K/dm^3 mol^{-1}
edta^{4-}	3.3	5.4	0.62
hedta^{3-} [a]	7.6	0.45	17
edtra^{3-} [b]	2.9×10^{-2}	1.6×10^{-3}	18
medta^{3-} [c]	7.3×10^{-4}	5.9×10^{-5}	12

[a] *N*-Hydroxymethylethylenediamine-*NN'N'*-triacetate ion. [b] Ethylenediamine-*NN'N'*-triacetate ion. [c] *N*-Methylethylenediamine-*NN'N'*-triacetate ion.

The effects of oxoanions upon the labilities of chromium(III) complexes of the type $[Cr(NH_3)_5X]^{n+}$, $[Cr(H_2O)_5(ONO_2)]^{2+}$, and $[Cr(H_2O)_n(DMSO)_{6-n}]^{3+}$ ($+NO_2^-$ or CO_2) were discussed in previous sections.[109,114,116]

Bridged Dichromium Complexes.—The thermodynamics and kinetics of the equilibria between di-μ-hydroxo and μ-hydroxo dinuclear complex ions of the type $[(en)_2Cr\text{-}\mu\text{-}(OH)_2\text{-}Cr(en)_2]^{4+}$ and $[(H_2O)(en)_2Cr\text{-}\mu\text{-}(OH)\text{-}Cr(en)_2(OH_2)]^{5+}$ have been investigated.[140] In acid solution (31) is rapidly converted into a mixture

$$\underset{(31)}{meso\text{-}[(en)_2Cr\text{-}\mu\text{-}(OH)_2\text{-}Cr(en)_2]^{4+}} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{(32)}{[(H_2O)(en)_2Cr\text{-}\mu\text{-}(OH)\text{-}Cr(en)_2(OH)]^{4+}}$$

$$\underset{(34)}{[(HO)(en)_2Cr\text{-}\mu\text{-}(OH)\text{-}Cr(en)_2OH]^{3+}} \quad (-H^+ \uparrow\downarrow +H^+)$$

$$\underset{(33)}{[(H_2O)(en)_2Cr\text{-}\mu\text{-}(OH)\text{-}Cr(en)_2(OH_2)]^{5+}}$$

of (32) and (33). At 274.0 K, I = 1.0 mol dm^{-3}, and $[H^+] = 10^{-5}$—1.0 mol dm^{-3}, $-d[(31)]/dt = d([(32)] + [(33)])/dt = k_1[(31)] - \{k_{-1}K_{a1}/(K_{a1} + [H^+])\}\{[(32)] + [(33)]\}$ with $10^4k_1 = 3.6$ s^{-1}, $10^4k_{-1} = 4.23$ s^{-1}, and $pK_{a1} = 0.67$, $pK_{a2} = 7.94$ for species (33). Activation energies associated with k_1 and k_{-1} are 19.6 and 20.7 kcal mol^{-1} respectively. The equilibrium constant $K_{eq} = [(32)]/[(31)] = 0.84$ at 274.0 K and 0.76

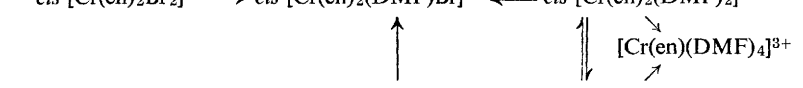
[139] H. Ogini, T. Watanabe, and N. Tanaka, *Inorg. Chem.*, 1975, **14**, 2093.

at 293.2 K. In strongly basic solution (31) (pK_a *ca.* 12 at 293.2 K) deprotonates to give the μ-hydroxo-μ-oxo-complex ion $[(en)_2Cr\text{-}\mu\text{-}(O,OH)\text{-}Cr(en)_2]^{3+}$, which was isolated as a triperchlorate dihydrate. (32) and (34) were also isolated as perchlorate salts.[140]

Dinuclear thiol-bridged complexes of chromium(III) are formed when the $[Cr(H_2O)_5SH]^{2+}$ ion is oxidized by I_2 or $[Fe(H_2O)_6]^{3+}$ [reactions (9)—(11)].[112] The conversion of the $[(H_2O)_4Cr\text{-}\mu\text{-}(S_2)\text{-}Cr(H_2O)_4]^{4+}$ ion into the mixed dinuclear Fe^{II}/Cr^{III} complex ion $[(H_2O)_4Cr\text{-}\mu\text{-}(S_2H)\text{-}Fe(H_2O)_4]^{4+}$ [reaction (11)] has the rate law $Rate = k_1[CrS_2Cr^{4+}][Fe^{2+}] + k_2[CrS_2Cr^{4+}]$. At 298.2 K and $I = 1.0$ mol dm^{-3} ($LiClO_4$), $10^2k_1 = 3.16 \pm 0.05$ dm^3 mol^{-1} s^{-1} and $10^5k_2 = 9.8 \pm 0.4$ s^{-1}, the reactions being acid-independent. Oxidation of the $[Cr(H_2O)_5SH]^{2+}$ ion by Fe^{3+}_{aq} [reaction (10)] follows the rate law $Rate = k_3[CrSH^{2+}][Fe^{3+}][H^+]^{-1}$, with $10^2k_3 = 1.50 \pm 0.02$ dm^3 mol^{-1} s^{-1}. A reaction between $[(H_2O)_5CrS]^+$ and $[Fe(H_2O)_6]^{3+}$ ions is believed to be involved.[113]

The kinetics of the formation of mononuclear complexes of triethanolamine $[N(CH_2CH_2OH)_3]$ at pH 2—4.6 have been investigated, and acid- and base-catalysed hydrolysis of a dinuclear species, stable at pH 9, is reported.[141]

Non-aqueous Solvents.—An extensive series of papers has appeared concerned with the solvolysis of complex ions of the type *cis*- and *trans*-$[Cr(en)_2LX]^+$ (L or X = Cl, Br, or solvent) in non-aqueous solvents (S) and the isomerization of the solvento-complex ions $[Cr(en)_2(S)X]^{2+}$ and $[Cr(en)_2(S)_2]^{3+}$ which are formed.[142–145] The results are collected in Table 19. The first step in the solvolysis of the *cis*- and *trans*-$[Cr(en)_2Br_2]^+$ and *cis*- and *trans*-$[Cr(en)_2BrCl]^+$ ions proceeds with the loss of bromide ion, and with retention of configuration. Addition of excess bromide ion produces up to 60% ion-pairing, but this does not significantly affect the rates of solvolysis.[142] At 313.2 K, *trans*-$[Cr(en)_2(DMF)_2]^{3+}$ isomerizes to the *cis*-complex (87%) and at the same time solvolyses with loss of en to give $[Cr(en)(DMF)_4]^{3+}$ (13%).[143] There is no significant formation of a species in which the en is acting as a unidentate ligand. At 321 K, *trans*-$[Cr(en)_2(DMF)Br]^{2+}$ undergoes parallel reactions to give *cis*-$[Cr(en)_2(DMF)Br]^{2+}$ (33%) and *cis*-$[Cr(en)_2(DMF)_2]^{3+}$ (67%). The solvolysis reaction does not proceed *via* the *trans*-$[Cr(en)_2(DMF)Br]^{2+}$ ion, the *cis*-product being obtained directly. The *cis*-$[Cr(en)_2(DMF)Br]^+$ ion solvates with retention of configuration and the Hg^{2+}- and Ag^+-catalysed solvolyses of *trans*-$[Cr(en)_2(DMF)Br]^{2+}$ proceed with retention of configuration as expected.[143] A summary of the kinetically significant pathways observed during the solvolysis of the bromo-complexes in DMF is shown in Scheme 2.



Scheme 2

[140] J. Springborg and H. Toftlund, *Acta Chem. Scand.*, 1976, **A30**, 171; *J.C.S. Chem. Comm.*, 1975, 422.
[141] M. Kunaszewska, *Roczniki Chem.*, 1975, **49**, 1455.
[142] W. G. Jackson and W. W. Fee, *Inorg. Chem.*, 1975, **14**, 1154.
[143] W. G. Jackson and W. W. Fee, *Inorg. Chem.*, 1975, **14**, 1161.
[144] W. G. Jackson and W. W. Fee, *Inorg. Chem.*, 1975, **14**, 1170.
[145] W. G. Jackson and W. W. Fee, *Inorg. Chem.*, 1975, **14**, 1174.

Table 19 *Rate data for the first step in the solvolysis in non-aqueous solvents of* cis- *and* trans-$[Cr(en)_2(L)X]^{n+}$ *ions* (X = *leaving group unless specified; data from refs.* 142—145)

L	X	*Solvent*	*Isomer*	*T*/K	10^5k/s^{-1}	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal K^{-1} mol^{-1}
Br	Br	DMF	*cis*	323.2	28.3[a]	22.0	−5.5
Cl	Cl	DMF	*cis*	323.2	5.01		−11.0
Cl	Cl	DMSO	*cis*	323.2	2.33		
Br	Br	DMF	*trans*	323.2	16.3[a]	20.5	
Cl	Cl	DMF	*trans*	323.2	0.70		
Cl	Cl	DMSO	*trans*	323.2	0.37		
Cl	Br	DMF	*cis*	322.5	37.3		
Cl	Br	DMSO	*cis*	322.8	56.7		
Cl	Br	DMF	*trans*	322.5	20.3		
Cl	Br	DMSO	*trans*	322.8	41.8		
DMF	Br	DMF	*cis*	323.2	16.2[b]	22.9	−5.5
DMF	Br	DMF	*trans*	323.2	2.25[c]	23.0	−8.5
DMSO	DMSO	DMSO	*trans*	323.2	8.8[d]	21.2	−12.0
DMSO	DMSO	DMSO	*trans*	323.2	1.2[e]	27.0	+2.5
DMSO	DMF	DMSO	*cis*	323.2	6.5[d]	23.2	−6.0
DMSO	DMF	DMSO	*cis*	323.2	0.6[e]	30.0	+10.0
DMF	DMF	DMSO	*trans*	323.2	2.7[d]	32.2	+20.0
DMF	DMF	DMSO	*trans*	323.2	1.4[e]	24.9	−4.0

trans→cis *Isomerization reactions at* 323.2 K

L	X	*Solvent*	10^5k/s^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
DMF	Br	DMF	1.2	27.4	+3.5
DMF	Cl	DMF	2.2	24.4	−4.5
DMSO	Cl	DMSO	3.7	22.3	−10.0
DMF	DMF	DMF	7.3	23.0	−6.5

[a] Rate constants corrected for a statistical factor of 2 (*i.e.* observed rate constant is twice this value). [b] Data for the reverse (anation) reaction also obtained. [c] Rate data for the loss of en to produce the $[Cr(en)(DMF)_4]^{3+}$ ion are: $10^5k = 1.3$ s^{-1}, $\Delta H^{\ddagger} = 26.4$ kcal mol^{-1}, and $\Delta S^{\ddagger} = +1.0$ cal K^{-1} mol^{-1}. [d] Rate data refer to solvolysis or solvent exchange. [e] Rate data refer to the loss of en.

The *trans*-$[Cr(en)_2(S)Cl]^{2+}$ ions (S = DMF or DMSO) undergo 100% isomerization to the corresponding *cis*-complexes except in the presence of added Cl^- ion when loss of en is the dominant reaction. The *trans*→*cis* isomerization occurs through the dissociation of a neutral group (*i.e. via* solvent exchange or a unidentate en intermediate).[144] For the *trans*-$[Cr(en)_2(S)_2]^{3+}$ ions (S = DMF or DMSO) and for *trans*-$[Cr(en)_2(DMSO)(DMF)]^{3+}$ the solvent exchange and isomerization reactions are synchronous, and loss of en is again significant (*ca.* 20%).[145]

A *D* mechanism is proposed for the solvolysis of the $[Cr(NCS)_6]^{3-}$ ion in non-aqueous solvents (S = DMSO, DMF, or Me_2NCOMe), and for the reactions of the product ion $[Cr(NCS)_5(S)]^{2-}$ with pyridine or thiocyanate ion in sulpholan.[11] Rate data for solvent exchange reactions of $[Cr(NCS)_5(S)]^{2-}$ ions are collected in Table 20.

Exchange of DMF with the $[Cr(DMF)_6]^{3+}$ ion has been studied as a function of pressure.[146] At 344.5 K and 0.1 MPa, $10^5k_{ex} = 7.4$ s^{-1}. The activation parameters which are independent of pressure up to 400 MPa are $\Delta H^{\ddagger} = 97.1$ kJ mol^{-1},

[146] S. T. D. Lo and T. W. Swaddle, *Inorg. Chem.*, 1975, **14**, 1878.

Table 20 *Rate data at* 298.2 K *for solvent exchange reactions with* $[Cr(NCS)_5(solvent)]^{2-}$ *ions (data from ref.* 11)

$$[Cr(NCS)_5S^1]^{2-} + S^2 \rightleftharpoons [Cr(NCS)_5S^2]^{2-} + S^1$$

S^1	S^2	$10^4k/s^{-1}$	E_a/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
$MeCONMe_2$	DMSO	1.57	85±3	−9±8
	DMF	4.40	114±3	100±20
DMF	DMSO	0.80	105±3	50±10
	$MeCONMe_2$	4.73	97±2	44±8
DMSO	DMF	0.71	171±6	280±30
	py	0.35	117±4	90±20

$\Delta S^{\ddagger} = 43.5$ JK^{-1} mol^{-1}, and $\Delta V^{\ddagger} = -6.3$ cm^3 mol^{-1}, the large negative value of $\Delta V^{\ddagger}$ being in accordance with an I_a mechanism. Perchlorate ion reduces the rate of solvent exchange slightly by ion-pair formation (K_{ip} *ca.* 6 dm^3 mol^{-1} at 344.5 K and 0.1 MPa). The rate of solvent exchange for the perchlorate ion pair is *ca.* 40% of its value in the free $[Cr(DMF)_6]^{3+}$ ion.

Catalysis.—*cis* Activation by co-ordinated oxoanions[109,114] and the catalytic effect of CO_2 and NO_2^- upon the rate of reaction of H_2O and DMSO with the $[Cr(H_2O)_n(DMSO)_{6-n}]^{3+}$ ions[116] were discussed in previous sections. The catalytic effect of chloride and bromide ions upon the rate of hydrolysis of $[Cr(NH_3)_5(ONO)]^{2+}$ was also noted earlier.[118]

IBr can be used to catalyse the removal of alkyl groups (R) from the $[Cr(H_2O)_5R]^{2+}$ ions in an S_E2 reaction:[147]

$$[Cr(H_2O)_5R]^{2+} + IBr + H_2O \longrightarrow [Cr(H_2O)_6]^{3+} + RI + Br^-$$

Rate constants at 298.2 K and $I = 1.0$ mol dm^{-3} are $k = 0.63 \pm 0.06$, 35.4 ± 2.2, $(1.16 \pm 0.09) \times 10^6$, $(1.0 \pm 0.2) \times 10^6$, and $(2.21 \pm 0.12) \times 10^5$ dm^3 mol^{-1} s^{-1} for R = CH_2Cl, $CHMe_2$, CH_2Ph, $CH_2C_6H_4Me$, and $CH_2C_6H_4CF_3$ respectively.

The rates of the Cr^{2+}_{aq} -ion-catalysed aquations of thiolatobis(ethylenediamine)-chromium(III) ions, $[Cr(en)_2(LL)]^{n+}$ (LL = $SCH_2CO_2^{2-}$, $SC_6H_4CO_2^{2-}$, or $SCH_2CH_2NH_2^-$), and of $[Cr(en)_2(ox)]^+$ ion have been measured, all the reactions proceeding by inner-sphere electron transfer. The thiolato-ligands are not such good bridging groups as were found in the analogous reactions of cobalt(III) complexes.[148]

4 Aquation: Other Complexes

***d*^{0}: Molybdenum(VI).**—The rapid hydrolysis of the $[MoOCl_5]^-$ ion ($k = 0.49$ s^{-1}) has been investigated by a spin-echo-method, and involves the formation of an intensely coloured, paramagnetic Mo^V intermediate.[149]

Base hydrolysis of the $[Mo_7O_{24}]^{6-}$ ion has been studied by the stopped-flow method using an excess of base (B):[150]

$$[Mo_7O_{24}]^{6-} + 4H_2O + 8B \longrightarrow 7[MoO_4]^{2-} + 8BH^+$$

The pseudo-first-order rate constant $k = k_0 + k_B[B] + k_{OH}[OH^-]$, with $k_0 =$

[147] J. H. Espenson and G. J. Samuels, *J. Organometallic Chem.*, 1976, **113**, 143.
[148] C. J. Weschler and E. Deutsch, *Inorg. Chem.*, 1976, **15**, 139.
[149] A. P. Filippov and U. M. Zyatkovskii, *Teor. i eksp. Khim.*, 1975, **11**, 272.
[150] J. P. Collin and P. Lagrange, *Bull. Soc. chim. France*, 1974, 773, 777.

4.72×10^{-2} s^{-1}, $k_{OH} = 8.5 \times 10^3$ dm^3 mol^{-1} s^{-1}, and $k_B = 580$, 600, 900, and 25 dm^3 mol^{-1} s^{-1} for B = PhO^-, gly^-, $digly^-$, and HPO_4^{2-}. Decondensation of the phosphomolybdate ions $[Mo_5P_2O_{23}]^{6-}$ and $[HMo_5P_2O_{23}]^{5-}$ has also been investigated. For $[Mo_5P_2O_{23}]^{6-}$ $k_{OH} = 16.7 \pm 0.9$ dm^3 mol^{-1} s^{-1}, and for $[Mo_7O_{24}]^{6-}$ a value of $k_{OH} = (1.30 \pm 0.13) \times 10^4$ dm^3 mol^{-1} s^{-1} is reported.[151]

The slow acid hydrolysis of 12-molybdogermanic acid has been studied in 1—11 mol dm^{-3} $HClO_4$:

$$H_4GeMo_{12}O_{40} + H^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} GeO_2 + \text{molybdate ions}$$

k_1 and k_2 are reported to have values of 0.304 and 4.34×10^{-2} h^{-1} respectively.[152]

The monomer–dimer equilibria in solutions of Mo^{VI} containing 0.2—3.0 mol dm^{-3} $HClO_4$ have been studied at 298.2 K and $I = 3.0$ mol dm^{-3} ($LiClO_4$) by the temperature-jump method.[153] The presence of $[HMoO_3]^+$, $[H_2Mo_2O_6]^{2+}$, and $[H_3Mo_2O_6]^{3+}$ ions is confirmed, and $[H_2MoO_3]$ is also present. The major equilibrium reaction observed is $2[HMoO_3]^+ \rightleftharpoons [H_2Mo_2O_6]^{2+}$, for which the rate constants for the forward and reverse reactions are $10^{-5}k_f = 1.71$ dm^3 mol^{-1} s^{-1} and $10^{-3}k_r = 3.20$ s^{-1} respectively. The reaction $[H_2MoO_3]^{2+} + [HMoO_3]^+ \rightleftharpoons [H_3Mo_2O_6]^{3+}$ also contributes to a small extent with $10^{-4}k_f = 3$ dm^3 mol^{-1} s^{-1} and $k_r = 30$ s^{-1}.

***d*^{0}: Vanadium(v).**—Although there are four types of V—O bonding in the $[V_{10}O_{28}]^{6-}$ ion, a study of the ^{18}O exchange with $H_2{}^{18}O$ at pH 6.7—7.2 and 298.2 K indicates that all of the oxygen atoms exchange at the same rate, with $10^5k_{ex} = 1.32 \pm 0.01$ s^{-1}.[154]

***d*^{1}: Molybdenum(v).**—The rate of the rapid reaction of the Mo^V-dimer ion $[Mo(H_2O)_3O_2]_2^{2+}$ with NCS^- ion has been studied by the temperature-jump method:[155]

$$[Mo(H_2O)_3O_2]_2^{2+} + NCS^- \rightleftharpoons [Mo(H_2O)_3O_2][Mo(H_2O)_2(NCS)O_2]^+ + H_2O$$

With excess dimer present only one relaxation time is observed, and at 298.2 K, $I = 2.0$ mol dm^{-3} ($LiClO_4$), and $[H^+] = 0.50$—2.0 mol dm^{-3}, the forward and reverse rate constants are $10^{-4}k_1 = 2.9$ dm^3 mol^{-1} s^{-1} and $k_{-1} = 120$ s^{-1} respectively, with $K_{eq} = 243$ dm^3 mol^{-1}.

The ease of substitution into $[Mo_2O_4(ox)_2(H_2O)_2]$ has been observed. Acid hydrolysis gives $[MoO_2(H_2O)_3]_2^{2+}$, and in concentrated HCl the $[MoOCl_5]^{2-}$ ion is formed. The oxalato-dimer reacts rapidly with thioglycollic acid to give a 1:1 complex, and then more slowly to give higher species.

***d*^{2}: Molybdenum(iv).**—Recently a dimeric structure, $[Mo_2O_2]^{4+}$, was rejected for acidic ($HClO_4$) solutions of Mo^{IV} on the basis of ion-exchange experiments, and a monomeric formulation, MoO^{2+} {or $[Mo(OH)_2]^{2+}$}, was proposed instead.[157] Further studies in CF_3CO_2H, notably cryoscopy in 5.1 mol dm^{-3} CF_3CO_2H, indicate that

151 R. Mellstrom and N. Ingri, *Acta Chem. Scand.*, 1974, **A28**, 703.
152 M. Biquard and P. Souchay, *Ann. Chim. (France)*, 1975, **10**, 163.
153 J. F. Ojo, R. S. Taylor, and A. G. Sykes, *J.C.S. Dalton*, 1975, 500.
154 R. K. Murmann, *J. Amer. Chem. Soc.*, 1974, **96**, 7836.
155 Y. Sasaki, R. S. Taylor, and A. G. Sykes, *J.C.S. Dalton*, 1975, 396.
156 A. Komura, Y. Ikeda, and H. Imanaga, *Bull. Chem. Soc. Japan*, 1976, **49**, 131.
157 T. Ramasani, R. S. Taylor, and A. G. Sykes, *J. Amer. Chem. Soc.*, 1975, **97**, 5918.

the originally proposed dimer formulation[158] is in fact correct.[33] The use of perchloric acid is not recommended for Mo^{IV} because reduction to Cl^- occurs.[33] The recently reported reactions of Mo^{IV} with thiocyanate ion[34,159] may therefore refer to reactions of the dimer $[Mo_2O_2]^{4+}$ ion, and although only a 1:1 complex was reported to be formed, the more recent work suggests that both the $[\{MoO\}_2NCS]^{3+}$ and $[\{MoO\}_2(NCS)_2]^{2+}$ ions are involved, the 2:1 species being more important in the presence of excess thiocyanate ion.[33]

Exchange of ^{18}O between $H_2{}^{18}O$ and the $[Mo(CN)_4(OH)O]^{3-}$ or $[Mo(CN)_4(O)_2]^{4-}$ ions has been shown to be complete in less than 2 min at 273 K.[160]

***d*²: Rhenium(v).**—Disproportionation of the $[Re^{V}OCl_5]^{2-}$ ion (3×10^{-3} mol dm^{-3}) to Re^{VII} and Re^{IV} has been studied at 293 K in aqueous solutions containing HCl (*ca.* 0.1 mol dm^{-3}) and K_2SO_4:

$$3[ReOCl_5]^{2-} + 5H_2O \rightleftharpoons [ReO_4]^- + 2[ReO_2] + 15Cl^- + 10H^+$$

The order with respect to Re^{V}, Cl^-, and H^+ ions is reported to be 2, 15.2, and 9.9 respectively.[161]

***d*³: Molybdenum(III).**—Formation and dissociation of 1:1 complexes of the $[Mo(H_2O)_6]^{3+}$ ion with Cl^- and NCS^- ions has been studied between 298.2 and 313.7 K in 0.17—1.0 mol dm^{-3} H^+ and $I = 1.0$ mol dm^{-3} (p-$MeC_6H_4SO_3Li$). The relative rates of reaction with these two ions indicate an I_a mechanism for complex formation.[162]

***d*³: Technetium(IV).**—Kinetic and equilibrium studies have been reported[163] for the aquation of the $[TcX_6]^{2-}$ ions (X = Cl or Br) and for the anation of the $[Tc(OH_2)X_5]^-$ ions in aqueous solutions containing HX–MX (M = Li, Na, or K):

$$[TcX_6]^{2-} + H_2O \underset{k_b}{\overset{k_f}{\rightleftharpoons}} [Tc(OH)_2X_5]^- + X^- \qquad (14)$$

The cations have a marked effect upon the rates of the reactions, and rates were measured in Na^+ or K^+ solutions. The observed rate constant (k) is given by equation (15):

$$k = k_f[H^+] + k_b[X^-] \qquad (15)$$

The values of k_f, k_d, and the equilibrium constant K_{eq} are collected in Table 21.

Table 21 *Rate and equilibrium data for reaction* (14). *Rate constants are defined by equation* (15) (*data from ref.* 163)

X	10^4k_f/ dm^3 mol^{-1} s^{-1}	$E_a(k_f)$/ kcal mol^{-1}	10^4k_b/ dm^3 mol^{-1} s^{-1}	$E_a(k_b)$/ kcal mol^{-1}	K_{eq}
Cl	1.18—9.07[a]	32.6±2.6	0.916—6.52[a]	30.7±2.3	1.25—1.39[a]
Br	2.77—21.7[b]	28.7±1.4	3.65—18.8[b]	23.7±1.1	0.756—1.14[b]

[a] Between 348.2 and 363.2 K. [b] Between 313.2 and 327.7 K.

158 M. Ardon and A. Pernick, *J. Amer. Chem. Soc.*, 1973, **95**, 6871; 1974, **96**, 1643.
159 J. F. Ojo, Y. Sasaki, R. S. Taylor, and A. G. Sykes, *Inorg. Chem.*, 1976, **15**, 1006.
160 R. K. Murmann and P. R. Robinson, *Inorg. Chem.*, 1975, **14**, 203.
161 A. I. Kostromin, M. I. Evgen'ev, and L. A. Novikova, *Zhur. fiz. Khim.*, 1975, **49**, 509.
162 Y. Sasaki and A. G. Sykes, *J.C.S. Dalton*, 1975, 1048.
163 M. Kawashima, M. Koyama, and T. Fujinaga, *J. Inorg. Nuclear Chem.*, 1976, **38**, 819.

d^4: Manganese(III).—The rates of oxidation of thiourea derivatives and of benzene-1,2-dithiol by the $[Mn(OH)]^{2+}$ ion have been shown to be controlled by the rate of substitution of the substrate at the Mn^{III} ion.[164]

d^4: Rhenium(III).—A very short-lived triplet excited state has been detected in the laser flash photolysis of $[Re_2X_8]^{2-}$ ions (X = Cl or Br). Photocleavage of $[Re_2Cl_8]^{2-}$ to the $[ReCl_4(MeCN)_2]^-$ ion was reported previously.[165]

d^5: Molybdenum(I).—The electrochemically generated Mo^I dinitrogen complex ion, *trans*-$[Mo(N_2)_2(Ph_2PCH_2CH_2PPh_2)]^+$ undergoes first-order solvolysis with loss of both dinitrogen ligands in THF–MeOH (26% v/v) and 0.1 mol dm^{-3} LiX (X = Cl^- or ClO_4^-). At 298.2 K in the presence of LiCl, $k = 0.24 \pm 0.02$ s^{-1}, $E_a = 24 \pm 2$ kcal mol^{-1}, and $\Delta S^{\ddagger} = 19 \pm 5$ cal K^{-1} mol^{-1}, and in $LiClO_4$ $k = 0.33 \pm 0.03$ s^{-1}, $E_a = 26 \pm 2$ kcal mol^{-1}, and $\Delta S^{\ddagger} = 26 \pm 7$ cal K^{-1} mol^{-1}. The product disproportionates into Mo^0 and Mo^{II} species.[166]

d^5: Iron(III).—A number of studies have been reported for the reaction of $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_5L]^{n-}$ ions with Co^{II} complexes.[167–169] These inner-sphere redox reactions often involve the formation of transient intermediates containing a ligand-bridged Fe^{II}/Co^{III} dinuclear complex. For example, reaction of $[Co^{II}(edta)]^{2-}$ with $[Fe^{III}(CN)_6]^{3-}$ or $[Fe^{III}(CN)_5PPh_3]^{2-}$ produces a deep-purple cyano-bridged intermediate:

$$[Fe^{III}(CN)_5L]^{n-} + [Co^{II}(edta)]^{2-} \longrightarrow [L(CN)_4Fe^{II}{-}C{\equiv}N{-}Co^{III}(edta)]^{(2+n)-}$$

At 303 K, pH 6.0, and $I = 0.26$ mol dm^{-3}, the rate constants for the formation (k_f) and dissociation (k_d) of the intermediate are $10^{-4}k_f = 3.8$ and 2.0 dm^3 mol^{-1} s^{-1} and $10^3k_d = 17.4$ and 2.10 s^{-1}, and the equilibrium formation constants are 201 and 1490 dm^3 mol^{-1} for L = CN^- and PPh_3 respectively.[167]

The high-temperature solution decomposition of $[Fe^{III}(TPP)N_3]$ (TPP = the tetraphenylporphyrinato-ion) gives the dimer complex $[(TPP)Fe]_2N$. The reaction is first-order and has an activation energy of 33.7 kcal mol^{-1}. $[(TPP)Fe]_2N$ is analogous to $[(TPP)Fe]_2O$ and contains one unpaired electron per dimer unit.[170]

The rates of dissociation of Fe^{III}, Ni^{II}, and Cu^{II} complexes of $\alpha,\beta,\gamma,\delta$-tetraphenylporphine have been measured in glacial acetic acid containing 0.5—5.0 mol dm^{-3} H_2SO_4,H_2O at 288—343 K. The relative rates are 300:6:1 for Cu^{II}, Ni^{II}, and Fe^{III} respectively, with activation energies in the range 16—20 kcal mol^{-1}. The Zn^{II} complex is much more labile.[171]

d^5: Ruthenium(III).—Aquation of the $[Ru(NH_3)_5Cl]^{2+}$ and *cis*-$[Ru(en)_2Cl_2]^+$ ions has been studied in mixed aqueous–organic solvents.[172] A dissociative mechanism is indicated from plots of the logarithm of the rate constants for aquation *versus* the Grunwald–Winstein Y values which are linear with gradients of *ca.* 0.25. The Hg^{2+}-

[164] G. Davies, *Inorg. Chim. Acta*, 1975, **14**, L13—14.
[165] R. H. Fleming, G. L. Geoffrey, H. B. Gray, A. Gupta, G. S. Hammond, D. S. Kliger, and V. M. Miskowski, *J. Amer. Chem. Soc.*, 1976, **98**, 48.
[166] C. M. Elson, *Inorg. Chim. Acta*, 1976, **18**, 209.
[167] R. X. Ewall and D. H. Huchital, *Inorg. Chem.*, 1975, **14**, 494.
[168] M. Takahashi and N. Tanaka, *Bull. Chem. Soc. Japan*, 1974, **47**, 1426.
[169] H. E. Toma, *J. Inorg. Nuclear Chem.*, 1975, **37**, 785.
[170] D. A. Summerville and I. A. Cohen, *J. Amer. Chem. Soc.*, 1976, **98**, 1747.
[171] B. D. Berezin, A. N. Drobysheva, and E. A. Venediktov, *Chem. Abs.*, 1976, **84**, 156224.
[172] L. A. P. Kane-Maguire and G. Thomas, *J.C.S. Dalton*, 1975, 1324.

ion-catalysed aquation of $[Ru(NH_3)_5Cl]^{2+}$ proceeds *via* a Ru^{III}—Cl—Hg^{II} intermediate, and a plot of log $k_{Hg^{2+}}$ with the Grunwald–Winstein Y values is non-linear.

The complexes *trans*-$[Ru(en)_2X_2]X,\frac{1}{2}H_2O$ (X = Cl or Br) have been prepared by isomerization of the *cis*-isomers in boiling ethylene glycol followed by ion-exchange separation. Aquation of *trans*-$[Ru(en)_2Cl_2]^+$ in $MeSO_3H$ solution proceeds with retention of configuration to give the *trans*-$[Ru(en)_2(OH_2)Cl]^{2+}$ ion.[173]

For the following reaction, the observed[174] rate constant is given by $k = k_1 + k_2/[H^+]$:

$$[(H_3N)_5RuNH_2CH_2CO_2H]^{3+} \longrightarrow [(H_3N)_5RuO_2CCH_2NH_3]^{3+}$$

At 298.2 K, $10^3k_1 = 2\ s^{-1}$ and $10^4k_2 = 1.25$ mol $dm^{-3}\ s^{-1}$. This isomerization from an *N*-bonded to an *O*-bonded glycine complex does not occur for the analogous cobalt(III) complex. The reverse reaction is complicated by side reactions.

Aquation of the $[Ru(NH_3)_5O_2CCH_2Cl]^{2+}$ ion is reported to proceed by an S_N2 mechanism and a seven-co-ordinate transition-state, whereas the reverse process, anation of $[Ru(NH_3)_5OH_2]^{3+}$ by $ClCH_2CO_2^-$, is claimed to involve an S_N1(lim) mechanism.[175]

Base hydrolysis of the $[Ru(NH_3)_5I]^{2+}$ ion is reported to proceed *via* an S_N2 and an S_N2cb mechanism.[176] Attack of OH^- ion at co-ordinated organonitriles (RCN) in $[Ru(NH_3)_5(NCR)]^{3+}$ ions is *ca.* 10^8 times as fast as in the unco-ordinated nitrile.[177]

d^6: Rhodium(III).—Electrophoresis has been used to study the kinetics of aquation and some redox and polymerization reactions of the $[IrCl_6]^{3-}$ and $[IrCl_6]^{4-}$ ions in neutral and alkaline solutions.[178]

A dissociative mechanism involving a square-pyramidal transition state is proposed for the aquation and chloride-ion anation reactions of *fac*- and *mer*-$[RhCl_3(H_2O)_3]$.[179]

The pseudo-first-order rate constant for the base hydrolysis of the *trans*-$[Rh(en)_2X_2]^+$ ions (X = Cl, Br, or I) varies with $[OH^-]$ according to equation (16).[180]

$$k = k_1 + k_2[OH^-] \qquad (16)$$

Rates and activation parameters associated with the values of k_1, the independently determined aquation rate constants (k_{aq}), and the base-hydrolysis rate constants (k_2) are collected in Table 22. The activation parameters associated with the k_1 and k_{aq} values are the same within experimental error. The hydroxide-ion-independent pathways lead to virtually complete *trans*→*cis* isomerization when X = Cl or Br, and to *ca.* 50% isomerization when X = I. The relatively small contribution of the k_2 term in equation (16) (k_2/k_1 *ca.* 1 $dm^3\ mol^{-1}$) arises from the lower values of $\Delta S^{\ddagger}(k_2) - \Delta S^{\ddagger}(k_1)$ than are observed for *cis*-$[Rh(en)_2(OH)X]^+$ or $[Rh(NH_3)_5X]^{2+}$. Values of $\Delta H^{\ddagger}(k_2)$ and $\Delta S^{\ddagger}(k_2)$ lie at the upper end of an isokinetic plot that includes data for the *trans*-$[Rh(en)_2(OH)X]^+$ ions. This isokinetic plot lies above that for complexes which contain NH groups in a *trans* position to the leaving group, the respective

[173] J. A. Broomhead, L. A. P. Kane-Maguire, and D. Wilson, *Inorg. Chem.*, 1975, **14**, 2575.
[174] S. E. Diamond and H. Taube, *J. Amer. Chem. Soc.*, 1975, **97**, 5921.
[175] H. Sakamoto, K. Yoshikuni, S. Ohno, K. Ohkubo, and A. Ohyoshi, *Chem. Letters*, 1974, 1309.
[176] H. Sakamoto, H. Makino, and K. Hamada, *Chem. Letters*, 1975, 631.
[177] A. W. Zanella and P. C. Ford, *Inorg. Chem.*, 1975, **14**, 42.
[178] W. J. Van Ooij and J. P. Whoutman, *Radiochim. Acta*, 1973, **20**, 47.
[179] D. A. Palmer and G. M. Harris, *Inorg. Chem.*, 1975, **14**, 1316.
[180] A. Poë and C. Vuik, *Canad. J. Chem.*, 1975, **53**, 1842; *J.C.S. Dalton*, 1976, 661.

Table 22 *Rate parameters for the aquation (k_1) and base hydrolysis (k_2) of* trans-$[Rh(en)_2X_2]^+$ *ions at* $I = 1.0$ mol dm^{-3} [*equation* (16); *data from ref.* 180]

X	Cl	Br	I
$10^6 k_1/s^{-1}$	5.33 ± 0.21^a	17.9 ± 0.6^b	384 ± 6^c
$\Delta H^{\ddagger}(k_1)$/kJ mol^{-1}	109.0 ± 2.6	107.9 ± 1.4	102.0 ± 0.5
$\Delta H^{\ddagger}(k_{aq})$/kJ mol^{-1} [d]	103 ± 1	105 ± 1	105 ± 1
$\Delta S^{\ddagger}(k_1)$/J K^{-1} mol^{-1}	-21.5 ± 7.7	-13.4 ± 4.0	-5.6 ± 1.6
$\Delta S^{\ddagger}(k_{aq})$/J K^{-1} mol^{-1} [d]	-38 ± 4	-21 ± 4	4 ± 4
$10^6 k_2$/dm^3 mol^{-1} s^{-1}	3.85 ± 0.43^a	16.8 ± 0.9^b	181 ± 11
$\Delta H^{\ddagger}(k_2)$/kJ mol^{-1}	146.7 ± 5.9	140.0 ± 2.7	130.5 ± 3.0
$\Delta S^{\ddagger}(k_2)$/J K^{-1} mol^{-1}	87.9 ± 17.3	84.8 ± 7.7	73.9 ± 9.0

[a] At 335.37 K. [b] At 333.56 K. [c] At 332.76 K. [d] Activation parameter for aquation for comparison with data associated with k_1 values.

isokinetic temperatures being *ca.* 373 and 463 K. The reactions which lead to extensive stereochemical rearrangement are believed to occur by an S_N1cb mechanism, and reactions further down the isokinetic plot are postulated to have a mechanism closer to the S_N1ip end of an S_N1cb–S_N1ip mechanistic spectrum.[180] The position of hydroxide ion in the intrinsic kinetic *trans*-effect series is shown to be $I^- \gg Br^- > NH_3 > OH^- \geqslant Cl^-$. The thermodynamic *trans*-influence series is $I^- > OH^- > NH_3 > Br^- > Cl^- > H_2O$. A comparison of the kinetic *trans* effect and thermodynamic *trans* influence has been made for complexes of the type *trans*-$[ML_4XCl]^{n+}$ and *trans*-$[ML_4(OH_2)X]^{n+}$ (M = Co^{III}, Rh^{III}, or Pt^{IV}, L_4 = amine ligands, X = OH, Cl, NCS, or NO_2).[181]

The rate of hydrolysis of the $[Rh(tren)Cl_2]^+$ ion has been measured at pH 1—5 in perchloric acid.[182] At 333.5 K, $10^3k = 1.14$ s^{-1} for loss of the first chloride ion, and there is no evidence for a second step involving loss of chloride ion from the $[Rh(tren)(OH_2)Cl]^{2+}$ ion. The activation parameters for the first step are $\Delta H^{\ddagger} = 18.7$ kcal mol^{-1} and $\Delta S^{\ddagger} = 16.0$ cal K^{-1} mol^{-1}.

The rate of reaction (17), which involves cleavage of the Rh—N bond in the Rh^{III} complex with the N,As-donor ligand 1,2-$Me_2NC_6H_4AsMe_2$ (L), has been investigated in alcoholic solvents (ROH); R = Me, Et, Pr^n, or Pr^i).[183] L′ represents the

$$trans\text{-}[Rh(L)_2Cl_2]^+ + X^- \rightleftharpoons mer\text{-}[Rh(L)(L')Cl_2X] \qquad (17)$$

unidentate As-donor ligand L, and X = Cl, Br, or NCS. The observed rate law is,

$$-d[Rh(L)_2Cl_2]/dt = k_1\gamma_{\pm}^2[Rh(L)_2Cl_2^+][X^-] - k_2[Rh(L)(L')Cl_2X]$$

where $\gamma_{\pm}$ is the mean ionic activity coefficient. The rate of the forward reaction (rate constant k_1) increases with decreasing polarity of the solvent as expected for reactions between ions of opposite charge. In MeOH, k_1 varies with X in the order NCS > I > Br > Cl, and this is explained by invoking some Rh—X bond formation in the transition state. The rates of the reverse reactions also vary with the nature of X and with change in the solvent. The solvent effect is rationalized using the Grunwald–Winstein Y values: $\log k_2 = mY +$ constant. The high values of m (1.24, 1.19, and 0.95 for X = Cl, Br, and I respectively) are taken as an indication of a dissociative

[181] A. V. Belyaev, S. Y. Dvurechenskaya, and B. I. Peshchevitskii, *Chem. Abs.*, 1975, 8021.
[182] S. G. Zipp and S. K. Madan, *J. Inorg. Nuclear Chem.*, 1975, **37**, 181.
[183] A. Peloso and L. Volponi, *J.C.S. Dalton*, 1976, 923.

mechanism, the rates varying with the strength of the Rh—X bond, NCS > Cl > Br > I.

Replacement of the chloro-ligands by bromide ion has been studied for the *trans*-$[Rh(LL)Cl_2]^+$ ions (LL = *N*-methyl, *NN'*-dimethyl-, *NN*-dimethyl-, *NNN'*-trimethyl-, or *NNN'N'*-tetramethyl-ethane-1,2-diamine).[184] The results are discussed in a later section concerned with ligand exchange.

Photochemistry. Photoaquation and luminescence results at 77 K have been reported from the ligand-field excitation of the $[Rh(NH_3)_5L]^{3+}$ ions (L = MeCN, PhCN, py, 3-Cl-py, or 4-Me-py).[185] Irradiation of the lowest-energy ligand-field band with 313 nm light leads to almost exclusive photoaquation of the unique ligand. For example, quantum yields for the loss of MeCN compared with NH_3 are 0.47 ± 0.04 and $< 2 \times 10^{-3}$ respectively, despite the fact that these ligands are close to each other in the spectrochemical series. Although the absorption band energies are approximately the same for all L, the emission band energies differ in a way which can be rationalized in terms of the σ- and π-bonding in the ground and excited states. In general those complexes which photoaquate most readily have the lower-energy emission band maxima and the shorter measured emission lifetimes in methanol–water glasses. It is concluded that there are close connections between the structure factors which affect the photochemical and photophysical radiationless decay processes. The $[Rh(ND_3)_5L]^{3+}$ ions (L = py or $[^2H_5]$-py) were also studied, and the quantum yield for photoaquation at 298 K and the emission lifetime at 77 K are increased. This effect is interpreted in terms of a weak coupling mechanism which contributes to the non-radiative deactivation pathways under both sets of conditions.

The photoaquations of the $[Rh(NH_3)_5X]^{2+}$ and $[Co(CN)_5X]^{3-}$ ions (X = N_3, NCS, or SCN) have been compared.[103] Ligand-field excitation of the Rh^{III} complexes leads to aquation of X with very small quantum yields (*ca.* 10^{-2}—10^{-4}), whereas for the Co^{III} complexes quantum yields are appreciable (0.2—0.03). The quantum yields vary with changes in the medium (*e.g.* viscosity), are not wavelength-dependent, and are not related to simple crystal-field parameters. This is in contrast to $[Co(NH_3)_5X]^{2+}$ ions which have quantum yields which are strongly wavelength-dependent.

The photochemistry of the *cis*- and *trans*-$[Rh(cyclam)X_2]^+$ ions (X = Cl, Br, or I) and *cis*-$[Rh(en)_2Cl_2]^+$ has been compared.[186] For the complexes of cyclam photoaquation proceeds with loss of X and retention of configuration, whereas loss of en is dominant for the *cis*-$[Rh(en)_2Cl_2]^+$ ion and isomerization occurs through a secondary reaction. In both cases the complexes are more sensitive to charge-transfer rather than ligand-field excitation. For ligand-field excitation of the *trans*-$[Rh(cyclam)X_2]^+$ ions the quantum yields vary in the order Cl < Br < I as predicted by the theory of Zink.[187] However, for ligand-field excitation of the *cis*-$[Rh(cyclam)X_2]^+$ ions the quantum yields are Cl (0.37) > Br (0.32) $\gg$ I (0.03). The behaviour of *cis*-$[Rh(en)_2Cl_2]^+$ and *cis*-$[Rh(cyclam)_2I_2]^+$ ions is consistent with preferential amine activation as predicted by Zink's model. The change in specificity observed with the *cis*-$[Rh(cyclam)X_2]^+$ ions (X = Cl or Br) is interpreted as the result of distortion from

[184] M. P. Hancock, B. T. Heaton, and D. H. Vaughan, *J.C.S. Dalton*, 1976, 931.
[185] J. D. Petersen, R. J. Watts, and P. C. Ford, *J. Amer. Chem. Soc.*, 1976, **98**, 3188.
[186] J. Sellan and R. Rumfeldt, *Canad. J. Chem.*, 1976, **54**, 1061.
[187] J. I. Zink, *J. Amer. Chem. Soc.*, 1972, **94**, 8039; *Mol. Photochem.*, 1973, **5**, 151; *Inorg. Chem.*, 1973, **12**, 1018, 1957.

tetragonal symmetry which causes the repulsive energy to become more localized in the Rh—X bond.

A comparison of the photochemistry of cyanocobalamin and Rh^{III} corrins was discussed previously.[106]

d^6: Iron(II).—Only low-spin (t_{2g}^6) complexes are considered here. A dissociative mechanism is confirmed for the aquation of $[Fe(LL)_3]^{2+}$ ions (LL = phen, 5-NO_2-phen, or 3,7-diMe-phen) from measurements of the volumes of activation.[188] At 308 K in 1 mol dm^{-3} H_2SO_4 values of $\Delta V^{\neq}$ are 15.4, 17.9, and 11.6 cm^3 mol^{-1} respectively. Aquation of $[Fe(5\text{-}NO_2\text{-phen})_3]^{2+}$ has also been investigated in binary aqueous–organic mixtures[189] and in aqueous gels.[190] The rates of aquation in aqueous–organic mixtures were correlated with the excess molar Gibbs energy of mixing for the binary mixtures.[189] The rates of aquation of the $[Fe(5\text{-}NO_2\text{-phen})_3]^{2+}$ ion in aqueous agar and gelatin gels and sols, and for the substitution reaction of the $[Fe(5\text{-Me-phen})_3]^{2+}$ ion with CN^- ion in aqueous agar, are very similar to the rates in aqueous solution.[190] The rates of dissociation and racemization of the $[Fe(phen)^3]^{2+}$ ion have been studied in a wide range of solvents (H_2O, MeOH, Me_2CO, $HCONH_2$, DMF, MeCN, and AcOH) and in mixed aqueous–organic solvents.[191] In all cases the rate of dissociation is much lower than the rate of racemization, indicating that racemization proceeds intramolecularly in these solvents. Ion association with ClO_4^- ion, when it occurs, retards the rate of racemization.

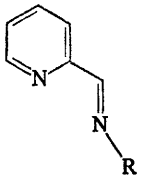
Dissociation of $[Fe(bipy)_3]^{2+}$ is accelerated by excess Cl^- and NO_3^- ions in HCl, $HClO_4$, and H_2SO_4 solutions (0.1—0.3 mol dm^{-3} H^+).[192] Co-ordination of the anion (X^-) in the half-bonded bipy intermediate $\{[Fe(bipy)_2(\text{unidentate bipy})X]^+\}$ is proposed. Limiting rates were observed below 10^{-2} mol dm^{-3} H^+ and above 2 mol dm^{-3} H^+.

Reaction of $[Fe(bipy)_3]^{2+}$ with CN^- ion has been studied in aqueous–organic mixtures [$\leqslant 30\%$ (vol) MeOH, EtOH, dioxan, and Me_2CO and $\leqslant 48\%$ Bu^tOH], and in aqueous solutions containing added electrolytes (KX, Me_4NX, or Bu_4NX; X = Cl or Br).[193] The reactivity trends are compared with those predicted from a consideration of the variation in the estimated chemical potentials of CN^- with solvent composition.

The rates of reaction of the optically active $[Fe(LL)_3]^{2+}$ ions with CN^- have been compared for LL = bipy and phen.[194] The $[Fe(bipy)_3]^{2+}$ ion reacts predominantly with retention of configuration whereas earlier studies showed that $[Fe(phen)_3]^{2+}$ reacts with a predominance of optical inversion. Values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are higher for the retention pathway than for the inversion pathway.

The rates of the simultaneous dissociation of the two types of Fe—N bond have been compared in complex ions of the type $[Fe(LL')_3]^{2+}$ (LL′ = (35), R = Me or Pr^n).[195]

[188] J. M. Lucie, D. R. Stranks, and J. Burgess, *J.C.S. Dalton*, 1975, 245.
[189] M. J. Blandamer, J. Burgess, and R. I. Haines, *J.C.S. Dalton*, 1976, 385.
[190] M. J. Blandamer, J. Burgess, and J. R. Membrey, *J.C.S. Faraday I*, 1075, **71**, 145.
[191] F. M. Van Meter and H. M. Neumann, *J. Amer. Chem. Soc.*, 1976, **98**, 1388.
[192] S. Raman, *J. Inorg. Nuclear Chem.*, 1976, **38**, 781; 1975, **37**, 1747.
[193] M. J. Blandamer, J. Burgess, and J. G. Chambers, *J.C.S. Dalton*, 1976, 606.
[194] D. D. Dollberg and R. D. Archer, *Inorg. Chem.*, 1975, **14**, 1888.
[195] E. J. S. Vichi and P. Krumholz, *J.C.S. Dalton*, 1975, 1543.



(35)

Rate constants for the dissociation of the tris-[2,3-bis-(2-pyridyl)pyrazine]iron(II) ion are reported to be $10^3k = 4.3$ and 6.8 s^{-1} at 298.2 and 308.2 K respectively.[196]

At 298.2 K, the rate of aquation of the $[Fe(CN)_5(4,4'\text{-bipyridyl})]^{3-}$ ion is $10^4k = 7.8\ s^{-1}$.[197]

For a long time the $[Fe(CN)_5OH_2]^{3-}$ ion has been known to exist in a monomer–dimer equilibrium. Recent kinetic studies indicate that the following equilibria exist:[198]

$$2[Fe(CN)_5OH_2]^{3-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [(H_2O)(CN)_4Fe\text{-}\mu\text{-}(CN)\text{-}Fe(CN)_5]^{6-} + H_2O \qquad (36)$$

$$[(H_2O)(CN)_4Fe\text{-}\mu\text{-}(CN)\text{-}Fe(CN)_5]^{6-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [(CN)_4Fe\begin{matrix}CN\\NC\end{matrix}Fe(CN)_4]^{6-} + H_2O \qquad (37)$$

At pH > 11, reaction of aqueous solutions of the $[Fe(CN)_5NH_3]^{3-}$ ion with excess CN^- or isonicotinamide (L) gives $[Fe(CN)_5L]^{n-}$ with two well resolved pseudo-first-order stopped-flow signals. The first reaction is attributed to L reacting with $[Fe(CN)_5OH_2]^{3-}$, this being the only iron species present at low dilution. The rate of the second, slower reaction is independent of [L], and can be ascribed to the conversion of the dicyano-bridged dimer (37) into the singly bridged cyano-dimer (36), which then reacts rapidly with L to give two moles of $[Fe(CN)_5L]^{n-}$; at 298.2 K and $I = 1.0$, $10^2k_{-2} = 1.63 \pm 0.01\ s^{-1}$, $\Delta H^{\ddagger}(k_{-2}) = 25$ kcal mol^{-1}, and $\Delta S^{\ddagger} = 18$ cal K^{-1} mol^{-1}. The rate constant reported by Emschwiller for the formation of the dimer (at 283.2 K and pH 10, $k_f = 5.1\ dm^3\ mol^{-1}\ s^{-1}$) is assigned as $k_f = k_2k_1/k_{-1}$. From data reported for the reaction of the $[Fe(CN)_5OH_2]^{3-}$ ion with $[Co(CN)_6]^{3-}$ (Higginson *et al.*), $k_1 = 3.5\ dm^3\ mol^{-1}\ s^{-1}$ and $10^{-3}K_1 \approx (2 \pm 1.5)\ dm^3\ mol^{-1}$ at 283 K. Hence $10^3k_{-1} \approx 1.7$ at 283 K, and since $K_1K_2 = k_1k_2/k_{-1}k_{-2} = 1.7 \times 10^3$ (Emschwiller) an estimate can be made for $10^3k_2 = 0.8$—5.6 at 283 K and pH 10. Species (36) and (37) are present in comparable amounts between pH 9 and 11 and at 283 K. The aquoligand in the dimer (36) is less labile than in the $[Fe(CN)_5OH_2]^{3-}$ ion.[198] A comparison of the rates of complexation of the $[Fe(CN)_5OH_2]^{3-}$ ion with pyrazine, Me_2CS, isonicotinamide, MeCN, CN^-, and NO_2^- ions, and the rate of oxidation by hydrogen peroxide and t-butyl peroxide, shows that the latter reactions are substitution controlled.[199]

[196] P. J. Guerney, R. J. Knight, and R. N. Sylva, *Austral. J. Chem.*, 1974, **27**, 2671.
[197] D. Gaswick and A. Haim, *J. Amer. Chem. Soc.*, 1974, **96**, 7845.
[198] G. Davies and A. R. Garafalo, *Inorg. Chim. Acta*, 1976, **19**, L3.
[199] G. Davies and A. R. Garafalo, *Inorg. Chem.*, 1976, **15**, 1101.

The rates of formation and dissociation of cyano-bridged dimers of the type $[(CN)_5Fe^{II}CNCo^{III}L_5]^{n-}$ and $[(CN)_5CoCNCo(en)_2SO_3]^{2-}$ have been investigated by the stopped-flow method.[200] Dinuclear complexes are formed on treating the *trans*-$[Co(en)_2(SO_3)(OH_2)]^+$ ion with $[Fe(CN)_5NO]^{2-}$, $[Fe(CN)_6]^{4-}$, and $[Fe(CN)_6]^{3-}$ ions. For example,

$$\begin{matrix} \textit{trans}\text{-}[Co(en)_2(SO_3)(OH_2)]^+ \\ + \\ [Fe(CN)_5(NO)]^{2-} \end{matrix} \longrightarrow [(ON)(NC)_4FeCNCo(en)_2SO_3]^- + H_2O$$

Reaction of the $[(ON)(NC)_4FeCNCo(en)_2SO_3]^-$ ion with $[Fe(CN)_6]^{3-}$ was also investigated, the rate being independent of $[Fe(CN)_6^{3-}]$:

$$\begin{matrix} [(ON)(NC)_4FeCNCo(en)_2SO_3]^- \\ + \\ [Fe(CN)_6]^{3-} \end{matrix} \longrightarrow [(NC)_5FeCNCo(en)_2SO_3]^{2+} + [Fe(CN)_5NO]^{2-}$$

$$-d[(ON)(NC)_4FeCNCo(en)_2SO_3^-]/dt = k[(ON)(NC)_4FeCNCo(en)_2SO_3^-]$$

The rate of dissociation of the $[(NC)_5CoCNCo(en)_2SO_3]^{2-}$ ion was investigated in the same way.

Photochemical studies of porphyrin complexes of the type [M(porphyrin)(pip)(CO)] or [M(porphyrin)$(pip)_2$] (M = Fe^{II}, or Ru^{II}, pip = piperidine) have appeared.[201]

***d*⁶: Ruthenium(II).**—The rates of formation and dissociation of $[Ru(NH_3)_5L]^{2+}$ ions (L = H_2S, Me_2S, EtSH, or thiophen) are collected in Table 23. The pK_a's of co-ordinated H_2S and EtSH were considered previously (Table 2). The affinity of Ru^{II}

Table 23 *Rate and equilibrium data at* 298.2 K *and* $[H^+]=0.1$ mol dm^{-3} *for the reactions* $[Ru(NH_3)_5OH_2]^{2+} + L \underset{k_d}{\overset{k_f}{\rightleftharpoons}} [Ru(NH_3)_5L]^{2+} + H_2O$ *(data from ref.* 37)[a]

L	10^2k_f/dm^3 mol^{-1} s^{-1}	10^5k_d/s^{-1}	$K = (k_f/k_d)$/dm^3 mol^{-1}
H_2S	10.0±0.4	6.7±0.5	1.5×10^3
Me_2S	8.0±0.6	(loss of NH_3)[b]	$\geqslant 9.5\times10^4$
EtSH	7.7±0.3	⩽3	$\geqslant 3\times10^3$
Thiophen		820±80	*ca.* 10

[a] The pK_a's of the H_2S and EtSH complexes are given in Table 2. [b] The rate constant for loss of NH_3 in 12% EtOH–H_2O is $10^6k = 4.2$ s^{-1}.

for these S-donor ligands is thiophen < H_2S < Me_2S and EtSH. The rates of the dissociation reactions were measured using the 4-cyanopyridinium ion (4-CN-pyH$^+$) as a scavenger:[37]

$$[Ru(NH_3)_5L]^{2+} \xrightarrow{k_d} [Ru(NH_3)_5OH_2]^{2+} + L$$

$$[Ru(NH_3)_5OH_2]^{2+} + \text{4-CN-pyH}^+ \xrightarrow{\text{rapid}} [Ru(NH_3)_5(\text{4-CN-py})]^{2+} + H^+$$

Reaction of the *trans*-$[Ru(NH_3)_4(isn)(OH_2)]^{2+}$ ion (isn = isonicotinamide) with H_2S was also investigated. Rate constants for the formation and dissociation of

[200] K. L. Scott, R. S. Murray, and W. C. E. Higginson, *J.C.S. Dalton*, 1975, 1339.
[201] A. Vogler and H. Kunkely, *Ber. Bunsengesellschaft phys. Chem.*, 1976, **80**, 425.

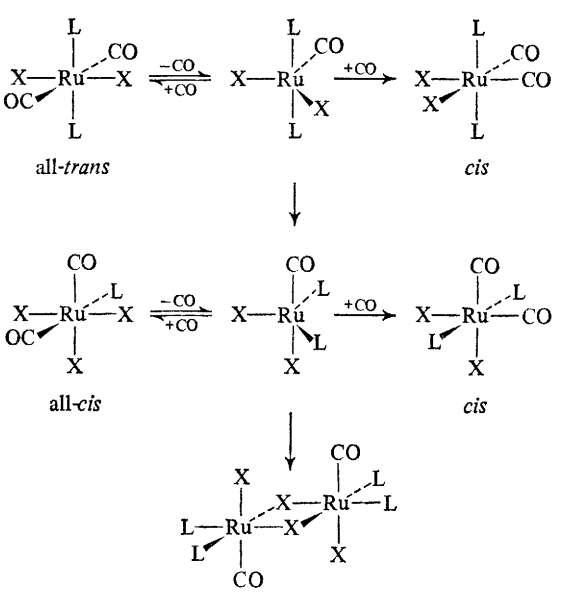
trans-$[Ru(NH_3)_4(isn)(SH_2)]^{2+}$ are $10^3k_f = 6.78$ dm^3 mol^{-1} s^{-1} and $10^3k_d = 0.94 \pm 0.04$ s^{-1} respectively in 0.5 mol dm^{-3} CF_3CO_2H ($k_f/k_d = 7.2$ dm^3 mol^{-1}). The *trans*-$[Ru(NH_3)_4(isn)(SH_2)]^{2+}$ ion is more stable to oxidation than $[Ru(NH_3)_5(SH_2)]^{2+}$, but aquates (with loss of H_2S) more readily. For the *trans*-$[Ru(NH_3)_4(isn)L]^{2+}$ ions, aquation in 0.5 mol dm^{-3} CF_3CO_2H leads to the loss of isonicotinamide with $k_d = 9 \times 10^{-6}$ and 1×10^{-3} s^{-1} for L = Me_2S and EtSH respectively.[38]

Reaction of $[Ru(NH_3)_5OH_2]^{2+}$ with HCN has also been investigated in 6 mol dm^{-3} CF_3CO_2H.[202] The immediate product is $[(H_3N)_5Ru(NCH)]^{2+}$, which rearranges in less acidic solutions to the *C*-bonded isomer with loss of H^+, and then polymerizes to cyano-bridged polynuclear *trans*-species:

$$[(H_3N)_5Ru(NCH)]^{2+} \longrightarrow [Ru(NH_3)_5CN]^+ + H^+$$
(polymerizes)

The rate constant for the rearrangement reaction is 10^{-2} s^{-1} at pH 3.6 and > 0.7 s^{-1} at pH 7. The *N*-bonded isomer does not deprotonate at pH 5.5 whereas the *C*-bonded isomer is fully deprotonated. Reaction of either $[Ru(NH_3)_5(NCH)]^{2+}$ or $[Ru(NH_3)_5CN]^+$ with isonicotinamide gives the *trans*-$[Ru(NH_3)_4(isn)(CN)]^+$ ion, the rate-determining step being loss of the *trans*-ammonia molecule ($10^3k = 5.3$ s^{-1} at pH 5—7.3).

Complexes of the type *cis*-$[Ru(CO)_2L_2X_2]$ (L = P- or As-donor ligands, X = halogen) are converted into their *trans*-isomers by u.v. irradiation. The process is reversed by heating, and a mechanism involving dissociation of CO is proposed (Scheme 3).[203] Reaction of *trans*-$[Ru(CO)_2L_2Cl_2]$ with HgR_2 (R = Me, Et, or Ph)



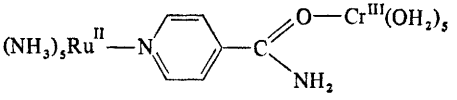
Scheme 3 *Mechanisms for the thermal rearrangements of complexes* $[Ru(CO)_2L_2X_2]$ *(from ref.* 203)

[202] S. S. Iseid and H. Taube, *Inorg. Chem.*, 1975, **14**, 2561.
[203] C. F. J. Barnard, J. A. Daniels, J. Jeffrey, and R. J. Mawby, *J.C.S. Dalton*, 1976, 953, 961.

or $SnMe_4$ also occurs with CO dissociation, the products being $[Ru(CO)_2(L)_2(Cl)R]$. The complexes *cis*-$[Ru(CO)_2L_2Cl_2]$ do not react in this way. Reactions between $[Ru(CO)(PMe_2Ph)_3Cl_2]$ and HgR_2 proceed with the intermediate formation of $[Ru(CO)(PMe_2Ph)_3ClR]$ in a reversible alkyl-group transfer mechanism. Halide-exchange reactions between *trans*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$ and Br^- or I^- ions also involve CO dissociation.

A dissociative mechanism is proposed for the reactions of *cis*-$[Ru(bipy)_2X_2]$ (X = F, Cl, or Br) with pyridine, 2- and 3-methylpyridine, and 2,6-lutidine in solutions of $PhNO_2$, DMSO, DMF, PhCl, or 1,2-dimethoxyethane.[204]

Complex (38) is produced during the inner-sphere reduction of the $[Ru(NH_3)_5$-



(38)

(nicotinamide)]$^{3+}$ ion by $[Cr(H_2O)_6]^{2+}$ ion.[205] The pseudo-first-order rate constant for the Cr^{2+}-catalysed aquation of this complex is given by

$$k = k_0 + k_1/[H^+] + k_2[Cr^{II}]/[H^+]$$

At 298.2 K and $I = 0.10$ mol dm^{-3}, $k_0 \approx 10^{-7}$ s^{-1}, $10^7 k_1 = 1.95 \pm 0.01$ mol dm^{-3} s^{-1}, and $10^5 k_2 = 4.05 \pm 0.26$ s^{-1}. When nicotinamide is replaced by thioisonicotinamide, the corresponding rate constants at 275.2 K and $I = 0.01$ mol dm^{-3} are $10^4 k_0 = 3.94 \pm 0.27$ s^{-1}, $10^5 k_1 = 8.97 \pm 0.21$ mol dm^{-3} s^{-1}, and $k_2 = 0.271 \pm 0.005$ s^{-1}. The significantly larger rate constants for the thioisonicotinamide complex arises from the aquation of an activated complex with a protonated sulphur atom.

Reactions of Co-ordinated Ligands. It is well known that ruthenium(II) can have a marked effect upon the reactivity of co-ordinated ligands. Aquation of the $[Ru(MeNH_2)_6]^{2+}$ ion in the presence of oxygen involves slow solvolysis and oxidation to give $[Ru(MeNH_2)_5OH]^{2+}$, which solvolyses further with oxidation of the co-ordinated methylamines to give $Ru(CN)_3,3H_2O$ as the final product.[206] Oxidation of co-ordinated amines also occurs in complex ions of the type $[Ru(bipy)_2(NH_2CH_2R)_2]^{2+}$ (NH_2CH_2R = allylamine, $PhCH_2NH_2$, or Bu^nNH_2) to give the $[Ru(bipy)_2$-$(NCR)_2]^{2+}$ ions.[207] The mechanism involves initial oxidation to Ru^{III} followed by stepwise dehydrogenation reactions involving imine intermediates.

$[Ru(bipy)_2(N_3)_2]$ and $[Ru(bipy)_2(L)(N_3)]^+$ (L = MeCN or py) are rapidly oxidized by Br_2 and Ce^{IV}, or electrochemically, to the Ru^{III} complexes, which then undergo thermal or photoinduced decomposition in acetonitrile with the release of dinitrogen,[208] *e.g.*

$$[Ru^{III}(bipy)_2(N_3)_2]^+ + MeCN \longrightarrow [Ru^{II}(bipy)_2(MeCN)(N_3)]^+ + \tfrac{3}{2}N_2$$

Azido-radicals are not involved, and either intramolecular electron transfer or nitrene formation is postulated. Dinitrogen complexes are not formed as inter-

[204] F. Maspero and G. Ortaggi, *Ann. Chim. (Italy)*, 1974, **64**, 115.
[205] R. W. Craft and R. G. Gaudner, *Inorg. Chem.*, 1975, **14**, 1283.
[206] J. D. Miller, J. B. Watts, and D. Y. Waddon, *Inorg. Chim. Acta*, 1975, **12**, 267.
[207] F. R. Keene, D. J. Salmon, and T. J. Meyer, *J. Amer. Chem. Soc.*, 1976, **98**, 1884.
[208] G. M. Brown, R. W. Callahan, and T. J. Meyer, *Inorg. Chem.*, 1975, **14**, 1915.

mediates in solution, but there is i.r. evidence for a low steady-state formation of a dinitrogen complex in the solid-state decomposition of $[Ru(bipy)_2(N_3)_2]Br$.

The ease of reduction of 1,4-pyrazine *N*-oxide (L) by V^{II} is lowered by co-ordination to Ru^{II} in the complex ion $[Ru(NH_3)_5L]^{2+}$ containing the *N*-bonded ligand L. At 298.2 K, the rates of ligand reduction are 2.29 and 0.209 $dm^3\ mol^{-1}\ s^{-1}$ for free and bound ligand respectively.[209] This behaviour is in marked contrast to the enormously enhanced rate of reduction of N_2O by V^{II} and Cr^{II} which occurs on co-ordination of N_2O to Ru^{II}.

The main products of the slow reaction of hydroxide ion (0.1 mol dm^{-3}) with the $[Ru(NH_3)_5NO]^{3+}$ ion are the ions *cis*-$[Ru(NH_3)_4(OH)NO]^{2+}$ (11%), $[Ru(NH_3)_5N_2]^{2+}$ (25%), and *trans*-$[Ru(NH_3)_4(OH)NO]^{2+}$ (8%). The reaction proceeds by the $[Ru(NH_3)_5NO]^{3+}$ ion reacting with its conjugate base, $[Ru(NH_3)_4(NH_2)NO]^{2+}$:[210]

$$[Ru(NH_3)_5NO]^{3+} + [Ru(NH_3)_4(NH_2)NO]^{2+} \longrightarrow [(H_3N)_5Ru\{N(O)NH_2\}Ru(NH_3)_4NO]^{5+} \longrightarrow [Ru(NH_3)_5N_2]^{2+} + \textit{cis}\text{-}[Ru(NH_3)_4(OH)NO]^{2+}$$

***d*⁶: Osmium(II).**—Electrochemical reduction of the $[Os(NH_3)_5X]^{2+}$ (X = Cl or Br) and $[Os(NH_3)_6]^{3+}$ ions at pH 11 gives $[Os^{II}(NH_3)_5OH]^+$ which is then oxidized to $[Os(NH_3)_5OH]^{2+}$. At pH 11 the pseudo-first-order rate constants for the hydrolysis of the $[Os(NH_3)_5X]^{2+}$ ions are 0.2 and 0.02 s^{-1} for X = Cl and Br respectively.[211]

5 Base Hydrolysis

In this section reactions of hydroxide ion will be discussed, including base hydrolysis and attack at co-ordinated ligands.

Cobalt(III) Complexes.—The Garrick conjugate-base mechanism for base hydrolysis has been further substantiated by the observation of the u.v.–visible spectrum of the conjugate bases, such as the $[Co(en)_2(en-H)]^{2+}$ ion, in 86.4% DMSO containing H_2O–Me_4NOH.[22] The pK_a's of the $[Co(en)_3]^{3+}$ and $[Co(NH_3)_5NO_2]^{2+}$ ions are estimated to be 15.2 and 16.8 respectively at $I = 3.1 \times 10^{-2}$ mol dm^{-3} in H_2O. An acidity function based on the solvent dependence of the rate of base hydrolysis of the $[Co(NH_3)_5Cl]^{2+}$ ion was used. Plots of log $k_{OH}(NO_2)$ and log $\{[Co(en)_2(en-H)^{2+}]/[Co(en)_3^{3+}]\}$ *versus* log $(k_{OH}(Cl))$ [$k_{OH}(X)$ = rate constant for base hydrolysis of anion X] in solutions of various DMSO concentrations are linear with slopes of 1.00 ± 0.02 and 1.05 ± 0.04 respectively. Values of $k_{OH}(Cl)$ increase by a factor of 10^5 over the solvent composition range studied. The results incidate that the behaviour both of cobalt ammines and of the $[Co(en)_3]^{3+}$ ion varies in the same way with solvent basicity, and the rate of dissociation of the conjugate bases changes only slightly in the range 15—40 mol % DMSO. The pK_a's in aqueous solution were estimated by extrapolation of the kinetic results to 0% DMSO. The red colours of the conjugate bases which are apparent in DMSO are not observed in H_2O. The kinetic data indicate that the conjugate base of the $[Co(NH_3)_5NO_2]^{2+}$ ion can be deprotonated further to give $[Co(NH_3)_3(NH_2)_2NO_2]$.

[209] M. A. Blesa and H. Taube, *Inorg. Chem.*, 1976, **15**, 1454.
[210] F. Bottomley, S. G. Clarkson, and E. M. R. Kiremire, *J.C.S. Chem. Comm.*, 1975, 91; *J.C.S. Dalton*, 1975, 1909.
[211] J. Gulens and J. A. Page, *J. Electroanalyt. Chem. Interfacial Electrochem.*, 1976, **67**, 215.

Insight into the site of deprotonation of co-ordinated amines has been gained by measuring the relative rates of *cis* and *trans* hydrogen–deuterium exchange between D_2O and complex ions of the type $[Co(NH_3)_5X]^{n+}$ and *cis*-$[Co(AA)_2X_2]^{n+}$ [AA = en or $(NH_3)_2$].[23] The results (Table 1) show that when X = CN^-, NO_2^-, and possibly SO_3^{2-}, the rates of deuteriation of amine protons in the *trans* position are less than for the *cis* positions, whereas when X = F^-, Cl^-, Br^-, H_2O, CO_3^{2-}, $NH_2CO_2^-$, N_3^-, $MeNH_2$, AcO^-, mal^{2-}, ox^{2-}, or fumarate, the rate of *trans* labilization is largest.

A study of the base hydrolysis of the two isomers of the $[Co(tren)(NH_3)Cl]^{2+}$ ion shows that deprotonation of a nitrogen centre in a *trans* position to the chloride ion leads to the most reactive conjugate-base intermediate for the loss of Cl^-. The stereochemistries of the two reaction pathways were related to the likely structures for the intermediates involved.[21]

A study of the steric course of the base hydrolysis of some optically active complex ions of the type *cis*-$[Co(en)_2(amine)Cl]^{2+}$ shows that a unique deprotonation site cannot be specified.[212] Results were compared for complex ions containing 12 different amines: RNH_2 (R = Me, $PhCH_2$, or cyclohexyl), py, 4-Me-, 4-benzyl-, 3,4-di-Me-, and 3,5-di-Me-pyridine, isoquinoline, imidazole, *N*-methylimidazole, and benzimidazole were studied. The results are best described by considering deprotonation at all possible sites rather than, say, the amino-groups in a *trans* position to a leaving group. The sites of deprotonation and transition states involved are indicated in Scheme 4.

The complexes involved can be divided into three classes with optical retention decreasing with the amine in the order RNH_2 > imidazole-type > pyridine-type. Complex ions containing an aliphatic amine (amine = RNH_2) react with a relatively high optical retention and considerable isomerization. This suggests that transition states (39) and (40) are important, together with one of the others [probably (43)] giving a racemic product. Complexes containing a pyridine-type ligand react *via* transition states (40)—(43), with some discrimination in transition state (40) such that entry to the *trans* position (pathway *b*) is favoured over the more open sites which lead to retained activity (pathways *a* and *c*), resulting in increased isomerization at the expense of retained activity. Compounds in which the amine is of the imidazole-type behave in a way intermediate between those containing aliphatic amines and pyridines.

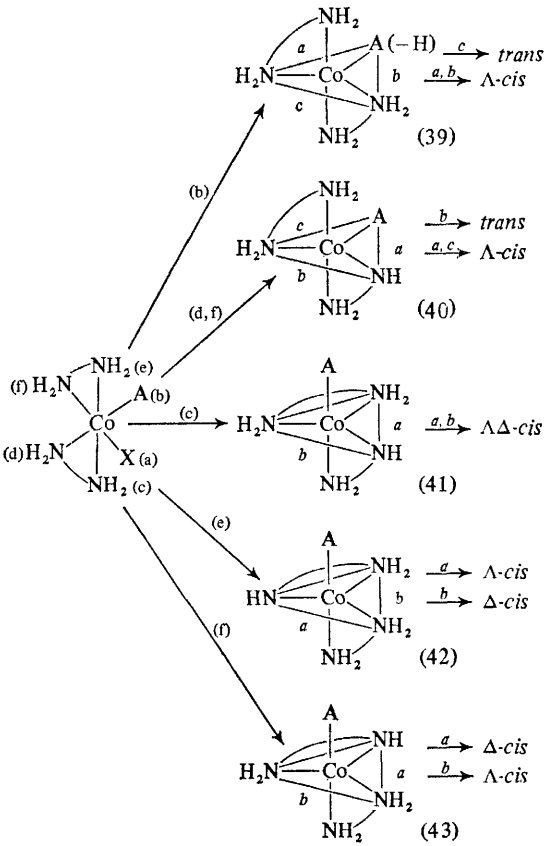
Rate data are also reported for the base hydrolysis of three stereoisomers of the $[Co(dien)(tmd)Cl]^{2+}$ ion and one isomer of $[Co(dpt)(tmd)Cl]^{2+}$ [structures (12)—(15)].[213] The results are compared with previous data in Table 24. Complexes with structures (13) and (15) in which the triamine is in a meridional position react 10^2—10^3 times faster than those in which the triamine is facial. Deprotonation of the secondary amine (NH) groups is indicated for these conjugate-base reactions.

The steric course and mechanism of the base hydrolysis of *cis*-$[Co(en)_2(CN)Cl]^+$ and *trans*-$[Co\{RS\text{- and }RR(SS)\text{-(2,3,2-tet)}\}Cl_2]^+$ ions has also been investigated.[67, 214] For the complexes of 2,3,2-tet the *N*-deuteriated analogues were also studied.[214] At 286.7 K (I=0.05 mol dm^{-3}) the undeuteriated compounds react with second-order

[212] D. Fenemor and D. A. House, *J. Inorg. Nuclear Chem.*, 1976, **38**, 1559.
[213] L. S. Dong and D. A. House, *Inorg. Chim. Acta*, 1976, **19**, 23.
[214] E. Ahmed, M. L. Tucker, and M. L. Tobe, *Inorg. Chem.*, 1975, **14**, 1.

Table 24 *Kinetic parameters for the base hydrolysis of some cobalt*(III) *complexes at* 298.2 K (I=0.1 mol dm^{-3}) (*data from ref.* 213)

Complex	*Isomer*	k/ dm^3 mol^{-1} s^{-1}	log (pZ/ dm^3 mol^{-1} s^{-1})	E_a/ kJ mol^{-1}	$\Delta S^{\ddagger}$/ J K^{-1} mol^{-1}
[Co(dien)(en)Cl]$^{2+}$	(12)	26.6			
[Co(dien)(tmd)Cl]$^{2+}$	(12)	138	18.16	91.4±2	94±3
[Co(dien)(en)Cl]$^{2+}$	(14)	7.26			
[Co(dien)(tmd)Cl]$^{2+}$	(14)	10.6	22.61	123±3	179±6
[Co(dien)(en)Cl]$^{2+}$	(13)	3 ± 10^4			
[Co(dien)(tmd)Cl]$^{2+}$	(13)	5.02×10^5	20.29	83.3±2	135±4
[Co(dpt)(en)Cl]$^{2+}$	(13)	2.2×10^3			
[Co(dpt)(tmd)Cl]$^{2+}$	(15)	2.75×10^4	22.39	102±3	175±6
[Co(dpt)(en)Cl]$^{2+}$	(15)	8.6×10^3			



Scheme 4 *Deprotonation sites and transition states for the base hydrolysis of* Λ-cis-[Co(en)$_2$(amine)X]$^{n+}$ *ions. Letters in parentheses above the arrows indicate the site of deprotonation. In* (39) A(−H) *represents a deprotonated aliphatic amine. Letters above the arrows and not in parentheses indicate the position of entry of the water molecule* (*from ref.* 212)

rate constants $10^{-4}k_{OH}=1.5$ and 3.0 $dm^3\ mol^{-1}\ s^{-1}$ for the *RS*- and *RR*(*SS*)-isomers, with primary isotope effects $k_{OH}(H)/k_{OH}(D)=1.7$ and 1.5 respectively. For the *RR*(*SS*)-isomer the activation parameters are $\Delta H^{\ddagger}=13.7$ kcal mol^{-1} and $\Delta S^{\ddagger}=12$ cal $K^{-1}\ mol^{-1}$, which reflects the rate-determining nature of the deprotonation step. General base catalysis was also observed with a Brönsted coefficient $\beta=0.67\pm0.07$. For the *cis*-$[Co(en)_2(CN)Cl]^+$ ion $10^3k_{OH}=8.9$ $dm^3\ mol^{-1}\ s^{-1}$ at 273.2 K, with $\Delta H^{\ddagger}=23.2$ kcal mol^{-1} and $\Delta S^{\ddagger}=18$ cal $K^{-1}\ mol^{-1}$, the reaction proceeding with $90\pm3\%$ retention of configuration.[67]

Circular dichroism has been used to study the base hydrolysis of the *Λ*-$[Co(en)_2Cl_2]^+$ ion, a reaction which proceeds in a concerted way with Bailar inversion:[215]

$$\Lambda\text{-}[Co(en)_2Cl_2]^+ + 2OH^- \longrightarrow \Delta\text{-}[Co(en)_2(OH)_2]^+ + 2Cl^- \qquad (18)$$

A reinvestigation of the base hydrolysis of the *Λ*-*cis*-$[Co(en)_2(OH)Cl]^+$ ion indicates that the reaction proceeds with 98% retention of configuration, in contrast to a previous report which indicated 61% retention, 36% inversion, and 3% *trans*-complex formation.[215] Reaction (18) is believed to occur by means of a momentary spin change, both chloride ions being lost during this period of intermediate spin. The proposed high-spin state must only exist for a very short period of time, otherwise complete decomposition or racemization would occur.[215]

Two reports have appeared of kinetic studies of the base hydrolysis of complex ions of the type $[Co(NH_3)_5(OCOR)]^{2+}$. Activation parameters are reported from rate constants extrapolated to zero ionic strength for $R = CH_{3-n}Cl_n$ ($n = 1, 2,$ or 3).[216] When RCO_2^- = salicylate ion a simple second-order rate law is not observed owing to the importance of the deprotonation of the phenolic group.[217] If K is the equilibrium constant for this deprotonation reaction, the pseudo-first-order rate constant (k) in the presence of an excess of OH^- ion is given by

$$k=(k_1K[OH^-]+k_2K[OH^-]^2)/(1+K[OH^-])$$

For RCO_2^- = *m*- or *p*-hydroxybenzoates a simple second-order rate law is observed: $k=k_2'[OH^-]$. Activation parameters are reported for these reactions from studies over a very narrow temperature range (313—323 K).

The base hydrolysis of the $[Co(NH_3)_5DMSO]^{3+}$ ion has been investigated in mixed aqueous–organic solvents and in the presence of added anions.[218] Increasing the non-aqueous component in aqueous–organic mixtures containing MeOH, EtOH, DMSO, Me_2CO, or dioxan increases the rate of hydrolysis at constant $[OH^-]$ (0.02 mol dm^{-3}). The rate acceleration amounts to a factor of more than 10^2 in organic-rich mixtures, and this is in line with the increased basicity of the ammine ligands due to the decreased solvation of the OH^- ion. In the presence of 1 mol dm^{-3} anions X^{n-} (X^{n-} = N_3^-, NCS^-, NO_2^-, OAc^-, or SO_4^{2-}) and 0.125 mol dm^{-3} OH^-, the yields of $[Co(NH_3)_5X]^{(3-n)+}$ ion are 12.8, 9.9, 7.8, 1.8, and 3.7 mol % respectively.

Studies of the ammonolysis of $[Co(NH_3)_5X]^{2+}$ ions continue to appear.[57,219] When X = Cl or Br the equilibrium constants for conjugate base formation and the rate

[215] W. S. Kwak and R. D. Archer, *Inorg. Chem.*, 1976, **15**, 986.
[216] O. Grancicova and V. Holba, *Chem. Zvesti*, 1975, **29**, 433.
[217] K. K. Mohanty and R. K. Nanda, *Indian J. Chem.*, 1976, **14A**, 39.
[218] M. Biruš, W. L. Reynolds, M. Pribanić, and S. Ašperger, *Croat. Chem. Acta*, 1975, **47**, 561
[219] S. Balt and G. F. Polthoff, *J. Coordination Chem.*, 1975, **4**, 167, 247.

constants for the dissociation of the $[Co(NH_3)_4(NH_2)X]^+$ ions can be separated by studies in liquid ammonia.[219] Ammonolysis of the *cis*-$[Co(en)_2(NH_3)Cl]^{2+}$ ion in liquid ammonia proceeds with retention of configuration to give *cis*-$[Co(en)_2(NH_3)_2]^{3+}$. Studies of the hydrolysis of the $[Co(NH_3)_5NO_2]^{2+}$ ion in ammonia–ammonium perchlorate buffers were considered previously (Table 3). These reactions involve loss of a *trans* ammonia molecule (aquation) as well as loss of nitrite ion (base hydrolysis).[57]

Results for the base hydrolysis of the *cis*-$[Co(en)_2(CN)Cl]^+$ ion were also considered previously.[67] The related base methanolysis of the *trans*-$[Co(en)_2(CN)Cl]^+$ ion has also been studied in MeOH–KCN solutions. The final product is the *cis*-$[Co(en)_2(CN)_2]^+$ ion which is formed *via* the intermediate $[Co(en)_2(OMe)CN]^+$.[220]

Base hydrolysis of the $[Co(en)_2(mal)]^+$ ion gives *cis*- and *trans*-$[Co(en)(OH)_2]^+$, and at $I = 3.7$ mol dm^{-3} an apparent limiting rate is reached above $[OH^-]=2$ mol dm^{-3}.[221]

For the *cis*-$[Co(en)_2(L)X]^{2+}$ ions (L = unidentate en, X = Cl or Br) the second-order rate constants at 298.2 K and $I=0.1$ mol dm^{-3} for base hydrolysis in aqueous media are 6.3 and 41 dm^3 mol^{-1} s^{-1} for X = Cl and Br respectively, and the main product is *cis*-$[Co(en)_2(L)OH]^{2+}$ (97%). Studies of $[Co(en)_2(L)X]^{2+}$ in mixtures of $BuNH_2$ and DMSO again established a second-order rate law, but this time the product is the $[Co(en)_3]^{3+}$ ion.[99]

For the *cis*-$[Co(phen)_2Cl_2]^+$ ion base hydrolysis of the first chloride ion is very fast and could only be studied at the lowest temperature and pH used. Loss of the second chloride ion is slower and was studied at pH 7.26—9.25 between 288 and 316 K.[222]

Two studies have appeared for the base hydrolysis of complex ions of the type *trans*-$[Co(L)XY]^{n+}$ containing a macrocyclic quadridentate ligand [L = (19) or (20)] and two unidentate ligands (X and Y). When X = NO_2 and Y = Cl, loss of chloride ion proceeds at much the same rate for L = (19) and (20), the extra methyl groups in (20) having little or no effect upon the base-hydrolysis rates.[82] Complex ions in which X = Y = NH_3 have also been prepared and rate data are reported for the base hydrolysis of the first ammonia molecule in 2,6-lutidinium buffers [L = (20), pH 6.0—6.8] or in carbonate buffers [L = (19), pH 9.8—10.6].[223] This time, the second-order rate constant at 298.2 K increases markedly from 3.2 dm^3 mol^{-1} s^{-1} [L = (19)] to 7.6×10^4 dm^3 mol^{-1} s^{-1} [L = (20)] as the number of peripheral methyl groups is increased.

Two studies of the base hydrolysis of dioximato-complexes of the type *trans*-$[Co(dmgH)_2(amine)X]$ (amine = NH_3, $PhNH_2$, or py, X = Cl, Br, or I)[224] and *trans*-$[Co(dioxime)_2(OH_2)X]$ (dioxime = methyl-, methylethyl-, α-benzyl-, or α-furfuryl-dioxime, X = Cl, Br, or occasionally I)[225] have appeared. The latter study shows that the rates increase with the inductive effect of the dioximato-substituents in the order Et < Me < H < Ph. Steric effects are also apparent since the

[220] M. Biruš, Z. Bradić, D. Pavlović, M. Pribanić, and S. Ašperger, *J. Inorg. Nuclear Chem.*, 1975, **37**, 600.
[221] M. E. Farago and I. M. Keefe, *Inorg. Chim. Acta*, 1975, **15**, 5.
[222] S. E. Campbell and J. A. Burke, *Chem. Abs.*, 1976, **84**, 22663.
[223] G. A. Lawrance, *Inorg. Nuclear Chem. Letters*, 1976, **12**, 85.
[224] N. M. Samus, G. A. Konunova, and A. V. Ablov, *Russ. J. Inorg. Chem.*, 1975, **20**, 1056.
[225] N. M. Samus, T. S. Luk'yanets, and A. V. Ablov, *Russ. J. Inorg. Chem.*, 1975, **20**, 1529.

α-furfurylglyoxime complex hydrolyses much faster than the methylglyoxime complex even though the pK_a's of these dioximes are very similar. For the *trans*-[Co(dmgH)$_2$(amine)X] complexes the rates decrease with the amine in the order $PhNH_2 > py \gg NH_3$.

The use of base-catalysed reactions for the template synthesis of co-ordinated, often macrocyclic ligands was discussed in the introduction to this chapter.[12–15]

Chromium(III) Complexes.—Studies of the base hydrolysis of chromium(III) complexes at high pH are relatively rare, probably because of the ease with which polymeric hydroxy-complexes can be precipitated. Studies of aqua-chromium(III) complexes even at low pH invariably show that conjugate-base formation is important owing to the acidity of the co-ordinated water molecules. Conjugate-base formation is apparent when the observed pseudo-first-order rate constant, k, varies with acidity according to the equation $k = k_0 + k_{-1}/[H^+]$. Recent examples include studies of the $[Cr(H_2O)_5(NH_3)]^{3+}$ and $[Cr(ox)_2(N_3)(H_2O)]^{2-}$ ions.[170,136]

Other Metal Ions.—Base hydrolysis of *trans*-$[Rh(en)_2X_2]^+$ ions leads to almost complete *trans*→*cis* isomerization when X = Cl or Br, and to *ca.* 50% isomerization when X = I.[180] Rates and activation parameters for the aquation and base hydrolysis reactions were considered previously (Table 22). An S_N1cb mechanism seems likely when X = Cl or Br, but an S_N1ip mechanism cannot be ruled out when X = I.

The activating effect of metal ions upon the base hydrolysis of co-ordinated organonitriles (RCN) in complex ions of the type $[M(NH_3)_5(NCR)]^{3+}$ was considered in Volume 4 (p. 130) of this series. Further reports have appeared for M = Ru, Co, Rh, and Ir and for R = Me and Ph.[177,226] Ru^{III} remains the most effective metal ion, accelerating the rate of base hydrolysis by a factor of 10^8 compared with the free organonitrile. Base attack at co-ordinated NO in the $[Ru(NH_3)_5NO]^{3+}$ ion gives the $[Ru(NH_3)_5N_2]^{2+}$ ion and *cis*- and *trans*-$[Ru(NH_3)_4(OH)NO]^{2+}$ ions.[210] S_N2 and S_N2cb mechanisms are postulated for the base hydrolysis of the $[Ru(NH_3)_5I]^{2+}$ ion.[227]

Base plays an important role in reducing Ru^{III} to Ru^{II} in a proposed solar energy storage system involving the $[Ru(bipy)_3]^{2+}$ ion.[35]

A review deals with the attack of hydroxide ion at the 2-position of co-ordinated bipyridyl-type ligands.[24]

6 Formation

In this section substitution reactions involving the formation (often anation) of inert metal complexes are discussed, with cations arranged in order of their increasing numbers of *d*-electrons. Metal ions with d^0, d^1, d^2, or d^{10} electronic configurations are usually labile and most references to these systems will be found in Chapter 4.

d^0: Titanium(IV) and Zirconium(IV).—The rates of formation and dissociation of complexes of Ti^{IV} and Zr^{IV} with metal-ion indicators such as methylthymol blue (Ti^{IV})[228] and xylenol orange (Zr^{IV})[229] have been reported. The reaction of Zr^{IV} with

[226] A. W. Zanella and P. C. Ford, *Inorg. Chem.*, 1975, **14**, 700.
[227] H. Sakamoto, H. Makino, K. Hamada, and A. Ohyoshi, *Chem. Letters*, 1975, 631.
[228] T. V. Mal'kova and L. A. Fomina, *Chem. Abs.*, 1975, **83**, 48095, 66142.
[229] T. I. Denisova and I. A. Shcheka, *Zhur. neorg. Khim.*, 1975, **20**, 660.

xylenol orange is reported to involve polymerization ($\Delta E^{\ddagger} = 11.2 \pm 0.5$ kcal mol^{-1}) as well as complex formation ($\Delta E^{\ddagger} = 23.6 \pm 0.7$ kcal mol^{-1}).

***d*^{1}: Molybdenum(v).**—The kinetics of reaction (19) have been studied in CH_2Cl_2 solution between 274 and 298 K (X = Cl or Br).[230] The rates are the same for

$$[MoOCl_3(OPPh_3)_2] + X^- \rightleftharpoons [MoOCl_3X(OPPh_3)] + Ph_3PO \qquad (19)$$

X = Cl and Br, independent of [X$^-$], and inversely proportional to [Ph_3PO]. An S_N1(lim) mechanism is proposed involving loss of the Ph_3PO ligand in the *trans* position to the Mo=O group to give a square-pyramidal intermediate. Following this substitution of the 'axial' Ph_3PO, a further reaction occurs in which the equatorial Ph_3PO is replaced. The reaction between Cl$^-$ and $[MoOCl_3Br(OPPh_3)]^-$ ions and those between $[MoOCl_4]^-$ ion and several nucleophiles were investigated at 298 K. Oxidation of $[MoOCl_3(OPPh_3)_2]$ to Mo^{VI} by nitrate and nitrite ions has also been studied.[231]

The reactivity of Mo^V dimers was considered earlier.[34,156]

***d*^{2}: Molybdenum(iv).**—The controversy over the nature of Mo^{IV} species in aqueous solution was discussed previously.[33,157] The reactions of the MoO^{2+} ion with thiocyanate ion[157] are claimed to involve the $[Mo_2O_2]^{4+}$ ion,[33] and both 1:1 and 1:2 metal:ligand complexes are believed to be formed in the recently reported studies of the 1:1 complex formation with thiocyanate ion. However, because of the different media used by these two groups (perchloric acid and 5.1 mol dm^{-3} CF_3CO_2H respectively), the position regarding the nature of the species involved is still uncertain.

Formation of $[MoX_2(SCR)_2]$ (R = Me_2N, Et_2N, or 1-piperidino) from the reaction between $[MoO(S_2CR)_2]$ and HX (X = Cl or Br) has been studied together with the oxidative addition reactions of $[MoO(S_2CR)_2]$ with X_2 to give $[MoOX_2(S_2CR)_2]$. The reactions with HX involve protonation of the oxygen atom, and it is claimed that this may be relevant to the function of ATP at molybdenum in nitrogenase.[232]

***d*^{3}: Chromium(iii).**—Studies of the rates of reaction of the $[Cr(H_2O)_6]^{3+}$ ion with unidentate[233] and multidentate[130,141,234] ligands have appeared. Formation of the $[Cr(H_2O)_5(HPO_4)]^+$ ion was investigated at pH 1.5—2.0,[233] and the formation of mononuclear complexes with triethanolamine was studied at pH 2.0—4.6.[141]

Formation of the $[Cr(H_2O)_4(bipy)]^{3+}$ ion does not involve the build up of a unidentate bipyridyl intermediate $[Cr(H_2O)_5(bipy)]^{3+}$, but rate constants were estimated for the ring-closure (k_2) and dissociation (k_{-1}) reactions of this intermediate:[130]

$$[Cr(H_2O)_6]^{3+} + bipy \underset{-1}{\overset{1}{\rightleftharpoons}} [Cr(H_2O)_5(bipy)]^{3+} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Cr(H_2O)_4(bipy)]^{3+}$$

[230] C. D. Garner, M. R. Hyde, F. E. Mabbs, and V. I. Routledge, *J.C.S. Dalton*, 1975, 1175.
[231] C. D. Garner, M. R. Hyde, F. E. Mabbs, and V. I. Vincent, *J.C.S. Dalton*, 1975, 1180, 1186.
[232] T. W. E. Newton, D. C. Bravard, and J. W. McDonald, *Inorg. Nuclear Chem., Letters*, 1975, **11**, 553.
[233] S. C. Lahiri, *Indian J. Chem.*, 1975, **52**, 479.
[234] A. J. Mahmood and A. Begum, *Chem. Abs.*, 1976, **84**, 127186.

In the presence of an excess of $[Cr(H_2O)_6]^{3+}$ ion the pseudo-first-order rate constant for the approach to equilibrium is given by

$$k = k_1[Cr^{III}] + (k_{-1}k_{-2}/k_2)$$

At 413.4 K, $10^6 k_1/dm^3\ mol^{-1}\ s^{-1} = (2.0 \pm 0.1) \times 10^3[H^+]^{-1} + (7.0 \pm 1.4)[H^+]^{-2}$ and $10^7 k_{-1}k_{-2}/k_2 = (9.5 \pm 0.2) \times 10^2 + (6.3 \pm 0.3)[H^+]^{-1}\ s^{-1}$. A credible but speculative breakdown of the composite term yields rate constants for ring closure, $k_2 = 5.3\ s^{-1}$, and dissociation, $10^2 k_{-1} = 1.3\ s^{-1}$, giving $k_2/k_{-1} = 408$.

Reaction of the $[Cr(H_2O)_6]^{3+}$ ion with nitrilotriacetic acid involves replacement of a co-ordinated water molecule in the first stage and Cr—N bond formation in the second stage.[234]

Complex formation between edta and the $[Cr(H_2O)_{6-n}(DMF)_n]^{3+}$ ions has been studied and the relative reactivities of the solvento-complexes are $Cr^{3+} < CrS^{3+} < CrS_2^{3+} < CrS_3^{3+} < CrS_4^{3+} < CrS_5^{3+} < CrS_6^{3+}$, where S = DMF and co-ordinated water molecules are omitted.[235]

Reaction of the $[CrS_6]^{3+}$ ions with X^- in non-aqueous solvents (S) have been studied for S = DMSO (X = N_3^-, NCS^-, or Cl^-) and S = DMF (X = Cl^-).[236] An I_d mechanism occurs with complications from ion aggregates including ion triplets as well as ion pairs.

Reaction of the $[Cr(H_2O)_4SH]^{2+}$ and thiocyanate ions in acidic solution produces an equilibrium mixture of $[Cr(H_2O)_4(NCS)(SH)]^+$ and $[Cr(H_2O)_4(NCS)(SH_2)]^{2+}$ ions.[111] Rate data associated with these complex formations were presented in the section concerned with aquation reactions.

Formation of the *cis*-$[Cr(H_2O)_2(mal)_2]^-$ ion occurs from the reaction between $[Cr(H_2O)_4(mal)]^+$ and malonic acid ($malH_2$) at pH 2.0—3.5. Rates and activation parameters were determined, and the reaction was shown to proceed by an I_d mechanism involving the $[Cr(H_2O)_4(mal)]^+Hmal^-$ ion pair.[237]

When the *trans*-$[Cr(ox)_2(H_2O)_2]^-$ ion is added to acidic solutions containing oxalic acid (oxH_2) and oxH^- ion, rapid *trans*→*cis* isomerization occurs first, followed by anation of the *cis*-$[Cr(ox)_2(H_2O)_2]^-$ ion which is formed to give an equilibrium mixture containing the $[Cr(ox)_3]^{3-}$ ion.[238] A half-bonded oxalato-intermediate is formed which is stabilized by interaction of the unco-ordinated carboxylate group with cations:

$$trans\text{-}[Cr(ox)_2(H_2O)_2]^- \rightleftharpoons cis\text{-}[Cr(ox)_2(H_2O)_2]^- \text{ rapid} \quad (20)$$

$$cis\text{-}[Cr(ox)_2(H_2O)_2]^- + H_2ox \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Cr(ox)_2(Hox)(OH_2)]^{2-} + H_3O^+ \quad (21)$$

$$[Cr(ox)_2(Hox)(OH_2)]^{2-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Cr(ox)_3]^{3-} + H_3O^+ \quad (22)$$

The rate constant for the *trans*→*cis* isomerization, reaction (20), was determined in aqueous acidic media containing $NaClO_4$ or KNO_3, and a dependence upon $[H^+]$

[235] B. S. Grigor'ev, Y. Y. Makarov-Zemlyanskii, and N. N. Pavlov, *Chem. Abs.*, 1975, **82**, 145727; *Zhur. fiz. Khim.*, 1974, **48**, 1173.
[236] S. T. D. Lo and D. W. Watts, *Austral. J. Chem.*, 1975, **28**, 491, 501.
[237] S. Sarkar and D. Banerjea, *J. Inorg. Nuclear Chem.*, 1975, **37**, 547.
[238] T. W. Kallen, *Inorg. Chem.*, 1976, **15**, 440.

and $[M^+]$ (M = Na or K) was observed:

$$k = k(H_2O) + k(M^+)[M^+] + k(H^+)[H^+]$$

Activation parameters associated with the rate constants $k(H_2O)$, $k(Na^+)$, $k(K^+)$, and $k(H^+)$ are $\Delta H^{\ddagger} = 17.9$, 15.1, 14.7, and 18.5 kcal mol^{-1} and $\Delta S^{\ddagger} = -14.7$, -23.9, -26.0, and -8.5 cal K^{-1} mol^{-1} respectively. The cation dependence is ascribed to the interaction of the one-ended oxalato-complex with the cations during this isomerization reaction. For reactions (21) and (22) the equilibrium constant, K, is given by:

$$K = [Cr(ox)_3^{3-}][H^+]^2/[cis\text{-}Cr(ox)_2(OH_2)_2^-][H_2ox]$$

At 323.2 K and I = 1.0 mol dm^{-3} (KNO_3), $K = 0.890 \pm 0.012$, and the observed rate constant for these reactions varies with $[H^+]$ according to the following equation in a nitrate medium:

$$k = \{k_1[H_2ox] + (k_{-2}k_{-1}/k_2)/[H^+]^2\}/\{1 + (k_{-1}/k_2)[H^+]\}$$

The ratio k_2/k_{-1}, which determines the relative rate at which the intermediate ring closes or aquates, is smaller in $NaClO_4$ than in KNO_3 media. In a perchlorate medium $(k_{-1}/k_2) \ll 1$ and the observed rate constant is given by $k = k_b\,[Hox^-] + k_{-2}[H^+]$. The reaction is postulated to proceed through the formation of steady-state amounts of two intermediates (A), one containing bidentate oxalate ion which is co-ordinated to chromium through two oxygen atoms of different carboxylate groups and the other containing bidentate oxalate co-ordinated through two oxygen atoms of the same carboxylate group (L = Hox^- or ox^{2-}):

$$cis\text{-}[Cr(ox)_2(H_2O)_2]^- \rightleftharpoons A; \quad d[A]/dt = 0$$

$$A + L \longrightarrow [Cr(ox)_2(L)(OH_2)]^{n-} + H_2O$$

$$[Cr(ox)_2(L)(OH_2)]^{n-} \xrightarrow{\text{rapid}} [Cr(ox)_3]^{3-} + H_2O$$

The rate of the *cis*→*trans* isomerization of $[Cr(ox)_2(H_2O)_2]^-$ has also been the subject of a separate investigation, and an equilibrium constant, [*trans*]/[*cis*] = 0.10, is reported at 298 K.[239]

Rates of formation and dissociation and the stability of $[Cr(Y)(OAc)]^{(n-2)-}$ ions for four quinquedentate aminopolycarboxylate ions (Y^{n-}) were considered previously and the data are collected in Table 18.

***d*³: Molybdenum(III).**—An S_N2 mechanism has been established for the 1:1 complex formation reactions of the $[Mo(H_2O)_6]^{3+}$ ion by comparing the rates of reaction with chloride and thiocyanate ions in 0.17—1.0 mol dm^{-3} H^+. The reactions were studied in 1 mol dm^{-3} RSO_3Li–RSO_3H (RSO_3H = toluene-*p*-sulphonic acid) and HBF_4 and are independent of $[H^+]$ at the high acidities used.[162]

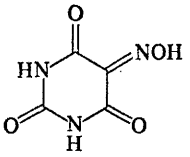
***d*³: Technetium(IV).**—Rates of anation of the $[Tc(OH_2)X_5]^-$ ions (X = Cl or Br) by X^- were considered previously (Table 21).[163]

***d*⁴: Manganese(III).**—Formation of an inner-sphere Mn^{III}–substrate complex is the rate-determining step in the oxidation of thioureas and benzene-1,2-dithiol by $[Mn(OH)]^{2+}$.[164]

[239] M. B. Davies and J. W. Lethbridge, *J. Inorg. Nuclear Chem.*, 1975, **37**, 141.

d^5: Iron(III).—Rates and equilibrium data are reported for the reaction of Fe^{III}-porphyrin monomers with cyanide ion at 298 K in 2% sodium lauryl sulphate and 0.1 mol dm^{-3} $M_4N^+Br^-$.[240] The porphyrins investigated were meso-, proto-, and deuterio-porphyrin-IX.

d^5: Ruthenium(III).—The kinetics and thermodynamics of the reactions between Ru^{III} and violuric acid [H_3L; (44)] have been studied at pH 2.0—5.5 and 298 K in 0.1 mol

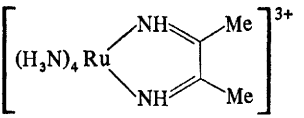


(44)

dm^{-3} Na_2SO_4 solutions.[241] Three successive complexes are formed, the last one being isolated as $Ba[Ru(H_2L)_3OH]_2$. The formation of $[Ru(H_2L)_2(NO)Cl]$ and $[Ru(H_2L)(NO)Br]$ is also reported.[242]

Anation of the $[Ru(NH_3)_5OH_2]^{3+}$ ion by $ClCH_2CO_2^-$ is reported to proceed by an S_N1(lim) mechanism.[175]

Formation of ruthenium(III) complexes by attack at co-ordinated amines promises to be a useful synthetic method. Recent examples include the reactions of the $[Ru(NH_3)_6]^{3+}$ ion with aldehydes (RCHO) to give the corresponding co-ordinated nitrile, $[Ru(NH_3)_5(NCR)]^{3+}$ (R = Me or Ph, and the oxidant is unknown),[243] or the reaction with glyoxal, MeCOCOMe, in the presence of hydroxide ion to give the ion (45).[244] From kinetic studies of the latter reaction, a mechanism is proposed in which the $[Ru(NH_3)_5NH_2]^{2+}$ ion attacks at one carbonyl centre of MeCOCOMe, followed by further deprotonation of the *cis* ammonia molecule, cyclization, and elimi-



(45)

nation of H_2O. The $[Pt(NH_3)_6]^{4+}$ ion also reacts with ketones such as acetylacetone and CF_3COCH_2COMe to give stable ring systems with completely delocalized electrons.[244]

d^6: Iron(II).—The rates of reaction of [Fe(pc)(DMSO)$_2$] (pc = phthalocyanine^{2-}) with imidazole and *N*-alkylated imidazole (*N*-methyl or *N*-butyl) have been studied in DMSO at 298—318 K. The second-order rate constants and activation parameters are very similar for all three imidazoles, the more basic *N*-alkylated derivatives being about twice as reactive as imidazole itself.[245]

[240] P. Hambright and P. B. Chock, *J. Inorg. Nuclear Chem.*, 1975, **37**, 2363.
[241] C. Bremard, *Bull. Soc. chim. France*, 1975, 953.
[242] S. Sueur, C. Bremard, and G. Nowogrocki, *Chem. Abs.*, 1976, **84**, 38129.
[243] K. Schug and C. P. Guengerich, *J. Amer. Chem. Soc.*, 1975, **97**, 4135.
[244] I. P. Evans, G. W. Everett, and A. M. Sargeson, *J.C.S. Chem. Comm.*, 1975, 139.
[245] J. G. Jones and M. V. Twigg, *Inorg. Chim. Acta*, 1975, **12**, L15.

Several reports have appeared for complex formation reactions involving the $[Fe(CN)_5(H_2O)]^{3-}$ ion. The tendency of this ion to dimerize at higher concentrations and the nature of the dimeric species involved were discussed previously.[198] Replacement of ligand X in the $[Fe(CN)_5X]^{n-}$ ions (X = *p*-$Me_2NC_6H_4NO$, PhNO, SO_3^{2-}, or H_2O) by ligands Y of differing charge (Y = *p*-$Me_2NC_6H_4NO$, PhNO, 3-CN-py, SCN^-, NO_2^-, CN^-, or SO_3^{2-}) shows that diffusion together of the reacting species could be rate limiting. Thus at 298 K and $I = 1.0$ mol dm^{-3} the second-order rate constants (k_f) vary with Y in the range 200—300, 40—60, and 3.3 dm^3 mol^{-1} s^{-1} for uncharged ions, uninegatively charged ions, and SO_3^{2-} respectively.[246] However, limiting rates are observed at high [Y] for all leaving groups except H_2O. The ionic-strength dependence of the rates of reaction between the $[Fe(CN)_5(H_2O)]^{3-}$ ion and Y = PhNO, NO_2^-, SCN^-, and SO_3^{2-} fits fairly well with the Brönsted–Bjerrum equation; plots of log k_f *versus* $I^{1/2}$ have slopes of 2.9 (NO_2^-), 2.5 (SCN^-), 4.4 (SO_3^{2-}), and zero (PhNO), in line with the product of the charges on the reacting ions.[247]

The use of $[Fe(CN)_5(H_2O)]^{3-}$ to bring about the inner-sphere reduction of cobalt(III) complexes often involves the formation of dinuclear ligand-bridged complexes as the rate-determining step. For example, at 298.2 K and pH 8, reaction with the $[Co(NH_3)_5LL]^{3+}$ ion (LL = 4,4′-bipyridyl) proceeds in two steps; the first step involves the formation of $[(H_3N)_5Co^{III}LLFe^{II}(CN)_5]$ (rate constant = 4.5×10^{-3} s^{-1}) and in the second step electron transfer to give $[(H_3N)_5Co^{II}LLFe^{III}(CN)_5]$ (rate constant = 2.6×10^{-3} s^{-1}) occurs.[197] Reduction of the $[Co(en)_2L]^{2+}$ ions (HL = pyrazinecarboxylic acid or pyridine-2-carboxylic acid) by $[Fe(CN)_5(H_2O)]^{3-}$ and $[Co(CN)_5]^{3-}$ ions has also been reported and a stable dinuclear species is formed between the pyrazinecarboxylato-complex and $[Fe(CN)_5(H_2O)]^{3-}$ [equilibrium constant, $K = 8.3 \times 10^6$ dm^3 mol^{-1} at 298.2 K and $I = 0.20$ mol dm^{-3} ($LiClO_4$)].[248] Inner-sphere and outer-sphere redox reactions occur with the pyridine-2-carboxylato-complex. Reaction of $[Co(NH_3)_5(O_2C\text{-}py)]^{2+}$ ions (py-CO_2^- = *O*-bonded pyridine-2-, -3-, or -4-carboxylate ions) with $[Fe(CN)_5H_2O]^{3-}$ gives dinuclear complexes for the pyridine-3- and -4-carboxylato-complexes, but steric effects prevent the formation of a dinuclear species with the pyridine-2-carboxylato-complex:[249]

$$\begin{matrix}[Co(NH_3)_5(O_2C\text{-}py)]^{2+} \\ + \\ [Fe(CN)_5(H_2O)]^{3-}\end{matrix} \underset{k_d}{\overset{k_f}{\rightleftharpoons}} [Co(NH_3)_5\text{-}(O_2C\text{-}py)\text{-}Fe(CN)_5]^- + H_2O$$

At 298.2 K, pH 8.0, and $I = 0.10$ mol dm^{-3} ($LiClO_4$), $10^{-3}k_f = 1.5 \pm 0.2$ and 1.9 ± 0.1 dm^3 mol^{-1} s^{-1} and $10^3 k_d = 2.54 \pm 0.05$ and 1.73 ± 0.01 s^{-1} for the pyridine-4- and -3-carboxylato-complexes respectively. Interestingly, only the dinuclear complex containing the pyridine-4-carboxylato-ligand was observed to undergo subsequent intramolecular electron transfer [rate constant = $(1.75 \pm 0.31) \times 10^{-4}$ s^{-1}], the rate constant for the pyridine-3-carboxylato-complex being estimated to be less than 3×10^{-5} s^{-1} under these conditions. Oxidation of $[Fe(CN)_5(H_2O)]^{3-}$ with H_2O_2 and t-butyl peroxide is also reported to be substitution controlled.[199]

[246] Z. Bradić, M. Pribanić, and S. Ašperger, *J.C.S. Dalton*, 1975, 353.
[247] A. Zmikić, M. Pribanić, D. Pavlović, and S. Ašperger, *Croat. Chem. Acta*, 1975, **47**, 117.
[248] H. E. Toma, *J. Inorg. Nuclear Chem.*, 1975, **37**, 785.
[249] J. J. Jwo and A. Haim, *J. Amer. Chem. Soc.*, 1976, **98**, 1172.

Rates and equilibrium constants for the formation of mixed dinuclear iron and cobalt complexes are also reported from stopped-flow studies of the reactions between *trans*-$[Co(en)_2(SO_3)(H_2O)]^+$ and $[Fe(CN)_5NO]^{2-}$ and $[Fe(CN)_6]^{4-}$ ions.[200] These reactions proceed by substitution of the labile water molecule in a *trans* position to the *S*-bonded sulphite ion to give cyano-bridged products such as $[(ON)(NC)_4FeCNCo(en)_2SO_3]^-$. The equilibrium and rate constants for the following reaction were also determined in alkaline solution:

$$[Fe(CN)_6]^{4-} + [Co(en)_2(SO_3)(OH)] \rightleftharpoons [(NC)_5FeCNCo(en)_2SO_3]^{3-} + OH^-$$

Reaction of the $[Fe(CN)_5NO]^{2-}$ ion with excess hydroxylamine in alkaline solution proceeds according to the equation:

$$[Fe(CN)_5NO]^{2-} + NH_2OH + OH^- \longrightarrow [Fe(CN)_5(H_2O)]^{3-} + N_2O + H_2O$$

A study of this reaction at 293.2 K and pH 4.0—5.6 indicates the following mechanism:[250]

$$[Fe(CN)_5NO]^{2-} + NH_2OH \rightleftharpoons [Fe(CN)_5N(NH_2OH)O]^{2-} \text{ (rapid)}$$

$$[Fe(CN)_5N(NH_2OH)O]^{2-} \longrightarrow [Fe(CN)_5(H_2O)]^{3-} + N_2O + H^+$$

$$[Fe(CN)_5N(NH_2OH)O]^{2-} + OH^- \rightleftharpoons [Fe(CN)_5N(NH_2O)O]^{3-} + H_2O \text{ (rapid)}$$

$$[Fe(CN)_5N(NH_2O)O]^{3-} \longrightarrow [Fe(CN)_5(H_2O)]^{3-} + N_2O$$

$$-d[Fe(CN)_5NO^{2-}]/dt = (k_0 + k_1[OH^-])[NH_2OH][Fe(CN)_5NO^{2-}]$$

At 293.2 K the rate constants are $10^3k_0 = 3.1$ dm^3 mol^{-1} s^{-1} and $10^{-6}k_1 = 3.1$ dm^6 mol^{-2} s^{-1}.

Reaction of the $[Fe(CN)_5NO]^{2-}$ ion with hydrazine hydrate in aqueous methanol or ethanol is reported to give the $[Fe(CN)_5(N_2H_4)]^{3-}$ and $[Fe(CN)_5N_2]^{3-}$ ions.[251] Further substitution reactions of $[Fe(CN)_5NO]^{2-}$ are also reported.[252]

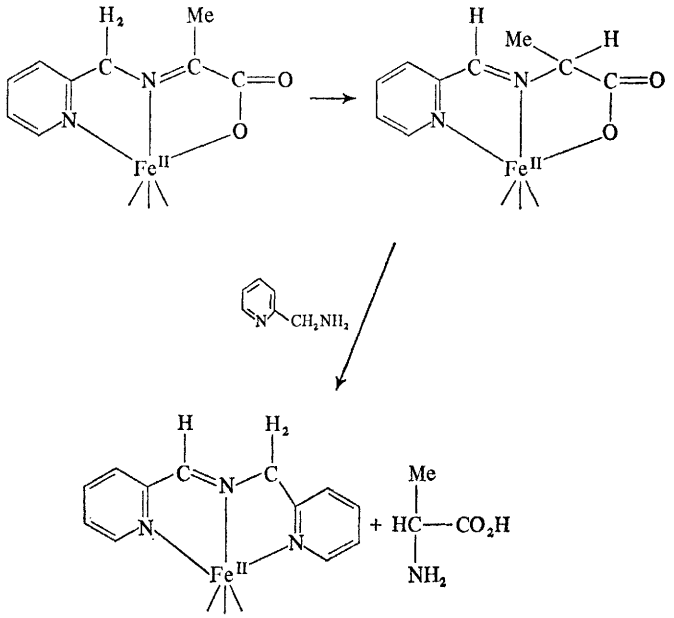
The rate constant for the hydration of the carbonyl group of the $[(NC)_5Fe$-(pyridine-4-aldehyde)$]^{3-}$ ion is reported to be 2.4×10^{-2} s^{-1} at 298.2 K, pH 4.7, and $I = 0.10$ mol dm^{-3}.[253]

Formation of an intensely coloured low-spin Fe^{II} complex is reported from the reaction between Fe^{II}(pyruvate) and 2-aminomethylpyridine.[254] The mechanism is shown in Scheme 5.

***d*^{6}: Ruthenium(II).**—The rates of reaction of the $[Ru(NH_3)_5OH_2]^{2+}$ ion with S-donor ligands (Table 23) and with HCN in 6 mol dm^{-3} CF_3CO_2H were considered[202] in the section concerned with aquation reactions. Formation of the *cis*-$[Ru(bipy)_2(NCR)_2]^{2+}$ ions by oxidation of $[Ru(bipy)_2(NH_2CH_2R)_2]^{2+}$ (RCH_2NH_2 = allylamine, benzylamine, or n-butylamine) was also considered previously.[207]

***d*^{6}: Cobalt(III).**—Several studies of the anation of the $[Co(NH_3)_5OH_2]^{3+}$ ion by carboxylic acids and their anions have been reported. They include reactions with oxalic,[225] formic,[256,257] acetic,[256,258] and propionic[256,259] acids, and with phthalate

[250] S. Luňák and J. Vepřek-Šiška, *Coll. Czech. Chem. Comm.*, 1974, **39**, 2719.
[251] A. N. Sergeeva, D. I. Zubritskaya, and D. I. Semenishin, *Zhur. neorg. Khim.*, 1975, **20**, 1925.
[252] V. Hankonyi, N. Burger, and V. Karas-Gasparec, *Z. phys. Chem.* (*Leipzig*), 1975, **256**, 87.
[253] H. Toma and J. M. Malin, *J. Amer. Chem. Soc.*, 1975, **97**, 288.
[254] M. I. D. Holanda, P. Krumholz, and H. L. Chum, *Inorg. Chem.*, 1976, **15**, 890.
[255] R. van Eldik and G. M. Harris, *Inorg. Chem.*, 1975, **14**, 10.
[256] P. R. Joubert and R. van Eldik, *Reaction Kinetics Catalysis Letters*, 1975, **3**, 23.
[257] P. R. Joubert and R. van Eldik, *Inorg. Chim. Acta*, 1975, **14**, 259.
[258] P. R. Joubert and R. van Eldik, *Inorg. Chim. Acta*, 1975, **12**, 205.
[259] P. R. Joubert and R. van Eldik, *J. Inorg. Nuclear Chem.*, 1975, **37**, 1817.



Scheme 5 *Mechanism of the transamination reaction involving* Fe^{II}, *2-aminomethylpyridine, and pyruvate ion*

ions.[260] Some of the earlier reported rate constants for the reactions with oxalic, formic, acetic, and propionic acids have been recalculated recently to take into account more than one simultaneous reaction pathway.[261] The results of these studies are collected in Table 25. An I_d mechanism applies in all cases and also to the reaction of $[Co(NH_3)_5OH_2]^{3+}$ with chloride ion discussed previously.[50]

Table 25 *Rate parameters for the reactions of carboxylic acids and carboxylate ions with the* $[Co(NH_3)_5OH_2]^{3+}$ *ion*

$$[Co(NH_3)_5OH_2]^{3+} + L \longrightarrow [Co(NH_3)_5L]^{n+} + H_2O$$

L	K_{1p}/[a] $dm^3\ mol^{-1}$	I/mol dm^{-3}	$10^5k/s^{-1}$ [b] (*temp.*/K)	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal $K^{-1}\ mol^{-1}$	*Ref.*
H_2ox	*ca.* 0	1.0	15.6[c] (343.2)	13.7±0.2	−35.5±0.6	261
Hox^-	1.8			22.4±2.1	−8.6±6.3	255
ox^{2-}	9.2			24.8±1.8	−2.1±5.4	255
AcO^-	5.2[g]	1.0	16 (343.2)	25.9±0.1[d]	−0.4±0.3[d]	261, 258
HCO_2^-	1.0[g]	1.0	56 (343.2)	17.6±2.8[e]	−22.1±10.1[e]	261, 257
$EtCO_2^-$	3.4[g]	1.0	25 (343.2)	25.4±3.2[f]	−1.5±11.5[f]	261, 295
phthalate$^-$	2.92	0.3	28.8 (333.2)	28.4±0.8	10.3±2.4	260
phthalate^{2-}	30.0	0.3	37.3 (333.2)	24.5±2.8	−0.7±8.0	260

[a] K_{1p} = Outer-sphere association constant. [b] $k = k_f/K_{1p}$, where k_f is the second-order formation rate constant. [c] k_f/l $mol^{-1}\ s^{-1}$. [d] $\Delta H^{\ddagger}(k_f) = 24.5 \pm 0.5$ kcal mol^{-1}; $\Delta S^{\ddagger}(k_f) = -1.3 \pm 1.8$ cal $K^{-1}\ mol^{-1}$. [e] $\Delta H^{\ddagger}(k_f) = 29.5 \pm 0.3$ kcal mol^{-1}; $\Delta S^{\ddagger}(k_f) = 12.4 \pm 1.2$ cal $K^{-1}\ mol^{-1}$. [f] $\Delta H^{\ddagger}(k_f) = 26.3 \pm 2.6$ kcal mol^{-1}; $\Delta S^{\ddagger}(k_f) = 4.2 \pm 9.3$ cal $K^{-1}\ mol^{-1}$. [g] At 343.2 K.

[260] A. C. Dash and N. Ray, *Indian J. Chem.*, 1976, **14A**, 78.
[261] R. van Eldik, *J. Inorg. Nuclear Chem.*, 1976, **38**, 884.

Replacement of one of the co-ordinated water molecules in the $[Co(NH_3)_4(H_2O)_2]^{3+}$ ion by polyphosphate ion is reported to proceed with an activation energy of 27.3 kcal mol^{-1}.[262]

The *cis*-$[Co(NH_3)_2(H_2O)_4]^{3+}$ and *fac*-$[Co(NH_3)_3(H_2O)_3]^{3+}$ ions have been isolated, and it has been shown that although *cis*-$[Co(NH_3)_2(H_2O)_4]^{3+}$ is a moderately powerful oxidizing agent, it is much more inert to substitution than $[Co(H_2O)_6]^{3+}$:[263]

$$cis\text{-}[Co(NH_3)_2(H_2O)_4]^{3+} + Cl^- \rightleftharpoons [Co(NH_3)_2(H_2O)_3Cl]^{2+} + H_2O \quad (23)$$

Reaction (23) was studied at 301.2—320.8 K in $NaClO_4$–$HClO_4$ solutions ($I = 2.0$ mol dm^{-3}) containing 0.01—1.20 mol dm^{-3} H^+ and excess (0.10—1.6 mol dm^{-3}) Cl^-. The pseudo-first-order rate constant (k) for the approach to equilibrium is characterized by

$$k/s^{-1} = A[Cl^-]/[H^+] + B/[H^+]$$

Both *cis*-$[Co(NH_3)_2(H_2O)_4]^{3+}$ and *cis*-$[Co(NH_3)_2(H_2O)_3(OH)]^{2+}$ ions are involved, and at 301.2 K $10^5A = 15.0 \pm 0.3$ s^{-1} and $10^5B = 2.7 \pm 0.2$ mol dm^{-3} s^{-1}. The rate-determining step in the oxidation of bromide ion[263] and hydrogen peroxide[264] by *cis*-$[Co(NH_3)_2(H_2O)_3(OH)]^{2+}$ is substitution of the reductant at the cobalt(III) centre.

The pK_a of $[Co(nta)(H_2O)_2]$ is 6.71 ± 0.01 at 298.2 K and $I = 1.0$ mol dm^{-3}. Rate constants for the reaction of $[Co(nta)(H_2O)_2]$ (k_a) and of its conjugate base (k_b) with potentially reducing ligands have been determined and complex formation is again rate determining.[94] The rate constants are collected in Table 26. The reaction with

Table 26 *Rate constants at* 298.2 K *and* $I = 1.0$ mol dm^{-3} *for the reaction of* $[Co(nta)(H_2O)_2]$ (k_a) *and its conjugate base* (k_b) *with potentially reducing substrates* (*data from ref.* 94)

Substrate	$N_2H_5^+$	N_2H_4	p-$C_6H_4(OH)_2$	NH_3OH^+	NH_2OH
10^2k_a/dm^3 mol^{-1} s^{-1}	0.16	< 640	0.82	0.022	< 26
10^2k_b/dm^3 mol^{-1} s^{-1}	< 46		86	< 120	420

Substrate	I^-	NO_2^-	NCS^-	$S_2O_3^{2-}$
10^2k_a/dm^3 mol^{-1} s^{-1}	2.17	< 0.88	*ca.* 2	0.50
10^2k_b/dm^3 mol^{-1} s^{-1}	164	140	*ca.* 30	120

NCS^- ion, and with NO_2^- ion at pH 4.5, does not lead to reduction, but at pH 5.6 NO_2^- like the other substrates causes reduction to Co^{II}. The anation reaction with SO_3^{2-} which can occur without Co—O bond fission is very rapid, and reduction is again involved in the rate-determining step.

The rapid uptake of CO_2 by $[Co(tren)(H_2O)_2]^{3+}$ to give $[Co(tren)(OH)(HCO_3)]^+$ and $[Co(tren)(OH)(CO_3)]$ has been studied by the stopped-flow method, and the rates of the subsequent chelation reactions of these first-formed products to give $[Co(tren)(CO_3)]^+$ have also been measured.[265] The reactions were studied between pH 7 and 9 and at 288—298 K at $I = 1.0$ mol dm^{-3} (NaCl), and the rate constants

[262] C. Stanisav and R. Vatulescu, *Chem. Abs.*, 1976, **84**, 65700.
[263] I. Bodek, G. Davies, and J. H. Ferguson, *Inorg. Chem.*, 1975, **14**, 1708.
[264] I. Bodek and G. Davies, *Inorg. Chem.*, 1975, **14**, 2580.
[265] T. P. Dasgupta and G. M. Harris, *J. Amer. Chem. Soc.*, 1975, **97**, 1737.

at 293.2 K and activation parameters for CO_2 uptake by the $[Co(tren)(OH)(H_2O)]^{2+}$ and $[Co(tren)(OH)_2]^+$ ions are reported to be $k = 30$ and 97 $dm^3\ mol^{-1}\ s^{-1}$, $\Delta H^{\ddagger} = 14.7 \pm 0.1$ and 32 ± 6 kcal mol^{-1}, and $\Delta S^{\ddagger} = -1.9 \pm 0.2$ and 53 ± 22 cal $K^{-1}\ mol^{-1}$ respectively. At 293.2 K the rate parameters for the ring closure of $[Co(tren)(OH)(HCO_3)]^+$ are $10^2k = 3.6\ s^{-1}$, $\Delta H^{\ddagger} = 12.5 \pm 0.5$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -22.7 \pm 1.6$ cal $K^{-1}\ mol^{-1}$, and for ring closure of $[Co(tren)(OH)(CO_3)]$ $10^4k = 1.3\ s^{-1}$.

Rate data for the formation of carbonato-complexes by substitution of amines into the $[Co(CO_3)_3]^{3-}$ ion have also appeared.[266] For the reaction of excess pyridine [$(1.2—29.8) \times 10^{-2}$ mol dm^{-3}] with green solutions of $Na_3[Co(CO_3)_3],3H_2O$[$(5.7—11.4) \times 10^{-4}$ mol dm^{-3}] in the presence of $NaHCO_3$ (0.14—0.865 mol dm^{-3}) and H^+ [$(0.15—9.52(\times 10^{-9}$ mol dm^{-3}], the rate law for the formation of the *cis*-$[Co(CO_3)_2(py)_2]^-$ ion is reported to be

$$-\mathrm{d}[\text{green reactants}]/\mathrm{d}t = \mathrm{d}[cis\text{-}Co(CO_3)_2(py)_2^-]/\mathrm{d}t = (A + B/[HCO_3^-])[H^+][\text{green reactants}][py]/(1 + C[H^+])$$

At 298.2 K and $I = 1.0$ mol dm^{-3}, $10^{-9}A = 1.70 \pm 0.22$ $dm^6\ mol^{-2}\ min^{-1}$, $10^{-8}B = 8.41 \pm 0.42$ $dm^3\ mol^{-1}\ min^{-1}$, and $10^{-9}C = 1.31 \pm 0.12$ $dm^3\ mol^{-1}$. The green reactants are a mixture of $[Co(CO_3)_3]^{3-}$, $[Co(CO_3)_2(H_2O)(HCO_3)]^{2-}$, and $[Co(CO_3)_2(H_2O)_2]^-$ ions in rapid equilibria ($10^{-9}K_h = 1.31 \pm 0.12$ $dm^3\ mol^{-1}$; $10^2K_2 < 6$ mol dm^{-3}):

$$[Co(CO_3)_3]^{3-} + H_3O^+ \overset{K_h}{\rightleftharpoons} [Co(CO_3)_2(HCO_3)(H_2O)]^{2-}$$

$$[Co(CO_3)_2(HCO_3)(H_2O)]^{2-} + H_2O \overset{K_2}{\rightleftharpoons} [Co(CO_3)_2(H_2O)_2]^- + HCO_3^-$$

The rate-determining steps involve the addition of one pyridine molecule to each of the three carbonato-species, followed by a rapid addition of a second pyridine molecule in each case. The rate constants for the addition of the first pyridine molecule to the $[Co(CO_3)_3]^{3-}$, $[Co(CO_3)_2(HCO_3)(H_2O)]^{2-}$, and $[Co(CO_3)_2(H_2O)_2]^-$ ions are estimated to be $\leqslant 0.4$, 1.3 ± 0.2, and $\geqslant 10$ $dm^3\ mol^{-1}\ min^{-1}$ respectively. Reactions with chelating diamines such as en, 1,2-pn, and 1,3-pn (tmd) in aqueous $NaHCO_3$ solutions at $8 \leqslant pH \leqslant 10.5$ are more complex, the formation of the $[Co(CO_3)_2(diamine)]^-$ ion occurring through an unusually stable half-bonded diamine species, $[Co(CO_3)_2(diamine)(HCO_3)]^{2-}$. Representing the diamine as L-L, the reactions involved are

$$[Co(CO_3)]^{3-} + \text{L-L} \xrightarrow[H^+]{(I_d)} [(HCO_3)(CO_3)_2Co—\text{L-L}]^{2-} \quad (24)$$

$$[(HCO_3)(CO_3)_2Co—\text{L-L}]^{2-} \xrightarrow{k_3} \left[(CO_3)_2Co\begin{matrix}\text{L}\\\text{L}\end{matrix}\right]^- + HCO_3^- \quad (25)$$

$$[(HCO_3)(CO_3)_2Co—\text{L-L}]^{2-} + H_2O \underset{k_2}{\overset{k_{-2}}{\rightleftharpoons}} [(H_2O)(CO_3)_2Co—\text{L-L}]^- + HCO_3^- \quad (26)$$

$$[(H_2O)(CO_3)_2Co—\text{L-L}]^- \xrightarrow{k_4} \left[(CO_3)_2Co\begin{matrix}\text{L}\\\text{L}\end{matrix}\right]^- + H_2O \quad (27)$$

$$[Co(CO_3)_2(diamine)]^- + diamine \longrightarrow [Co(CO_3)(diamine)_2]^+ + CO_3^{2-} \quad (28)$$

[266] G. W. Davies and Y. W. Hung, *Inorg. Chem.*, 1976, **15**, 704, 1358.

Reaction (25) is much more rapid than reaction (27) and the slowness of these chelate ring closures is attributed to a high conformational stability in the half-bonded intermediates, presumably as a result of hydrogen-bonding. The intermediate with 1,3-pn (tmd) is the slowest to ring-close, as might be expected since this involves the formation of a six-membered chelate ring. The mechanism of reaction (24) is analogous to that observed for the reaction with pyridine. An I_d mechanism is proposed involving the two ions $[Co(CO_3)_3]^{3-}$ and $[Co(CO_3)_2(HCO_3)(H_2O)]^{2-}$, which form two ion–dipole intermediates:

$$[Co(CO_3)_3]^{3-} + \text{L-L} \overset{K_0}{\rightleftharpoons} [Co(CO_3)_3]^{3-},\text{L-L} \quad \text{(rapid)} \tag{29}$$

$$[Co(CO_3)_2(HCO_3)(H_2O)]^{2-} + \text{L-L} \overset{K_1}{\rightleftharpoons} [Co(CO_3)_2(HCO_3)(H_2O)]^{2-},\text{L-L} \quad \text{(rapid)} \tag{30}$$

If k_0 and k_1 are the rate constants for the formation of the half-bonded intermediates from the ion–dipole complexes (formation constants K_0 and K_1), such that k_0K_0 and k_1K_1 are the second-order rate constants for the reactions of L-L with $[Co(CO_3)_3]^{3-}$ and $[Co(CO_3)_2(HCO_3)(H_2O)]^{2-}$ respectively, the observed overall rate constant (k) for reaction (24) is given by

$$k = \frac{(k_0K_0 + k_1K_1K_h[H^+])[\text{L-L}]}{1 + K_0[\text{L-L}] + K_h[H^+] + K_hK_1[H^+][\text{L-L}]} \tag{31}$$

Values of the rate and equilibrium constants associated with reactions (25)—(27) and (29)—(31) are collected in Table 27. The value of $K_2 = k_2/k_{-2} = 0.1$—0.4 dm^3 mol^{-1} between 274 and 298 K, and activation parameters associated with k_{-2} are $\Delta H^{\ddagger} = 18.2 \pm 1.1$ kcal mol^{-1} and $\Delta S^{\ddagger} = 2 \pm 4$ cal K^{-1} mol^{-1}.

Table 27 *Rate parameters and equilibrium constants estimated for reactions* (25)—(27) *and* (29)—(31) *at* 298.2 K *and* I = 1.0 mol dm^{-3} ($NaHCO_3/NaClO_4$) (*data from ref.* 266)

Ligand	py	en	1,2-pn	1,3-pn
K_0/dm^3 mol^{-1}	0.3	$\gtrsim 3000$	$\gtrsim 2000$	0.3
K_1/K_0	1	0.95 ± 0.2	0.55 ± 0.15	1
k_0/s^{-1}	<0.01	$\lesssim 0.1$	$\lesssim 0.08$	$\lesssim 5$
k_1/s^{-1}	0.07 ± 0.01	6.1 ± 1.0	7.1 ± 1.7	600
10^5k_4/[a] s^{-1}		92 ± 3	30 ± 13	19 ± 0.5
$\Delta H^{\ddagger}(k_4)$/kcal mol^{-1}		33 ± 2	47 ± 8	
$\Delta S^{\ddagger}(k_4)$/cal K^{-1} mol^{-1}		38 ± 8	84 ± 30	
$10^5k_3K_2$/dm^3 mol^{-1} s^{-1}		208 ± 8	300 ± 30	71 ± 3
$\Delta H^{\ddagger}(k_3K_2)$/kcal mol^{-1}		21.2 ± 0.7	11.7 ± 1.9	
$\Delta S^{\ddagger}(k_3K_2)$/cal K^{-1} mol^{-1}		0 ± 2	-31 ± 6	

[a] At 298.7 K.

References to studies of the formation of *trans*-$[Co(dmgH)_2(X)(Y)]^{n-}$ ions (X and Y are unidentate ligands) are collected in Table 28. Most of the reactions have been established to proceed by an S_N1(lim) mechanism.

A dissociative mechanism has also been demonstrated for the anation of the $[Co(P)(H_2O)_2]^{5+}$ ion [H_2P = 5,10,15,20-tetrakis-(4-*N*-methylpyridyl)porphine] by

Table 28 *References to studies of the rates of formation of* trans-$[Co(dmgH)_2(X)(Y)]$ *and other dioximato-complexes of cobalt* (III) (X *and* Y *are unidentate ligands*)

Reactants[a]	*Products*[a]	*Ref.*
$[Co(dmgH)_2(H_2O)_2]^+ + X^-$	$[Co(dmgH)_2(H_2O)X]$ (X = Cl or Br) $[Co(dmgH)_2X_2]^-$ (X = I or NCS)	267
$[Co(dmgH)_2(H_2O)X] + tu$	$[Co(dmgH)_2(tu)_2]^+$	268
$[Co(dmgH)_2(tu)(RC_6H_4NH_2)] + tu$	$[Co(dmgH)_2(tu)_2]^+$	269[b]
$[Co(dmgH)_2(SCN)(B)] + CN^-$	$[Co(dmgH)_2(SCN)(CN)]^-$	270[c]
$[Co(dmgH)_2(SCN)(CN)] + Q$	$[Co(dmgH)_2(CN)(Q)]$	270[c]
$[Co(dmgH)_2(RSO_2)(MeOH)] + L$	$[Co(dmgH)_2(RSO_2)(L)]$	84[d]
$[Co(dioxime)_2(SO_3)(H_2O)]^- + SO_3^{2-}$	$[Co(dioxime)_2(SO_3)_2]$	91[e]

[a] All reactants and products have a *trans* geometry. [b] R = H, *m*- or *p*-Me, *p*-OMe, *p*-Br, *p*-I, or *p*-NO_2. [c] B = NH_3 or py; Q = py, 3-Cl-py, 4-NH_2-py, NH_3 or piperidine. [d] R = Me or *p*-MeC_6H_4; L = tu, *p*-$MeC_6H_4NH_2$, py, Pr^n_2S, Ph_3P, Ph_3As, Ph_3Sb, or MeOH. [e] dioximeH = methyl-, dimethyl-, methylpropyl- or methylbutyl-glyoxime.

Cl^-, Br^-, I^-, and NCS^- ions.[271] Activation parameters for the loss of water are $\Delta H^{\ddagger} = 19 \pm 2$ kcal mol^{-1} and $\Delta S^{\ddagger} = 7 \pm 7$ cal K^{-1} mol^{-1}, and for the formation of the iodo-complex are $\Delta H^{\ddagger} = 20.3 \pm 0.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = 10.4 \pm 1.5$ cal K^{-1} mol^{-1}. The pK_a's of the co-ordinated water molecules are 5.5 and 10.7 at $I = 1.0$ mol dm^{-3}.

d^6: Rhodium(III).—Species of the type $[RhCl_n(H_2O)_{6-n}]^{(3-n)+}$ have been characterized for $n = 0$—6, and kinetic data are reported for the chloride-ion anation and aquation reactions of *fac*- and *mer*-$[RhCl_3(H_2O)_3]$.[179] A dissociative mechanism involving a square-pyramidal transition state is proposed for the aquation and anation reactions, and a similar conclusion has been reached for the bromide-ion anation of the $[Rh(H_2O)_6]^{3+}$ and $[Rh(H_2O)_5Br]^{2+}$ ions.[272] A *D* mechanism is consistent with the rate data and with the observation that the rates of anation by Cl^- and Br^- are very similar. The mechanism for anation involves both the $[Rh(H_2O)_6]^{3+}$ and $[Rh(H_2O)_5OH]^{2+}$ ions. For the $[Rh(H_2O)_5X]^{2+}$ ions the *trans* effect of X^- varies in the order $OH^- \gg Br^- > Cl^-$, and for *trans*-$[Rh(en)_2(H_2O)X]^{2+}$ ions the order is $OH^- > Br^- \gg Cl^-$.[273] The observation of a *D* mechanism for the anation of $[Rh(H_2O)_6]^{3+}$ is surprising in view of the evidence in favour of an I_a mechanism for the anation of $[Rh(NH_3)_5(H_2O)]^{3+}$,[274] and is in direct contrast to the behaviour for chromium(III) substitutions where an I_a mechanism is favoured for reactions of $[Cr(H_2O)_6]^{3+}$ and an I_d mechanism for anation of $[Cr(NH_3)_5(H_2O)]^{3+}$.[10] However, anation of $[Rh(NH_3)_5(H_2O)]^{3+}$ by ox^{2-} and Hox^- has been reported recently to proceed by an I_d mechanism,[275] and more work will be necessary to resolve this dichotomy.

267 N. M. Samus and T. S. Luk'yanets, *Zhur. neorg. Khim.*, 1975, **20**, 1010.
268 B. A. Bovykin and I. B. Leongardt, *Zhur. neorg. Khim.*, 1974, **19**, 3311.
269 B. A. Bovykin, *Zhur. neorg. Khim.*, 1974, **19**, 2464; B. A. Bovykin, N. V. Ivanov, and L. F. Vasil'eva, *Zhur. neorg. Khim.*, 1974, **19**, 2757.
270 A. L. Crumbliss and P. L. Gauss, *Inorg. Chem.*, 1976, **15**, 737.
271 K. R. Ashley, M. Berggren, and M. Cheng, *J. Amer. Chem. Soc.*, 1975, **97**, 1422.
272 R. J. Buchacek and G. M. Harris, *Inorg. Chem.*, 1976, **15**, 926.
273 M. J. Pavelich, *Inorg. Chem.*, 1975, **14**, 982.
274 T. W. Swaddle and D. R. Stranks, *J. Amer. Chem. Soc.*, 1972, **94**, 8347.
275 R. van Eldik, *Reaction Kinetics Catalysis Letters*, 1975, **2**, 251; *Z. anorg. Chem.*, 1975, **416**, 88.

The reaction between *trans*-$[Rh(en)_2(H_2O)_2]^{3+}$ and chloride ions gives the *trans*-$[Rh(en)_2Cl_2]^+$ ion, the second step of this two-step process being much more rapid than the first.[273] Thus there is no build up of the intermediate *trans*-$[Rh(en)_2(H_2O)Cl]^{2+}$ species.

d^6: Platinum(IV).—Substitutions at Pt^{IV} complexes are invariably complicated by Pt^{II} catalysis, and recent examples are no exception to this rule. For the formation of the *trans*-$[Pt(A_4)(N_3)Cl]^{2+}$ ions from *trans*-$[Pt(A_4)Cl_2]^{2+}$ [A_4 = $(NH_3)_4$ or $(en)_2$] the rate law is

$$d[Pt(A_4)(N_3)Cl^{2+}]/dt = k[Pt(A_4)Cl_2{}^{2+}][Pt(A_4)^{2+}][N_3^-]$$

At 298.2 K, the rate constants are $k = 36$ dm^6 mol^{-2} s^{-1} ($I = 0.23$ mol dm^{-3}) and $k = 120$ dm^6 mol^{-2} s^{-1} ($I = 0.40$ mol dm^{-3}) for A_4 = $(NH_3)_4$ and $(en)_2$ respectively. Substitution by azide ion is relatively slow for such reactions, indicating that this anion is an ineffective bridging ligand for the two-electron inner-sphere redox reaction involved. The result supports an earlier suggestion that the analogous reaction involving thiocyanate substitution only proceeds by bridging through the sulphur atom.[276]

Reductive elimination followed by oxidative addition has been found for the anation of the *trans*-$[Pt(CN)_4(H_2O)Cl]^-$ ion by bromide ion.[277]

$$\textit{trans}\text{-}[Pt(CN)_4(H_2O)Cl]^- + Br^- \longrightarrow [Pt(CN)_4]^{2-} + ClBr + H_2O$$

$$ClBr + \text{excess } Br^- \xrightarrow{\text{rapid}} Cl^- + Br_2$$

$$[Pt(CN)_4]^{2-} + Br_2 + H_2O \longrightarrow \textit{trans}\text{-}[Pt(CN)_4(H_2O)Br]^- + Br^-$$

The $[PtCl_5(H_2O)]^-$ ion is the primary product of the chloride-ion anation of *trans*-$[PtCl_4(H_2O)_2]$ and *trans*-$[Pt(CN)_4(H_2O)Cl]^-$ ion in the presence of $[PtCl_4]^{2-}$ ion and 1 mol dm^{-3} $HClO_4$. The importance of an aqua-adduct as well as a chloro-adduct of $[PtCl_4]^{2-}$ is demonstrated by these results, and the general mechanism shown in Scheme 6 applies for substitution reactions of this type in which the leaving group (Y) is not the solvent (X = entering ligand). Applying the steady-state approximation to the dinuclear species, the observed pseudo-first-order rate constant, k, in the presence of excess X is given by

$$k = k_1 \left(\frac{k_7(k_4 + k_5 + k_{10}) + k_3 k_5[X]}{k_4(k_2 + k_7) + (k_5 + k_{10})(k_2 + k_7 + k_3[X])} \right) [Pt^{II}] \qquad (32)$$

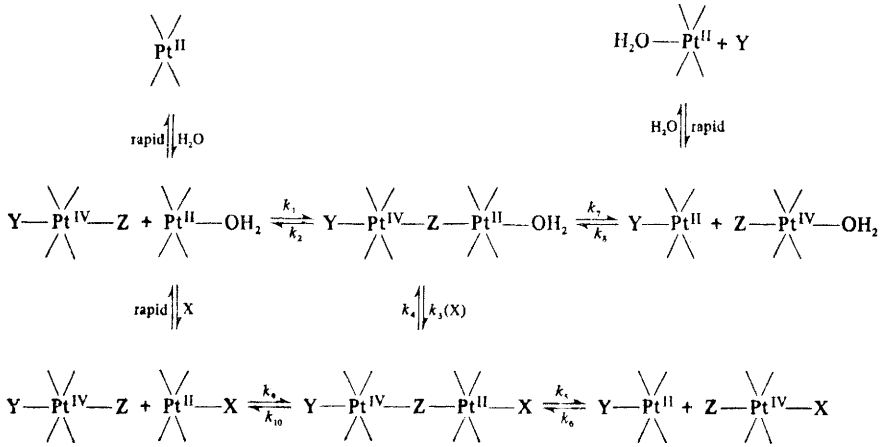
or

$$k = \{(k' + k''[X])/(1 + k'''[X])\}[Pt^{II}] \qquad (33)$$

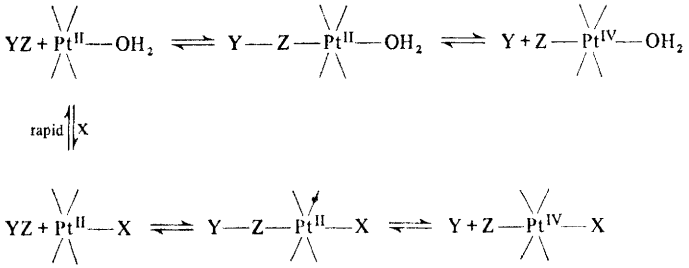
For reactions involving the $[PtCl_4]^{2-}$ ion, the above mechanism shows that k''' is *not* the equilibrium constant for the formation of the $[PtCl_5]^{3-}$ adduct as was previously supposed. A similar mechanistic scheme (Scheme 7) applies when the leaving group is a solvent molecule, and adducts with X and H_2O are important for oxidative addition reactions of Pt^{II}, *e.g.* $[Pt(CN)_4]^{2-} + I_2$.[277]

[276] H. A. Bryan, N. S. Pantalea, W. L. Dickinson, and R. C. Johnson, *Inorg. Chem.*, 1975, **14**, 1336.

[277] L. I. Elding and L. Gustafson, *Inorg. Chim. Acta*, 1976, **19**, 31, 165; 1976, **18**, L35.



Scheme 6



Scheme 7

Miscellaneous Metal Ions.—The rate of reaction of the $[UO_2]^{2+}$ ion with the metal ion indicator PAR has been measured at pH 1.0—3.9, and the reaction rate varies inversely with $[H^+]$. In this pH range, the dominant pathway is the reaction of $[UO_2]^{2+}$ with unionized PAR.[278] A low pH (2.3—2.9) has also been used to investigate the rate of the reactions between M^{III} (M = Eu, Am, or Cu) and cydta by an electromigration method.[279] Studies of the rates of reactions between Ti^{IV} and methylthymol blue[228] and between Zr^{IV} and xylenol orange[229] have also appeared.

7 Ligand Exchange and Replacement

Solvent Exchange.—References to solvent exchange studies will be found in previous sections. Data for the exchange between two non-aqueous solvents (S^1, S^2) in reactions of the type $[Cr(NCS)_5(S^1)]^{2-} + S^2 \rightleftharpoons [Cr(NCS)_5(S^2)]^{2-} + S^1$ are to be found in Table 20 (S^1 and S^2 = $MeCONMe_2$, DMF, or DMSO, S^2 = py).[11] For

[278] A. Ekstrom and D. A. Johnson, *J. Inorg. Nuclear Chem.*, 1974, **36**, 2549.
[279] A. V. Stepanov, *Chem. Abs.*, 1975, **82**, 145778.

the exchange of DMF with the $[Cr(DMF)_6]^{3+}$ ion the value of $\Delta V^{\ddagger}$ is -6.3 cm^3 mol^{-1} in line with an associative-interchange (I_a) mechanism.[146] Data for the exchange of DMF and DMSO with *cis*- or *trans*-$[Cr(en)_2(S^1)(S^2)]^{3+}$ ions (S^1 = S^2 = DMF or DMSO) are summarized in Table 19. The relative reactivities of $[Cr(H_2O)_n(S)_{6-n}]^{3+}$ ions (S = DMF[235] or DMSO[116]) were also considered previously.

For the *cis*-$[M(NO)_2(MeCN)_4]^{2+}$ ions (M = Mo or W), the two solvent molecules in a *trans* position to the nitrosyl groups are much more labile than the other two acetonitrile molecules.[280] Solvent exchange is stereoretentive, and a mechanism involving a trigonal-bipyramidal intermediate is proposed.

Binding of the $[Co(NH_3)_5(H_2O)]^{3+}$ ion with an ion-exchange resin (Dowex 50w) has no effect upon the water exchange rate, whereas the pH-dependence for ^{18}O-exchange between $H_2{}^{18}O$ and $[ReO_4]^-$ ion is modified on binding to the resin.[101]

Methanol exchange with *trans*-$[Co(dmgH)_2(RSO_2)(MeOH)]$ (R = Me or *p*-MeC_6H_4) has also been reported.[84]

Ligand Exchange and Replacement: Unidentate by Unidentate.—Exchange reactions of the type $[M^VX_5L] + L^* \rightleftharpoons [M^VX_5L^*] + L$ (M = Nb or Ta, X = Cl or Br, L = Me_2Y, Y = O, S, Se, or Te) were considered in Volume 4 of this series. Further studies have confirmed that the reactions are dissociative when Y = O, and associative when Y = S, Se, or Te.[281] Values of $\Delta H^{\ddagger}$ are *ca.* 11 kcal mol^{-1} and $\Delta S^{\ddagger}$ *ca.* 30—40 cal K^{-1} mol^{-1} less for the associative reactions than for the dissociative reactions, and the values of $\Delta V^{\ddagger}$ (determined by high-pressure ^{1}H n.m.r.) give an even more striking confirmation of this change in mechanism. For the dissociative exchange of Me_2O the value of $\Delta V^{\ddagger}$ is $+10$ cm^3 mol^{-1}, and for the associative exchange of Me_2Se $\Delta V^{\ddagger} = -12$ cm^3 mol^{-1}.

The kinetics and thermodynamics of the exchange of halide ions (X) in cluster compounds of the type $[M_6Cl_8]X_6$ have been reported for M = Mo and W. Replacement of chloride ion (X^-) by bromide ion involves aquation in the rate-determining step followed by rapid bromide-ion anation of the aqua-intermediate.[282] The activation energies for the forward and reverse reactions are both reported to be *ca.* 18 kcal mol^{-1}. The molybdenum clusters are about ten times as reactive as the analogous tungsten clusters.

An S_N1(lim) mechanism has been established for the exchange of Ph_3PO in $[MoOCl_3X(OPPh_3)]^-$ ions. These results were discussed previously.[230] ^{18}O Exchange between $H_2{}^{18}O$ and the $[Mo(OH)(O)(CN)_4]^{3-}$ or $[Mo(O)_2(CN)_4]^{4-}$ ions is complete in less than 2 min at 273 K.[160]

Replacement of chloride ions in *trans*-$[Rh(AA)_2Cl_2]^+$ ion (AA = *N*-methyl-, *NN'*-dimethyl-, *NN*-dimethyl-, or *NNN'*-trimethyl-ethane-1,2-diamine) by bromide ions has been studied kinetically,[184] and data are also reported for the replacement of halide ions in *cis*-$[Ru(bipy)_2X_2]$ (X = F, Cl, or Br) by pyridine or substituted pyridines.[204]

Data for the replacement of unidentate ligands X in the $[Fe(CN)_5X]^{n-}$ ions (X = *p*-$Me_2NC_6H_4NO$, PhNO, SO_3^{2-}, or H_2O) by ligands Y (PhNO, 3CN-py,

[280] B. F. G. Johnson, A. Khair, and C. G. Savory, *J.C.S. Chem. Comm.*, 1974, 744.
[281] R. Good and A. E. Merbach, *Inorg. Chem.*, 1975, **14**, 1030; A. E. Merbach and H. Vanni, Proc. XVII ICCC, Hamburg, 1976, p. 269.
[282] P. Lessmeister and H. Schaefer, *Z. anorg. Chem.*, 1975, **417**, 171.

p-$Me_2NC_6H_4NO$, SCN^-, NO_2^-, CN^-, or SO_3^{2-}),[246] and for the reaction of the $[Fe(CN)_5py]^{3-}$ ion with CN^-–HCN[283] have also been reported.

Ligand Replacement: Multidentate by Unidentate.—Cyanide ion is often used to displace multidentate ligands from nickel(II), and recently kinetic studies of such reactions have appeared:

$$[NiL]^{2+} + 4CN^- \longrightarrow [Ni(CN)_4]^{2-} + L$$

Striking differences in the reaction rates are observed for the demetalation of the Ni^{II} complexes of 12-, 13-, and 14-membered macrocyclic quadridentate N-donor ligands such as 1,4,7,10-tetra-azacyclododecane (and its 12,12-dimethyl derivative) and 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane (*N*-Me_4-cyclam).[284] The reactions with cyanide ion are reported to occur in two steps, the first step involving the rapid formation of 1:1 and sometimes 1:2 CN^- ion adducts, and the second, slower step giving the final products. Equilibrium constants for the rapidly formed adducts were determined. The lability of the (*N*-Me_4-cyclam)nickel(II) complex varies with the isomer involved. Thus the product of the reaction of *N*-Me_4-cyclam with Ni^{II} is labile, whereas when the $[Ni(cyclam)]^{2+}$ ion is methylated a much more inert isomer of $[Ni(N\text{-}Me_4\text{-cyclam})]^{2+}$ is formed.[285] The labile form has all four methyl groups on the same side of the macrocyclic ring. The affect of substituents upon the rates of formation of several Ni^{II} and Cu^{II} complexes of *C*-methyl-substituted derivatives of 1,4,7,10-tetra-azacyclotridecanes has been reported.[286] Nickel(III) complexes of the type $[Ni(L)(MeCN)_2]^{3+}$ decompose with the formation of radical species.[287]

Ligand Replacement: Unidentate by Multidentate.—The $[Co(CO_3)_3]^{3-}$ ion exists in aqueous solution together with the $[Co(CO_3)_2(H_2O)(HCO_3)]^{2-}$ and $[Co(CO_3)_2(H_2O)_2]^-$ ions. Replacement of the unidentate and bidentate carbonato-ligands by chelating amines was considered previously.[266]

The only other reactions in this category which have been reported involve displacement of co-ordinated solvent molecules, *e.g.* $[Cr(H_2O)_6]^{3+}$ + bipy,[130] and these were considered in the section concerned with complex formation.

Ligand Replacement: Multidentate by Multidentate.—^{14}C-Labelled oxalate ion has been used to study the rates of oxalate exchange with the $[Cr(ox)_2L]^{n-}$ ions (L = ox^{2-}, alinate, serinate, or cysteinate ions).[288] When L = ox^{2-}, the rate law is Rate = $k[Cr(ox)_3{}^{3-}][ox^{2-}]$, whereas when L = serinate ion $[HOCH_2CH(NH_2)CO_2^-]$ the reaction is first-order with rate = $k[Cr(ox)_2L^{2-}]$. Serinate ion accelerates the rate of oxalate exchange by lowering the activation energy; when L = ox^{2-}, $\Delta H^{\ddagger} = 23.2$ kcal mol^{-1}, and when L = serinate ion $\Delta H^{\ddagger} = 18.7$ kcal mol^{-1}. The rates of oxalate exchange decrease with L in the order cysteinate > serinate > alanate > oxalate.

[283] A. D. James and R. S. Murray, *J.C.S. Dalton*, 1975, 1530.
[284] L. Hertli and T. A. Kaden, *Chimia* (*Switz.*), 1975, **29**, 304.
[285] M. J. D'Aniello, M. T. Mocella, F. Wagner, E. K. Barefield, and J. C. Paul, *J. Amer. Chem. Soc.*, 1975, **97**, 192.
[286] W. Steinman and T. A. Kaden, *Helv. Chim. Acta*, 1975, **58**, 1358.
[287] E. K. Barefield and M. T. Mocella, *J. Amer. Chem. Soc.*, 1975, **97**, 4238.
[288] S. Wajda, M. Huza-Koralewicz, and E. Bezak, *Nukleonika*, 1974, **19**, 957; S. Wajda and M. Huza-Koralewicz, *Bull. Acad. polon. Sci. Sér. Sci. chim.*, 1975, **23**, 71.

Two pathways are reported for the formation of the $[Cr(edta)]^-$ ion from the reaction between $[Cr(ox)_3]^{3-}$ and edta at pH 8.5 in a bicarbonate buffer. One pathway is dependent on and one independent of [edta], and the reaction rate depends upon $[HCO_3^-]$.[289]

An S_N1 mechanism is reported for the exchange of ^{14}C-labelled acetylacetonate ion ($acac^-$) with $[Co(acac)_3]$. The activation parameters are $\Delta H^{\ddagger} = 6.7$ kcal mol^{-1} and $\Delta S^{\ddagger} = -110$ cal K^{-1} mol^{-1}.[290]

Second-order rate laws are observed for the reactions of $[Fe^{III}L]$ (L = tiron or salicylate ion) with edta,[291] and for the reactions of $[Ni^{II}L]$ (L = dien, nta, or edma) with triethyltetraminehexa-acetate ion ($ttha^{6-}$).[292] The latter reactions have rates which are the same as those reported previously for there actions with diethylenetriaminepenta-acetate ion (dtpa). The $[Ni(dien)]^{2+}$ ion reacts with $tthaH_2^{4-}$ and $tthaH^{5-}$ ions at approximately the same rate, whereas the $[Ni(nta)]^-$ and $[Ni(edma)]^+$ ions react much more slowly with the $tthaH_2^{4-}$ ion than with $tthaH^{5-}$. This suggests that the latter reactions involve a proton transfer from the entering group to the leaving group in the rate-determining step.

Data reported from ^1H n.m.r. line-broadening studies for the dissociation and exchange of aminopolycarboxylate ions (L^{4-}) from their respective Ca^{2+} complexes ($[CaL]^{2-}$) are summarized in Table 29.[293] Exchange of L^{4-} is a second-order process

Table 29 *Rate constants at* 298.2 K *for the dissociation of aminopolycarboxylate ions from their respective* Ca^{2+} *complexes (data from ref.* 293)

Rate of dissociation $= (k_0 + k_H[H^+])[CaL^{2-}]$

Ligand (L)	$10^5 k_0/s^{-1}$	$10^{-5} k_H/dm^3\ mol^{-1}\ s^{-1}$
edta[a]	1.28×10^5	144
1,2-pdta[b]	6.6×10^3	68.3
bdta[c]	10.4	12.8
cydta	3.0	4.43

[a] $\log_{10} A = 11.0$; $E_a = 12.4$ kcal mol^{-1} for ligand exchange [b] $\log_{10} A = 11.0$; $E_a = 15.0$ kcal mol^{-1} for ligand exchange. [c] 2,3-Diaminobutane-*NNN'N'*-tetra-acetate ion.

(rate $= k[CaL^{2-}][L]$) when L = edta or 1,2-pdta, but first-order (independent of [L]) when L = 2,3-diaminobutane-*NNN'N'*-tetra-acetate ion, $bdta^{4-}$, or $cydta^{4-}$. The reactions which are independent of [L] proceed by a dissociative mechanism:

$$[CaL]^{2-} \xrightarrow{k_0} Ca^{2+} + L^{4-}$$

$$[CaL]^{2-} + H^+ \xrightarrow{k_H} Ca^{2+} + HL^{3-}$$

$$Ca^{2+} + {}^*L^{4-} \xrightarrow{\text{rapid}} [Ca{}^*L]^{2-}$$

A chain mechanism has been established for the exchange of ligands between the

[289] M. N. Sastri and A. V. Raman, *Z. phys. Chem. (Leipzig)*, 1975, **256**, 993.
[290] S. Wajda and A. Szemik, *Bull. Acad. polon. Sér. Sci. chim.*, 1976, **24**, 111.
[291] E. Mentasti and E. Pelizzetti, *Talanta*, 1975, **22**, 930.
[292] M. Kodama, *Bull. Chem. Soc. Japan*, 1975, **48**, 2813.
[293] J. D. Carr and D. G. Swartzfager, *J. Amer. Chem. Soc.*, 1975, **97**, 315.

$[Cu(edta)]^{2-}$ and $[Zn(trien)]^{2+}$ ions at pH 7.0—10.5. The exchange rate is accelerated by traces of edta or trien, and the chain-propagation steps involve reactions between $[Cu(edta)]^{2-}$ and trien and between $[Zn(trien)]^{2+}$ and edta.[294]

Release of pan [1-(2-pyridylazo)-2-naphthol] from $[Cu(pan)]^{2+}$ by edta has been studied in the presence and absence of phen, and mixed complexes of pan and phen are shown to be involved.[295]

8 Metal Exchange and Displacement

References to kinetic studies of the displacement of a metal cation from its complexes with multidentate ligands are listed in Table 30.

Table 30 *Kinetic studies of the displacement and exchange of cations from largely multidentate ligand complexes*

Complex	*Displacing or arranging cation (conditions)*	*Ref.*
$[Al(edta)]^-$	In^{III} (pH 2—10)	296
$[Al(edta)(tartrate)]^{n-}$		
$[M(edta)]^-$ (M = Ga or In)	Fe^{III} (neutral pH—0.3 mol dm^{-3} H^+)	297
$[Cd(L)]^{3-}$ {L = $HO_2CCH_2N[(CH_2)_2N(CH_2CO_2H)_2]_2$}	H^+ (pH 2—7)	298
$[Pb(L)]^{n-}$ (L = $edta^{4-}$, $hedta^{3-}$, $cydta^{4-}$, or $dtpa^{5-}$)	Y^{III} (pH 2.5—5.6, 293 K, I=0.1, excess Pb^{2+})	299
	In^{III} (pH 1.8—4.8)	300
$[Eu(cydta)]^-$	Cu^{II}, HOAc	301, 302
$[Tm(edta)]^-$	Cu^{II}, HOAc	301, 302
$[Tm(L)]^-$ (L = $edta^{4-}$ or $cydta^{4-}$)	H^+	303
[Ln(methylthymol blue)] (Ln = Sm, Gd, Er, Tm, or La)	H^+	304
$[Ce(L)]^-$ (L = egta, eedta,[a] pdta, or edta)	*Ce^{III} (in presence of OAc^-, NO_3^-, ClO_4^-, or Cl^-)	305
$[Ln(cydta)]^-$	Er^{III} (1—1500 atmospheres)	306

[a] eedta = diamino(ethyl ether)-*NNN'N'*-tetra-acetate ion.

Values of $\Delta V^{\ddagger}$ for the reactions of $[Ln(cydta)]^-$ ions with Er^{3+} ion are in the range -4.7 to -0.6 cm^3 mol^{-1}, which is in line with a rate-determining dechelation of an aminodicarboxylate group.[306]

Dissociation of $[Pb(L)]^{n-}$ ions (L = $edta^{4-}$, $hedta^{3-}$, $cydta^{4-}$, or $dtpa^{5-}$) by In^{III} and Y^{III} proceeds by a dissociative mechanism for L = $cydta^{4-}$, but dinuclear species are involved for the other ligands investigated.[299,300]

Although acetic acid accelerates the rate of dissociation of $[Eu(cydta)]^-$ and $[Tm(edta)]^-$ ions, mixed acetato-complexes are not involved in the reactions.[302]

294 T. Katsuyama and T. Kumai, *Bull. Chem. Soc. Japan*, 1975, **48**, 3581.
295 G. Nakagawa and H. Wada, *Talanta*, 1975, **22**, 563.
296 M. Tsuchimoto, *Bull. Chem. Soc. Japan*, 1975, **48**, 417.
297 R. R. Das, *J. Indian Chem. Soc.*, 1974, **51**, 1024.
298 P. Letkemon and J. B. Westmore, *J.C.S. Dalton*, 1975, 480.
299 T. Nozaki and N. Suemitsu, *Chem. Abs.*, 1976, **84**, 80287.
300 T. Nozaki and N. Suemitsu, *Bull. Chem. Soc. Japan*, 1976, **49**, 445.
301 A. V. Stepanov and A. D. Gedeonov, *Zhur. fiz. Khim.*, 1975, **49**, 1706.
302 A. D. Gedeonov and A. V. Stepanov, *Russ. J. Inorg. Chem.*, 1975, **20**, 1873.

A short review of isotopic metal exchange and ligand exchange reactions has appeared.[41]

9 Isomerization and Racemization

General.—Two reviews dealing with the rearrangement reactions of metal chelates have appeared.[43,44] N.m.r. lineshape analysis plays a dominant role in mechanistic studies of this type, and a permutational analysis has been described for the coalescence behaviour of ^1H n.m.r. spectra in experiments involving complexes of the type *cis*-$[M(LL)_2X_2]$, *cis*-$[M(LL)_2XY]$, and *cis*-$[M(LL')X_2]$.[307]

Cobalt(III) Complexes.—Linkage isomers of thiocyanate ion are well known, and the ions $[Co(NH_3)_5NCS]^{2+}$ and $[Co(CN)_5SCN]^{3-}$, containing *N*-bonded and *S*-bonded thiocyanate ion, are frequently quoted as classic examples of symbiotic bonding in terms of Pearson's concept of hard and soft acids and bases. However, the results of i.r. and electronic spectral studies show that this concept is only valid in protic solvents, since the $[Co(CN)_5SCN]^{3-}$ ion isomerizes to $[Co(CN)_5NCS]^{3-}$ in CH_2Cl_2, Me_2CO, and $PhNO_2$. In DMF solutions an equilibrium is established between the *N*-bonded isomer and the $[Co(CN)_5(DMF)]^{2-}$ ion, and in MeCN or DMSO solvolysis is essentially complete.[308] The importance of hydrogen-bonding in stabilizing the *S*-bonded isomer in protic solvents is emphasized by the results in ethylene glycol where the *S*-bonded isomer prevails, and similar results are reported for the linkage isomers of selenocyanate ion. The size of the counteraction can also influence the stability of the $[Co(CN)_5SCN]^{3-}$ ion in the solid state; *S*-bonding dominates for K^+, Cs^+, and $MeNH_3^+$ salts, a mixture containing 25% of the *N*-bonded isomer is obtained with $Me_2NH_2^+$, and Me_4N^+ and Bu_4N^+ give only the *N*-bonded isomer. Isomerization in CH_2Cl_2, Me_2CO, $PhNO_2$, or DMF proceeds by a dissociative mechanism, possibly involving an ion pair. The rates of dissociation of the four isomers studied vary in the order CoSCN > CoSeCN > CoNCS ~ CoNCSe.

Novel linkage isomers of thiocyanate ion are also reported from studies of the reaction of Hg^{II} with the $[Co(NH_3)_5SCN]^{2+}$ ion. The immediate product is the $[Co(NH_3)_5(SCNHg)]^{4+}$ ion, which undergoes aquation and isomerization to yield the $[Co(NH_3)_5H_2O]^{3+}$ and $[Co(NH_3)_5(NCSHg)]^{4+}$ ions respectively.[55]

Two reports have appeared of the thermal and photochemical reactions of the $[Co(CN)_5(H_2O)]^{2-}$ and $[Co(CN)_4(H_2O)_2]^-$ ions, and their conjugate bases.[105,309] At 275 K and $I=1.0$, the pK_a's of the *cis*- and *trans*-$[Co(CN)_4(H_2O)_2]^-$ ions are 9.5 and 11.7, and 7.7 and 10.4 respectively. The rate of the thermal isomerization was studied at $I=1.0$ under acidic and basic conditions, and the results are summarized in Table 31. Quantum yields for the *cis*→*trans* photoisomerization in acidic solution are in the range 0.25—0.34 (254—405 nm irradiation), and for *trans*→*cis* isomerization are 4×10^{-3} at 546 nm and 4×10^{-2} at 313 nm. In 0.2—0.9 mol dm^{-3}

[303] A. V. Stepanov and T. P. Makarova, *Zhur. neorg. Khim.*, 1974, **19**, 2348.
[304] T. V. Mal'kova and L. V. Krasukhina, *Zhur. neorg. Khim.*, 1975, **20**, 3234; *Russ. J. Inorg Chem.*, 1975, **20**, 1470, 1787.
[305] C. I. Balcombe and B. Wiseall, *J. Inorg. Nuclear Chem.*, 1974, **36**, 881.
[306] E. Brucher and H. Kelm, *J. Coordination Chem.*, 1974, **4**, 133.
[307] D. G. Bickley and N. Serpone, *Inorg. Chem.*, 1976, **15**, 948.
[308] J. B. Melpolder and J. L. Burmeister, *Inorg. Chim. Acta*, 1975, **15**, 91.
[309] L. Viaene, J. D'Olieslager, and S. De Jaegere, *Inorg. Chem.*, 1975, **14**, 2736.

Table 31 *Rate data for the thermal* trans→cis *isomerization of the* $[Co(CN)_4(H_2O)_2]^-$ *ions at* 298.2 K *and* $I = 1.0$ (*data from ref.* 309)

Conditions	$10^4k/s^{-1}$	E_a/kcal mol^{-1}
1 mol dm^{-3} $HClO_4$	10.4	29.3
10^{-3} mol dm^{-3} $HClO_4$ and 1 mol dm^{-3} $NaClO_4$	9.0	
0.2 mol dm^{-3} NaOH and 0.8 mol dm^{-3} $NaClO_4$	4.5	26.9
0.5 mol dm^{-3} NaOH and 0.5 mol dm^{-3} $NaClO_4$	2.1	
0.9 mol dm^{-3} NaOH and 0.1 mol dm^{-3} $NaClO_4$	1.0	

[NaOH], $\Phi = 0.045$ for *cis*→*trans* isomerization at 405 nm. The thermal and photochemical reactions proceed by different mechanisms; an S_N1 mechanism is favoured for the thermal reactions and the photochemical reactions are believed to proceed by a twist mechanism and without metal–ligand bond cleavage.[309]

Concerted base hydrolysis and Bailar inversion of the *Λ-cis*-$[Co(en)_2Cl_2]^+$ ion has been established by a circular dichroism study [equation (18)]. Base hydrolysis of the *Λ-cis*-$[Co(en)_2Cl(OH)]^+$ ion is reported to proceed with complete retention of configuration in contrast to an earlier investigation of this reaction. The results of these studies were considered previously.[215]

Two reports of the rates and activation parameters for the racemization of $[Co(en)_2(amine)(H_2O)]^{3+}$ ions (amine = py or benzylamine[310] or $MeNH_2$, $BuNH_2$, γ-picoline, isoquinoline, imidazole, or benzimidazole[311]) have appeared. A mechanism involving dissociation of the co-ordinated water molecule to give a trigonal-bipyramidal intermediate is believed to be involved. The steric course of the base hydrolysis of $[Co(en)_2(amine)Cl]^{2+}$ ions was considered previously.[212]

Acid hydrolysis of the *cis*-$[Co(en)_2(CN)Cl]^+$ ion gives 100% *cis*-$[Co(en)_2(CN)(H_2O)]^{2+}$, but base hydrolysis gives 90% *cis*- and 10% *trans*-$[Co(en)_2(CN)(OH)]^+$. These results were considered earlier.[67]

High-speed liquid chromatography has been used to separate *cis*- and *trans*-$[Co(en)_2Cl_2]^+$ ions, and by this method the rate of the first-order isomerization process has been measured in methanol solution.[312]

The stereochemical course of the acid and base hydrolysis of $[Co(dien)(tmd)Cl]^{2+}$ and $[Co(dpt)(tmd)Cl]^{2+}$ ions was discussed previously (Tables 6 and 24).

The rate of the heterogenously catalysed racemization of solutions of $(\pm)_{589}$-$[Co(en)_3]^{3+}$ ion on carbon black has been investigated further, and several lines of evidence suggest that the catalysed reaction does *not* proceed *via* a Co^{II} intermediate.[313] Reduction to Co^{II} is, however, responsible in part for the halide-ion-catalysed rates of racemization of the $[Co(phen)_3]^{3+}$ ion.[314] Chloride ion brings about racemization completely by reduction, whereas bromide and iodide ions are only partly effective. The rate of the photocatalysed reaction was also investigated.

The reported *cis–trans* isomerization of the $[Co(phen)(OH)(OH_2)]^{2+}$ ion[315] is surprising since there are no authenticated examples of complex ions of the type

[310] I. J. Kindred and D. A. House, *J. Inorg. Nuclear Chem.*, 1975, **37**, 589.
[311] I. J. Kindred and D. A. House, *Inorg. Chim. Acta*, 1975, **14**, 185.
[312] Y. Yoshikawa, M. Kojima, M. Fujita, M. Iida, and H. Yamatera, *Chem. Letters*, 1974, *1163*
[313] P. D. Totterdell and M. Spiro, *J.C.S. Faraday I*, 1976, **72**, 1477.
[314] R. J. Mureinik, *Inorg. Nuclear Chem. Letters*, 1976, **12**, 319; M. Yamamoto and Y. Yamamoto, *Inorg. Nuclear Chem. Letters*, 1975, **11**, 691.
[315] R. F. Bogucki, G. McLendon, and A. E. Martell, *J. Amer. Chem. Soc.*, 1976, **98**, 3202.

trans-$[Co(AA)(X)(Y)]^{n+}$ (AA = bipy or phen), owing to non-bonded interactions between hydrogen atoms in the 2- and 9-positions of the two phen rings, or the 2- and 2′-positions of the two bipy rings, in the *trans*- but not the *cis*-complexes. These complexes are reported to be formed as follows:

$$[Co(phen)_2]^{2+} + O_2 \overset{H_2O}{\rightleftharpoons} [\{(phen)_2Co\}_2(O_2)OH] + H^+$$

$$[(phen)_2Co](O_2)OH \longrightarrow 2cis\text{-}[Co(phen)_2(OH)(OH_2)]^{2+} + H^+ + \text{peroxo-product}$$

$$cis\text{-}[Co(phen)_2(OH)(OH_2)]^{2+} \rightleftharpoons trans\text{-}[Co(phen)_2(OH)(OH_2)]^{2+}$$
(yellow) (red)

For the $[Co(bipy)_2]^{2+}$ ion, it was possible to separate the oxygenation and olation reactions so that the effect of dibridging upon the oxygenation could be investigated. The rate of conversion of the oxygenated species into the oxidized form was also measured.

Volumes of activation of +14.7 and +20.0 ml mol^{-1} have been reported from high-pressure studies of the rates of isomerization of β-$[Co(edda)(AA)]^+$ ions (AA = tmd and en respectively) to the α-isomers under basic conditions (0.2 mol dm^{-3} Na_2CO_3–$NaHCO_3$). An S_N1cb mechanism is favoured.[316]

The rates of racemization of diaquo-, hydroxoaquo-, and dihydroxo-complex ions of the type $[Co(3,2,3\text{-tet})X_2]^{n+}$ have been reported [3,2,3-tet = $NH_2(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$].[317]

For the *cis*→*trans* isomerization of the $[Co(dmgH)_2(H_2O)_2]^+$ ions between pH 2 and 4, the value of $\Delta H^{\ddagger}$ is 92 kJ mol^{-1}.[318]

Chromium(III) Complexes.—Rate parameters are reported for the racemization of the $(+)_{589}$-$[Cr(phen)_3]^{3+}$ ion in the presence of H^+, OH^-, or other anions (*e.g.* Cl^-, Br^-, I^-, ClO_4^-, and NO_3^-).[319] In aqueous solution at 348.2 K, $10^5k = 8.5$ s^{-1} and the activation parameters are $\Delta H^{\ddagger} = 23.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = -10.9$ cal K^{-1} mol^{-1}. An intramolecular twist mechanism is proposed.

Two reports of the *cis–trans* isomerization reactions of the $[Cr(ox)_2(H_2O)_2]^-$ ion have appeared.[238,239] At 298 K the equilibrium constant is given by [*trans*]/[*cis*] = 0.10. Formation of the $[Cr(ox)_3]^{3-}$ ion by anation of *trans*-$[Cr(ox)_2(H_2O)_2]^-$ in acidic solution involves a rapid prior isomerization to the *cis*-$[Cr(ox)_2(H_2O)_2]^-$ ion. These results were considered previously [reactions (20)—(22)].[238]

Rate data for the racemization of $[Cr(LL)_2(ox)]^+$ ions (LL = bipy or phen), and for the *trans*→*cis* isomerization reactions of $[Cr(en)_2(L)X]^{n+}$ ions (L = DMF or DMSO, X = halide ion; or L = X = DMF) were also discussed previously (Tables 14 and 19).

Intramolecular Rearrangement of Tris-chelate Complexes.—Co^{III} and Cr^{III} complexes were considered in the two previous sections and will not be discussed further in this section. A review deals with reactions in this category.[44]

$[Al(acac)_3]$ has been resolved by chromatography at 210 K. The rate of racemiza-

[316] Y. Kitamura, *Bull. Chem. Soc. Japan*, 1976, **49**, 1002.
[317] B. Bosnich, J. MacB. Harrowfield, and H. Boucher, *Inorg. Chem.*, 1975, **14**, 815, 836, **853**.
[318] T. B. Konunova and N. M. Samus, *Zhur. neorg. Khim.*, 1975, **20**, 706.
[319] N. A. P. Kane-Maguire and S. A. Edwards, *J. Inorg. Nuclear Chem.*, 1976, **38**, 1037.

tion was measured at 272 K in a mixture of isopentane and ether, and is characterized by a rate constant of 1.87×10^{-4} s^{-1}. The activation parameters are $\Delta H^{\ddagger} = 130 \pm 5$ kJ mol^{-1} and $\Delta S^{\ddagger} = 220 \pm 16$ J K^{-1} mol^{-1}, and a mechanism involving metal–ligand bond rupture is proposed.[320]

Two studies deal with the effect of varying the solvent upon the rate of racemization of the $[Fe(phen)_3]^{2+}$ ion[191] and the $[Ni(phen)_3]^{2+}$ ion.[321] The rates of racemization of the iodide and perchlorate salts of the $[Ni(phen)_3]^{2+}$ ion increase with the solvent in the order MeCN < H_2O < DMF < DMSO. Racemization also occurs in CH_2Cl_2 which contains H_2O, but not in anhydrous CH_2Cl_2.[321] The $[Fe(phen)_3]^{2+}$ ion racemizes by an intramolecular mechanism which does not involve metal–ligand bond cleavage. Solvent variation affects the rate of racemization because of changes in the solvation of the aromatic ligands in the transition state, and also because of viscous resistance to the solvent reorganization which occurs in the vicinity of the complex ion when it undergoes inversion.[191] The rate constant for racemization of the $[Fe(phen)_3]^{2+}$ ion (k) varies with the solvent viscosity (η) and the molar volume of the solvent (V_m) according to the equation

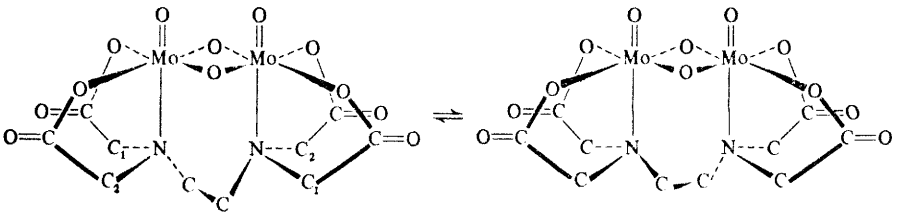
$$\log k = \text{constant} - (0.26\Delta G_L/2.303RT) - 0.48 \log (\eta/V_m)$$

where ΔG_L is the free energy of solvation of the phen ligand.

Miscellaneous.—A twisting rather than a bond-rupture mechanism has been established by n.m.r. line-broadening studies for the racemization of Ti^{IV} complexes of the type $[Ti(AA)(BB)_2]$ [BB = acac$^-$ or 3-acetylpentane-2,4-dionate ion; AA = $Me_2C(O^-)(CH_2)_nC(O^-)Me_2$, $n = 0$ or 1].[322]

N.m.r. has also been used to measure the rate of ring inversion in substituted derivatives of 1,2-diaminoethane (*e.g.* Me_4en) when co-ordinated to $[Pr(^2H_9\text{-fod})_3]$ [$^2H_9$-fod = $(CD_3)_3C(O^-)CHCOC_3F_7$].[323] For the complex with Me_4en, $\Delta G^{\ddagger} = 42.2$ kJ mol^{-1} at 235 K, which is much larger than the 'normally' expected value of *ca.* 20 kJ mol^{-1}.

^{13}C N.m.r. has been used to measure the conformational dynamics of dioxodi-μ-oxo-aminocarboxylatomolybdate(v) complexes of the type $[MoO_2]_2L$ (L = edta, pdta, or cydta).[324] The complexes with pdta and cydta are rigid on the n.m.r. timescale, but the isomeric equilibrium (46) which involves inversion at nitrogen is



(46)

[320] B. Nordan and I. Jonas, *J. Inorg. Nuclear Chem.*, 1976, **12**, 33.
[321] T. Fujiwara and Y. Yamamoto, *Inorg. Nuclear Chem. Letters*, 1975, **11**, 635.
[322] N. Baggett, D. S. P. Poolton, and W. B. Jennings, *J.C.S. Chem. Comm.*, 1975, 239.
[323] D. F. Evans and G. C. de Villardi, *J.C.S. Chem. Comm.*, 1976, 7.
[324] G. L. Blackmer, K. J. Johnson, and R. L. Roberts, *Inorg. Chem.*, 1976, **15**, 596.

characterized by $\Delta H^{\ddagger}(2/\tau) = 13 \pm 2$ kcal mol^{-1} and $\Delta S^{\ddagger}(2/\tau) = 0.2 \pm 0.04$ cal K^{-1} mol^{-1}.

10 Co-ordination Numbers Greater than Six

No reports of studies of metal ions with high co-ordination numbers have appeared apart from the lanthanide exchange reactions noted in Sections 7 and 8.

4
Labile Metal Complexes

BY D. N. HAGUE

1 Complex Formation involving Unsubstituted Metal Ions: Unidentate Ligands and Solvent Exchange

Univalent Ions.—The rate constant for the formation of the 1:1 thallium(I) tri-iodide complex in aqueous perchloric acid (10^{-2} mol l^{-1}) has been measured[1] over the temperature range 5—45 °C using the stopped-flow technique. The reaction is first-order in both ions when Tl^+ is kept in large excess over I_3^- (a ratio of at least 200:1) but the formation of higher complexes complicates the kinetic interpretation when the ion concentration ratio is reversed. Under pseudo-first-order conditions, the resultant second-order rate constant is 1.75×10^4 l mol^{-1} s^{-1} at 25 °C. This is comparatively low for substitution at a univalent ion and, as the authors point out, suggests that the rate-determining step is ligand-dependent. The activation parameters ($\Delta H^{\ddagger} = 7.24$ kcal mol^{-1} and $\Delta S^{\ddagger} = -14.8$ cal K^{-1} mol^{-1}) are also unusual for substitution at a univalent metal ion and it is suggested that the formation of the activated complex is accompanied by a drastic reorganization of the solvent around the Tl^I centre.

Bivalent Ions.—The complexation kinetics of Mg^{II} with CO_3^{2-} and HCO_3^- have been studied[2] in methanol and water by means of the stopped-flow and temperature-jump methods. The rate constants for CO_3^{2-} (6.8×10^5 and 1.5×10^6 l mol^{-1} s^{-1}, respectively) and for HCO_3^- (5.0×10^5 l mol^{-1} s^{-1} in both solvents) are analysed in terms of a dissociative mechanism.

Langford *et al.* conclude,[3] after a perusal of the literature concerning the kinetics of solvent exchange at Ni^{II}, that the process is remarkably insensitive to the nature of the bulk solvent. This implies, they suggest, that the correlations between complex formation kinetics and solvent properties (introduced by Bennetto and Caldin) provide a means of studying the solvent dependence of the encounter equilibria between a Ni^{II} complex and a ligand. The linear relationship between enthalpies and entropies of activation for reactions at Ni^{II} in different media is attributed to changes in the ligands bound to the metal but not undergoing substitution. Coetzee and Hsu, although agreeing that it is, in principle, preferable to base mechanistic conclusions on a detailed consideration of activation parameters rather than on rates at a single temperature, point out[4] that uncertainties in some or all of these data frequently lead to more rather than less confusion. Rate constants and activation parameters for the

[1] N. Purdie, M. M. Farrow, M. Steggall, and E. M. Eyring, *J. Amer. Chem. Soc.*, 1975, **97**, 1078.
[2] R. C. Patel, F. Garland, and G. Atkinson, *J. Solution Chem.*, 1975, **4**, 161.
[3] C. H. Langford, J. P. K. Tong, and A. Merbach, *Canad. J. Chem.*, 1975, **53**, 702.
[4] J. F. Coetzee and E. Hsu, *J. Solution Chem.*, 1975, **4**, 45.

formation and dissociation of the mono-complex of Ni^{II} with SCN^- in DMSO are consistent with an I_d mechanism, while a *D*-pathway cannot conclusively be ruled out ($k_f = 3.9 \times 10^4$ l mol^{-1} s^{-1}, $\Delta H_f^{\ddagger} = 7.8$ kcal mol^{-1}, $\Delta S_f^{\ddagger} = -10$ cal K^{-1} mol^{-1}; $k_d = 101$ s^{-1}, $\Delta H_d^{\ddagger} = 16.6$ kcal mol^{-1}, $\Delta S_d^{\ddagger} = +6$ cal K^{-1} mol^{-1}).

The spin–lattice relaxation time T_1 has been used[5] to measure the exchange rate of water molecules between the inner hydration sphere of Ni^{2+} ions and the bulk in concentrated solutions of $Ni(NO_3)_2$. (Previous n.m.r. methods have involved the determination of the spin–spin relaxation time, T_2.) An activation energy of 10.5 ± 1.0 kcal mol^{-1} is reported and the results indicate the existence of an inner-sphere nitrate complex with a stability constant of about 0.2 l mol^{-1}.

In the first of three reports on the kinetics of the Ni^{2+}–acetate reaction to appear during the review period, Fuentes, Morgan, and Matwiyoff have analysed[6] temperature-dependent [1-^{13}C]acetate line-broadening and chemical shift data. The results were considered in the framework of a two-term rate expression, $\tau_M^{-1} = k_{-1} + k_2 m_{Ac}$, where m_{Ac} is the acetate concentration and k_{-1} and k_2 are defined by

$$[Ni(H_2O)_6]^{2+} + Ac^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Ni(H_2O)_5Ac]^+ + H_2O$$

$$[Ni(H_2O)_5Ac]^+ + Ac^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Ni(H_2O)_xAc_2] + (5-x)H_2O$$

The rate constants at 300 K, $k_{-1} = (3.9 \pm 0.3) \times 10^3$ s^{-1} and $k_2 = (2.1 \pm 0.4) \times 10^4$ l mol^{-1} s^{-1}, and the activation enthalpies, $\Delta H_{-1}^{\ddagger} = 13.4 \pm 0.6$ kcal mol^{-1} and $\Delta H_2^{\ddagger} = 12.5 \pm 0.5$ kcal mol^{-1}, are consistent with acetate exchange controlled by loss of acetate and water, respectively, from $[Ni(H_2O)_5Ac]^+$. In the latter case, loss of water is followed by acetate entry and subsequent rapid dissociation of the diacetate species. As was to be expected, no dependence of either dissociation rate constant upon ionic strength was observed (in the range 1—4 mol l^{-1} and from 0 to 14 °C).

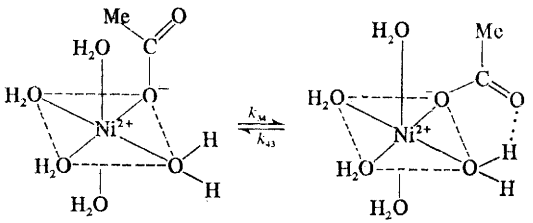
Yasunaga and co-workers found[7] that aqueous solutions of nickel acetate exhibit two ultrasonic absorption maxima, one in the kHz and the other in the MHz frequency range. They studied the relaxation phenomenon in the kHz range [which they interpreted in terms of an I_d (mono)complex-formation mechanism] in greater detail by means of the laser temperature-jump technique and were able to obtain rate constants and activation parameters. The rate-determining step in complex formation is, as usual, the loss of water from the inner co-ordination sphere of the metal (k_{23}), and the dissociation rate constants k_{32} (and stability constants K_{23}) for the monocarboxylate complexes of Ni^{2+} with acetate, propionate, butyrate, and β-chloropropionate are closely related to the acid dissociation constants of the protonated ligands (Table 1). The relaxation phenomenon in the MHz range was studied (by sound absorption) as a function of the concentrations of the metal and ligand and of the pH, temperature, and the nature of the solvent. The authors attribute this absorption to an intramolecular conversion of the nickel monocarboxylate complex, (1)$\rightleftharpoons$(2). On the assumption that $k_{34} \ll k_{43}$, it is estimated that $\Delta H_{43}^{\ddagger}$ is *ca.* 4 kcal mol^{-1}, a reasonable value for the rupture of a hydrogen bond. As

[5] H. Strehlow and J. Frahm, *Ber. Bunsengesellschaft phys. Chem.*, 1975, **79**, 57.
[6] R. Fuentes, L. O. Morgan, and N. A. Matwiyoff, *Inorg. Chem.*, 1975, **14**, 2774.
[7] S. Harada, T. Yasunaga, K. Tamura, and N. Tatsumoto, *J. Phys. Chem.*, 1976, **80**, 313.

Table 1 *Rate and equilibrium constants*[a] *for nickel carboxylate reactions*

Ligand	$10^{-4}k_{23}/s^{-1}$	$10^{-3}k_{32}/s^{-1}$	K/l mol^{-1}	$10^{-7}k_{43}/s^{-1}$	pK_a of acid
Acetate	2.7	5.0	34	6.0	4.76
Propionate	2.4	5.5	30	4.7	4.88
Butyrate	2.4	4.5	35	4.1	4.82
Acrylate	—	—	—	6.3	4.26
Chloroacetate	—	—	—	8.8	4.08
β-Chloropropionate	2.6	7.5	24	23	2.81

[a] Data, from ref. 7, refer to 25 °C and $I \rightarrow 0$ (I = 2 mol l^{-1} for k_{43}). See text for assignments of k_{23}, k_{32}, and k_{43}.



(1) (2)

shown in Table 1, the authors found that log k_{43} was inversely proportional to the pK_a for a series of carboxylate ligands.

The two ultrasonic absorption maxima found with aqueous solutions of nickel acetate have also been studied[8] by Bonsen *et al.* The slower of the two relaxation effects (attributed by them also to the formation of the mono-complex $NiAc^+$) was investigated further by the pressure-jump technique, and the rate constant and activation parameters for the rate-determining step are reported. The values for k_{23} at 25 °C (1.5×10^4 s^{-1}) and $\Delta H_{23}^{\ddagger}$ (12.9 ± 1.5 kcal mol^{-1}) compare quite well with those of Yasunaga and co-workers[7] (who obtained 2.7×10^4 s^{-1} and 12 kcal mol^{-1}, respectively), but the two groups differ in their assignments of the faster of the two relaxation effects. Whereas Yasunaga and co-workers invoke a conformational change of the monoacetate complex, Bonsen *et al.* favour the formation of the bis-complex, $NiAc_2$:

$$NiAc^+ + Ac^- \underset{k_{II}'}{\overset{k_{II}}{\rightleftharpoons}} NiAc_2$$

These authors base their assignment on the observations, first, that the relaxation time is independent of concentration and, secondly, that a change in the concentration of Ac^- influences the relaxation amplitude much more than does a change in the concentration of Ni^{2+} (indicating that this reaction 'involves more Ac^- than Ni^{2+}'). On this basis, the values of the rate constants at 10 °C are $k_{II} = (3.2 \pm 1.6) \times 10^7$ l mol^{-1} s^{-1} and $k_{II}' = (3.2 \pm 0.4) \times 10^7$ s^{-1}. Clearly, if this interpretation is the correct one, we must somehow find a way of rationalizing the apparent discrepancy between these results and those of Fuentes *et al.*[6]

[8] A. Bonsen, F. Eggers, and W. Knoche, *Inorg. Chem.*, 1976, **15**, 1212.

Metals of Valency Three and Higher.—There have been several reports of the measurement by n.m.r. of the kinetic characteristics of complexes of Group IIIA tervalent metal ions. Delpuech *et al.* have used[9] the spectra associated with the ^{27}Al and ^{31}P nuclei to identify the species present in solutions of the metal and a number of phosphorus-containing ligands, and to measure their exchange characteristics. It appears that the major solvates of Al^{3+} in trimethyl (TMPA) and triethyl phosphates (TEPA), dimethyl methyl- (DMMP) and diethyl ethyl-phosphonates (DEEP), and dimethyl hydrogen phosphite (DMHP) are octahedral. In each case the rate law for the exchange process,

$$[AlA_6]^{3+} + A^* \rightleftharpoons [AlA_5A^*]^{3+}$$

is zero-order in free ligand, suggesting a dissociative mechanism. Values of the rate constants (at 25 °C) and activation parameters are given in Table 2, together with

Table 2 *Kinetic parameters*[9] *for ligand substitution in aluminium solvates*

Ligand	k_{ex} (25 °C)/s^{-1}	$\Delta H_{ex}^{\ddagger}$/kcal mol^{-1}	$\Delta S_{ex}^{\ddagger}$/cal K^{-1} mol^{-1}
TMPA	0.38	23.5	18.2
DMMP	5.1	19.0	7.9
DMHP	1.33	19.8	6.9
HMPA	4.8×10^3[a]	7.7	−10.2
H_2O	0.16	27	28
DMSO	0.6	20	3.7
DMF	0.15	17.7	4.7

[a] Units are 1 mol^{-1} s^{-1}.

those for H_2O, DMSO, and DMF for comparison. Also quoted are the values for hexamethylphosphorotriamide (HMPA), where the spectra indicate that the major solvate is the tetrahedral $[Al(HMPA)_4]^{3+}$. Here, the rate law for the exchange process is first-order in free ligand – indicative of an associative process – and the kinetic parameters are markedly different from the rest. Clearly, this is an important result and, as the authors point out, the use of HMPA and similar solvents would be expected to change many aspects of the solution chemistry and electrochemistry of this element.

Richardson and Alger have measured[10] the solvation number and exchange rate for a number of Al^{III} and Ga^{III} salts in ethanol and methanol, using the OH proton signal from the free and bound alcohol. They obtain solvation numbers ranging from 4 to 7 but point out that the situation is sometimes complicated by the intrusion of the anion (chloride or nitrate) into the inner co-ordination sphere of the metal. They do conclude, however, that in all of the cases they studied the solvent-exchange process is S_N2.

In solutions of indium(III) and thallium(III) chloride in concentrated hydrochloric acid it appears that the major species are, respectively, $[InCl_4(H_2O)_2]^-$ and $[TlCl_6]^{3-}$ (or possibly $[TlCl_5]^{2-}$). Lincoln *et al.* have used[11] the ^{35}Cl resonance to study the

[9] J. J. Delpuech, M. R. Khaddar, A. A. Peguy, and P. R. Rubini, *J. Amer. Chem. Soc.*, 1975, **97**, 3373.
[10] D. Richardson and T. D. Alger, *J. Phys. Chem.*, 1975, **79**, 1733.
[11] S. F. Lincoln, A. C. Sandercock, and D. R. Stranks, *Austral. J. Chem.*, 1975, **28**, 1901.

kinetics of Cl^- exchange on these species and have compared their results with those of an earlier study[12] with gallium(III) chloride (where the predominant species is $[GaCl_4]^-$). Unfortunately, because of the difference in stoicheiometry in the three cases, it is not possible to use the simple electrostatic model to explain why the exchange lability increases in parallel with the ionic radius, $Ga^{3+} < In^{3+} < Tl^{3+}$.

The rate constants for the formation of $FeCl^{2+}$ from Fe^{III} and Cl^- have been measured[13] as a function of solvent composition in water–methanol mixtures. As with most complexation reactions of iron(III), the apparent rate constant k_{obs} is dependent on pH, indicating the existence of two parallel pathways (Scheme 1). Both

$$\begin{array}{ccc} Fe^{3+} + Cl^- & \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} & FeCl^{2+} \\ H^+ \uparrow\downarrow -H^+ & & H^+ \uparrow\downarrow -H^+ \\ Fe(OH)^{2+} + Cl^- & \underset{k_H'}{\overset{k_H}{\rightleftharpoons}} & Fe(OH)Cl^+ \end{array}$$

Scheme 1

k_1 and k_H increase with the mole fraction of methanol in the mixture x_m (Table 3), as is to be expected for reactions involving oppositely charged species, and the authors

Table 3 *Kinetic parameters*[13] *for formation of* $FeCl^{2+}$ *in water–methanol mixtures*

Mole fraction of MeOH	10^2D^{-1}	k_1(25 °C)/l mol^{-1} s^{-1}	k_1'(25 °C)/s^{-1}	$10^{-4}k_H$(25 °C)/l mol^{-1} s^{-1}
0	1.26	7	2	1.2
0.15	1.46	9	0.4	2.6
0.20	1.54	2	0.05	2.8
0.25	1.64	6	0.1	2.8
0.395	1.92	21	0.2	6.3
0.443	2.02	30	0.2	7.6
0.519	2.14	30	0.3	10.0

are able to show, from a calculation of the distance of closest approach of the charge centres, that the data for k_H are consistent with an activated complex containing the group $[OH^-—Fe^{3+}—H_2O—Cl^-]$. Moreover, it seems that the possible replacement of H_2O in the inner co-ordination sphere of the metal by methanol at high x_m has no effect on the kinetics of complex formation. (The data on k_1 are, unfortunately, insufficiently accurate to justify the corresponding calculation on k_1, so the authors are unable to comment on the activated complex for the low-pH pathway.) The same reaction has been studied[14] with a high-pressure laser-temperature-jump apparatus and an intriguing difference has been found between the two pathways. The volume of activation $\Delta V^{\neq}$ for the binding of Cl^- to $FeOH^{2+}$ is positive (7.8 ± 1.0 cm^3 mol^{-1}), which is consistent with a dissociative-interchange mechanism, whereas that for the binding of Cl^- to Fe^{3+} is negative (-4.5 ± 1.1 cm^3 mol^{-1}). The latter value is not

[12] S. F. Lincoln, A. C. Sandercock, and D. R. Stranks, *J.C.S. Dalton*, 1975, 669.
[13] G. Wada and Y. Kobayashi, *Bull. Chem. Soc. Japan*, 1975, **48**, 2451.
[14] B. B. Hasinoff, *Canad. J. Chem.*, 1976, **54**, 1820.

consistent with stretching of the metal ion–water bond to form the transition state in a dissociative mechanism and it is argued, by analogy with results which have been obtained in organic reactions, that the mechanism is an associative interchange in which the ligand in the outer sphere enters the inner sphere before the water leaves. The reason for the change in mechanism on going from $FeOH^{2+}$ to Fe^{3+} may well be that the higher charge density of Fe^{3+} raises the energy required to dissociate the metal cation–water bond; hence, the dissociative mechanism becomes energetically less favoured than the associative, in which the energy barrier is lowered through the formation of the new Fe^{3+}—Cl^- bond. A similar sort of difference has been observed[15] for the formation of the iron(III) thiocyanate complex: $\Delta V^{\ddagger}$ for the $FeOH^{2+}$ pathway is $+7.4$ cm^3 mol^{-1} at 25 °C and for the Fe^{3+} pathway *ca.* 0 cm^3 mol^{-1}. It will be particularly interesting to see how general this pattern is.

Measurements of the ultrasonic absorption of aqueous samarium(III) sulphate have been repeated[16] and the data analysed in terms of the usual two-step mechanism (diffusion, followed by water loss at the metal ion).

In a preliminary note, the kinetics of alcohol exchange with trialkyl arsenates and vanadates are reported,[17]

$$(R^1O)_3MO + R^2OH \rightleftharpoons (R^1O)_2(R^2O)MO + R^1OH$$

where M is As^V or V^V and R is an alkyl group. The lifetimes of the α-protons in the alcohol environment τ_A, together with the activation parameters, are shown in Table 4. A transition state involving little bond-breaking is indicated, but the substantial loss of entropy accompanying its formation suggests an associative exchange process. $\Delta H^{\ddagger}$ increases with the size of the alkyl group, while $\Delta S^{\ddagger}$ becomes less negative; thus, as the steric requirements become more stringent, the reaction mechanism apparently changes towards a displacement process with a greater degree of bond-breaking in the transition state.

Table 4 *Kinetic parameters*[17] *for* $[VO(OR)_3]$

R	τ_A(25 °C)/s	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
Pr^n	0.062	21.4±1.2	−150±9
Bu^n	0.057	22.4±0.9	−146±3
n-C_5H_{11}	0.110	26.4±1.5	−138±8
Pr^i	0.97	32.7±3.0	−129±9

2 Complex Formation involving Unsubstituted Metal Ions: Multidentate Ligands

Univalent Ions.—The technique of pulse radiolysis has been used[18] to measure the kinetics of the formation of the Cu^+ complexes (3) of maleic and fumaric acids.

$$Cu^+_{aq} + \textit{cis}\text{- or }\textit{trans}\text{-}HO_2CCH{=}CHCO_2H \underset{k_{-8}}{\overset{k_8}{\rightleftharpoons}} \left[\begin{array}{c} HO_2CCH{=}CHCO_2H \\ | \\ Cu \end{array}\right]^+$$

(3)

[15] A. Jost, *Ber. Bunsengesellschaft phys. Chem.*, 1976, **80**, 316.
[16] M. M. Farrow, N. Purdie, and E. M. Eyring, *J. Phys. Chem.*, 1975, **79**, 1995.
[17] P. J. White, M. J. Kaus, J. O. Edwards, and P. H. Rieger, *J.C.S. Chem. Comm.*, 1976, 429.
[18] D. Meyerstein, *Inorg. Chem.*, 1975, **14**, 1716.

Thus, at 22±2 °C and I = 0.04 mol l^{-1}, the values of k_8 and k_{-8} are, respectively, $(2.0 \pm 0.4 \times 10^9)$ l mol^{-1} s^{-1} and $(1.8 \pm 0.4) \times 10^5$ s^{-1} for maleic acid and $(1.7 \pm 0.4) \times 10^9$ l mol^{-1} s^{-1} and $(2.4 \pm 0.4) \times 10^5$ s^{-1} for fumaric acid.

Bivalent Ions.—*Manganese.* ^{31}P N.m.r. studies on the Mn^{II}–adenosine 5′-triphosphate system indicate[19] the existence of two parallel pathways for the exchange mechanism. These are, respectively, a dissociation–association process involving the free ligand and metal as intermediates (*viz.* the 'normal' mechanism for complex formation at labile metal ions),

$$M(aq) + L(aq) \underset{k_{-os}}{\overset{k_{os}}{\rightleftharpoons}} M(aq)L \underset{k_{-0}}{\overset{k_0}{\rightleftharpoons}} ML$$

and a direct ligand-exchange process

$$ML^1 + L^2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} ML^2 + L^1$$

The authors point out that the respective contributions of these two pathways to the observed n.m.r. linewidths and hence to the n.m.r. exchange rate depend on the concentration of the ligand ATP, and they conclude that the kinetic parameters evaluated on this basis compare favourably with those obtained from other kinetic techniques, such as temperature-jump.

Buck and Moore have extended[20] their low-temperature stopped-flow studies on the formation and dissociation of complexes of Mn^{2+} to bipyridyl-type ligands in DMSO. The rate constants for bipy are log k_f = 3.89 and log k_d [mercury(II)-induced dissociation] = 1.26 at 291.7 K.

Cobalt. The kinetics of formation and dissociation of the five-co-ordinate complex of Co^{2+} with 1,5-diazacyclo-octane-*NN′*-diacetic acid (H_2dacoda) have been studied[21] by the stopped-flow method. Formation of this square-pyramidal complex follows the rate law Rate = $k_f[Co^{2+}][Hdacoda^-]/[H^+]$, which can be interpreted as a bimolecular reaction either between Co^{2+} and $dacoda^{2-}$ or between $CoOH^+$ and $Hdacoda^-$. The second-order rate constant calculated on the basis of the former process (4.1×10^8 l mol^{-1} s^{-1}) is considerably higher than that expected from the known water-exchange rate constant and could only be explained by a large internal conjugate base (ICB) effect. In the limiting case, however, this is equivalent to the latter possibility, for which the rate constant 8.6×10^5 l mol^{-1} s^{-1} was calculated. The dissociation rate is given by Rate = $(k^{ML} + k_H^{ML}[H^+])[Co(dacoda)]$, where k^{ML} = 0.33 s^{-1} and k_H^{ML} = 640 l mol^{-1} s^{-1} (at 25 °C and I = 0.5 mol l^{-1}).

Nickel. The kinetics have been reported[22] for the reaction of Ni_{aq}^{2+} with the unprotonated and monoprotonated forms of dimethyl- and di-n-butyl-malonic acids (see Table 5). For the dimethyl derivative the results are similar to those previously found for some monosubstituted malonic acids except that the chelate-ring-opening rate is enhanced as a consequence of the increased steric hindrance between the two methyl groups. However, ring-opening is faster with dimethylmalonate (k = 1.5×

[19] G. P. P. Kuntz, Y. Lam, and G. Kotowycz, *Canad. J. Chem.*, 1975, **53**, 926.
[20] D. M. W. Buck and P. Moore, *J.C.S. Dalton*, 1976, 638.
[21] C. Chatterjee and T. A. Kaden, *Helv. Chim. Acta*, 1975, **58**, 1881.
[22] G. Calvaruso, F. P. Cavasino, and E. Di Dio, *J. Phys. Chem.*, 1976, **80**, 239.

10^4 s^{-1}) than with the di-n-butyl derivative (3.5×10^3 s^{-1}) in spite of the presence in the latter of the bulkier groups; evidently the incremental steric effect is outweighed by the greater basicity of di-n-butylmalonate.

Table 5 *Rate constants for complex formation between nickel*(II) *and bi- and ter-dentate ligands*

Ligand	*Rate constant*/ l mol^{-1} s^{-1}	*Temperature*/ °C	*Solvent*	*Ionic strength*/ mol l^{-1}	*Ref.*
$[O_2CCMe_2CO_2]^{2-}$	1.3×10^5	25	w[a]	0.10	22
$HO_2CCMe_2CO_2^-$	7.0×10^3	25	w	0.10	22
$[O_2CCBu^n{}_2CO_2]^{2-}$	1.4×10^5	25	w	0.10	22
$HO_2CCBu^n{}_2CO_2^-$	2.0×10^2	25	w	0.10	22
Picolinic acid (^-O—$\overset{+}{N}H$)	4.2×10^3	25	w	0.50	23
Picolinic acid (^-O—N)	3.6×10^4	25	w	0.50	23
Fusaric acid (^-O—$\overset{+}{N}H$)	8.1×10^3	25	w	0.50	23
Fusaric acid (^-O—N)	3.9×10^4	25	w	0.50	23
(4) (H_2L^+)	1.44×10^3	10	w	0.4	26
(4) (HL)	3.36×10^2	10	w	0.4	26
(5) (H_2L^+)	7.7×10^3	10	w	0.4	26
(5) (HL)	97	10	w	0.4	26
Hypoxanthine (H_2L)	1.9×10^3	10	w	0.4	26
Inosine (H_2L)	1.1×10^3	10	w	0.4	26
(6)	3.80×10^3	25	DMSO[b]	*c*	29
(6)	4.00×10^5	25	DMSO–$MeNO_2$[d, b]	*c*	29
pada	1.70×10^4	25.0	MeCN	*c*	30
pada	1.86×10^3	25.0	MeOH	*c*	30
pada	1.15×10^3	25.0	DMF	*c*	30
pada	1.01×10^3	25.0	D_2O	*c*	30
pada	$4.4_3 \times 10^3$	25.0	EtOH	*c*	30
pada	$20._5$	25.0	ETGLY[e]	*c*	30
pada	$5.1_3 \times 10^3$	25.0	DMMP	*c*	30
pada	7.4×10^2	25.0	DMSO	*c*	30
H_{-1} (8)	1.4×10^5	25	$MeNO_2$[f]	0.10	32

[a] w = water. [b] Rate constants also quoted at seven intermediate solvent compositions. [c] Not specified. [d] Mole fractions DMSO–$MeNO_2$ = 0.11—0.89. [e] ETGLY = ethylene glycol. [f] +0.0125 mol l^{-1} pyridine.

The pH dependence of the rates of complex formation between Ni^{2+} and picolinic acid (pyridine-2-carboxylic acid) and fusaric acid (5-butylpicolinic acid) are not linear functions of $[H^+]^{-1}$, but can be accounted for[23] by a reaction scheme in which initial complexing occurs at the carboxylate group and chelate ring closure (k_{35}) is an important kinetic factor (Scheme 2). If the rate law is expressed in the form

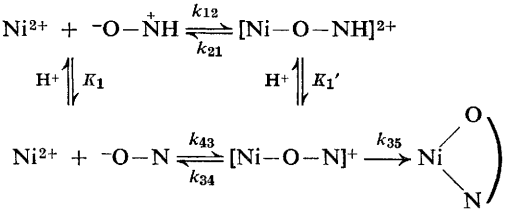
$$-d[Ni^{2+}]/dt = k_{obs}[Ni][\text{total ligand}]$$

then the relationship between k_{obs} and the individual rate constants is

$$\frac{k_{obs}(K_1 + [H^+])}{[H^+]} = \frac{(k_{12} + k_{43}K_1[H^+]^{-1})k_{35}K_1'}{k_{21}[H^+] + K_1'[k_{34} + k_{35}]}$$

The authors are able to show that the same scheme holds for the reaction of Ni^{2+} with various simple amino-acids but point out that it is necessary, for a complete

[23] R. H. Voss and R. B. Jordan, *J. Amer. Chem. Soc.*, 1976, **98**, 2173.



Scheme 2

analysis, to use the microacid dissociation constants in the calculations rather than the macroconstants, which have been employed by several authors. If this is done, the observed rate differences between the various ligands can be rationalized on the basis of a steric effect of α-substituents on the dissociation of the initially formed carboxylate complex.

The whole question of the correct analysis of kinetic data relating to the reaction of nickel(II) with amino-acids (and, indeed, other bifunctional ligands) has been carefully discussed[24] in an earlier paper by Jordan and co-workers. They report their own measurements on the reactions with cysteine, tyrosine, and seven related ligands over the pH range 6—7 and suggest that in five cases (methionine, glutathione, tyrosine, *m*-tyrosine, and *o*-tyrosine) the site of the initial metal–ligand bond formation is the carboxylate group of the zwitterion, while in two cases (cysteine and penicillamine) there is an additional pathway involving initial complexing at the sulphydryl group. The rate law, based on Scheme 2, simplifies for the amino-acids to

$$\frac{k_{obs}(K_1 + [H^+])}{[H^+]} = \frac{k_{43}K_1k_{35}}{k_{34}[H^+]} = \frac{k_{12}K_1'k_{35}}{k_{21}[H^+]}$$

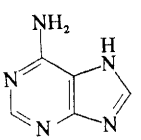
which implies, as above, that we have a rapid pre-equilibrium followed by rate-limiting ring closure. One important conclusion to be drawn from Letter and Jordan's analysis is that, contrary to the previously accepted view, the amino-acid zwitterion may be kinetically active when it is the dominant species in solution. Until now it had been assumed that the appearance of a term $[H^+]^{-1}$ in the experimental rate law meant that the zwitterionic species was not reactive but, as Letter and Jordan point out, such a term only means that a proton is lost before the transition state for the slowest step is reached; if the highest point in the reaction profile occurs after first-bond formation, there is no reason to insist that the proton is lost before the first water molecule leaves the inner co-ordination sphere of the metal.

In what amounts to another tilt at the windmills of conventional wisdom, Jordan has looked critically[25] at the evidence for the ICB effect and, in particular, the reasons for invoking it in the reaction of nickel with ethylenediamine (and the polyamines). He concludes that at pH < 6.8 the published data can be accounted for on the basis of normal reaction rates (including the well established labilizing effect of a co-ordinated amino-group in the unidentate intermediate) and require no special explanation such as the ICB mechanism. Moreover, if an ICB effect is to be established, experimental conditions must be such that $k_{43}K_1 \geqslant k_{12}[H^+]$ (*cf.* Scheme 2,

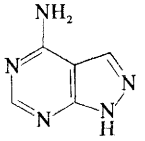
[24] J. E. Letter and R. B. Jordan, *J. Amer. Chem. Soc.*, 1975, **97**, 2381.
[25] R. B. Jordan, *Inorg. Chem.*, 1976, **15**, 748.

with N—$\overset{+}{N}$H and N—N replacing $^-$O—$\overset{+}{N}$H and $^-$O—N, respectively); in other words, the experiments must be performed at pH > 7. At these higher pH values, of course, care must be taken to ensure that the reactions of species such as $[(H_2O)_5Ni(OH)]^+$ are not being followed. In this connection it is, perhaps, worthwhile recalling the work of Chatterjee and Kaden with the quinquedentate ligand dacoda. They measured[21] the kinetics of formation and dissociation of the nickel complex in addition to that of cobalt(II) (see p. 246) and concluded (in both cases) that it was necessary either to invoke a particularly large ICB effect or to assume that the reactive form of the metal was the hydroxy-species. It is unlikely that we have heard the last of the ICB effect.

The interaction of Ni^{2+}_{aq} with adenine (4), 4-aminopyrazolo[3,4-*d*]pyrimidine (5), hypoxanthine, and inosine have been studied[26] by the stopped-flow technique. (4)



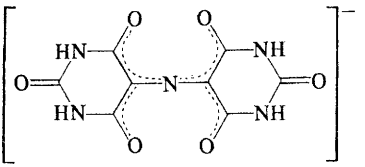
(4)



(5)

and (5) show a complex reaction pattern with both the neutral (HL) and protonated (H_2L^+) forms attacking the nickel ion, with subsequent deprotonation. The authors suggest that the preference, at first sight surprising, for the protonated ligand (Table 5) may be explained in terms of hydrogen bond formation between the neutral ligand and a water molecule in the inner co-ordination sphere of the metal, leading to poor alignment of the ligand (with respect to attack on the metal ion) in this case. Hypoxanthine and inosine show no pH dependence in the pH region 2—6 and give 'normal' rate constants. The dissociation kinetics of the nickel complexes of 1-nitroso-2-naphthol, 1-nitroso-2-naphthol-3,6-disulphonate, 2-nitroso-1-naphthol, and 2-nitroso-1-naphthol-4-sulphonate are strongly pH-dependent;[27] the rates also vary markedly with the relative positions of the NO and OH groups and of substitution in the rings by sulphonate groups.

The volume of activation for the reaction of Ni^{2+} with (6) in water is[28] 12.2 cm^3 mol^{-1} at 25 °C, a value which is consistent with rate-limiting replacement of the first



(6)

water molecule from the inner co-ordination sphere of the metal. The same I_d mechanism is suggested[29] for this reaction in DMSO–nitromethane solvent mixtures

[26] A. Casper and G. V. Fazakerley, *J.C.S. Dalton*, 1975, 1977.
[27] G. C. Lalor, *Inorg. Chim. Acta*, 1975, **14**, 179.
[28] A. Jost, *Ber. Bunsengesellschaft phys. Chem.*, 1975, **79**, 850.
[29] J. P. K. Tong and C. H. Langford, *Canad. J. Chem.*, 1976, **54**, 706.

but the authors are not able to say definitely whether or not a nitromethane-containing intermediate $[Ni(DMSO)_5(MeNO_2)]^{2+}$ is involved.

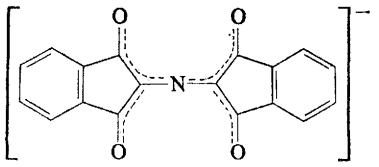
Bennetto and Imani have reported[30] the rates and activation parameters for the reaction of pyridine-2-azodimethylaniline (pada) with Ni^{II} in water and seven other solvents. They find a wide variation in the ratio of the rate constants for ligand substitution and solvent exchange and are able to correlate these ratios with various properties of the solvent in such a way as to lend support to the previously proposed 'concerted interchange' model for ligand substitution. This, it will be recalled, emphasizes the importance of solvent structure as an influence on the mechanism of reaction. As with the bipyridyl reaction, they obtain a good correlation between the activation enthalpies and activation entropies for the various solvents, but they find that the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for pada are all rather lower than in the corresponding reaction with bipy. They suggest that this may be rationalized in terms of the greater flexibility of pada: if it is more manoeuvreable and gives a better fit to the solvent structure, a greater degree of local order might be preserved. In terms of their model, this would be consistent with a greater availability of spaces in the solvent for reception of the leaving molecule, which would lead to a reaction of lower $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$, as is observed. In a preliminary note, the same authors have pointed out[31] that even small amounts of added water can have a large effect on the kinetics of this reaction in acetonitrile. Complex changes in the activation parameters suggest that the solvent can induce a change of reaction mechanism.

The kinetics of the reaction of nickel(II) with Ruhemann's Purple [the ammonium salt of (7)] and 4-(2-pyridylazo)resorcinol (8) have been reported[32] in nitromethane containing 0.0125 mol l^{-1} pyridine. In both cases the ligand appears to react in the monoanionic form and the kinetics are straightforward. The authors quote an apparent rate constant for the reaction with (7), $K_2k_2 = 2.1 \times 10^4$ s^{-1} at 25 °C (with

$$NH_4(7) \overset{K_2}{\rightleftharpoons} NH_4^+ + (7)$$

$$Ni^{2+} + (7) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Ni(7)]^+$$

an associated apparent activation energy of 19.6 kcal mol^{-1}). The activation energy for the reaction with H_{-1} (8) is 13.5 kcal mol^{-1}.



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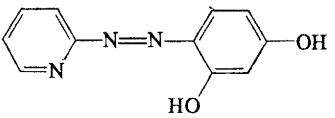
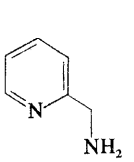


(8)

Rate data on the H^+- and Hg^{II}-ion induced dissociations of the mono-complexes of (9)—(12) in DMSO indicate[33] that the formation reactions are 'normal', *i.e.* that the

[30] H. P. Bennetto and Z. S. Imani, *J.C.S. Faraday I*, 1975, **71**, 1143.
[31] H. P. Bennetto and Z. S. Imani, *J.C.S. Chem. Comm.*, 1975, 333.
[32] H. L. Fritz and J. H. Swinehart, *Inorg. Chem.*, 1975, **14**, 1935.
[33] D. M. W. Buck and P. Moore, *J.C.S. Dalton*, 1975, 409.

chelate-ring-closure step is not rate limiting. Buck and Moore conclude, in the light of the marked acid dependence of these reactions, that their previous suggestion that ring closure is rate limiting for the bipy reaction was incorrect.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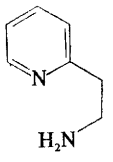
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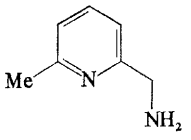
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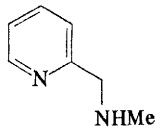
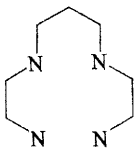

(12)

Copper. Much recent interest has centred on the unusually large stabilities of macrocyclic ligand complexes, particularly those of the crown polyethers (*cf.* Part III) and cyclic tetramines, as compared with the corresponding open-chain species, and the dependence of these stabilities on ligand ring size. Unfortunately, it is difficult to obtain direct kinetic data since the cyclic polyethers form extremely labile complexes while the polyamines protonate in the pH regions accessible to the solvated metal ions of general interest, thereby introducing interfering electrostatic and conformational effects which are difficult to isolate. In an attempt to overcome the difficulties associated with ligand protonation, Lin *et al.* have measured[34] the kinetics of Cu^{II} reacting with (13)—(18) in strongly basic aqueous media (0.1—2.0M-NaOH). Under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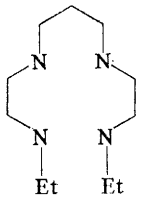
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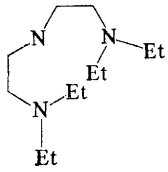
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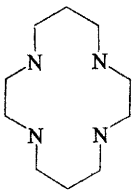
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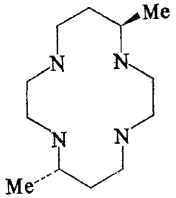
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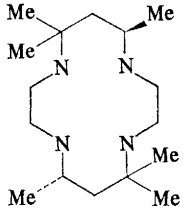

(18)

these conditions the copper is present as $[Cu(OH)_3]^-$ and $[Cu(OH)_4]^{2-}$, the former being the more reactive species (Table 6). It seems, from a comparison of the most closely correlated open-chain and cyclic ligands [*viz.* (14) and (16)] that ligand cyclization itself has only a relatively minor influence on the complex-formation rate constant, and more significant effects arise from substitution at the nitrogen donor atoms of the open-chain ligands or on the alkyl backbone of the cyclic compounds. It

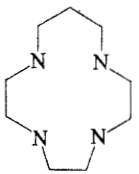
[34] C. T. Lin, D. B. Rorabacher, G. R. Cayley, and D. W. Margerum, *Inorg. Chem.*, 1975, **14**, 919.

Table 6 *Rate constants*[34] *for the reaction of hydroxycuprate*(II) *species with unprotonated cyclic and open-chain polyamines at* 25 °C

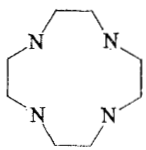
Ligand	$k^{L}_{Cu(OH)_3}$/l mol^{-1} s^{-1}	$k^{L}_{Cu(OH)_4}$/l mol^{-1} s^{-1}	$k^{L}_{Cu(OH)_4}/k^{L}_{Cu(OH)_3}$
(13)	$(1.0\pm0.7)\times10^7$	$(4.3\pm0.2)\times10^6$	2.4
(14)	$(3.0\pm0.3)\times10^6$	$(2.9\pm0.6)\times10^5$	10
(15)	4.0×10^5	$<10^3$	>400
(16)	$(2.7\pm0.4)\times10^6$	$(3.8\pm0.9)\times10^4$	72
(17)	5.6×10^5	0.9×10^4	60
(18)	$\sim10^4$	$<10^2$	$>10^2$

will be seen that all formation rate constants are well below the diffusion-controlled limit and are smaller than the values for $[Cu(H_2O)_6]^{2+}$ reacting with neutral unidentate ligands. The authors reject simple axial H_2O dissociation as the rate-determining step for both hydroxycuprate(II) complexes but argue that in the case of $[Cu(OH)_3]^-$ it is Jahn–Teller (tetragonal) inversion following the first-bond formation whereas in the case of the reaction of $[Cu(OH)_4]^{2-}$ with the macrocyclic ligands and the more sterically hindered open-chain polyamines it is the formation of the second metal–ligand bond. Since in both cases the ligands are co-ordinated at the time of the rate-determining step, the reactions can be said to exhibit associative character.

Kodama and Kimura have found[35] that the 13-membered cyclic tetramine (19), in



(19)



(20)

its reaction with copper(II), behaves kinetically rather like a non-cyclic tetramine. Thus, for the reactions in Scheme 3 they obtained the results shown in Table 7. The

$$\begin{array}{l} Cu(OAc)_2 \\ \quad \Big\Vert \text{ rapid} \\ Cu(OAc)^+ + \\ \quad \Big\Vert \text{ rapid} \\ Cu^{2+} \end{array} \left\{ \begin{array}{l} ZH^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CuZ^{2+} + HOAc \\ ZH_2^{2+} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CuZ^{2+} + HOAc + H^+ \\ \qquad Z = (19) \text{ or } (20) \end{array} \right.$$

Scheme 3

Table 7 *Rate constants*[a] *for the formation of copper*(II) *complexes*

Ligand	log k_1/ l mol^{-1} s^{-1}	$E_{A(1)}$/ kcal mol^{-1}	$\Delta S^{\ddagger}_1$/ cal K^{-1} mol^{-1}	log k_2/ l mol^{-1} s^{-1}	$E_{A(2)}$/ kcal mol^{-1}	$\Delta S^{\ddagger}_1$/ cal K^{-1} mol^{-1}	log k_{-1}/ l mol^{-1} s^{-1}	log k_{-2}/ l mol^{-1} s^{-1}
(19)	6.75	17.3	+26.9	1.01	12.8	−15.1	-14.2_3	−9.9
(20)	6.30	—	—	−0.74	—	—	−10.9	−8.2

[a] Data, from ref. 35, refer to 25 °C and I = 0.20 mol l^{-1}.

[35] M. Kodama and E. Kimura, *J.C.S. Chem. Comm.*, 1975, 326, 891.

contrast in the activation parameters for the reaction with $[H\text{-}(19)]^{+}$ and with $[H_2\text{-}(20)]^{2+}$ can be explained by assuming that the monoprotonated species has a conformation closer to that of the transition state than the diprotonated species and is more solvated by water molecules which will be released on forming the transition state.

Another ploy by which the lability/protonation difficulty mentioned at the start of this section can be overcome is to choose a series of macrocyclic ligands containing sulphur as the binding atoms: these ligands are free of protonation considerations even at moderately low pH and the stabilities of the copper(II) complexes are such as to permit the determination of both the formation and the dissociation rate constants by stopped-flow and/or temperature-jump methods. Jones *et al.* have studied[36] the reaction of Cu^{II} with (21)—(26) in a mixture of 80–20 methanol–water (by weight) and have obtained the results shown in Table 8. In agreement with previous studies on

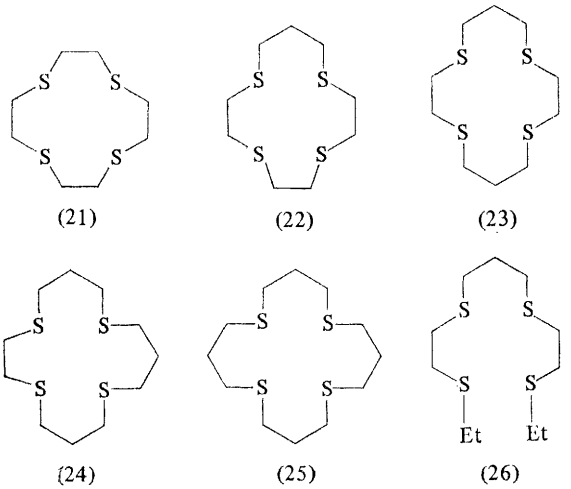


Table 8 *Kinetic and equilibrium data*[36] *for copper*(II) *reacting with macrocyclic tetrathiaethers in* 80% *methanol at* 25 °C (I = 0.10 mol l^{-1})

Ligand	k_f/l mol^{-1} s^{-1}	k_d/s^{-1}	K_{ML}/l mol^{-1} (*kinetic*)	K_{ML}/l mol^{-1} (*equil.*)
(21)	1.2×10^{3}	4.4	2.7×10^{2}	3.3×10^{2}
(22)	1.4×10^{4}	51	2.7×10^{2}	—
(23)	2.8×10^{4}	9	3.1×10^{3}	3.0×10^{3}
(24)	4.3×10^{4}	1.9×10^{2}	2.3×10^{2}	—
(25)	2.9×10^{4}	3.2×10^{3}	9	11
(26)	4.1×10^{5}	3.0×10^{4}	14	13

the tetramines, the 14-membered macrocycle exhibits the largest stability constant. Interestingly, the formation rate constants for the 13- to 16-membered macrocyclic complexes are fairly similar and the variation in stability constants is largely reflected

[36] T. E. Jones, L. L. Zimmer, L. L. Diaddario, D. B. Rorabacher, and L. A. Ochrymowycz, *J. Amer. Chem. Soc.*, 1975, **97**, 7163.

in changes in k_d. Moreover, the authors conclude that, as with the study involving $[Cu(OH)_4]^{2-}$ mentioned above,[34] the rate-determining step is the formation of the second water–ligand bond. Hence, the dependence of the dissociation rate constant (and therefore stability constant) on the size of the ring appears to be associated with the bonding of the third and fourth donor atoms and the associated conformational changes (such as folded to planar inversions). As the ring size increases, the constraints of the ring diminish, thereby reducing the macrocyclic effect.

Feltch *et al.* have studied[37] the kinetics of the interaction of Cu^{2+} with *NN*-dimethylglycine and L-proline and have observed two relaxation times, which they ascribe to the formation of the mono- and bis-complexes. Values of k_f for the former ligand were, respectively, 1.4×10^9 and 3.8×10^8 l mol^{-1} s^{-1} and for the latter ligand 2.6×10^9 and 2.2×10^8 l mol^{-1} s^{-1} (at 25 °C, $I = 0.1$ mol l^{-1}). The values of k_d for these (and related) ligands correlate with the pK_a of the amino-group.

Zinc, Cadmium, and Mercury. The lability of the metal–nitrogen bonds in the complexes of all three species with $(HO_2CCH_2)_2N(CH_2)_nN(CH_2CO_2H)_2$ ($n = 2$, 3, or 4) has been investigated[38] by ^{1}H n.m.r. In the Zn^{II} and Cd^{II} complexes, the metal–nitrogen bonds become more labile as the size of the internal chelate ring increases whereas they become more inert in the Hg^{II} complexes. It appears that this latter trend results from structural changes to a more linear N—Hg—N arrangement. Low-temperature stopped-flow studies in DMSO on the formation and dissociation of the Zn^{II} bipy complex have yielded[20] log $k_f = 4.27$ and log $k_d = 0.92$ at 292.2 K.

Metals of Valency Three and Higher.—Stopped-flow studies have been reported for iron(III) reacting with *o*-cresolsulphonphthalein[39] and with a series of substituted catechols,[40] including adrenaline and L-dopa. With the catechols, the value of k_f was more or less independent of the substituent groups present on the ligand.

The rate constants for the formation of 1:1 lanthanide–tartrate complexes have been determined[41] by the pressure-jump technique. The values of k_f range from 5.6×10^8 l mol^{-1} s^{-1} for samarium to 1.9×10^8 l mol^{-1} s^{-1} for lutetium (Table 9) and

Table 9 *Rate constants*[41] *for lanthanide*(III) *tartrate complexes at* 25 °C ($I \rightarrow 0$)

Metal	$10^{-8}k_f$/l mol^{-1} s^{-1}	$10^{-3}k_d$/s^{-1}
La	4.1±0.7	10.8±2.0
Nd	4.6±0.9	10.1±1.9
Sm	5.6±0.2	3.5±0.1
Gd	2.9±0.3	5.1±0.6
Dy	2.5±0.2	1.9±0.1
Ho	3.9±0.8	2.8±0.5
Tm	3.0±0.6	1.5±0.3
Lu	1.9±0.3	1.6±0.1

the fact that k_f/K_{os} is found to be about two orders of magnitude lower than the water-exchange rates suggests to the authors that the rate-determining step is ring closure.

[37] S. M. Feltch, J. E. Stuehr, and G. W. Tin, *Inorg. Chem.*, 1975, **14**, 2175.
[38] D. L. Rabenstein, G. Blakney, and B. J. Fuhr, *Canad. J. Chem.*, 1975, **53**, 787.
[39] H. Nakayama and M. Fujimoto, *Bull. Chem. Soc. Japan*, 1975, **48**, 3399.
[40] E. Mentasti, E. Pelizzetti, and G. Saini, *J. Inorg. Nuclear Chem.*, 1976, **38**, 785.
[41] S. S. Yun and J. L. Bear, *J. Inorg. Nuclear Chem.*, 1976, **38**, 1041.

It is argued,[42] on the basis of recent kinetic results, that the rate-limiting step in the formation of the (bidentate) glycine complex of oxovanadium(IV) is the direct interaction between the nitrogen of the unidentate glycine and the trigonal face of the oxovanadium(IV) complex. On this assumption, the rate constant for this process is 35 s^{-1} at 25 °C, and the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are 13.6 kcal mol^{-1} and -5.8 cal K^{-1} mol^{-1}, respectively.

3 The Effects of Bound Ligands

Reactions in Water.—The ultrasonic absorption technique has been applied[43] to silver(I) thiosulphate in solutions of which the predominant species is the ion $[Ag(S_2O_3)_2]^{3-}$. Both of the relaxation effects observed over the 15—230 MHz frequency range were attributed to the stepwise mutual approach of $[AgS_2O_3]^-$ and $[S_2O_3]^{2-}$ with the elimination of co-ordinated water. At 25 °C the rate constant for this association reaction is 1.0×10^9 l mol^{-1} s^{-1}, which is close both to the value calculated on the basis of the process being essentially diffusion controlled and to the literature value for the reaction of a second molecule of phen with the mono-complex $[Ag(phen)]^+$. The authors favour an associative mechanism for these reactions of Ag^+, with the bound ligand having essentially no effect on k_f.

Hunt and co-workers have published[44] the results of their ^{17}O n.m.r. studies on $[Ni(dien)(H_2O)_3]^{2+}$, $[Ni(trien)(H_2O)_2]^{2+}$, and $[Ni(tetren)(H_2O)]^{2+}$. The Ni–dien system shows at least two water-exchange rates which are not, however, well resolved (although the authors are confident that an approximately ten-fold rate difference exists between the two at 25 °C); it is suggested that two waters are 'fast' (Table 10)

Table 10 *Kinetic data*[44] *for water exchange at* 25 °C

Complex	$10^{-5}k^a/s^{-1}$	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
$[Ni(dien)(H_2O)_3]^{2+}$	34±6	9.0±0.7	1.5±2.8
	4.4±0.5	10.7±3	3.1±10
$[Ni(trien)(H_2O)_2]^{2+}$	5.7±1.6	8.23±0.92	−4.61±3.65
$[Ni(tetren)(H_2O)]^{2+}$	112±22	8.57±0.66	2.46±2.60
$[Ni(H_2O)_6]^{2+}$	3.07±0.05	14.4±0.2	10.3±0.6

[a] Rate constant per H_2O molecule.

and one is 'slow'. In a comparison of the Ni–trien data with published results for ternary complex formation, Rablen *et al.* point out that the value of K_{os} calculated (from $k_f = K_{os}k_{ex}$) for reaction with pada is rather lower than might have been predicted; perhaps the two water molecules are *trans* and the ring-closure step is slow because it is necessary for one of the 'arms' of trien to move from an equatorial to an axial position. The volumes of activation for the reaction of pada with five substituted nickel(II) species have been recorded.[45] They fall into two groups, +3 cm^3 mol^{-1} (where the bound ligand is tren or trien) and +6 cm^3 mol^{-1} (where it is nta^{3-}, $edda^{2-}$, or dien). The latter value, which is rather similar to that obtained previously

[42] H. Tomiyasu and G. Gordon, *Inorg. Chem.*, 1976, **15**, 870.
[43] M. M. Farrow, N. Purdie, and E. M. Eyring, *Inorg. Chem.*, 1975, **14**, 1584.
[44] D. P. Rablen, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, 1976, **15**, 931.
[45] M. W. Grant and C. J. Wilson, *J.C.S. Faraday I*, 1976, **72**, 1362.

for the reaction of pada with hexa-aquonickel(II), is interpreted in terms of the normal I_d mechanism in which the water-replacement step is rate determining, while the former is interpreted in terms of a mechanism in which ring closure is rate limiting. An n.m.r. study[6] on the kinetics of the $[Ni(H_2O)_5(Ac)]^+ + Ac^-$ reaction has already been discussed.

^1H N.m.r. has been used[46] to investigate the mechanism of 2:1 complex formation between the hydroxyethyliminodiacetate (himda) ion and praseodymium(III). A rather complex picture emerges in which three distinct pathways are identified for the exchange of the ligand, through the spontaneous dissociation of $[Pr(himda)_2]^-$ and its hydroxy-complex, through the acid-catalysed dissociation of $[Pr(himda)_2]^-$, and through a bimolecular process involving the free ligand and the 2:1 complex or its hydroxy-derivative.

In a preliminary note, Tanaka and Yamada have suggested[47] that the rate of water exchange at an acidoaquo-complex ML, $k_{ML}^{H_2O}$, is related to the electron-donating ability of the bound ligand L (measured by the Edwards parameter E_n) by the equation

$$\log (k_{ML}^{H_2O}/k_{M}^{H_2O}) = \gamma E_n$$

The proportionality constant γ has been estimated for chromium(III), cobalt(II), iron(III), nickel(II), and oxovanadium(IV), and is correlated with the 'softness parameter' σ (ref. 48) using the equation

$$\gamma = -5.5\sigma + 5.5$$

Since the value of σ has been evaluated for 26 metal ions, γ (and hence $k_{ML}^{H_2O}$) may be predicted for these metal ions – always provided, as the authors add cryptically, that the equation remains valid for all cases.

Reactions in Non-aqueous Solvents.—Coetzee and co-workers have determined the ratio N of the rate constants of the two reactions (a) $[NiXS_n]^+ + Y \rightarrow$ ternary complex and (b) $[NiS_6]^{2+} + Y \rightarrow$ simple complex (where X is a monoanion, S the solvent, and Y a neutral aromatic ligand) for the solvents acetonitrile[49] and methanol.[50] The accelerating effects produced by the inner-sphere substituents vary quite considerably from case to case (Table 11) and, in particular, between the two solvents. The fact that the rate of reaction (a) in acetonitrile is much less sensitive to the nature of Y than is the case for reaction (b) supports the authors' previous view on the importance of an 'extra' stabilization of the outer-sphere complex with this solvent (the latter being brought about by the interaction of the ligand with the polarized acetonitrile molecules of $[NiS_6]^{2+}$) since the S molecules will be less polarized in $[NiXS_n]^+$ than in $[NiS_6]^{2+}$. On the basis of these and other results, Coetzee and co-workers conclude that the accelerating influence of anionic inner-sphere substituents in non-aqueous solvents can be attributed to the net effect of solvent labilization and outer-sphere destabilization.

[46] F. Chastellain and A. E. Merbach, *Helv. Chim. Acta*, 1975, **58**, 1.
[47] M. Tanaka and S. Yamada, *J.C.S. Chem. Comm.*, 1976, 178.
[48] S. Yamada and M. Tanaka, *J. Inorg. Nuclear Chem.*, 1975, **37**, 587.
[49] P. K. Chattopadhyay and J. F. Coetzee, *Inorg. Chem.*, 1976, **15**, 400.
[50] J. F. Coetzee and D. M. Gilles, *Inorg. Chem.*, 1976, **15**, 405.

Table 11 *Accelerating effect of anionic inner-sphere substituents* (X) *on rates of reactions*[49,50] *of nickel*(II) *with various incoming ligands* (Y) *in methanol and acetonitrile*

		Methanol		*Acetonitrile*	
Y	X	$\log k_{N1X}$	$\log N^a$	$\log k_{N1X}$	$\log N^a$
4-Phenylpyridine	Cl	3.9	1.8	—	—
	Br	3.3	1.2	—	—
	I	2.8	0.7	—	—
	SCN	2.9	0.8	—	—
bipy	Cl	3.1	1.1	6.3	2.7
	Br	2.5	0.5	—	—
	I	2.3	0.3	—	—
	SCN	3.0	1.0	—	—
phen	Cl	3.1	0.3	6.6	1.9
terpy	Cl	2.8	1.2	6.3	2.9
	Br	2.2	0.6	5.7	2.3
	I	1.8	0.2	4.8	1.4
	SCN	2.8	1.2	5.5	2.1
	NO_3	—	—	4.4	1.0

[a] $N = k_{N1X}/k_{N1}$.

The lability of pyridine in bis-(β-alkanedionato)dipyridinenickel(II) complexes (Table 12) decreases[51] as the electron-withdrawing power of the β-alkanedionato-

Table 12 *Kinetic data*[51] *for pyridine exchange at* 25 °C

Complex	$10^{-4}k^a/s^{-1}$	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	$\Sigma\sigma^*$
$[Ni(acac)_2(py)_2]$	9.8±1.2	42±3	−9±10	0
$[Ni(bzac)_2(py)_2]$	4.6±0.5	38±3	−28±11	0.60
$[Ni(bzbz)_2(py)_2]$	2.7±0.3	38±3	−34±12	1.20
$[Ni(tfac)_2(py)_2]$	0.84±0.09	32±3	−58±11	2.75
$[Ni(hfac)_2(py)_2]$	<0.2	—	—	5.5

[a] Rate constant per py molecule.

ligand increases. The latter is measured as the sum of the Taft σ* parameters for the ligands and it seems that the progressive increase in $\Delta G^{\ddagger}$ at 298 K is a consequence of the increasingly negative $\Delta S^{\ddagger}$ contribution. (The negative $\Delta S^{\ddagger}$ values for a dissociative process may be rationalized by postulation of net ordering of solvent outside the first co-ordination sphere: *cf.* the Bennetto–Caldin model.) Although the accuracy of the data does not permit fine distinctions to be drawn for enthalpic and entropic contributions to the activation process, the authors feel that the CFAE contribution to the activation process is unlikely to vary significantly over this range of complexes.

The mechanism of ligand substitution on the five-co-ordinate 1,2-dithiolene complexes $[M\{S_2C_2(CF_3)_2\}_2X]^z$ (M is Fe or Co, X is a phosphine or phosphite) in benzene is associative when $z = 0$ and dissociative when $z = -1$;[52] second-order rate constants are given in Table 13.

[51] J. Crea and S. F. Lincoln, *Austral. J. Chem.*, 1975, **28**, 1523.
[52] D. A. Sweigart, *Inorg. Chim. Acta*, 1976, **18**, 179.

Table 13 *Rate constants*[52] *for the reaction* $[M\{S_2C_2(CF_3)_2\}_2 PR^1_3] + PR^2_3 \rightarrow [M\{S_2C_2(CF_3)_2\}_2PR^2_3] + PR^1_3$ *in benzene at* 25 °C

Metal	*Leaving group*	*Nucleophile*	$10^{-4}k$/l mol^{-1} s^{-1}
Co	PPh_3	P(*p*-tol)$_3$	3.0
Co	P(*p*-tol)$_3$	$P(OBu)_3$	5.2
Co	$P(OPh)_3$	PPh_3	1.7
Co	$P(OPh)_3$	P(*p*-tol)$_3$	15
Fe	P(*p*-tol)$_3$	$P(OBu)_3$	31
Fe	$P(OPh)_3$	PPh_3	2.5
Fe	$P(OPh)_3$	P(*p*-tol)$_3$	18

From n.m.r. studies on eight tetrahedral Co^{II} complexes of thiourea (tu) and substituted thioureas in acetone, it is concluded[53] that, in each case, two mechanisms are involved. The first is a direct associative exchange,

$$[Co(tu)_2X_2] + tu^* \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [Co(tu)_2(tu^*)X_2] \underset{k_3}{\overset{k_{-3}}{\rightleftharpoons}} [Co(tu)(tu^*)X_2] + tu$$

and the second is exchange *via* a solvated intermediate:

$$[Co(tu)_2X_2] + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Co(tu)_2SX_2] \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Co(tu)SX_2] + tu$$

As the authors point out, the lability of the complexes arises from the low enthalpies of activation (Table 14): indeed, the values are so low in many cases that the Reporter is forced to wonder whether we have heard the full mechanistic story about these interesting reactions.

[53] D. R. Eaton and K. Zaw, *Inorg. Chim. Acta*, 1975, **16**, 61.

Table 14 *Kinetic data*[53] *for ligand exchange reactions at room temperature*

Compound	k_1/ l mol^{-1} s^{-1}	$\Delta H_1^{\ddagger}$/ kcal mol^{-1}	$\Delta S_1^{\ddagger}$/ cal K^{-1} mol^{-1}	k_3/ l mol^{-1} s^{-1}	$\Delta H_3^{\ddagger}$/ kcal mol^{-1}	$\Delta S_3^{\ddagger}$/ cal K^{-1} mol^{-1}	k_{-2}/ l mol^{-1} s^{-1}	$\Delta H_{-2}^{\ddagger}$/ kcal mol^{-1}	$\Delta S_{-2}^{\ddagger}$/ cal K^{-1} mol^{-1}
$[Co[tu)_2Cl_2]$	180	3.6	−36	3.5×10^5	1.3	−29	3.4×10^7	0.9	−21
$[Co(tu)_2Br_2]$	130	3.5	−37	2.6×10^5	2.9	−24	2.3×10^7	0.6	−23
$[Co(tu)_2I_2]$	110	3.4	−38	1.6×10^5	3.2	−24	4.4×10^6	−0.2	−29
$[Co(metu)_2Cl_2]$	150	4.4	−34	2.9×10^5	2.3	−26	2.5×10^7	0.5	−23
$[Co(metu)_2Br_2]$	120	4.1	−35	2.3×10^5	3.1	−25	2.4×10^7	0.2	−26
$[Co(metu)_2I_2]$	37	4.0	−38	6.1×10^4	3.8	−23	2.2×10^7	0	−25
$[Co(dmtu)_2Br_2]$	43	3.6	−39	8.9×10^4	3.5	−24	1.9×10^7	1.7	−20
$[Co(dmtu)_2I_2]$	25	3.8	−40	8.5×10^4	4.8	−20	1.7×10^7	0.7	−24

5
Solvent Effects

BY J. BURGESS

1 Introduction

Interest in solvent and salt effects on reactivity in inorganic systems appears to be on the increase. The much larger number of references appropriate for inclusion in the present volume has resulted in a marked decrease in the space available per reference, and thus only a cursory mention of many investigations. Recent relevant reviews include a general discussion of solvent effects both for inorganic and for organic reactions in mixed aqueous media,[1] a review of specific solvent effects such as hydrogen-bonding on reactivity,[2] and a review of solvent effects in reactions of square-planar complexes.[3]

The arrangement of this chapter is similar to that in previous volumes of this Report, except that the division into pure and mixed solvents is no longer made in most topics. Before embarking on the classified sections on specific solvent and salt effects, a few general aspects of the usefulness of mixed and non-aqueous solvents in studies on inorganic kinetics and mechanisms are discussed. At the simplest level, choice of an appropriate medium may be dictated by the technical need to retard rates as much as possible, as in low-temperature stopped-flow studies of complex formation from very labile Mn^{2+} and Zn^{2+} in DMSO,[4] by the desire to avoid parallel hydrolysis or solvolysis paths, as in studies of cyanide attack at $[O_3SSeSO_3]^{2-}$, $[O_3SSeSeSO_3]^{2-}$, or sulphinates in acetonitrile,[5] or by reagent solubilities, as in some studies of dioximato-cobalt(III) complexes.[6] In recent years the use of crown ethers to permit dissolution of alkali-metal salts in organic solvents has become commonplace. Often the anion is practically unsolvated or 'naked', and thus very reactive, as illustrated by the ready attack of fluoride on organic substrates in reaction mixtures containing potassium fluoride, a crown ether, and the substrate dissolved in an organic solvent. Recently the use of 18-crown-6 to dissolve potassium fluoride or thiocyanate in benzene, THF, or acetonitrile and thus facilitate fluoride or thiocyanate substitution at hexachlorocyclotriphosphazene, $(PNCl_2)_3$, has been described,[7] while the present Reporter has observed very fast reaction of $[Fe(bipy)_3]^{2+}$ with potassium cyanide dissolved in non-aqueous solvents with the aid of 18-crown-6.

[1] M. J. Blandamer and J. Burgess, *Chem. Soc. Rev.*, 1975, **4**, 55.
[2] K. M. Ibne-Rasa and J. O. Edwards, *Internat. J. Chem. Kinetics*, 1975, **7**, 575.
[3] K. M. Ibne-Rasa, J. O. Edwards, and J. L. Rogers, *J. Solution Chem.*, 1975, **4**, 609.
[4] D. M. W. Buck and P. Moore, *J.C.S. Dalton*, 1976, 638.
[5] T. Austad, *Acta Chem. Scand.*, 1975, **A29**, 71, 241.
[6] N. M. Samus', G. A. Konunova, and A. V. Ablov, *Russ. J. Inorg. Chem.*, 1974, **19**, 849; N. M. Samus', A. V. Ablov, G. A. Konunova, and I. V. Khoroshun, *ibid.*, p. 1522.
[7] E. J. Walsh, E. Derby, and J. Smegal, *Inorg. Chim. Acta*, 1976, **16**, L9.

The non-co-ordinating properties of some organic solvents can be useful in mechanism elucidation, in that solvento-intermediates are ruled out. Replacement of one Lewis base by another in alkylcobaloximes, R[Co], *e.g.* reaction (1), is a dissoci-

$$Me[Co]py + PBu^n_3 \longrightarrow Me[Co]PBu^n_3 + py \quad (1)$$

ative process. It is not possible to tell whether the mechanism is I_d or D in aqueous solution, but in the non-co-ordinating solvent chloroform this distinction is possible. Both for the reaction specified above, and for the replacement of piperidine (pip) in Me[Co]pip by 4-substituted pyridines, substitution takes place by the D mechanism.[8] The non-co-ordinating properties of heptane, benzene, and ether are reflected in the non-variation of rate for reaction of *trans*-$[PtH_2\{P(C_6H_{11})_3\}_2]$ with carbon disulphide in these solvents; in co-ordinating solvents such as acetonitrile no reaction takes place.[9]

2 Pure and Mixed Solvents

Solvent Isotope Effects.—Solvent isotope effects on rates of tin–, germanium–, or silicon–carbon bond cleavage in $MR^1R^2_3$ (M = Sn, Ge, or Si) in various solvents and mixtures containing methanol and DMSO suggest that alcohols can provide electrophilic assistance in the case of some tin compounds, but that for most compounds of this type the rate-determining step involves carbanion generation.[10] The pH-variation of rates of decomposition of O_2NNH_2 and of O_2NND_2 in H_2O and in D_2O has been compared with that for analogous organic compounds.[11] Isotope (H/D) effects on base hydrolysis of $[PPh_4]Cl$ indicate that phosphorus–hydrogen bond-breaking is not an important feature of transition-state formation here.[12] Solvent isotope effects on Mg^{2+} catalysis of pyrophosphate hydrolysis are complicated.[13]

The reaction of Mg^{2+} with pyrophosphate is about twice as slow in D_2O as in H_2O (at 15 °C). This difference is attributed to a change in the outer-sphere association constant rather than to a change in the interchange rate constant.[14] Kinetics of solvolysis of $[Fe(bipy)_3]^{2+}$ in D_2O lend support[15] to the mechanism of dissociation *via* a unidentate-bipyridyl transient intermediate postulated, for aqueous solution, many years ago.[16]

Solvent Properties.—*Dielectric Constant.* The dependence of rate constants, for substitution and for redox reactions, on solvent dielectric constant (D) has long been a popular subject of investigation and source of mechanistic assignment and speculation. The linearity of plots of logarithms of rate constants ($\log k$) against $1/D$ or against $(D - 1)/(2D + 1)$ has been used to support the attribution of a dissociative mechanism for a variety of reactions of cobalt(III) complexes. Thus linear

[8] F. R. Jensen and R. C. Kiskis, *J. Amer. Chem. Soc.*, 1975, **97**, 5820.
[9] A. Albinati, A. Musco, G. Carturan, and G. Strukul, *Inorg. Chim. Acta*, 1976, **18**, 219.
[10] C. Eaborn and G. Seconi, *J.C.S. Perkin II*, 1976, 925; C. Eaborn, J. R. Jones, and G. Seconi, *J. Organometallic Chem.*, 1976, **116**, 83.
[11] J. R. Jones and T. G. Rumney, *J.C.S. Chem. Comm.*, 1975, 995.
[12] F. Y. Khalil and G. Aksnes, *Z. phys. Chem. (Frankfurt)*, 1975, **97**, 179.
[13] L. M. Konsowitz and B. S. Cooperman, *J. Amer. Chem. Soc.*, 1976, **98**, 1993.
[14] H. Silber and P. Wehner, *J. Inorg. Nuclear Chem.*, 1975, **37**, 1025.
[15] S. Raman, *J. Inorg. Nuclear Chem.*, 1975, **37**, 1747.
[16] F. Basolo, J. C. Hayes, and H. M. Neumann, *J. Amer. Chem. Soc.*, 1954, **76**, 3807.

log k *vs.* $1/D$ plots for aquation of *cis*-$[CoX(en)_2L]^{2+}$ (X = Cl or Br, L = ammonia, allylamine, or benzylamine) in aqueous mixtures containing methanol, ethanol, glycol, glycerol, or acetone (up to 40% w/w organic component),[17] for aquation of *trans*-$[Co(dmgH)_2(tu)_2]^+$ in aqueous ethanol, propan-2-ol, or glycol,[18] and for aquation of *trans*-$[Co(dmgH)_2(SO_3)L]^-$ (L = ammonia, aniline, or a picoline) in aqueous ethanol[19] have been used as evidence for dissociative mechanisms. Whether these be I_d or D mechanisms is not stated. The strong labilizing effects of thiourea and of sulphite[20] suggest a D mechanism for the last two series, but the linearity of log k *vs.* $1/D$ plots for reactions of *trans*-$[Co(dmgH)_2(tu)L]^+$, where L = (substituted) aniline, with thiourea in aqueous propanol, glycol, or acetone, has been held to indicate specifically (and surprisingly) an I_d mechanism.[21] Similar linearity of log k *vs.* $1/D$ plots for aquation of a series of *trans*-$[Co(dioxime)_2Cl_2]^-$ anions in aqueous ethanol, propan-2-ol, or glycol was also stated to indicate an I_d mechanism.[22]

In the case of reactions of *trans*-$[Co(dmgH)_2X(tu)]$ (X = Cl, Br, I,[23] or NCS[24]) with thiourea, linearity of plots of log k *vs.* $(D - 1)/(2D + 1)$ is said to indicate D mechanisms, which this time is consistent with strong *trans*-labilization by the thiourea. For aquation of *trans*-$[Rh(dmgH)_2Cl(tu)]$ in aqueous ethanol, propan-2-ol, or acetone, log k *vs.* $(D - 1)/(2D + 1)$ is linear; for the reverse anation reaction it is log k *vs.* $1/D$ which is linear. This time, in contrast to assignments above, the former reaction is assigned an I_d mechanism, the latter a D mechanism.[25]

The variation of rate constant with solvent dielectric constant for the formation reactions of nickel(II) with ammonia in aqueous alcohols[26] and of iron(III) with chloride in aqueous methanol[27] is in both cases consistent with dissociative activation.

Plots of log k *vs.* $1/D$ are smooth, gentle curves for two reactions thought to proceed by associative mechanisms, base hydrolysis of $[PPh_4]Cl$ in aqueous acetone or dioxan[12] and aquation of $[Cr(ox)_3]^{3-}$ in aqueous dioxan.[28]

Linear log k *vs.* $1/D$ plots have also been reported for some redox reactions which have, or may have, rate-determining substitution steps previous to electron transfer. Examples include reactions of $[Mn(ox)_2(OH_2)_2]^-$ in aqueous DMF or DMSO[29,30] and of iodide with bromate in aqueous ethanol.[31]

The majority of reactions whose kinetics have been discussed in terms of dielectric constant effects have been examined in mixed aqueous solution, but a few studies in series of pure solvents have been described in the past year and a half. Ionization of iodine thiocyanate is slow, and incomplete, in solvents with low dielectric constants,

[17] V. V. Udovenko, L. G. Reiter, and E. P. Stepanov, *Russ. J. Inorg. Chem.*, 1974, **19**, 550.
[18] G. P. Syrtsova and G. I. Shpakov, *Russ. J. Inorg. Chem.*, 1975, **20**, 1053.
[19] L. N. Istru and G. P. Syrtsova, *Russ. J. Inorg. Chem.*, 1974, **19**, 708.
[20] See, *e.g.*, J. E. Byrd and W. K. Wilmarth, *Inorg. Chim. Acta Rev.*, 1971, **5**, 7.
[21] B. A. Bovykin, N. V. Ivanov, and L. F. Vasil'eva, *Russ. J. Inorg. Chem.*, 1974, **19**, 1505.
[22] G. P. Syrtsova, *Russ. J. Inorg. Chem.*, 1974, **19**, 233.
[23] B. A. Bovykin and I. B. Leongardt, *Russ. J. Inorg. Chem.*, 1974, **19**, 1813.
[24] B. A. Bovykin, *Russ. J. Inorg. Chem.*, 1974, **19**, 421.
[25] G. P. Syrtsova and T. S. Bolgar', *Russ. J. Inorg. Chem.*, 1974, **19**, 856.
[26] G. A. Krestov, V. Shosmanov, and V. N. Afanas'ev, *Koord. Khim.*, 1976, **2**, 34.
[27] G. Wada and Y. Kobayashi, *Bull. Chem. Soc. Japan*, 1975, **48**, 2451.
[28] M. W. Rophael and M. A. Malati, *Inorg. Chim. Acta*, 1975, **12**, L11.
[29] T. Oncescu and E. Jurconi, *Rev. Roumaine Chim.*, 1976, **21**, 805.
[30] T. Oncescu and E. Jurconi, *Rev. Roumaine Chim.*, 1976, **21**, 985.
[31] M. S. Subhani and M. N. A. Lacewala, *J. Math. Sci.*, 1974, **1**, 41 (*Chem. Abs.*, 1975, **82**, 77547).

such as carbon disulphide or carbon tetrachloride, but faster in solvents with higher dielectric constants, *e.g.* nitrobenzene.[32] A log k *vs.* $(D - 1)/(2D + 1)$ graph gives a tolerable correlation for the reaction of *trans*-$[IrCl(CO)(PPh_3)_2]$ with dihydrogen in nine solvents.[33] A linear correlation of log k with $(D - 1)/(2D + 1)$ has also been reported for the reaction of $[Mn(SnMe_3)(CO)_5]$ with iodine in a range of six solvents.[34] Halide (X^-) exchange with $SnMe_3X$ has been assigned a mechanism in which bond-breaking is a significant feature of transition-state formation on the basis of solvent dielectric effects on rates.[35]

Attempts to correlate rate constants with solvent dielectric functions are not always successful. A marked lack of correlation between log k and D, $1/D$, or $(D - 1)/(2D + 1)$ has been reported for the addition of 2,2′-bipyridyl to $[Ni(dtp)_2]$[36] and for dissociation of the $[Fe(phen)_3]^{2+}$ cation.[37] Interestingly, aquation rates for the $[Fe(5\text{-}NO_2phen)_3]^{2+}$ cation in hydrogen peroxide–water mixtures vary markedly with solvent composition despite the almost isodielectric properties of these mixtures.[38]

Viscosity. Comparison between the kinetics of reaction of ferroprotoporphyrin IX with carbon monoxide in aqueous ethylene glycol and in glycerol, media whose viscosities differ very greatly, indicate diffusion control in the glycerol.[39] This work parallels an earlier investigation of rates of formation of M^{2+} complexes in glycerol, where slow diffusion-controlled reaction was also demonstrated, in contrast with the chemical activation control operating in other solvents,[40] including aqueous glycerol.[41] The effect of viscosity variation on reaction kinetics can conveniently be monitored by working over a range of applied pressures;[39] such viscosity variation effects on the reaction of Ni_{aq}^{2+} with ligands in aqueous solution has been probed by working in solutions of tetra-n-butylammonium nitrate.[42] Solvent viscosity is an important factor in determining rates of racemization of the $[Fe(phen)_3]^{2+}$ cation. The geometry of this complex is such that the solvent penetrates into pockets between the large planar ligand molecules and thus affects the barrier to intramolecular racemization.[37]

Water Concentration. The effect of varying the water concentration on the rate of a hydrolysis reaction is an obvious way of probing the mechanism, but one where interpretation may be far from straightforward. Rates of ring closure in amino-acid (aa) complexes of the type *trans*-$[Pt(aa)_2X_2]^{2-}$ and $[Pt(aa)_2X]^-$ in aqueous ethanol often depend on the square of the water concentration, which dependence has been

[32] C. Raby, J. Buxeraud, and J. Claude, *Ann. Chim. (France)*, 1976, **1**, 65.
[33] R. Schmidt, M. Geis, and H. Kelm, *Z. phys. Chem. (Frankfurt)*, 1974, **92**, 223.
[34] J. R. Chipperfield, J. Ford, A. C. Hayter, D. J. Lee, and D. E. Webster, *J.C.S. Dalton*, 1976, 1024.
[35] J. A. Ladd and B. R. Glasberg, *J.C.S. Dalton*, 1975, 2378.
[36] M. W. Grant and R. J. Magee, *Austral. J. Chem.*, 1976, **29**, 749.
[37] F. M. Van Meter and H. M. Neumann, *J. Amer. Chem. Soc.*, 1976, **98**, 1388.
[38] M. J. Blandamer, J. Burgess, and M. Dupree, *J.C.S. Dalton*, 1976, 1298.
[39] E. F. Caldin and B. B. Hasinoff, *J.C.S. Faraday I*, 1975, **71**, 515.
[40] See Vol. 3, pp. 316—317.
[41] A. P. G. Kieboom, T. Spoormaker, A. Sinnema, J. M. van der Toorn, and H. van Bekkum, *Rec. Trav. chim.*, 1975, **94**, 31; V. Djurkin, *Glas. Hem. Tehnol. Bosne Hercegovine*, 1972, **19–20**, 95 (*Chem. Abs.*, 1975, **82**, 38047).
[42] C. H. Langford, J. P. K. Tong, and A. Merbach, *Canad. J. Chem.*, 1975, **53**, 702.

ascribed to the incorporation of two water molecules into the transition state.[43] A similar dependence of rate on the square of the water concentration for reactions of the $[Mn(ox)_2(OH_2)_2]^-$ anion in aqueous DMF[29] and in aqueous DMSO[30] has been discussed in terms of rapid equilibrium incorporation of a water molecule into the complex, followed by rate-determining reaction of the $[Mn(ox)_2(OH_2)_3]^-$ anion thus generated with another water molecule and parallel electron transfer. Dependence of reaction rate on the first power of the water concentration has been reported for acetylacetone (acac) exchange with $[Ti(acac)_3]^+$ in aqueous acetonitrile,[44] for solvolysis of $[Cr(NCS)_4(benzylamine)_2]^-$ in aqueous ethanol,*[45] and for mercury(II)-catalysed hydrolysis of acetonitrile.[47] The dependence of rate constant on water concentration for substitution at $[W_6Cl_8]^{2-}$ is one of the pieces of evidence adduced for the assignment of rate-determining aquation here.[48]

Solvent Parameters.—Correlation of kinetic parameters, generally rate constants, with one or other of the various empirical solvent parameters, such as Grunwald–Winstein Y values, Kosower Z values, or Reichardt E_T values, in efforts to diagnose mechanisms of inorganic reactions continue. Recently Taft and Kamlet have proposed scales of α and β values,[49] based on the solvatochromic behaviour of a range of organic and inorganic species, which should prove of some use in the analysis of kinetic data for inorganic reactions. Gutmann has proposed a scale of solvent acceptor numbers to complement his well established scale of solvent donor numbers.[50]

Grunwald–Winstein Analysis. Plots of decadic logarithms of rate constants for aquation of the ruthenium(III) complexes $[RuCl(NH_3)_5]^{2+}$ and *cis*-$[RuCl_2(en)_2]^+$ in aqueous methanol, ethanol, and acetone against solvent Y values have slopes (m) of *ca.* 0.23. The similarity of this m value to that for aquation of chloro-cobalt(III) complexes suggests a predominantly dissociative mechanism for aquation of these ruthenium(III) complexes. However, one might reasonably have expected the m value for dissociative aquation of Ru^{III}–Cl complexes to be slightly higher than that for Co^{III}–Cl complexes: hence the observed near equality may betoken some associative character in the case of Ru^{III}–Cl aquation.[51] Logarithms of rate constants for substitution at the square-planar complexes $[PdX(dien)]^+$ and $[PdX(Et_4dien)]^+$ (X = Cl or I) against solvent Y values give good linear plots; for $[PdCl(Et_4dien)]^+$ the plot is linear all the way from water to pure ethanol. Estimated m values are quoted in the Table. Detailed reaction profiles were discussed in the light of these m values and other linear free-energy plots. The conclusion reached was that palladium–halide

* However, solvolysis rates of $[Cr(NCS)_4(aniline)_2]^-$ in aqueous acetone are not proportional to any simple power of the water concentration.[46]

[43] L. M. Volshtein, L. F. Krylova, and L. D. Dikanskaya, *Russ. J. Inorg. Chem.*, 1975, **20**, 1526.
[44] M. Nishizawa, H. Kido, I. Kinoshita, Y. Soma, and K. Saito, *Bull. Chem. Soc. Japan*, 1976, **49**, 819.
[45] J. Zsakó, C. Várhelyi, I. Gănescu, and D. Oprescu, *Roczniki Chem.*, 1974, **48**, 1141.
[46] I. Gănescu, V. Voiculescu, and C. Várhelyi, *Monatsh.*, 1975, **106**, 801.
[47] Y.-K. Sze and D. E. Irish, *Canad. J. Chem.*, 1975, **53**, 427.
[48] P. Lessmeister and H. Schäfer, *Z. anorg. Chem.*, 1975, **417**, 171.
[49] R. W. Taft and M. J. Kamlet, *J. Amer. Chem. Soc.*, 1976, **98**, 2886; M. J. Kamlet and R. W. Taft, *ibid.*, p. 377.
[50] U. Mayer, V. Gutmann, and W. Gerger, *Monatsh.*, 1975, **106**, 1235.
[51] L. A. P. Kane-Maguire and G. Thomas, *J.C.S. Dalton*, 1975, 1324.

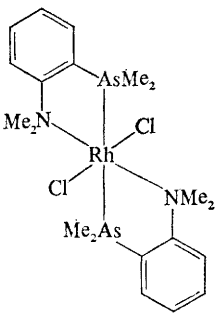
Table *Grunwald–Winstein m values for substitution at halogeno-palladium*(II) *complexes in mixed aqueous media*[52]

	k_1 *term*	k_2 *term*
$[PdI(dien)]^+$	0.33	0.63[a]
$[PdI(Et_4dien)]^+$	0.42	
$[PdCl(Et_4dien)]^+$	0.42—0.45	

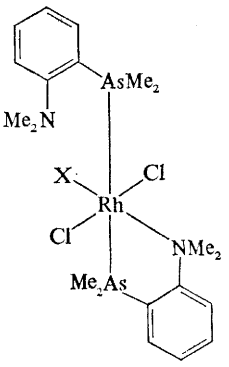
[a] For chloride substitution.

bond cleavage and leaving halide solvation are both important in determining reactivity trends for these complexes.[52]

A Grunwald–Winstein analysis was also found valuable in discussing kinetics of aquation and of formation of the rhodium(III) complexes (2) (X = Cl, Br, or I).[53] The reaction (1) + $X^- \rightarrow$(2) goes more rapidly in more polar solvents, as would be expected for a reaction between oppositely charged ions. Rate constants for the reverse reaction, (2)$\rightarrow$(1) + X^-, in aliphatic alcohols correlate with Grunwald–Winstein solvent *Y* values. The determined *m* values (1.24 for X = Cl, 1.19 for X = Br, and 0.95 for X = I) indicate extensive rhodium–halide bond stretching in transition-state formation.[53] Grunwald–Winstein plots for substitution in the $[W_6Cl_{14}]^{2-}$ anion are somewhat curved, with *m* tending to *ca.* 1.8 as pure water is approached.[48] A quasi-Grunwald–Winstein treatment of racemization rates for *cis*-$[PtClR(PEt_3)_2]$ has also been undertaken.[54]



(1)



(2)

Grunwald–Winstein analyses of kinetic results have proved less successful for the two-stage mercury(II)-catalysed aquation of the $[RuCl(NH_3)_5]^{2+}$ cation,[51] for associative attack of cyanide at the $[Fe(bipy)_3]^{2+}$ cation,[55] and for aquation of the $[Fe(phen)_3]^{2+}$ cation.[37] Logarithms of rates of isomerization of *trans*-$[Cr(ox)_2(OH_2)_2]^-$ correlate better with logarithms of rates of base hydrolysis of ethylene chlorohydrin than with solvent *Y* values (*i.e.* than with logarithms of rates of t-butyl chloride solvolysis).[56]

[52] L. A. P. Kane-Maguire and G. Thomas, *J.C.S. Dalton*, 1975, 1890.
[53] A. Peloso and L. Volponi, *J.C.S. Dalton*, 1976, 923.
[54] R. Romeo, D. Minniti, and S. Lanza, *Inorg. Chim. Acta*, 1976, **18**, L15.
[55] M. J. Blandamer, J. Burgess, and J. G. Chambers, *J.C.S. Dalton*, 1976, 606.
[56] H. Kelm, H. Stieger, and G. M. Harris, *Chem. Ber.*, 1971, **104**, 2743.

Other Solvent Parameters. Applications during the past year and a half have been to series of pure rather than mixed solvents. Correlations with Gutmann donor numbers have been reported for reaction of $[CoCl_3(solvent)]^-$ anions with chloride,[57] for formation reactions of M^{2+} cations,[58] and for racemization of $[Ni(phen)_3]^{2+}$.[59] Gutmann's latest review of solvent effects on reactivities suggests that solvent acceptor numbers[50] as well as solvent donor numbers may be needed for satisfactory correlations.[60] Correlations with E_T values have been discussed for decomposition of the alkyne complexes $[PtClMe(bipy)(MeO_2CC{\equiv}CCO_2Me)]$ and $[PtIMe(bipy)(F_3CC{\equiv}CCF_3)]$. In the former case rates vary greatly with solvent and correlate with solvent E_T values, suggesting rate-determining loss of chloride, whereas in the latter case rates vary very little with solvent, suggesting rate-determining alkyne loss.[61] Rates of addition of bipy to $[Ni(dtp)_2]$ do not correlate with empirical solvent parameters (*cf.* above).[36]

Thermodynamic Aspects.—The correlation of rates with thermodynamic characteristics of solutes (reactants) and solvents, particularly the former, has been a topic of increasing interest in the past year or two.

Reactant Solvation. Simple inorganic ions often become progressively less favourably solvated as the proportion of the organic component increases in series of binary aqueous mixtures. This has been established for, *e.g.*, hydroxide and chloride, whose Gibbs free energies of transfer (ΔG_{tr}) from water into binary aqueous mixtures are generally markedly positive. Thus if, for base hydrolysis of an inorganic complex, the Gibbs free energies of transfer of the relatively large complex and transition state from water into mixed solvents are relatively small, the reactivity trend for base hydrolysis will be predominantly determined by $\Delta G_{tr}(OH^-)$ and will be of increasing rate with increasing proportion of organic co-solvent. This seems to be the case for, *e.g.*, base hydrolysis of $[Co(DMSO)(NH_3)_5]^{3+}$ in alcohol–water mixtures,[62] of $[Co(en)_3]^{3+}$ in DMSO–water mixtures,[63] of polyphosphates in dioxan–water,[64] and of tetraphenylphosphonium chloride in acetone–water.[12,*] In the case of base hydrolysis of the $[Co(en)_3]^{3+}$ cation, which is S_N1cb in mechanism, the Gibbs free energy of transfer of the hydroxide affects the observed rate constant *via* the equilibrium constant for conjugate base generation rather than the rate constant for decomposition of the conjugate base.[63] Similarly, reactivity trends for reaction of Fe^{3+}_{aq} and of $Fe(OH)^{2+}_{aq}$ with chloride in methanol–water mixtures may be dominated by the effect of $\Delta G_{tr}(Cl^-)$ on the outer-sphere association constant in the Eigen–Wilkins formation mechanism.[27] Differences between rates of formation of ternary

* Increasing rates of base hydrolysis of ethyl acetate with increasing proportion of non-aqueous component in DMSO–water mixtures have been ascribed to an entropy effect rather than to hydroxide solvation enthalpy changes.[65]

[57] U. Mayer, *Pure Appl. Chem.*, 1975, **41**, 291.
[58] H. Hoffmann, *Pure Appl. Chem.*, 1975, **41**, 327.
[59] T. Fujiwara and Y. Yamamoto, *Inorg. Nuclear Chem. Letters*, 1975, **11**, 635.
[60] V. Gutmann, *Coordination Chem. Rev.*, 1976, **18**, 225.
[61] N. Chaudhury and R. J. Puddephat, *J. Organometallic Chem.*, 1975, **87**, C45.
[62] M. Birus, W. L. Reynolds, M. Pribanić, and S. Ašperger, *Croat. Chem. Acta*, 1975, **47**, 561.
[63] D. M. Goodall and M. J. Hardy, *J.C.S. Chem. Comm.*, 1975, 919.
[64] M. Watanabe, S. Sato, and H. Saito, *Bull. Chem. Soc. Japan*, 1975, **48**, 896.
[65] R. Fuchs, C. P. Hagan, and R. F. Rodewald, *J. Phys. Chem.*, 1974, **78**, 1509.

nickel(II) complexes in methanol and in acetonitrile correlate with Gibbs free energies of transfer of the incoming groups between the two solvents.[66]

The pattern of Gibbs free energies of transfer of cyanide from water to binary aqueous mixtures must be similar to that for hydroxide and, especially, chloride. On this assumption, it is possible to rationalize observed reactivity trends for the reaction of $[Fe(bipy)_3]^{2+}$ with cyanide in terms of a predominant effect of $\Delta G_{tr}(CN^-)$.[55] However, a subsequent publication which gave estimated values for $\Delta G_{tr}\{[Fe(phen)_3]^{2+}\}$ from water to binary aqueous mixtures and to pure solvents shows that these values and values of ΔG_{tr} (transition state) are significant in determining dissociation rate trends for this cation.[37] $\Delta G_{tr}(CN^-)$ must also make an important contribution to the rate trend for reaction of $[Re(CO)_5I]$ with cyanide in methanol–water mixtures.[67]

Hydrogen ions are known to have a marked catalytic effect on rates of dissociation of aminocarboxylato-complexes of metal cations. Addition of dioxan to an aqueous solution of such a ligand will have different effects on $pK_a(NH_2)$ and $pK_a(CO_2^-)$. The observed effect of dioxan–water solvent composition on rates of dissociation of edta and cydta complexes of thulium(III) suggests that the catalytic effect of added H^+ can be ascribed to protonation of nitrogen rather than oxygen in the co-ordinated ligand.[68]

Solvents. Solvent transfer parameters have been used from time to time in diagnosis of mechanisms of organic reactions. Now their first use in an inorganic system has been discussed. Comparisons between kinetic results and solvent transfer activity coefficients for solvolysis of $[Cr(NCS)_6]^{3-}$ in DMSO, DMF, and dimethylacetamide have been considered in terms of a dissociative mechanism. The DMSO results can be accommodated by a dissociative model for the transition state, but those in DMF and dimethylacetamide fit less well.[69] It is interesting to compare these conclusions with, for instance, the dissociative mechanism proposed by the same authors for anation of the $[Cr(DMSO)_6]^{3+}$ and $[Cr(DMF)_6]^{3+}$ cations,[70,71] and the associative mechanism suggested on the basis of the determined activation volume for exchange of DMSO with $[Cr(DMSO)_6]^{3+}$.[72]

The reflection of inter-solvent attractions in reactivity trends in binary aqueous mixtures has been considered.[1] In the particular case of dissociation of the $[Fe(5\text{-}NO_2phen)_3]^{2+}$ cation, as indeed in Bu^tCl solvolysis, there is a remarkably good correlation between $\Delta G^{\ddagger}$ and G^E, the excess Gibbs free energy of mixing for the respective solvent mixtures, for the so-called 'typically aqueous' mixtures.[73] These are mixtures with positive G^E values, and $|TS^E| > |H^E|$, and include such commonly studied mixtures as aqueous methanol, ethanol, t-butyl alcohol, acetone, dioxan, and THF. A similar $\Delta G^{\ddagger}/G^E$ correlation has been reported for *D* substitution by cyanide at the $[Fe(CN)_5(3,5\text{-}Me_2py)]^{3-}$ anion.[74]

[66] J. F. Coetzee and D. M. Gilles, *Inorg. Chem.*, 1976, **15**, 405.
[67] M. J. Blandamer, J. Burgess, S. J. Cartwright, and M. Dupree, *J.C.S. Dalton*, 1976, 1158.
[68] A. V. Stepanov and T. P. Makarova, *Russ. J. Inorg. Chem.*, 1974, **19**, 1282.
[69] S. T. D. Lo and D. W. Watts, *Austral. J. Chem.*, 1975, **28**, 1907.
[70] S. T. D. Lo and D. W. Watts, *Austral. J. Chem.*, 1975, **28**, 491.
[71] S. T. D. Lo and D. W. Watts, *Austral. J. Chem.*, 1975, **28**, 501.
[72] D. R. Stranks and T. W. Swaddle, *J. Amer. Chem. Soc.*, 1971, **93**, 2783.
[73] M. J. Blandamer, J. Burgess, and R. I. Haines, *J.C.S. Dalton*, 1976, 385.
[74] M. J. Blandamer, J. Burgess, and R. I. Haines, *J.C.S. Dalton*, 1976, 1293.

Solvent Structure.—Plots of activation enthalpies and entropies against solvent composition for the reaction of nickel(II) with pada in t-butyl alcohol–water mixtures show maxima and minima. These extrema are larger, and occur at a smaller mole fraction of alcohol, than in analogous plots for the same reaction in methanol–water mixtures. These results are consistent with currently accepted theories of the effects of added alcohols on water structure.[75] Solvent structural effects have also been invoked to explain some of the extrema in activation parameter *vs.* solvent composition plots for the same reaction in acetonitrile–water mixtures,[76] and some aspects of the kinetics of reaction of nickel(II) with acetate in aqueous mixtures and some non-aqueous solvents.[77] Solvent structural effects on observed rate constants for formation reactions of this type are thought to operate on the outer-sphere association constant rather than on the subsequent ligand interchange rate constant[42] (*cf.* solvent isotope section above). It is becoming increasingly clear that the possibilities of specific interactions with incoming ligands and, in the case of multidentate ligands, rate-determining chelate-ring closure, have to be considered alongside solvent structural effects in discussing kinetics of complex formation in mixed and non-aqueous solvents.[66,78]

Solvent structural factors seem to have little effect on activation parameters for aquation of $[Co(DMSO)(NH_3)_5]^{3+}$ in ethanol–water mixtures,[79] but are significant in polyphosphate hydrolysis (which is probably S_N2) in dioxan–water and formic acid–water media.[64,80] Solvent structure is important in determining kinetic parameters for reaction of copper(II) with chlorophyllic acid in mixed non-aqueous media (see below).

Photochemistry.—A few observations have been published on photochemical behaviour of chromium(III) complexes in aqueous acetone {$[CrCl(RNH_2)_5]^{2+}$ cations[81]} and in non-aqueous media {$[Cr(NCS)_6]^{3-}$ in methanol and ethanol;[82] $[Cr(bipy)_3]^{3+}$ and $[Cr(phen)_3]^{3+}$ in DMSO[83]}. Relevant photochemical reports and comments on cobalt(III) complexes refer to $[CoX(NH_3)_5]^{2+}$ cations (with X = Br,[84,85] NO_2,[85,86] or N_3 [86]) and to the $[Co(CN)_6]^{3-}$ anion in aqueous alcohols[87] and in a range of pure solvents.[88] Laser flash-photolysis studies of $[Re_2Cl_8]^{2-}$ in acetonitrile {product $[ReCl_4(MeCN)_2]^-$} and in methylene chloride (no net reaction) indicate stronger solvation by the former solvent, but no direct rhenium–acetonitrile interaction in or before the rate-determining step.[89]

[75] E. F. Caldin and P. Godfrey, *J.C.S. Faraday I*, 1974, **70**, 2260.
[76] H. P. Bennetto and Z. S. Imani, *J.C.S. Chem. Comm.*, 1975, 333.
[77] S. Harada, T. Yasunaga, K. Tamura, and N. Tatsumoto, *J. Phys. Chem.*, 1976, **80**, 313.
[78] P. K. Chattopadhyay and J. F. Coetzee, *Inorg. Chem.*, 1976, **15**, 400.
[79] M. Glavas and W. L. Reynolds, *J.C.S. Dalton*, 1975, 1706.
[80] M. Watanabe, S. Sato, and H. Saito, *Bull. Chem. Soc. Japan*, 1975, **48**, 3593.
[81] C. F. C. Wong and A. D. Kirk, *Canad. J. Chem.*, 1975, **53**, 419.
[82] I. B. Neporent and E. B. Sveshnikova, *Russ. J. Inorg. Chem.*, 1975, **20**, 375.
[83] N. A. P. Kane-Maguire and C. H. Langford, *Inorg. Chem.*, 1976, **15**, 464.
[84] J. F. Endicott, G. J. Ferraudi, and J. R. Barber, *J. Amer. Chem. Soc.*, 1975, **97**, 219.
[85] J. F. Endicott, *Inorg. Chem.*, 1975, **14**, 448.
[86] P. Natarajan, *J.C.S. Chem. Comm.*, 1975, 26.
[87] F. Scandola, M. A. Scandola, and C. Bartocci, *J. Amer. Chem. Soc.*, 1975, **97**, 4757.
[88] K. Nakamaru, K. Jin, A. Tazawa, and M. Kanno, *Bull. Chem. Soc. Japan*, 1975, **48**, 3486.
[89] R. H. Fleming, G. L. Geoffroy, H. B. Gray, A. Gupta, G. S. Hammond, D. S. Kliger, and V. M. Miskowski, *J. Amer. Chem. Soc.*, 1976, **98**, 48.

Pure Solvents: Miscellaneous.—*Solvent Exchange.* Recent examples of kinetic studies of solvent exchange at metal cations, formally the simplest substitution reaction in solution, include exchange of DMF at chromium(III)[90] and of DMSO at aluminium(III).[91] The latter investigation used an ingeniously modified stopped-flow device integrated with a pulse Fourier-transform n.m.r. spectrometer, an apparatus of considerable potential value in fast-reaction studies.[92]

Solvolysis. Solvolysis of the $[BH_4]^-$ anion has been studied in liquid ammonia[93] and in DMSO.[94] In both cases determined activation parameters are compared with those for hydrolysis. The comparison of rates in DMSO and in water underlines the importance of easy proton transfer in the latter solvent in determining reactivity. Kinetics of solvolysis of $[SnCl_4(py)_2]$ and of related compounds in acetonitrile and in nitromethane have large, positive values of $\Delta S^{\ddagger}$, betokening S_N1 mechanisms.[95]

Rates of solvolysis of $[CoX(NH_3)_5]^{2+}$ (X = Cl, Br, or I) in liquid ammonia have been reported. The mechanism is S_N1cb; interestingly it has proved possible to determine the equilibrium constants for generation of the conjugate bases and their rates of dissociation separately.[96] The S_N1cb solvolysis of *trans*-$[CoCl(CN)(en)_2]^+$ in methanol has been investigated.[97] Multitudinous publications on solvolysis of bis-dimethylglyoximato-complexes of cobalt(III) in mixed aqueous media[98] are now being followed by reports of studies in methanol[99] and in DMF.[100] Rather than risk a definite assignment of mechanism the authors sit safely but inelegantly on the fence by suggesting 'a mechanism involving the elements of both dissociation and association'.[99]

Several further papers have appeared on solvolysis,[101,102] anation,[102] and isomerization[102,103] reactions of $[CrX_2(en)_2]^+$, $[CrX(DMF)(en)_2]^{2+}$, and $[Cr(DMF)_2(en)_2]^{3+}$ (X = Cl or Br) and DMSO analogues. Solvent interchange between DMF and DMSO has also been investigated in the series *trans*-$[Cr(DMF)_2(en)_2]^{3+}$/*trans*-$[Cr(DMF)(DMSO)(en)_2]^{3+}$/*trans*-$[Cr(DMSO)_2(en)_2]^{3+}$; rate constants and activation parameters have been reported.[104] Discussion continues as to whether these reactions are I_d[101–104] or I_a.[105]

Ligand Exchange and Replacement. Three papers deal with ligand exchange at acetylacetonate complexes and the role of the solvent therein, for $[Cr(acac)_3]$ in

[90] S. T. D. Lo and T. W. Swaddle, *Inorg. Chem.*, 1975, **14**, 1878.
[91] A. J. Brown, D. A. Couch, O. W. Howarth, and P. Moore, *J. Magn. Resonance*,1976, **21**, 503.
[92] D. A. Couch, O. W. Howarth, and P. Moore, *J. Phys.* (*E*), 1975, **8**, 831.
[93] T. S. Briggs and W. L. Jolly, *Inorg. Chem.*, 1975, **14**, 2267.
[94] L. M. Abts, J. T. Langland, and M. M. Kreevoy, *J. Amer. Chem. Soc.*, 1975, **97**, 3181.
[95] S. S. Sandhu and J. C. Bhatia, *Res. J. Sci.*, 1974, **1**, 1 (*Chem. Abs.*, 1975,**83**, 16376); R. C. Paul, M. M. Mahajan, and J. C. Bhatia, *Indian J. Chem.*, 1975, **13**, 966.
[96] S. Balt and G. F. Pothoff, *J. Coordination Chem.*, 1975, **4**, 167, 247.
[97] M. Biruš, Z. Bradić, D. Pavlović, M. Pribanić, and S. Ašperger, *J. Inorg. Nuclear Chem.*,1975, **37**, 600.
[98] See the appropriate sections of Volumes 1—4 of these Reports.
[99] N. M. Samus', T. S. Luk'yanets, and Z. K. Fung, *Russ. J. Inorg. Chem.*, 1974, **19**, 1351.
[100] N. M. Samus', T. S. Luk'yanets, and A. V. Ablov, *Russ. J. Inorg. Chem.*, 1974, **19**, 1353.
[101] W. G. Jackson and W. W. Fee, *Inorg. Chem.*, 1975, **14**, 1154.
[102] W. G. Jackson and W. W. Fee, *Inorg. Chem.*, 1975, **14**, 1161.
[103] W. G. Jackson and W. W. Fee, *Inorg. Chem.*, 1975, **14**, 1170.
[104] W. G. Jackson and W. W. Fee, *Inorg. Chem.*, 1975, **14**, 1174.
[105] T. W. Swaddle, *Coordination Chem. Rev.*, 1974, **14**, 217.

dioxan,[106] for $[Co(acac)_3]$ again in dioxan,[107] and for the $[Ti(acac)_3]^+$ cation in acetonitrile.[44]

Kinetic results for the replacement of X (F, Cl, or Br) in $[RuX_2(bipy)_2]$ by pyridine in a variety of aprotic solvents indicate a dissociative mechanism with a transient $[RuX(bipy)_2]^+$ intermediate.[108] The range of rate constants for nucleophilic substitution in $[PdX(dien)]^+$ cations by a given series of incoming groups shows that there is a marked decrease in nucleophilic discrimination in going from, *e.g.*, water or methanol to the dipolar aprotic solvents DMF or DMSO.[109]

Complex Formation: Inert Cations. Several reports deal with the formation of chromium(III) complexes in dipolar aprotic solvents, especially DMF and DMSO. Reactions of $[Cr(DMSO)_6]^{3+}$ with N_3^- or NCS^- are I_d, the reaction with Cl^- perhaps more complicated.[70] Ion-triples as well as ion-pairs may be kinetically significant in DMSO.[71] Kinetics of reactions of complexes of the type *trans*-$[Cr(DMSO)_2(en)_2]^{3+}$ and *trans*-$[Cr(DMF)_2(en)_2]^{3+}$ with halide ions have also been described.[102,103]

Complex Formation: Labile Cations. Solvent effects on reactivity in the formation of complexes of metal(II) cations with unidentate ligands have been reviewed, with special reference to magnesium(II) and to the solvents methanol, acetonitrile, DMF, and DMSO.[58] There has been controversy over the mechanism of reaction of thiocyanate with nickel(II) in DMSO, with supporters of the usual Eigen–Wilkins I_d mechanism[110] and of a *D* mechanism.[111] The most recent investigators of this reaction report rate constants and activation parameters and favour the I_d mechanism.[112] There has been further discussion of the mechanism of the reaction between nickel(II) and bipy in DMSO; an earlier suggestion that the rate-determining step is ring closure is not supported by recent observations.[113] Rate constants for the reaction of acetate,[77] of other carboxylates,[114] and of pada[115] with nickel(II) in several non-aqueous solvents have been determined.

Kinetics of formation of ternary complexes of nickel(II) in acetonitrile[78] and in methanol,[66] solvents which are approximately isodielectric and have similar donor strengths towards Ni^{2+}, have been described. Some reactions in acetonitrile are unexpectedly fast, perhaps owing to favourable interactions between incoming groups such as phen with polarized acetonitrile bonded to Ni^{2+}.[78] Differences between reactivities with respect to incoming groups X^- between acetonitrile and methanol media can be correlated with free energies of transfer of X^- between these

[106] S. Wajda and A. Szemik, *Bull. Acad. polon. Sci., Sér. Sci. chim.*, 1975, **23**, 833 (*Chem. Abs.*, 1976, **84**, 80349).
[107] S. Wajda and A. Szemik, *Bull. Acad. polon. Sci., Sér. Sci. chim.*, 1976, **24**, 111 (*Chem. Abs.*, 1976, **84**, 185471).
[108] F. Maspero and G. Ortaggi, *Ann. Chim. (Italy)*, 1974, **64**, 115 (*Chem. Abs.*, 1975, **83**, 48898).
[109] M. Cusumano, V. Ricevuto, R. Romeo, and M. Trozzi, *Atti Accad. Peloritana Pericolanti, Cl. Sci. fis. mat. nat.*, 1974, **54**, 175 (*Chem. Abs.*, 1976, **84**, 185446).
[110] F. Dickert and H. Hoffmann, *Ber. Bunsengesellschaft phys. Chem.*, 1971, **75**, 1320; J. Williams, S. Petrucci, B. Sesta, and M. Battistini, *Inorg. Chem.*, 1974, **13**, 1968.
[111] L. S. Frankel, *Chem. Comm.*, 1969, 1254; *Inorg. Chem.*, 1971, **10**, 814; C. H. Langford and H. G. Tsiang, *Inorg. Chem.*, 1970, **9**, 2346.
[112] J. F. Coetzee and E. Hsu, *J. Solution Chem.*, 1975, **4**, 45.
[113] D. M. W. Buck and P. Moore, *J.C.S. Dalton*, 1975, 409.
[114] S. Harada, *J. Sci. Hiroshima Univ., Ser. A*, 1975, **39**, 197.
[115] H. P. Bennetto and Z. S. Imani, *J.C.S. Faraday I*, 1975, **71**, 1143.

two solvents.[66] The general discussion of these ternary complex formation reactions presents a consistent picture of these and earlier results.

Isomerization. Differences between kinetic parameters for intramolecular rearrangement within organotin β-diketonates of the $[Sn(acac)_2Ph_2]$ type in bromoform, chloroform, and dichloromethane are small.[116]

Rates of *cis*→*trans* isomerization for $[PtClR(PEt_3)_2]$ in methanol and propan-2-ol are consistent, from a qualitative Grunwald–Winstein analysis, with rate-determining chloride loss and generation of a three-co-ordinate intermediate.[54] The solvent must also play a vital role in *cis*⇌*trans* isomerizations involving five- or six-co-ordinate intermediates, as for example for $[Pd(N_3)_2(PPh_3)_2]$.[117]

Miscellaneous. Rates of palladium–carbene complex formation in reaction (2) depend on solvent nature, increasing in the order acetone ~ dioxan < 1,2-dichloro-

$$cis\text{-}[PdCl_2(p\text{-}CNC_6H_4Cl)(PPh_3)] + PhNHMe \longrightarrow cis\text{-}[PdCl_2\{C(NH\text{-}p\text{-}C_6H_4Cl)NMePh\}(PPh_3)] \quad (2)$$

ethane < benzene. This order can be rationalized in terms of variation of solvent–incoming *N*-methylaniline interactions.[118]

The majority of studies cited so far have been concerned with 'normal' solvents at temperatures around ambient. Kinetic studies at considerably higher temperatures can be conducted in molten salts. Recent examples include pyrophosphate degradation in molten nitrates, where a first-order reaction in pyrophosphate is reported in the presence of Li^+,[119] and a radiochemical investigation of rates of sulphur migration in thiosulphate in potassium thiocyanate melts.[120] Here the sulphur can move intramolecularly within the thiosulphate and can undergo exchange with the thiocyanate.

Mixed Aqueous Solvents: Miscellaneous.—*Solvolysis.* A dissociative mechanism operates for the solvolyses of $[CoCl(NH_3)_5]^{2+}$ in aqueous ethanol and in aqueous DMSO[121] and of *cis*-$[CoCl(OH)(en)_2]^+$ in a wide range of mixed solvents.[122] Kinetics of aquation of $[CrI(OH_2)_5]^{2+}$ in aqueous methanol and in aqueous DMSO can be interpreted as indicating a *D* or, less convincingly, an I_a mechanism.[123] Now the establishment of $\Delta V^{\neq}$ values indicates the I_a mechanism, though a *D* mechanism for the conjugate base $[CrI(OH)(OH_2)_4]^+$.[124] Some kinetic observations have been made relating to platinblau, the intensely coloured product from $[PtCl_4]^{2-}$ in aqueous acetonitrile.[125] Rates of hydrolysis of phosphonium ylides and salts in THF–water mixtures are very sensitive to solvent composition.[126]

[116] N. Serpone and K. A. Hersh, *Inorg. Chem.*, 1974, **13**, 2901.
[117] D. A. Redfield, L. W. Cary, and J. H. Nelson, *Inorg. Chem.*, 1975, **14**, 50.
[118] P. Uguagliati, B. Crociani, U. Belluco, and L. Calligaro, *J. Organometallic Chem.*, 1976, **112**, 111.
[119] J. L. Copeland, A. S. Metcalf, and B. R. Hubble, *J. Phys. Chem.*, 1976, **80**, 236.
[120] A. Siebert, *Z. phys. Chem. (Frankfurt)*, 1975, **97**, 11.
[121] W. L. Reynolds and E. S. Barber, *Internat. J. Chem. Kinetics*, 1975, **7**, 443.
[122] V. V. Udovenko, L. G. Reiter, and A. A. Andrieko, *Russ. J. Inorg. Chem.*, 1974, **19**, 1525.
[123] S. P. Ferraris and E. L. King, *J. Amer. Chem. Soc.*, 1970, **92**, 1215; D. B. Vanderheiden and E. L. King, *ibid.*, 1973, **95**, 3860.
[124] M. C. Weekes and T. W. Swaddle, *Canad. J. Chem.*, 1975, **53**, 3697.
[125] A. K. Johnson and J. D. Miller, *Inorg. Chim. Acta*, 1976, **16**, 93.
[126] A. Schnell and J. C. Tebby, *J.C.S. Chem. Comm.*, 1975, 134.

Formation. The dependence of rate on solvent composition for formation reactions of nickel(II) has been established for ethylenediamine in acetone–water,[127] for acetate in methanol–water and dioxan–water,[114] and for pada in acetonitrile–water.[76] For the last system it is suggested that the mechanism of the reaction may change as the solvent composition changes.

Some kinetic data are available for reactions of chromium(III) in methanol–water[128] and in DMSO–water mixtures,[129] and for (dissociative) replacement of water by DMSO in $[Cr(NO_3)(OH_2)_5]^{2+}$ in water–DMSO mixtures.[130] Kinetic results for reaction of *trans*-$[Co(dmgH)_2(O_2SC_6H_4Me)(solvent)]$ with pyridine or with triphenylphosphine in water, methanol, ethanol, and water–methanol mixtures are more easily accommodated by a *D* than by an I_d mechanism.[131]

Non-aqueous Solvent Mixtures.—The kinetic pattern for reaction between nickel(II) and murexide in mixtures consisting of the co-ordinating solvent DMSO and the non-co-ordinating solvent nitromethane fit an I_d but not a *D* mechanism.[132] Rate-limiting ring closure is not expected in this system, but may be a complicating factor in the reactions of nickel(II) with 4-(2-pyridylazo)resorcinol and with 2,2′-nitrilodiindane-1,3-dione in pyridine–nitromethane mixtures.[133] Trends and extrema in the kinetic parameters for reaction of copper(II) with chlorophyllic acid in pentanol–acetic acid and in methanol–acetic acid mixtures are explained in terms of solvent structural properties.[134]

The kinetics of thermal decomposition of nitrogen trichloride have been monitored in solutions in carbon tetrachloride containing electron-donor co-solvents such as benzene, toluene, cumene, and mesitylene.[135]

3 Salt Effects

The dependence of rate constant on ionic strength is still widely used, often in conjunction with the dependence of rate constant on dielectric constant, as an indicator of substitution mechanism. Recent instances of this classical approach include the reaction of *trans*-$[Co(dmgH)_2(SCN)(tu)]$ with thiourea (tu),[24] aquation of *trans*-$[Rh(dmgH)_2Cl(tu)]$,[25] aquation of the $[Co(O_2CCH_2Cl)(NH_3)_5]^{2+}$ cation,[136] and substitution at the $[Fe(CN)_5(OH_2)]^{3-}$ anion by nitrite, thiocyanate, sulphite, or nitrosobenzene.[137] Salt effects on observed rate constants for the reaction of nickel(II) with pyrophosphate operate *via* the outer-sphere association constant rather than *via* the interchange rate constant.[138]

[127] V. A. Shormanov, G. A. Krestov, E. A. Trupikov, and V. D. Gusev, *Russ. J. Inorg. Chem.*, 1975, **20**, 1521.
[128] C. M. Melsa and R. J. Baltisberger, *Analyt. Chem.*, 1976, **48**, 435.
[129] G. Rábai, G. Bazsa, and M. T. Beck, *Magyar Kém. Folyóirat*, 1976, **82**, 60.
[130] M. L. Mitchell, T. Montag, J. H. Espenson, and E. L. King, *Inorg. Chem.*, 1975, **14**, 2862.
[131] J. M. Palmer and E. Deutsch, *Inorg. Chem.*, 1975, **14**, 17.
[132] J. P. K. Tong and C. H. Langford, *Canad. J. Chem.*, 1976, **54**, 706.
[133] H. L. Fritz and J. H. Swinehart, *Inorg. Chem.*, 1975, **14**, 1935.
[134] B. D. Berezin and L. V. Klopova, *Russ. J. Phys. Chem.*, 1974, **48**, 186.
[135] B. A. Radbil, *Kinetika i Kataliz*, 1975, **16**, 360.
[136] O. Grancicova and V. Holba, *Chem. Zvesti*, 1975, **29**, 433 (*Chem. Abs.*, 1976, **84**, 65727).
[137] A. Zmikić, M. Pribanić, D. Pavlović, and S. Ašperger, *Croat. Chem. Acta*, 1975, **47**, 117 (*Chem. Abs.*, 1976, **84**, 35825).
[138] B. Perlmutter-Hayman and F. Secco, *Israel J. Chem.*, 1973, **11**, 623 (*Chem. Abs.*, 1975, **82**, 7954).

Salt effects on reactivities which can be ascribed to the consequences of ion-pairing include those of anions ($MeCO_2^-$, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}) on acid and base hydrolysis of the $[Co(ox)(NH_3)_5]^+$ cation[139] and of cations (Li^+, Na^+, K^+) on the reaction between $[Fe(CN)_6]^{4-}$ and $[NO(SO_3)_2]^{2-}$, the anion of Fremy's salt.[140] Specific effects of added halide ions on aquation of the $[Fe(bipy)_3]^{2+}$ cation[15,141] and on racemization of the $[Co(phen)_3]^{3+}$ cation[142] have been described. The close similarity of rates of aquation of $[Co(DMSO)(NH_3)_5]^{3+}$ in perchloric acid–sodium perchlorate media of constant perchlorate concentration has been held to be indicative of an I_d mechanism.[79,143] Effects of alkali metal and of tetra-alkylammonium cations on the hydrolyses of Me_3NSO_3[144] and of polyphosphates[80] can be discussed in terms of the effects of the added ions on water structure. Salt effects on Me_3NSO_3 hydrolysis strongly suggest a dissociative mechanism for this reaction in neutral solution.[144] In contrast to these hydrolyses, tetra-alkylammonium salts have no specific effect on rates of reaction of $[Fe(bipy)_3]^{2+}$ with cyanide.[55] Non-classical salt effects on the bromide–bromate reaction have been attributed to microdielectric and solvation variation.[145] Attention has been drawn to the need for great care over reagent purity when probing specific ion effects on reactivities, with special mention of base hydrolysis of the $[CoBr(NH_3)_5]^{2+}$ cation.[146]

Interest continues in the effects of micellar agents on rates of inorganic reactions. Aquation of oxalato-cobalt(III) and -chromium(III) complexes is mentioned in a review of reversed micellar systems;[147] predicted and actual rates have been compared for a variety of reactions, including the mercury(II)-catalysed aquation of $[CoX(NH_3)_5]^{2+}$ cations.[148,149] Micellar effects on uncatalysed aquation of *cis*- and of *trans*-$[CoCl_2(en)_2]^+$ are small (as expected) but real.[150] Other reactions for which the kinetic consequences of micelle or polyelectrolyte addition have been described include complex formation from nickel(II),[151] the conversion of ammonium cyanate into urea,[152] and the hydrolysis of pyrophosphate.[153]

[139] A. C. Dash and R. K. Nanda, *J. Indian Chem. Soc.*, 1975, **52**, 298.
[140] V. Holba and O. Volárová, *Coll. Czech. Chem. Comm.*, 1975, **40**, 355.
[141] S. Raman, *J. Inorg. Nuclear Chem.*, 1976, **38**, 781.
[142] M. Yamamoto and Y. Yamamoto, *Inorg. Nuclear Chem. Letters*, 1975, **11**, 691.
[143] W. L. Reynolds, *Inorg. Chem.*, 1975, **14**, 680.
[144] M. J. Blandamer, J. Burgess, and S. H. Morris, *J.C.S. Dalton*, 1975, 2118.
[145] M. Wronská and M. Wawrzeńczyk, *Z. phys. Chem.* (*Leipzig*), 1975, **256**, 183.
[146] P. Stopka and J. Vepřek-Šiška, *Coll. Czech. Chem. Comm.*, 1976, **41**, 1665.
[147] J. H. Fendler, *Accounts Chem. Res.*, 1976, **9**, 153.
[148] K. Mita, T. Okubo, and N. Ise, *J.C.S. Faraday I*, 1976, **72**, 1033.
[149] S. J. Dougherty and J. C. Berg, *J. Colloid Interface Sci.*, 1974, **49**, 135 (*Chem. Abs.*, 1975, **82**, 7985).
[150] M. J. Blandamer, J. Burgess, and J. G. Chambers, *Inorg. Chim. Acta*, 1976, **17**, L37.
[151] S. Kunugi and N. Ise, *Z. phys. Chem.* (*Frankfurt*), 1974, **92**, 69.
[152] K. Mita, S. Kunugi, T. Okubo, and N. Ise, *J.C.S. Faraday I*, 1975, **71**, 936.
[153] D. Turyn, E. Baumgartner, and R. Fernández-Prini, *Biophys. Chem.*, 1974, **2**, 269.

Part III

REACTIONS OF BIOCHEMICAL INTEREST

By
D. N. HAGUE

1 General

Three recently published[1] volumes of the third edition of Boyer's 'The Enzymes' will be of particular interest to readers of this section and for this reason the titles of relevant chapter headings are listed here. Volume 11 includes articles on alcohol, lactate, glutamate, and malate dehydrogenases and on types *b* and *c* cytochromes, Volume 12 includes the iron–sulphur proteins, iron- and copper-containing mono-oxygenases, molybdenum iron–sulphur flavin hydroxylases, and copper-containing oxidases and superoxide dismutase, and Volume 13 considers, amongst other topics, metal-containing flavoprotein dehydrogenases and the cytochrome *c* oxidases and peroxidases. McAuliffe's volume[2] on bioinorganic chemistry is concerned primarily with molybdenum- and iron-containing systems, although there are also small sections on zinc-containing metalloenzymes (carboxypeptidase and carbonic anhydrase) and calcium-binding proteins such as low molecular weight albumins and staphylococcal nuclease. Volume 5 in the series edited by Sigel[3] is entitled 'Reactivity of Coordination Compounds' and other interesting books in our general area include[4] Williams's 'An Introduction to Bioinorganic Chemistry'. Recognizing the difficulty experienced by many workers in the 'no-man's land' of bioinorganic model systems in getting their results published, the editors of the *European Journal of Biochemistry* have decided[5] to look favourably on such papers submitted to them. Reviews which have appeared during the relevant period include one on the role of calcium in biological systems,[6] one on the study of biochemical redox processes by the technique of pulse radiolysis,[7] and one on electron-transfer proteins.[8]

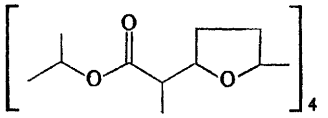
2 Metal Ion Transport through Membranes

Davis and Tosteson[9] have used ^{1}H and ^{13}C n.m.r. techniques to investigate the solution conformations of the cation (M^+) complexes of valinomycin (VAL) and to measure the rate constants and activation energies for the dissociation of the Na^+ and K^+ complexes in acetone and chloroform. Although there is a considerable body

[1] 'The Enzymes', ed. P. D. Boyer, 3rd Edn., Academic Press, New York, Vols. 11, 1975; 12, 1975; 13, 1976.
[2] 'Techniques and Topics in Bioinorganic Chemistry', ed. C. A. McAuliffe, Macmillan, London, 1975.
[3] 'Metal Ions in Biological Systems', ed. H. Sigel, Marcel Dekker, Basel, Vol. 5, 1976.
[4] 'An Introduction to Bioinorganic Chemistry', ed. D. R. Williams, Thomas, Springfield, Illinois, 1976.
[5] *European J. Biochem.*, 1975, **51**, 1.
[6] R. H. Kretsinger and D. J. Nelson, *Coordination Chem. Rev.*, 1976, **18**, 29.
[7] A. Shafferman and G. Stein, *Biochim. Biophys. Acta*, 1975, **416**, 287.
[8] G. R. Moore and R. J. P. Williams, *Coordination Chem. Rev.*, 1976, **18**, 125.
[9] D. G. Davis and D. C. Tosteson, *Biochemistry*, 1975, **14**, 3962.

of information about the structural and functional properties of free valinomycin and its K^+ complex (it will be recalled that VAL shows significant selectivity towards this metal, and there is evidence that conformational changes occur on forming the K–VAL complex), less is known about the structures of complexes formed with the other alkali-metal ions, especially Na^+. This lack of knowledge about the structure of Na–VAL arises partly because, until recently, there was little evidence to suggest that a stable complex is formed at all and partly because previous studies were carried out in polar solvents, in which the association constant of Na^+ for valinomycin is small. Davis and Tosteson conclude that the Na complex (but not the K complex) may exist in at least three different conformational states, depending on the anion and the polarity of the solvent: in acetone, it is distinct from but close to the conformation of free VAL; in chloroform with Br^-, SCN^-, or trinitro-*m*-cresolate (TNC) it is intermediate between that of uncomplexed VAL and K–VAL; and in chloroform with tetraphenylborate it is almost identical to that of K–VAL. (In the latter case the depsipeptide is disposed around the metal ion so that M^+ is shielded from the solvent and the anion whereas in the other two cases the Na^+ is partially co-ordinated to the polar groups of valinomycin while remaining exposed to the solvent and anions.) It seems that the dissociation rate of the NaTNC–VAL complex in $CDCl_3$ is about 20 times higher than that of KTNC–VAL and that the major factor governing this difference is entropic.

The antibiotic nonactin is particularly useful for studying the mechanism of ion transport because it selectively complexes with a wide variety of cations. Crystallographic and n.m.r. studies have shown that the cation is located near the middle of the nonactin molecule (1) and suggest that cation binding proceeds primarily through



(1)

the ester carbonyl oxygens. While it is generally agreed that electrostatic forces are primarily responsible for the stability of the antibiotic–cation complex, at least two distinct models have been advanced to account for the selectivity of nonactin. In the first, it is ascribed entirely to differences in the electrostatic free energy between the solvated ion in solution and the unsolvated ion bound to the antibiotic, whereas in the other it is suggested that the ability of the carrier to distinguish among the cations of one group of the periodic system by forming complexes over a large range of stabilities is largely due to steric interactions within the ligand itself. In a recent Raman study on (1) and its complexes with several M^+ ions, Phillies *et al.* were able to obtain direct evidence[10] that the interaction is primarily electrostatic, thus favouring the former interpretation. Talekar has addressed himself[11] to the question: given that (as the evidence seems to suggest) the nature of the metal–ligand bonding in ionophore complexes is *ca.* 80% ionic and 20% covalent and that these are about the same proportions as in the free aquo-ion, what is the driving force which induces

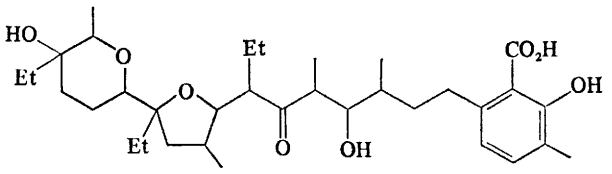
[10] G. D. J. Phillies, I. M. Asher, and H. E. Stanley, *Science*, 1975, **188**, 1027.
[11] S. V. Talekar. *Biochim. Biophys. Acta*, 1975, **375**, 157.

the metal ion to leave the aqueous environment and enter the ionophore? He suggests a model involving hydrogen-bonding in the inner hydration sphere of Li^+_{aq} and Na^+_{aq} which would enable the migration of these ions into the ionophores to be comparatively easily envisaged.

The kinetics of the reaction of K^+ with dibenzo-18-crown-6 (DBC) in methanol have been determined[12] from the longitudinal relaxation time (T_1) of ^{39}K. If the process is represented by

$$K^+ + DBC \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (K^+, DBC)$$

values for k_{-1} (at -34 °C) and its activation energy are, respectively, 610 s^{-1} and 12.6 kcal mol^{-1}. Only a lower limit (10^4 s^{-1}) was obtainable for the corresponding reaction of Rb^+ (at -50 °C), while the previously reported value for Na^+ was 800 s^{-1} at -13 °C (with activation energy 11.7 kcal mol^{-1}). This behaviour is consistent with the known structures of the solid complexes, as determined by *X*-ray crystallography: whereas both Na^+ and K^+ fit neatly into the cavity of the crown form of DBC, the much larger Rb^+ sticks out from it and is therefore, in all probability, less tightly bound. The kinetics of dissociation of the complexes of Ni^{2+} and Mn^{2+} with the ionophore X-537A (2) in methanol have also been measured[13] by the n.m.r. method. The rate constants at 25 °C are, respectively, $(2.4 \pm 0.4) \times 10^2$ s^{-1} (with $\Delta H^{\ddagger} = 4.5 \pm 1.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = -32 \pm 6$ cal K^{-1} mol^{-1}) and 1.4×10^4 $s^{-1} \leqslant k_d \leqslant 1 \times 10^6$ s^{-1}. The value of k_f at 25 °C for Ni^{2+} is $(2.2 \pm 0.4) \times 10^6$ l mol^{-1} s^{-1}, with associated $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger} = 6.8 \pm 1.5$ kcal mol^{-1} and -8 ± 7 cal K^{-1} mol^{-1}. On the assumption that the mechanism is I_d, the value of k_f calculated from the known k_{ex} and the Fuoss-equation value of K_{os} is about two orders of magnitude less than this, but the authors are unable to decide whether the discrepancy reflects a non-I_d mechanism or merely the breakdown of the Fuoss equation when applied to such large ligands as (2).

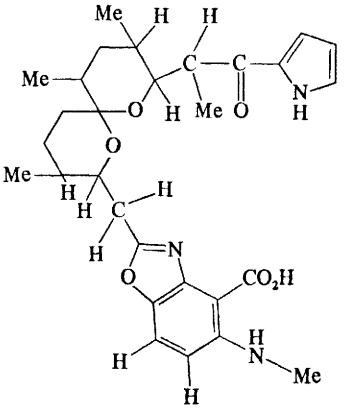


(2)

The naturally occurring ionophore A23187 (3) is being used increasingly to investigate the mechanism of complex physiological processes involving membranes since, in many cases, the presence of A23187 and Ca^{2+} has been found to mimic the effects of hormones or nervous excitation which normally control the processes *in vivo*. ^1H and ^{13}C n.m.r. spectroscopy have recently been used[14] to show that the conformation of the calcium complex differs from that of the free acid, and it has been suggested[15] that a lack of conformational mobility in A23187 is responsible for its high cation-size selectivity.

[12] M. Shporer and Z. Luz, *J. Amer. Chem. Soc.*, 1975, **97**, 665.
[13] H. Degani and H. L. Friedman, *Biochemistry*, 1975, **14**, 3755.
[14] C. M. Deber and D. R. Pfeiffer, *Biochemistry*, 1976, **15**, 132.
[15] D. R. Pfeiffer and H. A. Lardy, *Biochemistry*, 1976, **15**, 935.

A review has recently appeared[16] on the mechanism of the sodium pump.



(3)

3 Metal Complex Formation: Non-redox Systems

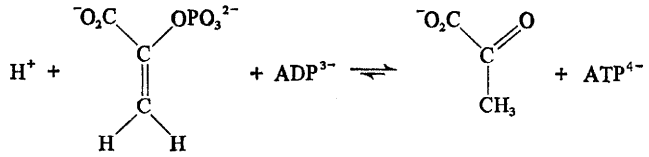
Systems involving Phosphate Groups.—The binding between Mn^{II} and inosine 5′-triphosphate (ITP) has been studied[17] by ^{13}C, ^{1}H, and ^{31}P n.m.r. techniques and it has been shown that the complex present in solution involves one Mn^{2+} ion interacting with one ITP molecule. Moreover, the metal interacts with two distinct sites on the inosine ring, namely the carbonyl group and N-7, but not at the same time. The lifetimes of the complexes in which the metal is bound to CO and N-7 are reported as being, respectively, 6.7×10^{-8} and 5×10^{-8} s, and the activation enthalpies for the dissociation processes are 14 and 9.4 kcal mol^{-1}. The computer mapping procedure in which lanthanide cations are used as n.m.r. probes has been applied[18] to ATP in aqueous solution. A small, closely interrelated family of conformations was obtained as 'best-fits' to the data, one of which (with an *anti* arrangement of the base–ribose unit and a right-handed helical phosphate chain folded towards the adenine part of the molecule) corresponds closely to one of the crystal structure forms. The dependence on metal ions of the rate of dephosphorylation of a group of nucleoside 5′-triphosphates has been investigated further[19] and the authors take pains to point out that care must be taken, in studies with this type of compound, to avoid the use of buffers which contain potential ligands. In a preliminary study with the fluorescence stopped-flow method, it has been shown[20] that the rate constants for several of the elementary steps in the reaction sequence for the ATP-ase action of myosin subfragment 1 with Mn^{2+} as the activating metal are very similar to those with the physiologically important ion Mg^{2+}, which means that the structural and dynamic information obtained by magnetic resonance techniques about the manganese-

[16] R. Whittam and A. R. Chipperfield, *Biochim. Biophys. Acta*, 1975, **415**, 149.
[17] G. P. P. Kuntz and G. Kotowycz, *Biochemistry*, 1975, **14**, 4144.
[18] P. Tanswell, J. M. Thornton, A. V. Korda, and R. J. P. Williams, *European J. Biochem.*, 1975, **57**, 135.
[19] H. Sigel, D. H. Buisson, and B. Prijs, *Bioinorganic Chem.*, 1975, **5**, 1; P. E. Amsler and H. Sigel, *European J. Biochem.*, 1976, **63**, 569.
[20] C. R. Bagshaw, *F.E.B.S. Letters*, 1975, **58**, 197.

containing intermediates may be assumed with a fair degree of confidence to apply to the magnesium analogues. Laser Raman spectroscopy has been used[21] to study the transfer of a phosphate group from ATP to orthophosphate or arsenate in DMSO. The results support a mechanism involving the binding of the Mg^{2+} to the α- and β-phosphates of ATP, leaving the third phosphate free for the transfer reaction. In a study of the factors controlling the association of Mg^{2+} with acyl phosphates, Kluger *et al.*[22] suggest that the failure of this metal to catalyse many non-enzymic reactions even though it is required for the corresponding enzyme reaction is consistent with the control function of enzymic catalysis; thus, enzymic binding is able to create minor perturbations in the distribution of the various complexes present and thereby bring about the observed catalytic patterns.

Mildvan and Grisham have reviewed[23] the role of bivalent cations in the mechanism of enzyme-catalysed phosphoryl and nucleotidyl transfer reactions.

Pyruvate kinase catalyses phosphoryl transfer reactions involving ATP. The reaction most important biologically is the transfer of a phosphoryl group from phosphoenolpyruvate (PEP) to ADP, to form ATP (Scheme 1), although other



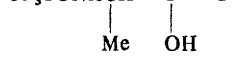
Scheme 1

phosphorylations involving ATP are catalysed by this enzyme (*e.g.* those of hydroxylamine and glycollate). All of these reactions require both bi- and uni-valent cations, which *in vivo* are Mg^{2+} and K^+ but which *in vitro* may be several others. Thus the order of catalytic efficiency for the bivalent ion has been reported to be $Mg^{II} > Mn^{II} > Co^{II} \gg Ni^{II}$ and a fair amount of effort has been expended in recent years in an attempt to elucidate the mechanism of the reaction through the use of the favourable spectral properties of the last three metals. The kinetics have recently been investigated[24] as a function of pH for all four activating metals and the results fall into two groups: Mg^{2+} and Mn^{2+} are quite similar, while Co^{2+} and Ni^{2+} are different from them but similar to one another. On spectral grounds, it is concluded that the co-ordination number of the metal at the active site in the Co^{II}- and Ni^{II}-activated enzymes (from rabbit muscle) is six, the same as that in the manganese case. From e.s.r. measurements on the cobalt(II) enzyme, it has been concluded[25] that, in the active quaternary pyruvate kinase–Co^{2+}–K^+–PEP complex, the interaction between PEP and Co^{II} is mainly outer-sphere. (This contrasts with the situation for the binary Co^{2+}–PEP complex, where the PEP enters the inner sphere of the metal.) N.m.r. results with the manganese(II)-activated enzyme have led Sloan and Mildvan to conclude[26] that there is a profound change in the conformation and structure of

[21] A. Lewis, N. Nelson, and E. Racker, *Biochemistry*, 1975, **14**, 1532.
[22] R. Kluger, P. Wasserstein, and K. Nakaoka, *J. Amer. Chem. Soc.*, 1975, **97**, 4298.
[23] A. S. Mildvan and C. M. Grisham, *Structure and Bonding*, 1974, **20**, 1.
[24] C. Y. Kwan, K. Erhard, and R. C. Davis, *J. Biol. Chem.*, 1975, **250**, 5951.
[25] E. Melamud and A. S. Mildvan, *J. Biol. Chem.*, 1975, **250**, 8193.
[26] D. L. Sloan and A. S. Mildvan, *J. Biol. Chem.*, 1976, **251**, 2412.

Mn^{II}–ATP (from a folded chelate to an extended outer-sphere complex) when the nucleotide binds to pyruvate kinase. It has also been established[27] that the substitution-inert complex Cr^{III}–ATP binds at the ATP binding site of the pyruvate kinase–M^{2+} complex, and studies with this magnetic probe have led[28] to the construction of molecular models for composite complexes of this important enzyme. Steady-state kinetic studies on the Mn^{2+}-, Ni^{2+}-, and Co^{2+}-activated systems suggest[29] that the substrates of pyruvate kinase are PEP, uncomplexed ADP, and free bivalent cations. Magnesium-complexed ADP and ATP bind[30] at the same site on yeast phosphoglycerate kinase, as do the uncomplexed nucleotides.

The importance of zinc in both catalysis and structure stabilization of alkaline phosphatase from *E. coli* has long been recognized but the presence of stoicheiometric amounts of magnesium has largely been overlooked. Vallee and co-workers have recently reaffirmed[31] the importance of the lighter metal for this enzyme and have found that it controls the occupancy of the catalytic and structural binding site and modulates the resultant enzymic activity. ^{31}P N.m.r. studies on phosphate and phosphonate complexes of a variety of metallo-alkaline phosphatases have indicated[32] that co-ordination of the phosphate group by the metal ion (and induction by the protein of unusual strain in the bond angles of the phosphoserine intermediate) are important in the catalytic mechanism. However, ^{19}F n.m.r. investigations of the binding of a fluorine-labelled phosphonate ion (4) to this enzyme have



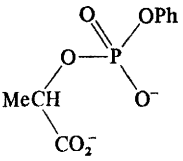
(4)

suggested[33] that there is 'a considerable distance' between the metal ions and the substrate binding site. ^{19}F and ^{31}P studies indicate[34] that dissociation of non-covalently bound phosphate is the rate-determining step at high pH. Recent proton relaxation rate data indicate[35] that there is at least one metal-bound water molecule in manganese(II)-, copper(II)-, and cobalt(II)-alkaline phosphatase and it has been suggested[36] that the *in situ* conversion of exchange-labile Co^{II} into exchange-inert Co^{III} with hydrogen peroxide offers a method of selectively and differentially 'freezing' the cobalt atoms at their respective binding sites; the accompanying

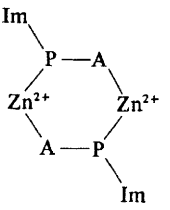
[27] R. K. Gupta, C. H. Fung, and A. S. Mildvan, *J. Biol. Chem.*, 1976, **251**, 2421.
[28] A. S. Mildvan, D. L. Sloan, C. H. Fung, R. K. Gupta, and E. Melamud, *J. Biol. Chem.*, 1976, **251**, 2431.
[29] S. Ainsworth and N. Macfarlane, *Biochem. J.*, 1975, **145**, 63.
[30] P. Tanswell, E. W. Westhead, and R. J. P. Williams, *European J. Biochem.*, 1975, **63**, 249.
[31] R. A. Anderson, W. F. Bosron, F. S. Kennedy, and B. L. Vallee, *Proc. Nat. Acad. Sci. U.S.A.*, 1975, **72**, 2989.
[32] J. F. Chlebowski, I. M. Armitage, P. P. Tusa, and J. E. Coleman, *J. Biol. Chem.*, 1976, **251**, 1207.
[33] H. Lilja, H. Csopak, B. Lindman, and G. Fölsch, *Biochim. Biophys. Acta*, 1975, **384**, 277.
[34] W. E. Hull and B. D. Sykes, *Biochemistry*, 1976, **15**, 1535; W. E. Hull, S. E. Halford, H. Gutfreund, and B. D. Sykes, *ibid.*, p. 1547.
[35] R. S. Zukin and D. P. Hollis, *J. Biol. Chem.*, 1975, **250**, 835.
[36] R. A. Anderson and B. L. Vallee, *Proc. Nat. Acad. Sci. U.S.A.*, 1975, **72**, 394.

spectral changes and retardation in ligand exchange reactions may then be used to differentiate between specific binding sites.

The binding of Co^{2+} to apo-alkaline phosphatase has been studied[37] by the stopped-flow technique and the process appears to be complex. Three reaction steps were detected, in the millisecond, second, and minute ranges; none of these was a bimolecular process but the authors suggest that they might all be associated with enzyme isomerization. The spontaneous hydrolysis of (5) is catalysed by bivalent metal ions and it seems[38] that optimal behaviour depends almost entirely on the cationic radius.



(5)



(6)

Adenosine 5′-phosphorimidazolide (Imp A) is an activated derivative of adenylic acid which polymerizes on a polyuridylate template to form short oligoadenylic acids. Zn^{2+} catalyses[39] the formation of oligonucleotides in aqueous solution, even in the absence of a template, although the mechanism of the reaction is unclear. [Perhaps[39] two imidazole molecules, bound in a single zinc complex (6), react together to form an intermediate bond; on the other hand, the reaction may occur between Imp A molecules attached to independent Zn^{2+} ions. In either case Imp A co-ordinates to Zn^{2+} and the internucleotide bond formation takes place in the co-ordination sphere of the metal ion.] The specific interaction of proteins with nucleic acids (in the replication and transcription processes, for example) takes place in the presence of Mg^{2+} or Mn^{2+}. ^1H and ^{13}C n.m.r. has recently been used[40] to show that either metal, complexed to tRNA, interacts with the carboxy-groups of simple amino-acids and dipeptides. E.s.r. results suggest[41] that manganese(II) binds at the major groove of the DNA helix, whereas alkali-metal ions (in particular, Na^+ and Rb^+) 'bind' to DNA in the form of a highly mobile ionic cloud around the phosphate groups.[42]

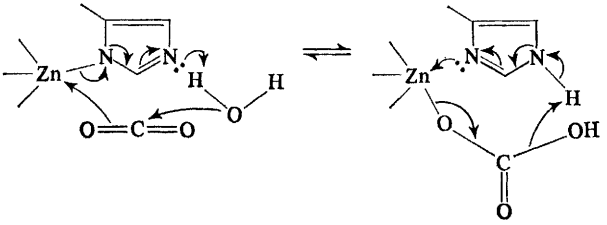
Carbonic Anhydrase (CA).—There has been continued interest in the mode of action of this widely found zinc-containing enzyme which catalyses the reversible interconversion of CO_2 and HCO_3^-. In a buffered solution not far from neutrality, the stoicheiometry of the reaction is

$$CO_2 + H_2O + B \rightleftharpoons HCO_3^- + BH^+$$

where B and BH^+ are the basic and acidic buffer components and, regardless of the actual mechanism, the hydration of CO_2 must be coupled to the splitting of water,

[37] H. Levine, T. Y. Tsong, and D. P. Hollis, *Arch. Biochem. Biophys.*, 1975, **169**, 140.
[38] J. J. Steffens, I. J. Siewers, and S. J. Benkovic, *Biochemistry*, 1975, **14**, 2431.
[39] H. Sawai and L. E. Orgel, *J. Amer. Chem. Soc.*, 1975, **97**, 3532.
[40] L. M. Weiner, J. M. Backer, and A. I. Rezvukhin, *Biochim. Biophys. Acta*, 1975, **383**, 316.
[41] J. Reuben and E. J. Gabbay, *Biochemistry*, 1975, **14**, 1230.
[42] J. Reuben, M. Shporer, and E. J. Gabbay, *Proc. Nat. Acad. Sci. U.S.A.*, 1975, **72**, 245.

formally into H^+ and OH^-. Thus, any postulated mechanism must involve proton transfer and the major point at issue between different groups of workers at present concerns the origin of the proton required for the formation of CO_2 from HCO_3^-: is it carried by the bicarbonate ion itself (*i.e.* is the true substrate H_2CO_3) or is it transported between solvent and active site by buffer components? Gupta and Pesando have assigned[43] an n.m.r. peak 15 p.p.m. downfield from TMS to a histidine imidazole-ring NH proton and have found that its movement under varying conditions is consistent with a mechanism for enzymatic catalysis which involves reversible deprotonation of the histidine and co-ordination of the imidazolate anion to the zinc. The argument is continued[44] elsewhere: this histidine, when bound to the metal as an anion, may act as a general base catalyst in the hydration of CO_2 and be replaced as a metal ligand by an oxygen of the substrate in the course of the reaction (Scheme 2). This concerted mechanism would allow the zinc to act as a Lewis acid by

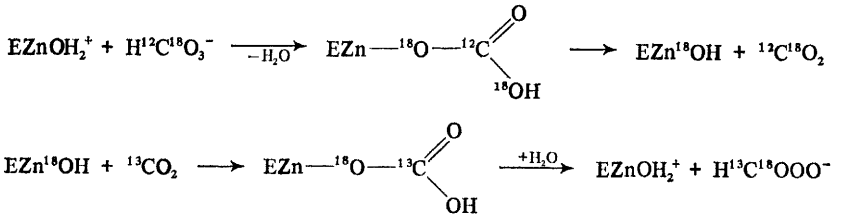


Scheme 2

co-ordinating to the incipient bicarbonate ion, as well as promoting the general base catalysis by imidazole. The histidine–metal complex would probably exist in a strained configuration in the active enzyme (indeed, space-filling models indicate that a strained configuration would be necessary to meet the steric requirements if only a single water molecule is involved) so that its imidazole–zinc bond is labile and readily broken on addition of substrates or inhibitors. Univalent anions would compete with the exchangeable histidine ligand for a site on the metal at low pH, displacing the equilibrium for generation of the active enzyme, while on binding to the high-pH form of the enzyme, sulphonamides would displace and protonate the exchangeable histidine (in accordance with a previously proposed model). It is also suggested[44] that the orientation of substrates may be facilitated by the formation of hydrogen bonds to water, to serine, or to threonine.

The catalysis by CA of the exchange of ^{18}O between CO_2 and water at chemical equilibrium has been measured.[45] To explain the observation that, near pH 6 and in the presence of excess CO_2, the rate of catalysed hydration is less than the known initial velocity of hydration in non-equilibrium experiments, the authors suggest that ^{18}O removed from bicarbonate during a catalysed dehydration step at low pH has a long lifetime in the active site compared with the turnover time for one catalytic cycle. As a result of these and other studies at higher pH, Tu and Silverman suggest[46] the following scheme:

[43] R. K. Gupta and J. M. Pesando, *J. Biol. Chem.*, 1975, **250**, 2630.
[44] J. M. Pesando, *Biochemistry*, 1975, **14**, 675, 681.
[45] D. N. Silverman and C. K. Tu, *J. Amer. Chem. Soc.*, 1976, **98**, 978.
[46] C. K. Tu and D. N. Silverman, *J. Amer. Chem. Soc.*, 1975, **97**, 5935.



The hydrolysis of *p*-nitrophenyl acetate catalysed by human CA-C is *ca.* 35% faster in D_2O than in H_2O and it is tentatively proposed[47] that the rate-limiting step at saturating concentrations of CO_2 or HCO_3^- is an intramolecular proton transfer between two ionizing groups at the active site, a 'catalytic group' and a 'proton transfer group' which is assumed to exchange H^+ rapidly with a buffered medium. In support of this proposal, HCO_3^- has been found[48] to be an inhibitor of CA-catalysed CO_2 hydration and ester hydrolysis.

The role of Zn^{II} in the folding of bovine CA-B has been investigated[49] by various physicochemical techniques. The metal appears to stabilize part of the molecule and enable the whole protein to act as a more co-operative unit but the authors feel that its presence is not vital for the enzyme to fold in the 'correct' manner.

The rate and equilibrium constants have been reported[50] for the binding of a series of sulphonamides to human CA-C. In all cases the increase in binding constant in a homologous series is due mainly to an increase in the association rate constant, as shown in Table 1 for 4-alkylsulphonamides. (Similar trends were found with other

Table 1 *Rate and equilibrium constants*[a] *for the binding of 4-alkylsulphonamides to human CA-C*

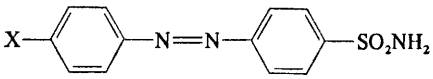
Substituent	K/l mol^{-1}	k_{on}/l mol^{-1} s^{-1}	$\tau(k_{off}^{-1})$/s
H	4.93×10^6	8.80×10^5	5.62
Me	1.22×10^7	1.12×10^6	10.9
Et	3.40×10^7	3.30×10^6	10.3
Pr	5.90×10^7	5.02×10^6	11.8
Bu^n	2.00×10^8	1.00×10^7	20.0
n-C_5H_{11}	7.24×10^8	2.46×10^7	29.4

[a] Data from ref. 50.

4-substituted benzenesulphonamides, with 3- and 2-substituted benzenesulphonamides, and with thiophen sulphonamides; in the case of the *meta-* and *ortho-*substituted compounds, the markedly lower binding constants were also due mainly to lower association rate constants.) It is argued that the sulphonamides bind initially to the enzyme without co-ordinating to the metal and that the initial complex formed then isomerizes into one in which complexation with the zinc has occurred. On the other hand, in the binding of the chromophoric sulphonamide (7a) to bovine CA, the rapid kinetics of the induced c.d. and difference spectra proceed[51] in parallel (with a

[47] H. Steiner, B. H. Jonsson, and S. Lindskog, *European J. Biochem.*, 1975, **59**, 253.
[48] H. Steiner, B. H. Jonsson, and S. Lindskog, *F.E.B.S. Letters*, 1976, **62**, 16.
[49] K. P. Wong and L. M. Hamlyn, *Arch. Biochem. Biophys.*, 1975, **170**, 12.
[50] R. W. King and A. S. V. Burgen, *Proc. Roy. Soc.*, 1976, **B193**, 107.
[51] P. Bayley and M. Anson, *Biochem. Biophys. Res. Comm.*, 1975, **62**, 717.

second-order rate constant of 5×10^6 l mol^{-1} s^{-1}), suggesting that a single classical binding process is being observed. N.m.r. studies on several sulphonamide complexes of human CA indicate[52] that an enzyme conformational change is involved. It is suggested that inhibition of CA involves the following: stabilization of an appropriately oriented initial complex through the hydrophobic binding of the aromatic



(7) a; X = OH
b; X = NMe_2
c; X = NH_2

ring of the inhibitor to residues of the cavity forming the active site; ionization of the sulphonamido-group, facilitated by its proximity to the zinc atom; protonation and displacement of the high-pH ligand to the metal controlling the catalytic activity (thought[44] by Pesando to be a histidine residue); and formation by the sulphonamido-group of an ionic bond to zinc and a hydrogen bond to the hydroxy-group of serine (in HCA-B) or threonine (in HCA-C). Evidence has been obtained[53] from resonance Raman spectra for the presence of the SO_2NH^- group in the complexes of (7a—c), with various isoenzymes of CA and it seems that hydrophobic bonding can be ruled out.

Although the essential Zn^{2+} can be replaced by other bivalent metals, the Co and Mn (and now[54] the Cd) enzymes are the only derivatives which have so far been shown to exhibit substantial esterase and CO_2 hydration activity. From ^{13}C n.m.r. measurements, Yeagle *et al.* have identified[55] two binding sites for HCO_3^- on bovine cobalt CA. One of these binds HCO_3^- loosely and inhibits *p*-nitrophenyl acetate activity, and is presumably the bicarbonate substrate binding site; the other binds HCO_3^- tightly and is non-inhibitory. Spin–lattice relaxation times for the C atom in bicarbonate indicate that the substrate bicarbonate is bound directly to the metal centre whereas the other bicarbonate remains in the outer co-ordination sphere of the metal. It is suggested that dehydration occurs only in the HCO_3^- which is bound directly to the metal, while the purpose of the outer-sphere bicarbonate is to facilitate catalytically important proton transfers. E.s.r. studies on cyanide complexes of the Co and Cu forms of CA have indicated[56] to Haffner and Coleman that the metal in this enzyme can expand its co-ordination sphere from four to five. Morpurgo *et al.* also propose[57] that halide complexes of the Cu, Co, and Zn enzymes give rise to five-co-ordinate metal species while Smith and Bryant find[58] that the co-ordination geometry of the zinc enzyme differs from those of the cadmium and mercury forms. Spin–lattice and spin–spin relaxation times of the water protons of the Mn enzyme indicate[59] that one water molecule remains bound to the metal at high pH whereas at

[52] J. M. Pesando and A. P. Grollman, *Biochemistry*, 1975, **14**, 689.
[53] K. Kumar, R. W. King, and P. R. Carey, *Biochemistry*, 1976, **15**, 2195.
[54] R. Bauer, P. Limkilde, and J. T. Johansen, *Biochemistry*, 1976, **15**, 334.
[55] P. L. Yeagle, C. H. Lochmüller, and R. W. Henkins, *Proc. Nat. Acad. Sci. U.S.A.*, 1975, **72**, 454.
[56] P. H. Haffner and J. E. Coleman, *J. Biol. Chem.*, 1975, **250**, 996.
[57] L. Morpurgo, G. Rotilio, A Finazzi Agró, and B. Mondoví, *Arch. Biochem. Biophys.*, 1975, **170**, 360.
[58] R. J. Smith and R. G. Bryant, *Biochem. Biophys. Res. Comm.*, 1975, **66**, 1281.
[59] A. Lanir, S. Gradstajn, and G. Navon, *Biochemistry*, 1975, **14**, 242.

low pH there is no H_2O in the inner co-ordination sphere of the metal. Woolley has extended[60] his studies on the zinc-catalysed hydration of acetaldehyde and has discussed[61] the general question of models for metal ion function in CA.

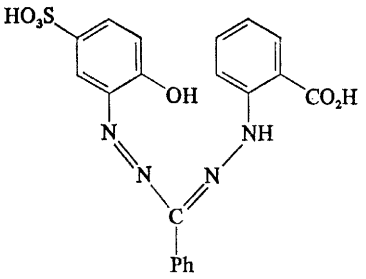
Carboxypeptidase.—Johansen and Vallee have used[62] their technique of chemically modifying carboxypeptidase A (CPA) with diazotized arsanilic acid (reported in Vol. 2, p. 235) to probe the conformational changes which occur at the active site when crystals of the enzyme are dissolved in water and when substrates or inhibitors bind. Evidence is presented that, during the catalytic process, Tyr-248 moves away from the zinc atom, which, incidentally, implies a mechanistic role for Tyr-248 different from that postulated on the basis of *X*-ray crystallographic analysis (a role which has been probed further[63] through the preparation of inert Co^{III} complexes of azotyrosine species). Subsequent work with the stopped-flow and temperature-jump methods has shown[64] that this conformational change is really two distinct processes, the faster being pH-dependent and having a relaxation time of *ca.* 10^{-5} s and the slower being pH-independent and having a relaxation time of *ca.* 0.2 s. Evidently the process is more complex than had originally been thought and, once again, the dangers inherent in the construction of a large mechanistic edifice based only, or largely, on the results of *X*-ray crystal studies are demonstrated.

The kinetics of chloride-ion exchange with the zinc, cadmium, mercury(II), and cobalt(II) derivatives of CPA have been obtained[65] from ^{35}Cl n.m.r. data. Interestingly, the mean residence time of the Cl^- ion at the metal sites is largely independent of the metal (being 4, 3, 4, and 2×10^{-7} s, respectively), as is the activation enthalpy (4.6, 2.9, and 3.5 kcal mol^{-1}, respectively, for Zn, Hg, and Co). A detailed analysis of the magnetic properties of the active Co^{II}–CPA supports[66] a co-ordination number of five rather than four at the metal, while the metal in the inactive copper(II) enzyme appears[67] to have a distorted square-planar geometry. [It has recently been shown[68] that the latter enzyme catalyses the hydrolysis of *S*-(*trans*-cinnamoyl)-L-α-mercapto-β-phenylpropionate at pH 7.5 and 25 °C at a rate similar to that produced by the native zinc enzyme.] N.m.r. studies on manganese(II) carboxypeptidase B indicate[69] the existence of one water molecule which can be displaced from the inner sphere of the metal ion by various inhibitors. Recent work with cobalt(III)–CPA suggests[70] that the substrate does not enter the inner co-ordination sphere of the metal during ester hydrolysis catalysed by the Co^{III} enzyme. Preliminary evidence has been published[71] which suggests that the CPA-catalysed hydrolysis of the (+)- and (−)-enantiomers of a thiol ester proceed by different mechanisms and there has been

[60] P. R. Woolley, *J.C.S. Chem. Comm.*, 1975, 579; *J.C.S. Dalton*, 1975, 1570.
[61] P. R. Woolley, *Nature*, 1975, **258**, 677.
[62] J. T. Johansen and B. L. Vallee, *Biochemistry*, 1975, **14**, 649; B. L. Vallee, *Pure Appl. Chem.*, 1975, **44**, 1.
[63] W. I. White and J. I. Legg, *J. Amer. Chem. Soc.*, 1975, **97**, 3937.
[64] L. W. Harrison, D. S. Auld, and B. L. Vallee, *Proc. Nat. Acad. Sci. U.S.A.*, 1975, **72**, 4356.
[65] R. S. Stephens and R. G. Bryant, *J. Biol. Chem.*, 1976, **251**, 403.
[66] R. C. Rosenberg, C. A. Root, and H. B. Gray, *J. Amer. Chem. Soc.*, 1975, **97**, 21.
[67] R. C. Rosenberg, C. A. Root, P. K. Bernstein, and H. B. Gray, *J. Amer. Chem. Soc.*, 1975, **97**, 2092.
[68] M. Schneider, J. Suh, and E. T. Kaiser, *J.C.S. Chem. Comm.*, 1976, 106.
[69] N. Zisapel, G. Navon, and M. Sokolovsky, *European J. Biochem.*, 1975, **52**, 487.
[70] E. P. Kang, C. B. Storm, and F. W. Carson, *J. Amer. Chem. Soc.*, 1975, **97**, 6723.
[71] J. Suh and E. T. Kaiser, *Biochem. Biophys. Res. Comm.*, 1975, **64**, 863.

further support[72] for the view that CPA-catalysed hydrolysis involves the binding of the zinc to the substrate.

Liver Alcohol Dehydrogenase.—The horse enzyme (LADH) contains one catalytic pair and one non-catalytic pair of zinc atoms per molecule. These have been replaced selectively with Co^{II} and/or ^{65}Zn and it has been found,[73] somewhat surprisingly, that the lability of the non-catalytic pair is markedly higher than that of the catalytic pair. (It had previously been assumed that the assignments were the other way round.) Substitution of the two rapidly exchanging zinc atoms by cobalt(II) is biphasic,[74] the faster process having a half-life of *ca.* 15 min and the slower about ten times longer than this. The involvement of the metal in catalysis and binding interactions with alcohol and NADH has been confirmed[75] by stopped-flow experiments. At pH 7.0, the only observable step in the reaction sequence with significantly different rate constants for totally cobalt-substituted and native enzymes is the catalytic hydrogen-transferring step; the values are 92 and 138 s^{-1}, respectively. Further stopped-flow experiments under conditions of excess substrate gave results[76] which were consistent with base-catalysed removal of a proton from alcohol substrates and subsequent acid catalysis of protonation of a zinc-alcoholate complex. The zinc ion is thought[77] to function as a Lewis acid in the activation by LADH of the carbonyl group in an aldehyde substrate analogue, while changes in the resonance Raman spectrum of the coenzyme competitive inhibitor (8) when it binds to the



(8)

enzyme have also been interpreted[78] in terms of complex formation with a zinc atom at the active site.

The three-dimensional structure of LADH has been reported[79] at 2.4 Å resolution and all four zinc atoms exhibit distorted tetrahedral co-ordination. The earlier assignment of the zinc atoms containing a water molecule (or hydroxy-group,

[72] R. Breslow, D. E. McClure, R. S. Brown, and J. Eisenach, *J. Amer. Chem. Soc.*, 1975, **97**, 194; R. Breslow and D. E. McClure, *J. Amer. Chem. Soc.*, 1976, **98**, 258; R. Breslow and D. Wernick, *ibid.*, p. 259.

[73] A. J. Sytkowski and B. L. Vallee, *Biochem. Biophys. Res. Comm.*, 1975, **67**, 1488; *Proc. Nat. Acad. Sci. U.S.A.*, 1976, **73**, 344.

[74] R. A. Harvey and A. Barry, *Biochem. Biophys. Res. Comm.*, 1975, **66**, 935.

[75] J. D. Shore and D. Santiago, *J. Biol. Chem.*, 1975, **250**, 2008.

[76] J. T. McFarland and Y. H. Chu, *Biochemistry*, 1975, **14**, 1140.

[77] M. F. Dunn, J. F. Biellmann, and G. Branlant, *Biochemistry*, 1975, **14**, 3176.

[78] J. T. McFarland, K. L. Watters, and R. L. Petersen, *Biochemistry*, 1975, **14**, 624.

[79] H. Eklund, B. Nordström, E. Zeppezauer, G. Söderlund, I. Ohlsson, T. Boiwe, B. O. Söderberg, O. Tapia, C. I. Brändén, and Å. Åkeson, *J. Mol. Biol.*, 1976, **102**, 27.

depending on the pH) in the inner co-ordination sphere as the 'catalytic' metal is retained (*cf.* ref. 73; note that the enzyme comprises two identical subunits) and the results of n.m.r. studies on the interaction of substrate with LADH are also discussed[80] in these terms.

Other Systems.—Dunn has reviewed[81] the mechanisms of zinc-ion catalysis in small molecules and enzymes, and Vallee and co-workers have considered[82] the use of m.c.d. spectra of cobalt(II)-substituted metalloenzymes for determining the co-ordination number of the metal.

It has been found[83] that Ca^{2+} and Mg^{2+} will form five-co-ordinate complexes with the unidentate ligands Me_3AsO and Ph_3AsO in the presence of the dehydrating agent triethyl orthoformate and it is suggested that complexes with this co-ordination number may well be involved in biological reactions of these metals. It is also suggested,[84] in a preliminary study with the class II aldolase from *Bacillus stearothermophilus*, that the role of the metal ion lies partly in its ability to help provide the correct orientation of the substrate and partly in its ability to act as an electrophile. The rate constants for the formation and dissociation of the complex between $GdOH^{2+}$ and bovine serum albumin are,[85] respectively, 1.0×10^8 l mol^{-1} s^{-1} and 9.3 s^{-1} at 7 °C, pH 8.2, and ionic strength 0.2 mol l^{-1}; the corresponding reaction with Ca^{2+} is too rapid to study kinetically. It is suggested[86] that ternary complexes play an important role in the exchange of Cu^{II} from L-histidine to human serum albumin or diglycyl-L-histidine.

Human serum transferrin is an iron(III) transport protein which gives up Fe^{3+} ions to bone marrow and placental tissues in preference to other cells such as liver cells; the protein can bind two iron atoms per molecule but an anion such as HCO_3^- must be present for binding to occur. Vanadyl ion has been used[87] (as an e.s.r. spin label) to show that the two metal-binding sites are non-equivalent and the same conclusion has been drawn[88] from studies on the dissociation of labelled protein-bound iron. On the other hand, Harris and Aisen have obtained evidence[89] from radiotracer experiments that the two sites are kinetically equivalent. The kinetics of iron(III) (in the form of ferric citrate) binding to the analogous apoprotein from hen's egg (apo-ovotransferrin) have been reported[90] and the following minimum mechanistic scheme has been proposed:

$$\text{ferric dicitrate} \rightleftharpoons \text{ferric citrate} + \text{citrate}$$

$$\text{protein} + \text{ferric citrate} \rightleftharpoons \text{protein–ferric citrate}$$

$$\text{protein–ferric citrate} + \text{bicarbonate} \rightleftharpoons \text{protein–ferric bicarbonate} + \text{citrate}$$

The authors feel unable to comment on the question of the equivalence of the two

[80] D. L. Sloan, J. M. Young, and A. S. Mildvan, *Biochemistry*, 1975, **14**, 1998.
[81] M. F. Dunn, *Structure and Bonding*, 1975, **23**, 61.
[82] B. Holmqvist, T. A. Kaden, and B. L. Vallee, *Biochemistry*, 1975, **14**, 1454.
[83] G. B. Jameson and G. A. Rodley, *Inorg. Nuclear Chem. Letters*, 1975, **11**, 547.
[84] H. A. O. Hill, R. R. Lobb, S. L. Sharp, A. M. Stokes, J. I. Harris, and R. S. Jack, *Biochem. J.*, 1976, **153**, 551.
[85] H. B. Silber and J. Rosen, *J. Inorg. Nuclear Chem.*, 1976, **38**, 1415.
[86] S. Lau and B. Sarkar, *Canad. J. Chem.*, 1975, **53**, 710.
[87] J. C. Cannon and N. D. Chasteen, *Biochemistry*, 1975, **14**, 4573.
[88] J. V. Princiotto and E. J. Zapolski, *Nature*, 1975, **255**, 87.
[89] D. C. Harris and P. Aisen, *Nature*, 1975, **257**, 821.
[90] C. E. Phelps and E. Antonini, *Biochem. J.*, 1975, **147**, 385.

Fe-binding sites, but Butterworth *et al.*[91] conclude from their e.s.r. results that each site can exist in two states and that there is no iron–iron interaction between the sites.

4 Reactions involving Metals in Porphyrins and Related Ring Systems

Haemoglobin and Similar Molecules.—The flow of papers relating to the mechanism of action of haemoglobin (Hb) has continued unabated and Shulman *et al.* have provided[92] a comprehensive review of the allosteric properties of this important macromolecule. Much of the recent work is discussed in terms of the model, proposed by Perutz and his colleagues, which relates changes in spin state and displacement of the iron atom (relative to the mean porphyrin plane) to the functional properties of Hb. A key feature of this model is 'tension at the haem' in the deoxyHb (T) structure, in which the globin is seen as exerting tension along the line of the iron–proximal histidine bond, thus distorting the haem conformation and lowering the oxygen affinity of the deoxy-haems. Co-operativity between the four subunits, as exhibited in the reaction with ligands, is mediated by conformational changes of the protein. Laser flash photolysis has recently been used[93] to measure the rate constants for the R→T change in human Hb (920, 6400, and 15 700 s^{-1}, respectively, at 3, 20, and 30 °C). Kinetic studies on the dissociation of ligands from the five principal components of normal adult Hb have been reported[94] and a new method of determining the ligand dissociation rates of carboxyHb (involving the binding of CO to microperoxidase) has been reported.[95]

Huestis and Raftery have used[96] ^{19}F and ^{31}P n.m.r. spectroscopy to study the ligand-binding process in human Hb and managed to identify signals from intermediates containing two and three ligands. They followed the behaviour of these signals in response to changes in pH and concluded that it was not completely consistent with either of the main theories of allostery (involving an 'all-or-none' transition or a simple sequential allosteric model). They found that α-chains exhibit higher ligand affinity than β-chains but concluded that any 'co-operative mechanism' based on the energetics of changes in a small region of the molecule or in a few interacting groups runs a risk of oversimplification.

The M haemoglobins are abnormal in that one pair of subunits (α) is in the normal ferrous state while the other pair (β) is in the ferric state; only the α-chains will bind oxygen. Recent stopped-flow results on the binding of O_2 and CO to (and dissociation from) the Saskatoon form of this mutant suggest[97] that the ligand-binding sites of the β-chains are independent of those of the α-chains. Thus, the similarity in the kinetics of the reaction of O_2 with normal Hb or the α-subunits of Hb M Saskatoon indicates that the latter undergo a structural transition from a low- (T) to a high-affinity (R) form on ligand-binding; in addition, the β-subunits react rapidly with CO even when the α-subunits are in the T-form. It therefore appears that the protein can exist in the $\alpha_2(T)\beta_2(R)$ form as well as the all-T and all-R forms. N.m.r.

[91] R. M. Butterworth, J. F. Gibson, and J. Williams, *Biochem. J.*, 1975, **149**, 559.
[92] R. G. Shulman, J. J. Hopfield, and S. Ogawa, *Quart. Rev. Biophys.*, 1975, **8**, 325.
[93] C. A. Sawicki and Q. H. Gibson, *J. Biol. Chem.*, 1976, **251**, 1533.
[94] R. C. Steinmeier and L. J. Parkhurst, *Biochemistry*, 1975, **14**, 1564.
[95] V. S. Sharma, H. M. Ranney, J. F. Geibel, and T. G. Traylor, *Biochem. Biophys. Res. Comm.*, 1975, **66**, 1301.
[96] W. H. Huestis and M. A. Raftery, *Biochemistry*, 1975, **14**, 1886.
[97] M. J. McDonald, H. M. Ranney, and R. W. Noble, *J. Mol. Biol.*, 1975, **91**, 471.

experiments with a similar mutant, Hb M Milwaukee, have also indicated[98] that the oxygenation process cannot be described in terms of the all-T/all-R two-structure model.

A new model, based on the bonding in ozone, has been proposed[99] for the bonding of an O_2 molecule to the iron of Hb and myoglobin (Mb). It involves basically a biradical with a singlet state stabilized by a three-centre four-electron π-bond and leads to an easy rationalization of the facile formation and dissociation of the Fe—O_2 bond since the O_2 would always retain its triplet ground state character.

Recent results from the laboratories of Perutz[100] and Caughey[101] show that the R(oxy)→T(deoxy) transition in the (low-spin) ferrous compounds of Hb with O_2, CO, and NO causes either a rupture or at least a very considerable stretching of the bond from the iron to the haem-linked histidine. Thus, an equilibrium is set up between five- and six-co-ordinated haems and this is biased towards the former in the α-subunits and the latter in the β-subunits. It seems that inositol hexaphosphate (IHP) can switch nitrosyl- but not carbon monoxy- or oxy-Hb A from the R to the T structure and that the reason for this is to be found in the weakening of the Fe—histidine bond by the unpaired NO electron and by the very short Fe—NO bond length. This ability of IHP to promote the R→T transition has also been demonstrated[102] by n.m.r. spectroscopy with nitrosyl-Hb Kansas, and the results of oxygen-pulse experiments with the same form of Hb suggest[103] that oxygen release and binding in the T form occur rather more rapidly than had been thought previously.

The resonance Raman spectra of the oxygen and carbon monoxide complexes of both Hb and Mb are[104] sufficiently similar to those of low-spin met (Fe^{III}) derivatives that the electronic distribution on the haem for both ligands can be interpreted as that of a low-spin ferrihaem (implying that the ligands are bound as O_2^- and CO^-). Similarly, it is suggested[105] that the metal in the NO complex of Hb is in the +3 oxidation state. The changes observed in the magnetic susceptibility of ferriHb on adding small quantities of t-butyl alcohol to an aqueous solution have led to the suggestion[106] that the high-spin–low-spin equilibrium may be intimately connected with changes in the hydration sphere of the metal, possibly controlled by factors mediated in part through the surrounding water shell to the protein.

Anusiem and Beetlestone found[107] that the Hill coefficient n (generally taken to represent the degree of co-operativity between subunits, a value of 1 reflecting total independence) for ferriHb can vary significantly with time. Thus, for example, the value of n for the binding of azide (which gives a low-spin complex) at pH 6 was found to be 1.01 ± 0.01 after equilibration for 11 h but 1.44 ± 0.04 after 48 h, whereas

[98] L. W. M. Fung, A. P. Minton, and C. Ho, *Proc. Nat. Acad. Sci. U.S.A.*, 1976, **73**, 1581.
[99] W. A. Goddard and B. D. Olafson, *Proc. Nat. Acad. Sci. U.S.A.*, 1975, **72**, 2335.
[100] M. F. Perutz, J. V. Kilmartin, K. Nagai, A. Szabo, and S. R. Simon, *Biochemistry*, 1976, **15**, 378.
[101] J. C. Maxwell and W. S. Caughey, *Biochemistry*, 1976, **15**, 388.
[102] J. M. Salhany, S. Ogawa, and R. G. Shulman, *Biochemistry*, 1975, **14**, 2180.
[103] J. M. Salhany, C. L. Castillo, M. J. McDonald, and Q. H. Gibson, *Proc. Nat. Acad. Sci. U.S.A.*, 1975, **72**, 3998.
[104] L. Rimai, I. Salmeen, and D. H. Petering, *Biochemistry*, 1975, **14**, 378.
[105] A. Szabo and L. D. Barron, *J. Amer. Chem. Soc.*, 1975, **97**, 660.
[106] A. C. I. Anusiem, *Biopolymers*, 1975, **14**, 1293.
[107] A. C. I. Anusiem and J. G. Beetlestone, *Biopolymers*, 1976, **15**, 403.

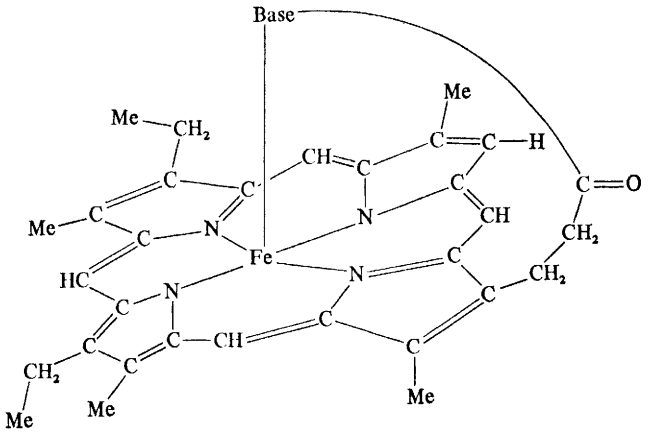
the value for fluoride (which gives a high-spin complex) was close to 1 and invariant with time. The implications of these findings are discussed.

The dissociation rate constant of water in human aquometHb is 1.4×10^4 s^{-1} at 30 °C ($\Delta H^{\ddagger} = 7.5$ kcal mol^{-1})[108] but in the presence of stoicheiometric quantities of IHP this is increased to 3.8×10^4 s^{-1} ($\Delta H^{\ddagger} = 6.8$ kcal mol^{-1}). IHP also has the effect of inducing co-operativity in the pH titration of aquometHb and it is suggested[108] that it alters the quaternary structure of metHb to the deoxy conformation without causing a change in spin state of the iron. The requirement for co-operativity appears to be the simultaneous occurrence of changes in the protein structure and changes in the haem spin state. In line with this, the co-operative interaction of aniline with metHb is accompanied[109] by a high-spin–low-spin change.

Reduction of one of the four haem groups of human aquometHb A has been studied[110] by pulse radiolysis. In unbuffered aqueous solution at 23 °C and pH 6.2 ($I = 0.1$ mol l^{-1}), the rate constant for the reaction with e_{aq}^- is 4.2×10^{10} l mol^{-1} s^{-1}. Similar results were obtained for cyano- and azido-metHb and for deoxyHb (4.7, 4.4, and 4.3×10^{10} l mol^{-1} s^{-1}, respectively). From studies on the redox equilibria of fluoro- and azido-metHb it is concluded[111] that the marked co-operativity and pH-dependence of E are not coupled to changes in the ferrihaem spin state.

Simple inductive electronic effects of the 2- and 4-substituents of the haem moiety in deuterio- and meso-Hb are insufficient to explain the results[112] of equilibrium and kinetic studies on ligand binding, and it is necessary to invoke additional steric effects. The binding of CO and weak- or strong-field ligands to deuteriohaem has been studied[113] over a very large concentration range and the results related to the relative σ-donor–π-acceptor character of the ligands. The kinetics of the binding of O_2 and CO to two synthetic analogues of Hb and Mb active sites (9a and b) have been measured[114] in different solvents. Both the association and the dissociation rate constants for oxygen could be made to match closely those of Mb, or of the α-chains of Hb, or of the various steps for Hb by varying the solvent composition or the basicity of the proximal base. These results suggest that the native protein may actually alter the association rate with oxygen by varying the basicity of the proximal base and the dissociation rate by changing the polarity of the distal environment. The authors feel that the protein serves more to protect the haems from oxidation than to bring about the binding of oxygen, and that variations in oxygen affinities among the haem proteins result more from changes in polarity of the haem environment than from stereochemical factors. Equilibrium studies have been extended[115] to other models of the type (9). Resonance Raman spectra of cobalt-substituted Mbs and Hbs imply[116] that the 'tension' imposed on the cobalt haem by the globin results in little distortion of the metal–porphyrin moiety from its unconstrained geometry.

[108] R. K. Gupta and A. S. Mildvan, *J. Biol. Chem.*, 1975, **250**, 246.
[109] J. J. Mieyal and L. S. Freeman, *Biochem. Biophys. Res. Comm.*, 1976, **69**, 143.
[110] J. R. Clement, N. T. Lee, M. H. Klapper, and L. M. Dorfman, *J. Biol. Chem.*, 1976, **251**, 2077.
[111] C. Bull and B. M. Hoffman, *Proc. Nat. Acad. Sci. U.S.A.*, 1975, **72**, 3382.
[112] D. W. Seybert, K. Moffat, and Q. H. Gibson, *J. Biol. Chem.*, 1976, **251**, 45.
[113] M. Rougee and D. Brault, *Biochemistry*, 1975, **14**, 4100.
[114] C. K. Chang and T. G. Traylor, *Proc. Nat. Acad. Sci. U.S.A.*, 1975, **72**, 1166.
[115] J. Geibel, C. K. Chang, and T. G. Traylor, *J. Amer. Chem. Soc.*, 1975, **97**, 5924.
[116] W. H. Woodruff, D. H. Adams, T. G. Spiro, and T. Yonetani, *J. Amer. Chem. Soc.*, 1975, **97**, 1695.



(9) a; Base = $-NH(CH_2)_3-$

b; Base = $-O(CH_2)_3-$

In a very detailed and closely argued paper, Austin *et al.* present the case[117] for a model to describe the steps involved in the rebinding of CO or O_2 to Mb after photodissociation. In this model, the ligand molecule, on its way from the solvent to the binding site at the ferrous haem iron, encounters four barriers in succession, which are tentatively identified[117] with known features of Mb. For CO, the heights of the barriers increase towards the inside and CO is therefore partially rejected at each of the four barriers; for O_2, on the other hand, the barriers are of approximately equal height and this ligand moves smoothly towards the binding site.

The kinetics of the binding of CO and O_2 to a series of haem-substituted Mbs from horse heart confirm[118] the reports that k_{on} tends to increase as the electron-withdrawing power of the side-chain increases. The kinetics have also been reported for the binding of O_2 and CO to dolphin fish Mb[119] and of azide to *Aplysia* metMb.[120] It appears[121] that the reactions of O_2 and CO with the monomeric Hb from the common bloodworm are more rapid than the corresponding reactions with Mb, and they are also biphasic in nature. The reactions of eight electrophoretic components of sperm whale ferriMb with F^-, N_3^-, and CN^- have been studied[122] by the stopped-flow technique and it seems that at pH 7.0 and 0.05 mol l^{-1} ionic strength (potassium phosphate) these reactions are insensitive to the net charge on the protein.

[117] R. H. Austin, K. W. Beeson, L. Eisenstein, H. Frauenfelder, and I. C. Gunsalus, *Biochemistry*, 1975, **14**, 5355.
[118] M. Sono, P. D. Smith, J. A. McCray, and T. Asakura, *J. Biol. Chem.*, 1976, **251**, 1418.
[119] J. V. Bannister, W. H. Bannister, P. Ascenzi, A. Focesi, and M. Brunori, *F.E.B.S. Letters*, 1976, **65**, 361.
[120] G. M. Giacometti, A. Da Ros, E. Antonini, and M. Brunori, *Biochemistry*, 1975, **14**, 1584.
[121] B. Seamonds, J. A. McCray, L. J. Parkhurst, and P. D. Smith, *J. Biol. Chem.*, 1976, **251**, 2579.
[122] L. J. Parkhurst and J. La Gow, *Biochemistry*, 1975, **14**, 1200.

The rate constant for the reduction of metMb by the iron(II) complex of *trans*-1,2-diaminocyclohexane-*NNN'N'*-tetra-acetate [Fe(cydta)$^{2-}$] at 25 °C is 28 l mol^{-1} s^{-1}, with $\Delta H^{\ddagger} = 13$ kcal mol^{-1} and $\Delta S^{\ddagger} = -11$ cal K^{-1} mol^{-1}.[123] Both CN^- and OH^- inhibit the reduction because of the relatively low reactivity of cyanometMb (Mb^+CN^-) and the ionized metMb (Mb^+OH^-) (rate constants $= 4.0 \times 10^{-2}$ and 4.8 l mol^{-1} s^{-1}, respectively). The kinetics of the reverse reaction, namely the oxidation of oxyMb by Fe(cydta)$^-$, are consistent with a scheme in which reaction occurs only through the deoxy form ($k = 1.45 \times 10^2$ l mol^{-1} s^{-1}). The authors interpret their data in terms of a simple outer-sphere mechanism.

Coenzyme B_{12} and Similar Molecules.—Two recent short reviews have considered[124] different aspects of the mechanism of action of the B_{12} series, while the e.s.r. spectra observed in B_{12}-dependent reactions (which strongly suggest a mechanism involving free radicals) have been interpreted[125] in terms of a four-membered-ring radical intermediate. The similar kinetic parameters for 3-fluoropropane-1,2-diol and the natural substrate in the adenosylcobalamin-mediated action of propanediol dehydrase suggest[126] that significant charge does not develop on the fluorinated (or, by implication, the natural) substrate during any rate-limiting steps of the reaction, lending further support to a radical pathway. Brown *et al.* have argued[127] in favour of a π-complex between cob(III)alamin and the enol form of acetophenone as an intermediate in the acid-promoted cleavage of phenacylcobalamin. Preliminary results from the use of stopped-flow rapid-scanning spectrophotometry have demonstrated[128] the rapid formation of a cobalt(II) species in the pre-steady-state phase of the ethanolamine–ammonia lyase-catalysed deamination of L-2-aminopropanol, but no evidence was found for the formation of an intermediate involving Co^I. Schrauzer has produced[129] more data in support of his claim that B_{12} dependent enzymatic reactions involve heterolytic bond cleavage.

Pulse radiolysis has been used[130] to measure the rate constant for the reaction of e^-_{aq} with coenzyme B_{12}; it is 3.0×10^{10} l mol^{-1} s^{-1}.

It has been shown[131] that axial base–ligand exchange in alkyl-(base)cobaloximes occurs by a purely dissociative (D) mechanism in chloroform but it was not possible[132] to distinguish between this and an I_d mechanism for the reaction of pyridine with a series of alkylcobaloximes in water.

Cytochromes and other Porphyrin-containing Systems.—At neutral pH, the haem group of horse-heart ferricytochrome *c* lies in a crevice in the globular protein; the (low-spin) iron atom is in the plane of the porphyrin ring, and its fifth and sixth coordination positions are occupied by the imidazole nitrogen of histidine-18 and the

[123] J. C. Cassatt, C. P. Marini, and J. W. Bender, *Biochemistry*, 1975, **14**, 5470.
[124] B. M. Babior, *Accounts Chem. Res.*, 1975, **8**, 376; R. H. Abeles and D. Dolphin, *ibid.*, 1976, **9**, 114.
[125] E. Ochiai, *J. Inorg. Nuclear Chem.*, 1975, **37**, 351.
[126] R. G. Eagan, W. W. Bachovchin, and J. H. Richards, *Biochemistry*, 1975, **14**, 5523.
[127] K. L. Brown, M. M. L. Chu, and L. L. Ingraham, *Biochemistry*, 1976, **15**, 1402.
[128] K. N. Joblin, A. W. Johnson, M. F. Lappert, M. R. Hollaway, and H. A. White, *F.E.B.S. Letters*, 1975, **53**, 193.
[129] G. N. Schrauzer, R. N. Katz, J. H. Grate, and T. M. Vickrey, *Angew. Chem. Internat. Edn.*, 1976, **15**, 170.
[130] R. Blackburn, M. Kyaw, G. O. Phillips, and A. J. Swallow, *J.C.S. Faraday I*, 1975, **71**, 2277.
[131] F. R. Jensen and R. C. Kiskis, *J. Amer. Chem. Soc.*, 1975, **97**, 5820.
[132] K. L. Brown, D. Lyles, M. Pencovici, and R. G. Kallen, *J. Amer. Chem. Soc.*, 1975, **97**, 7338.

sulphur atom of methionine-80. At alkaline pH the methionine residue is apparently displaced by the amino-group of a lysine, and below pH 4 the haem crevice opens and a high-spin form is obtained. Recent n.m.r. results at low pH are consistent[133] with there being two rapidly exchanging water molecules at the iron. The rate constant for the reduction of ferricytochrome *c* by Cr^{II} at 25 °C under these conditions is[134] $(3.2/[H^+]+10)$ l mol^{-1} s^{-1} (0.1 mol l^{-1} perchlorate). In 1.0 mol l^{-1} chloride, the rate constant becomes $(40/[H^+] + 3.6\times10^2 + 4.7\times10^3[H^+])$ l mol^{-1} s^{-1} and the authors postulate that the reaction occurs by an inner-sphere mechanism with an [Fe—Cl—Cr] transition state. Addition of thiocyanate ions markedly increases the reaction rate, the third-order rate constant for the thiocyanate-assisted reaction being 1.1×10^6 l^2 mol^{-2} s^{-1} in 1.0 mol l^{-1} chloride and 2.3×10^6 l^2 mol^{-2} s^{-1} in 0.1 mol l^{-1} chloride. The thiocyanate-assisted reaction is thought to occur mainly by an outer-sphere mechanism, with electron transfer taking place through the porphyrin ring system, but the detection of an unstable Cr^{III} product containing thiocyanate bound to the Cr through the S indicates the existence of an inner-sphere pathway with an [Fe—NCS—Cr] transition state.

The reduction of ferricytochrome *c* by e^-_{aq} at neutral pH appears[135] to be a three-step process. In the first step ($k=4.5\times10^{10}$ l mol^{-1} s^{-1}) a transient complex is formed between the cytochrome and the hydrated electron, in the second ($k=5\times10^6$ s^{-1}) the haem iron is reduced, and in the third ($k=1.3\times10^5$ s^{-1}) the protein conformation changes from that appropriate for Fe^{III} to that appropriate for Fe^{II}. The authors favour a specific pathway for the movement of the electron from the surface of the molecule to the haem iron (step 1). No intermediate complexes were observed[136] in the reduction of ferricytochrome *c* by the superoxide radical ion. At 20 °C the rate constant for the reaction at pH 4.7—6.7 is 1.4×10^6 l mol^{-1} s^{-1} and as the pH increases above 6.7 the rate constant steadily decreases (eventually reaching zero, indicating that the neutral and high-pH forms if ferricytochrome *c* are unreactive). The activation enthalpy is 18 kJ mol^{-1} and it seems that little protein rearrangement is required for the formation of the activated complex. The kinetics have been reported for the reduction by Cr^{2+} of 2-hydroxy-5-nitrobenzyltryptophyl cytochrome *c*[137] and of *N*-formyltryptophyl cytochrome *c*.[138]

Sutin's kinetic studies on the oxidation of horse-heart ferrocytochrome *c* by tris-(phen)cobalt(III) have recently been extended[139] to acid pH. The reaction is first-order with respect to each reactant but the dependence of the rate on $[H^+]$ is not simple. Measurements in chloride medium ($I=0.13$ mol l^{-1}) over the pH range 1—7 revealed a rate maximum at pH 2.9 ($k=6.7\times10^4$ l mol^{-1} s^{-1} at 25 °C). By contrast, the rate constants at pH 1.0 and 5.8 are 3.2×10^4 and 2.1×10^3 l mol^{-1} s^{-1}, respectively. Below pH 1.7, biphasic kinetics are observed, the slower reaction having a rate constant of *ca.* 2 s^{-1} (independent of oxidant concentration). The slow process is ascribed to a conformational change in the ferricytochrome *c* which is produced in

[133] A. Lanir and I. Aviram, *Arch. Biochem. Biophys.*, 1975, **166**, 439.
[134] T. J. Przystas and N. Sutin, *Inorg. Chem.*, 1975, **14**, 2103.
[135] J. Wilting, K. J. H. van Buuren, R. Braams, and B. F. van Gelder, *Biochim. Biophys. Acta*, 1975, **376**, 285.
[136] J. Butler, G. G. Jayson, and A. J. Swallow, *Biochim. Biophys. Acta*, 1975, **408**, 215.
[137] T. Brittain and C. Greenwood, *Biochem. J.*, 1975, **149**, 179.
[138] T. Brittain and C. Greenwood, *Biochem. J.*, 1975, **149**, 713.
[139] B. S. Brunschwig and N. Sutin, *Inorg. Chem.*, 1976, **15**, 631.

the mixed-spin form but rearranges to the more stable high-spin form. The large changes in rate occurring over the pH range 3—6 in the oxidation of ferrocytochrome *c* by bromomalononitrile are interpreted[140] in terms of a conformational isomerism of cytochrome *c*. It is suggested that the effective redox geometry alters from a predominantly 'short C' form (in which an axial position is available for substitution) at low pH to a predominantly 'C' form (axial positions encumbered) in the physiological region.

Two reports have appeared[141,142] on the kinetics of electron transfer between cytochrome *c* (P551) and the blue copper protein azurin, both from *Pseudomonas aeruginosa*, and the agreement between the two is fair. Two relaxation times are observed, the faster (in the range 0.4—8 ms) being assigned to the electron-exchange step and the slower (*ca.* 37 ms) to a conformational equilibrium of the reduced azurin, coupled[142] through the electron-transfer step to a faster conformational change of the oxidized cytochrome *c* (P551). The electron transfer is thought[142] to have an outer-sphere mechanism and its rate constant is close to that predicted by the Marcus theory.

Cytochrome P450 is the name given to the active site in a widespread class of iron-containing haem proteins which activate molecular oxygen during the hydroxylation of C—H bonds in metabolism, hormone regulation, and drug detoxification. Little is known about these proteins but it is generally accepted that sulphur (probably as a deprotonated cysteine residue[143]) is a necessary axial ligand in all low-spin ferric cytochromes P450. Recent preliminary work[144] with models indicates that this S is displaced by the O_2 when the latter binds to the Fe, and Chang and Dolphin have evidence[145] that Fe in the oxygenated form of P450 cannot be bound to a mercaptide ion. Holm[146] feels that the high-spin form of Fe^{III}-P450 cytochromes contains one axial sulphur ligand and has made[147] a determined attempt to decide what it might be. Spectroscopic evidence[148] suggests that considerable electron density is transferred to the iron by a mercaptide ligand in the axial position and the results of pulsed n.m.r. experiments[149] suggest that a water molecule, rather than an amino-acid residue of the protein, occupies the sixth co-ordination position at the ferric cation in the absence of added substrate or other ligand. (Its exchange rate of 9.3×10^4 s^{-1} at 25 °C is similar to those of the water molecules in acid met-Mb and -Hb.)

There have been several reports dealing with the kinetic behaviour of cytochrome *c* oxidase and peroxidase but in no case is it possible to conclude much about the

[140] C. E. Castro and E. W. Bartnicki, *Biochemistry*, 1975, **14**, 498.
[141] M. T. Wilson, C. Greenwood, M. Brunori, and E. Antonini, *Biochem. J.*, 1975, **145**, 449.
[142] P. Rosen and I. Pecht, *Biochemistry*, 1976, **15**, 775.
[143] C. K. Chang and D. Dolphin, *J. Amer. Chem. Soc.*, 1975, **97**, 5948.
[144] J. O. Stern and J. Peisach, *F.E.B.S. Letters*, 1976, **62**, 364.
[145] C. K. Chang and D. Dolphin, *J. Amer. Chem. Soc.*, 1976, **98**, 1607.
[146] S. Koch, S. C. Tang, R. H. Holm, R. B. Frankel, and J. A. Ibers, *J. Amer. Chem. Soc.*, 1975, **97**, 916; J. H. Dawson, R. H. Holm, J. R. Trudell, G. Barth, R. E. Linder, E. Bannenberg, C. Djerassi, and S. C. Tang, *ibid.*, 1976, **98**, 3707.
[147] S. C. Tang, S. Koch, G. C. Papaefthymiou, S. Foner, R. B. Frankel, J. A. Ibers, and R. H. Holm, *J. Amer. Chem. Soc.*, 1976, **98**, 2414.
[148] J. P. Collman and T. N. Sorrell, *J. Amer. Chem. Soc.*, 1975, **97**, 4133; J. P. Collman, T. N. Sorrell, J. H. Dawson, J. R. Trudell, E. Bannenberg, and C. Djerassi, *Proc. Nat. Acad. Sci. U.S.A.*, 1976, **73**, 6.
[149] B. W. Griffin and J. A. Peterson, *J. Biol. Chem.*, 1975, **250**, 6445.

mechanism of the reaction concerned. Rate constants of 2×10^4 (ref. 150) and 1.8×10^4 l mol^{-1} s^{-1} (ref. 151) have been reported for the reaction of CO with ascorbate-reduced oxidase, 22 l mol^{-1} s^{-1} for the reaction of cyanide with the oxygenated enzyme,[152] something in the range 10^6—10^7 l mol^{-1} s^{-1} for ferrocytochrome *c* with the oxidized enzyme,[153] and a complex picture for the reaction of azurin with the oxidase;[154] the highest value of the apparent rate constant for the oxidation of $[Fe(phen)_2(CN)_2]$ by compound II of cytochrome *c* peroxidase is[155] 2.9×10^5 l mol^{-1} s^{-1}.

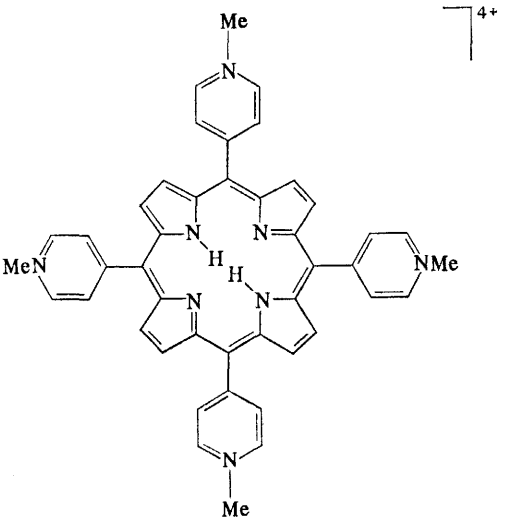
The debate on whether the pK_a of 8.6 for compound II of horseradish peroxidase (HRP-II) represents the ionization of an iron-bound water molecule continues. Dunford adduces[156] further kinetic evidence that it does while Schejter provides[157] additional n.m.r. evidence that there is no water molecule in the inner co-ordination sphere of the iron(III) atom; however, the latter interpretation of the data has been questioned[158] by Vuk-Pavlović and Benko, who suggest that the sixth ligand site of the metal contains what they term a 'sedentary' water molecule. The formation of HRP-I from the reaction of native horseradish peroxidase with H_2O_2 has[159] a rate constant of 2.5×10^7 l mol^{-1} s^{-1} at 25 °C (pH 7.10), with an activation energy of 3.5 ± 1.0 kcal mol^{-1}. The kinetics of cyanide and fluoride binding to turnip peroxidases P_1 and P_7 have also been measured.[160]

The results of pulsed n.m.r. experiments on high-spin haem iron-containing beef liver catalase suggest[161] that there is one rapidly exchanging water molecule per iron. The kinetics of the decomposition of H_2O_2 catalysed by Fe^{III}(edta) are consistent with a radical chain mechanism and it is suggested[162] that such redox chains may be quite a common feature of the catalase-like activity of transition-metal compounds.

Reviews have appeared on the kinetics and mechanism of metalloporphyrin formation[163] and inorganic oxygen carriers as models for biological systems.[164] Several new systems have been put forward[165] as models for the haem proteins. It has been shown[166] that the addition of CN^- to the five and six co-ordination positions in ferriprotoporphyrin (haemin) is slow on the n.m.r. time-scale, but the exchange of 1-methylimidazole (MI) between haemin$(MI)_2$ and the bulk solvent in MI–chloro-

150 S. R. Parr, M. T. Wilson, and C. Greenwood, *Biochem. J.*, 1975, **151**, 51.
151 D. C. Wharton and Q. H. Gibson, *Biochim. Biophys. Acta*, 1976, **430**, 445.
152 T. Brittain and C. Greenwood, *Biochem. J.*, 1976, **155**, 453.
153 M. T. Wilson, C. Greenwood, M. Brunori, and E. Antonini, *Biochem. J.*, 1975, **147**, 145.
154 M. Brunori, S. R. Parr, C. Greenwood, and M. T. Wilson, *Biochem. J.*, 1975, **151**, 185.
155 J. E. Erman, *Biochim. Biophys. Acta*, 1975, **397**, 36.
156 C. D. Hubbard, H. B. Dunford, and W. D. Hewson, *Canad. J. Chem.*, 1975, **53**, 1563.
157 A. Lanir and A. Schejter, *Biochem. Biophys. Res. Comm.*, 1975, **62**, 199.
158 S. Vuk-Pavlović and B. Benko, *Biochem. Biophys. Res. Comm.*, 1975, **66**, 1154.
159 W. D. Hewson and H. B. Dunford, *Canad. J. Chem.*, 1975, **53**, 1928.
160 D. Job and J. Ricard, *Arch. Biochem. Biophys.*, 1975, **170**, 427.
161 A. Lanir and A. Schejter, *Biochemistry*, 1976, **15**, 2590.
162 C. Walling, R. E. Partch, and T. Weil, *Proc. Nat. Acad. Sci. U.S.A.*, 1975, **72**, 140.
163 W. Schneider, *Structure and Bonding*, 1975, **23**, 123; see also 'Porphyrins and Metalloporphyrins', ed. K. M. Smith, Elsevier, Amsterdam, 1975.
164 G. McLendon and A. E. Martell, *Coordination Chem. Rev.*, 1976, **19**, 1.
165 J. P. Collman, R. R. Gagne, C. A. Reed, T. R. Halbert, G. Lang, and W. T. Robinson, *J. Amer. Chem. Soc.*, 1975, **97**, 1427; C. K. Chang and T. G. Traylor, *Biochem. Biophys. Res. Comm.*, 1975, **62**, 729; J. P. Collman, J. I. Brauman, and K. S. Suslick, *J. Amer. Chem. Soc.*, 1975, **97**, 7185.
166 J. T. Wang, H. J. C. Yeh, and D. F. Johnson, *J. Amer. Chem. Soc.*, 1975, **97**, 1968.

form is not.[167] The kinetics of the recombination of ferroprotoporphyrin IX with CO have been studied[168] at various pressures in aqueous ethylene glycol and glycerol. The activation enthalpies (at 1 bar) in the two solvents are, respectively, 7.5 and 12.2 kcal mol^{-1} and the activation volumes 2.0 and 14.0 cm^3 mol^{-1}, and it is concluded that the reaction is largely diffusion-controlled in the highly viscous glycerol but activation-controlled in the much more fluid glycerol–water mixture. The kinetics have also been reported for cyanide addition[169] to the monomeric iron(III) complexes of meso-, proto-, and deuterio-porphyrin IX in 2% sodium lauryl sulphate (above the CMC), for the interaction[170] of Cu^{II} with haematoporphyrin IX in aqueous acetic acid, and for the binding[171] of O_2 and CO to simple ferrous porphyrins in methylene chloride at low temperatures. It has been observed[172] that Mn^{II} in the manganese–tetraphenylporphyrin–(1-methylimidazole) complex exhibits a coordination number of five, and the rate constant for the addition of the first water molecule (with concomitant spin change) to the nickel(II) complex of (10) is[173] 2.5×10^5 l mol^{-1} s^{-1} at 25 °C.



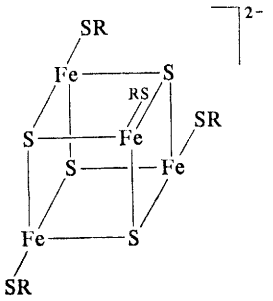
(10)

The high rate constant (2.0×10^{10} l mol^{-1} s^{-1}) for the reaction of e^-_{aq} with the hydroxy-protoferrihaem dimer suggests[174] that the mechanism is outer-sphere.

[167] E. V. Goldammer and H. Zorn, *Z. Naturforsch.*, 1976, **31b**, 242.
[168] E. F. Caldin and B. B. Hasinoff, *J.C.S. Faraday I*, 1975, **71**, 515.
[169] P. Hambright and P. B. Chock, *J. Inorg. Nuclear Chem.*, 1975, **37**, 2363.
[170] G. Paquette and M. Zador, *Canad. J. Chem.*, 1975, **53**, 2375.
[171] C. J. Weschler, D. L. Anderson, and F. Basolo, *J. Amer. Chem. Soc.*, 1975, **97**, 6707.
[172] B. Gonzalez, J. Kouba, S. Yee, C. A. Reed, J. F. Kirner, and W. R. Scheidt, *J. Amer. Chem. Soc.*, 1975, **97**, 3247.
[173] R. F. Pasternack, N. Sutin, and D. H. Turner, *J. Amer. Chem. Soc.*, 1976, **98**, 1908.
[174] J. Butler, G. G. Jayson, and A. J. Swallow, *J.C.S. Faraday I*, 1976, **72**, 1391.

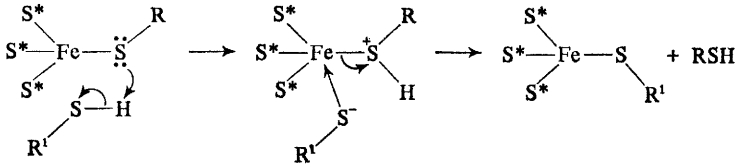
5 Redox Reactions involving Metals in other Biological and Model Systems

Synthetic iron–sulphur cluster compounds of general structure (11) serve as analogues of the active sites of $(Fe_4S_4)_n$ ferredoxins and high-potential iron proteins



(11)

(HIPIP). The rates of initial thiolate substitution in reactions of (11) (R = Et or Bu^t) with arylthiols in acetonitrile solution have been reported,[175] and the mechanism shown in Scheme 3 is proposed for the ligand-exchange process (S* represents a sulphide S in the Fe_4S_4 core).



Scheme 3

The kinetics for ligand exchange of the water-soluble (11; R = $CH_2CH_2CO_2^-$) as a function of pH and thiol concentration are[176] in accord with four reversible mercaptan–lyate species exchange reactions followed by product formation through specific acid and base catalysis. It has also been found[177] that (11) (R = Me, Bu^t, or Bu^i) represent the basic forms of weak acids, with pK_a comparable to those of carboxylic acids.

The kinetics of reduction [$K_4Fe(CN)_6$, SO_2^-, $S_2O_4^{2-}$, sodium ascorbate, and cytochrome c_2] and oxidation [$K_3Fe(CN)_6$ and cytochrome c_2] of HIPIP from *Chromatium vinosum* have been reported,[178] and it is concluded that HIPIP undergoes rapid outer-sphere electron transfer (there being no indication of complex formation with the various reactants). Moreover, steric restrictions and differences in oxidation–reduction potential are less important than electrostatic attraction and/or repulsion in determining the absolute rate constants (Table 2). Rawlings *et al.* have deter-

[175] G. R. Dukes and R. H. Holm, *J. Amer. Chem. Soc.*, 1975, **97**, 528.
[176] R. C. Job and T. C. Bruice, *Proc. Nat. Acad. Sci. U.S.A.*, 1975, **72**, 2478.
[177] T. C. Bruice, R. Maskiewicz, and R. Job, *Proc. Nat. Acad. Sci. U.S.A.*, 1975, **72**, 231.
[178] I. A. Mizrahi, F. E. Wood, and M. A. Cusanovich, *Biochemistry*, 1976, **15**, 343.

Table 2 *Rate constants for the oxidation and reduction of HIPIP*[a]

	k/l mol^{-1} s^{-1}	*Apparent charge interactions*
Oxidants		
Ferricyanide	890	minus–minus
Ferricytochrome c_2	1.4×10^6	plus–minus
Reductants		
Ferrocyanide	150	minus–neutral
Ferrocytochrome c_2	2.2×10^5	plus(?)–neutral
Na ascorbate	3.9	minus–neutral
SO_2^-	2.1×10^6	minus–neutral
$S_2O_4^{2-}$	1.2×10^3	minus–neutral

[a] Data from ref. 178.

mined[179] the kinetics of oxidation of reduced *Chromatium* HIPIP by $[Fe(CN)_6]^{3-}$ (where the agreement with Mizrahi *et al.* is fair) and $[Co(phen)_3]^{3+}$, and the kinetics of reduction of oxidized HIPIP by $[Fe(edta)]^{2-}$ (Table 3). It is concluded[179] that

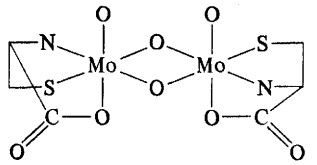
Table 3 *Kinetics of oxidation and reduction of HIPIP*[a]

Reactant	$10^{-3}k$/l mol^{-1} s^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
$[Fe(CN)_6]^{3-}$	(2.0 ± 0.1)	-0.4 ± 0.1	-45 ± 1
$[Co(phen)_3]^{3+}$	(2.8 ± 0.1)[b]	14.9 ± 0.7	7 ± 2
$[Fe(edta)]^{2-}$	(1.6 ± 0.1)	0.8 ± 0.3	-41 ± 1

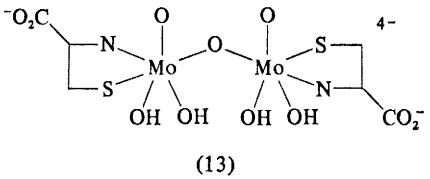
[a] Data, from ref. 179, refer to 25 °C, $I=0.1$ mol l^{-1}, and pH 7.0 (phosphate). [b] At 26 °C.

$[Co(phen)_3]^{3+}$ is able to attack the buried cluster of HIPIP directly, whereas $[Fe(edta)]^{2-}$ cannot do so and must therefore transfer its electron from long range in a process involving minimal protein activation.

Zumft and Mortenson have reviewed[180] the bacterial nitrogenases and Lawrence and Spence have noted[181] an interesting difference in the kinetics of reduction of ferricytochrome *c* (cyt c^{III}) by two apparently similar molybdenum-containing enzyme models (12) and (13). The reduction by the dioxo-bridged compound is



(12)



(13)

relatively slow and its rate is first-order in cyt c^{III} and zero-order in (12) ($k=1.09\times10^{-3}$ s^{-1} at pH 7.5 and 20 °C); the authors are unable to decide between three possible mechanisms for this reaction. On the other hand, the reduction by the mono-oxo-bridged complex is rapid and its rate is first-order in each reactant ($k=2.6\times10^7$ l mol^{-1} s^{-1} at pH 7.0, and 25 °C; at higher pH the picture is more

[179] J. Rawlings, S. Wherland, and H. B. Gray, *J. Amer. Chem. Soc.*, 1976, **98**, 2177.
[180] W. G. Zumft and L. E. Mortenson, *Biochim. Biophys. Acta*, 1975, **416**, 1.

complex); in this case, evidence is presented in favour of an outer-sphere mechanism. The biological implications of this difference in behaviour of mono-oxo- and dioxo-bridged molybdenum(v) complexes are discussed.[181]

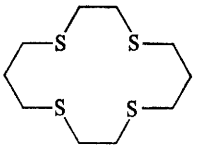
A preliminary report on the structure (to 2.8 Å resolution) of methaemerythrin from *Themiste dyscritum* shows[182] that the co-ordination about the two iron atoms in each subunit is rather unusual. The kinetics of anation (by azide, thiocyanate, fluoride and chloride) of methaemerythrin from *Golfingia gouldii* have been studied[183] over a wide pH range. An associative mechanism is preferred and the general decrease in the second-order rate constant with increasing anion concentration is attributed to the effect of a secondary anion-binding site; the behaviour of octameric and monomeric forms of the protein towards thiocyanate is identical. A further indication that octameric haemerythrin behaves kinetically as eight single units has been obtained[184] from data on the oxygen-binding and -dissociation reactions. There is no sign of anything other than a single reaction in either direction and the following kinetic parameters are reported (at 25 °C, pH 8.2, and $I=0.015$ mol l^{-1}): $k_{on}=7.4\times10^6$ l mol^{-1} s^{-1}, $\Delta H^{\ddagger}=8.2$ kcal mol^{-1}, and $\Delta S^{\ddagger}=+1$ cal K^{-1} mol^{-1}; $k_{off}=51$ s^{-1}, $\Delta H^{\ddagger}=20.6$ kcal mol^{-1}, and $\Delta S^{\ddagger}=+19$ cal K^{-1} mol^{-1}. Curiously, perchlorate ion (0.05 mol l^{-1}) enhances k_{off} by a factor of about 3, although it has little effect on k_{on}. The resonance Raman spectra of the oxygen complexes of several haemocyanins indicate[185] that the O_2-binding sites have essentially the same geometries; the oxygen is bound as O_2^{2-} and the two copper atoms both have oxidation states of +2.

Superoxide dismutases, which catalyse the conversion of the radical ion $O_2^{-\bullet}$ into molecular oxygen and hydrogen peroxide, are found in most, if not all, oxygen-using organisms. Many of these enzymes exist as dimers, both subunits of which contain one catalytic Cu atom and one Zn. The *X*-ray crystal structure at 3 Å resolution has recently been reported[186] for the Cu^{2+},Zn^{2+} superoxide dismutase from bovine erythrocytes, and the distance separating the copper (which has four histidine ligands in a somewhat distorted square plane) and the zinc atoms (three histidines, one of them in common with the Cu, and an aspartate in an approximately tetrahedral arrangement) in each subunit is about 6 Å. Further evidence has been produced[187] in support of a previous suggestion that Cu^{III} is an intermediate in catalysis by galactose oxidase (which contains a single Cu atom per molecule in an environment[188] of four in-plane N atoms with axial symmetry).

Fee has reviewed[189] the chemistry of proteins which contain the 'blue' copper centre and several groups have investigated the nature of the Cu sites in these interesting compounds. Low-temperature absorption c.d. and m.c.d. spectra of stellacyanin, plastocyanin, and azurin are consistent with[190] the presence of a tetra-

[181] G. D. Lawrence and J. T. Spence, *Biochemistry*, 1975, **14**, 3626.
[182] R. E. Stenkamp, L. C. Sieker, and L. H. Jensen, *Proc. Nat. Acad. Sci. U.S.A.*, 1976, **73**, 349.
[183] D. R. Meloon and R. G. Wilkins, *Biochemistry*, 1976, **15**, 1284.
[184] D. J. A. de Waal and R. G. Wilkins, *J. Biol. Chem.*, 1976, **251**, 2339.
[185] T. B. Freedman, J. S. Loehr, and T. M. Loehr, *J. Amer. Chem. Soc.*, 1976, **98**, 2809.
[186] J. S. Richardson, K. A. Thomas, B. H. Rubin, and D. C. Richardson, *Proc. Nat. Acad. Sci. U.S.A.*, 1975, **72**, 1349.
[187] G. R. Dyrkacz, R. D. Libby, and G. A. Hamilton, *J. Amer. Chem. Soc.*, 1976, **98**, 626.
[188] L. Cleveland, R. E. Coffman, P. Coon, and L. Davis, *Biochemistry*, 1975, **14**, 1108.
[189] J. A. Fee, *Structure and Bonding*, 1975, **23**, 1.
[190] E. I. Soloman, J. W. Hare, and H. B. Gray, *Proc. Nat. Acad. Sci. U.S.A.*, 1976, **73**, 1389.

hedral Cu^{II} centre which is distorted by *ca.* 6° towards a square-planar configuration. Two sets of resonance Raman spectra have been published recently but, whereas Siiman *et al.*[191] favour a distorted four-co-ordinate structure arising from the binding of Cu to one cysteine-S and three N atoms (at least one of which is an amide nitrogen), Miškowski *et al.*[192] prefer an approximately trigonal-bipyramidal co-ordination with an S and two N ligands in the equatorial plane and less strongly bound N or O ligands in the axial positions. Comparison of the spectra of Co^{II}- and Cu^{II}-stellacyanin and -carbonic anhydrase has led[193] Morpurgo *et al.* to the conclusion that 'blue' copper is five-co-ordinate, while Rorabacher and co-workers have found[194] that Cu^{2+}, in its complex with (14) (which has[195] very similar spectral and



(14)

redox properties to the 'blue' proteins), is at the centre of an undistorted planar square of S atoms. Resonance Raman results confirm[196] previous indications that the two 'blue' copper sites in ceruloplasmin are not equivalent.

The kinetics if the anaerobic reduction of stellacyanin, plastocyanin, azurin, and laccase by $[Fe(edta)]^{2-}$ have been reported.[197] Simple second-order behaviour was observed and the following rate constants, with their associated $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values, were measured (at 25 °C and pH 7): 4.3×10^5, 8.2×10^4, 1.3×10^3, and 2.6×10^2 l mol^{-1} s^{-1}; 3, 2, 2, and 13 kcal mol^{-1}; and −21, −29, −37, and −5 cal K^{-1} mol^{-1}, respectively. The authors favour an outer-sphere mechanism for azurin, plastocyanin, and stellacyanin but conclude that laccase employs a pathway which requires specific protein activation (of *ca.* 10 kcal mol^{-1} in $\Delta H^{\ddagger}$) to accept the reductant. The kinetics of the reduction of laccase by $[Fe(CN)_6]^{4-}$ are complicated,[198] as they are for the autoxidation of reduced laccase.[199] The results[141,142] for electron transfer between azurin and cytochrome *c* have already been mentioned.

[191] O. Siiman, N. M. Young, and P. R. Carey, *J. Amer. Chem. Soc.*, 1976, **98**, 744.
[192] V. Miskowski, S. P. W. Tang, T. G. Spiro, E. Shapiro, and T. H. Moss, *Biochemistry*, 1975, **14**, 1244.
[193] L. Morpurgo, A. Finazzi Agró, G. Rotilio, and B. Mondoví, *European J. Biochem.*, 1976, **64**, 453.
[194] M. D. Glick, D. P. Gavel, L. L. Diaddario, and D. B. Rorabacher, *Inorg. Chem.*, 1976, **15**, 1190.
[195] T. E. Jones, D. B. Rorabacher, and L. A. Ochrymowycz, *J. Amer. Chem. Soc.*, 1975, **97**, 7485.
[196] L. Tosi, A. Garnier, M. Herve, and M. Steinbuch, *Biochem. Biophys. Res. Comm.*, 1975, **65**, 100.
[197] S. Wherland, R. A. Holwerda, R. C. Rosenberg, and H. B. Gray, *J. Amer. Chem. Soc.*, 1975, **97**, 5260.
[198] R. A. Holwerda and H. B. Gray, *J. Amer. Chem. Soc.*, 1975, **97**, 6036.
[199] L. E. Andréasson, R. Brändén, and B. Reinhammer, *Biochim. Biophys. Acta*, 1976, **438**, 370.

Part IV

ORGANOMETALLIC COMPOUNDS

By
J. L. DAVIDSON

1
Substitution

BY J. L. DAVIDSON

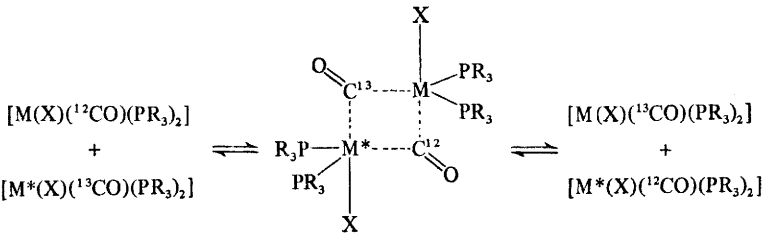
Reviews dealing with the photochemical reactions[1] of metal carbonyls and the photochemistry of metal carbonyls in matrices[2] have appeared. A third review is concerned with the kinetics and mechanisms of CO substitution in Group VI metal carbonyls.[3]

1 Exchange Reactions

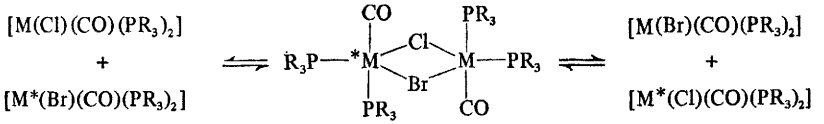
The exchange of isotopically labelled CO with $[Mn(Br)(CO)_5]$ and $[Re(Br)(CO)_5]$ has been the subject of several investigations and the results obtained to date generally support the idea that the rate-determining step is CO dissociation. Evidence has been obtained which indicates that the four equatorial CO groups undergo exchange more rapidly than the axial CO and also that fluxional behaviour is exhibited by the five-co-ordinate intermediate $[M(Br)(CO)_4]$.[4] A more detailed study confirms the above results and indicates that the rate constants for *cis*-CO dissociation are at least ten times greater than those for CO groups *trans* to Br.[5] The rate constants for *cis*-CO dissociation are $k_{cis} = 2.8 \times 10^{-5}$ s^{-1} at 23 °C and 5.1×10^{-7} s^{-1} at 30 °C for $[Mn(Br)(CO)_5]$ and $[Re(Br)(CO)_5]$ respectively. Calculations of the time dependence of the concentration of $[M(Br)(CO)_5]$ in which a ^{13}CO ligand is in an axial position can best be fitted to experimentally derived time dependencies if the intermediate $[M(Br)(CO)_4]$ is assumed to undergo fluxional motion. An estimate of the inverse lifetime of this intermediate in solution is 3×10^4 s^{-1} while the rate constant for CO axial–radial exchange is 10^6 s^{-1}, which indicates that CO scrambling occurs readily during the lifetime of the species. Stereochemical preference in CO exchange reactions has also been observed qualitatively by i.r. spectroscopy in reactions between $C^{18}O$ and *cis*-$[Mn(Br)(CO)_4(PPh_3)]$.[6] A comparison of the enthalpies of activation and the position of the Mn—C stretching modes of *E* symmetry in the i.r. spectra of $[Mn(X)(CO)_5]$ complexes demonstrates that the ΔH^* values parallel the inferred relative Mn—C bond strengths at the equatorial positions.[7] Thus for complexes of this type which undergo CO substitution or exchange *via* a dissociative mechanism an estimate of their relative reactivity can be made from the position of the ν(Mn—C)(*E*) mode.

[1] M. Wrighton, *Chem. Rev.*, 1974, **74**, 401.
[2] J. J. Turner, *Angew. Chem. Internat. Edn.*, 1975, **14**, 304.
[3] H. Werner, *J. Organometallic Chem.*, 1975, **94**, 285.
[4] A. Berry and T. L. Brown, *Inorg. Chem.*, 1972, **11**, 1165.
[5] J. D. Atwood and T. L. Brown, *J. Amer. Chem. Soc.*, 1975, **97**, 3380.
[6] I. S. Butler and H. K. Spendjian, *J. Organometallic Chem.*, 1975, **101**, 97.
[7] G. R. Dobson, *Ann. New York Acad. Sci.*, 1974, **239**, 237 (*Chem. Abs.*, 1975, **82**, 79878).

Halide, CO, and phosphines undergo intermolecular exchange between rhodium and iridium complexes $[M(X)(CO)(L)_2]$ (X = Cl or Br, L = tertiary phosphine, arsine, or stibine).[8] Exchange experiments indicate that CO and halide undergo random redistribution. Exchange of phosphines between rhodium complexes is also random but phosphine–phosphite exchange between Rh and Ir favours the mixed species $[MCl(CO)(PR_3)\{P(OR^1)_3\}]$. Thus exchange of CO and halide is considered to occur through four-centre associative mechanisms involving (doubly) five-co-ordinate bridging intermediates, (Schemes 1 and 2), while phosphine exchange is probably a dissociative process.



Scheme 1 CO *exchange*



Scheme 2 *Halide exchange*

Computer programmes applicable to intermolecular exchange in non-first-order spin systems have been developed and their scope has been illustrated with reference to the equilibrium[9]

$$[Pd(H)(PEt_3)_3]^+ + PEt_3 \rightleftharpoons [Pd(H)(PEt_3)_4]^+$$

Complexes $[M(PPh_3)_4]$ (M = Ni, Pd, or Pt) undergo rapid phosphine exchange in solution and are essentially dissociated completely to $[M(PPh_3)_3]$ and PPh_3. In contrast complexes $[M(SbR_3)_4]$ (M = Ni or Pd, R = Ph or *p*-MeC_6H_4) show little tendency to dissociate and undergo slow exchange in solution.[10] Phosphine exchange in the Ni^{II} complex $[(PPh_3)_2Ni(o\text{-tolyl})Br]$ also depends on steric factors since ligands such as PPh_2Me and $P(OMe)_3$ exchange readily with co-ordinated PPh_3 whereas no reaction was observed with sterically crowded $P(o\text{-}C_6H_4Me)_3$ and $P(o\text{-}C_6H_4OMe)_3$.[11] Variable-temperature ^{19}F n.m.r. studies of $[Pt\{P(CF_3)Ph_2\}_3]$ show that rapid phosphine exchange at room temperature is frozen out at -50 °C.[12] Addition of free phosphine increases the rate of exchange and also results in the formation of a new species believed to be $[Pt\{P(CF_3)Ph_2\}_4]$ which may exist in two different forms below -80 °C. Addition of PPh_3 to solutions of $[Ni(Et)(acac)(PPh_3)]$ also increases the rate

[8] P. E. Garrou and G. E. Hartwell, *Inorg. Chem.*, 1976, **15**, 646.
[9] P. Meakin, A. D. English, and J. P. Jesson, *J. Amer. Chem. Soc.*, 1976, **98**, 414.
[10] D. Garrou and G. E. Hartwell, *Inorg. Chem.*, 1976, **15**, 730.
[11] Y. Nakamura, K.-I. Maruya, and T. Mizoroki, *J. Organometallic Chem.*, 1976, **104**, C5.
[12] T. G. Attig, M. A. A. Beg, and H. C. Clark, *Inorg. Chem.*, 1975, **14**, 2986

of phosphine exchange, resulting in rate constants for PPh_3 dissociation in toluene varying from $1.6\times10^2\ s^{-1}$ at 25 °C to $4.2\times10\ s^{-1}$ at −80 °C.[13] The activation energies for PPh_3 dissociation from this complex and from $[Ni(Me)(acac)(PPh_3)_2]$ range from 16.8 to 25.2 kJ mol^{-1}, much less than values reported for other nickel complexes.

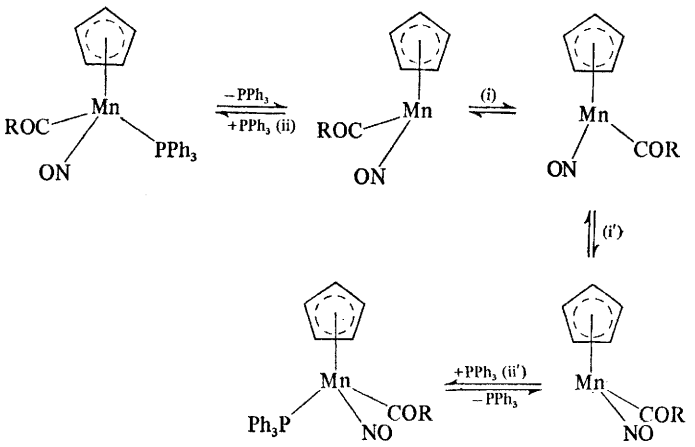
When equimolar amounts of $[Pd_2(Cl)_4(L^1)_2]$ and $[Pt_2(Cl)_4(L^2)_2]$ are mixed, complexes of the type $[PdPt(Cl)_4(L^1)(L^2)]$ are formed, according to ^{31}P n.m.r. studies (L^1 and L^2 are either the same or different phosphines, PPr_3 or PBu^n_3).[14,15] The three complexes are in dynamic equilibrium and a kinetic study suggests that exchange occurs *via* tetrameric intermediates. Thermodynamic data for the exchange processes (*a*) and (*b*) are given in Table 1.

$$P^*PdPdP^* + PPdPtP \longrightarrow P^*PdPtP + P^*PdPdP \quad (a)$$
$$P^*PtPtP^* + PPdPtP \longrightarrow P^*PtPdP + P^*PtPtP \quad (b)$$

Table 1 *Activation parameters for phosphine exchange (from ref.* 15)

Exchange process			(E_a/kJ mol^{-1})	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
Pd—P	L = PPr_3	(*a*)	34±8	−80±17
Pd—P	L = PBu^n_3	(*a*)	46±8	−50±17
Pt—P	L = PPr_3	(*b*)	80±17	—
Pt—P	L = PBu^n_3	(*b*)	59±17	—

The racemization of $[Mn(CO_2Me)(NO)(PPh_3)(\eta\text{-}C_5H_5)]$ occurs *via* exchange of PPh_3, which is a dissociative process unaffected by free PPh_3. However, racemization of the benzoyl complex (+579)-$[Mn(COPh)(PPh_3)(NO)(\eta\text{-}C_5H_5)]$ is retarded by the presence of PPh_3, and, to account for this, chiral intermediates are considered to be involved in the exchange process[16–18] (Scheme 3). The chiral intermediate may either

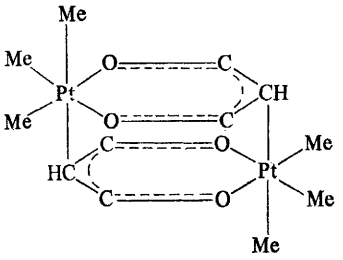


Scheme 3

[13] T. Yamamoto, T. Saruyama, Y. Nakamura, and A. Yamamoto, *Bull. Chem. Soc. Japan*, 1976, **49**, 589.
[14] C. Masters and J. P. Visser, *J.C.S. Chem. Comm.*, 1974, 932.
[15] A. A. Kiffen, C. Masters, and J. P. Visser, *J.C.S. Dalton*, 1975, 1311.
[16] H. Brunner, J. Aclasis, M. Langer, and W. Steger, *Angew. Chem. Internat. Edn.*, 1974, **13**, 810.
[17] H. Brunner and M. Langer, *J. Organometallic Chem.*, 1975, **87**, 223.
[18] H. Brunner, *J. Organometallic Chem.*, 1975, **94**, 189.

rearrange, step (i)(i'), to give a planar transition state or react with triphenylphosphine, step (ii)(ii'), to give the original compound. Since step (ii) will be preferred in the presence of excess PPh_3 the reduction in the rate of racemization observed on adding triphenylphosphine can be rationalized.

^1H N.m.r. studies of dimeric $[(acac)_2Pt_2(Me)_6]$ (1) in $CDCl_3$ at various tempera-



(1)

tures indicate that acac exchange follows first-order kinetics ($E_a = 61.5 \pm 0.8$ kJ mol^{-1}) consistent with Pt—C cleavage to give monomeric intermediates [(acac)Pt-$(Me)_3$].[19]

Photochemical exchange of cyclopentadienyl groups between $[(\eta\text{-}C_5D_5)_2TiCl_2]$ and $[(\eta\text{-}C_5H_5)_2TiCl_2]$ has been observed in benzene solution leading to formation of $[(\eta\text{-}C_5H_5)(\eta\text{-}C_5D_5)TiCl_2]$.[20] Lack of decomposition products from the reaction argues against a mechanism involving cyclopentadienyl free radicals. A later report[21] reveals that photochemical cyclopentadienide exchange also occurs between $[(\eta\text{-}C_5H_4Me)_2MCl_2]$ and $[(\eta\text{-}C_5H_5)_2MCl_2]$ but at a rate 0.1 times as great as for the cyclopentadienyl titanium system for M = V and 0.4 times as great for M = Ti.

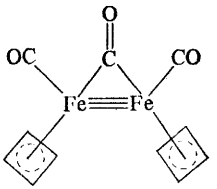
2 Substitution in Carbonyls: Carbon Monoxide Replacement

Simple Carbonyls.—A number of studies have been reported by Turner of the photochemistry of Group VI hexacarbonyls in low-temperature matrices which go some way to clarifying the nature of the species produced on photolysis of $[M(CO)_6]$ (see Vol. 3, p. 354). I.r. spectra of ^{13}CO-enriched carbonyls are consistent with the primary photolysis product $[M(CO)_5]$ (M = Cr, Mo, or W) with C_{4v} symmetry but are inconsistent with a D_{3h} pentacarbonyl.[22] Previously observed discrepancies in the position of maximum absorption of $[M(CO)_5]$ in the visible spectrum can be explained by exceptional sensitivity to the matrix since the matrix species generally occupy the sixth co-ordination site.[23] With noble gas matrices shifts in the visible band are interpreted in terms of changes in the bond angle between different $M(CO)_5$—(noble gas species). In CO-doped argon matrices evidence is provided for formation of both $[Cr(CO)_5 \cdots Ar]$ and $[Cr(CO)_5 \cdots CO]$ molecules on photolysis of $[Cr(CO)_6]$.[24] These

[19] N. S. Ham, J. R. Hall, and G. A. Swile, *Austral. J. Chem.*, 1975, **28**, 759.
[20] E. Vitz, P. J. Vagner, and C. H. Brubaker, jun., *J. Organometallic Chem.*, 1976, **107**, 301.
[21] E. Vitz and C. H. Brubaker, jun., *J. Organometallic Chem.*, 1976, **104**, C33.
[22] R. N. Perutz and J. J. Turner, *Inorg. Chem.*, 1975, **14**, 262.
[23] R. N. Perutz and J. J. Turner, *J. Amer. Chem. Soc.*, 1975, **97**, 4791.
[24] J. K. Burdett, M. A. Graham, R. N. Perutz, M. Poliakoff, A. J. Rest, J. J. Turner, and R. F. Turner, *J. Amer. Chem. Soc.*, 1975, **97**, 4805.

results provide a basis for rejecting claims that a more stable isomer (trigonal bipyramidal) of $[Cr(CO)_5]$ exists and that a species $[Cr(CO)_5S]$, where S is an *O*-bonded or sideways bonded isocarbonyl,[25] is feasible. Such a conclusion has been reached independently by Braterman and Black.[26] These workers also presumed the occurrence, under photoreversal conditions, of a degenerate, undetected photoisomerism in C_{4v} $[M(CO)_5]$ the reality of which was subsequently demonstrated by photolysing $[Cr(CO)_6]$ in a CH_4 matrix with plane-polarized light.[27] $[Mo(CO)_6]$ in a methane matrix on prolonged photolysis produces $[Mo(CO)_5]$ and secondary products $[Mo(CO)_4]$ and $[Mo(CO)_3]$ which, from ^{13}CO substitution studies, appear to have C_{2v} and C_{3v} structures respectively.[28] A brief report of the photosubstitution of a CO group in $[Cr(CO)_6]$ by pyridine gives a quantum yield of 0.67 ± 0.02 for $[Cr(CO)_6] = 3.10^{-4}$ mol l^{-1} when [pyridine] $= 10^{-2}$ mol l^{-1}. This compares with previous reports that a value of 1 is generally obtained for photodissociation of CO from $[M(CO)_6]$ (M = Cr, Mo, or W).[29] Thus radiationless processes must compete with M—CO cleavage. With $[V(CO)_6]^-$ slightly less efficient photosubstitution by MeCN and pyridine is suggested by a quantum yield of 0.5 ± 0.05.[30]

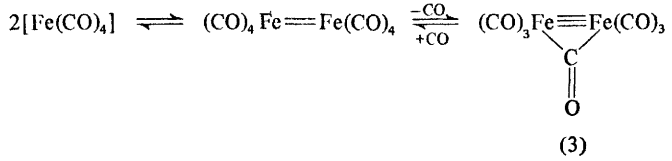
The co-ordinatively unsaturated species $[Fe(CO)_4]$ may be generated by a number of methods and reacts with phosphines and phosphites (L) to give a mixture of $[Fe(CO)_4(L)]$ and $[Fe(CO)_3(L)_2]$. However, the latter is not formed by attack of L on $[Fe(CO)_4(L)]$ under the same conditions and Cardaci has suggested that $[Fe(CO)_4]$ undergoes dissociation to $[Fe(CO)_3]$ first and that this subsequently reacts with L to give the disubstituted derivative.[31] An alternative hypothesis is offered by Koerner von Gustorf who observed that the complex (2), produced by photolysing tri-



(2)

carbonylcyclobutadienyliron, reacts with trimethyl phosphite to give $[(\eta\text{-}C_4H_4)Fe(CO)_2\{P(OMe)_3\}]$ and $[(\eta\text{-}C_4H_4)Fe(CO)\{P(OMe)_3\}_2]$.[32] He postulates that $[Fe(CO)_4]$ undergoes the transformation depicted in Scheme 4 to give the structurally related species (3) which can react with phosphines to give the aforementioned mono- and di-substituted complexes. Both of these theories adequately explain the available data for mono- and di-substitution and in fact may not be mutually exclusive since it is conceivable that $[Fe_2(CO)_7]$ (3) could be in equilibrium with $[Fe(CO)_4]$ and $[Fe(CO)_3]$. $[Fe(CO)_4]$ produced by photolysis of $[Fe(CO)_5]$ in hydrocarbon glasses, molar in

[25] E. P. Kundig and G. A. Ozin, *J. Amer. Chem. Soc.*, 1974, **96**, 3820.
[26] J. D. Black and P. S. Braterman, *J. Amer. Chem. Soc.*, 1975, **97**, 2908.
[27] J. K. Burdett, R. N. Perutz, M. Poliakoff, and J. J. Turner, *J.C.S. Chem. Comm.*, 1975, 157.
[28] R. N. Perutz and J. J. Turner, *J. Amer. Chem. Soc.*, 1975, **97**, 4800.
[29] J. Nasielski and A. Colas, *J. Organometallic Chem.*, 1975, **101**, 215.
[30] M. S. Wrighton, D. A. Handeli, and D. L. Morse, *Inorg. Chem.*, 1976, **15**, 434.
[31] G. Cardaci, *Inorg. Chem.*, 1974, **13**, 368.
[32] I. Fischler, K. Hildenbrand, and E. Koerner von Gustorf, *Angew. Chem. Internat. Edn.*, 1975, **14**, 54.

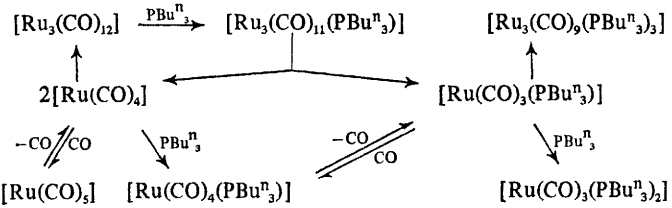


(3)

Scheme 4

MeTHF, exists as $[Fe(CO)_4(MeTHF)]$ (substituent axial) on the basis of i.r. studies.[33] Further photolysis produces $[Fe(CO)_3(MeTHF)_2]$ (bis-axial and axial–equatorial).

Polynuclear Carbonyls.—$[Ru_3(CO)_{12}]$ reacts with PBu^n_3 according to the rate law $k_{obs}=k_1+k_2[PBu^n_3]$ with activation parameters $\Delta H^{\ddagger}_2 = 50.43 \pm 0.80$ kJ mol^{-1}, $\Delta S^{\ddagger}_2 = -115.0 \pm 2.5$ J K^{-1} mol^{-1}, and $10^2 k_2$ (50 °C) $= 4.56 \pm 0.17$ l mol^{-1} s^{-1}.[34] The ratio of the quantities of the products obtained, $[Ru_3(CO)_9(PBu^n_3)_3]$, $[Ru(CO)_4(PBu^n_3)]$, and *trans*-$[Ru(CO)_3(PBu^n_3)_2]$, depends on the initial ratio $[Ru_3(CO)_{12}]/PBu^n_3$. These results can be accommodated by the mechanism shown in Scheme 5. Thus the relative yields (2:1) of $[Ru(CO)_4(PBu^n_3)]$ and $[Ru(CO)_3(PBu^n_3)_2]$



Scheme 5

obtained when the concentration of $[Ru_3(CO)_{12}]$ is low imply that $[Ru_3(CO)_{11}(PBu^n_3)]$ undergoes fission of the Ru_3 cluster rather than the parent carbonyl. If $[Ru_3(CO)_{12}]$ underwent fission only $[Ru(CO)_4(PBu^n_3)]$ would be obtained since this does not undergo further substitution under the conditions employed. The co-ordinatively unsaturated fragments $[Ru(CO)_4]$ and $[Ru(CO)_3(PBu^n_3)]$ exhibit a greater tendency to trimerize than to react with another ligand. These results are similar to those obtained earlier for reactions of $[Ru_3(CO)_{12}]$ with a range of phosphines.[35]

Mixed-ligand Carbonyls.—Further studies of the chelation reaction

$$[(LL)M(CO)_5] \longrightarrow [(LL)M(CO)_4] + CO$$

have been reported and substantiate the conclusions of previous reports.[36] For any given ligand the rate of chelation at Mo is greater than at Cr and for any particular metal the rate of chelation increases in the order LL = dmpe < dpe < dcpe. A dissociative reaction path is the dominating process for molybdenum complexes but with M = Cr an associative contribution to a concerted process increases in importance when steric hindrance is very great. Rate constants and activation parameters are given in Tables 2 and 3.

[33] J. D. Black and P. S. Braterman, *J. Organometallic Chem.*, 1975, **85**, C7.
[34] A. Poë and M. V. Twigg, *Inorg. Chem.*, 1974, **13**, 2982.
[35] A. Poë and M. V. Twigg, *J.C.S. Dalton*, 1974, 1860.
[36] J. A. Connor and P. I. Riley, *J. Organometallic Chem.*, 1975, **94**, 55.

Table 2 *Rate constants for chelation of* $[M(CO)_5(dcpe)]$ ($k \times 10^5/s^{-1}$) (*from ref.* 36)

T/K	M = Mo	T/K	M = Cr
363	4.5	393	18.5
373	14.5	403	61.0
383	49.5	413	168.0
393	132.0		

Table 3 *Activation parameters for chelation of* $[M(CO)_5(LL)]$ (*from ref.* 36)

M	LL[a]	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
Cr	dmpe	132	6
	dpe	135	27
	dcpe	147	46
Mo	dmpe	118	−7
	dpe	120	14
	dcpe	132	34

[a] dmpe = 1,2-bis(dimethylphosphino)ethane; dpe = 1,2-bis(diphenylphosphino)ethane; dcpe = 1,2-bis(dicyclohexylphosphino)ethane.

Similar studies[37] of chelation in dithioether complexes $[Mo(CO)_5L]$ (L = pte, tte, mte, dte, or bte) reveal that decomposition of $[Mo(CO)_5L]$ results in the two competing processes

$$[Mo(CO)_5L] \longrightarrow [Mo(CO)_4L] + CO$$

$$[Mo(CO)_5L] \rightleftharpoons L + [Mo(CO)_5] \xrightarrow{CO} [Mo(CO)_6] + L$$

Accordingly kinetic studies were carried out in the presence of a 20-fold excess of free ligand to eliminate the second reaction. Rate constants for the first-order process are given in Table 4.

Table 4 *Rate constants for* $[Mo(CO)_5L] \rightarrow [Mo(CO)_4L] + CO$ (*from ref.* 37)

L[a]	$10^4k/s^{-1}$
pte	4.5±0.1
tte	5.0
mte	5.4
dte	7.1
bte	0.4

[a] *pte = 1,2-diphenylthioethane*; tte = 1,2-di-*p*-tolylthioethane; mte = 1,2-di-*p*-methoxyphenylthioethane; dte = 1,2-di-*p*-dimethylaminophenylthioethane; bte = 1,2-di-t-butylthioethane.

The observations of steric hindrance (bte chelates more slowly than pte) and acceleration by electron donation (dte chelates more rapidly than pte) suggest that a greater contribution to the chelation reaction is made by an associative process with sulphur donors relative to phosphorus donors where dissociation is the dominant process.

Kinetic studies of CO substitution in thiocarbonyl complexes $[M(CO)_5(CS)]$ (M = Cr or W) by PPh_3 and I^- indicate that CS is much more inert to substitution

[37] J. A. Connor and G. A. Hudson, *J.C.S. Dalton*, 1975, 1025.

than CO and that the CS ligand in $[W(CO)_5(CS)]$ accelerates the rate of CO substitution relative to $[W(CO)_6]$.[38] For the reaction of $[W(CO)_5(CS)]$ and PPh_3 plots of k_{obs} *vs.* $[PPh_3]$ gave intercepts and slopes corresponding to rate constants for the S_N1 phosphine-independent reaction,

$$[W(CO)_5(CS)] \xrightarrow{k_1} [W(CO)_4(CS)] + CO \xrightarrow[\text{fast}]{PPh_3} [W(CO)_4(CS)(PPh_3)]$$

and for the S_N2 phosphine-dependent reaction,

$$[W(CO)_5(CS)] \xrightarrow{k_2[PPh_3]} [W(CO)_4(CS)(PPh_3)] + CO$$

In contrast, plots of k_{obs} *vs.* $[I^-]$ for the reaction between $[W(CO)_5(CS)]$ and $[Bu_4N]I$ point to a purely associative process. Comparison of rate constants with those for similar reactions involving $[W(CO)_6]$ shows that with PPh_3 the dissociative pathway (k_1) is 75 times faster in $[W(CO)_5(CS)]$ while the associative (k_2) route is 250 times faster. Substitution by I^- proceeds almost 1000 times faster in $[W(CO)_5(CS)]$. The activating effect of the CS ligand in $[Mn(CO)(CS)(C_8H_{14})(\eta\text{-}C_5H_5)]$ is not as pronounced, suggesting that its *trans* effect in $[W(CO)_5(CS)]$ may be significant.[39] Indeed, ^{13}CO exchange with $[W(CO)_5(CS)]$ proceeds 20 times faster with a *trans*-CO than with a *cis*-CO.[40]

The kinetics and mechanism of the reaction between $[(bipy)Cr(CO)_4]$ and the phosphites $P(OCH_2)_3CMe$ and $P(OEt)_3$ have been reinvestigated[41] in an attempt to explain the anomalous variation in the first-order rate constants with ligand. It was concluded that differences in the purity of the phosphites are responsible. The report on ^{13}CO exchange in $[M(Br)(CO)_5]$ (M = Mn or Re) reviewed earlier also gives an account of substitution in these complexes by PPh_3 (M = Mn or Re) and $P(OMe)_3$ (M = Mn).[5] Rate constants for the observed reactions are given in Table 5.

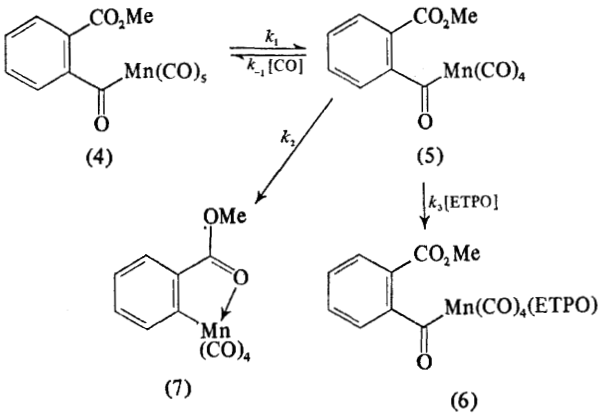
Table 5 *Rate constants for* CO *substitution in* $[M(Br)(CO)_5]$ *by phosphines and phosphites (from ref.* 5)

Reactants	*Products*	k/s^{-1} ($\times 10^{-5}$)
$[Mn(Br)(CO)_5] + PPh_3$	$[Mn(Br)(CO)_4(PPh_3)]$	8.23 ± 0.27
$[Mn(Br)(CO)_5] + P(OMe)_3$	$[Mn(Br)(CO)_3\{P(OMe)_3\}_2]$	8.54 ± 0.27
$[Re(Br)(CO)_5] + PPh_3$	$[Re(Br)(CO)_3(PPh_3)_2]$	1.71 ± 0.06

Differences in the rates of reactions of *cis*- and *trans*-carbonyls in $[Mn(X)(CO)_5]$ have already been noted in Section 1 and a further manifestation of this type of behaviour is found in the reaction of $P(OMe)_2Ph$ with *fac*-$[Mn(X)(CO)_3\{P(OMe)_2Ph\}_2]$ (X = Cl or Br) to give *mer-cis*-$[Mn(X)(CO)_2\{P(OMe)_2Ph\}_3]$.[42] Kinetic data suggest that the rate of reaction is controlled by the rate of isomerization of the former to the *mer-trans*-isomer which is reactive towards carbonyl substitution, presumably because of the *trans*-labilizing effect of the carbonyls.

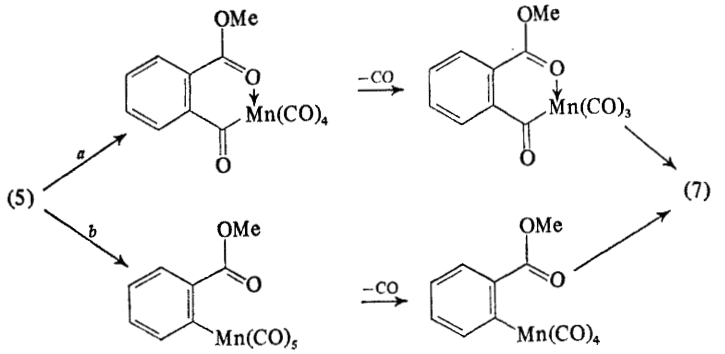
[38] B. D. Dombek and R. J. Angelici, *Inorg. Chem.*, 1976, **15**, 1089.
[39] I. S. Butler and A. E. Fenster, *Inorg. Chim. Acta*, 1973, **7**, 79.
[40] B. D. Dombeck and R. J. Angelici, *J. Amer. Chem. Soc.*, 1976, **98**, 4110.
[41] B. J. McKerley, G. C. Faber, and G. R. Dobson, *Inorg. Chem.*, 1975, **14**, 2275.
[42] D. J. A. de Waal, R. H. Reimann, and E. Singleton, *J. Organometallic Chem.*, 1975, **84**, 339.

Decarbonylation of *o*-methoxycarbonylbenzoylpentacarbonylmanganese(I) (4) has been studied in the presence and absence of the bicyclic phosphite 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2,2,2]octane (ETPO) and the kinetic data have been found to be consistent with the mechanism in Scheme 6.[43] The rate of ETPO substitution is



Scheme 6

first-order in complex (4) and independent of ETPO concentration between 0.06 and 0.56 mol l^{-1} ($k = 3.38 \times 10^{-4}$ s^{-1}), observations consistent with initial CO dissociation to give (5) which reacts rapidly and completely with ETPO (*i.e.* $k_3[\text{ETPO}] \gg k_2$) to give (6). Similar observations have been reported for the related system of ETPO and benzoylpentacarbonylmanganese(I).[44] A feature of the decarbonylation of (4) in the absence of ETPO to give (7) is the loss of a second molecule of CO by intermediate (5) at a much greater rate than loss of the first CO from (4). This may be interpreted in terms of co-ordination of the ester group to the 16-electron manganese accelerating the second decarbonylation (path *a*, Scheme 7). The alternative (path *b*) involves aryl migration prior to CO loss.

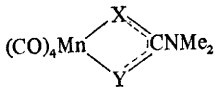


Scheme 7

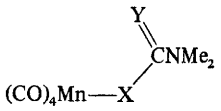
[43] C. P. Casey and C. A. Bunnel, *Inorg. Chem.*, 1975, **14**, 796.
[44] B. L. Booth, R. N. Haszeldine, and N. P. Woffenden, *J. Chem. Soc.* (*A*), 1970, 1979.

Similar studies on the decarbonylation and substitution reactions of [MeCOCO)-$Mn(CO)_5$][45] reveal that the reaction with ETPO is also first-order giving the product [(MeCOCO)$Mn(CO)_4$(ETPO)]. The decarbonylation reaction is discussed in Chapter 4.

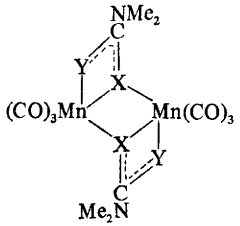
Differential scanning calorimetry has been employed in studies of the solid-state decarbonylation of carbamato-complexes $[Mn(CO)_4(L)]$ (8a) [L = $XYC(NMe_2)$,



(8)



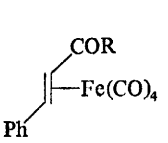
(9)



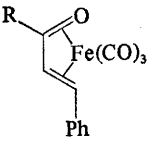
(10)

XY = SS, SSe, or SeSe] and $[Mn(CO)_5(L^1)]$ (9) [L^1 = $XY(NMe_2)$, XY = SO or SeO] which yields dinuclear carbamato-bridged complexes $[Mn(CO)_3(L)]_2$ (10a) and $[Mn(CO)_3(L^1)]_2$ (10b), the latter *via* $[Mn(CO)_4(L^1)]$ (8b) intermediates.[46] Activation energies (E_a/kJ mol^{-1}) are 23.06 ± 0.21, L = $SSC(NMe_2)$, 27.73 ± 0.11, L = SSeC-(NMe_2), and 33.9 ± 0.71, L = $SeSeC(NMe_2)$, for the reaction (8a)→(10a); 87.71 ± 3.20, L^1 = $SeC(O)(NMe_2)$, for (9)→(8b); 65.31 ± 1.31, L^1 = SeC(O)-(NMe_2), for (8b)→(10b); and 68.32 ± 1.42, L^1 = $SC(O)(NMe_2)$, for (9)→(10). The results suggest that CO co-ordinated to manganese with a large C—O stretching force constant is more subject to replacement and therefore that the rate-determining step in the above reactions is M—CO cleavage.

The kinetics of chelation of the COR group in (11) to give (12) follow the equation



(11)



(12)

$$[(L)Fe(CO)_4] \longrightarrow \alpha[(L)Fe(CO)_3] + (1-\alpha)Fe(CO)_5 + (1-\alpha)PhCH{=}CHCOR + (2\alpha-1)CO$$

(L = PhCHCHCOR; R = H, Me, or Ph) and are first-order with respect to (11). The first-order rate constants (k_c) decrease with increase in PhCH=CHCOR concentration and are dependent on CO concentration.[47] The kinetic results suggest that dissociation of the olefin occurs first, a process which may be common both to the step giving the chelate complex and to that leading to $[Fe(CO)_5]$. The mechanism in Scheme 8 is proposed (L = PhCH=CHCOR). The rate law

$$\frac{1}{k_c} = \frac{1}{k_1} = \frac{k_1k_2[L]^2 + k_{-1}k_{-1}'[CO][L]}{k_1k_2k_3[CO][L] + k_1k_1'k_2[L] + k_1k_{-1}'k_3[CO]^2}$$

[45] C. P. Casey, C. A. Bunnel, and J. C. Calabrese, *J. Amer. Chem. Soc.*, 1976, **98**, 1166.
[46] K. Tanaka, Y. Miya-Uchi, and T. Tanaka, *Inorg. Chem.*, 1975, **14**, 1545.
[47] G. Cardaci, *J. Amer. Chem. Soc.*, 1975, **97**, 1412.

reduces to

$$\frac{1}{k_e} = \frac{1}{k_1} + \frac{k_{-1}}{k_1 k_1'}[L]$$

when [CO]→0. It was concluded that the proposed mechanism may be generalized to all iron carbonyl complexes which yield $[Fe(CO)_4]$ in the first step of the reaction.

$$\underset{(11)}{[LFe(CO)_4]} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} L + [Fe(CO)_4] \xrightarrow[+CO]{k_3} [Fe(CO)_5]$$

$$k_{1'} \downarrow \uparrow k_{-1'}$$

$$[Fe(CO)_3] + CO \xrightarrow[+L]{k_2} \underset{(12)}{[LFe(CO)_3]}$$

Scheme 8

Kinetic studies of the reaction between $[Ru(CO)_4(L)]$ and excess L, (L = PPh_3, $PMePh_2$, or $PBu^n{}_3$) to give $[Ru(CO)_3(L)_2]$ are consistent with first-order reactions (with respect to complex), independent of phosphine concentration, and probably

$$[Ru(CO)_4L] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Ru(CO)_3L] + CO$$

$$\downarrow k_2[L]$$

$$[Ru(CO)_3L_2]$$

Scheme 9

proceed as shown in Scheme 9.[48] The observed rate constant is given by

$$k_{obs} = \frac{k_1 k_2[L]}{k_{-1}[CO] + k_2[L]}$$

Kinetic parameters for these reactions are shown in Table 6 and can be compared

Table 6 *Kinetic parameters for* $[M(CO)_4(L)] + L \rightarrow [M(CO)_3L_2] + CO$ *(from ref.* 48)

M	L	10^5k/s^{-1} (60 °C)	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
Ru	PPh_3	76	30.10±0.25	17.3±0.8
Ru	$PMePh_2$	29	29.66±0.22	14.1±0.6
Ru	$PBu^n{}_3$	13	31.57±0.18	18.3±0.5
Fe	PPh_3	3 (160 °C)	42.5±1.2	18.4±2.8

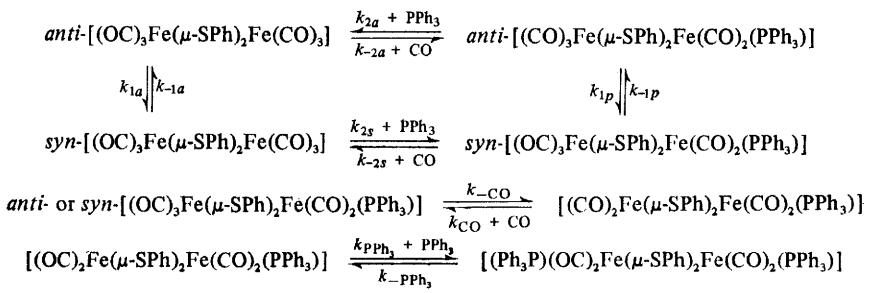
with data for the reaction between $[Fe(CO)_4(PPh_3)]$ and PPh_3 reported earlier. The ruthenium complexes are clearly much more reactive as a result of more favourable enthalpies of activation.

Previous studies of mono- and bis-CO substitution in mercapto-complexes $[Fe_2(CO)_6(\mu\text{-SR})_2]$ and isostructural nitrogen-bridged derivatives by Group Vb bases ER_3 provide evidence for an S_N2 or I_a bimolecular mechanism[49] (see Vol. 4 p. 281):

$$[Fe_2(CO)_6(\mu\text{-SR})_2] \xrightarrow{ER_3} [Fe_2(CO)_5(\mu\text{-SR})_2ER_3] \xrightarrow{ER_3} [Fe_2(CO)_4(\mu\text{-SR})_2(ER_3)_2$$

[48] B. F. G. Johnson, J. Lewis, and M. V. Twigg, *J.C.S. Dalton*, 1975, 1876.
[49] E. E. Siefert and R. J. Angelici, *J. Organometallic Chem.*, 1967, **8**, 374.

A more recent detailed study of the reaction between *syn*/*anti*-$[Fe_2(CO)_6(\mu\text{-SPh})_2]$ and PPh_3 indicates that the substitution does not go to completion in the presence of CO, and kinetic parameters for both forward and reverse reactions have been measured.[50] Data are consistent with the mechanism shown in Scheme 10. Thus the unsubstituted



Scheme 10

hexacarbonyl undergoes direct attack by PPh_3 on either the *syn*- or the *anti*-form in a bimolecular reaction to give the monosubstituted derivative which reacts with CO through an S_N2 mechanism. In contrast, reaction of the latter with PPh_3 is a first-order dissociative process and this change in mechanism can be attributed to steric inhibition of the second substitution step by the co-ordinated triphenylphosphine. Steric inhibition of a bimolecular mechanism may also be responsible for the recent observations that CO substitution in $[Fe_2(CO)_6(\mu\text{-}PPh_2)_2]$ by PPh_3, $P(OPh)_3$, and PBu^n_3 is a first-order reaction and that the rate constants for the replacement of one CO group are independent of concentration and nature of the nucleophile.[51] The activation parameters for CO dissociation from $[Fe_2(CO)_5(PPh_3)(\mu\text{-SPh})_2]$ and $[Fe_2(CO)_6(\mu\text{-}PPh_2)_2]$ are in fact rather similar and significantly higher than those for complexes which undergo bimolecular substitution (Table 7). Presumably substitution in $[Fe_2(CO)_6(\mu\text{-}PPh_2)_2]$ involves initial Fe—CO bond cleavage as with $[Fe_2(CO)_5(PPh_3)(\mu\text{-SPh})_2]$, but an alternative mechanism cannot be eliminated in which Fe—P bond fission (bridge-opening) is the rate-determining step.

Table 7 *Activation parameters for* CO *substitution in complexes* $[Fe_2(CO)_6(\mu\text{-L})_2]$ *(from ref.* 51)

Complex	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
$[Fe_2(CO)_5(\mu\text{-SPh})_2PPh_3]$	35.5	+16
$[Fe_2(CO)_6(\mu\text{-}PPh_2)]$	37.0	+10
$[Fe_2(CO)_6(\mu\text{-}N_2C_{12}H_8)]$	10.2	−34
$[Fe_2(CO)_6(\mu\text{-}S_2C_6H_3Me)]$	12.5	−31
$[Fe_2(CO)_6(\mu\text{-SPh})_2]$	21.6	−4

The influence of the apical group Y on the kinetics of CO substitution in methinyl tricobalt complexes $[Co_3(CY)(CO)_9]$ (Y = Ph, Me, H, Cl, or F), by PPh_3, $AsPh_3$, and $AsBu^n_3$ has been studied.[52] The evidence points to a simple dissociative mechan-

[50] M. Basato, *J.C.S. Dalton*, 1975, 911.
[51] J. N. Gerlach, S. L. McMullin, and P. C. Ellgen, *Inorg. Chem.*, 1976, **15**, 1232.
[52] A. Cartner, R. G. Cunninghame, and B. H. Robinson, *J. Organometallic Chem.*, 1975, **92**, 49.

ism (first-order kinetics) and since the parameters k_{obs} and E_a vary with the nature of Y (Table 8) it is concluded that the inductive effects of Y are transmitted through a delocalized Co_3C core. Addition of phosphines to the chlorine-bridged dimer $[Rh_2(Cl)_2(CO)_4]$ leads to bridge cleavage and CO substitution but it is not clear which

Table 8 *Activation parameters for* $[(CY)Co_3(CO)_9] + PPh_3 \rightarrow [(CY)Co_3(CO)_8(PPh_3)]$ *(from ref. 52)*

Y	E_a/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
Me	102.1	−18
H	97.9	−35.1
Ph	91.6	−40.2
F	89.1	−47.7

of these reactions is dominant. A recent report indicates that with PMe_2Ph the concentration of CO dissolved in the solvent can have significant effects.[53] Thus under an atmosphere of CO, bridge cleavage occurs first to give $[Rh(Cl)(CO)_2(PMe_2Ph)]$ and traces of $[Rh_2(Cl)_2(CO)_3(PMe_2Ph)]$. However, bubbling N_2 through the solutions obtained with successive addition of PMe_2Ph to $[Rh_2(Cl)_2(CO)_4]$ gives $[Rh_2(Cl)_2(CO)_3(PMe_2Ph)]$ and $[Rh_2(Cl)_2(CO)_2(PMe_2Ph)_2]$, *i.e.* bridge cleavage dominates in the presence of CO but in its absence CO substitution in the dimer is preferred.

The kinetics of decarbonylation of the five-co-ordinate iridium complexes $[Ir(CO)(dpe)_2]Cl$ and $[Ir(Cl)(CO)_2(PPh_3)_2]$ have been studied in different solvents at temperatures between −25 and +70 °C.[54] It is pointed out that the decarbonylation involves two processes,

$$[Ir(CO)(L)]^{m+}_{solv} \rightleftharpoons [Ir(L)]^{m+}_{solv} + CO_{solv} \quad (1)$$

$$CO_{solv} \rightleftharpoons CO_{gas} \quad (2)$$

i.e. the rate of CO appearance in the gas phase is determined by the 'chemical' rate (1) and the 'physical' rate (2). Accordingly diffusion coefficients of CO in the various solvents were determined and a relationship between these and the corresponding chemical rate constants was established. The relationship is interpreted by means of Scheme 11, which implies that a cage effect operates. k_1 refers to a process which

$$[Ir(CO)(L)]^{m+} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [IrL \ldots CO]^{m+} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} [Ir(L)]^{m+} + CO_{solv}$$

$$CO_{solv} \rightleftharpoons CO_{gas}$$

Scheme 11

may be isomerization of the carbonyl complex from trigonal-bipyramidal to the less stable square-pyramidal structure; k_3 corresponds to the transfer of CO from the intermediate to the bulk of solution while the third stage in the decarbonylation is diffusion of CO from the bulk of the solution to the gas–liquid interface. However, pre-exponential factors for the first step are *ca.* 10^7 times smaller than expected for a unimolecular reaction of this type and introduce some doubt as to whether or not the proposed isomerization from a trigonal bipyramid to a square pyramid is the correct interpretation of the results.

[53] A. J. Deeming and P. J. Sharratt, *J. Organometallic Chem.*, 1975, **99**, 447.
[54] R. d'Agostino, S. Gerardi, and E. Molinari, *Internat. J. Chem. Kinetics*, 1975, **7**, 249.

3 Formation of Carbonyls

The complexes $[(\eta\text{-}C_5H_5)_2M(CO)]$ (M = Mo or W) are well characterized stable compounds but formation of $[(\eta\text{-}C_5H_5)_2Cr(CO)]$ from chromocene and CO is found to be reversible.[55] Tungstenocene appears to be unique in forming a stable, formally 20-electron complex $[(\eta\text{-}C_5H_5)_2W(CO)_2]$. Attempts have been made to account for such behaviour.[56] Replacement of Br in $[Mn(CO)_{5-n}(CNMe)_n(Br)]$ by CO and CNMe in the presence of halogen acceptors is found to be stereospecific and a simple dissociative mechanism seems unlikely in view of the probability of fluxional behaviour in a five-co-ordinate intermediate.[57] A closely associated ion pair may therefore precede ligand attack and halide displacement.

The reactions of simple ferrous porphyrins such as [Fe(TPP)(base)$_2$] with small molecules are of current interest and the kinetics of the reactions of these complexes (base = pyridine, piperidine, or methylimidazole) with O_2 and CO at -79 °C in CH_2Cl_2 are the subject of a recent report.[58] The kinetics of the forward reaction,

$$[Fe(TPP)(py)_2] + CO \longrightarrow [Fe(TPP)(py)(CO)] + py$$

are essentially first-order under a pressure of 1 atm CO with $k_{obs} = 6.6 \pm 0.2 \times 10^{-3}$ s^{-1}. A similar rate constant is observed for the analogous reaction with O_2. Displacement of O_2 from [Fe(TPP)(base)(O_2)] by CO is also first-order with rates showing dependence on the base, *viz.* $k_{obs} = 5.6 \times 10^{-4}$ (pyridine), 5.1×10^{-5} (piperidine), and 5.4×10^{-6} s^{-1} (1-methylimidazole). Such reactions probably involve the mechanism shown in Scheme 12.

$$[Fe(TPP)(base)(L)] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Fe(TPP)(base)] + L$$

$$[Fe(TPP)(base)] + CO \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Fe(TPP)(base)(CO)]$$

L = base or O_2

Scheme 12

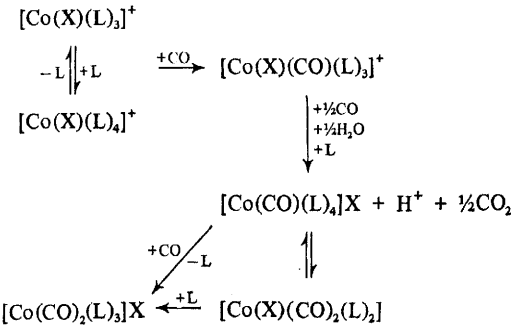
Kinetic studies of the recombination of haem with CO after photodissociation of the haem–CO complex in two solvents differing greatly in viscosity, *viz.* ethylene glycol + water (80% v/v) and glycerol, provide evidence that in the former the mechanism is dissociative, *i.e.* dissociation of a loosely bound solvent molecule occurs prior to co-ordination of CO.[59] The reaction is a normal activation-controlled process with $\Delta H^{\ddagger} = 31 \pm 3$ kJ mol^{-1}, $\Delta S^{\ddagger} = 4 \pm 12$ J K^{-1} mol^{-1}, and activation volume $\Delta V^{\ddagger} = 2.0 \pm 0.4$ cm^3 mol^{-1} (all at 1 bar). $\Delta H^{\ddagger}$ is similar to values found for reactions of CO with various types of myoglobin in water which lie in the range 27—42 kJ mol^{-1}. In glycerol, however, all data point to diffusion control as a result of the high viscosity of the solvent. The activation volume, $\Delta V^{\ddagger} = 14.0$ cm^3 mol^{-1}, and enthalpy, $\Delta H^{\ddagger} = 51 \pm 4$ kJ mol^{-1}, are significantly larger than in the aqueous solvent and in close agreement with values calculated for a diffusion-controlled reaction.

[55] K. L. T. Wong and H. H. Brintzinger, *J. Amer. Chem. Soc.*, 1975, **97**, 5143.
[56] H. H. Brintzinger, L. L. Lohr, jun., and K. L. T. Wong, *J. Amer. Chem. Soc.*, 1975, **97**, 5146.
[57] P. M. Treichel, H. J. Mueh, and B. E. Bursten, *J. Organometallic Chem.*, 1976, **110**, C49.
[58] C. J. Weschler, D. L. Anderson, and F. Basolo, *J. Amer. Chem. Soc.*, 1975, **97**, 6707.
[59] E. F. Caldin and B. B. Hasinoff, *J.C.S. Faraday I*, 1975, **71**, 515.

The previous suggestion[60] that a CO-bridged dimer is formed by the reaction of $[Co_2(CO)_8]$ and CO at 150 °C with CO pressures of ~150 atm may be in error. More recent studies assign most of the i.r. bands claimed to be due to such a species to $[Co_2(CO)_8]$.[61] Reductive carbonylation of $[Co(X)(L)_4]$ [X = Cl, Br, or I, L = $P(OEt)_2Ph$] proceeds according to the equation

$$2[Co(X)L_4]^+ + 5CO + H_2O \longrightarrow [Co(CO)_2L_3]^+ + [Co(X)(CO)_2L_2] + CO_2 + HX + 3L + H^+$$

I.r. monitoring of the reaction indicates initial formation of unstable $[Co(X)(CO)L_3]^+$ which was only partially characterized. Further reaction gives $[Co(CO)(L)_4]^+$ and finally the dicarbonyl complexes. The observations can be summarized in terms of Scheme 13.[62] Such a mechanism also explains the results of Klein's work.[63]



Scheme 13

The rate law for the carbonylation of $[Rh(Br)_4(H_2O)_2]^-$ was shown to be

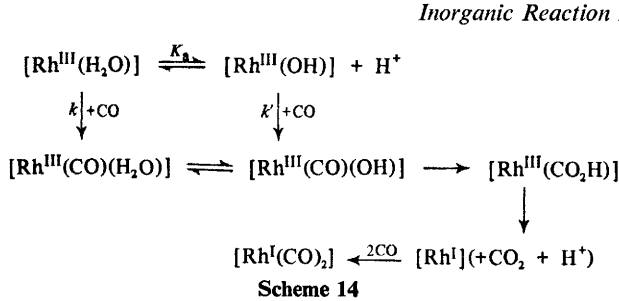
$$-d[CO]/dt = k_1^{CO}[Rh^{III}][CO] + k_2[Rh^{III}][Rh^{I}]$$

for an overall reaction

$$[Rh^{III}] + 3CO \xrightarrow{H_2O} [Rh^{I}(CO)_2] + CO_2 + 2H^+$$

The first term is concerned with the initial rate while the second is a contribution from an autocalalytic reaction which becomes dominant as the carbonylation progresses.[64] The k_1^{CO} step in the reaction to give the autocatalytic species $[Rh(CO)_2Br_2]^-$ involves a reductive carbonylation process *via* a carboxylate intermediate (Scheme 14). This assumes that co-ordinated H_2O or OH^- is involved in the reaction and migrates to a *cis* carbonyl. External H_2O/OH^- attack is also feasible but is considered less probable in view of previous observations that oxidation of ethylene to acetaldehyde using $[RhCl_n(H_2O)_{6-n}]^{(n-3)-}$ complexes does not occur when $n=6$, *i.e.* when co-ordinated H_2O is not present.[65] A comparison of kinetic data for the bromide with those of $[RhCl_5(H_2O)]^{2-}$ indicates that the former is some thirty

[60] R. Whyman, *Nature*, 1971, **230**, 139.
[61] E. E. Ernstbrunner and M. Kilner, *J.C.S. Dalton*, 1976, 417.
[62] G. Albertin, E. Bordignon, A. A. Orio, and G. Rizzardi, *Inorg. Chem.*, 1975, **14**, 944.
[63] H. F. Klein and H. H. Karsch, *Inorg. Chem.*, 1975, **14**, 473.
[64] B. R. James and G. Rosenberg, *Canad. J. Chem.*, 1976, **54**, 313.
[65] B. R. James and M. Kastner, *Canad. J. Chem.*, 1972, **50**, 1708.



Scheme 14

times more reactive towards CO (Table 9). For the autocatalytic step the data in Table 10 indicate that the bromide is 10 times more reactive. The kinetics of the

Table 9 *Rate and activation parameters for carbonylation of rhodium complexes (from ref.* 64)

System	k_I^{CO} l mol^{-1} s^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
$[RhBr_4(H_2O)_2]^-$/CO	0.14 (40 °C)	112.4	98
$[RhCl_5(H_2O)]^{2-}$/CO	0.005 (40 °C)	108	55

Table 10 *Rate and activation parameters for carbonylation of rhodium complexes (from ref.* 64)

System	k_2/l mol^{-1} s^{-1}	$\Delta H^{\ddagger}_2$/kJ mol^{-1}	$\Delta S^{\ddagger}_2$/J K^{-1} mol^{-1}
$[RhBr_4(H_2O)_2]^-/[Rh(CO)_2Br_2]^-$	0.05 (40 °C)	63.1	−69
$[RhCl_5(H_2O)]^{2-}/[Rh(CO)_2Cl_2]^-$	0.005 (40 °C)	52.2	−120

reversible addition of CO to $[Rh(diphos)_2]^+$ have been studied by cyclic voltammetry and the results compared with those available for the analogous cobalt and iridium systems.[66]

4 Metal–Metal Bonds

Metal–metal-bonded carbonyls generally undergo CO substitution and thermal decomposition *via* initial homolytic fission of the M—M bond rather than *via* CO dissociation, metal migration, and M—M bond heterolysis (see Vol. 3, p. 366), *i.e.*

$$[\{M(CO)_n\}_2] \longrightarrow 2[M(CO)_n] \longrightarrow \text{substitution or decomposition}$$

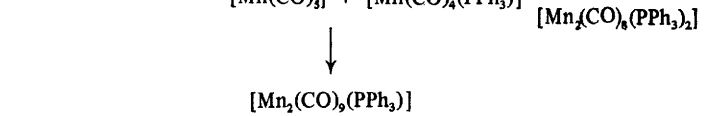
Recently reported studies of the thermal decomposition of $[Mn_2(CO)_{10}]$ and $[ReMn(CO)_{10}]$ in the presence and absence of oxygen[67] and the substitution of one PPh_3 ligand in $[Mn_2(CO)_8(PPh_3)_2]$[68] indicate that initial M—M homolysis also occurs in these reactions. CO substitution by phosphines and hydrogen in $[Re(H)(CO)_5]$ and $[Re_2(CO)_{10}]$[69,70] similarly follows radical pathways rather than M—CO cleavage in a dissociative mechanism.

[66] G. Pilloni, G. Zotti, M. Martelli, *J. Electroanalyt. Chem. Interfacial Electrochem.*, 1975, **62**, 397 (*Chem. Abs.*, 1975, **83**, 123201).
[67] J. P. Fawcett, A. Poë, and K. R. Sharma, *J. Amer. Chem. Soc.*, 1976, **98**, 1401.
[68] J. P. Fawcett, R. A. Jackson, and A. Poë, *J.C.S. Chem. Comm.*, 1975, 733.
[69] B. H. Byers and T. L. Brown, *J. Amer. Chem. Soc.*, 1975, **97**, 947.
[70] B. H. Byers and T. L. Brown, *J. Amer. Chem. Soc.*, 1975, **97**, 3260.

Photolysis of $[M_2(CO)_6(\eta\text{-}C_5H_5)_2]$[71,72] (M = Mo or W) and $[(CO)_5MnMo(CO)_3(\eta\text{-}C_5H_5)]$[73] (either continuous irradiation or flash photolysis) leads to efficient M—M cleavage. In the presence of halide-donor solvents such as CCl_4, $[M(Cl)(CO)_5]$ and/or $[M(Cl)(CO)_3(\eta\text{-}C_5H_5)]$ are obtained, again *via* radical processes. $[Mn_2(CO)_{10}]$ and $[Re_2(CO)_{10}]$[74] react similarly and these reactions are considered to arise from homolytic cleavage of the M—M bond in an excited state derived from a $\sigma \rightarrow \sigma^*$ one-electron transition associated with the M—M bond. I.r. spectroscopy has established that the $Mn(CO)_5^{\bullet}$ radical is formed when Mn atoms react with CO–argon mixtures at 10—15 K and that it has a C_{4v} square-pyramidal stereochemistry.[75] However, the nature of the species responsible for the e.s.r. spectrum observed during the photolysis of $[Mn_2(CO)_{10}]$ in THF has given rise to some controversy. This species was originally identified as $Mn(CO)_5^{\bullet}$ but later workers give convincing evidence that the spectrum is due to sextet Mn^{II} with $[Mn(CO)_5]^-$ as counterion and also reject the hypothesis that a manganese(0) quartet state is responsible.[76]

In addition to M—M cleavage, CO loss is claimed to occur on irradiation of $[Re_2(CO)_{10}]$ with thermal neutrons, giving $[Re(CO)_5]$ and $[Re(CO)_4]$,[77] while flash photolysis of $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ gives $[Mo(CO)_3(\eta\text{-}C_5H_5)]$ and an unidentified species which may be $[(\eta\text{-}C_5H_5)(Mo)_2(CO)_5]$.[78] Dimerization of $[Mo(CO)_3(\eta\text{-}C_5H_5)]$ and recombination of the pentacarbonyl with CO both follow second-order kinetics with rate constants which are solvent-dependent. Loss of CO on photolysis of such species is not unexpected in view of the thermal decomposition of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ to $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ which has a Mo—Mo triple bond.[79]

Photolysis of $[Mn_2(CO)_{10}]$ and PPh_3 leads to CO substitution which is explained by photolytic cleavage of the M—M bond followed by nucleophilic substitution of CO *via* $[Mn(CO)_4(PPh_3)]$[74] (Scheme 15). However, the intermediacy of $[Mn(CO)_4]$



Scheme 15

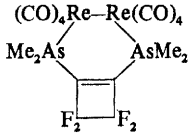
cannot be ruled out. The kinetic behaviour of the reversible thermal reaction

$$[Re_2(CO)_9(PPh_3)] + PPh_3 \rightleftharpoons [Re_2(CO)_8(PPh_3)_2] + CO$$

is quite simple and may be explained by reversible CO dissociation in the first step

[71] M. S. Wrighton and D. S. Ginley, *J. Amer. Chem. Soc.*, 1975, **97**, 4246.
[72] C. Giannotti and G. Merle, *J. Organometallic Chem.*, 1976, **105**, 97.
[73] D. S. Ginley and M. S. Wrighton, *J. Amer. Chem. Soc.*, 1975, **97**, 4908.
[74] M. S. Wrighton and D. S. Ginley, *J. Amer. Chem. Soc.*, 1975, **97**, 2065.
[75] H. Huber, E. P. Kundig, G. A. Ozin, and A. J. Poë, *J. Amer. Chem. Soc.*, 1975, **97**, 308.
[76] A. Hudson, M. F. Lappert, J. J. MacQuitty, B. K. Nicholson, H. Zainal, G. R. Luckhurst, C. Zennoui, S. W. Bratt, and M. C. R. Symons, *J. Organometallic Chem.*, 1976, **110**, C5 and references therein.
[77] I. Webber and D. R. Wiles, *J. Inorg. Nuclear Chem.*, 1976, **38**, 1103.
[78] J. L. Hughley, C. R. Bock, and T. J. Meyer, *J. Amer. Chem. Soc.*, 1875, **97**, 4440.
[79] R. J. Kingler, W. Butler, and M. D. Curtis, *J. Amer. Chem. Soc.*, 1975, **97**, 3535.

rather than by homolytic cleavage of the M—M bond.[80] However, it is not incompatible with the latter reaction nor with the metal-migration mechanism originally proposed for reactions of $[Mn_2(CO)_{10}]$[81] and $[Re_2(CO)_{10}]$[82] with iodine. In contrast, the reaction of $[Re_2(CO)_8(PPh_3)_2]$ with PPh_3 which leads to mononuclear carbonyl phosphine metal complexes most probably does go *via* reversible homolytic M—M fission.[79]



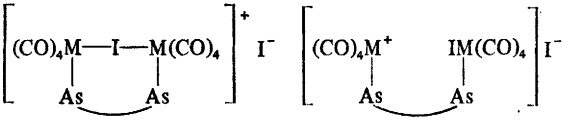
(13)

Cleavage of the M—M bond in $[(f_4fars)Re_2(CO)_8]$ (13) [f_4fars = tetrafluoro-1,2-bis(dimethylarsino)cyclobutene] and related complexes by iodine is first-order in both iodine and complex.[83] Rate and activation parameters are given in Table 11.

Table 11 *Rate and activation parameters for the reaction of* $[(f_nfars)M_2(CO)_8]$ *with iodine (from ref.* 83)

Reaction	*Temp.*/K	*Rate constant*/ $l\ mol^{-1}\ s^{-1}$	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal $K^{-1}\ mol^{-1}$
$[(f_4fars)Mn_2(CO)_8] + I_2$	294	3.40×10^{2}	14.2 ± 0.9	1.4 ± 3.2
$[(f_4fars)Re_2(CO)_8] + I_2$	292	3.40×10^{4}	6.9 ± 0.3	-13.8 ± 1.0
$[(f_6fars)Re_2(CO)_8] + I_2$	295	2.72×10^{3}	9.3 ± 0.9	-11.1 ± 3.0

Electrophilic addition of iodine to give intermediates such as (14) and (15) is deemed more plausible than initial homolysis of the M—M bond, particularly since addition of the radical scavenger 2,6-di-t-butyl-*p*-cresol has no effect on the rate of iodination.



(14) (15)

The results of a systematic study of the cleavage of transition-metal–Group IVb bonds by halogens have been reported during the present period and kinetic data for the following reactions are given:[84–88]

[80] D. G. de Wit, J. P. Fawcett, and A. Poë, *J.C.S. Dalton*, 1976, 528.
[81] L. I. B. Haines, D. Hopgood, and A. J. Poë, *J. Chem. Soc.* (*A*), 1968, 421.
[82] L. I. B. Haines and A. J. Poë, *J. Chem. Soc.* (*A*), 1969, 2826.
[83] W. R. Cullen and F. L. Hou, *Inorg. Chem.*, 1975, **14**, 3121.
[84] J. R. Chipperfield, A. C. Hayter, and D. E. Webster, *J.C.S. Chem. Comm.*, 1975, 625.
[85] J. R. Chipperfield, J. Ford, and D. E. Webster, *J.C.S. Dalton*, 1975, 2042.
[86] J. R. Chipperfield, A. C. Hayter, and D. E. Webster, *J.C.S. Dalton*, 1975, 2048.
[87] J. R. Chipperfield, J. Ford, A. C. Hayter, and D. E. Webster, *J.C.S. Dalton*, 1976, 360.
[88] J. R. Chipperfield, J. Ford, A. C. Hayter, D. J. Lee, and D. E. Webster, *J.C.S. Dalton*, 1976, 1024.

$$[M^1(MR_3)(CO)_3(\eta\text{-}C_5H_5)] + XY \longrightarrow [M^1(X)(CO)_3(\eta\text{-}C_5H_5)] + MR_3Y$$
(M^1 = Cr, Mo, or W)

$$[Fe(MR_3)(CO)_2(\eta\text{-}C_5H_5)] + XY \longrightarrow [Fe(X)(CO)_2(\eta\text{-}C_5H_5)] + MR_3Y$$

$$[Mn(MR_3)(CO)_5] + XY \longrightarrow [Mn(X)(CO)_5] + MR_3Y$$

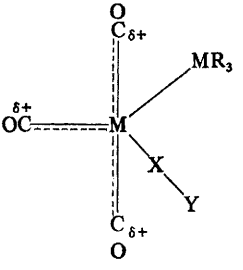
where M = Si, Ge, Sn, or Pb, R = alkyl or aryl group, and XY = Br_2, I_2, ICl, or IBr (not all of the possible combinations were studied). The results and conclusions can be summarized as follows. The rate of reaction depends principally on the electron-releasing power of the MR_3 group (for a given transition metal). The rates decrease in the order M = Fe > Mn ≈ W > Mn, all other factors being constant; bromine is *ca.* 4000 times more reactive than iodine (and hence less selective) while the interhalogen compounds react at approximately the same rate as iodine. Kinetic measurements in these reactions are consistent with the rate law

$$-d[XY]/dt = k_2^{obs}[XY][\text{organometallic}]$$

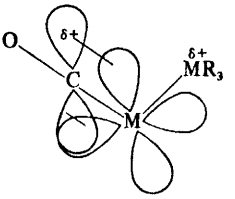
However, this disguises the complexity of the reactions which are considered to involve the following steps:

XY + organometallic ⟶ charge-transfer complex ⟶ intermediate ⟶ products

With XY = IBr and ICl 1:1 charge-transfer complexes were detected by optical studies. The complexity of the reactions is consistent with the low enthalpies of activation which in the case of iron are almost zero. This could be due to ΔH^+ values for the different stages compensating each other to give a small overall value. The entropies of activation are large and negative and in the range expected for a bimolecular reaction. The authors describe these reactions as pseudoaromatic electrophilic substitutions by virtue of their similarity to electrophilic substitution at aromatic carbon atoms. The intermediates in these reactions are considered to result from electrophilic attack by XY on the filled t_{2g} orbitals of the metal and the positive charge generated on the metal can then be delocalized on to the co-ordinated carbonyl ligands as in (16) and (17). The increased reactivity of the compounds observed when



(16)



(17)

Si is replaced by Ge, Sn, and finally Pb can be explained by the greater stability of MR_3 in such a transition state.

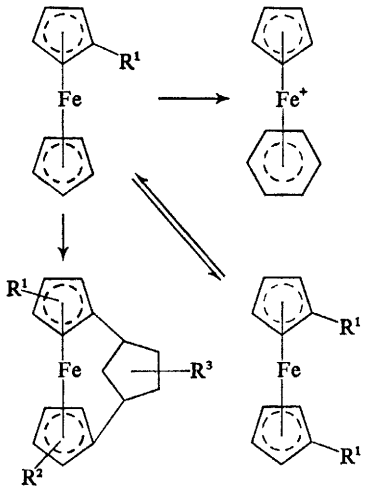
Cleavage of the metal–silicon bond in optically active silyl complexes by halogens has also been studied and the reaction between (+)-[(η-C_5H_5)$(CO)_2$FeSi(Ph)(1-naphthyl)Me] and chlorine proceeds with retention of configuration at silicon.[89]

[89] G. Cerveau, E. Colomer, R. Corriu, and W. E. Douglas, *J.C.S. Chem. Comm.*, 1975, 410.

Diastereoisomers (+)- and (−)-[(η-C_5H_5)(CO)(PPh_3)Fe{Si(Ph)(1-naphthyl)Me}] are also cleaved by Cl_2 with retention but in the presence of free PPh_3 inversion of configuration occurs on cleavage. The dicarbonyl, in contrast, is not cleaved by chlorine in the presence of PPh_3. These observations can be correlated with the fact that chlorine and triphenylphosphine react to give a 1:1 ionic adduct which probably cleaves the Fe—Si bond of the monocarbonyl *via* a different mechanism to that of chlorine. It also appears to be unreactive towards the dicarbonyl. Extension of these studies to (−)-[(η-C_5H_5)$(CO)_2$(H)Mn{Si(Ph)(1-naphthyl)Me}] reveals that cleavage of the Mn—Si bond by Cl_2 results in retention of configuration, but this complex reacts differently with triphenylphosphine.[90]

5 Cyclopentadienyls

Reactions between ferrocenes and $AlCl_3$ in the presence or absence of arenes give products according to Scheme 16.[91] The cleaved cyclopentadienyl rings can protonate



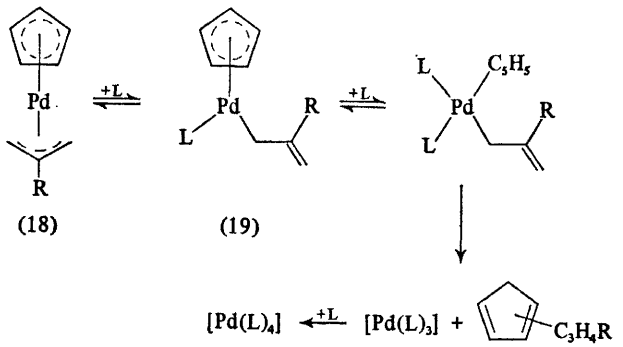
Scheme 16

and act as electrophiles in Friedel–Crafts alkylation of the alkylferrocenes and arenes. The presence of arene is found not to be necessary for ring cleavage since ferrocene, arene, and $AlCl_3$ lead to the same ferrocenophanes as were obtained in the absence of arenes. The sources of H required for formation of the cyclopentylene group, according to deuteriation studies, are traces of water in the solvent and the arene. Initial attack by $AlCl_3$ on ferrocenes to give these products depends on the substituents on the ferrocene ring. Complexation of $AlCl_3$ reversibly to a ring leads to Fe—C_5H_5 cleavage whereas irreversible attack at the iron atom, possible only in the absence of electron-withdrawing substituents, retards this cleavage reaction.

Further studies on the mechanism of formation of zero-valent phosphine complexes [Pd(P)$_4$] from [Pd(η-C_3H_5)(η-C_5H_5)] (18) have been reported[92] and the

[90] E. Colomer, R. Corriu, and A. Vioux, *J.C.S. Chem. Comm.*, 1976, 175.
[91] D. Astrue and R. Dabard, *J. Organometallic Chem.*, 1976, **111**, 339.
[92] D. J. Tune and H. Werner, *Helv. Chim. Acta*, 1975, **58**, 2240.

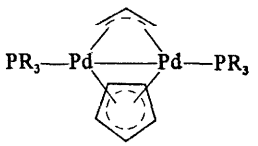
isolation of an intermediate σ-allyl complex has been achieved. Earlier kinetic[93] and low-temperature n.m.r. studies[94] indicated that a pathway (Scheme 17) involving



(18) (19)

Scheme 17

initial phosphine substitution and π–σ rearrangement of the allyl group is likely although intermediate (19) proved to be unstable. However, with R = Cl and L = $P(O\text{-}o\text{-}tol)_3$ a stable red oil has been isolated with spectral features consistent with such a structure. Under similar conditions [Pd(η-2-MeC_3H_4)(η-C_5H_5)] reacts with equimolar amounts of phosphine PR_3 (R = OMe, OPh, or Ph) to give dinuclear complexes (20).[95] In the case of R = Ph this has been confirmed by an



(20)

X-ray diffraction study. It therefore seems that either Scheme 17 may be an oversimplification or that alternative pathways are possible depending on the nature of R and L. Formation of organic products in reaction (17) obviously occurs by coupling of the cyclopentadienyl and allyl ligands. Similar compounds are isolated when nickelocene is allowed to react with allyl halides in the presence of phosphines.[96] Similar results are also obtained from the reaction of (η-crotyl)(η-cyclopentadienyl)-nickel and 5-chlorocyclopentadiene, implying that η-allyl nickel complexes may be involved in the former reaction, not an unreasonable conclusion in view of the observed coupling of organic ligands in the palladium reactions.

6 Olefin and Acetylene Complexes

This section deals with the formation as well as substitution of olefin and acetylene complexes.

[93] V. Harder and H. Werner, *Helv. Chim. Acta*, 1973, **56**, 549.
[94] G. Parker and H. Werner, *Helv. Chim. Acta*, 1973, **56**, 2819.
[95] D. J. Brauer, C. Kruyer, G. Parker, D. Tune, and H. Werner, *Angew. Chem. Internat. Edn.*, 1975, **13**, 185.
[96] C. Moberg, *J. Organometallic Chem.*, 1976, **108**, 125.

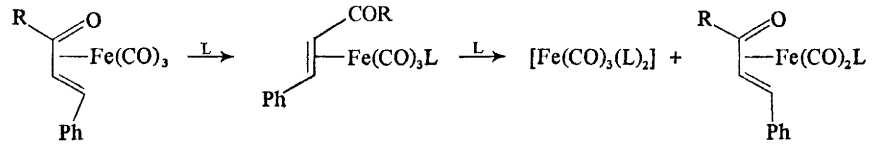
The 2,2-paracyclophane complex $[Mo(CO)_3(L)]$ decomposes in solution to give molybdenum metal, $[Mo(CO)_6]$, and 2,2-paracyclophane (L) according to a first-order rate law.[97] Kinetic data and activation parameters are $k \times 10^4/s^{-1} = 3.24$ (20 °C), 4.24 (25 °C), 4.83 (30 °C), 5.43 (35.4 °C), and 6.28 (40 °C); $\Delta H^{\ddagger} = 5.4 \pm 0.2$ kcal mol^{-1}; $\Delta S^{\ddagger} = -55.9 \pm 0.8$ cal K^{-1} mol^{-1}. A possible mechanism could be

$$[Mo(CO)_3L] \xrightarrow{\text{slow}} [Mo(CO)_3] + L$$

$$2[Mo(CO)_3] \longrightarrow [Mo(CO)_6] + Mo$$

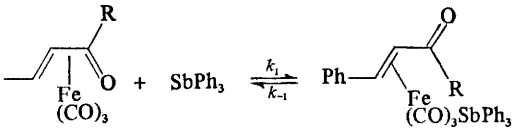
$[Fe(CO)_4(\eta\text{-}CH_2{=}CHPh)]$ and PPh_3 react *via* olefin dissociation to give $[Fe(CO)_4(PPh_3)]$ and $[Fe(CO)_3(PPh_3)_2]$. Two pathways for the formation of the latter product are *via* $[Fe(CO)_4]$, with a T_d structure, or *via* $[Fe(CO)_3]$ which results from CO dissociation from $[Fe(CO)_4]$.[31] More recent studies of the above reaction carried out under various pressures of carbon monoxide give kinetic results which favour an $[Fe(CO)_3]$ intermediate[98] although as pointed out in Section 2 other workers suggest that $[Fe(CO)_3(L)_2]$ complexes result from nucleophilic attack by ligands on a dinuclear species $[Fe_2(CO)_7]$. Substitution of the olefinic ligand in $[Fe(CO)_4(\eta\text{-}PhCH{=}CHCOR)]$[47] by $SbPh_3$ follows first-order kinetics and proceeds by olefin dissociation to give the intermediate $[Fe(CO)_4]$. However, $[Fe(CO)_4(SbPh_3)]$ is the sole substitution product.

The ligand PhCH=CHCOR can also act as a four-electron donor towards iron as in $[Fe(CO)_3(\eta\text{-}PhCH{=}CHCOR)]$ (12), where the carbonyl group is also co-ordinated. Cardaci has studied the kinetics of the reactions between these tricarbonyls (R = H, Me, or Ph) and the Group Vb ligands EPh_3 (E = P, As, or Sb) and a two-step process is described (Scheme 18).[99] The kinetics of the first step where



Scheme 18

L = $SbPh_3$ are the subject of a separate study[100] which gives kinetic parameters for the equilibrium reaction in Scheme 19. The forward reaction is first-order in complex

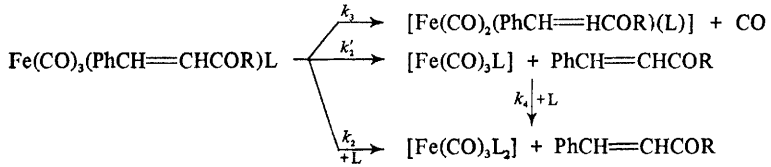


Scheme 19

and in $SbPh_3$ while the back reaction is first-order in complex. A simple associative mechanism can explain these observations although the alternative, reversible CO

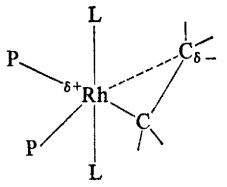
[97] F. Cristiani, D. de Filippo, P. Delano, F. Devillanova, A. Diaz, E. F. Troya, and G. Verani, *Inorg. Chim. Acta*, 1975, **12**, 119.
[98] G. Cardaci, *Inorg. Chem.*, 1974, 2974.
[99] G. Cardici and G. Concetti, *J. Organometallic Chem.*, 1974, **90**, 49.
[100] G. Cardici and S. Sorriso, *Inorg. Chem.*, 1976, **15**, 1242.

dissociation followed by nucleophilic attack by $SbPh_3$, is also conceivable. The variation of k_1 with the substituent R reveals that increased electron donation by R destabilizes the metal–diene bond and facilitates the forward reaction. The effect on k_{-1} leads to the conclusion that steric acceleration of the reverse reaction occurs and so cleavage of the Fe—Sb bond is an important factor in the back-chelation reaction. The variation of the ratio $[Fe(CO)_3(L)_2]/[Fe(CO)_2(\eta\text{-PhCH=CHCOR})(L)]$ with L suggests three different reaction pathways for the second step in the reaction (Scheme 20). The ratio k_2/k_2' gives the rate of the associative to that of the dissociative path for formation of $[Fe(CO)_3(L)_2]$, the value of which decreases in the order Ph > H > Me, *i.e.* R = Me favours a dissociative path.



Scheme 20

The kinetics of addition of tetracyanoethylene (tcne) to *trans*-$[Rh(R^1NC)_2(PR^2{}_3)_2]^+$ (R^1 = *p*-$MeOC_6H_4$, *p*-ClC_6H_4, or C_6H_{11}, R^2 = Ph or OPh) have been investigated and found to be first-order in both complex and tcne.[101] Reaction rates increase with increasing solvent polarity in the order THF < acetone < acetonitrile. This can be explained by formation of a dipolar intermediate (21) in the transition state which



(21)

will induce solvent orientation particularly with polar molecules. Activation parameters ΔH^{+} and ΔS^{+} are also markedly solvent-dependent.

Nucleophilic displacement of an ethylene molecule from $[Rh(\eta\text{-}CH_2{=}CH_2)_2(\eta\text{-}C_5H_5)]$ is generally initiated by ethylene dissociation to give a 16-electron complex which reacts with the nucleophile (L). However, recent kinetic studies[102] indicate that a variety of phosphines and phosphites react *via* second-order processes at a rate significantly greater than olefin dissociation. The kinetics indicate that an activated complex $[Rh(\eta\text{-}CH_2{=}CH_2)_2(\eta\text{-}C_5H_5):L]$ is formed in a bimolecular reaction and it is proposed that the rhodium atom retains its 18-electron configuration by reorganization of the η^5-C_5H_5 ring to the allylic η^3-C_5H_5 form. Subsequent expulsion of ethylene gives the product $[Rh(L)(\eta\text{-}CH_2{=}CH_2)(\eta\text{-}C_5H_5)]$.

Displacement of cod from $[M_2(Cl)_2(cod)_2]$ (M = Ir or Rh) by phosphines PCl_xPh_{3-x} (P) occurs in a stepwise manner *via* [M(Cl)(cod)(P)] and [M(Cl)(cod)$(P)_2$]

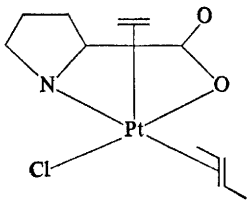
[101] M. A. Haga, K. Kawakami, and T. Tanaka, *Inorg. Chim. Acta*, 1975, **12**, 93.
[102] R. Cramer and L. P. Seiwell, *J. Organometallic Chem.*, 1975, **92**, 245.

to give $[M(Cl)(P)_3]$ though not every intermediate was isolated for each value of x:[103]

$$2[Ir(Cl)(cod)(PCl_xPh_{3-x})_2] \longrightarrow cod + [Ir(Cl)(cod)(PCl_xPh_{3-x})] + [Ir(Cl)(PCl_xPh_{3-x})_3]$$

The kinetics of the reaction are first-order in complex and zero-order in phosphine, and dechelation of cod is proposed as the rate-determining step. Triphenyl phosphite displaces one molecule of 1,4-bis(diphenylphosphino)butene (dpb) from $[Ni(CO)(dpb)_2]$ (in which one dpb ligand is unidentate).[104] Significant enhancement of the substitution rate is observed on addition of CF_3CO_2H and, to a lesser extent, H_2SO_4, which may indicate that protonation of the complex facilitates the reaction.

Further studies of the substitution of *trans*-but-2-ene in *trans*-(*N*,olefin)-[Pt(Cl)(L-pro)(*S*,*S*-*trans*-but-2-ene)] (L-pro = L-prolinato anion) by various olefins in the temperature range −20 to +23 °C indicate that second-order kinetics are followed.[105] Comparison of k_2 values shows that olefins with electronegative substituents react at a lower rate while *cis*-olefins give larger k_2 values than *trans*-olefins. The latter effect reflects steric inhibition at the rate-determining step as does the reduction in k_2 observed with olefins bearing increasing numbers of methyl groups. This is consistent with nucleophilic attack by the olefin at Pt to give an activated complex (22) which releases but-2-ene to give the product. Stereoselectivity in the



(22)

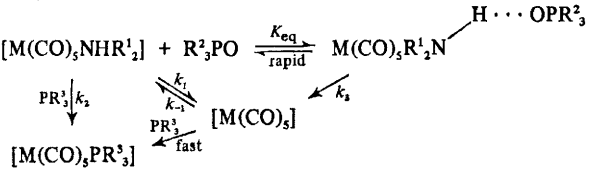
substitution reaction is also observed. With diastereoisomers of *trans*-(*N*,olefin)-[Pt(Cl)(L-pro)(*S*,*S*- or *R*,*R*-*trans*-but-2-ene)] as substrate the ratios of second-order rate constants for substitution with retention and inversion of configuration are 10 and 5 respectively for the *S*,*S*- and *R*,*R*-*trans*-but-2-ene ligands. Thus retention of configuration is the preferred pathway with both diastereoisomers. The mechanism suggested above for olefin exchange, *i.e.* formation of a five-co-ordinate intermediate (22), seems reasonable in view of the recent isolation of such intermediates in the substitution of Cl^- and ethylene in Zeise's salt by diamines.[106]

7 Amine Complexes

The reaction between $[Cr(CO)_5(py)]$ and pyridine (py) to give *cis*-$[Cr(CO)_4(py)_2]$ is first-order in complex and a predominantly dissociative mechanism is indicated.[107] The effect of phosphine purity on the kinetics of CO substitution by PR_3 in $[Cr(CO)_4(bipy)]$ was noted earlier (Section 2) and a reinvestigation of amine substitution by

[103] B. Denise and G. Pannetier, *J. Organometallic Chem.*, 1975, **99**, 455.
[104] B. Corain and L. de Nardo, *J. Organometallic Chem.*, 1976, **110**, C27.
[105] Y. Terai, H. Kido, J. Fujita, and K. Saito, *Bull. Chem. Soc. Japan*, 1975, **48**, 1233.
[106] L. Maresca, G. Natile, and L. Cattalini, *Inorg. Chim. Acta*, 1975, **14**, 79.
[107] J. A. Connor, J. P. Day, and R. M. Turner, *J.C.S. Dalton*, 1976, 108.

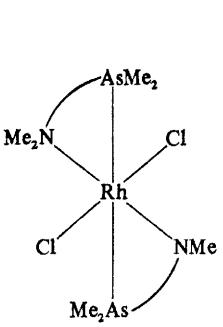
PPh_3 in $[W(CO)_5(aniline)]$ suggests that this reaction is affected similarly by the presence of traces of Ph_3PO since the rate is not reproducible even under strict exclusion of air and light.[108] The reaction is also affected dramatically by the presence of light and in view of these observations the reported thermodynamic parameters[109] must be viewed with caution. In the particular case where an amine is capable of hydrogen-bonding the deliberate addition of small quantities of phosphine oxides accelerates amine substitution by phosphines.[110] The mechanism for such a reaction is shown in Scheme 21 and the significant feature is the formation of a



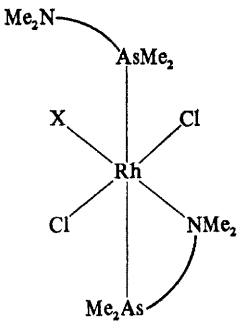
Scheme 21

kinetically labile hydrogen-bonded adduct which can be detected by differences in ν(CO) relative to the amine complex. The acceleration appears to be due to enhancement of the rate of dissociation in the first-order pathway: *e.g.* k_1 for piperidine dissociation in $[Mo(CO)_5(NHC_5H_{10})]$ is 1.36×10^{-5} s^{-1} at 34.5 °C; k_1 for dissociation of piperidine in the Bu^n_3PO adduct is 1.05×10^{-3} s^{-1} at 34.5 °C.

Photochemical studies of amine and CO substitution in $[W(CO)_5(L)]$[111] and $[M(CO)_4(L)_2]$[112] (M = Mo or W, L = amine) indicate that with L = py the M—N bond is much more labile than the M—CO bond in the excited state. When L = bidentate amine, *e.g.* 1,10-phenanthroline, M—CO cleavage occurs preferentially to give $[M(CO)_3(L)_2(X)]$ (X = PPh_3, py, MeCN, or *t*-4-styrylpyridine).[112]



(23)



(24)

Reaction with halide ion causes reversible dechelation of the N-donor end of aminoarsine bidentate ligands in *trans*-$[Rh(L)_2(Cl)_2]^+$ (23), giving *mer*-$[Rh(L)(L^1)$-

[108] J. Nasielski, M. Vermeulen, and P. Leempoel, *J. Organometallic Chem.*, 1975, **102**, 195.
[109] R. J. Angelici and C. M. Ingemanson, *Inorg. Chem.*, 1969, **8**, 83.
[110] J. Ewen and D. J. Darensbourg, *J. Amer. Chem. Soc.*, 1975, **97**, 6874.
[111] A. J. Rest and J. R. Sodeau, *J.C.S. Chem. Comm.*, 1975, 696.
[112] M. S. Wrighton and D. L. Morse, *J. Organometallic Chem.*, 1975, **97**, 405.

$(Cl)_2X]$ (24) [L and L^1 = (*o*-dimethylaminophenyl)dimethylarsine, *NAs*- and *As*-bonded].[113] The system obeys the rate law

$$-d[Rh(L)_2(Cl)_2^+]/dt = k_{(t\rightarrow m)0}\gamma_{\pm}^2[Rh(L)_2(Cl)_2^+][X^-] - k_{(m\rightarrow t)}[Rh(L)(L')(Cl)_2(X)]$$

where $\gamma_{\pm}$ is the mean ionic activity coefficient, since k_{obs} for the reactions with Br^- and Cl^- is concentration-dependent, *i.e.*

$$k_{obs} = k_1 + k_2[X^-]$$

The specific rate of the forward reaction (*trans*→*mer* conversion) at infinite dilution, $k_{(t\rightarrow m)0}$, is affected by X^- and the solvent, the latter dependency being due to changes in $\Delta S^{\ddagger}_{(t\rightarrow m)}$. The sensitivity of the rates to X^- can be ascribed to some bond-making during formation of the transition states. An associative interchange (I_a) mechanism can account for the observed results although a dissociative process in which M—N bond cleavage is the first step cannot be ruled out completely.

The kinetics and equilibria for axial ligation of pyridine to a number of neutral and anionic alkyl cobaloximes have been studied by stopped-flow techniques.[114] The neutral complexes appear to exist in solution as an equilibrium mixture of a six-co-ordinate aquo-species $[RCo(D_2H_2)(HOH)]$ and the five-co-ordinate compound $[RCo(D_2H_2)]$ and the mechanism of the formation of $[RCo(D_2H_2)(py)]$ is considered to involve initial dissociation of H_2O according to the equation

$$[RCo(D_2H_2)(HOH)] \xrightarrow{-H_2O} [RCo(D_2H_2)] \xrightarrow{+py} [RCo(D_2H_2)(py)]$$

This S_N1 reaction appears to be affected by the electron-withdrawing ability of the *trans* alkyl ligand. However, it is not possible to distinguish between S_N1 and I_d (dissociative interchange) mechanisms in the substitution of OH^- by pyridine in the anionic cobaloximes $[RCo(D_2H_2)(OH)]^-$ on the basis of the data obtained. Under certain conditions it is possible to distinguish clearly between I_d and dissociative mechanisms by mass-law retardation in a suitable non-co-ordinating solvent. The substitution of pyridine by tri-n-butylphosphine in $[MeCo(D_2H_2)(py)]$ proceeds to completion, *i.e.* the rate of reverse reaction is negligible, and so fulfils the main requirement. A recent kinetic study of this reaction using the above facts gave results consistent with a purely dissociative process in which the rate-determining step is pyridine dissociation to give the five-co-ordinate species $[MeCo(D_2H_2)]$.[115] Kinetic data indicate that other reactions studied involving substitution of piperidine in $[MeCo(D_2H_2)(piperidine)]$ by 4-substituted pyridines also proceed *via* metal–ligand (piperidine) dissociation.

8 Miscellaneous

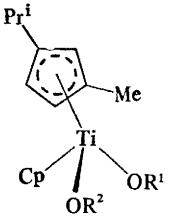
Substitution of the σ-bonded ligands in bis-cyclopentadienyltitanium(IV) compounds is the subject of some recent kinetic and stereochemical studies. Hydrolysis of $[(Cp(Cp^1)Ti(Cl)_2]$ (Cp = η-C_5H_5, Cp^1 = η-C_5H_4Me) proceeds according to Scheme 22.[116] Formation of $[(Cp)(Cp^1)TiCl]^+$ and of $[(Cp)(Cp^1)Ti]^{2+}$ is a first-order

[113] A. Peloso and L. Volponi, *J.C.S. Dalton*, 1976, 923.
[114] K. L. Brown, D. Lyles, M. Pencovici, and R. G. Kallen, *J. Amer. Chem. Soc.*, 1975, **97**, 7338.
[115] F. R. Jensen and R. C. Kiskis, *J. Amer. Chem. Soc.*, 1975, **97**, 5820.
[116] D. Pacheco, M. I. Hernandez, J. J. Lubinkowski, and J. L. Calderon, *Inorg. Chim. Acta*, 1976, **18**, L25.

$$[(Cp)(Cp^1)TiCl_2] \xrightarrow{k_{12}} [(Cp)(Cp^1)TiCl]^+ + Cl^-$$
$$[(Cp)(Cp^1)TiCl]^+ \xrightarrow{k_{23}} [(Cp)(Cp^1)Ti]^{2+} + Cl^-$$
$$[(Cp)(Cp^1)Ti]^{2+} + OH^- \xrightarrow{k_{3a}} [(Cp)(Cp^1)Ti(OH)]^+$$

Scheme 22

process whereas $[(Cp)(Cp^1)Ti(OH)]^+$ is produced at a rate dependent on the concentration of both $[(Cp)(Cp^1)Ti]^{2+}$ and OH^- and is consequently second-order. Tirouflet has succeeded in isolating optically active titanium complexes $[(Cp)(Cp^1)Ti(X)(Y)]$, some of which have an asymmetric titanium atom as the only chiral element.[117,118] Substitution of one RO^- group by Cl^- in (25) occurs stereospecifically with retention



(25) OR^1 = 2,6-$Me_2C_6H_3O$, R^2 = 2-ClC_6H_4O

of configuration at the metal.[119] Chlorination of $[W(H)_2(\eta\text{-}C_5H_5)_2]$ according to kinetic studies of the reaction

$$[W(H)_2(\eta\text{-}C_5H_5)_2] + 2PhCCl_3 \longrightarrow [W(Cl)_2(\eta\text{-}C_5H_5)_2] + 2PhCCl_2H$$

is first-order in complex.[120] Evidence was obtained that a free-radical mechanism is involved, with $[W(H)(Cl)(\eta\text{-}C_5H_5)_2]$ as a probable (though not detectable) intermediate.

Substitution of the organo-sulphide ligand L in complexes $[Mn(CO)_2(L)(\eta\text{-}C_5H_5)]$ (L = tetrahydrothiophen or SR_2, where R = Me, Et, Pr^n, Bu^n, Ph, or CH_2Ph) by tertiary phosphines and phosphites is first-order with respect to complex and a S_N1 mechanism is proposed.[121] The high positive entropies of activation, ~ 80 J K^{-1} mol^{-1}, are in accord with a dissociative mechanism which is also considered probable for olefin substitution reactions of $[Mn(CO)_2(olefin)(\eta\text{-}C_5H_5)]$ although rate constant comparisons indicate that olefins appear to be better leaving groups than the S-donor ligands.

In an effort to obtain a more detailed understanding of the much researched mechanisms of substitution of four-co-ordinate d^8 metal ions the temperature dependence of the second-order rate constants for replacement of X in *trans*-$[Pt(PEt_3)_2(R)X]^{n+}$ (R = Ph, *o*-tolyl, or mesityl) by a series of pyridine derivatives (X = MeOH, $n=1$) and thiourea derivatives (X = Cl, $n=0$) has been

[117] C. Moïse, J. C. Leblanc, and J. Tirouflet, *J. Amer. Chem. Soc.*, 1975, **97**, 6272 and references therein.
[118] A. Dormond, J. Tirouflet, and F. le Moigne, *J. Organometallic Chem.*, 1975, **101**, 71.
[119] J. Besançon, S. Top, J. Tirouflet, J. Dusausoy, C. Lecomte, and J. Protas, *J.C.S. Chem. Comm.*, 1976, 325.
[120] W. A. Morrison, J. A. Landgrebe, and J. Kleinberg, *J. Organometallic Chem.*, 1975, **91**, 315.
[121] I. S. Butler and T. Sawai, *Inorg. Chem.*, 1975, **14**, 2703.

studied[122] in methanol. The factors varied in studying the effect of increasing steric hindrance in the transition state were (i) methyl substitution in a position *ortho* to the carbon co-ordinated to platinum, (ii) methyl substitution *ortho* to the donor nitrogen in the entering heterocyclic amine, and (iii) methyl substitution on the nitrogens of the thiourea ligands. It was found that increasing the steric effects by methyl substitution (i) generally reduces the rate of reaction and leads to an increase in $\Delta H^{\ddagger}$, which is compensated for by a large increase in $\Delta S^{\ddagger}$. As a result $\Delta G^{\ddagger}$ does not change much relative to changes in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. This almost linear relationship between the two parameters is interpreted in terms of changes in the solvent 'cage' round the substrate as the activated complex is formed.

[122] R. Romeo, M. L. Tobe, and M. Trozzi, *Inorg. Chim. Acta*, 1974, **11**, 231.

2

Metal–Alkyl, –Aryl, and –Allyl Bond Formation and Cleavage

BY J. L. DAVIDSON

1 General

Photochemical cleavage of metal–carbon bonds constitutes a brief part of a recent review on the photochemistry of metal carbonyls.[1] Reviews of metal–alkyl and –aryl complexes have also appeared, one of which is concerned solely with metals in Groups IV—VII.[2] The other deals with the formation, stability, and decomposition pathways of transition metal–carbon σ-bonds,[3] subjects of much interest in recent years. Consequently the recent isolation of the first stable methylene complex $[Ta(Me)(CH_2)(\eta\text{-}C_5H_5)_2]$[4] and its unequivocal characterization by a single-crystal *X*-ray diffraction study[5] is of great interest in view of the probability that related derivatives are involved in the recently reported (see Vol. 4, p. 293) examples of α-hydride elimination in metal alkyls.

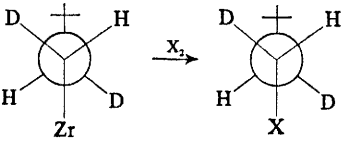
2 Group IV

Recent calorimetric studies of some Group IV metal alkyls $[MR_4]$ (M = Ti, Zr, or Hf) reveal that the mean M—C bond dissociation energies are not particularly low.[6] This adds weight to previous arguments that kinetic, rather than thermodynamic factors, are responsible for the instability of transition metal–carbon bonds (see Vol. 3, p. 372). Similar studies on $[TaMe_5]$ and $[WMe_6]$ provide further evidence to support such conclusions.[7] Thermal decomposition of $[Ti(Me)_2(\eta\text{-}C_5H_5)_2]$ in the solid state produces methane, ethane, ethylene, cyclopentadiene, and methylcyclopentadiene.[8] Comparison with products from the decomposition of $[Ti(CD_3)_2(\eta\text{-}C_5H_5)_2]$ indicates that methane, the major product, is formed by abstraction of hydrogen from both the C_5H_5 ring and the other methyl group. However, the cyclopentadienyl groups abstract hydrogen only from each other and not from the methyl groups. Ethylene is derived exclusively from the C_5H_5 rings while methylcyclopentadiene formation involves a simple combination of CH_3 and C_5H_5 substituents, in

[1] M. Wrighton, *Chem. Rev.*, 1974, **74**, 401.
[2] R. Schrock and G. W. Parshall, *Chem. Rev.*, 1976, **76**, 243.
[3] P. J. Davidson, M. F. Lappert, and R. Pearce, *Chem. Rev.*, 1976, **76**, 219.
[4] R. Schrock, *J. Amer. Chem. Soc.*, 1975, **97**, 6577.
[5] L. Guggenberger and R. Schrock, *J. Amer. Chem. Soc.*, 1975, **97**, 6578.
[6] M. F. Lappert, D. S. Patil, and B. J. Pedley, *J.C.S. Chem. Comm.*, 1975, 830.
[7] F. A. Adedeji, J. A. Connor, H. A. Skinner, L. Galyer, and G. Wilkinson, *J.C.S. Chem. Comm.*, 1976, 159.
[8] H. G. Alt, F. P. di Sanzo, M. D. Rausch, and P. C. Uden, *J. Organometallic Chem.*, 1976, **107**, 257.

contrast with the formation of ethane which is a complex process. Free-radical mechanisms are considered unlikely for this type of reaction and for reactions involving thermal decomposition of aryl- and benzyl-titanium derivatives $[Ti(R)_2(\eta\text{-}C_5H_5)_2]$ (R = aryl or CH_2Ph) in the solid state and in solution.[9–11] Decomposition of these derivatives and deuteriated analogues in all cases follows first-order kinetics to give toluene (R = CH_2Ph) or benzenes (R = aryl). Activation energies, E_a, are 20—22 kcal mol^{-1} (R = C_6D_5), 16 kcal mol^{-1} (R = CH_2Ph), and 19 kcal mol^{-1} (R = $CD_2C_6D_5$), which illustrates the effect of deuteriation. In contrast deuteriation of the cyclopentadienyl rings has no effect on E_a, proving that only the R groups are involved in the activation step. Mechanisms are proposed in which the σ-bonded ligand R is converted into a π-bonded activated state prior to H abstraction.

Cleavage of the Zr—C σ-bond of $[(\eta\text{-}C_5H_5)_2Zr(Cl)(CHDCHDBu^t)]$ (1) with bromine and iodine proceeds with retention of configuration at carbon, in contrast to M—C bond cleavage in alkyl-iron and -cobalt complexes in which inversion at carbon is the norm (see Scheme 1).[12] This difference is attributed to the fact that with



(1)

Scheme 1

the iron and cobalt complexes oxidation precedes backside nucleophilic attack by halide ion and the d^0 configuration of quadrivent zirconium effectively precludes the initial oxidation step. A closed transition state such as that proposed for halogenation of organomercurials is considered as an alternative in which the vacant low-lying orbital on the 16-electron zirconium can facilitate frontside attack. It is pointed out, however, that cleavage of the Mn—C σ-bond of $[Mn(CO)_5(CHMeCO_2Et)]$ with bromine occurs with retention of configuration[13] and so a d^0 configuration and vacant low-lying orbitals on the metal are not a prerequisite for this stereochemical pathway. (See also Vol. 4, p. 296.) $[Zr(Cl(H)(\eta\text{-}C_5H_5)_2]$ reacts with 4-chlorocyclohexene and 4-bromocyclohexane to give bicyclo[3,1,0]hexane.[14] These and other related reactions with chlorinated olefins are considered to proceed by Zr—X (X = Cl or Br) γ-elimination, while Zr—X β-elimination is also observed, but to a lesser extent.

3 Group V

Vanadium.—Thermal decomposition of $[V(CH_2Ph)_4],(Et_2O)_n(dioxan)_m$ in the solid

[9] C. P. Boekel, J. H. Teuben, and H. J. de Liefde Meijer, *J. Organometallic Chem.*, 1974, **81**, 371.
[10] C. P. Boekel, J. H. Teuben, and H. J. de Liefde Meijer, *J. Organometallic Chem.*, 1975, **102**, 161.
[11] C. P. Boekel, J. H. Teuben, and H. J. de Liefde Meijer, *J. Organometallic Chem.*, 1975, **102**, 317.
[12] J. A. Labinger, D. W. Hart, W. E. Seibert, and J. Schwartz, *J. Amer. Chem. Soc.*, 1975, **97**, 3851.
[13] R. W. Johnson and R. G. Pearson, *J.C.S. Chem. Comm.*, 1970, 986.
[14] W. Tam and M. F. Rettig, *J. Organometallic Chem.*, 1976, **108**, C1.

state gives toluene *via* H abstraction from the other benzyl groups.[15] In ether solution at 90 °C the solvent appears to function as a source of hydrogen.

4 Group VI

Chromium.—Deuteriation studies support the proposal that thermal decomposition of $[Cr(Cl)_2(Me)(amine)_2]$ complexes proceeds *via* α-hydrogen elimination[16] but no definite evidence is available. Oxidation of $[Cr(CH_2Ph)(H_2O)_5]^{2+}$ in perchloric acid is effected by Fe^{3+}, Cu^{2+}, $[Co(NH_3)_5(X)]^{2+}$ (X = Cl or Br), O_2, and H_2O_2 at a rate independent of the oxidizing agent.[17] Concomitant homolysis of the Cr—C bond is also observed with a first-order rate constant of $10^3k/s^{-1} = 2.63 \pm 0.21$ at 25 °C and activation parameters $\Delta H^{\ddagger} = 133 \pm 3$ kJ mol^{-1} and $\Delta S^{\ddagger} = 153 \pm 11$ J K^{-1} mol^{-1}. The preferred mechanism is a unimolecular homolysis of the Cr—C bond by an S_H1 dissociation in which the transition state is $[(H_2O)_5Cr^{2+}\cdots CH_2Ph]$. With *para*-substituted benzyl derivatives $[Cr(CH_2C_6H_4X)(H_2O)_5]^{2+}$ electron-donating substituents lead to increased rates of reaction whereas decreased rates of reaction are observed with electron-withdrawing groups X. This is expected if the above mechanism operates.

Cleavage of the M—C bond in alkyl-chromium complexes $[Cr(R)(H_2O)_5]^{2+}$ (R = CH_2Cl, $CHMe_2$, CH_2Ph, $CH_2C_6H_4Me$, or $CH_2C_6H_4CF_3$) with the interhalogen IBr has also been the subject of kinetic studies.[18] The reaction gives RI and $[Cr(H_2O)_6]^{3+}$ exclusively with rates comparable to those of bromine and much higher than those of iodine. This contrasts with the cleavage of M—ER_3 bonds (E = Si, Ge, or Sn) by ICl and IBr which, as noted earlier (p. 323), react at rates similar to those of iodine. The rate reaction follows the bimolecular expression

$$d[RI]/dt = k_{IBr}[Cr-R^{2+}][IBr]$$

and an S_E2 mechanism is postulated in this case.

5 Group VII

Manganese.—Photolysis of $[Mn(R)(CO)_5]$ and $[Mn(COR)(CO)_5]$ (R = Me or CH_2Ph) leads to homolytic cleavage of the Mn—C bond and both radicals formed can be trapped by addition of nitrosodurene.[19]

6 Group VIII

Iron.—Cleavage of the iron–methyl bond in optically pure $(-)_{356}$-[Fe(Me)(CO)(L)-(η-C_5H_5)], where L = (S)-$(+)_{365}$-[$Ph_2PNMe(CHMePh)$], by chlorine, bromine, or iodine gives the metal halide [Fe(X)(CO)(L)(η-C_5H_5)] with predominant retention of configuration at the metal.[20] The reverse reaction of the iodide with methyl-lithium regenerates the methyl complex, again with significant retention at iron. Cleavage of

[15] G. A. Razuvaev, V. N. Latyaeva, L. I. Vyshinskaja, A. N. Linyova, U. V. Drobotenko, and V. K. Cherkasov, *J. Organometallic Chem.*, 1975, **93**, 113.
[16] A. Yamamoto, Y. Kano, and T. Yamamoto, *J. Organometallic Chem.*, 1975, **102**, 57.
[17] R. S. Nohr and J. H. Espenson, *J. Amer. Chem. Soc.*, 1975, **97**, 3392.
[18] J. H. Espenson and G. J. Samuels, *J. Organometallic Chem.*, 1976, **113**, 143.
[19] A. Hudson, M. F. Lappert, P. W. Lednor, and B. K. Nicholson, *J.C.S. Chem. Comm.*, 1974, 966.
[20] H. Brunner and G. Wallner, *Chem. Ber.*, 1976, **109**, 1053.

the Fe—C σ-bond in $[Fe(R)(CO)_2(\eta\text{-}C_5H_5)]$ by $HgCl_2$ gives products which depend on the nature of the alkyl group R and three distinct pathways are observed (Scheme 2).[21] The kinetics of reaction (i) where R = Me obey a third-order rate law, first-

$$[Fe(R)(CO)_2(\eta\text{-}C_5H_5)] + HgCl_2 \xrightarrow{(i)} [Fe(Cl))CO)_2(\eta\text{-}C_5H_5)] + RHgCl$$

$$[Fe(R)(CO)_2(\eta\text{-}C_5H_5)] + HgCl_2 \xrightarrow{(ii)} [Fe(HgCl)(CO)_2(\eta\text{-}C_5H_5)] + RCl$$

$$[Fe(R)(CO)_2(\eta\text{-}C_5H_5)] + HgCl_2 \xrightarrow{(iii)} \text{Fe-containing material} + \tfrac{1}{2}Hg_2Cl_2 + \text{organic products} + CO$$

Scheme 2

order in complex and second-order in $HgCl_2$ with a rate constant $k = 4.6 \times 10^{-4}$ $l^2\ mol^{-2}\ s^{-1}$. The same rate law is followed in equation (ii) (R = Bu^t) with $k = 9.3 \times 10^{-3}\ l^2\ mol^{-2}\ s^{-1}$. However, with R = Pr^i the reaction proceeds according to equation (iii) with second-order kinetics, first-order in each reactant, with $k = 4.3 \times 10^{-5}\ l\ mol^{-1}\ s^{-1}$. The proposed mechanism for the above reactions is shown in Scheme 3.

$$[Fe{-}R] + HgCl_2 \overset{K_1}{\rightleftharpoons} Fe(HgCl_2)R \xrightarrow{k'} \tfrac{1}{2}Hg_2Cl_2 + [Fe{-}R]Cl \longrightarrow \text{Decomposition}$$

$$+HgCl_2 \uparrow\downarrow K_2$$

$$[Fe(HgCl)R]HgCl_3 \xrightarrow{k''} Fe{-}Cl + RHgCl + HgCl_2$$

$$or \quad \downarrow k''$$

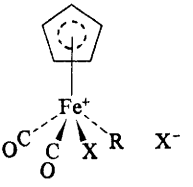
$$Fe{-}HgCl + RCl + HgCl_2$$

Fe = $[Fe(CO)_2(\eta\text{-}C_5H_5)]$

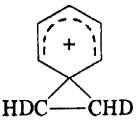
Scheme 3

Cleavage of the Fe—C bond of $[Fe(CHDCHDBu^t)(CO)_2(\eta\text{-}C_5H_5)]$ and $[Fe(CHDCHDPh)(CO)_2(\eta\text{-}C_5H_5)]$ by halogens proceeds with inversion and retention of configuration at carbon respectively and steric effects were originally cited as factors responsible for these two seemingly contradictory results. A later report, in which electrophilic cleavage of the Fe—C bond of $[Fe(CD_2CH_2Ph)(CO)_2(\eta\text{-}C_5H_5)]$ is described, attributes these differences to the fact that in the intermediate (2) which precedes Fe—C cleavage $[(\eta\text{-}C_5H_5)Fe(CO)_2X]$ functions as a stable leaving group with S_N2 attack by X^- on carbon leading to inversion (R = $CHDCHDBu^t$).[22] However, with R = CHDCHDPh the phenyl group is considered to compete with X^- in attack from the rear at carbon resulting in formation of the phenonium ion (3).

[21] L. Dizikes and A. Wojcicki, *J. Amer. Chem. Soc.*, 1975, **97**, 2540.
[22] T. C. Flood and F. J. di Santi, *J.C.S. Chem. Comm.*, 1975, 18.



(2)



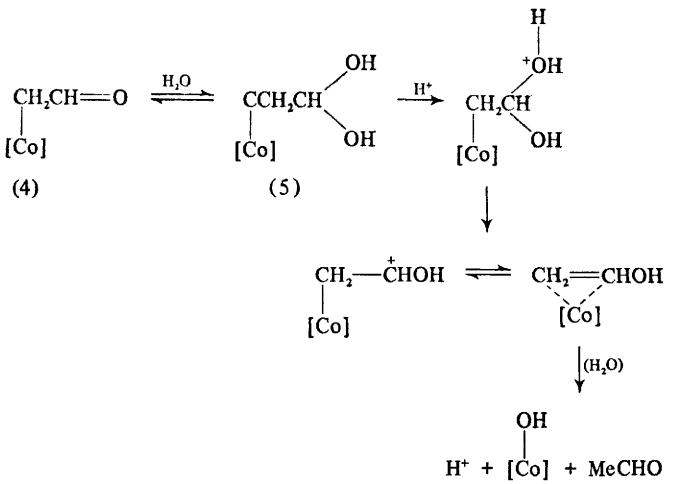
(3)

The double inversion at carbon resulting from this mechanism accounts for the observed retention of configuration. The relative reactivities of some carbonyl-metal anions have been determined by measuring second-order rate constants for their reactions with pentafluoropyridine which give M—C_5F_4N derivatives.[23] The rate constants and reactivities decrease in the order $[\eta\text{-}C_5H_5Fe(CO)_2]^- > [Rh(CO)_2(PPh_3)_2]^- > [Ir(CO)_2(PPh_3)_2]^- > [Co(CO)_2(PPh_3)_2]^-$.

Cobalt.—A number of reviews have appeared in recent years concerned with the chemistry of vitamin B_{12} and one published in the present period has some sections relevant to this chapter.[24] A variety of studies have also been published which are concerned with cleavage of the Co—C bond in vitamin B_{12} model compounds. Formylmethylcobalamin (CoR) (4) undergoes decomposition between pH 4 and 6 according to the second-order rate law

$$\frac{d(CoR)}{dt} = \frac{(k_2K_a + k_2'[H^+])[H^+][CoR]}{K_a + [H^+]}$$

with the rate constant $k_2 = 4.3 \pm 0.5$ l mol^{-1} s^{-1}.[25] This is accompanied by significant Co—C cleavage which is considered to occur *via* the hydrate (5) in Scheme 4.



Scheme 4

[23] B. L. Booth, R. N. Haszeldine, and I. Perkins, *J.C.S. Dalton*, 1975, 1843.
[24] R. H. Abeles and D. Dolphin, *Accounts Chem. Res.*, 1976, **9**, 114.
[25] T. M. Vickrey, R. N. Katz, and G. N. Schrauzer, *J. Amer. Chem. Soc.*, 1975, **97**, 7248.

Decomposition of the diethyl acetal of formylmethylcobalamin occurs *via* a multistage reaction the initial step of which has a second-order rate constant k_1 of 2.6×10^4 l mol^{-1} s^{-1}. These kinetic results are used to explain conflicting reports concerning the synthesis and nature of formylmethylcobalamin. A second communication has appeared with the same objective,[26] but the studies are not as extensive as those in ref. 25. Electrophilic cleavage of cobalt–alkyl σ-bonds by Hg^{2+} has been studied extensively in recent years and the general consensus of opinion is that such reactions frequently involve an S_E2 mechanism. This applies to reactions between Hg^{2+} and complexes $[Co(Me)(L)(H_2O)]$ (L = macrocyclic chelate) in which the rate-determining step is considered to be reaction of Hg^{2+} with the neutral cobalt complex according to the equation

$$[Co(Me)(L)(H_2O)] + Hg^{2+} \longrightarrow [Co(L)(H_2O)_2]^+ + HgMe^+$$

The neutral complexes appear to be in equilibrium with an unreactive protonated species which is not attacked by Hg^{2+},

$$[Co(Me)(L)(H_2O)] + H^+ \overset{K_B}{\rightleftharpoons} [Co(Me)(LH)(H_2O)]^+$$

and the apparent second-order rate constant is given by

$$k_2 = k/(1 + K_B[H^+])$$

Accordingly the rates are sensitive to pH. The observed influence of the chelate L on the rate of reaction is explained by changes in electron density at cobalt affecting the rate of cleavage of the Co—Me bond in the transition state, the greater the electron density the faster the reaction.[27] Similar effects were noted in the cleavage of the Cr—R bond of $[Cr(R)(H_2O)_5]^{2+}$ as discussed earlier.[17] Related kinetic studies[28] of the dealkylation of the analogous complexes $[RCo(salen)(H_2O)]$ and $[R^1Co(DO)(DOH)(pn)(H_2O)]^+$ (R = alkyl, R^1 = alkyl or aryl) with Hg^{2+} indicate that intermediates (5) are sometimes formed as follows, where M = $Co(chelate)H_2O$:

$$RM + Hg^{2+} \rightleftharpoons RM{-}Hg^{2+}$$
(5)

$$RM{-}Hg^{2+} + H_2O \rightleftharpoons MH_2O^+ + RHg^+$$

Intermediates of this type have been detected previously in methyl-transfer reactions from methylcobalamin to mercury(II) and palladium(II) (see Vol. 4).

Studies of the stereochemistry of Co—alkyl bond cleavage by electrophiles Br_2 and Hg^{2+} in complexes $[Co(R)(dmg)_2(py)]$ [R = *cis*-2-methoxycyclohexyl (i), *cis*- and *trans*-4-t-butylcyclohexyl (ii) and (iii), or *trans*-2-hydroxycyclohexyl (iv)] are the subject of another report in this area.[29] The bonds to (i), (ii), and (iii) are all cleaved by both electrophiles with exclusive inversion of stereochemistry at carbon. These reactions can be considered to proceed *via* an S_E2 mechanism which usually involves retention at carbon, particularly with Hg^{2+} as the electrophile. However, steric effects are considered to be responsible for inversion reactions when large macrocyclic

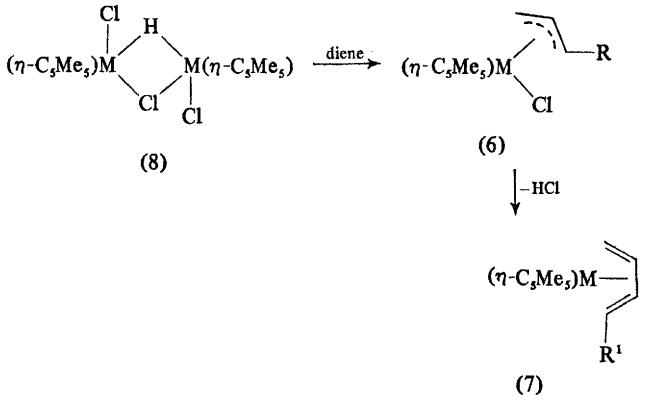
[26] R. B. Silverman and D. Dolphin, *J. Amer. Chem. Soc.*, 1975, **97**, 2924.
[27] J. H. Espenson, W. R. Bushley, and M. E. Chmielewski, *Inorg. Chem.*, 1975, **14**, 1302.
[28] G. Tauzher, R. Dreos, G. Costa, and M. Green, *J. Organometallic Chem.*, 1974, **81**, 107.
[29] H. Shinozaki, H. Ogawa, and M. Tada, *Bull. Chem. Soc. Japan*, 1976, **49**, 775.

ligands are present on the metal[30] and the above results are not unique. Products resulting from β-elimination were also detected in reactions of (i) and (iv) and in the case of the latter these were the only species isolated since, in this case, simple Co—C cleavage does not appear to be favoured. The role of the anion associated with Hg^{2+} in cobalt–carbon bond-cleavage reactions with methylcobalamin has also been assessed and results indicate that the effects are significant.[31] The rates of reaction are proportional to the concentration of both cobalt complex and $HgCl_2$ in the case of mercuric chloride, whereas those for $Hg(OAc)_2$ depend little on the concentration of this substrate, but are proportional to $[OAc^-]$. Moreover the rates decrease in the order $OAc^- \gg Cl^- \geqslant SCN^- \geqslant Br^- \gg CN^-$ which, it was noted, is inversely related to the stability constant of the equilibrium

$$HgL_{n-1} + L \rightleftharpoons HgL_n \quad (n=1 \text{ or } 2)$$

This may identify HgL^+ as the active electrophile in these cleavage reactions.

Rhodium and Iridium.—Full details are now available of the formation of π-allyl M^{III} (6) and π-diene M^{I} (7) (M = Rh or Ir) complexes from μ-hydrido-derivatives (8) and acyclic dienes (Scheme 5).[32,33] A mechanism was originally proposed to

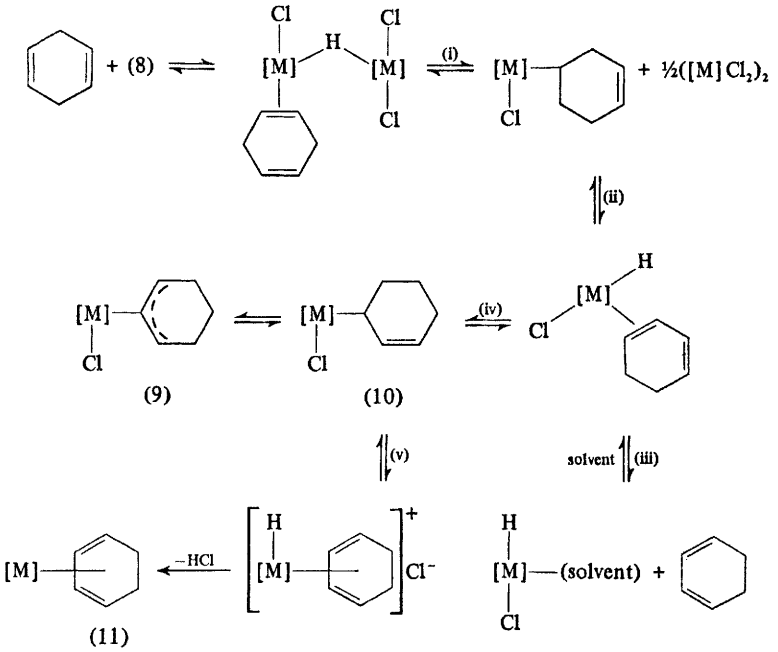


Scheme 5

account for these transformations but the results of additional studies with a wider variety of dienes indicated that some modification was necessary. Thus with both 1,3- and 1,4-cyclohexadiene it is possible to obtain intermediates identified as (1–3)-π-cyclohexadienyl complexes (9) (Scheme 6). Isomerization of the 1,4- to the complexed 1,3-diene may occur *via* addition (i) and elimination (iii) of M—H as shown. In the presence of 'good' solvents such as ethanol, loss of cyclohexa-1,3-diene (iii) competes with insertion (iv) to give the σ- (10) and π-allylic (9) intermediates so that free 1,3-diene is obtained, whereas in CH_2Cl_2 only the π-allylic intermediate (9)

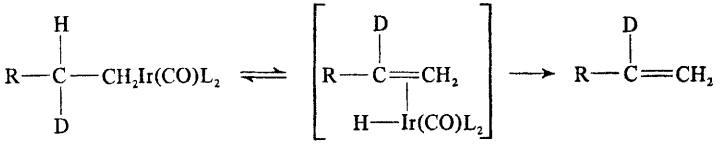
[30] H. L. Fritz, J. H. Espenson, D. A. Williams, and G. A. Molander, *J. Amer. Chem. Soc.*, 1974, **96**, 2378.

[31] H. Yamamoto, Y. Yokoyama, Ju.-L. Chen, and T. Kwan, *Bull. Chem. Soc. Japan*, 1975, **48**, 844.
H.-B. Lee and P. M. Maitlis, *J.C.S. Dalton*, 1975, 2316.
H.-B. Lee, K. Mosely, C. White, and P. M. Maitlis, *J.C.S. Dalton*, 1975, 2322.



Scheme 6 [M] = $M(C_5Me_5)$ (M = Rh or Ir)

is detected. The final step to give the π-diene (11) complex is HCl elimination (vi), possibly *via* β-hydride abstraction (v) as shown. The octyliridium(I) complex (12) is considered to decompose *via* β-elimination to give octene according to the mechanism shown in Scheme 7.[34] Measurement of the isotope effect, $k_H/k_D = 2.28 \pm 0.20$,



Scheme 7

indicates that a transition state (13) is involved in which the iridium inserts into the C—H bond of the alkyl group.

Nickel.—The thermal decomposition of alkyl-nickel complexes $[Ni(R)(PPh_3)(\eta\text{-}C_5H_5)]$ (R = Me, Et, Pr^n, Pr^i, Bu^n, s-Bu, $PhCH_2$, or Me_3SiCH_2) in aromatic solvents has been studied by n.m.r. spectroscopy.[35] In most cases olefins are produced probably by β-hydride elimination although the other product of such a reaction, $[Ni(H)(PPh_3)(\eta\text{-}C_5H_5)]$, was not detected. The trimethylsilylmethyl derivative decomposes with first-order kinetics to give tetramethylsilane and when the reaction is

[34] J. Evans, J. Schwartz, and P. Urquhart, *J. Organometallic Chem.*, 1974, **81**, C37.
[35] J. Thompson and M. C. Baird, *Inorg. Chim. Acta*, 1975, **12**, 105.

conducted in [$^2H_8$]toluene gives no deuteriated product. Thus a radical mechanism is rather unlikely. Disproportionation of methyl- and ethyl-nickel complexes [Ni(R)(acac)$(PPh_3)_n$] (R = Et, $n=1$; R = Me, $n=2$) in pyridine is considered to follow Scheme 8.[36] The ethyl derivative decomposes according to the second-order

$$2[Ni(R)(acac)(PPh_3)_n] \xrightarrow{2py} [Ni(acac)_2 2py] + [Ni(R)_2(PPh_3)_2]$$

$$\downarrow R = Et \qquad \downarrow R = Me$$

$$[Ni(C_2H_4)(PPh_3)_2] + C_2H_6 \qquad [Ni(PPh_3)_n] + CH_4 + C_2H_6$$

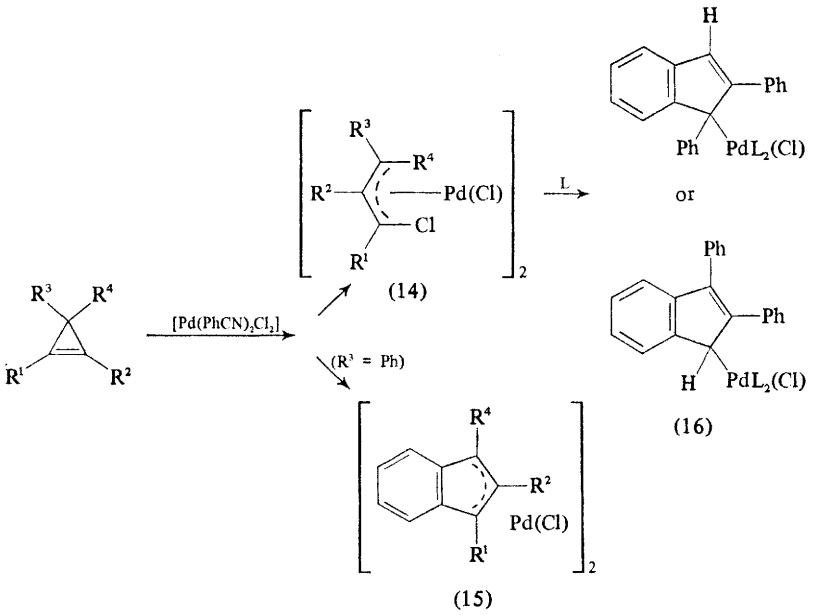
Scheme 8

rate law

$$-d[Ni]/dt = k[Ni]^2 \quad \{Ni = [Ni(Et)(acac)(PPh_3)]\}$$

When a deuteriated ethyl derivative (R = CH_2CD_3) was studied only $CH_2{=}CD_2$ was detected, which suggests that Ni—C bond fission in the proposed diethylnickel intermediate proceeds through a β-hydride elimination mechanism.

Palladium.—[$Pd(Cl)_2(PhCN)_2$] reacts with phenyl-substituted cyclopropenes *via* ring-opening to give η^3-allyl complexes (14) according to Scheme 9.[37] The influence of



Scheme 9

substituents on the rate of reaction has been studied and the results obtained were analysed in terms of a rate-controlling step in which the cyclopropene becomes co-

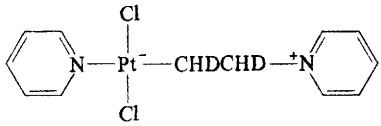
[36] T. Yamamoto, R. Saruyama, Y. Nakamura, and A. Yamamoto, *Bull. Chem. Soc. Japan*, 1976, **49**, 589.

[37] M. A. Battiste, L. E. Friedrich, and R. A. Fiato, *Tetrahedron Letters*, 1975, 45.

ordinated symmetrically to palladium. Different effects of substituents on the reaction are demonstrated in a later communication in which an alternative pathway is described whereby intramolecular cyclization of the organic moiety takes place to give indenyl complexes (15).[38] Allyl complexes similar to (14) are considered to be probable intermediates in the latter type of reaction in view of the observed transformation of the allyl (14; $R^1 = R^2 = R^3 = Ph$, $R^4 = H$) to the η^1-indenyl complexes (16) on addition of two equivalents of triphenylphosphine (L).

Cleavage of the mercury–carbon bond of *threo*- and *erythro*-MeCH(NMe_2)—CH(HgCl)Me with $[Pd(Cl)_2(PhCN)_2]$ to give the palladium derivatives is completely stereospecific and proceeds with retention of configuration.[39] This is consistent with an S_E2 (cyclic) or S_E2 (open) reaction. Similar stereochemical effects have been noted when a variety of organomercurials RHgCl are carbonylated in the presence of lithium tetrachloropalladate.[40] The exchange of mercury for palladium proceeds with predominant retention at carbon. Steric effects are claimed to be important in determining the stereochemical course of reactions between $[Pd(Cl)_2(PhCN)_2]$ and the steroidal olefins cholest-4-ene and cholest-5-ene which yield diastereoisomeric η^3-allyl complexes.[41] Subsequent oxidation of these complexes with 3-chloroperbenzoic acid in light petrol releases allylic alcohols regiospecifically with high stereoselectivity.[42]

Platinum.—*trans*-$[Pt(Cl)_2$(*cis*-[1,2-$^2H_2$]ethylene)(py)] reacts reversibly with pyridine to give the σ-bonded zwitterion (16) with slow release of the *cis*-ethylene.[43] No trace



(16)

of the *trans*-ethylene was detected so the olefin addition–elimination must be stereospecific. Halide–methyl-group exchange in reactions (1), (2), and (3) (L = PMe_2Ph) follows second-order kinetics with rate constants $k = 2.1 \times 10^{-4}$ l mol^{-1} s^{-1} (1), $k = 5.5 \times 10^{-6}$ l mol^{-1} s^{-1} (2), and $k = 2.0 \times 10^{-4}$ l mol^{-1} s^{-1} (3).[44] These results, in conjunction with qualitative data from a variety of other reactions of similar

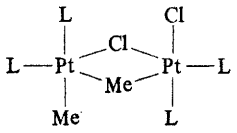
$$cis\text{-}[Pd(Cl)_2(L)_2] + [Au(Me)_3(L)] \longrightarrow cis\text{-}[Au(Cl)(Me)_2(L)] + trans\text{-}[Pd(Cl)(Me)(L)_2] \quad (1)$$

$$cis\text{-}[Pt(Me)_2(L)_2] + cis\text{-}[Pt(Cl)_2(L)_2] \longrightarrow 2cis\text{-}[Pt(Cl)(Me)(L)_2] \quad (2)$$

$$cis\text{-}[Pt(Me)_2(L)_2] + [Au(Cl)(L)] \longrightarrow [Au(Me)(L)] + [Pt(Cl)(Me)(L)_2] \quad (3)$$

complexes, are considered to be indicative of an S_E2 (cyclic) mechanism of electrophilic substitution at carbon. In particular, cyclic intermediates, *e.g.* (17), are

[38] R. A. Fiato, P. Mushak, and M. A. Battiste, *J.C.S. Chem. Comm.*, 1975, 869.
[39] J. E. Bäckvall and B. Åkermark, *J.C.S. Chem. Comm.*, 1975, 82.
[40] J. K. Stille and P. K. Wong, *J. Org. Chem.*, 1975, **40**, 335.
[41] D. N. Jones and S. D. Knox, *J.C.S. Chem. Comm.*, 1975, 165.
[42] D. N. Jones and S. D. Knox, *J.C.S. Chem. Comm.*, 1975, 166.
[43] F. Pesa and M. Orchin, *J. Organometallic Chem.*, 1976, **108**, 135.
[44] R. J. Puddephatt and P. J. Thompson, *J.C.S. Dalton*, 1975, 1810.

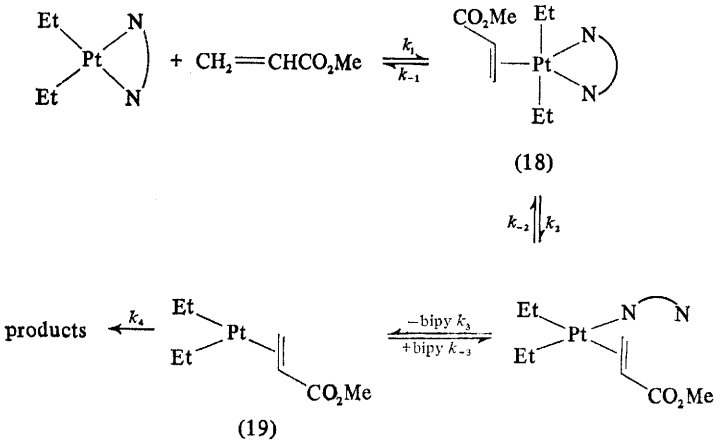


(17)

considered to be involved in view of the observation that reaction (2) initially gives *cis*-$[Pt(Cl)(Me)(L)_2]$ as the kinetically controlled product which slowly isomerizes in solution to the thermodynamically favoured *trans*-isomer. Thus the configuration at both platinum atoms is retained. The symmetrization of *cis*-$[Pt(Me)_2(PMe_2Ph)_2]$ and *cis*-$[Pt(NO_3)_2(PMe_2Ph)_2]$ is completely analogous to that of the chloride and gives *cis*-$[Pt(Me)(NO_3)(PMe_2Ph)_2]$ which then isomerizes to the *trans*-isomer.[45] Evidence is not directly available for cyclic intermediates in exchange reactions of the gold complexes studied but the reactivity towards $[Pt(Me)_2(L)_2]$ decreases in the order $[Au(I)(L)] \geqslant [Au(Br)(L)] \geqslant [Au(Cl)(L)]$. Since iodine is a much better bridging ligand than bromine or chlorine it can be inferred that bridge formation to give a cyclic intermediate is important in these reactions also.

2,2′-Bipyridyl(diethyl)platinum(II) reacts with methyl acrylate with release of ethylene and formation of $[Pt\{CH(Me)CO_2Me\}_2(bipy)]$.[46] No ethane was detected in the products and ethyl radicals are considered unlikely intermediates in the reaction. This contrasts with earlier studies of $[Pt(R)_2(L)_2]$ complexes which react with diethyl fumarate to give $[Pt(CHCO_2Et)_2(L)_2]$ with release of alkyl radicals which could be trapped by Bu^tNO.[47] Second-order kinetics were followed in the methyl acrylate reaction and if the stationary-state approximation is made for the intermediate $[Pt(Et)_2(CH_2{=}CHCO_2Me)]$ (19) in Scheme 10 the rate expression is

$$-d[Pt]/dt = k_1k_2[Pt][CH_2{=}CHCO_2Me]/(k_{-1}[bipy] + k_2)$$



(18)

(19)

Scheme 10

[45] R. J. Puddephatt and P. J. Thompson, *J.C.S. Chem. Comm.*, 1975, 841.
[46] N. Chaudhury and R. J. Puddephatt, *J.C.S. Dalton*, 1976, 915.
[47] N. G. Hargreaves, R. J. Puddephatt, L. H. Sutcliffe, and P. J. Thompson, *J.C.S. Chem. Comm.*, 1973, 861.

For the reaction in neat methyl acrylate $k_1(CH_2{=}CHCO_2Me) = 0.13\ min^{-1}$ and $k_{-1}/k_2 = 870\ l\ mol^{-1}$. The proposed mechanism illustrated in Scheme 10 involves preliminary methyl acrylate co-ordination (18) followed by displacement of bipy to give (19). Since a vacant co-ordination site is available on (19) elimination of ethylene can occur readily whereas intermediate (18) and $[Pt(Et)_2(bipy)]$ are necessarily less reactive in this respect since they are co-ordinatively saturated. Consequently complete loss of bipy may be a prerequisite for the β-elimination step which precedes fast insertion of methyl acrylate into the Pt—H bonds formed to give the final complex.

7 Group I

Gold.—Full details are available of the reactions between benzenethiol and Au^{I} and Pt^{II} complexes [Au(Me)(L)] and *cis*-$[Pt(Me)(L)_2]$ (L = PMe_3, PMe_2Ph, $PMePh_2$, or PPh_3) which give methane and [Au(SPh)(L)] and *trans*-$[Pt(Me)(SPh)(L)_2]$ or *trans*-$[Pt(SPh)_2(L)_2]$ respectively.[48] Inhibition of these reactions by the radical scavenger galvinoxyl and rapid acceleration by the radical initiator azobis(isobutyronitrile) provide evidence that free-radical chain mechanisms are involved. In contrast, neither of these reagents affects the formation of *cis*-$[Au(Me)_2(SPh)(L)]$ from PhSH and the Au^{III} complexes $[Au(Me)_3(L)]$, so radical mechanisms do not seem to operate in these reactions. Two mechanisms, (4) and (5) are considered for the radical reactions and the fact that only (4) leads to formation of methyl radicals serves to dis-

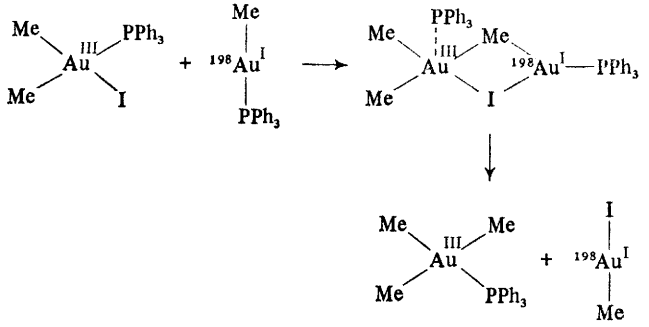
$$\begin{aligned} PhS^{\bullet} + MeM &\longrightarrow (\dot{M}eMSPh) \longrightarrow M + Me^{\bullet} \\ Me^{\bullet} + PhSH &\longrightarrow CH_4 + PhS^{\bullet} \end{aligned} \qquad (4)$$

$$\begin{aligned} PhS^{\bullet} + MeM &\longrightarrow \dot{M}eMSPh \xrightarrow{PhSH} Me{-}MH{-}SPh + PhS^{\bullet} \\ Me{-}MH{-}SPh &\longrightarrow CH_4 + MSPh \end{aligned} \qquad (5)$$

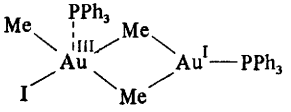
tinguish between them. E.s.r. experiments detected the presence of $Bu^{t}MeNO$ when the reactions of PhSH with *cis*-$[Pt(Me)_2(PMe_2Ph)_2]$ and $[Au(Me)(PMe_3)]$ were carried out in the presence of $Bu^{t}NO$, showing that Me radicals had been formed. However, $Bu^{t}NO$ had little effect on the rates of reaction and since it does not scavenge thiyl radicals it was concluded that mechanism (5) constitutes the main reaction pathway. Radical reactions are also observed when $[Au(Me)(PPh_3)]$ is irradiated in $CDCl_3$ solution.[49] Methyl and solvent-derived radicals in triplet-pairs were detected in addition to S_H2 substitution by Me radicals at the metal. Use of ^{198}Au-labelled $[Au(Me)(PPh_3)]$ in reactions with $[Au(Me)_2(I)(PPh_3)]$ indicates that in the methyl–iodine transfer reaction illustrated the gold does not undergo redox during the transfer since ^{198}Au is found only in the univalent product (Scheme 11).[50] Simple methyl–methyl exchange between the Au^{I} and Au^{III} complexes also occurs, possibly *via* a doubly methyl-bridged intermediate (20).

Recent studies have resulted in the isolation of a variety of four-co-ordinate Au^{III}

[48] A. Johnson and R. J. Puddephatt, *J.C.S. Dalton*, 1975, 115.
[49] P. W. N. M. van Leeuwen, R. Kaptein, R. Huis, and C. F. Roobeck, *J. Organometallic Chem.*, 1976, **104**, C44.
[50] G. W. Rice and R. S. Tobias, *J. Organometallic Chem.*, 1975, **86**, C37.



Scheme 11



(20)

complexes $[AuR_4]^+$ which exhibit exceptional thermal stability.[51,52] This is attributed to the co-ordinative saturation of the gold centre which may inhibit hydride elimination and subsequent decomposition. This is supported by kinetic studies (summarized in Vol. 4, p. 303) of the decomposition of the less thermally stable complex $[Au(Me)_3(PPh_3)]$ which undergoes thermolysis *via* initial dissociation of triphenylphosphine.

8 Actinides

The observation that thermolysis of σ-alkyl uranium complexes $[U(R)(\eta\text{-}C_5H_5)_3]$ to give alkanes RH does not proceed *via* β-hydride elimination has prompted similar studies on some thorium analogues.[53] Qualitatively the reactions are identical to those of uranium although quantitatively the first-order reactions exhibit slight differences (see Table).

Table *Comparative data for thermolysis of* $[M(R)(\eta\text{-}C_5H_5)_3]$ *complexes (from ref.* 53)

	M = U		M = Th	
R	$\Delta G^{\ddagger}$/kcal mol^{-1}	$t_{1/2}$/h	$\Delta G^{\ddagger}$/kcal mol^{-1}	$t_{1/2}$/h
n-Butyl	33.3	1130	37.6	96
Neopentyl	32.2	270	41.4	7500
i-Propyl	29.8	201	35.3	7.1
Allyl	28.7	40	38.6	566
trans-But-2-enyl	34.6	6730	36.3	21

[51] G. W. Rice and R. S. Tobias, *Inorg. Chem.*, 1975, **14**, 2402.
[52] G. W. Rice and R. S. Tobias, *Inorg. Chem.*, 1976, **15**, 489.
[53] T. J. Marks and W. A. Wachter, *J. Amer. Chem. Soc.*, 1975, **98**, 703.

3
Homogeneous Catalysis

BY J. L. DAVIDSON

1 General

The subject matter covered in this chapter is more extensively reviewed than most and each sub-section is preceded by mention of reviews dealing specifically with the subject in question. Other reviews of a more general nature are given in refs. 1—10.

Interest in the olefin disproportionation (metathesis) reaction catalysed by transition-metal compounds has increased markedly during the present period and although a number of features of such reactions remain unexplained or are topics of controversy, sufficient evidence has now been obtained to suggest that carbene intermediates are involved in most catalytic systems. The exact nature of the catalytic sites remains obscure but the recent discovery of one-component metathesis catalysts may enable more rapid advances to be made in this direction.

2 Isomerization

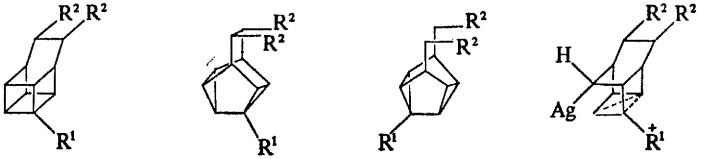
Strained Carbocyclic Systems.—The rearrangement of polycyclic organic compounds catalysed by Ag^+ and other metals has been reviewed.[11,12] The silver(I)-catalysed isomerization of bishomocubanes (1) (R^1=Me or CH_2OAc, R^2=CO_2Me) could follow four mechanistic pathways to give the two isomeric snoutane diesters (2) and (3) but the latter is formed preferentially (82% when R^1=Me; 65% when R^1=CH_2OAc) in both cases.[13] The isomerizations of bishomocubanes substituted at the 9,10-positions, the C-4 corner, at C-4 and C-3, and at C-2 and C-3, to the structurally related snoutane follow the second-order rate law

$$d[\text{bishomocubane}]/dt = k_{Ag}[\text{bishomocubane}][Ag^+]$$

and with excess bishomocubane pseudo-first-order kinetics are observed.[14] The

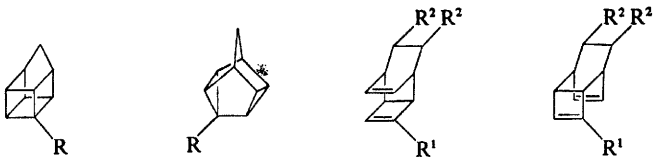
[1] F. D. Mango, *Coordination Chem. Rev.*, 1975, **15**, 109.
[2] D. M. Roundhill, *Adv. Organometallic Chem.*, 1975, **13**, 273.
[3] D. M. Hearg, *Adv. Organometallic Chem.*, 1975, **13**, 363.
[4] M. Wrighton, *Chem. Rev.*, 1974, **74**, 401.
[5] W. Strohmeier, *J. Organometallic Chem.*, 1975, **94**, 273.
[6] P. S. Braterman, *J. Organometallic Chem.*, 1975, **103**, 386.
[7] M. M. T. Khan and A. E. Martell, 'Homogeneous Catalysis by Metal Complexes', Academic Press, New York, 1974, Vols. 1 and 2.
[8] G. W. Parshall, *Accounts Chem. Res.*, 1975, **8**, 113.
[9] F. Minisci, *Accounts Chem. Res.*, 1975, **8**, 165.
[10] H. Felkin and G. Swierczewski, *Tetrahedron*, 1975, **31**, 2735.
[11] L. A. Paquette, *Synthesis*, 1975, 347.
[12] K. C. Bishop, *Chem. Rev.*, 1976, **76**, 461.
[13] L. A. Paquette and R. S. Beckley, *J. Amer. Chem. Soc.*, 1975, **97**, 1084.
[14] L. A. Paquette, R. S. Beckley, and W. B. Farnham, *J. Amer. Chem. Soc.*, 1975, **97**, 1089.

probable mechanism involves a pre-equilibrium with complex formation between Ag^+ and the bishomocubane in which the C-2—C-5 bond is attacked preferentially (edge argentation). The rates are dependent on the electronic properties of R groups substituted at the C-4 position and the intermediate at the rate-determining step (4) is thought to dissipate the positive charge over four carbon atoms. Bis-substitution at C-4 and C-5 results in anomalous rate effects which suggest that steric effects are significant in this case and may over-ride electronic rate enhancement of the rearrangement.



(1) (2) (3) (4)

Ag^+-catalysed isomerization of 4-substituted homocubanes (5) to norsnoutanes (6) also proceeds *via* pre-equilibrium complex formation and follows second-order kinetics.[15] In the case R = Me adherence to Michaelis–Menten kinetics could also be demonstrated. C-4 Substituents capable of resonance interaction in the cationic transition state promote deviations in the rate of reaction relative to substituents which exhibit inductive effects only. With R = Bu^t bond-switching is reduced in rate, presumably because of steric inhibition of Ag^+ attack on the homocubane to give an intermediate analogous to (4). Placement of deuterium or CD_3 at C-4 produces only a minor inverse kinetic deuterium isotope effect ($k_H/k_D = 0.97$) which implies that a completely free carbonium ion intermediate is not involved and so argues in favour of a delocalized species analogous to (4).



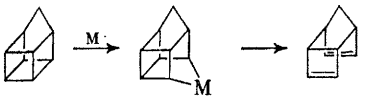
(5) (6) (7) (8)

The mode of rearrangement of 1,8-bishomocubanes (1) catalysed by Rh^I and Pd^{II} complexes depends, not only on the metal and the ligands attached, but also on the level of substitution at the C-4 and C-5 positions of the carbocyclic species.[16] Both snoutanes and the *exo*- and *endo*-diolefins (7) and (8) can be produced, the amount of the former increasing in the order $[Rh_2(nbd)_2(Cl)_2] < [Pd(I)_2(PPh_3)_2] < [Pd(Cl)_2(PPh_3)_2] < [Pd(Cl)_2(PhCN)_2]$ which is the order of decreasing softness of the metals. Steric effects are significant and since the *endo*-isomer (8) of the diene is formed preferentially in reactions of 9,10-disubstituted compounds, attack by the metal from the direction *syn* to the 9,10-substituted position must occur in most cases.

[15] L. A. Paquette, J. S. Ward, R. A. Boggs, and W. B. Farnham, *J. Amer. Chem. Soc.*, 1975, **97**, 1101.

[16] L. A. Paquette, R. A. Boggs, W. B. Farnham, and R. S. Beckley, *J. Amer. Chem. Soc.*, 1975, **97**, 1112.

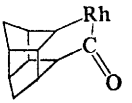
Diene formation is thought to result from an oxidative-addition mechanism (Scheme 1) rather than edge metalation which leads to snoutanes. Kinetic studies of the Rh^{I}- and Pd^{II}-catalysed rearrangement of homocubanes to the diene (9) also provide



(9)

Scheme 1

evidence for an oxidative addition pathway since the electronic properties of substituents at the C-4 position have little effect on the rates, *i.e.* charge development at the C-4 position is insignificant in the transition state.[17] The absence of a deuterium isotope effect with CD_3 as the C-4 substituent is in accord with such a conclusion and suggests that oxidative addition into C-2—C-5 is kinetically favoured (Scheme 1).



(10)

The isolation of (10) from the reaction of $[Rh_2(Cl)_2(CO)_4]$ and 1,3-bishomocubane also provides evidence for such a mechanism since its formation probably involves oxidative addition followed by carbonyl insertion.[18]

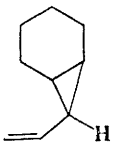
A separate report of the Ni^0-catalysed isomerization of (1) ($R^1=H$, $R^2=CO_2Me$) to *exo*- and *endo*-diolefins (7) and (8) suggests that formation of co-ordinatively unsaturated nickel complexes is a prerequisite for the isomerization to take place.[19] However, addition of tcne to $[Ni(cod)_2]$ in the reaction mixture results in a considerable change in product distribution with the snoutane being formed preferentially. This is probably due to formation of Ni^{2+} which mimics Ag^+ in its catalytic activity. Results of molecular orbital calculations are in general agreement with Paquette's conclusions regarding the transition state (4) for Ag^+-catalysed reactions and oxidative addition of transition metals into the C-2—C-5 bond leading to diolefin production. Concerted cyclobutane–diolefin isomerization promoted by face-on co-ordination to a metal (unidentate or bidentate) is considered unlikely since the appropriate sets of MO's required are not available.

The ease of the silver(I)-promoted rearrangement of dehydronoriceane to 2,4-ethenonoradamantane according to empirical force-field calculations cannot be rationalized in terms of strain release in the former and stabilization of a Ag^I–dehydronoriceane intermediate complex by hyperconjugative effects is considered to be responsible.[20]

The $[Rh_2(Cl)_2(CO)_4]$-catalysed rearrangement of (11) to (13), (14), and (15) follows zero-order kinetics for at least two half-lives and doubling the catalyst concentration doubles the rate of reaction.[21] The *syn*-isomer (12) gives the same products

[17] L. A. Paquette, R. A. Boggs, and J. S. Ward, *J. Amer. Chem. Soc.*, 1975, **97**, 1118.
[18] J. Blum, C. Zlotogorski, and A. Zoran, *Tetrahedron Letters*, 1975, 1117.
[19] R. Noyori, M. Yamakawa, and H. Takoya, *J. Amer. Chem. Soc.*, 1976, **98**, 1471.
[20] T. Katsushima and M. Kawanisi, *J.C.S. Chem. Comm.*, 1976, 39.
[21] M. F. Salomon and R. G. Salomon, *J.C.S. Chem. Comm.*, 1976, 89.

but in addition epimerizes to (11) in a separate competing reaction. The kinetic behaviour and product selectivity provide evidence for initial co-ordination of the vinyl group to rhodium followed by stereospecific *cis*-β-hydride elimination from the metallocyclic intermediate (16) formed by rearrangement of the π-complex. This gives (17) and (18) which on reductive elimination release (13), (14), and (15).



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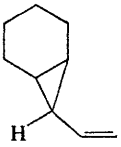

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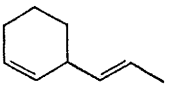

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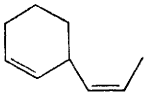

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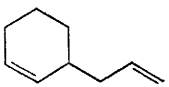

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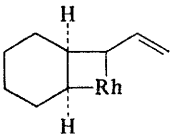

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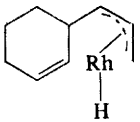

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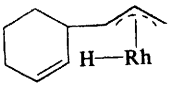

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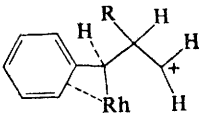
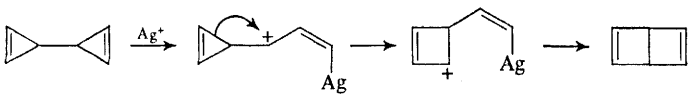


(19)

Phenylmethylcyclopropanes isomerize to conjugated phenylalkenes in the presence of $[Rh(Cl)_2(CO)_4]$ according to a first-order rate law, but under catalytic conditions this becomes pseudo-zero-order in the cyclopropyl compounds.[22] Ring-opening occurs predominantly across the ring from the Me group but adjacent to the Ph substituent, probably reflecting steric and conjugative control of rhodium co-ordination prior to formation of an intermediate carbocation (19) which undergoes hydride migration and product formation. The Ag^I-catalysed rearrangement of bicyclopropenyls to Dewar-benzenes is considered to follow a stepwise pathway (Scheme 2) in which carbocations (20) and (21) are plausible intermediates. Evidence



(20) (21)

Scheme 2

for such species has now been obtained by intercepting the cations by solvolysis.[23]

Alkenes.—The isomerization of but-1-ene to *cis*- and *trans*-but-2-ene by $[NiL_4]$ (L = tertiary phosphine) in acid solution exhibits a rate dependence on the nature of L, is preceded in many cases by an induction period, and is drastically retarded by

[22] P. W. Chum and J. A. Roth, *J. Catalysis*, 1975, **39**, 198.
[23] F. C. Peelen, G. G. A. Rietveld, I. J. Landheer, W. H. de Wolf, and F. Bickelhaupt, *Tetrahedron Letters*, 1975, 4187.

addition of excess ligand. This is considered as evidence for $[Ni(H)(L)_3]^+$ as the catalytic species.[24] Isomerization of pent-1-ene to *cis*-pent-2-ene and *trans*-pent-2-ene is catalysed by $[Ru_3(CO)_{12}]$ and during the reaction complexes $[Ru_3(CO)_9(C_5H_{10})]$ and $[Ru_3(CO)_9(C_5H_8)]$ (two isomers) are formed but these do not contribute significantly to the catalytic process.[25] The rate of conversion is proportional to $[Ru_3(CO)_{12}]$ concentration and is retarded by carbon monoxide, which suggests that CO dissociation is the rate-determining step. The isomerization of pent-1-ene to *cis*- and *trans*-pent-2-ene (mainly the latter) is also catalysed by $[Ru(H)_4(PPh_3)_3]$ and $[Ru(H)_2(N_2)(PPh_3)_3]$[26] and is accompanied by stoicheiometric hydrogenation of the olefin although this proceeds 250 times more slowly than isomerization. The reaction is a two-stage process with the first (rapid) step involving formation of $[Ru(H_2)$(pent-1-ene)$(PPh_3)_3]$. The slower second stage which follows first-order kinetics involves the catalytic species $[Ru(PPh_3)_3]$. The reactions are retarded significantly by nitrogen which is thought to compete effectively with the olefin for a co-ordination site on the metal. $[Co(H)(N_2)(PPh_3)_3]$ also catalyses the transformation of pent-1-ene to *cis*- and *trans*-pent-2-ene in toluene but in this case the *cis*-isomer is formed preferentially. The reaction is second-order in pent-1-ene, first-order in complex, and is retarded by PPh_3 but promoted by dinitrogen. In addition dinitrogen also reduces the ratio of the *cis*- to *trans*-isomers. The observation of second-order kinetics (in olefin) provides evidence for an olefin exchange reaction as the rate-determining step in the isomerization and the rate enhancement by dinitrogen could therefore result from assistance by N_2 of the substitution process.

The allyl complex $[Fe(CO)_3(\eta^3\text{-}C_3H_5)]$ exists in solution as a monomer–dimer equilibrium and isomerizes hex-1-ene to *trans*-hex-2-ene.[27] When dissolved in hex-1-ene a reaction occurs to give $[Fe(CO)_3$(hex-1-ene)$(\eta^1\text{-}C_3H_5)]$ with an activation energy of 10 kcal mol^{-1} suggesting that olefin co-ordination is the first stage in the catalytic reaction. A possible isomerization mechanism is shown in Scheme 3.

$$[Fe(CO)_3(\text{hex-1-ene})(\eta^1\text{-}C_3H_5)] \rightleftharpoons [(\eta^1\text{-}C_3H_5)(CO)_3Fe(H')(\eta^1\text{-}CH_2CH{=}CH(CH_2)_2Me]$$

$$\Updownarrow$$

$$[Fe(CO)_3(\eta^3\text{-}C_3H_5)] + \text{hex-2-ene} \rightleftharpoons [Fe(CO)_3\{CH_2H'CH{=}CH(CH_2)_2Me\}(\eta^1\text{-}C_3H_5)]$$

Scheme 3

Addition of dec-1-ene to toluene solutions of $[Rh_2(Cl)_2(PF_3)_4]$ affords *cis*-dec-2-ene initially which is subsequently isomerized to the *trans*-isomer. Kinetic studies give an activation energy of 40 kJ mol^{-1} for the reaction.[28] An allyl-metal hydride intermediate is suggested for the isomerization but its existence could not be demonstrated by low-temperature n.m.r. studies although previous work has confirmed the existence of such species.

The photochemical rearrangement of cyclo-octa-1,5-diene in the presence of $[Rh_2(Cl)_2(\eta\text{-}1,5\text{-cod})_2]$ gives the 1,4-diene as the exclusive primary photoproduct but this undergoes subsequent isomerization to other compounds as the reaction

[24] C. J. Rix and J. G. Verkade, *Coordination Chem. Rev.*, 1975, **16**, 129.
[25] M. Castiglioni, L. Milone, D. Osella, G. A. Vaglio, and M. Valle, *Inorg. Chem.*, 1976, **15**, 394.
[26] F. Pennella, *Coordination Chem. Rev.*, 1975, **16**, 51.
[27] E. L. Meutterties, B. A. Sosinsky, and K. I. Zamaraev, *J. Amer. Chem. Soc.*, 1975, **97**, 5299.
[28] J. F. Nixon and B. Wilkins, *J. Organometallic Chem.*, 1975, **87**, 341.

progresses.[29] $[^2H_8]$-1,5-cod Rearranges under similar conditions to $[^2H_8]$-1,4-cod with a structure which implies a 1,3-shift of deuterium. A deuterium isotope effect $k_H/k_D = 1.55$ is in accord with a mechanism involving rate-determining cleavage of an allylic C—H bond to give an η^3-allylrhodium hydride intermediate which undergoes reductive elimination of the 1,4-diene. The reaction is thought to be initiated by photolytic dechelation of a 1,5-cod ligand in $[Rh_2(Cl)_2(1,5\text{-cod})_2]$ thus facilitating the oxidative addition of co-ordinatively unsaturated rhodium into a C—H bond of 1,5-cod to give the allyl-rhodium hydride intermediate.

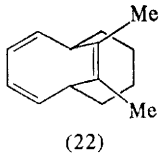
$[Ir_2(H)_2(Cl)_2(1,5\text{-}C_8H_{12})(PPh_3)_2]$ promotes the isomerization of 1,5-cyclo-octadiene to both the 1,4- and 1,3-forms in a stepwise manner according to equation (1). The rate of isomerization decreases at a rate dependent on both the initial

$$1,5\text{-cod} \rightleftharpoons 1,4\text{-cod} \longrightarrow 1,3\text{-cod} \qquad (1)$$

catalyst concentration and the reaction temperature as a result of catalyst conversion into the catalytically inert complex $[Ir(Cl)(1,5\text{-}C_8H_{12})(PPh_3)]$,[30] The active intermediate is considered to be $[Ir(H)_2(Cl)(1,5\text{-}C_8H_{12})(PPh_3)]$ since under nitrogen this can lose hydrogen to give $[Ir(Cl)(1,5\text{-}C_8H_{12})(PPh_3)]$. In addition the latter readily becomes active towards promotion of 1,5-cod isomerization at low temperatures in the presence of hydrogen. The isomerization of bicyclo[4,2,0]oct-7-ene to bicyclo-[4,2,0]oct-2-ene in the presence of $[Fe_2(CO)_9]$ proceeds *via* olefin co-ordination to an $Fe(CO)_4$ moiety followed by hydrogen migration.[31]

A unique example of a metal-catalysed two-fold circumambulatory rearrangement is illustrated by the hexacarbonyl molybdenum-promoted rearrangement of (22) to (23).[32,33] Two other isomers (24) and (25) are also formed but these do not undergo conversion to (23). The observed 1,5-carbon shifts presumably involve specific co-ordination to the metal which controls the subsequent suprafacial migration. The tricyclic alcohol (26; R = H) on heating in the presence of $[Fe(CO)_5]$ undergoes isomerization to the ketone (27; R = H) although its epimer is unreactive under similar conditions.[34] The deuterium-labelled analogue of (26; R = D) gives (27; R = D) exclusively, demonstrating that deuterium incorporation is stereospecific as a result of an intramolecular 1,3-suprafacial shift of deuterium. A primary kinetic isotope effect of 1.23 is more easily rationalized on this basis than in terms of an allyl-metal hydride intermediate.

Kinetic studies[35] of the Ni^{II}-catalysed Beckmann rearrangement of *syn*-benzaldoxime to benzamide indicate that two distinct consecutive steps are involved (k_a and



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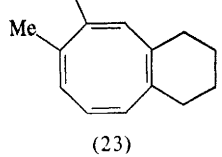
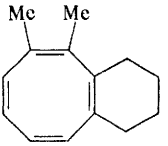


(23)

[29] R. G. Salomon and N. E. Sanadi, *J. Amer. Chem. Soc.*, 1975, **97**, 6214.
[30] M. Gargano, P. Giannoccaro, and M. Rossi, *J. Organometallic Chem.*, 1975, **84**, 389.
[31] K. Cann and J. C. Barborak, *J.C.S. Chem. Comm.*, 1975, 190.
[32] L. A. Paquette, J. M. Photis, K. B. Gifkins, and J. Clardy, *J. Amer. Chem. Soc.*, 1975, **97**, 3536.
[33] L. A. Paquette and J. M. Photis, *Tetrahedron Letters*, 1975, 1145.
[34] J. U. Strauss and P. W. Ford, *Tetrahedron Letters*, 1975, 2917.
[35] A. K. Johnson and J. D. Miller, *Inorg. Chim. Acta*, 1976, **16**, 181.



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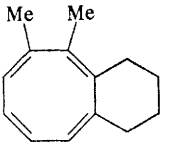

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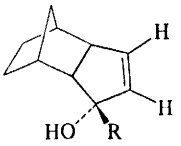

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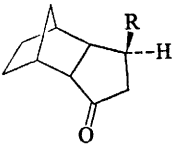


(27)

k_b) and amide formation follows equation (2). The overall sequence is described by Scheme 4.

$$[\text{amide}] = [\text{amide}]_\infty \left\{1 - \frac{k_b}{(k_b - k_a)} \exp(-k_a t) + \frac{k_a}{(k_b - k_a)} \exp(-k_b t)\right\} \quad (2)$$

$$\text{Ni}^{II} + \textit{syn}\text{-oxime} \overset{K_1}{\rightleftharpoons} \text{Ni}^{II}(\textit{anti}\text{-oxime})$$

$$\text{Ni}^{II}(\textit{anti}\text{-oxime}) \xrightarrow{k_2} \text{Ni}^{II}(\text{imidate})$$

$$\text{Ni}^{II} + \text{imidate} \overset{K_3}{\rightleftharpoons} \text{Ni}^{II}(\text{imidate})$$

$$\text{imidate} \xrightarrow{k_4} \text{benzamide}$$

$$\text{imidate} \xrightarrow{k_5} \text{side-products}$$

Scheme 4

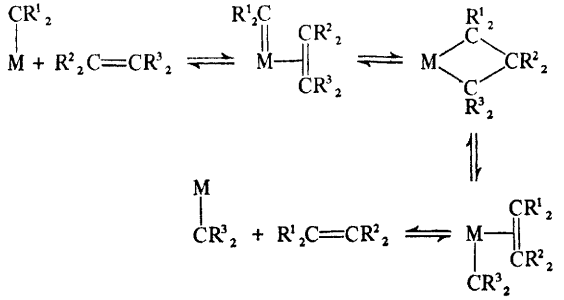
The composite rate constant $k_a (= K_1 k_2 [\text{Ni}])$ corresponds to a series of reactions in which attack by solvent on co-ordinated oxime leads to side-chain C—H bond cleavage, yielding a benzimidate complex. In the second stage (k_b) the imidate is released into solution (K_3) and converted thermally (k_4) into benzamide or into side-products (k_5).

3 Disproportionation

Disproportionation of olefins induced by homogeneous and heterogeneous catalysts has been reviewed.[36,37]

Following the period during which a variety of mechanisms were proposed for olefin disproportionation reactions there appears to be a general move towards acceptance of the view that metal–carbene and metalacyclobutane intermediates are involved, particularly when the catalysts are based on tungsten (Scheme 5). Casey, for example, has studied a model system in which the carbene complex [$W(CO)_5$-(CPh_2)] was allowed to react with isobutylene and the organic products (28) and (29)

[36] R. J. Maines and G. J. Leigh, *Chem. Soc. Rev.*, 1975, **4**, 155.
[37] J. C. Mol and J. A. Moulijn, *Adv. Catalysis*, 1975, **24**, 131.



Scheme 5

were isolated. This and related experiments demonstrate fission of the C=C bond of the olefin and combination of the resulting methylene group with the carbene ligand to give (29).[38] A number of studies have established the selectivity of metathesis

(28) (29)

reactions with relative rates decreasing in the order (i) degenerate (non-productive) exchange of CH_2 groups between terminal olefins; (ii) cross-metathesis of terminal and internal alkenes; (iii) metathesis of internal alkenes; (iv) metathesis of terminal alkenes to give ethylene and internal alkenes. This order of reactivity is partially explained by studies of reactions between $[W(CO)_5\{C(tol)_2\}]$ and unsymmetrical olefins which suggest that the least substituted alkylidene is transferred to the carbene ligand preferentially.[39] Thus the predominant reaction (ii), cross-metathesis of terminal and internal olefins, is likely to be a favoured process as is found experimentally.

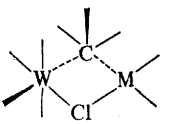
Not only are carbene complexes useful for studies of model systems, but recently they have also been found to initiate genuine metathesis reactions, illustrating that Lewis acid co-catalysts are not always essential components of active catalysts.[40] This holds considerable promise for future investigations since such catalysts can possibly be used to promote metathesis of olefins which are sensitive to Lewis acids. Another aspect of the one-carbene exchange mechanism (Scheme 5) is that chain transfer of methylene groups is involved unlike earlier mechanisms which require that pair-wise exchange occurs exclusively. Further support for a carbenoid intermediate mechanism is therefore provided by the results of Katz[41] and Grubbs[42] who have independently reported evidence for a non-pair-wise exchange process.

Carbene exchange mechanisms also account for CH_2–CD_2 exchange in the following reaction

[38] C. P. Casey and T. J. Burkhardt, *J. Amer. Chem. Soc.*, 1974, **96**, 7803.
[39] C. P. Casey, H. E. Tuinstra, and M. C. Saeman, *J. Amer. Chem. Soc.*, 1976, **98**, 608.
[40] J. McGinnis, T. J. Katz, and S. Hurwitz, *J. Amer. Chem. Soc.*, 1976, **98**, 605.
[41] T. J. Katz and J. McGinnis, *J. Amer. Chem. Soc.*, 1975, **97**, 1592.
[42] R. H. Grubbs, P. L. Burk, and D. D. Carr, *J. Amer. Chem. Soc.*, 1975, **97**, 3266.

$$\text{hex-1-ene} + [1,1\text{-}^2H_2]\text{hept-1-ene} \xrightarrow{WCl_6\text{–}2Bu^nLi} [1,1\text{-}^2H_2]\text{hex-1-ene} + \text{hept-1-ene}$$

and in the mixture [$^2H_{10}$]-pent-1-ene + hex-1-ene–WCl_6 + $EtAlCl_2$.[43] Such non-productive metathesis reactions are also accompanied by productive disproportionation but the ratio of the former to the latter varies between 1000:1 and 100:1 depending on the system. The underlying reasons for such high ratios are unknown but catalyst stereochemistry, which will depend on the interaction between WCl_6 and the Lewis acid co-catalyst, may be responsible.[43] Interactions between Lewis acids, *e.g.* $EtAlCl_2$, and the metal halide produced in catalyst mixtures from reactions with WCl_6 are thought to promote α-hydride elimination from the other reaction products, *i.e.* alkyl tungsten halides.[44] This provides the catalytically active tungsten complex required for metathesis. The precursor is postulated to have structure (30). Other



(30)

evidence points to the necessity for a tungsten–hydrogen bond in order to promote metathesis in such catalytic systems[45] while in catalysts derived from [$W(CO)_5L$] [L = CO, PPh_3, PBu^n_3, or $P(OPh)_3$], and $EtAlCl_2$, molecular oxygen is necessary to ensure high activity.[46] The co-catalyst $EtAlCl_2$ apparently forms an adduct with O_2, thus enhancing its Lewis acidity and so promoting attack on [$W(CO)_5(L)$] to produce the disproportionation catalyst. The latter probably contains aluminium bound to the oxygen of a CO group *trans* to ligand L since a ν(CO) mode at 1667 cm^{-1} is observed in the i.r. spectrum of catalyst solutions. Whatever the nature of the catalyst, whether derived from zerovalent tungsten or from WCl_6, the stereochemistry (*cis* or *trans*) of the C_4 (butenes) and C_6 (hexenes) olefins obtained by metathesis of *cis*-pent-2-ene remains invariant.[47] The *trans*:*cis* ratio of the C_4 olefin lies in the range 0.69—0.78 whereas that of the C_6 olefin from 0.83 to 0.89, which suggests that, despite the nature of the catalyst precursor, the active species has a constant co-ordination sphere during the catalytic steps which govern the stereochemistry of the products.

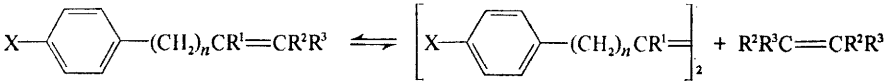
Photolysis of [$W(CO)_6$] in CCl_4 yields a disproportionation catalyst the nature of which has given rise to some controversy since McNelis considers the active species to be [$W(Cl)_2(CO)_4$][48] whereas the stoicheiometry [$W(Cl)(CO)_5$] is favoured by Dubois.[49] The former has prepared the dichloride by a separate route and demonstrated its catalytic activity with respect to disproportionation of *cis*-pent-2-ene to but-2-enes and hex-3-enes. Flash photolysis or irradiation of [$W(CO)_6$] in CCl_4, according to Dubois, gives [$W(Cl)(CO)_5$] and $COCl_2$ *via* the reaction

[43] M. T. Mocella, M. A. Busch, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1976, **98**, 1283.
[44] E. L. Muetterties, *Inorg. Chem.*, 1975, **14**, 951.
[45] J. Levisalles, H. Rudler, and D. Villemin, *J. Organometallic Chem.*, 1975, **87**, C7.
[46] J. L. Bihou, J. M. Basset, and R. Mutin, *J. Organometallic Chem.*, 1975, **87**, C4.
[47] J. M. Basset, J. L. Bilhou, R. Mutin, and A. Theolier, *J. Amer. Chem. Soc.*, 1975, **97**, 7376.
[48] A. Agapiou and E. McNelis, *J. Organometallic Chem.*, 1975, **99**, C47 and refs. cited therein.
[49] P. Krausz, F. Garnier, and J. E. Dubois, *J. Organometallic Chem.*, 1976, **108**, 197.

$$[W(CO)_6] \xrightarrow{h\nu} [W(CO)_5] + CO \xrightarrow{CCl_4} [W(Cl)(CO)_5] + COCl_2$$

but some doubt is cast upon these conclusions by the report that oxygen is necessary for the formation of phosgene and that CCl_4 functions as the source of the carbonyl group.[48] Suggestions that metathesis reactions catalysed by co-ordination complexes derived from WCl_6 are heterogeneous in nature (see Vol. 4 of these Reports) have been refuted by some workers who have separated the soluble and insoluble constituents of the catalytic mixture WCl_6–$EtAlCl_2$ and found that catalytic activity resides only in the soluble fraction.[50]

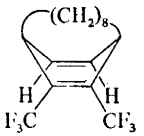
The effect of the structure of ω-aryl-olefins on their reactivity towards disproportionation (Scheme 6) has been studied in terms of three variables, (i) length of chain



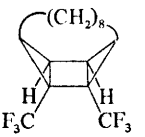
Scheme 6

(n) between the aryl group and the double bond, (ii) substituent effects at the double-bond, and (iii) substituent effects on the aryl group.[51] The results can be accounted for by a one-carbene exchange mechanism and, to explain a marked increase in the rate of reaction with $n=2$ (4-phenylbut-1-ene), relative to $n=1$ or 3—6, an interaction between the aromatic ring and the transition metal during one of the catalytic steps is postulated. Substitution at the double bond by more than one methyl group produces a significant decrease in the rate of metathesis which may reflect steric and possibly electronic retardation. Bulky substituents on the aromatic ring do not, however, affect the rates of metathesis nor do halogens, but a methoxy-group retards the reaction while the highest rate of reaction is observed with X=H.

Finally, despite the plethora of reports providing evidence for the one carbene exchange mechanism, in certain circumstances cyclobutanes can be converted quantitatively into diolefins and, of greater importance, two non-conjugated olefinic groups (31) can be converted into a cyclobutane (32) almost quantitatively by the methathesis catalyst $PhWCl_3$–$AlCl_3$.[52] This suggests that the carbene mechanism is not a unique pathway for olefin disproportionation and that in some circumstances cyclobutane intermediates may be formed.



(31)



(32)

4 Oligomerization

Reviews in this area are concerned with the oligomerization of acetylenes induced by

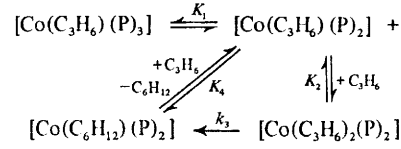
[50] R. Wolovsky and Z. Nir, *J.C.S. Chem. Comm.*, 1975, 302.
[51] P. Chevalier, D. Sinou, G. Descotes, R. Mutin, and J. Basset, *J. Organometallic Chem.*, 1976, **113**, 1.
[52] P. G. Gassman and T. H. Johnson, *J. Amer. Chem. Soc.*, 1976, **98**, 861.

palladium(II),[53] one-component catalysts for olefin polymerization,[54] and more general aspects of acetylene oligomerization catalysed by transition metals.[55] A book concerned with the mechanistic aspects of co-ordination polymerization has also appeared.[56]

The kinetics of homogeneous propylene dimerization in benzene catalysed by $[Co(H)(N_2)(PPh_3)_3]$ or $[Co(N_2)(PPh_3)_3]$ can be described by the rate equation (3).

$$\text{Rate} = \frac{k_3K_1K_2[\text{Co}][C_3H_6]}{[\text{PPh}_3] + K_1 + K_1K_2[(C_3H_6)]} \quad (3)$$

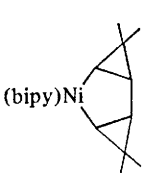
The major products are *trans*-4-methylpent-2-ene (17%) and 2-methylpent-1-ene (65%) and activation parameters are $E_a = 22.9$ kcal mol^{-1}, $\Delta H^{\ddagger} = 22.3$ kcal mol^{-1}, and $\Delta S^{\ddagger} = 13$ cal K^{-1} mol^{-1}.[57] Since both complexes have equal catalytic ability both must produce the same active species, possibly a Co^0 complex. The proposed mechanism is illustrated in Scheme 7 and it appears that the Co—H bond plays no



Scheme 7

part in the initial stages of dimerization although this does not exclude hydride participation during the reaction. In fact, *ortho*-metalation of a phenyl group is postulated which can initiate the catalytic cycle.

Nickelacyclopentane derivatives (33) and (34), isolated from the reactions of the Ni^0 complex [Ni(bipy)(cod)] with 3,3-dimethylcyclopropene and norbornadiene



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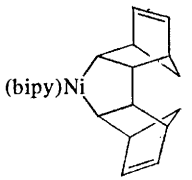


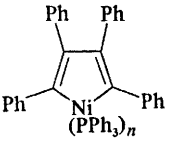
(34)

respectively at 25 °C, catalyse the cyclodimerization of these two olefins at higher temperature, thus illustrating the importance of metala-ring systems in cyclodimerization reactions.[58] Photodimerization of *trans,trans*-dibenzylideneacetone in the presence of uranyl salts gives the 'truxillic'-type dimer while the 'truxinic' dimer is obtained in the absence of a metal salt.[59] The structure of bis(dibenzylideneacetone)-uranyl dichloride requires that dimerization *via* uranyl salts is an intermolecular reaction between two uranyl intermediate complexes such that head-to-tail linkage of

[53] P. M. Maitlis, *Accounts Chem. Res.*, 1976, **9**, 93.
[54] Yu. Yermakov and V. Zakharov, *Adv. Catalysis*, 1975, 173.
[55] L. P. Yur'eva, *Russ. Chem. Rev.*, 1974, **43**, 48.
[56] 'Coordination Polymerisation', ed. J. C. W. Chien, Academic Press, New York, 1975.
[57] G. Speier, *J. Organometallic Chem.*, 1975, **97**, 109.
[58] M. J. Doyle, J. McMeeking, and P. Binger, *J.C.S. Chem. Comm.*, 1976, 376.
[59] N. W. Alcock, N. Herron, T. J. Kemp, and C. W. Shoppee, *J.C.S. Chem. Comm.*, 1975, 785.

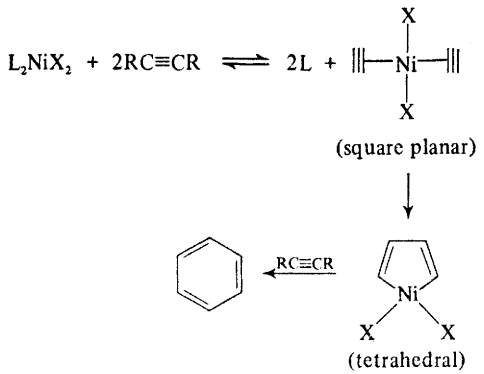
dibenzylideneacetone can occur. This results from the bulk of the rest of the molecule $[UO_2Cl_2(dba)]$ precluding any other mode of approach by another similar species. The rate of linear dimerization of isoprene to 2,6-dimethylocta-1,3,6-triene in the presence of $[Ni(Cl)_2(PPh_3)_2]$–$NaBH_4$ is accelerated significantly by amines and the rate increase shows a correlation with a combination of σ^* and E_S values of alkyl groups on the amine.[60] This indicates that steric as well as electronic factors play a role in the catalytic dimerization which is to be expected since the amine is considered to function as a hydrogen transfer agent.

Intermediates containing metallapentadiene rings are frequently involved in metal-catalysed cyclotrimerization of acetylenes to benzenes, a fact illustrated by the facile catalysis of the cyclotrimerization of PhC_2Ph by the nickelole complex (35).[61]



(35)

However, the nature of the intermediate stages in such reactions is not well understood. The mechanism of Ni^{II}-catalysed reactions is depicted in Scheme 8 and since

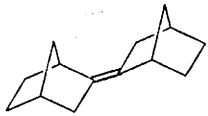


Scheme 8

$[NiX_2(L)_2]$ complexes (L = neutral ligand, X = halide, CN^-, *etc.*) can exist in square-planar or tetrahedral forms it is proposed that the two acetylenes cyclize by movement towards each other (as a result of a vibration of a_1 symmetry) to give the tetrahedral structure.[62] Since the acetylenes possess empty π-orbitals this is facilitated by the large amplitude of the a_1 vibration which arises from a second-order Jahn–Teller effect.

Norbornene undergoes polymerization and dimerization to four isomeric dimers (36) in the presence of WCl_6 or $ReCl_5$, and when the reaction is carried out in benzene norbornylbenzene is also obtained.[63] Kinetic studies show that while the alkylation

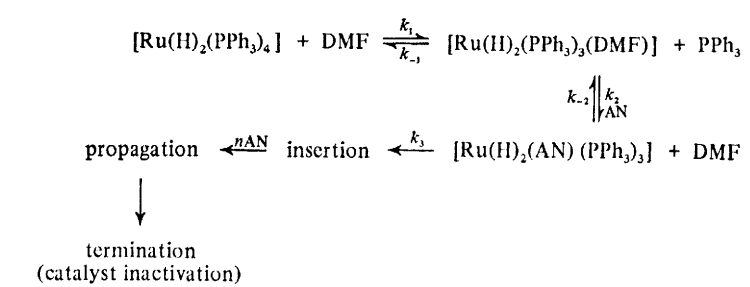
[60] I. Mochida, S. Yuasa, and T. Seiyama, *J. Catalysis*, 1976, **41**, 101.
[61] J. J. Eisch and J. E. Galle, *J. Organometallic Chem.*, 1975, **96**, C23.
[62] A. W. Parkins and R. Slade, *J.C.S. Dalton*, 1975, 1352.
[63] D. T. Laverty, M. A. McKervey, J. J. Rooney, and A. Stewart, *J.C.S. Chem. Comm.*, 1976, 193.



(36)

reaction is independent of polymerization the same intermediate is involved in both the latter reaction and in dimerization. Trace amounts of water enhance the reactivity of the system towards polymerization, which may implicate metal hydrides as the active catalysts which promote dimerization and polymerization. A carbene-intermediate mechanism analogous to that discussed in Section 2 in relation to olefin disproportionation is considered plausible.

$[Ru(H)_2(PPh_3)_4]$ initiates the polymerization of α-substituted olefins of intermediate electronegativity such as acrylonitrile and methyl acrylate but olefins of high or low electronegativity preferentially form π-complexes.[64] The molecular weight of the polymer obtained from acrylonitrile is independent of polymerization time but increases linearly with monomer concentration. The complex decomposes during the reaction (in DMF) at a rate equivalent to the rate of polymer initiation according to the rate law $-d[Ru]/dt = k[Ru]$, where $1/k = A + \{B + C[PPh_3]\}/[\text{monomer}]$. This can be correlated with the mechanism of Scheme 9 in which the rate-determining step is



Scheme 9 (AN = olefin monomer)

the first insertion (k_3) into the Ru—H bond with an activation energy of 20 kcal mol^{-1}. This is followed by rapid monomer insertions in the propagation step. Triphenylphosphine apparently competes with monomer in the propagation step and also promotes termination in a complex with a growing polymer chain. This latter is probably accomplished by hydrogen migration from metal to polymer since loss of hydride will deactivate the catalyst in accord with experimental observations. A similar mechanism can also account for the kinetic data obtained from studies of polymerizations using $[Co(H)(L)(PPh_3)_2]$ ($L = N_2$ or CO) as catalysts.[65]

Polymerization of styrene in the presence of $[Ti(NEt_2)_3(Me)]$ follows a third-order rate law, first-order in complex and second-order in styrene,[66] with an activation energy of 9.56 kcal mol^{-1}. Radical inhibitors have no effect on the reaction rate and

[64] S. Komiya, A. Yamamoto, and S. Ikeda, *Bull. Chem. Soc. Japan*, 1975, **48**, 101.
[65] A. Yamamoto and S. Ikeda, *J. Macromol. Sci.*, 1975, **A9**, 931.
[66] N. Koide, K. Iimura, and M. Takeda, *J. Macromol. Sci.*, 1975, **A9**, 961.

an anionic mechanism is proposed in which the first step is styrene co-ordination to titanium followed by insertion into the Ti—Me bond. The latter step accounts for the disappearance of the methyl peak ($\tau = 9.52$) in the ^{1}H n.m.r. spectrum of the catalyst when monomer is added.

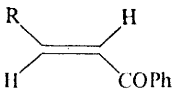
Previous kinetic studies of the $[Ni_2(I)_2(\eta\text{-allyl})_2]$-catalysed polymerization of butadiene suggest that the active metal species is $[Ni(I)(\eta\text{-allyl})]$ but studies of the $[Ni(I)(\eta\text{-1-Me}C_3H_4)]$–butadiene system indicate that if the complex concentration is sufficiently high the undissociated dimeric form acts as the catalyst.[67] ^{1}H N.m.r. studies indicate that butadiene insertion into the Ni—(η-allyl) bond is the first step in the polymerization and follows a first-order rate law with respect to the catalyst. The polymerization then proceeds by similar multiple insertions in the propagation step of the reaction.

The rates of photopolymerization of methyl methacrylate catalysed by $[Fe(triene)_3]^{3+}$–CCl_4 exhibit a complex dependence on the concentrations of the reacting species.[68] At low concentrations of complex the rate is $\frac{1}{2}$-order in concentration but as [complex] is raised this is reduced to a zero-order dependency, possibly as a result of less efficient free-radical formation. The rate is also proportional to monomer concentration at low concentrations of complex but changes to a $\frac{3}{2}$-order dependency at higher concentrations. Addition of CCl_4 accelerates the reaction up to a point where the rate does not increase with increased CCl_4 concentration. From these findings a radical mechanism is proposed in which the initiation step is

$$[Fe(triene)_n] + CCl_4 \rightleftharpoons [Fe(triene)_n \cdots CCl_4] \xrightarrow{h\nu} Fe(triene)_{n-1} + {}^{\cdot}CCl_3 + (triene)Cl^-$$

$$^{\cdot}CCl_3 + \text{monomer} \longrightarrow \text{monomer radical}$$

Further evidence for a co-ordination–addition mechanism in the polymerization of vinyl ketones by alkyl zinc complexes has been obtained from kinetic studies of the model system $[Zn(Et)_2]$–(37; R = Ph).[69] A second-order rate law is observed for



(37)

the reaction of the two compounds in toluene solution and can be explained by the sequence shown in Scheme 10.

$$PhCH{=}C(H)COPh + ZnEt_2 \rightleftharpoons [Zn(Et)_2 \cdots (37)]$$

$$2[Zn(Et)_2 \cdots (37)] \longrightarrow PhEtCH{-}CHCPh(OZnEt) + Zn(Et)_2 \cdots$$

Scheme 10

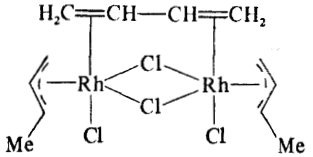
Kinetic studies of acrylonitrile polymerization catalysed by a variety of Cu^{II} complexes have also been reported by Takemota and the results interpreted in terms

[67] V. I. Klepikova, G. B. Erusalimskii, M. I. Lobach, L. A. Churlyaeva, and V. A. Kormer, *Macromolecules*, 1976, **9**, 217, and refs. cited therein.
[68] Y. Inaki, M. Takahashi, and K. Takemoto, *J. Macromol. Sci.*, 1975, **A9**, 1133.
[69] T. Tsuruta and R. Tsushima, *Makromol. Chem.*, 1976, **177**, 337.

of preliminary reduction of Cu^{II} to Cu^{I} generating an acrylonitrile monomer radical which initiates the polymerization.[70,71,72]

5 Co-addition and Co-oligomerization

The η^3-crotyl complex (38) is known to be a precursor to the active species which catalyses the formation of hexa-1,4-diene from ethylene and butadiene. In non-polar solvents (38) is inactive but becomes active in the presence of donor ligands (D) which promote monomer formation (39).[73]



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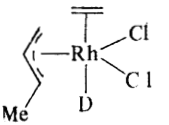
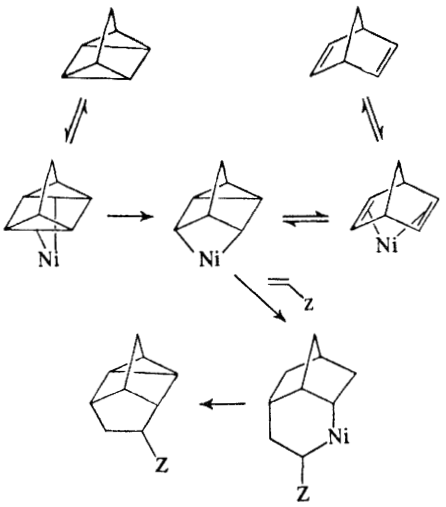


(39)

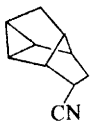
The Ni^0-catalysed (2+2) cycloaddition of activated olefins such as acrylonitrile or acrylic acid esters to quadricyclane which gives *endo*- and *exo*-substituted products is complicated particularly in the case of 1,2-disubstituted olefins by a competing isomerization of quadricyclane to norbornadiene.[74] Norbornadiene gives identical cycloadducts under these conditions with a similar isomer ratio. Kinetic studies of the cycloaddition reactions of quadricyclane gave a plot of log $[\text{quadricyclane}]_{t=0}/[\text{quadricyclane}]_{t=t}$ against time which exhibited a marked deviation from linearity due to the retarding effect of norbornadiene which is also formed and in turn co-ordinates to the Ni^0 catalyst. Scheme 11 accounts for these observations.



Scheme 11

[70] Y. Inaki, H. Shirai, and K. Takemoto, *Angew. makromol. Chem.*, 1975, **45**, 51.
[71] Y. Inaki, S. Nakagawa, K. Kimura, and K. Takemoto, *Angew. makromol. Chem.*, 1975, **48**, 29.
[72] Y. Inaki, M. Ishiyama, K. Hibino, and K. Takemoto, *Makromol. Chem.*, 1975, **176**, 3135.
[73] A. C. L. Su and J. W. Collette, *J. Organometallic Chem.*, 1975, **90**, 227.
[74] R. Noyori, I. Umeda, H. Kawauchi, and H. Takaya, *J. Amer. Chem. Soc.*, 1975, **97**, 812.

At higher temperatures > 90 °C the alternative [4+2] cycloaddition reaction gives (40) (*endo*) and (41) (*exo*) with norbornadiene and acrylonitrile as substrates and the *endo*:*exo* isomer ratio is affected by added phosphines.[75] The ratio shows little dependence on the electronic properties of PR_3 but bulky phosphines promote the formation of the *exo*-isomer which can be explained in terms of a preference for intermediate (43) rather than (42).



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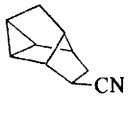

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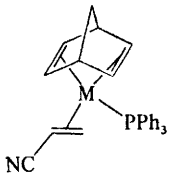

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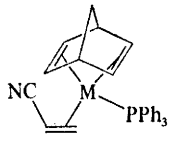
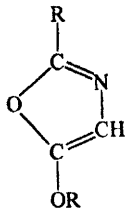
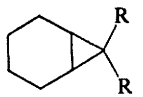


(43)

The Cu^{II}-catalysed 1,3-dipolar addition of ketocarbenes (generated from alkyl diazoacetates N_2CHCO_2R) to nitriles RCN gives oxazoles (44) and obeys first-order kinetics with respect to both N_2CHCO_2R and the catalyst, *i.e.* Rate = $k[N_2CHCO_2R][Cu^{II}]$ when the reaction is conducted with the nitrile as solvent.[76] The reactions proceed by an initial fast stoicheiometric evolution of N_2 which is indicative of preliminary reduction of Cu^{II} to the active catalyst Cu^{I}. Moreover the Cu^{II} signal in the e.s.r. spectrum disappears completely on addition of N_2CHCO_2R at a rate comparable to that of the preliminary stoicheiometric reaction. The available data point to an intermediate Cu^{I} species containing co-ordinated RCN and N_2CHCO_2R. The situation is less clear with the copper(I)-catalysed decomposition of dimethyl diazomalonate in the presence of cyclohexene since cyclopropanation, insertion, and dimerization can all occur to give (45), (46), and the olefin $R_2C{=}CR_2$ respectively



(44)



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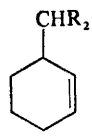


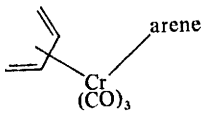
(46)

(R = CO_2Me).[77] Some evidence is presented for the initial oxidation of Cu^{I} to Cu^{II} by peroxide impurities in the olefin and this functions as the active catalyst. Cyclopropanation of olefins by reaction with $ZnEt_2$–$CHBr_3$ mixtures in the presence of oxygen probably proceeds *via* a radical pathway in view of the observed rate inhibition by styrene.[78] The bromocarbenoid intermediate generated (Br_2HCZnR; R = H or Et) shows high *syn*-selectivity for the addition to cyclo-octene and *cis*-but-2-ene.

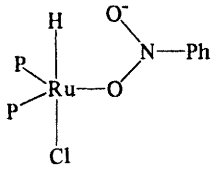
[75] S. Yoshikawa, K. Aoki, J. Kiji, and J. Furukawa, *Bull. Chem. Soc. Japan*, 1975, **48**, 3239.
[76] Ph. G. Moniotte, A. J. Hubert, and Ph. Teyssie, *J. Organometallic Chem.*, 1975, **88**, 115.
[77] D. S. Wulfman, N. van Thinh, R. S. McDaniel, B. W. Peace, C. W. Heitsch, and M. T. Jones, jun., *J.C.S. Dalton*, 1975, 522.
[78] S. Miyano and H. Hashimoto, *Bull. Chem. Soc. Japan*, 1975, **48**, 3665.

6 Homogeneous Hydrogenation

The complex *trans,trans*-hexa-2,4-dienetetracarbonylchromium has been shown to be an intermediate in the photocatalytic hydrogenation of *trans,trans*-hexa-2,4-diene with $[Cr(CO)_6]$.[79] The complexes $[Cr(CO)_3(L)]$ (L = phenanthrene, naphthalene, or anthracene) are much more active in the catalysis of diene hydrogenation than typical arenetricarbonylchromium complexes in addition to which induction times are significantly lower. This can be correlated with the asymmetry of the Cr—arene bonding which may facilitate formation of an intermediate (47) during the induction period.[80,81]



(47)



(48)

A number of reports have appeared concerning the details of hydrogenation reactions catalysed by $[Ru(X)_2(P)_3]$ (X = halide or CO_2R, P = tertiary phosphine) and a feature of such catalysts is their selectivity. The first step in such reactions is generally phosphine dissociation and when X = Cl this is followed by transformation of the dichloride to $[Ru(Cl)(H)(P)_2]$ by addition of hydrogen and elimination of HCl:

$$[Ru(Cl)_2(P)_2] + H_2 \longrightarrow [Ru(Cl)(H)(P)_2] + HCl$$

This catalyst promotes the hydrogenation of olefins and addition of aluminium alkyls is found to enhance the rate of reaction apparently as a result of HCl scavenging by AlR_3:[82]

$$HCl + AlR_3 \longrightarrow AlR_2Cl + RH$$

Addition of phosphine retards the catalytic reduction of $PhNO_2$ to aniline,

$$PhNO_2 + 3H_2 \xrightarrow{[Ru(Cl_2)(PPh_3)_3]} PhNH_2 + 2H_2O$$

as might be expected if phosphine dissociation from the tris-phosphine complex is important.[83] The reaction rate is also comparable to the rate for the $[Ru(H)(Cl)(PPh_3)_3]$-catalysed reaction in accord with the intermediate formation of the bis-phosphine complex which is then attacked by $PhNO_2$ to give (48). The sensitivity of rates to H_2 pressure and [Ru] in addition to a small isotope effect suggests that oxidative addition of H_2 to (48) may be the rate-determining step and this, in conjunction with repeated H transfer to the nitrogen-containing ligand, produces $PhNH_2$ and H_2O. The rate of hydrogenation of 1,4-androstadiene-3,17-dione over $[Ru(Cl)_2\{P(p\text{-}MeOC_6H_4)_3\}_3]$ obeys first-order kinetics with respect to steroid concentrations.[84] The

[79] I. Fischler, M. Budzwait, and E. A. Koerner von Gustorf, *J. Organometallic Chem.*, 1976, **105**, 325.
[80] M. Cais, D. Fraenkel, and K. Weidenbaum, *Coordination Chem. Rev.*, 1975, **16**, 27.
[81] G. Yagupsky and M. Cais, *Inorg. Chim. Acta*, 1975, **12**, L27.
[82] R. A. Porter and D. F. Schriver, *J. Organometallic Chem.*, 1975, **90**, 41.
[83] J. F. Knifton, *J. Org. Chem.*, 1976, **41**, 1200.
[84] S. Nishimura, O. Yumoto, K. Tsuneda, and H. Mori, *Bull. Chem. Soc. Japan*, 1975, **48**, 2603.

presence of MeO groups on the phosphine aryl substituents enhances the activity of the catalyst significantly. Rate enhancement of the $[Ru(CO_2Me)_2(PPh_3)_2]$- and $[Rh(CO_2Me)_2(PPh_3)_3]$-catalysed hydrogenation of mono- and diolefins by toluene-*p*-sulphonic acid is attributed to dissociation of acetate as $MeCO_2H$, thus facilitating olefin co-ordination.[85]

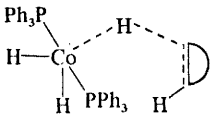
Kinetic data for the $[Co(H)_3(PPh_3)_3]$-catalysed hydrogenation of cyclohexene in benzene solution is most easily explained by mechanism of Scheme 12, in which the

$$\begin{array}{ccccccccc} AB_2 & \rightleftharpoons & AH_2 & \rightleftharpoons & AH_3B & \rightleftharpoons & AH_3S & \rightleftharpoons & AH_2R \longrightarrow AH + RH \\ \Downarrow & & & & \Downarrow & & & & \\ ABP & & & & AH_3P & & & & \end{array}$$

A = $Co(PPh_3)_2$; B = benzene; P = PPh_3; S = cyclohexane; R = cyclohexyl

Scheme 12

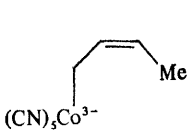
rate-determining step is assumed to be transfer of the first hydride ligand to a co-ordinated olefin *via* a transition state (49). Activation parameters are $\Delta H^{\ddagger} = 20 \pm 2$



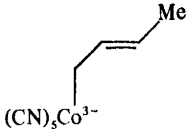
(49)

kcal mol^{-1} and $\Delta S^{\ddagger} = 0 \pm 5$ kcal mol^{-1}.[86] A kinetic isotope effect $k_H/k_D = 1.54$ is in accord with this.

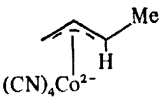
The $[Co(CN)_5]^{3-}$-catalysed hydrogenation of butadiene is thought to proceed *via* a butenyl cobalt complex the structure of which depends on the concentration of CN^-. At high values of $[CN^-]$ equal amounts of *cis*- and *trans*-forms (50) and (51) are present but on reduction of $[CN^-]$ the *syn*-π-complex (52) is favoured.[87] These results correlate with the observations that but-1-ene is the principal hydrogenated product at high values of $[CN^-]$ but at low values *trans*-but-2-ene is obtained preferentially. The mechanism of formation of $[Co(CN)_5(H)]^{3-}$, the precursor to butenyl complexes (50), (51), and (52), is the subject of computational studies.[88]



(50)



(51)



(52)

The complex $[Co\{P(OMe)_3\}_3(\eta\text{-}C_3H_5)]$ is one of the few homogeneous catalysts capable of promoting the hydrogenation of aromatic systems and in addition

[85] A. Spencer, *J. Organometallic Chem.*, 1975, **93**, 389.
[86] J. L. Henikse, J. H. Kaspersma, and J. W. E. Coenen, *Internat. J. Chem. Kinetics*, 1975, **7**, 557.
[87] H. J. Clase, A. J. Cleland, and M. J. Newlands, *J. Organometallic Chem.*, 1975, **93**, 231.
[88] K. Ohkuba, K. Tsuchihashi, H. Ikebe, and H. Sakamoto, *Bull. Chem. Soc. Japan*, 1975, **48**, 1114.

exhibits remarkable selectivity.[89,90] Benzene is hydrogenated to cyclohexane at a rate 3—4 times greater than that for cyclohexene and 1.3 times that for cyclohexadiene. This, in addition to the selective hydrogenation of C_6D_6 to all-*cis*-$C_6D_6H_6$, suggests that the arene ring rarely leaves the co-ordination sphere of cobalt during the hydrogenation. The catalysis is preceded by reaction of the complex with hydrogen to give $[Co(H)_2(\eta^1\text{-}C_3H_5)\{P(OMe)_3\}_3]$ which is then postulated to undergo phosphine dissociation to allow arene co-ordination and hydrogen transfer. The rhodium complex $[Rh\{P(OMe)_3\}_3(\eta\text{-}C_3H_5)]$ catalyses the hydrogenation of olefins but is inactive towards arenes.[91]

A reassessment of the experimental data concerning the catalytic hydrogenation of polyaromatic hydrocarbons by cobalt carbonyl under 'oxo' conditions has resulted in the postulate that the reaction involves free radicals rather than organocobalt complexes.[92]

Atactic poly(methallyl)alcohol reacts with $PClPh_2$ to give a polyphosphite P_n, and on treatment with $[Rh_2(Cl)_2(CO)_4]$ or $[Rh_2(Cl)_2(\text{norbornadiene})_2]$ polymer-bound catalysts are obtained which are active in the hydrogenation of a variety of olefins.[93] The species derived from the norbornadiene complex catalyses oct-1-ene hydrogenation at a rate dependent on catalyst concentration with solutions 0.125 mol l^{-1} in olefin and at a rate $\propto[\text{olefin}]^{1/2}$ up to a concentration of 0.3 mol l^{-1}. No attempt is made to rationalize these results in mechanistic terms.

Kinetic and potentiometric studies have been made of the hydrogenation of maleic acid, hex-1-ene, styrene, phenylacetylene, hex-1-yne, and nitrobenzene in the presence of a catalyst prepared from a Pt—Sn chloro-complex and cyclo-octa-1,5-diene.[94]

7 Hydrogen Exchange

Two reviews of catalytic transfer hydrogenation have appeared.[95,96] The complex $[Ru(Cl)(H)(PPh_3)_3]$ not only functions as a useful hydrogenation catalyst as described in the previous section but also catalyses H_2–D_2 exchange in benzene solution.[97] The D_2–H_2 exchange follows the rate law

$$-d[D_2]/dt = k[D_2]^{1.5}[Ru]^{0.38}$$

at 297 K with an activation energy of 25.9 kJ mol^{-1}. The exchange is extremely rapid compared with D_2 exchange with the Ru bond of the catalyst which may be accounted for by the equilibria of Scheme 13. The rate law can be explained if the rate-determining step is uptake of H_2 by $[Ru(D)_2(PPh_3)_3]$ but in practice the observed rates are limited by the rate of hydrogen diffusion to the catalyst. The observation

[89] F. J. Hirsekorn, M. C. Rakowski, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1975, **97**, 238.
[90] E. L. Muetterties, M. C. Rakowski, F. J. Hirsekorn, W. D. Larson, V. J. Basas, and F. A. L. Anet, *J. Amer. Chem. Soc.*, 1975, **97**, 1266.
[91] M. Bottrill and M. Green, *J. Organometallic Chem.*, 1976, **111**, C6.
[92] H. M. Feder and J. Halpern, *J. Amer. Chem. Soc.*, 1975, **97**, 7186.
[93] W. R. Cullen, D. J. Patmore, A. J. Chapman, and A. D. Jenkins, *J. Organometallic Chem.* 1975, **102**, C12.
[94] Ya. A. Dorfman and L. V. Lyaschchenko, *Izvest. Akad. Nauk Kazakh. S.S.R., Ser. khim.*, 1976, **26**, 84 (*Chem. Abs.*, 1976, **84**, 141148).
[95] G. Brieger and T. J. Nestrick, *Chem. Rev.*, 1974, **74**, 567.
[96] I. S. Kolomnikev, V. P. Kukolev, and M. E. Vol'pin, *Russ. Chem. Rev.*, 1974, **43**, 399.
[97] G. Strathdee and R. Given, *Canad. J. Chem.*, 1975, **53**, 106.

$$[Ru(Cl)(H)(PPh_3)_3] + D_2 \rightleftharpoons [Ru(D)_2(PPh_3)_3] + HCl$$

$$[Ru(D)_2(PPh_3)_3] + H_2 \rightleftharpoons [Ru(H)_2(D)_2(PPh_3)_3]$$

$$\Big\downarrow\Big\uparrow$$

$$[Ru(H)(D)(PPh_3)_3] + HD$$

$$[Ru(D)_2(PPh_3)_3] + N_2 \rightleftharpoons [Ru(D)_2(N_2)(PPh_3)_3]$$

Scheme 13

that the Ru—H bond is not directly involved in the catalysis leads to the conclusion that the active species in $[Ru(Cl)(H)(PPh_3)_3]$- (and presumably $[Ru(Cl)_2(PPh_3)_3]$-) catalysed olefin hydrogenation reactions is not the chloro-hydride complex but more likely $[Ru(H)_4(PPh_3)_3]$. The related complex $[Ru(H)_2(PPh_3)_4]$ is an excellent catalyst for hydrogen transfer from propan-2-ol to olefins as the rates in Table 1 show.[98]

Table 1 *Rates of hydrogen transfer from propan-2-ol to olefins*[98]

Olefin	*Rate* $\times 10^4$/l mol^{-1} min^{-1}	*Product*
Cyclopentene	3.1	Cyclopentane
Cyclohexene	4.0	Cyclohexane
Cycloheptene	3.5	Cycloheptane
Cyclo-octene	3.4	Cyclo-octane
Norbornadiene	0.5	Norbornene

The rates are solvent-dependent and for cyclohexene in toluene at 80 °C the rate law shown in equation (4) is obeyed. The zero-order dependence on olefin is ascribed to

$$\text{Rate} = \frac{0.04\,[\text{catalyst}][\text{propan-2-ol}]}{1+24[PPh_3]} \qquad (4)$$

the fact that olefin co-ordination to the catalyst occurs after the rate-determining step, which from an isotope effect $R_H/R_D = 2.7$ is assumed to be hydrogen transfer from co-ordinated alcohol to ruthenium to give acetone. The active species is thought to be a Ru^0 complex (53) which can accept hydrogen by undergoing oxidative addition to Ru^{II} (see Scheme 14, step *a*). The reaction is initiated by hydrogen transfer

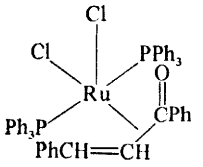
$$\begin{array}{ccc}
RuP_4L & & \\
\Big\downarrow\Big\uparrow -P & & \\
Ru(P)_3L & \overset{+D,\,-L}{\rightleftharpoons} & RuP_3D \\
(54) & & (53) \\
+L,\,-SH_2\Big\uparrow b & & \Big\downarrow\Big\uparrow a \\
RuH_2P_3S & \underset{+S,\,-A}{\rightleftharpoons} & RuH_2P_3A \\
 & & \Big\downarrow\Big\uparrow -A,\,+L \\
 & & RuH_2P_3L
\end{array}$$

P = PPh_3; S = olefin; D = propan-2-ol; A = acetone; L = solvent, PPh_3, or propan-2-ol

Scheme 14

[98] H. Imai, T. Nishiguchi, M. Kabayashi, and K. Fukuzumi, *Bull. Chem. Soc. Japan*, 1975, **48**, 1585.

from Ru to a co-ordinated olefin, step *b*, giving a zerovalent ruthenium complex (54). This mechanism is related to those proposed for hydrogen transfer from indoline to cycloheptene in the presence of $[Rh(Cl)(PPh_3)_3]$[99] and from alcohols to aldehydes catalysed by $[Ru(H)_2(PPh_3)_4]$.[100] However, the isotope effect measured in the latter reaction, $R_H/R_D = 0.9$, and other data suggest that the rate-determining step is alcohol co-ordination rather than hydrogen transfer. It is proposed that the mechanism of hydrogen transfer differs from established routes in that oxidative addition of the O—H bond of the alcohol to Ru occurs, generating a monohydride alkoxide complex. The hydride ligand then transfers to the carbonyl carbon of a co-ordinated aldehyde. Kinetic studies of the transfer hydrogenation of benzilideneacetophenone by 1-phenylethanol in the presence of $[Ru(Cl)_2(PPh_3)_3]$ give results in accord with a contrasting mechanism involving preliminary phosphine dissociation followed by ketone co-ordination.[101] The resulting complex (55) reacts with the alcohol to give the alkoxide derivative (56) and in the rate-determining step the β-hydrogen atom of



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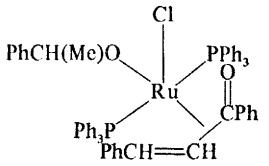


(56)

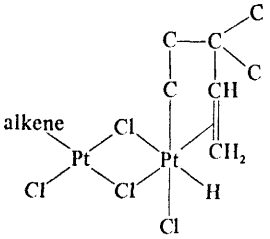
the alkoxide ligand is transferred directly to the β-carbon of the ketone in a concerted reaction. The stereochemistry of this step was established by deuterium labelling and contrasts with the hydride transfer mechanism of ref. 100.

The $[Rh(Cl)(PPh_3)_3]$-catalysed hydrogenation of the cyclo-olefins in Table 1 by dioxan gives the corresponding saturated hydrocarbon and dioxen stoicheiometrically.[102] Isolation of an intermediate $[Rh(Cl)(PPh_3)_2(dioxan)]$ indicates that dioxan co-ordination is the first step in the reaction while kinetic data including a kinetic isotope effect $R_H/R_D = 3.1$ show that the rate-determining step is dehydrogenation, *i.e.* formation of the monohydride complex $[Rh(Cl)(H)(C_4H_7O_2)(PPh_3)_2]$ by oxidative addition of dioxan involving cleavage of a C—H bond. The results of an independent study of these reactions differ considerably in several details although there is agreement that the transfer-hydrogenation reaction is first-order in dioxan.[103] The 'intermediate complex' is thought to be merely $[Rh_2(Cl)_2(PPh_3)_4]$ containing dioxan occluded in the crystal structure. Although concluding that oxidative-addition of a C—H bond of dioxan is the rate-determining step there is also disagreement with the proposal that the following step necessarily involves formation of a dihydro-complex $[Rh(Cl)(H)_2(PPh_3)_2]$ or $[Rh(Cl)(H_2)(PPh_3)_2S]$ (S = solvent). The observation of an apparent first-order rate-dependence on olefin (for the particular case of cyclopentene) is explained in terms of competing reversible complex formation between the catalytic species and both cyclopentene and the product dioxen, *i.e.* dioxen inhibits the reaction.

[99] T. Nishiguchi, K. Tachi, and K. Fukuzumi, *J. Org. Chem.*, 1975, **40**, 240.
[100] H. Imai, T. Nishiguchi, and K. Fukuzumi, *J. Org. Chem.*, 1976, **41**, 665.
[101] Y. Sasson and J. Blum, *J. Org. Chem.*, 1975, **40**, 1887.
[102] T. Nishiguchi and K. Fukuzumi, *J. Amer. Chem. Soc.*, 1974, **96**, 1893.
[103] C. Masters, A. A. Kiffen, and J. P. Visser, *J. Amer. Chem. Soc.*, 1976, **98**, 1357.

Isotopic hydrogen exchange in both the side-chain and the aromatic ring of alkylbenzenes catalysed by $RhCl_3$ has several features in common with analogous reactions carried out in the presence of heterogeneous catalysts.[101] This has led to the conclusion that a similar type of mechanism operates, *i.e.* the terminal abstraction π-complex process.

Alkenes of the type $RC(Me)_2CH{=}CH_2$ (R = Et, Pr, or Bu) undergo regiospecific H—D exchange in $MeCO_2D$–D_2O solutions containing perchloric acid and a Pt^{II} catalyst.[105] The reactions obey first-order kinetics and with 3,3-dimethylpentene the activation energy for exchange is 72 ± 10 kJ mol^{-1}. Evidence was obtained for a dimeric active catalyst and since deuteriation in the alkyl moiety occurs predominantly at C-5 an intermediate (57) or (58) is indicated. Since the main deuteriated species is $—CH_2D—$, H—D exchange must be not only a stepwise process but occur at a much lower rate than exchange between free and co-ordinated diene. Deuterium is incorporated regiospecifically into the phosphine R groups of $[Pt_2(Cl)_4(PR_3)_2]$ under similar conditions, *i.e.* $MeCO_2D$–D_2O solution, and a comparable mechanism involving metallation and formation of the intermediate (59) can be postulated.[106]



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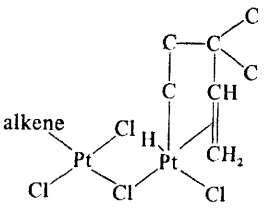

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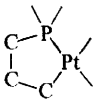


(59)

8 Homogeneous Oxidation

Several reviews published recently concerned with transition-metal-catalysed oxidations include sections on kinetics and mechanisms of such reactions.[107–109]

Kinetic studies of the oxidation of organic compounds catalysed by transition-metal derivatives are listed in Table 2, which is arranged in Periodic Table order of the metals.

Activation of molecular oxygen has often been proposed to explain the catalytic effect of certain transition-metal complexes in the oxidation of organic compounds, but in most cases critical examination has shown that the catalyst merely assists in the homolysis of hydroperoxides leading to the familiar radical-chain process. This mechanism is now proposed for the metal-phthalocyanine-catalysed autoxidation of cumene, originally considered to be an example of an oxygen activation reaction.[110] However, the controversy does not seem to be resolved as yet since a

[104] M. R. Blake, J. L. Garnett, I. K. Gregor, W. Hannan, K. Hoa, and M. A. Long, *J.C.S. Chem. Comm.*, 1975, 930.
[105] P. A. Kramer and C. Masters, *J.C.S. Dalton*, 1975, 849.
[106] A. A. Kiffen, C. Masters, and L. Raymond, *J.C.S. Dalton*, 1975, 853.
[107] A. V. Savitskii and V. I. Nelyubin, *Russ. Chem. Rev.*, 1975, **44**, 110.
[108] I. P. Skibida, *Russ. Chem. Rev.*, 1975, **44**, 789.
[109] D. J. Hucknall, 'Selective Oxidation of Hydrocarbons', Academic Press, London, 1974.
[110] W. J. M. von Tilborg and A. D. Vreugdenhil, *Tetrahedron*, 1975, **31**, 2825.

Table 2 *Transition-metal-catalysed oxidation of organic substrates*

Catalyst	*Substrate(s)*	*Product(s)*	*Ref.*
$Mo(CO)_6$, molybdenum–oxo-complexes	olefins	epoxides	*a*
$[Rh_2(Cl)_2(C_2H_4)_4]$	styrene	acetophenone + benzaldehyde	*b*
$[Rh(Cl)(PPh_3)_3]$	cyclohexenyl peroxide	cyclohex-2-ene-1-ol + cyclohex-2-ene-1-one	*c*
$[Ir(Cl)(CO)(PPh_3)_2]$	cyclohexene	cyclohex-2-ene-1-ol + epoxide + hydroperoxide	*d*
Pd^{II}	$ArCH_2CH_2Ph$	$ArCH_2COPh$ + $ArCOCH_2Ph$	*e*
Pd^{II}	oct-1-ene	octan-2-one	*f*
Cu^{II}	ascorbic acid	dehydroascorbic acid	*g*, *h*

[a] J. Sobczak and J. J. Ziolkowski, *Inorg. Chim. Acta*, 1976, **19**, 15. [b] J. Farrar, D. Holland, and D. J. Milner, *J.C.S. Dalton*, 1975, 815. [c] H. Arzoumanian, A. A. Blanc, J. Metzger, and J. E. Vincent, *J. Organometallic Chem.*, 1974, **82**, 261. [d] W. Strohmeier and E. Eder, *J. Organometallic Chem.*, 1975, **94**, C14. [e] F. R. S. Clark, R. O. C. Norman, and C. B. Thomas, *J.C.S. Perkin I*, 1975, 1230. [f] J. S. Coe and J. B. Unsworth, *J.C.S. Dalton*, 1975, 645. [g] R. F. Jameson and N. J. Blackburn, *J. Inorg. Nuclear Chem.*, 1975, **37**, 809. [h] R. F. Jameson and N. J. Blackburn, *J.C.S. Dalton*, 1976, 534.

metal-polyphthalocyanine complex, which has no effect on the decomposition of cumene hydroperoxide, has been found to catalyse cumene and acrolein oxidation, probably *via* a dioxygen complex.[111]

Radical-chain processes have not been detected in the $[Rh(Cl)(PPh_3)_3]$- and $[Rh(H)(CO)(PPh_3)_2]$-catalysed oxidation of hex-1-ene, hept-1-ene, and oct-1-ene to the corresponding methyl ketones and evidence is presented for an oxygen activation mechanism in which dioxygen rhodium complexes play a significant part.[112] Dioxygen complexes also catalyse the oxidation of α-methylstyrene and cyclohexene.[113] The reaction involving the styrene proceeds by an addition mechanism to give polyperoxide while a hydrogen abstraction mechanism gives a hydroperoxide in the case of cyclohexene. An attempt is also made to correlate the reactivity of the catalysts with the length of the oxygen–oxygen bond but failure to do so is not surprising in view of the recent realization of inaccuracies in reported O—O distances of certain dioxygen complexes.[114]

9 Exchange Reactions

Kinetic studies of the Pd^{II}-catalysed exchange of VP (vinyl propionate) with acetic acid solvent to give vinyl acetate in the presence of sodium acetate are complicated by equilibria between three Pd^{II} species (Scheme 15).[115] The dimer is significantly more

$$2Pd_3(OAc)_6 + 6NaOAc \rightleftharpoons 3Na_2Pd_2(OAc)_6$$

$$Na_2Pd_2(OAc)_6 + 2NaOAc \rightleftharpoons 2Na_2Pd(OAc)_4$$

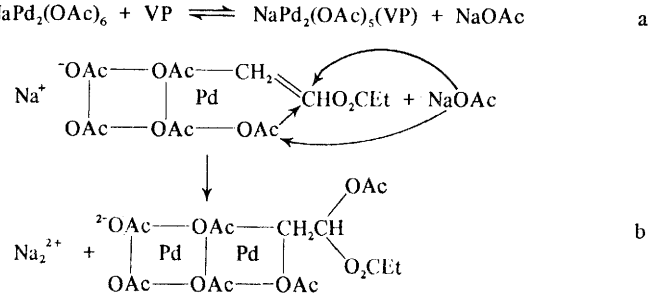
Scheme 15

[111] T. Hara, Y. Ohkatsu, and T. Osa, *Bull. Chem. Soc. Japan*, 1975, **48**, 85.
[112] C. W. Dudley, G. Read, and P. J. C. Walker, *J.C.S. Dalton*, 1974, 1927.
[113] S. Muto and Y. Kamiya, *J. Catalysis*, 1976, **41**, 148.
[114] M. J. Nolte, E. Singleton, and M. Laing, *J. Amer. Chem. Soc.*, 1975, **97**, 6396.
[115] R. N. Pandey and P. M. Henry, *Canad. J. Chem.*, 1975, **53**, 2223 and refs. cited therein.

reactive than the trimer while the monomer which is formed at high concentrations of sodium acetate shows no catalytic activity. The exchange rate is sensitive to NaOAc concentration with a maximum at 0.2 M, but the rate equation,

$$\text{Rate} = (k_0 + k_t[Pd_3(OAc)_6] + k_d[Na_2Pd_2(OAc)_6])[CH_2{=}CHCO_2Et]$$

does not contain a term in NaOAc, possibly because of cancellation of an inhibitory term for π-complex formation (Scheme 16a) by a catalytic term in [NaOAc] in the rate-determining conversion of a π-complex into a σ-complex (Scheme 16b). In the



Scheme 16

second step, (b), acetoxypalladation can occur from either within or outwith the co-ordination sphere which explains the observed non-stereospecificity of the exchange reaction. Steps (a) and (b) correspond to the k_d term in the rate equation but unfortunately the significance of the k_t and k_0 terms is less well understood.

The conversion of acetylene or monosubstituted acetylenes into aryl- and vinyl-substituted acetylenes by reaction with aryl and vinyl halides,

$$NaOMe + R^1C{\equiv}CH + R^2X \longrightarrow R^1C{\equiv}CR^2 + NaX + MeOH$$

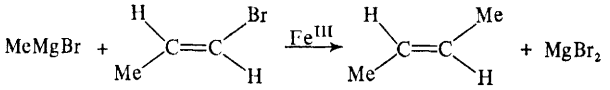
can be accomplished in the presence of zerovalent Ni and Pd triarylphosphine complexes and a base such as NaOMe or NaOPh.[116] The rates of exchange are influenced by the substituents on the aryl group and the leaving halide in a manner similar to that found for oxidative addition of $[Pd(PPh_3)_4]$ to aryl halides, suggesting that such a process may be the first step in the reaction. Reaction of the intermediate $[Pd(X)(Ar)(PPh_3)_2]$ with acetylide anion produced by the reaction

$$RC{\equiv}CH + NaOMe \longrightarrow RC{\equiv}C^-\,Na^+ + MeOH$$

will ultimately give the observed products. The situation is more complicated in the nickel-catalysed displacement of halide from aryl halides by primary and secondary amines and the intermediacy of aryl nickel species is open to doubt even though evidence for their existence during the reaction was found.[117] The amination reactions exhibit first-order kinetics and are inhibited by aryl halide also with a first-order rate-dependence. Dramatic inhibition by nitroaromatics, copper, or iron salts was also observed which suggests that electron transfer to the aromatic ring may be important and a tentative suggestion is made that Ni^I species are the active catalysts.

[116] L. Cassar, *J. Organometallic Chem.*, 1975, **93**, 253.
[117] R. Cramer and D. R. Coulson, *J. Org. Chem.*, 1975, **40**, 2267.

The iron(III)-catalysed cross-coupling of MeMgBr with 1-bromopropene (Scheme 17) has been found to proceed stereospecifically. The reaction rate is virtually



Scheme 17

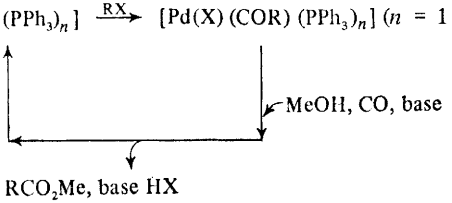
independent of MeMgBr concentration but is roughly first-order in alkenyl bromide and iron catalyst. The instability of the active catalytic species precluded detailed mechanistic studies but an iron(I) derivative produced by Grignard reduction of iron(III) may be a key intermediate.[118]

10 Carbonylation, Hydroformylation, and Hydration

A brief review concerned with technical aspects of the industrially important 'oxo' reaction has appeared.[119] Palladium complexes $[Pd(CO)(PPh_3)_3]$, $[Pd_3(CO)_3(PPh_3)_4]$, $[Pd_3(CO)_3(PPh_3)_3]$, and $[Pd(Cl)_2(PPh_3)_2]$ are catalysts for the carbomethoxylation of organic halides in the presence of methanol and a base.[120] Since $[Pd^I(COPh)(PPh_3)(L)]$ ($L = PPh_3$ or toluene), which is obtained from the reaction of these complexes

$$RX \xrightarrow{Pd\text{–}CO\text{–}MeOH\text{–}Et_2NH} RCO_2Me + Et_2NHHX$$

with PhI, gives the same product (methyl benzoate) as the catalytic reactions it probably functions as an intermediate as illustrated in the proposed mechanism (Scheme 18). The purpose of the base is to enhance attack of methoxide ion on the



Scheme 18

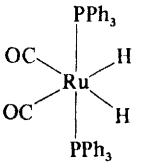
Pd—COPh moiety rather than to neutralize the acidity generated during the reaction. A similar sequence is proposed to explain the rhodium-catalysed carbonylation of methanol to acetic acid.[121] Full details of the carbonylation of *cis*- and *trans*-but-2-ene in methanol with a Pd^{II}–Cu^{II} Wacker-type catalyst have now appeared;[122] the stereospecificity of the resulting methoxypalladation (*trans*) was found to be similar to that involving chelating di-olefins which until now has been considered anomalous.[123]

Alkyl and acyl cobalt carbonyls $[Co(R)(CO)_4]$ and $[Co(COR)(CO)_4]$, which are

[118] S. M. Neumann and J. K. Kochi, *J. Org. Chem.*, 1975, **40**, 599.
[119] J. Falbe, *J. Organometallic Chem.*, 1975, **94**, 213.
[120] M. Hidai, T. Hikita, Y. Wada, Y. Fujikura, and Y. Uchida, *Bull. Chem. Soc. Japan*, 1975, **48**, 2075.
[121] D. Foster, *J. Amer. Chem. Soc.*, 1976, **98**, 846.
[122] D. E. James, L. F. Hines, and J. K. Stille, *J. Amer. Chem. Soc.*, 1976, **98**, 1806.
[123] J. K. Stille and D. E. James, *J. Organometallic Chem.*, 1976, **108**, 401.

thought to be intermediates in the 'oxo' reaction, undergo isomerization in solution and this has been considered as an explanation for the production of isomeric aldehydes in the 'oxo' reaction. However, the recent demonstration that normal and secondary alkyl and acyl cobalt carbonyls do not undergo isomerization under 'oxo' conditions indicates that the step responsible for the formation of the isomeric aldehydes must precede the formation of alkyl or acyl cobalt intermediates.[124,125] The results of i.r. spectroscopic studies of the hydroformylation of various olefins in the presence of $[Co_2(CO)_8]$ and $[Co_2(CO)_8]$–PBu^t_3 as catalyst precursors are generally consistent with present views on the reaction mechanism.[126] However, only with reactions involving terminal olefins and $[Co_2(CO)_8]$ as catalyst where the rates are relatively high is the hydrogenolysis of the acyl species $[Co(COR)(CO)_4]$ found to be rate-determining. In slower reactions, *e.g.* involving hydroformylation of internal olefins or $[Co_2(CO)_8]$–PBu^t_3-catalysed systems, olefin attack on the intermediate hydride $[Co(H)(CO)_3(L)]$ (L = CO or PBu^t_3) determines the rate of reaction. These conclusions find support in the results of earlier kinetic experiments.

The rate-determining step in the $[Ru(CO)_3(PPh_3)_2]$-catalysed hydroformylation of olefins is probably oxidative addition of hydrogen to give (60) since the reaction is



(60)

facilitated by high pressures of H_2 and is also inhibited by carbon monoxide.[127] The proposed mechanism is similar to that of cobalt- and rhodium-catalysed olefin hydroformylation reactions. The initial rates of hydroformylation of hept-1-ene and cyclohexene at 75 °C with $[Rh_4(CO)_{12}]$ as catalyst exhibit a zero-order and first-order dependence respectively on the olefin concentration. The hydroformylation is also promoted by $[Rh_6(CO)_{16}]$ since this can also function as a source of $[Rh(H)(CO)_3]$ which is considered to be the active catalyst.[128]

The chirality of aldehydes resulting from rhodium-(−)-(diop)-catalysed hydroformylation of olefins is different from those obtained from Pt^{II}–$SnCl_2$–(−)-diop catalyses. Since asymmetric induction has been shown to occur before CO insertion with the rhodium catalyst it is suggested that with platinum it takes place after alkyl–platinum complex formation.[129]

Raman spectroscopy has been used to study the Hg^{II}-catalysed hydrolysis of acetonitrile since MeCN co-ordinated to Hg^{2+} has two distinct lines at 2275 and 2305 cm^{-1}.[130] The intensities of these decrease according to a second-order rate law,

[124] F. Piacenti, M. Bianchi, G. Bimbi, P. Frediani, and U. Matteoli, *Coordination Chem. Rev.*, 1975, **16**, 9.
[125] F. Piacenti, M. Bianchi, P. Frediani, and U. Matteoli, *J. Organometallic Chem.*, 1975, **87**, C54.
[126] R. Whyman, *J. Organometallic Chem.*, 1974, **81**, 97.
[127] R. A. Sanchez-Delgado, J. S. Bradley, and G. Wilkinson, *J.C.S. Dalton*, 1976, 399.
[128] G. Csontos, B. Heil, and G. Bor, *Ann. New York Acad. Sci.*, 1974, 239 (*Chem. Abs.*, 1975, **82**, 97411).
[129] G. Consiglio and P. Pino, *Helv. Chim. Acta*, 1976, **59**, 642.
[130] Y. K. Sze and D. E. Irish, *Canad. J. Chem.*, 1975, **53**, 427.

Rate = k[MeCN][H_2O], and an activation energy of 18.9 kcal mol^{-1} was obtained for the hydrolysis. A mechanism is proposed whereby H_2O attacks co-ordinated MeCN to form an acetamide Hg^{II} complex $MeC(O)NH_2,Hg(MeCN)_n$ (detected spectroscopically), which is slowly hydrolysed further to give acetic acid and Hg^{II} ammine complexes.

11 Decarbonylation

The reaction between acyl halides and [Rh(Cl)(PPh_3)$_3$] follows the sequence shown in Scheme 19 and is stoicheiometric at low temperatures, but catalytic above 170 °C.[131]

$$RCOBr + [Rh(Cl)(PPh_3)_3] \longrightarrow [Rh(Br)(Cl)(COR)(PPh_3)_2]$$

$$[Rh(Br)(Cl)(R)(CO)(PPh_3)_2] \longrightarrow [Rh(Cl)(CO)(PPh_3)_2] + RBr$$

Scheme 19

Above *ca.* 210 °C the rhodium catalyst becomes deactivated rapidly and the optimum temperature range for the decarbonylation is 200—210 °C. The activation energy for the process is *ca.* 30 kcal mol^{-1}.

12 Hydrosilylation

Hydrosilylation studies by Hetflejs reported during the present period are listed in Table 3. Although kinetic data are not available the effects of changing (i) the ligands on the catalyst, (ii) the metal, (iii) the structure of the silane, and (iv) the solvent, on the mode of reaction allow some conclusions to be reached about possible mechanisms.

Table 3 *Catalytic hydrosilylation studies*

Catalyst	*Substrate*	*Ref.*
CoX_2–$NaAlH_2(OC_2H_4OMe)$	buta-1,3-diene	*a*
[Rh(X)(PPh_3)$_3$], [Rh(X)(CO)(PPh_3)$_3$], or [Rh(PPh_3)$_2$(η-C_3H_5)]	buta-1,3-diene	*b*
[Rh(Cl)(CO)(PPh_3)$_2$][Rh(H)(CO)(PPh_3)$_3$] or [Rh(X)(PPh_3)$_3$]	hex-1-ene	*c*
Ni^{II} / Ni^0	buta-1,3-diene	*d*, *e*
Ni^{II}/Na(2-methoxyethoxy)$_2AlH_2$	buta-1,3-diene	*f*
Pd^{II}	buta-1,3-diene	*g*, *h*

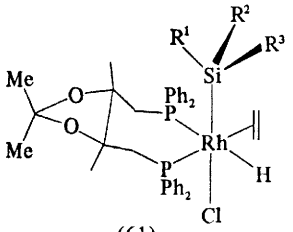
[a] M. Capka and J. Hetflejs, *Coll. Czech. Chem. Comm.*, 1976, **41**, 1024. [b] J. Rejhon and J. Hetflejs, *ibid.*, 1975, **40**, 3190. [c] J. Rejhon and J. Hetflejs, *ibid.*, p. 3680. [d] M. Capka and J. Hetflejs, *ibid.*, p. 3020. [e] M. Capka and J. Hetflejs, *ibid.*, p. 2073. [f] M. Capka and J. Hetflejs, *ibid.*, p. 3186. [g] J. Langova and J. Hetflejs, *ibid.*, p. 420. [h] J. Langova and J. Hetflejs, *ibid.*, p. 432.

The mode of hydrosilylation of $\alpha\beta$-unsaturated esters catalysed by [Rh(Cl)(PPh_3)$_3$] can be divided into three groups, (i) α-addition, (ii) β-addition and disilylation, and (iii) 1,2- and 1,4-addition.[132] A general feature of mechanisms proposed for hydrosilylation reactions is oxidative addition of the Si—H bond to the metal and in

[131] W. Strohmeier and P. Pfohler, *J. Organometallic Chem.*, 1976, **108**, 393.
[132] I. Ojima, M. Kumagai, and Y. Nagai, *J. Organometallic Chem.*, 1976, **111**, 43.

reactions of Et_3SiH with ketones catalysed by $[Rh(Cl)(PPh_3)_3]$ the intermediate $[Rh(H)(Cl)(SiEt_3)(PPh_3)_2]$ has been isolated.[133]

Asymmetric hydrosilylation can be accomplished (i) by $[RhCl(PPh_3)_3]$ if the organic substrate is optically active, *e.g.* (−)-menthane or (+)-camphor, or (ii) if chiral phosphine–rhodium catalysts are used.[134] In the particular case where the catalyst is a (diop)rhodium(I) derivative molecular models of intermediates based on oxidative addition of the silane to Rh, *e.g.* (61), can be used to predict the chirality of products



(61)

resulting from hydrosilylation (and hydrogenation) of olefin with a fair degree of certainty.[135] The rigidity of the dioxolan ring of the diop ligand apparently imposes steric restraints on the orientation of the diop phenyl groups in the intermediate, thus controlling the product stereochemistry.

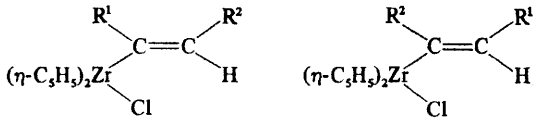
[133] I. Ojima, M. Nihonyanagi, T. Kogure, M. Kumagai, S. Horiuchi, and K. Nakatsugawa, *J. Organometallic Chem.*, 1975, **94**, 449.
[134] J. P. Corriu and J. J. E. Moreau, *J. Organometallic Chem.*, 1975, **91**, C27.
[135] R. Glaser, *Tetrahedron Letters*, 1975, 2127.

4
Insertion Reactions

BY J. L. DAVIDSON

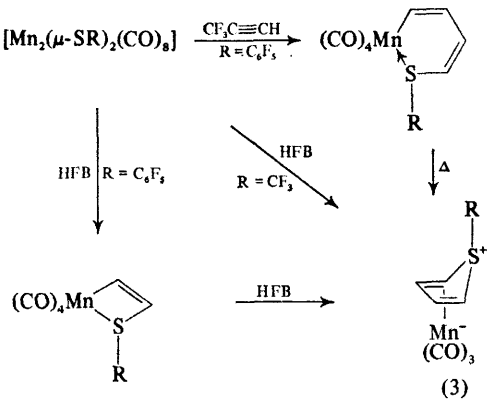
1 Alkenes and Alkynes

The insertion of disubstituted unsymmetrical acetylenes $R^1C{\equiv}CR^2$ into the Zr—H bond of $[Zr(Cl)(H)(\eta\text{-}C_5H_5)_2]$ gives mixtures of the two isomeric *cis*-vinylic products (1) and (2) in which the direction of the *cis* addition is dictated by the bulk of the substituents R^1 and R^2.[1] The initial mixture is catalytically converted after a few hours by excess hydride into one with higher regioselectivity, possibly *via* an intermediate dimetallated alkyl, $[(\eta\text{-}C_5H_5)_2Zr(Cl)CHR^1CHR^2(Cl)Zr(\eta\text{-}C_5H_5)_2]$.



(1) (2)

Insertion of fluorinated acetylenes into the Mn—S bonds of $[Mn_2(\mu\text{-}SR)_2(CO)_8]$ ($R = CF_3$ or C_6F_5) is stereospecific and follows Scheme 1.[2] The primary insertion



(3)

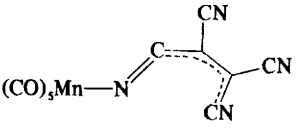
HFB = $CF_3C{\equiv}CCF_3$

(substituents H and CF_3 omitted for clarity)

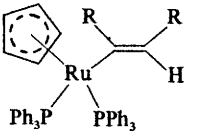
Scheme 1

[1] D. W. Hart, T. F. Blackburn, and J. Schwartz, *J. Amer. Chem. Soc.*, 1975, **97**, 679.
[2] J. L. Davidson and D. W. A. Sharp, *J.C.S. Dalton*, 1975, 2283.

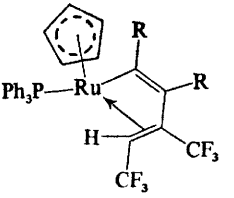
reactions give only *cis*-olefinic products, thus enabling further insertion or cyclization to give the zwitterionic heterocycle (3) without bond-breaking, which would be necessary with *trans*-olefinic products. Similar reactions are observed with $[Fe(SR)(CO)_2(\eta\text{-}C_5H_5)]$. Tetracyanoethylene reacts with alkyl-iron complexes $[Fe(R)(CO)(L)(\eta\text{-}C_5H_5)]$ [L = CO, PPh_3, $P(OPh)_3$, or PBu^n_3, R = Me or CH_2Ph] to give products of insertion of tcne or CO into the Fe—R bond.[3] A radical mechanism is considered possible for such reactions and this now seems probable in view of the independent report that $[Mn(CH_2Ph)(CO)_5]$ reacts with tcne to give the radical (4).[4] $[Ru(H)(PPh_3)_2(\eta\text{-}C_5H_5)]$ reacts with electrophilic acetylenes RC≡CR to give, initially, σ-vinyl complexes (5) (R = CF_3 or CO_2Me). Further reaction of $CF_3C{\equiv}CCF_3$ with (5; R = CO_2Me) gives a butadienyl derivative assigned structure (6) in which the fluorinated acetylene has apparently inserted into the C—H bond of the vinyl ligand; *X*-ray studies have now confirmed the postulated structure.[5] $[Ru(H)(CO)_2(\eta\text{-}C_5H_5)]$ reacts with $CF_3C{\equiv}CCF_3$ to give analogues of (5) and (6) but with the



(4)



(5)



(6)

alternative *trans* geometry of the $-CCF_3{=}CHCF_3$ moiety which emphasizes the importance of ancillary ligands in deciding the stereochemical course of insertion reactions.[6] The insertion of dienes into M—H bonds (M = Rh or Ir) to give η-allyl complexes has been reviewed on p. 339. Communications describing *exo-cis*-insertion of norbornadiene into Ni—allyl bonds were reviewed in Volume 4, p. 424, and have now been superseded by full publications.[7,8] The reactions can be compared with the insertion of norbornadiene into the Pd—allyl bond of $[Pd(hfac)(\eta\text{-}CH_2CClCH_2)]$ which follows a second-order rate law (Vol. 4, p. 333).

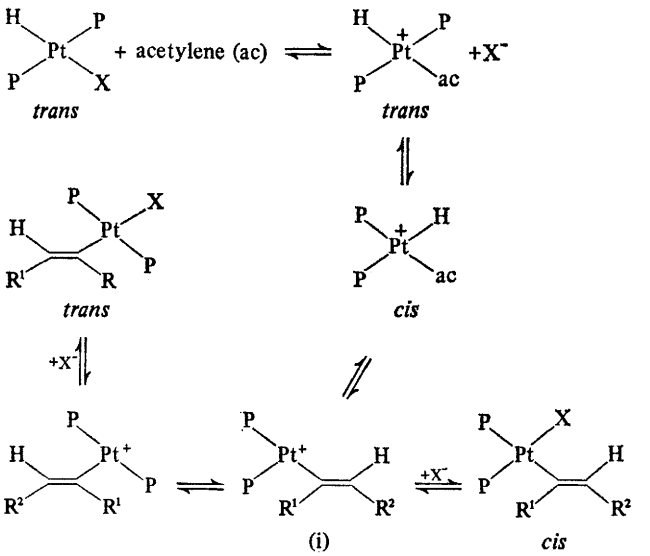
Insertion of olefins into the Pt—H bond of square-planar hydrides *trans*-$[(Pt(H)(X)(L)_2]$ was originally assumed to involve olefin co-ordination to give a five-co-ordinate intermediate which underwent migratory rearrangement to the alkyl *trans*-$[Pt(R)(X)(L)_2]$. Recent MO calculations of the insertion reaction between ethylene and $[Pt(H)(Cl)(PH_3)_2]$ suggest that collapse of the five-co-ordinate intermediate is

[3] S. R. Su and A. Wojcicki, *Inorg. Chem.*, 1975, **14**, 89.
[4] P. J. Krusic, H. Stoklosa, L. E. Manzer, and D. Meakin, *J. Amer. Chem. Soc.*, 1975, **97**, 667.
[5] L. E. Smart, *J.C.S. Dalton*, 1976, 390.
[6] J. L. Davidson, M. Green, F. G. A. Stone, and A. J. Welch, *J.C.S. Chem. Comm.*, 1975, 286.
[7] M. C. Gallazi, L. Porri, and G. Vitulli, *J. Organometallic Chem.*, 1975, **97**, 131.
[8] M. Zocchi and G. Tieghi, *J.C.S. Dalton*, 1975, 1740.

initiated by alkene migration to the hydrogen[9] but independent calculations[10] show that a lower-energy process is realized by hydrogen migration to the alkene with concomitant movement of Cl to the *trans* position. The situation is more complex in practice since, if the ligand X *trans* to hydride is weakly co-ordinating, the incoming olefin can displace this species to give a four-co-ordinate intermediate $[Pt(H)(olefin)(L)_2]^+$ prior to the insertion step. However, it has now been demonstrated that during the insertion of ethylene and PhC_2Me into the Pt—H bond of *trans*-$[Pt(H)(CO)(PEt_3)_2]^+$ the *trans* ligand CO does not leave the co-ordination sphere.[11] It is apparent that the mechanism of insertion depends on the nature of the *trans* ligand present in the complexes. It was therefore suggested that a five-co-ordinate intermediate is formed initially which has a stability dependent on the nature of the other ligands. This can undergo direct insertion or Pt—X cleavage to give the four-co-ordinate species $[Pt(H)(olefin)P_2]^+$ if X is not bound strongly. The insertion reaction

trans-$[Pt(H)(X)(PEt_3)_2]$ + $R^1C{\equiv}CR^2$ ⟶ *trans*- or *cis*-$[Pt(X)(CR^1{=}CR^2H)(PEt_3)_2]$

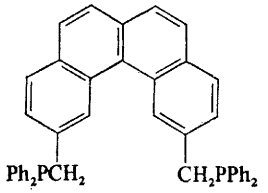
where X = Cl, NO_3, or solvent, probably goes *via* the latter mechanism and the stereochemical implications of this have been investigated by Clark.[12] The formation of a *cis*-isomer is favoured by (*a*) electron-withdrawing substituents on the acetylene, (*b*) use of co-ordinating solvents for cationic complexes (X = solvent) and non-polar solvents when X = Cl or NO_3, and (*c*) the presence of strongly co-ordinating anions X^-. Previously it was suggested that, prior to insertion, the four-co-ordinate species *trans*-$[Pt(H)(R^1C_2R^2)P_2]^+$ rearranges to the *cis*-isomer. This accounts for the observation that *trans*-hydrides sometimes yield *cis*-insertion products. The mechanism of Scheme 2 takes this into account and explains why *cis*- or *trans*-products are obtained



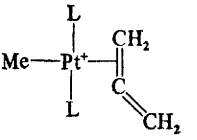
Scheme 2

[9] D. R. Armstrong, R. Fortune, and P. G. Perkins, *J. Catalysis*, 1976, **41**, 51.
[10] S. Sakaki, H. Kato, H. Kanai, and K. Tarama, *Bull. Chem. Soc. Japan*, 1975, **48**, 813.
[11] H. C. Clark, C. R. Jablonski, and C. S. Wong, *Inorg. Chem.*, 1975, **14**, 1332.
[12] H. C. Clark and C. S. Wong, *J. Organometallic Chem.*, 1975, **92**, C31.

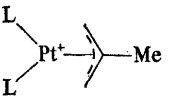
since this will depend on the relative rates of the isomerization of (i) and its recombination with X. These are obviously dependent on the properties of the solvent and the identity of X, R^1, and R^2; *e.g.* electronegative substituents R^1 will increase the rate of nucleophilic attack by X on (i), thus favouring the *cis*-product, and this correlates with experimental observations. Recently the insertion of ethylene into the Pt—H bond of *trans*-[Pt(H)(acetone)(LL′)]$^+$ has been demonstrated.[13] Since the bidentate ligand LL′ (7) cannot form *cis*-complexes owing to severe overlap of the phenyl groups the insertion mechanism involving a *cis*-intermediate must be excluded for this reaction. Kinetic studies of the insertion of co-ordinated allene into the Pt—methyl bond of (8) to give η-allylplatinum complexes (9) have been carried out.[14] The



(7)



(8)



(9)

reaction is first-order in [Pt(Me)(L)$_2$(η-C_3H_4)]Z (L = PMe_2Ph), and according to activation parameters in Table 1 the size of the anion Z^- is important. However,

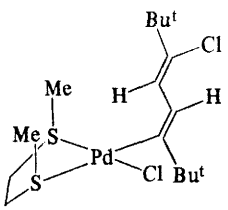
Table 1 *Thermodynamic data for the reaction* [Pt(Me)(L)$_2$(η-C_3H_4)]Z → [Pt(L)$_2$(η-2-MeC_3H_4)]Z (*from ref.* 14)

Z^-	E_a/kcal mol^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$ (298 °C)/ cal K^{-1} mol^{-1}	$\Delta G^{\ddagger}$/kcal mol^{-1}
$[SbF_6]^-$	29.6±1.4	24.0±1.4	4.6±1.8	27.7±1.7
$[PF_6]^-$	19.3±1.2	18.7±1.2	−5.6±1.0	20.3±1.5
$[BF_4]^-$	27.5±1.2	26.9±1.2	3.0±1.1	26.0±1.6

addition of Z^- in the form of *cis*-[Pt(PMe_2Ph)$_2$(η-C_4H_7)]Z has no effect on the rate of insertion and direct participation by Z^- in a five-co-ordinate transition state is unlikely, particularly in view of the almost zero entropies of activation. No definitive evidence is available which enables a conclusion to be reached about the nature of the transition state but a distorted square-planar geometry is possible.

In the reaction of t-butylacetylene with [Pd(Cl)$_2$($PhCN$)$_2$] the acetylene is consumed according to a first-order rate law up to the point where three equivalents of acetylene per Pd is reached after which the rate decreases by a factor of ten.[15] Addition of 2,5-dithiahexane at the three-equivalents point gives complex (10) which has the structure illustrated, according to *X*-ray studies. This indicates that the first stage in the reaction, *cis* insertion into the Pd—Cl bond, is followed by a second *cis* insertion to give the σ-butadienyl ligand. Since three moles of acetylene are consumed at the point where the dithiahexane is added, complex (11) is considered to be the precursor of (10).

[13] G. Bracher, P. S. Pregosin, and L. M. Venanzi, *Angew. Chem. Internat. Edn.*, 1975, **8**, 563.
[14] M. H. Chisholm and W. S. Johns, *Inorg. Chem.*, 1975, **14**, 1189.
[15] B. E. Mann, P. M. Bailey, and P. M. Maitlis, *J. Amer. Chem. Soc.*, 1975, **97**, 1275.



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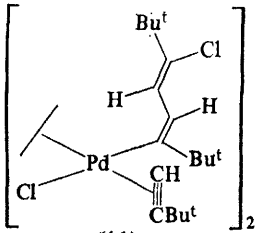
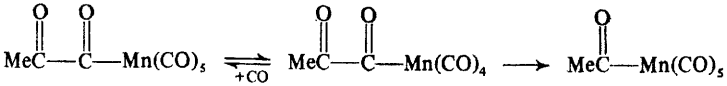


(11)

2 Carbon Monoxide

Insertion of carbon monoxide into the Zr—C σ-bond of [Zr(CHDCHDBu^t)(Cl)(η-C_5H_5)$_2$] to give the corresponding acyl complex proceeds with complete retention of configuration.[16]

Studies of the thermal decarbonylation of [Mn(COCOMe)(CO)$_5$] (12) were undertaken to explore the possibility that ligand substitution and decarbonylation reactions of [Mn(COMe)(CO)$_5$] might proceed *via* acetyl migration to give pyruvoyl species as unstable intermediates (see Scheme 3).[17] However, (12) undergoes decarbonylation



(12)

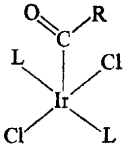
Scheme 3

twenty-one times more slowly than [Mn(COMe)(CO)$_5$] and this, in conjunction with evidence that CO dissociation is the first step in the decarbonylation of (12), provides evidence that such a mechanism is unlikely. The kinetic data obtained from the decarbonylation and substitution reactions of (12) enable the construction of a free-energy diagram for Scheme 3 from which ΔG for the formation of [Mn(COCOMe)-(CO)$_4$] from [Mn(COMe)(CO)$_5$] was calculated to be 7.2 kcal mol^{-1} higher than ΔG for formation of [Mn(COMe)(CO)$_4$]. This corresponds to a rate preference for decarbonylation of [Mn(COMe)(CO)$_5$] *via* [Mn(COMe)(CO)$_4$] of over 77 500, making acyl migration to give a pyruvoyl intermediate a highly unfavourable route. Decarbonylation and substitution reactions of *o*-methoxycarbonylbenzoyl(pentacarbonyl)manganese(I) also involve Mn—CO bond cleavage as the rate-determining step and are discussed in Chapter 1. Similarly decarbonylation of [Fe(^{13}COMe)(CO)$_2$-(η-C_5H_5)] photochemically or in a mass spectrometer follows the established route of CO dissociation followed by alkyl group migration to the metal.[18] The intermediate [Fe(^{13}COMe)(CO)$_2$(η-C_5H_5)] undergoes nucleophilic attack by triphenylphosphine to give [Fe(^{13}COMe)(CO)(PPh$_3$)(η-C_5H_5)] faster than methyl migration to give [Fe(Me)-(^{12}CO)(^{13}CO)(η-C_5H_5)]. This is also a feature of the decarbonylation reactions of the manganese complexes discussed above. Photochemical decarbonylation of (+)- and (−)-[Fe(COMe)(CO)(PPh$_3$)(η-1-Me-3-Ph-C_5H_3)] gives the corresponding methyl

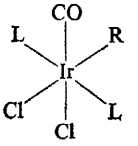
[16] J. A. Labinger, D. W. Hart, W. E. Seibert, and J. Schwarz, *J. Amer. Chem. Soc.*, 1975, **97**, 3851.
[17] C. P. Casey, C. A. Bunnel, and J. C. Calabrese, *J. Amer. Chem. Soc.*, 1976, **98**, 1166.
[18] J. J. Alexander, *J. Amer. Chem. Soc.*, 1975, **97**, 1729.

derivative with > 84% retention of inversion at the iron atom.[19] Prolonged irradiation reduces the stereospecificity or the reaction but solvent effects are negligible. The rate constant for the decarbonylation reaction is 2×10^{-4} s^{-1} while the epimerization of the methyl derivative (+)- or (−)-[Fe(Me)(CO)(PPh_3)(η-1-Me-3-Ph-C_5H_3)] has $k = 6 \times 10^{-4}$ s^{-1}.

Rate constants and activation parameters for the carbonyl migration reactions of fluoroacyl derivatives (13) to give six-co-ordinate fluoroalkyl complexes (14) are given in Table 2.[20] The rates decrease in the order $CFH_2 > CF_3 > CF_2H$, which does not



(13) L = PPh_3



(14)

Table 2 *Rate constants and activation parameters for the* CO *migration reaction of* $[Ir(Cl)_2(COR)(PPh_3)_2]$ *in toluene (from ref.* 20)

R	10^4k/s^{-1} (343 K)	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
CFH_2	15.88	85.5±1.4	−49.8±6
CF_2H	0.45	104.4±1.4	−24.7±2
CF_3	3.03	94.4±0.2	−38.1±1

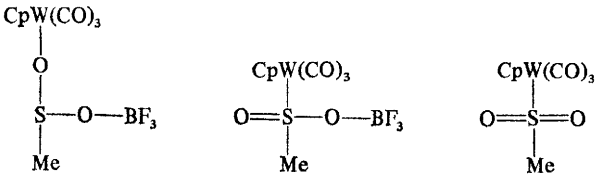
correlate with the expected trend in electronegativities. However, the observed trend is also reflected in the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values. The values of $\Delta H^{\ddagger}$ obtained, in conjunction with the enthalpy change measured by differential scanning calorimetry, enable an estimate to be made of the activation enthalpy for the insertion of co-ordinated CO into the Ir—R bond of (14), *i.e.* $\Delta H^{\ddagger}$ for (14)→(13). With R = CF_3, $\Delta H^{\ddagger} = 178 \pm 5$ kJ mol^{-1}, which suggests a slow reaction, although thermodynamically the reaction should be favourable. These results are of interest in view of the well known reluctance of perfluoroalkyl ligands to migrate on to co-ordinated carbon monoxide.

3 Sulphur Dioxide

Insertion of SO_2 into the Zr—C σ-bond of [Zr(CHDCHDBu^t)(Cl)(η-C_5H_5)$_2$] gives [Zr(SO_2CHDCHDBu^t)(Cl)(η-C_5H_5)$_2$] with retention of configuration at carbon[16] in contrast with the reaction of [Fe(CHDCHDPh)(Cl)(η-C_5H_5)] which proceeds with inversion.[21] This is an agreement with previous proposals that co-ordinatively unsaturated complexes can co-ordinate SO_2 prior to insertion by frontside attack on the metal–alkyl bond whereas backside attack frequently occurs with co-ordinatively saturated species. Insertion of SO_2 into metal–alkyl bonds is facilitated by the use of the Lewis acid adduct SO_2BF_3 which attacks M—R bonds inert to insertion with pure SO_2.[22] The reaction with [W(Me)(CO)$_3$(η-C_5H_5)] gives, initially, the *O*-bonded adduct

[19] T. G. Attig and A. Wojcicki, *J. Organometallic Chem.*, 1974, **82**, 397.
[20] D. M. Blake, A. Winkelman, and Y. L. Chung, *Inorg. Chem.*, 1975, **14**, 1326.
[21] D. Slack and M. C. Baird, unpublished results quoted in ref. 23.
[22] R. G. Severson and A. Wojcicki, *Inorg. Chim. Acta*, 1975, **14**, L7.

(15) which on precipitation isomerizes to the *S*-bonded complex (16) and this, on pumping *in vacuo*, gives the insertion product (17). *O*-Sulphinates have been detected

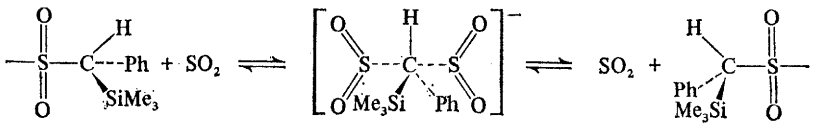


(15) (16) (17)

in previous reactions of pure SO_2 with metal alkyls but on removal of excess SO_2 rapid rearrangement to the *S*-sulphinate occurs. The enhanced stability in the presence of SO_2 may therefore be due to interaction of free SO_2 with the co-ordinated —O—S(O)R ligand in a manner similar to BF_3. SO_2 also reacts with (*RS,SR*)-[Fe(CHPhSiMe$_3$)(CO){P(OPh)$_3$}(η-C$_5$H$_5$)] (18) to give a mixture of the above compound and its thermodynamically less stable diasteroisomer (*RR,SS*)-[Fe(CHPhSiMe$_3$)(CO){P(OPh)$_3$}(η-C$_5$H$_5$)] (19), apparently *via* reversible insertion of SO_2 to give the unstable *S*-sulphinate (20) of the former.[23] This loses SO_2 to give a mixture of the above complexes according to the equilibrium

$$(18) + SO_2 \rightleftharpoons (20) \rightleftharpoons (21) \rightleftharpoons (19)$$

Thus, decomposition of (20) gives (18) alone in the solid state, but if isomerization to (21) [the sulphinate of (19)] is allowed to occur (in solution) loss of SO_2 gives a mixture of diastereoisomers (18) and (19). The interconversion of (20) and (21), which involves epimerization at one of the chiral centres, is proposed to proceed *via* ionization and an SO_2-assisted Walden-like inversion at the asymmetric carbon atom as shown in Scheme 4. This is consistent with the observed inability of SO_2 to epimerize (18) in non-polar solvents.



Scheme 4

4 Miscellaneous

Carbon Disulphide.—Kinetic data for the insertion reaction

$$trans\text{-}[Pt(H)_2\{P(C_6H_{11})_3\}_2] + CS_2 \longrightarrow trans\text{-}[Pt(H)(S_2CH)\{P(C_6H_{11})_3\}_2]$$

suggest initial formation of a five-co-ordinate intermediate which rearranges to the insertion product.[24] This mechanism was also considered in MO calculations of CS_2 insertion into the Pt—H bond of [Pt(H)(Cl)(PH$_3$)$_2$].[13] The former reaction follows the rate law $k_{obs} = k_2[CS_2]$, and the k_2 values obtained show little solvent dependence in heptane, benzene, or diethyl ether. However, no reaction occurs in the co-ordinating

[23] K. Stanley, D. Groves, and M. C. Baird, *J. Amer. Chem. Soc.*, 1975, **97**, 6599.
[24] M. Albinati, A. Musco, G. Carturan, and G. Strukul, *Inorg. Chim. Acta*, 1976, **18**, 219.

solvents THF and acetonitrile, observations which could be rationalized in terms of formation of stable 1:1 solvent–complex adducts which prevent CS_2 co-ordination.

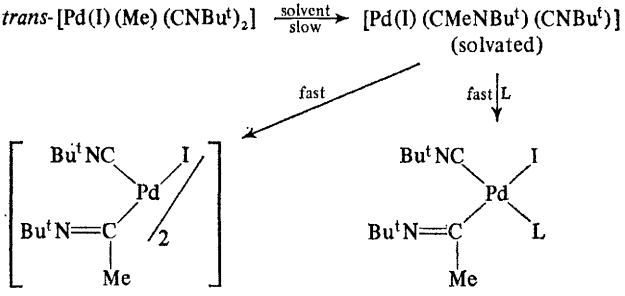
Carbon Dioxide.—CO_2 insertion into the metal–nitrogen bonds of dimethylamido-complexes $[M(NMe_2)_n]$ (M = Ti or Zr, $n = 4$; M = Nb or Ta, $n = 5$; M = W, $n = 3$ or 6) gives *NN*-dimethylcarbamato-complexes which undergo exchange reactions with isotopically labelled CO_2.[25] Activation energies for the exchange are 54 ± 8 kJ mol^{-1} (M = Zr) and 96 kJ mol^{-1} (M = W). Preliminary kinetic studies involving $[W(NMe_2)_3(O_2CNMe_2)_3]$ indicate that the exchange reaction is first-order in complex and zero-order in CO_2 and the de-insertion of CO_2 is considered to be the first step in the reaction, *i.e.*

$$M(O_2CNMe_2)_n \rightleftharpoons [M(O_2CNMe_2)_{n-1}(NMe_2)] + CO_2$$

Alternative mechanisms cannot, however, be excluded.

Oxygen.—Photochemically induced insertion of molecular oxygen into the Co—C σ-bond of optically active 2-butylpyridine cobaloxime occurs with complete racemization and the loss of optical activity can be attributed to a free-radical mechanism for which evidence has been obtained.[26] Re-investigation of the corresponding reaction of O_2 with 2-hydroxy-1-phenethylpyridine cobaloxime, which was originally reported to yield an optically active insertion product, also resulted in isolation of a racemic complex and the mechanistic details of these reactions at present remain obscure.

Isocyanides.—Insertion of a co-ordinated isocyanide ligand into the Pd—Me bond of $[Pd(Me)(I)(CNBu^t)_2]$ occurs on addition of nucleophiles L = $CNBu^t$, PPh_3, or $P(OPh)_3$ (Scheme 5), with a first-order rate dependence on the complex.[27] The rate is

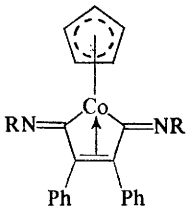


Scheme 5

independent of nucleophile but is significantly greater in polar aromatic solvents than in hexane. The first-order rate constants, 1.05×10^{-4}, 1.98×10^{-4}, and 3.51×10^{-4} s^{-1}, obtained at 0, 10, and 20 °C respectively, yield activation parameters $\Delta H^{\ddagger} = 9.4 \pm 0.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = -22 \pm 1$ cal K^{-1} mol^{-1}. The large negative entropy may reflect a solvent-assisted alkyl migration mechanism, particularly in view of the solvent effects noted. However, co-ordination of solvent is unlikely in view of the observed lack of dependence of the rate on the nucleophile and it is

[25] M. H. Chisholm and M. Extine, *J.C.S. Chem. Comm.*, 1975, 438.
[26] F. R. Jensen and R. C. Kiskis, *J. Amer. Chem. Soc.*, 1975, **97**, 5825.
[27] S. Otsuka and K. Ataka, *J.C.S. Dalton*, 1976, 327.

proposed that the role of the solvent is to assist in polarizing the Pd—halogen bond so as to increase the negative charge on the alkyl carbon and thus facilitate migration. Addition of isocyanides to $[Co(PPh_3)(PhC{\equiv}CPh)(\eta\text{-}C_5H_5)]$ results in a series of stepwise insertion reactions to give the cyclopentene (24) *via* the cobaltacyclopentenes (22) and (23).[28] The reaction is stoicheiometric rather than catalytic.



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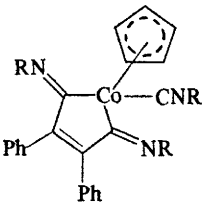

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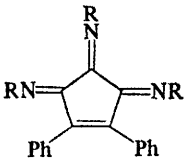


(24)

R = Ph, 4-MeC_6H_4, or 2,5-$Me_2C_6H_3$

Carbenes.—A communication describing kinetic data for the reactions of $[Cr(CO)_5\{C(OMe)Ph\}]$ with R_3MH (R = Si, Ge, or Sn) which lead to carbene insertion into the M—H bond was reported in Vol. 3, p. 428. Full details of these and other related reactions have now been published.[29,30]

Stannous Chloride.—The kinetics of the insertion of $SnCl_2$ into the M—M bond of $[Co_2(CO)_6\{P(OPh)_3\}_2]$ have been studied over the temperature range 35—55 °C in THF.[31] The activation enthalpy and entropy are 24.7 ± 0.4 kcal mol^{-1} and 2.4 ± 1.3 cal K^{-1} mol^{-1} respectively. The observed rate constants increase with increasing $SnCl_2$ concentration, which may be explained by considering that the mechanism is a two-step process, but no definite conclusions could be reached.

[28] H. Yamazaki, K. Aoki, Y. Yamamoto, and Y. Wakatsuki, *J. Amer. Chem. Soc.*, 1975, **97**, 3546.
[29] J. A. Connor, J. P. Day, and R. M. Turner, *J.C.S. Dalton*, 1976, 108.
[30] J. A. Connor, J. P. Day, and R. M. Turner, *J.C.S. Dalton*, 1976, 283.
[31] P. F. Barret, *Canad. J. Chem.*, 1974, **52**, 3773.

5
Reactions of Co-ordinated Ligands

BY J. L. DAVIDSON

1 Carbonyls and Nitrosyls

Carbonyls.—Substitution and exchange of the carbonyl groups in $[M(X)(CO)_5]$ (M = Mn or Re, X = halide) occurs preferentially at the *cis* position as described in Chapter 1 and a recent report indicates that this stereochemical selectivity also extends to incorporation of ^{18}O into $[M(CO)_5(L)]^+$ (M = Mn or Re, L = PMe_2Ph, MeCN, or py) on reaction with $H_2{}^{18}O$.[1] The importance of the degree of positive charge on the carbonyl carbon in reactions of carbonyls with strong nucleophiles has been commented on previously (see Volumes 3 and 4 of this Report) and this could be cited as the factor responsible for inducing attack by LiMe on the carbonyl rather than the acyl carbon of $[Mn(COPh)(CO)_5]$:[2]

$$[Mn(COPh)(CO)_5] \xrightarrow{LiMe} Li[\textit{cis}\text{-}Mn(COMe)(COPh)(CO)_4]$$

However, MO calculations suggest that nucleophilic attack is not charge-controlled although it is not possible to predict the site of attack since too many closely spaced empty energy levels are associated with both acyl and carbonyl carbons.[3] Similar calculations on $[Cr(CO)_5\{C(OMe)Me\}]$ indicate that the lowest unoccupied MO is localized on the carbene carbon and frontier orbital control predicts nucleophilic attack on the carbene carbon. The electron density on the sulphur atom of co-ordinated thiocarbonyl ligands, as indicated by ν(C=S), is considered to control the reactivity towards electrophiles and only those with C—S stretching modes above 1200 cm^{-1} have been found to react.[4]

Nitrosyls.—A review of the reactions of co-ordinated nitric oxide points out the fact that the reactivity depends on the mode of bonding of NO to a metal.[5] Thus linearly co-ordinated NO with ν(NO) greater than *ca.* 1850 cm^{-1} undergoes nucleophilic attack at the nitrosyl nitrogen atom whereas bent NO ligands are susceptible to electrophilic attack at nitrogen. Complexes $[Ir(Cl)(X)(CO)(NO)(PPh_3)_2]$ in which ν(NO) is *ca.* 1550 cm^{-1} undergo oxidation to nitrate complexes according to the equation

$$[Ir(Cl)(X)(CO)(NO)(PPh_3)_2] + O_2 \longrightarrow [Ir(Cl)(X)(CO)(PPh_3)_2(NO_3)]$$

and under pseudo-first-order conditions with dioxygen at a partial pressure of

[1] D. J. Darensbourg and D. Drew, *J. Amer. Chem. Soc.*, 1976, **98**, 275.
[2] C. P. Casey and C. A. Bunnel, *J. Amer. Chem. Soc.*, 1976, **98**, 436.
[3] T. F. Block, R. F. Fenske, and C. P. Casey, *J. Amer. Chem. Soc.*, 1976, **98**, 441.
[4] B. D. Dombeck and R. J. Angelici, *J. Amer. Chem. Soc.*, 1975, **78**, 1261.
[5] R. Eisenberg and C. D. Meyer, *Accounts Chem. Res.*, 1975, **8**, 26.

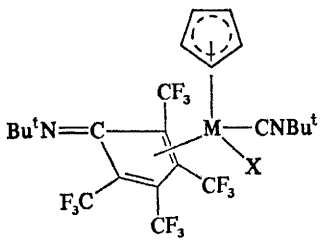
619 Torr the rates were found to decrease in the order X = I > Br > Cl > NCS > NCO > N_3 (see Table 1) which approximates to the order of electron-releasing power of X.[6] Oxygenation probably proceeds by electrophilic attack of dioxygen on the NO^- ligand to give the *N*-co-ordinated O—N—O—O ligand which subsequently rearranges to the nitrato-form.

Table 1 NO *stretching frequencies for* [Ir(Cl)(X)(CO)(NO)(PPh_3)$_2$] *and rate constants for reaction with dioxygen (from ref.* 6)

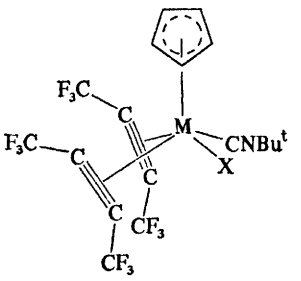
X	ν(NO)/cm^{-1}	$10^3 k_{obs}$/s^{-1}
I	1550	184.0
Br	1560, 1530	40.4
Cl	1560, 1520	8.25
NCS	1545	6.68
NCO	1540	3.42
N_3	1540	1.59

2 Alkenes and Alkynes

Linear Alkenes and Alkynes.—Addition of Bu^{t}NC to bishexafluorobut-2-yne complexes [M(X)($CF_3C_2CF_3$)$_2$(η-C_5H_5)] (M = Mo, X = CF_3; M = W, X = Cl) results in cyclization of the two acetylenes and Bu^{t}NC to give (1).[7] Under certain conditions the intermediate (2) can be isolated which illustrates that the cyclization reaction probably requires prior co-ordination of the isocyanide to the metal.



(1)

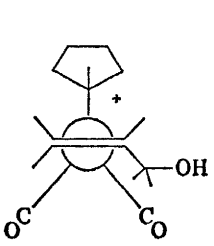


(2)

Deprotonation of cationic olefin complexes [Fe(CO)$_2$(olefin)(η-C_5H_5)]$^+$ gives η^1-allyl complexes with a stereochemistry which is accounted for by preferred abstraction of an allylic proton *trans* to the Fe—olefin bond.[8] The reverse reaction, protonation of the allyl complexes, is, however, non-stereospecific. Proton abstraction from the allyl alcohol derivative (3) by Et_3N gives the lactone (4) in only one diastereoisomeric form, probably as a result of the alcohol in (3) having a preference for the conformation illustrated. Addition of MeO^- to similar olefinic cations (5) proceeds with high regioselectivity while amines add similarly to give complexes of

[6] M. Kubota and D. A. Philips, *J. Amer. Chem. Soc.*, 1975, **47**, 5637.
[7] J. L. Davidson, M. Green, J. Z. Nyathi, F. G. A. Stone, and A. J. Welch, *J.C.S. Chem. Comm.*, 1975, 803.
[8] A. Cutler, D. Ehntholt, P. Lennon, K. M. Nicholas, D. F. Marten, M. Madhavarao, S. Raghu, A. Rosan, and M. Rosenblum, *J. Amer. Chem. Soc.*, 1975, **97**, 3149.

type (6) or (7) in contrast to the deprotonation reactions described above.[9] Phosphines also form 1:1 adducts with high regioselectivity but mixtures of isomers are



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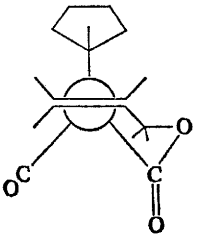

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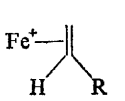
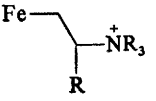


(5)



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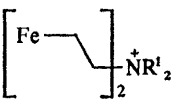
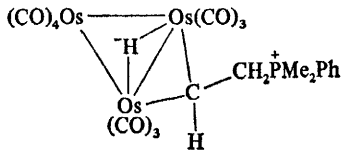
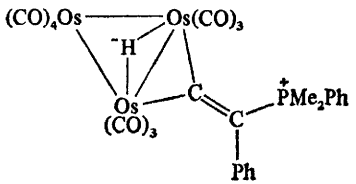


(7)

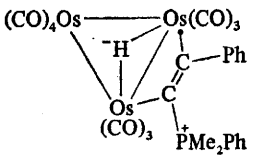
formed in reactions with t-butyl mercaptan. Steric factors are claimed to be responsible for the selectivity exhibited, but, since some reactions are reversible, thermodynamic rather than kinetic product control may be operating in some cases. The situation seems even less clear in reactions of cationic η^2-allene complexes $[Fe(CO)_2(\eta\text{-}CH_2{=}C{=}CHR)(\eta\text{-}C_5H_5)]^+$ with nucleophiles in which nucleophilic attack at C-1 or C-2 of the allene, deprotonation, or attack at a carbonyl can occur.[10] The site of nucleophilic attack by phosphines on $[Os_3(H)(CH{=}CH_2)(CO)_{10}]$ is one of the vinyl carbon atoms and results in reversible formation of a zwitterion (8) which is converted on further reaction with phosphine into $[Os_3(CO)_{10}(PMe_2Ph)_2]$ and ethylene.[11] The phenylacetylide analogue $[Os_3(H)(C{\equiv}CPh)(CO)_{10}]$ similarly adds PMe_2Ph to give a zwitterion with structure (9) or (10). Both types of bonding have



(8)



(9)



(10)

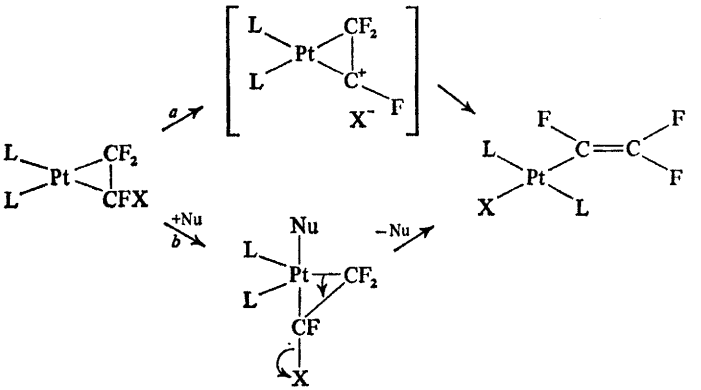
[9] P. Lennon, M. Madhavarao, A. Rosan, and M. Rosenblum, *J. Organometallic Chem.*, 1976, **108**, 93.

[10] D. W. Lichtenberg and A. Wojcicki, *J. Organometallic Chem.*, 1975, **94**, 311.

[11] A. J. Deeming and S. Hasso, *J. Organometallic Chem.*, 1976, **112**, C39.

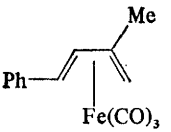
been reported recently in complexes resulting from nucleophilic attack of phosphines on co-ordinated acetylides.[12,13] Addition of HCl to *trans*-[Pt(C≡CH)$_2$(L)$_2$] (L = PMe_2Ph) gives *trans*-[Pt(Cl)(C≡CH)(L)$_2$] *via* intermediates *trans*-[Pt(C≡CH)-(CCl=CH_2)(L)$_2$], *trans*-[Pt(CCl=CH_2)$_2$(L)$_2$], and *trans*-[Pt(Cl)(CCl=CH_2)(L)$_2$].[14] A feature of the reaction is facile addition of HCl to the acetylide ligand and its ready elimination from the α-chlorovinyl ligand formed. Preliminary kinetic and labelling experiments support a mechanism in which platinum-vinyl carbonium ions Pt—$\overset{+}{C}$=CH_2 play a significant role.

The so called vinyl rearrangement (Scheme 1) may involve dissociation of X^- to give a tight ion pair followed by Pt—X bond formation and rearrangement (path *a*)



Scheme 1

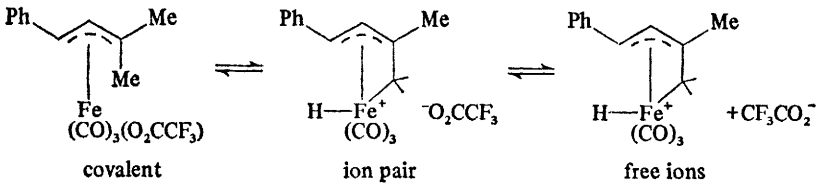
to the product (Vol. 4, p. 343). The reactions are sensitive to solvent and do not take place in benzene, but if nucleophiles (Nu) such as cyclo-octa-1,5-diene or ethylene are added ready conversion takes place. This has led to the suggestion that an alternative mechanism may be considered (path *b*) whereby preliminary co-ordination of a solvent (or nucleophile) molecule precedes C—X bond fission.[15] Solutions of 1-phenyl-3-methylbutadienetricarbonyliron (11) in trifluoroacetic acid have been



(11)

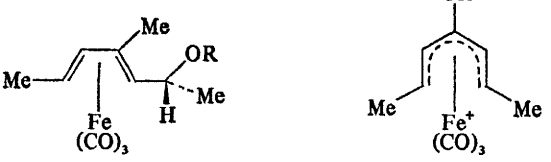
shown to contain at least three species in equilibrium (see Scheme 2), which confirms an earlier suggestion as to the nature of the species produced by protonation of (11).[16]

[12] Y. S. Yong, H. N. Paik, P. C. Chieh, and A. J. Carty, *J.C.S. Chem. Comm.*, 1975, 309.
[13] A. J. Carty, N. J. Taylor, H. N. Paik, W. Smith, Y. G. Yule, *J.C.S. Chem. Comm.*, 1976, 41.
[14] R. A. Bell and M. H. Chisholm, *J.C.S. Chem. Comm.*, 1976, 200.
[15] V. A. Mukhedkar, B. J. Kavathekar, and A. J. Mukhedkar, *J. Inorg. Nuclear Chem.*, 1975, **37** 483.
[16] T. H. Whitesides and R. W. Arhart, *Inorg. Chem.*, 1975, **14**, 209.

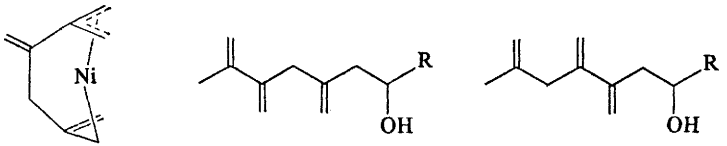


Scheme 2

Solvolysis of dienylester complexes generally proceeds stereospecifically to give dienyl alcohol complexes of the same configuration but the *ψ-endo*-ester (12) (R = 3,5-dinitrobenzoyl) gives a mixture of both *ψ-exo-* and *ψ-endo*-isomers whereas the *ψ-exo*-isomer of (12) undergoes the normal stereospecific hydrolysis to the *ψ-exo*-alcohol only.[17] An intermediate cation (13) is not involved in the hydrolysis of the



ψ-endo-isomer according to deuterium labelling experiments and non-stereospecific ionization is therefore assumed to be responsible for the lack of stereospecificity in the reaction. Reaction of the bisallylnickel complex (14) with acetaldehyde or acrolein followed by treatment with aqueous KCN affords two isomeric alcohols (15) and (16) (R = Me or CH=CH$_2$) in addition to other organic products.[18] It is apparent



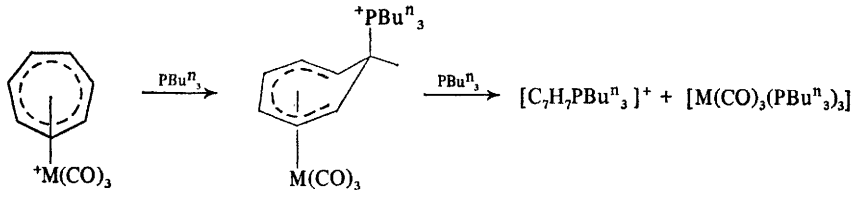
that reaction of the aldehyde occurs preferentially at the σ-allyl–nickel bond in contrast with reactions of nucleophilic reagents, *e.g.* amines or active methylene compounds, where reaction occurs predominantly at the π-allyl system.

Cyclic Alkenes.—A number of studies have established that tertiary phosphines react with polyolefin metal carbonyl complexes in a variety of ways: (i) by CO displacement, (ii) by displacement of the polyolefin, or (iii) by nucleophilic addition of phosphine to the ring system. The last reaction now appears to be the first step in some examples of type (ii), *e.g.* the addition of PBu$^n_3$ to [M(CO)$_3$(η-C$_7$H$_7$)]$^+$ (M = Cr, Mo, or W) which follows Scheme 3.[19] An independent investigation gives similar

[17] J. W. Burril, B. R. Bonazza, D. W. Garret, and C. P. Lillya, *J. Organometallic Chem.*, 1975, **104**, C37.

[18] R. Baker and A. H. Cook, *J.C.S. Perkin II*, 1976, 447 and references cited therein.

[19] D. A. Sweigart, M. Gower, and L. A. P. Kane-Maguire, *J. Organometallic Chem.*, 1976, **108**, C15.



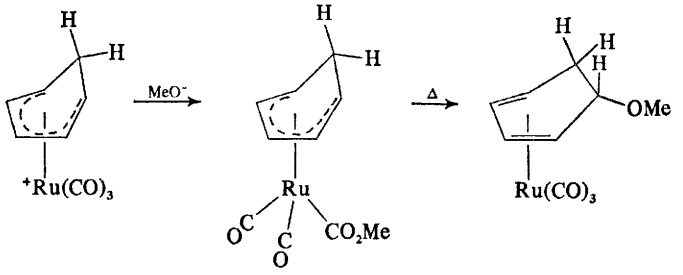
Scheme 3

results but suggests that addition to the ring is possible only with hard bases whereas soft bases preferentially attack the metal centre, leading to CO substitution.[20] On introducing a basic ligand for one CO the direction of nucleophilic attack can be changed but the results are rather unpredictable. Addition of PBu^n_3 to $[Mn(CO)_3(\eta\text{-}C_6H_6)]^+$ gives, in a reversible reaction ($K = 300$ l mol^{-1}), the ring-addition product $[Mn(CO)_3(\eta\text{-}C_6H_6PBu^n_3)]^+$, provided that the reaction is carried out (*a*) in air or (*b*) under nitrogen in the dark.[21] Under nitrogen an equilibrium mixture is quickly converted into the substitution product $[Mn(CO)_2(PBu^n_3)(\eta\text{-}C_6H_6)]^+$ on exposure to light. However, in this case, the precursor to the final product is thought to be the benzene complex and not the ring-addition compound. Similarly equimolar quantities of PPh_3 and $[Mo(CO)_3(\eta\text{-}C_7H_7)]^+$ give $[Mo(CO)_2(PPh_3)(\eta\text{-}C_7H_7)]^+$ and, since ring addition was not observed, an intermediate $[Mo(CO)_3(PPh_3)(\eta^5\text{-}C_7H_7)]^+$ is proposed which results from phosphine attack at the metal.[22] The kinetics of the addition of other nucleophiles MeO^- and acetylacetone to the tropylium ring of cations $[M(CO)_3(\eta\text{-}C_7H_7)]^+$ (M = Cr, Mo, or W) have been reported and are obviously of interest in relation to the phosphine reactions.[23] Under pseudo-first-order conditions (excess nucleophile) the rate of addition of both nucleophiles is virtually independent of the nature of the metal, which supports a mechanism involving direct attack at the tropylium ring. This is compatible with stereochemical evidence indicating a general preference for *exo*-addition of nucleophiles to the ring.

exo-Addition of nucleophiles to the arene ring of arenecyclopentadienyliron cations is fairly well documented and the directing influence of arene substituents exerting $+I$ or $-I+R$ electronic effects has been the subject of earlier studies. The $(-I-R)$ group CO_2Me has now been found to activate the *ortho* carbon such that H^- attack gives *ortho*-, *para*-, and *meta*-substituted derivatives with a ratio (corrected for statistical effects) of 12.7:1.0:1.1 respectively.[24] Selectivity in arenetricarbonylmanganese cation reactions follows similar patterns but in general nucleophilic attack is less facile. These directive effects are rationalized on the basis of localized positive charge generation by inductive and related effects of the ring substituent. However, MO calculations reveal that no correlations of this type exist with the cation $[Fe(CO)_3(\eta\text{-}C_6H_7)]^+$.[25] Instead the bond-index values correctly predict the site of attack, which may suggest formation of an early transition state in nucleophilic additions to this complex, *e.g.* an ion pair for addition of anions. Nucleophilic attack

[20] A. Salzer, *Inorg. Chim. Acta*, 1976, **17**, 221.
[21] D. A. Sweigart and L. A. P. Kane-Maguire, *J.C.S. Chem. Comm.*, 1976, 13.
[22] G. Deganomello, T. Boshi, L. Toniolo, and G. Albertin, *Inorg. Chim. Acta*, 1974, **10**, L3.
[23] K. M. Al-Kamuthi and L. A. P. Kane-Maguire, *J. Organometallic Chem.*, 1975, **102**, C4.
[24] J. F. McGreer and W. E. Watts, *J. Organometallic Chem.*, 1976, **110**, 103.
[25] D. W. Clack, M. Monshi, and L. A. P. Kane-Maguire, *J. Organometallic Chem.*, 1976, **107**, C40.

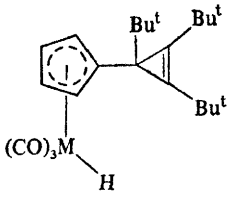
on cyclohexadienyltricarbonyliron by MeO^- gives the expected 5-*exo*-derivative initially but with longer reaction times this is converted into a mixture of *exo*- and *endo*-isomers in the ratio 35:65.[26] Formation of the *endo*-isomer may result from nucleophilic attack at a carbonyl ligand to give a dienyl ester which undergoes MeO^- transfer to an *endo* position on the ring. Subsequent demonstration of this was possible with the ruthenium complex in Scheme 4.



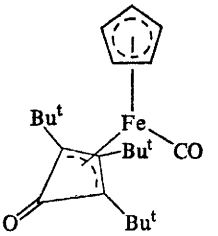
Scheme 4

Electrophilic attack of the tri-t-butylcyclopropenium cation on $[M(CO)_3(\eta\text{-}C_5H_5)]^-$ (M = Mo or W) takes place at the C_5H_5 ring to give complexes (17) and, since the displaced hydrogen is transferred to the metal, *exo* attack is implied.[27] With $[Fe(CO)_2(\eta\text{-}C_5H_5)]^-$ attack at co-ordinated CO is observed preferentially since the oxocyclobutenyl complex (18) is obtained. This stereoselectivity is difficult to rationalize on steric grounds and differences in electron density distribution in these complexes are consequently thought to control the site of attack.

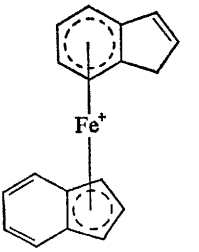
Protonation of di-indenyliron gives the η^5-indenyl-η^6-indeneiron(II) cation (19) as a result of stereospecific addition to the indenyl ring, probably at the *endo* position *via*



(17)



(18)



(19)

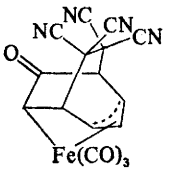
an intermediate metal hydride species.[28] Deprotonation with the strong base n-butyl-lithium regenerates the starting material by preferential abstraction of an *exo*-proton in line with the known ability of nucleophiles to attack at this side of co-ordinated rings. The protonation reaction is accompanied by a shift in the site of co-ordination of the hydrocarbon ligand from the C_5 to the C_6 ring, a phenomenon also

[26] K. E. Hine, B. F. G. Johnson, and J. Lewis, *J.C.S. Chem. Comm.*, 1975, 81.
[27] M. Green and R. P. Hughes, *J.C.S. Chem. Comm.*, 1975, 862.
[28] P. M. Treichel and J. W. Johnson, *J. Organometallic Chem.*, 1975, **88**, 207.

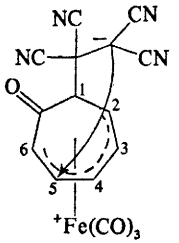
observed, but in the reverse direction, on deprotonation of η^6-indene and indole complexes $[M(L)(\eta\text{-}C_5Me_5)]^{2+}$ (M = Rh or Ir, L = η^6-indene or indole).[29]

Interestingly, protonation of nickelocene with CF_3CO_2H gives $[Ni(\eta\text{-}C_5H_6)(\eta\text{-}C_5H_5)]^+$, in which the entering proton occupies the *exo*-methylene position, according to deuteriation experiments with CF_3CO_2D.[30] In this case the metal does not function as the initial site of attack so that a metal hydride cannot be involved in the reaction.

Cycloaddition.—Reactions of electrophilic olefins and acetylenes with tricarbonyliron complexes of cycloheptatriene and cyclo-octatetraene lead to 1,3-*exo*-products. Troponetricarbonyliron and tcne, however, have now been found to give complex (20) which results from previously unobserved 1,5-*exo*-cycloaddition.[31] A dipolar intermediate (21) resulting from initial attack by the electrophile on the hydrocarbon



(20)



(21)

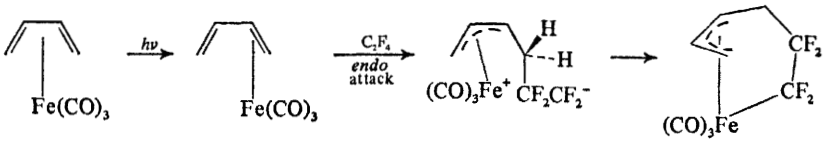
is thought to be involved and deuterium labelling experiments clearly indicate that attack at a non-co-ordinated double bond occurs preferentially at C-1. The site of initial attack by tcne on substituted η^4-cyclo-octatetraenetricarbonyliron derivatives leading to 1,3-cycloaddition is influenced significantly by the nature of the substituent and the results are summarized in Table 2.[32] Elucidation of the role of the substituent is complicated by the existence of various tautomers of $[Fe(CO)_3(\eta\text{-}C_8H_7X)]$ which may have different reactivities towards tcne, and in addition the position of the tautomeric equilibrium is different for different substituents X. Some rationalization of the results is possible since the positions of the equilibria have been determined independently by n.m.r. methods.

Table 2 *Effect of substituents on the site of attack by* tcne *on* $[Fe(CO)_3(\eta\text{-}C_8H_7X)]$ *(from ref.* 32)

	Site attacked (%)			
Substituent (X)	α	β	γ	δ
Me	71	—	—	21.5
Ph	39	—	16	23
CO_2Me	23	64	—	—

[29] C. White, S. J. Thompson, and P. M. Maitlis, *J.C.S. Chem. Comm.*, 1976, 409.
[30] G. K. Turner, W. Kläui, M. Scotti, and H. Werner, *J. Organometallic Chem.*, 1975, **102**, C9.
[31] Z. Goldschmidt and Y. Bakal, *Tetrahedron Letters*, 1976, 1229.
[32] L. A. Paquette, S. V. Ley, S. Maiorano, D. F. Schneider, M. J. Broadhurst, and R. A. Boggs, *J. Amer. Chem. Soc.*, 1975, **97**, 4658.

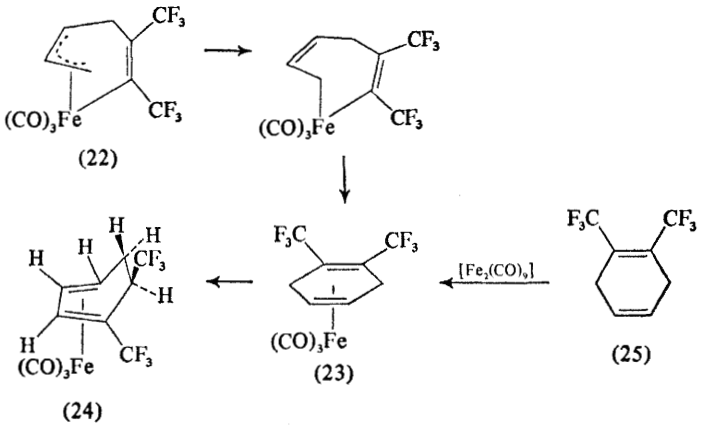
A series of reports describing cycloaddition reactions of fluorocarbons with co-ordinated olefins has appeared; generally *endo* attack at a co-ordinated double bond is observed.[33,34] This contrasts with electrophilic attack at unco-ordinated double bonds as described above where *exo* attack is preferred. The mechanism of photo-initiated addition of C_2F_4 to butadienetricarbonyliron is considered to follow Scheme 5, *i.e.* photolysis promotes dechelation of the hydrocarbon rather than CO



Scheme 5

dissociation, and C_2F_4 then attacks the co-ordinated rather than the free double bond. This has been refuted in an independent report since in the presence of ^{13}CO similar reactions gave analogous products containing substantial quantities of co-ordinated ^{13}CO, *i.e.* CO exchange occurs readily, possibly *via* CO dissociation.[35]

Thermal decomposition of (22) proceeds according to Scheme 6, possibly *via* an unstable intermediate (23) which undergoes a familiar and, in this case, regioselective



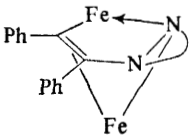
Scheme 6

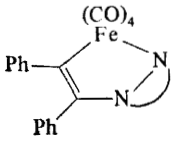
1,3-hydrogen shift to give the final product.[36] This is supported by the isolation of (24) from the reaction of (25) and $[Fe_2(CO)_9]$. This demonstrates stepwise Diels–Alder addition of $CF_3C{\equiv}CCF_3$ to a co-ordinated diene, which is a thermally allowed process, whereas a number of so-called thermally forbidden reactions have been reported which, by implication, may involve stepwise addition of electrophiles to the co-ordinated olefin and are therefore allowed. Consequently it is suggested that re-examination of these forbidden reactions may now be necessary with a view to eliminating the possibility of stepwise addition.

[33] A. Bond, B. Lewis, and M. Green, *J.C.S. Dalton*, 1975, 1109.
[34] M. Green, B. Lewis, J. J. Daly, and F. Sanz, *J.C.S. Dalton*, 1975, 1118.
[35] R. C. Kerber and E. A. Koerner von Gustorf, *J. Organometallic Chem.*, 1976, **110**, 345.
[36] R. Davis, M. Green, and R. P. Hughes, *J.C.S. Chem. Comm.*, 1975, 405.

The reaction of μ-(*cis*-azo)-hexacarbonyldi-iron complexes (26) with diphenylacetylene results in [4+4] cycloaddition probably in a stepwise manner to give (27) and (28) followed by [4+2] addition to give ultimately (29).[37] Preliminary kinetic

(26)


(27)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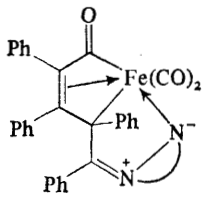
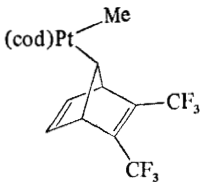
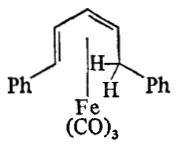

(29)

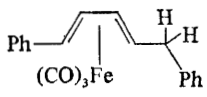
studies favour a concerted cycloaddition of the first acetylene (26)→(27) followed by thermal decomposition to (28), CO dissociation, and reaction of the second alkyne to give (29). Accordingly, carbon monoxide inhibits the second cycloaddition, (28)→(29), but not the first, (26)→(27). Intermediates detected by flash photolysis studies and low-temperature i.r. monitoring of the photolysis of (28) in the presence of PhC_2Ph support a dissociative mechanism for the (28)→(29) step. Addition of electrophilic acetylenes to nickelocene is postulated to proceed *via* acetylene co-ordination to the metal and $\eta^5 \rightarrow \eta^1$ rearrangement of an η^5-C_5H_5 ring. However, addition of $CF_3C{\equiv}CCF_3$ to [Pt(Me)(cod)(η^1-C_5H_5)] gives a 1:1 adduct (30) structurally characterized by


(30)

X-ray diffraction studies and, since the acetylene adds to the η^1-C_5H_5 ring on the side opposite to the metal, preliminary co-ordination of $CF_3C{\equiv}CCF_3$ to platinum is considered unlikely in this case.[38]

Isomerization and Exchange.—Thermolysis of (31) leads to the *trans*-isomer (32) and in a competing reaction to metal epimerization and C-5 methylene hydrogen *exo–endo* scrambling.[39] The isomerization reaction obeys first-order kinetics and the


(31)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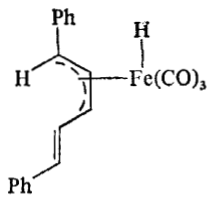
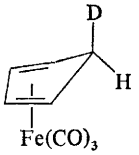
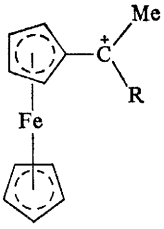

(33)

[37] A. Albini and H. Kisch, *J. Organometallic Chem.*, 1975, **101**, 231.
[38] H. C. Clark, D. G. Ibbot, N. C. Payne, and A. Shaver, *J. Amer. Chem. Soc.*, 1975, **97**, 3555.
[39] T. H. Whitesides and J. P. Neilan, *J. Amer. Chem. Soc.*, 1976, **98**, 63.

thermolysis of specifically deuteriated complexes gives products in accord with a mechanism involving preliminary dechelation of the diene. This leads to an allyl-metal hydride intermediate (33) through which the isomerization can take place. The formation of $[Fe_2(CO)_4(\eta^5\text{-}C_5H_5)_2]$ from $[Fe(CO)_5]$ and cyclopentadiene has been shown to involve the intermediate $[Fe(CO)_3(\eta^4\text{-}C_5H_6)]$ which undergoes CO dissociation and hydride transfer to the metal followed by dimerization with loss of the hydride ligand. Detailed studies of the thermal decomposition of the *exo*-deuteriated complex (34) provide evidence for a much more complex mechanism since a number of side-products are obtained and the reaction does not follow any simple rate law.[40] Dechelation of the diene to give an $\eta^2\text{-}C_5H_6$ complex is proposed as the first step in a process leading to the hydride $[Fe(H)(CO)_2(\eta\text{-}C_5H_5)]$ and finally the dimer. However, the reaction is autocatalytic, probably as a result of Fe—Fe bond fission in the product to give $[Fe(CO)_2(\eta\text{-}C_5H_5)]$ radicals which stereospecifically abstract deuterium from (34) to provide an alternative radical-chain pathway to the dimer. The photolytic decomposition of (34) to the dimer, in contrast, involves initial CO loss and hydride transfer of the *endo*-isotope to the metal, *i.e.* the pathway originally postulated for the thermal reaction.



(34)

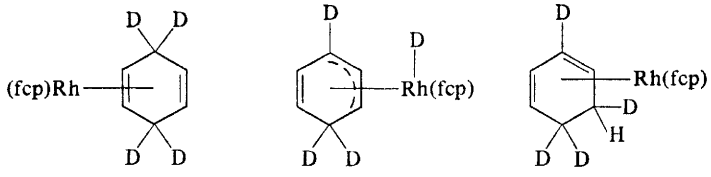


(35)

Intramolecular proton transfer to the metal also accounts for slow H/D exchange of protons attached to carbon atoms bonded to the carbenium atom in tertiary 1-ferrocenylalkylium ions (35) in CF_3CO_2D solution.[41] Rates of exchange in the methyl group increase in the series $R = Me < Ph < Et < CH_2Ph < Pr^i < Bu^t$.

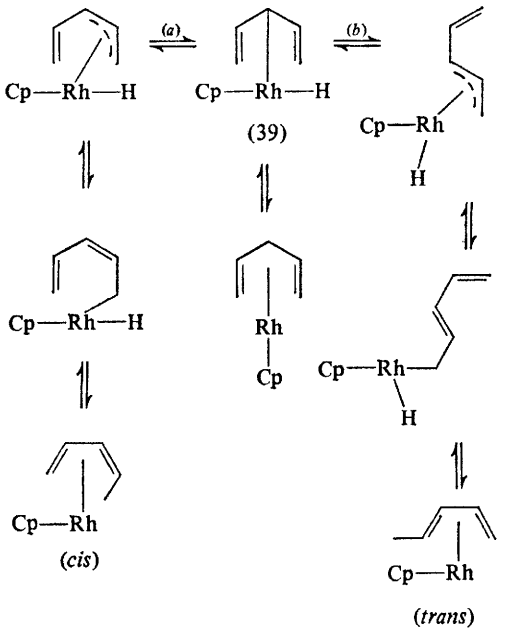
The methyl hydrogens of 1,1′-dimethylcobalticinium ion exchange in 0.91M-NaOD in D_2O with a rate constant of 1.40×10^{-2} min^{-1} at 70 °C and an activation energy of 25.4 ± 1 kcal mol^{-1}.[42] The ring protons exchange at a rate *ca.* 100 times less, possibly as a result of resonance stabilization of the carbanion formed by removal of a methyl hydrogen. Metal participation is not considered likely. A mechanism involving the allyl-metal hydride intermediate (37) can account for the observation of a 1,3-deuterium shift in the thermal isomerization of (36) to (38) (fcp = η^5-formylcyclopentadienyl) which follows first-order kinetics.[43] Isomerizations of penta-1,4-diene and 3-methylpenta-1,4-diene complexes of rhodium to the corresponding complexes of the *cis*- and *trans*-1,3-dienes also follow first-order kinetics and the *cis*-products subsequently isomerize to the *trans*-forms in a separate process (Scheme 7).

[40] T. H. Whitesides and J. Shelly, *J. Organometallic Chem.*, 1975, **92**, 215.
[41] W. Crawford and W. E. Watts, *J. Organometallic Chem.*, 1976, **110**, 257.
[42] J. E. Sheats, W. Miller, and T. Kirsh, *J. Organometallic Chem.*, 1975, **91**, 97.
[43] M. Arthurs, M. Sloan, M. G. B. Drew, and S. M. Nelson, *J.C.S. Dalton*, 1975, 1794.



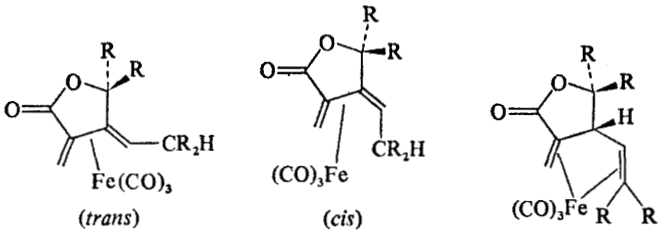
(36) (37) (38)

To account for the observed formation of the *cis*- and *trans*-1,3-diene complexes at equal rates (initially) the authors find it necessary to propose that isomerization (1,4-→1,3-diene) proceeds *via* a symmetrical η^1-allyl intermediate (39) which can collapse in two ways (*a*) or (*b*) to give the *cis*- or *trans*-form of the 1,3-diene *via* allyl-hydride intermediates. Interestingly an intermediate η^1-allyl complex analogous to (39) is also postulated by Green to account for the formation of *cis*- and *trans*-isomers of (40) from (41) (R = H or D).[44] However, prolonged refluxing in hexane did not result in *cis–trans* isomerization. The 1,4-→1,3-rearrangement involves regiospecific 1,3-hydrogen shifts and, in view of the configuration of the products, a mechanism which proceeds *via* allyl-metal hydrides is possible whereas metal-promoted suprafacial 1,3-hydrogen shift processes can be ruled out. The importance of this result lies in the fact that although both mechanisms are possible the latter cannot compete effectively with the former as a low-energy isomerization pathway.



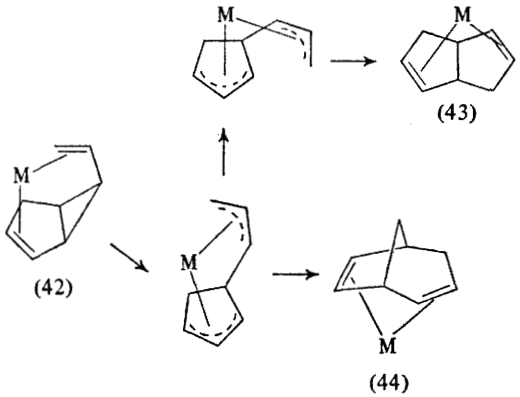
Scheme 7

[44] M. Green and R. P. Hughes, *J.C.S. Chem. Comm.*, 1975, 619.



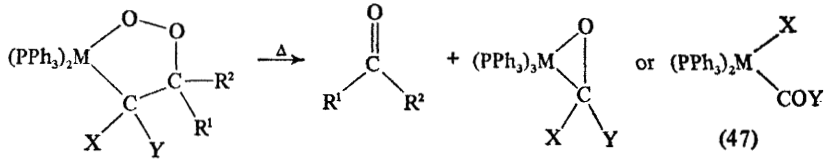
(40) (41)

Vinylcyclopropane complexes (42) (M = Rh, Ir, or Pd) undergo thermal isomerization to the cyclopentane derivatives (43) although in some cases small quantities of a third isomer (44) are produced.[45] The latter can be produced by a single-stage concerted reaction in which bonding to rhodium is maintained throughout but the requirement of *cis* stereochemistry in the new double bond of (43) suggests that different pathways, involving bisallyl intermediates, are followed (Scheme 8).



Scheme 8

Thermal decomposition of the complexes (45) (M = Pd or Pt) proceeds according to Scheme 9 and kinetic studies of the palladium system give an activation energy of



(45) (46) (47)

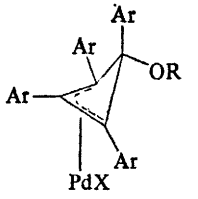
Scheme 9

82.5 ± 3 kJ mol^{-1} (X = Y = CN, $R^1 = R^2$ = Me) for the first-order reaction.[46] The structure of the metal complex is unknown but could be (46) or (47), and similarly a

[45] V. Aris, J. M. Brown, J. A. Conneely, B. T. Golding, and D. H. Williamson, *J.C.S. Perkin II*, 1975, 4.

[46] R. A. Sheldon and J. A. van Doorn, *J. Organometallic Chem.*, 1975, **94**, 115.

number of mechanisms could be fitted to the data available which means that assignment of a unique mechanism is not possible. The cyclobutenyl complexes (48) undergo reversible ring-opening to (49) according to low-temperature n.m.r. studies and

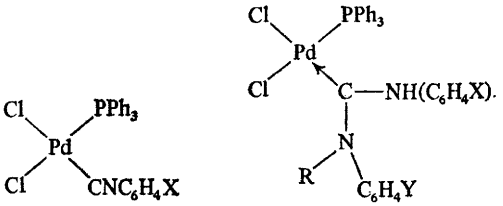


(48) (49)

the stereochemistry of the rearrangement has been elucidated by an *X*-ray structural study of the adduct [{(EtO)C_4Ph_4}Pd(acac)(PMe_2Ph)].[47] The —PhC=CPhOEt moiety is *trans*, confirming that initial *trans* attack of diphenylacetylene on $PdCl_2$ has occurred to give (49; X = Cl), the precursor to (48; X = acac). An estimate of $\Delta G^{\ddagger}$ for ring-opening is 80 kJ mol^{-1}.

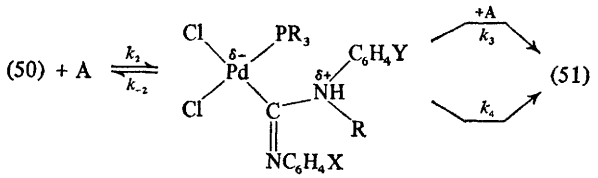
3 Isocyanides

Primary and secondary amines react with the co-ordinated isocyanide in (50) to give carbene complexes (51).[48] Kinetic studies of the reaction with Y = MeO, Me, or H,



(50) (51)

X = Me, H, or Cl, and R = Me or Et, carried out under pseudo-first-order conditions (excess amine, A), gave pseudo-first-order rate constants k_{obs} which exhibit a complex dependence on the concentration of amine since the second-order coefficient $k_A = k_{obs}/[A]$ is a function of [A]. Two types of behaviour were found: (i) plots of k_A *vs.* [A] are linear or (ii) plots of k_A *vs.* [A] are curvilinear although $1/k_A$ *vs.* 1/[A] is linear, to account for which a stepwise mechanism is proposed (Scheme 10). The



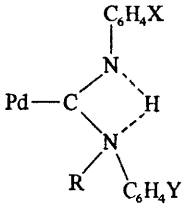
(52)

Scheme 10

[47] P.-T. Cheng, T. R. Jack, C. J. May, S. C. Nyburg, and J. Powell, *J.C.S. Chem. Comm.*, 1975, 369.

[48] L. Calligaro, P. Uguagliati, B. Crociani, and U. Belluco, *J. Organometallic Chem.*, 1975, **92**, 399.

intermediate (52) in the scheme is thought to result from nucleophilic attack of A on the carbon atom of the isocyanide. Proton transfer in (52) to give the final product can occur intramolecularly *via* a four-centre transition state (53) or intermolecularly with a second amine acting as a catalyst in a six-membered transition state (54).



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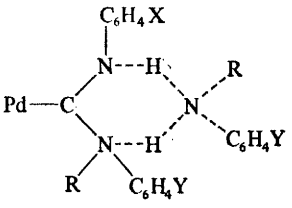


(54)

A later communication describes the effect of solvents on such reactions. Overall rates were found to increase with the decreasing ability of the solvent to form hydrogen bonds with the attacking amine.[49] The rates are also affected by solvent–complex interactions, probably of a dipolar nature. The effects of the *cis*-ligand (L) were assessed by studying the reaction between *N*-methylaniline and *cis*-$[Pd(Cl)_2(CN\text{-}p\text{-}C_6H_4Me)(L)]$ and the second-order rate constants k_2 were found to increase in the order $L = PEt_3 < PMePh_3 < PPh_3 < PMe_2Ph < P(OMe)_2Ph < P(OMe)_3$. Thus a balance between steric and electronic factors is in evidence with bulky ligands reducing the rate but good π-acceptor, poor σ-donor ligands enhancing the reactivity by decreasing the d–π^* palladium–isocyanide back donation. Activation parameters for the k_2 step ($L = PPh_3$) are $\Delta H^{\ddagger} = 9.8 \pm 0.7$ kcal mol^{-1} and $\Delta S^{\ddagger} = -30 \pm 3$ cal K^{-1} mol^{-1}. The low enthalpy of activation fits the proposed k_2 step of nucleophilic attack by the amine on the isocyanide ligand since no energy-demanding bond-breaking processes are involved.

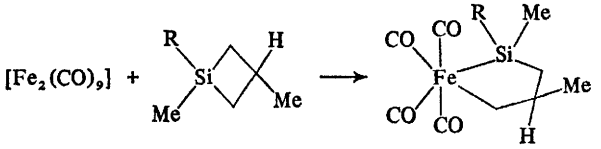
[49] P. Uguagliati, B. Crociani, U. Belluco, and L. Calligaro, *J. Organometallic Chem.*, 1976, **112**, 111.

6
Oxidative Addition and Reductive Elimination

BY J. L. DAVIDSON

1 Group VIII

Iron.—$[Fe_2(CO)_9]$ reacts with stereoisomeric mixtures of silacyclobutanes according to Scheme 1 to give product mixtures in isomer ratios unchanged from those of the starting materials.[1] This can be explained by (*a*) a concerted ring-opening mechanism or (*b*) formation of a dipolar or biradical intermediate which has a lifetime short in comparison with bond rotation, which would lead to racemization.



two isomers two isomers

R = Bu^n or MeO

Scheme 1

Cobalt.—The isolation [2] of an intermediate cobalt(III) complex $[Co(SC_6F_5)_2(CO)(\eta\text{-}C_5H_5)]$ from the reaction of $[Co(CO)_2(\eta\text{-}C_5H_5)]$ and $C_6F_5SSC_6F_5$, which leads to dinuclear $[Co_2(\mu\text{-}SC_6F_5)_2(\eta\text{-}C_5H_5)_2]$, confirms earlier suggestions[3] that oxidative addition of disulphides to metal complexes is the first stage in some reactions leading to mercapto-bridged dimers.

Rhodium.—$[Rh(CN)_4]^{3-}$ exhibits exceptionally high reactivity in oxidative addition reactions with alkyl halides (RX)[4] which follow second-order kinetics according to the rate law

$$-d[Rh(CN)_4^{3-}]/dt = k_2[Rh(CN)_4^{3-}][RX]$$

In aqueous solution MeI gives the product *trans*-$[Rh(CN)_4(Me)(I)]^{3-}$ while in methanol $PhCH_2Cl$ similarly gives $[Rh(CN)_4(PhCH_2)(Cl)]^{3-}$. In aqueous methanol MeI and other organic halides, EtI, PrI, $PhCH_2I$, and $PhCH_2Br$, although exhibiting similar kinetics, give hydroxy-complexes $[Rh(CN)_4(OH)(X)]^{3-}$ which are thought to result from $[Rh(CN)_4]^-$-induced decomposition of the primary product $[Rh(CN)_4(R)(X)]^{3-}$. The reactions follow trends typical of oxidative addition, *i.e.* the rates decrease in the orders MeI ≫ EtI > PrI, reflecting increasing steric hindrance, and

[1] C. S. Cundy, M. F. Lappert, J. Dubac, and P. Mazerolles, *J.C.S. Dalton*, 1976, 910.
[2] J. L. Davidson and D. W. A. Sharp, *J.C.S. Dalton*, 1975, 813.
[3] C. T. Lam and C. V. Senoff, *Canad. J. Chem.*, 1973, **51**, 3790.
[4] J. Halpern and R. Cozens, *Coordination Chem. Rev.*, 1975, **16**, 141.

$PhCH_2I > PhCH_2Br > PhCH_2Cl$, reflecting the decreasing ease of carbon–halogen bond cleavage. Iodide ion has been found to catalyse the oxidative addition of methyl iodide to $[Rh(I)(CO)(EPh_3)_2]$ (E = P, As, or Sb) although compared with reactions with E = As or Sb the effect is small with E = P.[5] The active species appears to be $[Rh(I)_2(CO)(EPh_3)]^-$ but the rates of reaction of this complex with MeI are so great that accurate kinetic data could not be obtained. The proposed mechanism is illustrated in Scheme 2 and in order to produce a catalytic effect it is necessary that halide

$$[Rh(L)_2(CO)I] + I^- \underset{}{\overset{K_1}{\rightleftharpoons}} [Rh(L)(CO)I_2]^- + L$$

$L = EPh_3$

slow ↓ MeI

very fast ↓ MeI

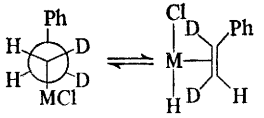
$$[Rh(Me)(L)_2(CO)I_2] + I^- \underset{k_2}{\overset{L}{\rightleftharpoons}} [Rh(Me)(L)(CO)I_3]^-$$

or

$$[Rh(Me)(L)(CO)I_2] + I^- \qquad (1)$$

Scheme 2

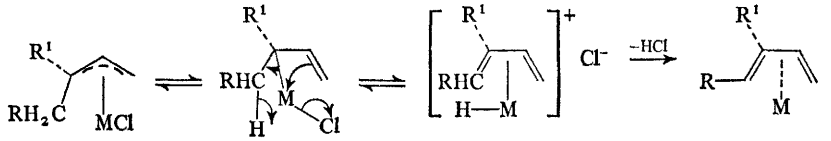
ion is ejected from the anion (1) which in practice is made possible by the strong *trans*-labilizing effect of the methyl ligand. Oxidative addition of *threo*-PhCHDCHDCOCl to $[Rh(Cl)(PPh_3)_3]$ or $[Ir(Cl)(N_2)(PPh_3)_2]$ gives $[M(Cl)_2(dpp)(PPh_3)_2]$ (M = Rh or Ir, dpp = *threo*-2,3-dideuterio-3-phenylpropionyl) and $[Ir(Cl)_2(dpe)(CO)(PPh_3)_2]$ (dpe = *threo*-α,β-dideuteriophenethyl).[6] The oxidative addition reactions and alkyl migration to produce the latter from the dpp complex therefore proceed with retention of configuration of the alkyl group. Thermal decomposition of these complexes leads to mixtures of deuteriated 1-chloro-1-phenylethanes, the products of Markovnikov addition of the liberated HCl (DCl) to liberated styrenes. This reductive elimination process is probably preceded by hydride transfer to the metal according to Scheme 3. Since mixtures of deuteriated organic products are obtained, a series of such reversible reactions must occur leading to H–D scrambling.



Scheme 3

Allylic complexes formed from the reaction of acyclic 1,3-dienes and μ-hydrido-complexes $[M_2(H)(Cl)_3(\eta\text{-}C_5Me_5)_2]$ (M = Rh or Ir) (described in Chapter 2) exhibit differences in the readiness with which they undergo reductive elimination of HCl to give diene complexes $[M(\eta\text{-diene})(\eta\text{-}C_5Me_5)]$.[7,8] A common feature of those which undergo this reaction readily is the existence of methyl groups in both the *syn*-1- and *anti*-1-positions and, as it is probably the *anti*-1-isomers which undergo HCl elimination (Scheme 4), the reaction is facilitated since the carbon skeleton is already *cisoid*

[5] D. Forster, *J. Amer. Chem. Soc.*, 1975, **97**, 951.
[6] N. A. Dunham and M. C. Baird, *J.C.S. Dalton*, 1975, 774.
[7] H. B. Lee and P. M. Maitlis, *J.C.S. Dalton*, 1975, 2316.
[8] H. B. Lee, K. Mosely, C. White, and P. M. Maitlis, *J.C.S. Dalton*, 1975, 2322.



Scheme 4

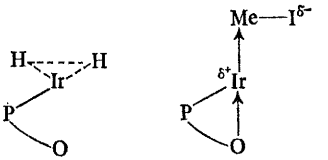
and close to the conformation needed for formation of the *cis*-diene. Complexes with alkyl groups in both *syn*-1- and -2-positions require to rearrange to the *anti*-1-isomer and, particularly when the substituents are small, an activation barrier has to be overcome, so that it is not surprising that HCl elimination is observed to be difficult. When only hydrogen is present at the 2-position the activation energy for the preliminary rearrangement is probably quite high and consequently reductive elimination is not possible.

Iridium.—Kinetic studies have been carried out on the oxidative addition of hydrogen to *trans*-[Ir(Cl)(CO)(L)$_2$] [L = PMe_2Ph or $PMe_2(o\text{-}MeOC_6H_4)$] and the activation parameters were found to be comparable to those reported earlier for *trans*-[Ir(Cl)(CO)(PPh_3)$_2$][9] (Table 1). The reactions are first-order in Ir^I and since the pressure of hydrogen was kept constant a first-order dependence on H_2 was assumed such that $-d[Ir^I]/dt = k_{obs}[Ir^I]$, where $k_{obs} = k_1[H_2]$. k_1 values are listed in Table 1.

Table 1 *Rate constants and activation parameters for the oxidative addition of* H_2 *to* trans-[Ir(Cl)(CO)(L)$_2$] (*from ref.* 9)

L	10^2k_1/l mol^{-1} s^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
PMe_2Ph	28	46	−105
$PMe_2(o\text{-}MeOC_6H_4)$	20	50	−94
PPh_3	67	45	−96

The *o*-methoxy-group on $PMe_2(o\text{-}MeOC_6H_4)$ obviously has little effect on the rates whereas an acceleration of ~100 times is observed in oxidative additions involving methyl iodide. This effect is attributed to anchimeric assistance due to interaction of the methoxy oxygen with iridium. However, in the present case the lack of effect is probably a reflection of the much lower polarity of the transition state (2) compared with that for methyl iodide addition (3).



(2) (3)

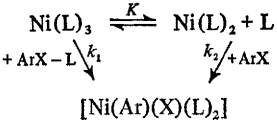
Nickel.—Although a number of oxidative addition reactions follow free-radical pathways the nature of the initiation process is not well defined. Additions of nickel(0) and platinum(0) complexes, *e.g.* [Ni(PEt_3)$_4$] or [Pt(PEt_3)$_3$], to the one-electron acceptors tcne, dichlorodicyano-*p*-benzoquinone, and chloranil give radical

[9] E. M. Hyde and B. L. Shaw, *J.C.S. Dalton*, 1975, 765.

anions of these three compounds.[10] It is therefore suggested that electron transfer from the metal to the attacking species may be the initiation step in some oxidative addition reactions. Oxidative addition of aryl halides, *p*-chloranisole, *p*-dichlorobenzene, and *m*-dichlorobenzene to $[Ni(PPh_3)_3]$ follows first-order kinetics with respect to both reactants and can therefore be accommodated by the mechanism in Scheme 5 ($L = PPh_3$).[11] This gives a rate law

$$dx/dt = (k_1[L] + k_2K)[ArX](a-x)/(K + [L]) = k_{obs}(a-x)$$

where a is the initial concentration of Ni^0 complexes and $(a-x)$ is the concentration at time t. Since [ArX] is constant and K is assumed to be less than 10^{-6} mol l^{-1} this



Scheme 5

reduces to

$$k'[L] = k_1[L] + k_2K$$

In accord with this, linear plots of $k'[L]$ were obtained against [L] and the rate constants k_1 and k_2K were computed (see Table 2). Since K is probably $< 10^{-6}$ mol l^{-1}

Table 2 *k values for oxidative addition of* ArX *to* $[Ni(PPh_3)_3]$ *(from ref.* 11)

Aryl halide	10^4k_1/l mol^{-1} s^{-1}	10^5k_2K/s^{-1}
p-Chloroanisole	1.0	1.1
p-Dichlorobenzene	1.8	0.9
m-Dichlorobenzene	85	20

it is apparent that $[Ni(L)_3]$ and its dissociation product $[Ni(L)_2]$ exhibit significantly different reactivities towards the aryl halide although both show the same trends. Competition experiments with these and other aryl halides also reveal a relationship between reactivity and the Hammett σ-parameter of the aryl substituent and it is proposed that the reactants form an asymmetric three-centre transition state which, with electron-withdrawing substituents, approaches an aromatic nucleophilic substitution. 1,2-Bisdiethylphosphinoethane (dee) reacts with $[Ni(CN)(Ph)(PEt_3)_2]$ to give $[Ni(dee)_2]$ as a result of reductive elimination of PhCN.[12] Kinetic studies are in accord with the mechanism shown in Scheme 6 in which dee initially displaces PEt_3 leading to a five-co-ordinate intermediate [Ni(CN)(Ph)(dee)(dee)] where one of the dee ligands is unidentate. The basic role of dee is that of a unidentate ligand and consequently the so called *cis* 'effect' does not operate although it has been invoked in other reductive elimination reactions.

[10] I. H. Elson, D. G. Morrel, and J. K. Kochi, *J. Organometallic Chem.*, 1975, **84**, C7.
[11] M. Fou and L. Cassar, *J.C.S. Dalton*, 1975, 2572.
[12] G. Favero and A. Turco, *J. Organometallic Chem.*, 1976, **105**, 389.

$$[Ni(CN)(Ph)(PEt_3)_2] + dee \xrightarrow[fast]{-2\,PEt_3} [Ni(CN)(Ph)(dee)]$$

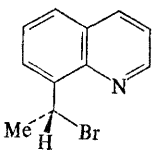
$$PhCN + [Ni(dee)(dee)] \underset{}{\overset{k_1\,slow}{\rightleftharpoons}} [Ni(CN)(Ph)(dee)(dee)]$$

(with $+dee$ / $-dee$, fast, between the two Ni species)

$$PhCN + [Ni(dee)_2]$$

Scheme 6

Platinum.—*Oxidative Addition.* The oxidative addition of (+)-(8-bromoethyl) quinoline (4) to $[Pt(PPh_3)_3]$ gives the platinum(II) complex (5) with inversion of configuration at carbon.[13] Benzocyclobutene-1,2-dione (6) and [Pt(diphenylacetylene)$(PPh_3)_2$] react to give the platinum(II) complex (7) with first-order kinetics, *i.e.* first-order in complex, zero-order in organic substrate; the rate-determining step would appear to be acetylene dissociation from the zero-valent platinum complex in view of the high entropy of activation, 85 ± 12 J K^{-1} mol^{-1}.[14] This is in accord with the observation that reactions of (6) with $[Pt(PPh_3)_4]$ and [Pt(PhCH=CHPh)$(PPh_3)_2$]



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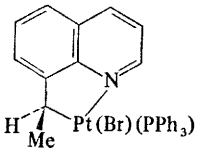
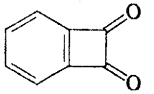


(5)



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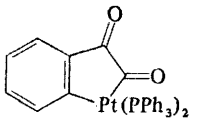

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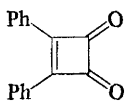

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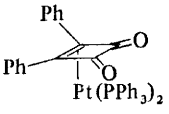

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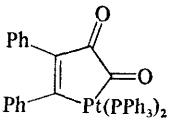
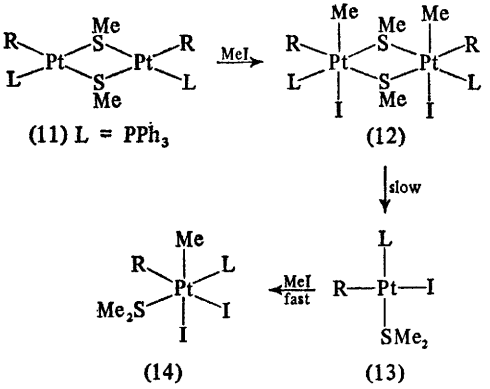


(10)

give the same product but at significantly different rates. Moreover, the rate constant for (6)→(7) is similar to that for (8)→(9) when the zero-valent substrate is [Pt(PhC_2-Ph)$(PPh_3)_2$], which again implies that acetylene dissociation is the slow step. The kinetics of the rearrangement of (9) to the platinacyclopentene (10) have been examined in different solvents and activation parameters for this first-order reaction calculated. In chloroform the low activation entropy, -3 ± 13 J K^{-1} mol^{-1}, is clearly indicative of an intramolecular pathway whereas the large positive value obtained for the reaction in benzene, 122 ± 25 J K^{-1} mol^{-1}, implies that a dissociative mechanism operates in this solvent. Of the two possibilities, (*a*) rate-determining loss of $Pt(PPh_3)_2$ from the complex followed by rapid attack of the metal at the C—C σ-bond of the cyclobutenedione and (*b*) PPh_3 dissociation leading to ring-opening followed by recombination of the two species, the former mechanism is preferred.

[13] V. I. Sokolov, *Inorg. Chim. Acta*, 1976, **18**, L9.
[14] J. Burgess, R. I. Haines, E. R. Hamner, R. D. W. Kemmitt, and M. A. R. Smith, *J.C.S. Dalton*, 1975, 2579.

Evidence has been obtained for the involvement of intermediates (12) and (13) in the reaction of dinuclear Pt^{II} complexes (11) with methyl iodide which gives Pt^{IV} compounds (14) (Scheme 7).[15] Thus with R = Me (12) was isolated and identified by



(11) L = PPh_3 (12) (14) (13)

Scheme 7

n.m.r. spectroscopy. The stereochemistry of the methyl iodide addition (*trans*) was confirmed by reaction with CD_3I to give the deuteriated analogue of (12), which gave only one peak in the ^1H n.m.r. spectrum. With R = Ph (12) was not isolated but the final product proved to be the methyl-migration product (13) which is unreactive to further oxidation to (14), possibly as a result of the lower stability of Pt^{IV} with the phenyl group attached.

Platinum(II) complexes $[Pt(R)(Cl)(L)_2]$ undergo oxidation in the presence of $[AuCl_4]^-$ and chloride ion according to the equation

$$[Pt(R)(Cl)(L)_2] + [AuCl_4]^- \longrightarrow [Pt(R)(Cl)_3(L)_2] + [AuCl_2]^-$$

where L = PEt_3 and R = Cl, Ph, *m*-FC_6H_4, *p*-FC_6H_4, *p*-ClC_6H_4, or *p*-$MeOC_6H_4$.[16] $[Pt(Cl)_2(bipy)]$ and *trans*-$[Pt(Cl)_2(SEt_2)_2]$ react similarly and obey the rate law

$$\text{Rate} = k_3[Pt(Cl)_2(L)][AuCl_4^-][Cl^-] + k_s[Pt(Cl)_2(L)_2]$$

whereas the rate law for the triethylphosphine complexes is more complex:

$$\text{Rate} = k_3[Pt(R)(Cl)(L)_2][AuCl_4^-] + k_s\frac{[Pt(R)(Cl)(L)_2][AuCl_4^-]}{k + [AuCl_4^-]}$$

These rate laws suggest that oxidation follows two reaction pathways, (1) and (2)+(3), the latter of which is solvent (S) assisted and gives rise to k_s. The overall mechanism is considered to be

$$[Pt(R)(Cl)(L)_3] + [AuCl_4]^- + Cl^- \xrightarrow{k_3} [Pt(R)(Cl)_3(L)_2] + [AuCl_2]^- + Cl^- \quad (1)$$

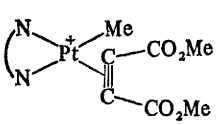
$$[Pt(R)(Cl)(L)_2] + S \underset{k_{-s}}{\overset{k_s}{\rightleftharpoons}} [Pt(R)(L)_2(S)]^+ + Cl^- \quad (2)$$

$$[Pt(R)(L)_2(S)]^+ + [AuCl_4]^- + Cl^- \xrightarrow{k_3'} [Pt(R)(Cl)_3L_2] + [AuCl_2]^- + S \quad (3)$$

[15] R. J. Puddephatt and C. E. E. Upton, *J. Organometallic Chem.*, 1975, **91**, C17.
[16] A. Peloso, *Coordination Chem. Rev.*, 1975, **16**, 95.

Since the rate law for the triethylphosphine complexes reduces to that of the bipy and $AsEt_3$ compounds when k_{-s}/k_3' (k) is small it can be inferred that Cl^- is much more reactive towards triethylphosphine solvent–complex intermediates than those formed by the bipy and $AsEt_3$ complexes. Values of $\Delta H^{\ddagger}$ lie in the range 7.8—9.7 kcal mol^{-1} while $\Delta S^{\ddagger} = -30$ to -33 cal K^{-1} mol^{-1}, which is taken as evidence for an intermediate activated complex with Cl^- bridging the Pt^{II} and Au^{III} species. Since at least three mechanisms involving such an intermediate can account for the kinetic data the actual redox pathway cannot be assigned unambiguously.

Reductive Elimination. The bonding between metals and acetylenes bearing electronegative substituents is frequently assumed to approximate to a metallacyclopropene ring and consequently the following kinetic study is included in this section. The complex [Pt(Cl)(Me)(dmac)(bipy)] (dmac = $MeO_2CC{\equiv}CCO_2Me$) decomposes to [Pt(Cl)(Me)(bipy)] and free dmac by a complex mechanism involving preliminary dissociation of Cl^- to give the complex cation (15).[17] The rate constant, given by $k = 0.0122 + 1/(9.2 \times 10^5[Cl]) + 5.59$, the dependence of decomposition rate on solvent, and the retardation of reaction rate by added Cl^- support such a mechanism. The analogous hexafluorobut-2-yne complex loses $CF_3C{\equiv}CCF_3$, apparently by simple acetylene dissociation rather than *via* an intermediate such as (15).



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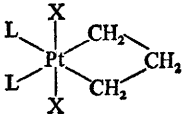

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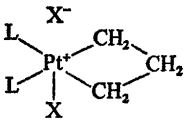


(17)

A number of mechanistic studies have been carried out on the thermally induced reductive elimination of hydrocarbons from platinum(II) and platinum(IV) complexes. Pyrolysis of *cis*-$[Pt(Ar)_2(L)_2]$ complexes [Ar = Ph or 4-MeC_6H_4, $L_2 = (PPh_3)_2$, $\{P(4\text{-}MeC_6H_4)_3\}_2$, dpe, or dpm] gives biphenyls Ar_2 quantitively which indicates that concerted reductive elimination is the primary decomposition pathway.[18] Addition of neutral nucleophiles (L) in all cases studied facilitates Pt—C bond cleavage. Puddephatt has examined the thermal decomposition of the trimethylene Pt^{IV} compounds (16) by isothermal differential scanning calorimetry in the solid state[19] and by u.v. spectrophotometry in solution.[20] The first step in the solid-state reactions appears to be dissociation of X^- to give (17) followed by elimination of C_3H_6 as cyclopropane and propene, but kinetic data were difficult to interpret. In *o*-dichlorobenzene solution the complexes $[Pt(X)_2(C_3H_6)(LL)]$ (X = Cl or Br, LL = bipy or phen) decompose at 130 °C with first-order kinetics to $[Pt(X)_2(LL)]$, cyclopropane (75—85%), and propene (15—25%). In the solid-state decompositions only 36—40% cyclopropane is formed. With $[Pt(Cl)_2(C_3H_6)(bipy)]$ addition of Cl^- had little effect on the rate whereas marked retardation was observed on addition of bipyridyl,

[17] N. Chaudhury and R. J. Puddephatt, *J. Organometallic Chem.*, 1975, **87**, C45.
[18] P. S. Braterman, R. J. Cross, and G. B. Young, *J.C.S. Chem. Comm.*, 1975, 627.
[19] P. W. Hall, R. J. Puddephatt, K. R. Seddon, and C. F. H. Tipper, *J. Organometallic Chem.*, 1975, **81**, 423.
[20] F. Iwanciw, M. A. Quyser, R. J. Puddephatt, and C. F. H. Tipper, *J. Organometallic Chem.*, 1976, **113**, 91.

which strongly suggests that the primary step is dissociation of the chelate LL rather than halide ion in this case. The proposed mechanism is shown in Scheme 8 (S=

$$[Pt(X)_2(C_3H_6)(bipy)] + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Pt(X)_2(C_3H_6)S] + bipy$$

$$\downarrow k_2$$

$$S + [Pt(X)_2(bipy)] \xleftarrow[fast]{bipy} [Pt(X)_2S] + C_3H_6$$

Scheme 8

solvent). Assuming a stationary concentration of the labile intermediate $[Pt(X)_2(C_3H_6)S]$ (Pt′), the rate of decomposition of $[Pt(X)_2(C_3H_6)(bipy)]$ (Pt),

$$d[Pt]/dt = k_1[Pt][S] - k_{-1}[Pt'][bipy]$$

reduces to

$$1/k_{obs} = k_{-1}[bipy]/k_1k_2[S] + 1/k_1[S]$$

This predicts a linear relationship between the reciprocal of k_{obs} and [bipy] and this is observed experimentally.

The trimethylene moiety can also be displaced from $[Pt(X)_2(C_3H_6)(L)_2]$ by other ligands, particularly those with high *trans* effects, and generally cyclopropane is evolved.[21] For the reaction

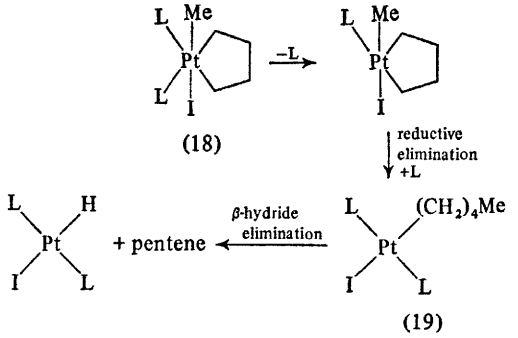
$$[Pt(X)_2(C_3H_6)(L^1)_2] + 2L^2 \longrightarrow [Pt(X)_2(L^2)_2] + 2L^1 + C_3H_6$$

the yield of cyclopropane depends on the nature of L^1, L^2, and X and on the solvent and temperature. The rate constants and even the reaction order vary with L^1, L^2, and solvent but with tractable systems in which X=Cl, L^1=pyridine or 4-methylpyridine, and $L^2=SbPh_3$, in DMF, reasonable Arrhenius plots were obtained from rates at three temperatures which allowed the derivation of activation energies $E_a = 82 \pm 14$ and 46 ± 3 kJ mol^{-1} respectively for the two reactions. In some systems where yields of cyclopropane were too low to enable the collection of kinetic data other products were detected in which the cyclopropane ring may still be intact but stability problems prevented isolation or identification of these species. A mechanism is proposed for these reactions which, like that suggested for the solid-state decomposition of $[Pt(X)_2(C_3H_6)(L)_2]$, involves ionic intermediates (17) due to X^- rather than L dissociation but, as the authors admit, some of the steps are rather speculative.

In these reactions, as with the thermally induced decomposition of the complexes described above, it is obvious that reductive elimination of cyclopropane is preferred to β-elimination, which would give propene. This can be compared with later reports that tetramethylene platinum complexes decompose mainly *via* β-hydride elimination to give but-1-ene[22] and it appears that the PtC_n ring size may to some extent control the decomposition pathway. This could be due to the rigidity of the PtC_3 ring which makes β-hydrogen abstraction more difficult than with the flexible PtC_4 ring.[20] Thermal decomposition studies on tetramethylene Pt^{IV} complexes in fact provide evidence for such conclusions but also show that the identity of the other ligands is

[21] P. W. Hall, R. J. Puddephatt, and C. F. H. Tipper, *J. Organometallic Chem.*, 1975, **84**, 407.
[22] M. P. Brown, A. Hollings, K. J. Houston, R. J. Puddephatt, and M. Rashidi, *J.C.S. Dalton*, 1976, 786.

important.[22] Thus $[Pt(Me)(C_4H_8)(I)(L)_2]$ (18) decomposes largely by β-elimination when L is a nitrogen donor ligand (*e.g.* L_2 = bipy) to give butene and methane but by reductive elimination when L is a tertiary phosphine. The proposed mechanism for the latter reaction involves preliminary phosphine dissociation and reductive elimination to give, after β-elimination from the pentyl Pt^{II} complex formed (19), pentene and *trans*-$[Pt(H)(I)(L)_2]$ (Scheme 9).



Scheme 9

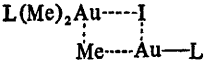
2 Group I

Gold.—Reactions of methyl iodide with [Au(Me)(L)] (L = tertiary phosphine) depend significantly on the nature of L, but when $L = PMe_3$ $[Au(Me)_3(L)]$ and [Au(I)(L)] are obtained first and this is followed by slow formation of *cis*-$[Au(Me)_2(I)(L)]$.[23] The first stage was followed by n.m.r. spectroscopy, and with high concentrations of MeI pseudo-first-order kinetics are obeyed with observed rate constants showing an approximate linear dependence on the methyl iodide concentration. Addition of the radical scavenger galvinoxyl had no effect on the rates, which rules out a free-radical mechanism. The first stage in the reaction takes place in two steps (4) and (5),

$$[Au(Me)(L)] + [MeI] \longrightarrow cis\text{-}[Au(Me)_2(I)(L)] \quad (4)$$

$$cis\text{-}[Au(Me)_2(I)(L)] + [Au(Me)(L)] \rightleftharpoons [Au(Me)_3(L)] + [Au(I)(L)] \quad (5)$$

according to an independent report, and reaction (4), in view of the kinetic studies, possibly follows an ionic pathway as proposed in related systems involving, *e.g.* $[Pt(PPh_3)_2]$. Methyl–iodo exchange (5) may involve a four-centre transition state (20)



(20)

and, as described on p. 344, the gold atoms do not undergo redox during the reaction. The second stage of the reaction to give $[Au(Me)_2(I)(L)]$ follows pseudo-second-order kinetics in neat methyl iodide, $k_{obs} = 1.63 \times 10^{-3}$ l mol^{-1} min^{-1}, but since satisfactory kinetic plots using methyl iodide solutions in benzene could not be obtained the order with respect to methyl iodide could not be determined. It is suggested that the second stage involves two processes,

[23] A. Johnson and R. J. Puddephatt, *J. Organometallic Chem.*, 1975, **85**, 115.

$$[Au(Me)_3L] + [Au(I)L] \rightleftharpoons cis\text{-}[Au(Me)_2(I)(L)] + [Au(Me)(L)]$$

$$[Au(Me)(L)] + MeI \longrightarrow cis\text{-}[Au(Me)_2(I)(L)]$$

but in the absence of data concerning the rate dependence with respect to [MeI] an unequivocal conclusion cannot be reached.

7

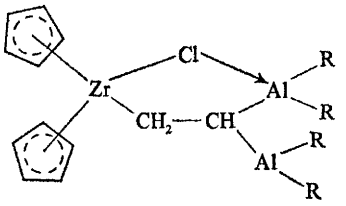
Isomerization: Intramolecular Processes

BY J. L. DAVIDSON

A number of reviews containing details of isomerization processes, or at least isomerism relevant to this chapter, have appeared.[1–5] Particularly welcome is the appearance of a book concerned wholly with the study of dynamic molecular rearrangements by n.m.r. techniques which, in addition to dealing with basic theory, contains comprehensive reviews on stereochemical non-rigidity in organometallic compounds and includes separate chapters on fluxional allyl compounds and carbonyl complexes.[6] However, as remarked by the author of the last chapter, this field is expanding so rapidly that the review is already somewhat dated. The rate of publication in this and other areas requires that a degree of selectivity must be exercised in the present Report, and although as many publications as possible have been included here the limitations of space have resulted in the exclusion of others.

1 Groups IV and V

Two independent isomerization processes are exhibited by organo-zirconium-aluminium compounds (1) according to ^1H n.m.r. spectroscopic studies.[7] The first



(1)

equilibrates the four methyl-group signals in the deuteriated complex with $R = CD_2$-Me and is considered to result from Al—Cl bond fission and rotation of the $(AlR_2)_2$-CH group about the C—C bond with $\Delta G^{\ddagger} = 17.1 \pm 0.3$ kcal mol^{-1}. The second phenomenon, with $\Delta G^{\ddagger} = 19.8 \pm 0.4$ kcal mol^{-1}, is probably a conformational

[1] M. H. Chisholm and S. Godleski, *Progr. Inorg. Chem.*, 1976, **20**, 299.
[2] R. K. Sheline and H. Mahnke, *Angew. Chem. Internat. Edn.*, 1975, **14**, 314.
[3] H. Brunner, *Topics Current Chem.*, 1975, **56**, 67.
[4] F. A. Cotton, *J. Organometallic Chem.*, 1975, **100**, 29.
[5] G. Deganello, P. Uguagliati, L. Calligaro, P. L. Sandrini, and F. Zingales, *Inorg. Chim. Acta*, 1975, **13**, 251.
[6] 'Dynamic Nuclear Magnetic Resonance Spectroscopy', ed. L. M. Jackman and F. A. Cotton, Academic Press, New York, 1975.
[7] W. Kaminsky and H. J. Vollmer, *Annalen*, 1975, 438.

exchange between two forms of the five-membered $ZrClC_2Al$ ring. I.r. spectroscopic studies of the allyl complexes $[MA_4]$, $[MA_2(cot)]$, $[M(Met)_2(cot)]$ and $[M(Crot)_2(cot)]$ (M = Zr or Hf; A = allyl, Met = methyl allyl and Crot = crotyl) distinguishes between three types of allyl complex σ, π, and $\sigma+\pi$, each of which, on the basis of variable-temperature ^1H n.m.r. studies, can be further subdivided into the categories static or dynamic.[8] As can be seen in Table 1 the classification of allyl complexes requires specification of temperature since one form can change to another.

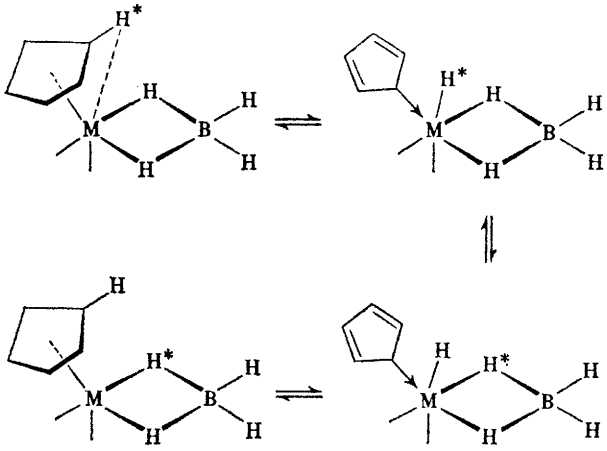
Table 1 *Classification of selected allyl complexes on the basis of i.r. and* ^1H *n.m.r. data (from ref.* 8)

Complex	*Solvent*	*T*/°C	*N.m.r. spectral type*	*Category*
$[ZrA_4]$	toluene	0	AX_4 (dynamic)	π-dynamic
$[ZrA_4]$	toluene	−80	AM_2X_2	π-static
$[Zr(Met)_2(cot)]$	toluene	+35	AX_4 (dynamic)	σ-dynamic
$[Hf(A)_2(cot)]$	THF	−90	$AMNX_2$	σ-static
$[Zr(A)_2(cot)]$	THF	−80	AX_4 (dynamic)	$(\sigma + \pi)$-dynamic
$[Hf(Crot)_2(cot)]$	toluene	−70		$(\sigma + \pi)$-static

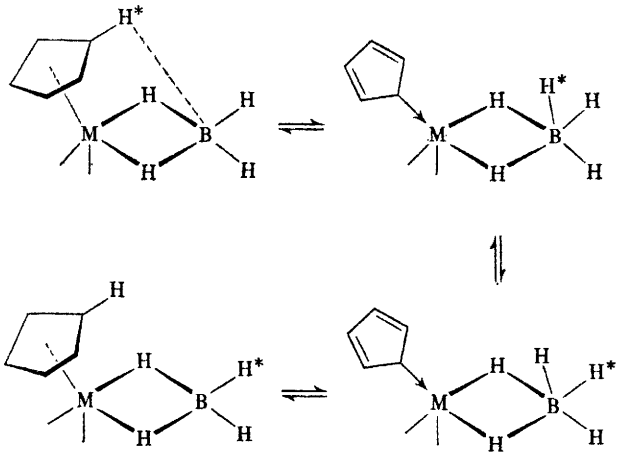
The ^1H n.m.r. spectrum of $[V(BH_4)(\eta\text{-}C_5H_5)_2]$ reveals the bridging and terminal BH_4 protons to be magnetically equivalent at ambient temperatures owing to an exchange process for which variable-temperature n.m.r. studies give a free energy of activation of 7.6 ± 0.3 kcal mol^{-1}.[9] This represents the first reported case of a transition-metal borohydride complex with a sufficiently high free-energy barrier to bridge–terminal hydrogen exchange to allow observation of a frozen structure at low temperature. The barrier to hydrogen exchange in the iridium complexes $[Ir(H)_2(BH_4)(L)_2]$ ($L = PMeBu^t_2$, PBu^t_3) must be significantly higher since fluxional character is not observed even at room temperature.[10] Dynamic intramolecular processes in $[M(BH_4)_2(\eta\text{-}C_5H_5)_2]$ (M = Zr or Hf) and $[Zr(H)(BH_4)(\eta\text{-}C_5H_5)_2]$ have been studied by variable-temperature n.m.r. methods and identified as hydrogen exchange between the C_5H_5 ring(s) and the tetrahydroborate ligand.[11] The free energies of activation are 21.3 ± 0.4, 19.4 ± 0.4, and 19.6 ± 0.4 kcal mol^{-1} respectively for the process which is also observed in the solid state. At temperatures which lead to this exchange the hydride signal of $[Zr(H)(BH_4)(\eta\text{-}C_5H_5)_2]$ remains sharp but eventually this also broadens as the hydride becomes involved in the hydrogen exchange and the barrier for this was found to be $\Delta G^{\ddagger} = 20.9$ kcal mol^{-1}. Proposed mechanisms for the process are illustrated in Schemes 1 and 2 and, although they cannot be distinguished at this stage, both involve a similar carbenoid intermediate regardless of whether the hydrogen is transferred initially to the boron (Scheme 1) or to the metal (Scheme 2).

Equilibration of the non-equivalent η-C_5H_5 and benzyl α-protons in the n.m.r. spectrum of the carbene complex $[Ta(CH_2Ph)(CHPh)(\eta\text{-}C_5H_5)_2]$ is attributed to the onset of rotation of the carbene ligand with a free-energy value of 19.3 ± 0.1 kcal

[8] E. G. Hoffman, R. Kallweit, G. Schroth, K. Seevogel, W. Stempfle, and G. Wilke, *J. Organometallic Chem.*, 1975, **97**, 183.
[9] T. J. Marks and W. J. Kennelly, *J. Amer. Chem. Soc.*, 1975, **97**, 1439.
[10] H. D. Empsall, E. Mentzer, and B. L. Shaw, *J.C.S. Chem. Comm.*, 1975, 861.
[11] T. J. Marks and J. R. Kolb, *J. Amer. Chem. Soc.*, 1975, **97**, 3397.



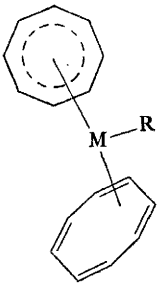
Scheme 1



Scheme 2

mol^{-1} at 393 K.[12] In the related complexes [Ta(Cl)(CHBu^t)(η-C_5H_5)$_2$] and [TaMe(CH_2)(η-C_5H_5)(η-C_5H_4Me)] the corresponding values are estimated to be 16.8 and 21.4 kcal mol^{-1} respectively, the differences possibly reflecting different steric requirements of the substituents on the carbene. The temperature dependence of the ^{1}H n.m.r. spectra of biscyclo-octatetraene complexes [M(R)(η^4-C_8H_8)(η^8-C_8H_8)] (2) (M = Nb or Ta; R = Me or Ph) is probably due to an intramolecular redox process involving exchange of the two C_8H_8 rings between η^4 and η^8 forms as found in the related complex [Ti(η-C_8H_8)$_2$].[13] The free energies of activation at 393 K are for M = Nb, R = Me 17.5 and R = Ph $\geq$17, and for M = Ta, R = Me 15.7 and R = Ph 16.5 kcal mol^{-1}.

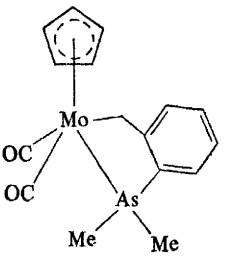
[12] L. J. Guggenberger and R. R. Schrock, *J. Amer. Chem. Soc.*, 1975, **97**, 6578.
[13] R. R. Schrock, L. J. Guggenberger, and A. D. English, *J. Amer. Chem. Soc.*, 1976, **98**, 903.



(2)

2 Group VI

The isomerization of *trans*-$[Mo(CO)_2(dpe)_2]$ to the *cis*-form has activation parameters $\Delta H^{\ddagger} = 13.3 \pm 0.4$ kcal mol^{-1} and $\Delta S^{\ddagger} = -16 \pm 3$ cal K^{-1} mol^{-1} and a rate constant at 25 °C of $1.1 \pm 0.06 \times 10^{-1}$ s^{-1}.[14] The isomerization of the corresponding tungsten complex takes place at a slightly greater rate but as with the molybdenum reaction follows first-order kinetics. A dissociative mechanism is favoured despite the negative entropy of activation and the rate-determining step is considered to be opening of one of the chelate rings. It should be noted however that an independent report indicates that an atmosphere of carbon monoxide stabilizes the *trans*-isomer, which suggests that CO dissociation is in fact the rate-controlling process.[15] The fluxional character of the arsenic donor compounds (3) is attributed to isomerization between the normal square-pyramidal form (3) and a trigonal-bipyramidal structure (4).[16] Free-energy values for the isomerization are 82.2 and 85.3 kJ mol^{-1} for R = Me and *p*-tolyl respectively.



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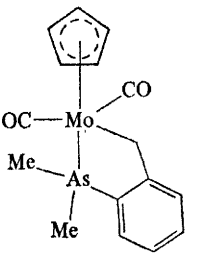
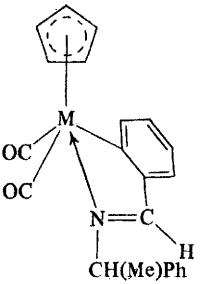


(4)



(5) a; M = Mo
b; M = W

Epimerization of diastereoisomers of related complexes $[M(CO)_2(LL')(\eta\text{-}C_5H_5)]$ (M = Mo or W) where LL′ is a bidentate ligand derived from Schiff bases of benzaldehyde (5) follows first-order kinetics with the activation parameters given in Table 2.[17] In these cases the epimerization process, as with pyridine carbaldehyde

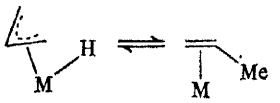
[14] C. M. Elson, *Inorg. Chem.*, 1976, **15**, 469.
[15] L. K. Holden, A. H. Mawby, D. C. Smith, and R. Whyman, *J. Organometallic Chem.*, 1973, **55**, 343.
[16] M. Mickiewicz, K. P. Wainwright, and S. B. Wild, *J.C.S. Dalton*, 1976, 262.
[17] H. Brunner and J. Wachter, *J. Organometallic Chem.*, 1976, **107**, 307.

Table 2 *Activation parameters for the racemization of benzaldimine complexes* (+)-$[M(CO)_2(LL')(\eta\text{-}C_5H_5)]$ *(from ref.* 17)

Metal	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta G^{\ddagger}$/kcal mol^{-1}	E_a/kcal mol^{-1}
Mo	-8.5 ± 0.8	18.9 ± 0.5	21.4 ± 0.6	19.5 ± 0.5
W	-8.6 ± 0.8	19.3 ± 0.4	21.8 ± 0.7	17.9 ± 0.4

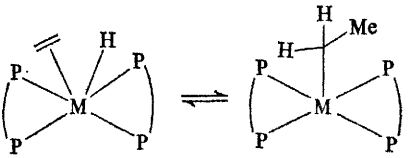
derivatives, probably involves a metal-centred intramolecular rearrangement *via* an intermediate analogous to (4). Interconversion of diastereoisomers of thioamide complexes $[Mo\{SC(R)NR'\}(CO)_2(\eta\text{-}C_5H_5)]$ [R = H, Me, or Ph, R' = (*S*)-α-phenylethyl] also follows first-order kinetics but, whereas the ^1H n.m.r. spectra of these complexes show only two $\eta\text{-}C_5H_5$ singlets and two CH_3 doublets, twice as many signals are observed for the complex with R = 1-naphthyl.[18] This is probably due to the existence of rotational isomers of each diastereoisomer with the 1-naphthyl groups in different orientations. The epimerization process has activation energies $\Delta G^{\ddagger} = 23.3\pm4.1$ and 24.3 ± 0.1 kcal mol^{-1} while the barrier to rotation of the 1-naphthyl group in the two diastereoisomers has $\Delta G^{\ddagger}$ values of 19.2 ± 0.3 and 18.8 ± 0.3 kcal mol^{-1}.

The ^1H n.m.r. of $[Mo(H)(\eta\text{-}C_3H_5)(dpe)_2]$ at +5 °C gives a metal–hydride resonance at τ 12.60 and characteristic η-allyl signals at τ 9.62, 8.84, and 6.28 (ratio 2:2:1).[19] The peaks at τ 12.60, 9.62, and 8.84 collapse to a single resonance at τ = 10.12 (5H) on raising the temperature, *i.e.* exchange of the hydride with the terminal protons of the η-allyl ligand occurs. This can be explained by the process in Scheme 3. Similarly the hydrido-ligand in $[Mo(H)(C_2H_4)_2(dpe)_2]^+$ exchanges



Scheme 3

rapidly and reversibly with the hydrogens of one of the ethylene ligands at 7 °C as a result of an insertion–de-insertion process, the first to be observed directly (Scheme 4). This is of particular interest in view of its relevance to many catalytic mechanisms

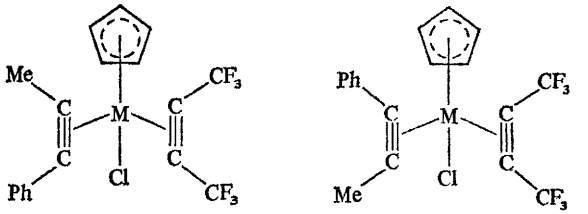


Scheme 4

and to the role of β-hydride elimination in the decomposition of metal alkyls. The precursor to the above complex $[Mo(C_2H_4)_2(dpe)_2]$ exhibits fluxional behaviour due to propeller rotation of the ethylene molecule with a barrier of 15.3 kcal mol^{-1}.[19] Propeller rotation of the two co-ordinated acetylenes is found in co-ordinatively unsaturated complexes $[Mo(X)(RC_2R)_2(\eta\text{-}C_5H_5)]$ (X = Cl, Br, or I, R = CF_3 or Me).[20]

[18] H. Brunner and J. Wachter, *Angew. Chem. Internat. Edn.*, 1976, **15**, 316.
[19] J. W. Byrne, H. U. Blaser, and J. A. Osborn, *J. Amer. Chem. Soc.*, 1975, **97**, 3871.
[20] J. L. Davidson and D. W. A. Sharp, *J.C.S. Dalton*, 1975, 2531.

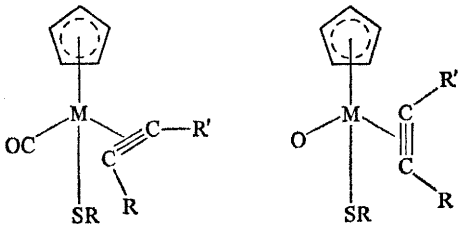
Free energies of activation are for X = Cl 9.3, Br 14.4, and I 12.7 kcal mol^{-1} for the but-2-yne complexes and 11.2 (Cl), 11.5 (Br), and 11.1 (I) kcal mol^{-1} for the hexafluorobut-2-yne derivatives. The observed trend in $\Delta G^{\ddagger}$ values may indicate that the steric and inductive properties of the halogens exert opposing effects on the rotational barrier. In a later paper[21] complexes containing two different co-ordinated acetylenes are described, a situation which leads to more complicated low-temperature behaviour. $[Mo(Cl)(CF_3C_2CF_3)(PhC_2Me)(\eta\text{-}C_5H_5)]$ for instance exists in two isomeric forms (6) and (7) at −90 °C as a result of the asymmetry of the acetylene



(6) (7)

PhC_2Me and the octahedral geometry of the complex. On warming to −70 °C the onset of rotation of this acetylene is observed in the ^1H n.m.r. spectrum with coalescence of the two methyl group signals. However, the two CF_3 signals of $CF_3C_2CF_3$ do not coalesce in the ^{19}F n.m.r. spectrum until the temperature reaches +30 °C. The difference in rotational barriers reflects the greater ability of $CF_3C_2CF_3$ to participate in π-back-bonding with the metal, which also results in a reduction of the coalescence temperature of the PhC_2Me rotation relative to that in $[Mo(Cl)(PhC_2Me)_2(\eta\text{-}C_5H_5)]$ (*ca.* −45 °C).

Co-ordinatively unsaturated monoacetylene complexes $[M(SR)(RC_2R')(CO)(\eta\text{-}C_5H_5)]$ (8) (M = Mo or W, R = CF_3 or C_6F_5, R′ = CF_3, Me, or Ph) have also been isolated, some of which undergo oxidation to $[M(SR)(O)(RC_2R')(\eta\text{-}C_5H_5)]$ (9).[22] Unlike the acetylenes in $[M(X)(RC_2R)_2(\eta\text{-}C_5H_5)]$ complexes propeller rotation is not observed in these compounds but *X*-ray studies have revealed that the orientation of the alkyne in (8) and (9) differs by *ca.* 90°, which may be explained by simple bond-



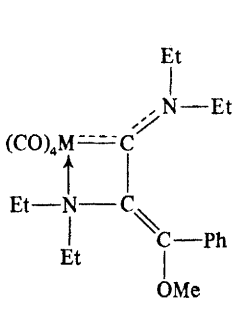
(8) (9)

ing arguments. Dynamic behaviour in the carbonyl complexes is attributed to restricted rotation of the SR group about the M—SR bond but this is prevented in the

[21] J. L. Davidson, M. Green, F. G. A. Stone, and A. J. Welch, *J.C.S. Dalton*, 1976, 738.
[22] P. S. Braterman, J. L. Davidson, and D. W. A. Sharp, *J.C.S. Dalton*, 1976, 241.

oxo-complexes by steric interaction with the acetylene ligand. It is speculated that the two rotamers found at low temperature result from preferred orientations of the SR group which coincide with the requirements of maximum p–d_π bonding from sulphur to the metal.

Hindered rotation of carbenes about the carbene carbon–metal bond is described in a recent publication[23] which gives $\Delta G^{\ddagger}$ values for the rotational barrier in the complexes *cis*-[M(CO)$_4$(carbene)$_2$] (M = Cr, Mo, or W). The fluxional behaviour observed in the carbene complexes [Cr(CO)$_4$(L){C(OMe)Me}] (L = tertiary phosphine, arsine, or stibine) is, however, due to rotation of the OMe substituent about the carbene C—O bond.[24] Free-energy values (*ca.* 11.3 kcal mol^{-1}) are close to those for analogous rotation of the NEt_2 group about the carbene C—N bond in (10) (11.9 kcal mol^{-1}).[25] The observation of one CO signal in the ^{13}C n.m.r. spectra of triazenido-complexes [M(NArNNAr′)(CO)$_2$(η-C$_5$H$_5$)] (M = Mo, or W, Ar and Ar′ = aryl groups) is attributed to intramolecular CO exchange rather than fluxional behaviour of the bidentate ligand.[26] In accord with this the signals due to the α-carbon atoms of the cyclopentadienyl group in (11) remain distinct and sharp at temperatures where the ^{13}CO signals have collapsed to a



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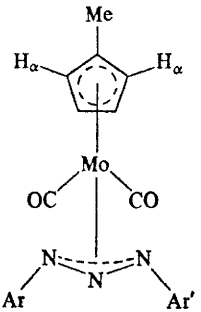

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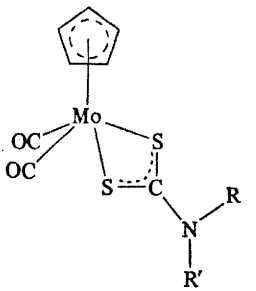
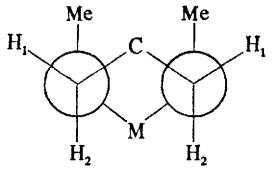


(12)

singlet. Intermolecular ligand exchange can also be excluded and it appears that CO exchange must involve a Berry-type pseudorotation with a trigonal-bipyramidal transition state. Dithiocarbamato-complexes [MoS$_2$C(NRR′)(CO)$_2$(η-C$_5$H$_5$)] (12) (R′ = H, R = CMe$_2$H or CMeHPh) similarly show no evidence for metal-centred rearrangements involving the bidentate ligand although fluxional behaviour due to rotation of the amido-group NRR′ results in epimerization in these chiral complexes with free energies of activation of *ca.* 15 kcal mol^{-1}.[27] Well resolved temperature-dependent ^{1}H n.m.r. spectra of the chelate complexes [M(CO)$_4$(msdp)] [M = Cr, Mo, or W, msdp = 1,3-bis(methylseleno)-(2,2-dimethylpropane)] have enabled lineshape fitting analysis and calculation of activation parameters for the dynamic processes exhibited by these compounds (Table 3).[28] Total inversion of the six-membered chelate ring from one *syn*-chair conformation (13) to the other (14) is

[23] C. G. Kreiter, K. Ofele, and G. W. Weiser, *Chem. Ber.*, 1976, **109**, 1749.
[24] E. O. Fischer and K. Richter, *Chem. Ber.*, 1976, **109**, 1140.
[25] K. H. Dotz and C. G. Kreiter, *Chem. Ber.*, 1976, **109**, 2026.
[26] E. Pfeiffer, J. Kuyper, and K. Vrieze, *J. Organometallic Chem.*, 1975, **105**, 371.
[27] H. Brunner, T. Burgemeister, and J. Wachter, *Chem. Ber.*, 1975, **108**, 3349.
[28] G. Hunter and R. C. Massey, *J.C.S. Dalton*, 1975, 209.



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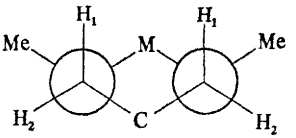


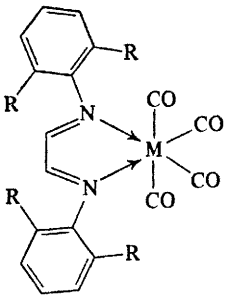
(14)

Table 3 *Thermodynamic parameters for the dynamic process in complexes* $[M(CO)_4(msdp)]$ *(from ref.* 28)

M	$\Delta G^{\ddagger}$ (I→II) (kJ mol^{-1})	$\Delta G^{\ddagger}$ (II→I) (kJ mol^{-1})	$\Delta H^{\ddagger}$ (I→II) (kJ mol^{-1})	$\Delta H^{\ddagger}$ (II→I) (kJ mol^{-1})	$\Delta S^{\ddagger}$ (I→II) (J K^{-1} mol^{-1})	$\Delta S^{\ddagger}$ (II→I) (J K^{-1} mol^{-1})
Cr	61.6	61.5	50.2	50.6	−38.0	−36.0
Mo	55.9	57.3	49.3	50.6	−22.0	−22.0
W	62.6	63.2	66.5	66.9	+13.0	−12.0

considered to be responsible for the changes in the n.m.r. spectra rather than lone pair inversion at selenium which is favoured by other workers to account for dynamic behaviour of 1,2-bis(ethylseleno)ethane palladium and platinum compounds. The significant differences in $\Delta S^{\ddagger}$ between the three complexes may be due to the greater symmetry of the transition state conformation of the ring system in chromium relative to tungsten complexes. The latter presumably has a twist-chair conformation in the transition state (*cf.* cyclohexane) whereas with chromium severe non-bonding interactions might lead to flattening of the ring and hence a more negative $\Delta S^{\ddagger}$.

The ^{13}C n.m.r. spectra of complexes $[M(CO)_4(LL)]$ (15) (LL = substituted glyoxal

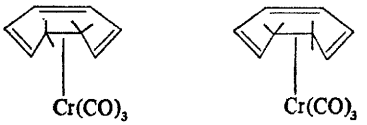


(15)

bis-arylimine) indicate that *cis–trans* interchange of carbonyl ligands occurs intramolecularly, possibly *via* a trigonal-prismatic transition state.[29] Intermolecular exchange can be ruled out since no exchange was observed between CO gas and the complexes containing ^{13}C isotopically enriched CO ligands. $\Delta G^{\ddagger}$ values are sensitive to the steric requirements of the substituents R and range from 10.0 ± 0.3 kcal mol^{-1} for R = *p*-MeC_6H_4 to *ca.* 25 kcal mol^{-1} for R = Bu^t. The cyclic olefins in complexes

[29] W. Majunke, D. Leibfritz, T. Mack, and H. tom Dieck, *Chem. Ber.*, 1975, **108**, 3025.

$[M(CO)_3(L)]$ (L = 1,3,5-cycloheptatriene, M = Cr, Mo, or W; L = 1,3,5-cyclo-octatriene or 1,3,5,7-cyclo-octatetraene, M = Cr or Mo) undergo restricted rotation about the three-fold axis of the $M(CO)_3$ moiety with free energies of activation ranging from 11.3 to 12.7 ± 0.3 kcal mol^{-1}.[30] In addition the cyclo-octatriene complex $[Cr(CO)_3(\eta\text{-}C_8H_{10})]$ exists in two enantiomeric forms (16) and (17) at



(16) (17)

-120 °C which interconvert at higher temperatures over a barrier of 8.3 ± 0.1 kcal mol^{-1}. Detailed studies of the dynamic behaviour of the cyclo-octatetraene complexes have been reported previously (see ref. 39) and are discussed in the next section (Group VII).

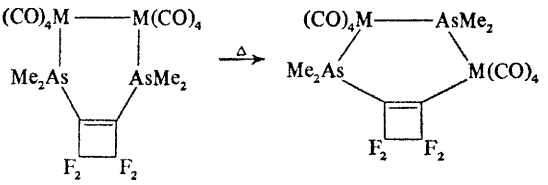
3 Group VII

The mechanism of isomerization of *fac*-$[Mn(X)(CO)_3\{P(OMe)_2Ph\}_2]$ to the *mer-trans*-form is most probably S_N1, with phosphite rather than carbonyl dissociation as the rate-determining step.[31] These conclusions are based on the observed first-order kinetics, the positive entropies of activation (Table 4), and the observation that the

Table 4 *Activation parameters for the isomerization of* fac-$[Mn(X)(CO)_3\{P(OMe)_2Ph\}_2]$ *(from ref.* 31)

X	$k_{obs} \times 10^6/s^{-1}$	E_a/kcal mol^{-1}	ΔS^*/cal K^{-1} mol^{-1}	*Solvent*
Cl	12.6	30.0 ± 0.5	17.7	C_6H_6
Cl	8.0	30.6 ± 0.5	18.7	DMF
Br	2.5	31.3 ± 0.2	18.8	C_6H_6

isomerization goes to completion even when reaction solutions are flushed with nitrogen. The addition of free phosphite has no effect on the reaction rate in contrast to the observed suppression of isomerization of *fac*-$[Mn(Br)(CO)_3\{P(OPh)_3\}_2]$ by excess $P(OPh)_3$.[32] The thermal rearrangement of $[MM'(CO)_8(f_4fars)]$ (M = M' = Mn or Re; M = Re, M' = Mn) to their structural isomers (Scheme 5) involves ligand

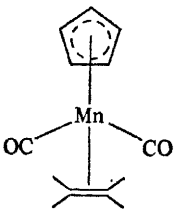


Scheme 5

[30] C. G. Kreiter, M. Lang, and H. Strack, *Chem. Ber.*, 1975, **108**, 1502.
[31] D. J. A. de Waal, R. H. Reimann, and E. Singleton, *J. Organometallic Chem.*, 1975, **84**, 339.
[32] R. J. Angelici, F. Basolo, and A. Poë, *J. Amer. Chem. Soc.*, 1963, **85**, 2215.

cleavage but kinetic studies do not allow positive conclusions to be reached about the mechanism.[33] The high activation entropies of $+15.0 \pm 4.7$ (Mn_2), $+23.2 \pm 1.1$ (Re_2), and 20.9 ± 2.8 (MnRe) cal K^{-1} mol^{-1} may imply that M—As cleavage is the rate-determining step but this does not exclude other possibilities. The racemization of complexes $[Mn(R)(NO)(PR'_3)(\eta\text{-}C_5H_5)]$, which proceeds by dissociative phosphine exchange, has already been described in Chapter 1, Section 1 and is one of the subjects reviewed in reference 3. Variable-temperature ^1H n.m.r. spectroscopy shows that the isocyanide ligands in $[Mn_2(CO)_7(CNMe)_3]$ are rapidly exchanged between the two metal atoms in a unimolecular intramolecular process with thermodynamic parameters $E_a = 12.9 \pm 1.0$ kcal mol^{-1}, $\log A = 8.9$, and $\Delta G^{\ddagger} = 18.2 \pm$ kcal mol^{-1}.[34] Two isocyanides or one isocyanide and a carbonyl group are considered to function as bridging ligands during the exchange reaction.

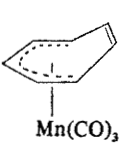
Herberhold has investigated fluxional behaviour in a variety of olefin compounds of stoicheiometry $[Mn(CO)_2(olefin)(\eta\text{-}C_5H_5)]$ and concluded that restricted rotation of the olefin about the metal–olefin bond is responsible.[35–37] The preferred orientation of the olefin is illustrated (18) which contrasts with the conformation found in



(18)

$[Mo(SC_6F_5)(CO)(CF_3C_2CF_3)(\eta\text{-}C_5H_5)]$ (8) or its oxo analogue (9) described earlier. The barrier to rotation is influenced by the nature of the substituents on the olefin, *e.g.* for ethylene $\Delta G^{\ddagger} = 8.4 \pm 0.2$ kcal mol^{-1} and for dimethyl fumarate $\Delta G^{\ddagger} = 11.0 \pm 0.4$ kcal mol^{-1}, values which are significantly lower than those for the structurally analogous chromium compounds $[Cr(CO)(NO)(olefin)(\eta\text{-}C_5H_5)]$,[35] 11.4 ± 0.2 and 15.9 ± 0.3 kcal mol^{-1} respectively for ethylene and dimethyl fumarate. The tetramethoxyethylene derivative $[Mn(CO)_2\{C_2(OMe)_4\}(\eta\text{-}C_5H_5)]$, in addition to olefin rotation ($\Delta G^{\ddagger} = 9.8 \pm 0.6$ kcal mol^{-1}), exhibits an independent process in which hindered rotation of the four methoxy-groups occurs about the olefin carbon C—O bond with $\Delta G^{\ddagger} = 13.8 \pm 0.3$ kcal mol^{-1}.[38] The ^{13}C n.m.r. spectra of the π-excessive molecule (η-cycloheptatrienyl)tricarbonylmanganese at low temperatures exhibits the pattern expected for the η^5 structure (19) but as the temperature is raised the lines broaden at unequal rates.[38] This rules out a random pathway for the exchange process and a 1,2-shift mechanism is favoured with $\Delta G^{\ddagger} = 14$ kcal mol^{-1} at 300 K. Thus the similarity between (19) and (20) (cyclo-octatetraenetricarbonyl-

[33] W. R. Cullen and F. L. Hou, *Canad. J. Chem.*, 1975, **53**, 1735.
[34] R. D. Adams and D. F. Chodosh, *J. Organometallic Chem.*, 1975, **87**, C48.
[35] H. Alt, M. Herberhold, C. G. Kreiter, and H. Strack, *J. Organometallic Chem.*, 1975, **102**, 491.
[36] M. Herberhold, G. O. Wiedersatz, and C. G. Kreiter, *J. Organometallic Chem.*, 1976, **104**, 209.
[37] M. Herberhold, C. G. Kreiter, S. Stuber, and G. O. Wiedersatz, *J. Organometallic Chem.*, 1975, **96**, 89.
[38] T. H. Whitesides and R. A. Budnik, *Inorg. Chem.*, 1976, **15**, 874.

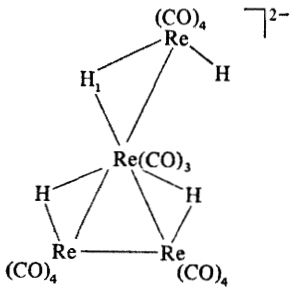


(19)

(20)

molybdenum), *i.e.* both have an uncomplexed double bond, is not sufficient to induce a random exchange mechanism in the former although this is found in the latter. It is further pointed out that an alternative to Cotton's mechanistic proposals[39] regarding the dynamic stereochemistry of this molybdenum compound exists, namely a dissociative process to give an η^4-cot ring rather than an associative one to give an η^8-ring.

Protonation of $[Re(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$ gives both *cis*- and *trans*-isomers of $[Re(H)(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]^+$ which interconvert within the time-scale of n.m.r. techniques.[40] Line-shape analysis gives an activation energy of 20 kcal mol^{-1} for the isomerization. Hydrogen tautomerism in $[Re_4(H)_4(CO)_{15}](NEt_4)_2$ (21) has been



(21)

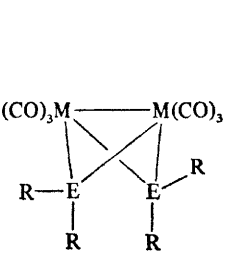
studied by ^{1}H n.m.r. spectroscopy over the temperature range -39 to 46 °C.[41] At 46 °C two equal-intensity singlets are present one of which does not change on cooling whereas the other broadens at 0 °C, collapses, and at lower temperatures splits into two well separated bands. Analysis of the spectra gives $E_a = 12.32 \pm 0.66$ kcal mol^{-1}, $\log A = 12.90 \pm 0.53$, $\Delta H^{\ddagger} = 11.73 \pm 0.66$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -1.35 \pm 2.21$ cal K^{-1} mol^{-1}. The changes in the spectra are thought to result from exchange of the terminal hydride with one of the three bridging hydrides (H_1) in a concerted bridge-making–bridge-breaking process.

4 Group VIII: Iron Triad

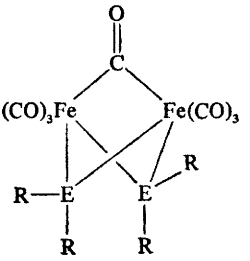
Iron.—The optically active complexes $(-)_{365}$-$[Fe(X)(CO)(PPh_2R)(\eta\text{-}C_5H_5)]$ {X = Cl or Br, $PPh_2R = (S)$-$(+)_{365}$-$[Ph_2PN(Me)CH(Me)Ph]$} epimerize in solution according to a first-order rate law.[42]

[39] F. A. Cotton, D. L. Hunter, and P. Lahuerta, *J. Amer. Chem. Soc.*, 1974, **96**, 7926.
[40] G. A. Panosyan, P. V. Petrovskii, N. I. Pyshnograyeva, N. E. Kolobova, V. N. Setkina, and E. I. Fedin, *J. Organometallic Chem.*, 1976, **108**, 209.
[41] P. Fantucci, *J. Organometallic Chem.*, 1976, **108**, 203.
[42] H. Brunner and G. Wallner, *Chem. Ber.*, 1976, **109**, 1053.

Two mechanisms have been considered for the dynamic process which equilibrates axial and equatorial groups R in complexes $[M_2(CO)_6(\mu\text{-}ER_2)_2]$ (M = Co, E = Ge or Sn; M = Fe, E = P or As) (22) and $[Fe_2(CO)_7(\mu\text{-}ER_2)]$ (E = Si or Sn) (23).

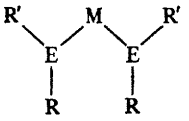


(22)



(23)

The first involves bridge cleavage prior to rearrangement while the second requires deformation (flapping) of the M_2E bridges without bond fission. Variable-temperature ^1H and ^{13}C n.m.r. studies of a number of compounds of type (22) have identified three independent processes, (i) CO scrambling, (ii) axial–equatorial R group exchange in a concerted fashion involving both ER_2 ligands without leading to isomer interconversion, and (iii) axial–equatorial R group exchange leading to interconversion of isomers.[43] The three isomers possible are structures (24), (25), and (26).



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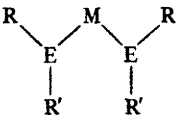
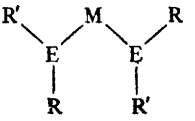


(25)



(26)

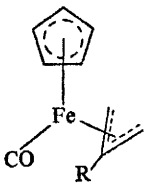
In view of the observation of (ii) and (iii) as distinct processes it would appear that isomer interconversion, which is the energy-demanding and slowest of the three processes, proceeds *via* a different mechanism to that which exchanges R groups within a single isomer. Accordingly (ii) is presumed to involve rearrangement without bridge cleavage whereas this is required in (iii). In addition to this, isomer interconversion also requires rotation about the M—E bond and inversion of configuration at the pyramidal atom E, both of which probably have high activation energies. No information about either process (ii) or (iii) is gained from the ^{13}CO n.m.r. data for the carbonyl ligands since CO scrambling is sufficiently facile that the signals have collapsed long before the onset of (ii) or (iii) is observed. This is in direct contrast to CO scrambling and R group exchange in $[Fe_2(CO)_7(\mu\text{-}SnBu^n_2)_2]$, type (23), which proceed concurrently with similar free energies of activation $\Delta G^{\ddagger} = 12.6 \pm 0.7$ and 13.0 ± 0.5 kcal mol^{-1} respectively.[44] These values are comparable to that for methyl-group exchange in the asymmetric isomer (26) of $[Fe_2(CO)_7(\mu\text{-}SnMePh)_2]$ ($\Delta G^{\ddagger} = 12.7 \pm 0.3$ kcal mol^{-1}). Significantly, however, this isomer undergoes exchange with a symmetric isomer at considerably higher temperatures.

[43] R. D. Adams, F. A. Cotton, W. R. Cullen, D. L. Hunter, and L. Mihichuk, *Inorg. Chem.*, 1975, **14**, 1395.

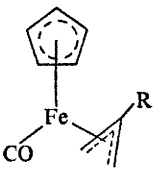
[44] T. J. Marks and G. W. Grynkewich, *J. Organometallic Chem.*, 1975, **91**, C9.

If the CO scrambling and methyl-group exchange are initiated by the same dynamic process and the comparable $\Delta G^{\ddagger}$ values and coalescence temperatures are not due to coincidence (as Cotton's results might suggest), then the low-energy exchange can be ascribed to the deformation mechanism while the high-energy exchange presumably arises from Fe—Sn bond cleavage.

The *endo*-isomer (27) of [Fe(CO)(η-2-RC_3H_4)(η-C_5H_5)] (R = H or Me) rearranges to the thermally stable *exo*-isomer (28) with $\Delta G^{\ddagger} = 24.1$ kcal mol^{-1}, $\Delta H^{\ddagger} = 26.2$



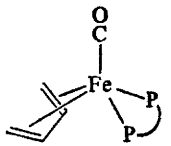
(27)



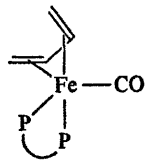
(28)

kcal mol^{-1}, and $\Delta S^{\ddagger} = 7.0$ cal K^{-1} mol^{-1} (R = Me).[45] The rates of interconversion of *syn*- and *anti*-isomers of Cl-substituted derivatives are similar to the rates of *endo–exo* isomerization, which leads to the suggestion that the same mechanism is responsible for both types of exchange *viz.* η^3–η^1–η^3 transformations. The *exo-syn*-isomers are the most stable and the *endo-anti* are the least stable in all cases studied, which contrasts with the lack of stability of the *exo*-isomers in [$M(CO)_2$(η^3-allyl)(η-C_5H_5)] (M = Mo or W). The latter undergo *endo–exo* isomerization by pseudorotation about the metal—allyl bond axis, a mechanism which fails to exchange the *syn* and *anti* substituents. A pseudorotation mechanism is symmetry allowed in the Group VI complexes but in the iron derivatives such a process leads to a significant decrease in metal—allyl bonding and the η^3–η^1–η^3 mechanism is therefore preferred for the latter.

PF_3 exhibits preference for an apical site in complexes [$Fe(CO)_{(3-x)}(PF_3)_x$-(butadiene)] rather than either of the two basal sites and in asymmetric methyl-substituted butadiene derivatives with $x = 2$ a secondary preference for the basal position *trans* to the methyl group is found.[46] Intramolecular exchange of PF_3 groups occurs in compounds with $x = 2$ or 3 and leads to equivalence of the PF_3 ^{19}F n.m.r. resonances, possibly *via* Berry pseudorotation. [Fe(CO)(dpe)(η-C_4H_6)] exists in two isomeric forms assigned structures (29) [basal–basal (bb) phosphine] and (30) [apical–basal (ab) phosphine] on the basis of their n.m.r. spectra.[47] Variable-temperature ^{31}P n.m.r. spectra provide evidence that interconversion of (29) and (30)



(29)

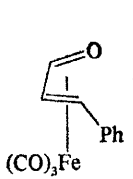


(30)

[45] R. W. Fish, W. P. Giering, D. Marten, and M. Rosenblum, *J. Organometallic Chem.*, 1976, **105**, 101.
[46] M. A. Bush and R. J. Clark, *Inorg. Chem.*, 1975, **14**, 226.
[47] C. B. Ungermann and K. G. Caulton, *J. Organometallic Chem.*, 1975, **94**, C9.

is rapid at 30 °C and that (30) undergoes an exchange process (30)⇌(30′) as a result of permutation of the non-equivalent apical and basal phosphorus nuclei. The main pathway for the latter process does not involve (29) as an intermediate according to ^{31}P n.m.r. spectra simulation, which gives $\Delta G^{\ddagger} = 12.6$ and 13.4 kcal mol^{-1} for the b–b and a–b exchanges respectively. Scrambling of phosphines (L) between apical and basal sites of complexes $[M(CO)_x(L)_{3-x}(diene)]$ (diene = cyclohexadiene or cycloheptadiene, M = Fe or Ru, L = 4-ethyl-1-phospha-2,6,7-trioxabicyclo[2,2,2]-octane, $x = 0$, 1, or 2) has also been studied by n.m.r. methods and both isomers, *i.e.* apical or basal L, were detected for most monosubstituted compounds ($x = 2$).[48] As with [Fe(CO)(dpe)(η^4-C_4H_6)] the bis-substituted complexes exist in two isomeric forms, the basal–basal (bb) and the apical–basal (ab), but only the (ab) isomer could be detected in some related Mn and Re complexes. In the iron and ruthenium compounds where both isomers are observed, examples are noted in which the rate of exchange between (bb) and (ab) is greater than that between (ab) and (ab′) which contrasts with the rates for exchange in [Fe(CO)(dpe)(η-C_4H_6)]. The phosphine ligand L also appears to have little preference for either an apical or basal site, unlike the PF_3 ligand in the diene complexes discussed earlier and in earlier reports (Vol. 3, p. 469). It is apparent from these three studies that the nature of the phosphine plays a significant role in determining the stability and rates of interconversion.

The free energy of activation for basal–apical CO exchange in tricarbonyl(1-methoxycyclohexa-1,3-diene)iron is 7.3 ± 0.2 kcal mol^{-1} which is almost identical to that in tricarbonyl(hexa-1,3-diene)iron.[49] Higher barriers are found in π-bonded heterodiene complexes; *e.g.* for compound (31) $\Delta G^{\ddagger} = 14.0$ kcal mol^{-1} whereas the σ–π and σ–σ azadiene derivatives (32; R = Bu^t) and (33; R′ = Pr^i) have barriers of less than 9 kcal mol^{-1}.[50]



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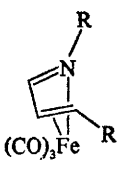

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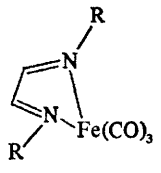


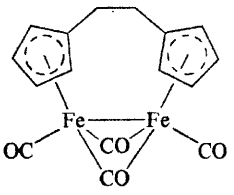
(33)

Six-co-ordinate Complexes. Graham originally reported that facile interconversion of *cis*- and *trans*-isomers of $[Os(SiMe_3)_2(CO)_4]$ at 55 °C is an intramolecular process which is rarely observed with six-co-ordinate compounds. Extensive ^{13}C n.m.r. studies of $[M(EMe_3)_2(CO)_4]$ (M = Fe, E = Si, Ge, or Sn; M = Ru or Os, E = Si, Ge, Sn, or Pb) and $[M(SiMe_{3-n}Cl_n)_2(CO)_4]$ (M = Fe, Ru, or Os, $n = 1$—3) have shown that this behaviour is fairly common in this type of complex.[51] Axial–equatorial CO exchange in the *cis*-isomers is also observed and detailed lineshape analysis of the ^{13}C n.m.r. data for $[Os(SiMe_3)_2(CO)_4]$ provides evidence that this occurs *via* the *trans*-isomer. The stereochemical rigidity of the chelate *cis*-[Fe($Me_2SiCH_2CH_2$-$SiMe_2$)$(CO)_4$] in which the *trans*-isomer is inaccessible is consistent with such a

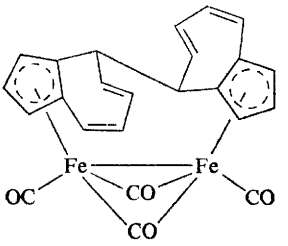
[48] T. H. Whitesides and R. A. Budnik, *Inorg. Chem.*, 1975, **14**, 664.
[49] J. Y. Lallemand, P. Laszlo, C. Muzette, and A. Stockis, *J. Organometallic Chem.*, 1975, **91**, 71.
[50] D. Liebfritz and H. tom Dieck, *J. Organometallic Chem.*, 1976, **105**, 255.
[51] L. Vancea, R. K. Pomeroy, and W. A. G. Graham, *J. Amer. Chem. Soc.*, 1976, **98**, 1407.

mechanism. The barriers to equatorial–axial exchange (and hence *cis–trans* isomerization) depend significantly on the central metal and are 6—8 kcal mol^{-1} higher with Ru and Os complexes.

In Volume 4 of these Reports the Adams–Cotton mechanism, which accounts for fluxional behaviour in $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and similar CO bridged complexes, was discussed at some length. This requires that CO bridge-opening leads directly to a staggered conformation of the non-bridged form, but other rotamers are also possible which allow both interconversion of isomers and bridge–terminal CO exchange to take place. When the η^5-rings are tied together as in (34) and in the azulenyl complex $[Fe_2(CO)_4(C_{10}H_{10}\text{—}C_{10}H_{10})_2]$ (35) some of these rotamers are rendered inaccessible



(34)



(35)

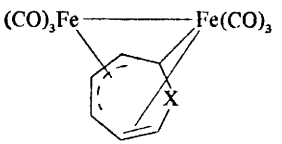
but this does not prevent bridge–terminal CO exchange taking place, although in the latter it is slowed down significantly.[52] The energy barrier to exchange in (34), $\Delta G^{\ddagger} = 11 \pm 1.5$ kcal mol^{-1}, is similar to that of the parent cyclopentadienyl complex whereas it is *ca.* 6 kcal mol^{-1} higher in (35). The Adams–Cotton scheme also requires that for a molecule such as $[Fe_2(CO)_3(L)(\eta\text{-}C_5H_5)_2]$, where L is a non-bridging ligand, bridge–terminal CO exchange must proceed with the same activation barrier as *cis–trans* isomerization. Any pathway allowing direct bridge–terminal exchange should be significantly slower and when $L = P(OPh)_3$ it is satisfying to note that no exchange is found even at 100 °C, since this complex cannot undergo exchange within the scheme.

The observation of a single C_5H_5 resonance in the ^{1}H n.m.r. spectrum of $[Fe_2(CO)_3(CNBu^t)(\eta\text{-}C_5H_5)_2]$ down to −120 °C originally led to the conclusion that *cis*- and *trans*-isomers were undergoing rapid interconversion even at this temperature. Since the Adams–Cotton scheme requires that, for this complex, isomerism must be accompanied by CO exchange the observation that the latter process does not occur below −30 °C is incompatible with this conclusion.[53] Clearly at −120 °C only one isomer is present in sufficient quantities to enable detection. Cotton and Todd have independently reported ^{13}C n.m.r. investigations of CO scrambling in $[Fe_2(CO)_6(C_4Ph_4CO)]$ and both give similar results, *i.e.* three distinct CO environments exist at −30 °C but above this CO exchange is observed with coalescence of signals at +30 °C (or +41 °C).[54,55] The activation energy E_a is *ca.* 13.4 (Todd) or 14.7 kcal

[52] F. A. Cotton, D. L. Hunter, P. Lahuerta, and A. J. White, *Inorg. Chem.*, 1976, **15**, 557.
[53] J. A. S. Howell, T. W. Matheson, and M. J. Mays, *J.C.S. Chem. Comm.*, 1975, 865.
[54] F. A. Cotton, D. L. Hunter, and J. M. Troup, *Inorg. Chem.*, 1976, **15**, 63.
[55] J. P. Hickey, J. R. Wilkinson, and L. J. Todd, *J. Organometallic Chem.*, 1975, **99**, 281.

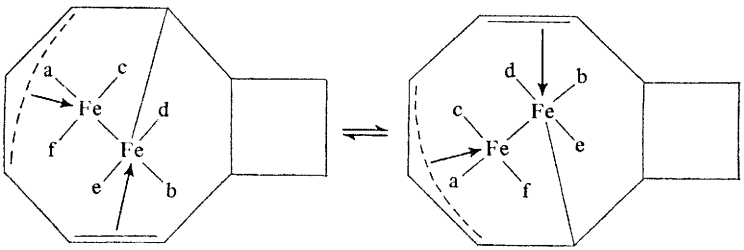
mol^{-1} (Cotton) while $\Delta G^{\ddagger} = 15.1$ kcal mol^{-1}, $\Delta H^{\ddagger} = 14.1$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -3.2$ cal K^{-1} mol^{-1} (Cotton). The data do not allow specification of a mechanism but local CO scrambling is preferred to exchange between the two metals *via* CO bridges. Local CO scrambling has been reported recently in guaiazulene-hexacarbonyldimolybdenum,[56] 4*H*-indenepentacarbonyldi-iron,[57] acenaphthylene-pentacarbonyldi-iron, and cycloheptatrienehexacarbonyldi-iron.[58]

Three dynamic intramolecular rearrangements have been identified in the cyclic-triene complexes (36a)[59] and (36b)[60] by variable-temperature ^{13}C n.m.r. methods. The spectrum of (36b) at -120 °C exhibits six signals of equal intensity for



(36) a; X = CH_2CH_2
b; X = $CHCH_2CH_2CH$

the carbonyl carbons consistent with the ground-state structure established by *X*-ray crystallography. Four of these collapse symmetrically on warming to -88 °C, an observation consistent with the onset of the twitching process illustrated in Scheme 6.



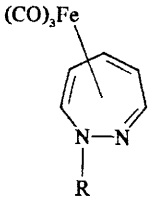
Scheme 6

Above this other changes are observed which imply that local scrambling of CO groups in the allyl-bonded $Fe(CO)_3$ group takes place followed at higher temperatures by the onset of local CO scrambling in the other $Fe(CO)_3$ moiety. An alternative explanation can account for the first set of changes (-120 to -88 °C) but this was eliminated by similar studies on a substituted derivative $[Fe_2(CO)_5(PEt_3)(C_{10}H_{12})]$. The above conclusions apply equally to complex (36a).

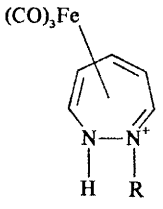
The isomerization to the 1,3-form of cyclohepta-1,4-diene co-ordinated to iron was the subject of earlier kinetic investigations and the preliminary communication has been followed up by a full report.[61] Fluxional behaviour in diazepineiron tricarbonyls (37) has been shown to require proton transfer *via* an intermolecular

[56] F. A. Cotton, D. L. Hunter, and P. Lahuerta, *J. Organometallic Chem.*, 1975, **87**, C42.
[57] D. G. Leppard, H. J. Hansen, K. Bachmann, and W. von Philipsborn, *J. Organometallic Chem.*, 1976, **110**, 359.
[58] F. A. Cotton, D. L. Hunter, and P. Lahuerta, *Inorg. Chem.*, 1975, **14**, 511.
[59] F. A. Cotton, D. L. Hunter, and P. Lahuerta, *J. Amer. Chem. Soc.*, 1975, **97**, 1046.
[60] F. A. Cotton and D. L. Hunter, *J. Amer. Chem. Soc.*, 1975, **97**, 5739.
[61] B. F. G. Johnson, J. Lewis, I. E. Ryder, and M. V. Twigg, *J.C.S. Dalton*, 1976, 421.

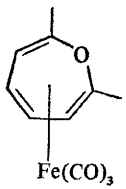
process.[62] The reaction is strongly acid-catalysed and proceeds through a fluxional η^4-imminium ion complex (38) which has been isolated and structurally characterized. However, η^4-imminium ions which result from protonation of non-fluxional diazepine derivatives are themselves non-fluxional. Oxepintricarbonyliron and its 2,7-dimethyl-substituted derivative (39) undergo rapid valence tautomerism with, in the case of the latter, an activation barrier of $\Delta G^{\ddagger} = 15.8 \pm$ kcal mol^{-1}.[63]



(37)

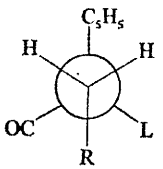


(38)



(39)

Rotational Isomerization. Steric effects strongly influence the relative energies of the staggered conformations of compounds [Fe(CH_2R)(CO)(L)(η-C_5H_5)] (R = Ph or $SiMe_3$, L = tertiary phosphine), the lowest-energy form (40) having the bulky C_5H_5 and R groups mutually *trans*.[64] Two higher-energy rotamers are also possible but with very crowded molecules, *e.g.* L = PPh_3, R = $SiMe_3$, one of these could not be detected. In addition to restricted rotation about Fe—C bonds, complexes of the above type may also exhibit isomerism of a rotational nature involving the Fe—P bond. In [Fe(CN)(CO)(L)(η-C_5H_5)] (L = PMe_2Ph or $PMePh_2$) the preferred conformer surprisingly is one in which the phenyl group(s) lies adjacent to the cyclopentadienyl ligand and the barrier to rotation is $\Delta G^{\ddagger} = 8.0$ kcal mol^{-1}.[65] ^{13}C and ^{1}H n.m.r. spectra contain averaged signals for *ortho* and *meta* nuclei on the aryl rings {in



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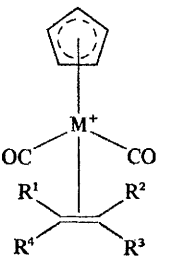


(41)

the presence of [Eu(fod)$_3$]}, which is attributed to rotation about the carbon—phosphorus bond of the phosphine. The free energy of activation for this process is 7.6 kcal mol^{-1}. Olefin rotation in [Fe$(CO)_2$(olefin)(η-C_5H_5)]$^+$ (olefin = C_2H_4, C_3H_6, 1-C_4H_8, *trans*-2-C_4H_8, or i-C_4H_8) and related indenyl complexes has also attracted attention and the energy barriers to free rotation of co-ordinated ethylene have been

[62] A. J. Carty, C. R. Jablonski, and V. Snieckus, *Inorg. Chem.*, 1976, **15**, 601.
[63] R. Aumann, H. Averbeck, and C. Kruger, *Chem. Ber.*, 1975, **108**, 3336.
[64] K. Stanley and M. C. Baird, *J. Amer. Chem. Soc.*, 1975, **97**, 4292.
[65] J. W. Faller and B. V. Johnson, *J. Organometallic Chem.*, 1975, **96**, 99.

calculated from ^{1}H n.m.r. data.[66] Values are $\Delta G^{\ddagger} = 7.8$ and 7.7 kcal mol^{-1} for the iron-C_5H_5 and -C_9H_7 complexes respectively, which are comparable to the barrier in $[Ru(CO)_2(C_2H_4)(\eta\text{-}C_5H_5)]^+$ (7.6 kcal mol^{-1}). The stable ground-state conformation (41) is analogous to that found in chromium and manganese complexes discussed earlier.[35–37] Consequently isomerism is possible with the substituted olefin derivatives, but the n.m.r. data do not allow unequivocal identification of preferred structures. Barriers to rotation are higher in the tin complexes $[Fe(SnR_3)(CO)(olefin)(\eta\text{-}C_5H_5)]$ (R = Me or Ph) by *ca.* 5 kcal mol^{-1}, probably as a result of the increased Fe—olefin back-bonding permitted by the greater electron density at the metal.[67] The presence of a chiral atom also permits diastereoisomers with propene complexes and in each case one is less stable than the other by *ca.* 3 kcal mol^{-1}. The orientation of the propene ligand deviates by 10—15° from a plane parallel to the plane of the C_5H_5 ring.

Hindered rotation of the NMe_2 groups about the C—N bond of both the carbene ligand and the amidinium cation of the complex $[Fe(CO)_4(CONMe_2)][C(H)(NMe_2)_2]$ is observed which leads to different coalescence temperatures (+7 °C and 40 °C respectively) for the two sets of methyl signals.[68] Energy barriers are also different, being 13.7 kcal mol^{-1} for the carbene ligand and 15.3 kcal mol^{-1} for the cation. Rotation of the NRH group about the C—N bond in the dithiocarbamate complex $[Fe(CO)(S_2CNRH)(\eta\text{-}C_5H_5)]$ ($R = CHMe_2$) has a barrier height $\Delta G^{\ddagger} = 16.6 \pm 0.3$ kcal mol^{-1} and results in racemization. Barriers to acyl group rotation in a number of acylferrocenes [FcCOR] have also been determined by ^{1}H and ^{13}C dynamic n.m.r. techniques which give values in the range 6.8—8.8 kcal mol^{-1} for $\Delta G^{\ddagger}$.[69] The rotational barrier of 1,1′-diacetylferrocene is lower than that of [FcCOMe] by 0.7 kcal mol^{-1} which may be due to interannular effects in which one acetyl group inductively diminishes the interaction of the other ring with its acetyl group.

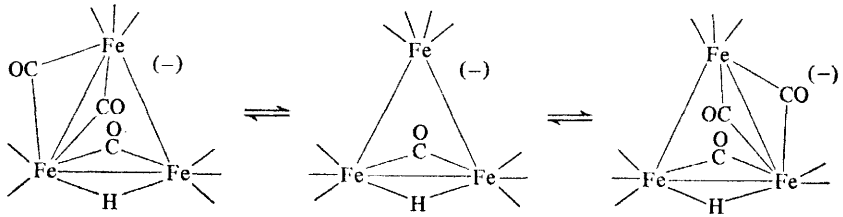
Ruthenium and Osmium.—Square-pyramidal compounds $[M(X)(Y)(PPh_3)_3]$ exhibit a dynamic process in solution which according to ^{31}P n.m.r. spectroscopy equilibrates apical and basal phosphine sites.[70] The measured values of $\Delta S^{\ddagger}$ (Table 5) are consistent with this being an intramolecular rearrangement (probably Berry pseudorotation) and since addition of PPh_3 does not effect the process a bimolecular exchange is also excluded.

Table 5 *Activation parameters for phosphine site exchange in* $[M(X)(Y)(PPh_3)_3]$ *(from ref.* 70)

M	X	Y	E_a/kcal mol^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
Ru	Cl	Cl	10.4	10.0	0.9
Ru	Cl	H	13.9	13.4	9.4
Os	Cl	Cl	11.5	11.0	−2.3
Os	Br	Br	13.6	12.0	0.4

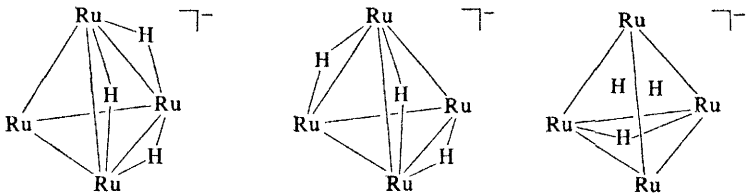
[66] J. W. Faller and B. V. Johnson, *J. Organometallic Chem.*, 1975, **88**, 101.
[67] J. W. Faller, B. V. Johnson, and C. D. Schaeffer, jun., *J. Amer. Chem. Soc.*, 1976, **98**, 1395.
[68] J. Schmetzer, J. Daub, and P. Fischer, *Angew. Chem. Internat. Edn.*, 1975, **14**, 487.
[69] J. Sandström and J. Seitz, *J. Organometallic Chem.*, 1976, **108**, 371.
[70] P. R. Hoffmann and K. G. Caulton, *J. Amer. Chem. Soc.*, 1975, **97**, 4221.

Scrambling of axial and equatorial CO groups on the $Ru(CO)_4$ unit of $[Ru_3(CO)_{10}(NO)_2]$ is observed in the ^{13}C n.m.r. spectrum but no scrambling in the $Ru(CO)_3$ units is detectable between -50 and $+40$ °C. Thus the axial–equatorial exchange must be a localized process since CO-bridged intermediates are not available for scrambling.[71] Ten of the eleven CO ligands in $[HFe_3(CO)_{11}]^-$ undergo scrambling *via* pair-wise opening and closing of CO bridges at -30 °C (Scheme 7). This corresponds



Scheme 7

to an oscillation rather than the complete CO migration process found in $Fe_3(CO)_{12}$. At higher temperatures all the carbonyls undergo site exchange. The slow exchange limit of $[H_2FeRu_3(CO)_{12}]$ is reached at -92 °C and eight CO resonances are observed in the ^{13}C n.m.r. spectrum which correlates with the structure given by *X*-ray crystallography.[72] As the temperature is raised complete localized scrambling at iron is observed first, possibly *via* bridge opening on the ruthenium side, followed by CO scrambling on the $Ru(CO)_3$ groups and finally over the whole cluster. Three distinct sets of carbonyls undergo localized scrambling in $[Os_6(CO)_{18}]$ at different temperatures with $\Delta G^{\ddagger}$ values of 61, 53, and 31 kJ mol^{-1} but CO migration is not observed between different metals.[73] $[Ru_4(H)_3(CO)_{12}]^-$ exists in solution as two rapidly interconverting isomers, one with C_{3v} symmetry (42) and the other with C_{2v} or C_2 symmetry (43).[74] The former is favoured in polar solvents and of three structures



C_{3v} C_2 C_{2v}

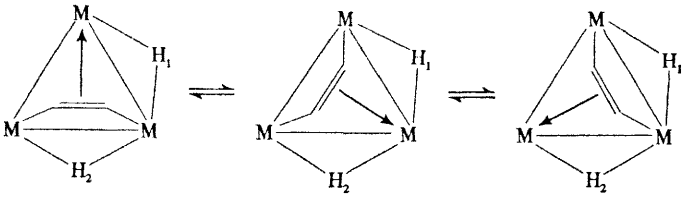
(42) (43)

considered the most polar and hence preferred isomer is (42). The three peaks in the ^1H n.m.r. spectrum at -79 °C due to isomer (42) (singlet) and isomer (43) (doublet + triplet) collapse simultaneously to a singlet at higher temperatures. This could be due

[71] A. Forster, B. F. G. Johnson, J. Lewis, T. W. Matheson, B. H. Robinson, and W. G. Jackson, *J.C.S. Chem. Comm.*, 1974, 1042.
[72] L. Milone, S. Aime, E. W. Randall, and E. Rosenberg, *J.C.S. Chem. Comm.*, 1975, 452.
[73] C. R. Eady, W. G. Jackson, B. F. G. Johnson, J. Lewis, and T. W. Matheson, *J.C.S. Chem. Comm.*, 1975, 958.
[74] J. W. Koepke, J. R. Johnson, S. A. R. Knox, and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1975, **97**, 3947.

solely to isomer exchange or alternatively to a combination of isomer exchange and intramolecular tautomerism. Lineshape analysis in conjunction with spin-saturation transfer experiments give results in accord with the latter and activation parameters are $\Delta H^{\ddagger} = \sim 11$ kcal mol^{-1}, $\Delta S^{\ddagger} = 0.2$—8 cal K^{-1} mol^{-1}.

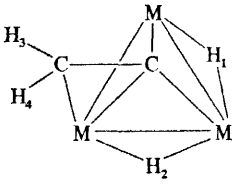
Previous studies have established that complexes of the type $[M_3(H)_2(RR'C_2)(CO)_9]$ obtained from the reactions of $[M_3(CO)_{12}]$ (M = Ru or Os) and olefins exist in two structural forms [(44) and (45)] and undergo two separate H-migration processes which equilibrate the two hydride-ligand positions. In addition an olefin rotation mechanism must also be considered for structure (44) (M = Ru, $RR'C_2$ = cyclo-octene; M = Os, $RR'C_2$ = cyclo-octene or MeC=CMe) according to ^{13}C n.m.r. studies.[75] On warming from the frozen limit hydrogen scrambling is observed resulting in collapse of a nine-line spectrum to five resonances for the CO ligands which further reduces to a four-line spectrum ($RR'C_2$ = cyclo-octene). The latter is ascribed to localized CO scrambling on the unique metal while for $RR'C_2 = Me_2C_2$ the observation of a two-line spectrum at this stage is consistent with localized CO scrambling or olefin rotation (Scheme 8). At higher temperatures all three complexes



(44)

Scheme 8

exhibit one CO peak as a result of total CO scrambling and/or localized scrambling accompanied by olefin rotation. Olefin rotation also accomplishes $H_1 \rightleftharpoons H_2$ site exchange and in favour of this mechanism is the fact that $\Delta G^{\ddagger}$ values for the highest-energy CO scrambling process calculated from ^{13}C n.m.r. data are identical to those obtained from ^{1}H n.m.r. data. Detailed studies of the H-exchange process in complexes of type (45) confirm the original suggestion that both $H_1 \rightleftharpoons H_2$ and $H_3 \rightleftharpoons H_4$



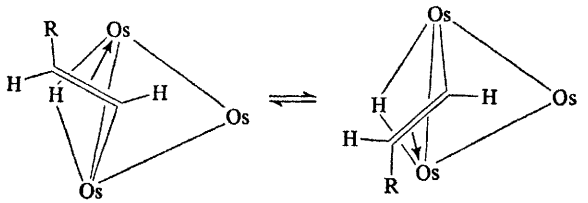
(45)

interconversion is achieved by H-migration from one edge of the metal triangle to the other.[76] Related complexes $[Os_3(H)(CH{=}CHR)(CO)_{10}]$ also undergo fluxional

[75] J. Evans, B. F. G. Johnson, J. Lewis, and T. W. Matheson, *J. Organometallic Chem.*, 1975, **97**, C16.

[76] W. G. Jackson, B. F. G. Johnson, and J. Lewis, *J. Organometallic Chem.*, 1975, **90**, C13.

motion which is considered to interchange the vinyl bonding mode (σ–π, π–σ) between the H-bridged metal atoms ($\Delta G^{\ddagger} = 10.3$ kcal mol^{-1}, R = H) (Scheme 9).[77]



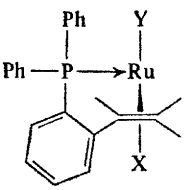
Scheme 9

The simultaneous collapse of the four ^{13}C signals of the η^6-cot ring in the variable-temperature ^{13}C n.m.r. spectrum of [Ru(cot)(nbd)] at the same rate parallels the behaviour of [M(CO)$_3$(cot)] (M = Cr, Mo, or W) and a similar mechanism for the fluxional process is proposed, *i.e.* random site exchange *via* an intermediate with an η^8-cot ring.[78] Approximate thermodynamic parameters are $\Delta S^{\ddagger} = -3 \pm 3$ cal K^{-1} mol^{-1} and $E_a = 14.0 \pm 1.5$ kcal mol^{-1} for the exchange process. However, the alternative mechanism proposed by Whitesides[38] for the exchange in [M(CO)$_3$(cot)] may also be applicable here. ^{13}C N.m.r. data confirm previous proposals that 1,2-shifts are responsible for fluxionality in [Ru(CO)$_3$(η-C$_8$H$_8$)] and are of more significance in [Fe(CO)$_3$(η-C$_8$H$_8$)] since an unequivocal decision could not be reached previously regarding the behaviour of this complex.[79] Hindered rotation of the cycloheptadienyl ligands about the metal–ligand axis is claimed to be responsible for the temperature dependence of the ^{13}C n.m.r. spectrum of [Ru(η-C$_7$H$_9$)$_2$], analysis of which yields $\Delta G^{\ddagger} = 8.1 \pm 0.2$ kcal mol^{-1} for the barrier to rotation.[80] Similar behaviour is exhibited by [Os(MR$_3$)(CO)$_2$(η-C$_7$H$_9$)] (MR$_3$ = SiMe$_3$, SiMe$_2$Ph, or GeMe$_3$) which gives two sets of ^{1}H n.m.r. signals at -100 °C due to different rotamers which interconvert at higher temperatures.[81] The precise nature of the fluxional behaviour which leads to pair-wise averaging of the ring protons of [Ru$_2$(I)(CO)$_4$(η-C$_7$H$_6$R)] (R = Me or Ph) cannot be ascertained from the n.m.r. data reported but two oscillatory processes are possible.[82]

A full report of ethylene rotation in [Os(CO)(NO)(C$_2$H$_4$)(PPh$_3$)$_2$]$^+$ has now appeared[83] and studies of this type have been extended to acetylene rotation in [Os(CO)(NO)(C$_2$H$_2$)(L)$_2$]$^+$,[84] which has energy barriers of $\Delta G^{\ddagger} = 11.5 \pm 0.2$ for L = PPh$_3$ and 14.4 ± 0.5 kcal mol^{-1} for L = P(C$_6$H$_{11}$)$_3$, dependent on the nature of L. The possibility that rotation is coupled with a Berry rearrangement as in [Fe(CO)$_4$(olefin)] cannot be excluded. Isomerization and exchange in [RuX(CO)(*o*-MeCHC$_6$H$_4$PPh$_2$)SP] (SP = *o*-styryldiphenylphosphine, X = Cl or CO$^+$) which have $\Delta G^{\ddagger}$ values of 15.2 ± 0.5 (44 °C) and $17.7 \pm$ kcal mol^{-1} (70 °C) respectively have been

[77] J. R. Shapley, S. I. Richter, M. Tachikawa, and J. B. Keister, *J. Organometallic Chem.*, 1975, **94**, C43.
[78] F. A. Cotton and J. R. Kolb, *J. Organometallic Chem.*, 1976, **107**, 113.
[79] F. A. Cotton and D. L. Hunter, *J. Amer. Chem. Soc.*, 1976, **98**, 1413.
[80] J. Muller, C. G. Kreiter, B. Mertschenk, and S. Schmitt, *Chem. Ber.*, 1975, **108**, 273.
[81] S. A. R. Knox, R. P. Philips, and F. G. A. Stone, *J.C.S. Dalton*, 1976, 552.
[82] J. C. Burt, S. A. R. Knox, and F. G. A. Stone, *J.C.S. Dalton*, 1975, 731.
[83] J. A. Segal and B. F. G. Johnson, *J.C.S. Dalton*, 1975, 677.
[84] J. A. Segal and B. F. G. Johnson, *J.C.S. Dalton*, 1975, 1990.

attributed to the existence of (46) and (47) which undergo exchange with (48) and (49).[85]



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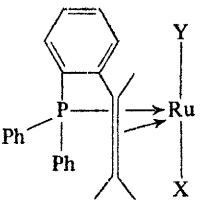

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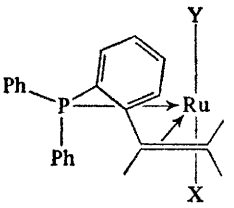

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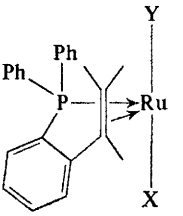


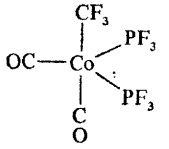
(49)

5 Group VIII: Cobalt Triad

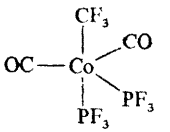
Cobalt.—Studies of fluxional behaviour in five-co-ordinate complexes are generally hampered by very low activation barriers and only in certain circumstances can the problem be overcome (see Vol. 4). However, the barriers in $[Co(SnR_3)(CO)_4]$ are sufficiently high to enable observation in the ^{13}C n.m.r. of separate resonances due to equatorial and axial carbonyl ligands.[86] $\Delta G^{\ddagger}$ values are 7.1, 7.2, 7.2, and 6.8 kcal mol^{-1} for R = Bz, Bu^n, Ph, and Me respectively. In addition $\Delta H^{\ddagger} = 8.2$ kcal mol^{-1} and $\Delta S^{\ddagger} = 7.1$ cal K^{-1} mol^{-1} for the benzyl derivative. It may be that the π-acceptor abilities of X in $[Co(X)(CO)_4]$ contribute significantly to raising or lowering the barrier to axial–equatorial CO interchange and hence determining whether the lower exchange rate limit is accessible. Such limits can generally be reached with less difficulty in molecules such as $[Co(Rf)(PF_3)_x(CO)_{4-x}]$ (Rf = CF_3, C_2F_5, or C_3F_7, $x = 1$—4) although even in these cases the limiting structure is not always observed at −100 °C.[87] Assuming an axial position for the Rf ligand and a trigonal-bipyramidal geometry the PF_3 groups can take up axial or equatorial positions in the molecule. Low-temperature ^{19}F n.m.r. spectra suggest that the equatorial isomer is increasingly favoured with $x = 2$ and 3 for Rf = CF_3 while axial PF_3 substituents are favoured with C_2F_5 and C_3F_7 derivatives. Isomer exchange can occur *via* Berry or turnstile mechanisms to give a high-energy intermediate with an equatorial Rf group which would return to the favoured axial site on the next inversion. A second dynamic process is also apparent in $[Co(CF_3)(CO)_{(4-x)}(PF_3)_x]$ ($x = 2$ or 3) since the minor isomer (50) still equilibrates at temperatures at which the major isomer (51) is static and this

[85] M. A. Bennet, R. N. Johnson, and I. B. Tomkins, *Inorg. Chem.*, 1975, **14**, 1908.
[86] D. L. Lichtenberger, D. R. Kidd, P. A. Loeffler, and T. L. Brown, *J. Amer. Chem. Soc.*, 1976, **98**, 629.
[87] C. A. Udovich, M. A. Krevalis, and R. J. Clark, *Inorg. Chem.*, 1976, **15**, 900.

equilibration process, of necessity, cannot involve a rearrangement which leads to isomer (51) since the latter is rigid.

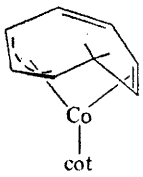


(50)

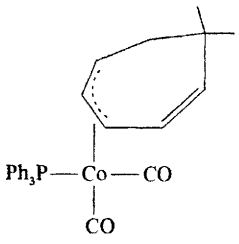


(51)

CO scrambling leads to equivalence of all carbonyl groups in $[Co_3(CMe)(CO)_8(L)]$ (L = tertiary phosphine) but only with the $P(C_6H_{11})_3$ derivative could the $\Delta G^{\ddagger}$ value be obtained for the barrier to exchange (-41.2 kJ mol^{-1}) from ^{13}C n.m.r. studies.[88] The complexes exist as equilibrium mixtures of two isomers, one with three bridging carbonyls the other with eight terminally bonded carbonyls. Conrotatory movement of *ca.* 100° about individual Co atoms around the basal triangle scrambles terminal-axial and bridging CO groups only and additional axial–equatorial CO interconversion *via* a twist mechanism about individual Co atoms is necessary to account for the total scrambling observed in the ^{13}C n.m.r. spectra. $[Co_4(CO)_{10}(RC_2R)]$ (R = CO_2Me or Ph) has a 'butterfly' structure with two asymmetrically bridging carbonyls. Above -70 °C CO scrambling over the whole cluster is observed in the ^{13}C n.m.r. spectra but in the region -104 to -70 °C each of the asymmetrically bonded CO groups only seem to interchange with one of the terminal carbonyls attached to the cobalt which has the shorter Co—CO(bridge) bond.[89] Complexes (52) and (53) exhibit fluxional behaviour in solution as a result of interconversion of



(52)



(53)

the two enantiomeric forms generated by the asymmetry of the Co—ring bonding.[90] Activation parameters for the process are $\Delta H^{\ddagger} = 14.5 \pm 1.5$, $\Delta G^{\ddagger} = 16.5 \pm 2$ kcal mol^{-1}, $\Delta S^{\ddagger} = -6.8 \pm 1.5$ cal K^{-1} mol^{-1} for (52) and $\Delta H^{\ddagger} = 11.3 \pm 1$, $\Delta G^{\ddagger} = 17.6 \pm 1.5$ kcal mol^{-1}, $\Delta S^{\ddagger} = -21.4 \pm 3$ cal K^{-1} mol^{-1} for (53).

Rhodium.—The temperature dependence of the ^1H n.m.r. spectra of trigonal-bipyramidal compounds [Rh(dtc)(RNC)$_2$(olefin)] (dtc = $Me_2NCS_2^-$, R = *p*-MeC_6H_4 or 2,4,6-$Me_3C_6H_2$, olefin = tcne, fumaronitrile, maleonitrile, or maleic anhydride)[91]

[88] T. W. Matheson and B. H. Robinson, *J. Organometallic Chem.*, 1975, **88**, 367.
[89] J. Evans, B. F. G. Johnson, J. Lewis, and T. W. Matheson, *J. Amer. Chem. Soc.*, 1975, **97**, 1245.
[90] P. V. Rinze, *J. Organometallic Chem.*, 1975, **90**, 343.
[91] T. Kaneshima, Y. Yumoto, K. Kawakami, and Tanako, *Inorg. Chim. Acta*, 1976, **18**, 29.

is thought to result from olefin rotation accompanied by Berry pseudorotation with the olefin as the pivot. This combination of intramolecular rearrangements is also found in acetylacetonato derivatives [Rh(acac)(RNC)$_2$(tcne)].[92] In addition the dtc–maleonitrile complexes appear to undergo dissociative exchange of the olefin at 25 °C which leads to loss of spin–spin coupling between the ^{103}Rh nucleus and the olefinic protons. The high barriers to rearrangement (see Table 6) contrast with the

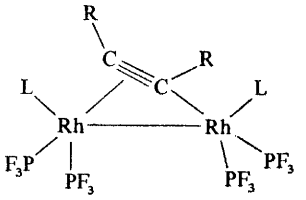
Table 6 *Barriers to intramolecular rearrangement in* [Rh(LL)(RNC)$_2$(olefin)] *(from ref.* 92)

LL	*Olefin*	R	$\Delta G^{\ddagger}$/kcal mol^{-1}
dtc	maleic anhydride	*p*-MeC$_6$H$_4$	10.9
dtc	maleonitrile	*p*-MeC$_6$H$_4$	13.4
dtc	maleonitrile	2,4,6-Me$_3$C$_6$H$_2$	13.3
dtc	fumaronitrile	*p*-MeC$_6$H$_4$	14.1
dtc	fumaronitrile	2,4,6-Me$_3$C$_6$H$_2$	14.1
dtc	tcne	*p*-MeC$_6$H$_4$	18.2
dtc	tcne	2,4,6-Me$_3$C$_6$H$_2$	18.4
acac	tcne	*p*-MeC$_6$H$_4$	14.8
acac	tcne	2,4,6-Me$_3$C$_6$H$_2$	14.6

values of 6—12 kcal mol^{-1} expected for the Berry process alone and further illustrate the effect of olefin rotation on barrier heights in five-co-ordinate metal-olefin complexes. Ethylene propeller rotation in [Rh(C$_2$H$_4$)$_2$(η-C$_5$Ph$_4$Cl)] has a free energy of activation $\Delta G^{\ddagger} = 16.4$ kcal mol^{-1}, similar to that calculated for [Rh(C$_2$H$_4$)$_2$(η-C$_5$H$_5$)].[93]

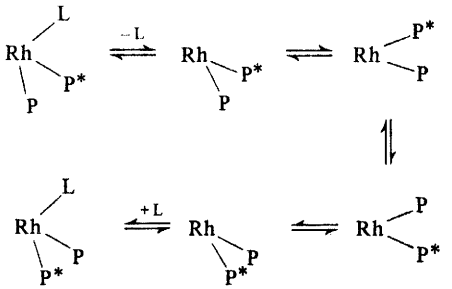
The ^{13}C n.m.r. spectra of [Rh$_2$(CO)$_2$P(OPh)$_3$(η-C$_5$H$_5$)] demonstrate that exchange between the bridging and terminal CO groups occurs readily and the energy barrier was found to be $\Delta G^{\ddagger} = 8.8 \pm 0.5$ kcal mol^{-1}.[94] The ^{1}H and ^{31}P n.m.r. spectra are temperature invariant between −90 and 20 °C, which clearly indicates that the phosphite ligand remains attached to the same metal atom during the exchange, and a mechanism for CO scrambling involving a bridging phosphite is therefore eliminated. Carbonyl exchange in rhodium cluster compounds is speculated to be facilitated by the accessibility of an intermediate which involves minimal changes in symmetry, co-ordination numbers of the metal atoms, and total back-bonding relative to the solid-state structure.[95] On this basis carbonyl scrambling in [Rh$_6$(CO)$_{15}$]$^{2-}$ is possible but not in [Rh$_6$(CO)$_{16}$] while only restricted exchange is possible in [Rh$_7$(CO)$_{16}$]$^{3-}$. Fluxional behaviour in [Rh$_2$(PF$_3$)$_6$(acetylene)] derivatives was discussed in Volume 3, p. 475, and full details of this[96] in addition to further studies of related systems are the subject of a series of recent reports. Complexes of this type undergo substitution reactions to give [Rh(PF$_3$)$_4$(L)$_2$(RC$_2$R′)] (L = tertiary phosphine or arsine) and when R ≠ R′ the ^{19}F n.m.r. spectra show two signals due to PF$_3$ groups in two different environments near ambient temperatures.[97] This is explicable, according to *X*-ray

[92] T. Kaneshima, K. Kawakami, and T. Tanaka, *Inorg. Chim. Acta*, 1975, **15**, 161.
[93] K. J. Reimer and A. Shaver, *J. Organometallic Chem.*, 1975, **93**, 239.
[94] J. Evans, B. F. G. Johnson, J. Lewis, and T. W. Matheson, *J.C.S. Chem. Comm.*, 1975, 576.
[95] B. T. Heaton, A. D. C. Towl, P. Chini, A. Fumagalli, D. J. A. McCaffrey, and S. Martinengro, *J.C.S. Chem. Comm.*, 1975, 523.
[96] M. A. Bennet, R. N. Johnson, and T. W. Turney, *Inorg. Chem.*, 1976, **15**, 90.
[97] M. A. Bennet, R. N. Johnson, G. B. Robertson, T. W. Turney, and P. O. Whimp, *Inorg. Chem.*, 1976, **15**, 97.



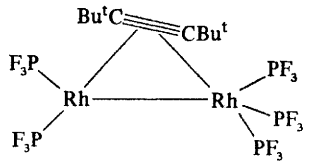
(54)

studies, in terms of structure (54) (L = PPh_3, R = R′ = Ph). Raising the temperature results in intramolecular PF_3 exchange and lineshape analysis gives free energies of activation ranging from 13.5 ± 0.3 kcal mol^{-1} for L = $AsPh_3$ to 17.9 ± 0.5 kcal mol^{-1} for L = $PMePh_2$ (R = Ph, R′ = Me). Exchange of free and co-ordinated diphenylmethylarsine occurs in $[Rh_2(PF_3)_4(AsMePh_2)_2(PhC_2Me)]$ simultaneously with intramolecular PF_3 exchange and consequently the latter process is probably triggered by initial dissociation of L. Since addition of free phosphine or arsine does not alter the rate of PF_3 exchange M—L bond fission is most likely the rate-determining step in the rearrangement. A possible mechanism for PF_3 exchange is illustrated in Scheme 10 and finds support in the isolation of a di-t-butylacetylene complex which has been



Scheme 10

assigned structure (55).[98] The two PF_3 ligands of the $Rh(PF_3)_2$ moiety undergo mutual exchange simultaneously with, but independently of, PF_3 exchange in the $Rh(PF_3)_3$ group and with the same energy of activation ($\Delta G^{\ddagger} = 15.1 \pm 0.5$ kcal



(55)

mol^{-1}) which suggests that exchange is due to rotation of $Rh(PF_3)_2$ and $Rh(PF_3)_3$ about the metal—metal double bond. If the intermediate produced by dissociation of L from $[Rh_2(PF_3)_4(L)_2(RC_2R)]$ has a structure similar to (55) then recombination of

[98] M. A. Bennet, R. N. Johnson, and T. W. Turney, *Inorg. Chem.*, 1976, **15**, 111.

L can occur on either side of the $Rh(PF_3)_2$ plane and so provide an alternative mechanism for PF_3 exchange in (54). (55) also reversibly adds on equivalent of PF_3 to give $[Rh_2(PF_3)_6(Bu^tC_2Bu^t)]$ which exchanges PF_3 both intermolecularly and intramolecularly, the latter with a free energy of activation of 13.3 ± 0.2 kcal mol^{-1}. Dimethyl acetylenedicarboxylate and methyl propiolate react with $[Rh_2(PF_3)_8]$ to give rhodiacyclopentadienes $[Rh_2(PF_3)_5\{C_4(CO_2Me)_2R_2\}]$ (R = CO_2Me or H) rather than monoacetylene complexes.[99] The $Rh(PF_3)_3$ unit exhibits fluxional behaviour in the ^{19}F n.m.r. spectra with $\Delta G^{\ddagger} = 10.5 \pm 0.5$ and 10.3 ± 0.2 kcal mol^{-1} for R = CO_2Me and H respectively but no changes were observed in the spectrum of $Rh(PF_3)_2$ moiety. Concerted PF_3 rotation around the metal about a general axis is the favoured mechanism for this exchange process.

Conformational isomerism in the chelate ring of [Rh(Cl)(CO)(PCN)] (PCN = *o*-diphenylphosphino-*NN*-dimethylbenzylamine) is thought to be responsible for the observed *N*-methyl group site exchange in the ^1H n.m.r. spectrum.[100] The free energy of activation for the interchange is 8.8 kcal mol^{-1}.

Iridium.—The activation entropies for phosphorus site exchange in complexes $[Ir(CO)(LL)_2]^+$ (LL = dpe, dpp, or dpm) are characteristic of an intramolecular process although the simplicity of the ^{31}P n.m.r. spectra precludes more detailed discussion of the mechanism.[101] Rearrangement is also facilitated by CO dissociation but this pathway is much slower than the intramolecular one. Activation parameters indicate that the ring size of the co-ordinated chelate affects the barrier to rearrangement such that smaller rings facilitate the site exchange. Values are for LL = dpe $\Delta H^{\ddagger} = 12.2$ kcal mol^{-1}, $\Delta S^{\ddagger} = -6.3$ cal K^{-1} mol^{-1} and for LL = dpp, $\Delta H^{\ddagger} = 10.2$ kcal mol^{-1}, $\Delta S^{\ddagger} = 4.9$ cal K^{-1} mol^{-1}. Stereochemical non-rigidity in five-co-ordinate compounds $[IrL'_5]^+$, $[IrL'_4L]^+$, and $[Ir(CO)L'_4]^+$ [L = PPh_3, L' = $P(OCH_2)_3CMe$] probably results from site exchange *via* Berry pseudorotation.[102] However, equilibration of axial and equatorial ligands L' in $[Ir(CO)(L')_3(L)]^+$ requires four Berry motions while a tetrahedral edge-traverse mechanism achieves this in a more economical fashion.

The higher energy barriers to intramolecular rearrangements in six-co-ordinate octahedral complexes have already been commented upon and it is interesting therefore to find a report of site exchange in *cis*-$[Ir(Cl)(H)(dpp)_2]^+$ which has activation parameters $\Delta H^{\ddagger} = 11.3$ kcal mol^{-1} and $\Delta S^{\ddagger} = -0.3$ cal K^{-1} mol^{-1}.[101] This corresponds to equilibration of axial and equatorial phosphorus atoms between -74 and $+35$ °C. The lack of molecular symmetry in this cation requires four different phosphorus signals in the ^{31}P n.m.r. spectrum at the slow exchange limit but, even at -93 °C, there is no evidence for more than two, so that a second, faster process which permutes the equatorial sites *trans* to H and Cl is indicated. With $[Ir(Cl)(H)(dpe)_2]^+$ no change in the spectrum occurs on lowering the temperature so that even the slow process has too low an energy barrier to be affected. Comparison of these compounds with other octahedral complexes suggests that rearrangement barriers in six-co-ordinate species may be reduced by introducing five-membered chelate rings (such as dpe) in conjunction with a hydride ligand.

[99] M. A. Bennet, R. N. Johnson, and T. A. Turney, *Inorg. Chem.*, 1976, **15**, 107.
[100] T. B. Rauchfuss, F. T. Patino, and D. M. Roundhill, *Inorg. Chem.*, 1975, **14**, 652.
[101] J. S. Miller and K. G. Caulton, *J. Amer. Chem. Soc.*, 1975, **97**, 1067.
[102] J. S. Miller and K. G. Caulton, *Inorg. Chem.*, 1975, **14**, 2296.

6 Group VIII: Nickel Triad

General.—Reference has already been made in Chapter 1 to the development of computer programmes applicable to intermolecular exchange in $[M(H)(L)_3]^+$ (M = Ni, Pt, or Pd) and these are also of interest to readers of this section particularly since intramolecular rearrangements are also considered.[103,104] $[M(H)(L)_3]^+$ and free ligand L exist in equilibrium with $[M(H)(L)_4]^+$ (L = PEt_3) according to n.m.r. studies but with M = Pt or Pd very low temperatures are required to detect the five-co-ordinate species.[104] Generally the rate of ligand dissociation is greater than the rate of intramolecular rearrangement but in the absence of free ligand the n.m.r. spectra are independent of temperature, *i.e.* $[M(H)(L)_3]^+$ does not show fluxional behaviour. Fluxional behaviour in $[M(H)(L)_4]^+$ could not be studied owing to its low concentration. However, $[Ni(H)(PEt)_3)_3]^+$ undergoes two types of rearrangement above −90 °C, one of which is thought to be mutual exchange of ligands between different sites since the entropy of activation is low (−7.9 cal K^{-1} mol^{-1}) but the nature of the other process (above −20 °C) is unknown. Addition of PEt_3 gives $[Ni(H)(PEt_3)_4]^+$ in equilibrium with PEt_3 and $[Ni(H)(PEt_3)_3]^+$ but this time an analysis of the intramolecular rearrangement in the five-co-ordinate complex was possible since the equilibrium strongly favours the latter. Thus for M = Pt or Pd the equilibrium

$$[M(H)(L)_3]^+ + L \rightleftharpoons [M(H)(L)_4]^+$$

lies so far to the left that only parameters for the associative intramolecular process could be studied whereas with nickel it lies so far to the right that both intramolecular processes could be analysed. The thermodynamic parameters are given in Table 7.

Table 7 *Thermodynamic parameters for intramolecular and intermolecular processes exhibited by* $[M(H)(L)_3]^+$ *and* $[M(H)(L)_4]^+$ (M = Ni, Pd, *or* Pt) (*from ref.* 104)

Process	$\Delta G^{\ddagger}$/ kcal mol^{-1}	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal K^{-1} mol^{-1}	*T*/K
L + $[Pt(H)(L)_3]^+ \rightarrow [Pt(H)(L)_4]^+$	10.9	2.4	−28.5	209
L + $[Pd(H)(L)_3]^+ \rightarrow [Pd(H)(L)_4]^+$	10.2	1.9	−27.8	298
$[Ni(H)(L)_4]^+ \rightarrow [Ni(H)(L)_3]^+$ + L	9.5	9.7	1.0	200
$[Ni(H)(L)_3]^+$ (intramolecular)	11.2	9.6	−7.9	200
$[Ni(H)(L)_4]^+$ (intramolecular)	5.6	—		126

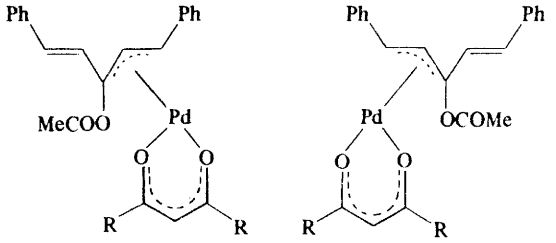
Nickel.—Dechelation of the (acac) ligand in $[Ni(Me)(acac)(PPh_3)_2]$ and $[Ni(R)(acac)(PPh_3)]$ (R = Et, COMe, or COEt) seems the most probable mechanism by which the (acac) methyl groups undergo exchange.[105,106] The ethyl derivative has a $\Delta G^{\ddagger}$ value of *ca.* 42 kJ mol^{-1} for the process.

Palladium.—A number of mechanisms have been considered for phosphine-catalysed *cis–trans* isomerism in square-planar $[M(X)_2(L)_2]$ complexes of the nickel subgroup (Vol. 4, p. 383). One of these, solvent- or phosphine-assisted consecutive displace-

[103] P. Meakin, A. D. English, and J. P. Jesson, *J. Amer. Chem. Soc.*, 1976, **98**, 414.
[104] A. D. English, P. Meakin, and J. P. Jesson, *J. Amer. Chem. Soc.*, 1976, **96**, 422.
[105] T. Yamamoto, T. Sayuyama, T. Nokamura, and A. Yamamoto, *Bull. Chem. Soc. Japan*, 1976, **49**, 589.
[106] T. Saruyama, T. Yamamoto, and A. Yamamoto, *Bull. Chem. Soc. Japan*, 1976, **49**, 546.

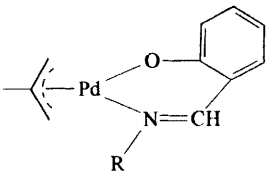
ment of phosphine *via* an intermediate $[Pd(X)_2(P)_2(S)]$ [X = Cl^- or N_3^-, P = $P(p\text{-}ZC_6H_4)_nMe_{3-n}$, S = solvent or catalysing phosphine], is preferred for the rearrangement of *cis*-$[Pd(X)_2(P)_2]$ to the *trans*-isomer.[107,108] Activation energies lie in the range 21.0—24.0 kcal mol^{-1} for these entropy-controlled reactions.

Previous studies of isomerism in dialkylsulphurdi-imine complexes $[Pt(Cl)_2(L)(RN{=}S{=}NR)]$ have been extended to their palladium analogues.[109] While intramolecular rearrangements similar to those exhibited by the platinum complexes are found, the dominating features are intermolecular processes resulting from facile cleavage of the Pd—N bond. Fluxional behaviour in the acetylacetonato-complex (56) is thought to arise from dynamic exchange between the two allylic forms



(56)

illustrated.[110] Lineshape analysis of the vinylic protons in $[^2H_8]$toluene gave activation parameters $\Delta H^{\ddagger} = 62 \pm 6$ (R = Me) and 55 ± 3 (R = CF_3) kJ mol^{-1} and $\Delta S^{\ddagger} = -44 \pm 17$ (R = Me) and -37 ± 9 (R = CF_3) J K^{-1} mol^{-1}. The asymmetry of the N,O-donor chelate in (57) places the two ends of the allyl group in different

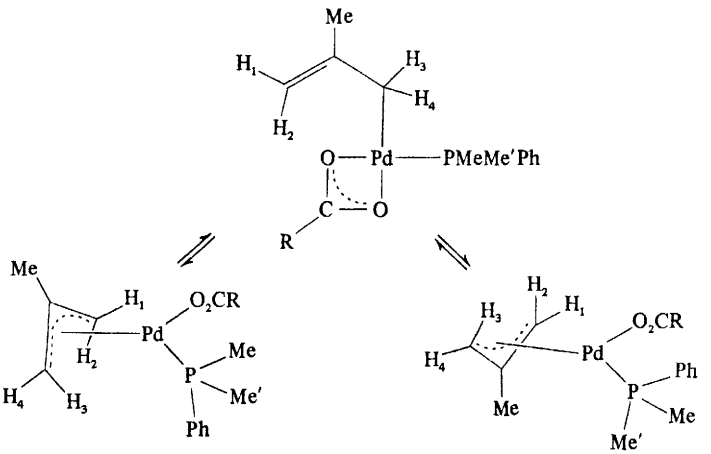


(57)

environments but low-temperature ^1H n.m.r. data show that end-to-end exchange occurs readily.[111] This is achieved by simple rotation of the allyl group but, since the rate of exchange exhibits some dependence on the complex concentration, a bimolecular mechanism is also considered to contribute to the isomerism. The latter may be similar to that postulated for *syn–syn* and *anti–anti* exchange in allylic palladium picolinate complexes whereby the co-ordination sites of the N—O donor ligand are interchanged. Free energies of activation range from 73.3 to 82.9 kJ mol^{-1} for the exchanges in (57). In contrast 3,4-(*syn–anti*) allylic proton site exchange is found in $[Pd(O_2CR)(PR'_3)(\eta\text{-allyl})]$ and a π–σ–π intramolecular mechanism is reasonably well

[107] A. W. Verstuyft and J. H. Nelson, *Inorg. Chem.*, 1975, **14**, 1501.
[108] D. A. Redfield, L. W. Cary, and J. H. Nelson, *Inorg. Chem.*, 1975, **14**, 50.
[109] J. Kuyper, P. I. van Vliet, and K. Vrieze, *J. Organometallic Chem.*, 1976, **108**, 257.
[110] A. Sonoda, B. E. Mann, and P. M. Maitlis, *J. Organometallic Chem.*, 1975, **96**, C16.
[111] I. D. Rae, B. E. Rechert, and B. O. West, *J. Organometallic Chem.*, 1974, **81**, 227.

established for processes such as this.[112] The intermediate σ-allyl complex is stabilized by chelation of the carboxylate group (Scheme 11) and the increasing inductive



Scheme 11

influence of the substituent R, $CH_3 < CH_2Ph < CH_2Cl$ results in a reduction in stability of the intermediate according to the data in Table 8. With dimethylphenylphosphine complexes ($R = CF_3$ or CCl_3) loss of ^{31}P coupling to the 1,2-allylic proton

Table 8 *Free energies of activation for* 3,4-*allylic proton exchange in* $[Pd(O_2CR)(L)(\eta\text{-}CH_2C(Me)CH_2)]$ *in* $CDCl_3$ *solution (from ref.* 112)

	$\Delta G^{\ddagger}$/kcal mol^{-1}	
R	PPh_3	PMe_2Ph
Me	13.9	13.6
Bu^t	14.3	14.0
CH_2Ph	14.5	14.4
CPh_3	14.4	15.0
CH_2Cl	15.7	15.1
CCl_3	17.7	15.2
CF_3	17.8	15.2

resonances is also observed prior to coalescence of the 3,4-allylic resonances and at higher temperatures all the allylic signals collapse to a singlet in accord with intermolecular phosphine exchange and simultaneous *syn–anti*, *syn–syn*, and *anti–anti* proton exchange. This accounts for the unusually low $\Delta G^{\ddagger}$ values for the exchange process in these two cases.

Allyl ligand exchange in $[Pd_2(\eta\text{-allyl})_2(LL)_2]$ is inferred to proceed through solvolytic cleavage of the bridge system when the bridging ligands LL are carboxylato-species. Consequently addition of bridge-splitting ligands facilitates allyl-group exchange. The absence of any such effect on the rate of allyl group interchange in μ-*NN*-diarylformamidido analogues (LL = ArNCHNAr) has been taken to imply that

[112] T. R. Jack and J. Powell, *Canad. J. Chem.*, 1975, **53**, 2558.

the alternative intramolecular rearrangement, boat inversion of the $C_2N_4Pd_2$ ring *via* a chair conformation, is a more favourable pathway.[113,114] The former, partially dissociative process is also considered to be responsible for the n.m.r. equivalence of the diastereotopic methyl groups of the PMe_2Ph ligands in $[Pd_2(X)_2(O_2CR)_2(PMe_2Ph)_2]$ (X = halide) (see Vol. 3, p. 481) and more recently in related complexes with $X = O_2CR$ containing both bridging and terminal carboxylate groups.[114] This mechanism also accounts for the simultaneous exchange of both the PMe_2Ph methyl groups and the terminal–bridge carboxylate sites. The role of the solvent in promoting bridge cleavage is further emphasized by the observation that $[Pd_2(O_2CCF_3)_2(PMe_2Ph)_2]$ is dimeric in $CDCl_3$ or $[^2H_8]$toluene but exists as a monomer–dimer equilibrium in $[^2H_6]$acetone.

The coalescence temperature of the ethyl signals in the ^1H n.m.r. spectrum of *trans*-$[Pd(Cl)_2(Et_2S)_2]$ (249 K) does not change when free diethyl sulphide is added.[115] A second coalescence at 350 K, however, is lowered by the addition of Et_2S, which is a characteristic feature of an associative process. The lower-temperature coalescence is therefore identified unambiguously as being due to inversion of configuration at sulphur.

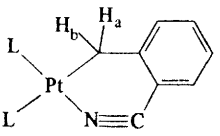
Platinum.—The *cis–trans* isomerization of *cis*-$[Pt(Cl)(CH_2CN)(PPh_3)_2]$ in the presence of varying amounts of free PPh_3 has been followed by ^{31}P n.m.r. spectroscopy and the second-order rate constants k_2 and k_{-2} for the forward and reverse reactions have been evaluated.[116] The rate is first-order in complex and in PPh_3 with $k_2 = 9.1 \times 10^{-6}$ mol^{-1} s^{-1} and the equilibrium constant $K = k_2/k_{-2} = 4.0$. Similar results were obtained with *cis*-$[Pt(X)(CH_2C_6H_4CN)(PPh_3)_2]$ (X = Cl or Br).[117] Studies of uncatalysed *cis–trans* isomerization of square-planar platinum compounds have also been reported during the present period and yield results which have been interpreted in terms of a dissociative process to give a three-co-ordinate intermediate, a mechanism which has not been considered previously.[118,119] *cis*-$[Pt(R)(Br)(PEt_3)_2]$ undergoes isomerization in methanol according to first-order kinetics at rates which increase with temperature but which decrease on addition of bromide ion. The mass-law retardation by bromide suggests that the rate-determining step involves Pt—Br bond cleavage to yield a three-co-ordinate *cis*-like intermediate which rearranges to a *trans*-like species, and on uptake of Br gives the *trans*-isomer. Bimolecular attack by the solvent on the *cis*-complex is also possible, leading to bromide release and the formation of a solvated intermediate $[Pt(R)(PEt_3)_2S]$. The enthalpies and entropies of activation in Table 9 also support a dissociative process while the observed rate increase when electron-releasing groups are introduced into group R has also been noted in other systems which are dissociative in nature.

Coalescence of the H_a and H_b proton resonances in the ^1H n.m.r. spectrum of (58) is observed at 27 °C as a result of conformational interconversion which has an

[113] S. C. de Sanctis, L. Toniolo, T. Boshi, and G. Deganello, *Inorg. Chim. Acta*, 1975, **12**, 251.
[114] L. Toniolo, T. Boshi, and G. Deganello, *J. Organometallic Chem.*, 1975, **93**, 405.
[115] R. J. Cross, T. H. Green, R. Keat, and J. F. Paterson, *Inorg. Nuclear Chem. Letters*, 1975, **11**, 145.
[116] R. Ros, J. Renaud, and R. Roulet, *Helv. Chim. Acta*, 1975, **58**, 133.
[117] T. Ros, J. Renaud, and R. Roulet, *J. Organometallic Chem.*, 1975, **87**, 379.
[118] R. Romeo, D. Minniti, and M. Trozzi, *Inorg. Chim. Acta*, 1975, **14**, L15.
[119] R. Romeo, D. Minniti, and M. Trozzi, *Inorg. Chem.*, 1976, **15**, 1134.

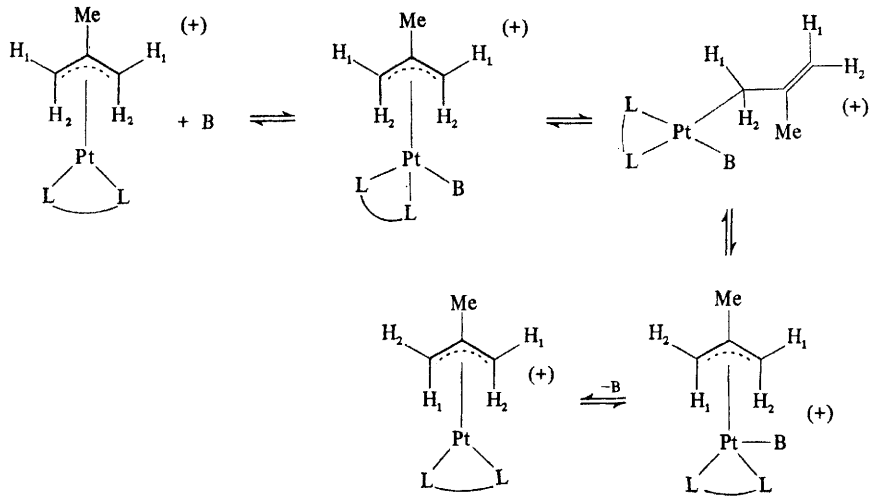
Table 9 *Activation parameters for the* cis–trans *isomerization of* cis-[Pt(R)(Br)-$(PEt_3)_2$] (*from ref.* 119)

R	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
Ph	21.0	−3.0
p-MeC_6H_4	19.5	−6.2
o-MeC_6H_4	23.6	+5.0
o-EtC_6H_4	24.0	+5.7
2,4,6-$Me_3C_6H_2$	16.1	−22.6



(58)

energy barrier $\Delta G^{\ddagger}_{300} = 15.3 \pm 0.2$ kcal mol^{-1}.[120] The magnetic non-equivalence of the *syn* protons H_1 and H_4 of the allyl ligand in $[Pt(\eta\text{-}C_3H_5)(PR_3)_2]^+$ (R = C_6H_{11}), which is attributed to restricted rotation of the phosphines, is lost as the temperature is raised and free rotation commences.[121] The η^3-allyl ligand in $[Pt(\eta\text{-}CH_2CMeCH_2)$-(LL)]$^+$ (LL = dpe or diars) is bonded rigidly to the metal but addition of neutral bases, *e.g.* PPh_2Me or pyridine, leads to *syn–anti* allylic proton exchange and averaging of the arsine methyl-group signals[122] in the complex with LL = diars. When the added base is $PMePh_2$ phosphine exchange (intermolecular) is observed but this is frozen out at −10 °C, whereas the dynamic behaviour involving the other ligands continues down to −70 °C and σ–π allyl interconversion is thought to be responsible (Scheme 12). Limiting ^{1}H n.m.r. spectra for $[Pt(cod)(\eta^1\text{-}C_5H_4R)_2]$ (R = H or Me) could not be



Scheme 12

[120] R. Ros, J. Renaud, and R. Roulet, *J. Organometallic Chem.*, 1975, **87**, 379.
[121] T. G. Attig and H. C. Clark, *J. Organometallic Chem.*, 1975, **94**, C49.
[122] H. C. Clark and C. R. Jablonski, *Inorg. Chem.*, 1975, **14**, 1518.

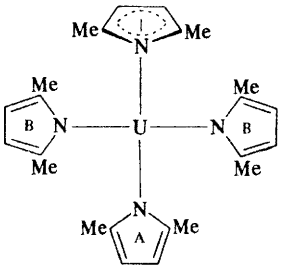
obtained but with R = Me sufficient line-broadening was observed such that estimates of the activation parameters for cyclopentadienyl ring 'whizzing' could be obtained[123] [$\Delta H^{\ddagger} = 2.2 \pm 6.2$ (R = H) and 3.1 ± 0.6 kcal mol^{-1} (R = Me); $\Delta S^{\ddagger} = -31 \pm 12$ (R = H) and -34 ± 17 cal K^{-1} mol^{-1} (R = Me)].

7 Group II

Mercury.—Variable-temperature ^{13}C n.m.r. spectroscopy has been employed in an attempt to elucidate the mechanism of ring 'whizzing' in [Hg(Cl)(η^1-C_5H_5)] and Hg(η^1-C_5H_5)$_2$] which turns out, not surprisingly, to involve 1,2-shifts.[124] The dynamic process has an activation energy $E_a = 7.7 \pm 0.7$ kcal mol^{-1} for the chloride.

8 Actinides

Tetrakis-(2,5-dimethylpyrollyl)uranium(IV) (59) undergoes two types of exchange



(59)

process according to variable-temperature ^1H n.m.r. studies.[125] The higher energy rearrangement ($\Delta G^{\ddagger} = 17.0 \pm 1.0$ kcal mol^{-1}) is assigned to rapid interconversion of *monohapto-* and *pentahapto*-pyrollyl rings while the second process interconverts ring A with rings B by rotation of the η^1-bonded rings about the U—N bond. Isomerism due to rotation of the η^5-ring about the metal–ring axis is also indicated.

The paramagnetism of [U(BH_4)(η-C_5H_5)$_3$] induces large contact shifts in the BH_4 proton resonances thus increasing the time resolution of the n.m.r. technique.[126] This has enabled observation for the first time of slowing of bridge–terminal H-exchange in a tetrahydroborate complex. The estimated $\Delta G^{\ddagger}$ value is 5.0 ± 0.6 kcal mol^{-1}. As mentioned in Section 1 non-fluxionality has been induced in or is inherent in other tetrahydroborate complexes isolated more recently. Marks has also observed fluxional behaviour in the η^1-allyl complexes [M(C_3H_5)(η-C_5H_5)$_3$] (M = Th or U) due to a σ–π–σ interconversion process.[127] Free energies of activation range from 7.6 to 8.7 kcal mol^{-1} for M = Th and 8 ± 1 kcal mol^{-1} for M = U, although the value for the thorium compound is only a rough estimate since sufficiently low temperatures required to observe the 'frozen' spectrum could not be reached.

[123] M. N. S. Hill, B. F. G. Johnson, T. Keating, and J. Lewis, *J.C.S. Dalton*, 1975, 1197.
[124] F. A. Cotton, D. L. Hunter, and J. D. Jamerson, *Inorg. Chim. Acta*, 1975, **15**, 245.
[125] T. J. Marks and J. R. Kolb, *J. Organometallic Chem.*, 1974, **82**, C35.
[126] T. J. Marks and J. R. Kolb, *J. Amer. Chem. Soc.*, 1975, **97**, 27.
[127] T. J. Marks and J. R. Kolb, *J. Amer. Chem. Soc.*, 1976, **98**, 703.

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