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Inorganic Reaction Mechanisms

Volume 7

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Inorganic Reaction Mechanisms

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Foreword

The number of journals and amount of literature generally continue to increase and accumulate, with the area of inorganic mechanisms no exception. Relevant journals are not always in libraries, making surveys of the kind attempted here an essential part of literature contact and coverage. The literature referred to in this volume covers an eighteen month period from January 1978 to June 1979, where the writing and checking of manuscripts was completed by December 1979. While the aim is comprehensive reporting, in the bioinorganic and organometallic areas some barriers have had to be erected restricting coverage which would otherwise impinge on other S.P.R. volumes. The reading of Dr. Cannon's text on electron transfer reactions must be in conjunction with the continuing series of Tables at the end of his section which together refer to all relevant work in this area.

Three new contributors, Drs. Buxton, Elding, and Deeming, are to be welcomed to this volume. In a further change Dr. Lappin has taken over the bioinorganic coverage. The new chapter on pulse radiolysis by Dr. Buxton is highly desirable in view of the increasing use being made of the now well established techniques in this area to generate radicals and unusual oxidation states of metal ions.

Some attempt has been made to make the contents pages more systematic and meaningful. A first-time reader will require to familiarize himself/herself with these pages, which in the absence of indexes are the only lead-in. Minor adjustments in approach have been necessary. For example it has become increasingly difficult to arrange metal-ion substitution reactions in terms of labile and inert systems. To some extent this has resulted from the increasing importance of associative processes, the identification of which necessarily introduces a wide span of rate constants for any one metal oxidation state. Therefore it has become essential to divide the substitution section more rigorously into first of all different co-ordination numbers and then different oxidation states. Although at this time redox studies in non-aqueous solvents are all too few, substitution studies using non-aqueous solvents are receiving increasing attention, and Dr Burgess has covered relevant aspects of this area. Substitution studies in the organometallic area have been included in Part II, which now has comprehensive coverage of substitution reactions. It was not at this time as easy (or as appropriate) to transfer the oxidative addition chapter to the redox section.

Most researchers have become much more conscious of units and no one would today list rate constants without giving units, now almost always in seconds, although (not very long ago) there are otherwise classic papers in which no units are specified but *specific rates* are referred to (*e.g.* papers by Bray and Liebhafsky, *J. Am. Chem. Soc.*, 1930—1936). The same cannot always be said for

absorption coefficients (ϵ), where sometimes no units are given and ambiguities can arise ($M^{-1}\,cm^{-1}$, which is most often used, or $m^2\,mol^{-1}$?). For easy reading (and to economize in space) this volume, like many journals, continues to use the widely understood abbreviation M for mol l^{-1} or mol dm^{-3}. Also a majority of those researching in this area continue to use calories rather than joules (1 cal ≡ 4.2 J), and again we conform to this preference. Furthermore, it seems pointless to refer to temperatures in four digits, *e.g.* 298.2 K, when virtually every reader thinks and translates back into °C. Interestingly working at 300 K rather than 25 °C as a standard condition appears to have been adopted by only one group (Dr. Lincoln's in Adelaide).

Finally, as far as new trends and new thinking are concerned, the involvement (in some cases extensive) of those interested primarily in inorganic mechanisms in work on metalloproteins and bio-related studies continues. However, perhaps the most interesting single development is the recent work on Mn^{II} by Merbach and colleagues in Lausanne, and the suggestion that this and other 2+ ions substitute by an associative mechanism (see Dr. Moore's sections).

A. G. SYKES

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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)
bzba	1,3-diphenylpropane-1,3-dionate
CDP	cytosine-5′-diphosphate
chxn	*trans*-1,2-diaminocyclohexane
cod	cyclo-octadiene
Cp	cyclopentadienyl
CTP	cytosine-5′-triphosphate
cyclam	1,4,8,11-tetra-azacyclotetradecane
dacoda	1,5-diazacyclo-octane-*NN*′-diacetate
diars	*o*-phenylenebisdimethylarsine
dien	diethylenetriamine
dien−H	diethylenetriamine minus one nitrogen proton
diene-N_4	5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene
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
dop	*NN'*-bis-(2-hydroxyimino-1-methylpropylidene)propane-1,3-diamine anion
DPE	deuterioporphyrin IX dimethyl ester
dpt	dipropylenetriamine
dtc	dithiocarbamate
dto	dithio-oxalate
dtp	diethyldithiophosphate
dtpa	diethylenetriaminepenta-acetate
edda	ethylenediaminediacetate
eddda	ethylenediaminediacetatedipropionate
edds	*NN'*-ethylenedeiaminedisuccinate
edma	ethylenediaminemonoacetate
edta	ethylenediamineteta-acetate
egta	ethylene glycol bis-(2-aminoethyl ether)-tetra-acetate
en	ethylenediamine
Et_4dien	*NNN"N"*-tetraethyldiethylenetriamine
ete	4,8-dithia-1,11-diazaundecane
Fc	ferrocenyl
fum	fumarate
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

OTs	toluene-*p*-sulphonate
ox	oxalate
pada	pyridine-2-azo-*p*-dimethylaniline
pdc	propylene carbonate
pdta	propylenediaminetetra-acetate
phen	1,10-phenanthroline
pm	pyrimidine
pn	propylenediamine
py	pyridine
py-py	4,4′-bipyridyl
pyz	pyrazine
$pyzCO_2$	pyrazinecarboxylate
salen	*NN′*-bis(salicylaldehydo)ethylenediamine
SDS	sodium dodecylsulphonate
tar	tartrate
tcne	tetracyanoethylene
tea	triethanolamine
tep	tetraethylenepentamine
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-tetra-azacyclotetradecane
tetraene-N_4	2,3,9,10-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-1,3,8,10-tetraene
tetren	tetraethylenepentamine
tfa	trifluoroacetate
tfac	1,1,1-trifluoroacetylacetonate
thiox	monothio-oxalate
tmd	trimethylenediamine
tmeda	*NNN′N′*-tetramethylethylenediamine
TP	tripolyphosphate
TPP	$\alpha,\beta,\gamma,\delta$-tetraphenylporphine
TPPS	tetrakis-(*p*-sulphonatophenyl)porphinate
tren	triaminotriethylamine
trien	triethylenetetramine
trigly	triglycine
ttha	triethylenetetraminehexa-acetate
tu	thiourea

Part I

ELECTRON TRANSFER PROCESSES

By
G. V. BUXTON
R. D. CANNON
A. McAULEY

1
Electron Transfer Reactions

BY R. D. CANNON

1 Introduction

This Report covers the period January 1978—June 1979 inclusive, with the addition of some earlier references which were not available at the time of writing the previous Report. Likewise, the most recent issues of some journals are not covered, and these omissions will be rectified in the next Report.

As in previous volumes, it has not been possible to discuss every paper published, but the Tables of rate data at the end of the chapter have been made as comprehensive as possible. It is hoped that the cumulative series of these Tables will be of lasting value as a guide to the literature.

2 General and Theoretical

A short review on 'electron tunnelling' contains references to the development of electron-transfer theory, and to some more recent experimental work.[1] A review on inelastic atom–atom collisions includes the theory of gas-phase electron-transfer processes.[2] Developments within the Marcus adiabatic theory are considered under the first two headings.

Effect of Internuclear Distance.—Brown and Sutin[3] have discussed the rates of a series of ruthenium(III) + ruthenium(II) exchanges. These increase in the order $[Ru(NH_3)_6]^{n+} < [Ru(NH_3)_5py]^{n+} < [Ru(NH_3)_4(bipy)]^{n+} < [Ru(NH_3)_2(bipy)_2]^{n+} < [Ru(bipy)_3]^{n+}$, and this is attributed to the increasing internuclear distance due to increasing bulk of the ligands. Two main effects can be distinguished: a decreasing coulombic work term ω_r, and decreasing reorganization energy λ, mainly due to the outer-sphere contribution. Two alternative expressions were considered for the second-order rate constant k:

$$k = Z \exp(-\omega_r/RT) \exp(-\Delta G^*/RT) \quad (1)$$

$$k = K_0 k_{et} = K_0(RT/Lh) \exp(-\Delta G^*/RT) \quad (2)$$

where Z is the bimolecular rate constant for uncharged species and K_0, k_{et} are the formation constant of the precursor complex and the rate constant for intramolecular electron transfer. The reorganization energy, defined by

$$\Delta G^* = \tfrac{1}{4}\lambda(1 + \Delta G^\ominus/\lambda)^2 \quad (3)$$

[1] W. F. Libby, *Annu. Rev. Phys. Chem.*, 1977, **28**, 105.
[2] J. S. Briggs and K. Taulbjerg, 'Theory of Inelastic Atom–Atom Collisions', in *Top. Curr. Phys.*, ed. I. A. Sellin, Springer Verlag, Berlin, Heidelberg, New York, Vol. 5, 1978, pp. 105—153.
[3] G. M. Brown and N. Sutin, *J. Am. Chem. Soc.*, 1979, **101**, 883.

is subdivided into inner- and outer-sphere contributions,

$$\lambda = \lambda_{in} + \lambda_{out} \tag{4}$$

where

$$\lambda_{in} = NLf_1f_2(\Delta a)^2/2(f_1 + f_2) \tag{5}$$

$$\lambda_{out} = \frac{L}{4\pi\varepsilon_0} \cdot \frac{q^2}{4}\left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r}\right)\left(\frac{1}{D_0} - \frac{1}{D_s}\right) \tag{6}$$

Here f_1 and f_2 are force constants for the breathing modes of the metal–ligand bonds, N is the co-ordination number, and Δa is the change in bond length associated with the electron transfer; q is the amount of charge transferred, a_1 and a_2 are the overall radii of the complexes, and r is the distance of closest approach, assumed to be $r = a_1 + a_2$; D_0 and D_s are the optical and static dielectric constants of the medium. The difference varies from a ratio of 20 to 75 along the series from $[Ru(NH_3)_6]^{n+}$ to $[Ru(bipy)_3]^{n+}$, the values from equation (1) being smaller and also closer to the experiment values. Final theoretical and calculated rates agree within a factor of 2 or better, and for the complex $[Ru(NH_3)_5py]^{n+}$ the calculated value of ΔG^* is close to the value for intramolecular thermal electron transfer in the complex $[(NH_3)_5Ru(4,4'\text{-bipy})Ru(NH_3)_5]^{5+}$, predicted from the energy of the intervalence charge-transfer absorption. Thus the evidence is generally in favour of the Marcus kinetic formulation, equation (1), rather than the equilibrium formulation, equation (2).

Long-range electron transfer involving relatively mobile electrons produced by radiolysis continues to receive attention, but will not be reviewed at length. Recent theoretical developments include studies of electron mobility in molecular crystals, by the process of hopping from one trap to another.[4,5] On the other hand, for systems in which electrons are produced by pulse radiolysis, in a glassy matrix which also contains strongly accepting centres, it has been argued that trap-to-trap hopping is unimportant compared with direct transfer from the initial site to the acceptor, and that the latter process is controlled by the well known principles of outer-sphere electron transfer.[6] Further experimental evidence has been reported for long-range transfer of mobile electrons in glassy matrixes such as 10M-NaOH in H_2O at 77 K. Experiments showing long-range electron transfer between reactants in widely separated monolayers have been mentioned in an abstract, but not described in detail.[7]

Effect of Driving Force.—Linear free-energy relationships, or rate comparisons along a series of apparently similar electron-transfer reactions, are now widely used as criteria of mechanism, but Gould[8] has provided a timely warning against the undiscriminating use of such arguments. He shows a correlation of rates of reduction of 16 penta-ammine cobalt complexes, by Cr^{2+} and Eu^{2+}, eight of which are structurally constrained to outer-sphere pathways whereas the others are known to be mainly inner-sphere; they all fit a single linear correlation:

$$\log k_{Eu} = 0.93 \log k_{Cr} + 0.97 \tag{7}$$

[4] S. Efrima and H. Metiu, *Chem. Phys. Lett.*, 1979, **60**, 226.
[5] M. Tachiya, *J. Chem. Soc., Faraday Trans. 2*, 1979, **75**, 271.
[6] J. R. Miller, *J. Phys. Chem.*, 1978, **82**, 767.
[7] D. Möbius, *Ber. Bunsenges. Phys. Chem.*, 1978, **82**, 867.
[8] E. S. Gould, *Inorg. Chem.*, 1979, **18**, 900.

The same applies to a series of $U^{3+} + Cr^{2+}$ reactions:

$$\log k_U = 1.23 \log k_{Cr} + 3.05 \quad (8)$$

Electron-transfer quenching of excited $[RuL_3]^{2+}$ ions (L = 2,2′-bipyridyl or related ligands) by organic oxidants as reductants can be used to test the Marcus relationship between ΔG^* and ΔG° since the redox potentials of the donors can be varied over a wide range by means of substituent groups. Previously, Rehm and Weller observed a non-Marcus dependence (in a different, wholly organic system), in that as $\Delta G^\ominus$ passed into the range for inverted behaviour ΔG^* levelled off.[9] What might be termed the converse behaviour has since been observed[10] in the system $[RuL_3]^{2+} + ArNO_2$ with various nitro-aromatics as oxidative quenchers. As $\Delta G^\ominus$ is made more positive, rates diminish at first, according to the Marcus parabolic law, but then there is a change to a linear dependence of ΔG^* on $\Delta G^\ominus$, of slope 1.0. The proposed mechanism[11] is shown in equation (9), where A denotes the quencher. If step 2 is rate determining, the

$$\begin{array}{ccccc} [RuL_3]^{2+} + A & & & [RuL_3]^{3+} + A^- & [RuL_3]^{2+},A \\ \Big\downarrow \tau_0^{-1} + h\nu & & & \nwarrow k_3 & \nearrow k_3' \\ [RuL_3^{2+}]^* + A & \overset{K_1}{\rightleftharpoons} & [RuL_3^{2+}]^*,A & \underset{-2}{\overset{2}{\rightleftharpoons}} & [RuL_3]^{3+},A^- \end{array} \quad (9)$$

overall quenching rate constant is given by

$$k_q' = K_1 k_2 \quad (10)$$

and a decrease in the oxidizing power of A produces a decrease in k_2, and an increase in k_{-2}, according to the Marcus equation. After a certain point, however, step 3 becomes rate determining, and the quenching constant is given by

$$k_q' = K_1 K_2 k_3 \quad (11)$$

after which k_q' is proportional to K_2, as observed.

Mention has been made previously[12] of the possibility that the maximum electron-transfer rate observed in a series of reactions, as the driving force is increased, may be due to the onset of diffusion control, unrelated to the redox properties of the reactants. This has usually been discussed by amending the value of Z in the Marcus equation (1). Thus for uncharged reactants in water at room temperature $Z \approx 10^{11}$ M^{-1} s^{-1}, but for like-charged reactants it may be very much less. Brunschwig and Sutin[13] have now proposed a different formulation in which Z is a parameter independent of the encounter rate. Writing the general bimolecular electron-transfer mechanism as

$$A^+ + B \underset{-1}{\overset{1}{\rightleftharpoons}} A^+ \cdot B \quad (12)$$

$$A^+ \cdot B \xrightarrow{2} \text{products} \quad (13)$$

[9] D. Rehm and A. Weller, *Ber. Bunsenges. Phys. Chem.*, 1969, **73**, 834; *Isr. J. Chem.*, 1970, **8**, 259.
[10] C. R. Bock, T. J. Meyer, and D. G. Whitten, *J. Am. Chem. Soc.*, 1975, **97**, 2909.
[11] C. R. Bock, J. A. Connor, A. R. Gutierrez, T. J. Meyer, D. G. Whitten, B. P. Sullivan, and J. K. Nagle, *Chem. Phys. Lett.*, 1979, **61**, 522.
[12] This series, Vol 5, p. 5, and references cited therein; *cf.* also Vol. 6, p. 11.
[13] B. Brunschwig and N. Sutin, *J. Am. Chem. Soc.*, 1978, **100**, 7568.

where $A^{+}{\cdot}B$ is the outer-sphere precursor complex and k_1 is the specific rate of encounter, the overall specific rate is obtained in the steady-state approximation as

$$k_{obs} = \text{Rate}/[A^{+}][B] = k_1k_2/(k_{-1}+k_2) \quad (14)$$

The limiting cases are $k_{obs}=k_1$, when $k_2 \gg k_{-1}$, in the diffusion-controlled limit, and

$$k_{obs} = k_1k_2/k_{-1} = k_{12} \quad (15)$$

when $k_2 \ll k_{-1}$. The specific rate given by the Marcus theory is the second of these, *i.e.* k_{12}. Hence the theoretical curve of $\log k_{obs}$ as a function of $\log K_{12}$ takes different limiting forms. When $Z \ll k_1$ it is a parabola with its maximum at $k_{obs}=Z$; when $Z \gg k_1$ the parabola is truncated, with a flat maximum at $k_{obs} \simeq k_1$. A consequence is that at low driving force, where $\partial(\log k_{12})/\partial(\log K_{12}) \approx 0.5$, rates of electron transfer depend very little on Z, and at high driving force, if diffusion control takes over, rates again depend very little on Z. The feature which does depend strongly on Z is the value of $\log K_{12}$ beyond which the curve turns down again into the inverted region. Data for a series of reactions involving electronically excited complexes are cited in support of this model. The $\log k_{obs}$–$\log K_{12}$ curve shows a pronounced flattening which can be attributed to the diffusion effect. At the highest driving force, there is an apparently significant deviation, but not to the extent required by the Marcus theory. As already discussed,[14] this is attributed to nuclear tunnelling effects.

The Role of Bridging Groups.—The mechanisms of bridged electron-transfer reactions, and the structures of bridged dinuclear complexes, have been reviewed from the standpoint of molecular orbital theory.[15] For the M—X—M unit (precursor or successor complex, or transition state), MO's are constructed from the orbitals of the metal ion M, and are used to predict whether the symmetric configuration $L_5M—X—ML_5$ is more or less stable than the asymmetric form $L_5M—X\cdots ML_5$. In this way the symmetric structures observed in the basic rhodochromic ion $[\{Cr(NH_3)_5\}_2O]^{4+}$ and the nearly symmetric bridging in 'ruthenium red' $[(NH_3)_5RuORu(en)_2ORu(NH_3)_5]^{6+}$ are rationalized, as are the asymmetric structures of the CrFCr units in Cr_2F_5 and the PtBrPt units in various mixed-valence Pt^{II}/Pt^{IV} compounds.

For electron-transfer reactions, extended Hückel-type calculations are mentioned which rationalize the order of rates F < Cl < Br < I, or *vice versa*. Calculations of the amount of charge located on the bridging atom at the symmetrical configurations are used to distinguish 'chemical' transfer from double exchange or resonance processes.[16] For a model system $[Cl_5Cr^{III}\cdots Cl\cdots Cr^{II}Cl_5]^{6-}$, resonance transfer is favoured. A further distinction is drawn between 'smooth' electron transfer, in which the symmetry of the orbital containing the transferred electron remains unchanged, and 'sudden' transfer, in which one or more electrons change from a σ- to a π-orbital or *vice versa* or in which the electron must change between two orbitals of the same symmetry but very different energy.

[14] C. Creutz and N. Sutin, *J. Am. Chem. Soc.*, 1977, **99**, 241.
[15] J. K. Burdett, *Inorg. Chem.*, 1978, **17**, 2537.
[16] J. Halpern and L. E. Orgel, *Discuss. Faraday Soc.*, 1960, No. 29, p. 32.

It is suggested that, in general, reactions of the first type will tend to involve net transfer of the bridging group, whereas the second type will not. In some cases, however, if not all, the argument is tantamount to rationalizing the relative inertness or lability of the metal centres before and after the reaction; hence this theory overlaps with previous discussions to a considerable extent.

Outer-sphere reactions are also considered. For the hypothetical reaction $[Cr^{III}Cl_6]^{3-} + [Cr^{II}Cl_6]^{4-}$, it is suggested that the inclusion of a Na^+ ion in the transition state is sufficient to transform the reaction from non-adiabatic to adiabatic, and that the overall effects of counterions on such reactions are too great to be regarded as mere electrostatic stabilization of the encounter complex. Less credible is the conclusion that water molecules themselves can act as effective 'catalysts' for outer-sphere electron transfer, a single water molecule between the reacting complexes leading to a resonance energy increase of 6 kcal mol^{-1}.

Non-adiabatic Theories.*—In the biological field, increasing use is being made of the non-adiabatic multiphonon theories of Hopfield[18,19] and Jortner,[20] These theories take account of the vibrational states associated with the reactants' and products' electronic configurations. The overall transfer probability involves probabilities from all reactant states to all product states, expressed in Hopfield's formalism as a double integral involving the bandshapes of the photoelectron emission and absorption spectra of the reducing and oxidizing centres respectively. When these are approximated by Gaussian functions of equal width, so that the dependence of electronic energy on nuclear configuration becomes parabolic with equal curvature, and when the temperature is high enough so that the separation of vibrational states is smaller than k_BT (where k_B is the Boltzmann constant), the rate constant is given by

$$k = (2\pi/\hbar)|T_{ab}(r)|^2(4\pi k_B)^{-1/2} \exp(-E_A/k_BT) \quad (16)$$

where the activation energy E_A is given by

$$E_A = (\Delta E + \Delta)^2/4\Delta \quad (17)$$

$\Delta E = E_b - E_a$ being the overall energy change for the reaction and Δ the vibronic coupling parameter. This equation has the familiar Marcus form, with Δ corresponding to the reorganization energy λ [*cf.* equation (3)]. The tunnelling integral T_{ab} is estimated by performing an electron tunnelling calculation with a barrier of suitable chosen energy.

The main differences between Hopfield's theory and the earlier theory of Marcus are the explicit use of the spectral shape functions $D(E)$ (though this difference is removed when Gaussian functions are used), the lack of reference to a transition state, and the extension to lower temperatures where equation (16) is replaced by a non-Arrhenius form, not quoted here. Jortner,[20] however, later argued that at low temperatures the Hopfield theory is inapplicable, since

* Rates of atom transfer processes at low temperatures have been considered using a quantum mechanical tunnelling model.[17]

[17] J. Jortner and J. Ulstrup, *Chem. Phys. Lett.*, 1979, **63**, 236.
[18] J. J. Hopfield, *Proc. Natl. Acad. Sci. USA*, 1974, **71**, 3640.
[19] J. J. Hopfield, *Biophys. J.*, 1977, **18**, 311.
[20] J. Jortner, *J. Chem. Phys.*, 1976, **64**, 4860.

the separation of vibrational energy levels becomes large compared with k_BT. In his theory, the transition probability is written separately for each pair of reactants' and products' vibronic levels, and appropriate summations are performed. Results are obtained for different temperature ranges, based on the fact that the relevant vibrations fall into two main frequency ranges: 1—10 cm^{-1} for solvent molecular motions (or 10—100 cm^{-1} for lattice vibrations in a solid) and 300—3000 cm^{-1} for bond vibrations. In the extreme low-temperature limit, the rate is temperature-independent, corresponding to horizontal tunnelling[21] from the zero-point energy level of the reactants' electronic configuration to the nearest available level of the products' electronic configuration. At higher temperatures, where the medium vibrations are excited but the molecular modes are still frozen, the apparent activation energy $[E_A = d \ln k/d(T^{-1})]$ becomes positive:

$$E_A = (\Delta E + \Delta_{out} + \Delta_{in})^2/4\Delta_{out} \quad (18)$$

where Δ_{out} and Δ_{in} are separate contributions to the total coupling constant.* As the temperature is raised, the activation energy increases further until when both sets of modes are activated it assumes the constant value given by equation (17), where $\Delta = \Delta_{in} + \Delta_{out}$, corresponding to the reorganization energy of the Marcus–Hush theories [*cf.* equation (4); see also p. 32 below]. The first test[20] of these equations was in fitting the temperature dependence of the light-induced cytochrome–chlorophyll electron transfer observed in the bacterium *Chromatium*.[22] This shows a transition from a temperature-independent to a temperature-dependent regime at around 80 K. A good fit to the experimental data was obtained using $\nu_{in} \approx 400$ cm^{-1}, $\Delta E \approx 0.1$ eV, and $S = \Delta_{in}/\hbar\langle\omega_{in}\rangle \approx 20$ so that $\Delta_{in} \approx 1.0$ eV $= 23$ kcal mol^{-1}. These parameters seem physically reasonable.

Hopfield[19,23] subsequently discussed the corresponding optically induced electron-transfer process (*i.e.* what in metal–metal systems is now generally called intervalence charge transfer). For the charge-transfer energy at the absorption maximum he obtained the equation

$$Lh\nu_{CT} = E_a - E_b + \Delta \quad (19)$$

as previously derived by Kubo[24] and by Hush,[25] and for the oscillator strength

$$f = \tfrac{1}{3}|T_{ab}|^2\hbar^2/h\nu_{CT}mr^2 \quad (20)$$

where m is the mass of the oscillator and the other terms have already been defined. The bands are expected to be very weak: assuming $\Delta E = 0.1$ eV, $r = 12$ Å,

* The subscrips 'in' and 'out' introduced here refer to inner- and outer-sphere by analogy with the two reorganization energies of the Marcus theory [equation (4)]. Actually the theory does not assume that high frequencies are associated exclusively with inner-sphere bond vibrations, though this is probably a good approximation. In Jortner's notation ν_{in} and ν_{out} are written ω_s and ω, and are referred to as 'molecular' and 'medium' vibrations, respectively.

[21] V. G. Levich, *Adv. Electrochem. Eng.*, 1966, **4**, 249.
[22] (*a*) D. De Vault and B. Chance, *Biophys. J.*, 1966, **6**, 825; (*b*) D. De Vault, J. H. Parkes, and B. Chance, *Nature (London)*, 1967, **215**, 642.
[23] M. J. Potasek and J. J. Hopfield, *Proc. Natl. Acad. Sci. USA*, 1977, **74**, 229.
[24] R. Kubo and Y. Toyozawa, *Prog. Theoret. Phys.*, 1955, **13**, 160.
[25] N. S. Hush, *Prog. Inorg. Chem.*, 1967, **8**, 391.

and $T_{ab} = 10^{-3}$ eV, Hopfield calculates the relationship between ν_{CT} and f and shows that, for example, when $\nu_{CT} = 9.5 \times 10^3$ cm^{-1}, the maximum extinction coefficient is about $\varepsilon = 0.25$ M^{-1} cm^{-1}. Given the low concentrations normally accessible with biological molecules, this is below the limits of measurement by conventional spectrophotometric methods. Hopfield and Potasek have, however, developed a method of difference spectroscopy using rapidly oscillating concentrations of the complex to be measured, and have reported examples of absorption bands with energy and intensity in the expected range.[23,26,27]

In the system cytochrome *c*-ferrocyanide, a rough comparison can be made between parameters obtained from the thermal and the optical electron-transfer process.[27] For the optical process

$$c^{III} \cdot Fe^{III} \xrightarrow{h\nu_{CT}} (c^{II} \cdot Fe^{III})^* \qquad (21)$$

the energy of the absorption band maximum is $h\nu_{CT} = 1.10 \pm 0.04$ eV ($Lh\nu_{CT} = 31.4$ kcal mol^{-1}). The free-energy change of the thermal reaction

$$c^{III} \cdot Fe^{II} \rightleftharpoons c^{II} \cdot Fe^{III} \qquad (22)$$

is $\Delta G^{\ominus} = 3.7 \pm 3.5$ kcal mol^{-1}, and if this is taken to represent ΔE it gives $\Delta = 27.7 \pm 3.4$ kcal mol^{-1}. The predicted value of the activation enthalpy depends on the value assumed for the dominant vibrational frequency, but reasonable estimates lie in the range $\Delta H^{\ddagger} = 7$—10 kcal mol^{-1}. The experimental value is also subject to some uncertainty, but agrees quite well: $\Delta H^{\ddagger} = 8$—10 kcal mol^{-1}.[28]

Hopfield has extended his theory to cover bimolecular as well as unimolecular electron transfers.[29] The derivation has not yet been published, but the result has been quoted.[30,31] Chien[31] has compared this formulation with the Marcus theory, and has used it to calculate rates of electron transfer between iron or cobalt cytochromes and various small inorganic complexes. Taking $\Delta = 0.5$ eV for the iron cytochrome couple and $\Delta = 1.0$ eV for the cobalt cytochrome couple, and calculating $|T_{ab}|$ for carbon–carbon $2p\pi$ interactions with distance r estimated from *X*-ray data, he obtains good agreement between theory and experiment. Rate constants of some 30 reactions generally agree within a factor of 2, and activation enthalpies, where available, agree within 3 or 4 kcal mol^{-1} in most cases.

Early on in the development of this subject, R. Lumry remarked on the apparent 'yearning for the appearance in biological systems of exotic processes depending upon the quantum mechanics of highly ordered systems and the like' and suggested that biochemists should not neglect the effects of other phenomena such as changes in protein configuration.[32] Although this comment may not be directly applicable to the systems under review, one cannot help noticing both the experimental difficulties encountered in the study of biological molecules and the number of parameters which so far can only be crudely

[26] M. J. Potasek, *Science*, 1978, **201**, 151.
[27] M. J. Potasek and J. J. Hopfield, *Proc. Natl. Acad. Sci. USA*, 1977, **74**, 3817.
[28] E. Stellwagen and R. G. Shulman, *J. Mol. Biol.*, 1973, **80**, 559.
[29] J. J. Hopfield, *Int. Congr. Soc. Chim. Phys., 29th* (cited in ref. 30).
[30] J. C. W. Chien, H. L. Gibson, and L. C. Dickinson, *Biochemistry* 1978, **17**, 2579.
[31] J. C. W. Chien, *J. Phys. Chem.*, 1978, **82**, 2159.
[32] R. Lumry, *Discuss. Faraday Soc.*, 1959, No. 27, p. 109.

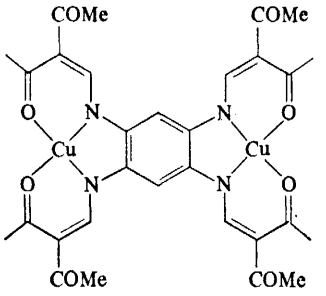
estimated. For example, the electron energy difference ΔE is usually either unknown or else is assumed to be the same as $\Delta G^{\ominus}$;* the locations of the oxidizing and reducing centres are not accurately defined (in fact the above theories have been used to calculate the electron transfer distance[14]), and the vibrational frequencies have not been independently measured. The evidence for non-adiabatic electron transfer in biological systems is already impressive, but it seems that more experiments will be required to settle the question beyond doubt. In principle, both the energy Δ and the tunnelling integral T_{ab} can now be obtained for the same system by different methods, and the extent of agreement between them should be a powerful test of the non-adiabatic theory.[19] Still more convincing would be the extension of such experiments to simple inorganic systems such as mixed-valence, crystalline solids with bond distances and vibrational frequencies accurately determined. Some years ago it was predicted that electron-transfer rates between simple inorganic couples should show the non-Arrhenius-type temperature dependence exhibited by *Chromatium*, and the relevant temperature ranges were calculated using estimated vibration frequencies.[34]

Magnetic Studies.—As was remarked previously,[35] studies of magnetic interaction between metal ions have a bearing on the electron-transfer probability, especially where the double exchange mechanism is involved, but possibly more generally. Hendrickson and co-workers have made a preliminary study of the relationship between magnetic coupling in a copper(II)–copper(II) dinuclear complex, and electronic interaction in the copper(II)–copper(I) mixed-valence system with the same bridging group.[36] The complex (1), which has an appreciable ferromagnetic interaction ($J = -12\,cm^{-1}$), also shows two polarographic reduction waves of (just) distinguishable potential ($E_{1/2} = -1.050$ and -1.125 V, in DMSO, *vs.* s.c.e.), whereas complex (2), with no measurable interaction, shows only one wave ($E_{1/2} = -1.058$ V). It is too early to predict whether or not a relationship will be established between J and (for example) the comproportionation energy† of the mixed-valence system, but that such a relationship will not be a simple one is suggested by two recent magnetic studies of ruthenium dimers. In the series $[(bipy)_2(Cl)Ru^{III}LRu^{III}(Cl)(bipy)_2]^{4+}$ [L = pyrazine, 4,4′-bipyridyl, *trans*-1,2-bis-(4-pyridyl)ethylene, or 1,2-bis-(4-pyridyl)ethane] there is negligible magnetic interaction, the effective magnetic moment per ruthenium atom being similar to that of the monomer $[Ru(bipy)_2(py)Cl]^{2+}$ over the temperature range 1.7—77 K. The coupling constant is evidently not larger than $|J| = 2\,cm^{-1}$. The authors express surprise at these results in view of the significant metal–metal interaction found in the corresponding mixed-valence systems, as evidenced by intervalence charge transfer. It appears that in the Ru^{III}–Ru^{II} system orbital mixing of the type $d\pi(Ru^{II})$–$\pi^*(pyr)$ is significant, whereas in the Ru^{III}–Ru^{III} system it is not.

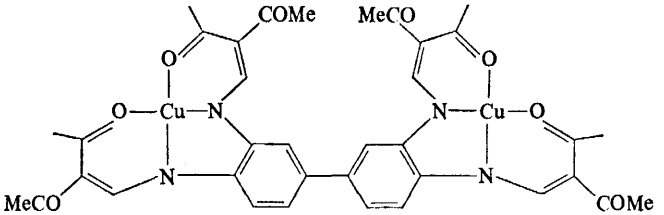
* Gray and co-workers point out that there are surprisingly few data on $\Delta G^{\ominus}$, $\Delta H^{\ominus}$, and $\Delta S^{\ominus}$ of electron-transfer reactions of metal proteins, and they have embarked on a programme of measuring reduction potentials and temperature dependences.[33]

† See equation (42) below.

[33] N. Sailasuta, F. C. Anson, and H. B. Gray, *J. Am. Chem. Soc.*, 1979, **101**, 455.
[34] N. R. Kestner, J. Logan, and J. Jortner, *J. Phys. Chem.*, 1974, **78**, 2148.
[35] This series, Vol. 6, p. 14.
[36] E. F. Hasty, L. J. Wilson, and D. N. Hendrickson, *Inorg. Chem.* 1978, **17**, 1834.



(1)

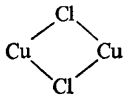


(2)

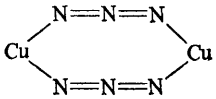
The difference may be associated with contraction of the $d\pi$-orbitals upon oxidation of the metal.[37] Still more remarkable is the lack of interaction in the ion $[(NH_3)_5Ru^{III}(pyz)Ru^{III}(NH_3)_5]^{6+}$ ($J < ca.$ 0.2 cm^{-1}).[38,39] Drago, Hendrickson, *et al.*[38] have used this result in connection with the Ratner–Ondrechen theory of bridged electron transfer[40] to predict the rate of intramolecular electron transfer in the $[(NH_3)_5Ru^{III}(pyz)Ru^{II}(NH_3)_5]^{5+}$ complex. The mixed-valence complex is considered to be localized on the e.p.r. time-scale, with $k < 10^9$ s^{-1} at -50 °C. This conflicts with previous i.r. data[41] and with conclusions drawn from the width of the IT band.[42] The authors suggest that the i.r. data may be affected by other factors such as lattice energy effects, but they accept the possibility that the rate may be substantially higher in solutions at room temperature, so that the electron is effectively delocalized in the time-scale of solvent reorganization. It should perhaps be emphasized that the Ratner–Ondrechen theory neglects vibronic coupling (*i.e.* bond-stretching and solvent reorganization effects), so that strictly it is concerned with predicting electron-transfer probabilities in the transition state, *i.e.* with the difference between adiabatic and non-adiabatic reactions. Drago, Hendrickson, *et al.* do not overlook this point, but they argue that because of the small magnitude of the tunnelling integral 'the unpaired electron has no effective electronic pathway for short circuiting the vibronic barrier to electron transfer'.

[37] E. C. Johnson, R. W. Callahan, R. P. Eckberg, W. E. Hatfield, and T. J. Meyer, *Inorg. Chem.*, 1979, **18**, 618.
[38] B. C. Bunker, R. S. Drago, D. N. Hendrickson, R. M. Richman, and S. L. Kessell, *J. Am. Chem. Soc.*, 1978, **100**, 3805; *cf. ibid.*, 1979, **101**, 512.
[39] I. Treitel, Ph.D. Thesis, California Institute of Technology, 1971, cited in refs. 37 and 38.
[40] M. A. Ratner and M. J. Ondrechen, *Mol. Phys.*, 1976, **32**, 1233.
[41] J. Beattie, N. S. Hush, and P. Taylor, *Inorg. Chem.*, 1976, **15**, 992.
[42] C. Creutz and H. Taube, *J. Am. Chem. Soc.*, 1973, **95**, 1086.

Numerous other magnetic studies, especially of copper(II) complexes, involve structures which resemble known mixed-valence systems or electron-transfer transition states. Examples include doubly bridged structures (3)[43] and (4),[44] single-atom bridges (CuOHCu),[45] bridging by heterocyclic rings [Cu(imida-



(3)



(4)

zolate)Cu *etc.*][46,47] and by lengthy aromatic molecules [Cu(benzidine)Cu *etc.*],[48,49] and outer-sphere dinuclear structures $[Mn_2(tren)_2X_2](BPh_4)_2$ (X= Cl^-, Br^-, NCS^-, *etc.*).[50]

3 Intramolecular Electron Transfer

Various reactions involving dinuclear complexes as reactants, intermediates, or products are summarized in Table 1 on p. 33.

Labile Systems.—Where the dinuclear species is in labile equilibrium with the reactants, the general rate law is

$$\text{Rate} = kK[A^+][B]_T/(1+K[A^+]) \quad (23)$$

$$\text{or} \quad \text{Rate} = kK[A^+]_T[B]/(1+K[B]) \quad (24)$$

depending whether oxidant (A^+) or reductant (B) is in excess. This is consistent with the mechanism in which the complex $A^+ \cdot B$ functions as an intermediate,

$$A^+ + B \rightleftharpoons A^+ \cdot B \text{ rapid}, K \quad (25)$$

$$A^+ \cdot B \rightarrow \text{products}, k \quad (26)$$

though the alternative mechanism in which the complex is a 'dead end', and the electron transfer is bimolecular, cannot be distinguished kinetically, namely

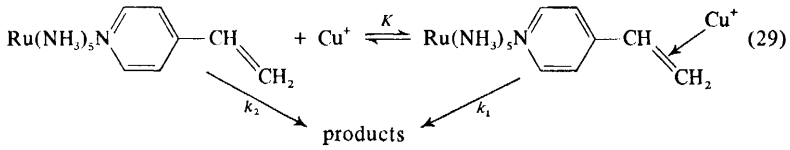
$$A^+ + B \rightleftharpoons A^+ \cdot B \text{ rapid}, K \quad (27)$$

$$A^+ + B \rightarrow \text{products}, k_2 \quad (28)$$

since this gives the same rate law, with k_2 in place of kK. Where the reaction is between outer-sphere reagents, the mechanistic distinction is too subtle to be of much concern in the present state of the subject. An outer-sphere dead-end mechanism would be one in which the encounter complex is thermodynamically stable, but in which electron transfer takes place preferentially over some longer distance.

The reaction $[Ru(NH_3)_5(4\text{-vinylpyridine})]+Cu^+$ conforms to both equations (23) and (24), and the values of K and of the associated $\Delta H^\ominus$ and $\Delta S^\ominus$ are close

[43] J. A. C. Van Ooijen and J. Reedijk, *J. Chem. Soc., Dalton Trans.*, 1978, 1170.
[44] T. R. Felthouse and D. N. Hendrickson, *Inorg. Chem.*, 1978, **17**, 444.
[45] M. S. Haddad and D. N. Hendrickson, *Inorg. Chim. Acta*, 1978, **28**, L121.
[46] M. S. Haddad and D. N. Hendrickson, *Inorg. Chem.*, 1978, **17**, 2622.
[47] M. S. Haddad, E. N. Duesler, and D. N. Hendrickson, *Inorg. Chem.*, 1979, **18**, 141.
[48] T. R. Felthouse, E. N. Duesler, and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1978, **100**, 618.
[49] T. R. Felthouse and D. N. Hendrickson, *Inorg. Chem.*, 1978, **17**, 2636.
[50] E. J. Laskowski and D. N. Hendrickson, *Inorg. Chem.*, 1978, **17**, 457.



(29)

to the stability parameters of the complex (4-vinylpyridine)copper(I), determined spectrophotometrically.[51] The authors argue in favour of direct electron transfer through the organic ligand and against the 'dead-end' mechanism, pointing out that the value of k_2 should be similar to the second-order rate constant for the reaction $[Ru(NH_3)_5(4\text{-ethylpyridine})] + Cu^+$. On this basis, less than 2% of the observed reaction proceeds by the k_2 pathway. The same paper includes an interesting discussion of the thermodynamics of formation of dinuclear complexes.

Some further examples of the 'dead-end' mechanism have been reported[54] (*cf.* refs 52 and 53) [equations (30) and (31); Y = edta^{4-}, pdta^{4-}, or cydta^{4-}; X = CN^- or Ph_3P].

$$[Fe^{III}(CN)_5X] + Co^{II}Y \underset{-2}{\overset{K_1}{\rightleftharpoons}} [Fe^{II}(CN)_5XCo^{III}Y] \qquad (30)$$

$$3 \downarrow \quad \uparrow -3 \qquad 2 \uparrow \downarrow -2$$

$$[Fe^{II}(CN)_5X] + Co^{III}Y \qquad (31)$$

The overall reaction (31) was studied in both directions. Rates of the reverse reaction are too high for the substitution-controlled path (−2, −1), but are consistent with an outer-sphere single step (−3); hence by the principle of microscopic reversibility the main forward path is the step (3).[54] The complex $[(NC)_5Fe^{III}CNCo^{III}(edta)]$ has been prepared pure in solution and the rate of dissociation into $[Fe(CN)_6]^{3-}$ and $[Co(edta)]^-$ has been measured. The slowness of this reaction (analogous to step 2 of the mechanism above) is further confirmation of the mechanism.[55]

Reactions of $[Co(NH_3)_5(dmso)]^{3+}$ with several complexes $[Fe^{II}(CN)_5L]^{3-}$, where L is a non-bridging ligand, have given evidence of ion-pairing,[56,57] all with similar formation constants K and with intramolecular rates k depending on the redox potential as predicted by Marcus, the trend residing in the ΔH^* values. The intramolecular activation entropies remain nearly constant, at 17—18 cal K^{-1} mol^{-1}. The reaction $[Co(NH_3)_5(dmso)]^{3+} + [Fe^{II}(CN)_5(OH_2)]^{3-}$, however, leads to bridge transfer without electron transfer, the products being $[Co(NH_3)_5(OH_2)]^{3+}$ and $[Fe(CN)_5(dmso)]^{3-}$.[57]

[51] K. A. Norton and J. K. Hurst, *J. Am. Chem. Soc.*, 1978, **100**, 7237.
[52] L. Rosenhein, D. Speiser, and A. Haim, *Inorg. Chem.*, 1974, **13**, 1571.
[53] R. X. Ewall and D. H. Huchital, *Inorg. Chem.*, 1975, **14**, 494.
[54] D. H. Huchital and J. Lepore, *Inorg. Chem.*, 1978, **17**, 1134.
[55] D. H. Huchital and J. Lepore, *J. Inorg. Nucl. Chem.*, 1978, **40**, 2073.
[56] L. A. A. Oliveira, E. Giesbrecht, and H. E. Toma, *J. Chem. Soc., Dalton Trans.*, 1979, 236.
[57] L. A. A. Oliveira, H. E. Toma, and E. Giesbrecht, *Inorg. Chim. Acta*, 1977, **22**, 269.

On reaction of $[(NH_3)_5Ru(OH_2)]^{2+}$ with chelate vanadium(IV) complexes, dinuclear species are formed,

$$[(NH_3)_5Ru(OH_2)]^{2+} + [VOL]^{(2-n)+} \xrightarrow{1} [(NH_3)_5RuOVL]^{(4-n)+} \quad (32)$$

where L^{n-} = edta^{4-}, hedta^{3-}, or edta^{2-}.[58] The e.s.r. spectrum indicates that the V^{IV} oxidation state is retained, and the formation rate constant ($k_1 = 2.8\ M^{-1}\ s^{-1}$ for the hedta complex) is consistent with substitution at the ruthenium(II) centre. The complexes are dark green with intense bands near 605 nm, assigned to the Ru^{II} $d_{xy}(B_2) \rightarrow VO^{2+}$ $\pi^*(E)$ transition. This is similar to the MLCT bands observed in other ruthenium(II) complexes with π-acceptor ligands. The complexes show no thermal electron transfer unless the pH is changed, shifting the balance of redox potentials. On a sudden pH jump, the reaction

$$[(NH_3)_5Ru^{II}OV^{IV}L]^{(4-n)+} \rightarrow [(NH_3)_5Ru(OH_2)]^{3+} + [V^{III}L]^{(3-n)+} \quad (33)$$

follows, with the rate law (for the hedta case)

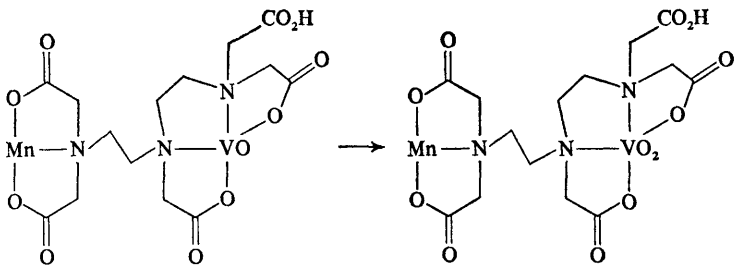
$$-\mathrm{d}\ \ln\ [Ru^{II}V^{IV}]/\mathrm{d}t = k_2 + k_3[H^+]^2 \quad (34)$$

and on reversing the pH change the dinuclear complex is reformed, according to the equation

$$[(NH_3)_5Ru(OH)]^{2+} + [V^{III}L(OH)]^- \rightarrow [(NH_3)_5RuOVL] \quad (35)$$

The rate constant for equation (35) corresponds to the reverse of the k_2 term in equation (34), the reverse of the k_3 term not being detected. This behaviour contrasts with that of the previously characterized complex $[(NH_3)_5Ru^{II}OV^{IV}(OH_2)_4]^{4+}$, which does not undergo intramolecular electron transfer under the range of conditions studied.[59]

When manganese(III) is mixed with the [VO(dtpa)]$^{3-}$ ion in an acetate buffer medium, a reaction occurs to form a complex that retains the characteristic visible absorptions of Mn^{III} and V^{IV} but slowly bleaches to Mn^{II} and V^{V}. The disappearance of V^{IV} and formation of Mn^{II} can also be detected by the e.s.r. spectrum. It is proposed[60] that the initial product is the dinuclear complex (5), which slowly undergoes electron transfer and rearrangement to form (6).



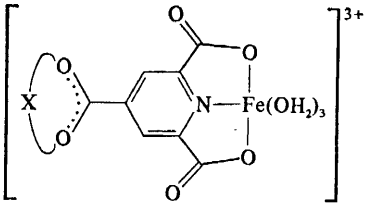
(5) (6)

[58] F. J. Kristine and R. E. Shepherd, *Inorg. Chem.*, 1978, **17**, 3145.
[59] H. De Smedt, A. Persoons, and L. De Maeyer, *Inorg. Chem.*, 1974, **13**, 90.
[60] J. Nelson and R. E. Shepherd, *Inorg. Chem.*, 1978, **17**, 1030.

Inert Systems.—The important distinction between these and the previous systems is that the structure of the precursor complex is unambiguously determined. The complex (7) undergoes intramolecular electron transfer with $k = 6\ s^{-1}$ (22 °C, $I = 0.02$ M).[61] This is faster than the rate for the analogous pyrazine-bridged system, despite the fact that π-electronic coupling (between two rutheniums) is less with imidazole than with pyrazine.



(7)

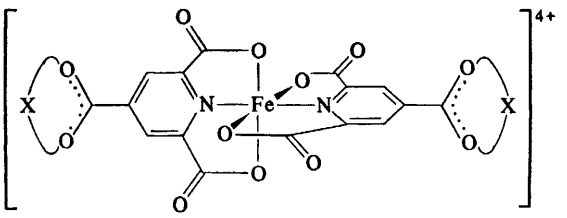


(8)

The complex (8) containing the dinuclear cobalt(III) moiety shown [X = $(H_3N)_3Co(OH)_2Co(NH_3)_3$] does not strictly come into the present category since it is formed in a labile equilibrium from the cobalt–organic component and free Fe^{2+} ion; but the structure of the organic bridge imposes a fixed metal—metal distance, as in the inert systems. The complex is remarkably long-lived; it can be stored for several hours without decomposition. With excess of the cobalt(III) component, a second complex is formed, which undergoes electron transfer according to equation (36)

$$\text{Rate} = \frac{kK[A^+][B]_T}{1 + K[A^+]} \qquad (36)$$

where A^+ denotes the complex $[\{Co(NH_3)_3\}_2(OH)_2L]$ (L = pyridine-2,4,6-tricarboxylate) and B denotes the complex (8). This implies a precursor complex (9) with a lifetime of 200 s at 25 °C. The difference in reactivity of the two complexes is attributed to the increased reducing power of Fe^{II} in the complex (9), and a 'chemical' mechanism is suggested involving transfer of the electron from Fe^{II} into one of the pyridine rings, and thence to one of the cobalt(III) centres.[62]



(9)

[61] S. S. Isied and C. G. Kuehn, *J. Am. Chem. Soc.*, 1978, **100**, 6754.
[62] H. Bertram and K. Wieghardt, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 205.

Some other mixed dinuclear complexes of potential electron-transfer interest include Cu^{II}–Fe^{II},[63] Sn^{IV}–Cu^{I},[64] Fe^{III}–Sn^{II},[65] and V^{V}–Cu^{I}[66] systems.

Intervalence Charge Transfer.—Two reviews have appeared dealing with optical electron transfer between metal ions in trapped-valency systems.[67,68] The present writer[67] has assembled literature data on optical charge-transfer energies, which when combined with appropriate redox potential data yield the reorganization energies ΔG_{FC} [λ in equation (3)] by means of cycles such as that in equation (37).

$$\begin{array}{ccccc} A^+(env) + B(env) & \longrightarrow & A^+\cdot B(env) & & \\ & & p & \searrow^{h\nu_{CT}} & \\ \downarrow \quad \downarrow & & & & \\ A(env) + B^+(env) & \longrightarrow & A\cdot B^+(env) & \xrightarrow{\Delta G_{FC}} & A\cdot B^+(env^*) \\ & & s & & s^* \end{array} \qquad (37)$$

This example relates to a ground-state outer-sphere complex (p) existing in labile equilibrium with reactants A^+ and B. Other systems considered include photoelectron emission, directly bonded systems (such as $Fe^{III}Cl^{2+} \rightarrow Fe^{II}Cl^{\cdot 2+}$), and charge transfer to and from the solvent. Meyer[68] concentrates on intervalence charge transfer and intramolecular thermal electron transfer in homonuclear mixed-valence complexes. He remarks that 'the ideal experiment will be to measure both IT band energies and the rate of intramolecular electron transfer directly for an ion like $[(bipy)_2ClRu^{II}(pyz)Ru^{III}Cl(bipy)_2]^{3+}$', since it will then be possible to sketch the complete energy profile and to obtain the frequency factor for the thermal process.

This follows from Hush's model of the intervalence transfer process according to which the energy of the band maximum is given by

$$Lh\nu = E_{op} = \Delta E^{\ominus} + \lambda \qquad (38)$$

[*cf.* equation (19) above] while the activation energy of the thermal intramolecular reaction is

$$E_{act} = \lambda(1 + \Delta E^{\ominus}/\lambda)^2/4 \qquad (39)$$

and the rate is

$$k_{et} = A \exp(-E_{act}/RT) \qquad (40)$$

Thus where $\Delta E^{\ominus}$ for the overall reaction is known (it being zero for the symmetrical complex just mentioned), the reorganization energy λ can be calculated and thence the frequency factor A. In the theory of radiationless transitions, A is identified with the frequency of the vibrational mode which causes the electron transfer; thus $A \approx 10^{12}$ s^{-1}. In the transition state theory, equation (40) is replaced by

$$k_{et}' = A' \exp(-\Delta G^*/RT) \qquad (41)$$

[63] R. H. Petty and L. J. Wilson, *J. Chem. Soc., Chem. Commun.*, 1978, 483.
[64] D. Petridis, *Inorg. Chem.*, 1978, **17**, 3719.
[65] B. Binder, *J. Inorg. Nucl. Chem.*, 1979, **41**, 257.
[66] H. Okawa and S. Kida, *Inorg. Chim. Acta*, 1977, **23**, 253.
[67] R. D. Cannon, *Adv. Inorg. Chem. Radiochem.*, 1978, **21**, 179.
[68] T. J. Meyer, *Acc. Chem. Res.*, 1978, **11**, 94.

where $A' = RT/Lh \approx 10^{13}\ s^{-1}$ at room temperature. On the other hand, if the activating process is solvent reorganization, the frequency factor should presumably be as low as the dielectric relaxation frequency, $\sim 10^{11}\ s^{-1}$ for water.[69]

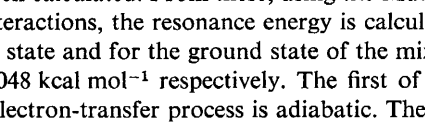
It will be appreciated that although the idea of measuring E_{op} and k_{et} for the same system is still unrealized for simple dinuclear complexes in solution there are several solid-state systems for which the relevant data are available, the thermal reaction rate having been measured by resonance methods or by its manifestation as hopping conductivity. A recent example is the complex $[W_4O_8Cl_8(H_2O)_4]^{2-}$, containing trapped W^{VI} and W^{V} valency states. Intervalence charge transfer has been detected ($\tilde{\nu}_{IT} = 15.4$ and $18.3 \times 10^3\ cm^{-1}$), and the thermal electron-transfer reaction is found by e.s.r. measurements, with $k_{et} = 2.5 \times 10^8\ s^{-1}$ at $-50\ °C$.[70]

As far as solution work is concerned, the example of cytochrome c^{III}+ $[Fe(CN)_6]^{4-}$ has already been mentioned (p. 9), and among smaller molecules the system $[(hedta)V^{IV}ORu^{II}(NH_3)_5]^+$ comes close to fulfilling the objective mentioned above. Besides the thermal electron transfer already described [equation (33)], the complex shows an absorption band at 600 nm which is not characteristic of either VO^{2+} or Ru^{2+} complexes, and is assigned to charge transfer, $Ru(dxy) \rightarrow VO(\pi^*)$. However, it is not certain that the thermal and the optical processes are truly analogous, since (*a*) the thermal reaction is competitive with dissociation of the $hedta^{3-}$ ligand and (*b*) in the optical process the receptor π^*-orbital is significantly delocalized away from the V atom.*

Examples of other dinuclear systems showing intervalence transfer are listed in Table 2 (p. 35). The compilation is not exhaustive, but is biased towards the kinds of complexes most often postulated as intermediates in electron-transfer reactions. Only a selection of studies, and those concerned with solution chemistry, will be reviewed here.

A spectrophotometric titration study of the complexes (10) ($n = 4$, 5, or 6) has yielded the comproportionation† constant $K_{com} = 24$ for the equilibrium

$$[Ru^{III}\cdots Ru^{III}] + [Ru^{II}\cdots Ru^{II}] \rightleftharpoons 2[Ru^{III}\cdots Ru^{II}] \qquad (42)$$



(10)

and from the intervalence charge-transfer spectrum the energy E_{op} and the mixing coefficient have been calculated. From these, using the Mulliken theory for weak charge-transfer interactions, the resonance energy is calculated for the electron-transfer transition state and for the ground state of the mixed-valence complex: $H_{12} = 1.65$ and 0.048 kcal mol^{-1} respectively. The first of these figures ensures that the thermal electron-transfer process is adiabatic. The second measures the

* The Reporter is indebted to a Referee for emphasizing these two points.
† Note the revised spelling of this word (see ref. 71, note 10).

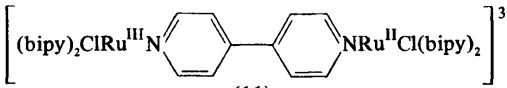
[69] C. Creutz, personal communication; *cf.* C. Creutz, P. Kroger, T. Matsubara, T. L. Netzel, and N. Sutin, *J. Am. Chem. Soc.*, 1979, **101**, 5442.
[70] Y. Jeannin, J.-P. Launay, J. Livage, and A. Nel, *Inorg. Chem.*, 1978, **17**, 374.

contribution of electronic energy to the stability of the mixed-valence complex, and this is remarkably small compared with $\Delta G_{com} = RT \ln (K_{com}/4) = 0.50$ kcal mol^{-1}. It is suggested that ΔG_{com} is largely electrostatic in origin, the charge configuration 2+,3+ being favoured relative to the 2+,2+ and 3+,3+ configurations. An attempt to calculate the electrostatic energy gave an underestimate, 0.09 kcal mol^{-1}, however.[71] On the other hand the electrostatic contribution to the IT energy has been calculated in good agreement with experiments.[72] The variation of E_{op} with different solvents is interpreted according to the equation

$$E_{op} = \lambda = \lambda_{in} + \lambda_{out} \qquad (43)$$

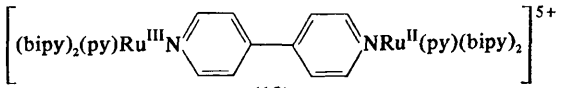
with Δ_{in} and Δ_{out} calculated, using equations (5) and (6) above. For the complex (10; $n=5$) both λ_{in} and λ_{out} are obtained in good agreement with experiment (for λ_{out} better agreement than with the ellipsoidal model previously suggested).[67,73]

For the complex (11) the calculated value of λ_{in} is too small. It is suggested that in general the IT spectrum will be an overlay of two bands, since the transferring electron may originate from either a bonding or a non-bonding π-orbital, and that in this case the higher-energy band may dominate the spectrum.[72]



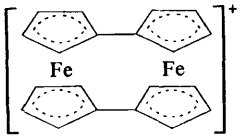
(11)

A recent study of the complex (12) also indicates that λ_{in} is larger than theoretically expected, while λ_{out} is smaller. Whether the above consideration applies here as well has not yet been discussed. The suggestion so far made is that the electron is transferring rapidly on the solvent reorganizational time-scale but not on the vibrational time-scale.[74]

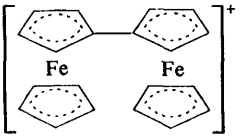


(12)

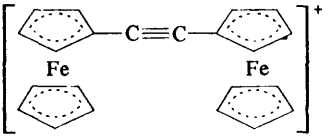
The three ions (13)—(15) have increasing valence trapping in the order shown, as evidenced by the width of the IT band, and the IT energies correlate with internuclear distance and solvent dielectric properties according to equation (6).[75]



(13)



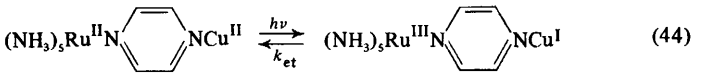
(14)



(15)

[71] J. E. Sutton, P. M. Sutton, and H. Taube, *Inorg. Chem.*, 1979, **18**, 1017.
[72] C. Creutz, *Inorg. Chem.*, 1978, **17**, 3723.
[73] R. D. Cannon, *Chem. Phys. Lett.*, 1977, **49**, 299.
[74] M. J. Powers and T. J. Meyer, *Inorg. Chem.*, 1978, **17**, 1785.
[75] M. J. Powers and T. J. Meyer, *J. Am. Chem. Soc.*, 1978, **100**, 4393.

The dimers $[L_2Mn^{III}(O)_2Mn^{II}L_2]^{3+}$ (L = bipy or phen) have the valence-trapped structure on the e.s.r. time-scale ($k_{et} < 10^8\ s^{-1}$)[76] and the difference in Mn^{III}—O and Mn^{II}—O bond lengths is measurable in the *X*-ray crystal structure.[77] Intervalence charge-transfer bands are found, but the solvent dependence is in the opposite direction to that required by equation (6). The reasons for this are not understood but specific interactions with the solvent are one possibility.[78] Also, the degree of delocalization of the electron is greater than in the ruthenium complexes such as (11; $n = 5$), no doubt reflecting the shorter metal–metal distance.[78] Electrochemical oxidation is reversible, but reduction leads to dissociation into mononuclear species.[79] The dimer with L = bipy has strong antiferromagnetic coupling.[76] The photoelectron-transfer process (44) was



(44)

reported by Durante and Ford in 1975.[80] The back reaction, $k_{et} \approx 7.8 \times 10^3\ s^{-1}$, is an intramolecular electron transfer. The excitation process is considered to be not intervalence (*i.e.* direct metal-to-metal) charge transfer, but metal-to-ligand, and this is confirmed by the resonance Raman spectrum of the Ru^{II}–Cu^{II} complex. The totally symmetric vibrations of the pyrazine molecule are enhanced, and the same effect is seen in the analogous Ru^{II}–Ni^{II} complex. A difference between the two complexes, however, is that with the copper complex continuous irradiation converts the whole of the ruthenium into Ru^{III} and the resonance enhancement is lost.[81]*

4 Bimolecular Reactions

A review on pulse radiolysis contains references to a number of intriguing metal–metal electron-transfer reactions with relatively unfamiliar reagents such as Zn^+, Cd^+, and Ag^0.[83]

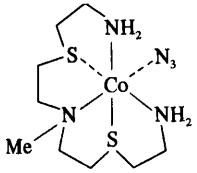
Lists of bimolecular electron-transfer reactions are given in Tables 3—6 (beginning on p. 37). Space prevents discussion of more than a small proportion of these.

Consideration of Specific Oxidants and Reductants.—In this section systems in which one or both of the metal ions involved is the centre of attention are described.

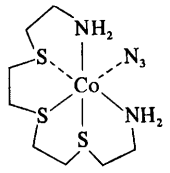
* A review on the resonance Raman effect contains some other references to electron-transfer systems, notably Pt^{IV}–Pt^{II} compounds.[82]

[76] S. R. Cooper, G. C. Dismukes, M. P. Klein, and M. Calvin, *J. Am. Chem. Soc.*, 1978, **100**, 7248.
[77] P. M. Plaksin, R. C. Stoufer, M. Mathew, and G. J. Palenik, *J. Am. Chem. Soc.*, 1973, **94**, 2121.
[78] S. R. Cooper and M. Calvin, *J. Am. Chem. Soc.*, 1977, **99**, 6623.
[79] M. M. Morrison and D. T. Sawyer, *J. Am. Chem. Soc.*, 1977, **99**, 257; *Inorg. Chem.*, 1978, **17**, 333.
[80] V. A. Durante and P. C. Ford, *J. Am. Chem. Soc.*, 1975, **97**, 6898.
[81] H. E. Toma and P. S. Santos, *Inorg. Chim. Acta*, 1977, **24**, L61.
[82] R. J. H. Clark and B. Stewart, *Struct. Bonding (Berlin)*, 1979, **36**, 1.
[83] D. Meyerstein, *Acc. Chem. Res.*, 1978, **11**, 43.

Cobalt(III). Using the specially synthesized ligands shown in formulae (16) and (17), two cobalt(III) complexes have been prepared, with tertiary N or thioether S



(16)



(17)

placed *trans* to the azide group, all other ligand atoms being the same. Both react with Fe^{2+} much more rapidly than does $[Co(NH_3)_5N_3]^{2+}$, but there is only a slight difference between the two complexes.[84] Likewise, the complex $[Co(NSSN)(N_3)_2]^+$ (NSSN = 1,8-diamino-3,6-dithiaoctane) reacts at much the same rate as *cis*-$[Co(NH_3)_4(N_3)_2]^+$. Thus there are no significant rate enhancements on replacing co-ordinated NH_3 by thioether S. This seems to be a peculiarity of azide-bridged systems, since with bromide, chloride, and oxalate bridges enhancements of 10^2—10^4 were observed.[85] The fact that thioether sulphur can function as an electron-transfer bridge has been proved in an extensive series of experiments[86] with reactions of the type $[Co(en)_2\{S(R)CH_2CH_2NH_2\}]^{3+} + Cr^{2+}$.

Reduction of the N-bonded glycinatopenta-amminecobalt(III) complex by Cr^{2+} yields O-bonded glycinatopenta-aquochromium(III), indicating a remote attack mechanism. The rate law is

$$-\mathrm{d}\ln[Co^{III}]/\mathrm{d}t = k_1 + k_2[H^+]^{-1} \qquad (45)$$

where the second term predominates throughout the acidity range studied. The proposed mechanism entails a bridged precursor complex but since the bridging chain offers no apparent assistance the electron-transfer process is similar to that of an outer-sphere reaction. The intramolecular electron-transfer rate constant is estimated to be $k_{et} = 0.25\ s^{-1}$ (25 °C). The *N*-alaninato-complex reacts similarly. With vanadium(II) as reductant the same rate law is observed, but control of the rate by substitution at $[V(H_2O)_6]^{2+}$ is a possibility. With $[Ru(NH_3)_6]^{2+}$, which must react by an outer-sphere path, no $[H^+]^{-1}$ term occurs in the rate law.[87]

Reactions of cobalt complexes of macrocyclic tetramine ligands with various couples (including the highly oxidizing $MnCl^{2+/+}$, hitherto little studied) have been reported. Inner-sphere and outer-sphere reactions involving, for example, $[Ru(NH_3)_5py]^{3+/2+}$ have been characterized. A free-energy correlation for reactions between $[Co(N_4)(OH_2)_2]^{2+}$ with inner-sphere oxidants shows the expected slope $\partial\Delta G^{\ddagger}/\partial\Delta G^{\ominus} \approx 0.5$ down to a limit of $\Delta G^{\ddagger} \approx 7$ kcal mol^{-1}, which is believed to represent diffusion control. Application of the Marcus equations (1) and (3) to reactions of both types leads to an assessment of the factors con-

[84] J. H. Worrell, R. Goddard, and T. Jackman, *Inorg. Chim. Acta*, 1979, **32**, L71.
[85] J. H. Worrell and T. A. Jackman, *J. Am. Chem. Soc.*, 1971, **93**, 1044; J. H. Worrell, R. A. Goddard, E. M. Gupton, and T. A. Jackman, *Inorg. Chem.*, 1972, **11**, 2734; R. A. Goddard and J. H. Worrell, *ibid.*, 1977, **16**, 1249.
[86] G. J. Kennard and E. Deutsch, *Inorg. Chem.*, 1978, **17**, 2225.
[87] C. S. Glennon, J. D. Edwards, and A. G. Sykes, *Inorg. Chem.*, 1978, **17**, 1654.

tributing to the intrinsic barrier λ. The barrier is greater for outer-sphere than for inner-sphere reactions, and for the outer-sphere mechanisms the inner-sphere part λ_{in} [equation (4)] is about twice the outer-sphere part λ_{out}.[88]

Titanium(III). For the reaction $[Co(phen)_3]^{3+} + Ti^{III}$ the acid dependence of the second-order rate constant can be fitted to either of the expressions (46) or (47).

$$k = (a + b[H^+]^{-1}) \quad (46)$$

$$k = c/(d + [H^+]) \quad (47)$$

The former is preferred since it avoids the need for a pathway with Ti^{3+} as the effective reducing agent, and allows the mechanism

$$Ti^{3+} \overset{K_a}{\rightleftharpoons} TiOH^{2+} + H^+ \quad (48)$$

$$[Co(phen)_3]^{3+} + TiOH^{2+} \xrightarrow{k_1} \text{products} \quad (49)$$

with $K_a = b = (1.52 \pm 0.34) \times 10^{-3}$ M^{-1}, which is similar to values obtained in other studies. On the other hand, data for the analogous reaction with $[Fe(phen)_3]^{3+}$ as oxidant, fitted to the same rate law, yield $K_a = 4.3 \times 10^{-2}$ M^{-1}.[89]

The rates of reduction of $[Co(edta)]^-$, $[Co(edtaH)(OH_2)]$, and $[Co(edtaH)Cl]^-$ by Ti^{III} have been reported.[90] Again the hydrogen-ion dependences show that $TiOH^{2+}$, not Ti^{3+}, is the effective reducing agent. With the first-named complex there is also a rate term in $[Ti^{III}]^2$, which seems curious, especially since the complex, with sexadentate edta and no free carboxy-group, apparently offers fewer sites for binding titanium ions than do the other two. Reduction rates of a series of ruthenium complexes, all expressible as a rate term $k[Ru^{III}][TiOH^{3+}]$, increase in the order $[Ru(NH_3)_5Cl]^{2+} < [Ru(NH_3)_6]^{3+} < [Ru(NH_3)_5py]^{3+} < [Ru(NH_3)_5pyz]^{3+} <$ *cis*-$[Ru(NH_3)_4(isonicotinamide)_2]^{3+}$. The increase is mainly due to decreasing $\Delta H^{\ddagger}$, and the values of $\log k$ correlate with reduction potentials of the ruthenium complexes as predicted by the Marcus equation.[91] The reduction potential of titanium(IV),

$$TiOH^{3+} + e^- \rightleftharpoons TiOH^{2+} \quad (50)$$

is estimated to be $E^{\ominus} = 0.08$ V, from polarographic data.[92]

Iron. Volumes of activation for the reactions $[Co(NH_3)_5X]^{2+} + Fe^{2+}$ in DMSO as solvent are 0.0, 3.8, and 10.3 cm^3 mol^{-1} for X = Br, Cl, and F, respectively.[93] These are interpreted in terms of an inner-sphere mechanism for all three reactions, and the trend is assigned to changes in solvation and to steric crowding. A previous suggestion[94] that the co-ordination number of the Fe ion changes from 6 to 4 on going from reactants to intermediate for X = Cl or Br is not supported by these data.

[88] B. Durham, J. F. Endicott, C.-L. Wong, and D. P. Rillema, *J. Am. Chem. Soc.*, 1979, **101**, 847.
[89] N. Akinyugha, J. Ige, J. F. Ojo, O. Olubuyide, and R. Simoyi, *Inorg. Chem.*, 1978, **17**, 218.
[90] R. Marčec and M. Orhanović, *Inorg. Chem.*, 1978, **17**, 3672.
[91] K. M. Davies and J. E. Earley, *Inorg. Chem.*, 1978, **17**, 3350.
[92] R. A. Lee, unpublished experiments cited in ref. 91.
[93] R. Van Eldik, D. A. Palmer, and H. Kelm, *Inorg. Chim. Acta*, 1978, **29**, 253.
[94] B. A. Matthews and D. W. Watts, *Aust. J. Chem.*, 1976, **29**, 97; *cf.* also B. A. Matthews, J. V. Turner, and D. W. Watts, *ibid.*, p. 551.

Self-exchange rates of the three tetrakis-(4-pyridyl)porphine complexes $[Fe(P)(imidazole)_2]^{5+/4+}$, $[Fe(P)(OH)(OH_2)]^{4+/3+}$, and $[Fe(P)(OH_2)]^{5+/4+}$ have been estimated as $>10^7$, $>10^9$, and 1.2×10^6 M^{-1} respectively.[95] Of the iron(III) complexes in this series, the first is low-spin, the second is believed to be an equilibrium mixture of high-spin and low-spin forms, and the third is high-spin.[96] These results support a previous suggestion that electron transfer to or from a low-spin iron porphyrin system has a negligible Franck–Condon barrier.[97]

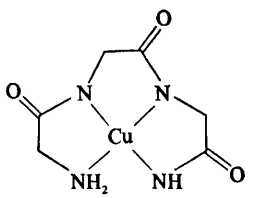
Copper. Copper(II) phenanthroline- and bipyridine-type complexes catalyse the 'autoxidation' (*i.e.* the net oxidation by molecular oxygen) of cytochrome *c* according to the mechanism[98,99]

$$Cu^{II} + c^{II} \rightarrow Cu^{I} + c^{III} \quad (51)$$

$$Cu^{I} + \tfrac{1}{4}O_2 \rightarrow\!\!\!\!\rightarrow Cu^{II} \quad (52)$$

the first step being rate determining. The data have been used to calculate self-exchange rates for the copper(II)/copper(I) couples $[Cu(2,9\text{-}Me_2phen)_2]^{2+/+}$, $[Cu(5\text{-}NO_2\text{-}phen)_2]^{2+/+}$, and $[Cu(phen)_2]^{2+/+}$. These decrease in the order stated, and are all much less than the self-exchange rate of, for example, $[Fe(phen)_3]^{3+/2+}$. The effects are ascribed to differences in co-ordination geometry between the two oxidation states of copper.

Copper(III) is an interesting new addition to the list of electron-transfer oxidants. Complexes with peptides such as triglycineamide (18) [the ligand has



(18)

lost three protons and hence the formula is conventionally written $Cu(H_{-3}Ga)$] are relatively inert to substitution. Rates of reduction[100] of a variety of peptide Cu^{III} complexes with $[IrCl_6]^{2-}$ support the general mechanism

$$[Cu^{III}(H_{-x}L)] + [IrCl_6]^{3-} \underset{-1}{\overset{1}{\rightleftharpoons}} [Cu^{II}(H_{-x}L)]^{-} + [IrCl_6]^{2-} \quad (53)$$

$$[Cu^{II}(H_{-x}L)]^{-} \xrightarrow{2} Cu^{2+} + HL \quad (54)$$

retardation by $[IrCl_6]^{2-}$ being significant in some cases. Values of k_{-1} calculated from K_1 and k_1 are close to the diffusion-controlled limit (typically $\sim10^8$ M^{-1} s^{-1}). The correlation of k_1 with K_1 for the uncharged Cu^{III} peptide complexes fits

[95] R. F. Pasternack and E. G. Spiro, *J. Am. Chem. Soc.*, 1978, **100**, 968.
[96] R. F. Pasternack, H. Lee, P. Malek, and C. Spencer, *J. Inorg. Nucl. Chem.*, 1977, **39**, 1865.
[97] N. Sutin, *Chem. Br.*, 1972, **8**, 148.
[98] M. A. Augustin and J. K. Yandell, *J. Chem. Soc., Chem. Commun.*, 1978, 370.
[99] M. A. Augustin and J. K. Yandell, *Inorg. Chem.*, 1979, **18**, 577.
[100] G. D. Owens, K. L. Chellappa, and D. W. Margerum, *Inorg. Chem.*, 1979, **18**, 960.

the Marcus equation and gives the value 7×10^7 M^{-1} s^{-1} for the (average) self-exchange rate constant.

Actinides. The reactions $[Ru(NH_3)_6]^{3+} + U^{3+}$, $[Ru(NH_3)_5H_2O]^{3+} + U^{3+}$, and $[Ru(en)_3]^{3+} + U^{3+}$ are second-order, are independent of H^+ concentration, and have almost zero enthalpy of activation.[101] The latter feature is attributed to the concentration of charge in the transition state, as with other reactions between highly charged cations which have been noted to have low, even negative ΔH^*, and highly negative ΔS^*.[102] By means of the Marcus cross-relation, the self-exchange rate for the reaction $U^{4+} + U^{3+}$ is obtained as 5.9×10^{-5} M^{-1} s^{-1} (25 °C). This is much lower than a previously reported value, obtained[103] by extrapolation of a free-energy plot (ΔG^* *vs.* $\Delta G^\ominus$ for various reactions) which the authors criticize. A similar low value is obtained for the reaction $Np^{4+} + Np^{3+}$, 4.6×10^{-4} M^{-1} s^{-1}, comparable with a previous estimate[104] for $Eu^{3+} + Eu^{2+}$, $\sim 10^{-4}$ M^{-1} s^{-1}. These low rates may be associated with the heavy shielding of the transferring *f* electron. It is implied that a previously reported value[105] for $Pu^{4+} + Pu^{3+}$, 22 M^{-1} s^{-1} at 25 °C, with a strong temperature dependence, may be in error.

Rates of reduction by U^{3+} of a series of cobalt(III) ammine complexes, with ligands such as to ensure an outer-sphere mechanism (see Table 3), correlate with rates of reduction by $[Ru(NH_3)_6]^{2+}$ according to the equation

$$\log k_U = 1.08 \log k_{Ru} + 1.76 \qquad (55)$$

For reactions of carboxylatopenta-amminecobalt(III) complexes with U^{3+}, inner-sphere mechanisms are suggested: the reaction $[Co(NH_3)_5OAc]^{2+} + U^{3+}$ proceeds more than 10^4 times faster than the reaction $[Co(NH_3)_6]^{3+} + U^{3+}$, whereas in the absence of bridging the two oxidants are reduced at nearly the same rate. For the carboxylato series, reductions by U^{3+} and by Cr^{2+} are correlated as follows:

$$\log k_U = 1.14 \log k_{Cr} + 4.15 \qquad (56)$$

Gould and co-workers point out that for reactions of carboxylato-ammine cobalt(III) complexes, on comparing the four reductants Cr^{2+}, V^{2+}, Eu^{2+}, and U^{3+}, it is the most reactive of the four, U^{3+}, which shows the greatest sensitivity to steric effects of substituents (as defined by Taft's E_S parameter). They relate this behaviour to a detailed consideration of the geometry of the *f*-orbital which provides the transferring electron.[106]

Other Transition Metals. A study[107] of the reaction $[IrCl_6]^{2-} + [Mo(NCS)_6]^{3-}$ is concerned with the oxidation of Mo^{III} through Mo^{IV} to Mo^V and the restraints imposed by the need to provide an aquo/oxo ligand prior to formation of Mo^V. In organic solvents (acetone or acetonitrile) the reaction is rapid and conforms to the stoicheiometry

$$[IrCl_6]^{2-} + [Mo(NCS)_6]^{3-} \rightarrow [IrCl_6]^{3-} + [Mo(NCS)_6]^{2-} \qquad (57)$$

[101] C. Lavallee, D. K. Lavallee, and E. A. Deutsch, *Inorg. Chem.*, 1978, **17**, 2217.
[102] R. C. Patel, R. E. Ball, J. F. Endicott, and R. G. Hughes, *Inorg. Chem.*, 1970, **9**, 23.
[103] A. Adegite, H. Egboh, J. F. Ojo, and R. Olieh, *J. Chem. Soc., Dalton Trans.*, 1977, 833.
[104] M. Chou, C. Creutz, and N. Sutin, *J. Am. Chem. Soc.*, 1977, **99**, 5615.
[105] T. K. Keenan, *J. Phys. Chem.*, 1957, **61**, 1117.
[106] M. K. Loar, M. A. Sens, G. W. Loar, and E. S. Gould, *Inorg. Chem.*, 1978, **17**, 330.
[107] A. B. Soares, R. S. Taylor, and A. G. Sykes, *Inorg. Chem.*, 1978, **17**, 496.

In aqueous solution the same reagents when mixed in the 1 : 1 ratio react rapidly, probably to give the same initial products, but the Mo^{IV} species then decomposes at a rate independent of Ir^{IV} or Mo^{III} concentrations. The water addition reaction is suggested:

$$[Mo(NCS)_6]^{2-} + nH_2O \rightarrow [Mo(NCS)_6(OH_2)_n]^{2-} \quad (58)$$

Substitution reactions of the type

$$[Ru^{II}(edta)(OH_2)]^{2-} + L \xrightarrow{1} [Ru^{II}(edta)L]^{2-} \quad (59)$$

(L = isonicotinamide, pyrazine, or acetonitrile) are catalysed by traces of ruthenium(III), as a result of the reactions

$$[Ru^{III}(edta)(OH_2)]^{-} + L \underset{-2}{\overset{2}{\rightleftharpoons}} [Ru(edta)L]^{-} \quad (60)$$

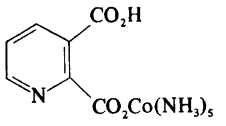
$$[Ru(edta)I]^{-} + [Ru(edta)]^{2-} \xrightarrow{3} [Ru(edta)L]^{2-} + [Ru(edta)]^{-} \quad (61)$$

the ruthenium(III)–water bond being unexpectedly more labile than the ruthenium(II)–water bond ($k_3/k_1 \approx 10^5$ for isonicotinamide).[108]

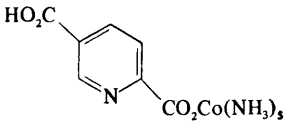
Organic Bridging Groups—In most of the systems to be mentioned here, the point of discussion is the distinction between 'chemical transfer' and 'resonance transfer' mechanisms. In the former, an intermediate occurs in which the electron (or a positive hole) is temporarily trapped by the ligand, which may thus be considered a free radical; in the latter, there is no such intermediate, or, more strictly, if there is an intermediate its lifetime is comparable with the lifetimes of the transition states which separate it from reactants and products.

Chromium(II) reductions of $Co(NH_3)_5$ complexes of various dicarboxylic acid derivatives of pyridine have been studied in order to determine the effect of placing the cobalt centre at different positions relative to the ring nitrogen.[109] It is found that in general complexes with cobalt attached to carboxyl in the 2-position react 10—10^4 times faster than those with cobalt attached at a more remote position. This is attributed to chelation in the transition state.

The two complexes (19) and (20), with cobalt(III) specifically attached to the 2-position, have been prepared by the action of nitrosyl perchlorate on the



(19)



(20)

corresponding 3-$CONH_2$ and 5-$CONH_2$ complexes. Reduction rates with chromium(II) conform to the expression (62)

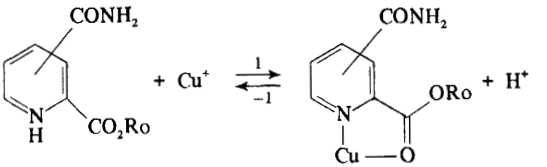
$$k_{obs} = k_0 + k_1[H^+]^{-1} \quad (62)$$

[108] T. Matsubara and C. Creutz, *J. Am. Chem. Soc.*, 1978, **100**, 6255.
[109] J. C.-K. Heh and E. S. Gould, *Inorg. Chem.*, 1978, **17**, 3138.

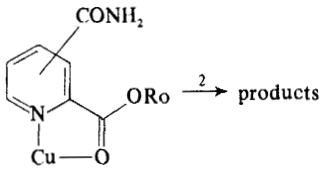
or alternatively the same expression without the k_0 term, the k_1 term corresponding to the reaction with the ring nitrogen unprotonated. Reactions of the corresponding amides with copper(I), however, gave the expression[110]

$$k_{obs} = a/(1+b^{-1}[H^+]) \quad (63)$$

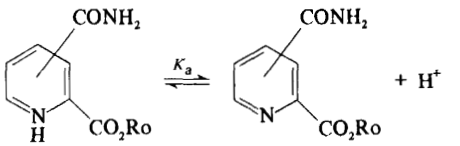
Two mechanisms are considered, exemplified by equations (64) and (65) [Ro = $Co(NH_3)_5$], giving $a = k_1$ and $ab^{-1} = K_1k_2$, or equations (66) and (67), giving $a = K_aK_1'k_2'$ and $ab^{-1} = K_ak_1'$.



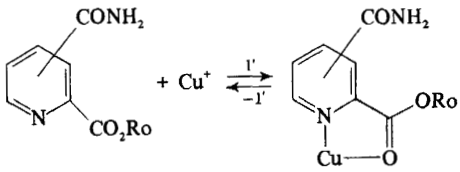
(64)



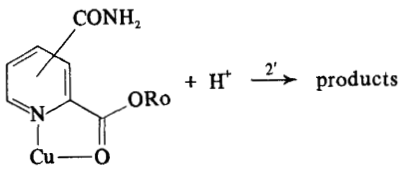
(65)



(66)



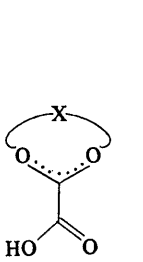
(67a)

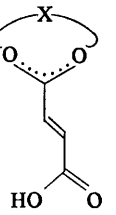


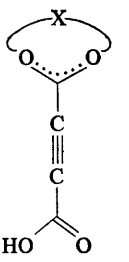
(67b)

The titanium(III) reductions of the series of complexes (21)—(23) [*cf.* formula (8)] all feature two rate terms of the type $[Ti^{III}][(Co^{III})_2LH][H^+]^{-n}$ ($n = 1$ or 2), suggesting attack of $TiOH^{2+}$ on the protonated and the deprotonated complex.[111] It is suggested that the first of the two terms in each corresponds to an outer-sphere pathway; this is borne out by a correlation of the rates of these and

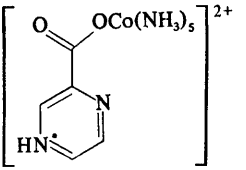
[110] J. C.-K. Heh and E. S. Gould, *Inorg. Chem.*, 1978, **17**, 3142.
[111] M. Hery and K. Wieghardt, *Inorg. Chem.*, 1978, **17**, 1130.

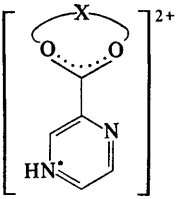

(21)


(22)

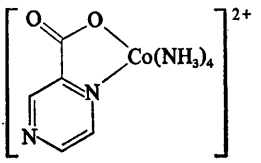

(23)

other $TiOH^{2+}$ reactions with those of reductions by V^{2+}. The second of the two terms, however, may well correspond to inner-sphere remote attack, at least in the case of complexes (21) and (22), the rates being considerably higher than the $TiOH^{2+}/V^{2+}$ correlation would predict.[111] The radical ion complexes (24) and (25), previously postulated as intermediates in the reductions of the corresponding pyrazinecarboxylate cobalt(III) complexes by Cr^{2+},[112,113] * have now


(24)


(25)

been directly characterized.[114] They are generated by the use of the propan-2-ol radical $Me_2\dot{C}OH$ as reductant, and detected by e.s.r. spectra. Intramolecular electron-transfer rates have been measured. In contrast to complexes (24) and (25), the complex (26) is reduced directly to Co^{II} by $Me_2\dot{C}OH$, with no detectable intermediate.[114] The incorporation of a reducible pyridine-type function in the carboxylato-penta-ammine series leads to a marked rate enhancement, even when there is no conjugated bond system linking the pyridine ring to the cobalt,[115]


(26)

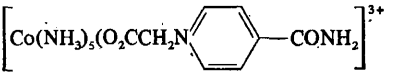
* Strictly speaking, the intermediates in the Cr^{II} reductions are the Cr^{III} adducts of these complexes.

[112] E. S. Gould, *J. Am. Chem. Soc.*, 1972, **94**, 4360.
[113] H. Spiecker and K. Wieghardt, *Inorg. Chem.*, 1977, **16**, 1290.
[114] K. Wieghardt, H. Cohen, and D. Meyerstein, *Angew. Chem. Int. Ed. Engl.*, 1978, **17**, 608.
[115] C. A. Radlowski and E. S. Gould, *Inorg. Chem.*, 1979, **18**, 1289.

e.g. a ratio of $\sim 10^4$ for Cr^{2+} reductions of (27) and (28). Moreover, the chromium(III) product is carboxyl-bound not amide-bound. A chemical mechanism is suggested in which the chromium(II), while attached to the carbonyl group nearest to the cobalt, also participates in a charge-transfer interaction with the pyridine ring.

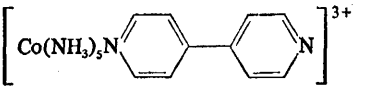
$[Co(NH_3)_5(O_2CCH_2NH_3)]^{2+}$

(27)



(28)

Leopold and Haim have sought evidence for the chemical mechanism by studying the reactions of a series of cobalt complexes such as (29) with excited $[Ru(bipy)_3]^{2+}$, *i.e.* by luminescence quenching experiments (*cf.* Section 4



(29)

below). Quenching rate constants for the cobalt complexes are similar to those of the free organic ligands, and it is noteworthy that some at least of the latter give transient radical species as products. A chemical mechanism is proposed, but attempts to detect the intermediate were unsuccessful.[116] Chemical mechanisms are thought to be involved in reactions of various complexes of the type $[Co(NH_3)_5(O_2CC_5H_3NCONH_2)]^{2+}$ with Cr^{2+},[109] but not with Cu^+,[110] and in reactions of complexes of the type $[Co(NH_3)_5\{O_2CC_6H_3(R)NO_2\}]^{2+}$ with V^{2+} but not with $[Ru(NH_3)_6]^{2+}$.[117]

The product of reaction of pyrazinecarboxamide with Cr^{2+} is a dark green complex of chromium(III) and the pyrazinecarboxamide radical ion, first characterized in 1965 (see ref. 118 and references cited therein). Evidence has now been presented to show that in reactions with various cobalt(III) complexes, the effective reducing agent is, not the radical-ion complex but free Cr^{2+} present in equilibrium with it (Pz = substituted pyrazine):

$$Cr^{III}(Pz) \underset{-1}{\overset{1}{\rightleftharpoons}} Pz + Cr^{2+} \qquad (68)$$

$$Co^{III} + Cr^{2+} \xrightarrow{2} Co^{2+} + Cr^{III} \qquad (69)$$

The kinetics yield values of k_1 and K_1k_2, but k_2 is known already from previous studies, and hence K_1 can be calculated, as 3×10^{-8} M. From the known and

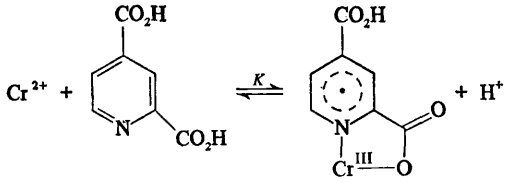
[116] K. R. Leopold and A. Haim, *Inorg. Chem.*, 1978, **17**, 1753.
[117] R. Reid, F.-R. F. Fan, Y.-T. Fanchiang, and E. S. Gould, *Inorg. Chem.*, 1978, **17**, 2766.
[118] M.-Y. Wu, S. J. Paton, Y.-T. Fanchiang, E. Gelerinter, and E. S. Gould, *Inorg. Chem.*, 1978 **17**, 326.

estimated standard potentials of the Cr^{3+}/Cr^{2+} and Pz/Pz· couples, respectively, the following equilibrium is obtained:

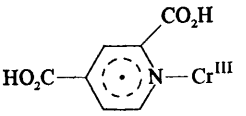
$$Cr^{III}(Pz^{\cdot})^{2+} \rightleftharpoons Cr^{3+} + (Pz^{\cdot})^{-} \qquad (70)$$

with $K = 0.1$ M.*

Reaction of chromium(II) with pyridine-2,4-dicarboxylic acid yields two radical complexes of Cr^{III}, one of which is active in reducing cobalt(III) complexes, the other not. The inactive form is formed in reversible equilibrium, and is believed to be the chelate (30), with apparent formation constant $K_{app} = K/[H^+] \approx 50\ M^{-1}$ at 20 °C in 1.2M-$HClO_4$. The active form, possibly (31), is not detected as such, but is an intermediate postulated in the reaction $[Co(NH_3)_5py]^{3+} + Cr^{2+}$, when accelerated by the presence of the organic acid.[119]

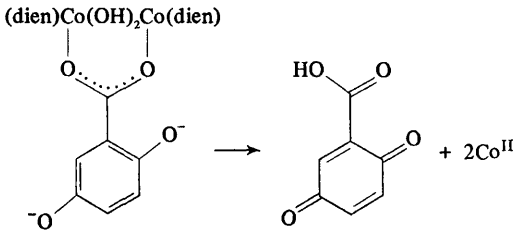


(30)



(31)

Reaction (71) may involve a radical intermediate of the semiquinone type, though this is not certain. The alternative is a one-step, two-electron transfer.[120] †



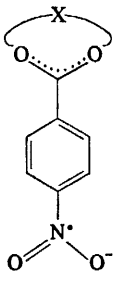
(71)

The radical ions (32) and (33) have been generated by the action of $Me_2\dot{C}OH$ radical on the appropriate complexes, and intramolecular reduction of Co^{III} has been observed.[121]

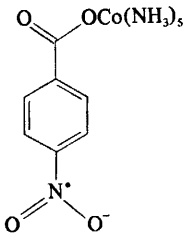
* The authors reach a different conclusion thus. '[The $Pz-Pz^{\cdot}_{m}$ potential of -0.020 V], in combination with a Cr^{3+} potential of -0.41 V, leads to an equilibrium constant of 3×10^{-7} for a redox reaction uncomplicated by chromium–pyrazine co-ordination. The discrepancy between this value and the observed constant, 3×10^{-8} M, indicates that the chromium(III) radical complex is 10 times as stable toward heterolysis . . . as is the (unobservable) chromium(III)–pyrazine complex, but in the absence of further information we cannot assign individual formation constants to these isomeric species.' It seems that the authors have attributed the equilibrium constant of 3×10^7 M to the equilibrium $Cr^{III}(Pz^{\cdot})^{2+} \rightleftharpoons Cr^{II}(Pz)^{2+}$, whereas in fact it relates to the outer-sphere process $Cr^{3+} + (Pz^{\cdot})^{-} \rightleftharpoons Cr^{2+} + Pz$, leading directly to the conclusion stated in the text above.

† Stable analogues of the complex shown in equation (71) are known with Fe^{III} as the metal. Although formed from $[Fe^{II}(salen)]$ and various *para*-quinones, they are formulated $[\{Fe^{III}(salen)\}_2Q]$ where Q^{2-} is the dianion of hydroquinone.[125]

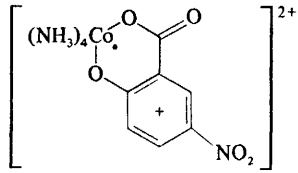
[119] Y.-T. Fanchiang, J. C.-K. Heh, and E. S. Gould, *Inorg Chem.*, 1978, **17**, 1142.
[120] H. Bertram and K. Wieghardt, *Chem. Ber.*, 1978, **111**, 832.
[121] K. Wieghardt, H. Cohen, and D. Meyerstein, *Ber. Bunsenges. Phys. Chem.*, 1978, **82**, 388.



(32)



(33)



(34)

Of related interest are cobalt(III) complexes such as (34) with oxidized radical ions, *i.e.* with a hole in the ligand instead of an electron. These were originally reported as cobalt(IV) complexes.[122] and are still so described in the title of the most recent paper,[123] but are now characterized as cobalt(III) species on the basis of the i.r. spectrum of the $Co(NH_3)_4$ group.[123]

Reversible thermal electron transfer between the metal ion and the ligand is now well characterized for Ni^{III} complexes of macrocyclic tetra-amines, such as tetraphenylporphine.[124]

Electron-transfer 'chains', sequences of reactions of the type

$$A^+ + X \rightleftarrows A + X^+ \quad (72)$$

$$X^+ + B \rightarrow X + B^+ \quad (73)$$

in which the overall reaction is faster than the direct process $A^+ + B$, so that reagent X is a catalyst, were reported previously by Gould and co-workers (previous Report in this series) and further examples are listed in Table 3. From the same laboratory comes a report of a four-membered chain, with two catalysts, isonicotinamide (I) and methylviologen (V),

$$I + Eu^{2+} \underset{-1}{\overset{1}{\rightleftharpoons}} I^- + Eu^{3+} \quad (74)$$

$$V + I^- \underset{-2}{\overset{2}{\rightleftharpoons}} V^- + I \quad (75)$$

$$Co^{III} + V^- \rightleftharpoons Co^{II} + V \quad (76)$$

with the overall rate law

$$-d[Co^{III}]/dt = K_1K_2k_3[V][Eu^{2+}][Co^{III}][Eu^{3+}]^{-1} \quad (77)$$

The effect is described as 'synergistic', *i.e.* the two catalysts together are more effective than either one alone, and this is explained by the fact that isonicotinamide has an effective lead-in group for a bridged electron transfer, so that step 1 is faster than the reaction $V + Eu^{2+}$, and the redox potentials of the catalysts are such that the steady-state concentration of V^- is greater than that of I^-.[126]

[122] Y. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1969, **49**, 999, and references cited therein.
[123] Y. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 2894.
[124] E. C. Johnson, T. Niem, and D. Dolphin, *Can. J. Chem.*, 1978, **56**, 1381.
[125] S. L. Kessell and D. N. Hendrickson, *Inorg. Chem.*, 1978, **17**, 2630.
[126] Y.-T. Fanchiang and E. S. Gould, *Inorg. Chem.*, 1978, **17**, 1138.

5 Reactions of Electronically Excited States

It has been remarked[127] that 'in many respects, the chemistry of the luminescent excited state of tris-(2,2′-bipyridyl)ruthenium(II) . . . is as well characterized as that of many ground-state metal complexes'. Certainly kinetic data on the electron-transfer reactions of $*[Ru(bipy)_3]^{2+}$, both as oxidant and as reductant, are becoming plentiful year by year. These, and data for other excited metal ions, are listed in Table 6 (p. 58). Emission quenching of a series of polypyridyl-type ruthenium(II) complexes with Cu^{2+} proceeds by electron transfer,

$$*[RuL_3]^{2+} + Cu^{2+} \xrightarrow{k_1} [RuL_3]^{3+} + Cu^{+} \qquad (78)$$

and the back reactions,

$$[RuL_3]^{3+} + Cu^{+} \rightarrow [RuL_3]^{2+} + Cu^{2+} \qquad (79)$$

have also been measured.[128,129] Rate constants k_1 correlate with thermodynamic driving force, but the selectivity is not as great as that predicted by the Marcus equation. Among other quenching ions, Eu^{3+} shows normal selectivity, and Cr^{3+} and Fe^{3+} none at all, but Fe^{3+} reacts at the diffusion-controlled limit and Cr^{3+} operates by energy transfer, not electron transfer. It is suggested that the salient difference between Eu^{3+} and Cu^{2+} is that the latter is the more powerful oxidant, and these data are a further example of departure from the Marcus free-energy dependence in the highly 'exergonic' range.[128,129] The absolute rates of some $*[RuL_3]^{2+} + Eu^{2+}$ reactions are[130] somewhat lower than predicted from the Marcus cross-relation, as has been noted previously for other Eu^{2+} reductions.[131]

The emitting state of $[Ru(bipy)_3]^{2+}$ which has hitherto been studied, conventionally written $*[Ru(bipy)_3]^{2+}$, is a metal-to-ligand charge-transfer state* (more strictly it is a mixture of the three lowest-lying CT states in thermal equilibrium).[133] Another high-energy state has now been detected[134] in the reaction of $[Ru(bipy)_3]^{2+}$ with e^-_{aq} and has a longer lifetime than $*[Ru(bipy)_3]^{2+}$. This species has not been fully characterized and it is thought that it may be 'another excited state or a co-ordinated radical' – the latter term perhaps implying some structural change in the ligand as opposed to mere residence of an odd electron in the ligand orbitals. The reaction $[Ru(bipy)_3]^{3+} + e^-$ thus yields three products:

$$[Ru(bipy)_3]^{3+} + e^- \longrightarrow \begin{cases} {}^{\ddagger}[Ru(bipy)_3]^{2+} & (> 55\%) \\ *[Ru(bipy)_3]^{2+} & (38\%) \\ [Ru(bipy)_3]^{2+} & (< 7\%) \end{cases} \qquad (80)$$

* The absorption spectrum of this excited complex has now been measured in detail.[128,132]

[127] C. Creutz, N. Sutin, and B. S. Brunschwig, *J. Am. Chem. Soc.*, 1979, **101**, 1297; see also ref. 128.
[128] N. Sutin and C. Creutz in 'Inorganic and Organometallic Photochemistry', ed. M. S. Wrighton, *Adv. Chem. Ser.*, No. 168, A.C.S. Washington D.C., 1978, p. 1.
[129] M. A. Hoselton, C.-T. Lin, H. A. Schwarz, and N. Sutin, *J. Am. Chem. Soc.*, 1978, **100**, 2383.
[130] C. Creutz, *Inorg. Chem.*, 1978, **17**, 1046.
[131] M. Chou, C. Creutz, and N. Sutin, *J. Am. Chem. Soc.*, 1977, **99**, 5615.
[132] U. Lachish, P. Infelta, and M. Grätzel, *Chem. Phys. Lett.*, 1979, **62**, 317.
[133] Ref. 134, note 2, and references cited therein.
[134] C. D. Jonah, M. S. Matheson, and D. Meisel, *J. Am. Chem. Soc.*, 1978, **100**, 1449.

the yields correlating inversely with the overall free-energy charge. This is considered to be another example of the slowness of highly exergonic electron transfer. The reaction to produce ($[Ru(bipy)_3]^{2+}$ has $\Delta G^{\ominus} = -4.17$ eV and must be well into the inverted region. The authors note that this situation was predicted by Marcus in 1965,[135] with numerical data, chosen as example, remarkably close to those of the present case.

Two studies of the quenching of excited chromium(III) complexes by Fe^{2+} have appeared.[13,136] Rates correlate with redox potentials of the $*Cr^{III}$ complex,* and this is the main, though not the only[13] reason for assigning an electron-

$$*[CrL_3]^{3+} + Fe^{2+} \rightarrow [CrL_3]^{2+} + Fe^{3+} \quad (81)$$

transfer mechanism. (With O_2 as quencher, rates are independent of redox potential, but correlate with the energy of the ^2E excited state of chromium, implying an energy-transfer mechanism;[13] with I^-, the redox correlation is found, implying again the electron-transfer mechanism[136]). By fitting the data to the Marcus equations (82) and (83) the unknown rate constant k_{22} for the self-

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2} \quad (82)$$

$$\log f = (\log K_{12})^2/4 \log (k_{11}k_{22}/Z^2) \quad (83)$$

exchange (84) can be obtained, using the known k_{11} and K_{12}. Over a small

$$*[CrL_3]^{3+} + [CrL_3]^{2+} \rightarrow [CrL_3]^{2+} + *[CrL_3]^{3+} \quad (84)$$

range of $\log K_{12}$, the segment of the Marcus curve is a straight line, of which slope and intercept yield two independent experimental parameters, whereas according to the theory there is only one to be determined. In other words two estimates of k_{22} can be obtained, one from the slope and one from the intercept. Brunschwig and Sutin[13] found that the two estimates were significantly different, and to eliminate the discrepancy they propose that the cross-reactions are non-adiabatic. On the other hand, Serpone, Hoffman, and co-workers,[136] using similar and in some cases identical chromium(III) complexes, found approximately the same slope for the $\log k_{12}$–$\log K_{12}$ plot but a higher intercept so that no non-adiabatic correction was required. The only obvious difference between the two sets of experiments is in the reaction media, 1M-H_2SO_4 and 1M-HCl respectively. Rates of quenching of the same chromium(III) oxidant by $[Ru(bipy)_3]^{2+}$ and $[Os(bipy)_3]^{2+}$ can be fitted to the Marcus equation without this difficulty, implying that the reactions $*[CrL_3]^{3+} + [Ru(bipy)_3]^{2+}$ and $*[CrL_3]^{3+} + [Os(bipy)_3]^2$ are adiabatic.

It is of interest that the rates of the self-exchange reactions involving excited complex are similar to those of the corresponding reactions of ground-state species, *i.e.*

$$*[Cr(bipy)_3]^{3+} + [Cr(bipy)_3]^{2+} \rightarrow [Cr(bipy)_3]^{2+} + *[Cr(bipy)_3]^{3+} \quad (85)$$

$$[Cr(bipy)_3]^{3+} + [Cr(bipy)_3]^{2+} \rightarrow [Cr(bipy)_3]^{2+} + [Cr(bipy)_3]^{3+} \quad (86)$$

* The redox potential of the $*Cr^{III}/Cr^{II}$ couple is calculated by combining that of the ground-state Cr^{III}/Cr^{II} couple with the excitation energy $Cr^{III} \rightarrow *Cr^{III}$ obtained by averaging the energies of the absorption maximum of Cr^{III} and the emission of $*Cr^{III}$, so that Franck–Condon effects cancel out.

[135] R. A. Marcus, in 'Solvated Electron', ed. E. J. Hart, *Adv. Chem. Ser.* No. 50, A.C.S., Washington D.C., 1965, p. 138; cited in ref. 175.

[136] N. Serpone, M. A. Jamieson, M. S. Henry, M. Z. Hoffman, F. Bolletta, and M. Maestri, *J. Am. Chem. Soc.*, 1979, **101**, 2907.

for which $k \approx 10^8$ and 2×10^9 M^{-1} s^{-1} respectively. It is argued[17] that work terms and outer-sphere reorganization energies will be the same, and inner-sphere terms will be small.

6 Postscript: Energy Terms in Optical and Thermal Electron Transfer

In this Report, the same symbol, λ, is used for the reorganization energy, regardless of whether the other energy terms in the equations are total energy (U), electronic energy (E), enthalpy (H), or free energy (G). This reflects the prevailing confusion in the literature of electron-transfer theory. In the derivation of equation (5) from a bond-stretching model[137] it is clear that λ_{in} is either energy or enthalpy (depending on what assumptions are made about the averaging of molecular energies at temperatures above absolute zero). In equation (6), derived from dielectric continuum theory,[138] λ_{out} is free energy.* It is well known that equations of the Marcus form can be derived in terms of either model,[139] or both.[140] In contexts of spectroscopy λ is usually assumed to be energy.[24,25] In Ref. 67 the present writer treated the spectroscopic λ as free energy, ΔG_{FC} [see *e.g.* equation (37)]. This is tantamount to assuming that the associated entropy change ΔS_{FC} is zero. The same assumption was made earlier by Stein and Treinin,[141] and justified intuitively by noting that in the optical transition no structural reorganization occurs (Franck–Condon principle). The key assumption, however, is that the excited state produced in the intervalence transition can even be said to possess thermodynamic entropy and free energy. Strictly, it cannot, since it has a non-equilibrium distribution of vibrational states. There is also a fallacy in ascribing a free energy or entropy to the transition state of the thermal electron-transfer reaction. Here we follow Adamson[142] and regard ΔG^* as a purely conventional quantity, namely the free energy that would be ascribed to a chemical intermediate which underwent unimolecular decomposition with a specific rate equal to RT/Lh. In the more sophisticated state-to-state theories of electron transfer, both of these problems disappear: instead of calculating ΔG_{FC} or E_{opt} the complete spectral bandshape can in principle be obtained from the relevant Franck–Condon factors, and instead of calculating ΔG^* or E_{act} the complete temperature dependence of the reaction rate can in principle be obtained from the relevant tunnelling integrals. Nevertheless, it would be a service to experimental workers in solution kinetics and spectroscopy if theorists would comment on this problem and investigate the range of validity of the simple equations quoted here.

* See, however, ref. 67 p. 213, footnote.

137 N. Sutin, *Ann. Rev. Nucl. Sci.*, 1962, **12**, 285.
137a F. J. Kristine and R. E. Shepherd, *J. Am. Chem. Soc.*, 1978, **100**, 4398.
138 R. A. Marcus, *J. Chem. Phys.*, 1956, **24**, 966, 979.
139 T. W. Newton, *J. Chem. Educ.*, 1968, **45**, 571.
140 N. S. Hush, *Trans. Faraday Soc.*, 1961, **57**, 557.
141 G. Stein and A. Treinin, *Trans. Faraday Soc.*, 1959, **55**, 1091; this reference was given incorrectly in Ref. 67.
142 A. W. Adamson, 'Mechanisms of Inorganic Reactions', ed. R. K. Murmann, R. T. M. Fraser, and J. Bauman, *Adv. Chem. Ser.*, No. 49, A.C.S., Washington, 1965, p. 248.

Table 1 *Kinetics of electron-transfer reactions involving dinuclear complexes* $[A^{+}\cdot B]$ *(precursor) or* $[A\cdot B^{+}]$ *(successor.) Unless otherwise stated the overall reactions are one-electron transfer and the expression in the column headed Rate law is the complete expression for the rate of disappearance of reactants. Thus the first entry indicates the rate law* $-d[A^{+}]_T/dt = -d[B]_T/dt = k[A^{+}\cdot B]$, *where* $[A^{+}]_T = [A^{+}] + [A^{+}\cdot B]$, $[B]_T = [B] + [A^{+}\cdot B]$, *and* A^{+} *and* B *are defined in the first two columns. For other conventions used, see Table* 3

Oxidant, A^{+}	*Reductant*, B	*Rate law*	*Medium*	*T*/°C	*Rate data and notes*	*Ref.*
$[VO(cydta)]^{2-}$	$[V(hedta)]^{-}$	$k[A^{+}\cdot B]$	0.2 ($NaClO_4$) pH 6.86	26.5	k 2.88×10^{2}, ΔH^{*} 6.27, ΔS^{*} −30.4	137*a*
$[VO(hedta)]^{-}$	[V(hedta)]	$(a+b[H^{+}])[A^{+}\cdot B]$	0.2 ($NaClO_4$)	25	*a* 25.5, ΔH^{*} −8.0, ΔS^{*} −25.4; *b* 1.22×10^{7}, ΔH^{*} −7.0, ΔS^{*} −49.7	137*a*
$[Mn(O_2CMe)_3]^{+}$	$[VO(dtpa)]^{3-}$	$k[A^{+}\cdot B]$	0.1	25	*a*	60
$[Co(NH_3)_5(dmso)]^{3+}$	$[Fe(CN)_5(im)]^{3-}$	$kK[A^{+}][B]/(1+K[A^{+}])$	0.1 $LiClO_4$, pH 4.6	25	k 2.6, ΔH^{*} 22.0, ΔS^{*} 17.0; K 450, $\Delta H\sim0$, ΔS 12.4	56
$[Co(NH_3)_5(dmso)]^{3+}$	$[Fe(CN)_5NH_3]^{3-}$	$kK[A^{+}][B]/(1+K[A^{+}])$	0.1 $LiClO_4$, pH 4.6	25	k 2.3, ΔH^{*} 22.5, ΔS^{*} 17.2; K 420, $\Delta H\sim0$, ΔS 12.4	56
$[Co(NH_3)_5(dmso)]^{3+}$	$[Fe(CN)_5py]^{3-}$	$kK[A^{+}][B]/(1+K[A^{+}])$	0.1 $LiClO_4$, pH 4.6	25	k 1.5×10^{-1}, ΔH^{*} 23.9, ΔS^{*} 17.9; K 490, $\Delta H\sim0$, ΔS 12.2	56
$[Co(NH_3)_5(dmso)]^{3+}$	$[Fe(CN)_5$-$(pyCONH_2$-4$)]^{3-}$	$kK[A^{+}][B]/(1+K[A^{+}])$	0.1 $LiClO_4$, pH 4.6	25	k 5.0×10^{-2}, ΔH^{*} 24.4, ΔS^{*} 17.0; K 600, $\Delta H\sim0$, ΔS 12.4	56
$[Co(NH_3)_5(dmso)]^{3+}$	$[Fe(N)_5(pyz)]^{3-}$	$kK[A^{+}][B]/(1+K[A^{+}])$	0.1 $LiClO_4$, pH 4.6	25	k 8.9×10^{-3}, ΔH^{*} 28.5, ΔS^{*} 17.9; K 360, $\Delta H\sim0$, ΔS 12.0	56
$[Co(NH_3)_5(dmso)]^{3+}$	$[Fe(CN)_5(pyz$-$CONH_2$-2$)]^{3-}$	$kK[A^{+}][B]/(1+K[A^{+}])$	0.1 $LiClO_4$, pH 4.6	25	k 4.7×10^{-3}, ΔH^{*} 26.1, ΔS^{*} 17.9; K 560, $\Delta H\sim0$, ΔS 12.7	56

[a] Slow intramolecular redox reactions; also some oxidation of dtpa ligand.

Table 1 (*continued*)

Oxidant, A^+	*Reductant*, B	*Rate law*	*Medium*	*T*/°C	*Rate data and notes*	*Ref.*
$(Co^{III})_2$ complex[b]	$(Co^{III})_2$–Fe^{II} complex[b]	$\frac{kK[A^+][B]_T}{1+K[A^+]}$	0.04, pH 5.5	25	K 3.7×10^{-3}, ΔH^* 24.0, ΔS^* 11	62
$[Co(edta)]^-$	$[Fe(CN)_6]^{4-}$	$k[A^+\cdot B]$	0.26 ($NaClO_4$), pH 6.0	25	k 9.56×10^{-3}, ΔH^* 22.3, ΔS^* 7.1	54
$[Co(pdta)]^-$	$[Fe(CN)_6]^{4-}$	$k[A^+\cdot B]$	0.26 ($NaClO_4$), pH 6.0	25	k 4.79×10^{-3}, ΔH^* 20.6, ΔS^* 0.27	54
$[Co(cydta)]^-$	$[Fe(CN)_6]^{4-}$	$k[A^+\cdot B]$	0.26 ($NaClO_4$), pH 6.0	25	k 2.21×10^{-2}, ΔH^* 17.9, ΔS^* −5.9	54
$[Co(edta)]^-$	$[Fe(CN)_5PPh_3]^{3-}$	$k[A^+\cdot B]$	0.26 ($NaClO_4$), ph 6.0	25	k 1.09×10^{-3}, ΔH^* 23.0, ΔS^* 6.4	54
$[VO(hedta)]^-$	$[Ru(NH_3)_5(OH_2)]^{2+}$	$(k_2+k_3[H^+]^{-2})[A^+\cdot B]$	0.1 (NaCl)	25.2	k_2 0.11; k_3 3.55×10^3, ΔH^* 6.68, ΔS^* −19.2	58
$[Ru(NH_3)_5pyz]^{3+}$	Cu^+	$k[A^+\cdot B]$	1 (Cu^{2+}), pH 6	25	k 7.8×10^3	80
$[Ru(NH_3)_5(py\text{-}CH{=}CH_2\text{-}4)]$	Cu^+	$\frac{kK[A^+][B]_T}{1+K[A^+]}$ / $\frac{kK[A^+]_T[B]}{1+K[B]}$ [c]	0.1 CF_3CO_2H	23	k 0.24, ΔH^* 15.1, ΔS^* −10; K 1.3×10^3, $\Delta H^\ominus$ −9.7, $\Delta S^\ominus$ −18[d]	51
$[Co(NH_3)_5(im)]^{3+}$	*trans*-$[Ru(NH_3)_4(SO_4)]$	$k[A^+\cdot B]$	0.02, pH 3	22	k 6	61

[b] See text, formulae (8) and (9). [c] The two rate laws are observed depending on whether A^+ or B is in excess. [d] Similar values of $\Delta H^\ominus$ and $\Delta S^\ominus$ were obtained spectrophotometrically.

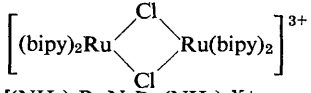
Table 2 *Properties of some mixed-valence dinuclear complexes*

Complex	*Ground-state valencies* $A^+\cdots B$	*Conditions*	K_{com}	$\bar{\nu}_{IT}/10^3$ cm^{-1}	*Half-width* $\Delta_{1/2}/10^3$ cm^{-1}	α^2	*Ref.*
$[(bipy)_2Mn(O)_2Mn(bipy)_2]$	$Mn^{IV}\cdots Mn^{III}$	D_2O, pD 4.1	—	12.0	4.6	0.01	79
$Fe[Fe(CN)_5(OH_2)],2.9H_2O$	$Fe^{III}\cdots Fe^{II}$	Solid	—	15.5	—	—	143
$Fe[Fe(CN)_5(NH_3)],3.7H_2O$	$Fe^{III}\cdots Fe^{II}$	Solid	—	16.4	—	—	143
$Fe[Fe(CN)_5(CO)],4.9H_2O$	$Fe^{III}\cdots Fe^{II}$	Solid	—	19.5	—	—	143
$[(NC)_5Fe(pyz)Fe(CN)_5]^{5-}$	$Fe^{III}\cdots Fe^{II}$	1 ($NaClO_4$)	~50	8.3	4.8[a]	1×10^{-2}	144
$[NC)_5Fe(pypy)Fe(CN)_5]^{5-}$	$Fe^{III}\cdots Fe^{II}$	1 ($NaClO_4$)	~4	8.3	5.0[a]	2×10^{-3}	144
$[(NC)_5Fe(pyCH{=}CHpy)Fe(CN)_5]^{5-}$	$Fe^{III}\cdots Fe^{II}$	1 ($NaClO_4$)	~4	7.7	4.8	8×10^{-4}	144
$[(H_2O)_5FeNCFe(CN)_4CO]$	$Fe^{III}\cdots Fe^{II}$	0.1 ($LiClO_4$)	—	17.5	—	—	145[b]
$[Fc{-}Fc]^+$	$Fe^{III}\cdots Fe^{II}$	CD_2Cl_2[c]	—	5.00	3.70	—	75
$[Fc{-}C{\equiv}C{-}Fc]^+$	$Fe^{III}\cdots Fe^{II}$	CH_2Cl_2[c]	—	6.18	5.20	—	75
$[Cu_2(PhCOCHCOCHCOMe)_2]^-$	$Cu^{II}\cdots Cu^{I}$[e]	DMF; 0.1 Me_4NClO_4	~1[d]	—	—	—	146
$[(NH_3)_5Ru(pyz)Fe(CN)_5]$	$Ru^{III}\cdots Fe^{II}$[f]	Solid	—	[g]	—	—	147
$[(NH_3)_5Ru(pypy)Fe(CN)_5]$	$Ru^{III}\cdots Fe^{II}$	Solid	—	[g]	—	—	147
$[Ru(NH_3)_5py]^{3+}[Fe(CN)_6]^{4-}$[h]	$Ru^{III}\cdots Fe^{II}$	H_2O, pH 5, 22 °C	—	10.9	6.5	1.4×10^{-3}	148

[a] Temperature dependence fits the equation $\Delta_{1/2}(T)=[\Delta_{1/2}(0)]\,[\coth(h\nu/2kT)]^{1/2}$, with $\nu=490$ cm^{-1} (pyz), 540 cm^{-1} (pypy). [b] Kinetics of the reaction $A^+ + B \rightarrow A^+\cdot B$ are reported. [c] Other solvents also reported. [d] Polarographic reduction potentials are the same for the two processes $Cu^{II}Cu^{II} + e^- \rightleftharpoons Cu^{II}Cu^{I}$ and $Cu^{II}Cu^{I} + e^- \rightleftharpoons Cu^{I}Cu^{I}$. [e] The assignment of Class II (mixed valency) or Class III (average valency) has not been reported. [f] Valencies assigned from a comparison of bond stretching and MLCT frequencies with those of related compounds, $Ru^{III}\cdots Fe^{III}$, $Rh^{III}\cdots Fe^{II}$, and $Ru^{II}\cdots Co^{III}$. [g] No IT band observed. [h] Ion pair in solution; formation constant $K=3\times10^3$ M^{-1}.

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Table 2 (*continued*)

Complex	Ground-state valencies	Conditions	K_{com}	$\bar{\nu}_{IT}$/10^3 cm^{-1}	Half-width $\Delta_{1/2}/10^3$ cm^{-1}	α^2	Ref.
	$Ru^{III}\cdots Ru^{II}$ [j]	CH_2Cl_2 0.1 $(Bu^n_4N)PF_6$	2×10^9 [i]	—	—	—	149
$[(NH_3)_5RuN_2Ru(NH_3)_5]^{5+}$	$Ru^{III}\cdots Ru^{II}$ [k]	—	—	—	—	—	150
$[(NH_3)_5Ru(pyz)Ru(NH_3)_5]^{5+}$	$Ru^{III}\cdots Ru^{II}$ [l]	—	—	—	—	—	38
$pyz[Ru(NH_3)_4pyz]_n$, $n=1$—4	—	—	see text	—	—	—	151
$NH_3[Ru(NH_3)_4pyz]_n$, $n=3$—6	—	—	see text	—	—	—	151
$[(bipy)_2ClRu(pm)RuCl(bipy)_2]^{3+}$	$Ru^{III}\cdots Ru^{II}$	MeCN, 25 °C	107	7.35	5.52	3.0×10^{-4}	152
$[(bipy)_2pyRu(pypy)Rupy(bipy)_2]^{3+}$	$Ru^{III}\cdots Ru^{II}$	MeCN, 0.1 $(Bu^n_4N)PF_6$, 25 °C	4	7.90[e]	4.10[e]	$\sim2\times10^{-4}$	74
trans-$[(NH_3)_5Ru(im)Ru(NH_3)_4(SO_4)]^{3-}$ [n]	$Ru^{III}\cdots Ru^{II}$ [m]	D_2O	8.5×10^5 [i]	7.27	—	—	61
trans-$[SO_4(NH_3)_4Ru(im)Ru(NH_3)_4(SO_4)]^{3-}$ [n]	$Ru^{III}\cdots Ru^{II}$	D_2O	3.5×10^2 [i]	7.7	—	—	61
$[(NH_3)_5Ru(pypy)Ru(NH_3)_5]^{5+}$	$Ru^{III}\cdots Ru^{II}$	D_2O	24	9.71	—	1.7×10^{-3}	71
$[Ru(NH_3)_5py]_4[(Fe(CN)_6]_3,7H_2O$	$Ru^{III}\cdots Fe^{II}$	Solid	—	10.0[o]	—	—	148
$[Ru(NH_3)_5py]_4[(Ru(CN)_6]_3,7H_2O$	$Ru^{III}\cdots Ru^{II}$	Solid	—	14.2[o]	—	—	148
$[Ru(NH_3)_6]_4[(Fe(CN)_6]_3,5H_2O$	$Ru^{III}\cdots Fe^{II}$	Solid	—	13.5[o]	—	—	148
$[Ru(NH_3)_6]_4[(Ru(CN)_6]_3,5H_2O$	$Ru^{III}\cdots Ru^{II}$	Solid	—	18.5[o]	—	—	148

[i] Present writer's calculated value from the reported reduction potentials, $Ru^{III}Ru^{III}+e^- \rightleftharpoons Ru^{III}Ru^{II}$ and $Ru^{III}Ru^{II}+e^- \rightleftharpoons Ru^{II}Ru^{II}$. [j] Assigned as Class II (mixed valency) on theoretical grounds. [k] Presumably Class III (average valency) species; no data reported. [l] Magnetic susceptibility and n.m.r. data are interpreted in terms of valence trapping (Class II, mixed valence), with thermal electron transfer activation energy, $3.4 \leqslant E_a \leqslant 6.7$ kcal mol^{-1}. [m] Or *vice versa*. [n] Under the conditions of the experiment it is not certain whether some or all of the SO_4^{2-} has been replaced by D_2O or OD^-. [o] Estimated from graphs in the original reference.

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Table 3 *Rate and activation parameters for one-electron transfer reactions, involving ground-state metal ion complexes,* $A^+ + B \rightarrow A + B^{+*}$†

Oxidant, A^+	*Reductant*, B	*Rate expression*	*Medium*	*Temp./* °C	*k*	ΔH^*	ΔS^*	*Ref.*
Reductant = Titanium(III)								
$[Fe(phen)_3]^{3+}$	Ti^{III}	$(a+b[H^+])^{-1}$	1 (LiCl)	25	a 0.14×10^{-5} b 3.17×10^{-5}			89
$[Co(C_2O_4)_3]^{3-}$	Ti^{III}	$k_3k_4/(k_{-3}[H^+]+k_4)$	1 (LiCl)	25	k_3 1.89×10^{3} k_4/k_3 0.102			89
$[Co(phen)_3]^{3+}$	Ti^{III}	$k_0+k_1[H^+]^{-1}$	1 (LiCl)	25	k_0 0.038 k_1 0.24			89
		$k_1/(K_a+[H^+])$	1 (LiCl)		k_1 0.25 [a] K_a 1.52×10^{-3} [a]			
$[Co(edta)]^-$	Ti^{III}	$a[H^+]^{-1}/(1+K_h[H^+])$ $+c[H^+]^{-1}[Ti^{III}]$	1 (Na)Cl	25	a 0.29 K_h 4.6×10^{-3} c 8.2			90
$[CoH(edta)(OH_2)]^-$	Ti^{III}	$a[H^+]^{-1}/(1+K_h[H^+]^{-1})$	1 (Na)Cl	25	a 3.0 K_h 3.3×10^{-3}			90
$[CoH(edta)Cl]^-$	Ti^{III}	$a[H^+]^{-1}/(1+K_h[H^+]^{-1})$	1 (Na)Cl	25	a 9.0 K_h 5.7×10^{-3}			90
$[Co(NH_3)_5(SCN)]^{2+}$	Ti^{III}	$a[H^+]/(K_a+[H^+])$- $(b+[H^+])$	1	25	K_a 2×10^{-3} [b] a 11.0 b 5.3×10^{-3}			152*a*

* Rate constants are quoted in $(M^{-1})^n\ s^{-1}$ or $(dm^3\ mol^{-1})^n\ s^{-1}$, where n is defined by the rate law; ΔH^* and ΔS^* are 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 rate expression given is the second-order rate coefficient. Media are specified as noted previously (Vol. 6, p. 39). For example, 1 denotes an ionic strength of 1 mol dm^{-3}, salts unspecified; 1 ($LiClO_4$) denotes an ionic strength of 1 mol dm^{-3} maintained by the addition of $LiClO_4$; 1 $LiClO_4$ denotes a concentration 1 mol dm^{-3} of $LiClO_4$ in addition to the reacting species; 1 (Li)ClO_4 denotes a constant concentration 1 mol dm^{-3} of ClO_4^- ion maintained by the addition of $LiClO_4$.

† Reactions are grouped according to the nature of the reductant (*i.e.* the metal and its formal oxidation state), and within these groups they are arranged according to the nature of the oxidant. For both reductants and oxidation, the order of elements is Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn; Mo, W; Ru, Os; Rh, Ir; Ag; Cd; Tl; lanthanides; actinides; and oxidation states are arranged in increasing order. For a given element and a given oxidation state, complexes are classified roughly according to the nature of the inner-sphere ligands.

[a] Alternative expression fitting the same data. [b] Assumed.

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Table 3 (*continued*)

Oxidant, A^+	*Reductant*, B	*Rate expression*	*Medium*	*Temp./* °C	*k*	ΔH^*	ΔS^*	*Ref.*
$[Co(NH_3)_5N_3]^{2+}$	Ti^{III}	$a[H^+]/(K_a+[H^+])-(b+[H^+])$	1	25	*a* 2.7 *b* 4.4×10^{-2} K_a 2×10^{-3} [b]			152*a*
$[\{Co(NH_3)_3\}_2(OH)_2(O_2CCO_2H)]^{3+}$	$TiOH^{2+}$	$(k_{aH}+k_aK_b[H^+]^{-1})$	1 (NaOTs)	25	k_{aH} 0.62 [d] k_a 4.8 [c,e]			111
$[\{Co(NH_3)_3\}_2(OH)_2(O_2CCH{=}CHCO_2H\text{-}trans)]^{3+}$	$TiOH^{2+}$	$(k_{aH}+k_aK_b[H^+]^{-1})$	1 (NaOTs?)	25	k_{aH} 0.092 [d] k_a 8.6 [c,e]			111
$[\{Co(NH_3)_3\}_2(OH)_2(O_2CC{\equiv}CCO_2H)]^{3+}$	$TiOH^{2+}$	$(k_{aH}+k_aK_b[H^+]^{-1})$	1 (NaOTs)	25	k_{aH} 0.18 [d] k_a 0.3 [c,f]			111
$[\{Co(NH_3)_3\}_2(OH)_2(O_2CPh)]^{3+}$	Ti^{3+}	$k_1[H^+]^{-1}$ [g]	1 (LiCl or NaOTs) [h]	25	1.92×10^{-5}			111
$[\{Co(NH_3)_3\}_2(OH)_2(O_2CC{\equiv}CH)]^{3+}$	Ti^{3+}	$k_1[H^+]^{-1}$	1 (LiCl or NaOTs) [h]	25	1.26×10^{-4}			111
$[\{Co(NH_3)_3\}_2(OH)_2(O_2CC_6H_4OH\text{-}2)]^{3+}$	Ti^{3+}	$k_1[H]^{-1}$	1 (LiCl or NaOTs) [h]	25	0.86×10^{-4}			111
$[(\{Co(NH_3)_3\}_2(OH)_2)_2(C_2O_4)]^{6+}$	Ti^{3+}	$k_1[H]^{-1}$	1 (LiCl or NaOTs) [h]	25	0.95×10^{-4}			111
$[(\{Co(NH_3)_3\}_2(OH)_2)_2(fum)]^{6+}$	Ti^{3+}	$k_1[H]^{-1}$	1 (LiCl or NaOTs) [h]	25	2.05×10^{-4}			111
$[(\{Co(NH_3)_3\}_2(OH)_2)_2(O_2CC{\equiv}CCO_2)]^{6+}$	Ti^{3+}	$k_1[H]^{-1}$	1 (LiCl or NaOTs) [h]	25	1.74×10^{-4}			111
$[Co(NH_3)_4(C_2O_4)]^{2+}$	Ti^{3+}	$k_1[H]^{-1}$	1 (LiCl or NaOTs) [h]	25	0.12			111
Cu^{II}	Ti^{3+}	—	1 HCl	25	*i*			153
$[Ru(NH_3)_5(OH_2)]^{3+}$	Ti^{3+}	$kK_a[H^+]^{-1}$	1 (CF_3SO_3Li)	25	*k* 66 [l]			91
$[Ru(NH_3)_5py]^{3+}$	Ti^{3+}	$kK_a[H^+]^{-1}$	1 ($LiCl/LiClO_4$) [j]	25	*k* 4.2×10^3 [l]	3.3 [l]	−29 [l]	91
$[Ru(NH_3)_5pyz]^{3+}$	Ti^{3+}	$kK_a[H^+]^{-1}$	1 ($LiCl/LiClO_4$) [j]	25	*k* 1.5×10^5 [l] K_a 5×10^{-3} [l]	2.9 [l] 10.0	−23 [l]	91
cis-$[Ru(NH_3)_4(isn)_2]^+$	Ti^{3+}	$k_0+kK_a[H^+]^{-1}$	1 ($LiCl/LiClO_4$) [j]	25	*k* 1×10^6 [k] k_0 2×10^4			91

$[Ru(NH_3)_5Br]^{2+}$	Ti^{3+}	$k_2K_a[H^+]^{-1}$	1 (LiCl or CF_3SO_3Li)	25	k_2 56 [m] K_a 5×10^{-3} [n]			154
$[Ru(NH_3)_5I]^{2+}$	Ti^{3+}	$k_2K_a[H^+]^{-1}$	1 (LiCl or CF_3SO_3Li)	25	k_2 112 K_a 5×10^{-3} [n]			154
Reductant = *Vanadium*(II)								
$[Co(en)_3]^{3+}$	V^{2+}	k	0.1 (H) CF_3SO_3	25	9.4×10^{-4}	59	−110	155
$[Co(chxn)_3]^{3+}$	V^{2+}	k	0.1 (H) CF_3SO_3	25	5.8×10^{-4}	62	−106	155
$[Co(en)_3]^{3+}$	V^{2+}	$\dfrac{k_1k_2[\text{diquat}]}{k_{-1}[V^{3+}]+k_2[Co^{III}]}$	1 $HClO_4$	25	k_1 19 k_2/k_1 0.26			156
$[Co(NH_3)_5(NH_2CH_2CO_2H)]$	V^{2+}	$k_1+k_2[H^+]^{-1}$	1 ($LiClO_4$)	25	k_1 0.41 k_2 0.106			87
$[Co(NH_3)_5(NH_2C_2H_4CO_2H)]$	V^{2+}	$k_1+k_2[H^+]^{-1}$	1 ($LiClO_4$)	25	k_1 2.36×10^{-2}			87
$[Co(NH_3)_5(NCMe)]$ and 7 related oxidants	V^{2+}	k	1 $HClO_4$	25	1.18			157
$[Co(NH_3)_5Cl]^{2+}$	V^{2+}	k	1 H^+, 1.1 ClO_4^-	25	7.9			158
trans-$[Co(NH_3)_4(NH_2Me)Cl]^{2+}$	V^{2+}	k	1 H^+, 1.1 ClO_4^-	25	1.6×10			158
$[Co(NH_2Me)_5Cl]^{2+}$	V^{2+}	k	1 H^+, 1.1 ClO_4^-	25	9.6×10			158
$[Co(NH_2Pr^n)_5Cl]^{2+}$	V^{2+}	k	1 H^+, 1.1 ClO_4^-	25	1.9×10^2			158
$[Co(NH_3)_5(OH_2)]^{3+}$	V^{2+}	k	1 H^+, 1.1 ClO_4^-	25	2.6×10^{-1}			158
trans-$[Co(NH_3)_4(NH_2Me)(OH_2)]^{3+}$	V^{2+}	k	1 H^+, 1.1 ClO_4^-	25	8.7			158
$[Co(NH_2Me)_5(OH_2)]^{3+}$	V^{2+}	k	1 H^+, 1.1 ClO_4^-	25	1.3×10			158
$[Co(NH_2Pr)^n{}_5(OH_2)]^{3+}$	V^{2+}	k	1 H^+, 1.1 ClO_4^-	25	1.7×10			158

[c] Using values of K_b reported previously. [d] Outer-sphere pathway. [e] Possibly inner-sphere pathway. [f] Possibly outer-sphere pathway. [g] There is also a rate term $k_0[H^+][\text{Co complex}][Ti^{III}]^0$, $k_0 = 0.8\times10^{-1}$ M^{-1} s^{-1}. [h] The same rates were observed in the two media. [i] Fast reaction. [j] 'The Ru^{III} complexes at 1.0 M ionic strength ($LiClO_4/HClO_4$) were mixed in the stopped-flow instrument with Ti^{III} solutions which had also been adjusted previously to an ionic strength of 1.0 M, but with HCl'. [k] Assumed. [l] Using assumed values of K_a. [m] Reaction catalysed by Cl^-, N_3^-, NCS^-, effect increasing in that order (data tabulated). [n] Obtained from kinetic studies at low H^+ (no details given).

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Table 3 (*continued*)

Oxidant, A^+	*Reductant*, B	*Rate expression*	*Medium*	*Temp./* °C	*k*	ΔH^*	Δ_3^*	*Ref.*
trans-(O,Cl)-[Co(glyO)-(dien)Cl]$^+$	V^{2+}	k	1 H^+, 1.1 ClO_4^-	25	11.0 [o]			158
trans-(O,Cl)-[Co(leuO)-(dien)Cl]$^+$	V^{2+}	k	1 H^+, 1.1 ClO_4^-	25	6.5			158
$[Co(NH_3)_5\{OC_6H_3(NO_2)_2$-2,4$\}]^{2+}$	V^{2+}	k	0.12 $HClO_4$	25	21			117
			0.12 H^+, 1.2 ($LiClO_4$)	25	47			
$[Co(NH_3)_5\{OC_6H_3(NO_2)_2$-2,5$\}]^{2+}$	V^{2+}	k	0.12 $HClO_4$	25	50			117
			0.12 H^+, 1.2 ($LiClO_4$)	25	92			
$[Co(NH_3)_5\{O_2CCH(Me)$-py$CONH_2$-4$\}]^{3+}$	V^{2+}	k	1 $HClO_4$	25	1.59			115
$[\{Co(NH_3)_3\}_2(OH)_2$-$\{O_2Cpyz$-4$\}]^{3+}$	V^{2+}	k_v	1 ($LiClO_4$)	25	0.198			159
$[\{Co(NH_3)_3\}_2(OH)_2$-$\{(O_2CpyzMe_2$-4,6)-2$\}]^{3+}$	V^{2+}	k	1 ($LiClO_4$)	25	0.357			159
$[\{Co(NH_3)_3\}_2(OH)_2$-$(O_2CC_4H_3NMe$-6)-2$]^{3+}$	V^{2+}	k	1 ($LiClO_4$)	25	0.221			159
$[Mn^{III}(edta)]^-$	$[VO(hedta)]^-$	$k[H^+]$	1 HOAc, 0.12 ($^-$OAc)	25	3.5×10^2	11.8	−7	60
$[Mn^{III}(edta)]^-$	$[VO(nta)]^-$	$k_0+k_1[H^+]^{-1}$	1 HOAc, 0.1 ($^-$OAc)	25	k_0 10.2 k_1 1.06×10^{-2}			60
$[Mn^{III}(hedta)]$ and 4 other related reactions	$[VO(hedta)]^-$	k	0.1 NaOAc, pH 3.76	25	6.66			60
			0.1 NaOAc, pH 3.00	25	4.20			60
$[VO(hedta)]^-$	$[V(hedta)]^-$	k_1+k_2 [p]	0.2 ($NaClO_4$) pH 6.75	25	k_1 2.7×10^4 k_2 4.0×10^4 [q]	6.1	−17	137
$[VO(hedta)]^-$	$[(hedta)V^{IV}OV^{II}$-$(hedta)]^{-2}$	k_6	0.2 ($NaClO_4$), pH 6.75		9.3×10^3			137

$[(hedta)V^{IV}OV^{II}(hedta)]^{2-}$	$[V(hedta)]^-$	k_7	0.2 ($NaClO_4$), pH 6.75		4.6×10^3			137
Reductant = *Vanadium*(III)								
$[Ru(NH_3)_5(OH)]^{2+}$	$[V^{III}(hedta)(OH)]^-$ [r]	k_4	0.1 (NaCl)	25	1.32×10^6	12.1	9.4	58
Reductant = *Vanadium*(IV)								
$[Mn^{III}(edta)]^-$	VO^{2+}	$k_0+k_1[H^+]^{-1}$	1 HOAc, 0.1 (^-OAc)	25	k_0 7.78 k_1 4.54	11.5	−17	60
Reductant = *Chromium*(II)								
$[Cr(NH_3)_5(O_2Cpy\text{-}2)]^{2+}$	Cr^{2+}	$k[H^+]^0$	1 ($LiClO_4$)	25	3.3×10^{-2}			160
$[Cr(NH_3)_5(O_2CpyCO_2H)]^{2+}$ [s]	Cr^{2+}	$k[H^+]^{-1}$	1 ($LiClO_4$)	25	1.40			160
$[Cr(NH_3)_5(O_2CpyCO_2H)]^{2+}$ [t]	Cr^{2+}	—	1	25	*v*			160
$[Cr(NH_3)_5(O_2CCOMe)]^{2+}$	Cr^{2+}	k	0.12 H^+, 1.2 ($LiClO_4$)	25	$\sim3\times10^2$			160
$[Cr(NH_3)_5(O_2CMe)]^{2+}$	Cr^{2+}	k [u]		25	$<10^{-4}$			160
$[Fe^{III}(DPDME)]$ [w]	Cr^{2+}	$k_2K_1[H^+]^{-1}$	0.5 ($NaClO_4$), 2% Triton X-100	25	k_2 5.5×10^5 pK_1 4.7 [y]			161
$[Fe^{III}(MPDME)]$ [x]	Cr^{2+}	$k_2K_1[H^+]^{-1}$	0.5 ($NaClO_4$), 2% Triton X-100	25	k_2 1.7×10^5 pK_1 5.0 [y]			161
$[Co(NH_3)_5(O_2CCH_2NC_5H_4)]^{3+}$ and 6 related oxidants	Cr^{2+}	k	1 $HClO_4$	25	0.039			115

[o] Other H^+ concentrations also reported; effects of added DMF also reported. [p] k_1 refers to the reaction $[VO(hedta)]^- + [V(hedta)]^- \rightarrow 2[V(hedta)]$; k_2 refers to the reaction $[VO(hedta)]^- + [V(hedta)]^- \rightarrow [V_2O(hedta)_2]^{2-}$. [q] The reverse rate constant is estimated to be $k_{-2} = 2 \pm 2\ s^{-1}$. [r] The ligand written here as $hedta^{3-}$ is apparently the trianion of *N*-2-hydroxy-ethyl-*NN'N'*-tricarboxymethyl-1,2-diaminoethane, written $HEDTA^{3-}$ in the original paper, the acid being written $H_3(HEDTA)$. It is not to be confused with the trianion of 1,2-diaminoethane-*NNN'N'*-tetra-acetic acid, which some other authors write $HEDTA^{3-}$, the acid being written H_4EDTA. [s] Ligand is pyridine-2,3-dicarboxylic acid; from the value of the rate constant it is concluded that chromium(III) is attached to the 2-carboxy-group. [t] Ligand is pyrazine-2,3-dicarboxylic acid. [u] Assumed. [v] Reaction too fast to follow by stopped-flow; dark green product. [w] DPDME = deuteroporphyrin IX dimethyl ester. [x] MPDME = mesoporphyrin IX dimethyl ester. [y] From spectrophotometric acid–base titrations.

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Table 3 (*continued*)

Oxidant, A^+	*Reductant*, B	*Rate expression*	*Medium*	*Temp./* °C	*k*	ΔH^*	ΔS^*	*Ref.*
$[2\text{-}Co(NH_3)_5(O_2CC_6H_4NCO_2\text{-}Me\text{-}3)]^{3+}$ and 9 related oxidants	Cr^{2+}	$k_0+k_{-1}[H^+]^{-1}$	1.2 ($LiClO_4$)	25	k_0, k_{-1} various			109
$[Co(NH_3)_5(OH_2)]^{3+}$	Cr^{2+}	k	$1H^+$, 1.1 ClO_4^-	25	5.5×10^{-1}			158
trans-$[Co(NH_3)_4(NH_2Me)(OH_2)]^{3+}$	Cr^{2+}	k	$1H^+$, 1.1 ClO_4^-	25	3.4			158
$[Co(NH_2Me)_5(OH_2)]^{3+}$	Cr^{2+}	k	$1H^+$, 1.1 ClO_4^-	25	4.9			158
$[Co(NH_2Pr^n)_5(OH_2)]^{3+}$	Cr^{2+}	k	$1H^+$, 1.1 ClO_4^-	25	6.5			158
$[Co(NH_3)_5(NCMe)]$	Cr^{2+}	k	1 $HClO_4$	25	0.020			157
$[Co(NH_3)_5(NCC_6H_4CN\text{-}2)]$	Cr^{2+}	k	1 $HClO_4$	25	0.142			157
$[Co(NH_3)_5(NCCH{=}CHPh\text{-}cis)]$	Cr^{2+}	k	1 $HClO_4$	25	0.033			157
$[Co(NH_3)_5\{OC_6H_3(NO_2)_2\text{-}2,4\}]^{2+}$	Cr^{2+}	k [z]		25	$>10^3$			117
$[Co(NH_3)_5\{OC_6H_3(NO_2)_2\text{-}2,5\}]^{2+}$	Cr^{2+}	k [z]		25	$>10^3$			117
$[Co(NH_3)_5(NH_2CH_2CO_2H)]$	Cr^{2+}	$k_1+k_2[H^+]^{-1}$	1 ($LiClO_4$)	25	k_1 1.2×10^{-3} k_2 9.3×10^{-3}			87
$[Co(NH_3)_5(NH_2C_2H_4CO_2H)]$	Cr^{2+}	$k_1+k_2[H^+]^{-1}$	1 ($LiClO_4$)	25	k_1 7.9×10^{-4} k_2 5.2×10^{-5}			87
$[Co(en)_2\{S(Me)CH_2CH_2NH_2\}]^{2+}$ and 7 related oxidants	Cr^{2+}	k	1 ($LiClO_4$)	25	0.337	4.9	−44.2	86
$[Co^{III}(TPPS)]^{3-}$	Cr^{2+}	$k_0+k_2[H^+]^{-1}$	1 ($LiClO_4$)	25	k_0 173 k_2 2.1			162
$[Co(NH_3)_5py]^{3+}$	Cr^{2+}	$\frac{k_1k_2[X]}{(k_{-1}+k_2[Co^{III}])}$ [aa]	1 ($LiClO_4$)	25	k_1 94 k_2/k_{-1} 92			119
$[Co(NH_3)_5(pyrazole)]^{3+}$	Cr^{2+}	$\frac{k_1k_2[X]}{(k_{-1}+k_2[Co^{III}])}$ [aa]	1 ($LiClO_4$)	25	k_1 85 k_2/k_{1-1} 31			119
$[Co(en)_3]^{3+}$	Cr^{2+}	$\frac{k_1k_2[X]}{(k_{-1}+k_2[Co^{III}])}$ [aa]	1 ($LiClO_4$)	25	k_1 94 k_2/k_{-1} 1.3			119

$[Co(en)_3]^{3+}$	Cr^{2+}	$\frac{k_1k_2[\text{diquat}]}{k_{-1}[Cr^{3+}]+k_2[Co^{III}]}$	1 $HClO_4$	25	k_1 0.38			156
$[\{Co(NH_3)_3\}_2(OH)_2(O_2CC_3H_3N_2\text{-}4)]^{3+}$	Cr^{2+}	$k_aK_1[H^+]/(1+K_1[H^+])$	1 ($LiClO_4$)	25	k_a 3.93 [ab]	3.1	−40.3	159
			1 ($LiClO_4$)	25	K_I 13.7	*ac*		
$[\{Co(NH_3)_3\}_2(OH)_2(O_2CC_3H_3N_2\text{-}5)]^{3+}$	Cr^{2+}	$\frac{k_aK_{II}[H^+]+k_b}{(1+K_1[H^+])}$	1 ($LiClO_4$)	25	k_a 1.74×10^4 [ad]			159
			1 ($LiClO_4$)	25	k_b 2.93×10^3			
			3 ($LiClO_4$)	25	K_{II} 1.09			
$[\{Co(NH_3)_3\}_2(OH)_2\{(O_2CC_3HN_2Me_2\text{-}4,6)\text{-}2\}]^{3+}$	Cr^{2+}	k	1 ($LiClO_4$)	25	9.5×10^{-3} [ad]			159
$[\{Co(NH_3)_3\}_2(OH)_2\{(O_2CC_4H_3NMe\text{-}6)\text{-}2\}]^{3+}$	Cr^{2+}	k	1 ($LiClO_4$)	25	4.8×10^{-3} [ad]			159
$[Co(en)_3]^{3+}$	$[Cr(bipy)_3]^{2+}$	k	0.1 NaCl, pH 4.4	25	35	47	−59	155
$[Co(chxn)_3]^{3+}$	$[Cr(bipy)_3]^{2+}$	k	0.1 NaCl, pH 4.4	25	40	54	−32	
$[VO(hedta)]^-$	$[Cr(hedta)]^-$	—	—		rapid reaction			137
$[Co(en)_3]^{3+}$	$[Cr(hedta)]^-$	k	1 ($NaClO_4$)	25	3.14×10^3			163
$[Co(NH_3)_5(NCS)]^{2+}$	$[Cr(hedta)]^-$		1 ($NaClO_4$)	25	1.19×10^5 [ae]			163
$[Co(NH_3)_5(OH_2)]^{3+}$	$[Cr(hedta)]^-$		1 ($NaClO_4$)	25	1.3×10^5			163
$[Co(NH_3)_5(OH)]^{2+}$	$[Cr(hedta)]^-$		1 ($NaClO_4$)	25	2.06×10^7			163
$[Co(NH_3)_5Cl]^{2+}$	$[Cr(hedta)]^-$		1 ($NaClO_4$)	25	$>1\times10^6$ [ae]			163
$[Co(NH_3)_5Br]^{2+}$	$[Cr(hedta)]^-$		1 ($NaClO_4$)	25	$>1\times10^6$ [ae]			163
$[Co(en)_3]^{3+}$	$[Cr(edta)]^{2-}$		1 ($NaClO_4$)	25	4.24×10^3			163
$[Co(NH_3)_5(C_5H_4NCOPh\text{-}4)]^{3+}$	$[Cr(Pz)]^{2+}$ [af]	$K_1k_2[Pz]^{-1}$	1 $HClO_4$	25	K_1k_2 1.4×10^{-3}			118
$[Co(NH_3)_5(C_5H_4NCOMe\text{-}4)]^{3+}$	$[Cr(Pz)]^{2+}$ [af]	$K_1k_2[Pz]^{-1}$	1 $HClO_4$	25	K_1k_2 2.9×10^{-3}			118
$[Co(NH_3)_5(pyz)]^{3+}$	$[Cr(Pz)]^{2+}$ [af]	$K_1k_2[Pz]^{-1}$	1 $HClO_4$	25	K_1k_2 2.6×10^{-3}			118
					k_2 8.7×10^4 [ag]			
$[Co(NH_3)_5F]^{2+}$	$[Cr(Pz)]^{2+}$ [af]	$\frac{k_1k_2}{k_1[Pz]+k_2[Co^{III}]}$	1 $HClO_4$	25	K_1k_2 1.16×10^{-2}			118
					k_1 0.060			

[z] Assumed. [aa] X = 2,4-$C_5H_2N(CO_2Me)_2$. [ab] Inner-sphere mechanism. [ac] K_I independent of temperature from 10 to 41 °C. [ad] Outer-sphere mechanism. [ae] Inner-sphere mechanism. [af] Pz = pyrazine-carboxamide; the complex is actually the radical ion species $[Cr^{III}(Pz^-)]^{2+}$. [ag] Calculated from K_1k_2, using K_1 calculated from the data.

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Table 3 (*continued*)

Oxidant, A^+	*Reductant*, B	*Rate expression*	*Medium*	*Temp./* °C	k	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
$[Co(NH_3)_5Cl]^{2+}$	$[Cr(Pz)]^{2+}$ [af]	$\frac{k_1k_2}{k_{-1}[Pz]+k_2[Co^{III}]}$	1 $HClO_4$	25	K_1k_2 4.5×10^{-2} k_1 0.063			118
$[Co(NH_3)_5Br]^{2+}$	$[Cr(Pz)]^{2+}$ [af]	$\frac{k_1k_2}{k_{-1}[Pz]+k_2[Co^{III}]}$	1 $HClO_4$	25	K_1k_2 7.8×10^{-2} k_1 0.073			118
$[Co(NH_3)_5I]^{2+}$	$[Cr(Pz)]^{2+}$ [af]	k_1	1 $HClO_4$	25	$k_1 \sim 0.15$?			118
Reductant = *Iron*(II)								
$[Mn(acac)_3]$	$[Fe(dmf)_6]^{2+}$	*ah*	pdc	25	—	—	—	164
$[Fe(phen)_3]^{3+}$	Fe^{2+}	k [ai]	0.05 $HClO_4$; $NaClO_4$ var.	20	*a*			165
		k [ai]	0.05 $HClO_4$, 0.45 $NaClO_4$, MeOH or EtOH var.	20	*aj*			165
Co^{3+}	Fe^{2+}	k	3 $HClO_4$	25	3.57×10^2	*ak*	*ak*	166
Co^{3+}	Fe^{2+}	$(k_0+k_1K_h[H^+])^{-1}$	3 ($LiClO_4$	25	k_0 k_1K_H	14.7 14.7	1.2 2.0	166[al] *al*
$[Co(acac)_3]$	$[Fe(dmf)_6]^{2+}$	*ah*	pdc	25	—	—	—	164
$[Co(NH_3)_5Br]^{2+}$	Fe^{2+}	k	DMSO, 0.1—5% H_2O	25	2.51×10^{-3}	21.7	1.9	93
$[Co(NH_3)_5Cl]^{2+}$	Fe^{2+}	k	DMSO, 0.1—5% H_2O	25	9.72×10^{-3}	21.2	2.9	93
$[Co(NH_3)_5F]^{2+}$	Fe^{2+}	k	DMSO, 0.1—5% H_2O	25	4.73	8.8	−26	93
$[Co(Q)N_3]^{2+}$ [am]	Fe^{2+}	$k[H^+]^0$	1 $(Li)ClO_4$	25	1.35	14.1	−10.8	84
$[Co(QS)N_3]^{2+}$ [am]	Fe^{2+}	$k[H^+]^0$	1 $(Li)ClO_4$	25	0.914	13.2	−14.7	84
trans(O, Cl)-[Co(glyO)-(dien)Cl]$^+$	Fe^{2+}	k	1 H^+, 1.1 ClO_4^-	25	2.7×10^{-5}			158
trans-(O, Cl)-[Co(leuO)-(dien)Cl]$^+$	Fe^{2+}	k	1 H^+, 1.1 ClO_4^-	25	1.0×10^{-5}			158

cis-$[Co(NSSN)(N_3)_2]^+$ [an]	Fe^{2+}	$k_0+k_1[H^+]$	1 (Li) ClO_4; I=1.15M	25	k_0 0.127 k_1 0.030			165*a*
			1 ($Ba_{1/2}$)ClO_4	25	k_0 0.134 k_1 0.032			165*a*
$[Ru(bipy)_3]^{3+}$	Fe^{2+}	k [ao]	>0.005 SDS	25	$>5\times10^7$			168
Tl^{2+}	Fe^{2+}	K	1 $HClO_4$	25	3.3×10^6			169
$[Fe(phen)_3]^{3+}$	$[Fe(dmf)_n]^{2+}$	$k_aK/(1+K$-$[Fe(phen)_3^{3+}])$ [ap]	MeCN		k_a 130 K 513			170
$[Fe(CN)_6]^{3-}$	$[Fe(CN)_5$-$(NC_5H_3NH_2$-4)$]^{3-}$	k	0.05 ($LiClO_4$), pH 9.0	25	4.3×10^5	2.0	−26	171
$[Fe(CN)_5(NC_5H_3NH_2$-4)$]^{2-}$	$[Fe(CN)_5$-$(NC_5H_3NH_2$-4)$]^{3+}$	k	0.05 ($LiClO_4$), pH 9.0	25	7×10^5 [aq]			171
$[Co^{III}(edta)]^-$	$[Fe(CN)_6]^{4-}$	k	0.26 ($NaClO_4$), pH 6.0	25	29.7	15.4	−9.3	54
$[Co^{III}(pdta)]^-$	$[Fe(CN)_6]^{4-}$	k	0.26 ($NaClO_4$), pH 6.0	25	13.9	15.0	−12.0	54
$[Co^{III}(cydta)]^-$	$[Fe(CN)_6]^{4-}$	k	0.26 ($NaClO_4$), pH 6.0	25	2.59	16.3	−11.2	54
$[Co^{III}(edta)]^-$	$[Fe(CN)_5(PPh_3)]^{3-}$	k	0.26 ($NaClO_4$), pH 6.0	25	3.08	16.8	−8.8	54

[ah] Autocatalytic reaction, complicated mechanism. [ai] Assumed rate law. [aj] Data not tabulated; dependence of k (or of k_{obs}?) on ionic strength and dielectric constant shown in graphs. [ak] Temperature dependence agrees with ref. 167. [al] Data of ref. 167 recalculated in ref. 166. [am] Q = 7-methyl-4,10-dithia-1,7,13-triazatridecane; QS = 1,11-diamino-3,3,9-trithiaundecane; see formulae (16) and (17). [an] NSSN = 1,8-diamino-3,6-dithiaoctane. [ao] Assumed. [ap] k_a is the specific rate for a reaction between $[Fe(phen)_3]^{3+}$ and an 'active' species, $[Fe(dmf)_5]^{2+}$, formed from 'inactive' $[Fe(dmf)_6]^{2+}$ at measurable rate; data for reactions in propanediol carbonate as solvent are also given. [aq] Computed from the rate of the reaction $[Fe(CN)_6]^{3-}+[Fe(CN)_5(NC_5H_3NH_2$-4)$]^{3-}$, using the Marcus cross-relation.

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Table 3 (*continued*)

Oxidant, A^+	*Reductant*, B	*Rate expression*	*Medium*	*Temp./* °C	*k*	ΔH^*	ΔS^*	*Ref.*
$[Ru(bipy)_3]^{3+}$	$[Fe(CN)_6]^{4-}$	*k*	0.005 SDS	8	$\sim 2.4\times10^7$			168
$[Ru(3,4,7,8\text{-}Me_4phen)_3]^{3+}$	$[Fe(3,4,7,8\text{-}Me_4\text{-}phen)_3]^{2+}$	*k*	~90%HCOOH, 10%H_2O [as]	25	$\gtrsim 20\times10^6$			168
$[Ru(4,7\text{-}Ph_2phen)_3]^{3+}$	$[Fe(4,7\text{-}Ph_2phen)_3]^{2+}$	*k*	0.13 H_2SO_4 [as]	25	$\gtrsim 40\times10^6$			168
$[Ru(4,7\text{-cyclo-}C_6H_{11}phen)_3]^{3+}$	$[Fe(4,7\text{-cyclo-}C_6H_{11}phen)_3]^{2+}$	*k*	0.13 H_2SO_4 [as]	25	$\gtrsim 50\times10^6$			168
Ce^{IV}	$[Fe(C_5H_5)\text{-}(C_5H_4COMe)]$		H_2SO_4, var.	25	*at*			172
Ce^{IV}	$[Fe(C_5H_4COMe)_2]$		H_2SO_4, var.	25	*at*			172
$[Fe^{III}P(im)_2]^{5+}$ [au]	$[Fe^{II}P(im)_2]^{4+}$	*k* [av]	0.5	25	$>10^7$ [aw]			95
$[Fe^{III}P(OH)(OH_2)]^{4+}$ [au]	$[Fe^{II}P(OH)(OH_2)]^{3+}$	*k* [av]	0.05	25	$>1\times10^9$ [aw]			95
$[Fe^{III}P(OH_2)]^{5+}$ [au]	$[Fe^{II}P(OH_2)]^{4+}$	*k* [av]	0.05	25	1.2×10^6 [aw]			95
$[Ru(NH_3)_6]^{3+}$	$[Fe^{II}P(H_2O)_5]^{4+}$ [au]	$k_{-1}+k_{-2}K_{a1}$	0.05 ($MeSO_3^-$)		$k_{-2}K_{a1}'$ 4.3			95
Reductant = Cobalt(I)								
$[Ru(bipy)_3]^{2+}$	Co^+	*k*	pH 6.9	24	6.3×10^9			173
		k	pH 6.9, 0.01 SDS	24	1.75×10^9			173
Reductant = Cobalt(II)								
$[Co(CO_3)_3]^{3-}$	Co^{2+}	$k_1K_1[N_2H_4]+k_2\beta_2[N_2H_4]^2$	0.283 HCO_3^-, pH 9.22	26	k_1 26.3 k_2 0.0 K_1 348 [ax] β_2 300 [ax]			174
$[Mn(cydta)]^-$	$[Co(cydta)]^{2-}$	*k* [ay]	CTAB var. [az]	25	*ay*			
$[Fe(CN)_6]^{3-}$	$(Co(edta)]^{2-}$	*k* [ba]	0.26 ($NaClO_4$), pH 6.0	25	2.61	9.5	−24.8	54
$[Fe(CN)_6]^{3-}$	$[Co(pdta)]^{2-}$	*k* [ba]	0.26 ($NaClO_4$), pH 6.0	25	1.70	9.4	−25.7	54
$[Fe(CN)_6]^{3-}$	$[Co(cydta)]^{2-}$	*k* [ba]	0.26 ($NaClO_4$), pH 6.0	25	0.577	5.3	−40.7	54

$[Fe(CN)_5(PPh_3)]^{2-}$	$[Co(edta)]^{2-}$	k [ba]	0.26 ($NaClO_4$), pH 6.0	25	2.19	12.3	−15.8	54
$[Co(NH_3)_5Br]^{2+}$	[Co([14]tetraene-N_4)]$^{2-}$ [bb]	k	0.1 $NaClO_4$, pH 2	24	247	7.4	−23	88
$[Co(NH_3)_5Cl]^{2+}$	[Co([14]tetraene-N_4)]$^{2+}$	k	1 HCl	24	22			88
Co^{3+}	[Co([14]tetraene-N_4)]$^{2+}$	k	3 $HClO_4$	25	337			88
Mn^{3+}	[Co([14]tetraene-N_4)]$^{2+}$	k	3 $HClO_4$	25	1.7×10^5			88
$CoCl^{2+}$	[Co([14]tetraene-N_4)]$^{2+}$	k	1 HCl	25	1.5×10^7			88
$MnCl^{2+}$	[Co([14]tetraene-N_4)]$^{2+}$	k	1 HCl	25	2.4×10^7			88
$[IrCl_6]^{2-}$	[Co([14]tetraene-N_4)]$^{2+}$	k	1 HCl	25	2.9×10^6			88
			0.5 HCl, 0.5 $HClO_4$	25	5.2×10^6			88
$[Co(NH_3)_5Br]^{2+}$	[Co([14]diene-N_4)]$^{2+}$ [bb]	k	0.1 $NaClO_4$, pH 2	25	0.69	8.6	−30	88
$[Co(NH_3)_5Cl]^{2+}$	[Co([14]diene-N_4)]$^{2+}$	k	0.1 $NaClO_4$, pH 2	25	0.042			88
Co^{3+}	[Co([14]diene-N_4)]$^{2+}$	k	3 $HClO_4$	25	66			88

[ar] Effects of increasing SDS concentration, and of ionic strength ($NaClO_4$), are also tabulated. [as] Oxidant and reductant present as perchlorates over various concentration ranges up to 2.5M. For details of concentration ranges, see the original reference. [at] Reaction 'practically immediate'. [au] P = tetrakis-(4-*N*-methylpyridyl)porphine; im = imidazole. [av] Assumed. [aw] Calculated from rates of $Fe^{III} + [Ru(NH_3)_6]^{2+}$, using the Marcus cross-relation. [ax] K_1 and β_2 are stability constants of $[Co(N_2H_4)]^{2+}$ and $[Co(N_2H_4)_2]^{2+}$. Other combinations of values of k_1, k_2, K_1, and K_2 are consistent with the data. [ay] Dependence of k on CTAB concentration is reported and discussed. [az] CTAB = cetyltrimethylammonium bromide. [ba] Outer-sphere pathway: see also Table 1. [bb] [14]tetraene-N_4 = 2,3,9,10-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-1,3,8,10-tetraene; [14]diene-N_4 = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-aza-cyclotetradeca-4,11-diene.

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Table 3 (*continued*)

Oxidant, A^+	*Reductant*, B	*Rate expression*	*Medium*	*Temp./* °C	*k*	ΔH^*	ΔS^*	*Ref.*
Mn^{3+}	[Co([14]diene-N_4)]$^{2+}$	*k*	3 $HClO_4$	25	1.7×10^4			88
$CoCl^{2+}$	[Co([14]diene-N_4)]$^{2+}$	*k*	0.1 $NaClO_4$, pH 2	25	1.6×10^6			88
$MnCl^{2+}$	[Co([14]diene-N_4)]$^{2+}$	*k*	0.1 $NaClO_4$, pH 2	25	5.3×10^6			88
[Co([14]tetraene-N_4)Cl]$^{2+}$ and 7 related reactions	[Co([14]diene-N_4)]$^{2+}$	*k*	0.1 ($HClO_4$)	23	0.15×10^4	6.3	−23	88
[Cu(2,9-Me_2phen)$_2$]$^{2+}$	[Co(phen)$_3$]$^{3+}$	*k*	0.1, pH 6.1	25	8.81×10^4	10.3	−1.4	99
Reductant = *Nickel*(II)								
$Ni^{III}Pp$ [bc]	$[Ni^{II}(H_{-3}G_4)]^{2-}$ [bd]	k_7			*be*			175
Reductant = *Copper*(I)								
$[Fe(CN)_6]^{3-}$	Cu^+	*k*			*bf*			176
[2-$Co(NH_3)_5(O_2CC_5H_4$-NCO_2Me-3)]$^{3+}$ and 4 related oxidants	Cu^+	$a/(1+b^{-1}[H^+])$	1.1 ($LiClO_4$)	25	*a* 6.7 *b* 0.29			110
[Cu(2,9-Me_2phen)$_2$]$^{2+}$	[Cu(2,9-Me_2phen)$_2$]$^+$	*k*	0.1	25	1.8×10^4 [bg] 1.9×10^4 [bg] 4.9×10^4 [bh]			98 99 99
[Cu(phen)$_2$]$^{2+}$	[Cu(phen)$_2$]$^+$	*k*	0.1	25	7.4×10^1 [bg] 5.0×10^1 [bg] 7.5×10^1 [bg]			98 99 99
[Cu(5-NO_2phen)$_2$]$^{2+}$	[Cu(5-NO_2phen)$_2$]$^+$	*k*	0.1	25	1.0×10^2 [bg]			98, 99
[Cu(bipy)$_2$]$^{2+}$	[Cu(bipy)$_2$]$^+$	*k*	—	25	2.5×10^2 [bg] 1.8×10^2 [bg]			99 99
[Ru(NH_3)$_5$(NC_5H_4)]$^{3+}$ and 2 related oxidants	Cu^+	*k*	0.1 CF_3CO_2H	23	0.40	14.6	−11	51
[Ru(4,4′-Me_2bipy)$_3$]$^{2+}$	Cu^+	*k*	0.5 H_2SO_4	25	8.7×10^7			129

$[Ru(bipy)_3]^{3+}$	Cu^+	k	0.5 H_2SO_4	25	9.7×10^8		129
			0.5 $HClO_4$	25	4.3×10^8		129
			2.5 $HClO_4$	25	3×10^8		129
$[Ru(phen)_3]^{3+}$ and 7 related oxidants	Cu^+	k	0.5 H_2SO_4	25	1.2×10^9		129
Reductant = Copper(II)							
$[Cu^{III}(H_{-3}G_4)]^-$	$[Cu^{II}(H_{-2}G_4)]^{-}$ [bd]	k [bi]	0.1 $NaClO_4$	25	—		177
Reductant = Zinc(I)							
$[Ru(bipy)_3]^{2+}$	Zn^+	k	pH 5.2	24	2.9×10^9		173
		k	pH 5.2, 0.01 SDS	24	1.6×10^9		173
Reductant = Molybdenum(IV)							
$[Ru(bipy)_3]^{3+}$	$[Mo(CN)_8]^{4-}$	k	0.005 SDS [ar]	8	1.4×10^7		168
Reductant = Tungsten(IV)							
$[MnO_4]^-$	$[W(CN)_8]^{4-}$	$(k_1+k_2K_H[H^+])$	dil.	11	k_1 2.40×10^3		178
				11	k_2 3.55×10^8		
				11	K_H 2.99×10^{-3} [bj]		
				25	k_2 2.78×10^8	3.35 [bk] -17.5 [bk]	
Reductant = Ruthenium(I)							
$[Ru(bipy)_3]^{3+}$	$[Ru(bipy)_3]^+$	k	0.5 Bu^tOH, pH 4.6	24	3.4×10^9		134

[bc] Pp = various N-hydroxymethylated peptides. [bd] Peptide ligands are made up from the following amino-acid units: G, glycyl; A, L-alanyl; V, L-valyl; leu, L-leucyl; P, L-prolyl; terminal a denotes an amide, thus G_3a, glycylglycylglycylamide; terminal OMe denotes the methyl ester. The expression H_{-x} in the formula denotes the number of protons lost from amide groups. The total ionic charge, however, takes account of the loss of a proton from a terminal carboxy-group, where this occurs. [be] Postulated step in the oxidation of Ni^{II} peptide complex by O_2. [bf] Postulated rapid step in the Cu^{II}-catalysed oxidation of citric acid by $[Fe(CN)_6]^{3-}$. [bg] Calculated from the Cu^{II} + cytochrome c^{II} rate using the Marcus cross-relation. [bh] Calculated from the Cu^{II} + $[Co(phen)_3]^{2-}$ rate using the Marcus cross-relation. [bi] Postulated step in the mechanism of the autocatalysis of the reaction of $[Cu^{II}(H_{-3}G_4)]^{2-}$ with oxygen. [bj] Protonation constant of $(MnO_4)^-$. [bk] Calculated using estimated values of $\Delta H_H^{\ominus}$.

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Table 3 (*continued*)

Oxidant, A+	*Reductant*, B	*Rate expression*	*Medium*	*Temp./* °C	*k*	ΔH^*	ΔS^*	*Ref.*
Reductant = *Ruthenium*(II)								
$[Fe^{III}P(im)_2]^{5+}$ [au]	$[Ru(NH_3)_6]^{2+}$		0.25 im, 0.5 ($MeSO_3^-$), pH 4.5	25?	*bl*			95
$[Fe^{III}P(H_2O)]^{5+}$	$[Ru(NH_3)_6]^{2+}$	$k_1+k_2K_{a1}[H^+]^{-1}$	0.05 ($MeSO_3^-$)		k_1 1.6×10^5 k_2 5.1×10^6 K_{a1} 2.0×10^{-5} k_{-1} 4.5×10^3			95
$[Co(NH_3)_5(NH_2CH_2CO_2H)]$	$[Ru(NH_3)_6^{2+}$	k	1 (LiCl)	25	1.33			87
$[Co(NH_3)_5(NH_2C_2H_4CO_2H)]$	$[Ru(NH_3)_6^{2+}$	k	0.1 (LiCl)	25	5.5×10^{-2}			87
$[Co(NH_3)_5\{OC_6H_3(NO_2)_2$-2,4$\}]^{2+}$	$[Ru(NH_3)_6]^{2+}$	k	0.12 HCl	25	7.4			117
			0.12 H^+, 1.0 (LiCl)	25	21			
$[Co(NH_3)_5\{OC_6H_3(NO_2)_2$-2,5$\}]^{2+}$	$[Ru(NH_3)_6]^{2+}$	k	0.12 HCl	25	5.1×10^2			117
			0.12 H^+, 1.0 (LiCl)	25	1.3×10^3			
$[Co(NH_3)_5(NCMe)]$ and 7 related oxidants	$[Ru(NH_3)_6]^{2+}$	k	0.03H^+, 0.5 (LiCl)	25	~6			157
$[Co(NH_3)_5(SCN)]^{2+}$	$[Ru(NH_3)_5(OH_2)]^{3+}$	$k[H^+]^0$	0.2 (LiCl)	25	1.7×10^2	8.4	−20.2	179
$[Co(NH_3)_5(NCS)]^{2+}$	$[Ru(NH_3)_5(OH_2)]^{3+}$	$k[H^+]^0$	0.2 (LiCl)	25	0.28	14.8	−11.3	179
$[Co(NH_3)_5N_3]^{2+}$	$[Ru(NH_3)_5(OH_2)]^{3+}$	$k[H^+]^0$	0.2 (LiCl)	25	0.61	13.2	−15.1	179
$[Co(en)_3]^{3+}$	$[Ru(NH_3)_5Cl]^+$	k	0.01 H^+, 0.1 (Na)Cl	25	6.2×10^{-3}	17.2	−11.2	155
$[Co(Chxn)_3]^{3+}$	$[Ru(NH_3)_5Cl]^+$	k	0.01 H^+, 0.1 (Na)Cl	25	3.8×10^{-3}	17.7	−10.5	155
$[Co(NH_3)_5Br]^{2+}$	$[Ru(NH_3)_5py]^{2+}$	k	0.1 $NaClO_4$, pH 2	24	20	7.9	−26.1	88
$[Co([14]tetraene\text{-}N_4)Cl_2]^+$ [bb]	$[Ru(NH_3)_5py]^{2+}$	k	0.1 NaCl, pH 2	24	2.9×10^5	1.9	−27.0	88
$[Co([14]diene\text{-}N_4)Cl_2]^+$ [bb]	$[Ru(NH_3)_5py]^{2+}$	k	0.1 NaCl, pH 2	24	1.2×10^4	4.6	−25.1	88
$[Co([14]tetraene\text{-}N_4)]^{3+}$	$[Ru(NH_3)_5py]^{2+}$	k	0.1 $HClO_4$	25	8.3×10^3	0.95	−37.0	88

$[Co([14]diene\text{-}N_4)]^{3+}$	$[Ru(NH_3)_5py]^{2+}$	k	0.1 $HClO_4$	25	36	6.95	−28.0	88
$[Co(NH_3)_5Cl]^{2+}$	$[Ru(NH_3)_5py]^{2+}$	k	0.1 $NaClO_4$, pH 2	24	3.9			
$[Co(edtaH)Cl]^{-}$	$[Ru(NH_3)_5py]^{2+}$	k	0.1 NaCl, pH 2	24	6.2×10^4			
$[Co([14]tetraene\text{-}N_4)Br_2]^{+}$	$[Ru(NH_3)_5py]^{2+}$	k	0.1 NaBr, pH 2	24	9.1×10^4			
$[Co([14]diene\text{-}N_4)Br_2]^{+}$	$[Ru(NH_3)_5py]^{2+}$	k	0.1 NaBr, pH 2	24	1.0×10^5			
$[Co([14]diene\text{-}N_4)]^{2+}$	$[Ru(bipy)_3]^{+}$	k	?	25	1.8×10^8			180
Cu^{2+}	$[Ru^{II}(NH_3)_5$-$(NC_5H_4$-$CH{=}CH_2\text{-}4)]$	k	0.1 CF_3CO_2H	23	2.3	10.2	−22	51
$[Ru(en)_3]^{3+}$	$[Ru(en)_3]^{2+}$	k [bm]	1 (CF_3SO_3Li)	25	3.6×10^4			101
$[Ru(NH_3)_5(OH_2)]^{3+}$	$[Ru(NH_3)_5(OH_2)]^{2+}$	k [bm]	1 (CF_3SO_3Li)	25	2.9×10^3			101
$[Ru(NH_3)_4(bipy)]^{3+}$	$[Ru(NH_3)_4(phen)]^{2+}$	k	→0	25	4.14×10^4			3
			0.1 $HClO_4$ [bo]	25	2.2×10^6 [bn]	1.9	−23	3
			0.1 CF_3SO_3H [bo]	25	7.7×10^5	3.1	−21	
$[Ru(NH_3)_2(bipy)_2]^{3+}$	$[Ru(NH_3)_2(phen))_2]^{2+}$	k	0.1 $HClO_4$	25	8.4×10^7 [bp]	2.4	−30	3
$[Ru(en)_3]^{3+}$	$[Ru(NH_3)_6]^{2+}$	k	0.1 CF_3SO_3H	25	2.7×10^4 [bq]	2.4 [br]	−30 [br]	3
$[Ru(NH_3)_6]^{3+}$	$[Ru(NH_3)_6]^{2+}$	k	0.1 CF_3SO_3H	25	3.2×10^3 [bs]	4.5 [bs]	−27 [bs]	3
$[Ru(NH_3)_6]^{3+}$	$[Ru(bipy)_3]^{+}$	k	0.5	25	4.7×10^9			130
$[Ru(NH_3)_5Cl]^{2+}$	$[Ru(NH_3)_5Cl]^{+}$	k	0.1	25	3×10^5 [bt]			130
$[Ru^{III}(edta)(NC_5H_3$-$CONH_2\text{-}4)]^{-}$	$[Ru(edta)]^{2-}$	k	0.2 (CF_3SO_3K), pH 5.5	25	k 2.8×10^6			108
$[Ru^{III}(edta)(NCMe)]^{-}$	$[Ru(edta)]^{2-}$	k	0.2 (CF_3SO_3K), pH 5.5	25	k 3.3×10^5			108
$[Ru(TPP)(py)_2]^{+}$ [bu]	$[Ru(NH_3)_6]^{2+}$	k	0.3	22	1.2×10^9			181

[bl] $k_{obs}=700$ s^{-1} when $[Ru(NH_3)_6]^{2+}=1.2\times10^{-3}$ M, $[Ru(NH_3)_6]^{3+}=1.2\times10^{-3}$ M, $[Fe]_T=2.7\times10^{-5}$ M. [bm] Assumed. [bn] From kinetic data, $\Delta H^{\ominus}=\Delta S^{\ominus}=\Delta G^{\ominus}=0$ within experimental error; from electrochemical data $\Delta H^{\ominus}=-0.1$ kcal mol^{-1}, $\Delta S^{\ominus}=0.8$ cal K^{-1} mol^{-1} at 25 °C. [bo] Data also recorded at other medium concentrations, up to 1.0 M. [bp] From kinetic and electrochemical measurements, $\Delta G^{\ominus}=0$ within experimental error. [bq] From electrochemical measurements the equilibrium constant of the overall reaction is 73; $\Delta H^{\ominus}=-4.3$ kcal mol^{-1}, $\Delta S^{\ominus}=-6.4$ cal K^{-1} mol^{-1}. [br] Stated in the paper to be activation parameters of a different reaction apparently by a misprint ('reaction 8' for 'reaction 9'). [bs] Calculated from data on the reaction $[Ru(en)_3]^{3+}+[Ru(NH_3)_6]^{2+}$, using the Marcus cross-relation. [bt] Estimated from the $[Co(en)_3]^{3+}+[Ru(NH_3)_5Cl]^{+}$ rate by means of the Marcus cross-relation. [bu] TPP = tetraphenylporphine.

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Table 3 (*continued*)

Oxidant, A^+	*Reductant*, B	*Rate expression*	*Medium*	*Temp./* °C	*k*	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
Reductant = Osmium(II)								
$[Fe(phen)_3]^{3+}$	$[Os(phen)_3]^{2+}$	*k*	5×10^{-4} M H_2SO_4 *bv*	25	47×10^6			182
			HCO_2H *bv*	25	$\sim17\times10^6$			
			90% HCO_2H, 10% H_2O *bv*	25	$\sim24\times10^6$			
			MeCN *bv*	25	$\sim14\times10^6$			
$[Fe(bipy)_3]^{3+}$	$[Os(phen)_3]^{2+}$	*k*	HCO_2H *bv*	25	19×10^6			182
			90% HCO_2H, 10% H_2O *bv*	25	$\sim52\times10^6$			
$[Fe(bipy)_3]^{3+}$	$[Os(bipy)_3]^{2+}$	*k*	MeCN *bv*	25	$\sim1.0\times10^6$			182
$[Fe(4,4'\text{-}Me_2bipy)_3]^{3+}$	$[Os(phen)_3]^{2+}$	*k*	5×10^{-4} M H_2SO_4 *bv*	25	32×10^6			182
			HCO_2H *bv*	25	0.49×10^6			
			90% HCO_2H, 10% H_2O *bv*	25	3.5×10^6			
$[Fe(4,4'\text{-}Me_2bipy)_3]^{3+}$	$[Os(4,4'\text{-}Me_2bipy)]_3]^{2+}$	*k*	MeCN *bv*	25	1.9×10^6			182
$[Fe(4,7\text{-}Me_2bipy)_3]^{3+}$	$[Os(4,7\text{-}Me_2phen)_3]^{2+}$	*k*	~90% HCO_2H, 10% H_2O *bv*	25	$\sim20\times10^6$			182
$[Fe(5,6\text{-}Me_2phen)_3]^{3+}$	$[Os(5,6\text{-}Me_2phen)_3]^{2+}$	*k*	~90% HCO_2H, 10% H_2O *bv*	25	$\sim12\times10^6$			182
$[Fe(bipy)_3]^{3+}$	$[Os(3,5,6,7\text{-}Me_4\text{-}phen)_3]^{2+}$	*k*	~90% HCO_2H, 10% H_2O *bv*	25	$\sim13\times10^6$			182
$[Fe(3,5,6,8\text{-}Me_4phen)_3]^{3+}$	$[Os(3,5,6,8\text{-}Me_4\text{-}phen)_3]^{2+}$	*k*	5×10^{-4} M H_2SO_4 *bv*	25	$\sim47\times10^6$			182
			~90% HCO_2H, 10% H_2O *bv*	25	44×10^6			
$[Fe(4,4'\text{-}Me_2bipy)_3]^{3+}$	$[Os(4,4'\text{-}Me_2bipy)_3]^{2+}$	$(k_1+k_2[ClO_4^-]+k_3[PF_6^-])$	MeCN	25	k_1 5.0×10^5 k_2 1.3×10^{10} k_3 5.6×10^9 k_1 4.0×10^5 *bw* k_2 1.0×10^{10} *bw* k_3 3.4×10^9 *bw*			182

Reductant = *Silver*(I)								
Ag^+	Ag [bx]	— [by]	—	—	—	—	—	183
Ag^+	Ag [bx]	*k*	NH_3 liquid	23	1.3×10^{10}			184
Reductant = *Cadmium*(I)								
$[Ru(bipy)_3]^{3+}$	Cd^+	*k*	0.5 Bu^tOH, pH 4.6	24	2.8×10^9			134
$[Ru(bipy)_3]^{2+}$	Cd^+	*k*	pH 5.9	24	4.1×10^9			173
		k	pH 5.9, 0.01 SDS	24	6.1×10^8			173
Reductant = *Iridium*(III)								
$[Cu^{III}(H_{-3}G_3a)]$ and 15 related oxidants [ba]	$[IrCl_6]^{3-}$	$k_1[H^+]^0$	0.1 ($NaClO_4$ + NaOAc), 0.05 HOAc	25	3.1×10^4			100
Reductant = *Cerium*(III)								
Np^{VII}	Ce^{III}	—	0.1 H^+; $I = 1.0$ M	25	*bz*			185
Reductant = *Europium*(II)								
$[Cr(NH_3)_5(O_2CC_4H_3N_2\text{-}CO_2H)]^{2+}$ [ca]	Eu^{2+}	—	—	—	*cb*			160
$[Co(NH_3)_5(O_2CCH_2NC_5H_4)]^{3+}$ and 6 related oxidants	Eu^{2+}	*k*	1 $HClO_4$		0.82			115
$[2\text{-}Co(NH_3)_5(O_2CC_6H_4\text{-}NCONH_2\text{-}4)]^{3+}$ and 2 related oxidants	Eu^{2+}	*k*	1.2 $HClO_4$	25	1.2×10^3 [cc]			109
$[Co(NH_3)_5(NCMe)]$ and 6 related oxidants	Eu^{2+}	*k*	1 $HClO_4$	25	0.41			157

[bv] Oxidant and reductant present as perchlorates, in various concentration ranges, up to 25×10^{-6} M; for details see the original reference. [bw] The same data recalculated by a procedure in which 'ion atmosphere effects are considered by inclusion of the Debye–Hückel limiting law in the calculation'. [bx] Mononuclear, solvated species; reaction product is Ag_2^+. [by] Decomposition of Ag_2^+ in anionic micelles. [bz] Rapid reaction (stopped flow). [ca] Ligand is pyrazine-2,3-dicarboxylic acid. [cb] Reaction product is a strongly absorbing yellow species; kinetics 'not simple', but no details recorded. [cc] Autocatalytic reaction, specific rate calculated from the initial rate.

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Table 3 (*continued*)

Oxidant, A^+	*Reductant*, B	*Rate expression*	*Medium*	*Temp./* °C	*k*	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref*
$[Co(NH_3)_5py]^{3+}$	Eu^{2+}	$\frac{k_1k_2[X]}{k_{-1}[Eu^{3+}]+k_2[Co^{III}]}$	1.5 ($LiClO_4$)	25	k_1 1.3×10^3 *cd* k_2/k_{-1} 13			119
$[Co(en)_3]^{3+}$	Eu^{2+}	$K_1K_2k_3[V][Eu^{3+}]^{-1}$	1 $HClO_4$	25	$K_1K_2k_3$ 1.2×10^2 *ce*			126
$[Co(NH_3)_5\{OC_6H_3(NO_2)_2$-2,4$\}]^{2+}$	Eu^{2+}	*k* *cf*		25	$>10^3$			117
$[Co(NH_3)_5\{OC_6H_3(NO_2)_2$-2,5$\}]^{2+}$	Eu^{2+}	*k* *cf*		25	$>10^3$			117
Reductant = *Uranium*(III)								
$[Cr(NH_3)_5(O_2CCH{=}CHCO_2H$-*cis*$)]^{2+}$	U^{3+}	*k*	0.24 $HClO_4$	25	4×10^3 *cg*			160
$[Cr(NH_3)_5(O_2CCOMe)]^{2+}$	U^{3+}	*k*	0.24 $HClO_4$	25	6×10^3 *cg*			160
$[Cr(NH_3)_5(O_2CC_5H_4N$-2$)]^{2+}$	U^{3+}	—	—	—	*cg*, *ch*			160
$[Co(en)_3]^{3+}$	U^{3+}	*k*	0.2 ($HClO_4$) 0.35 ($HClO_4$?)	25 25	0.18 0.22			106
$[Co(NH_3)_6]^{3+}$	U^{3+}	*k*	0.2 ($HClO_4$)	25	1.38			106
$[Co(NH_3)_5$(imidazole)$]^{3+}$	U^{3+}	*k*	0.2 ($HClO_4$)	25	2.7			106
$[Co(NH_3)_5$(pyrazole)$]^{3+}$	U^{3+}	*k*	0.2 ($HClO_4$)	25	14			106
$[Co(NH_3)_5py]^{3+}$	U^{3+}	*k*	0.2 ($HClO_4$)	25	26			106
$[Co(NH_3)_5(OCHNMe_2)]^{3+}$ and 6 related oxidants	U^{3+}	*k*	0.2 ($HClO_4$)	25	33			106
$[Co(en)_3]^{3+}$ *ci*	U^{3+}	$\frac{k_1k_2[isn]}{k_{-1}[U^{4+}]+k_2[Co^{III}]}$	0.25 H^+, 0.5 ($LiClO_4$)	25	k_1 2.1×10^3 k_1k_2/k_{-1} 5.9×10^{-3} k_2 3×10^4			186
$[Ru(NH_3)_5(OH_2)]^{3+}$	U^{3+}	$k[H^+]^0$	1 $(Li)CF_3SO_3$	25	1.11×10^4 *cj*	−0.6	−38	101
$[Ru(NH_3)_6]^{3+}$	U^{3+}	$k[H^+]^0$	1 $(Li)CF_3SO_3$	25	1.10×10^4 *cj*	1.0	−38	101
$[Ru(en)_3]^{3+}$	U^{3+}	$k[H^+]^0$	1 $(Li)CF_3SO_3$	25	1.62×10^5	−1.3	−39	101
U^{4+}	U^{3+}	*k* *cl*	1 (CF_3SO_3Li)	25	5.9×10^{-5} *ck*			101
U^{4+}	U^{3+}		1	25	0.05 *cm*			101

Reductant = *Uranium*(IV)								
Am^{V}	U^{IV}	k	0.2 H^+			25.0	34.0	187
Np^{VI}	U^{IV}	k	1 $HClO_4$		*cn*			188
Reductant = *Neptunium*(III)								
Np^{4+}	Np^{3+}	k	1 (CF_3SO_3Li)	25	4.6×10^{-4} *co*			101
Reductant = *Neptunium*(IV)								
V^{V}	Np^{IV}	*cp*	2 ($NaClO_4$)		436	25.4	29.5	189
Fe^{III}	Np^{IV}	$k_1[H^+]^{-3}$	2 ($LiNO_3$)	25.1	7.7×10^{-3} *cq*	E_a 32 ± 0.5		190
$[Fe(CN)_6]^{3-}$	Np^{VI}	k	2.5 OH^-, 3 (K^+)	10	9.4			191
			3 KOH			E_a 9.4		
Reductant = *Plutonium*(IV)								
Ce^{IV}	Pu^{IV}	k	4 HNO_3	30	0.21	21.8	14	192
		$k[H^+]^{-2.2}$	4 ($NaNO_3$)	10	0.22	—	—	
		$k[H^+]^{-2.6}$	3.7 ($NaNO_3$)	15	—	—	—	
		k	3.7 HNO_3	—	—	24.0	17	
		k	4.9 HNO_3	—	—	23.1	13	

cd X = 2,4-$(MeO_2C)_2C_5H_3N$. *ce* K_1, K_2 are equilibrium constants for the reactions Eu^{2+} + isn ⇌ Eu^{3+} + isn^- and isn^- + Vn ⇌ isn + Vn^- (isn = isonicotinamide, Vn = Methylviologen); data for other combinations of organic catalysts, and other reaction conditions are reported in the original reference. *cf* Assumed. *cg* The reaction observed is reduction of the ligand, not the chromium(III) centre. *ch* No kinetic data. *ci* Results with three other organic catalysts also reported. *cj* Ionic strength dependence also determined. *ck* Calculated from the $[Ru(NH_3)_6]^{3+/2+}$ rate and the cross-reaction, using the Marcus equation. *cl* Assumed. *cm* Calculated from rates of three other reactions using the Marcus cross-relation. *cn* Data shown graphically for various mixtures of water with MeOH, EtOH, or Me_2CHOH. *co* Calculated from the $[Ru(NH_3)_6]^{3+}$ + $[Ru(NH_3)_6]^{2+}$ and $[Ru(NH_3)_6]^{3+}$ + Np^{3+} rates using the Marcus equation. *cp* Rate = $k[Np^{4+}][V^V]^{0.33}[H^+]^{-0.8}$. *cq* Initial step in Fe^{III}-catalysed oxidation of Np^{IV} by HNO_2.

186 M. K. Loar, Y.-T. Fanchiang, and E. S. Gould, *Inorg. Chem.*, 1978, **17**, 3689.
187 N. B. Blokhin and A. G. Rykov, *Sov. Radiochem.* (*Engl. Transl.*) 1977, **19**, 52.
188 L. M. Frolova and A. G. Rykov, *Sov. Radiochem.* (*Engl. Transl.*), 1977, **19**, 56.
189 V. S. Koltunov, V. I. Marchenko, and M. P. Shapovalov, *Radiokhimiya*, 1977, **19**, 56.
190 I. V. Shilin, T. A. Rumyantseva, and A. V. Belyaev, *Sov. Radiochem.* (*Engl. Transl.*), 1975, **17**, 615.
191 N. N. Krot, M. P. Mefod'eva, and T. V. Afanas'eva, *Sov. Radiochem.* (*Engl. Transl.*), 1977, **19**, 193.
192 G. P. Nikitina, V. G. Shumkov, V. P. Egorova, and Yu. E. Ivanov, *Sov. Radiochem.* (*Engl. Transl.*), 1975, **17**, 550.

Table 3 (*continued*)

Oxidant, A^+	*Reductant*, B	*Rate expression*	*Medium*	*Temp./* °C	*k*	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
Reductant = *Americium*(IV)								
Am^{IV}	Am^{IV}	k	0.11 ($LiClO_4$), pH 5.2	23	5×10^6			193
Reductant = *Americium*(V)								
Np^{VII}	Am^{V}	$\frac{\beta c[H^+]}{1+c[H^+]}$	1	25	β 4.42×10^5 c 1.30	5.58 −1.8	−14.1 −5.5	185

[193] S. Gordon, W. A. Mulac, K. H. Schmidt, R. K. Sjoblom, and J. C. Sullivan, *Inorg. Chem.*, 1978, **17**, 294.

Table 4 *Rate and activation parameters for complementary two-equivalent electron transfer reactions. For conventions used, see Table* 3

Oxidant	*Reductant*	*Rate expression*	*Medium*	*Temp.*	*k*	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
	$[(OC)_2L_3CoCo(CO)_5]$	—	—	—	*a*			194
Sn^{IV}	Sn^{II}	$k[HCl]^{1.14}$	2—4 HCl	22	5.3×10^{-4}	E_a 8.05		195
		$k[HCl]^{0.5}$	4—8 HCl	22	1.3×10^{-3}			
		$k[HCl]^{3.2}$	8—12 HCl [b]	22	5.3×10^{-6}	E_a 11.05		

[a] $[(OC)_2L_3CoCo(CO)_5] \rightarrow [Co(CO)_2L_3]^+ + [Co(CO)_4]^- + CO$; postulated step in the disproportionation of $[Co_2(CO)_8]$; L = piperidine. [b] Data also given for various mixtures of $HClO_4$ and HCl.

Table 5 *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* $Rate = -(1/a)d[A]/dt = -(1/b)d[B]/dt$ *etc. For other conventions, see Table* 3

Reaction	*Rate*	*Medium*	*Temp.*	*Rate data and notes*	*Ref.*
$[HCrO_4]^- + 3[Fe(CN)_6]^{4-} + 7H^+ = Cr^{3+} + 3[Fe(CN)_6]^{3-} + 4H_2O$	$(k_0 + k_M[M^+])[H^+][HCrO_4^-][Fe(CN)_6^{4-}]$	0.25 (NO_3^-)	30	k_0 2.0×10^6 k_{Na} 6.5×10^6 k_K 3.0×10^6	196
	$\dfrac{k_1[HCrO_4^-][Fe(CN)_6^{4-}]^2}{[Fe(CN)_6^{4-}] + (k_{-1}/k_2)[Fe(CN)_6^{3-}]}$	1.91×10^{-5} H^+, 0.5 K(NO_3)	30	k_1 5.03×10^{-3} k_{-1}/k_2 0.18	
		1.91×10^{-5} H^+(?), 0.2 K(NO_3)	30	k_{-1}/k_2 0.25	
$Np^{VII} + Cr^{III}$	—	0.1 H^+; I = 1.0M	25	*a*	185
$Np^{VII} + Pd^{II}$	—	0.53 H^+; I = 1.0M	25	*a*	185

[a] 'Complex multiphasic kinetics, consistent with, but not establishing, the existence of transient, oxidized intermediates'; stoicheiometry not reported.

194 P. L. Stanghellini, R. Rossetti, E. Mentasti, and E. Pelizzetti, *Inorg. Chim. Acta*, 1977, **22**, 19.
195 J. Sedláček, A. Gosman, P. Podhájecký, and J. Tarasová, *J. Radioanal. Chem.*, 1976, **30**, 273.
196 K. E. Howlett and Y. Sulfab, *Inorg. Chim. Acta*, 1976, **17**, 129.

Table 6 *Rate and activation parameters for electron transfer reactions involving electronically excited metal complexes. For conventions used, see Table 3*

Oxidant	*Reductant*	*Rate law*	*Medium*	*Temp.*	*k*	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
$[Co(NH_3)_5py]^{3+}$	$*[Ru(bipy)_3]^{2+}$	*k*	0.1 ($LiClO_4$), pH 5.6	25	1.72×10^8			116
$[Co(NH_3)_5$-$(NC_5H_4C_2H_4C_5H_4N)]^{3+}$ and 3 related oxidants	$*[Ru(bipy)_3]^{2+}$	*k*	0.1 ($LiClO_4$), pH 5.6	25	2.02×10^8			116
Fe^{3+}	$*[Ru(terpy)_2]^{2+}$	*k*	1 $HClO_4$	26	$\leqslant 2.9\times10^9$			181
$[Ru(bipy)_3]^{3+}$	$*[Ru(bipy)_3]^{2+}$	*k*	0.5 Bu^tOH, pH 4.6	24	1.8×10^9			134
$[Ru(bipy)_3]^{3+}$	$\ddagger[Ru(bipy)_3]^{2+}$ [a]	*k*	0.5 Bu^tOH, pH 4.6	24	3.6×10^9			134
Cu^{2+}	$*[Ru(phen)_3]^{2+}$ and 6 substituted phen complexes	*k*	0.5 H_2SO_4	25	7.5×10^7			129
Cu^{2+}	$*[Ru(bipy)_3]^{2+}$ and 2 substituted bipy complexes	*k*	0.5 H_2SO_4	25	6.2×10^7			129
			0.5 $HClO_4$	25	6.6×10^7 [b]			129
Cu^{2+}	$*[Os(bipy)_3]^{2+}$	*k*	0.5 H_2SO_4	25	20×10^7			129
Cu^{2+}	$*[Os(5,6\text{-}Me_2phen)_3]^{2+}$	*k*	0.5 H_2SO_4	25	21×10^7			129
Cu^{2+}	$*[Ru(bipy)_3]^{2+}$	— [c]		24	—	—	—	197
Fe^{III}	$*[Ru(bipy)_3]^{2+}$	*c*		25	—	—	—	197
Fe^{III}	$*[Ru(bipy)_3]^{2+}$	*c*		25	—	—	—	198
[Fe(nta)]	$*[Ru(bipy)_3]^{2+}$	*k*		22	3.7×10^9			199
		c		22	—			
$[Co(acac)_3]$	$*[Ru(bipy)_3]^{2+}$	*k*		22	1.1×10^9			199
		c		22	—			
$[Ru(acac)_3]$	$*[Ru(bipy)_3]^{2+}$	*k*		22	3.1×10^9			199
		c		22	—			
Cu^{2+}	$*[Ru(bipy)_3]^{2+}$	*k*	1.9 ($Ca(ClO_4)_2$) 0.04 ($Mg(ClO_4)_2$), 0.01 SDS [d]		8×10^7			173
					1.7×10^8			
$[Fe(CN)_6]^{3-}$	$*[Ru(bipy)_3]^{2+}$	*k*	0.01 SDS [d]		*e*			173
$*[Ru(4,4\text{-}Me_2bipy)_3]^{2+}$	Eu^{2+}	*k*	0.5	25	0.15×10^7			130
$*[Ru(bipy)_3]^{2+}$	Eu^{2+}	*k*	0.5	25	2.8×10^7	−2.2	−32	130

*$[Ru(phen)_3]^{2+}$ and 2 substituted phen complexes	Eu^{2+}	k	0.5	25	4.9×10^7	130
*$[Cr(bipy)_3]^{3+}$	$[Ru(bipy)_3]^{2+}$	k	1 H_2SO_4	25	6.1×10^8	13
*$[Cr(bipy)_3]^{3+}$	$Ru(4,4\text{-}Me_2bipy)_3]^{2+}$	k	1 H_2SO_4	25	11×10^8	13
*$[Cr(bipy)_3]^{3+}$	$[Ru(phen)_3]^{2+}$ and 5 substituted phen complexes	k	1 H_2SO_4	25	9.1×10^8	13
*$[Cr(bipy)_3]^{3+}$	$[Os(bipy)_3]^{2+}$	k	1 H_2SO_4	25	15×10^8	13
*$[Cr(phen)_3]^{3+}$	$[Ru(bipy)_3]^{2+}$	k	1 H_2SO_4	25	8.3×10^8	13
*$[Cr(phen)_3]^{3+}$	$[Ru(4,7\text{-}Me_2phen)_3]^{2+}$	k	1 H_2SO_4	25	14×10^8	13
*$[Cr(phen)_3]^{3+}$	$[Ru(5\text{-}Clphen)_3]^{2+}$	k	1 H_2SO_4	25	8.1×10^8	13
*$[Cr(phen)_3]^{3+}$	$[Ru(5\text{-}NO_2phen)_3]^{2+}$	k	1 H_2SO_4	25	2.6×10^8	13
*$[Cr(phen)_3]^{3+}$	$[Os(bipy)_3]^{2+}$	k	1 H_2SO_4	25	15×10^8	13
*$[Cr(bipy)_3]^{3+}$	Fe^{2+}	k	1 H_2SO_4	25	1.6×10^7	13
*$[Cr(4,4'\text{-}Me_2bipy)_3]^{3+}$	Fe^{2+}	k	1 H_2SO_4	25	8.2×10^5	13
*$[Cr(phen)_3]^{3+}$ and 3 substituted phen complexes	Fe^{2+}	k	1 H_2SO_4	25	1.5×10^7	13
*$[Cr(bipy)_3]^{3+}$ and 2 substituted bipy complexes	Fe^{2+}	k	1 HCl	25	3.7×10^7	136
*$[Cr(phen)_3]^{3+}$ and 4 substituted phen complexes	Fe^{2+}	k	1 HCl	25	3.2×10^7	136
$[Co(NH_3)_5(H_2O)]^{3+}$	*$[Os(bipy)_3]^{2+}$	k	pH 3, 0.5 (Na_2SO_4)	24	2.1×10^8	200

[a] Reductant is different excited state from the others listed in this Table; see text, p. 30. [b] Data at other temperatures also reported. [c] Study of the effects of poly(vinyl sulphate) on emission quenching; data tabulated and shown in graphs. [d] SDS = sodium dodecylsulphate. [e] Lower rate than in the absence of SDS.

[197] C. D. Jonah, M. S. Matheson, and D. Meisel, *J. Phys. Chem.*, 1979, **83**, 257.
[198] D. Meisel, J. Rabani, D. Meyerstein, and M. S. Matheson, *J. Phys. Chem.*, 1978, **82**, 985.
[199] D. Meyerstein, J. Rabani, M. S. Matheson, and D. Meisel, *J. Phys. Chem.*, 1978, **82**, 1879.
[200] E. Kinkenberg, P. Fisher, S.-M. Y. Huang, and H. D. Gafney, *J. Phys. Chem.*, 1978, **82**, 526.

Table 6 (*continued*)

Oxidant	*Reductant*	*Rate law*	*Medium*	*Temp.*	*k*	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
$[Co(NH_3)_5(CO_3)]^+$	$*[Os(bipy)_3]^{2+}$	*k*	pH 3, 0.5 (Na_2SO_4)	24	1×10^8			200
$[Co(NH_3)_5N_3]^{2+}$	$*[Os(bipy)_3]^{2+}$	*k*	pH 3, 0.5 (Na_2SO_4)	24	3.7×10^8			200
$[Co(NH_3)_5(SO_4)]^+$	$*[Os(bipy)_3]^{2+}$	*k*	pH 3, 0.5 (Na_2SO_4)	24	2.1×10^8			200
$[Co(NH_3)_5Cl]^{2+}$	$*[Os(bipy)_3]^{2+}$	*k*	pH 3, 0.5 (Na_2SO_4)	24	5.7×10^8			200
$[Co(NH_3)_5Br]^{2+}$	$*[Os(bipy)_3]^{2+}$	*k*	pH 3, 0.5 (Na_2SO_4)	24	8.9×10^8			200
$[Co(NH_3)_4(C_2O_4)]^+$	$*[Os(bipy)_3]^{2+}$	*k*	pH 3, 0.5 (Na_2SO_4)		*f*			200
cis-$[Co(ida)_2]^-$	$*[Cu(2,9\text{-}Me_2phen)]^+$	—	0.01 HOAc, 0.01 $^-$OAc,	20	*g*			201,
trans-$[Co(ida)_2]^-$	$*[Cu(2,9\text{-}Me_2phen)]^+$	—	30% EtOH,					202
			0.1 ($LiNO_3$,	20	*g*			
trans-$[Co(NH_3)_4(CN)_2]^+$	$*[Cu(2,9\text{-}Me_2phen)]^+$	—	LiCl, or NaCl)	20	*g*			202

[f] Electron-transfer reaction; rate not measured. [g] Evidence of 1:1 bimolecular electron-transfer reaction.

[201] D. R. McMillin, M. T. Buckner, and B.-T. Ahn, *Inorg. Chem.*, 1977, **16**, 943.
[208] B.-T. Ahn and D. R. McMillin, *Inorg. Chem.*, 1978, **17**, 2253.

2

Metal Complexes with Inorganic (Main Group) Substrates

BY A. McAULEY

With the division of reaction types into those involving inorganic and organic reagents (see next chapter), the presentation of material differs somewhat from that used in previous Reports. In this chapter, reactants have been identified according to groups in the periodic table. Also, with the inclusion of a section in the bio-inorganic chapter on reactions of dioxygen and hydrogen peroxide the coverage in this section of the Report relates more exclusively to the inorganic redox reactions of these reagents.

1 Reactions with Nitrate

A number of studies have been reported on the reduction of nitrate by metal ions. In dilute HNO_3 solution, the ruthenium(II) species $[(py)(bipy)_2Ru(OH_2)]^{2+}$ is oxidized by NO_3^- to the corresponding Ru^{III} complex.[1] The metal nitrosyl cation $[(py)(bipy)_2Ru(NO)]^{3+}$ is also formed as a product, resulting from the nitrosation reaction of (initial product) HNO_2 with ruthenium(II) aquo-species. This side reaction is eliminated when the HNO_2 scavenger sulphamate ion ($NH_2SO_3^-$) is present. The reaction mechanism involves an initial substitution of the nitrate to yield the species $[(py)(bipy)_2Ru(O\text{-}NO_2)]^+$, which in an intramolecular redox step produces HNO_2 and a ruthenium(IV) ion,

$$[L_nRu(OH_2)]^{2+} \overset{NO_3^-}{\rightleftharpoons} [L_nRu(O\text{-}NO_2)]^+ \rightarrow [L_nRuO]^{2+} + HNO_2$$

$$[L_nRuO]^{2+} + [L_nRuOH_2]^{2+} \xrightarrow{\text{fast}} 2[L_nRu(OH)_2]^{3+}$$

where L_n is used to represent the ligands indicated. The rapid reaction of Ru^{IV} and Ru^{II} provides the route to the observed Ru^{III} product.

Monomeric molybdenum(v) complexes of the type $[MoOCl_3L]$ (L = bipy or phen), $[MoOClL_2]$ (L = 8-hydroxy- or 8-mercapto-quinoline), and [MoOCl-(MeOH)L] [L = *O*-(salicylidenimino)phenol] reduce NO_3^- in a one-electron step (in DMF) producing NO_2 and the corresponding Mo^{VI} complex.[2] The kinetics are complex with some deviations from linearity under first-order conditions. In the presence of added Cl^- and excess NO_3^-, however, linearity to 87% reaction is observed. The rate law is of the form

$$-d[Mo^V]/dt = a[NO_3^-][Mo^V]/(b[Cl^-] + [NO_3^-])$$

[1] B. A. Moyer and T. J. Meyer, *J. Amer. Chem. Soc.*, 1979, **101**, 1326.
[2] R. D. Taylor, P. G. Todd, N. D. Chasteen, and J. T. Spence, *Inorg. Chem.*, 1979, **18**, 44.

Omitting the ligand groups, a mechanism is proposed in which the initial dissociation of a chloride ion is followed by the formation of a nitrato-complex:

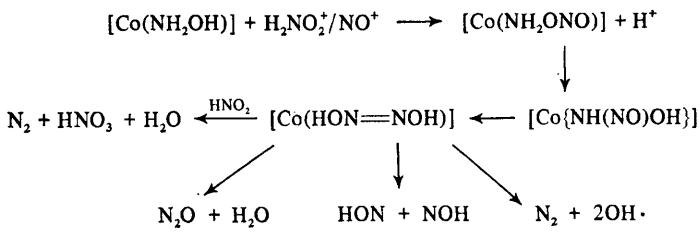
$$Mo^{V}OCl \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Cl^- + Mo^{V}O^+ \overset{+NO_3^-,k_2}{\underset{k_{-2}}{\rightleftharpoons}} Mo^{V}O(NO_3) \xrightarrow{k_3} Mo^{VI}O_2 + NO_2$$

It is probable that the intermediate nitrate is *O*-bonded as in the ruthenium reaction. The rates are, however, highly dependent on structure, *cis*-complexes being generally more reactive than *trans*. An interpretation of this finding is that the nitrate is required to co-ordinate with an oxygen atom *cis* to the MoO group in order to achieve proper overlap of the Mo^{V} d_{xy} orbital (which contains the electron) and the nitrate oxygen π-orbital. In the cases of *cis*-[$MoOCl_3$(bipy)] and *cis*-[$MoOCl_3$(phen)], the initial rapid replacement of Cl^- occurs at the position *trans* to the co-ordinated oxygen and either a rapid rearrangement or rapid formation of a chelated nitrato-group takes place prior to the electron transfer.

Reaction of a nickel(II) tetra-aza-annulene with NO_3^- in methanol results in the formation of a dinuclear nickel(III) complex.[3] In conditions of dilute acid, the reaction is slower than the corresponding reaction of HNO_2 (which is reduced to N_2O). In the reaction of the related tetra-azacyclotetradecadienenickel(II) ion with HNO_3, however, oxidation takes place on the ring with tetraimine formation.[4]

2 Reactions with Nitrite

Kinetic studies have been made on the reaction of nitrous acid with *cis*-chlorobis-(ethylenediamine)hydroxylaminecobalt(III).[5] The reaction is hydrogen-ion dependent, with rate $\propto$ $[H^+][HNO_2]$[complex] at $[H^+] > 0.1M$ whereas at lower acidities hydrogen ion retardation is observed with rate $\propto [^+]^{-1}[HNO_2]$[Complex]. The corresponding complex with *O*-methylhydroxylamine does not react with HNO_2. At the higher acid ranges the reaction is considered to proceed *via* a rate-determining formation of an *O*-nitroso-species which undergoes rearrangement to give a co-ordinated hyponitrite with subsequent decomposition to N_2O or, *via* a nitrous acid-catalysed reaction, to yield N_2. Omitting other ligands on the cobalt, Scheme 1 is proposed. Using labelled N atoms, it was shown that the formation of N_2O of mass numbers 44 and 46 requires cleavage of the



Scheme 1

[3] G. P. Ferrara and J. C. Dabrowiak, *Inorg. Nuclear Chem. Letters*, 1978, **14**, 223.
[4] T. Ito, *Bull. Chem. Soc. Japan*, 1978, **51**, 3647.
[5] M. N Hughes, K. Shirmanker, and P. E. Wimbledon, *J.C.S. Dalton*, 1978, 1634.

hyponitrite species into nitryl fragments. Some catalysis by SCN^- is noted since the formation of NOSCN provides an effective carrier for NO^+.

The kinetics and mechanism of the oxidation of $[Fe(phen)_2(CN)_2]$ by HNO_2 have been reported.[6] At low acidities ($\sim 0.1M$) in H_2SO_4, the rate equation is of the form $Rate = k[H^+][HNO_2][Fe^{II}]^2$, and the reaction proceeds *via* diffusion-controlled oxidation of the complex by NO^+. Under more concentrated conditions ($[H_2SO_4] \sim 6M$) protonation of the iron(II) species to yield $[Fe(phen)_2(CNH)_2]^{2+}$ is invoked in the interpretation of the rate variations.

3 Reactions with Hydrazine

Autocatalysis by Co^{II} has been shown to be a feature in the reduction of carbonatocobaltate(III) complexes by hydrazine.[7] The reduction proceeds according to the equation

$$(1 + 3x)Co^{III} + N_2H_4 \longrightarrow (1 + 3x)Co^{II} + N_2 + \tfrac{1}{2}(1-x)(N_2 + 2NH_3)$$

where x varies between 0.86 and 2.02 depending on relative reactant concentrations. In the pH range 8—10 the rate expression involves two terms; in pseudo-first-order conditions (N_2H_4 in excess), $-d[Co^{III}]/dt = k_1[Co^{III}] + k_2[Co^{III}][Co^{II}]$, where k_1 and k_2 represent pseudo-first- and second-order rate constants respectively. A mechanism in agreement with the observed data and with a suppression of the second term in the presence of edta involves (k_1) a rate-determining substitution process followed by a fast inner-sphere redox decomposition of the carbonatocobalt(III)-hydrazine complex and (k_2) an outer-sphere electron transfer between $[Co(CO_3)_3]^{3-}$ and a cobalt(II)-hydrazine complex. Similar effects are observed when copper(II) and manganese(II) are present in place of cobalt(II).

The kinetics of the reaction of plutonium(IV) with hydroxylamine in $HClO_4$ have been investigated.[8] The rate equation again shows a hydrogen-ion dependence with $Rate = k[Pu^{IV}]^2[NH_3OH^+]/[Pu^{III}][H^+]^2$. In this case it is suggested that the intermediate $[PuNHOH]^{4+}$ is formed.

Complex formation is proposed in the mechanism of oxidation of hydrazinium ion by hexachloroiridate(IV).[9] The observed rate law, $-d[Ir^{IV}]/dt = kK[Ir^{IV}][N_2H_5^+]/([H^+] + K[N_2H_5^+])$, is consistent with a mechanism involving the rapid formation of the outer-sphere species $[N_2H_4IrCl_6]^{2-}$ with a slow subsequent redox step:

$$[IrCl_6]^{2-} + [N_2H_5^+] \overset{K}{\rightleftharpoons} [H^+] + [N_2H_4IrCl_6]^{2-} \xrightarrow[\text{slow}]{k} \text{products}$$

At 30°C, $K = 16.4$ and $k = 3.3 \times 10^{-4}\ s^{-1}$. The rationalization of this mechanism and K value is not clear. No retarding effects of added Ir^{III} were observed and although a slight increase in rate was noted there is no anion (ClO_4^-, Cl^-, SO_4^{2-}) specificity.

[6] P. Reveco, and G. Stedman, *Z. analyt. Chem.*, 1979, **295**, 252 (*Chem. Abs.*, 1979, **91**, 128 404v).
[7] S. P. Tanner, *Inorg. Chem.*, 1978, **17**, 600.
[8] V. S. Koltunov and G. I. Zhuravleva, *Radiokhimiya*, 1978, **20**, 661 (*Chem. Abs.*, 1979, **90**, 44 436j).
[9] K. K. Sengupta and P. K. Sar, *Inorg. Chem.*, 1979, **18**, 979.

4 Reactions with Azide

The reaction of azide with peroxodisulphate in neutral or acidic solutions proceeds with the stoicheiometric amounts of dinitrogen being formed:[10]

$$S_2O_8^{2-} + 2N_3^- \rightarrow 2SO_4^{2-} + 3N_2$$

Retardation of the rate by $[H^+]$ is attributed to protonation of azide. The rate-determining step proposed is a one-electron transfer from N_3^- to $S_2O_8^{2-}$. The authors cite a positive salt effect as supportive evidence for this proposal although the possibility of catalysis *via* ion-pairing (involving Cu^{II}, Co^{II}, Mn^{II}, and Fe^{III}) must leave this interpretation open to further substantiation.

Oxidation of the Mo^{III} dimer $[Mo_2(O_2CMe)(edta)\mu(OH)_2]^-$ with azide has provided a means[10a] of preparing tetrameric $Mo^{III,IV}$ mixed oxidation state species.

5 Reactions with Water

The kinetics of decomposition of silver(III) in dilute acid have been studied using a stopped-flow technique.[11] Although $[Ag(OH)_4]^-$ is stable for several hours in 1.2M-NaOH, reduction of the base concentration to ~ 0.1M greatly decreases the stability of the ion. Also, whereas the products of the decomposition reaction under basic conditions are AgO and O_2, in acidic media Ag^I is formed. The reaction mechanism may be described as

$$[Ag(OH)_4]^- + H^+ \xrightarrow{k_2} [Ag(OH_2)(OH)_3] \xrightarrow{k_3} \text{products}$$

The initial protonation is outwith the detection limits of the apparatus and is probably diffusion controlled. The second reaction is independent of $[H^+]$, $[Ag^+]$, and $[Ag^{III}]_0$ ($k_3 = 142 \pm 13$ s^{-1}), the product being Ag^+, O_2, and a rapidly neutralized hydroxide ion. There is no evidence for H_2O_2 involvement either as an intermediate or as a product. Oxygen formation in the oxidation of water by Mn^{IV} sulphate[12] is thought to be preceded by several disproportionation reactions of the metal ion leading to Mn^{VII} and a dinuclear species $[Mn^{IV}HMnO_4]$. The reduction of permanganate by alkali[13] proceeds *via* the formation of MnO_4^{2-}. The growth and decay of this ion are linear functions of $[OH^-]$. The reaction of H_2O with $Ce(SO_4)_2$ results in dioxygen formation when Pt^{IV} and Ir^{IV} redox catalysts are present.[14]

6 Reactions with Hydrogen Peroxide

Although a section of this Report (Part III) deals with the reactions of hydrogen peroxide and of oxygen in their biochemical interactions, several papers have appeared which have a more pronounced inorganic emphasis. It is such studies

[10] V. Ponnuraj, M. S. Ramachandran, T. S. Vivekanadam, and U. C. Singh, *Bull. Chem. Soc. Japan*, 1978, **51**, 460.

[10a] T. Shibahara and A. G. Sykes, *J.C.S. Dalton*, 1978, 100.

[11] L. J. Kirschenbaum and L. Mrozowski, *Inorg. Chem.*, 1978, **17**, 3718.

[12] V. Y. Shafirovich, N. K. Khannanov, and A. E. Shilov, *Kinetika i Kataliz*, 1978, **19**, 1502 (*Chem. Abs.*, 1979, **90**, 93 128u).

[13] O. Farooq and M. A. Nawab, *Bangladesh. J. Sci. Ind. Res.*, 1978, **13**, 9 (*Chem. Abs.*, 1979, **90**, 128 404v).

[14] J. Kiwi and M. Graetzel, *Angew. Chem.*, 1978, **90**, 900.

that are highlighted in this section. For fuller coverage of reactions of these substrates, however, the reader is referred to both contributions.

The reaction of thallium(III) with H_2O_2 ($Tl^{III} + H_2O_2 \rightarrow Tl^{I} + O_2 + 2H^+$) has been studied using both iodometric and edta titrimetry.[15] Over the range 0.5—3.0M-$NaClO_4$ the rate is independent of ionic strength and of the presence of Tl^{I}. The rate law is of the form

$$-\frac{d[Tl^{III}]}{dt} = \left(\frac{k_2}{[H^+]} + \frac{k_3[H_2O_2]}{[H^+]^2}\right)[Tl^{III}](H_2O_2]^2$$

Sulphate and chloride ions and radical scavengers inhibit the reaction. Although the reaction stoicheiometry is 1:1, the variation with respect to order in $[H_2O_2]$ of between 2 and 3 indicates an interaction between Tl^{III} and the substrate other than the redox step. A mechanism consistent with these data involves the initial formation of complexes:

$$Tl^{3+}aq \rightleftharpoons [Tl(OH)]^{2+} + H^+ \quad (1)$$

$$[Tl(OH)]^{2+} \rightleftharpoons [Tl(OH)_2]^+ + H^+ \quad (2)$$

$$[Tl(OH)]^{2+} + H_2O_2 \rightleftharpoons [Tl(O_2H)]^{2+} + H_2O \quad (3)$$

$$[Tl(OH)_2]^+ + H_2O_2 \rightleftharpoons [Tl(O_2H)(OH)]^+ + H_2O \quad (4)$$

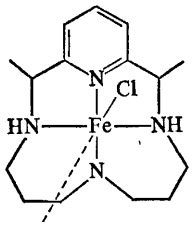
$$[Tl(O_2H)(OH)]^+ + H_2O \rightleftharpoons [Tl(O_2H)_2]^+ + H_2O \quad (5)$$

$$[Tl(O_2H)]^{2+} + H_2O \xrightarrow{k_6} Tl^{I} + O_2 + H_2O_2 + H^+ \quad (6)$$

$$[Tl(O_2H)_2]^+ + H_2O \xrightarrow{k_7} Tl^{I} + O_2 + 2H_2O_2 + H^+ \quad (7)$$

The redox step is considered to proceed *via* two one-electron transfers in which the first is an inner-sphere reaction leading to a Tl^{II}-peroxyl complex. The inhibiting role of SO_4^{2-} or Cl^- is through reduction of the number of co-ordinating sites on the metal ion. No consideration is given by the authors to an outer-sphere process. The results differ from those of a previous study[16] and comment is made on what are seen to be deficiencies in the former investigation.

In the reaction of the iron(III) macrocycle dichloro-*meso*-2,12-dimethyl-3,7,11,17-tetra-azobicyclo[11.3.1]heptadeca-1(17),13,15-trieneiron(III) tetrafluoroborate, $[Fe(CRH)Cl_2]BF_4$ (1), the reactive form of the complex is the *trans*-aquo-hydroxo-species where the axial chloride ions are lost in the pH range (4—6) under consideration. Reaction with H_2O_2 was followed by monitoring O_2



(1)

[15] Z. Boti, I. Horvath, Z. Szil, and L. J. Csanyi, *J.C.S. Dalton*, 1978, 1012.
[16] P. D. Sharma and Y. K. Gupta, *J.C.S. Dalton*, 1975, 81.

pressure as a function of time. Corrections were made for iron(III) dimer which is formed in the presence of oxygen in acetate buffer. The rate law is of the form $\text{Rate} = k_\alpha[Fe^{III}][H_2O_2]_0^2/[H^+][OAc^-]_0$ and inhibition by acetate is observed.[18] A mechanism, similar to that above in which complexes of the type $[Fe(CRH)(OH)(O_2H)]^+$ are formed, is given some consideration by the authors, but is found to be untenable. A free-radical process is favoured,

$$H_2O_2 + [Fe(CRH)(OH)(H_2O)]^{2+} \rightarrow Fe^{II} + H^+ + HO_2\cdot \quad (8)$$

$$Fe^{II} + H_2O_2 \rightarrow [Fe^{III}(CRH)] + HO^- + HO\cdot \quad (9)$$

$$HO\cdot + H_2O_2 \rightarrow H_2O + HO_2\cdot \quad (10)$$

$$HO_2\cdot + [Fe^{III}(CRH)] \rightarrow O_2 + Fe^{II} + H^+ \quad (11)$$

$$HO_2\cdot + Fe^{II} \rightarrow HO_2^- + [Fe^{III}(CRH)] \quad (12)$$

where Fe^{II} is the reduced form of the complex and (8) is the chain initiation step with (9)—(11) as propagation and (12) a termination reaction. Retardation by organic radicals occurs *via* reaction with $OH\cdot$ and the inhibiting effects of acetate are thought to involve competition of this type.

The decomposition of hydrogen peroxide catalysed by configurationally different iron(III) complexes,[17] *e.g. cis*-$[Fe(b\text{-}men)X_2]^{n+}$ and *trans*-$[Fe(tetpy)X_2]^{n+}$, where b-men = *N*,*N*′-bis-(-2-methylpyridyl)ethylenediamine, tetpy = 2,2′:6′,2″:6″, 2‴-tetrapyridyl and X = OH^- or OH_2, has been studied over the range pH = 3.5—7.3. Unlike the previous investigation,[18] however, in these systems the reaction order is dependent on the complex configuration and metal–substrate complex formation is invoked. In the case of *cis*-$[Fe(b\text{-}men)X_2]^{n+}$, the reaction order is unity with respect to both [complex] and $[H_2O_2]$. A scheme consistent with the data is of the form (L = ligand) shown in Scheme 2, where the protolytic equilibria

$$\begin{array}{ccccc} [FeL(OH)_2] + H_2O_2 & \rightleftharpoons & [FeL(O_2H)OH] & \xrightarrow{k_3} & [FeLO_2] + H_2O_2 \\ \Big\downarrow\Big\uparrow H^+ & & \Big\downarrow\Big\uparrow H^+ & & \Big\downarrow \text{fast} \\ [FeL(H_2O)(OH)] + H_2O_2 & \rightleftharpoons & [FeL(O_2H_2)(OH)] & & [FeL(OH)_2] + O_2 \end{array}$$

Scheme 2

of the iron(III) complex and of the peroxo-species provide the rationale for the observed pH effects. In the reaction of the *trans*-complex, however, a higher order in $[H_2O_2]$ is observed as seen in the *trans*-$[Fe(CRH)X_2]^+$ study. The interpretation of the data differs, however, in that for the *trans*-$[Fe(tetpy)X_2]^+$ system the irreversible decomposition of the peroxo-metal ion complex is considered as rate determining. Steric hindrance is considered a factor in the differences in reactivity of the *cis*- and *trans*-complexes with, in the former case, little likelihood of two peroxide molecules co-ordinated in adjacent sites of the complex. A radical pathway has been invoked in the reaction of Fe^{II} with

[17] M. Barteri, M. Farinella, B. Pispisa, and L. Splendorini, *Inorg. Chem.*, 1978, **17**, 3366.
[18] A. C. Melnyk, N. H. Kildahl, A. R. Rendina, and D. H. Busch, *J. Amer. Chem. Soc.*, 1979, **101**, 3232.

hydrogen peroxide in acidic sulphate and nitrate media.[19] The reaction is second order overall and independent of $[H^+]$, the rate-determining step being

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO\cdot$$

The iron(III) reaction has been investigated in MeCN–H_2O solutions[20] where the extent of decomposition is dependent on the relative concentrations of H_2O_2 and acetonitrile present. Again, a radical mechanism with production of ·OH is proposed.

Hydrogen peroxide catalyses the reaction between $[Cr(H_2O)_6]^{3+}$ and edta and the Cr^{III}–edta complex accelerates the decomposition of the substrate.[21] In the absence of edta, the analysis of the kinetic trace suggests that Cr^{IV} and/or Cr^{V} are catalysts for the decomposition reaction in acidic media. The rate of oxygen evolution decreases markedly in the presence of edta, suggesting that the complexes are less active catalysts for the decomposition process. Any catalytic edta-containing species are considered as having chromium in an oxidation state greater than +3. A detailed reaction scheme for the redox process may be simplified to include the reactions (ox = oxidation, sub = substitution):

$$Cr^{III} + H_2O_2 \xrightarrow{k_1^{ox}} Cr^{IV} \xrightarrow[edta]{k_1^{sub}} Cr^{IV}\text{-edta} \xrightarrow{H_2O_2} + Cr^{III}\text{-edta} + (0.25)O_2$$

The aminopolycarboxylate ligand also increases the rate of the Cr^{VI}–H_2O_2 reaction. The stoicheiometry of formation of the peroxochromium(IV) complex and its decomposition to Cr^{III} have been studied[22] over the range $[H^+] = 0.1$—3.0M. For the reactions

$$[HCrO_4]^- + H^+ + 2H_2O_2 \overset{K_f}{\rightleftharpoons} 3H_2O + [CrO(O_2)_2] \overset{K_f^H(+H^+)}{\rightleftharpoons} [Cr(OH)(O_2)_2]^+$$

$K_f = 2 \times 10^7\ M^{-3}$ and $K_f^H = 0.15\ M^{-1}$ respectively ($T = 25\ °C$). The overall reaction of $[HCrO_4]^-$ with H_2O_2 yields 1.50 ± 0.05 moles of dioxygen per g atom of Cr and the decomposition reaction may be written as

$$2[CrO(O_2)_2] + 6H^+ \rightarrow 2Cr^{2+} + 3O_2 + H_2O_2 + 2H_2O$$

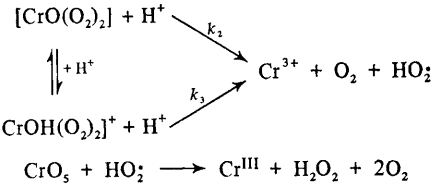
The first-order rate constant, k_d, for this reaction was studied under various conditions. k_d is independent of $[H_2O_2]$ but depends on $[H^+]$, the rate law being of the form

$$-d[CrO_5]/dt = k_2[CrO(O_2)_2][H^+] + k_3[Cr(OH)(O_2)_2^+][H^+]$$

This result differs from that of a previous study[23] where a second-order dependence on hydrogen ion concentration was observed. The present work is substantiated, however, by determination of the rate of oxygen evolution which corresponded with the rate of disappearance of the oxydiperoxochromium(VI) at 580 nm. Also, most studies of decomposition of peroxo-species have been

[19] I. A. Kulikov, V. S. Koltunov, V. I. Marchenko, A. S. Milovanova, and L. K. Nikishova, *Zhur. fiz. Khim.*, 1979, **53**, 647 (*Chem. Abs.* 1979, **91**, 27 993s).
[20] H. Yamamoto, H. Takei, T. Yamamoto, and M. Kimura, *Chem. and Pharm. Bull. (Japan)*, 1979, **27**, 789.
[21] M. T. Beck and Z. Toth, *Bull. Chem. Soc. Japan*, 1979, **52**, 598.
[22] S. Funahashi, F. Uchida, and M. Tanaka, *Inorg. Chem.*, 1978, **17**, 2784.
[23] M. Orhanovic and R. G. Wilkins, *J. Amer. Chem. Soc.*, 1967, **89**, 278.

carried out at higher concentrations than those (10^{-4} M) employed in this study. Two mechanisms are postulated. The hydrogen ion catalysis is considered to result from protonation of a co-ordinated oxo-group and k_3 is about 10 times greater than k_2:



The second mechanism differs in that [Cr(III)(O_2·)] is formed with subsequent rapid reaction with Cr^{VI}. There is no e.s.r. evidence for Cr^{V} and the three-electron redox process is similar to that proposed previously by Rocek. Hydrogen ion catalysis has also been demonstrated in the interconversion of diperoxovanadate(v) and monoperoxovanadate(v) species co-ordinated to organic ligands.[24, 25] In this case there appears to be no evidence for any redox process.

Metal-ion oxidation is observed in the reaction of cobalt(II) macrocycles.[26] The products are diaquocobalt(III) species and only in the case of $[(H_2O)_2Co^{II}(14\text{-ane-}N_4)]^{2+}$ does the reaction follow a clean 2:1 $Co^{II}:H_2O_2$ stoicheiometry. In all cases, the rate law is of the form $-d[H_2O_2]/dt = k_2[Co^{II}][H_2O_2]$ and rate constants are shown in Table 1. The stoicheiometry varies with complex, how-

Table 1 *Reactions of cobalt*(II) *macrocycle complexes with* H_2O_2, $I = 0.1$M, $[H^+] = 0.05$–0.1M[26]

Ligand	*Stoicheiometry*[a]	$k_2/M^{-1}\,s^{-1}$
14-ane-N_4	2.0:1	3.97×10^3
$(dmgH)_2$	0.99:1	1.92×10^3
dpnH	—	4.62×10^2
ms-Me_6-14-ane-N_4	0.95:1	2.65×10^2
Me_4-14-tet-ane-N_4	0.98:1 (1.06:1)[b]	1.42×10^2
corrin	1.20:1	1.32×10^2
Me_6-14-4,11-diene-N_4	1.06:1	7.7×10^1

[a] $[Co^{II}]:[H_2O_2]$ in aqueous $HClO_4$. [b] in 1M-t-butyl alcohol.

ever, as is shown. In some reactions special effects were observed; *e.g.*, with cobal(II)oxime, addition of 10% t-butyl alcohol gave no change in the rate constant from that in an aqueous solution and addition of Br^- caused a gradual increase in the rate constant for the Me_4-14-tet-ane-N_4 complex. The latter effect is attributed to formation of a bromo-cobalt(II) species which reacts more rapidly than the aquo-complex. Only in the case of $[Co^{II}(14\text{-ane-}N_4)]^{2+}$ is there evidence for formation of ·OH radicals. It is probable that for the other systems this free radical is not an intermediate and a modified mechanism involving either simultaneous (or immediately consequential) attack at both the metal centre and

[24] K. Wieghardt, *Inorg. Chem.*, 1978, **17**, 57.
[25] U. Quilitzsch and K. Wieghardt, *Inorg. Chem.*, 1979, **18**, 869.
[26] R. A. Heckman and J. H. Espenson, *Inorg. Chem.*, 1979, **18**, 38.

either a ring imine NH or an adjacent methyl group is proposed. The disproportionation of H_2O_2 by $Cu^{2+}aq$ and $[Cu(bipy)]^{2+}$ has been investigated[27] over the pH range 4—6.5. An intermediate peroxo-complex has been proposed in the reaction mechanism although the formal oxidation state of the metal centre in this species is still not certain.

Using a continuous-flow system, an e.s.r. study has been made[29] of the reaction of Sn^{II} with H_2O_2 in HCl. Two pathways are described (*a*) a reaction to yield Sn^{III}, $HO^{\cdot}$, and OH^-, similar to the one-electron process described for the corresponding iron(II) system,[19] and (*b*) a direct interaction to Sn^{IV} and $2OH^-$. The contribution from (*a*) is small both in aqueous media and in the presence of organic solvents, the second-order rate constant for the process ($T=25\,°C$ 0.5M-HCl) being $24\pm3\ M^{-1}\ s^{-1}$. Some consideration is given to (*b*) resembling two consecutive one-electron reactions. Flow e.s.r. has also been used in the detection of radical peroxo-complexes of composition $[Zr^{IV}(O_2^-)]$ which are formed[29] on the reaction of Ce^{IV} with H_2O_2–Zr^{IV}. Reactions were studied in acid sulphate media and two major decomposition rates were observed:

$$Zr^{IV} + H_2O_2 \rightleftharpoons [Zr^{IV}(O_2^{2-})] + Ce^{IV} \overset{K_1}{\rightleftharpoons} [Zr^{IV}(O_2^{2-})Ce^{IV}]$$

$$[Zr^{IV}(O_2^{2-})Ce^{IV}] \xrightarrow{k_1} [Zr^{IV}O_2] + Ce^{III}$$

$$[Zr^{IV}O_2^-] + Ce^{IV} \overset{K_2}{\rightleftharpoons} [Zr^{IV}O_2\text{–}Ce^{IV}] \xrightarrow{k_2} Zr^{IV}, O_2, Ce^{III}$$

where $K_1=710\ M^{-1}$, $K_2=40\ M^{-1}$, $k_1=160\ s^{-1}$, and $k_2=8\ s^{-1}$. Studies have been made of the oxidation of ethanol in the aerobic Fe^{II}–C_2H_5OH–H_2O_2 system. Unlike the anaerobic process, it has been shown[30] that the oxidation of alcohol in the aerobic Fenton system proceeds without appreciable decrease of $[H_2O_2]$ and that the extent of acetaldehyde formation exceeds by a factor of 2—3 the initial peroxide concentration. The mechanism proposed invokes a radical chain mechanism where the extreme reactivity of the alcohol radicals towards O_2 leads to the formation of an α-peroxy-alcohol radical. This strongly oxidizing species then propagates the chain with further reaction with ethanol. It is of interest that there appears to be no reaction of the peroxy-alcohol radical with Ce^{IV}. The complex tris-(2-mercaptoethylamine)cobalt(III) (CoL_3) can function as a terdentate ligand and co-ordinate to such metals as Ni^{II} and Pb^{II} using the bound mercapto-groups as donor atoms.[31] Mixed complex ions of the type $[Ni(CoL_3)_2]^{2+}$ and $[Pb(CoL_3)_2]^{2+}$ have been identified and on reaction with H_2O_2 oxidation at sulphur takes place yielding a cobalt(III) ion with three co-ordinated sulphinato-groups. The complex $[Co(NH_2CH_2CH_2SO_2)_3]$ is extremely stable in both acid (concentrated) and base (5M-NaOH) and in large excess of peroxide shows no tendency to further oxidation to the sulphonato-complex.

[27] H. Sigel, K. Wyss, B. E. Fischer, and B. Prijs, *Inorg. Chem.*, 1979, **18**, 1354.
[28] A. P. Morarskii and V. F. Shuvalov, *Kinetika i Kataliz*, 1979, **20**, 314 (*Chem. Abs.*, 1979, **91**, 9993n).
[29] V. M. Berdnikov, L. L. Makarshin, and L. S. Ryvkina, *React. Kinet. Catal. Letters*, 1978, **9**, 211 (*Chem. Abs.*, 1979, **90**, 61 869v).
[30] A. Y. Sychev, Y. I. Skurlatov, V. G. Isak, and M. K. Khiev, *Russ. J. Phys. Chem.*, 1978, **11**, 1686.
[31] P. R. Butler and E. L. Blinn, *Inorg. Chem.*, 1978, **17**, 2037.

7 Reactions of Dioxygen

As in the above section, the reader is referred to Part III where details of the biologically oriented reactions of dioxygen are described. Several reviews[32–34] have been published relating to the inorganic and bio-inorganic aspects of oxygenation and redox reactions. Recent studies[34] indicate that the primary electron-transfer step for the reduction of O_2 is a one-electron process which is followed under acidic conditions by chemical disproportionation to yield H_2O_2 (an overall 2e process) and under basic conditions by production of OH^- (a 4e process overall). The primary reaction reduction potential is -0.33 V and is independent of pH.

The reaction of di-μ-oxo-bis(oxo{L-(+)-cysteinato}molybdate(v)]$^{2-}$, [$(Mo^V{}_2$-$(cys)_2$], with dioxygen has been investigated in phosphate and ammonia buffers.[35] At pH 6.5 (HPO_4^{2-}–$H_2PO_4^-$) the reaction proceeds (O_2 in excess) according to the scheme

$$[Mo^V{}_2(cys)_2] \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [Mo^{IV}(cys)] + [Mo^{VI}(cys)]$$

$$O_2 + [Mo^{IV}(cys)] \xrightarrow[H^+]{k_2} [Mo^{VI}(cys)\,(H_2O_2)]$$

At least one phosphate group is considered bound to the molbydenum(v). H_2O_2 reacts about 20 times faster than O_2 with $[Mo^V{}_2(cys)_2]$ and addition of peroxide to Mo^{VI} yields the same product as that of the dioxygen reaction. If the metal complex is present in excess, however, there is evidence for adduct formation:

$$[Mo^V{}_2(cys)_2] + O_2 \rightleftharpoons [Mo^V{}_2(cys)_2O_2] \rightarrow 2[Mo^{VI}(cys)] + H_2O_2$$

This is followed by a further process where the H_2O_2 formed reacts with the Mo^V to form OH^- and $OH^\cdot$ leading to further oxidation of the dimeric complex. The presence of the base (phosphate, hydroxide, ammonia) is considered significant since complexing to $[Mo^V{}_2cys)_2]$ causes a co-ordination asymmetry resulting in a change in oxidation state from (v)–(v) to (iv)–(vi). The latter species are the reactive agents towards O_2. The formation of peroxo intermediates may also be significant in the oxygenation of bis-(2-pyridyl)methane and 6-methylbis-(2-pyridyl)methane to the corresponding ketones.[36] These reactions are catalysed by copper(ii). Pyridino-complexes are formed which may act as a template for reaction of the oxidant which attacks at the metal centre. There is still some uncertainty as to the oxidation state of the metal, and an intramolecular ligand redox reaction leading to a Cu^I–radical complex may be invoked. In the auto-oxidation of deprotonated copper(ii) tetraglycine, however, catalysis by copper(iii) has been demonstrated.[37] Disproportionation of $[Cu^{II}(H_{-2}G_4)]$ to Cu^I and Cu^{III} species is followed by decomposition of the copper(iii) complex to give a species which reacts with O_2 and eventually generates more Cu^{III} as well as the

[32] A. B. P. Lever and H. B. Gray, *Accounts Chem. Res.*, 1978, **11**, 348.
[33] R. D. Jones, D. A. Summerville, and F. Basolo, *Chem. Rev.*, 1979, 139.
[34] J. Wilshire and D. T. Sawyer, *Accounts Chem. Res.*, 1979, **12**, 105.
[35] T. M. Tam and J. H. Swinehart, *Inorg. Chem.*, 1979, **18**, 975.
[36] F. L. Urbach, U. Knopp, and A. D. Zuberbuhler, *Helv. Chim. Acta*, 1978, **61**, 1097.
[37] J. L. Kurtz, G. L. Bruce, and D. W. Margerum, *Inorg. Chem.*, 1978, **17**, 2454.

oxidized peptide. A similar result has been observed in the nickel(III) catalysis of the corresponding reaction of nickel(II) tetraglycine.[38] In this case, however, electrochemical generation of the Ni^{III}–peptide complex has enabled a resolution of the rate order which at low concentrations is unity with respect to $[Ni^{II}]_{total}$, $[Ni^{III}]$, and $[O_2]$. At higher concentrations the order tends to zero for each reagent.

8 Reactions with Halide Ions

The rapid oxidation of bromide by aquocerium(IV) has been investigated.[39] The rate law, Rate $\propto [Ce^{IV}][Br^-]^2[H^+]^2$, can be explained only by the reaction proceeding *via* the formation of intermediate complexes. The overall reaction is represented by the equation

$$2Ce^{IV} + 2Br^- \rightarrow 2Ce^{III} + Br_2$$

Additional evidence for a rapid pre-equilibrium is provided by the transmission–time traces where a large initial decrease in transmission can be attributed to the formation of such a complex. From a consideration of the hydrolysis equilibria of the aquo-metal ion and of the complexes formed, and since at least two bromide ions must be present in the transition state, the simplest pre-equilibria may be written as

$$\begin{array}{ccccc} Ce^{4+} + 3Br^- & \overset{\beta_3}{\rightleftharpoons} & CeBr_3^+ & & \\ \Big\| K_h & & & & \\ CeOH^{3+} + 3Br^- & \overset{\beta_3'}{\rightleftharpoons} & [Ce(OH)Br_3] & \overset{k_3}{\rightleftharpoons} & [Ce(OH)_2Br_3]^- + H^+ \end{array}$$

Two mechanisms are consistent with the data:

(*a*) where the intermediate complexes participate directly,

e.g.

$$CeBr_3^+ \xrightarrow{k_1} Ce^{III} + {\cdot}Br_2^- + Br^-$$

$$[Ce(OH)Br_3] \xrightarrow{k_2} Ce^{III} + {\cdot}Br_2^- + Br^-$$

$$[Ce(OH)_2Br_3]^- \xrightarrow{k_3} Ce^{III} + {\cdot}Br_2^- + Br^-$$

or

(*b*) where further reaction with an additional bromide ion takes place,

e.g.

$$CeBr_3^+ + Br^- \xrightarrow{k_4} Ce^{III} + {\cdot}Br_2^- + 2Br^-$$

$$[Ce(OHBr_3] + Br^- \xrightarrow{k_5} Ce^{III} + {\cdot}Br_2^- + 2Br^-$$

$$[Ce(OH)_2Br_3]^- + Br^- \xrightarrow{k_6} Ce^{III} + {\cdot}Br_2^- + 2Br^-$$

followed in both cases by the rapid process

$$Ce^{IV} + {\cdot}Br_2^- \rightarrow Ce^{III} + Br_2$$

[38] F. P. Bossu, E. B. Paniago, D. W. Margerum, S. T. Kirksay, and J. L. Kurtz, *Inorg. Chem.*, 1978, **17**, 1034.

[39] C. F. Wells and A. F. M. Nazer, *J.C.S. Faraday II*, 1979, **75**, 816.

In a comparison of the oxidation of ligands with other highly oxidizing cations, the suggestion is made that Ce^{IV} resembles more closely the reactions of Mn^{III} rather than those of Co^{III} since in general the reactivity order is $M^{n+} > M(OH)^{(n+1)+}$. The contrary is true for cobalt(III) where hydrolysed species usually oxidize ligands more rapidly than the unhydrolysed aquocobalt(III) ions. Some ambiguities exist and further work is needed with these cations before unequivocal comparisons can be made.

Two studies have been made of the outer-sphere oxidation of iodide by tervalent metal ion complexes. In both cases the reaction is

$$2M^{III} + 2I^- \rightarrow 2M^{II} + I_2$$

although the mechanisms postulated differ. In the reaction[40] with $[Os(bipy)_3]^{3+}$ and $[Os(phen)_3]^{3+}$ (M^{III}) the experimental rate law is

$$-d[ML_3^{3+}]/dt = 2k_1'[M^{III}][I^-] + 2k_2'[M^{III}][I^-]^2$$

and is consistent with the mechanism

$$M^{III} + I^- \overset{K_f}{\rightleftharpoons} M^{III}I^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} M^{II} + I\cdot$$

$$M^{III}I^- + I^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} M^{II} + I_2^-$$

$$I\cdot + I^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} I_2^-$$

$$M^{III} + I_2^- \xrightarrow{k_4} M^{II} + I_2$$

where $k_1' = k_1K_f$, $k'_2 = k_2K_f$, $k_{-1}[M^{II}] \ll k_3[I^-]$, $k_{-3} < k_4[M^{III}]$, and $k_{-2}[M^{II}] \ll k_4[M^{III}]$. The rapid pre-equilibrium step has $K_f < 1$. The rate constants (k_1K_f) together with those for other oxidants, $[Fe(bipy)_3]^{3+}$, $[IrBr_6]^{2-}$, $[IrCl_6]^{2-}$, $[Mo(CN)_8]^{3+}$ and $[NpO_2]^{2+}$, extending over a range of 10^7 have been shown to be in agreement with a Marcus cross relation when the work terms are neglected. A similar correlation was made for k_2K_f constants. Formal redox potentials of the $I\cdot$–I^- (1.38 V) and I_2^-–$2I^-$ (1.08 V) couples have been derived. For the reaction involving the ion pair reacting with I^-, an oriented ion triplet is envisaged $[M^{III}I^- \cdots I^-]$ as an intermediate. The I^-–I^- bond formation in the succeeding precursor complex for electron transfer is required to be essentially that of the I_2^- radical. Use has been made of the Marcus equation and associated equilibrium constants to derive the individual rate constants outlined (Table 2).

Table 2 *Reactions of metal complexes with halide ions and halogen radicals*[40]

Reaction	k_2[a]	$\Delta H^{\ddagger}$[c]	$\Delta S^{\ddagger}$[d]
$[Os(bipy)_3]^{3+} + I^-$	17	17.4	−7
$[Os(bipy)_3]^{3+} + 2I^-$	9.2×10^3[b]	9.1	−10
$[Os(bipy)_3]^{3+} + I_2^-$	2.9×10^{10}		
$[Os(bipy)_3]^{2+} + I\cdot$	2.2×10^{10}		
$[Os(bipy)_3]^{2+} + I_2^-$	1×10^8		
$[Os(phen)_3]^{3+} + I^-$	1.4×10^4	13.7	−4
$[Fe(bipy)_3]^{3+} + I^-$	3.5×10^4		
$[Fe(phen)_3]^{3+} + I^-$[41]	6.0×10^4	11.0	0.2

[a] Units in $M^{-1}\,s^{-1}$ except where indicated. [b] $M^{-2}\,s^{-1}$. [c] kcal mol^{-1}. [d] cal $K^{-1}\,mol^{-1}$.

[40] G. Nord, B. Pedersen, and O. Farver, *Inorg. Chem.*, 1978, **17**, 2233.

In the oxidation by $[Fe(phen)_3]^{3+}$ ionic strength and permittivity (dielectric constant) dependences of the rate constants have been determined,[41] the linear relationships $\log k_2$ *vs.* $I^{1/2}/(I+1^{1/2})$ and $\log k$ *vs.* D^{-1} being established. Significant thermodynamic parameter variations were observed depending on the ionic strength used. Unlike the case of $[Os(bipy)_3]^{3+}$, however, no second-order dependence on reductant was identified, the oxidation proceeding with atomic iodine as the initial product. Ion pair formation is again invoked in keeping with the ionic strength effects. A slight increase in rate with increasing hydrogen ion concentration is attributed to the formation of $[HFe(phen)_3]^{4+}$ which would associate more easily with iodide. This oxidant is stable only in moderately acidic media. It becomes extremely stable in 11M-$HClO_4$ and under these conditions oxidizes even Fe^{II} slowly. This finding is attributed to a strong association between $[Fe(phen)_3]^{3+}$ and ClO_4^- which may inhibit the approach of the reductant to the feri-in ion. The mechanism of reduction of In^{III} by I^- has been studied using chronovoltammetric techniques.[42]

9 Reactions with Halate Ions

Several studies have been published in which bromate ion has been used as an oxidant. In the rections with cyano(bipyridyl)iron(II) complexes and $[Fe(bipy)_3]^{2+}$ autocatalysis is observed.[43] The reaction stoicheiometry in excess BrO_3^- is considered to be in accord with the reaction

$$BrO_3^- + 5Fe^{II} + 6H^+ \rightarrow 0.5Br_2 + 5Fe^{III} + 3H_2O$$

although it is not possible in the absence of spectroscopic confirmation to rule out HOBr as an initial product which would then lower the number of moles of Fe^{II} reacting to four. In the reaction with $[Fe(bipy)(CN)_4]^{2-}$, Guggenheim plots were linear for most of the reaction although near to the end an abrupt change of slope was observed similar to that expected for the Br^-–BrO_3^- system. The reaction sequence

$$Fe^{II} + BrO_3^- \xrightarrow[2H^+]{k_1} Fe^{III} + BrO_2 + H_2O$$

$$4Fe^{II} + BrO_2 + H^+ \xrightarrow{\text{fast}} 4Fe^{III} + 0.5Br_2 + 2H_2O$$

$$Fe^{II} + 0.5Br_2 \xrightarrow{\text{rapid}} Fe^{III} + Br^-$$

$$Br^- + BrO_3^- + 2H^+ \xrightarrow[4Br^-,\,4H^+]{k_3} 3Br_2 + 3H_2O$$

The reaction with $[Fe(CN)_2(bipy)_2]$ is similar in mechanism. In both cases the first electron-transfer step is rate determining although there are probably parallel pathways having different dependencies. In the reaction as written, comparison of oxidation rates with those of Ce^{IV} and V^V suggests the process to be outer-sphere in nature. For the complex $[Fe(bipy)_3]^{2+}$, however, under

[41] M. Kimura and G. Wada, *Inorg. Chem.*, 1978, **17**, 2239.
[42] C. Tran Thi Minh and M. Turowska, *Polish J. Chem.*, 1978, **52**, 1869 (*Chem. Abs.*, 1979, **90**, 45 958t).
[43] J. P. Birk and S. G. Kozub, *Inorg. Chem.*, 1978, **17**, 1186.

some conditions the reaction was autocatalytic but in others the aquation of $[Fe(bipy)_3]^{2+}$ was rate determining. The oxidation of $[IrCl_6]^{3-}$ conforms to a stoicheiometry similar to that for Fe^{II} with Br_2 as the reaction product.[44] The reaction kinetics are in accord with the rate law $-d[Ir^{III}]/dt=(k_0+k_2[BrO_3^-][H^+]^2)[Ir^{III}]$ in which the minor (bromate-independent) term is not completely explicable. The principal term may be summarized by the scheme

$$BrO_3^- + 2H^+ \rightleftharpoons H_2BrO_3^+ \quad K \ll 1$$

$$[IrCl_6]^{3-} + H_2BrO_3^+ \xrightarrow{k_2} [IrCl_6]^{2-} + H_2O + BrO_2$$

$$BrO_2 + 4Ir^{III} + 4H^+ \xrightarrow{\text{fast}} 0.5Br_2 + 4Ir^{IV} + 2H_2O$$

In this case, the slow step is though to proceed *via* an inner-sphere process with rate-limiting loss of a water molecule from the bromine(v) ion. The monoprotonated species $HBrO_2$ has been proposed as the oxidant in the reaction with $[Fe(phen)_3]^{2+}$ in sulphuric acid solution.[45] A variety of reduction products, from Br^{IV} to Br^{-I}, has been suggested in the reaction of cerium(III) with bromate ions in sulphate media.[46] At high acid concentrations Br^{IV} and Br^{III} are favoured whereas at low acid Br^- is formed.

In the oxidation of hexachloroiridate(III) by iodate ion[47] the stoicheiometry is identical to that of the corresponding bromate system. The rate law is of the form

$$-d[Ir^{III}]/dt = k_1'[H^+][IO_3^-]/(1 + K_f[IO_3^-])$$

where K_f is the equilibrium constant for formation of an Ir^{III}–I^V complex. The reaction mechanism shown in Scheme 3 shows some similarity to the

$$HIO_3 \rightleftharpoons IO_3^- + H^+$$

$$[IrCl_6]^{3-} + IO_3^- \overset{K_f}{\rightleftharpoons} [IrCl_6 \cdot IO_3]^{4-}$$

$$[IrCl_6 \cdot IO_3]^{4-} \xrightarrow[k_1]{H^+} Ir^{IV} + I^{IV}$$

$$[IrCl_6 \cdot IO_3]^{4-} \xrightarrow[k_2]{2H^+} Ir^{IV} + I^{IV}$$

$$I^{IV} + 4Ir^{III} \xrightarrow{\text{fast}} 4Ir^{IV} + I^0$$

Scheme 3

chlorate and bromate oxidations. In particular, the occurrence of the net activation process

$$XO_3^- + [IrCl_6]^{3-} + 2H^+ \xrightarrow{k_\alpha} [H_2XO_3 \cdot IrCl_6]^{2-}$$

is a common feature. The calculated values for k_α are of the order 5×10^{-5}, 50, and

[44] J. P. Birk, *Inorg. Chem.*, 1978, **17**, 504.
[45] A. B. Rovinskii and A. M. Zhabotinskii, *Teor. Eksp. Khim.*, 1979, **15**, 25 (*Chem. Abs.*, 1979, **90**, 157 667d).
[46] K. Prasad and M. S. Prasad, *Indian J. Chem., Sect. A*, 1979, **17**, 83.
[47] J. P. Birk, *Inorg. Chem.*, 1978, **17**, 1372.

5 $M^{-1}\,s^{-1}$ for X = Cl, Br, and I respectively. This is consistent with the general observation that I^V and Br^V oxidations are more facile than the corresponding Cl^V oxidations, possibly owing to easier substitution on the larger and softer halogens.

10 Reactions with Halogens

A series of cobalt(II) complexes of N-donor quadridentate 14-membered macrocyclic ligands is oxidized by Br_2 and I_2 to the corresponding monohalogenocobalt(III) products.[26] The rate laws show a first-order dependence on each reactant. The stoicheiometry was found to be 2:1 (Co^{II}:I_2) for reactions with iodine, which were sufficiently rapid that competition was minimized between the reaction with halogen and the subsequent aquation of the I–[Co^{III}]–H_2O product. For the complex $[(H_2O)_2Co^{II}(14\text{-ane-}N_4)]$, the aquo-iodocobalt(III) ion was identified using ion-exchange chromatography, and the monoiodo-complex of B_{12} was identified spectrophotometrically. No hydrogen-ion or ionic-strength effects were observed. For the reactions with bromine, several experiments were performed to confirm the stoicheiometry, which is identical to that for the reactions with I_2. Again interference from the secondary aquation process presented difficulties in some instances. The reaction mechanisms (X = halogen) may be written as

$$[(H_2O)_2Co^{II}L]^{2+} + X_2 \xrightarrow[\text{slow}]{k_1} [(H_2O)Co(L)X]^{2+} + X\cdot$$

$$[(H_2O)_2Co^{II}L]^{2+} + X\cdot \xrightarrow[\text{fast}]{k_2} [(H_2O)Co(L)X]^{2+}$$

although the atom recombination ($2X \rightarrow X_2$) or, if halide ion is present, the disproportionation ($2X_2^- \rightarrow X_2 + 2X^-$) could also be plausible subsequent rapid reactions. The identification of the monohalogeno-cobalt(III) complexes precludes any outer-sphere mechanism for the k_1 pathway. For the reaction of the complex $[(H_2O)_2Co(14\text{-ane-}N_4)]^{2+}$ with I_2, it is possible to compute the individual rate constants for the equilibrium

$$[(H_2O)_2Co^{II}(14\text{-ane-}N_4)]^{2+} + I_2 \underset{k_\beta}{\overset{k_\alpha}{\rightleftharpoons}} [ICo^{III}(14\text{-ane-}N_4)(H_2O)]^{2+} + I\cdot aq$$

where $k_\alpha = 2.9 \times 10^3\ M^{-1}\,s^{-1}$ and $k_\beta = 2.4 \times 10^{11}\ M^{-1}\,s^{-1}$. The latter value not only exceeds the diffusion-controlled rate but is too large to allow for the simple kinetic pattern observed where k_2 (above) must be greater than k_β. For this system a modified mechanism is proposed in which a cobalt(III)–iodine adduct is formed which undergoes rate-limiting internal redox:

$$[Co^{II}] + X_2 \rightleftharpoons X_2\text{–}[Co^{II}] \xrightarrow{\text{slow}} X_2^-\text{–}[Co^{III}] \xrightarrow{[Co^{II}]} 2X[Co^{III}]$$

Rate data for the reactions are presented in Table 3. As in the case of the reaction with H_2O_2 the kinetic effect of substitution of methyl groups at peripheral positions is quite marked. Of the two saturated systems $[Co^{II}(14\text{-ane-}N_4)]^{2+}$ reacts more rapidly than its hexamethyl analogue (by a factor of > 200 with Br_2 and 570 with I_2). Although part of this difference is reflected in a difference of 0.15 V

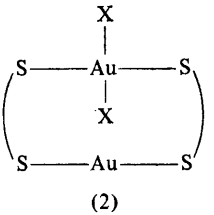
Table 3 *Kinetic data for the oxidation of cobalt*(II) *macrocycles by halogens*[26] (I=0.1M, [H$^+$]=0.01—0.13M)[a]

Ligand	k_2/M^{-1} s^{-1} (*bromine oxidation*)[b]	k_2/M^{-1} s^{-1} (*iodine oxidation*)[b]
corrin	$6(\pm 1)\times 10^6$	6.1×10^4
dpnH	3.3×10^7	9.2×10^4
14-ane-N_4	$>1\times 10^7$	2.9×10^3
Me_4-14-ane-N_4	1.13×10^5	6.9×10^3
ms-Me_6-14-ane-N_4	5.03×10^4	5.0 ± 1
ms-Me_6-14-4,11-diene-N_4	1.81×10^4	4.0 ± 0.2

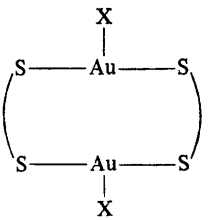
[a] Reactions show no [H$^+$] dependence. [b] Observed second-order rate constants.

in E^0, the blocking of axial co-ordination sites may be responsible for the retardation in rates observed.

A 1:1 charge-transfer adduct is formed as the initial process in the oxidation of bis-(μ-dibutyldithiocarbamato-*S*,*S*')-digold(I) by halogens.[48] This species has been identified spectrophotometrically at low temperatures. The rates in CH_2Cl_2 are almost identical for Br_2, I_2, and IBr and are independent of both [Au(Bu^n_2-dtc)]$_2$ and [halogen]. The charge-transfer intermediate is considered to decompose in the rate-determining step to give the final product [$Au^{III}(Bu^n_2dtc)_2$][Au^IX_2]. Although there is no direct evidence for another transient species, two possible intermediates are suggested depending on whether the halogen attacks at a single Au centre (2) or simultaneously at two metal atoms (3). In (2) the mixed Au^I–Au^{III} complex is postulated whereas in (3) both metal centres are gold(II). Precedents for both types of complex are discussed, although (2) is favoured since less reorganization is required and reductive elimination at the gold(III) centre affords the final product.



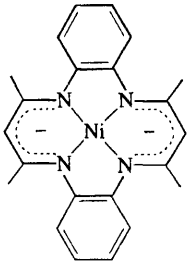
(2)



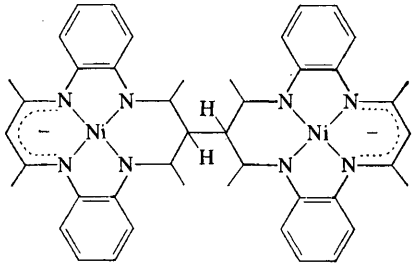
(3)

The reaction of Br_2 (and other oxidants) with organo-bis(dioximato)cobalt(III) complexes results in one-electron oxidations[49] to generate the cobalt(IV) complex cations [RCo(dmgH)$_2$L]$^+$. In the corresponding reaction[50] with the nickel(II) tetra-aza-annulene (4) ligand oxidation occurs prior to metal oxidation and a radical cation is formed which rapidly dimerizes to (5), which may be further deprotonated.

[48] H. Kita, K. Itoh, K. Tanaka, and T. Tanaka, *Bull. Chem. Soc. Japan*, 1978, **51**, 3530.
[49] J. Topich and J. Halpern, *Inorg. Chem.*, 1979, **18**, 1339.
[50] G. P. Ferrara and J. C. Dabrowiak, *Inorg. Nuclear Chem. Letters*, 1978, **14**, 223.



(4)



(5)

11 Other Redox Reactions

The oxidation kinetics of *trans*-aquabis(ethylenediamine)isothiocyanatocobalt(III) ion with peroxodisulphate have been investigated in 0.01 M-$HClO_4$.[51] The reaction products *trans*-$[Co(OH_2)(en)_2CN]^{2+}$ and *trans*-$[Co(OH_2)(en)_2NH_3]^{3+}$ were identified by ion-exchange procedures. The rate law may be expressed as

$$-d[Co^{III}]/dt = k_2[Co(en)_2(H_2O)(NCS)^{2+}][HS_2O_8^-]$$

The variation of rate constant with ionic strength was measured and values of Z_AZ_B of -2.00 in accord with a transition state involving the reactants were observed when the distance of closest approach of the reactants was 0.5 nm. Comparison of the present data with those for oxidation of free thiocyanate shows the latter to have a lower activation energy (12 compared with 15 kcal mol^{-1}) but a more negative activation entropy (-32 compared with -18.5 cal K^{-1} mol^{-1}).

The reactions of thiocyanate with $[Os(bipy)_3]^{3+}$ and $[Os(phen)_3]^{3+}$ have been studied.[40] The rate law derived is of the form

$$\frac{-d[Os^{III}]}{dt} = \frac{[Os^{III}][SCN^-]}{1 + A[Os^{II}]/[Os^{III}]}(2k_2'[SCN^-]) + \frac{[Os^{III}][SCN^-]\,C}{1 + A[Os^{II}]/[Os^{III}]}$$

and was computed from a numerical analysis of the data. An outer-sphere complex formation is considered to precede several redox pathways, as shown in Scheme 4. This scheme is in accord with the rate law where $A = k_{-2}/k_4 = 1$ and

$$[Os^{III}]^{3+} + NCS^- \overset{K_f}{\rightleftharpoons} [Os^{III}(NCS)]^{2+}$$

$$[Os^{III}(NCS)]^{2+} \overset{k_1}{\underset{k_{-1}}{\rightleftharpoons}} [Os^{II}]^{2+} + NCS\cdot$$

$$[Os^{III}(NCS)]^{2+} \overset{+NCS^-,\ k_2}{\underset{k_{-2}}{\rightleftharpoons}} [Os^{II}]^{2+} + [NCS]_2^-$$

$$NCS\cdot + NCS^- \overset{k_3}{\underset{k_{-3}}{\rightleftharpoons}} [NCS]_2^-\ (K_3)$$

$$[NCS^-]_2 + [Os^{III}]^{3+} \xrightarrow{k_4} [NCS]_2 + [Os^{II}]^{2+}$$

Scheme 4

[51] O. Volarova and V. Holba, *Coll. Czech. Chem. Comm.*, 1979, **44**, 1052.

$C = 2k_1K_f$. The latter parameter was very small for the $[Os(bipy)_3]^{3+}$ system and varied from 0.017 at 17.2 °C to 0.03 $M^{-1}s^{-1}$ at 33 °C. For $[Os(phen)_3]^{3+}$, however, C was much larger but the second-order ligand-dependent pathway was barely detectable at higher temperatures. An estimate for the $E^{0\prime}(SCN^{\cdot}/SCN^{-}) = 1.62$ V has been made using the Marcus cross correlation and assuming an equilibrium constant $K_3 = 2.1 \times 10^5$, $E^{0\prime}([SCN]_2^{-}/2SCN^{-}) = 1.31$ V. As in the case of the corresponding reactions with iodide,[40] values of k_1, k_{-1}, k_2, k_{-2} have been determined using the Marcus free-energy relationship.

The osmium(VIII)-catalysed oxidation of Te^{IV} by $[M(CN)_8]^{3-}$ has been studied[52] in alkaline media (M = Mo or W), the reactions being first order in both [octacyanometallate] and catalyst. The overall stoicheiometry is

$$2[M(CN)_8]^{3-} + Te^{IV} \rightarrow 2[M(CN)_8]^{4-} + Te^{VI}$$

with TeO_3^{2-} used as the reducing ion. A first-order $[OH^-]$ dependence is attributed to the pre-equilibrium

$$OsO_4 + OH^- \overset{K}{\rightleftharpoons} [HOsO_5]^- \quad K = 302\ M^{-1}$$

The reaction mechanism consistent with the observed rate law may be expressed as

$$[HOsO_5]^- + [M(CN)_8]^{3-} \rightleftharpoons [Complex]$$

$$[Complex] + Te^{IV} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Te^{V} + [M(CN)_8]^{4-} + [HOsO_5]^-$$

$$Te^{V} + [M(CN)_8]^{3-} \xrightarrow{\text{rapid}} Te^{VI} + [M(CN)_8]^{4-}$$

There is some evidence of a positive salt effect and the rate-determining step is that of complex formation. The reduction of Te^{IV} by BH_4^- has also been reported.[53] In acidic media ($pH \leqslant 1.5$) TeO_3^{2-} is reduced to several tellurium oxidation states. In borate buffer solutions, however, a hydrosol of Te^0 is formed by reaction of BH_3OH^- and/or other hydrolysed species. Hydroxide ion attack is considered the slow step in the disproportionation[54] of molybdate(V) complexes $[Mo_2O_4L]^{n-}$ (L = edta or cysteine) in the presence of CN^-. The initial opening of the μ-dioxo-bridge also depends on the ligands attached and is followed by attack by CN^- at the molybdenum centre. Of the ligands studied, the edta complex dissociates much less rapidly than other ligand systems and e.p.r. shows that $[Mo_2O_4(cysteine)]^{2-}$ and other species dissociate more readily into Mo^V monomers. Although the reaction of As^{III} with $[Fe(CN)_6]^{3-}$ is too slow to be studied[55] with $[OH^-] \leqslant 0.05$M, it takes place smoothly in the presence of Os^{VIII}. Unlike the reaction of $[M(CN)_8]^{3-}$, described above where the cyanometallate complex is involved in the rate law, in the arsenic(III) reaction the rate may be expressed as $Rate = k_0[As^{III}][OH^-][Os^{VIII}]$ with a zero-order dependence of $[Fe(CN)_6]^{3-}$. At higher hydroxide ion concentrations, $> 10^{-2}$ M, the rate

[52] J. G. Leipoldt, C. R. Dennis, A. J. Van Wyk, and L. D. C. Bok, *Inorg. Chim. Acta*, 1979, **34**, 237.
[53] E. S. Kotelevets, V. S. Khain, and E. N. Marinova, *Russ. J. Inorg. Chem.*, 1978, **23**, 374.
[54] P. R. Robinson and C. R. Landis, *Inorg. Chim. Acta*, 1979, **33**, 63.
[55] K. K. Sengupta and B. Basu, *Indian J. Chem., Sect A.*, 1978, **16**, 808.

becomes independent of [OH^-]. In the oxidation of As^{III} by platinum(IV), however,[56] the rate law is of the form Rate $= k[PtCl_6^{2-}][As^{III}][OH^-]$. There is an observed positive salt effect, consistent with the presence of two negatively charged ions in the transition state, and on increasing dielectric constant the reaction also occurs more readily.

The products of reaction of manganese(VII) with BH_4^- are dependent on the reaction conditions.[57] In alkaline media (0.1—1.0M-NaOH) permanganate is reduced quantitatively to manganate(VI) with no further reaction even in excess reductant. At lower pH's there is evidence of Mn^{IV} and in strongly acidic conditions Mn^{II} is formed.

[56] K. K. Sengupta and P. Kumar, *J. Inorg. Nuclear Chem.*, 1978, **40**, 1657.
[57] V. S. Khain and V. F. Martynova, *Russ. J. Inorg. Chem.*, 1978, **23**, 376.

3

Metal Complexes with Organic Substrates

BY A. McAULEY

1 Introduction

In this chapter, unlike the treatment for inorganic main-group substrates, data are sub-divided into metal-ion oxidants or reductants. In this way the format of previous Reports is maintained. A short section has also been added on systems where intramolecular redox has been shown to take place.

Several reviews have been published which deal either exclusively or in part with this area of chemistry. A general structural principle has been developed[1] for multistage organic redox systems where there is the capacity for two-stage electron transfer. It is in this aspect that the main differences arise between the inorganic and organic areas, since there are many examples of unit change in oxidation state between stable metal ions whereas for ligands a two-electron transfer is generally required to proceed to a new stable state. The importance of thermodynamically stable ($K \sim 10^6$—10^{10}) radical cations (L^+) involved in the process

$$L \rightleftharpoons L^+ \rightleftharpoons L^{2+}$$

where L^{n+} is the organic substrate in various oxidation states and $K = [L^+]^2/[L][L^{2+}]$. Detection of L^+ by a variety of electrochemical and spectrophotometric methods is providing new insights into redox potentials and kinetic stability. Complexes of cations in unstable oxidation states, generated by pulse radiolysis, have been reviewed[2] and are described more fully elsewhere in this Report. A survey has also been made of one-electron transfer reactions of free radicals with organic donors and acceptors and transition-metal complexes.[3] The importance of the complexing of radicals to metal ions is described, especially since complex formation may alter greatly the reactivity of the radicals and possibly modify their mechanism of reaction. The use of e.s.r. methods in fast reaction kinetics has been discussed and information derived on the rates of conformational changes in radicals.[4] The importance of macrocyclic ligands in modifying the spin states of metal complexes has been reviewed[5] together with the substantial range of redox potentials ensuing from substitution on the macrocyclic ring. A review has also been published on the oxidation of thiones

[1] K. Denchert and S. Hunig, *Angew Chem. Internat. Edn.*, 1978, **17**, 875.
[2] D. Meyerstein, *Accounts Chem. Res.*, 1978, **11**, 43.
[3] I. V. Khudyakov and V. A. Kuz'min, *Russ. Chem. Rev.*, 1978, **47**, 22.
[4] R. O. C. Norman, *Pure Appl. Chem.*, 1979, **51**, 1009.
[5] D. H. Busch, *Accounts Chem. Res.*, 1978, **11**, 392.

and phosphine sulphides by metal ions and halogens.[6] The significance of metal complex formation in the mechanisms is described.

2 Reactions of Manganese-(III), -(IV), and -(VII)

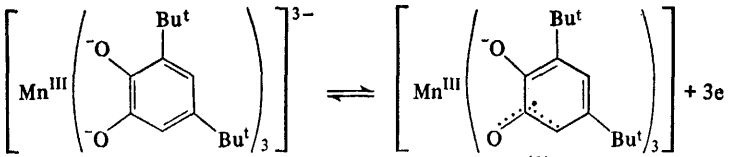
The hydrolysis of manganese(III) has been re-examined[7] and equilibrium data have been derived for the reactions

$$Mn^{3+} + H_2O \overset{K_h}{\rightleftharpoons} MnOH^{2+} + H^+$$

$$Mn^{3+} + 2H_2O \overset{\beta_2}{\rightleftharpoons} [Mn(OH)_2]^+ + 2H^+$$

$\log K_h = 0.4 \pm 0.1$ and $\log \beta_2 = 0.1 \pm 0.1$. The data are in reasonable agreement with previous results which were generally obtained under more acidic conditions. In 3M-$LiClO_4$, the standard reduction potential for the Mn^{3+}/Mn^{2+} couple has been determined to be 1.559 ± 0.003 V.

Complexes of manganese with aliphatic and aromatic ligands formed in basic media have been studied using a variety of methods.[8] The stabilization of Mn^{II}, Mn^{III}, and Mn^{IV} complexes by glucarate, glycerate, L-tartrate, and *meso*-tartrate is similar to that for gluconate. For sorbitol, mannitol, and other polyol ligands, however, stability of the +3 and +4 oxidation states is more marked. The manganese(II) complexes are stable in the absence of oxygen.[9] Reduction potentials for the Mn^{IV}/Mn^{III} and Mn^{III}/Mn^{II} couples have been determined[10] for polyhydroxy and polyhydroxy-amine complexes and the higher oxidation state species may also be produced by reaction with one or two equivalents of $[Fe(CN)_6]^{3-}$. Different manganese(III) complexes have been identified depending on reversible oxidation of the Mn^{II} species at less negative potentials, although some are irreversibly reduced to Mn^{II} at more negative values. From studies with triethanolamine as ligand it is suggested that at least two hydroxy-groups are required for complex formation and that two ligands are incorporated in the Mn^{III} complexes. The tris-catechol complex of Mn^{III} is oxidized by either dioxygen or $[Fe(CN)_6]^{3-}$ to a short-lived intensely blue species which appears to be the semiquinone of catechol. With 3,5-di-butylcatechol (DTBC) the corresponding reaction is observed. Addition of the oxidant to the free ligand in alkaline media, however, yields the blue semiquinone radical which shows a reduction current of about the same magnitude as for the Mn^{III}–semiquinone complex. Interestingly, further reaction of the Mn^{III} species with oxidant is consistent with the formation of the tris-ligated semiquinone (1)



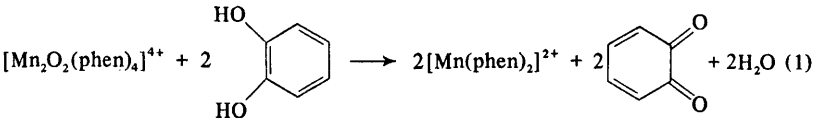
(1)

[6] E. W. Ainscough and A. M. Brodie, *Coordination Chem. Rev.*, 1978, **27**, 59.
[7] G. Biederman and R. Palombari, *Acta Chem. Scand.*, 1978, **A32**, 381.
[8] K. D. Magers, C. G. Smith, and D. T. Sawyer, *Inorg. Chem.*, 1978, **17**, 516.
[9] D. T. Richens, C. G. Smith, and D. T. Sawyer, *Inorg. Chem.*, 1979, **18**, 706.
[10] M. M. Morrison and D. T. Sawyer, *Inorg. Chem.*, 1978, **17**, 333.

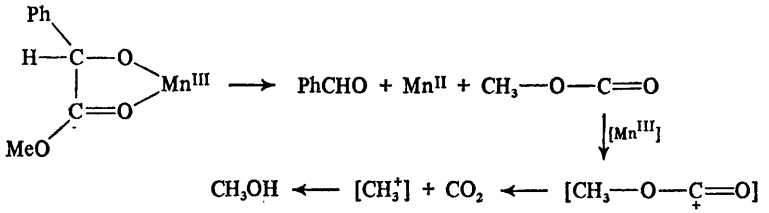
which may act as a four-electron oxidizing agent, giving $[Mn^{II}(DTBC)_3]^{4-}$. The irreversible oxidation of $[MnL_3]^{2+}$ to the corresponding Mn^{III} complexes (L = bipy, phen, or substituted derivatives) in acetonitrile solution is followed by rapid decomposition to a dimeric manganese(III)/(IV) species, the overall reaction being

$$2[MnL_3]^{2+} + 2H_2O \rightleftharpoons [Mn_2O_2L_4]^{3+} + 4H^+ + 3e^- + 2L$$

Further oxidation to the (IV)/(IV) complex is also observed. The latter ion, $[Mn_2O_2(phen)_4]^{4+}$, is reduced by a variety of substrates including OH^-, Cl^-, and catechols. Addition of one equivalent of OH^- or Cl^- yields $[Mn_2O_2(phen)_4]^{3+}$ while excess of these reagents induces breakdown of the μ-dioxo-bridge. Reaction with catechols results in the formation of quinones and manganese(II) complexes [equation (1)].



Radical formation is proposed in the oxidation of methyl mandelate by $[Mn^{III}(H_2P_2O_7)_3]^{3-}$. Following removal of a pyrophosphate ligand (omitted for clarity) the formation of methanol is *via* the mechanism[11] shown in Scheme 1.

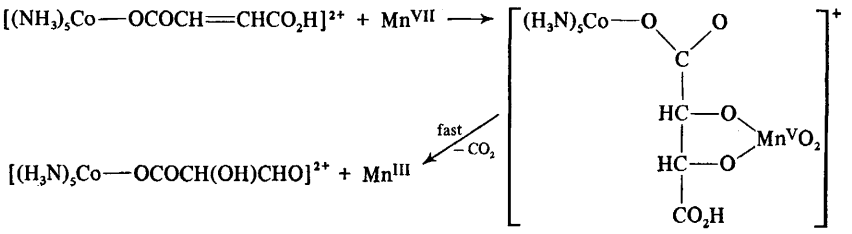


Scheme 1

In the interaction of manganese(III) pyrophosphate with cydta,[12] two processes are observed. Slow substitution by cydta results in an inner-sphere redox, while a more rapid outer-sphere oxidation of the ligand by $[Mn(H_2P_2O_7)_3]^{3-}$ also takes place.

Evidence has been provided[13] for an even-electron process in the oxidation of maleatopenta-amminecobalt(III) by MnO_4^-. The reaction is rapid in acid media up to a mole ratio of 1:1, but with Mn^{VII} in excess it takes place more slowly. Manganese(IV) is not a product unless pH > 3. Manganese(III) is observed as a short-lived intermediate. The data are consistent with the initial mechanistic steps shown in Scheme 2. Further attack by Mn^{III} produces radical-ion complexes since about 30% of total cobalt is converted into cobalt(II). In the reaction

[11] R. K. Malkani, K. S. Kuresch, and G. V. Bakore, *J. Indian Chem. Soc.*, 1978, **55**, 215.
[12] V. V. Lapkin and N. I. Pechurova, *Deposited Doc.*, 1977, *VINITI* 2663 (*Chem. Abs.*, 1979, **90**, 61 879y).
[13] L. I. Simandi, Z. Szeverenyi, and M. Jaky, *Inorg. Chim. Acta*, 1978, **31**, L397.



Scheme 2

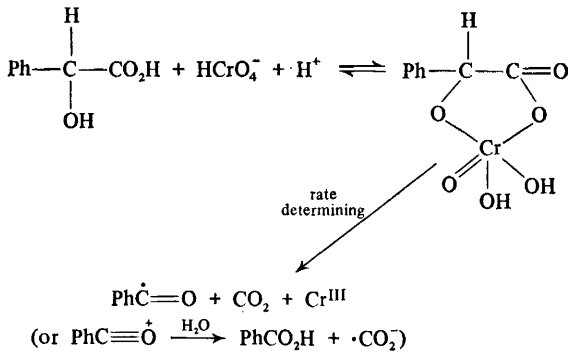
of Mn^{VII} with ethoxyethanol,[14] the reaction order of unity with respect to each reagent is consistent with the formation of a permanganate ester which decomposes *via* a radical pathway. The corresponding oxidation of substituted benzaldehydes has also been studied.[15] The kinetics of the rapid stage of reduction of oxalate in the presence of Mn^{II} have been investigated using stopped-flow methods.[16] Rates of formation of Mn^{III} and loss of Mn^{VII} are identical and a rate law of the form $-d[Mn^{VII}]/dt = k[Mn^{II}]^2[ox^{2-}]^2[Mn^{VII}]$ is reported.

3 Reactions of Chromium(VI)

The oxidation of mandelic acid has been reinvestigated in the light of recent suggestions of three-electron oxidations.[17] In this system, equimolar amounts of benzaldehyde and benzoic acid are formed and a large kinetic isotope effect is observed ($k_H/k_D = 7.6$). The rate law is of the form (MA = mandelic acid)

$$-d[Cr^{VI}]/dt = \{k_a + k_b[H^+] + k_c[MA]\}[HCrO_4^-][MA]$$

The data provide convincing evidence that neither benzaldehyde nor phenylglyoxylic acid is an intermediate in the benzoic acid formation. The mechanism proposed is shown in Scheme 3. This oxidation represents the first example of a



Scheme 3

[14] R. Gopalan and G. R. R. Sankar, *J. Indian Chem. Soc.*, 1978, **55**, 1011.
[15] P. R. Rao and E. V. Sunderam, *J. Indian Chem. Soc.*, 1978, **55**, 107.
[16] T. Ernst, M. Wawrzenczyk, and M. Wronska, *Mater. Sci.*, 1976, **2**, 123 (*Chem. Abs.*, 1979, **90**, 110 587n).
[17] D. Ip and J. Rocek, *J. Org. Chem.*, 1979, **44**, 312.

three-electron oxidation of a molecule in which a C—C and a C—H bond on the same carbon atom are broken simultaneously in the rate-determining step. The free-radical intermediates formed in this step can reduce Cr^{VI} to Cr^{V} and in order to account for the products the latter is assumed to oxidize the mandelic acid directly:

$$PhCH(OH)CO_2H + Cr^{V} \longrightarrow PhCHO + CO_2 + Cr^{III}$$

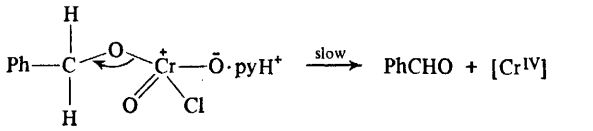
Rate differences have been monitored in the reaction of formic acid[18] with various Cr^{VI} species, and in the presence of an oxalic acid–formic acid mixture[19] simultaneous oxidation occurs at a rate much greater than with either of the substrates under identical conditions. This has been observed previously by Rocek and his co-workers (see previous Reports) and is consistent with a three-electron oxidation of a mixed formate–oxalate ester. The oxidation of methyl phenyl sulphoxides in aqueous acetic acid is first order with respect both to substrate and to $[Cr^{VI}]$,[20] the suggested mechanism involving a one-electron transfer, $PhS(O)Me + Cr^{VI} \rightarrow Ph\overset{+}{S}(O)Me + Cr^{V}$, followed by oxygen transfer from the oxidant to yield the sulphone $PhMeSO_2$. In non-aqueous media, the reaction with dithizone proceeds by differing mechanisms depending on the [oxidant]: [substrate] ratio.[21] In a more complete study,[22] principally in amide solvents, the redox and co-ordination reactions involving Cr^{V} complexes with phosphorus and sulphur ligands (L) have been identified. Following a one-electron transfer, e.s.r. spectra typical of equilibria $Cr^{V} + nL \rightleftharpoons Cr^{V}L_n$ were observed prior to further reduction. Two chromium(v) complexes have been identified using e.s.r. techniques. At low dithizone concentrations two-electron transfers are operative whereas at higher levels a 1e process to yield a radical and one of the Cr^{V} species is observed. This latter complex is further reduced in a two-electron step.

The oxidations of benzyl alcohols[23] and substituted mandelic acids[24] by pyridinium chlorochromate have been described. This oxidant is a complex of CrO_3,pyridine and hydrochloric acid, and is known to convert alcohols into carbonyl compounds in high yield. In the reaction with benzyl alcohol the reaction is

$$3PhCH_2OH + 2Cr^{VI} \rightarrow 3PhCHO + 6H^{+} + 2Cr^{III}$$

The rate is first order with respect to both [oxidant] and [alcohol] and is catalysed by H^{+}. A kinetic isotope effect $k_H/k_D = 5.07$ is consistent with a rate-determining C—H cleavage from the alcohol carbon. A protonated Cr^{VI} species is proposed as the reactant and a mechanism involving hydride ion transfer within a chromate ester is invoked, *e.g.* equation (2). The possibility of direct

[18] A. V. Mahajani and S. Mahajani, *J. Sci. Res. (Bhopal) India*, 1978, **1**, 25 (*Chem. Abs.*, 1979, **90**, 157 705q).
[19] R. C. Pawar, G. L. Agrawal, and A. V. Mahajani, *Indian J. Chem. Sect. A*, 1978, **16**, 984.
[20] V. Baliah and P. V. V. Satyanarayana, *Indian J. Chem. Sect. A*, 1978, **16**, 966.
[21] P. Rusev, P. R. Bonchev, M. Miteva, and A. Malinovski, *Inorg. Chim. Acta*, 1979, **34**, 103.
[22] M. Miteva, P. Bonchev, K. Kabasanov, G. Petrov, P. Rusev, and M. Natskova, *Doklady bolgarsk. Akad. Nauk*, 1978, **31**, 1437.
[23] K. K. Banerji, *J.C.S. Perkin II*, 1978, 639.
[24] K. K. Banerji, *J. Chem. Res. (S)*, 1978, 193.



reaction cannot be ruled out, however. A similar mechanism is considered to describe the reactions of the mandelic acids.[24] For the unsubstituted substrate $k_H/k_D = 6.09$ and the species $PhC^{+}(OH)CO_2H$ is formed on H^- transfer. In both studies the reactions were carried out in 1:1 methylene chloride–nitrobenzene mixtures.

4 Reactions of Cerium(IV)

Kinetic studies have been carried out in both perchlorate and sulphate media. In many instances the former provides a better background electrolyte since complexation with the oxidant is generally small. The exact nature of the reacting aquo-metal ion is still the subject of debate, however, and for this reason some investigators prefer the use of sulphate where the sulphato-cerate species are well identified. The oxidation of propionic acid in $HClO_4$ exhibits[25] first-order behaviour with respect to $[Ce^{IV}]$ but tends to a limiting rate with increasing substrate. This is indicative of complex formation prior to the rate-determining electron transfer. The intermediate species has been confirmed by spectrophotometry. A mechanism consistent with the findings is

$$Ce^{4+}aq + C_2H_5CO_2H \overset{K_1}{\rightleftharpoons} [Ce\cdot C_2H_5CO_2H]_{aq}^{4+} + H_2O$$

$$[Ce\cdot C_2H_5CO_2H]_{aq}^{4+} \underset{k_1}{\overset{\text{slow}}{\longrightarrow}} \text{radical} + H^+ + Ce^{III}$$

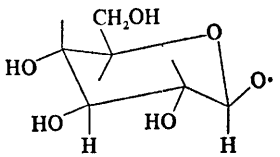
$$[Ce^{IV}] + \text{radical} \overset{\text{fast}}{\longrightarrow} CH_3CO_2H + H^+ + Ce^{III} + CO_2$$

At higher $[Ce^{IV}]$ (>4 mM) the rate decreases owing to dimerization of the oxidant.

Ionic strength and specific ion effects have been investigated in the oxidation of mandelic acid by cerium(IV) sulphate.[26] Unlike the reaction in $HClO_4$ where there is spectrophotometric and kinetic evidence for complex formation, under these conditions there is a first-order rate dependence of both oxidant and reductant. The replacement of H^+ by Li^+, Na^+, or K^+ produces only a minor change in rate and has no effect on the activation parameters. Rate laws which are essentially similar have been established in the reactions with cyclohexane-1,4-diol[27] cyclopentanone,[28] and methyl isopropyl ketone.[29] The enol form of the substrate is favoured as the active reagent in the latter two reactions.

[25] I. C. Tewari and S. R. Tripathi, *J. Inorg. Nuclear Chem.*, 1977, **39**, 2095.
[26] G. Atcoleo, G. Calvaruso, F. P. Cavasino, and E. Di Dio, *Internat. J. Chem. Kinetics*, 1979, **11**, 415.
[27] R. K. Khanna, K. Behari, and B. Krishna, *Proc. Nat. Acad. Sci., India Sect. A*, 1976, **46**, 239 (*Chem. Abs.*, 1979, **90**, 21 950h).
[28] H. Chatterjee and K. Behari, *Chem. Scripta*, 1977, **12**, 40.
[29] B. Singh, P. K. Saxena, K. M. Richards, and B. Krishna, *Z. phys. Chem.* (*Leipzig*), 1978, **259**, 801.

Acceleration of the rate by HSO_4^- ions also appears as a common feature of these oxidations. In the reaction with glucose,[30] a number of products, principally glycollic and formic acids, and CO_2 are formed with one-electron oxidants (Ce^{IV}, Fe^{3+}, Cu^{2+}). The initial redox process yields the radical (2), which undergoes further rapid oxidation. Hydrogen-ion dependences were not investigated. The roles of H^+, HSO_4^-, and SO_4^{2-} have been discussed in the cerium(IV)–arsenic(III) (H_3AsO_3) reaction catalysed by Os^{VIII}.[31]



(2)

Although ferrocenes are only sparingly soluble and rather unstable in water, by employing a method involving dissolution in glacial acetic acid and dilution with H_2SO_4 solution it has been possible to prepare solutions ($\sim 2 \times 10^{-3}$M) of acetylferrocene [Fe(cp) (acp)] and 1,1′-bisacetylferrocene [$Fe(acp)_2$].[32] Several redox and dissociation processes are observed in reaction with cerium(IV) sulphate. Using acetylferrocene as an example, the oxidative decomposition is described by

$$[Fe(cp)\,(acp)] \xrightarrow[k_1]{Ce^{IV}} [Fe(cp)\,(acp)]^+ \xrightarrow{k_2} [Fe(cp)]^{2+} + (acp)^-$$

$$[Fe(cp)]^{2+} \xrightarrow{k_3} Fe^{2+} + (cp)^0$$

$$(acp)^- \xrightarrow[k_4]{Ce^{IV}} (acp)^0 + Ce^{III}$$

with further rapid reaction of $(cp)^0$, $(acp)^0$, and Fe^{II} with oxidant. Increase of acidity by one H_0 unit results in a fall of rate constant by $\sim 50\%$ and under highly acidic conditions the decomposition is arrested sufficiently to enable a value (0.48 V) to be determined for the reduction potential of the [Fe(cp) (acp)]/[Fe(cp) (acp)]$^+$ couple. The role of strong one-electron oxidants (Co^{III}, Mn^{III}, and Ce^{IV}) in the oxidative coupling of aromatic systems has been reviewed.[33]

Oscillating chemical reactions continue to be investigated[34,35] in sulphate media. Addition of α-monobromo-ketone, one of the products of the BrO^-_3–Ce^{IV}–cyclohexanone and BrO_3^-–Ce^{IV}–cyclopentanone systems has been shown to decrease and, in some instances, suppress the initial induction period.[34] The inhibitory effects of Cl^- ions have also been described. In the gallic acid–bromate reaction catalysed by $[Fe(phen)_3]^{+/2+}$ the enol is the reactive form of the organic substrate.[35] The mechanism proposed is essentially that of

[30] V. I. Kruparskii, *J. Gen. Chem. U.S.S.R.*, 1978, **48**, 2023.
[31] Y. A. El-Tantawy, I. Abu-Shady, and I. I. Ezzat, *J. Inorg. Nuclear Chem.*, 1978, **40**, 1683.
[32] J. Holecek, K. Handlir, and J. Klikorka, *Coll. Czech. Chem. Comm.*, 1979, **44**, 1060.
[33] I. V. Kozhevnikov and T. I. Mateev, *Russ. Chem. Rev.*, 1978, **47**, 649.
[34] V. J. Farage and D. Janjic, *Helv. Chim. Acta*, 1978, **61**, 1539.
[35] J. S. Babu and K. Srinivasula, *Z. phys. Chem. (Leipzig)*, 1978, **259**, 1191.

Noyes[36] for bromate–malonic acid reaction and involves formation of $BrO_2\cdot$ radicals which oxidize the reduced metal complex. Silver(I) inhibition in the gallic acid reaction is observed, presumably by reduction of the Br^- present

5 Reactions of Cobalt(III)

The standard electrode potential for Co^{III}/Co^{II} has been determined from a calorimetric study of the Co^{III}–Fe^{II} reaction.[37] The value obtained (1.73 V) is somewhat lower than that estimated previously, possibly owing to differences in the perchloric acid concentrations used. The recommended figure 1.85 V ($T=25$ °C, 4M-$HClO_4$) is based on potentiometric measurements.[38] The oxidations of acetamide, formamide, and *N*-methyl- and *NN*-dimethyl-formamides have been studied in aqueous $HClO_4$.[39] The rate law is of the form

$$-d[Co^{III}]/dt = (k_1+k_2[H^+])\,[Co^{III}]\,[\text{amide}]$$

and a free-radical mechanism is proposed. This study is of interest in that it is one of the few oxidation reactions of cobalt(III) identified so far which is acid catalysed. The mechanism involves reaction of only Co_{aq}^{3+} as metal ion reactant with $R^1CONR^2_2$ and its protonated conjugate $R^1C(OH)=\overset{+}{N}R^2_2$ as reductants, *e.g.*

$$Co^{3+} + R^1C(OH)=\overset{+}{N}R^2_2 \xrightarrow[H_2O]{k_0} R^1CO_2H + \cdot NR^2_2 + Co^{II} + 2H^+$$

$$\cdot NR^2_2 + H_2O \xrightarrow{\text{fast}} HNR^2_2 + HO\cdot$$

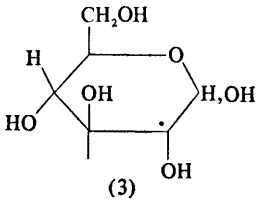
$$2HO\cdot \xrightarrow{\text{fast}} H_2O + \tfrac{1}{2}O_2$$

No further oxidation of the amine products occurs. In the reaction with 2-mercaptoisobutyric acid,[40] there is no evidence for intermediate complex formation and the increase of rate with decreasing $[H^+]$ is consistent with the rate law $\text{Rate}=k_2K_h[Co^{III}]\,[RSH]/[H^+]$ in which the ion $CoOH^{2+}$ is the oxidant. The radical character involved in the oxidation of hydroxy-compounds by cobalt^{III} has been confirmed by e.s.r.[41] The reductants chosen in this study were glucose, sorbitol, and methyl-α-glucoside. Careful removal of oxygen resulting from the oxidation of water has shown well defined triplets of intensity 1:2:1 ($g=2.004\pm0.002$) which are consistent with displacement of H from a secondary carbon atom. Thus with glucose the radical (3) is formed. The mechanism of reaction involves an intermediate complex formation,

$$ROH + Co^{3+} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [\text{complex}] \xrightarrow{k_3} \cdot ROH + H^+$$

$$\cdot ROH + Co^{3+} \xrightarrow{k_4} R{=}O + Co^{2+} +$$

[36] J.-J. Jwo and R. M. Noyes, *J. Amer. Chem. Soc.*, 1975, **97**, 5422.
[37] C. W. Mowforth, D. R. Rosseinsky, and K. Stead, *J.C.S. Faraday I*, 1978, **74**, 1268.
[38] B. Warnqvist, *Inorg. Chem.*, 1970, **9**, 682.
[39] F. Ahmad and V. S. Baswami, *Austral. J. Chem.*, 1979, **32**, 537.
[40] R. Shanker and G. V. Bakore, *Indian J. Chem. Sect. A.*, 1978, **16**, 648.
[41] V. I. Kurlyankina, V. N. Shadrin, E. N. Kazbekov, and V. A. Molotkov, *J. Gen. Chem. U.S.S.R.*, 1978, **48**, 387.



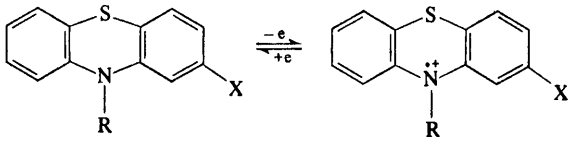
(3)

where $k_3/k_4 \approx 0.3$—0.5×10^{-6} and the equilibrium constants (k_1/k_2) are 145, 80, and 23 M^{-1} respectively for glucose, sorbitol, and methyl-α-glucoside.

Reactions of amminecobalt(III) complexes as oxidants are being further investigated.[42] Under pseudo-first-order conditions, the two reactions observed in the reduction of $[Co(NH_3)_4(OH)_2]^{3+}$ by cysteine have been ascribed to the faster redox involving the *trans*-isomer and a slower *cis* reaction. The order with respect to complex is unity and that for cysteine is zero. The mechanism proposed involves the rapid pre-equilibrium to form $[(RS)Co(NH_3)_4(OH_2)]^{2+}$ complexes which then undergo a rate-determining internal redox process. More data are required for these systems which appear to involve a pre-equilibrium rate much greater than expected for a low-spin d^6 cobalt(III) centre.

6 Reactions of Iron(III)

The oxidations of *N*-alkylphenothiazines (PTZ) by Fe^{3+} and $[Fe(CN)_6]^{3-}$ have been reported.[43] The reactions are of considerable interest since they give rise to cation radicals which are long lived in aqueous acidic media, *e.g.* (4), where



(4)

R = substituted alkyl (*e.g.* $CH_2CH_2CH_2NMe_2$) and X = OH, H, Cl, or OMe. For the redox reaction

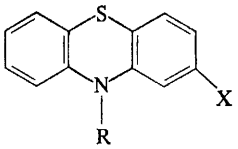
$$Fe^{3+}_{aq} + PTZ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Fe^{2+}_{aq} + PTZ^+$$

the observed rate is of the form (pseudo-first-order conditions) $k_{obs} = k_1[Fe^{III}] + k_2[Fe^{II}]$. The rate data are presented in Table 1. An interesting feature of these systems is the invariance of the rate in the acidity range 0.05—1.00M-$HClO_4$, consistent with Fe^{3+} (and not $FeOH^{2+}$ which is present under optimum conditions at only ~3%) as the main outer-sphere electron-transfer agent. A comparison of calculated and experimental rate constants for the Fe^{3+}/Fe^{2+} reactions shows the former values to be ~300—500 times higher than the observed constants. In this regard, the systems behave like the ML_3^{3+}–Fe^{2+} reactions where L = a phenanthroline-like ligand. In contrast, the reactions of $[Fe(CN)_6]^{3-}$

[42] K. Kumari, S. Prakash, and B. Krishna, *Z. phys. Chem. (Leipzig)*, 1978, **259**, 219.,
[43] E. Pelizzetti and E. Mentasti, *Inorg. Chem.*, 1979, **18**, 583.

Table 1 *Rate constants and activation parameters for redox reactions or* Fe^{III}, Fe^{II}, *complexes*[a]

N-*Alkylphenothiazine complexes*



(5) R = $CH_2CH_2CH_2NMe$ = (A), X = OH; (6) R = $CH_2CH_2CH_2N$⟨ ⟩NMe, X = H;

(7) R = (A), X = OMe; (8) R = (A), X = H; (9) R = (A), X = Cl;
(10) R = $CH_2CH_2NEt_2$, X = H; (11) R = $CH_2CH(Me)NMe_2$, X = H;
(12) R = $CH(Me)CH_2NMe_2$, X = H

$$Fe^{3+} + PTZ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Fe^{2+} + PTZ^{+}$$

PTZ	k_1[b]	$\Delta H_1^{\ddagger}$[c]	$\Delta S_1^{\ddagger}$[d]	k_2[b]	$\Delta H_2^{\ddagger}$[c]	$\Delta S_2^{\ddagger}$[d]	*Ref.*
(5)	5.7×10^2	10.9	−20	12	7.3	−29	43
(6)	1.4×10^2	8.5	−20	80	5.8	−30	43
(7)	1.1×10^2	8.6	−20	65	4.4	−36	43
(8)	1.3×10^2	9.9	−16	1.0×10^2	5.7	−30	43
(9)	60	11.9	−11	2.8×10^2	4.9	−31	43
(10)	14	11.1	−16	4.7×10^2	5.1	−29	43
(11)	8.3	12.0	−14	1.1×10^3	6.0	−25	43
(12)	7.6	11.9	−14	1.7×10^3	5.0	−27	43
(6)[e]	2.1×10^6	—	—				43
(7)[e]	1.6×10^6	—	—				43
(8)[e]	1.5×10^6	—	—				43
(9)[e]	5.9×10^5	—	—				43

Heteroaromatic diols (13)—(16)

$$[FeL_3]^{3+} + H_2X \xrightarrow{k_3} [FeL_3]^{2+} + H_2X^{+}$$

Reaction	k_3[b,f]	$\Delta H_3^{\ddagger}$[c]	$\Delta S^{\ddagger}$[d]	*Ref.*
$[Fe(phen)_3]^{3+}$+(13)	$\sim2\times10^7$	—	—	44
$[Fe(Mephen)_3]^{3+}$+(13)	$\sim9\times10^6$	—	—	44
$[Fe(Me_2phen)_3]^{3+}$+(13)	2.3×10^6	0.0	−29	44
$[Fe(bipy)_3]^{3+}$+(13)	3.3×10^6	3.4	−17	44
$[Fe(Me_2bipy)_3]^{3+}$+(13)	4.6×10^4	8.1	−9	44
$[Fe(NO_2phen)_3]^{3+}$+(14)	4.5×10^6	1.2	−24	44
$[Fe(Clphen)_3]^{3+}$+(14)	6.8×10^5	5.0	−15	44
$[Fe(phen)_3]^{3+}$+(14)	2.7×10^4	9.4	−7	44
$[Fe(Me_2phen)_3]^{3+}$+(14)	1.4×10^3	11.5	−6	44
$[Fe(bipy)_3]^{3+}$+(14)	5.0×10^3	7.9	−15	44
$[Fe(Mephen)_3]^{3+}$+(15)	$\sim9\times10^6$	—	—	44
$[Fe(Me_2phen)_3]^{3+}$+(15)	6×10^6	(−0.6)	−29	44
$[Fe(bipy)_3]^{3+}$+(15)	$\sim1\times10^7$	—	—	44
$[Fe(Me_2bipy)_3]^{3+}$+(15)	9×10^4	5.2	−19	44
$[Fe(NO_2phen)_3]^{3+}$+(16)	6.9×10^5	3.4	−21	44
$[Fe(Clphen)_3]^{3+}$+(16)	6.2×10^4	3.9	−23	44
$[Fe(phen)_3]^{3+}$+(16)	1.9×10^3	3.7	−31	44

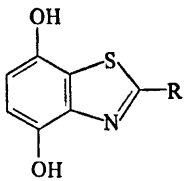
Table 1 (*continued*)

Reaction	k_3[b,f]	$\Delta H_3^{\ddagger}$ [c]	$\Delta S^{\ddagger}$ [d]	*Ref.*
$[Fe(phen)_2(CN)_2]^+ + H_2A$[g]	~40	—	—	45
$[Fe(bipy)_2(CN)_2]^+ + H_2A$	≤10	—	—	45
$[Fe(phen)(CN)_4]^- + H_2A$	~0.6	—	—	45
$[Fe(SO_3phen)_3]^{3+} + H_2A$	7.6×10^5	1.0	−28	45
$[Fe(Brphen)_3]^{3+} + H_2A$	4.6×10^5	1.3	−28	45
$[Fe(phen)_2(CN)_2]^+ + HA^-$[h]	8.3×10^6	0.0	−27	45
$[Fe(bipy)_2(CN)_2]^+ + HA^-$	4.0×10^6	2.1	−22	45
$[Fe(phen)(CN)_4]^- + HA^-$	4.8×10^4	1.6	−32	45
$[Fe(SO_3phen)_3]^{3+} + HA^-$	3.2×10^9	—	—	45
$[Fe(Brphen)_3]^{3+} + HA^-$	2.8×10^9	—	—	45

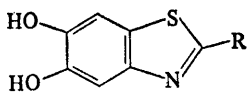
[a] $I = 1.00$M $HClO_4$ ($[H^+] = 1.00$M), $T = 25$ °C unless indicated otherwise. [b] $M^{-1}\ s^{-1}$. [c] kcal mol^{-1}. [d] cal $K^{-1}\ mol^{-1}$. [e] reactions of $[Fe(CN)_6]^{3-}$. [f] $T = 20$ °C. [g] H_2A = ascorbic acid. [h] HA^- = ascorbate ion.

with PTZ derivatives are in agreement with Marcus predictions. Linear free-energy plots have also been observed in the electron-transfer reactions of heteroaromatic diols with $[Fe(phen)_3]^{3+}$ complexes.[44] For substrates (H_2X) of the types (13)—(16) the reduction potentials have been measured: (13) 0.68 V, (14) 0.87 V, (15) 0.66 V, (16) 0.93 V, and the overall reaction is of the form

$$2FeL_3^{3+} + H_2X \longrightarrow 2[Fe(phen)_3]^{2+} + X + 2H^+$$



(13) R = H
(14) R = Me



(15) R = H
(16) R = Me

where X is the corresponding quinone. Comparison of the rates with ligand displacement reactions confirms the outer-sphere nature of the redox processes and the mechanism proposed involves the rate-determining formation of a radical which undergoes further rapid oxidation to the product:

$$Fe^{III}L_3^{3+} + H_2X \overset{\text{slow}}{\rightleftharpoons} H_2X^+ + FeL_3^{2+}$$

$$H_2X^+ + Fe^{III} \longrightarrow Fe^{II} + X + 2H^+$$

Rate and thermodynamic data are presented in Table 1. Correlation of the data with the Marcus theory has enabled estimates to be made for the reduction potentials and the intrinsic parameters of the cation radicals which are formed in the rate-limiting reaction. A similar procedure has been adopted in an analysis of the outer-sphere oxidation of ascorbic acid by a series of one-electron acceptor metal complexes.[45] In this case, however, reactions of both H_2A and HA^- are

[44] E. Pelizzetti, E. Mentasti, and E. Barni, *J.C.S. Perkin II*, 1978, 623.
[45] E. Pelizzetti, E. Mentasti, and E. Pramauro, *Inorg. Chem.*, 1978, **17**, 1181.

observed. Rate constants for both reductants are listed in Table 1. The reactions of FeL_3^{3+} with HA^- are extremely fast and in these instances a diffusion-controlled rate constant correction has been introduced. In the reduction of ascorbic acid by a water-soluble bis(histidine)ferriporphyrin,[46] the first-order rate constants are independent of reductant concentration and are related to the $[H^+]$ dependence in accordance with the expression $k_{obs} = k_{diss}(1 + K_a[H^+]^{-1})$, where K_a and k_{diss} represent the deprotonation equilibrium quotient of the bis(histidine)ferriporphyrin and the rate of dissociation of the histidine ligand.

Catalysis by metal complexes of the oxidation of various organic substrates by alkaline hexacyanoferrate(III) has been the subject of several papers. In the mechanism of oxidation of alcohols catalysed by Ru^{III},[47,48] a complex is formed which is involved in the rate-determining step. The rate law (with zero-order dependence on Fe^{III}),

$$\text{Rate} = -\mathrm{d}\frac{[Fe(CN)_6^{3-}]}{dt} = \frac{2k_1k_2[ROH]\,[Ru^{III}]_{tot}}{k_2 + k_1[ROH] + k_{-1}[OH^-]}$$

is consistent with a scheme where the initial steps

$$[Ru(OH_2)_6(OH)_x]^{(3-x)+} + ROH \underset{k_{-1}}{\overset{k_1}{\longrightarrow}} [Ru(ROH)]^{(4-x)+}_{aq} + OH^-$$

$$\downarrow k_2$$

$$[Ru^{III\prime}] + \text{products}$$

are followed by redox reactions of $[Fe(CN)_6]^{3-}$. Secondary alcohols are oxidized to ketones, the rate decreasing in the order of formation constant of Ru^{III} complexes. The existence of a seven-co-ordinate ruthenium(III) hydride $[Ru^{III\prime}]$ proposed as a reaction intermediate will require further substantiation. In the Os^{VIII}-catalysed oxidation of cinnamate, the reaction scheme proposed[49] (Scheme 4) again involves an intermediate although in this instance a two-

$$[OsO_4(OH)_2]^{2+} + PhCH{=}CHCO_2^- \rightleftharpoons [\text{complex}] + OH^-$$

$$\downarrow \text{slow}$$

$$PhCO_2^- \xleftarrow{Fe^{III}} PhCHO + HCO_2^- \xleftarrow[\substack{(4)[Fe(CN)_6]^{3-}\\(4)OH^-}]{\text{rapid}} PhCH(OH){-}CH(OH)CO_2^- + [OsO_4(OH)_2]^{4-}$$

$$+ Fe^{II}$$

Scheme 4

electron transfer to yield Os^{VI} is invoked. The kinetics of the corresponding oxidation of lysine are complex.[50] The oxidation of citric acid, catalysed by Cu^{II}, has also been reported.[51]

[46] J. C. Oxley and D. L. Toppen, *Inorg. Chem.*, 1978, **17**, 3119.
[47] R. N. Singh, R. K. Singh, and H. S. Singh, *J. Chem. Res. (S)*, 1978, 176.
[48] R. N. Singh and H. S. Singh, *Indian J. Chem., Sect. A*, 1978, **16**, 145.
[49] S. Kumar and P. C. Mathur, *J. Inorg. Nuclear Chem.*, 1979, **41**, 599.
[50] S. K. Upadhyay and M. C. Agrawal, *Monatsh.*, 1979, **110**, 413 (*Chem. Abs.*, 1979, **90**, 210 713u).
[51] S. Kumar and P. C. Mathur, *J. Inorg. Nuclear Chem.*, 1978, **40**, 581.

7 Reactions of Iridium(IV)

Studies of oxidation reactions of differing substrate types have been described. The nature of oxidant species in $HClO_4$ and H_2SO_4 media has been examined by investigation of catalysis of the Ce^{IV}–Hg^{I} reaction.[52] It is suggested that at 2.0M-$HClO_4$ the iridium(IV) is hydrolysed with protonation constant of 0.4 M^{-1} for $[Ir(H_2O)_5OH]^{3+}$. Most kinetic studies, however, refer to reaction of the hexachloro and hexabromo ions. The oxidation of thiourea (tu), *N,N'*-dimethylthiourea (dmtu), and 2-imidazolidinethione (it) follows a rate law[53] second order in [substrate] and first in $[Ir^{IV}]$. The rate of oxidation follows the reactivity trend established previously for aquo-metal ions. The mechanism proposed involves rapid pre-equilibria followed by disulphide radical formation,

$$tu + OH^- \rightleftharpoons tu^- + H_2O$$

$$tu^- + Ir^{IV} \rightleftharpoons [tu^- Ir^{IV}]$$

$$[tu^- Ir^{IV}] + tu \xrightarrow{\text{slow}} tu_2\cdot + Ir^{III}$$

$$tu_2\cdot + Ir^{IV} \longrightarrow tu_2 + H^+ + Ir^{III}$$

the initial reaction being required to explain a pH dependence at values >2.3. Rate data for the reactions are provided in Table 2.

Table 2 *Reactions of iridium*(IV) *complexes*

Reaction	k_2[a]	$\Delta H^{\ddagger}$[b]	$\Delta S^{\ddagger}$[c]	*Ref.*
$[IrCl_6]^{2-}$ + tu[d]	368[e]	6.1	−26	53
$[IrCl_6]^{2-}$ + dmtu[d]	394[e]	5.7	−27	53
$[IrCl_6]^{2-}$ + it[d]	297[e]	7.5	−27	53

Benzene diols and heteroaromatic diols

(17)=2-methylbenzene-1,4-diol; (18)=benzene-1,4-diol; (19)=2,5-dihydroxybenzoic acid; (20)=2,5-dihydroxybenzenesulphonic acid; (21)=2,3-dicyanobenzene-1,4-diol; (22)=4-methylbenzene-1,2-diol; (23)=benzene-1,2-diol; (24)=(−)-4-[1-hydroxy-2-(methylamino)ethyl]benzene-1,2-diol; (25)=3,4-dihydroxybenzoic acid; (26)=4-[1-oxo-2-(methylamino)ethyl]benzene-1,2-diol; (27)=4-cyanobenzene-1,2-diol; (28)=4,5-dihydroxybenzene-1,3-disulphonic acid.

Reaction with $[IrBr_6]^{2-}$ *(substrate)*[f]	k_2[a]	$\Delta H^{\ddagger}$[b]	$\Delta S^{\ddagger}$[c]	*Ref.*
(17)	4.1×10^5	4.0	−20	54
(18)	7.4×10^4	4.7	−21	54
(19)	1.75×10^3	4.6	−28	54
(20)	1.45×10^3	4.9	−28	54
(22)	3.8×10^4	5.4	−20	54
(23)	2.7×10^3	6.5	−21	54
(24)	3.6×10^3	5.8	−22	54
Reactions with $[IrCl_6]^{2-}$				
(13)[g]	3.5×10^4	3.1	−27	43
(14)[g]	1.3×10^2	3.4	−37	43
(15)[g]	5.6×10^4	4.0	−23	43

[52] K. B. Yatsimirskii, L. P. Tikhonova, and V. Y. Zayats, *Tezisy Doklady Vses. Soveshch. Khim.*, 1976, No. 1, 23 (*Chem. Abs.*, 1979, **90**, 62 018d).

[53] H. N. Po, H. Eran, Y. Kim, and J. E. Byrd, *Inorg. Chem.*, 1979, **18**, 197.

Reaction with $[IrBr_6]^{2-}$ *(substrate)*[f]	k_2[a]	$\Delta H^{\ddagger}$[b]	$\Delta S^{\ddagger}$[c]	*Ref.*
Reaction with $[IrCl_5(OH_2)]^-$				
(13)	3.8×10^5	0.2	−32	43
(14)	2.6×10^3	1.8	−37	43
(15)	5.3×10^5	0.7	−30	43
(18)	8.8×10^5	4.6	−16	54
(19)	5.5×10^4	5.2	−20	54
(20)	4.6×10^4	4.7	−22	54
(21)	7.0×10^2	3.9	−32	54
(23)	6.2×10^4	3.9	−23	54
(24)	8.9×10^4	1.9	−30	54
(25)	2.7×10^3	6.5	−21	54
(26)	2.3×10^3	5.8	−24	54
(27)	7.2×10^2	6.9	−22	54
(28)	1.4×10^2	7.0	−25	54
Reactions with $[IrCl_4(OH_2)_2]$				
(13)	2.0×10^6	0.4	−28	43
(14)	2.7×10^4	4.3	−24	43
(15)	4.4×10^6	0.8	−25	43
(19)	6.6×10^5	6.8	−9	54
(20)	5.4×10^5	6.2	−11	54
(21)	9.0×10^3	4.8	−24	54
(23)	6.4×10^5	5.1	−15	54
(24)	7.8×10^5	2.8	−22	54
(25)	3.2×10^4	6.2	−17	54
(26)	2.2×10^4	5.8	−19	54
(27)	8.6×10^3	7.0	−17	54
(28)	3.6×10^3	6.0	−22	54
$[IrCl_6]^{2-}+H_2A$[g]	$\sim4\times10^2$	—	—	45
$[IrCl_5(OH_2)]+H_2A$	$\sim5\times10^3$	—	—	45
$[IrCl_4(OH_2)_2]+H_2A$	1.05×10^5	~0	−36	45
$[IrBr_6]^{2-}+H_2A$	$\leqslant2\times10^2$	—	—	45
$[IrCl_6]^{2-}+HA^-$[h]	2.8×10^7	1.2	−20	45
$[IrCl_5(OH_2)]^-+HA^-$	2.6×10^8	~0.1	−20	45
$[IrCl_4(OH_2)_2]+HA^-$	2×10^9	—	—	45
$[IrBr_6]^{2-}+HA^-$	5.9×10^7	1.3	−18	45

[a] M^{-1} s^{-1}, $T=25$ °C. [b] kcal mol^{-1}. [c] cal mol^{-1} K^{-1}. [d] $I=0.15$M. [e] Third-order rate constant. [f] $I=1.0$M, $[HClO_4]=1.0$M. [g] $T=20$ °C. [h] H_2A = ascorbic acid. [i] HA^- = ascorbate ion.

An outer-sphere mechanism is proposed[54] in the electron transfer between benzene diols and $[IrCl_5(OH_2)]^-$, $[IrCl_4(OH_2)_2]$, and $[IrBr_6]^{2-}$. In these systems the stoicheiometry $2Ir^{IV}+H_2Q\rightarrow2Ir^{III}+Q+2H^+$ has been confirmed as with other one-electron oxidants. The rate law is of the form $Rate=k_2[Ir^{IV}][H_2Q]$, with no dependences on $[H^+]$ or $[Ir^{III}]$. Rate data are presented in Table 2. Good agreement with the Marcus cross correlation has been observed and an estimation of the intrinsic parameters for the self-exchange reactions of the Ir^{IV}–Ir^{III} pairs has been attempted. The three oxidants have also been studied[44] in their reactions with the heteroaromatic diols (13)—(16). Again the rate law is of identical form to that expressed above. Adherence to the Marcus theory has been observed through a linear correlation between $\log k_2$ and the standard

[54] E. Pelizzetti, E. Mentasti, and E. Pramauro, *J.C.S. Perkin II*, 1978, 620.

reduction potentials. The rate-determining step is considered to be the formation of a cation radical which rapidly reduces a further mole of iridium(IV).

8 Reactions of Copper(II)

Several pathways have been identified in the oxidation of 2-mercaptosuccinic acid (H_3L) in perchlorate media (pH 2—4).[55] In conditions of excess of either oxidant or organic substrate, a sulphur-bonded copper(II) transient absorbing at 350 nm ($\varepsilon = 1.6 \times 10^3$ M^{-1} cm^{-1}) was detected within the time of mixing. The assignment of oxidation state was confirmed by e.s.r. measurement. In excess reductant, the kinetics of decay of the intermediate showed a second-order dependence on transient. The reaction is acid catalysed, suggesting that opening of the chelate ring is necessary before reaction can proceed:

$$CuL^- + H^+ \rightleftharpoons CuLH$$

$$CuL^- + CuLH \xrightarrow{k_3} [Cu_2L_2H]^-$$

$$[Cu_2L_2H]^- + H_3L \xrightarrow{k_4} [Cu^I{}_2LH] + HL'—L'H_2^-$$

$$[Cu_2L_2H]^- + H_2L^- \xrightarrow{k_5} [Cu^I{}_2LH] + HL'—L'H^{2-}$$

$$[Cu^I{}_2LH] + H_3L \xrightarrow{\text{fast}} [Cu_2L_2H_4]$$

The formation of a dimer provides a two-electron template on which direct oxidation to the mercaptide can occur. After redox the copper(I) complex is stabilized by further co-ordination of thiol.

The influence of anions on the rate of reduction of copper(II) in the Cu^{II}–piperidine–benzene–A^- ($A^- = NO_3^-$, Cl^-, Br^-, or ClO_4^-) systems has been investigated.[56] No redox is shown where $A^- = Cl^-$, but for the other counter-ions Cu^I formation takes place. The results are interpreted in terms of the relative influence of σ-donor and π-acceptor ligands present in the Cu^{II} co-ordination sphere.

9 Reactions of Vanadium(V)

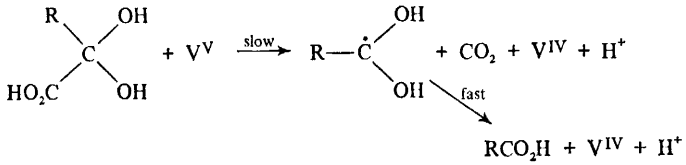
The kinetics of oxidation of glyoxylic and pyruvic acids have been investigated in the presence of perchloric acid.[57] Two moles of oxidant are required in the reaction to yield formic and acetic acids respectively. The rate law is of the form

$$-d[V^V]/dt = k_0K[V^V][S][H^+]/(1 + K[H^+])$$

The mechanism of reaction (Scheme 5) involves the proton equilibrium of vanadium(V), followed by reaction with the hydrated form of the α-keto-acid. The values $K = 3.4$ (35 °C) and 2.0 (30 °C) have been derived kinetically. Initial oxidation of glyoxylic acid to oxalic acid is ruled out in view of the complex reaction of the latter with V^V. A study has been made, however, of the oxalic acid catalysis of the oxidation of iodide by vanadium(V).[58]

[55] A. G. Lappin and A. McAuley, *J.C.S. Dalton*, 1978, 1606.
[56] H. Langfelderova, B. Przeczek, and J. Gazo, *Z. anorg. Chem.*, 1979, **451**, 143.
[57] K. K. SenGupta and H. R. Chatterjee, *Inorg. Chem.*, 1978, **17**, 2429.
[58] P. V. Subba Rao, P. S. Murty, and R. V. Murty, *J. Inorg. Nuclear Chem.*, 1978, **40**, 295.

$$[V(OH)_4]^+ + H^+ \rightleftharpoons [V(OH)_3]^{2+} + H_2O \quad K$$



Scheme 5

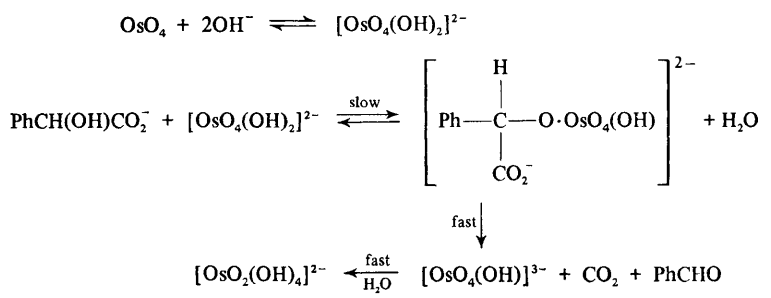
10 Miscellaneous Reactions

A kinetic study has been made of the oxidation of ascorbic acid (H_2A) by neptunium(VI).[59] The rate law is of the form $-d[Np^{VI}]/dt = k_2[H_2A][Np^{VI}]$ with no evidence for a hydrogen-ion dependence over the range $0.05 < [H^+] < 1.00$M. In aqueous media Np^{VI} exists as the $[O—Np—O]^{2+}$ ion with between four and six equatorial water molecules. A comparison with the reactions with aquo-ions, *e.g.* V^V or Fe^{III}, where inner-sphere reactivity is established and with $[Fe(phen)_3]^{3+}$ indicates that the preferred pathway is outer sphere. The exchange rate for $[(5\text{-nitrophen})_3Fe]^{3+/2+}$ and the redox potential are both greater than for the Np^{VI}/Np^V couple and these features are considered the reason for the rate of the present reaction being ~40 times slower than that of the iron^{III} system.

Radiochromatographic techniques have been used to determine the rates of oxidation of cysteine[60] by pertechnate ion, $^{99}TcO_4^-$. The technetium(VII) is reduced by the thiol (and cysteine ethyl ester) to form a Tc^V complex which involves both *S*- and *N*-co-ordination of the amino-acid. The rate law is first order with respect to both $[Tc^{VII}]$ and [RSH]. A hydrogen-ion dependence observed is attributed to the formation of pertechnic acid, the rate-determining step being the nucleophilic attack by the thiol at the metal centre of $HTcO_4$. The oxidation of RSH (R = Et, Pr, or Bu) has been studied over the range 20—40 °C in aqueous alkaline solutions in the presence of metal phthalocyanines.[61] The reaction is zero order with respect to [thiol], first order in phthalocyanin and decreases in the order $M = Co > Mn > V > Fe^{III}$. No effects are observed from the nature of the alkali cation.

Varying kinetic dependences on hydroxide ion concentration have been identified in the oxidation of mandelic acid by osmium(VIII).[62] Although extensive data are available on osmium-catalysed systems, relatively little is known on the nature of the ion as an independent oxidant. The reaction mechanism may be written as in Scheme 6. The kinetic order is unity with respect to oxidant and organic substrate, indicating an ester intermediate of low thermodynamic stability. The change in order of $[OH^-]$ from two to zero on increasing hydroxide ion is not, however, satisfactorily explained.

[59] M. Woods, C. A. Hoenich, and J. C. Sullivan, *J. Inorg. Nuclear Chem.*, 1978, **40**, 1907.
[60] H. Spies, B. Johannsen, R. Muenze, and K. Unverferth, *Z. anorg. Chem.*, 1978, **447**, 215.
[61] Yu. M. Afanas'ev, A. V. Gladkii, L. F. Sokolina, and V. A. Borodataya. *Zhur. priklad. Khim.*, 1979, **52**, 408 (*Chem. Abs.*, 1979, **91**, 27 998x).
[62] B. L. Chandwani and G. D. Menghani, *J. Inorg. Nuclear Chem.*, 1978, **40**, 1946.



Scheme 6

Thallium(III) acetate has been used as the reactant in the oxidative hydrolysis of aldoximes RCH=NOH (R=Me, Et, Pr, or Ph) to the corresponding ketones.[63] The reactions were studied in 50% aqueous acetic acid with a rate law Rate=k_2[Tl^{III}] [oxime]. A rate-limiting decomposition of an outer-sphere complex to yield an iminoxyl radical is considered to take place prior to further hydrolysis.

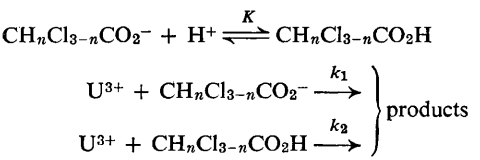
Mixed complex formation has been postulated in the oxidation of sulphite catalysed by transition-metal ions.[64] Several reactions are observed in the presence of copper(II). The auto-oxidation rate is catalysed with formation of the species $[Cu(SO_3)_2O_2]^{3-}$ as intermediate. In the presence of propan-2-ol (ROH), however, an inhibition reaction, dependent on $[SO_3^{2-}]$ and [ROH], is observed. Induced oxidation of the inhibitor by copper(II) is also a factor, the rate being a function of $[Cu^{II}]$. In the latter system the complex $[Cu(SO_3)(ROH)O_2]^-$ is considered as the reactive species.

11 Metal Ions as Reductants

Two parallel paths have been identified in the reduction of monochloro- and dichloro-acetic acids by uranium(III).[65] The reactions have been studied in various binary alcohol–water mixtures as well as in aqueous media. Under the latter conditions the rate may be described by

$$-d[U^{3+}]/dt=(k_1 + k_2K[H^+])\,[U^{3+}]\,[CH_nCl_{3-n}CO_2H]/(1 + K[H^+])$$

in accord with the scheme



For $n=1$, $k_1=0.8\ M^{-1}\ s^{-1}$ and $k_2=0.22\ M^{-1}\ s^{-1}$ respectively. In mixtures of water with MeOH, EtOH, Pr^iOH, and Bu^tOH the dependence of the overall second-order rate constant on mole fraction of the alcohol shows both a minimum

[63] T. Balakrishnan and M. Sankappa, *J. Indian Chem. Soc.*, 1978, **55**, 1014.
[64] S. Lunak, A. El-Wakil, and J. Vepřek-Šiška, *Coll. Czech. Chem. Comm.*, 1978, **43**, 3306.
[65] L. Adamciķova and L. Treindl, *Coll. Czech. Chem. Comm.*, 1979, **44**, 401.

and a maximum. The influence on reaction rate from solvent composition and structure is considered to be more important than dielectric constant changes although the reactions are considered to be outer sphere in character.

The stoicheiometric oxidations of both cobalt(II) and manganese(II) acetates in aqueous acetic acid by *m*-chloroperbenzoic acid[66] are non-free-radical processes. In the cobalt(II) reaction, the rapid pink $Co^{II} \rightarrow$green Co^{III} colour change observed occurs in two stages, (*a*) pink to apple green, followed by a slower conversion (*b*) to give a stable olive-green product. For (*a*) the process is first order in per-acid and second order in Co^{II} whereas in (*b*) in excess oxidant the reaction is first order in the apple-green species. A mechanism consistent with these observations is

$$2Co^{II} \rightleftharpoons [Co^{II}]_2$$

$$ClC_6H_4CO_3H + [Co^{II}]_2 \longrightarrow ClC_6H_4CO_2H + [Co^{III}]_2^{I}$$

$$[Co^{III}]_2^{I} \longrightarrow [Co^{III}]_2^{II}$$

where I and II are the intermediate and stable complexes respectively. In the corresponding reaction of Mn^{II}, however, a two-electron process,

$$Mn^{II} + ClC_6H_4CO_3H \longrightarrow Mn^{IV} + ClC_6H_4CO_2H$$

is considered to account for the slow initiation of an autocatalytic sequence involving

$$Mn^{IV} + Mn^{II} \rightleftharpoons [Mn^{III}]_2$$

$$[Mn^{III}]_2 + ClC_6H_4CO_3H \longrightarrow 2Mn^{IV} + ClC_6H_4CO_2H$$

Preferential reaction thus appears to take place *via* metal dimers in both systems.

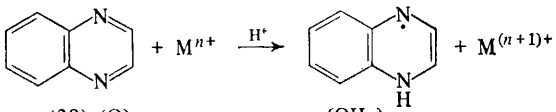
Ligand transfer has been suggested as the initial step in the reduction of aromatic aldehydes by Cr^{II} in acid solution.[67]

The reaction of nitrosylpenta-ammineruthenium(II) with RNH_2 (R = Me or Et) may be written[68] as

$$[Ru(NH_3)_5NO]^{3+} + 2RNH_2 \longrightarrow [Ru^{II}(NH_3)_5N_2]^{2+} + ROH + RNH_3^+$$

The dinitrogen complex formation is considered to take place *via* a series of steps including interaction of the electrophilic NO^+ with the nucleophilic NH_2 group of the free amine and elimination of water to form a co-ordinated diazonium ligand with subsequent ligand redox to the observed ruthenium product.

The reduction of quinoxaline (29) with V^{II}, Eu^{II}, or Ti^{III} in 1.2M-$HClO_4$ yields the strongly absorbing quinoxalinium radical (QH·), which under favour-



(29) (Q) (QH·)

[66] G. H. Jones, *J.C.S. Chem. Comm.*, 1979, 536.
[67] B. Reddy, R. Siva, and S. Rajam, *Indian J. Chem. Sect. A*, 1978, **16**, 878.
[68] C. P. Guengerich and K. Schug, *Inorg. Chem.*, 1978, **17**, 1378.

able conditions persists for over an hour in aqueous media.[69] The reactions with $M = Eu^{2+}$ or Ti^{3+} are inner sphere whereas the vanadium(II) reduction proceeds *via* an outer-sphere path. Rate data are presented in Table 3, where it is seen that the specific rate for reaction of V^{II} far exceeds the substitution-controlled upper

Table 3 *Redox reactions of metal-ion complexes*

Reaction	k_2[a]	*Ref.*
Np^{VI} + ascorbate[b]	1.23×10^5[b]	65
$Eu^{2+} + Q$[c,d]	$> 2.5 \times 10^4$	77
$V^{2+} + Q$[c,d]	1.7×10^3	77
$Ti^{3+} + Q$[c,d]	0.44	77
$QH\cdot + [(H_3N)_5CoBr]^{2+}$[c,d]	9.0[e]	77
$QH\cdot + [(H_3N)_5CoBr]^{2+}$[c,d]	8.3[f]	77

[a] $M^{-1}\ s^{-1}$. [b] $\Delta H^{\ddagger} = 7.0$ kcal mol^{-1}; $\Delta S^{\ddagger} = -11.7$ cal $K^{-1}\ mol^{-1}$. [c] $[H^+] = 1.00M$, $I = 1.00M$. [d] Q = quinoxaline, QH· = quinoxalinium radical. [e] Eu^{2+} present as initial reductant in QH· formation. [f] V^{2+} as initial reductant.

limit for inner-sphere reactions of this reagent. The stability of the radical has permitted investigation of its oxidation by $[(H_3N)_5CoBr]^{2+}$. The reaction is first order in both $[Co^{III}]$ and [QH·] and the rate is unaffected by addition of Eu^{3+} or V^{3+}, indicating that the reductant is the radical itself rather than a small amount of reducing metal ion in dynamic equilibrium with it (see above). In the case of the Ti^{III}–Ti^{IV} system, however, the lower rate observed may be attributed to an interaction between the radical and Ti^{IV}. Since bromide is formed,

$$QH\cdot + [(H_3N)_5CoBr]^{2+} + 4H^+ \longrightarrow Q + 5NH_4^+ + Co^{II} + Br^-$$

rather than a product in which the bromine is bound to the benzene ring, the oxidation takes place *via* an outer-sphere mechanism.

12 Processes Involving Redox of a Ligand

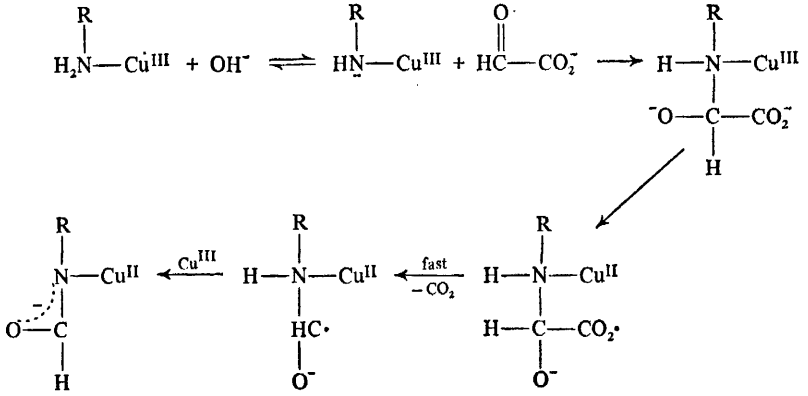
Co-ordinated oxalate is oxidized by thallium(III),[70]

$$[CrL_2(ox)]^+ + Tl^{III} \longrightarrow Tl^I + [CrL_2(OH_2)_2]^{3+} + 2CO_2$$

(L = phen or bipy), when the rate is considerably greater than that for the acid-catalysed aquation. A similar process is observed with Ce^{IV} and Fe^{III} as oxidants. The mechanism is considered to involve the formation of a bridged oxalato intermediate and a rate-determining electron transfer to the oxidizing cation. No aquation was detected on replacement of these metal ions by Zn^{II}, Cd^{II}, Hg^{II}, or $[Fe(bipy)_3]^{3+}$. In the latter case, there is sufficient oxidizing power for the reaction to proceed but the mechanism is limited to an outer-sphere route. Oxidative decarboxylation has also been investigated in a deprotonated copper(III) peptide complex.[71] The reversible deprotonation of the amine terminus of copper(III) peptides is known to take place in basic media. In the presence of glyoxylate ion ($CHOCO_2^-$) rapid reduction of the metal centre and elimination of CO_2 are observed. The initial step involves the nucleophilic

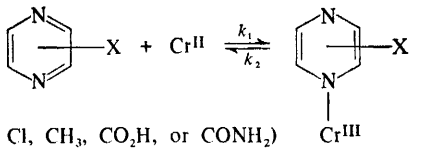
[69] C.-R. Chang, S. J. Paton, E. Gelerinter, and E. S. Gould, *Inorg. Chem.*, 1979, **18**, 1294.
[70] O. Farver and G. Nord, *Acta Chem. Scand.*, 1978, **A32**, 963.
[71] S. T. Kirksey and D. W. Margerum, *Inorg. Chem.*, 1979, 966.

attack of the amide on glyoxylate to yield an adduct which then undergoes internal electron transfer (Scheme 7). The two-electron transfer from Cu^{III} to Cu^{I} cannot, however, be ruled out.



Scheme 7

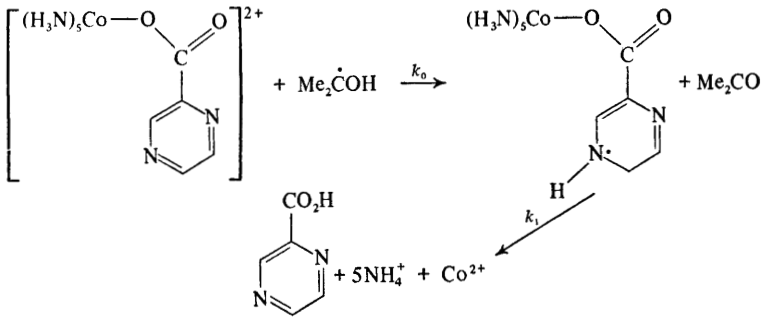
The reaction between cobalt(II) and pyridine-2-aldoxime takes place in several steps.[72] The initial rapid complex formation is followed by a rate-determining redox reaction where oxidation of the cobalt(II) by the ligand provides a route to an inert cobalt(III) species. The mode of reaction of some chromium(III)-bound pyrazine radicals with cobalt(III) complexes has been clarified.[73] In the reaction shown in equation (3) the green complexed radicals formed have been



(X = Cl, CH_3, CO_2H, or $CONH_2$) (3)

identified using e.s.r. techniques. The rates of dissociation (k_2) are considerably lower than for chromium(II) species but several orders of magnitude above the heterolysis rates for chromium(III) complexes in water, suggesting that the rate-determining step is the rate of internal electron transfer within the radical cation. Reactions with cobalt(III) complexes have been shown to proceed not by an electron transfer involving the radical but with the small concentrations of free [Cr^{II}] in equilibrium with this species. Reaction of propan-2-ol radical with cobalt(III) pyrazinecarboxylato-complexes[74] leads to the formation of ligand radical species which can undergo intramolecular electron transfer, *e.g.* Scheme 8. k_0 is independent of pH but the first-order reaction (k_1) is

[72] G. Bazsa, H. G. Shinouda, and M. T. Beck, *J. Inorg. Nuclear Chem.*, 1978, **40**, 1665.
[73] M. Y. Wu, S. J. Paton, Y. T. Fanchiang, E. Gelerinter, and E. S. Gould, *Inorg. Chem.*, 1978, **17**, 326.
[74] K. Wieghardt, H. Cohen, and D. Meyerstein, *Angew. Chem. Internat. Edn.*, 1978, **17**, 608.



Scheme 8

hydrogen-ion dependent. The ligand-radical species may be protonated,

$$Co^{III}\dot{L}H_2 \rightleftharpoons Co^{III}\dot{L}H + H^+$$

and both complexes undergo internal redox, the doubly protonated species being more slow to react. Reaction of organocobal(III)oximes with $[IrCl_6]^{2-}$ or Ce^{IV} results in the formation[75] of cobalt(IV) complexes $[RCo^{IV}(dmgH)_2(OH_2)]^+$ (CoR^+) which have been confirmed as having this description rather than the $[Co^{III}—R\cdot]^+$ structure. The latter is suggested (on n.m.r. evidence) for the corresponding nitrosalicylato-species.[76] Decomposition of the cobalt(IV) oximes may occur in several ways. In 80 vol% aqueous methanol, first-order kinetics are observed for the rate of loss of $[C_6H_5CH_2Co^+]$, $[iso\text{-}C_3H_7Co^+]$, and $[2\text{-}C_8H_{17}Co^+]$. In typical experiments approximately 10—20% of the cobalt could be recovered in the +3 oxidation state (CoR) with the remainder as cobalt(II). Also, in the case of the benzyl (*a*) and 2-octyl (*b*) species, there is

$$[RCo(dmgH)_2(OH_2)]^+ \xrightarrow[-H_2O]{H^+} \begin{cases} Co^{II} + 2(dmgH_2) + ROH & (a) \\ Co^{II} + 2(dmgH_2) + R_{-H} & (b) \end{cases}$$

evidence for both alcohol and 1- and/or 2-octene (R_{-H}) formation. In the presence of *ca.* 2.5M-HCl the latter reaction is accompanied by about 25% chloride-induced nucleophilic decomposition,

$$[RCo(dmgH)_2(H_2O)]^+ + Cl^- \xrightarrow{H^+} Co^{II} + 2(dmgH_2) + RCl$$

in which there is inversion of configuration at the cobalt-bound carbon atom.[77]

[75] J. Halpern, M. S. Chan, T. S. Roche, and G. M. Tom, *Acta Chem. Scand.*, 1978, **A33**, 141.
[76] Y. Yamamoto, *Bull. Chem. Soc. Japan*, 1978, **51**, 2894.
[77] M. D. Johnson, *Accounts Chem. Res.*, 1978, **11**, 57

4

Reactions between Two Non-metallic Compounds

BY A. McAULEY

1 Dioxygen with Sulphite

Several papers have appeared dealing with aspects of S^{IV} chemistry in reaction with O_2. The rates of oxidation of sulphur dioxide by oxygen [1] have been studied in buffered media over the pH range 4—12, the overall expression being of the form

$$d[SO_4^{2-}]/dt = (k_1 + k_2[H^+]^{0.5} + k_3 P_{O_2}[H^+]^{-1})[SO_3^{2-}]$$

and in acidic conditions there is a zero-order $[O_2]$ dependence. The rate of absorption of dioxygen by SO_3^{2-} in the presence of Co^{II} reaches a limiting value [2] dependent on catalyst concentration. Under these conditions reaction orders with respect to $[SO_3^{2-}]$ and $[O_2]$ are zero and two respectively. Using electrochemical techniques, it has been shown [3] that the first transition-row divalent metal ions act as catalysts for the oxidation of sulphite when present at concentrations below micromolar. If $[M^{2+}] > 10^{-4}$M, however, inhibition of the reaction is observed. A radical chain mechanism has been proposed in this case. From the foregoing it is evident that processes involved in these reactions are not well understood and there is a need for additional studies of these reactions, which have considerable significance in commercial and environmental terms.

2 Reactions of Peroxodisulphate

Oxidation rates involving this anion are usually slow and in many instances the rate-determining step is the homolytic cleavage of the O—O bond. The presence of a metal cation may increase the rate although the mode of reaction and the rate law vary with the nature of M^{n+}. The copper(II)-catalysed oxidation of succinic acid proceeds [4] according to the rate law:

$$\text{Rate} = \{k_1 + k_2[Cu^{II}]^{1/2}\}[S_2O_8^{2-}]$$

where k_1 refers to the cleavage reaction and k_2 to the catalytic pathway. The zero-order dependence on reductant is a feature noted previously in these systems. A radical mechanism is involved, with H^+ and O_2 decreasing the reaction rate.

[1] T. V. Larson, N. R. Horike, and H. Halsread, *Atoms. Environ.*, 1978, **12**, 1597.
[2] N. Sathyamurthy, T. E. Degaleesan, K. Chandrasekharan, and G. S. Ladda, *Can. J. Chem. Eng.*, 1979, **57**, 145 (*Chem. Abs.*, 1979, **90**, 193 062).
[3] L. A. Kiseleva and Y. U. Orlov, *J. Gen. Chem. USSR* (*Engl. Trans.*), 1978, **48**, 1673.
[4] S. C. Agarwal, P. S. Pal, and V. B. Agarwal, *Bull. Soc. Chim. Fr.*, 1979, Part 1, 43.

A Cu^{II}–succinate (CuL_2) complex is postulated which may undergo oxidation to a transient Cu^{III} species, *e.g.*

$$S_2O_8^{2-} \xrightarrow{k_1} 2SO_4^{\cdot -}$$

$$CuL_2 + SO_4^{\cdot -} \longrightarrow Cu^{III}L_2 + SO_4^{2-}$$

$$Cu^{III}L_2 \longrightarrow Cu^{II}L^+ + L^{\cdot}$$

The hydrogen ion dependence is attributed to the inhibition of formation of the copper complex but the mechanism will hold only if $[L] \gg [Cu^{II}]$. A similar half-order dependence on Cu^{II} is exhibited in the corresponding oxidation of glycollic acid.[5] In this instance, however, the copper complex $[Cu(gly)_2]$ is involved directly in a redox reaction with the oxidant:

$$[Cu(gly)_2] + S_2O_8^{2-} \longrightarrow [Cu^{III}(gly)_2]^+ + SO_4^{\cdot -} + SO_4^{2-}$$

A feature of both systems is the autocatalysis by $SO_4^{\cdot -}$ and $CO_2^{\cdot -}$ (derived from the reductant) radicals. A simple rate law is observed in the Ag^I-catalysed oxidation of aspartic acid[6] ($Rate = k_a[S_2O_8^{2-}][Ag^I][Asp]^0$). Medium effects are important with inhibition by ions in the order $Mg^{2+} > K^+ > Na^+ > H^+$ and $NO_3^- > SO_4^{2-}$. The uncatalysed oxidations of glyoxal[7] and glyoxylic acid[8] have also been investigated. Potassium ruthenate (K_2RuO_4), which can be readily prepared from reaction of ruthenium trichloride with aqueous persulphate, can be used catalytically in the presence of $S_2O_8^{2-}$ for the oxidation of organic substrates under mild conditions.[9] RuO_4^{2-} is considered to act as a two-electron oxidant.

Catalysis by cobalt(II) has been observed in the oxidation of iodide by peroxodisulphate,[10] the mechanism involving formation of the reactant complex CoI^+. It is perhaps of interest that this is the first paper concerned with a redox mechanism that the Reporter has seen from this source.

3 Reactions of Peroxodiphosphate

Copper(II)-ion catalysis has been shown to take place in the oxidation of iodide by peroxodiphosphate.[11] The results conform to the rate law

$$Rate = k_a[P_2O_8^{4-}][H^+] + k_b[P_2O_8^{4-}][Cu^{II}]^2[I^-]/[H^+]; (k_a = k_c[I^-] + k_d)$$

In most kinetic studies involving this oxidant, a rate-determining hydrolytic path has been proposed. This pathway is evident in the present investigation (k_d) and k_c is the rate constant for the uncatalysed pathway,

$$H^+ + P_2O_8^{4-} \rightleftharpoons HP_2O_8^{3-} + I^- \xrightarrow{k_c} \text{products}$$

With copper(II) present, there is spectrophotometric evidence for complex

[5] S. C. Agarwal and L. K. Saxena, *Indian J. Chem., Sect. A*, 1978, **16**, 602.
[6] S. P. Srivastava, S. K. Singhal, and B. B. L. Mathur, *Indian J. Chem., Sect. A*, 1978, **16**, 899.
[7] W. C. Vasudeva, A. Hossady, S. N. Srivastava, and S. Wasif, *Z. Phys. Chem. (Leipzig)*, 1978, **259**, 825.
[8] W. C. Vasudeva, Z. Sherif, and A. Hossady, *Libyan J. Sci.*, 1977, **7B**, 24 (*Chem. Abs.*, 1979, **90**, 137 057).
[9] M. Schroder and W. P. Griffith, *J. Chem. Soc. Chem. Commun.*, 1979, 59.
[10] M. Zhu and R.-H. Jzu, *Hua Hsueh Tung Pao*, 1979, **1**, 38 (*Chem. Abs.*, 1979, **91**, 45 023).
[11] L. M. Bhardwaj, D. N. Sharma, and Y. K. Gupta, *Inorg. Chem.*, 1978, **17**, 2469.

formation and the second-order dependence on metal ion is attributed to the pre-equilibrium

$$HP_2O_8^{3-} + 2Cu^{II} \rightleftharpoons [CuHP_2O_8\,Cu]^-$$

followed by the reaction of the 2:1 complex with iodide. The role of the copper ion appears to be to lower the activation barrier by formation of the complex since there is no evidence for a Cu^{II}–Cu^{I} cycle in the system. The phosphate ion radical PO_4^{2-} has been reported in the oxidation of iron(II) complexes but no evidence was found for its production in the present study.

4 Reactions of Halate Ions

The kinetics and mechanisms of some reactions of aqueous bromite have been reported.[12] In the reaction with iodide in alkaline solution,

$$3BrO_2^- + 2I^- \longrightarrow 3Br^- + 2IO_3^-$$

the rate law is of the form

$$-1/3d[BrO_2^-]/dt = (k_1 + k_2[OH^-]^{-1})[BrO_2^-][I^-]$$

The hydroxide-ion dependent pathway probably reflects a reaction of bromous acid although thermodynamic data are not yet available for the ionization of this acid. The second route involves the reaction

$$BrO_2^- + I^- \xrightarrow{k_1} BrO^- + IO^-$$

with k_1 (25 °C) $= 2.75 \times 10^5$ M^{-1} s^{-1} and $\Delta S_1 = -169$ J K^{-1} mol^{-1}. A second oxygen transfer completes the reduction to bromide,

$$BrO^- + I^- \xrightarrow{\text{rapid}} Br^- + IO^-$$

and the known decomposition of hypoiodite ions to iodate and iodide may follow, although the further oxidation ($BrO_2^- + IO^- \rightarrow Br^- + IO_3^-$) is thermodynamically feasible. A similar rate law and oxygen transfer mechanism are postulated for the corresponding reaction of sulphite although for thiosulphate a more complex reactivity pattern is apparent.

The reaction of chlorine dioxide and sulphur(IV) has been investigated[13] in the pH range 8—13 (phosphate and borate buffers), where in the presence of a slight excess of S^{IV} (sulphite) the major products are chlorite and sulphate ions with only miorr amounts of chloride and chlorate formed. In the overall reaction,

$$nClO_2 + mS^{IV} \longrightarrow pClO_2^- + qClO_3^- + rCl^- + mSO_4^{2-}$$

the coefficients n, m, p, q, and r are dependent on pH and the specific buffer solution used. Several hydroxide-ion catalysed pathways are invoked, the reaction

$$2ClO_2 + S^{IV} + 2OH^- \longrightarrow 2ClO_2^- + SO_4^{2-} + H_2O$$

predominating at high pH. The overall reaction is first order with respect to both $[ClO_2]$ and $[S^{IV}]$ and the absence of any higher-order term in the latter in the pH

[12] C. L. Lee and M. W. Lister, *Can. J. Chem.*, 1979, **57**, 1524.
[13] K. Suzuki and G. Gordon, *Inorg. Chem.*, 1978, **17**, 3115.

range 7—11 is consistent with the absence of dithionate ion as product. The reaction scheme

$$S^{IV} + ClO_2 \xrightarrow{k_1} S^V + ClO_2^-$$

$$S^V + ClO_2 \xrightarrow{k_2} SO_4^{2-} + ClO_2^-$$

$$S^{IV} + ClO_2 \xrightarrow{k_3} SO_4^{2-} + Cl^{II}$$

$$Cl^{II} + S^V \xrightarrow{k_4} SO_4^{2-} + OCl^-$$

$$S^{IV} + OCl^- \xrightarrow{k_5} Cl^- + SO_4^{2-}$$

accounts for the variation in the stoicheiometry. The initial one-electron transfer reaction is the primary process. The chlorine(II) radical is formed *via* a two-electron transfer. The small amount of chlorate ion derives from an alternative reaction of Cl^{II} with ClO_2 or ClO_2^-. Chlorine dioxide is thermodynamically a more powerful oxidant than ClO_2^-.

Formate ions are oxidized to carbonate by bromite[12] in the overall reaction

$$BrO_2^- + 2HCO_2^- + 2OH^- \longrightarrow Br^- + 2CO_3^{2-} + 2H_2O$$

The rates of reaction (monitored by loss of Br^V) show acceleration initially before slowing down, the catalytic agent being the CO_3^{2-} produced. The mechanism proposed is written as

$$2BrO_2^- \xrightarrow{k_1} BrO^- + BrO_3^-$$

$$BrO^- + BrO_2^- \xrightarrow{k_2} BrO_3^- + Br^-$$

$$BrO_2^- + HCO_2^- \xrightarrow{k_3} BrO^- + HCO_3^-$$

$$BrO^- + HCO_2^- \xrightarrow{k_4} Br^- + HCO_3^-$$

$$HCO_3^- + OH^- \xrightarrow{\text{fast}} CO_3^{2-} + H_2O$$

and hypobromite ions react much faster than bromite.

The pH dependence and mechanism of oxidation of iodide by chloramine-T have also been described.[14] Palladium(II) has been shown to be a catalyst in the oxidation of chloride by manganese(III).[15] The complex $MnCl^{2+}$ is formed during the reaction possibly *via* a chloride-bridged dinuclear intermediate with the catalyst. There is also evidence for Pd^{IV} formation.

Methanol is oxidized by aqueous Br_2 in alkaline solutions.[16] The reaction order is unity with respect to oxidant and reductant. Hydroxide ion promotes the reaction at lower concentrations but acts as an inhibitor as $[OH^-]$ is increased.

[14] J. M. Antelo, F. Arce, A. Varela, and J. M. Cachaza, *Acta Cienc. Compostelana*, 1979, **16**, 55 (*Chem. Abs.*, 1979, **91**, 63 312).
[15] L. P. Tikhonova and S. N. Barkovets, *Russ. J. Inorg. Chem.* (*Engl. ransl.*), 1978, **23**, 1687.
[16] S. Bharat, P. K. Saxena, M. Richards, K. N. Srivastava, and B. Krishna, *Acta Cienc. Indica*, 1978 **4**, 138 (*Chem. Abs.*, 1979, **90**, 44 474).

5 Reactions of Hydrazine with Iodine

The oxidation of hydrazine by iodine has been re-investigated in perchloric acid media.[17] This system has been studied previously but with conflicting results, especially in the $[I^-]$-dependence term. Over the pH range 1.5–9.0, the stoicheiometry is consistent with the reaction

$$2I_2 + N_2H_5^+ \longrightarrow N_2 + 4I^- + 5H^+$$

The rate law may be expressed as

$$-0.5d[I_2]_{tot}/dt = k_1K_a[N_2H_5^+]_{tot}[I_2]_{tot}/[H^+](1 + K_1[I^-])(1 + k_{-1}[I^-]/k_2)$$

and may be derived from the steady-state mechanism

$$I_2 + N_2H_4 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2H_4I^+ + I^-$$

$$N_2H_4I^+ \xrightarrow{k_2} \text{products}$$

and the rapid equilibria

$$I_2 + I^- \rightleftharpoons I_3^- \ (K_1)$$

$$N_2H_5^+ \rightleftharpoons N_2H_4 + H^+ \ (K_a)$$

A $[H^+]$-independent term suggested previously is not substantiated, and mechanistically the involvement of iodide both in non-productive equilibria and in the steady-state production of intermediates is explained.

6 Reactions of Xenon Difluoride

The reaction of phenol with aqueous xenon difluoride has been investigated at pH 3—4, the primary stable product being *p*-benzoquinone.[18] Under these conditions, the rate of consumption of XeF_2 in water is independent of the substrate present. The initial hydrolysis reaction is followed by a series of rapid redox steps depending on the substrate present:

$$XeF_2 \xrightarrow[k_1]{H_2O} XeO \xrightarrow[k_2]{H_2O} H_2O_2 \xrightarrow{XeF_2} 2HF + Xe + O_2$$

$$XeO \xrightarrow[k_3]{PhOH} H_2Q \xrightarrow{k_4} Q$$

where QH_2 and Q represent hydroquinone and quinone respectively. A similar reaction scheme holds for the oxidation of allyl alcohol. Formation of radicals is confirmed and $k_2/k_3 = 1.2 \times 10^{-5}$ in keeping with the preferential oxidation of the phenol.

[17] S. E. King, J. N. Cooper, and R. D. Crawford, *Inorg. Chem.*, 1978, **17**, 3306.
[18] A. A. Goncharov and Y. N. Kozlov, *Russ. J. Phys. Chem.* (*Engl. Transl.*), 1978, **52**, 539.

5
Pulse Radiolysis Studies

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1 Introduction

The contribution of pulse radiolysis to redox chemistry in aqueous solution continues to grow as the potential of this powerful and versatile technique becomes more widely recognized and utilized. A major development in recent years has been the use of fast digital signal recorders linked to on-line computing facilities which permit the unravelling of kinetically complex sequences of fast reactions and the identification of the nature and role of transient intermediates. In this respect increasing attention is being paid to the measurement of conductivity changes, in conjunction with optical kinetic spectroscopy, which pinpoint the uptake or release of protons in redox processes as well as the state of hydrolysis of metal ions in unstable oxidation states.

This chapter covers all topics studied by pulse radiolysis which are relevant to this Report. The material is divided into sections, the main themes of which are (i) the reactions of inorganic free radicals, (ii) systems involving non-metallic compounds, (iii) aquo-metal ions in unusual oxidation states, (iv) reactions of transition-metal complexes, and (v) metalloproteins and related systems.

Extensive compilations of rate constants for the reactions of metal ions in unusual valency states[1] and of inorganic free radicals[2] in aqueous solution have appeared, as well as short reviews on pulse radiolysis studies in general chemistry[3] and on complexes of metal ions in unstable oxidation stages.[4]

2 Reactions of Inorganic Free Radicals

Inorganic free radicals are receiving increasing attention as mechanistic probes of one-electron redox processes. Comparison of their rates of reaction with substrates helps to distinguish between electron transfer, hydrogen-atom abstraction, and free-radical addition. The greater selectivity of oxidizing radicals such as $Br_2^{\cdot -}$ and $(SCN)_2^{\cdot -}$, as compared with $^{\cdot}OH$, in their reactions with amino-acids for example, has proved valuable in identifying crucial residues in the active sites of a number of enzymes.[5]

[1] G. V. Buxton and R. M. Sellers, 'Compilation of Rate Constants for the Reactions of Metal Ions in Unusual Valency States', NSRDS – NBS 62.
[2] A. B. Ross and P. Neta, 'Rate Constants for Reactions of Inorganic Radicals in Aqueous Solutions', NSRDS – NBS 65.
[3] J. H. Baxendale and M. A. J. Rodgers, *Chem. Soc. Rev.*, 1978, **7**, 235.
[4] D. Meyerstein, *Accounts Chem. Res.*, 1978, **11**, 43.
[5] G. E. Adams, R. H. Bisby, R. B. Cundall, J. L. Redpath, and R. L. Willson, *Radiat. Res.*, 1972, **49**, 290.

$CO_3^{\bullet-}$.—Combined conductivity and kinetic spectroscopy measurements lead to the conclusion that the bimolecular reaction between two $CO_3^{\bullet-}$ radicals involves transfer of O^-:

$$CO_3^{\bullet-} + CO_3^{\bullet-} \longrightarrow CO_2 + CO_4^{2-} \quad (1)$$

This is based on pH-dependent changes in conductivitivy which correlate with the rate of hydrolysis of CO_2 in alkaline solution. Other reactions in which CO_2 is formed by this mechanism are between $CO_3^{\bullet-}$ and NO_2, $SO_3^{\bullet-}$, or $^{\bullet}CH_3$.[6] In the last example a long-lived intermediate ($t_{1/2} > 5$ s), postulated to be $CH_3OCO_2^-$, is formed:

$$CO_3^{\bullet-} + {}^{\bullet}CH_3 \longrightarrow CH_3OCO_2^- \quad (2)$$

Analogous, but much shorter-lived, intermediates may be formed in the reactions with NO_2 and $SO_3^{\bullet-}$. So far no examples of O^- transfer to non-radicals has been found.

Reactions of the acidic form of the carbonate radical, $^{\bullet}CO_3H$, with several metal complexes[7] are reported in Section 4.

$SO_4^{\bullet-}$.—Reactions of $SO_4^{\bullet-}$ radicals with alcohols and ethers in aqueous solution occurs by hydrogen-atom abstraction from a C—H bond since the corresponding deuteriated compounds react 2—3 times more slowly.[8] The radical reacts 100 times more slowly than $^{\bullet}OH$ with alcohols which contain H atoms on C_α, and this ratio increases to 10^4 for 2-methylpropan-2-ol where abstraction occurs at C_β. A plot of log $[k(SO_4^{\bullet-} + S)/k(SO_4^{\bullet-} + MeOH)]$ *vs.* log $[k(^{\bullet}OH + S)/k(^{\bullet}OH + MeOH)]$, where S = MeOH, EtOH or Me_2CHOH, is linear with a slope of 3 which demonstrates that $SO_4^{\bullet-}$ is much more sensitive than $^{\bullet}OH$ to inductive effects at C_α, and is in keeping with $SO_4^{\bullet-}$ being a stronger electrophile.

$SeO_4^{\bullet-}$.—The spectrum of this radical has λ_{max} at 525 nm and $\varepsilon_{max} = 610$ M^{-1} cm^{-1}.[9] It is formed by oxidizing SeO_4^{2-} with $^{\bullet}OH$ ($k = 4.1 \times 10^9$ M^{-1} s^{-1}) or $CO_3^{\bullet-}$ ($k = 4.3 \times 10^7$ M^{-1} s^{-1}), and reacts with itself to form unidentified products ($2k = 1.1 \times 10^9$ M^{-1} s^{-1}).

$(SeCN)_2^{\bullet-}$.—This radical has an absorption spectrum with λ_{max} at 440 nm and $\varepsilon_{max} = 9.3 \times 10^3$ M^{-1} s^{-1} in neutral aqueous solution.[10] It reacts at a measurable rate with cysteine ($k = 6.7 \times 10^7$ M^{-1} s^{-1}) but immeasurably slowly, if at all ($k < 10^7$ M^{-1} s^{-1}), with other amino-acids. This selectivity makes it a useful probe for investigating enzymes where cysteine residues are crucial to their function.

$H_2PO_4^{\bullet}$, $HPO_4^{\bullet-}$, $PO_4^{\bullet 2-}$.—The spectral and acid–base properties of these radicals are:[11]

$$\underset{(\lambda_{max}\ 520\ nm,\ \varepsilon_{max}\ 1850\ M^{-1}\ cm^{-1})}{H_2PO_4^{\bullet}} \overset{pK_1\ 5.7}{\rightleftharpoons} \underset{(\lambda_{max}\ 510\ nm,\ \varepsilon_{max}\ 1550\ M^{-1}\ cm^{-1})}{HPO_4^{-\bullet}} \overset{pK_2\ 8.9}{\rightleftharpoons} \underset{(\lambda_{max}\ 530\ nm,\ \varepsilon_{max}\ 2150\ M^{-1}\ cm^{-1})}{PO_4^{\bullet 2-}}$$

[6] J. Lilie, R. J. Hanrahan, and A. Henglein, *Radiat. Phys. Chem.*, 1978, **11**, 225.
[7] V. W. Cope, M. Z. Hoffman, and S. Chen. *J. Phys. Chem.*, 1978, **82**, 2665.
[8] H. Elbenberger, S. Steenken, P. O'Neill, and D. Schulte-Frohlinde, *J. Phys. Chem.*, 1978, **82**, 749.
[9] M. S. Subhani and M. Khalid, *Rev. Roumaine Chim.*, 1978, **23**, 1117.
[10] R. Badiello and M. Tamba, *Radiochem. Radioanalyt. Letters*, 1979, **37**, 165.
[11] P. Maruthumuthu and P. Neta, *J. Phys. Chem.*, 1978, **82**, 710.

Rate constants for reactions of these radicals with several inorganic compounds have been measured and compared[11] with the corresponding reactions of $SO_4^{\bullet-}$ and ·OH. For inorganic compounds which contain abstractable H atoms, *e.g.* $H_2PO_3^-$, HPO_3^{2-}, N_2H_4, NH_2OH, *etc.*, the order of reactivity is $\cdot OH > SO_4^{\bullet-} \sim H_2PO_4^{\bullet-} > HPO_4^{\bullet-} \sim PO_4^{\bullet 2-}$, and $HPO_4^{\bullet-}$ is slightly more selective than $SO_4^{\bullet-}$. This order of reactivity is similar to that observed for reaction of these radicals with alcohols,[12] so it is likely that the mechanism is one of H-atom abstraction.

For inorganic anions which do not contain abstractable hydrogen the pattern of reactivity is quite different. In this case the redox potentials of both radical and substrate are important. Strongly reducing anions such as SO_3^{2-}, N_3^-, and I^- react rapidly with all the radicals, but weaker reductants such as Br^- and Cl^- suggest that the oxidation potentials of the radicals decrease in the order $SO_4^{\bullet-} > HPO_4^{\bullet-} > PO_4^{\bullet 2-}$. Oxidation of OH^- by $SO_4^{\bullet-}$ and $H_2PO_4^\bullet$ indicates that these radicals are stronger oxidants than ·OH.[11] Because of this it is suggested[11] that the reaction of ·OH with anions such as NO_2^- and SO_3^-, which is faster than that of $SO_4^{\bullet-}$, involves ·OH addition, as in the case of halides and pseudohalides, rather than electron transfer.

$Cl_2^{\bullet-}$.—This radical may abstract hydrogen, add to unsaturated compounds, or oxidize by electron transfer. Extensive measurements of rate constants for its reaction with aliphatic, aromatic, and inorganic compounds have helped to clarify the relative importance of these reaction modes.[13]

Rate constants for H-atom abstraction by $Cl_2^{\bullet-}$ from organic compounds are generally smaller than, but show a similar pattern to, those for the hydrogen atom itself. This shows that the energy of the C—H being broken is a controlling factor. With amino-acids, however, $Cl_2^{\bullet-}$ and H· react at similar rates, so it seems unlikely that $Cl_2^{\bullet-}$ reacts only by H-atom abstraction in this case.

Like H· and ·OH, $Cl_2^{\bullet-}$ adds to olefinic compounds but the rate is lower and depends strongly on substituent groups attached directly to the double-bonded carbon; for example, cyano- and carboxy-groups are strongly inhibiting. Thus $Cl_2^{\bullet-}$ shows a greater selectivity than either ·OH or H· which react at nearly diffusion-controlled rates.

The reaction of $Cl_2^{\bullet-}$ with aromatic compounds can occur through addition to the benzene ring ($k \leqslant 10^7$ M^{-1} s^{-1}),[13] but the important reaction is direct oxidation by electron transfer which becomes possible when the ring is substituted with OH, OMe, NH_2, or related groups ($k > 10^8$ M^{-1} s^{-1}).[13]

In its reactions with inorganic compounds $Cl_2^{\bullet-}$ abstracts hydrogen from substrates such as H_2O_2, NH_2OH, and N_2H_4 ($k \approx 10^5$—10^7 M^{-1} s^{-1}) and oxidizes anions by electron transfer ($k \approx 10^7$—10^9 M^{-1} s^{-1}).[13] Cl_2^- abstracts hydrogen 10—100 times more slowly than $SO_4^{\bullet-}$ and $HPO_4^{\bullet-}$, but oxidizes by electron transfer at rates intermediate between those of $SO_4^{\bullet-}$ and $HPO_4^{\bullet-}$. Thus the order of oxidation potentials may be written as $SO_4^{\bullet-} > Cl_2^{\bullet-} > HPO_4^{\bullet-}$.

$Br_2^{\bullet-}$.—In aqueous solutions containing micelles of hexadecyltrimethylammonium bromide the reaction

$$Br_2^{\bullet-} + Br_2^{\bullet-} \longrightarrow Br_2 + 2Br^- \qquad (3)$$

[12] P. Maruthumuthu and P. Neta, *J. Phys. Chem.*, 1977, **81**, 1622.
[13] K. Hasegawa and P. Neta, *J. Phys. Chem.*, 1978, **82**, 854.

is retarded.[14] This is attributed to occurrence of

$$Br_2^{\bullet-} + Br_2^{\bullet-}(\text{mic}) \longrightarrow Br_2 + 2Br^- \quad (4)$$

$$Br_2^{\bullet-}(\text{mic}) + Br_2^{\bullet-}(\text{mic}) \longrightarrow Br_2 + 2Br^- \quad (5)$$

where $Br_2^{\bullet-}$(mic) represents $Br_2^{\bullet-}$ adsorbed at the micelle. Below the critical micellar concentration (c.m.c.) the observed rate constant ($2k$) for dismutation of $Br_2^{\bullet-}$ is $2k_3$; above the c.m.c. $2k$ decreases. Kinetic analysis of the data, assuming that the equilibrium

$$Br_2^{\bullet-}(\text{mic}) \rightleftharpoons Br_2^{\bullet-} + \text{mic} \quad (6)$$

is rapid, indicates that $Br_2^{\bullet-}$ radicals that are singly absorbed at different micelles react only after detachment. There is no evidence that reaction (5) takes place (consistent with strong repulsion by the charged surfaces of the micelles), and on this basis $K_6k_4 = 6.4 \times 10^4$ s^{-1} is obtained. Reaction (4) occurs in two steps: (*a*) diffusion of $Br_2^{\bullet-}$ from the bulk solution to the micelle surface and (*b*) reaction with the other $Br_2^{\bullet-}$ adsorbed there. This latter, two-dimensional, reaction is rapid and so the residence time of $Br_2^{\bullet-}$ is obtained as $(K_6k_4)^{-1} = 1.5 \times 10^{-5}$ s.[14] A related study of Ag_2^+ is described in Section 4.

3 Systems Involving Non-metallic Compounds

Peroxynitric Acid (HO_2NO_2).—Evidence has been obtained[15] for the reactions

$$HO_2 + NO_2 \rightleftharpoons HO_2NO_2 \quad (7)$$

from a study of aqueous oxygenated solutions containing formic acid and tetranitromethane in which formation of nitroform was monitored. Under the chosen conditions HO_2 and NO_2 are formed by

$$e_{aq}^- + C(NO_2)_4 \longrightarrow C(NO_2)_3^- + NO_2 \quad (8)$$

$$e_{aq}^- + O_2 \longrightarrow O_2^- \overset{H^+}{\rightleftharpoons} HO_2 \quad (9)$$

and corresponding reactions of $CO_2^{\bullet-}$ radicals, all of which are rapid. However, nitroform was also formed in a slow reaction ($k = 1.4 \times 10^2$ s^{-1}) which is identified with the decomposition of HO_2NO_2 followed by

$$O_2^- + C(NO_2)_4 \longrightarrow C(NO_2)_3^- + NO_2 + O_2 \quad (10)$$

No absorption spectrum attributable to HO_2NO_2 was observed.

Triazene (N_3H_3).—The radiation chemistry of hyrdazine continues to attract attention. Recent work[16] has been concerned with a long-lived ($t_{1/2} > 5$ ms) intermediate identified as triazene (N_3H_3). This species is amphiprotic and the following acid–base equilibria are rapidly established:

$$N_3H_4^+ \overset{pK_1=4.9}{\rightleftharpoons} N_3H_3 + H^+, \quad \Delta H_1^\circ = -4.9 \text{ kcal mol}^{-1}; \quad \Delta S_1^\circ = -39 \text{ cal K}^{-1} \text{ mol}^{-1},$$

$$N_3H_3 \overset{pK_2=11.37}{\rightleftharpoons} N_3H_2^- + H^+, \quad \Delta H^\circ = -4.2 \text{ kcal mol}^{-1}; \quad \Delta S_2^\circ = -66 \text{ cal K}^{-1} \text{ mol}^{-1}$$

[14] T. Proske and A. Henglein, *Ber. Bunsengesellschaft phys. Chem.*, 1978, **82**, 711.
[15] H. C. Sutton, W. A. Seddon, and F. C. Sopchyshyn, *Canad. J. Chem.*, 1978, **56**, 1961.
[16] J. W. Sutherland, *J. Phys. Chem.*, 1979, **83**, 779.

The rate constants for decomposition of the acidic and basic forms are $k(N_3H_4^+) = 1.97 \times 10^{11} \exp(-12\,600/RT)\ s^{-1}$ and $k(N_3H_2^-) = 2.14 \times 10^{14} \exp(-19\,200/RT)\ s^{-1}$. The neutral form is much more stable and $k(N_3H_3)$ is estimated to be $\leqslant 10^{-3}\ s^{-1}$ at 297 K.

The triazene species have absorption spectra with λ_{max} in the range 220—230 nm, and the extinction coefficients at 230 nm are estimated to be: $\varepsilon(N_3H_4^+) = 3.9 \times 10^3\ M^{-1}\ cm^{-1}$, $\varepsilon(N_3H_3) = 5.2 \times 10^3\ M^{-1}\ cm^{-1}$, and $\varepsilon(N_3H_2^-) \sim 50\ M^{-1}\ cm^{-1}$.

4 Aquo-metal Ions in Unusual Oxidation States

Hydrolysis.—Oxidation of Tl^+, Ag^+, Cu^{2+}, and Sn^{2+} by ·OH proceeds *via* the adduct,

$$\cdot OH + M^{n+} \longrightarrow M(OH)^{n+} \qquad (11)$$

and data have been obtained[17] for the hydrolysis equilibria:

$$M^{(n+1)+} \overset{pK_1}{\rightleftharpoons} M(OH)^{n+} \overset{pK_2}{\rightleftharpoons} M(OH)_2^{(n-1)+} \overset{pK_3}{\rightleftharpoons} \ldots\ldots$$

For $M = Ag^+$, $pK_1 = 5.35$ and $pK_2 = 8.35$. The data for Cu and Sn are explained in terms of reaction (12):

$$\cdot OH + M^{2+} + 2H_2O \longrightarrow M(OH)_3 + 2H^+ \qquad (12)$$

Because of experimental limitations it was only possible to obtain pK_3 for Cu^{III} ($pK_3 = 4.0 \pm 0.2$) and an estimate of pK_3 for Sn^{III} ($pK_3 \approx 2.9 \pm 0.3$). These data are in keeping with the principle that metal ions tend to be more hydrolysed in their higher oxidation states. Polarographic measurements[17] indicate that the oxidative properties of these unstable metal ions decrease as the ions become more hydrolysed.

Hydrolysis constants of stable reducible metal ions can be measured by pulse radiolysis combined with conductivity measurements, and this method yields data for low concentrations and ionic strengths.[18] The change in conductance accompanying reactions (13) is largely due to protons formed with e_{aq}^- during the radiation pulse. If M^{n+} is partially hydrolysed,

$$e_{aq}^- + M^{n+} \longrightarrow M^{(n-1)+} \qquad (13)$$

$$M^{n+} + H_2O \rightleftharpoons M(OH)^{(n-1)+} + H^+ \qquad (14)$$

equilibrium (14) is disturbed by the sudden decrease in $[M^{n+}]$ brought about by reaction (13). This results in a post-pulse decrease in conductance as some of the radiation-produced H^+ ions are consumed in restoring equilibrium (14).

By use of appropriate equations for material and charge balance and hydrolysis, pK_{14} can be evaluated. Data obtained in this way include:[18] $Yb(ClO_4)_3$, $pK_{14} = 8.7 \pm 0.2$; $Eu(ClO_4)_3$, $pK_{14} = 8.7 \pm 0.25$; $UO_2(ClO_4)_2$, $pK_{14} = 5.2 \pm 0.1$.

[17] K.-D. Asmus, M. Bonifacic, P. Toffel, P. O'Neill, D. Schulte-Frohlinde, and S. Steenken, *J.C.S. Faraday I*, 1978, **74**, 1820.

[18] K. H. Schmidt, J. C. Sullivan, S. Gordon, and R. C. Thompson, *Inorg. Nuclear Chem. Letters*, 1978, **14**, 429.

$Zn^+ + Mn^{III}$ System.[19]—This is an example of a system containing one metal ion in an unstable reduced state and the second in an oxidized state. As well as providing interesting inorganic chemistry, such systems are relevant to the problems of energy storage.

The lower oxidation state Mn^{2+} is oxidized by ·OH to $MnOH^{2+}$ (referred to as Mn^{III}). Under totally oxidizing conditions in the absence of Zn, Mn^{III} forms a precipitate (turbid solution) in which the average valence of Mn is *ca.* 3.65, showing that Mn^{III} is involved in turbidity formation. The kinetics are complex but consistent with Mn^{III} as the nucleating species.

When Zn^+ and Mn^{III} are generated together in approximately equal concentrations, the kinetics of turbidity formation are largely unchanged, showing that a considerable fraction of Mn^{III} escapes reduction by Zn^+ even though $k(Zn^+ + Mn^{III}) = 2.4 \times 10^9\ M^{-1}\ s^{-1}$.[19] Some of the Zn^+ reacts to form Zn^0 and, ultimately, hydrogen. A consequence of this formation of gas (H_2) and precipitate (MnO_2) in an initially homogeneous redox system, through a fraction of the redox intermediates escaping back reaction, is that chemical storage of some of the energy of the system becomes possible.

Lead(I).—The Pb^{2+} ion is rapidly reduced to Pb^+ by the hydrated electron ($k = 3.5 \times 10^{10}\ M^{-1}\ s^{-1}$).[20] The unstable Pb^+ has an absorption spectrum with maxima at 275 and 315 nm ($\varepsilon_{275} = 6.4 \times 10^3$, $\varepsilon_{315} = 1.1 \times 10^4\ M^{-1}\ cm^{-1}$). Rate constants for the reaction of Pb^+ with $[Co(NH_3)_5X]^{3+}$ (X = NH_3, H_2O, Cl^-, or Br^-) have been measured[20] and compared with the corresponding rates for Co^+, Zn^+, Cd^+, and Ni^+. The order of their reactivity is generally $Co^+ > Zn^+ \sim Cd^+ > Pb^+ > Ni^+$.

Mercury.—Reduction of Hg_2^{2+} by e_{aq}^- produces a transient species which, at pH 3.45, has an absorption spectrum with λ_{max} at 280—285 nm and $\varepsilon_{max} = 1.4 \times 10^3\ M^{-1}\ cm^{-1}$,[21] and is assigned as Hg_2^+. At pH < 1 the absorption band is slightly narrower but ε_{285} is practically unaltered. At the lower pH reduction is by H atoms [$k(H + Hg_2^{2+}) = 4.5 \times 10^9\ M^{-1}\ s^{-1}$], and the first step may be formation of Hg_2H^+. The species Hg_2^+ decays by second-order kinetics at pH 3.45, independent of ionic strength ($2k = 2.6 \times 10^9\ M^{-1}\ s^{-1}$), suggesting that the absorbing species at this pH is Hg_2OH. At the lower pH the species is thought to be Hg_2^+.[21] This conclusion is supported by the observation[21] that $k(Hg_2^+ + O_2) = 1.1 \times 10^9\ M^{-1}\ s^{-1}$ at pH 3.45 and $7 \times 10^8\ M^{-1}\ s^{-1}$ in 1M-$HClO_4$ solution.

Reduction of mecuric halides by e_{aq}^- produces short-lived light-emitting species, assigned[22] as HgX* (X = Cl, Br, or I), which are quenched by HgX_2. This emitted light is thought to be chemiluminescence resulting from reaction of e_{aq}^- (*cf.* $[Ru^{III}(bipy)_3]^{3+}$, Section 5),

$$e_{aq}^- + HgX_2 \xrightarrow{k_1} A \xrightarrow{k_2} HgX^* \xrightarrow{k_3} \text{product} \qquad (15)$$

where A is an electron or H atom adduct. For X = I, $k_1 = 3 \times 10^{10}\ M^{-1}\ s^{-1}$, $k_2 = 7 \times 10^5\ s^{-1}$, and $k_3 \approx (7—10) \times 10^{10}\ M^{-1}\ s^{-1}$. The natural lifetimes of HgX*

[19] J. Rabani and M. S. Matheson, *Radiat. Phys. Chem.*, 1978, **11**, 1.
[20] I. Mihalcea and R. R. Hentz, *Radiochem. Radioanalyt. Letters*, 1978, **34**, 15.
[21] A. K. Pikaev and G. K. Sibirskaya, *Radiochem. Radioanalyt. Letters*, 1979, **38**, 39.
[22] S. Fujita, H. Horii, T. Mori, and S. Taniguchi, *J. Phys. Chem.*, 1978, **82**, 1693.

are estimated[22] to be >2 μs for HgI* and 0.3 μs for HgCl*, and an intermediate time for HgBr*.

Copper.—Reactions of simple hydroxyalkyl radicals with Cu^{I} and Cu^{II} have been investigated.[23] For the reaction of α-radicals with Cu^{II} the order of reactivity is primary > secondary > tertiary and $k \approx 10^8$ M^{-1} s^{-1}. This is consistent with reaction proceeding *via* organocopper complexes, but these complexes have not been directly observed. β-Radicals react more slowly than α-radicals and epoxides are formed.

Organocopper intermediates are formed in the reactions of the radicals with Cu^{I} and have absorption spectra in the 300—500 nm range. β-Radicals oxidize Cu^{I} to Cu^{II} and are themselves reduced to the corresponding olefin in the overall reaction, *e.g.*

$$Cu^{+} + \cdot CH_2CMe_2OH \longrightarrow Cu^{2+} + CH_2{=}CMe_2 + OH^{-} \qquad (16)$$

which is acid-catalysed. α-Radicals cannot reduce Cu^{I} to Cu^{0} and it is suggested[23] that the complexes decay according to

$$CuROH^{+} \rightleftharpoons Cu^{+} + \cdot ROH \qquad (17)$$

$$ROH + Cu^{2+} \longrightarrow Cu^{+} + H^{+} + \text{products} \qquad (18)$$

This mechanism accounts satisfactorily for the reaction of $\cdot CH_2OH$, which is pH-independent, but doubt exists in the case of $Me\dot{C}HOH$ and $Me_2\dot{C}OH$ which show an apparent pH dependence. An alternative proposal[24] is that the last two radicals do not complex with Cu^{I} but rather it is the small fraction of β-radicals, $\cdot CH_2CH_2OH$ and $\cdot CH_2C(Me)HOH$, which are also present in these systems, that are responsible for the observed organocopper complexes.

Silver.—Radiolytically reduced silver exists in a number of forms in aqueous solution ranging from Ag^{0} and Ag_2^{+} to larger aggregates and colloidal particles. Ag^{+} is reduced to Ag^{0} by e_{aq}^{-} and $\cdot H$; in the latter reaction AgH^{+} is postulated as an intermediate on energetic grounds ($t_{1/2} < 10^{-8}$ s).[25] Organic free radicals cannot reduce Ag^{+} by a single electron transfer, but may do so *via* complex formation:

$$Ag^{+} + \cdot RH \rightleftharpoons AgRH^{+} \qquad (19)$$

$$AgRH^{+} + Ag^{+} \longrightarrow Ag_2^{+} + R + H^{+} \qquad (20)$$

Both Ag^{0} and Ag_2^{+} are electron-donating agents with approximate standard redox potentials of -1.8 and -1.2 V respectively.[25] On the other hand Ag_2^{+} is reduced by organic radicals, *e.g.*

$$\cdot CH_2OH + Ag_2^{+} \longrightarrow CH_2O + H^{+} + Ag_2 \qquad (21)$$

and E° for Ag_2^{+}/Ag_2 is estimated to be -0.6 V.[25]

The cation Ag_2^{+} also reacts to form 'dimeric silver':

$$Ag_2^{+} + Ag_2^{+} \longrightarrow Ag_4^{2+} \overset{-Ag^{+}}{\rightleftharpoons} Ag_3^{+} \overset{-Ag^{+}}{\rightleftharpoons} Ag_2 \qquad (22)$$

[23] G. V. Buxton and J. C. Green, *J.C.S. Faraday I*, 1978, **74**, 697.
[24] D. Meyerstein, personal communication.
[25] R. Tausch-Treml, A. Henglein, and J. Lilie, *Ber. Bunsengesellschaft phys. Chem.*, 1978, **82**, 1335.

with $2k_{22} = 3 \times 10^8$ M^{-1} s^{-1},[25] and Ag_4^{2+} disappears by reacting with itself ($2k = 1.1 \times 10^7$ M^{-1} s^{-1}). Colloidal silver is ultimately formed and the agglomeration process is accelerated by sulphate ions. Under these conditions the decay of Ag_4^{2+} becomes first order, showing that it reacts with colloidal silver particles.[25]

In solutions containing micelles of sodium hexadecyl trioxyethylene sulphate or sodium dodecyl sulphate Ag_2^+ becomes adsorbed on the micelles and its decay kinetics are profoundly changed.[26] A fraction of the Ag_2^+ cations decays in 1—2 μs and the remainder in 10^{-4}—10^{-2} s. The rapid decay is attributed to a two-dimensional reaction between two Ag_2^+ cations adsorbed on the same micelle and the slow decay to a three-dimensional reaction between Ag_2^+ adsorbed singly on different micelles. A kinetic analysis of the dependence of the slow reaction on tenside concentration indicates that reaction occurs when an Ag_2^+ is exchanged between two colliding micelles so that, on separating, one of the micelles carries two Ag_2^+ cations which undergo the rapid two-dimensional reaction. This behaviour is different from that observed for Br_2^- radicals (see Section 2).

Gallium and Indium.[27]—Ga^{III} and In^{III} are reduced by e_{aq}^- to the unstable bivalent ions. In perchlorate solution Ga^{II} has a spectrum with λ_{max} at 268 nm and $\varepsilon_{max} = 1.7 \times 10^4$ M^{-1} cm^{-1}. For In^{II} these parameters are 260 nm and 2×10^4 M^{-1} cm^{-1}. No spectral differences are observed between pH 2 and 3. Since M^{3+} (M = Ga or In) predominates at the lower pH and MOH^{2+} at the higher, the reduction products are expected to be M^{2+} and MOH^+, so the lack of a pH effect suggests either that both forms of M^{II} have similar spectra or that the equilibrium

$$MOH^+ \rightleftharpoons M^{2+} + OH^- \qquad (23)$$

lies well to the right. In sulphate solution, where M^{II} is largely MSO_4^+, the spectra of the M^{II} species show a small (~5 nm) blue shift, which may be an indication that MSO_4 is formed.

Both bivalent metal ions decay by second-order kinetics at diffusion-controlled rates: for Ga^{II} $2k = 8.1 \times 10^9$ M^{-1} s^{-1}, and for In^{II} $2k = 1.8 \times 10^{10}$ M^{-1} s^{-1}. It seems likely under the experimental conditions[27] that the reaction is mainly reoxidation of M^{II} by ·OH.

Americium.[28]—Absorption spectra of the transient species Am^{II} (λ_{max} 312 nm) and Am^{IV} (λ_{max} 320—340 nm) in aqueous perchlorate solution have been obtained using the streak-camera technique.[28] The Am^{II} state is generated by reduction of Am^{III} with e_{aq}^- ($k = 1.55 \times 10^8$ M^{-1} s^{-1}), and Am^{IV} by oxidation of Am^{III} with ·OH ($k = 4.1 \times 10^8$ M^{-1} s^{-1}) or reduction of Am^V with e_{aq}^- ($k = 3.2 \times 10^{10}$ M^{-1} s^{-1}).

The Am^{II} species decays by a first-order process ($k = 9.7 \times 10^4$ s^{-1}) which may be a reaction with water. Americium(IV) disproportionates [$k = (5 \pm 1) \times 10^6$ M^{-1} s^{-1}] at a rate which is qualitatively consistent with the decreasing stability of quadrivalent actinides observed in going from U^{IV} to Pu^{IV}.

[26] A. Henglein and T. Proske, *Ber. Bunsengesellschaft phys. Chem.*, 1978, **82**, 471.
[27] N. L. Sukhov, I. E. Makarov, and B. G. Ershov, *Khim. vysok. Energii*, 1978, **12**, 375.
[28] S. Gordon, W. A. Mulac, K. H. Schmidt, R. K. Sjoblom, and J. C. Sullivan, *Inorg. Chem.*, 1978, **17**, 294.

Compared with Sm^{III}, which has similar radius, charge, and formal potential, Am^{III} is 100 times less reactive with e_{aq}^-. This is probably a reflection of the greater overlap of 5*f* orbitals, compared with 4*f* orbitals, with ligands in the first co-ordination shell of Am^{III}, resulting in a larger rearrangement free energy of formation of the activated complex.[28]

Technetium.—Technetium(VI) has been shown to be a viable chemical species in alkaline aqueous solution.[29] It is generated by reduction of $[^{99}TcO_4]^-$ with e_{aq}^- in 0.1 M-NaOH solution ($k = 2.5 \times 10^{10}$ M^{-1} s^{-1}) and exhibits a broad absorption band in the visible region of the spectrum [ε (500—600 nm) ~ 250 M^{-1} s^{-1}]. The spectrum remained unchanged for 10^{-3} s, the maximum time of observation by the streak-camera technique, so that Tc^{VI} has a lifetime of at least a few milliseconds.

5 Reactions of Transition-metal Complexes

Reactivity of The Carbonate Radical.[7]—Rate constants for the reaction of CO_3H radicals with several complexes have been measured.[7] Of the labile aquo-ions Co^{2+}, Zn^{2+}, Ni^{2+}, Cu^{2+}, and Mn^{2+}, only Co^{2+} ($k = 2.8 \times 10^6$ M^{-1} cm^{-1}), Cu^{2+} ($k \approx 4.5 \times 10^4$ M^{-1} s^{-1}), and Mn^{2+} ($k = 1.5 \times 10^7$ M^{-1} s^{-1}) react at measurable rates; the oxidation potential of the metal ion appears to be a governing factor. Two Co^{II}–macrocycle complexes, $[Co^{II}(2)]$ and $[Co^{II}(3)]$ (see below), whose equatorial co-ordination sites are substitution inert and axial sites have labile H_2O, react ~200 times faster than Co_{aq}^{2+}, and here the rate is probably substitution limited.[7]

For six-co-ordinate complexes of Cr^{III}, Co^{III}, Rh^{III}, Ir^{III}, and Ru^{III} which are substitution inert, direct addition of CO_3H to the metal centre is precluded and oxidation can only take place if there is an accessible M^{IV} state. Iridium(IV) is such a case, and reaction of CO_3H with $[Ir(NH_3)_5Cl]^{2+}$ is significantly faster than with the analogous Cr^{III}, Co^{III}, and Rh^{III} complexes.

Reaction with $[Co(NH_3)_6]^{3+}$ is immeasurably slow, ruling out H-atom transfer, but reaction does occur when an oxidizable ligand is substituted for NH_3, *e.g.* $[Co^{III}(NH_3)_5X]$ ($X = HPO_4^{2-}$, Cl^-, Br^-, SO_4^{2-}, NO_2^- or SO_3^{2-}), and the most easily oxidized ligand (NO_2^-) has the highest rate constant ($k = 10^8$ M^{-1} s^{-1}). However, when X is Cl^- or Br^- the ultimate product is $[Co(NH_3)_5(OH_2)]^{3+}$, so the overall reaction is one of ligand replacement; it is suggested[7] that CO_3H initially couples to the halide ligand in this reaction.

Complexes of the composition $[M^{III}(NH_3)_5(OH)]^{2+}$ (M = Cr, Co, Rh, or Ru) are more reactive than their conjugate acids and, except for Co^{III}, than the corresponding $[M^{III}(NH_3)_5Cl]^{2+}$ complexes. This seems to rule out oxidation of the ligand by direct electron or H-atom transfer.

Oxidation by Free Radicals.—The Co^{III}–polyamine complexes $[Co(en)_3]^{3+}$, $[Co(dien)_2]^{3+}$, $[CoCl_2(en)_2]^+$, and $[CoCl_2(trien)]^+$ all react with ·OH with $k = (3 \pm 0.2) \times 10^8$ M^{-1} s^{-1}.[30] Conductivity measurements are consistent with H-atom abstraction from the ligand, followed by electron transfer to the metal

[29] E. Deutsch, W. R. Heineman, R. Hurst, J. C. Sullivan, W. A. Mulac, and S. Gordon, *J.C.S. Chem. Comm.*, 1978, 1038.
[30] N. Shinohara and J. Lilie, *Inorg. Chem.*, 1979, **18**, 434.

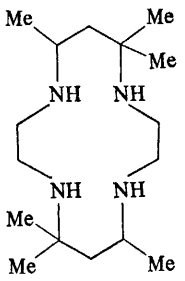
centre from the ligand radical and eventual dissociation of the degraded ligand. In all cases the degraded ligand dissociates faster than the undegraded ligand and the rates increase with decreasing pH. The alternative mechanism of oxidation of the metal centre followed by ligand oxidation, which is proposed for Cu^{II}–en and Ni^{II}–en complexes,[31] is ruled out for Co^{III}–en.[30]

Both types of oxidation are reported[32] for oxidation by ·OH of the first-row bivalent metal complexes containing ethylenediaminetetra-acetate (edta) or nitriloacetate (nta) ligands. For $M=Ni^{II}$, Cu^{II}, or Fe^{II} the metal centre is oxidized directly, whereas for $M=Zn^{II}$, Mn^{II}, or Co^{II} hydrogen-atom abstraction from the ligand occurs. With $[Co^{II}(edta)]^{2-}$ partial oxidation of the metal centre is observed. All these reactions have rate constants in the range $(2—5)\times 10^9\ M^{-1}\ s^{-1}$.

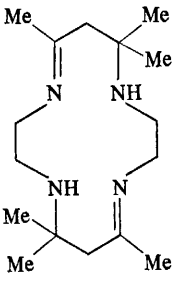
These results follow no obvious pattern; thus they do not fit in with the redox potentials of the $M^{III}L/M^{II}L$ couples nor with stability of the $M^{III}L$ complexes (L=edta or nta). A suggested explanation[32] is that all the reactions proceed through formation of an intermediate in which ·OH interacts strongly with the complex. The reorganization energy required in the oxidation of the metal centre may then determine whether electron transfer or H-atom abstraction follows. When the oxidizing radical is $Br_2^{\bullet-}$, $(SCN)_2^{\bullet-}$, $I_2^{\bullet-}$, $O_2^{\bullet-}$, or $^{\bullet}O_2CCH_2CMe_2OH$, no H-atom abstraction is observed.[32] Instead, there is a clear indication that oxidation of $Co^{II}L$ and $Mn^{II}L$ occurs by an inner-sphere mechanism which may involve seven-co-ordination.

From a wider survey[32a] of available data on the reactions of ·OH with complexes containing organic ligands, it is argued that such properties as the Lewis acidity of the metal centre and metal–ligand π-bonding, as well as redox potentials and the oxidation state of the metal, help to determine the kinetics and mechanism of these reactions.

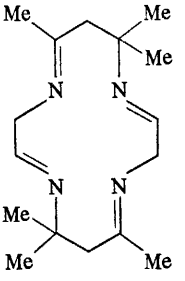
Free-radical Oxidation of Metal Complexes Containing Macrocyclic Ligands.—*Nickel*(II). The radicals $Cl_2^{\bullet-}$, $Br_2^{\bullet-}$, $(SCN)_2^{\bullet-}$, and ·OH oxidize NiL^{2+} [L= (1), (2), or (3)] to form transient species identified from their absorption bands at



(1)



(2)



(3)

[31] J. Lati and D. Meyerstein, *Inorg. Chem.*, 1972, **11**, 2393, 2397.
[32] J. Lati and D. Meyerstein, *J.C.S. Dalton*, 1978, 1105.
[32a] W. L. Waltz, R. J. Woods, and K. D. Whitburn, *Photochem. and Photobiol.*, 1978, **28**, 681.

300—400 nm as Ni^{III} complexes.[33–35] Comparison of the data for oxidation by $X_2^{\bullet -}$ and ·OH shows that a transient intermediate is produced in the former case, *e.g.*

$$Br_2^{\bullet -} + Ni^{II}L \longrightarrow Ni^{III}L{-}Br + Br^- \quad (24)$$

which decomposes to give the same intermediate formed directly by ·OH:

$$Ni^{III}L{-}Br \longrightarrow Ni^{III}L + Br^- \quad (25)$$

Reaction (25) is pH dependent, the rate increasing rapidly between pH 4.9 and 5.3 for L=(2), and from conductometric measurements is interpreted as a base-catalysed ligand exchange.[34] The absorption spectrum of the product of reaction (25) depends strongly on pH; as the pH is raised from 3 to 5 the absorption band at 320 nm decreases and a band at 540 nm appears. These observations, together with measured changes in conductivity, are consistent with equilibrium (26) and a pK of 3.45 ± 0.1:

$$[Ni^{III}(2)]^{3+} + H_2O \rightleftharpoons [Ni^{III}(2)(OH)]^{2+} + H^+ \quad (26)$$

Such a large spectral change requires considerable distortion of the planar complex. It is significant, therefore, that the 540 nm band is most intense when L=(1) where there are no double bonds to provide rigidity in the planar complex.[33]

A different interpretation of the spectral and kinetic data has been put forward,[35] namely that ·OH abstracts an H atom from the NH groups in (1) and (2) to form a ligand radical species $Ni^{II}L^{\bullet}$ which absorbs at 540 nm, as well as oxidizing the metal centre directly, and that the pH-dependent spectral changes are due to interconversion of $Ni^{III}L$ and $Ni^{II}L^{\bullet}$:

$$Ni^{III}L + H_2O \rightleftharpoons Ni^{II}L^{\bullet} + H_3O^+ \quad (27)$$

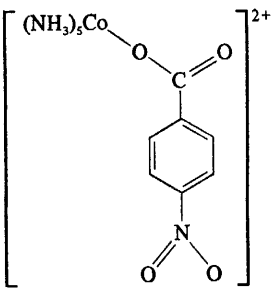
The $Ni^{III}L$ species are powerful oxidants and the rates of oxidation of Cl^-, Br^-, SCN^-, and N_3^- depend on the reduction potentials of the complexes.

Copper(II). Oxidation of $[Cu^{II}(2)]$ by ·OH ($k = 1.5 \times 10^{10}$ M^{-1} s^{-1}) produces a transient species having a broad absorption spectrum with λ_{max} at 315 nm and $\varepsilon_{max} = 5.5 \times 10^3$ M^{-1} cm^{-1} independent of pH (1—5).[36] From a comparison with $[Cu^{III}(2)]$ prepared electrochemically in acetonitrile[37] it is concluded[36] that $[Cu^{II}(2)]^{\bullet}$ is the initial product of oxidation of $[Cu^{II}(2)]$ by ·OH, and that the equilibrium corresponding to (27) lies to the right at $1 < pH < 5$.

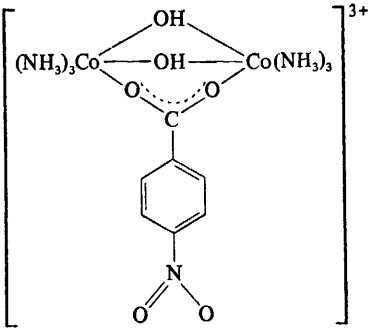
The radicals $Cl_2^{\bullet -}$ oxidize $[Cu^{II}(2)]$ about 100 times more slowly than ·OH to produce the same transient species $[Cu^{II}(2)]$, but the initial product is thought to be[36] $[Cu^{III}(2)]$ which is rapidly transformed to $[Cu^{II}(2)]^{\bullet}$. Oxidized $[Cu^{II}(2)]$ is a powerful oxidant, and in this respect it is mechanistically more straightforward if the oxidant is $[Cu^{III}(2)]$ rather than $[Cu^{II}(2)]^{\bullet}$.

[33] P. Maruthumuthu, L. K. Patterson, and G. Ferraudi, *Inorg. Chem.*, 1978, **17**, 3157.
[34] M. Jaacobi, D. Meyerstein, and J. Lilie, *Inorg. Chem.*, 1979, **18**, 429.
[35] K. D. Whitburn and G. S. Laurence, *J.C.S. Dalton*, 1979, 139.
[36] K. D. Whitburn and G. S. Laurence, *J.C.S. Dalton*, 1979, 334.
[37] D. C. Olson and J. Vasilevskis, *Inorg. Chem.*, 1971, **10**, 463.

Reduction by Free Radicals.—*Cobalt.* Reduction of two cobalt(III) complexes (4) and (5) by $Me_2\dot{C}OH$ radicals has been studied to assess the role of the carboxylate group in intramolecular electron-transfer processes.[38] In each case



(4)



(5)

transient species are formed rapidly and have absorption spectra resembling those of the free *p*-nitrobenzoato-radicals $^-O_2C_6H_4NO_2^{\bullet-}$ and $HO_2CC_6H_4N\dot{O}_2H$, indicating that the initial product is a complexed radical. In (5) the unprotonated form undergoes intramolecular electron transfer to form Co^{II} ($k = 3.3 \times 10^3\ s^{-1}$), whereas a disproportionation reaction occurs with the protonated form ($pK_a = 2.5$). Although co-ordination of two Co^{III} centres to the carboxylic group has a strong effect compared with one Co^{III} on the properties of the *p*-nitrobenzoato-ligand, the intramolecular transfer has practically the same rate ($k = 2.6 \times 10^3\ s^{-1}$) in (4). This is attributed[38] to the poor electron permeability of the carboxylate group, which may result in electron transfer directly to the Co^{III} centre in an intramolecular 'outer-sphere' mechanism.

The complex $[Co(bipy)_3]^{3+}$ reacts rapidly ($k = 10^8$—$10^{10}\ M^{-1}\ s^{-1}$) with reducing radicals (e_{aq}^-, $CO_2^{\bullet-}$, $Me_2\dot{C}OH$, and $\cdot CH_2OH$) to form a common intermediate which has a spectrum with λ_{max} at 300 nm and $\varepsilon_{max} = 4.2 \times 10^4\ M^{-1}\ cm^{-1}$. This species does not react with *p*-benzoquinone or O_2 and is assigned[39] as high-spin ($t_{2g}^5 e_g^2$) $[Co(bipy)_3]^{2+}$ formed by one-electron reduction. This reduced transient loses a bipy ligand in a first-order process ($k = 3.4 \pm 0.4\ s^{-1}$; pH 0.5—10.5) to form an equilibrium mixture:

$$[Co(bipy)_3]^{2+} \overset{H_2O}{\rightleftharpoons} [Co(bipy)_2(H_2O)_2]^{2+} + bipy \qquad (28)$$

These results conflict with previous work,[40,41] and it is speculated[39] that the effects observed there were caused by a small fraction of e_{aq}^- reacting with $[Co(bipy)_n]^{2+}$ ($n = 1$, 2, or 3) or free bipy.

[38] K. Wieghardt, H. Cohen, and D. Meyerstein, *Ber. Bunsengesellschaft phys. Chem.*, 1978, **82**, 388.
[39] M. G. Simic, M. Z. Hoffman, R. P. Cheney, and Q. G. Mulazzani, *J. Phys. Chem.*, 1979, **83**, 439.
[40] W. L. Waltz and R. G. Pearson, *J. Phys. Chem.*, 1969, **73**, 1941.
[41] J. H. Baxendale and M. Fiti, *J.C.S. Dalton*, 1972, 1995.

Limited data[39] for $[Co(phen)_3]^{3+}$ are explicable on the same basis as those for $[Co(bipy)_3]^{3+}$, except that detachment of a phen ligand [reaction (28)] was not observed.

Iron. $[Fe(phen)_3]^{3+}$ shows similar behaviour to its cobalt analogue; it is rapidly reduced by ·H to stable $[Fe(phen)_3]^{2+}$ ($k = 5 \times 10^9$ M^{-1} s^{-1}).[42] There is no evidence for an intermediate H-atom adduct of co-ordinated phen, suggesting that adduct formation is the rate-controlling step in the overall reduction.

Ruthenium. Reduction of $[Ru(bipy)_3]^{3+}$ by e^-_{aq} ($k = 5 \times 10^{10}$ M^{-1} s^{-1}) results[43] in the simultaneous formation of (*a*) $*[Ru(bipy)_3]^{2+}$ (38% yield), the lowest charge-transfer state of $[Ru(bipy)_3]^{2+}$; (*b*) $^{\dagger}[Ru(bipy)_3]^{2+}$ (>55% yield), which is a different excited state or co-ordinated radical complex that is longer lived than $*[Ru(bipy)_3]^{2+}$ and is not converted into it; and (*c*) ground-state $[Ru(bipy)_3]^{2+}$ (<7% yield). Since by its nature e^-_{aq} most probably reduces by direct electron transfer, the formation of $*[Ru(bipy)_3]^{2+}$ as a major product can be rationalized in terms of the Marcus theory which predicts that transfer will occur into excited states of the acceptor if the redox reaction is highly exoergic.

Radicals such as ·H, $\cdot CH_2CMe_2OH$, and Cd^+ reduce $[Ru(bipy)_3]^{3+}$ to ground-state $[Ru(bipy)_3]^{2+}$ directly; ·H may react *via* adduct formation, but direct electron transfer is more likely in the other two cases.[43]

Reactions of $[Ru(bipy)_3]^+$ have been reinvestigated.[44] This complex is the product of reduction of $[Ru(bipy)_3]^{2+}$ in alkaline solution by reducing radicals such as e^-_{aq}, $\cdot CH_2O^-$, $MeC\dot{H}O^-$, and $MeC\dot{O}^-$, and is itself a powerful reductant. At pH 11—13 $[Ru(bipy)_3]^+$ is long-lived ($t_{1/2} \approx 5$ s) and decays by a first-order process which appears to be reaction with water, although no H_2 or free bipy is generated. In less alkaline solution where the organic free radicals are not ionized they do not reduce $[Ru(bipy)_3]^{2+}$, but in their presence the decay of $[Ru(bipy)_3]^+$ is accelerated and is consistent with

$$[Ru(bipy)_3]^+ + \cdot RH \longrightarrow \text{products} \qquad (29)$$

This reaction is thought[44] to be the correct explanation of the much lower stability of $[Ru(bipy)_3]^+$ observed in earlier work and attributed[41] to

$$2[Ru(bipy)_2(bipy^{\cdot -})]^+ \xrightarrow{2H^+} [Ru(bipy)_3]^{2+} + [Ru(bipy)_2(bipyH_2)]^{2+} \qquad (30)$$

The complex $[Ru(bipy)_3]^+$ transfers an electron rapidly to $[Ru(bipy)_3]^{3+}$ ($k = 3.4 \times 10^9$ M^{-1} s^{-1}) but there is no clear evidence that $*[Ru(bipy)_3]^{2+}$ is an intermediate in this reaction.

It is known that $[Ru(bipy)_3]^{2+}$ forms a water-insoluble salt with dodecyl sulphate ions which is solubilized by sodium dodecyl sulphate micelles. Kinetic measurements[45] reveal that all the $[Ru(bipy)_3]^{2+}$ are bound to micelles and reside in a negatively charged ionic atmosphere. As a consequence the reaction of $[Ru(bipy)_3]^{2+}$ with e^-_{aq} is retarded and those of Zn^+, Cd^+, and Co^+ are accelerated. The micellar environment also has a dramatic effect on the quenching of

[42] I. Janovsky, *Radiochem. Radioanalyt. Letters*, 1979, **39**, 337.
[43] C. D. Jonah, M. S. Matheson, and D. Meisel, *J. Amer. Chem. Soc.*, 1978, **100**, 1449.
[44] Q. G. Mulazzani, S. Emmi, P. G. Fuochi, M. Z. Hoffman, and M. Venturi, *J. Amer. Chem. Soc.*, 1978, **100**, 981.
[45] D. Meisel, M. S. Matheson, and J. Rabani, *J. Amer. Chem. Soc.*, 1978, **100**, 117.

*$[Ru(bipy)_3]^{2+}$, the rate by Cu^{2+} being enhanced and that by $[Fe(CN)_6]^{3-}$ diminished as compared with the rates in the absence of micelles. In the latter case Cu^{2+} has been shown[46] to quench *$[Ru(bipy)_3]^{2+}$ by an electron-transfer mechanism.

The influence of the negative potential field of poly(vinyl sulphate) (PVS) on the quenching of *$[Ru(bipy)_3]^{2+}$ by eletcron acceptors has been demonstrated.[47] In general PVS slows the quenching rate by about 40%, and for two uncharged quenchers, [Fe(nta)] and $[Co(acac)_3]$, the fraction of electron-transfer products, $[Ru(bipy)_3]^{3+}$ and $(acceptor)^-$, that escape geminate recombination is enhanced by a factor of three. This latter effect is attributed[47] to expulsion of $(acceptor)^-$ from the negatively charged environment of the ruthenium complex. Such systems are potentially useful in solar energy conversion.[47]

Aquation of $[M^{II}(acac)_3]^-$.[48]—The kinetics of ligand exchange in labile complexes can be readily obtained using pulse radiolysis combined with conductivity measurements. For the complexes $[M(acac)_3]^-$ ($M=Co^{2+}$, Cr^{2+}, or Ru^{2+}; $acac^-$ = acetylacetonate) the conductance changes in the pH range 3.1—7.0 are in accord with the following reactions:

$$e^-_{aq} + [M(acac)_3] \longrightarrow [M(acac)_3]^- \quad (31)$$

$$[M(acac)_3]^- + H^+ \longrightarrow [M(acac)_2] + acacH \quad (32)$$

$$[M(acac)_2] + H^+ \longrightarrow [M(acac)]^+ + acacH \quad (32)$$

$$[M(acac)]^+ + H^+ \longrightarrow M^{2+}_{aq} + acacH \quad (34)$$

with small contributions from the equilibria

$$[M(acac)_3]^- \overset{-acac^-}{\rightleftharpoons} [M(acac)_2] \overset{-acac^-}{\rightleftharpoons} [M(acac)]^+ \overset{-acac^-}{\rightleftharpoons} M^{2+}_{aq} \quad (35)$$

For $M=Co^{2+}$ reactions (32)—(34) are well separated kinetically with $k_{31}=7.2\times10^8\ M^{-1}\ s^{-1}$ and $k_{31} : k_{32} : k_{33} \approx 1 : 0.004 : 0.0001$. For $M=Cr^{2+}$ reaction (32) is too fast to be measured, and both (33) and (34) are faster than for the cobalt analogues ($k_{33}=4\times10^7\ M^{-1}\ s^{-1}$, $k_{34}=0.1\ k_{33}$). For $M=Ru^{2+}$ the reactions are all extremely slow and only an upper limit for (32) ($k_{32}<10^2\ M^{-1}\ s^{-1}$) has been estimated. The corresponding non-acid-catalysed equations (35) are all 10^4—10^5 times slower.

A mechanism of aquation is proposed[48] in which the bidentate ligand becomes unidentate-bound in a pre-equilibrium and is then lost in an acid-catalysed process with a small contribution from an acid-independent path.

Carbon–Cobalt(III) Bonds.—These bonds are readily formed in reactions of aliphatic free radicals with Co^{II} complexes. Reaction of $\cdot CH_2OH$, $MeCHOH$, $HOCHCH_2OH$, or $\cdot CH_2CHO$ with the macrocyclic complex $[Co^{II}(2)]$ produces the unstable intermediate $[Co^{III}(2)-RH]$ containing a σ-carbon–cobalt bond:[49]

$$\cdot RH + [Co^{II}(2)] \longrightarrow [Co^{III}(2)-RH] \quad (36)$$

Such complexes serve as models for coenzyme B_{12}.

[46] M. A. Hoselton, C.-T. Lin, H. A. Schwarz, and N. Sutin, *J. Amer. Chem. Soc.*, 1978, **100**, 2383.
[47] D. Meyerstein, J. Rabani, M. S. Matheson, and D. Meisel, *J. Phys. Chem.*, 1978, **82**, 1879.
[48] D. Meisel, K. H. Schmidt, and D. Meyerstein, *Inorg. Chem.*, 1979, **18**, 971.
[49] H. Elroi and D. Meyerstein, *J. Amer. Chem. Soc.*, 1978, **100**, 5540.

The mechanism by which these complexes decompose depends on the nature of RH.[49] Thus [Co^{III}(2)—CH_2OH] undergoes heterolytic cleavage of the carbon–cobalt bond to form [Co^{I}(2)] and CH_2O. On the other hand, [Co^{III}(2)—CH(Me)OH] seems to decompose by hydride transfer from the β-carbon whereas [Co^{III}(2)—$CH(OH)CH_2OH$] rearranges by loss of H_2O to [Co^{III}(2)—CH_2CHO] which then hydrolyses to [Co^{III}(2)] and MeCHO, both steps being acid-catalysed. This last reaction is a model of the diol dehydrogenase enzyme which contains coenzyme B_{12}.

Alkylnitroso Complexes.—Reduced nitrosyl complexes such as $[Fe(CN)_5(NO)]^{3-}$ and $[Ru(NH_3)_5(NO)]^{2+}$ react with alkyl free radicals to yield the corresponding *N*-bound alkylnitroso-complexes:[50]

$$M^{II}—NO^{+} \xrightarrow{e^-_{aq}} M^{II}—\dot{N}O \xrightarrow{\cdot R} M^{II}—N(O)R$$

β-Carbon radicals (·R) generated by abstraction of H by ·OH from t-butyl alcohol, t-butylamine, *N*,*N*-dimethylacetamide, α-aminoisobutyric acid, pivalic acid, or α-hydroxyisobutyric acid react rapidly: $k = 6 \times 10^8$—3.5×10^{10} M^{-1} s^{-1} for $[Fe(CN)_5(NO)]^{3-}$; $k = (2—4) \times 10^9$ M^{-1} s^{-1} for $[Ru(NH_3)_5(NO)]^{2+}$. These reactions are sufficiently rapid to compete favourably with bimolecular combination/disproportionation reactions of ·R, so that aqueous radiation chemistry provides a useful general synthetic route to alkylnitroso-complexes.[50]

Metal Carbonyls.—The pentacarbonylmanganese(0) radical has been generated and characterized[51] by pulse radiolysis of ethanolic solutions of $[Mn_2(CO)_{10}]$, $[Mn(CO)_5Br]$, and $[Mn(CO)_5I]$ in which dissociative electron attachment occurs ($k \approx 10^{10}$ M^{-1} s^{-1}):

$$e^-_{sol} + [Mn(CO)_{10}] \longrightarrow [\cdot Mn(CO)_5] + [Mn(CO)_5]^- \quad (37)$$

$$e^-_{sol} + [Mn(CO)_5X] \longrightarrow [\cdot Mn(CO)_5] + X^- \quad (38)$$

The free radical $[\cdot Mn(CO)_5]$ has an optical absorption band with λ_{max} at 830 nm and $\varepsilon_{max} = 800$ M^{-1} cm^{-1}, and decays by second-order kinetics ($2k = 1.2 \times 10^9$ M^{-1} s^{-1}) to form $[Mn_2(CO)_{10}]$; it also reacts rapidly with O_2 ($k = 1.8 \times 10^9$ M^{-1} s^{-1}). This species exemplifies a broad class of radicals of general importance to organometallic and polymer chemistry.[51]

The pentacarbonyls of Cr, Mo, and W have been produced by pulse radiolysis of cyclohexane solutions of the corresponding hexacarbonyls[52] by the following reactions:

$$e^-_{sol} + [M(CO)_6] \longrightarrow [M(CO)_6]^- \quad (39)$$

$$[M(CO)_6]^- + C_6H_{12}^+ \longrightarrow [M(CO)_5] + CO + C_6H_{12} \quad (40)$$

The absorption spectra of these pentacarbonyls have λ_{max} at 505, 410, and 415 nm respectively. In the absence of other solutes the $[M(CO)_5]$ decay by first-order kinetics to form unknown products. They react moderately rapidly ($k = 10^6$—

[50] R. P. Cheney, S. D. Pell, and M. Z. Hoffman, *J. Inorg. Nuclear Chem.*, 1979, **41**, 489.
[51] W. L. Waltz, O. Hackelberg, L. M. Dorfman, and A. Wojcicki, *J. Amer. Chem. Soc.*, 1978, **100**, 7259.
[52] L. Flamigni, *Radiat. Phys. Chem.*, 1979, **13**, 133.

10^8 M^{-1} s^{-1}) with cyclohexene, H_2, N_2, and CO, and spectra attributed to $[M(CO)_5(C_6H_{10})]$ and $[M(CO)_5N_2]$ have been observed.[52]

6 Metalloproteins and Related Systems

Haemoglobin.—The kinetics of the binding of CO to human methaemoglobin, in which only one haem group is reduced by e_{aq}^- to the ferrohaem form, have been measured[53] in unbuffered solution at pH 6.2:

$$[HbFe_3^{3+}Fe^{2+}] + CO \longrightarrow [HbFe_3^{3+}Fe^{2+}CO] \quad (41)$$

Reaction (41) was followed by monitoring changes in the concentrations of $[HbFe_3^{3+}Fe^{2+}]$ and $[HbFe_3^{3+}Fe^{2+}CO]$, and both observations gave $k_{41} = (4.1 \pm 0.2) \times 10^6$ M^{-1} s^{-1} under conditions where the dimer–tetramer equilibrium of haemoglobin favours the dimeric form (2 : 1). Addition of 2×10^{-4} M inositol hexaphosphate (IHP), which shifts the equilibrium in favour of the tetrameric form, lowered k_{41} to 1.1×10^5 M^{-1} s^{-1}. Both these values of k_{41} are consistent with rate constants in previous reports of biphasic kinetics which have been ascribed to reactions of the dimeric and tetrameric forms respectively. They also lie between values for the reaction of CO with the valency hybrids $(\alpha^{2+}\beta^{3+})_2$ and $(\alpha^{3+}\beta^{2+})_2$, suggesting that the singly reduced haem group is distributed equally between the α- and β-chains of haemoglobin. Since k_{41} is measured for singly reduced methaemoglobin it cannot involve any ferrohaem–ferrohaem interaction.[53]

The kinetics of binding of O_2 and CO to singly reduced methaemoglobin have also been measured to investigate the quaternary structure of tetrameric methaemoglobin.[54] In the absence of IHP at pH 6.8 the rates and activation energies of O_2 and CO binding agree well with those measured by other methods for binding of the fourth ligand to haemoglobin. On this basis it is concluded[54] that the valency hybrid and the parent methaemoglobin have a quaternary structure resembling that of haemoglobin in its high-affinity (R) state). IPH lowered the binding rate constants at pH 6.8, but not at pH 8.9 where the binding of IPH itself to the protein is drastically lowered, and it is concluded that the IPH-bound valency hybrid simulates low-affinity (T) haemoglobin at pH 6.8 but reverts to the R state at pH > 8. However, this structural transition does not coincide with the switch of spin state of the haem-iron that accompanies ionization of aquomethaemoglobin to hydroxymethaemoglobin in this pH range.

The alternative explanation of the effect of IHP on binding rates in terms of a shift in the dimer–tetramer equilibrium (see above) was discounted[54] on the grounds that the reaction kinetics were independent of protein concentration (10—40 μM based on tetramer). In contrast to the data of ref. 53, the kinetics of CO binding in the presence of IPH were biphasic at pH 6.8, and it is suggested[54] that IHP induces different reactivity in the α- and β-chains towards CO.

Methaemoglobin is reduced[55] by $\cdot OH$ ($k = 3.6 \times 10^{10}$ M^{-1} s^{-1}), $\cdot CH_2OH$ [$k = (9.5 \pm 1.5) \times 10^6$ M^{-1} s^{-1}), and $MeC\dot{H}OH$ [$k = (4.0 \pm 0.4) \times 10^7$ M^{-1} s^{-1}].

[53] K. Ho, M. H. Klepper, and L. M. Dorfman, *J. Biol. Chem.*, 1978, **253**, 238.
[54] Y. A. Ilan, A. Samuni, M. Chevion, and G. Czapski, *J. Biol. Chem.*, 1978, **253**, 82.
[55] J. W. Van Leeuwen, J. Tromp, and H. Nauta, *Biochim. Biophys. Acta*, 1979, **577**, 394.

Both organic radicals are 100% efficient in reducing the iron centre, indicating direct interaction with the haem group, whereas only about 40% of the ·OH reaction leads to reduction. A likely reason for this is that ·OH forms a radical on the protein that can undergo other reactions as well as transfer an electron to the haem group.

The superoxide ion $O_2^{\cdot -}$ shows no reaction with oxyhaemoglobin and reacts very slowly ($k = 1.4 \times 10^3$ M^{-1} s^{-1}), if at all, with methaemoglobin.[56] The reaction observed in the latter case is slow enough to be due to H_2O_2 formed by the disproportionation of $O_2^{\cdot -}$.

Myoglobin.—Metmyoglobin is reduced[55] in 100% yield by $\cdot CH_2OH$ [$k = (2.4 \pm 0.5) \times 10^7$ M^{-1} s^{-1}] and $MeC\dot{H}OH$ [$k = (5.5 \pm 0.5) \times 10^7$ M^{-1} s^{-1}] but not at all by ·OH (*cf.* methaemoglobin).

γ-Radiolysis of low-temperature ethylene glycol–water glass has been used to gain information on transient intermediates formed in the reduction of metmyoglobin–ligand complexes by electrons.[57] Reduction leads to the formation of low-spin liganded Fe^{II} myoglobin, in which the haem configuration is strained, when the sixth ligand is azide, inidazole, or water, and to two products corresponding to ligand-off and ligand-on when this ligand is fluoride. Spectral changes observed on raising the temperature of the irradiated glass from 77 to 160 K are consistent with dissociation of the ligand and transition of the low-spin intermediate to the high-spin final state. There is evidence[58] in the case of the azide and imidazole derivatives that more than one bound state is involved when these ligands dissociate.

Cytochrome *c*.—Rate constants for reduction of ferricytochrome *c* [cyt(III)-*c*] by several organic free radicals show that reaction is generally rapid ($k \approx 10^8$—2×10^9 M^{-1} s^{-1}) and that the electron is transferred from the radical directly to the iron centre.[55, 58] An exception is the pentaerythritol radical, $(CH_2OH)_3C\dot{C}HOH$, which has a neopentane structure. At pH < 7 this radical is less reactive ($k < 10^6$ M^{-1} s^{-1}) than most, although it becomes more reactive at higher pH ($k = 1.6 \times 10^8$ M^{-1} s^{-1} at pH 10). It is suggested[58] that the reduction path is through the crevice in cyt(III)-*c* which widens at high pH. Aromatic donor radicals generally are found to react faster than others, which may be due to π–π interactions with the porphyrin ring and other aromatic residues in the protein.

Reaction with ·OH leads to reduction of cyt(III)-*c* in less than stoicheiometric amounts[55, 58] (*cf.* methaemoglobin). Although ·OH reacts extremely rapidly ($k = 4 \times 10^{10}$ M^{-1} s^{-1}), changes in the absorption spectrum of cyt(III)-*c* continue up to seconds after the initial attack. On the assumption that these changes are due to electron tunnelling from a radical site on the surface of the protein to the iron centre, a tunnelling model has been constructed[59] which fits the experimental kinetics reasonably well. However, slow spectral changes are also observed after

[56] C. Ferradini, J. Foos, L. Gilles, D. Haristoy, and J. Pucheault, *Photochem. and Photobiol.*, 1978, **28**, 851.
[57] Z. Gasyna, *Biochim. Biophys. Acta*, 1979, **577**, 207.
[58] M. G. Simic and I. A. Taub, *Biophys. J.*, 1978, **24**, 285.
[59] J. W. Van Leeuwen, A. Raap, W. H. Koppenol, and H. Nauta, *Biochim. Biophys. Acta*, 1978, **503**, 1.

direct reduction of the iron centre and have been ascribed to conformational changes,[60] so the fit of the electron tunnelling model may be fortuitous.

Protoferrihaem IX intercalated in sodium dodecyl sulphate (SDS) micelles has been studied as a model system for cytochrome *c*.[61] Hydrated electrons reduce the solubilized haemin with $k = 5.2 \times 10^9$ M^{-1} s^{-1} at pH 9.2, and MeĊHOH radicals reduce it with $k = 5.6 \times 10^8$ M^{-1} s^{-1} at pH 9.2 and $k = 1.6 \times 10^9$ M^{-1} s^{-1} at pH 4. At both pHs reduction is accompanied by changes in the haemin spectrum consistent with production of the same ferrohaem in 100% yield, but at pH 9.2 further changes occur over several milliseconds. These slow changes, which are not observed at pH 4, have an activation energy of 15.8 kcal mol^{-1} and are independent of pH (9.2—10.7) and ionic strength (0.05—0.2 M); they are attributed[61] to protonation of the hydroxy-ligand in the reduced haemin:

$$[H_2O—Fe^{II}(por)\text{-}OH]^- \xrightarrow{H_2O} [H_2O\ –Fe^{II}(por)\text{-}H_2O]^0 + OH^-$$

·SDS radicals formed by ·OH attack on the surfactant cause marked changes in the haemin spectrum over several milliseconds. It is suggested[61] that these may be due to degradation of the porphyrin ring.

The kinetics of reduction by e^-_{aq} and $CO_2^{\bullet -}$ radicals of cytochrome c_3 from *Desulfovibrio vulgaris* have been reported.[62] The four haem groups in the molecule are kinetically equivalent towards attack by e^-_{aq} ($k = 2 \times 10^{10}$ M^{-1} s^{-1}), but CO_2^- reduces only two of the haem groups rapidly ($k = 2.1 \times 10^8$ M^{-1} s^{-1}). These biphasic kinetics are analogous to those observed for reduction by SO_2^- ($k = 6.8$ and 2.1×10^6 M^{-1} s^{-1}),[62] and the data are consistent with lack of electron transfer between haem groups within a single protein molecule.

Vitamin B_{12}.—The rate of electron transfer between the Co^I and Co^{III} derivatives of vitamin B_{12} has been reinvestigated:[63]

$$Co^I + Co^{III} \longrightarrow 2Co^{II} \qquad (42)$$

It was previously shown[64] by stopped-flow methods that $k_{42} = 5.8 \times 10^3 + 70.7\text{-}[OH^-]^{-1}$, whereas pulse radiolysis measurements gave $k_{42} = 3.2 \times 10^7$ M^{-1} s^{-1} in CO_2-saturated solution.[65] In the new study[63] it is reported that $k_{42} = 1.5 \times 10^7$ M^{-1} s^{-1} at pH 4 and decreases to 2.9×10^4 M^{-1} s^{-1} at pH 11.1, in substantial agreement with results in ref. 64.

Oxidation of vitamin B_{12r} by $Br_2^{\bullet -}$ occurs in three stages, as shown by changes in absorbance at 365 nm.[66] The sequence of reactions is represented as

$$Br_2^{\bullet -} + Co^{II} \longrightarrow [Br_2—Co^{III}] \qquad (43)$$

$$[Br_2—Co^{III}] \longrightarrow Br^- + [Br—Co^{III}] \qquad (44)$$

$$[Br—Co^{III}] + H_2O \longrightarrow [H_2O—Co^{III}] + Br^- \qquad (45)$$

[60] E. J. Land and A. J. Swallow, *Arch. Biochem. Biophys.*, 1971, **145**, 365.
[61] E. L. Evers, G. G. Jayson, and A. J. Swallow, *J.C.S. Faraday I*, 1978, **74**, 418.
[62] V. Favaudon, C. Ferradini, J. Pucheault, L. Gilles, and J. Le Gall, *Biochem. Biophys. Res. Comm.*, 1978, **84**, 435.
[63] D. A. Ryan, J. H. Espenson, D. Meyerstein, and W. A. Mulac, *Inorg. Chem.*, 1978, **17**, 3725.
[64] E. J. Kaufman and J. H. Espenson, *J. Amer. Chem. Soc.*, 1977, **99**, 7051.
[65] R. Blackburn, M. Kyaw, and A. J. Swallow, *J.C.S. Faraday I*, 1977, **73**, 250.
[66] D. Meyerstein, J. H. Espenson, D. A. Ryan, and W. A. Mulac, *Inorg. Chem.*, 1979, **18**, 863.

in which reaction of B_{12r} with $Br_2^{\bullet-}$ proceeds by an inner-sphere mechanism with $k_{43} = (3.4 \pm 0.6) \times 10^9\ M^{-1}\ s^{-1}$, $k_{44} \approx 10^4\ s^{-1}$, and $k_{45} = (6.4 \pm 0.7) \times 10^2\ s^{-1}$. This last value is in good agreement with a previously measured rate of aquation of bromocob(III)alamin.[67]

Superoxide Dismutase.—Rate constants for the reactions between $O_2^{\bullet-}$ and the Cu^{II} chelates of salicylate, acetylsalicylate, *p*-aminosalicylate, and di-isopropylsalicylate at pH 7.5 range[68] from 0.8 to $2.4 \times 10^9\ M^{-1}\ s^{-1}$ compared with native cuprein-copper for which $k = 1.3 \times 10^9\ M^{-1}\ s^{-1}$ per g atom of Cu. Thus, these chelates act as perfect model superoxide dismutases.

[67] D. Thusius, *J. Amer. Chem. Soc.*, 1971, **93**, 2629.
[68] M. Younes, R. Lengfelder, S. Zienau, and U. Weser. *Biochem. Biophys. Res. Comm.*, 1978, **81**, 576.

Part II

SUBSTITUTION REACTIONS

By

J. BURGESS

A. J. DEEMING

L. I. ELDING

P. MOORE

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Introduction

BY P. MOORE

This introduction summarizes progress made in the eighteen months January 1978—July 1979, and includes references to related reviews and topics of a more general nature. The subdivision into chapters differs from that of previous volumes, the attempted classification according to lability having been superseded by the metal ion co-ordination number or geometry as the most relevant feature. Since studies of six co-ordinated complexes are by far the largest part, this section is further subdivided (as before) into sections on solvolysis, base hydrolysis, formation, solvent exchange, isomerization, and racemization. Octahedral metal ions in different oxidation states are now considered separately. A chapter on linear complexes is included for the first time, although it is realized that here in particular for solvated aqua ions the classification may be somewhat arbitary. Another minor difference is that organometallic substitution reactions are also included in Part II rather than Part IV.

An extremely useful and comprehensive review (836 references) of the kinetics and mechanism of complex formation and ligand exchange (including water exchange) has appeared.[1] Tabulation of rate data for metal complex formations in aqueous media is comprehensive, but studies in non-aqueous media are largely excluded.* A compilation of rate constants for reactions of metal ions in unusual valency states has also been produced.[2] This covers reactions of mostly transient species, generated usually by pulse radiolysis and sometimes by flash photolysis or γ-radiolysis. Reviews which have appeared of a more general nature, and of relevance to mechanistic work, include studies of synthetic oxygen carriers related to biological systems,[3] the activation of co-ordinated amino-acids and related ligands, including the stereoselective synthesis of amino-acids and Schiff-base formation,[4] template reactions involving the synthesis of multidentate ligands (straight chain, branched chain, and macrocycles),[5] and the stereochemistry of chromium(III) complexes.[6] Although primarily of interest to organic chemists, a review of empirical parameters of solvent polarity as linear free-energy relationships is also of interest to inorganic kineticists.[7] A short review on ligand exchange

* A book by J. Burgess entitled 'Metal Ions in Solution', Ellis Horwood, 1978, is also strongly recommended, both for teaching and for research.

[1] D. W. Margerum, G. R. Cayley, D. C. Weatherburn, and G. K. Pagenkopf, 'Kinetics and Mechanisms of Complex Formation and Ligand Exchange', in 'Co-ordination Chemistry', Vol. 2, A.C.S. Monograph No. 174, ed. A. E. Martell, A.C.S., 1978.

[2] G. V. Buxton and R. M. Sellers, *Nat. Stand. Ref. Data Ser.* (*U.S. Nat. Bur. Stand.*), 1978, **62**, 80 pp.

[3] R. D. Jones, D. A. Summerville, and F. Basolo, *Chem. Rev.*, 1979, **79**, 139.

[4] D. A. Phipps, *J. Mol. Catal.*, 1979, **5**, 81.

[5] M. de Sousa Healy, and A. J. Rest, *Adv. Inorg. Chem. Radiochem.*, 1978, **21**, 1.

[6] I. D. Brown, *Coord. Chem. Rev.*, 1978, **26**, 161.

[7] C. Reichardt, *Angew. Chem. Int. Ed. Engl.*, 1979, **18**, 98.

reactions in inert solvents, with emphasis on non-polar solvents, has been presented in Japanese.[8] Russian workers have recently reviewed (in English) their extensive work on the kinetics and mechanisms of substitution reactions of *trans*-$[CoL_2XY]^{n+}$ (L = dioxime, X and Y = unidentate ligands) complexes.[9] An article by Pearson entitled 'Modern Kinetics, Use and Misuse' has appeared.[10]

Recent interest has focused upon work aimed at measuring volumes of activation (ΔV^*) in solution from high-pressure studies. Studies of inert systems continue to flourish,[11–19] and investigations of labile systems by *p*-jump, *T*-jump, n.m.r. line-broadening,[20] and even stopped-flow[21,22] are now possible. The proceedings of the sixth conference on High Pressure in Science and Technology held in 1977 have been published this year.[23] Articles include those by Swaddle on 'Pressure Effects in Inorganic Solution Chemistry' and by Jost on the 'Effect of Pressure on Complex Formations of Transition Metal Ions in Aqueous Solutions up to 2 kbar'. A striking example of the importance of high-pressure studies has recently appeared from Merbach's group. The variation of rate constants for methanol exchange with pressure for the bivalent metal ions Ni^{2+}, Co^{2+}, Fe^{2+}, and Mn^{2+} is illustrated in the Figure. A gradual shift in the slopes of the lines in the Figure indicates that the mechanism for solvent exchange changes from a dissociative I_d process for Ni^{2+} to an associative I_a process for Mn^{2+}. The volumes of activation are +11.4, +8.9, +0.4, and −5.0 $cm^3\ mol^{-1}$ for hexa(methanol) complexes of Ni^{2+}, Co^{2+}, Fe^{2+}, and Mn^{2+} ions respectively.[24] The associativity of Mn^{2+} solvent exchange is also confirmed by measurement of a negative value of ΔV^* for $[Mn(H_2O)_6]^{2+}$ ion.[25] One great advantage of ΔV^* measurements is the considerable accuracy in comparison with measurements of ΔS^*. Nevertheless, correlations between ΔV^* and ΔS^* continue to be found, a recent example being for racemization and isomerization reactions of octahedral complexes. It is argued that a correlation is to be expected for this type of reaction except in the case of a twist mechanism for the interconversion of optical and geometric isomers. Excluding data available for $[Cr(L)_3]^{3+}$ and $[Cr(L)_2(ox)]^+$ (L = phen or bipy), for which twist mechanisms are believed to occur, $\Delta S^* = (13.7 \pm 5.8) +$

[8] T. Sekine, *Chem. Abs.*, 1978, **89**, 139 563s.
[9] N. M. Amus and A. V. Ablov, *Coord. Chem. Rev.*, 1979, **28**, 177.
[10] R. G. Pearson, *Chemtech.*, 1978, **8**, 552.
[11] P. L. Kendall, G. A. Lawrance, and D. R. Stranks, *Inorg. Chem.*, 1978, **17**, 1166.
[12] G. A. Lawrance and D. R. Stranks, *Inorg. Chem.*, 1978, **17**, 1804.
[13] S. T. D. Lo, M. J. Sisley, and T. W. Swaddle, *Can. J. Chem.*, 1978, **56**, 2609.
[14] K. E. Hyde, H. Kelm, and D. A. Palmer, *Inorg. Chem.*, 1978, **17**, 1647.
[15] D. A. Palmer and H. Kelm, *Inorg. Chim. Acta*, 1978, **29**, L278.
[16] D. A. Palmer and H. Kelm, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1095.
[17] D. A. Palmer, R. van Eldik, T. P. Dasgupta, and H. Kelm, *Inorg. Chim. Acta*, 1979, **34**, 91.
[18] R. van Eldik, D. A. Palmer, and H. Kelm, *Inorg. Chem.*, 1979, **18**, 1520.
[19] D. A. Palmer and H. Kelm, *Z. Anorg. Allg. Chem.*, 1979, **450**, 50.
[20] H. Vanni, W. L. Earl, and A. E. Merbach, *J. Magn. Reson.*, 1978, **29**, 11.
[21] K. Heremans, 'Fast Reactions in Solution under High Pressure', in 'High Pressure Chemistry' ed. H. Kelm, Reidel, Dordrecht, 1978; Abstracts of the Second International Symposium on the Mechanisms of Reactions in Solution, University of Kent at Canterbury, 1979.
[22] S. Funahashi, K. Ishihara, and M. Tanaka, *Inorg. Chim. Acta*, 1979, **35**, 6351.
[23] High Pressure in Science and Technology, AIRAPT Conf., 6th, 1977, ed. K. D. Timmerhaus and M. S. Barber, Plenum, New York, 1979.
[24] F. K. Meyer, K. E. Newman, and A. E. Merbach, *J. Am. Chem. Soc.*, 1979, **101**, 5588.
[25] Y. Ducommun, K. E. Newman, and A. E. Merbach, personal communication.

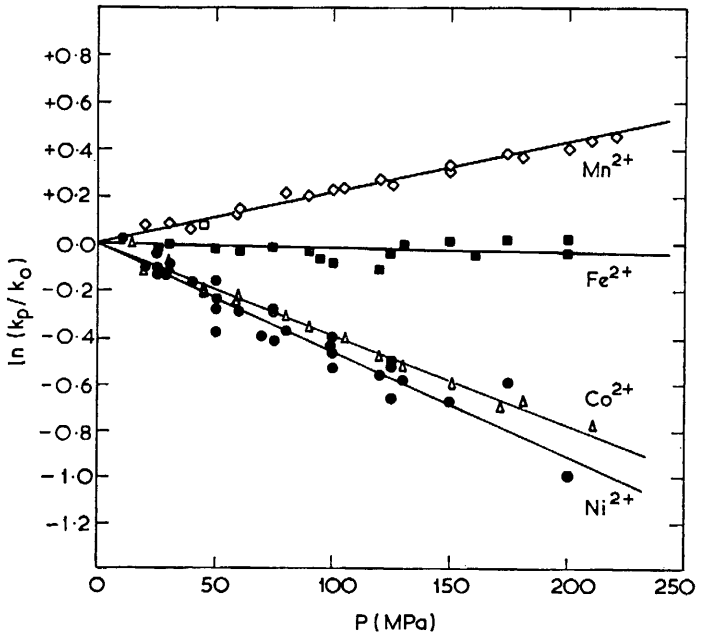


Figure *Variation of rate constants for methanol exchange with pressure for some bivalent metal ions*
(Reproduced by permission from *J. Am. Chem. Soc.*, 1979, **101**, 5588)

$(5.4 \pm 0.5)\Delta V^*$ for other racemizations and isomerizations.[26] One way of improving the accuracy of ΔS^* values is to study systems over as wide a temperature range as possible. For example, by combining conventional n.m.r. line-broadening experiments with stopped-flow n.m.r. studies, data for solvent exchange with moderately labile $[M(S)_6]^{3+}$ ions (M = Al or Ga, S = DMSO or DMF) have recently been obtained over a temperature range of more than 100 K.[27] Such results obtained from a combination of two techniques avoid the systematic errors which are inherent in many n.m.r. line-broadening studies alone.

In Volume 6 of this series, evidence was summarized for a relatively new mechanism involving covalent hydrate and pseudo-base formation in hydrolysis reactions of complexes of bipy, phen, and terpy.[28] Attack by H_2O or OH^- ion usually occurs at the carbon atoms adjacent to the co-ordinated *N*-donors (*e.g.* the 2,9-positions of phen), or at the 4,7-positions of phen, and at similar positions for bipy and terpy. However, for 5-nitro-1,10-phenanthroline, ^1H n.m.r. evidence has been found for attack by MeO^- ion at the 6-position of free and co-ordinated

[26] G. A. Lawrance and S. Suvachittanont, *Inorg. Chim. Acta*, 1979, **32**, L13.
[27] A. E. Merbach, P. Moore, O. W. Howarth, and C. H. McAteer, *Inorg. Chim. Acta*, 1980, **39**, 129; C. Ammann, C. H. McAteer, A. E. Merbach, and P. Moore, *Helv. Chim. Acta*, 1980, **63**, 268.
[28] P. Moore, in 'Inorganic Reaction Mechanisms', ed. A. McAuley, Specialist Periodical Reports, The Chemical Society, London, 1979, Vol. 6, p. 175.

ligand molecules.[29] For tervalent metal ions, hydrates formulated as $[M(LL)_3]X_3 . nH_2O$ (LL = bipy, phen) may even be covalent hydrates *e.g.* $[Ir(bipy)_2(bipy . H_2O)]Cl_3 . 3H_2O$.[30] Contrary to earlier reports, neither $[Ru(bipy)_3]^{3+}$ nor $[Ru(phen)_3]^{3+}$ racemizes or dissociates in aqueous solution, although covalent hydrates are believed to form reversibly.[31] Supporting evidence from *X*-ray crystallographic studies is still required, however, in this interesting area.*

Substitution reactions of aquachromium(III) complexes are now believed to proceed by an associative interchange I_a, mechanism. Negative volumes of activation support this conclusion, and recent theoretical calculations using an angular overlap model indicate that the most likely seven-co-ordinate transition state is one in which the entering and leaving groups are symmetrically disposed with respect to the four-fold axis defined by the five non-reacting ligands.[32]

The way in which aromatic aldehydes in 0.1M-NaOH catalyse the removal of the *trans*-NH_3 in $[Ru^{II}(NH_3)_5NO]^{3+}$ to give *trans*-$[Ru(NH_3)_4(OH)(NO)]^{2+}$ has been investigated.[33]

Reactions of ligands co-ordinated to cobalt(III) continue to be explored, and several examples are considered later.

* *Note added in proof.* Recent ^1H and ^{13}C n.m.r. studies of the reaction between $[Pt(bipy)_2]^{2+}$ and OH^- ions indicate that, contrary to previous reports, attack occurs at the metal centre in this case (O. Farver, O. Moensted, and G. Nord, *J. Am. Chem. Soc.*, 1979, **101**, 6118).

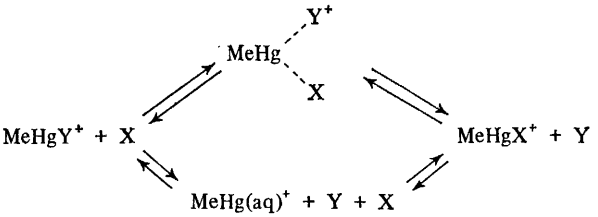
[29] P. Roberts, M. V. Twigg, and M. B. Williams, *Inorg. Chim. Acta*, 1979, **34**, L281.
[30] R. D. Gillard, R. J. Lancashire, and P. A. Williams, *J. Chem. Soc., Dalton Trans.*, 1979, 190.
[31] J. A. A. Sagüés, R. D. Gillard, R. J. Lancashire, and P. A. Williams, *J. Chem. Soc., Dalton Trans.*, 1979, 193.
[32] O. Moensted, *Acta Chem. Scand., Ser A.*, 1978, **32**, 297.
[33] C. P. Guengerich and K. Schuz, *Inorg. Chem.*, 1978, **17**, 2819.

1

Substitution Reactions of Linear Complexes

BY L. I. ELDING

Complex formation at linear mercury(II) is extremely rapid, and experiments in aqueous solution are further complicated by easy formation of hydroxo-complexes. Methylmercury compounds have received attention, partly on account of their molecular simplicity and partly because of their significance in the natural environment, but kinetic studies are scarce. Erni and Geier[1,2] have continued their comprehensive investigation of exchange reactions at linear mercury(II), using a high time-resolution *T*-jump method. The ligand exchange can be described by a two-path mechanism according to the Scheme. One of the paths



Scheme

consists of a concerted process *via* an associative transition state, whereas the other one, comparable to the solvent path in the square-planar substitutions, involves the formation of an intermediate aqua-complex and a subsequent substitution of water by the entering ligand. The reactions are almost diffusion controlled, except when hydroxide is involved. In this case the rates are lower, but the metal complex is not responsible for the intrinsic barrier, which instead is due to the specific structure of the hydrated hydroxide, which is supposed to react as $[H_7O_4]^-$. The term I_{al}, where the subscript 'l' denotes an activation energy caused by the ligand, is suggested for this type of associative interchange.

The symmetrization of methylmercury(II) chloride in non-aqueous media is a rather slow process.[3]

An ultrasonic absorption study of the kinetics for the formation of the second acetate complex of mercury(II) in acidic aqueous solution, reaction (1), gives rate

$$HgAc^+ + Ac^- \rightleftharpoons HgAc_2 \qquad (1)$$

[1] I. Erni and G. Geier, *Helv. Chim. Acta*, 1979, **62**, 1007.
[2] I. Erni, Thesis, E.T.H., Zürich, 1977.
[3] K. Stanley, J. Martin, J. Schnittker, R. Smith, and M. C. Baird, *Inorg. Chim. Acta*, 1978, **27**, L111.

constants for the forward (7.8×10^9 M^{-1} s^{-1}) and reverse (1.6×10^6 s^{-1}) reactions at zero ionic strength and 30 °C.[4] The close agreement between the rate constant for this complex formation and that obtained previously[5] for $HgCl_2$ formation indicates that the Eigen mechanism is operative for the acetate complexes also, involving a loss of a water molecule in the rate-determining step.

Another ultrasonic absorption study[6] of the rates of complexation–decomplexation of 15-crown-5 and 18-crown-6 complexes for a series of bivalent cations in aqueous solution shows that non-spherically co-ordinated Hg^{2+} (similarly to the previously studied[7,8] Ag^+) reacts faster with the crown ethers than spherically co-ordinated metal ions, which gives additional evidence for water loss as the rate-determining step. The more rigid crown ethers have to undergo considerable conformational strain to accommodate themselves to the linear geometry of silver(I) and mercury(II), so the rigidity of the ligand is especially important for the rate of complexation with these metal ions.[6]

Gold(I) is usually two-co-ordinate, although three- and four-co-ordinate species have also been detected. Two ^{31}P n.m.r. studies of mixed halide–tertiary phosphine systems show that both the co-ordination number and the exchange behaviour are functions of the ligand.[9,10] At >213 K, ligand exchange is rapid on the n.m.r. time-scale. Both associative and dissociative exchanges occur in these systems, but the linear bis-complex $[AuL_2]^+$ probably exchanges with free L by an associative path *via* $[AuL_3]^+$.[10]

Substitutions at linear Ag^I in aqueous solution are very fast and involve displacement of water as the rate-determining step.[11] Reaction between silver(I) ions and diphenylmethylenebismercaptoethanol is reported to be seven orders of magnitude slower, and can be followed using stopped-flow techniques.[12] The experiments give further support to the associative mechanism.

[4] K. Tamura, S. Harada, M. Hiraishi, and T. Yasunaga, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 2928.
[5] M. Eigen and E. M. Eyring, *Inorg. Chem.*, 1963, **2**, 636.
[6] L. J. Rodriguez, G. W. Liesegang, M. M. Farrow, N. Purdie, and E. M. Eyring, *J. Phys. Chem.*, 1978, **82**, 647.
[7] G. W. Liesegang, M. M. Farrow, F. A. Vazquez, N. Purdie, and E. M. Eyring, *J. Am. Chem. Soc.*, 1977, **99**, 3240.
[8] L. J. Rodriguez, G. W. Liesegang, R. D. White, M. M. Farrow, N. Purdie, and E. M. Eyring, *J. Phys. Chem.*, 1977, **81**, 2118.
[9] M. J. Mays and P. A. Vergnano, *J. Chem. Soc., Dalton Trans.*, 1979, 1112.
[10] C. B. Colburn, W. E. Hill, C. A. McAuliffe, and R. V. Parish, *J. Chem. Soc., Chem. Commun.*, 1979, 218.
[11] M. M. Farrow, N. Purdie, and E. M. Eyring, *Inorg. Chem.*, 1975, **14**, 1584.
[12] D. P. N. Satchell and T. J. Weil, *Inorg. Chim. Acta*, 1978, **29**, L239.

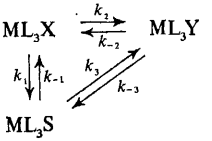
2

Substitution Reactions of Square-planar Complexes

BY L. I. ELDING

1 General

The mechanism for square-planar substitutions can be written as in Scheme 1, if the reactions are assumed to be associative. If the solvento intermediate is present



Scheme 1

in steady-state concentration, the rate constant for pseudo first-order conditions is given by equation (1), which simplifies to (2) if reverse reactions are suppressed.

$$k_{exp} = \frac{k_1 + k_1k_2[X]/(k_2[Y])}{1 + k_{-1}[X]/(k_3[Y])} + k_{-2}[X] + k_2[Y] \quad (1)$$

$$k_{exp} = \frac{k_1}{1 + k_{-1}[X]/(k_3[Y])} + k_2[Y] \quad (2)$$

If, furthermore, $k_{-1}[X] \ll k_3[Y]$, which is the usual case when the concentration of the leaving ligand is small, equation (2) reduces to the usual simple rate law $k_{exp} = k_1 + k_2[Y]$. One review[1] and several experimental studies[2-6] discuss this reaction scheme, with special emphasis on the nature of the solvent path. One point might be stressed. The absence of an observable solvent path in the experimental rate expressions does not necessarily indicate that the solvento species is unreactive with the entering nucleophile, which has been claimed in some cases.[4,7-9] For instance, platinum(II) aqua-complexes have now been shown to react readily with thiocyanate[3] and ethene,[10] contrary to the conclusions in some of the previous studies.[8,9] So far, there seems to be no example of a solvento intermediate ML_3S reacting more slowly with the nucleophile than the parent complex ML_3X.

Another important mechanistic aspect on the associative process is the possible existence of intermediates with increased co-ordination number. In the

[1] R. J. Mureinik, *Coord. Chem. Rev.*, 1978, **25**, 1.
[2] D. J. A. De Waal and W. Robb, *Inorg. Chim. Acta*, 1978, **26**, 91.
[3] L. I. Elding and A.-B. Gröning, *Inorg. Chim. Acta*, 1978, **31**, 243.
[4] P. V. Z. Bekker, *Inorg. Chim. Acta*, 1978, **31**, 109.
[5] R. J. Mureinik and M. Bidani, *Inorg. Chim. Acta*, 1978, **29**, 37.
[6] L. I. Elding and A.-B. Gröning, *Acta Chem. Scand., Sect. A*, 1978, **32**, 867.
[7] P. V. Z. Bekker and W. Robb, *Int. J. Chem. Kinet.*, 1975, **7**, 87.
[8] R. M. Milburn and L. M. Venanzi, *Inorg. Chim. Acta*, 1968, **2**, 97.
[9] R. J. Mureinik, *Inorg. Chim. Acta*, 1975, **13**, 127.

case of gold(III) halide systems, it has been suggested that *persistent* five-co-ordinate complexes exist, the formation and decay of which can be observed as separate processes.[11] According to a recent study of the $[AuCl_4]^-$–bromide reaction, however, it seems more reasonable that the observed processes are due to stepwise halide substitutions.[6]

Controversy over the interpretation of the kinetics for *cis–trans* isomerizations of square-planar complexes continues. The topic is important for the understanding of substitution mechanisms in general. Associative[12] and dissociative[13–15] mechanisms have been proposed, as well as intramolecular rearrangements *via* tetrahedral intermediates.[15,16]

Dissociative mechanisms for square-planar substitutions are discussed in a review.[1] A molecular orbital study of insertion of ethene into Pt—H bonds concludes that the reaction can be best described by a series of, preferably, dissociative steps.[17] Rearrangements of three-co-ordinate ML_3 T- or Y-shaped d^8-structures are discussed in this context. Three-co-ordinate intermediates are also suggested in the mechanisms for palladium(II)-catalysed oxidations of olefins,[18,19] and for electrophilic cleavage of platinum–carbon σ-bonds by protons.[20] Parallel associative and dissociative processes have been proposed for a substitution reaction of a square-planar rhodium(I) complex in benzene solution.[21] Especially, sterically crowded complexes have been thought to stabilize three-co-ordinate intermediates more easily. Recently determined activation volumes for sterically hindered square-planar complexes both of platinum[12] and palladium[21,22] are not compatible with dissociative activation, however.

Determination of activation volumes from the pressure dependence of rate constants is a useful tool for the classification of mechanisms. A comprehensive review of a wide range of reactions with data in tabular form covering the period 1966—1976 has appeared.[23] Kelm and co-workers have summarized results for co-ordination compounds, including square-planar complexes.[24–26]

[10] M. Green and C. J. Wilson, *J. Chem. Soc., Dalton Trans.*, 1977, 2302.
[11] A. J. Hall and D. P. N. Satchell, *J. Chem. Soc., Dalton Trans.*, 1977, 1404.
[12] R. van Eldik D. A. Palmer, and H. Kelm, *Inorg. Chem.*, 1979, **18**, 572; *Ber. Bunsenges. Phys. Chem.*, 1978, **82**, 1242.
[13] R. Romeo, *Inorg. Chem.*, 1978, **17**, 2040.
[14] J. H. Price, J. P. Birk, and B. B. Wayland, *Inorg. Chem.*, 1978, **17**, 2245.
[15] C. J. May and J. Powell, *Inorg. Chim. Acta*, 1978, **26**, L21.
[16] S. H. Strauss, S. E. Diamond, F. Mares, and D. F. Shriver, *Inorg. Chem.*, 1978, **17**, 3064.
[17] D. L. Thorn and R. Hoffmann, *J. Am. Chem. Soc.*, 1978, **100**, 2079.
[18] J. K. Stille and R. Divakaruni, *J. Organomet. Chem.*, 1979, **169**, 239.
[19] J. E. Bäckvall, B. Åkermark, and S. O. Ljunggren, *J. Am. Chem. Soc.*, 1979, **101**, 2411.
[20] R. Romeo, D. Minniti, S. Lanza, P. Uguagliati, and U. Belluco, *Inorg. Chem.*, 1978, **17**, 2813.
[21] Y. Othani, A. Yamagishi, and M. Fujimoto, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 1537.
[22] D. A. Palmer, R. Schmidt, R. van Eldik, and H. Kelm, *Inorg. Chim. Acta*, 1978, **29**, 261.
[23] T. Asano and W. J. Le Noble, *Chem. Rev.*, 1978, **78**, 456.
[24] H. Kelm and D. A. Palmer, *NATO Adv. Study Inst. Ser., Ser. C*, 1978, **41**, 281 (*Chem. Abs.*, 1979, **90**, 61 774).
[25] D. A. Palmer and H. Kelm, *NATO Adv. Study Inst. Ser., Ser. C*, 1978, **41**, 435 (*Chem. Abs.*, 1979, **90**, 61 776).
[26] D. A. Palmer, M. Cikovic, M. Mares, and H. Kelm, High-Pressure Sci. Technol., AIRAPT Conf., 6th, 1977, Vol. 1, p. 673, ed. K. D. Timmerhaus and M. S. Barber, Plenum, New York, 1979, (*Chem. Abs.*, 1979, **90**, 175 298).

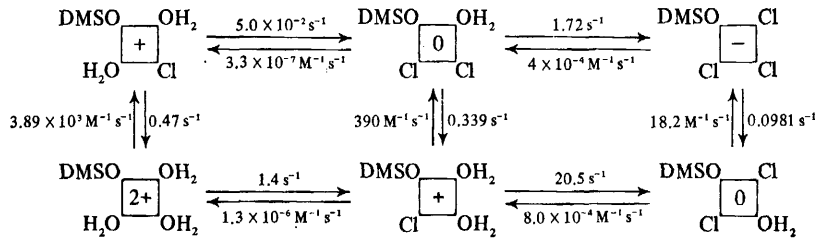
A special issue of *Biochimie*[27] devoted to a symposium on co-ordination chemistry and cancer therapy held in 1978 and a review article on mechanisms of antitumour activity[28] summarize the present state of knowledge in this field of research. A few recent articles dealing with mechanistic aspects on metal–nucleotide interaction will be mentioned below (see refs. 66—69, 79, 80, 98).

2 Platinum(II)

Reactions Involving Aqua-complexes.—Kinetic studies of various aqua-complexes $[PtCl_n(H_2O)_{4-n}]^{(2-n)+}$ ($n=0$—4) with a series of nucleophiles including halides, thiocyanate, DMSO,[3,29] and ethene[10,30] show that in all cases the solvated species are at least ten times more reactive than the corresponding parent complexes. The entering-ligand efficiency order is as follows:

$$\underset{\sim 10^{-3}}{H_2O} < \underset{0.3}{DMSO} \approx \underset{0.4}{C_2H_4} < \underset{1}{Cl^-} < \underset{4}{Br^-} < \underset{40}{SCN^-} < \underset{100}{I^-}$$

Aquation and chloride anation reactions for a chloro–DMSO–aqua-complex system have been studied in detail (Scheme 2).[31] Experimental data from these



Scheme 2 (*Data from ref. 31*)

studies have been used for a general MO description of the kinetic *cis*- and *trans*-effects.[32] The *trans*-effects for the ligands used span eleven orders of magnitude (for chloride as entering and water as leaving ligand),[31]

$$\underset{1}{H_2O} < \underset{200}{NH_3} < \underset{330}{Cl^-} < \underset{3\times10^3}{Br^-} < \underset{4\times10^4}{I^-} < \underset{1\times10^5}{SCN^-} < \underset{2\times10^6}{DMSO} < \underset{\sim10^{11}}{C_2H_4}$$

whereas the *cis*-effects vary only by a factor of 100 under the same conditions:[31]

$$\underset{0.05}{C_2H_4} < \underset{0.3}{Br^-} \approx \underset{0.4}{Cl^-} < \underset{1}{NH_3} \approx \underset{1}{H_2O} < \underset{2}{I^-} < \underset{5}{DMSO}$$

Nitro-complexes of platinum and palladium react with amidosulphuric acid according to reaction (3).

$$[M(NO_2)_4]^{2-} + 2NH_2SO_2OH \longrightarrow 2N_2 + HSO_4^- + [Pt(NO_2)_2(H_2O)_2] \quad (3)$$

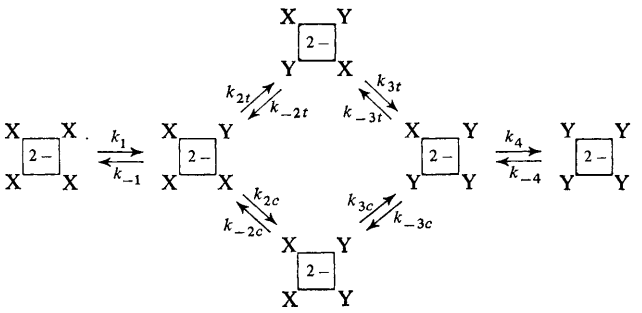
[27] *Biochimie*, 1978, **60**, No. 9.
[28] J. J. Roberts and A. J. Thomson, *Prog. Nucleic Acid Res. Mol. Biol.*, 1979, **22**, 71.
[29] L. I. Elding, *Inorg. Chim. Acta*, 1978, **28**, 255.
[30] M. Green and C. J. Wilson, *J. Chem. Res.* (*S*), 1978, 175.
[31] L. I. Elding and Ö. Gröning, *Inorg. Chem.*, 1978, **17**, 1872.
[32] J. K. Burdett, *Inorg. Chem.*, 1977, **16**, 3013.

The mechanism is proposed to be a rate-determining aquation of nitro-ligands followed by a redox process.[33] The rate constants obtained from volumetric measurements of initial rates differ only by a factor of 100 between platinum (3×10^{-5} s^{-1}), and palladium (4×10^{-3} s^{-1}).

Unidentate Ligand Exchange.—Exchange of chloride for a series of nucleophiles Y in the complexes *trans*-[PtL_2RCl], where L represents PEt_2 and R a large variety of *trans*-groups, takes place *via* the usual two-term rate law, but for most of the entering groups the k_1 term is predominant and can be used directly as a measure of the relative *trans*-effect of the groups R:[34] C_6F_5 < mesityl < *o*-tolyl < *p*-$NO_2C_6H_4 \approx$ *m*-$FC_6H_4 \approx$ *m*-$CF_3C_6H_4$ < Ph < Et ≈ Me < H. The *trans*-effect for these ligands spans six orders of magnitude. Similarly, for *trans*-[$Pt(NH_3)_2R(Cl)]^+$, the *trans*-ligands R can be ordered in the following series:[35] Me_2S, Et_2S < DMSO < $P(OEt_3) \approx PPh_3$. The *trans*-effects of the ligands L in the complexes *trans*-[$PtL(am)Cl_2$], where am represents various amines, can be estimated using ^{15}N and ^{195}Pt n.m.r. spectroscopy.[36] η-C_2H_4 has a much larger *trans*-effect than PPh_3 and σ-bonded (am)CH_2CH_2.

The pressure and temperature dependence for the substitution of bromide by iodide and thiourea in the sterically crowded complexes *cis*- and *trans*-[$Pt(PEt_3)$-(2,4,6-$Me_3C_6H_2$)Br] have been determined by van Eldik, Palmer, and Kelm.[12] For both the k_1 and k_2 paths, the activation entropies are strongly negative and the activation volumes vary between −11 and −16 cm^3 mol^{-1}. This is consistent with an associative mechanism, contrary to previous suggestions.[37]

Halide exchange in the $[PtCl_4]^{2-}$–$[PtBr_4]^{2-}$ system has been studied in detail[38] and compared with corresponding reactions for gold(III)[6] (see Table 1 and Scheme 3). The solvent path is predominant for the platinum complexes but not observable for those of gold (*cf.* p. 147). The previously well studied kinetics



Scheme 3

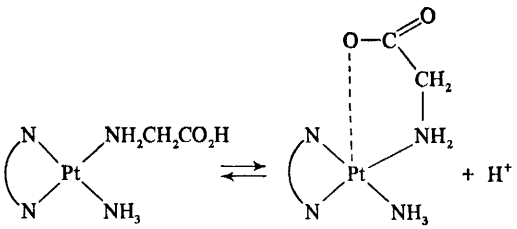
[33] Y. N. Kukushkin and O. V. Stefanova, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1977, **22**, 1844.
[34] M. Cusumano, P. Marricchi, R. Romeo, V. Ricevuto, and U. Belluco, *Inorg. Chim. Acta*, 1979, **34**, 169.
[35] E. A. Andronov, Y. N. Kukushkin, Y. S. Shcherbakov, G. N. Sedova, and T. M. Lukicheva, *Koord. Khim.*, 1978, **4**, 681.
[36] I. M. Al-Najjar, M. Green, S. J. S. Kerrisson, and P. Sadler, *J. Chem. Res.* (*S*), 1979, 206.
[37] R. Romeo, D. Minniti, and M. Trozzi, *Inorg. Chem.*, 1976, **15**, 1134.
[38] L. I. Elding and A.-B. Gröning, *Chemica Scr.*, 1977, **11**, 8.

for the halide substitution reactions of $[Pt(dien)X]^+$ have been reinvestigated.[39] Cyanide as entering ligand has been used for the displacement of nitro and chloride ligands in the substrates *trans*-$[Pt(NH_3)_2(NO_2)_2]$ and *trans*-$[Pt(NH_3)_2(NO_2)Cl]$, respectively.[40] In both cases, the first substitution step is rate determining.

Mureinik and Bidani[5] have performed a study of the reaction of $[Pt(terpy)Cl]^+$ with various nucleophiles with the aim of comparing the reactivity of the terpy and dien complexes. The rate constant for the solvent path is found to vary with the leaving ligand concentration according to $1/(a[X]+b)$, a and b being constants. This is believed to indicate a deviation from the normal mechanism. The reason for this conclusion is not quite clear, since the experimental expression reported by the authors conforms to the first term of equation (2) if the experiments are performed at constant [Y] and varying excess of [X].

Ring Opening and Closure.—Formation and cleavage of five-membered rings in several glycine complexes have been studied. In aqueous acidic media, the mechanism for chelate formation in *cis*-$[PtCl_2(glyH)_2]$ and in $[PtCl(en)(glyH)]$ involves rate-determining acid hydrolysis of the chloride ligands, followed by rapid ring closure in the intermediate aqua complex. In alkaline media, direct displacement of chloride by the chelating oxygen is rate determining.[41] An analogous study of the formation of the five-membered serine ring in *trans*-$[PtCl_2(serH)_2]$ has also been performed.[42]

In this context it is interesting to note that glycine ring closure in the octahedral *trans*-$[Pt(en)NH_3(glyH)Cl_2]^{2+}$ is accelerated by square-planar $[Pt(en)NH_3(glyH)]^{2+}$. A four-co-ordinate–five-co-ordinate equilibrium (4) followed by



(4)

formation of a chloride-bridged Pt^{II}/Pt^{IV} complex and subsequent electron transfer and bridge cleavage is a reasonable interpretation of these experiments.[43]

The ring-opening reactions of $[Pt(en)(gly)]^+$ and *cis*-$[Pt(gly)_2]$ take place *via* a base hydrolysis mechanism.[44] Studies of the influence of solvents (various water–alcohol–aprotic solvent mixtures) on the kinetics of ring-closure reactions

[39] R. M. Alcock, F. R. Hartley, and D. E. Rogers, *J. Chem. Soc., Dalton Trans.*, 1978, 123.
[40] R. S. Omarova, A. V. Babkov, and A. I. Busev, *Koord. Khim.*, 1978, **4**, 575.
[41] G. D. Malchikov, V. J. Kazbanov, and A. G. Molokanov, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1978, **23**, 885.
[42] T. P. Lastushkina, G. D. Malchikov, and A. V. Nikolaev, *Deposited Doc.*, 1977, VINITI 3211–77. (*Chem. Abs.*, 1979, **90**, 157 653).
[43] A. V. Nikoalev, T. K. Kazbanova, G. D. Malchikov, and V. I. Kazbanov, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1979, **24**, 60.
[44] V. I. Kazbanov, G. D. Malchikov, A. K. Starkov, and G. V. Khrustaleva, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1979, **24**, 73.

of various bidentate ligands including glycine have continued (*cf.* Volume 5 of this Report).[45–47]

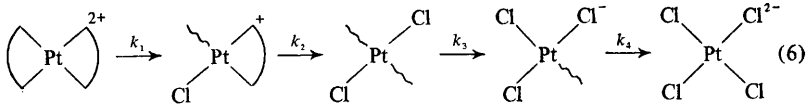
Ring closure for terdentate ligands has been studied in two cases. Gray and co-workers[48] determined rate constants and activation parameters for the closure of the first and second five-membered rings of the complex $[PtCl_3(basH_2)]^+$ [bas = $S(CH_2CH_2NH_2)_2$]. The rate constants for both reactions are inversely dependent on the hydrogen-ion concentration (as usual for ring closures involving amine or carboxylate ligands), indicating rapid acid–base equilibria preceding the rate-determining displacement of chloride by the chelating NH_2 groups. Both activation enthalpy and entropy are less favourable for the closure of the second ring which involves more internal strain than the first ring closure. Activation parameters for the second ring closure of $[PtCl(NH_2CH_2CH_2NHCH_2CO_2)]^+$ have also been reported.[49]

A comprehensive discussion of the factors that influence the kinetics for ring closure and opening has been made by Tobe, Romeo, and co-workers.[50] They studied the formation and cleavage of six- and seven-membered rings under the large *trans*-effect of DMSO, reaction (5),

$$cis\text{-}[Pt(DMSO)(N\text{–}NH)Cl_2]^+ \rightleftharpoons [Pt(DMSO)(N\text{–}N)Cl]^+ + H^+ + Cl^- \quad (5)$$

where N–N denotes chelated 1,3-diaminopropane (forming six-membered rings) or 1,4-diaminobutane (forming seven-membered rings). The authors discuss their results in relation to previous studies of five- and six-membered chelates, especially with regard to ring size, internal strain, and basicity of the amine ligands. The solid-state structure of the complex containing the seven-membered chelate indicates considerable internal strain.[51]

Displacement of oxalate from $[Pt(ox)_2]^{2-}$ by chloride takes place by a series of first-order reactions in the pH range 5—8.[52] In the proposed reaction sequence (6)



(6)

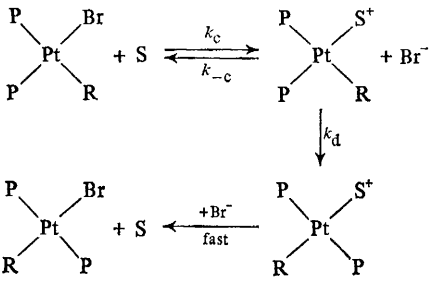
k_1 and k_3 denote the two rate-determining processes under the small *trans*-effect of oxalate oxygen. The conclusions of a previous study[53] are rebutted.

Isomerization.—In a comment to a previous paper by Louw,[54] which favoured a pseudorotation of a five-co-ordinate intermediate or a consecutive displacement

[45] L. F. Krylova, J. G. Lukyanova, and L. M. Volshtein, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1977, **22**, 1336.
[46] L. F. Krylova and L. D. Dikanskaya, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1978, **23**, 1696.
[47] L. M. Volshtein, L. F. Krylova, and N. S. Slyudkina, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1978, **23**, 59.
[48] G. Albertin, E. Bordignon, A. A. Orio, B. Pavoni, and H. B. Gray, *Inorg. Chem.*, 1979, **18**, 1451.
[49] K. B. Nolan and A. A. Soudi, *J. Chem. Res.* (*S*), 1978, 118.
[50] R. Romeo, S. Lanza, D. Minniti, and M. L. Tobe, *Inorg. Chem.*, 1978, **17**, 2436.
[51] N. B. Pahor, M. Calligaris, L. Randaccio, and R. Romeo, *Inorg. Chim. Acta*, 1978, **26**, L13.
[52] J. Hock and R. M. Milburn, *Inorg. Chem.*, 1979, **18**, 886.
[53] D. Banerjea and P. Banerjee, *Z. Anorg. Allg. Chem.*, 1973, **401**, 189.
[54] W. J. Louw, *Inorg. Chem.*, 1977, **16**, 2147.

mechanism for the *cis–trans* isomerization, Romeo[13] shows that the rate law used in Louw's paper is incorrect. He also summarizes the experimental results, which are claimed to support the dissociative type of mechanism. Price, Birk, and Wayland[14] studied uncatalysed *cis–trans* isomerizations of dimethyl, diethyl, and di-n-propyl sulphoxide complexes of the type $[PtL_2Cl_2]$ in deuteriochloroform using n.m.r. Two multistep mechanisms are proposed by these authors, which include respectively three- and four-co-ordinate intermediates which undergo geometric conversion to enable isomerization. May and Powell,[15] in an n.m.r. study of rearrangement of square-planar β-diketonate complexes of palladium and platinum, reject both pseudorotation of a five-co-ordinate species between the complex and the solvent and an associative solvent displacement. Their experiments favour instead either a square-planar–tetrahedral rearrangement (which has recently been independently suggested[16] for rapid isomerization of some rhodium complexes) or a partial dissociation to a three-co-ordinate intermediate.

Kelm and co-workers[12] have carefully analysed the data of Romeo *et al.*[37] for isomerization and solvolysis. They conclude that the rate law reported by these authors (involving a mass-law retardation for addition of halide) can also be described by a mechanism involving a rapid reversible solvolysis step followed by a rate-determining isomerization (k_d) of the solvento intermediate, according to Scheme 4. A prerequisite for this interpretation is that k_c and $k_{-c} \gg k_d$, which



Scheme 4

seems to be fulfilled for all reactions studied by Romeo *et al.*,[37] except in one case, where instead the rate of isomerization is determined by k_c, according to the model by Kelm *et al.*[12] The values of the activation parameters also speak in favour of an associative mechanism.[12]

The *cis–trans* isomerization of bis-chelate complexes of (*o*-aminophenyl)-diphenylphosphine (PNH_2) in ethanol is catalysed by anions.[55] The proposed mechanism involves equilibrium association of the anion, followed by rearrangement of the five-co-ordinate intermediate according to (7):

$$\textit{trans}\text{-}[Pt(PNH_2)_2]^{2+} + X^- \rightleftharpoons [Pt(PNH_2)_2X]^+ \longrightarrow \textit{cis}\text{-}[Pt(PNH_2)_2]^{2+} + X^- \quad (7)$$

Photoisomerization of *cis-* and *trans*-$[PtCl_2$(ethylene)(amine)] complexes have been studied, but mechanisms are not discussed.[56]

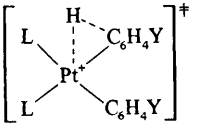
[55] M. C. Cooper and J. M. Downes, *Inorg. Chem.*, 1978, **17**, 880.
[56] R. Rumin and P. Courtot, *J. Organomet. Chem.*, 1979, **169**, 225.

The linkage isomerization of $[Pt(\eta^2\text{-PhC}{\equiv}CCl)(PPh_3)_2]$ to the alkynyl complex probably takes place by an intramolecular mechanism.[57]

Cleavage of Platinum–Carbon σ-Bonds.—Electrophilic cleavage of metal–carbon bonds may take place either by a direct attack on the bond or by an oxidative addition of the central metal followed by reductive elimination, *cf.* a recent review.[58] Romeo and co-workers[20] have studied reaction (8), which is first order

$$cis\text{-}[Pt(PEt_3)_2(YC_6H_4)_2] + H^+ + Cl^- \longrightarrow cis\text{-}[Pt(PEt_3)_2(YC_6H_4)Cl] + YC_6H_5 \quad (8)$$

with respect to complex and protons but independent of chloride concentration. The proposed mechanism involves a rate-determining electrophilic cleavage of the Pt—C σ-bond *via* the three-centred transition state (1). This is supported by



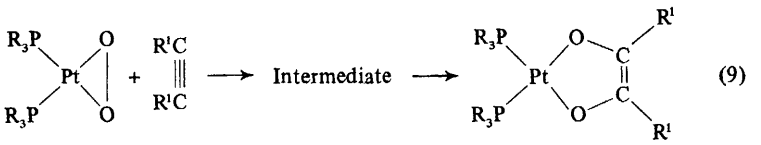
(1)

the observations that the rate increases with increasing electron density on the Pt—C axis, as determined by the electron-donating ability of the substituent Y, and that it also increases with the ease of electron detachment from platinum, as measured by anodic oxidation potentials.[59] Subsequent reactions in the proposed model are fast and involve a tentative three-co-ordinate intermediate.[20] An analogous mechanism is proposed for the cleavage of the Pt—C(alkyl) bond in *trans*-$[Pt(PEt_3)_2RMe]$, where R denotes various aryl substituents.[60] It is noteworthy that this mechanism contradicts earlier predictions[61] that these systems prefer attack by the electrophile on the metal (*cf.* also ref. 62).

On the other hand, protolysis of the Pt—C bond in *trans*-$[PtH(CH_2CN)(PPh_3)_2]$ takes place by a two-step oxidative addition–reductive elimination mechanism.[63] Obviously, which mechanism is preferred will probably depend on many factors, such as electronic and steric properties of the complex and its substituents, the nature of the electrophile, and the solvent.

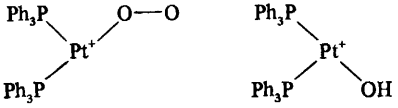
Miscellaneous.—The reaction between dioxygen platinum(II) complexes and substituted acetylenes takes place *via* two discernible steps, according to reaction (9), where $R^1 = CO_2Me$ and R = cyclohexyl. There is a direct attack by the acetylene on the dioxygen ligand.[64] Formation of μ-peroxo-μ-hydroxo-complexes

[57] J. Burgess, M. E. Howden, R. D. W. Kemmitt, and N. S. Sridhara, *J. Chem. Soc., Dalton Trans.*, 1978, 1577.
[58] M. D. Johnson, *Acc. Chem. Res.*, 1978, **11**, 57.
[59] R. Seeber, G. A. Mazzocchin, D. Minniti, R. Romeo, P. Uguagliati, and U. Belluco, *J. Organomet. Chem.*, 1978, **157**, 69.
[60] R. Romeo, D. Minniti, and S. Lanza, *J. Organomet. Chem.*, 1978, **165**, C36.
[61] J. K. Jarwad and R. J. Puddephatt, *J. Chem. Soc., Chem. Commun.*, 1977, 892.
[62] J. Behan, R. A. W. Johnstone, and R. Puddepatt, *J. Chem. Soc., Chem. Commun.*, 1978, 444.
[63] P. Uguagliati, R. A. Michelin, U. Belluco, and R. Ros, *J. Organomet. Chem.*, 1979, **169**, 115.
[64] C. H. Clark, A. B. Goel, and C. S. Wong, *J. Am. Chem. Soc.*, 1978, **100**, 6241.



(9)

of platinum(II) is suggested to take place *via* three-co-ordinate intermediates of the types (2) and (3).[65]

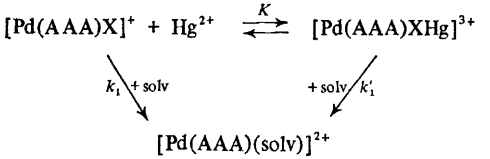


(2) (3)

Some mechanistic information about the interaction between platinum complexes and nucleotides has recently appeared;[66-69] see also the reviews[27,28] and refs. 79, 80, and 98.

3 Palladium (II)

Solvolysis and Complex Formation.—The mercury(II)-accelerated solvolysis of a series of thiocyanato- and selenocyanato-complexes and their N-bonded linkage isomers can be described by Scheme 5, where X stands for the thio- or seleno-



Scheme 5

cyanate and AAA denotes the terdentate chelating ligands Et_4dien or $MeEt_4$dien.[70] The studied systems represent two limiting cases of the general rate law (10).

$$k_{exp} = (k_1 + k_1'K[Hg^{2+}])/(1 + K[Hg^{2+}]) \quad (10)$$

For the N-bonded isomers, the Hg^{2+} can easily attack the free sulphur or selenium atoms of the ligands, so the equilibrium is displaced to the right and the rate law reduces to $k_{exp}=k_1'$ since k_1 for the spontaneous solvolysis is approximately 3×10^3 times smaller than k_1' for the mercury(II)-accelerated one. For the sulphur- or selenium-bonded isomers on the other hand, the rate law (10) reduces to $k_{exp}=k_1'K[Hg^{2+}]$. It should be noted that in this case the experiments cannot

[65] G. R. Hughes and D. M. P. Mingos, *Transition Met. Chem.*, 1978, **3**, 381.
[66] T. Boon-Keng, P. Eisenberger, J. Reed, J. K. Barton, and S. J. Lippard, *J. Am. Chem. Soc.*, 1978, **100**, 3225.
[67] G. Y. H. Chu, S. Mansy, R. E. Duncan, and R. S. Tobias, *J. Am. Chem. Soc.*, 1978, **100**, 593, 607.
[68] W. M. Scovell and R. S. Reaoch, *J. Am. Chem. Soc.*, 1979, **101**, 174.
[69] B. Nordén, *Inorg. Chim. Acta*, 1978, **31**, 83.
[70] M. Cusumano, G. Guglielmo, and P. Marricchi, *Inorg. Chim. Acta*, 1978, **30**, 29.

distinguish between the pre-equilibrium mechanism in Scheme 5 and a mechanism involving as a rate-determining step a direct electrophilic attack by Hg^{2+} on the substrate complex.

Irradiation of $[Pd(MeEt_4dien)(NO_2)]^+$ in methanol solution using wavelengths in the charge-transfer and ligand-field regions causes linkage isomerization followed by parallel photosolvolysis and thermal solvolysis of the formed nitrito-complex:[71]

$$[Pd(MeEt_4dien)(ONO)]^+ + MeOH \longrightarrow [Pd(MeEt_4dien)(MeOH)]^{2+} + ONO^- \quad (11)$$

Activation parameters for the anation by chloride of the sterically hindered $[Pd(MeEt_4dien)(OH_2)]^{2+}$ have been determined using a newly developed high-pressure stopped-flow instrument for moderately fast reactions. A negative activation volume and a zero activation entropy are compatible with an associative mechanism, probably I_a.[22] This study is the first in a series in which the effect of pressure on such relatively fast reactions will be studied. A summary of published and current work on pressure effects on the kinetics of sterically hindered palladium(II) complexes by the Frankfurt group has appeared.[26]

Steric effects of bulky entering ligands have been studied using the classical $[Pd(dien)(H_2O)]^{2+}$ complex as the substrate:

$$[Pd(dien)(H_2O)]^{2+} + R_2S \longrightarrow [Pd(dien)(R_2S)]^{2+} + H_2O \quad (12)$$

R_2S represents a series of symmetrical dialkyl sulphides of increasing complexity. As expected, the rate constants decrease with increasing chain length and branching of the alkyl substituents. The effects on the activation parameters are rather small, but it is obvious that the activation enthalpies for the branched substituents are larger than for the linear ones, and that there is a decrease of the negative activation entropies with increasing complexity within each series (linear and branched, respectively).[72]

Substitution of Unidentate Ligands.—The reactions

$$[PdX_4]^{2-} + L \longrightarrow [PdX_3L]^- + X^- \quad (13)$$

(X = Cl or Br; L = *N*-alkyl-substituted thioureas) have enthalpies of activation of the order of 5—7 kcal mol^{-1} and negative entropies of activation.[4] The experimental design in this study was similar to that used in a previous report by Bekker and Robb,[7] and rate law (2) was assumed to be applicable. In none of these two investigations, however, could the authors detect the solvent path corresponding to the first term in the rate law, which was reduced to $k_{exp} = k_2[Y]$. Their conclusion that the aqua-species $[PdX_3(H_2O)]^-$ is less reactive than $[PdX_4]^{2-}$ with thioureas (or about equally reactive) seems not to be justified by the experiments, however. The steady-state conditions were fulfilled only for the highest concentrations of chloride used, and in these experiments $k_1k_3/(k_3[Y]+k_{-1}[X]) \ll k_2$ even if $k_3 \gg k_2$ (*cf.* Scheme 1). For the smaller concentrations of chloride used in ref. 7 the steady-state condition for $[PdX_3(H_2O)]^-$ was not satisfied, so the rate

[71] L. Costanzo, A. Giuffrida, G. Guglielmo, and V. Richevuto, *Inorg. Chim. Acta*, 1979, **33**, 29.

[72] T. E. Jones, J. R. Cole, and B. J. Nusser, *Inorg. Chem.*, 1978, **17**, 3680; *Abs. Pap. A.C.S.*, 1978, **176**, 141.

expressions used were not applicable. Independent studies of the $[PdX_3(H_2O)]^-$–thiourea reaction have not been reported so far.

Bromide substitution in the sterically hindered complexes $[Pd(Et_4dien)XCN]^+$ and $[Pd(MeEt_4dien)XCN]^+$ (X = S or Se) follows the usual two-term rate law in methanol solution, whereas in the case of the nitrogen-bonded linkage isomers only the solvolytic path is observable.[70]

Previous kinetic studies of palladium complexes containing sulphide ligands have dealt mainly with relatively inert systems with chelating or sterically hindered sulphides. The replacement of a variety of organic sulphides R^1SR^2 (where R^1 and R^2 denote alkyl or phenyl groups) with pyridine and substituted pyridines according to reaction (14),

$$trans\text{-}[Pd(R^1SR^2)_2Cl_2] + am \longrightarrow [trans\text{-}Pd(am)_2Cl_2] + 2R^1SR^2 \qquad (14)$$

(am = amine) takes place *via* a two-stage process. The kinetics for the first, rapid substitution of one R^1SR^2 by am can be followed using a stopped-flow technique independent of the subsequent slower substitution. The reaction obeys the usual two-term rate equation.[73]

Analysis of the results shows that there are very small differences in the discriminating ability of one complex against the various entering amines, whereas, when the reactivity of the series of complexes towards a given amine is compared, there is a marked decrease in rate when the donor ability of the sulphur atom is increased; *i.e.* the lability decreases when the bond strength increases.[73]

In an effort to elucidate the influence of the non-reacting chelate ligands terpyridyl (terpy) and 3-azapentane-1,5-diamine (3-NHpd) on the reactivity of square-planar palladium complexes, the kinetics for the substitution reaction (15)

$$[Pd(terpy)X]^+ + Y^- \longrightarrow [Pd(terpy)Y]^+ + X^- \qquad (15)$$

have been studied[74] and compared with those of the previously investigated $[Pd(3\text{-}NHpd)X]^+$ complexes.[75] The terpy complexes are both more reactive (~ 1000 times) and more discriminating between various entering ligands than their 3-azapentane-1,5-diamine analogues, but the order of reactivity of the entering group Y^- is the same for both series of complexes (thiourea > I^- > Br^- > N_3^- > Cl^-). The lability sequence for the leaving groups X^- is dependent of the nature of Y^-, being $I^- > Br^- > Cl^- > N_3^- > NO_2^-$. The higher reactivity of the terpy complexes might be explained by the possibility of extensive π-interaction between the metal atom and the coplanar nitrogen atoms of the ligand, which enhances the electrophilicity of the reaction centre.[74]

Some qualitative n.m.r. studies on exchange reactions of palladium(II) tertiary phosphine complexes have been reported.[76] Exchange between the complexes $[PdL_2X_2]$ and $[PdL_3X]^+$ (L = a tertiary phosphine, X = Cl, Br, or I) is fast on the n.m.r. time-scale at room temperature but slow at −50 °C in $CDCl_3$ solvent. The line-broadenings observed can be explained if the exchange is assumed to take place *via* a reaction in which a halide of $[PdX_2L_2]$ is exchanged directly with the

[73] L. Cattalini, M. Cusumano, S. Degetto, *J. Chem. Soc., Dalton Trans.*, 1978, 12.
[74] M. Cusumano and G. Guglielmo, *Inorg. Chim. Acta*, 1978, **27**, 197.
[75] L. Cattalini, M. Cusumano, V. Ricevuto, and M. Trozzi, *J. Chem. Soc., Dalton Trans.*, 1975, 771.
[76] W. J. Louch and D. R. Eaton, *Inorg. Chim. Acta*, 1978, **30**, 243.

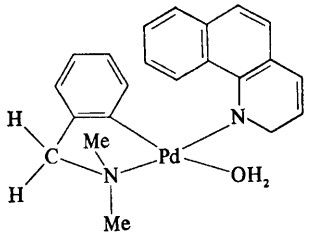
phosphine *trans* to the X of $[PdXL_3]^+$ *via* a halide-bridged intermediate. Exchange between the cationic complex $[PdXL_3]^+$ and free phosphine can also be observed.[76]

Isomerization.—Linkage isomerization rate constants for the reactions

$$[Pd(Et_4dien)(XCN)] \longrightarrow [Pd(Et_4dien)(NCX)] \qquad (16)$$

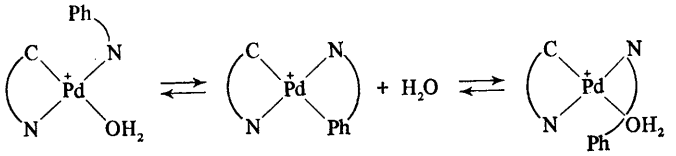
(X = S or Se) agree closely with the corresponding solvolysis rate constants, indicating that the mechanism for the isomerization involves a rate-determining formation of a solvento intermediate, followed by a rapid anation by NCX^- to form the nitrogen-bonded isomer.[70] Nitro–nitrito linkage isomerizations in the complexes $[Pd(AAA)(NO_2)]^+$, where AAA is the sterically hindered $MeEt_4$dien or Et_4dien or the unhindered dien, is induced by irradiation of methanol solutions of the complexes in the charge-transfer or ligand-field bands.[71]

Enantiometric forms of $[Pd(dmp)L(OH_2)]^+$ [dmp = 2-(dimethylaminomethyl)-phenyl, L = benzoquinoline] (4) rapidly interconvert in $(CD_3)_2CO$ solution to give



(4)

coalescence of the methyl ^1H n.m.r. singlets of the L ligand. A kinetic study[77] of the process supports a unimolecular displacement of H_2O associated with the ligand L rotating from largely above to largely below the co-ordination plane, *e.g.*



(17)

The intermediate (or transition state) is formally three-co-ordinate with a hydrogen occupying the fourth co-ordination site.

The isomerization of *trans*-$[Pd(MePh_2P)_2Cl_2]$ to the corresponding *cis*-isomer is accelerated by addition of catalytic amounts of the free phosphine ligand.[76] The isomerization probably takes place *via* formation of the $[Pd(MePh_2P)_3Cl]^+$ complex. *trans* → *cis*-Isomerization of bis(triphenylphosphine)diacetatopalladium(II) is a first-order process with an activation enthalpy of 16 kcal mol^{-1} and an activation entropy of -21 cal K^{-1} mol^{-1}.[78]

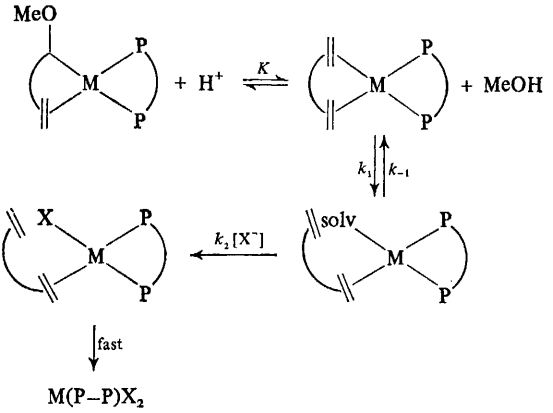
[77] A. J. Deeming and J. P. Rothwell, *J. Chem. Soc., Dalton Trans.*, 1978, 1497.
[78] A. D. Ryabov and A. K. Yatsimirskii, *Kinet. Katal.*, 1979, **20**, 106 (*Chem. Abs.*, 1979, **90**, 185 980).

Ring Opening and Closure.—The reactions between $[PdCl_4]^{2-}$ and inosine and guanosine have been studied with the aim of comparing the reactions of the palladium complexes with those of platinum previously studied.[79] Both ligands have a ketone oxygen atom at the 6-position which can be enolized, making possible the formation of five-membered chelate rings with the metal. The possibility of formation of such chelates has been proposed[80] to explain the mechanism of action of *cis*-$[Pt(NH_3)_2Cl_2]$ as an antitumour agent reacting with DNA, and is now clearly demonstrated, both for platinum and palladium. As expected, the palladium complexes react much faster with inosine and guanosine than those of platinum, and both metals form quantitatively the bis-complexes $[M(Nucl)_2]$ as the final reaction product. The N-bonded nucleosides exhibit a smaller *trans*-effect than chloride and bromide, which is also reasonable (*cf.* NH_3).

The displacement of the substituted bidentate dien ligand from palladium and platinum complexes by $X^- = Cl^-$ or Br^-, according to (18),

$$[M(C_{10}H_{12}Me)(P\text{–}P)]^+ + H^+ + 2X^- \longrightarrow [M(P\text{–}P)X_2] + C_{10}H_{12} + MeOH \quad (18)$$

takes place in one single observable step in aqueous methanol (P–P = 1,2-bisdiphenylphosphinoethane).[81] The observed rate constants are proportional to $[H^+]$ and independent of the nature and concentration of halide. They decrease with increasing water content. A mechanism consistent with these findings is given in Scheme 6. The rate-determining solvolysis (k_1) is preceded by an initial



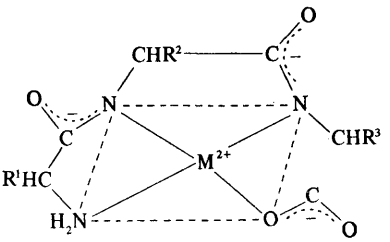
Scheme 6

fast $[H^+]$-dependent pre-equilibrium, giving $k_{exp} = k_1K[H^+]$. The palladium complexes react *ca.* 2—2.5 times faster than those of platinum, which is suggested to be a result of a balance between thermodynamic (K) and kinetic (k_1) factors.

[79] G. Pneumatikakis, N. Hadjiliadis, and T. Theophanides, *Inorg. Chem.*, 1978, **17**, 915.
[80] M. M. Millard, J. P. Macquet, and T. Theophanides, *Biochim. Biophys. Acta*, 1975, **402**, 166.
[81] R. Pietropaolo and F. Cusmano, *J. Organomet. Chem.*, 1979, **168**, 363.

The acid dissociation kinetics for doubly deprotonated palladium(II) triglycine complexes, $[Pd(H_{-2}GGG)]^-$ (5), takes place *via* four sequential bond-dissociation steps:[82]

$$[Pd(H_{-2}GGG)]^- \xrightarrow{k_1} X \xrightarrow{k_2} Y \xrightarrow{k_3} Z \xrightarrow{k_4} H_2GGG^+ + [PdCl_n]^{(2-n)+}$$



(5)

When solutions of $[Pd(H_{-2}GGG)]^-$ are mixed with acid, there is an initial, rapid absorbance change (k_1) complete within the stopped-flow dead-time. The three subsequent first-order reactions (k_2, k_3, k_4) are separated in rate by only about one order of magnitude each. Equilibrium c.d.–pH profiles help to characterize the intermediates, X, Y, Z, which each appear in appreciable concentration and are shown to contain three, two, and one nitrogen co-ordinated to palladium respectively. A stepwise unwrapping mechanism, starting at the carboxylate end (k_1) and ending with the slow cleavage of the terminal Pd—ammine bond (k_4), is proposed. Comparison with previous studies of triglycine complexes shows a regular trend in the reactivites $Cu^{II} > Ni^{II} > Pd^{II}$, covering a range of more than three orders of magnitude for similar species. This parallels the relative rates of substitution of these metal ions. Equilibrium protonation constants indicate that the Pd—N(peptide) bond is thermodynamically more stable than the Ni—N-(peptide) bond.[82]

Bridged Complexes.—Superoxide ion, O_2^-, reacts with dinuclear chloride-bridged palladium(II) complexes to form dioxygen products. The suggested mechanism involves bridge-splitting in two steps *via* nucleophilic displacement of chloride by superoxide.[83]

Reactions of allylpalladium chloride dimers with *N,N'*-diarylformamidines or 1,3-diaryltriazenes (L) in CH_2Cl_2 or $CHCl_3$ solution splits the chloride bridge and gives complexes of the type $[PdCl(L)(1,3\text{-}\eta\text{-}C_3H_5)]$, which show two distinct dynamic processes, interpreted as a dissociation of L and as a chloride–L exchange *via* a five-co-ordinate chloro-bridged species.[84]

4 Gold(III)

A monograph on gold chemistry which also contains a chapter on reaction

[82] J. C. Cooper, L. F. Wong, and D. W. Margerum, *Inorg. Chem.*, 1978, **17**, 261.
[83] H. Suzuki, K. Mizutani, Y. Moro-oka, and T. Ikawa, *J. Am. Chem., Soc.*, 1979, **101**, 748.
[84] T. Boschi, U. Belluco, L. Toniolo, R. Favez, and R. Roulet, *Inorg. Chim. Acta*, 1979, **23**, 37.

mechanisms in gold(III) systems with literature references dating to 1977 has appeared.[85] So far few mechanisms have been investigated in detail.

Two comprehensive studies of stepwise substitutions in gold(III) systems have appeared.[6,86] One of them describes the kinetics for the overall process (19)

$$[Au(NH_3)_4]^{3+} + 4H^+ + 4Br^- \rightleftharpoons [AuBr_4]^- + 4NH_4^+ \qquad (19)$$

and is the first part of a series of papers on substitutions in ammine–gold(III) systems.[86] Reaction (19) takes place in two discernible steps differing greatly in rate. The intermediate can be identified as *trans*-$[Au(NH_3)_2Br_2]^+$. In principle, the stoicheiometric mechanism for this overall reaction is analogous to that for the chloride–bromide exchange in platinum(II) systems (Scheme 3), the reaction *via* the *cis*-isomer of the 2,2-complex being negligibly slow. Scheme 3 can also be applied to reaction (20):[6]

$$[AuCl_4]^- + 4Br^- \rightleftharpoons [AuBr_4]^- + 4Cl^- \qquad (20)$$

In this case also, the contribution to the overall reaction by the path *via* the *cis*-isomer is of minor importance. The study[6] shows conclusively that there is no evidence for the build-up and subsequent slow decay of five-co-ordinate intermediates in this particular system (*cf.* ref. 11) and completes the results of some previous studies,[87–89] which have treated reaction (20) in a more superficial manner.

The data from refs. 6, 38, 88, and 89 enable a comparison of the reactivities for analogous Au^{III} and Pt^{II} complexes, which is given in Table 1. For bromide as entering nucleophile, the former react *ca.* 2×10^6 times faster than the latter, whereas for chloride the ratio decreases to *ca.* 10^5 and for water to only *ca.* 10^3. Since the influence of the leaving groups on the rate is similar for gold(III) and platinum(II) substrates, the variation of reactivity for various nucleophiles shown in the Table demonstrates that the nature of the entering nucleophiles is much more important for gold(III) complexes than for those of platinum(II). This is also in agreement with the observation[6,86] that both reactions (19) and (20) take place without any significant contribution from the solvent path, contrary to the corresponding platinum reactions. For halide as the entering nucleophile, the relative contribution of the solvent path to the overall reaction is *ca.* 100—1000 times smaller for the gold complexes than for the platinum. This confirms early conclusions that bond formation in the transition state is more important for gold(III) complexes than for those of platinum(II).[90]

Substitution of azide at *NNN″N″*-tetraethyldiethylenetriaminechlorogold(III) in binary aqueous solvent mixtures has been studied.[91]

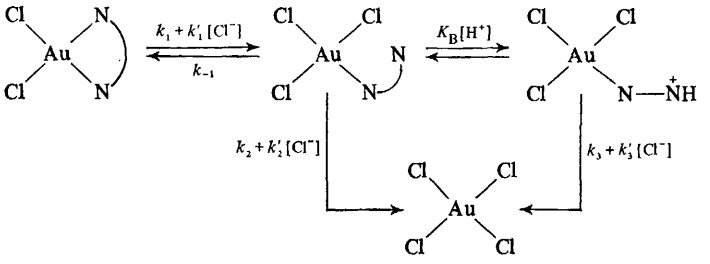
The displacement of ethylenediamine (en) and propylenediamine (pn) from the complexes $[Au(en)Cl_2]^+$ and $[Au(pn)Cl_2]^+$ occurs in two consecutive steps which

[85] R. J. Puddephatt, 'The Chemistry of Gold', Elsevier, Amsterdam and New York, 1978.
[86] L. H. Skibsted, *Acta Chem. Scand., Sect. A*, 1979, **33**, 113.
[87] L. Cattalini, A. Orio, and M. L. Tobe, *J. Am. Chem. Soc.*, 1967, **89**, 3130.
[88] W. J. Louw and W. Robb, *Inorg. Chim. Acta*, 1974, **9**, 33.
[89] W. Robb, *Inorg. Chem.*, 1967, **6**, 382.
[90] W. H. Baddely and F. Basolo, *Inorg. Chem.*, 1964, **3**, 1087.
[91] M. J. Blandamer, J. Burgess, S. J. Hamshere, and P. Wellings, *Transition Met. Chem.*, 1979, **4**, 161.

Table 1 *Rate constants at* 25 °C, 1.00 M *perchlorate medium, for reactions of analogous gold*(III) *and platinum*(II) *complexes*; $j=1$ for M = Au and $j=2$ for M = Pt. *Data from refs*, 6, 38, 88, and 89

Reaction	$k_{Au}/M^{-1}\,s^{-1}$ *Ref.* 6	$10^5 k_{Pt}/M^{-1}\,s^{-1}$ *Ref.* 38	k_{Au}/k_{Pt}	
$[MCl_4]^{j-}+Br^- \rightarrow [MCl_3Br]^{j-}+Cl^-$	63	4.8	1.3×10^6	
$[MCl_3Br]^{j-}+Br^- \rightarrow$ *trans*-$[MCl_2Br_2]^{j-}+Cl^-$	240	8.9	3×10^6	
$[MCl_3Br]^{j-}+Br^- \rightarrow$ *cis*-$[MCl_2Br_2]^{j-}+Cl^-$	29	2.6	1.1×10^6	$\sim2\times10^6$
trans-$[MCl_2Br_2]^{j-}+Br^- \rightarrow [MClBr_3]^{j-}+Cl^-$	30	0.94	3×10^6	
cis-$[MCl_2Br_2]^{j-}+Br^- \rightarrow [MBr_4]^{j-}+Cl^-$	460	10.0	5×10^6	
$[MCl_3Br]^{j-}+Cl^- \rightarrow [MCl_4]^{j-}+Br^-$	0.26	0.45	0.6×10^5	
trans-$[MCl_2Br_2]^{j-}+Cl^- \rightarrow [MCl_3Br]^{j-}+Br^-$	7.0	4.2	1.3×10^5	
cis-$[MCl_2Br_2]^{j-}+Cl^- \rightarrow [MCl_3Br]^{j-}+Br^-$	0.45	0.60	0.8×10^5	$\sim10^5$
$[MClBr_3]^{j-}+Cl^- \rightarrow$ *trans*-$[MCl_2Br_2]^{j-}+Br^-$	0.19	0.15	1.1×10^5	
$[MClBr_3]^{j-}+Cl^- \rightarrow$ *cis*-$[MCl_2Br_2]^{j-}+Br^-$	6.2	3.1	1.8×10^5	
$[MBr_4]^{j-}+Cl^- \rightarrow [MClBr_3]^{j-}+Br^-$	10.7	3.0	4×10^5	
	k_{Au}/s^{-1} *Refs.* 88, 89	k_{Pt}/s^{-1} *Ref.* 38		
$[MCl_4]^{j-}+H_2O \rightarrow [MCl_3(OH_2)]^{(1-j)+}+Cl^-$	0.022	4	6×10^2	$\sim10^3$
$[MBr_4]^{j-}+H_2O \rightarrow [MBr_3(OH_2)]^{(1-j)+}+Br^-$	0.245	19	12×10^2	

are kinetically separated.[92] The rapid ring opening and the subsequent slower displacement of the singly bonded amine can be described by Scheme 7. The



Scheme 7

results allow a comparison between the reactivities for five- and six-membered chelate rings. Ring formation is easier and ring opening more difficult for the five-membered than for the six-membered ring. The rate of displacement of the half-detached diamines is similar to that of unidentate amines if allowance is made for the differences in basicity. A comparison of estimated rate constants for the ring-closure reaction (21) (ionic charges omitted; en′ denotes unidentate

$$[M(en)(en')Cl] \longrightarrow [M(en)_2] + Cl^- \qquad (21)$$

unprotonated ethylenediamine) is given in Table 2. For amine nitrogen as the nucleophile there is a ratio of reactivity k_{Au}/k_{Pt} of about five orders of magnitude.

Table 2 *Rate constants at* 25 °C *for ring closure, reaction* (21)

M	k/s^{-1}	*Medium*	*Ref.*
Pd^{II}	~2—20	aq., 1M ClO_4^-	93
Pt^{II}	0.73	aq., 1M ClO_4^-	94
Au^{III}	$\sim 7 \times 10^4$	MeOH–aq., 1.7M ClO_4^-	92

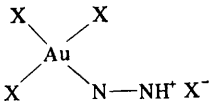
The formation of chelate complexes according to reaction (22),

$$[AuCl_4]^- + am \longrightarrow [Au(am)Cl]^+ + 3Cl^- \qquad (22)$$

where am represents various terdentate methyl-substituted diethylenetriamines, takes place with the entering of the first nitrogen as the rate-determining step, subsequent ring-closing reactions being fast.[95] The observed rates depend on the hydrogen- and chloride-ion concentrations in a rather complicated manner. To explain the chloride dependence for the tetra- and penta-methyl-substituted amines the authors suggest that formation of ion pairs between halide and deprotonated amines precedes the rate-determining ligand exchange. They arrive at a reaction model very similar to that proposed by Cattalini and co-workers[92] shown in Scheme 7, but they also consider the possibility of ion pairs of the type

[92] G. Annibale, G. Natile, B. Pitteri, and L. Cattalini, *J. Chem. Soc., Dalton Trans.*, 1978, 728.
[93] J. S. Coe, J. R. Lyons, and M. D. Hussain, *J. Chem. Soc.* (*A*), 1970, 90.
[94] M. J. Carter and J. K. Beattie, *Inorg. Chem.*, 1970, **9**, 1233.
[95] W. J. Louw and D. J. A. De Waal, *Inorg. Chim. Acta*, 1978, **28**, 35.

(6) which might account for the additional chloride-dependent terms obtained in some previous studies.[96, 97] They also suggest the possibility of a 'chelate effect' for long-chain amine ligands, caused by hydrogen-bonding between a co-ordinated halide and the positively charged end of the amine, which might explain the difficult detachment of the second (and third) nitrogen of some multi-dentate amines.



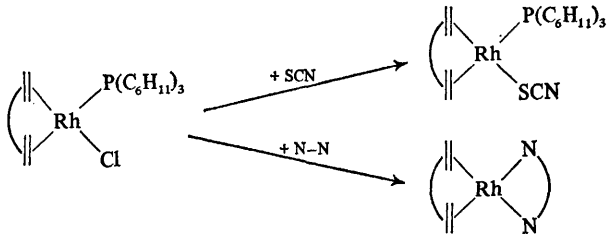
(6)

The reaction between $[AuCl_4]^-$ and ribonucleic acid can be followed spectrophotometrically. The reaction is first order with respect to gold and second order with respect to the nucleotide unit of RNA. pH and ionic strength dependences of the reaction rate indicate that various hydrolysed gold(III) species are probably involved in the reaction.[98]

Redox processes in gold(III) systems involving initial fast substitution steps have been described in previous volumes of this Report. Further examples are given by the reactions between $[AuCl_4]^-$ and dialkyl sulphides[99] and thiourea.[100] Both reactions take place in two discernible steps. The first corresponds to the formation of substitution products in equilibrium with $[AuCl_4]^-$, and the second one to the reduction of the gold(III) species to gold(I).

5 Rhodium(I), Iridium(I), and Cobalt(I)

The substitution reactions (23), where the chelate ligands are cyclo-octa-1,5-diene (cod), ethylenediamine (en), or *N*,*N*′-dimethylethylenediamine, offer two further illustrative examples of square-planar substitution reactions, where reversible solvolysis of the substrate complex has to be considered.[2] In these cases also, the observed rate constants depend on the concentration of the leaving ligand (X = Cl^-), so the more complete rate law (2) applies.



(23)

[96] G. Annibale, L. Cattalini, A. A. El-Awady, and G. Natile, *J. Chem. Soc., Dalton Trans.*, 1974, 802.
[97] A. J. Poë and D. H. Vaughan, *Inorg. Chim. Acta*, 1967, **1**, 255.
[98] C. Mandal and U.S. Nandi, *Chem.-Biol. Interactions*, 1978, **21**, 125.
[99] G. Annibale, L. Canovese, L. Cattalini, and G. Natile, 2nd International Symposium on the Mechanisms of Reactions in Solution, Canterbury, 1979.
[100] E. V. Makotchenko, B. I. Peshchevitskii, and R. I. Novoselov, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1978, 44 (*Chem. Abs.*, 1979, **90**, 93 116).

A stopped-flow study of the displacement of a series of chelating diamines (N–N) such as bipy and phen by ethylenediamine (en) in the complex [Rh(cod)-(N–N)]$^+$ shows that the complexes containing the less rigid diamines N–N react faster. The rate also depends on the basicity of the leaving N–N ligands, those having low pK_a reacting faster.[101]

The interpretation by Robb and Nicholson of the kinetics for amine displacements in [Rh(cod)Cl(am)] by 2,2′-bipy,[102] for piperidine displacement by amine in [Rh(cod)Cl(pip)],[103] and for the reaction between DMF and the dimer $[Rh(cod)Cl]_2$,[104] described partly in Volume 4 of this Report, has been questioned in a recent critical paper by Simmons and Laing.[105] Moreover, Mureinik and Bidani[5] have pointed out that the mathematical treatment of the rate laws in ref. 103 is erroneous. Simmons and Laing observed that both the dimer and the monomer yield essentially the same observed rate constants, and that the rate constants for the slow reaction are proportional to the initial total concentration of complex. They propose an alternative reaction model, where all the rhodium is initially assumed to be present as the dimer $[Rh(cod)Cl]_2$ and where ion pairs of the type [Rh(cod)(bipy)]$^+$[Rh(cod)Cl$_2$]$^-$ are suggested to be the reacting species in the slow step of the reaction between bipy and $[Rh(cod)Cl]_2$. In the original mechanism of Robb and Nicholson[102] for the [Rh(cod)(am)Cl]-bipy reaction, the fast and the slow reactions observed were (quite reasonably) interpreted as the [Rh(cod)(solvent)Cl]–bipy and the [Rh(cod)(am)Cl]–bipy reactions, respectively. The Simmons and Laing paper does not contain any new experimental results. To settle this discussion definitely, a supplementary experimental check will probably be necessary.

Addition of trimethyl phosphite to benzene solutions of the chloro-bridged dimer $[Rh(cod)Cl]_2$ in the stoicheiometric amount 3:1 causes simultaneous bridge-splitting and olefin displacement, the final product being the monomeric species $[Rh\{P(OMe)_3\}_3Cl]$.[106] In the reaction with $[Rh(CO)_2Cl]_2$, trimethyl phosphite preferentially displaces one carbon monoxide at each rhodium atom and then proceeds to cleave the dimer. Further addition of phosphite causes displacement of chloride rather than carbon monoxide from *trans*-[Rh(CO)-$\{P(OMe)_3\}_3$Cl]. Both reactions can be followed using $^{31}P\{^1H\}$ n.m.r. and i.r. spectroscopy, which enables a characterization of most of the species formed in solution. It is noteworthy that for the ratio $P(OMe)_3$:Rh = 4:1 the spectra suggest the presence of five-co-ordinate $[Rh(CO)\{P(OMe)_3\}_4]^+$, which probably has a trigonal-bipyramidal structure with axial CO.[106]

The previously mentioned substitution of acetonitrile in the complex [RhCl-(MeCN)$(PPh_3)_2$] by triphenylphosphine was followed in benzene solution using a stopped-flow technique and excess of both entering and leaving ligands. The observed first-order rate constants show an unusual dependence on these concentrations:

$$k_{exp} = (k + k'/[MeCN])[PPh_3] \qquad (24)$$

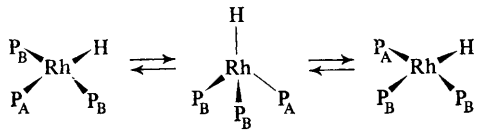
[101] W. Robb and C. G. Nicholson, *S. Afr. J. Chem.*, 1978, **31**, 1.
[102] W. Robb and C. G. Nicholson, *Inorg. Chim. Acta*, 1973, **7**, 645.
[103] C. G. Nicholson and W. Robb, *Inorg. Chim. Acta*, 1974, **8**, 41.
[104] C. G. Nicholson, Ph. D. Thesis, University of Natal, 1975.
[105] E. L. Simmons and M. Laign, *Inorg. Chim. Acta*, 1978, **27**, 43.
[106] M. L. Wu, M. J. Desmond, and R. S. Drago, *Inorg. Chem.*, 1979, **18**, 679.

It is noteworthy that the authors suggest parallel associative and dissociative pathways to explain this rate law.[21]

Five-co-ordinate species have previously been suggested as intermediates when substituted phosphines react with dinuclear Rh^I compounds.[107] A stable five-co-ordinate compound $[Rh(nbd)\{P(p\text{-}ClC_6H_4)_3\}_2Cl]$ has now been isolated in the reaction between $P(p\text{-}ClC_6H_4)_3$ and $[Rh(nbd)Cl]_2$.[108]

Ethene displacement from $[Rh(\eta^5\text{-}C_9H_7)(C_2H_4)_2]$ by incoming ligands such as carbon monoxide and trimethyl phosphite can be described by the mechanism previously proposed by Cramer and Siewell[109] for other Rh^I complexes which was discussed in Volume 5 of this Report. The observation that phosphine ligands containing strongly electron-withdrawing substituents, for example PF_3, displace ethene at significantly greater rates than other phosphines might indicate that a different mechanism is operating for such entering ligands, however,[110]

Variable-temperature $^{31}P\{^1H\}$ n.m.r. measurements[16] indicate that hydrido-(triphenylphosphine)rhodium(I), $[RhH(PPh_3)_3]$, has a square-planar C_s or C_{2v} structure in toluene solution. Interestingly, these experiments also give compelling evidence for a rapid intramolecular rearrangement ($230\ s^{-1}$ at $-13\ °C$) of the three PPh_3 ligands, which is unprecedented behaviour for a four-co-ordinate $4d^8$ or $5d^8$ complex (*cf.* $[RhCl(PPh_3)_3]$ or $[PtH(PPh_3)_3]$ which are structurally rigid in solution). Another similar case might be $[Rh(Me)(PPh_3)_3]$, for which early n.m.r. measurements indicated three equivalent phosphine ligands, interpreted as evidence for a stable tetrahedral structure.[111,112] Shriver and co-workers now suggest as a more reasonable explanation a square-planar structure undergoing a rapid intramolecular rearrangement, as in the case of $[RhH(PPh_3)_3]$:

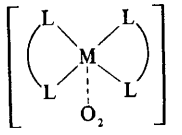


(25)

In equation (25), the three phosphines are equivalent in the tetrahedral intermediate. The mechanism (25) has been demonstrated for a large number of four-co-ordinate $3d^8$ complexes,[113] but is hitherto unknown for $4d^8$ or $5d^8$ complexes because of the increasing energy difference between square-planar and tetrahedral conformations, $3d^8 < 4d^8 < 5d^8$. An analogous mechanism has been proposed as an alternative for isomerization of a platinum complex.[15]

The oxygenation kinetics of some square-planar Co^I, Rh^I, and Ir^I complexes of the type $[M(LL)_2]^-$ (LL is diphosphine chelate) have been reinvestigated with the aim of finding out whether a chemically significant five-co-ordinate intermediate 'dot complex' (7) between the oxygen molecule and the square-planar complex exists. The lack of saturation effects for high $[O_2]$, the activation para-

[107] R. R. Schrock and J. A. Osborn, *J. Am. Chem. Soc.*, 1971, **93**, 2397.
[108] L. A. Oro and J. V. Heras, *Inorg. Chim. Acta*, 1979, **32**, L37.
[109] R. Cramer and L. P. Siewell, *J. Organomet. Chem.*, 1975, **92**, 245.
[110] H. Eshtiagh-Hosseini and J. F. Nixon, *J. Less-Common Met.*, 1978, **61**, 107.
[111] W. Keim, *J. Organomet. Chem.*, 1967, **8**, P25.
[112] K. C. Dewhirst, W. Keim, and C. A. Reilley, *Inorg. Chem.*, 1968, **7**, 546.
[113] R. H. Holm, *Acc. Chem. Res.*, 1969, **2**, 307.



(7)

meters, and the observed absorbance changes all indicate that such intermediates are *not* chemically significant in the mechanisms for oxygenation reactions.[114]

Square-planar *trans*-[IrCl($N_2C_5Cl_4$)(PPh_3)$_2$] reacts with phosphines, phosphites, isocyanides, nitrosyl, and diazonium to form five-co-ordinate species, whereas CO and SO_2 displace the diazo-ligand, giving square-planar products.[115]

6 Nickel(II)

Comparative studies of rates and mechanisms for square-planar nickel(II), palladium(II), and platinum(II) complexes containing bidentate sulphur ligands, which were discussed in the previous volume of this Report, have continued.[116]

Sterically hindered complexes of the type *trans*-[Ni(PEt_3)$_2$RX], where R denotes bulky substituted aryl groups, are suitable model systems for studies of substitutions at square-planar nickel. The complexes react slowly (conventional or stopped-flow range) and the bulky ligands block the axial positions, thereby preventing complications from square-planar–octahedral equilibria. The substitution reactions (26)

$$\textit{trans}\text{-[Ni(PEt}_3)_2\text{RX]} + \text{Y} \longrightarrow \textit{trans}\text{-[Ni(PEt}_3)_2\text{RY]} + \text{X} \qquad (26)$$

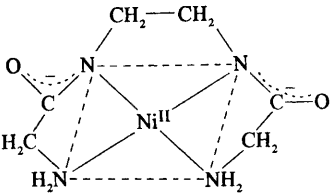
where X and Y represent a series of leaving and entering ligands, have been studied in ethanol and butanol solvent.[117] The usual two-term rate law compatible with Scheme 1 applies. As expected the contribution from the k_1 path is smaller for butanol solvent than for ethanol, in accord with poorer co-ordinating properties of the former, and also decreases with increasing excess of X according to equation (2). The reason for the author's classification of the k_1 path as dissociative interchange is not clear. The nucleophilicity order for the entering ligands is $N_3^- > SCN^- > Br^- > Cl^-$. Obviously, azide is a much better nucleophile for nickel(II) complexes than for those of platinum and palladium (*cf.* for instance ref. 72).

Exchange of acetylacetonate in [(PhCO)Ni(acac)(PPh_3)] and in [(PhCO)Ni(acac)(PEt_3)] can be followed using ^{1}H n.m.r. spectroscopy. Rate constants at 30 °C are *ca.* 500 s^{-1} and 200 s^{-1}, respectively. The phosphine ligands in these complexes are not exchanged.[118] Exchange of *N*-methylsalicylaldimines between square-planar nickel(II) and tetrahedral zinc(II) followed by ^{1}H n.m.r. spectroscopy (*ca.* 8×10^3 M^{-1} s^{-1} at 329 K) indicates a bridging associative mechanism.[119]

[114] L. Vaska, R. C. Patel, and R. Brady, *Inorg. Chim. Acta*, 1978, **30**, 239.
[115] K. D. Schramm and J. A. Ibers, *J. Am. Chem. Soc.*, 1978, **100**, 2932.
[116] M. J. Hynes and P. F. Brannick, *Proc. R. Ir. Acad., Sect. B*, 1977, 77 (19–47), 479 (*Chem. Abs.*, 1979, **89**, 49 501).
[117] M. Cusumano and V. Ricevuto, *J. Chem. Soc., Dalton Trans.*, 1978, 1682.
[118] K. Maruyama, T. Ito, and A. Yamamoto, *J. Organomet. Chem.*, 1978, **157**, 463.
[119] J. R. Blackborow, S. Karunaratne, J. C. Lockhart, and M. N. S. Hill, *J. Chem. Res.* (*S*), 1979, 93.

Displacement of multidentate ligands from square-planar nickel(II) has been the subject of several studies. Interest in cyanide as the displacing ligand has continued, and the nature of the intermediate species and the rate-determining steps in these reactions have been discussed.[120–122] Interactions between the multidentate leaving ligands and axial co-ordination sites of the metal have been suggested for these intermediates.[121] The mechanistic description of an earlier study[123] has been revised.[122]

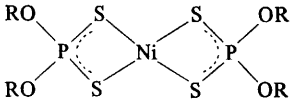
Displacement of the multidentate short-chain peptide ligand *N,N'*-diglycylethylenediamine from its square-planar complex (8) by edta proceeds through



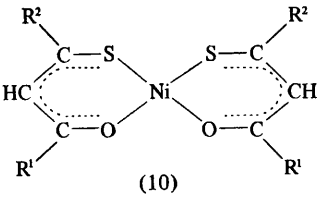
(8)

two paths. One of them is dissociative and the other involves direct displacement by deprotonated edta. Both reactions are accelerated through reaction with bicarbonate to form a protonated intermediate.[124] The rate for the reaction of triethylenetetramine (trien) with a series of deprotonated nickel(II)–dipeptide-amide–cyanide complexes varies with the dipeptide structure, which can be rationalized in terms of steric interactions during the rotation of chelate rings.[125]

Grant and co-workers have continued their studies of addition reactions of square-planar nickel(II) substrates to form octahedral products. Addition of 1,10-phenanthroline to complexes of the types (9) and (10) is first order with



(9)

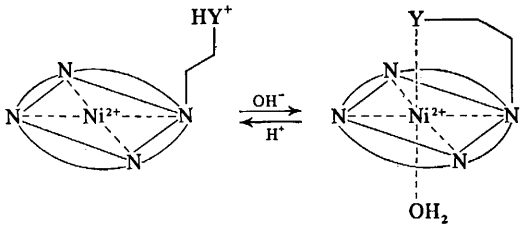


(10)

respect to complex and phenanthroline and probably takes place *via* an associative mechanism. The rate-determining step is believed to be a concerted process in which the formation of the first axial metal—N bond is accompanied by the movement of the ligands in the square plane to produce a five-co-ordinate

[120] K. Kumar and P. C. Nigam, *Indian J. Chem., Sect. A*, 1978, **16**, 518 (*Chem. Abs.*, 1979, **89**, 153 559).
[121] K. Kumar, P. C. Nigam, and G. S. Pandey, *J. Phys. Chem.*, 1978, **82**, 1955.
[122] K. Kumar and P. C. Nigam, *J. Coord. Chem.*, 1979, **9**, 139.
[123] V. Stara and M. Kopanica, *Collect. Czech. Chem. Commun.*, 1972, **37**, 2882.
[124] R. Pearson and G. K. Pagenkopf, *Inorg. Chem.*, 1978, **17**, 1799.
[125] G. K. Pagenkopf and W. A. Marchese, *J. Coord. Chem.*, 1978, **7**, 249.

intermediate; ring closure of the phenanthroline then occurs rapidly.[126] Square-planar–octahedral pH-dependent rearrangements according to equation (27) have also been proposed for complexes between nickel(II) and branched macrocycles, but no kinetic information is available.[127]



(27)

7 Copper(II)

Rapid ligand exchange in copper(II) glycine[128] and serine[129] systems can be followed by n.m.r. spectroscopy. The rate of exchange in the glycine system becomes comparable to the rate of NH_2–H_2O proton exchange for high copper concentrations. It is necessary to consider this effect when determining the rate constant for the ligand exchange.[128] The kinetics for formation of the first and second complexes between copper(II) and acetylacetonate and bipyridyl have been determined using *T*-jump.[130]

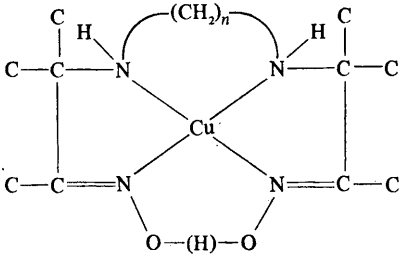
There is a direct correlation between the structural distortion and the kinetic reactivity of copper(II) complexes. This is excellently illustrated by a stopped-flow study of ligand exchange reactions of a series of bis(salicylaldimine) copper-(II) complexes, in which the ligand donor set remains constant whereas the co-ordination geometry varies from square-planar to nearly tetrahedral. The reaction is first order with respect to complex and entering ligand for both types of complexes, compatible with an associative mechanism.[131] The distorted complexes react faster, which contradicts previous suggestions[132] that Jahn–Teller effects might enhance the rate for the square-planar species. A simultaneous study of analogous complexes, including also those of nickel(II), reports the usual two-term rate law for square-planar substitutions.[133] Similarly, the ligand exchange in a series of bis(salicylaldiminato) complexes follows that rate law, but in that case the k_1 term is due to residual water in the aprotic solvents used.[134]

Slow isotopic exchange of the central ion in various square-planar copper(II) complexes with multidentate ligands has also been studied, with special reference

[126] M. U. Fayyaz and M. W. Grant, *Aust. J. Chem.*, 1978, **31**, 1439.
[127] T. J. Lotz and T. A. Kaden, *Helv. Chim. Acta*, 1978, **61**, 1376.
[128] I. Nagypál, E. Farkas, F. Debreczeni, and A. Gergely, *J. Phys. Chem.*, 1978, **82**, 1548.
[129] A. A. Popel, A. V. Zakharov, I. I. Evgeneva, and L. V. Vasileva, *Russ. J. Inorg. Chem.* (*Engl. Trans.*), 1978, **23**, 1351.
[130] M. Munakata and K. Yamada, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 3500.
[131] G. R. Dukes and S. L. Lovelady, *J. Chem. Soc., Chem. Commun.*, 1978, 583.
[132] G. Cayley, D. Cross, and P. Knowles, *J. Chem. Soc., Chem. Commun.*, 1976, 837.
[133] H. Elias, M. Schumann, and K. J. Wannowius, 2nd International Symposium on the Mechanisms of Reactions in Solution, Canterbury, 1979.
[134] H. Voss, K. J. Wannowius, and H. Elias, *Inorg. Chem.*, 1979, **18**, 1454.

to steric effects.[135,136] A study of a slow randomization reaction suggests an associative mechanism.[137]

Copper(II) has a strong tendency to form five-co-ordinate species. The reaction between cyanide and square-planar copper(II) ions of the structure (11) takes place in two steps. The initial fast reaction (too fast for stopped-flow) is an



(11)

addition of cyanide to form a five-co-ordinate tetragonal-pyramidal intermediate, which is subsequently slowly reduced to copper(I).[138] Axial co-ordination of the carboxylate groups in bis(triglycine) complexes of copper(II) is also proposed, and axial interactions are important in the mechanism for displacements in these complexes.[139] A series of papers describing complex formation between solvated copper(II) and macrocyclic ligands suggests reaction products with probably pseudo-octahedral structures.[140–144]

[135] H. Winkler, K. J. Wannowius, and H. Elias, *Z. Phys. Chem. (Frankfurt am Main)*, 1977, **107**, 57.
[136] G. Köhler and H. Elias, *Inorg. Chim. Acta*, 1979, **34**, L215.
[137] S. S. Eaton and G. R. Eaton, *Inorg. Nucl. Chem. Lett.*, 1979, **15**, 29.
[138] R. K. Murmann and B. Monzyk, *Inorg. Chem.*, 1978, **17**, 2461.
[139] J. M. T. Raycheba, F. R. Dukes, and D. W. Margerum, *Inorg. Chem.*, 1978, **17**, 2449.
[140] A. P. Leugger, L. Hertli, and A. Kaden, *Helv. Chim. Acta*, 1978, **61**, 2296.
[141] P. Schultz-Grunow and T. A. Kaden, *Helv. Chim. Acta*, 1978, **61**, 2291.
[142] T. J. Riedo and T. A. Kaden, *Helv. Chim. Acta*, 1979, **62**, 1089.
[143] L. D. Diaddario, L. L. Zimmer, R. E. Jones, L. S. W. L. Sokol, R. B. Cruz, E. L. Yee, L. A. Ochrymowycz, and D. B. Rorabacher, *J. Am. Chem. Soc.*, 1979, **101**, 3511.
[144] M. Kodama and E. Kimura, *J. Chem. Soc., Dalton Trans.*, 1979, 325.

3

Substitution Reactions of Tetrahedral Complexes

BY L. I. ELDING

Formation of inner-sphere sulphate complexes of beryllium(II) in water–formamide and water–DMSO mixtures studied by pressure-jump relaxation can be described by an extended Eigen–Tamm mechanism, which makes allowance for the different reactivities of the various solvated beryllium species. In principle, eight different relaxation processes should be expected, four for the replacement of water and four for the replacement of formamide/DMSO by a sulphate ion in the inner co-ordination sphere of beryllium. Some of these processes are very close in rate, however, so that only two relaxations are observed in water–formamide and five in water–DMSO solvent.[1,2] The kinetics for solvent exchange have also been studied in this context using ^{1}H n.m.r.[3] Formation of chelated [BeL] complexes with dicarboxylate anions L^{2-} takes place with ring closure as the rate-determining step. In the case of hydroxycarboxylates, only unidentate complexes are formed with a rate constant independent of the nature of the ligand and equal to the rate constant for formation of sulphato-complexes (200 s^{-1} at 25 °C).[4]

^{1}H N.m.r. spectroscopy has been used to study enantiomeric inversions of a series of tetrahedral chelates of zinc(II), cadmium(II), and lead(II). The rates of inversion depend on the nature of the metal, the donor atoms, and the structure and substituents of the chelate rings. An intramolecular diagonal-twist mechanism is suggested.[5] Rapid complex formation kinetics between zinc(II) and the glycine zwitterion[6] and pada (pyridine-2-azo-*p*-dimethylaniline)[7] have been studied using relaxation methods.

Associative mechanisms for ligand exchange in tetrahedral complexes of transition metals have been reported in several cases. Studies of tetrahedrally distorted copper and nickel complexes have already been mentioned above (see Chapter 2, refs. 131 and 133). Activation parameters for the solvent exchange in the tetrahedral nickel(II) solvento complex in hexamethylphosphoramide, determined using ^{31}P n.m.r. spectroscopy, are compatible with an associative

[1] R. Lachmann, I. Wagner, D. H. Devia, and H. Strelow, *Ber. Bunsenges. Phys. Chem.*, 1978, **82**, 492.
[2] D. H. Devia and H. Strelow, *Ber. Bunsenges. Phys. Chem.*, 1979, **83**, 627.
[3] H. H. Füldner, D. H. Devia, and H. Strelow, *Ber. Bunsenges. Phys. Chem.*, 1978, **82**, 499.
[4] B. Gruenewald and W. Knoche, *J. Chem. Soc., Dalton Trans.*, 1978, 1221.
[5] V. I. Minkin, L. E. Nivorozhkin, L. E. Konstantinovskii, and M. S. Korobov, *Koord. Khim.*, 1977, **3**, 174.
[6] S. Harada, Y. Uchida, M. Hiraishi, H. L. Kuo, and T. Yasunaga, *Inorg. Chem.*, 1978, **17**, 3371.
[7] B. H. Robinson and N. C. White, *J. Chem. Soc., Faraday Trans. 1*, 1978, **74**, 2625.

mechanism, the entropy of activation being -28 cal K^{-1} mol^{-1}.[8] Similarly, the activation volume for the triphenylphosphine (tpp) exchange in $[CoBr_2(tpp)_2]$ in deuteriated chloroform is -12 cm^3 mol^{-1} at 303 K, which is also in good agreement with a bimolecular mechanism *via* a five-co-ordinate transition state (I_a).[9] Oxygen exchange between water and $[MoO_4]^{2-}$ and $[WO_4]^{2-}$ in aqueous alkaline solutions takes place by a two-term rate law, corresponding to parallel spontaneous and hydroxide-assisted paths. Both pathways are proposed to be associative.[10] Similarly, a preliminary report concerning the stepwise substitutions $[MoO_4]^{2-} \rightarrow [MoS_4]^{2-}$ indicates associative activation.[11]

A study of reactions of chelating ligands with $[Ni(CO)_4]$, $[Co(NO)(CO)_3]$, and $[Fe(NO)_2(CO)_2]$ reveals both associative and dissociative pathways. Reactions with the tetracarbonylnickel complex take place in two steps, the first being a rapid dissociation to give a three-co-ordinate intermediate. The rate constants for this step are independent of the nature of the entering chelate ligand. The subsequent ring-closure reaction is associative and involves a displacement of a second carbonyl by the unattached donor atom of the chelate ligand. The complex $[Fe(NO)_2(CO)_2]$ reacts with 1,10-phenantroline by a purely second-order associative process. Reactions of the cobalt(II) complexes are less clear-cut, involving mixtures of first- and second-order kinetics.[12]

Complex formation between cobalt(II) and pyridine-2-aldoxime has previously been reported to be a slow process.[13] The reaction has now been reinvestigated, and the new study shows that the mechanism is not so simple as was believed. It probably involves redox processes, in which finally cobalt(III) is formed.[14]

Ligand exchange of peroxide between hydrogen peroxide and tetraperoxochromate(V) ion, $[Cr(O_2)_4]^{3-}$, has been studied and gives relevant information for the mechanisms of tetraperoxochromate decomposition reactions.[15]

Possible mechanisms for substitutions in tetranuclear clusters $[Fe_4S_4(SR)_4]^{2-}$, which contain tetrahedrally co-ordinated iron, have been discussed, but quantitative kinetic data are not available.[16]

The relevance of square-planar–tetrahedral rearrangements for reaction mechanisms of square-planar complexes was mentioned in Chapter 2 (references 15 and 16).

[8] J.-C. Boubel, J.-C. Delpuech, and A. Peguy, *Mol. Phys.*, 1977, **34**, 1093.
[9] F. K. Meyer, W. L. Earl, and A. Merbach, *Inorg. Chem.*, 1979, **18**, 888.
[10] H. von Felten, B. Wernli, H. Gamsjäger, and P. Baertschi, *J. Chem. Soc., Dalton Trans.*, 1978, 496.
[11] M. Harmer and A. G. Sykes, 2nd International Symposium on the Mechanisms of Reactions in Solution, Canterbury, 1979.
[12] B. J. Plankey and J. V. Rund, *Inorg. Chem.*, 1979, **18**, 957.
[13] M. W. Blackmore and R. J. Magee, *J. Inorg. Nucl. Chem.*, 1969, **31**, 2859.
[14] G. Bazsa, H. G. Shinouda, and M. T. Beck, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1665.
[15] S. B. Brown, P. Jones, and K. Prudhoe, *Inorg. Chim. Acta*, 1979, **34**, 9.
[16] R. W. Johnson and R. H. Holm, *J. Am. Chem. Soc.*, 1978, **17**, 5338.

4

Substitution Reactions of Five-co-ordinate Complexes

BY L. I. ELDING

1 Substitution and Intermolecular Exchange

Substitution at five-co-ordinate nickel(II) according to equation (1),

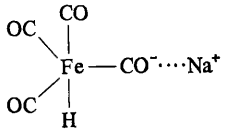
$$[NiX(qas)]^+ + Y^- \rightarrow [NiY(qas)]^+ + X^- \quad (1)$$

where qas is a tripod quadridentate ligand and X is axially co-ordinated, probably takes place *via* an I_a mechanism, since the rates are more sensitive to the nature of the entering ligand than to the leaving one, and are proportional to $[Y^-]$. The nucleophilicity order for $[NiBr(qas)]^+$ as the substrate is $PPh_3 \ll NO_2^- < I^- < SCN^- < N_3^- < CN^- < SC(NH_2)_2$.[1] The activation entropy of -12 cal K^{-1} mol^{-1} for the acetonitrile exchange at the probably trigonal-bipyramidal complex $[NiL(NCMe)]^{2+}$ also indicates an associative mechanism (L represents a quadridentate ligand and NCMe equatorially co-ordinated acetonitrile).[2] On the other hand, intermolecular phosphine exchange between trigonal-bipyramidal $[Ni(CN)_2(PMe_3)_3]$ and $[NiX(PMe_3)_4]^+$ (X = Cl or Br) and free phosphine takes place *via* a dissociative mechanism with square-planar intermediates.[3]

In the case of five-co-ordinate cobalt(II) complexes, it has been suggested that square-pyramidal complexes are more susceptible to nucleophilic attack than those having a trigonal-bipyramidal structure.[4] So far, however, only two trigonal-bipyramidal complexes (reacting purely dissociatively)[4,5] and one square-pyramidal (reacting associatively)[6] have been studied.

Carbonyl exchange at $[FeH(CO)_4]^-$ in tetrahydrofuran solution is catalysed by sodium ions. Formation of ion pairs (1) is thought to be responsible for the catalysis.[7] A kinetic study of diene exchange at five-co-ordinate iron complexes of the type $[(\eta^4\text{-enone})Fe(CO)_3]$ shows that the reaction proceeds *via* competing associative and dissociative pathways.[8]

[1] H. L. Collier, Thesis, Mississippi State University, 1977; *Diss. Abs. Int. B*, 1978, **38**, 3188 (*Chem. Abs.*, 1978, **88**, 126 910).
[2] N. Herron and P. Moore, *J. Chem. Soc., Dalton Trans.*, 1979, 441.
[3] P. F. Meier, A. E. Merbach, M. Dartiguenave, and Y. Dartiguenave, *Inorg. Chem.*, 1979, **18**, 610.
[4] M. J. Hynes and P. F. Brannick, *Inorg. Chim. Acta*, 1979, **33**, 11.
[5] P. M. Enriques, S. S. Zumdahl, and L. Forshey, *Chem. Commun.*, 1970, 1527.
[6] P. Meier, A. Merbach, S. Burki, and T. A. Kaden, *J. Chem. Soc., Chem. Commun.*, 1972, 36.
[7] M. Y. Darensbourg, D. J. Darensbourg, and H. L. C. Barros, *Inorg. Chem.*, 1978, **17**, 297.
[8] J. A. S. Howell and P. M. Burkinshaw, *J. Organomet. Chem.*, 1978, **152**, C5.



(1)

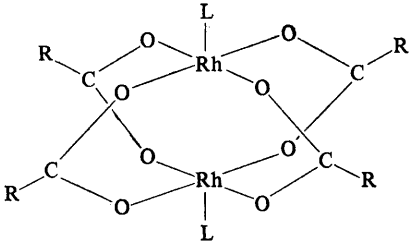
The acetylacetonate exchange with square-pyramidal $[VO(acac)_2]$ in dichloroethane solution is first order with respect to complex and free acetylacetonate. The activation entropy of -15 cal K^{-1} mol^{-1} is compatible with an associative rate-determining step. Addition of a donor solvent like DMSO inhibits the reaction by interaction with the proposed intermediate.[9]

The mechanism for substitution of X^- at five-co-ordinate [Ir(cod)(phen)X] (X=I or SCN) by ethylenediamine is dissociative.[10] Substitutions and exchange at five-co-ordinate nickel and palladium complexes containing tertiary phosphines and uni- or bi-dentate carbaboranyldithiocarboxylate ligands have been studied, but quantitative kinetic data are not yet available.[11]

A *T*-jump and stopped-flow study of the rapid anation of a five-co-ordinate copper(II) aqua-complex by azide and thiocyanate has its main interest as a model system for the active site of a metalloenzyme. The kinetics conform to the Eigen–Wilkins mechanism (rate-determining water release, I_d).[12]

2 Adduct Formation

Rate constants for exchange of axial water molecules in the tetra-μ-carboxylato-rhodium(II) complex (2) by nucleophiles L (pyridine, picolinic acid, niacin, or isonicotinic acid) have been determined using *T*-jump. The rate-determining step



(2)

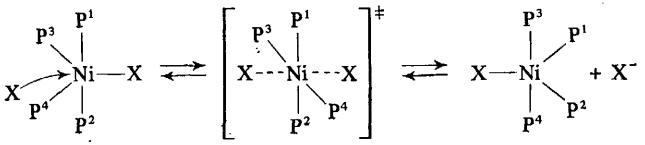
is suggested to be release of the axially co-ordinated water, but detailed kinetic data are not reported.[13] Axial addition of phosphines to bis(dialkylglyoximato)-palladium(II) complexes has also been studied.[14] A kinetic search for five-co-ordinate complexes formed by axial addition of oxygen to square-planar species

[9] M. Nishizawa and K. Saito, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 483.
[10] W. J. Louw and J. E. Singleton, *Inorg. Chim. Acta*, 1978, **27**, 21.
[11] B. Longato, F. Morandini, and S. Bresadola, *Inorg. Chim. Acta*, 1978, **26**, 157.
[12] J. H. Coates, P. S. Collins, and S. F. Lincoln, *J. Chem. Soc., Faraday Trans. 1*, 1979, **75**, 1236.
[13] J. L. Bear, R. A. Howard, and J. E. Korn, *Inorg. Chim. Acta*, 1979, **32**, 123.
[14] D. P. Graddon and I. A. Siddiqi, *Inorg. Chim. Acta*, 1978, **29**, L245.

was mentioned in Chapter 2 (ref. 114). See also relevant sections on reactions of square-planar nickel(II) and copper(II).

3 Intramolecular Rearrangements and Changes of Co-ordination Number

Merbach and co-workers have extended their comprehensive studies of solution structure and dynamics of five-co-ordinate nickel(II) phosphine complexes, *viz.* $[NiX_2(PMe_3)_3]$ (X = CN, Cl, Br, or I), $[NiX(PMe_3)_4]^+$ (X = Cl, Br, or I), and $[Ni(PMe_3)_5]^{2+}$. These complexes are all trigonal bipyramidal and stereochemically non-rigid on the n.m.r. time-scale. They display a variety of mechanisms for the intramolecular phosphine exchange (*i.e.* exchange from axial to equatorial co-ordination or reverse). For instance, a Berry pseudorotation is proposed for $[NiL_5]^{2+}$[15] and $[NiXL_4][BF_4]$,[3] a dissociative mechanism involving loss of an axial phosphine to form a four-co-ordinate intermediate for $[NiX_2L_3]$,[3] and an I_a mechanism *via* a 20-electron transition state for $[NiX(PMe_3)_4]X$[16] (see Scheme 1). Previously, a tetrahedral jump had been proposed for $[NiHL_4]^+$.[17]



Scheme 1

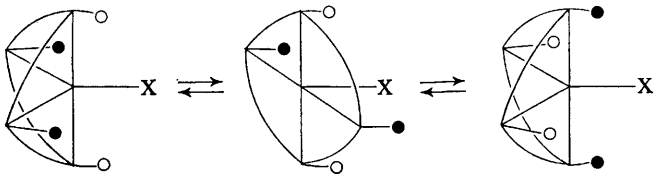
Square-pyramidal metal carbonyls $[M(CO)_5]$ (M = Cr, Mo, or W) are generated on u.v. photolysis of metal hexacarbonyls and related compounds and appear as intermediates in photochemical replacement reactions of the six-co-ordinate species. The reaction step relevant in this context is an internal rearrangement of the square-pyramidal $[M(CO)_5]$ *via* a trigonal-bipyramidal intermediate, and back to the square-pyramidal ground state. This spy → tbp → spy process represents an inverse Berry mechanism and also accounts for many other aspects of the photochemistry of these compounds.[18]

Intramolecular rearrangement in five-co-ordinate cobalt(I) and rhodium(I) complexes of the type $[ML_4\{(CN)_2C{=}C(CN)_2\}]^+$, where L represents various cyano-substituted organic ligands, are shown to be due to Berry pseudorotation, to rotation around the tetracyanoethylene double bond, and to catalysis by anions due to formation of ion pairs.[19]

^{13}C N.m.r. spectroscopy in nitromethane solutions of the complex $[ZnXL]^+$ (X = halide, NCS^-, or ClO_4^-, L is a quadridentate methyl-substituted tetra-azacyclotetradecane ligand) demonstrates a dynamic process which probably

[15] M. Dartiguenave, Y. Dartiguenave, A. Gleizes, C. Saint-Joly, J. Galy, P. Meier, and A. E. Merbach, *Inorg. Chem.*, 1978, **17**, 3503.
[16] P. Meier and A. S. Merbach, *J. Chem. Soc., Chem. Commun.*, 1979, 49.
[17] A. D. English, P. Meakin, and J. P. Jesson, *J. Am. Chem. Soc.*, 1976, **98**, 422, 7590.
[18] J. K. Burdett, J. M. Grzybowski, R. N. Perutz, M. Poliakoff, J. Turner, and R. F. Turner, *Inorg. Chem.*, 1978, **17**, 147.
[19] K. Sato, K. Kawakami, and T. Tanaka, *Inorg. Chem.*, 1979, **18**, 1532.

involves interconversion of axial and equatorial *N*-methyls. Scheme 2 shows a possible model for this dynamic process.[20]



Scheme 2

Spin-state changes which are accompanied by changes in the co-ordination sphere have been demonstrated by kinetic studies of the paramagnetic five-co-ordinate ⇌ diamagnetic four-co-ordinate equilibrium (2)[21]

$$[Ni(aex)(H_2O)]^{2+} \rightleftharpoons [Ni(aex)]^{2+} + H_2O \qquad (2)$$

(aex = 2,4,4-trimethyl-10,11-benzo-1,5-diaza-8,13-dithiacyclopentadeca-1,10-diene) and by five-co-ordinate high-spin ⇄ four-co-ordinate low-spin equilibria in the tetraphenylporphinatoiron(III) chloride system.[22]

[20] N. W. Alcock, N. Herron, and P. Moore, *J. Chem. Soc., Dalton Trans.*, 1978, 1282.
[21] L. Campbell, J. J. McGarvey, and N. S. Samman, *Inorg. Chem.*, 1978, **17**, 3378.
[22] D. Burdige and D. A. Sweigart, *Inorg. Chim. Acta*, 1978, **28**, L131.

5

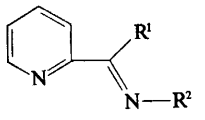
Octahedral Complexes: Aquation and Solvolysis

BY J. BURGESS AND P. MOORE

1 Oxidation State II

Iron(II) (d^6).—Rate constants, and in some cases activation enthalpies and entropies, for the dissociation of a range of anions $[Fe^{II}(CN)_5L]^{n-}$ have been reported. Ligands L include benzonitrile and the three dicyanobenzenes;[1] imidazole, glycine, and L-histidine;[2] and ammonia, alkylamines, and aniline.[3] Fully reversible photoaquation has been demonstrated for the anion with L = benzonitrile.[4] In many of these systems, rate constants for the reverse (formation) reaction, or for ligand replacement, have also been determined (see Chapters 7 and 8).

As for the pentacyano-complexes just dealt with, nucleophilic substitution at low-spin iron(II) di-imine complexes, $[Fe(LL)_3]$, appears in this section as well as in the chapters on base hydrolysis and ligand replacement. Schiff-base di-imine ligands such as (1) are unsymmetrical, with non-equivalent iron–nitrogen bonds in their complexes. There is thus the possibility of two simultaneous paths for the aquation of such complexes. Kinetic parameters for the various paths and steps in the reaction sequence for aquation of the complex of (1; $R^1 = R^2 = Me$) have been reported and compared with analogous constants from earlier studies of complexes of (1; $R^1 = H$).[5] The effects of ligand denticity (from 2 up to 6) and structure on aquation rates have been probed for related Schiff-base–iron(II) complexes.[6]



(1) R^1 = H or Me
R^2 = Me or Pr^i

Acid-dependent terms in rate laws for aquation of iron(II) complexes of flexible di-imine ligands, such as the above Schiff bases or 2,2′-bipyridyl, are ascribed to protonation of unidentate-ligand intermediates. Attempts have been made to

[1] A. P. Szecsy, S. S. Miller, and A. Haim, *Inorg. Chim. Acta*, 1978, **28**, 189.
[2] H. E. Toma, J. M. Martins, and E. Giesbrecht, *J. Chem. Soc., Dalton Trans.*, 1978, 1610.
[3] N. E. Katz, P. J. Aymonino, M. A. Blesa, and J. A. Olabe, *Inorg. Chem.*, 1978, **17**, 556.
[4] G. Calzaferri and H.-R. Grüniger, *Helv. Chim. Acta*, 1979, **62**, 1112.
[5] M. Tubino and E. J. S. Vichi, *Inorg. Chim. Acta*, 1978, **28**, 29.
[6] M. J. Blandamer, J. Burgess, R. I. Haines, F. M. Mekhail, and P. Askalani, *J. Chem. Soc., Dalton Trans.*, 1978, 1001.

measure the protonation constant for the $[Fe(bipy)_3]^{2+}$ cation,[7] but unfortunately these experiments were conducted in acidic nitrate media where both aquation and oxidation occur fairly rapidly. Kinetic parameters have been determined for aquation of the $[Fe(5\text{-Br-phen})_3]^{2+}$ cation;[8] here the rigidity of the phenanthroline ligand means that there is no acid-dependent term in the rate law. Kinetics of acid solvolysis of the cations $[Fe(LL)_3]^{2+}$ (LL = phen, 5-NO_3-phen, or bipy) in DMSO have been described. Here the kinetic evidence suggests that unidentate bipyridyl intermediates do not play a significant role. Comparison of rates in chloride and in sulphate media shows competitive ion-pair formation; the ion pair with chloride is of greatly enhanced reactivity.[9] Salt effects on reactivity of the bipy,[10,11] phen,[11] and 5-NO_2-phen[12] complexes and aquation rates in ethylene carbonate– or propylene carbonate–water solvent mixtures[13] are mentioned in Chapter 13 of this Part.

Further evidence has been presented for a dissociative mechanism for solvolysis of bis-imidazole- and bis-4-aminopyridine-phthalocyanineiron(II) complexes in DMSO. The dependence of rates on DMSO concentration in solvent mixtures with acetone or benzene indicates a limiting dissociative (*D*) mechanism.[14]

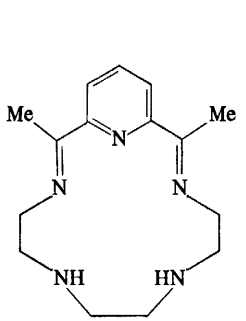
Ruthenium(II) (*d*^{6}).—Contrary to earlier reports, the $[Ru(bipy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ cations do not dissociate in aqueous media, but there is evidence for covalent hydration.[15] In connection with this, it may be mentioned that $[Ir(bipy)_3]Cl_3.4H_2O$ does not contain the earlier proposed unidentate bipyridyl ligand, but rather has one ligand covalently hydrated.[16] The complex $[Ru(bipy)_2(CN)_2]$ reacts in aqueous solution to give the ruthenium(III) complex $[Ru(bipy)_2(OH_2)_2]^{3+}$ by a complicated reaction sequence.[15] Excited-state $^*[Ru(bipy)_3]^{2+}$ is, like the ground state, substitution-inert.[17] A transient intermediate containing the substituted pyridine ligand π-bonded to the ruthenium has been proposed for photoaquation of $[Ru(NH_3)_5(X\text{-py})]^{2+}$ cations. This arrangement permits reversible protonation of the pyridine nitrogen in the photoaquated intermediate.[18]

Nickel(II) (*d*^{8}).—The activation volumes for aquation and racemization of the $[Ni(phen)_3]^{2+}$ cation are equal within experimental uncertainty at -1.2 and -1.5 cm^3 mol^{-1}, as is also the case for $[Fe(phen)_3]^{2+}$, where $\Delta V^{\ddagger}_{aq} = +15.6$ and $\Delta V^{\ddagger}_{rac} = +15.4$ cm^3 mol^{-1}. The simplest explanation, of a common rate-determin-

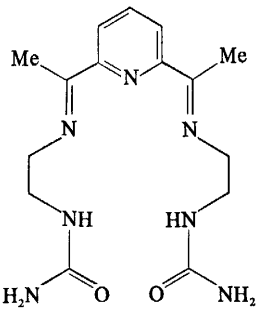
[7] V. I. Kravtsov, E. A. Mambetkaziev, and V. N. Statsyuk, *Elektrokhimiya*, 1978, **14**, 1120, (*Chem. Abs.*, 1978, **89**, 95850).
[8] J. Burgess and F. M. Mekhail, *Transition Met. Chem.*, 1978, **3**, 162.
[9] D. J. Farrington, J. G. Jones, and M. V. Twigg, *J. Chem. Soc., Dalton Trans.*, 1979, 221.
[10] S. Raman, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1073.
[11] A. P. Chagas, M. Tubino, and E. J. S. Vichi, *Inorg. Chim. Acta Lett.*, 1978, **28**, L137.
[12] N. F. Ashford, M. J. Blandamer, J. Burgess, D. Laycock, M. Waters, P. Wellings, R. Woodhead, and F. M. Mekhail, *J. Chem. Soc., Dalton Trans.*, 1979, 869.
[13] M. J. Blandamer, J. Burgess, S. J. Hamshere, and F. M. Mekhail, *Transition Met. Chem.*, 1979, **4**, 77.
[14] J. G. Jones and M. V. Twigg, *J. Chem. Soc., Dalton Trans.*, 1978, 1709.
[15] J. A. A. Sagues, R. D. Gillard, R. J. Lancashire, and P. A. Williams *J. Chem. Soc., Dalton Trans.*, 1979, 193.
[16] R. D. Gillard, R. J. Lancashire, and P. A. Williams, *J. Chem. Soc., Dalton Trans.*, 1979, 190.
[17] C. Creutz, N. Sutin, and B. S. Brunschwig, *J. Am. Chem. Soc.*, 1979, **101**, 1297; *Adv. Chem. Ser.*, 1978, No. 168, p.1.
[18] V. A. Durante and P. C. Ford, *Inorg. Chem.*, 1979, **18**, 588.

ing step for racemization and aquation, cannot be wholly true as rate constants differ somewhat. This problem, and that of the large difference between the nickel(II) and iron(II) values, is discussed in detail.[19] The relevance of $\Delta V^{\ddagger}$–$\Delta S^{\ddagger}$ correlations to the diagnosis of mechanism in this area has also been considered.[20] Perhaps surprisingly, in view of the possibility and impossibility of unidentate intermediates in loss of 2,2′-bipyridyl and 1,10-phenanthroline respectively, activation volumes for aquation of the series of cations $[Ni(phen)_{3-n}(bipy)_n]^{2+}$ ($n=0$—2), are all equal. But $\Delta H^{\ddagger}$ values do vary, with loss of bipy easier than loss of phen.[21] Reactions of tptz complexes of nickel(II) are mentioned with other cations below.

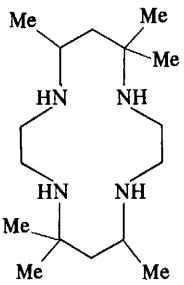
Some kinetic data on the dramatic effect of ring size on reactivity for dissociation of four-nitrogen-donor macrocycles from nickel(II) have been reviewed.[22] The nickel(II) complex of the five-nitrogen-donor Schiff-base ligand (2) readily undergoes ring opening in aqueous solution, to give the ligand (3) still bonded to the metal.[23] The complex $[Ni(LLLL)(DMSO)_2]^{2+}$, where LLLL = the four-nitrogen-donor macrocycle (4), loses DMSO by a limiting dissociative mechanism.[24]



(2)



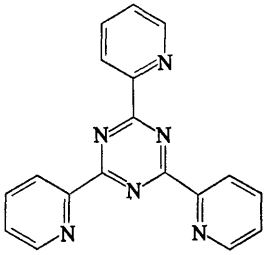
(3)



(4)

Other Studies.—The kinetics and mechanisms of reactions of tptz (5) complexes of cobalt(II), copper(II), and nickel(II) with water and with hydroxide have been established and compared. Covalent hydrates are believed to be important intermediates in aquation of the $[M(tptz)(OH_2)_3]^{2+}$ complexes.[25] Kinetics of aquation of the anions $[M(acac)_3]^-$ (M = Co, Cr, or Ru) have been studied in pulse radiolysis experiments. All three steps were monitored for the cobalt(II) complex, but the first step for the chromium(II) complex was too fast to follow and, predictably, all steps for the ruthenium(II) complex were too slow to follow by this technique. The mechanism of acac loss is thought to involve equilibrium

[19] G. A. Lawrance and D. R. Stranks, *Inorg. Chem.*, 1978, **17**, 1804.
[20] G. A. Lawrance and S. Suvachittanont, *Inorg. Chim. Acta Lett.*, 1979, **32**, L13.
[21] G. A. Lawrance, D. R. Stranks, and S. Suvachittanont, *Inorg. Chem.*, 1978, **17**, 3322.
[22] D. H. Busch, *Acc. Chem. Res.*, 1978, **11**, 392.
[23] C. Cairns, S. G. McFall, S. M. Nelson, and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, 1979, 446.
[24] Y. Masuda, T. Ito, N. Yoshida, and M. Fujimoto, *Chem. Lett.*, 1979, 565.
[25] R. D. Gillard and P. A. Williams, *Transition Met. Chem.*, 1979, **4**, 18.



(5)

formation of a unidentate intermediate, which dissociates from the metal ion by parallel acid-catalysed and uncatalysed paths.[26]

2 Oxidation State III

Cobalt(III).—*Unidentate Leaving Groups.* Volumes of activation for the aquation of $[Co(CN)_5X]^{3-}$ ions and for the anation of $[Co(CN)_5(OH)_2]^{2-}$ ion are collected in Table 1. The data are entirely consistent with the well established extreme dissociative *D*-mechanism for ligand substitution (see Introduction, ref. 19).

Table 1 *Volumes of activation for the aquation of* $[Co(CN)_5X]^{3-}$ *ions and for the anation of* $[Co(CN)_5(OH_2)]^{2-}$ *ion (at* 25 °C *and* $I = 1.0$ M *unless specified; data from Introduction, ref.* 19)

X^-	Cl^-	Br^-	I_3^-	NCS^-
$\Delta V^*/cm^3\ mol^{-1}$				
(aquation)	$+7.8\pm0.5$[a]	$+7.6\pm0.6$	$+14.0\pm0.7$	$+16.8\pm0.5$[b]
(anation)		8.4 ± 1.0	9.4 ± 1.6	8.2 ± 0.9

[a] At $I = 0.10$ M, $\Delta V^* + 10.0\pm0.6$ and 9.1 ± 0.3 $cm^3\ mol^{-1}$ at 40 and 25 °C respectively. [b] 0.1 M $[HClO_4]$.

Much smaller values of ΔV^* are observed for the Hg^{2+} ion-induced aquation reactions of $[M(NH_3)_5X]^{2+}$ ions (M = Co, Cr, or Rh) (Introduction, ref. 17). At 15 °C in 0.31M $[H^+]$, when M = Co, $\Delta V^* = -1.7\pm1.0$ $cm^3\ mol^{-1}$ (X = Cl) and $\Delta V^* = +0.8\pm0.5$ $cm^3\ mol^{-1}$ (X = Br), and similarly when $M = Cr^{3+}$, $\Delta V^* = +0.7\pm0.4$ $cm^3\ mol^{-1}$ (X = Cl, 15 °C) and when $M = Rh^{3+}$, $\Delta V^* = -1.0\pm0.4$ $cm^3\ mol^{-1}$ (X = Cl, 25 °C). Again, these data are consistent with the known mechanism involving rate-determining dissociation of a rapidly formed M—X—Hg bridge precursor complex. For the Hg^{2+} ion-induced aquation of $[Co(NH_3)_5N_3]^{2+}$ ion, $k_{obs} = kK[Hg^{2+}]/(1 + K[Hg^{2+}])$, and, from studies between 60 and 80 °C and $I = 1.0$ M, the precursor formation constant, $K = 7.3\ M^{-1}$, $\Delta S°(K) = -15.5$ cal $K^{-1}\ mol^{-1}$, and $\Delta H°(K) = -5.8$ kcal mol^{-1}, and the dissociation rate constant $10^5k = 1.0\ s^{-1}$, $\Delta S^*(k) = 9.8$ cal $K^{-1}\ mol^{-1}$, and $\Delta H^*(k) = 27$ kcal mol^{-1} at 25 °C. The association constant for the $Co^{III}NNNHg^{II}$ adduct is much smaller than the value of $K = 9.8 \times 10^4\ M^{-1}$ found for the analogous

[26] D. Meisel, K. H. Schmidt, and D. Meyerstein, *Inorg. Chem.*, 1979, **18**, 971.

Co^{III}–NCS–Hg^{II} precursor, in line with the greater affinity of Hg^{2+} ion for S-donor ligands.[27]

The induced aquation of $[Co(NH_3)_5N_3]^{2+}$ ion in the presence of nitrous acid *and* Hg^{2+} ion has also been investigated in aqueous perchlorate solutions.[28] In this case, the pseudo-first-order rate constant $k_{obs} = A[H^+]^2[NO_2^-]_{total}/([H^+] + B[Hg^{2+}])$, where A and B are constants. The Hg^{2+} ion inhibits attack of NO^+ ion by competing with H^+ ion for the nitrite which is present. In mixed acetonitrile–aqueous solutions, formation of $[HgNO_2]^+$ is more complete, $B[Hg^{2+}] \gg [H^+]$, and then $k_{obs} = k[H^+]^2[NO_2^-]_{total}/[Hg^{2+}]$. For the Hg^{2+} ion-induced aquation of $[Co(NH_3)_5Cl]^{2+}$ ion in nitrate media, $k_{obs} = (k_0 + k_1[NO_3^-])$-$[Hg^{2+}]$, with two pathways postulated involving $[CoClHg]^{4+}$ and $[CoClHgNO_3]^{3+}$ precursors.[28] It is concluded from competition experiments that if the five-co-ordinate, $[Co(NH_3)_5]^{3+}$, intermediate is formed in the reaction of $[Co(NH_3)_5N_3]^{2+}$ with NO^+ ion, this intermediate is not formed in either of the Hg^{2+} ion-induced pathways.[28]

A comparison of the relative *trans*-effects of *S*-bonded sulphite and sulphinate ions (X^-) in $[Co(NH_3)_5X]^{n+}$ ions has been made.[29] The ground-state *trans*-influence of sulphite ion is greater than that of p-$MeC_6H_4SO_2^-$ ion, as shown by the lengthening of the *trans*-Co—N bond by an average of 8.9 ± 0.3 and 5.4 ± 1.2 pm respectively. In two other sulphinato-complexes ($X^- = NH_2CH_2$-$CH_2SO_2^-$ and $PhSO_2^-$) increase in the *trans*-Co—N bond length by 4.9 ± 0.5 and 6.0 ± 0.6 pm have been observed, giving an average of 5.4 ± 0.6 pm for the *trans*-influence of sulphinato-groups. The greater *trans*-influence of sulphito-groups is reflected in a larger kinetic *trans*-labilization by a factor of 160 ± 7 at 25 °C. Anation of $[Co(NH_3)_5X]^{n+}$ ions ($X = SO_3^{2-}$, p-$MeC_6H_4SO_2^-$, or $PhSO_2^-$) by NCS^- was studied as a function of excess NH_3 and NCS^- at several temperatures, and the observed pseudo-first-order rate constant found to vary as follows:

$$k_{obs} = (a + bc[SCN^-]/[NH_3])/(1 + c[SCN^-]/[NH_3])$$

This rate expression supports the *D*-mechanism established previously for such reactions:

$$[Co(NH_3)_5X]^{n+} \rightleftharpoons [Co(NH_3)_4X]^{n+} + NH_3$$

$$[Co(NH_3)_4X]^{n+} + SCN^- \longrightarrow trans\text{-}[Co(NH_3)_4(X)(SCN)]^{(n-1)+}$$

The greater *trans*-effect of SO_3^{2-} ions is attributable to a lower value for ΔH^* (by 9 ± 1 kcal mol^{-1}), partly offset by a less positive value of ΔS^*. Using a simple harmonic oscillator model, it is estimated that the Co—N bond must be stretched to 320 pm to achieve a dissociative transition state, and this estimate agrees with previous values calculated from measurements of ΔV^*.

Studies of the aquation and spontaneous reduction of *trans*-$[Co(py)_4(H_2O)_2]^{3+}$ ion have been reported.[30] The aquation step involves stereochemical change since *fac*-$[Co(py)_3(H_2O)_3]^{3+}$ ion is the immediate product. Spontaneous reduction is believed to occur for *cis*-$[Co(py)_2(H_2O)_4]^{3+}$ ion, which is produced from

[27] V. Butkovic, M. Orhanovic, and A. Stivin, *Inorg. Chim. Acta* 1979, **35**, 215.
[28] W. L. Reynolds and E. R. Alton, *Inorg. Chem.*, 1978, **17**, 3355.
[29] R. C. Elder, M. J. Heeg, M. D. Payne, M. Trkula, and E. Deutsch, *Inorg. Chem.*, 1978, **17**, 431.
[30] K. E. Hyde and G. M. Harris, *J. Phys. Chem.*, 1978, **82**, 2204.

fac-$[Co(py)_3(H_2O)_3]^{3+}$ and polynuclear forms of *cis*- and *trans*-$[Co(py)_2(H_2O)_4]^{3+}$ ions. The possibility of covalent hydrate formation was considered as a possibility to account for the greater reactivity of such species.

Rates and activation parameters have been determined for the acid hydrolysis of $[Co(NH_3)_5X]^{2+}$ ions (X = glyoxylate or pyruvate);[31] as expected, $k_{obs} = k_0 + k_1[H^+]$. The acid and base hydrolysis of $[Co(NH_3)_5(S_2O_3)]^+$ ion has also been investigated.[32]

Rate and activation parameters for the aquation of $[M(NH_3)_5Br]^{2+}$ ions (M = Co^{III} or Cr^{III}) in H_2O–ROH mixtures (R = Me, Et, Pr^n, or Bu^t) show that alcohols affect ΔS^* rather than ΔH^*. Plots of ΔH^* *versus* ΔS^* are linear with isokinetic temperatures of 30 °C (M = Cr) and 39 °C (M = Co).[33]

At 25 °C, loss of DMF from $[Co(NH_3)_5(DMF)]^{2+}$ ion is characterized by $\Delta H^* = 28$ kcal mol^{-1}, $\Delta S^* = +5.3$ cal K^{-1} mol^{-1}, and $\Delta V^* = +3.2$ cm^3 mol^{-1}. For the analogous Rh^{III} complex, $\Delta H^* = 24$ kcal mol^{-1}, $\Delta S^* = -4.8$ cal K^{-1} mol^{-1}, and $\Delta V^* = -1.4$ cm^3 mol^{-1}. These data are consistent with an I_d mechanism for Co^{III} and an I_a mechanism for Rh^{III}. The Co^{III} complex had to be studied under acidic conditions to avoid reduction to Co^{II} ion (see Introduction, ref. 13).

Several studies of carbonato-complexes have been reported.[34–38] A recent study of the acid-catalysed decarbonylation of $[Co(py)_4(CO_3)]^+$ ion showed a rate acceleration in D_2O which is consistent with a proton pre-equilibrium mechanism:

$$[(py)_4Co(CO_3)]^+ + H^+ \rightleftharpoons [(py)_4Co(HCO_3)]^{2+}$$

$$[(py)_4Co(HCO_3)]^{2+} + H_2O \rightleftharpoons [(py)_4Co(HCO_3)(OH_2)]^{2+}$$

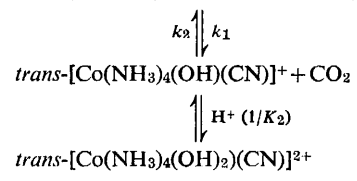
$$[(py)_4Co(HCO_3)(OH_2)]^{2+} + H^+ \rightleftharpoons [(py)_4Co(OH)_2)_2]^{3+} + CO_2$$

This observation directly contradicts earlier results for $[Co(en)_2(CO_3]^+$ ion which indicated a rate deceleration in D_2O. A re-investigation of $[Co(en)_2(CO_3)]^+$ ion over a wider range of acid concentration shows that earlier work was in error, and a proton pre-equilibrium step is now believed to be involved for all $[CoL_4(CO_3)]^+$ ions (L_4 = various tetra-amine ligand groupings of uni, bi-, and quadri-dentate type). Unexpectedly for $[Co(en)_2(CO_3)]^+$ ion in the 0.1—1.0 M $[H^+]$-range, the observed rate constant for chelate-ring opening overtakes and becomes larger than the first-order rate of loss of CO_2.[35] Other carbonato-complexes investigated recently include α,β,S-$[Co(tetren)(CO_3)]^+$ ion (studied over the range 15—30 °C in 0.5 M-NaCl and pH 1—7.5)[36] and *trans*-$[Co(NH_3)_4(CN)(OCO_2)]$.[37] For the latter species, the pseudo-first-order rate constant is given by:

$$k_{obs} = \{k_1[H^+]/([H^+] + K_1)\} + \{k_2K_2[CO_2]/([H^+] + K_2)\}$$

[31] A. Mishra, R. K. Nanda, and N. K. Moharty, *Indian J. Chem., Sect. A*, 1978, **16**, 871.
[32] C. A. N. Viana, M. M. Humanes, and M. R. Nunes, *Chem. Abs.*, 1979, **91**, 32101.
[33] V. Holba and O. Gracicova, *Collect. Czech. Chem. Commun.*, 1979, **44**, 495.
[34] C. R. Karl-MacColl and L. Beyer, *Z. Chem.*, 1978, **18**, 417.
[35] G. M. Harris and K. E. Hyde, *Inorg. Chem.*, 1978, **17**, 1892.
[36] T. P. Dasgupta and G. M. Harris, *Inorg. Chem.*, 1978, **17**, 3304.
[37] C. R. Krishnamoorthy, D. A. Palmer, R. van Eldik, and G. M. Harris, *Inorg. Chim. Acta*, 1979, **35**, L361.

In the absence of added CO_2, the second term is negligible ($k_1 = 0.36 \pm 0.04\ s^{-1}$ and $pK_1 = 6.89 \pm 0.04$ at 25 °C, $I = 0.5$ M) (Scheme 1). Studies of CO_2 uptake gave $k_2 = 338 \pm 32\ M^{-1}\ s^{-1}$ and $pK_2 = 7.55$.



Scheme 1

For the reaction of $[Co(CO)_3)_3]^{3-}$ ion with excess sulphite ion, two intermediates are formed which are believed to be mono- and bis-sulphite complexes. The mono-complex is either $[Co(CO_3)_2(OH_2)(SO_3)]^{3-}$ or $[Co(CO_3)_2(HCO_3)(SO_3)]^{4-}$ ion. Surprisingly, reduction to Co^{II} was not observed, and oxidation of Co^{II} by sulphite and oxygen in the presence of carbonate gives $[Co(CO_3)_3]^{3-}$ ion.[38]

A kinetic study of the acid hydrolysis of a μ-carbonato-bridged species, $[(H_3N)_5Co\text{-}\mu(OCO_2)\text{-}Co(NH_3)_5]^{4+}$, giving $2[Co(NH_3)_5(OH_2)]^{3+}$ and CO_2, has also been reported.[34] All of these reactions proceed without Co—O bond fission.

Powerful methylating and acetylating agents (*e.g.* acetyl perchlorate in DMF) are reported to catalyse the removal of acetate from $[Co(NH_3)_5(OAc)]^{2+}$ ion, and in this way acetate can be replaced by weakly co-ordinating ligands such as tetramethylene sulphone. A mechanism involving attack at the carbonyl oxygen is proposed.[39] In solvents of low polarity, acetylation of $[Co(NH_3)_5(^{18}OH)]^{2+}$ ion shows that the reaction proceeds without Co—OH bond fission, but in more polar media linkage isomerization of co-ordinated acetate ($Co\text{—}^{18}OCOMe \rightarrow Co\text{—}OC^{18}OMe$) occurs.

Multidentate Leaving Groups. Further studies have appeared of the acid-induced and/or metal-ion-induced dissociation of biguanidine (LL) from $[M(LL)_3]^{3+}$ ($M = Co^{III}$ or Cr^{III}),[40] from $[Co(LL)_2(en)]^{3+}$ and $[Co(LL)(en)_2]^{3+}$ ions,[41] and from *trans*-$[Co(LL)_2(CN)_2]^+$ and *cis*-$[Co(LL)_2(H_2O)_2]^{3+}$ ions.[42] For $[M(LL)_3]^{3+}$ ions ($M = Co^{III}$ or Cr^{III}), the catalytic effectiveness of bivalent metal ions parallels their ability to co-ordinate to bound LL: Cu < Ni < Co < Zn < Mn.[40] Studies of $[Co(LL)_2(en)]^{3+}$ and $[Co(LL)(en)_2]^{3+}$ show that only the biguanidine molecules are lost between 55 and 90 °C.[41] In the case of *trans*-$[Co(LL)_2(CN)_2]^+$ ion, the product is *cis*-diaqua-*trans*-dicyano-mono-biguanidinecobalt(III), and the activation parameters for loss of the first biguanidine are $\Delta H^* = 15.6$ kcal mol^{-1} and $\Delta S^* = -24$ cal K^{-1} mol^{-1}. Similarly, for *cis*-$[Co(LL)_2(H_2O)_2]^{3+}$, the activation parameters are $\Delta H^* = 15.2$ kcal mol^{-1} and $\Delta S^* = -32$ cal K^{-1} mol^{-1}.

[38] D. R. Rosseinsky and G. A. Jauregui, *J. Chem. Soc., Dalton Trans.*, 1979, 805.
[39] L. M. Jackman, J. F. Dormish, R. M. Scott, R. H. Portman, and R. D. Minard, *Inorg. Chem.*, 1979, **18**, 1503.
[40] R. N. Banerjee and D. Banerjea, *J. Indian Chem. Soc.*, 1978, **55**, 969.
[41] B. Chakravarty and P. K. Das, *Indian J. Chem., Sect. A*, 1978, **16**, 583.
[42] B. Chakravarty and A. K. Sil, *J. Indian Chem. Soc.*, 1978, **55**, 211, 452.

Table 2 *Activation parameters (at 25 °C) for the acid hydrolysis of* $[M(ox)_3]^{3-}$ *ions in* 1 M $[HClO_4]$ *(data from Introduction, ref. 16)*

M	ΔV^*/cm^3 mol^{-1}	ΔH^*/kcal mol^{-1}	ΔS^*/cal K^{-1} mol^{-1}
Co	10.8 ± 0.4^a	30	+20
Cr	-6.3 ± 0.4^a	21	− 9.1
Rh	-7.9 ± 0.6^b	19.7	+22

[a] 50 °C. [b] 60 °C.

Values of ΔV^*, ΔH^*, and ΔS^* for the acid hydrolysis of $[M(ox)_3]^{3-}$ ions (M = Co^{III}, Cr^{III}, or Rh^{III}) are collected in Table 2. The pseudo-first-order rate constant varies with acidity as follows:

$$k_{obs} = k_1' + k_2'[H^+] + k_3'[H^+]^2$$

This is consistent with rapid $[M(ox)_2(OC_2O_3)(OH_2)]^{3-}$ and $[M(ox)_2(OC_2O_3H)(OH_2)]^{2-}$ formation in which one oxalato-ligand is unidentate:

$$[M(ox)_3]^{3-} + H_2O \overset{K_1}{\rightleftharpoons} [M(ox)_2(OC_2O_3)(OH_2)]^{3-}$$

$$[M(ox)_3]^{3-} + H_3O^+ \overset{K_2}{\rightleftharpoons} [M(ox)_2(OC_2O_3H)(OH_2)]^{2-}$$

The rate-determining steps are then as follows:

$$[M(ox)_2(OC_2O_3)(OH_2)]^{3-} + H_2O \xrightarrow{k_1} [M(ox)_2(OH_2)_2]^- + ox^{2-}$$

$$[M(ox)_2(OC_2O_3H)(OH_2)]^{2-} + H_2O \xrightarrow{k_2} [M(ox)_2(OH_2)_2]^- + oxH^-$$

$$[M(ox)_2(OC_2O_3H)(OH_2)]^{2-} + H_3O^+ \xrightarrow{k_3} [M(ox)_2(OH_2)]^- + oxH_2$$

Since the activation parameters in Table 2 are composite values associated with k_{obs}, assumptions have to be made to dissect the observed values into those associated with k_1, k_2, and k_3. It is concluded that $\Delta V^*(k_1) = \Delta V^*(k_2) = +3 \pm 3$ cm^3 mol^{-1} and $\Delta V^*(k_2) = \Delta V^*(k_3) = -18 \pm 3$ cm^3 mol^{-1} for Cr^{III} and Rh^{III} respectively. The cobalt complex is known to react with rate-determining bond breaking and the formation of radical intermediates. The Cr^{III} and Rh^{III} complexes react with an I_a mechanism (see Introduction, ref. 16).

A dissociative mechanism is favoured for the acid-catalysed hydrolysis of $[Co(phen)_2(mal)]^{2+}$ ion in 0.5—2.5 M [HCl].[43] Protonation of the malonate carboxylate group occurs, and in 1 M [HCl] the activation parameters are $\Delta H^* = 22$ kcal mol^{-1} and $\Delta S^* = -10.5$ cal K^{-1} mol^{-1} (40—60 °C).

Effects of Non-leaving Ligands. Complexes of the type $[Co(en)_2XY]^{n+}$ are considered first. The stereochemistry of the spontaneous and Hg^{II} ion-induced aquations of resolved (+)-*cis*-$[Co(en)_2XY]^{n+}$ ions has been re-examined by spectrophotometry and polarimetry at 25 °C in dilute $HClO_4$ for the cases where X = Y = Cl or Br; X = Cl or Br, Y = OH; X = Cl, Br, or DMSO, Y = N_3. It appears that both *cis*- and *trans*-$[Co(en)_2XY]^{n+}$ ions aquate spontaneously with steric change, and should be regarded no longer as fundamentally different. The widely held belief that *cis*-complexes aquate *without* stereochemical change

[43] B. Chattopadhyay, J. Roy, and D. Banerjea, *J. Inorg. Nucl. Chem.*, 1978, **40**, 2041.

is shown to be in gross error, since 15—30% conversion into a *trans*-product is observed in all cases.[44] However, the chiral *cis*-product retains full optical activity. The results of these important studies are collected in Tables 3 and 4.

Table 3 *Product stereochemistry and rates of aquation of* (+)-cis-$[Co(en)_2XY]^{n+}$ *ions at* 25 °C (Y = *leaving group*; *data from ref.* 44)

X	Y	%(+)-cis-*product*	$10^4k_a/s^{-1}$
Br	Br	72±2	
Cl	Cl	76±2	
OH	Br	85±1	
OH	Cl	84.5±1.5	
N_3	Br	85±2	11.6±0.3
N_3	Cl	84±3	2.4+0.1
N_3	DMSO	85±3	2.1±0.1

Table 4 *Rates of isomerization* (k_i) *and racemization* (k_r) *of* (+)-cis- *and* trans-$[Co(en)_2(OH_2)X]^{2+}$ in 0.1 M $HClO_4$ *at* 25 °C (*data from ref.* 44)

X^-	Br^-	N_3^- [a]
$10^5k_i/s^{-1}$		16.3±0.5
$10^2k_r/s^{-1}$	4.6±0.2	4.3±0.2

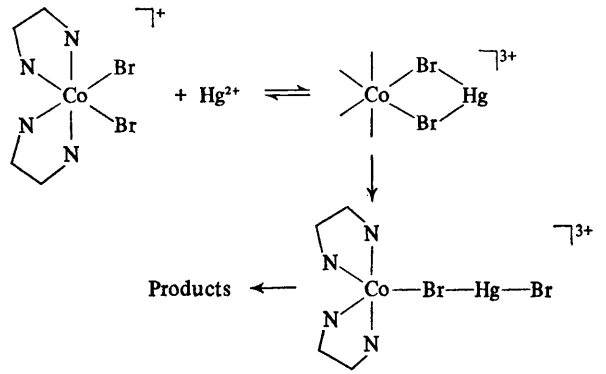
[a] 68±1 (+)-*cis*-product at equilibrium.

The data establish that racemization occurs exclusively by isomerization to the inactive *trans*-isomer. Data were also obtained for the sterochemistry of the Hg^{II} ion-induced aquations of (+)-*cis*-$[Co(en_2)X_2]^+$ ions (X = Cl or Br) and for the Hg^{II} and NO^+ ion-induced aquations of (+)-*cis*-$[Co(en)_2(N_3)Y]^{n+}$ ions (Y = Cl, Br, or DMSO). The Cl_2-induced hydrolysis of DMSO from (+)-*cis*-$[Co(en)_2X(DMSO)]^{2+}$ ions (X = Cl or Br) was also investigated. It is concluded that for most (+)-*cis*-$[Co(en)_2XY]^{n+}$ ions the steric courses of the spontaneous and induced aquation reactions are the same and are independent of the nature of the leaving group. The case for the presence of five-co-ordinate intermediates in the induced aquations of $[Co(en)_2XY]^{n+}$ and $[Co(NH_3)_5Y]^{n+}$ ions (Y = N_3, $OCONH_2$, Cl, Br, I, DMSO, and others) rests on the demonstration of the independence of the stereochemistry and competition results from the nature of the leaving group. The unexpected observation of identical stereochemistries for the spontaneous and induced aquation reaction is, therefore, surprising especially as *cis*-$[Co(en)_2(NH_3)Y]^{n+}$ and $[Co(NH_3)_5Y]^{n+}$ ions were shown earlier to aquate without stereochemical change.

The Hg^{II} ion-induced aquation of *cis*-$[Co(en)_2Br_2]^+$ ion is unusual since only 61.5±1.5% *cis*-product is formed compared with 73.5±1.5% *cis*-product for the spontaneous aquation. This exception is accounted for by a special mechanism shown in Scheme 2, involving a μ-dibromo-bridge between Co^{III} and Hg^{II}.

The aquation of *trans*-$[Co(en)_2(NO_2)(MeCN)]^{3+}$ ion in D_2O is accelerated by crown ethers such as 18-crown-6 and, to a lesser extent, 15-crown-5. A mechanism involving 'complexation' of the methyl group protons of the co-ordinated

[44] W. G. Jackson and A. M. Sargeson, *Inorg. Chem.*, 1978, **17**, 1348.



Scheme 2

acetonitrile followed by rate-determining Co—NCMe bond dissociation is proposed.[45]

Rate data for the spontaneous, Hg^{II} ion-induced, and base hydrolyses of *trans*-$[Co(en)_2Cl(RCH_2CO_2)]^+$ ions (R = H, Cl, Br, I, CN, or NH_2/NH_3^+) are collected in Table 5. Spontaneous aquation gives $80 \pm 3\%$ *cis*-product after a long period of time, and the more rapid Hg^{II} ion-induced aquation gives $88 \pm 4\%$ *cis*-product. On the other hand, base hydrolysis *via* the S_N1cb mechanism gives $71 \pm 5\%$ *trans*-product and $29 \pm 5\%$ *cis*-product.[46]

Table 5 *Rate data for the spontaneous* (k_{aq}), *mercury*(II) *ion-induced* (k_{Hg}) *and base hydrolysis* (k_{OH}) *of* trans-$[Co(en)_2Cl(RCH_2CO_2)]^+$ *ions at* 25 °C, $[H^+] = 0.5$ M, *and* $I = 1.1$ M (*data from ref.* 46)

R	H	Cl	Br	I	CN	NH_2	NH_3^+
$10^4 k_{aq}/s^{-1}$	5.46	1.95	1.50	1.36	1.47		0.86
$10^2 k_{Hg}/M^{-1}\,s^{-1}$	27.0	15.7	9.37	9.25	6.56		5.30
$k_{OH}/M^{-1}\,s^{-1}$	37.4	50.9	42.4	39.4	113	6.30	

For the Hg^{II}-assisted hydrolysis of *cis*-$[Co(en)_2(RNH_2)Cl]^{2+}$ ions (R = Ph or *m*- or *p*-MeC_6H_4) under basic conditions, the mechanism shown in Scheme 3 is proposed.[47] The rate law is Rate $= k_2[Hg^{II}][Co(en)_2(RNH_2)Cl^{2+}]$, where $k_2 = k_1'K_1 + k_{cb}'K_1'K'[OH^-]$.

Rates of the acid, Hg^{II} ion-induced, and base hydrolyses of *cis*-$[Co(tmd)_2(RNH_2)Cl]^{2+}$ ions (R = H, Me, Et, Pr^n, Bu^n, Bu^i, or Ph) are *ca.* 10^2 faster than for the analogous $[Co(en)_2(RNH_2)Cl]^{2+}$ ions.[48] This arises primarily from a reduction in the activation energy by *ca.* 2.5 kcal mol^{-1}. A comparison of the rate data for acid, Hg^{II}-assisted, and base hydrolysis reactions is given in Table 6. *cis–trans* isomerization was not observed in the aquation reactions.

[45] G. L. Blackmer, M. D. Nordyke, T. M. Vickrey, and R. A. Bartsch, *Inorg. Chem.*, 1978, **17**, 3310.
[46] K. B. Nolan and A. A. Soudi, *J. Chem. Res.* (*S*), 1979, 130.
[47] P. D. Ford and K. B. Nolan, *Inorg. Chim. Acta*, 1979, **35**, L377.
[48] B. M. Oulaghar and D. A. House *Inor . Chem* 1978 **17** 197

$$\begin{array}{ccc}
[Co(en)_2(RNH_2)Cl]^{2+} + OH^- & \overset{K'}{\rightleftharpoons} & [Co(en)_2(RNH)Cl]^+ + H_2O \\
\Big\uparrow\Big\downarrow +Hg^{2+}\ K_1 & & \Big\uparrow\Big\downarrow +Hg^{2+}\ K_1' \\
[Co(en)_2(RNH_2)ClHg]^{4+} & \overset{(OH^-)}{\rightleftharpoons} & [Co(en)_2(RNH)ClHg]^{3+} \\
-HgCl\ \Big\downarrow +H_2O\ k_1' & & -HgCl\ \Big\downarrow +H_2O\ k_{cb}' \\
[Co(en)_2(RNH_2)(OH_2)]^{3+} & \underset{H^+}{\rightleftharpoons} & [Co(en)_2(RNH)(OH_2)]^{2+}
\end{array}$$

Scheme 3

Table 6 *Comparison of rate data for the spontaneous* (k_{aq}), *mercury*(II) *ion-induced* (k_{Hg}), *and base hydrolysis* (k_{OH}) *of* cis-$[Co(tmd)(RNH_2)Cl]^{2+}$ *ions at* 25 °C *and* $I = 1.0$ M (*data from ref.* 48)

R	H	Me	Et	Pr^n	Bu^n	Bu^i	Ph
$10^2k_{Hg}/M^{-1}\ s^{-1}$	12.2	170	209	213	206	198	74
$10^5k_{aq}/s^{-1}$	6.5	43.5	44.3	36.7	42.8	39.0	29.0
$\Delta H^{\ddagger}(k_{aq})$/kcal mol^{-1}	24	18.4	20	22	21.5	22.5	20
$\Delta S^{\ddagger}(k_{aq})$/cal $K^{-1}\ mol^{-1}$	−3.4	−16.7	−10.3	−4.1	−5.5	−3.6	−13.9
$k_{OH}/M^{-1}\ s^{-1}$	508	765	915	997	916	1470	1397
$\Delta H^{\ddagger}(k_{OH})$/kcal mol^{-1}	21.0	16.2	19.1	19.7	20	18.8	18.3
$AS^{\ddagger}(k_{OH})$/cal $K^{-1}\ mol^{-1}$	+21.5	+9.1	+19.5	+21.5	+22 .0	+19.0	+17.6

Aquation of *cis*-$[Co(en)_2(HL)Br]^{2+}$ ion (HL = 2-aminothiazole) has been studied between 30 and 50 °C in perchloric acid and in acetate buffer at $I = 0.3$ M. The pseudo-first-order rate constant is given by $k_{obs} = k_1 + k_2K/[H^+] + k_3'[OAc^-]$, where k_1 and k_2 are rare constants for loss of Br^- from $[Co(en)(HL)Br]^{2+}$ and its conjugate base, $[Co(en)_2(L)Br]^+$ respectively and K is the conjugate-base formation constant. At 45 °C, $10^4k_1 = 2.95 \pm 0.04\ s^{-1}$, $10^9k_2K = 5.18 \pm 0.15\ M\ s^{-1}$, and $10^4k_3' = 4.75 \pm 0.25\ M^{-1}\ s^{-1}$.[49]

Acid-catalysed hydrolysis of *cis*-$[Co(en)_2(L)(NO_2)]^{n+}$ ions (L = NH_3, $PhNH_2$, NCS^-, or H_2O) and of *trans*-$[Co(en)_2(NCS)(NO_2)]^+$ ion has been investigated in perchloric acid over a wide acidity range. Protonation and loss of the co-ordinated nitro-group is involved. The effect of organic solvents on the reaction rates was also investigated.[50] For the aquation of *cis*-$[Co(en)_2(L)I]^{2+}$ ions (L = NH_3, $MeNH_2$, $BuNH_2$, allylamine, $PhNH_2$, or py) an S_N1 reaction is proposed for all cases except L = py for which an S_N2 mechanism is proposed.[51] Perhaps covalent hydrate formation is involved with the pyridine complex (for a discussion of this topic, see the Introduction).

Aquation of *cis*-$[Co(en)_2(OH_2)Br]^{2+}$ ion has been studied in a range of aqueous/alcohol mixtures.[52] In aqueous solution at 25 °C and $10^3I = 1.4$ M, $\Delta H^{\ddagger} = 31$ kcal mol^{-1} and $\Delta S^{\ddagger} = 22$ cal $K^{-1}\ mol^{-1}$. The free energy of activation is not sensitive to the alcohol/water composition except in aqueous methanol solutions.

[49] A. C. Dash and S. K. Mahapatra, *Indian J. Chem., Sect. A*, 1977, **15**, 871.
[50] L. G. Reiter, V. V. Udovenko, and T. V. Batyushkima, *Koord. Khim.*, 1978, **4**, 752.
[51] L. G. Reiter and V. S. Podil'chuk, *Koord. Khim.*, 1979, **5**, 239.
[52] O. Grancicova and V. Holba, *Coll. Czech. Chem. Comm.*, 1978, **43**, 2512.

Two further studies of the strong *trans*-effect of *S*-bonded sulphite have appeared.[53,54] For the anation of *trans*-$[Co(en)_2(SO_3)(OH_2)]^+$ ion an I_d rather than a *D*-mechanism is favoured.[53] Aquation of *cis*-$[Co(en)_2(SO_3)N_3]$ at acidities between 10^{-2} and 0.2 M gives *trans*-$[Co(en)_2(SO_3)(OH_2)]^+$ ion as the only cobalt(III) product; $10^5 k_{obs}/s^{-1} = 1.0 + 49[H^+]$ at 25 °C, $I = 1.0$ M. The Hg^{II} and NO^+ ion-induced reactions also gave the *trans*-product and a stereochemical change at the five-co-ordinate intermediate rather than rapid isomerization of a first formed *cis*-product is proposed. The preference for an I_d rather than a *D*-mechanism is at variance with previous studies of *trans*-$[Co(NH_3)_4(SO_3)L]^+$ ions. The *trans*-labilizing effect of *S*-bonded sulphite ion is of the order of 10^8—10^{10}, corresponding to a reduction in $\Delta H^{\ddagger}$ by *ca.* 20 kcal mol^{-1}.

Rate data for the release of X^{n-} from *trans*-$[Co(LL)_2(SO_3)X]^{(1-n)}$ ions (k_{-X}) and for the reactivity ratio (k_X/k_{OH}) of X^{n-} and OH^- ions for five-co-ordinate $[Co(LL)_2SO_3]^+$ ion (LL = en or tmd) are collected in Table 7. The equilibrium constants for the anation of *trans*-$[Co(en)_2(SO_3)(OH_2)]^+$ ion vary from 1.24 ($X^- = Br^-$) to 1.23×10^7 ($X^- = CN^-$) and the values correlate with the Edwards parameter, E_n. A dissociative *D*-mechanism is favoured for these reactions. The greater lability of the tmd complexes compared with the en complexes is in agreement with their lower stability.[54]

Table 7 *Rate constants for the release of* X^{n+} *ions from* trans-$[Co(LL)_2(SO_3)X]^{(1-n)+}$ *ions* (k_{-X}) *and the reactivity ratios* (k_X/k_{OH}) *of* X^{n-} *and* OH^- *ions for* $[Co(LL)SO_3]^+$ *ion at* 25 °C *and* $I = 1.0$ M $[NaClO_4]$ (*data from ref.* 54)

	LL = en		LL = tmd	
X^{n-}	$10^3 k_{-X}/s^{-1}$	$10^2 k_X/k_{OH}$	$10^3 k_{-X}/s^{-1}$	$10^2 k_X/k_{OH}$
N_3^-	556	3.0±2.3	6750	3.28±0.78
NO_2^-	82.1	1.1±1.5	810	1.81±0.37
NCS^-	40.0	2.1±1.6	1000	2.08±0.49
CN^-	0.0241	1.1±0.8	3.6	3.23±0.94
SO_3^{2-}	111	3.4±2.4	1410	2.38±0.6
OH^-	1190	100	13900	100

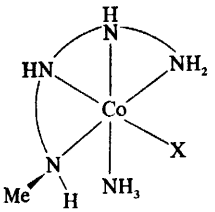
Facile solvolysis of *cis*- and *trans*-$[Co(en)_2Cl_2]^+$ ions has been studied between 218 and 233 K in liquid ammonia.[55] The final products are *cis*- and *trans*-$[Co(en)_2(NH_3)_2]^{3+}$ ions. *trans*-$[Co(en)_2Cl_2]^+$ and *cis*-$[Co(en)_2(NH_3)Cl)]^{2+}$ ions react with retention of configuration, whereas *cis*-$[Co(en)_2Cl_2]^+$ gives only 20% *cis*-product and *trans*-$[Co(en)_2(NH_3)Cl]^{2+}$ only 30% *trans*-product. The reactions proceed with an S_N1cb mechanism (as in most base hydrolyses), and at 208 K the pK_a's of the *trans*-$[Co(en)_2Cl_2](NO_3)$ and *cis*-$[Co(en)_2(NH_3)Cl](NO_3)_2$ salts were estimated to be 7.84 and 7.71 respectively. The high rate of these reactions in liquid ammonia arises largely from the more favourable heat of solvation of the released proton in the conjugate-base mechanism.

[53] J. K. Yandell and L. A. Tomlins, *Aust. J. Chem.*, 1978, **31**, 561.
[54] Y. Ito, A. Terada, and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 2898.
[55] S. Balt, J. Breman, and W. de Kieviet, *J. Inorg. Nucl. Chem.*, 1979, **41**, 331.

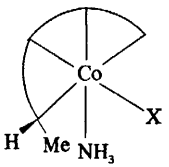
Acid and base hydrolyses of $[Co(LL)(NO_2)_4]^-$ ions (LL = en or tmd) give $[Co(LL)(NO_2)_3(OH_2)]$ (pH 4—6) and $[Co(LL)(NO_2)_3(OH)]^-$ ion (pH 9.5—12.2) respectively.[56] A mechanism involving a five-co-ordinate intermediate, $[Co(LL)(NO_2)_3]$, is proposed, with $10^4k/s^{-1} = 9.27 \pm 0.03$ and 2.08 ± 0.01 at 25 °C for LL = tmd and en respectively. The corresponding rate constants for $[Co(LL)(NO_2)_3(OH_2)]$ are $10^4\,k/s^{-1} = 3.95 \pm 0.12$ and 0.546 ± 0.01 for LL = tmd and en respectively.

The complexes $[Co(LL)_2(L)X]^{n+}$ and $[Co(LLL)(LL)X]^{n+}$ are now considered, where L, LL, and LLL are uni-, bi-, and ter-dentate ligands respectively and X is the leaving group. The Hg^{2+}- and base-catalysed hydrolyses of β_2-(*RR*,*SS*)-$[Co(trien)(glyOR)Cl]^{2+}$ ions (glyO = $NH_2CH_2CO_2$, R = H or Et) have been investigated and the site of deprotonation in the conjugate-base mechanism has been established.[57] Acid hydrolysis of the ester function (R = Et) of the Δ-β_2-(*RR*)-isomer gives optically pure Δ-β_2-(*RR*)-$[Co(trien)(glyOH)Cl]^{2+}$, which reacts with Hg^{2+} ion (at 25 °C and $I = 1.0$ M, $10^2k_{Hg} = 1.36 \pm 0.03$ $M^{-1}\,s^{-1}$) to give Δ-β_2-(*RR*)-$[Co(trien)(glyO)]^{2+}$ ion. Some competition occurs between the dangling carboxylate arm, water, and added nitrate ion (1 M) for the five-co-ordinate intermediate which is presumed to be formed. Rapid ring closure occurs following capture of the five-co-ordinate intermediate by H_2O.

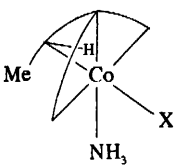
Common intermediates are not involved in the Hg^{2+}-, Ag^+-, and NO^+-induced aquation and base hydrolysis reactions of $[Co(Metren)(NH_3)X]^{n+}$ ions (X = Cl, Br, N_3, or NH_3) which have structures (6)—(8).[58] The stereochemistries of the H_2O/OH-product ions were established using *N*-Me ^{13}C-enriched materials related to known crystal structures. An I_d mechanism is favoured for these reactions with H_2O involved prior to complete Co—X bond fission.



(6)



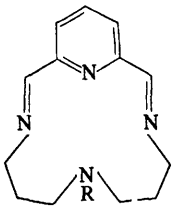
(7)



(8)

The reaction of *trans*-$[Co(LLLL)X_2]^+$ ions (X = Cl or Br) with NCS^- ion [LLLL = (9; R = Me or H)] has been investigated between 4 and 67.2 °C.[59] The first substitution of X^- by NCS^- ion proceeds at the same rate for R = Me and H, whereas the second substitution process is much faster (by a factor of *ca.* 10^2) when R = H than when R = Me. This is interpreted by assuming that the first loss of X^- occurs farthest from the N—R group, with the amine-H atom involved in promoting the reaction rate when R = H. Hydrolysis of $[Co(LLLL)(NCS)(X)]^+$

[56] Y. Ito and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 1083.
[57] D. A. Buckingham, W. Marty, and A. M. Sargeson, *Helv. Chim. Acta*, 1978, **61**, 2223.
[58] D. A. Buckingham, J. D. Edwards, T. W. Lewis, and G. M. McLaughlin, *J. Chem. Soc., Chem. Commun.*, 1978, 892.
[59] C. K. Poon and S. T. Sarah, *J. Chem. Soc., Dalton Trans.*, 1978, 1180.



(9)

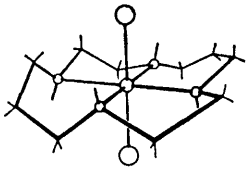
ions [LLLL = (9; R = Me, X = Cl or Br)] involves concurrent loss of both NCS^- and X^- ion. This behaviour and the ratio k_{Br}/k_{Cl} for loss of Br^- and Cl^- indicate that (9) is a much 'softer' ligand than saturated tetra-aza macrocycles.

A very labile form of *trans*-$[Co(cyclam)Cl_2]^+$ ion has been prepared in which the HN-donor atoms of cyclam have conformations *RRRR* (10).[60] A comparison of the rates of hydrolysis of various *cis*- and *trans*-$[Co(cyclam)Cl_2]^+$ ions is shown in Table 8. Only the labile *trans-RRRR* isomer aquates with stereochemical change, the immediate products of aquation being 75% *trans*- and

Table 8 *Comparison of rates and activation parameters at* 25 °C *for the aquation of three isomers of* $[Co(cyclam)Cl_2]^+$ *ion (data from ref.* 60)

Isomer	$10^4k/s^{-1}$	ΔH^*/kcal mol^{-1}	ΔS^*/cal K^{-1} mol^{-1}
trans-RSSR	0.011	25.0	−3.1
trans-RRRR	17.5	24.5	+9.9
cis-RRRR	160	18.3	−6.0

25% *cis-RRRR*-$[Co(cyclam)(OH_2)Cl]^{2+}$ ion. Isomerization to 100% *cis*-isomer then occurs with $10^2k_i = 1.3\ s^{-1}$, $\Delta H_i^* = 26$ kcal mol^{-1}, and $\Delta S_i^* = 19.2$ cal K^{-1} mol^{-1} at 25 °C ($I = 1.0$ M, pH 2). The stereochemical change which is observed is typical of that found during the aquation of other *trans*-$[Co(L)_4X_2]^+$ ions in which $(L)_4$ represents non-macrocyclic ligands [*e.g.* $(en)_2$, 2,3,2-tet]. The positive ΔS^* value is also in line with previous studies in which stereochemical change occurs. The Hg^{2+}-catalysed aquation of (10) takes place with retention of configuration.



(10) The *trans*-$[Co(R,R,R,R\text{-cyclam})Cl_2]^+$ cation. Predicted structure showing the sequence of skew six-membered rings and *gauche* five-membered rings

References to studies of complexes of the type *trans*-$[Co(dioxime)_2LX]^{n+}$ (X = leaving group) are collected in Table 9. A review of substitution reactions of dioximato-complexes has appeared (Introduction, ref. 9).

[60] C. J. Cooksey and M. L. Tobe,., *Inorg. Chem* 1978, **17**, 1558.

Table 9 *References to studies of dioximato-complexes of the type* trans-[Co-(dioxime)$_2$LX]$^{n+}$ (X = *leaving group*) (*for a review, see Introduction, ref.* 9)

Dioxime	L	X	*Reactions studied and conditions*	*Ref.*
dmgH$^-$	Me	4-CN-py	CH_2Cl_2 solution; reaction with 4-Bu^t-py, 1-Me-imidazole, $(MeO)_3P$, Me_3P, Me_2PhP, Bu^n_3P, or (n-octyl)$_3$P	61
	Me	4-Bu^t-py, 4-CN-py, Ph_3P	reaction wth Bu^n_3P	61
	p-$SO_2C_6H_4Me$, $CHBr_2$, $SCPh_3$, CH_2Br, *p*-C_6H_4Br, *p*-C_6H_4OMe, Ph, *p*-$CH_2C_6H_4CN$, CH_2Ph, Et	4-CN-py	reaction with Bu^n_3 P or $(MeO)_3P$	61
dmgH$^-$	RNH_2 (R = H, Me, Et, or Br) or Me_2NH	Cl, Br, or I	solvolysis by ROH (R = Et or Pr), DMSO, or MeCN	62
MeC(NOH)C(NOMe)Me MeC(NO)C(NOMe)Me$^-$	Cl, Br, or I	Cl, Br, or I	solvolysis by H_2O, MeOH, or DMF	63, 64

In a major paper, the relative *trans*-effect of alkyl- and *S*-bonded ligands in *trans*-[Co(dmgH)$_2$(L)X] complexes has been established as *p*-$SO_2C_6H_4Me$ < $CHBr_2$ < $SCPh_3$ < CH_2Br < *p*-C_6H_4Br < *p*-C_6H_4OMe < Ph < *p*-$CH_2C_6H_4CN$ < Me < CH_2Ph < Et.[61] Addition of the leaving group leads to mass law retardation and establishes a dissociative *D*-mechanism. The discriminating ability of the five-co-ordinate intermediates for the nucleophiles present is small except when bulky Bu^n_3 P and trioctylphosphine are involved, which are poor competitors.

Activation parameters for the solvolysis of *trans*-[Co(L)(LH)X_2] (HL = MeC(NOH)C(NOMe)Me, X = Cl or Br) in H_2O, MeOH, and DMF are collected in Table 10. Although values of ΔS^* are significantly negative, it is surprising

Table 10 *Activation parameters for the solvolysis of* trans-[Co(HL)(L)X_2], *where* HL = MeC(NOH)C(NOMe)Me (*data from refs.* 63 *and* 64)

	In H_2O		*In* MeOH		*In DMF*	
X	ΔH^*/ kcal mol^{-1}	ΔS^*/ cal K^{-1} mol^{-1}	ΔH^*/ kcal mol^{-1}	ΔS^*/ cal K^{-1} mol^{-1}	ΔH^*/ kcal mol^{-1}	ΔS^*/ cal K^{-1} mol^{-1}
Cl	26	−1.9	21.5	−12.2	10.8	−42
Br	29	−6.7	21.0	−14.8	13.6	−33

that an associative mechanism is proposed. Rates of solvolysis decrease with solvent in the order DMF > MeOH > H_2O.[62,63] For *trans*-[Co(dmgH)$_2$(L)X] (L = RNH_2, R = H, Me, Et, Br, or Me_2NH, X = halide), the rates decrease with solvent in the order EtOH > PrOH > DMSO, MeCN.[64]

Cobaloximes are models for cobalamins, and the rates of reaction of B_{12a} co-enzyme with 6-mercaptopurine and 8-azaguanine (HL) (Scheme 4) have been reported.[65] Rate and equilibrium constants associated with this Scheme are collected in Table 11.

$$\begin{array}{ccc} [\text{bzmCoOH}_2]^+ + \text{HL} & \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} & [\text{bzmCoLH}]^+ + \text{H}_2\text{O} \\ \Big\Uparrow K_1 & & \Big\Uparrow K_2 \\ [\text{bzmCoOH}_2]^+ + \text{L}^- & \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} & [\text{bzmCoL}] + \text{H}_2\text{O} \end{array}$$

Scheme 4

Table 11 *Rates and equilibrium constants associated with Scheme 4* (*data from ref.* 65)

Ligand	k_1/M^{-1} s^{-1}	k_2/M^{-1} s^{-1}	10^4k_{-1}/s^{-1}	10^4k_{-2}/s^{-1}	K_1	10^6K_2
6-Mercaptopurine	40.0	800	184000	140	2.17	0.0517
8-Azaguanine	62.0	220	200	8.8	3100	2.5

[61] R. C. Stewart and L. G. Marzilli, *J. Am. Chem. Soc.*, 1978, **100**, 817.
[62] N. M. Samus, T. H. Nguyen, and O. A. Bologa, *Zh. Neorg. Khim.*, 1979, **24**, 98.
[63] N. M. Samus, N. T. Hong, and O. A. Bologa, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1979, **24**, 55.
[64] N. M. Samus, T. H. Nguyen, and J. A. Fridman, *Zh. Neorg. Khim.*, 1978, **23**, 994.
[65] K. Kano, F. Nome, and J. H. Fendler, *J. Chem. Soc., Dalton Trans.*, 1978, 1226.

Bridged Complexes.—The $[(edta)Co^{III}-NC-Fe^{III}(CN)_5]^{4-}$ ion has been prepared and the rate of its bridge-cleavage (ring-closure) reaction measured for comparison with the behaviour observed during the inner-sphere redox reaction between $[Co(edta)]^{2-}$ and $[Fe(CN)_6]^{3-}$ ions;[66] $10^5k = 3.0 \pm 0.4\ s^{-1}$ at 25 °C, pH 4.8, and $I = 0.66$ M. Formation of $[Co(edta)]^-$ ion during the redox reaction results not from the bridge-cleavage reaction but rather from the outer-sphere redox pathway, thus providing evidence for a 'dead-end' mechanism in this reaction.

The μ-carbonato-species $[(H_3N)_5Co-OCO_2-Co(NH_3)_5]^{4+}$ undergoes facile acid hydrolysis to two moles of $[Co(NH_3)_5(OH_2)]^{3+}$ ion, and the rate of the reaction has been measured.[34]

Reactions of Co-ordinated Ligands. Rates of mercuration of *o*-, *m*-, and *p*-hydroxybenzoates (L) in $[Co(NH_3)_5L]^{2+}$ ions[67] and iodination of salicylate (L) in $[Co(en)_2(L)]^+$ and in free salicylate ion have been compared.[68] At 40 °C [$(H^+) = 0.1$—0.25 M) the mercuration reactions have rates (k) and activation energies (E_a) which are very similar (*o*-, *m*-, and *p*-hydroxybenzoates: $10^3k/M^{-1}\ s^{-1} = 3.5$, 3.0, and 2.0; $E_a = 13.4$, 12.3, and 11.7 kcal mol^{-1} respectively). Iodination of free and co-ordinated salicylate ions is catalysed by acetate ion and by water, the rates varying in the order $L^- < [Co(en)_2(L)]^+ < L^{2-}$ (H_2L = salicylic acid). Chelation of the dianion of salicylic acid to Co^{III} reduces its rate of iodination by a factor of 10^7.

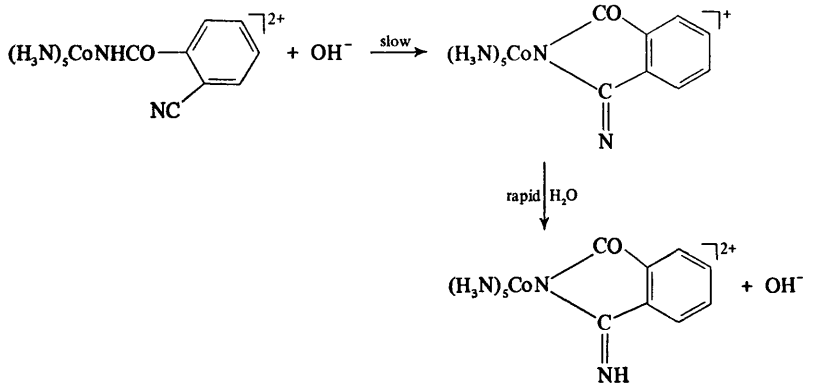
The rate of reaction of bromide ion with *trans*-$[Co(dmgH)_2\{P(OMe)_3\}X]$ to give *trans*-$[Co(dmgH)_2\{P(O)(OMe)_2\}X]$ varies by a factor of 10^5 as X is varied from NO_3 to Et.[69] The logarithm of the constant for nucleophilic attack at the methyl group of co-ordinated trimethyl phosphite correlates well with the ^{13}C chemical shift of this group.

Base hydrolysis of the amino-acid esters in *cis*-$[Co(en)_2\{NH_2(CH_2)_3CO_2R\}X]^{2+}$ ions (R = H, X = Cl; R = Et, X = Br; R = Me, X = Cl or Br) follows the more rapid loss of halide ion.[70] At 298.2 K and $I = 0.1$ M, $k_{OH}^{Cl} = 15.2\ M^{-1}\ s^{-1}$ and $k_{OH}^{ester} = 0.72\ M^{-1}\ s^{-1}$ (X = Cl, R = Me), and when X = Br, $k_{OH}^{Br} = 1.25 \pm 3\ M^{-1}\ s^{-1}$. The un-co-ordinated ester hydrolysis is slower by a factor of *ca.* 7.2, and lactamization to give 2-pyrrolidinone also occurs.

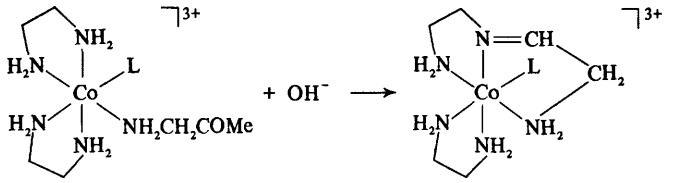
The base-catalysed cyclization of 2-cyanobenzamide (L) in $[Co(NH_3)_5L]^{3+}$ ion gives 3-iminoisoindolin-1-one (Scheme 5).[71] At 25 °C, $k = 1.13 \pm 0.03\ M^{-1}\ s^{-1}$, $\Delta H^{\ddagger} = 18.3$ kcal mol^{-1}, and $\Delta S^{\ddagger} = 3.1$ cal K^{-1} mol^{-1}. The reaction of co-ordinated 1,2-dicyanobenzene has also been investigated.[72]

In the reaction of *cis*-$[Co(en)_2(NH_2CH_2R)(NH_2CH_2COMe)]^{3+}$ ion with base, imine complexes (11) are formed by condensation of the co-ordinated aminoacetone with the NH_2 group of co-ordinated en and not with the co-ordinated RCH_2NH_2 (L).[73] Favourable orientation of the carbonyl group is invoked to

[66] D. H. Huchital and J. Lepore, *J. Inorg. Nucl. Chem.*, 1978, **40**, 2073.
[67] N. Mullick and R. K. Nanda, *J. Indian Chem. Soc.*, 1977, **54**, 1018.
[68] A. C. Dash, N. Mullick, and R. K. Nanda, *Transition Met. Chem.*, 1977, **2**, 244.
[69] P. J. Toscano and L. G. Marzilli, *Inorg. Chem.*, 1979, **18**, 421.
[70] R. W. Hay, R. Bennett, and D. P. Piplani, *J. Chem. Soc., Dalton Trans.*, 1978, 1046.
[71] R. J. Balahura and W. L. Purcell, *Inorg. Chim. Acta*, 1978, **31**, L383.
[72] R. J. Balahura and W. L. Purcell, *Inorg. Chem.*, **18**, 937.
[73] A. R. Gainsford and A. M. Sargeson, *Aust. J. Chem.*, 1978, **31**, 1679.



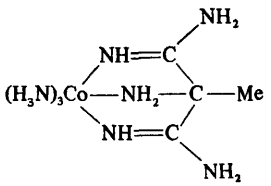
Scheme 5



(11)

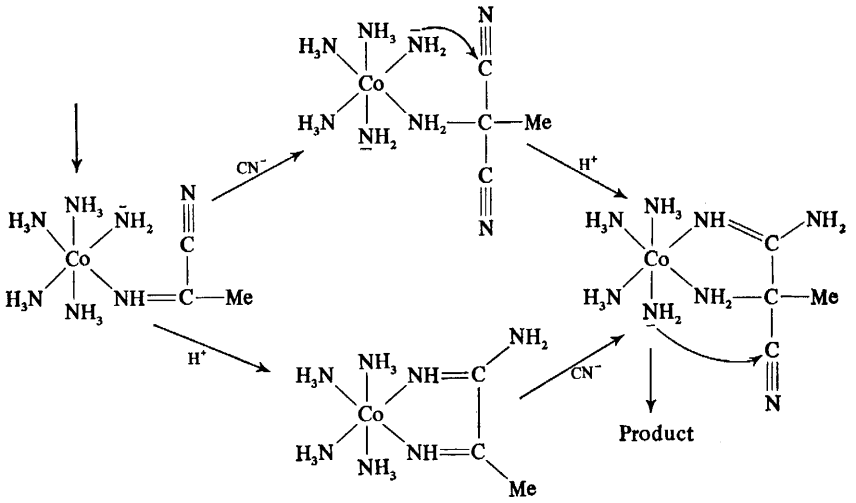
account for this observation. The imine group of the product can be reduced stereospecifically with $[BH_4]^-$ ion to give $[Co(en)\{NH_2CH_2CH_2NHCH(Me)CH_2NH_2\}(NH_2CH_2R)]^{3+}$, with no reduction of Co^{III}.

In the reaction of $[Co(NH_3)_5(NCCH_2R)]^{2+}$ ions (R = Ph or $CH{=}CH_2$) with base, deprotonation of the α-CH_2 group is followed by rapid intramolecular oxidation to give nitrile radicals which dimerize.[74] Reduction of co-ordinated nitriles with $[BH_4]^-$ ion and Michael additions of carbanions and phosphate to co-ordinated acrylonitrile occur more than 10^4 times faster than the corresponding reactions of the un-co-ordinated nitriles. Scheme 6 is proposed to account for the formation of (12) from the reaction between $[Co(NH_3)_5(NCMe)]^{3+}$ and CN^- ions.[74]



(12)

[74] D. G. Butler, I. I. Creaser, S. F. Dyke, and A. M. Sargeson, *Acta Chem. Scand., Ser. A*, 1978, **32**, 789.



Scheme 6

Co-ordinated water is more reactive than co-ordinated hydroxide in the intramolecular reaction

$$cis\text{-}[Co(en)_2(OH_2/OH)(glyNHR)]^{3+/2+} \longrightarrow [Co(en)_2(gly)]^{2+} + RNH_2$$

where R = H, CH_2CO_2Pr, or $CH_2CO_2^-$, owing to a more positive ΔS^* value. When R = CH_2CO_2Pr, loss of OH^- also occurs to give $[Co(en)_2(glyNHR)]^{3+}$, with the cyclization reaction rate determining ($glyNH_2$ = glycinamide).[75,76] The Hg^{2+}-catalysed removal of Br^- ion from *cis*-$[Co(en)_2Br(glyNHR)]^{2+}$ gives $[Co(en)_2(glyNHR)]^{3+}$ with retention of configuration at Co^{III} and without the formation of an aqua- or hydroxo-intermediate.[76] In basic solution, the cyclization of *cis*-$[Co(en)_2(OH)(glyNHR)]^{2+}$ to $[Co(en)_2(gly)]^{2+}$ and $[Co(en)_2(glyNHR)]^{3+}$ proceeds without Co—O bond fission, whereas in acidic solution, although the products are the same, only the $[Co(en)_2(gly)]^{2+}$ ion retains the O-atom of the co-ordinated H_2O. Reaction of *cis*-$[Co(en)_2Br(glyglyOPr^i)]^{2+}$ with hypochlorous acid gives *cis*-$[Co(en)_2(glyglyOPr^i)]^{3+}$ and *cis*-$[Co(en)_2Br(glyglyOPr^i)]^{3+}$, again with retention of configuration at Co^{III}. Base hydrolysis at pH 9—14 gives some *trans*- as well as *cis*-$[Co(en)_2(OH)(glyNHR)]^{3+}$ ion.[76]

For the reaction of *cis*-$[Co(en)_2Cl(NH_2OH)]^{2+}$ ion with nitrous acid, the rate is inversely dependent on $[H^+]$ below 0.1 M $[H^+]$, and the major N-product is N_2O. Some N_2 is also released from the co-ordinated hyponitrite formed:

$$[Co(NH_2OH)] + H_2NO_2^+/NO^+ \longrightarrow [Co(NH_2ONO)] + H^+$$

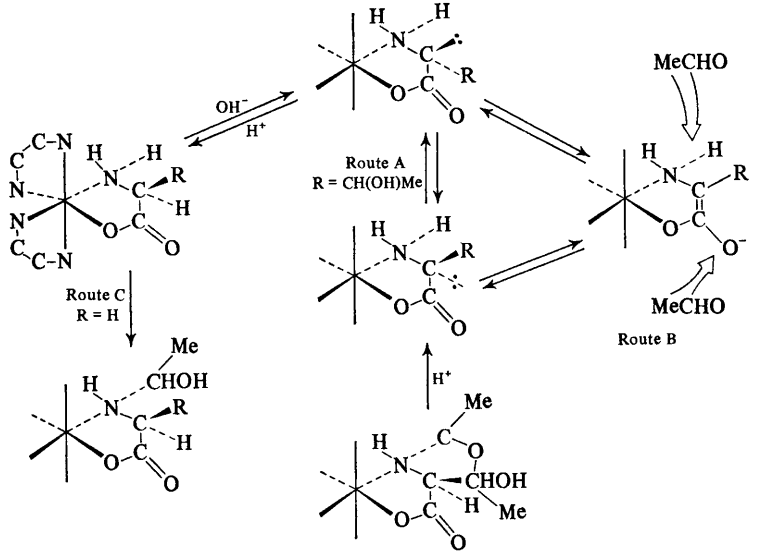
$$[Co(NH_2ONO)] \longrightarrow [Co\{NH(NO)OH\}] \longrightarrow [Co(HON{=}NOH)]$$

The Co(HON=NOH) dissociates to give N_2O and some N_2, and is also attacked by HNO_2 to give N_2 and HNO_3.[77]

[75] C. J. Boreham, D. A. Buckingham, and F. R. Keene, *J. Am. Chem. Soc.*, 1979, **101**, 1409.
[76] C. J. Boreham, D. A. Buckingham, and F. R. Keene, *Inorg. Chem.*, 1979, **18**, 28.
[77] M. N. Hughes, K. Shirmanker, and P. E. Wimbledon, *J. Chem. Soc., Dalton Trans.*, 1978, 1634.

Several studies of base-catalysed H/D exchange reactions have appeared.[78–81] In *mer*-$[Co(gly)_3]$ the α-hydrogens in *trans*-positions with respect to co-ordinated O are more labile than those in a *trans*-position to co-ordinated N.[78] In $[Co(mal)_2(L)]^{n-}$ ions (L = en, *N*-Me-en, gly, or sarcosine) the H/D exchange occurs first at the malonate methylenes closest to L, but in *cis*-$[Co(mal)_2(NH_3)_2]^-$ H/D exchange is not stereospecific.[79] For the H/D exchange with glycinate ion in $[Co(en)_2(gly)]^{2+}$, *N*-1,2,6-$[Co(gly)_3]$, and *trans*-*N*-$[Co(ox)(gly)_2]^-$ ions the rates show a gradual decrease with change in overall charge.[81] For the $[Co(en)_2L]^+$ ions (L = malonate or ethylmalonate) the α-protons undergo acid- and base-catalysed H/D exchange, and $[Co(en)_2(mal)]^+$ ion also undergoes rapid chelate-ring opening at the same time.[80]

Three possible mechanisms (Scheme 7) have been discussed to account for stereoselectivity in the formation of $[Co(L)_3]$ (L = threonine) from the condensation of acetaldehyde with $[Co(gly)_3]$. Pathway C is shown to be most likely.[82]

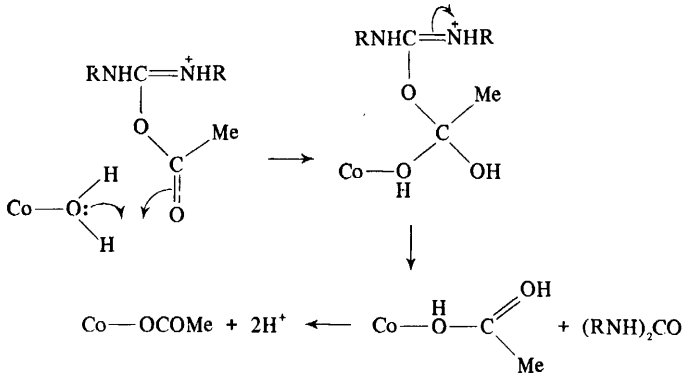


Scheme 7

At 25 °C, the rate of inversion of sulphur in co-ordinated Co^{III}-thioethers has been shown to be relatively low ($0.1 < k_i < 10\ s^{-1}$). The $[Co(tren)L]^{n+}$ ions (L = *R*-cysteine, cysteamine, or their *S*-methylated derivatives) were investigated.[83]

Scheme 8 is proposed to account for the formation of $[Co(NH_3)_5OAc]^{2+}$ from the reaction of $[Co(NH_3)_5(OH_2)]^{3+}$ with dicyclohexylcarbodi-imide (RN=C=NR) and acetic acid.[84]

[78] U. Sakaguchi, H. Yoneda, and Y. Morimoto, *Inorg. Chim. Acta*, 1978, **31**, L473.
[79] U. Sakaguchi, K. Morito, and H. Yoneda, *Chem. Lett.*, 1979, 19.
[80] S. Amirhaeri, M. E. Farago, J. A. P. Gluck, and M. A. R. Smith, *Inorg. Chim. Acta*, 1979, **33**, 57.
[81] P. R. Norman and D. A. Phipps, *Inorg. Chim. Acta*, 1978, **28**, L161.
[82] D. A. Phipps, *Inorg. Chim. Acta*, 1978, **27**, L103.
[83] W. G. Jackson and A. M. Sargeson, *Inorg. Chem.*, 1978, **17**, 2165.
[84] L. M. Jackson, R. M. Scott, and J. F. Dormish, *Inorg. Chem.*, 1979, **18**, 2023.



Scheme 8

Electrophilic attack of the co-ordinated water molecule in $[Co(CN)_5(OH_2)]^{2-}$ by $HSeO_3^-$ ion has also been investigated.[85]

Photochemical Studies. A study of the ligand-field photolysis of *cis*-β-[M(2,3,2-tet)Cl(X)]$^{n+}$ ions (M = Co or Rh, X = Cl^- or H_2O) is reported together with the thermal aquation of *cis*-α- and *cis*-β-$[Rh(trien)Cl_2]^+$ and *cis*-β-$[Rh(2,3,2\text{-tet})Cl_2]^+$ ions in acidic solutions. For the Co^{III} complexes the only product of photolysis is *trans*-$[Co(2,3,2\text{-tet})Cl(OH_2)]^{2+}$, the quantum yields being typical of those found for other Co^{III} amines.[86]

The primary step in the charge-transfer photolysis of $[Co(NH_3)_5Cl]^{2+}$ ion is the formation of $[Co(NH_3)_5]^{2+}$ and Cl·. This is followed by the reaction of Cl· with Cl^- to give $Cl_2^{\cdot-}$ and loss of NH_3 from $[Co(NH_3)_6]^{2+}$ in five successive steps.[87]

Photosubstitution of Cl^- in Λ-*cis*-$[Co(en)Cl_2]^+$ by CO_3^{2-} and hydroxamate ions is reported to be facilitated by absorption on to silica gel.[88]

Chromium(III).—*Unidentate Leaving Groups.* Following measurements of ΔV^* values for substitution reactions of chromium(III) by Stranks, Swaddle, and co-workers, there is a general belief that the majority of such reactions proceed by an associative interchange, I_a, mechanism. Nevertheless recent evidence suggests that in some cases dissociative, I_d or D, mechanisms are also possible. For example, the values of ΔV^* for the Hg^{II}-catalysed aquation of $[M(NH_3)_5X]^{2+}$ ions (Table 12) are very similar for M = Co^{III}, Rh^{III}, or Cr^{III} and in line with a

Table 12 *Volumes of activation for the mercury(II)-catalysed aquations of* $[M(NH_3)_5X]^{2+}$ *ions in* 0.31 M $[H^+]$ *(data from Introduction, ref.* 17)

M	Co	Co	Rh	Cr
X	Cl	Br	Cl	Cl
ΔV^*/cm^3 mol^{-1}	−1.7±1.0	+0.8±0.5	+0.7±0.4	−1.0±0.4
T/°C	15	15	25	15

[85] K. R. Ashley and Y. Jon, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1099.
[86] E. Martins, E. B. Kaplan, and P. S. Sheridan, *Inorg. Chem.*, 1979, **18**, 2195.
[87] J. Lilie, *J. Am. Chem. Soc.*, 1979, **101**, 4417.
[88] F. Benda and B. Hájek, *Inorg. Chim. Acta*, 1979, **36**, L401.

dissociative mechanism following rapid M—X—Hg bridge formation (Introduction, ref. 17). An earlier report that ΔV^* for the aquation of $[Cr(NCS)_6]^{3-}$ ion is as large as $+16\pm2$ cm^3 mol^{-1} has been corrected by recent workers who found $\Delta V^* = +2.9\pm0.8$ cm^3 mol^{-1} for the same reaction (Introduction, ref. 15). It is suggested that earlier work may have involved loss of two NCS^- ions. The small positive ΔV^* indicates an I_d mechanism as found previously for *trans*-$[Cr(NH_3)_2(NCS)_4]^-$ ion but *not* for $[Cr(NH_3)_5(NCS)]^{2+}$, which is claimed to react *via* an I_a mechanism. The *trans*-effect of thiocyanate ion is invoked to account for the I_d mechanisms ascribed to the anionic complexes.

Solvolysis of *trans*-$[Cr(NH_3)_2(NCS)_4]^-$ ion (Reinecke's salt) has been studied recently in methanolic and ethanolic perchloric acid.[89] Loss of thiocyanate from *trans*-$[Cr(NCS)_4(benzylamine)_2]^-$ ion in aqueous acetone,[90] and [^{14}C]thiocyanate exchange with *trans*-$[Cr(NH_3)_2(NCS)_4]^-$ ion[91] have also been reported.

A comparison of the rates of solvolysis of $[M(NH_3)_5Br]^{2+}$ ions (M = Co or Cr) has been made in H_2O–ROH mixtures (R = Me, Et, Pr^i, or Bu^t) The alcohol affects ΔS^* rather than ΔH^* and plots of ΔH^* *versus* ΔS^* are linear with isokinetic temperatures of 30 °C (Cr) and 39 °C (Co).[33]

The acid aquation of four complexes of the type $[Cr(NH_3)_x(OH_2)_{4-x}Cl_2]^+$, all of which contain *trans*-dichloro configurations, have been investigated together with the rates of isomerization to a *cis*-dichloro structure with an unchanged ammine configuration.[92] The aquation reactions were followed using a chloride ion specific electrode, and the results are collected in Table 13.

Table 13 *Rate data* ($I = 1.0$ M) *for the acid aquation* (*loss of* Cl^-) *of some chromium*(III) *ammines with* trans-*dichloro-configurations* (*data from ref.* 92)

Complex	10^3k (*at* 70 °C)/s^{-1}	E_a/kcal mol^{-1}
mer-$[Cr(NH_3)_3(OH_2)Cl_2]^+$	7.45 ± 0.14	25
cis-$[Cr(NH_3)_2(OH_2)_2Cl_2]^+$	9.9 ± 0.3	23
trans-$[Cr(NH_3)_2(OH_2)Cl_2]^+$	4.39 ± 0.05	23.5
$[Cr(NH_3)(OH_2)_3Cl_2]^+$	7.2 ± 0.3^a	23[a]

[a] These data differ from those of an earlier investigation.

A comparison of the thermal aquation and photoaquation of *trans*-$[Cr(NH_3)_4(DMF)Cl]^{2+}$ ion has been made.[93] The products of the thermal reaction are 85% *trans*-$[Cr(NH_3)_4(OH_2)Cl]^{2+}$ and 15% *trans*-$[Cr(NH_2)_4(DMF)(OH_2)]^{3+}$, whereas photoaquation yields 89% *cis*-$[Cr(NH_3)_4(OH_2)Cl]^{2+}$, 9% *cis*-$[Cr(NH_3)_4(DMF)(OH_2)]^{3+}$, and 2% $[Cr(NH_3)_3(OH_2)(DMF)Cl]^{2+}$ ions. Similarly, thermal aquation of $[Cr(NH_3)_5(DMF)]^{3+}$ proceeds with loss of DMF, whereas photoaquation gives 84% *cis*-$[Cr(NH_3)_4(DMF)(OH_2)]^{3+}$ and only 16% $[Cr(NH_3)_5(OH_2)]^{3+}$ ion. The ease of photodissociation of Cr—ligand bonds increases in the order $Cl^- < NCS < DMF < H_2O < NH_3$, in parallel with the decreasing ligand π-bonding ability.[93]

[89] P. Kita, R. Kostrzewska-Zeidler, *Pol. J. Chem.*, 1978, **52**, 187.
[90] J. Zsakó, Cs. Várhelyi, D. Oprescu, and I. Ganescu, *Acta Chim. Acad. Sci. Hung.*, 1978, **97**, 159.
[91] S. Wajda and B. Kurzak, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, 1977, **25**, 987.
[92] L. Mönsted and O. Mönsted, *Acta Chem. Scand., Ser. A*, 1978, **32**, 917.
[93] P. Riccieri and E. Zinato, *Chem. Abs.*, 1979, **80**, 132 011.

Replacement of DMF by H_2O in *cis*-$[Cr(ox)_2(DMF)_2]^-$ ion proceeds in two consecutive steps without stereochemical change. The rates are independent of pH in the range pH 1—5, and at 25 °C and $I = 1.0$ M [$NaNO_3$], $10^4k_1 = 6.95 \pm 0.28$ s^{-1}, $\Delta H^* = 14.3$ kcal mol^{-1}, $\Delta S^* = -25$ cal K^{-1} mol^{-1} and $10^4k_2 = 3.27 \pm 0.18$ s^{-1}, $\Delta H^* = 14.3$ kcal mol^{-1}, $\Delta S^* = -27$ cal K^{-1} mol^{-1}. The reverse solvolysis reaction of *cis*-$[Cr(ox)_2(OH_2)_2]^-$ ion in DMF was also studied, and for the first step $10^3k_{-2} = 1.75 \pm 0.04$ s^{-1}, $\Delta H^* = 14.4$ kcal mol^{-1}, $\Delta S^* = 47$ cal K^{-1} mol^{-1} and for the second step $10^4k_{-1} = 1.87 \pm 0.05$ s^{-1}, $\Delta H^* = 14.7$ kcal mol^{-1}, $\Delta S^* = -26$ cal K^{-1} mol^{-1} at 25 °C. The equilibrium formation constants are $K_1 = 5.55 \pm 0.27$ and $K_2 = 0.437 \pm 0.069$.[94] The negative ΔS^* values are consistent with an I_a mechanism.

A dissociative mechanism is proposed for the aquation of *trans*-$[Cr(en)_2Cl_2]^+$ ion from studies in aqueous–organic solvent mixtures (0—50% MeOH, ethylene glycol, glycerol, acetone, and dioxan).[95] Plots of ln k with ε^{-1} (ε = dielectric constant of solvent) or the Grunwald–Winstein Y-values are linear, and comparison with the analogous Co^{III} systems indicates far less charge separation in the transition state.

Studies of the aquation of *cis*-$[Cr(en)_2(NCS)_2]^+$ ion below pH 3 have been interpreted in terms of reactions of the parent ion (k_1) and its conjugate base, $[Cr(en-H)(en)(NCS)_2]$ (k_2); $k_{obs} \simeq k_1 + K(k_2 - k_1)[H^+]^{-1}$, where K is the equilibrium constant for conjugate-base formation, $\Delta H^*(k_1) = 28$ kcal mol^{-1}, $\Delta S^*(k_1) = +7.8$ cal K^{-1} mol^{-1}, $\Delta H^*(k_2) = 21.5$ kcal mol^{-1}, and $\Delta S^*(k_2) = -9.3$ cal K^{-1} mol^{-1}. Similar results were obtained previously for the analogous *trans*-complex.[96]

Very few carbonato-complexes of Cr^{III} are known, and so the recent study of the formation and aquation of *cis*-$[Cr(ox)_2(OCO_2)]^{3-}$ ion is particularly interesting. For the aquation reaction, only the acid-catalysed ring-opening process is observed with $k = 2.04$ M^{-1} s^{-1} at 25 °C and $I = 2.0$ M [$NaClO_4$]. Studies of the reaction of *cis*-$[Cr(ox)_2(OH_2/OH)]^{-/2-}$ with CO_2 between pH 7 and 9.3 gives *cis*-$[Cr(ox)_2(HCO_3)(OH_2)]^{2-}$ ion which slowly ring-closes.[97]

Bidentate Leaving Groups. A comparison of the rates of the acid-catalysed removal of pentane-2,4-dione (acac) from [Cr(hedta)(acac)]$^-$ ion and [Cr(edda)(acac)] has been made.[98] The pendant carboxylate arm in the former complex accelerates the rate of acac loss by a factor of 10^3 compared with the usually observed rate, and this complex is more reactive than the protonated derivative, [Cr(hedtaH)(acac)]. For [Cr(edda)(acac)], a normal rate is observed at 25 °C, $10^5k = 2.99$ s^{-1} ($I = 1.0$ M).

Values of ΔH^*, ΔS^*, and ΔV^* for the acid-catalysed aquation of *cis*-$[Cr(LL)_2(OH_2)_2]^-$ ions (LL = ox or mal) are collected in Table 14 (see Introduction, ref. 11). The small positive ΔV^* values for the aquation reactions are consistent with a mechanism in which proton attack at the co-ordinated uniden-

[94] K. R. Ashley, D. K. Pal, and V. D. Ghanekar, *Inorg. Chem.*, 1979, **18**, 1517.
[95] L. G. Reiter, V. V. Udovenko, and I. Berna, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1979, **24**, 27.
[96] Cs. Várhelyi, J. Zsakó, and B. Gagyi, *Monatsh. Chem.*, 1978, **109**, 1321.
[97] D. A. Palmer, T. P. Dasgupta, and H. Kelm, *Inorg. Chem.*, 1978, **17**, 1173.
[98] J. Guardalabene, S. Gulnak, N. Keder, and R. E. Shepherd, *Inorg. Chem.*, 1979, **18**, 22.

Table 14 *Activation parameters for the H^+-catalysed aquation of* cis-$[Cr(LL)_2(OH_2)_2]^-$ *ions and for the isomerization of* trans-$[Cr(LL)_2(OH_2)_2]^-$ *ions (data from Introduction, ref.* 11)

Aquation of cis-$[Cr(LL)_2(OH_2)_2]^-$ *ions*

LL	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	$\Delta V^{\ddagger}$/cm^3 mol^{-1}
ox^{2-}	24	−2.4	+1.7±0.7
mal^{2-}	21	−8.4	+2.4±0.6

Isomerization of trans-$[Cr(LL)_2(OH_2)_2]^-$ *ions*

LL	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	$\Delta V^{\ddagger}$/cm^3 mol^{-1}	$\Delta\beta^{\ddagger}$/ cm^3 mol^{-1} kbar^{-1}
ox^{2-}	17.5	−14.6	−16.6±0.5	−1.8±0.6
mal^{2-}	30.1	+17.6	+8.9±0.3	0

tate carboxylato-intermediate occurs. The large negative $\Delta V^{\ddagger}$ values for the isomerization reactions support a mechanism involving one-ended dissociative (I_d) chelate-ring opening. Values of $\Delta V^{\ddagger}$ for the acid hydrolysis of $[Cr(ox)_3]^{3-}$ ion were compared with those for the analogous Co^{III} and Rh^{III} complexes in Table 2 (Introduction, ref. 16).

For the H^+-catalysed aquation of $[CrL_3]$ (L = bromomalonate ion), $10^4k_1 = 3.9\ M^{-1}\ s^{-1}$ and $E_a = 24$ kcal mol^{-1}, with *cis*-$[Cr(L)_2(OH_2)_2]^-$ ion the first-formed product.[99]

Some of the steps in the reaction of $[Cr(ox)_2(gly)]^{2-}$ ion with oxalic acid (H_2ox) in acidic nitrate media are as follows:[100]

$$[Cr(ox)_2(gly)]^{2-} + H_3O^+ \longrightarrow cis\text{-}[Cr(ox)_2(O_2CCH_2NH_3)(OH_2)]^-$$

$$[Cr(ox)_2(gly)]^{2-} + H_2O \longrightarrow cis\text{-}[Cr(ox)_2(O_2CCH_2NH_3)(OH)]^-$$

$$[Cr(ox)_2(O_2CCH_2NH_3)(OH_2)]^- + H_2ox \longrightarrow [Cr(ox)_3]^{3-} + glyH_2^+ + H_3O^+$$

$$[Cr(ox)_2(O_2CCH_2NH_3)(OH_2)]^- + H_3O^+ \longrightarrow cis\text{-}[Cr(ox)_2(OH_2)_2]^- + glyH_2^+$$

$$[Cr(ox)_2(O_2CCH_2NH_3)(OH_2)]^- + NO_3^- + H^+ \longrightarrow [Cr(ox)_2(ONO_2)(OH_2)]^{2-} + glyH_2^+$$

All three steps in the successive H^+-catalysed loss of salicylaldehyde (L) from $[CrL_3]$ have been examined. For each step, $k_{obs} = k_0 + k_1[H^+]$, with the H^+-independent pathways catalysed by anions such as NO_3^- and SO_4^{2-}, except for the first step (*i.e.* when co-ordinated H_2O is not present). Anation of $[Cr(H_2O)_6]^{3+}$ by sulphate ion was also investigated and proceeds *via* an I_a mechanism.[101]

Hydrolysis of $[CrL_3]$ ($L = NH_2CH_2CH_2O^-$) has been studied in aqueous solution and in aqueous methanol. In aqueous solution $\Delta H^{\ddagger} = 13.3$ kcal mol^{-1} and in methanol $\Delta H^{\ddagger} = 17.6$ kcal mol^{-1} for all three steps, whereas $\Delta S^{\ddagger}$ decreases from −33 to −34 cal K^{-1} mol^{-1} in H_2O and from −18.9 to −19.4 cal K^{-1} mol^{-1} in methanol. The reactions proceed with Cr—O bond fission.[102]

[99] A. A. Abdel Khalek, M. S. Al-Obadie, and A. A. K. Al-Mahdi, *Inorg. Chim. Acta*, 1978, **31**, 141.
[100] T. W. Kallen and R. E. Hamm, *Inorg. Chem.*, 1979, **18**, 2151.
[101] K. Bauer, H. Elias, R. Gaubatz, and G. Lang, *Inorg. Chim. Acta*, 1979, **36**, 55.
[102] E. G. Timofeeva and A. A. Koroleva, *Koord. Khim.*, 1978, **4**, 1223.

Several studies involving H_3PO_4 reacting with the Cr^{III} complexes $[Cr(L)_3]^{3-}$ (L = methylmalonate),[103] $[Cr(OH_2)_4(ox)]^+$,[104] and $[Cr(mal)_3]^{3-}$ and *cis*-$[Cr(mal)_2(OH_2)_2]^-$[105] have appeared. For the first of these reactions,[103] Rate = $(k_1[H_3O^+] + k_2[H_3PO_4])[CrL_3^{3-}]$ with $10^3 k_1 = 4.22$ M^{-1} min^{-1} and $10^3 k_2 = 5.1$ M^{-1} min^{-1}, and for the reaction of $[Cr(mal)_3]^{3-}$ and *cis*-$[Cr(mal)_2(OH_2)_2]^-$ ions, Rate = $(k_1[H_3O^+] + k_2)[Cr(mal)_3^{3-}][H_3PO_4]^2[H_2mal]^{-1}$ with $10^2 k_1 = 1.38$ and 1.11 M^{-1} min^{-1} and $10^3 k_2 = 15.6$ and 1.07 min^{-1} for the tris- and bis-complexes respectively.[105]

Bridged Complexes. From the reaction of $\Delta,\Lambda[(en)_2Cr\text{-}\mu(OH)_2\text{-}Cr(en)_2]^{4+}$ ion with sulphuric acid, the $\Delta,\Lambda[(en)_2Cr\text{-}\mu(OH,SO_4)\text{-}Cr(en)_2]^{3+}$ ion can be isolated.[106] This μ-sulphato-complex is robust in acidic media, but in basic solution it deprotonates (pK_a *ca.* 12) to give blue $\Delta,\Lambda\text{-}[(en)_2Cr\text{-}\mu(O,SO_4)\text{-}Cr(en)_2]^{2+}$ which rapidly undergoes sulphate-bridge cleavage to give $\Delta,\Lambda\text{-}[(HO)(en)_2Cr\text{-}\mu(OH)\text{-}Cr(en)_2(OH)]^{3+}$ ion as a major product. Similarly, reaction of $\Delta,\Lambda\text{-}[(en_2Cr\text{-}\mu(OH)_2\text{-}Cr(en)_2]^{4+}$ ion with RCO_2H (R = Me, H, $H_3\overset{+}{N}CH_2$, or NH_2CH_2) gives $\Delta,\Lambda\text{-}[(en)_2Cr\text{-}\mu(OH,RCO_2)\text{-}Cr(en)_2]^{4+}$ ion, and at 25 °C in 4 M RCO_2H the formation rate is relatively high [k_{obs} in the range $(1—7) \times 10^{-4}$ s^{-1}]. In strong base the μ-hydroxo-bridge again deprotonates (pK_a *ca.* 12) to give the μ-oxo-μ-carboxylato-complex.[107]

Photochemical Studies Various factors affecting the quantum yield (Φ) for the photoaquation of $[Cr(bipy)_3]^{3+}$ ion have been investigated. The yield is increased by: (i) increasing $[H^+]$, (ii) increasing ionic strength, (iii) increasing [phosphate], especially at low $[H^+]$, (iv) lowering *T*, and (v) incorporating O_2 in the solution.[108,109] A seven-co-ordinate intermediate, $[Cr(bipy)_3(OH_2)]^{3+}$, is believed to be involved, which undergoes H^+-assisted formation of *cis*-$[Cr(bipy)_2(OH)_2)_2]^{3+}$ ion ($k = 2 \times 10^4$ M^{-1} s^{-1}), $[H_2PO_4]^-$-ion-assisted reconversion into $[Cr(bipy)_3]^{3+}$ ($k = 8 \times 10^3$ M^{-1} s^{-1}), and $[H_2PO_4]^-$-ion-assisted conversion into *cis*-$[Cr(bipy)_2(OH)_2]^+$ ion ($k = 8 \times 10^5$ M^{-1} s^{-1}). Scheme 9 is proposed, in which the photo-

$$[Cr(bipy)_2]^{3+} \underset{\text{non-radiative}}{\overset{h\nu}{\rightleftharpoons}} [Cr(bipy)_3]^{3+}(^2E)$$

$$[Cr(bipy)_3]^{3+}(^2E) \overset{H_2O}{\rightleftharpoons} [Cr(bipy)_3(OH_2)]^{3+}$$

$$[Cr(bipy)_2(OH_2)]^{3+} \rightleftharpoons [Cr(bipy)_3]^{3+} + H_2O$$

$$[Cr(bipy)_2(OH_2)]^{3+} \overset{H^+}{\rightleftharpoons} [Cr(bipy)_3]^{3+} + H_2O$$

$$[Cr(bipy)_2(OH_2)]^{3+} \rightleftharpoons [Cr(bipy)_3(OH)]^{2+} + H^+$$

$$[Cr(bipy)_3(OH)]^{2+} \overset{OH^-}{\rightleftharpoons} [Cr(bipy)_2(OH)_2] + bipy$$

Scheme 9

[103] N. R. Anipindi, V. A. Ramam, and M. N. Sastri, *Indian J. Chem., Sect. A*, 1978, **16**, 711.
[104] N. R. Anipindi, V. M. Rao, and V. A. Ramam, *J. Indian Chem. Soc.*, 1978, **55**, 736.
[105] N. R. Anapindi, V. M. Rao, and V. A. Ramam, *J. Indian Chem. Soc.*, 1978, **55**, 647.
[106] J. Springborg, *Acta Chem. Scand., Ser. A*, 1978, **32**, 231.
[107] J. Springborg and H. Toftlund, *Acta Chem. Scand., Ser. A*, 1979, **33**, 31.
[108] R. Sriram, M. S. Henry, and M. Z. Hoffmann, *Inorg. Chem.*, 1979, **18**, 1727.
[109] M. A. Jamieson, N. Serpone, M. S. Henry, and M. Z. Hoffman, *Inorg. Chem.*, 1979, **18**, 214.

excited ^2E state is reached with unitary efficiency *via* spin-allowed excited states and rapid intersystem crossing. The Gillard mechanism, involving covalent hydrate formation is rejected, but on the flimsiest of evidence.[110] The pK_a of the proposed seven-co-ordinate intermediate is estimated to be *ca.* 5—6,[108] and on the basis of Scheme 9 $\Phi = k_1/k_0$, where k_1 is the rate constant for associative attack by H_2O on the ^2E excited state and k_0 is the rate of non-radiative decay of this state. Activation parameters associated with k_1 are $\Delta H^*(k_1) = 9.6$ kcal mol^{-1}, $\Delta S^*(k_1) = -10$ cal K^{-1} mol^{-1}, compared with $\Delta H^* = 23$ kcal mol^{-1} and $\Delta S^* = -8.7$ cal K^{-1} mol^{-1} for the thermal aquation reaction involving the ^4A ground state.[109] The quantum yield at pH 9.6 ($\Phi = 0.11$) is much larger than that at pH 4.3 (Φ *ca.* 10^{-3}; 313—464 nm irradiation).

An autocatalytic chain reaction is reported[111] for the solvolysis of $[Cr(bipy)_3]^{3+}$ ion in DMF solution involving reduction to Cr^{II}:

$$[Cr(bipy)_3]^{3+} \xrightarrow{h\nu} [Cr(bipy)_3]^{3+*} \longrightarrow [Cr(bipy)_3]^{2+}$$

$$[Cr(bipy)_3]^{2+} + 2DMF \longrightarrow [Cr(bipy)_2(DMF)_2]^{2+} + bipy$$

$$[Cr(bipy)_3]^{3+} + [Cr(bipy)_2(DMF)_2]^{2+} \longrightarrow [Cr(bipy)_2(DMF)_2]^{3+} + [Cr(bipy)_3]^{2+}$$

A new theory has been proposed to account for the observed stereochemistry in the photolysis of chromium(III) acido-amines,[112] only to be rejected since it does not explain the high proportion of *trans*-product resulting from the loss of the equatorial (*cis*) ammonia molecule in $[Cr(NH_3)_5F]^{2+}$ ion.[113] It is argued that the unique stereochemistry of chromium(III) photoreactions must reside in the vacant t_{2g} orbital in an excited state which enables bonding of an entering ligand to give a seven-co-ordinate transition state.[113] Recent further studies in this area include a comparison of the photolysis and thermal aquation of *trans*-$[Cr(NH_3)_4(DMF)Cl]^{2+}$ and $[Cr(NH_3)_5(DMF)]^{3+}$ ions,[93] and the ligand-field photolysis of *cis*-$[Cr(NH_3)_4Cl_2]^+$ ($\Phi_{NH_3} = 0.32$, $\Phi_{Cl^-} = 0.15$) and *cis*-α-[Cr(trien)-$Cl_2]^+$ ion (Φ_{NH_3} *ca.* 0, $\Phi_{Cl^-} = 0.10$), the latter two reactions proceeding with retention of configuration.[114] A correlation between log k for the thermal aquation and Φ_{total} for the photolysis of $[Cr(NH_3)_4XY]^{n+}$, $[Cr(en)_2XY]^{n+}$, and $[Cr(trien)XY]^{n+}$ ions was noted.[114]

Scandium(III) (d^0).—A number of years ago this Reporter found the reaction between $[Sc(DMSO)_6]^{3+}$ ion and the metal ion indicator pada too fast to measure by conventional stopped-flow spectrophotometry.[115] However, it now appears that in other solvents stopped-flow experiments are possible, as shown by the recent solvent-exchange studies of Lincoln *et al.* in nitromethane and acetonitrile solutions of $[Sc(L)_6]^{3+}$ ions (L = trimethyl phosphate[116] or dimethyl

[110] M. Maestri, F. Bolletta, L. Moggi, V. Balzani, M. S. Henry, and M. Z. Hoffmann, *J. Am. Chem. Soc.*, 1978, **100**, 2694.
[111] G. B. Porter and J. van Houten, *Inorg. Chem.*, 1979, **18**, 2053.
[112] L. G. Vanquickenborne and A. Ceulemans, *J. Am. Chem. Soc.*, 1978, **100**, 475; 1977, **99**, 2208.
[113] A. D. Kirk, *Inorg. Chem.*, 1979, **18**, 2326.
[114] M. S. Thompson and P. S. Sheridan, *Inorg. Chem.*, 1979, **18**, 1580.
[115] P. Moore and D. M. W. Buck, unpublished results.
[116] D. L. Pisaniello, S. F. Lincoln, and E. H. Williams, *J. Chem. Soc., Chem. Commun.*, 1978, 1074.

methylphosphonate[117]). Some interestingly different rate laws are reported in the supposedly non-co-ordinating solvents nitromethane and acetonitrile. For example, in CD_3CN the observed rate constant for solvent exchange with $[Sc\{OPMe(OMe)_2\}_6]^{3+}$ ion is of the form $k_{ex}=k_1+k_2[solvent]$ [at 300 K, $k_1=3.2\pm0.2$ s^{-1}, $\Delta H^{\ddagger}(k_1)=10.4$ kcal mol^{-1}, $\Delta S^{\ddagger}(k_1)=-22$ cal K^{-1} mol^{-1}; $k_2=14.8\pm0.4$ M^{-1} s^{-1}, $\Delta H^{\ddagger}(k_2)=5.8$ kcal mol^{-1}, $\Delta S^{\ddagger}(k_2)=-34$ cal K^{-1} mol^{-1}], whereas in CD_3NO_2 solution only a second-order term is observed [at 300 K, $k_2=13.7\pm0.5$ M^{-1} s^{-1}, $\Delta H^{\ddagger}(k_2)=7.1$ kcal mol^{-1}, $\Delta S^{\ddagger}=-30$ cal K^{-1} mol^{-1}].

Titanium(III) (d^1).—$[Ti(edtaH)(OH_2)]$, containing quinquedentate protonated edta, is remarkably more labile than the $[Ti(H_2O)_6]^{3+}$ ion, the relative water exchange rates being $>10^7$ s^{-1} and *ca.* 10^5 s^{-1} respectively.[118] It is suggested that the un-co-ordinated carboxylate arm labilizes the water molecule in $[Ti(edtaH)(OH_2)]$, possibly *via* a seven-co-ordinate ring-closed transition state. Despite its lability, $[Ti(edtaH)(OH_2)]$ still chooses to react with certain oxidants, *e.g.* $[Co(NH_3)_5Cl]^{2+}$, through an outer-sphere rather than an inner-sphere mechanism.

Vanadium(III) (d^2).—Two papers have appeared concerned with V^{III} β-diketonate complexes.[119] Replacement of pentane-2,4-dionate ion (acac) in $[V(acac)_3]$ by its hexafluoro-analogue proceeds with a two-term rate law, first- and second-order with respect to incoming ligand respectively, whereas replacement by its deuterio-analogue has a two-term rate law zero- and first-order in incoming ligand. The reactions are markedly catalysed by acids and bases, and a chelate-ring opening mechanism is proposed, with an intermediate involving a unidentate, 'dangling' acac ligand. These ligand-exchange reactions are much slower than isomerization.

Molybdenum(III) (d^3).—An S_N2 mechanism is proposed for [^{14}C]oxalate exchange with $[Mo^{III}_2(ox)(L)(OH_2)_4]$ (L = hydroxyproline).[120]

Iron(III) (d^5).—Studies of Fe^{III} systems fall into two groups, the labile, high-spin $t_{2g}^3e_g^{*2}$ and the inert t_{2g}^5 complexes.

The importance of covalent hydrates has been stressed in the aquation of the low-spin $[Fe(terpy)_2]^{3+}$ ion in aqueous sulphuric acid. The rate of the reaction increases upon addition of small amounts of acid, reaches a maximum, and then falls to zero as the activity of water approaches zero.[121] A similar mechanism can be expected for $[Fe(L)_3]^{3+}$ ion (L = 5-Br-phen).[122]

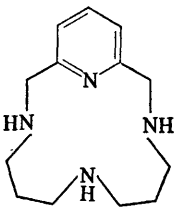
A dissociative I_d mechanism has been established for substitution reactions of low-spin $[Fe(cyclam)(NCS)X]^+$ ions (X = NCS^-, $CH_2ClCO_2^-$, $CHCl_2CO_2^-$, Cl^-, or Br^-).[123] Of the complexes studied, only the $[Fe(cyclam)Br]^{2+}$ ion was found to be in a high-spin/low-spin equilibrium (*ca.* 71% low-spin at 20 °C). A plot of the logarithm of the rate constant for the loss of ligand X (k_{-X}) against the logarithm of the equilibrium constant for its formation (K) is linear over 5 log units with a slope of 1.00 ± 0.05. The data are summarized in Table 15.

[117] D. L. Pisaniello and S. F. Lincoln, *Inorg. Chim. Acta*, 1979, **36**, 85.
[118] G. A. K. Thompson and A. G. Sykes, *Inorg. Chem.*, 1979, **18**, 2025.
[119] A. J. C. Nixon and D. R. Eaton, *Can. J. Chem.*, 1978, **56**, 1005, 1012.
[120] S. Wajda and B. Kurzak, *Bull. Acad. Pol. Sci. Ser. Sci. Chim.*, 1978, **26**, 709.
[121] W. S. Walters, R. D. Gillard, and P. A. Williams, *Aust. J. Chem.*, 1978, **31**, 1959.
[122] J. Burgess and F. M. Mekhail, *Transition Met. Chem.*, 1978, **3**, 162.
[123] C. K. Poon and W. M. Andrew, *Inorg. Chem.*, 1979, **18**, 1277.

Table 15 *Rate constants at* 22.4 °C *for the loss of* X^- *from low-spin* trans-$[Fe^{III}(cyclam)(NCS)X]^+$ *ions* (k_{-X}) *and the equilibrium constants for aquation reaction* (Q) *(data from ref.* 123)

X^-	$10^4 k_{-X}/s^{-1}$	$10^6 Q/M$
NCS^-	3.5	4.5
$CH_2ClCO_2^-$	440	500
$CHCl_2CO_2^-$	1000	1400
Cl^-	3.2×10^4	3.6×10^4
Br^-	4.2×10^5	4.4×10^5

The complex $[Fe^{III}(L)Cl_2]^+$ [L = (13)] is an effective catalyst for the decomposition of H_2O_2.[124] In an acetate buffer, $[Fe(L)(OH)(OH_2)]^{2+}$ ion was identified as the active species ($pK_1 = 2.88$, $pK_2 = 7.43$) which dimerizes to the μ-oxo-dimer with $10^{-3}k_{obs} = 9.82\ M^{-2}\ min^{-1}$.



(13)

Properties of the cyano-bridged species $[(edta)Co^{III}—NC—Fe^{III}(CN)_5]^{4-}$ were referred to in the cobalt(III) section.[66]

From studies of the high-spin monophenolate complexes of Fe^{III} using the temperature-jump method, it is suggested that pathways involving $[Fe(H_2O)_6]^{3+}$ and $[Fe(H_2O)_5(OH)]^{2+}$ ions (*i.e.* proton ambiguity) can be distinguished by measuring values of $\Delta S_d^{\ddagger}$ for the phenolate dissociation reactions. The pertinent data are collected in Table 16.[125] Comparison with related systems shows that $\Delta S_d^{\ddagger}$ is rather different for the two reactions $[Fe(H_2O)_6]^{3+} + L^-$ and $[Fe(H_2O)_5(OH)]^{2+} + HL$.

The kinetics of ligand exchange between $[Fe(acac)_3]$ and 2-thenoyltrifluoroacetone have been studied in organic solvents.[126] In CCl_4, C_6H_6, Me_2CO, and 4-methylpentan-2-one the rates are about the same, but catalysis by EtOH, H_2O, and acids is observed. The reaction is independent of the concentrations of acac and incoming ligand.

Reaction of $[Fe(DMF)_6]^{3+}$ with $[Mn(acac)_3]$ involving exchange of acac between the two metal ions has been reported.[127]

[124] A. C. Melnyk, N. K. Kildahl, A. R. Rendina, and D. H. Busch, *J. Am. Chem. Soc.*, 1979, **101**, 3232.
[125] G. Calvaruso, F. P. Cavasina, and E. di Dio, *J. Chem. Soc., Faraday Trans. 1*, 1978, **74**, 525.
[126] T. Sekine, H. Honda, M. Kokiso, and T. Tasak, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 1046.
[127] R. Schmid and V. N. Sapunov, *Int. J. Chem. Kinet.*, 1979, **11**, 1.

Table 16 *Approximate activation parameters for the aquation of mono-complexes of iron*(III) *in aqueous solution* (*data from ref.* 125)

Species involved in transition-state	*I*/M	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S_d^{\ddagger}$/cal K^{-1} mol^{-1}
Fe^{3+}, HF	0.5	9	−32
Fe^{3+}, Cl^-	1.0	10—11	−21
Fe^{3+}, Br^-	1.2	6	−29
Fe^{3+}, NCS^-	0.4	15	−10
Fe^{3+}, SO_4^{2-}	0.5	11	−15
$FeOH^{2+}$, RC_6H_4OH[a]	0.1	14—17	0 to +9
$FeOH^{2+}$, $MeCO_2H$	0.5	15	3
$FeOH^{2+}$, HF	0.5	20	5
$FeOH^{2+}$, HN_3	0.1	17	3
$FeOH^{2+}$, Cl^-	0.64	18	6
$FeOH^{2+}$, NCS^-	0.4	22	10
$FeOH^{2+}$, SO_4^{2-}	0.5	16	−3

[a] R = *p*-Me, H, *p*-Cl, *m*-Cl, *m*-NO_2, or *p*-NO_2.

Ruthenium(III) (d^5).—The Hg^{2+} ion-induced aquation of $[Ru(NH_3)_5Cl]^{2+}$ ion in perchloric or nitric acids is characterized by $\Delta H^{\ddagger} = 16.9$ kcal mol^{-1}, $\Delta S^{\ddagger} = -14.5$ cal K^{-1} mol^{-1}. The effectiveness of Hg^{2+} as an electrophile increases in the order $Ru^{III} < Rh^{III} < Co^{III}$.[128]

The $[Ru(NH_3)_5(XMe_2)]^{2+/3+}$ ions have been prepared (X = S, Se, or Te) and for the Ru^{III} complexes the rate constants for loss of Me_2X were found to be $10^6k = 1.59 \pm 0.04$ s^{-1} for X = Se and $10^7k = 2.6 \pm 0.1$ s^{-1} for X = S at 25 °C in 0.2 M [HCl] and 0.1 M [LiCl]. The Me_2Te complex is more difficult to study but is approximately as labile as the Me_2Se analogue. Ligand → metal charge transfer is invoked to account for the low rates observed. The Ru^{II} complexes aquate with loss of NH_3 (primarily in a *trans*-position to Me_2X) rather than Me_2X.[129]

The oxime complexes *trans*-$[Ru^{III}(L)_2(OH_2)_2]^+$ (HL = α-furyl mono- and di-oximes) have been investigated, including measurements of equilibrium constants and rate constants for the formation and dissociation of mono- and bis-species.[130]

Two groups report studies of $[Ru^{III}(edta)OH_2]^-$ ion.[131,132] Rate data reported for the following equilibria are collected in Table 17:[131]

$$[Ru(edta)(OH_2)]^- + L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Ru(edta)(L)]^{n-} + H_2O$$

Values of k_1 are much larger than those observed for other Ru^{III} complexes containing unidentate O- and N-donor atoms, with $\Delta H^{\ddagger}$ much smaller. The picture is similar to that observed for the analogous Ti^{III} complex discussed

[128] V. V. Tatarchuk and A. V. Belyaev, *Koord. Khim.*, 1978, **4**, 1059.
[129] C. A. Stein and H. Taube, *Inorg. Chem.*, 1979, **18**, 1168.
[130] V. M. Savostina, O. A. Shpigun, N. V. Klimova, I. Y. Kolotyrkina, and V. M. Peshkova, *Chem. Abs.*, 1979, **90**, 128332.
[131] T. Matsubara and C. Creutz, *Inorg. Chem.*, 1979, **18**, 1956; *J. Am. Chem. Soc.*, 1978, **100**, 6255.
[132] Y. Yoshino, T. Uehiro, and M. Saito, *Bull. Chem. Jpn.*, 1979, **52**, 1060.

Table 17 *Rate data at* 25 °C *for the formation* (k_1) *and dissociation* (k_{-1}) *of* $[Ru^{III}(edta)(L)]^{n-}$ (*data from ref.* 131)

L	$k_1/M^{-1}\,s^{-1}$	$\Delta H_1^{\ddagger}$/kcal mol^{-1}	$\Delta S_1^{\ddagger}$/cal K^{-1} mol^{-1}	k_{-1}/s^{-1}	$k_1([Ru^{II}(edta)L]^{m-}/M^{-1}\,s^{-1}$
MeCN	30 ± 7	8.3	−24.0	3.2 ± 0.2	13 ± 1
NCS^-	270 ± 20	8.9	−17.9	0.5 ± 0.1	2.7 ± 0.2
py	6300 ± 500			0.061 ± 0.002	
isonicotinamide	8300 ± 600	6.6	−18.8	0.7 ± 0.2	30 ± 15
pyrazine	$20\,000\pm1000$	5.7	−20	2.0 ± 0.5	

previously,[118] and for some other $[M^{III}(edta)(OH_2)]^-$ complexes. For example, when M = Cr, Ru, or Os, the edta complexes are 10^5—10^{10} times as labile as the corresponding $[M(NH_3)_5(OH_2)]^{3+}$ ions. An I_a mechanism is proposed for these very labile systems, with hydrogen-bonding between the co-ordinated water molecule and the un-co-ordinated carboxylate arm thought to be important in the transition state. It is interesting that the analogous Co^{III}, Rh^{III}, and Ru^{II} complexes, which are known to react *via* an I_d mechanism, are only 10^2 times as labile as their corresponding ammine complexes. Because the $[Ru^{III}(edta)(OH_2)]^-$ ion is so labile, study of the analogous Ru^{II} complex, $[Ru(edta)(OH_2)]^{2-}$, is complicated by traces of Ru^{III} which can catalyse substitution reactions *via* a redox pathway in which substitution occurs first at Ru^{III} followed by rapid electron transfer between Ru^{II} and Ru^{III}.[131] For the reaction of $[Ru(edta)(OH_2)]^-$ with $S_2O_3^{2-}$ ion, $k_1 = 2.94 \pm 0.11$ at 303.2 K (pH 4—6, $I = 0.1$ M), and above pH 6 the reaction is slower owing to $[Ru(edta)(OH)]^{2-}$ ion formation. The equilibrium formation constant is $10^{5.02}$ at 30 °C.[132]

When edta complexes of Ru^{II} and Ru^{III} are attached to a graphite surface by means of co-ordinated 4-(aminomethyl)pyridine, which is synthetically introduced on to the graphite surface through an amide bond, the rate of Ru—heterocyclic nitrogen bond fission is significantly reduced.[133]

Chloride exchange between $^{36}Cl^-$ and *cis*-$[Ru(bipy)_2Cl_2]^+$ ion is reported to proceed with an S_N2 mechanism.[134]

Rhodium(III) (d^6).—Systems considered previously include measurements of ΔV^* for the acid hydrolysis of $[M(ox)_3]^{3-}$ ions (M = Co, Cr, or Rh; Table 2) (Introduction, ref. 16), for the Hg^{II}-ion induced aquations of $[M(NH_3)_5X]^{2+}$ ions (M = Co, Cr, or Rh; Table 12) (Introduction, ref. 17), and for solvent exchange with $[M(NH_3)_5(DMF)]^{3+}$ ions (M = Co or Rh) (Introduction, ref. 13). The small negative ΔV^* value for solvent exchange with $[Rh(NH_3)_5(DMF)]^{3+}$ ion is ascribed to an I_a mechanism. However, a dissociative mechanism is favoured for aquation of $[RhCl_6]^{3-}$ and $[RhCl_5(H_2O)]^{2-}$ ions based on the values of ΔV^* of 21.5 ± 0.6 and 14.3 ± 0.5 cm^3 mol^{-1} respectively. Anation of $[RhCl_5(H_2O)]^{2-}$ and *cis*-$[RhCl_4(H_2O)_2]^+$ ions by chloride ion was also studied and ΔV^* found to be 15.7 ± 6.5 and 14.7 ± 1.6 cm^3 mol^{-1} respectively (Introduction, ref. 14).

A *D*-mechanism rather than an $S_N1$ip (or I_d) mechanism is favoured for chloride exchange reactions involving *trans*-$[Rh(NH_3)_4Cl_2]^+$, *cis*-$[Rh(en)_2Cl_2]^+$, and *trans*-$[Ir(trien)Cl_2]^+$ ions. If the ion-pairing mechanism were involved, values of the outer-sphere ion-pair constant, K_{os}, in the range 10—60 would be required and these values are regarded as too large for interactions of +1 and −1 ions.[135]

The Ag^+ ion-assisted aquation of $[Rh(NH_3)_5I]^{2+}$ ion[136] and the Hg^{2+} ion-induced aquations of $[Rh(NH_3)_5Cl]^{2+}$,[137] *trans*-$[Rh(L)_4Cl_2]^+$ [$L_4 = (NH_3)_4$,

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[134] S. Wajda, K. Rachlewicz, and E. Krawczyk, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, 1978, **26**, 399.
[135] J. Burgess, K. W. Bowker, E. R. Gardner, and F. M. Mekhail, *J. Inorg. Nucl. Chem.*, 1979 **41**, 1093.
[136] C. St.E. Boyce, G. C. Lalor, and H. Miller, *J. Inorg. Nucl. Chem.*, 1979, **41**, 857.
[137] S. F. Chan and L. Lang, *Chem. Abs.*, 1979, **90**, 157707.

$(py)_4$, or $(en)_2$],[138] and *fac*-$[RhCl_3(H_2O)_3]$[139] have all been investigated. For the reaction of $[Rh(NH_3)_5I]^{2+}$ ion in the presence of 1 M $[Ag^+]$ ion,

$$k_{obs} = k_{aq} + \sum_{n=1}^{n=3} k_n\beta_n[Ag^+]^n \Big/ \left(1 + \sum_{n=1}^{n=3} \beta_n[Ag^+]^n\right)$$

where k_{aq} is the rate constant for aquation in the absence of Ag^+ ion, k_n is the rate constant for the aquation of each species of the type $[Rh(NH_3)_5IAg_n]^{(2+n)+}$, and β_n is the overall formation constant for this species. At 113 °C, $10^3k_{aq} = 2.0\ s^{-1}$, $10^5k_1 = 7.4\ s^{-1}$ ($\beta_1 = 77$), $10^3k_2 = 7.0\ s^{-1}$ ($\beta_2 = 87$), and $k_3 = 0.1\ s^{-1}$ ($\beta_3 = 34$). The rate constant k_{aq} varies with temperature according to the Arrhenius equation with $PZ = 7.422 \times 10^{10}\ s^{-1}$ and $E_a = 26$ kcal mol^{-1}.[136] The Hg^{2+} ion-induced aquation reactions of *trans*-$[Rh(L)_4Cl_2]^+$ ions give *trans*-$[Rh(L)_4(H_2O)Cl]^{2+}$ ions with rates 10^6 times as fast as the spontaneous aquations. When $L = NH_3$, ΔH^* is lowered by 6.8 kcal mol^{-1} and when $L_4 = (en)_2$ by 5.4 kcal mol^{-1}. Side reactions were observed for the complexes with L = py.[138]

The Hg^{2+} ion-induced aquation of *fac*-$[RhCl_3(H_2O)_3]$ gives *cis*-$[RhCl_2(H_2O)_4]^+$ ion which reacts further at a lower rate to give $[Rh(H_2O)_5Cl]^{2+}$ and finally $[Rh(H_2O)_6]^{3+}$ ion. For each step $k_{obs} = kK[Hg^{2+}]/(1 + K[Hg^{2+}])$, and at 40 °C $K = 137 \pm 5$, 10.0 ± 1.0, and $3.0 \pm 0.6\ M^{-1}$ and $10^6k/s^{-1} = 10700 \pm 400$, 43 ± 3, and 8.9 ± 1.8 for the trichloro-, dichloro-, and monochloro-species respectively. Values of ΔH^* and ΔS^* associated with the values of k are 18.9, 22.0, and 24.0 kcal mol^{-1} and -6.4, -7.5, and -5.0 cal K^{-1} mol^{-1} respectively.

The kinetics of the equilibration of *trans*-$[Rh(L)_2Cl_2]^+$ ion (L = *o*-dimethylaminophenyldimethylarsine) with RNH_2 (R = H, Me, Et, Pr^n, Bu^n, $PhCH_2$, Pr^i, Bu^i, Bu^s, or CH_2Bu^t) proceeds with Rh—N bond fission to give *mer*-$[Rh(L)(L')(RNH_2)Cl_2]^+$ in which L′ = L co-ordinated through the As-donor atom only. The pseudo-first-order rate constant is given by $k_{obs} = k_{t\rightarrow m}[RNH_2] + k_{m\rightarrow t}$, where $k_{t\rightarrow m}$ and $k_{m\rightarrow t}$ are the forward and reverse rate constants respectively. Values of $k_{t\rightarrow m}$ are not sensitive to R, whereas values of $k_{m\rightarrow t}$ are, as one might expect. The importance of steric effects was noted, and a dissociative mechanism proposed.[140]

Aquation of $[Rh(LL)_2Cl_2]^+$ ions (LL = Me-, Et-, or Ph-substituted biguanidines) have been investigated in aqueous solution and in aqueous methanol.[141] The results obtained in aqueous solution are collected in Table 18. In aqueous methanol the rates decrease as the percentage of methanol increases, and associative mechanisms are proposed.

Ligand-field photoaquation of *cis*- and *trans*-$[Rh(en)_2(X)Cl]^{n+}$ ions (X = Cl^- or NH_3) has been investigated. All of the complexes lose Cl^- ion to give $[Rh(en)_2X(OH_2)]^{(n-1)+}$ ions. The *trans*-complexes react without sterochemical change, and the quantum yields are $\Phi = 0.061$ (X = Cl^-) and 0.062 (X = NH_3). For the *cis*-complexes when X = Cl^-, $\Phi = 0.43$ and the product is the *trans*-isomer, whereas when X = NH_3, $\Phi = 0.145$ and a *cis*-product is formed.[142]

[138] A. B. Venediktov and A. V. Belyaev, *Chem. Abs.*, 1979, **90**, 29604.
[139] S. F. Chan and G. M. Harris, *Inorg. Chem.*, 1979, **18**, 717.
[140] A. Peloso and L. Volponi, *J. Chem. Soc., Dalton Trans.*, 1979, 952.
[141] B. Chakravarty, P. K. Das, and A. K. Sil, *Inorg. Chim. Acta*, 1978, **30**, 149.
[142] J. D. Petersen and F. P. Jakse, *Inorg. Chem.*, 1979, **18**, 1818.

Table 18 *Activation parameters for the stepwise aquation of dichlorobis(substituted biguanidine)rhodium*(III) *ions (data from ref.* 141)

Complex[a]	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
$[Rh(LH)_2Cl_2]^+$	14.0	−25
$[Rh(LMe)_2Cl_2]^+$	14.8	−24
$[Rh(LEt)_2Cl_2]^+$	14.4	−24
$[Rh(LPh)_2Cl_2]^+$	14.4	−25.5
$[Rh(LH)_2(H_2O)Cl]^{2+}$	12.3	−35
$[Rh(LMe)_2(H_2O)Cl]^{2+}$	11.5	−37
$[Rh(LEt)_2(H_2O)Cl]^{2+}$	11.7	−36
$[Rh(LPh)_2(H_2O)Cl]^{2+}$	10.6	−40

[a] LR = biguanidine with substituent R.

Photoluminescence spectra, excited-state lifetimes, and quantum yields for photosubstitution reactions of $[Rh(NH_3)_5X]^{2+}$ and $[Rh(ND_3)_5X]^{2+}$ ions (X = Cl or Br) have been determined. Individual rate constants for deactivation of the excited states by radiative, non-radiative, and reactive pathways were determined. For the deuterio-complexes, the rate of non-radiative deactivation is lower, and consequently quantum yields for photosubstitution and photoemission are larger. The rate constant for the excited-state substitution pathway is estimated to be 10^{14}—10^{15} times greater than for the thermal substitution process.[143]

Ligand-field photolysis of *cis*-*β*-$[M(2,3,2\text{-tet})Cl(X)]^{n+}$ ions (M = Co or Rh, X = Cl^- or H_2O) and the thermal aquation of *cis*-*α*- and *cis*-*β*-$[Rh(LLLL)Cl_2]^+$ ions (LLLL = trien or 2,3,2-tet) have been studied in aqueous acidic solution. Photoaquation of *cis*-*β*-$[Rh(2,3,2\text{-tet})Cl_2]^+$ ion gives *cis*-*β*- and *trans*-chloro-aquo products in a ratio 1 : 3 ($\Phi_{total} = 0.26$). The *cis*-chloro-aquo product photoisomerizes to the *trans*-isomer with $\Phi = 0.13$. For the *cis*-*α*- and *cis*-*β*-$[Rh(trien)Cl_2]^+$ and *cis*-*β*-$[Rh(2,3,2\text{-tet})Cl_2]^+$ ions, *cis*-chloro-aquo products are formed, and at 25 °C and pH 1—4, $\Phi = 0.15$ and $10^4 k/s^{-1} = 1.8$, 16.7, and 3.7 respectively. The greater photoisomerization of *cis*-*β*-$[M(LLLL)Cl(X)]^+$ ions observed when LLLL = 2,3,2-tet rather than trien is interpreted in terms of a dissociative mechanism.[86]

Iridium(III) (d^6).—Aquation of the $[IrCl_6]^{3-}$ ion has been studied in 4 and 6 M $HClO_4$/HCl solutions,[144] and in the presence of K^+, Rb^+, Cs^+, and In^{3+} ions.[145, 146] At 5 °C, equilibrium constants for the aquation are estimated to be 0.96 ± 0.08 at $I = 6.0$ M, and 0.42 ± 0.06 at $I = 4.0$ M, and the rate constants at 50 °C are 1.3 ± 0.2 (h^{-1} ?) and 2.2 ± 0.2 (h^{-1} ?) respectively at these two ionic strengths.[144] The ion-pair constants with Cs^+, Rb^+, and K^+ ions were estimated to be 1400 ± 30, 110 ± 30, and 23 respectively.[145]

A *D*-mechanism is favoured for Cl^- ion exchange with *trans*-$[Ir(trien)Cl_2]^+$ as explained in the section on Rh^{III}.[135]

[143] M. A. Bergkamp, J. Brannon, D. Magde, R. J. Watts, and P. C. Ford, *J. Am. Chem. Soc.*, 1979, **101**, 4549.

[144] S. M. Zinina, G. P. Tsayun, V. I. Kravtsov, and L. Y. Smirnova, *Electrokhimiya*, 1979, **15**, 578.

[145] V. I. Kravtsov, L. Y. Smirnova, and G. P. Tsayun, *Chem. Abs.*, 1978, **89**, 118638.

[146] I. Salma, V. I. Kravtsov, L. Y. Smirnova, and G. P. Tsayun, *Chem. Abs.*, 1979, **90**, 142624.

3 Oxidation State IV

Vanadium(IV) (d^1).—Stopped-flow studies of the reaction of $[VO(L)(OH_2)]$ [L = (2-pyridylmethyl)iminodiacetate ion] with thiocyanate and azide ions, reactions which involve replacement of the basal water molecule in a *cis*-position to V=O) gave data for both the rate of formation (k_f) and the rate of dissociation (k_d), as shown in Table 19.[147] An associative mechanism is favoured for the formation reactions.

Table 19 *Rate constants and activation parameters at 25 °C for the formation (k_f) and dissociation (k_d) of $[V^{IV}O(L)X]^-$ ions [L = (2-pyridylmethyl)-iminodiacetate ion; data from ref.* 147]

X	k_d/s^{-1}	ΔH_d^*/ kcal mol^{-1}	ΔS_d^*/ cal K^{-1} mol^{-1}	k_f/M^{-1} s^{-1}	ΔH_f^*/ kcal mol^{-1}	ΔS_f^*/ cal K^{-1} mol^{-1}
N_3^-	0.13	15.2	−11.2	3.7	11.3	−17.9
NCS^-	0.061	14.7	−14.6	0.26	11.7	−22.0

Ligand exchange between $[VO(acac)_2]$ and ^{14}C-labelled acacH in CH_2Cl_2 solution has a second-order rate law, first-order in $[VO(acac)_2]$ and first-order with respect to the enol form of acacH; at 240 K, $10^2k = 7.1$ M^{-1} s^{-1}, $\Delta H^* = 11.2$ kcal mol^{-1}, and $\Delta S^* = -14.8$ cal K^{-1} mol^{-1}. An isotope effect, $k_H/k_D = 1.3 \pm 0.2$, was observed, and a mechanism involving rate-determining chelation and H^+ transfer from a half-bonded acacH molecule is proposed. Addition of donor solvents lowers the exchange rate: for example, in 0.06 M [DMSO] at 240 K, $10^3k = 3.8$ M^{-1} s^{-1}, $\Delta H^* = 17.2$ kcal mol^{-1}, and $\Delta S^* = -1.0$ cal K^{-1} mol^{-1}. Inhibition of the associative rate-determining step by co-ordinated DMSO is proposed.[148]

Osmium(IV) (d^4).—Full kinetic and thermodynamic data have been reported for the aquation of 13 complexes of general formula *trans*-$[Os(L)_4(I)X]^{2-}$, where the leaving group X^- is F^-, Cl^-, Br^-, or I^- and the four in-plane ligands L are Cl^- or I^-. The replacement of each L = Cl^- by L = I^- lowers ΔG^* for aquation by *ca.* 1.0 kcal mol^{-1}, and this *cis*-effect is less than the *trans*-effect of I^- which results in a lowering of ΔG^* by 5—6 kcal mol^{-1}. The reactions appear to proceed via an associative mechanism.[149]

4 Oxidation State V

Vanadium(V) (d^0).—The kinetics of $H_2{}^{18}O$ exchange[150] and $H_2{}^{17}O$ exchange[151] and decomposition[150,152] of $[V_{10}O_{28}]^{6-}$ ion have been reported. At 25 °C and 0.01 M ionic strength, incorporation of ^{18}O into this ion is very slow ($t_{1/2}$ *ca.* 15 h), and all of the oxygen atoms appear to exchange with $H_2{}^{18}O$ at the same rate. At a fixed pH the reaction is approximately first-order with a rate which shows

[147] M. Nishizawa and K. Saito, *Inorg. Chem.*, 1978, **17**, 3676.
[148] M. Nishizawa and K. Saito, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 483.
[149] U. Dietl and W. Preetz, *Z. Anorg. Allg. Chem.*, 1979, **451**, 93.
[150] R. K. Murmann, *Inorg. Chem.*, 1978, **17**, 1160.
[151] M. A. Fedotov and R. I. Maksimovskaya, *Chem. Abs.*, 1978, **89**, 118422.
[152] F. Corigliano and S. di Pasquale, *J. Chem. Soc., Dalton Trans.*, 1978, 1329.

a small ionic-strength dependence. Between pH 4.0 and 6.3 the rate is approximately constant, but there is a sharp increase in rate with increasing $[H^+]$ below pH 4, and a decrease in rate above pH 6.3. The depolymerization and ^{18}O exchange with this ion in slightly basic media are believed to proceed through a common intermediate in which there is a one-ended dissociation of a V_4 group. The activation parameters for this process are $\Delta V^* = 5.0 \pm 2.0$ cm^3 mol^{-1}, $\Delta H^* = 21$ kcal mol^{-1}, and $\Delta S^* = -7$ cal K^{-1} mol^{-1}. A $[^{49}VO_4]^{3-}$ transfer experiment confirms the proposed mechanism.[150] Protonation of $[V_{10}O_{28}]^{6-}$ ion decreases the decomposition rate, whereas deprotonation gives $[HV_{10}O_{29}]^{7-}$ ion with an increased decomposition rate.[152]

Oxygen-17 n.m.r. has been used in studies of the rates of $^{17}O/^{16}O$ exchange between $H_2{}^{17}O$ and the molybdophosphovanadic hetereopolyanions $[HPMo_{11}VO_{40}]^{3-}$ and $[H_2PMo_{10}VO_{40}]^{3-}$ as well as with $[H_3PMo_{12}O_{40}]$ and $[V_{10}O_{28}]^{6-}$ ion. Exchange is claimed to involve cleavage of monomeric MO_x (M = Mo or V) from the polyanions, and the rate was observed to decrease with an increase in the number of V^V atoms.[151]

Stopped-flow studies of the base hydrolysis of aminocarboxylato-complexes of V^V (as well as Mo^{VI} and W^{VI}) have been reported. The 1 : 1 complexes are involved with $edda^{2-}$, nta^{3-}, and $edta^{4-}$, and a 1 : 2 (V : ligand) complex with ida^{2-}. The observed pseudo-first-order rate constant varies with OH^- according to the equation $k_{obs} = (k_1 + k_2 K_{os}[OH^-]^n)/(1 + K_{os}[OH^-]^n)$ where $n = 2$ for V^V and $n = 1$ for Mo^{VI} and W^{VI}, K_{os} is the outer-sphere formation constant between complex and OH^- ion, and k_1 and k_2 are rate constants for attack by H_2O and OH^- ion respectively.[153] The non-bonded carboxylate arms of the ligands increase values of k_1 and k_2 by factors of 10^2—10^3.

Aquation of $[VO(O_2)_2L]^{n-}$ ions (L = ox^{2-}, bipy, phen, 3,4,7,8-tetramethylphen, picolinate, or isoquinolate) has been studied in $HClO_4/LiClO_4$ solutions at 25 °C and $I = 1.0$ M. The rate of the reaction is inversely dependent on $[H_2O_2]$ for L = ox^{2-}, bipy, or phen, but independent of $[H_2O_2]$ for the rest. The reactions are acid catalysed.[154]

Molybdenum(V) (d^1).—The μ-oxo-complexes $[O\{Mo^VO(XYCNEt_2)_2\}_2]$ (XY = SS, SSe, or SeSe) have been prepared and the kinetics of their disproportionation to $[Mo^{IV}O(XYCNEt_2)_2]$ and $[Mo^{VI}O_2(XYCNEt_2)_2]$ investigated. The rates of disproportionation increase with XY in the order SS < SeS < SeSe, whereas the reverse coupling reactions show the inverse trend.[155]

Disproportionation of the μ-dioxo-dimer $[LMoO\text{-}\mu(O)\text{-}MoOL]^2$ (L = cysteine) is also implicated in the reaction of this species with excess O_2 (Scheme 10).

$$[Mo^V{}_2O_4(L)_2]^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Mo^{IV}O(L)]^{2-} + [Mo^{VI}O(L)]$$

$$k_2 \downarrow O_2, 2H^+$$

$$[Mo^{VI}O(L)(H_2O_2)]$$

Scheme10

[153] K. Zare, J. Lagrange, and P. Lagrange, *Inorg. Chem.*, 1979, **18**, 568.
[154] U. Quilitzsch and K. Wieghardt, *Inorg. Chem.*, 1979, **18**, 869.
[155] T. Matsuda, K. Tanaka, and T. Tanaka, *Inorg. Chem.*, 1979, **18**, 454.

At least one phosphate is bound to the Mo^{V} dimer, and the rate law is Rate = $k_1k_2[O_2][\text{dimer}]/(k_{-1}[Mo^{VI}OL]+k_2[O_2])$ with $10^3k_1 = 1.5 \pm 0.2\ s^{-1}$ and $k_{-1}/k_2 = 0.9 \pm 0.2$ at 25 °C. In the case where $[Mo_2O_4(L)_2] \gg [O_2]$ a first-order reaction is observed and an oxygen adduct $[Mo^{V}{}_2O_4(L)_2,O_2]$ is implicated.[156]

Reaction of $[Mo_2O_4(L)_2]^{n-}$ ions (L = cysteine, histidine, citric acid, $[HP_2O_{10}]^{4-}$, H_2O, or $edta^{4-}$) with cyanide ion in aqueous solution gives $[MoO_4]^{2-}$ and $[Mo^{IV}O(OH)(CN)_4]^{3-}$ ions with a rate law of the form Rate = $k[Mo_2O_4L_2{}^{n-}][OH^-]$.[157] When L = edta or cysteine, at 25 °C $k = 0.02$ and 77 $M^{-1}\ s^{-1}$ respectively, and for the other systems studied $k = ca.\ 150\ M^{-1}\ s^{-1}$.

Oxidation of $[Mo(NCS)_6]^{3-}$ ion with $[IrCl_6]^{2-}$ gives $[Mo^{IV}(NCS)_6]^{2-}$ as an intermediate which rapidly aquates and disproportionates to Mo^{V} and the original $[Mo(NCS)_6]^{3-}$ ion. One step in the aquation reaction (loss of NCS^-) was identified by the stopped-flow technique prior to the disproportionation process.[158].

Tungsten(V) (d^1).—Binding of O_2 is involved in the demetalation of W^{V} porphyrins (Scheme 11); Rate = $k_2K[W^{V}O(OH_2)L]^2[O_2]$ (L = tetraphenylporphinate).

$$[LW^{V}O(OH_2)]^{3+} + O_2 \underset{\text{rapid}}{\overset{K}{\rightleftharpoons}} [LW^{V}(O)(O_2)] + H_2O$$

$$[LW^{V}(O)(O_2)] + [LW^{V}O(OH_2)]^{3+} + H_2O \underset{\text{slow}}{\overset{k}{\rightleftharpoons}} 2[LW^{VI}O(OH)]^{3+} + H_2O_2$$

$$2[LW^{VI}O(OH)]^{3+} \xrightarrow[\text{rapid}]{H^+} 2[LW^{VI}(O)(OH_2)]^{4+}$$

$$2[LW^{V}O(OH_2)]^{3+} + H_2O_2 \longrightarrow 2[LW^{VI}O(OH_2)]^{4+} + 2OH^- + 2L$$

$$[LW^{VI}O(OH_2)] + H_2O \xrightarrow{\text{rapid}} H_4L^{2-} + [H_3W_6O_{21}]^{3-}$$

Scheme 11

At pH < 2, the rate law changes, the order with respect to $[W^{V}O(OH_2)L]$ becoming inexplicably −1.[159]

5 Oxidation State VI

Chromium(VI) (d^0).—A further study of the formation and decay of peroxochromic acid, $[CrO_5(OH_2)]$ has appeared.[160] The authors appear to have neglected the first extensive study of the formation reaction,[161] whilst acknowledging a subsequent study aimed at resolving the two possible mechanisms that were first postulated.[162] The equilibrium constant for the formation process is estimated at $I = 3.0$ M and 25 °C:

$$[HCrO_4]^- + H^+ + 2H_2O_2 \rightleftharpoons [Cr(O)(O_2)_2(OH_2)] + 2H_2O$$

156 T. M. Tam and J. H. Swinehart, *Inorg. Chem.*, 1979, **18**, 975.
157 P. R. Robinson and C. R. Landis, *Inorg. Chim. Acta*, 1979, **33**, 63.
158 A. B. Soares, R. S. Taylor, and A. G. Sykes, *Inorg. Chem.*, 1978, **17**, 496.
159 E. B. Fleischer, R. D. Chapman, and M. Krishnamurthy, *Inorg. Chem.*, 1979, **18**, 2156.
160 S. Funahashi, F. Uchida, and M. Tanaka, *Inorg. Chem.*, 1978, **17**, 2784.
161 P. Moore, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, 1966, **5**, 466.
162 M. Orhanović and R. G. Wilkins, *J. Am. Chem. Soc.*, 1967, **89**, 278.

$K_f = [CrO_5(OH_2)]/[HCrO_4^-][H^+][H_2O_2]^2 = (2.0 \pm 0.2) \times 10^7\ M^{-3}$, $\Delta H^\circ = -13.9$ kcal mol^{-1}, and $\Delta S^\circ = 37$ cal K^{-1} mol^{-1}. Protonation of $[HCrO_4]^-$ ion occurs with $K_a^{-1} = [H_2CrO_4]/[H^+][HCrO_4^-] = 0.16 \pm 0.02\ M^{-1}$, $\Delta H^\circ = 0$ kcal mol^{-1}, and $\Delta S^\circ = -3.6$ cal K^{-1} mol^{-1}, and the rate of formation of $[CrO_5(OH_2)]$ and its conjugate acid $[Cr(OH)(O_2)_2(OH_2)]^+$ ($K_a^{-1} = 0.15 \pm 0.02\ M^{-1}$) is given by: Rate $= k_1[H_2CrO_4][H_2O_2] - k_{-1}[CrO_5OH_2][H_2O_2]$. At 25 °C, $10^{-4}k_1 = 9.3 \pm 0.2$ M^{-1} s^{-1}, $\Delta H^*(k_1) = 19$ kcal mol^{-1}, and $\Delta S^*(k_1) = 22.5$ cal K^{-1} mol^{-1} and $10^4 k_{-1} = 6.1 \pm 0.2$ M^{-1} s^{-1}, $\Delta H^*(k_{-1}) = 19$ kcal mol^{-1}, and $\Delta S^*(k_{-1}) = 8.6$ cal K^{-1} mol^{-1}. Decomposition of the $[CrO_5(OH_2)]$ and its conjugate acid gives Cr^{III} and O_2 with an overall stoicheiometry:

$$2[HCrO_4]^- + 8H^+ + 3H_2O_2 \longrightarrow 2Cr^{3+} + 3O_2 + 8H_2O$$

The rate law for this process is given by Rate $= k_2[CrO_5(OH_2)][H^+] + k_3[Cr(O_2)_2(OH)(OH_2)^+][H^+]$, with $k_2 = 0.25 \pm 0.02$ M^{-1} s^{-1}, $\Delta H^*(k_2) = 19.3$ kcal mol^{-1}, and $\Delta S^*(k_2) = 4.1$ cal K^{-1} mol^{-1} and $k_3 = 1.8 \pm 0.3$ M^{-1} s^{-1}, $\Delta H^*(k_3) = 17.4$ kcal mol^{-1}, and $\Delta S^*(k_3) = 1.4$ cal K^{-1} mol^{-1} at 25 °C.[160] It has been suggested that CrO_5 contains Cr^{III} and should be reformulated as $[Cr_2(Cr_2O_{10})_3]$[163]

Tungsten(VI) (d^0).—Reference to a study also appears in the V^V section.[161] Base hydrolysis of $[PW_{12}O_{40}]^{3-}$, $[BW_{12}O_{40}]^{5-}$, and $[H_2W_{12}O_{40}]^{6-}$ ions has also been investigated at $I = 1.0$ M [MCl] (M = Li, Na, or K) and 25 °C. The rates depend on the choice of counter-cation, owing to ion-pairing with these highly charged anions.[164]

Studies of ^{18}O exchange between tetrahedral $[WO_4]^{2-}$ and $[MoO_4]^{2-}$ ions and $H_2{}^{18}O$ are reported elsewhere.[165]

[163] D. R. Singh and O. P. Kulshrestha, *Chem. Abs.*, 1979, **90**, 96713.
[164] D. L. Kepert, and J. H. Kyle, *J. Chem. Soc., Dalton Trans.*, 1978, 1781.
[165] H. von Felten, B. Wernli, H. Gamsjäger, and P. Baertschi, *J. Chem. Soc., Dalton Trans.*, 1978, 496.

6

Octahedral Substitution: Base Hydrolysis

BY P. MOORE

This chapter continues to be dominated by studies on cobalt(III) complexes, which are reported in the first section. A section on other oxidation state III studies is then followed by a consideration of other oxidation states.

1 Cobalt(III) Studies

Further support for the conjugate-base mechanism comes from a comparison of calculated and observed values of ΔV^*. The experimental results agree fairly closely with those calculated from the simple equation $\Delta V^* = 117.5 - \bar{V}[Co(NH_3)_5X^{2+}]$ which is derived by making reasonable assumptions regarding the volume changes involved in the cb mechanism. The reactivity of the conjugate base is attributed to large volume increase on passing to the dissociative transition stage.[1]

Studies of hydrogen–deuterium exchange in the complexes *mer*-$[Co(gly)_3]$, $[Co(mal)_2(L)]^{n-}$ [L = en, *N*-Me-en, gly, sarcosine, or $(NH_3)_2$], $[Co(en)_2(L)]^{2+}$ (L = gly, L-alanine, or phenylglycine), and *trans*-*N*-$[Co(ox)(gly)_2]^-$ were considered in Chapter 5 (refs. 78, 79, and 81).

Base hydrolyses of $[Co(NH_3)_5X]^{n+}$ ions (X = Cl^-, Br^-, NO_3^-, or DMSO) have been studied in the presence of N_3^- ion and the product ratios $[Co(NH_3)_5N_3]^{2+}/[Co(NH_2)_5(OH_2)]^{3+}$ determined at three temperatures. An interchange mechanism, I_d, is postulated for the reactive conjugate base (Scheme 1). The

$$[Co(NH_3)_5X]^{n+} + OH^- \overset{K}{\rightleftharpoons} [Co(NH_3)_4(NH_2)X]^{(n-1)+} + H_2O \quad (1)$$

$$[Co(NH_3)_4(NH_2)X]^{(n-1)+} + N_3^- \xrightarrow{k_{N_3}} [Co(NH_3)_4(NH_2)N_3]^+ + X^{m-} \quad (2)$$

$$[Co(NH_3)_4(NH_2)X]^{(n-1)+} + H_2O \xrightarrow{k_w} [Co(NH_3)_5(OH)]^{2+} + X^{m-} \quad (3)$$

$$[Co(NH_3)_4(NH_2)N_3]^+ + H_2O \xrightarrow{\text{rapid}} [Co(NH_3)_5N_3]^{2+} + OH^- \quad (4)$$

Scheme 1

product ratio is then identified as $[Co(NH_3)_5N_3^{2+}]/[Co(NH_3)_5(OH_2)^{3+}] = k_{N_3}[N_3^-]/k_w$. This mechanism differs from the usual S_N1cb mechanism, since it does not require a common five-co-ordinate intermediate, $[Co(NH_3)_4(NH_2)]^{2+}$, to be generated for all leaving groups, X. Since the product ratios are not very

[1] S. Balt, *Inorg. Chem.*, 1979, **18**, 333.

temperature sensitive, an I_d mechanism rather than I_a is favoured for reactions (2) and (3).[2]

For the base hydrolysis of $[Co(NH_3)_5X]^{2+}$ ions (X = *o*-, *m*-, or *p*-$MeOC_6H_4$-CO_2^-) the activation parameters are reported to be $\Delta H^{\ddagger}$/kcal mol^{-1} = 24.2 ± 0.6, 30.3 ± 0.7, and 33.7 ± 2.2, and $\Delta S^{\ddagger}$/cal K^{-1} mol^{-1} = 8.4 ± 0.2, 26.6 ± 2.2, and 38.0 ± 0.7 respectively.[3]

Studies of the base hydrolysis of $[Co(NH_3)_4(ox)]^+$ ion in 0.2—0.4 M $[OH^-]$ show that below 60 °C $k_{obs} = k_0 + k_2[OH^-]^2$, whereas above 60 °C $k_{obs} = k_0 + k_1[OH^-]$. By analogy with other carboxylato-complexes, the rate constant k_1 is associated with Co—O bond fission and k_2 with C—O bond fission.[4] The relevant activation parameters are $\Delta H_1^{\ddagger} = 26.5$ kcal mol^{-1}, $\Delta S_1^{\ddagger} = 5.9$ cal K^{-1} mol^{-1}, $\Delta H_2^{\ddagger} = 15.5$ kcal mol^{-1}, and $\Delta S_2^{\ddagger} = -25$ cal K^{-1} mol^{-1} from studies between 40 and 70 °C.

Studies of the hydrolysis of $[Co(NO_2)_4(LL)]^-$ ions (LL = en or tmd) between pH 9.5 and 12.2 show that $[Co(NO_2)_3(OH)(LL)]^-$ ions are the products, and the reactions are believed to proceed *via* a *D*-mechanism (rather than S_N1cb) involving the five-co-ordinate intermediate $[Co(NO_2)_3(LL)]$:[5]

$$[Co(NO_2)_4(LL)]^- \rightleftharpoons [Co(NO_2)_3(LL)] + NO_2^-$$

$$[Co(NO_2)_3(LL)] + H_2O \rightleftharpoons [Co(NO_2)_3(LL)(OH_2)]$$

$$[Co(NO_2)_3(LL)(OH_2)] + OH^- \overset{\text{rapid}}{\rightleftharpoons} [Co(NO_2)_3(LL)(OH)]^- + H_2O$$

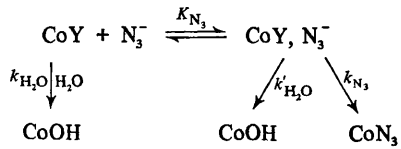
For LL = en, $\Delta H^{\ddagger} = 27.2 \pm 0.7$ kcal mol^{-1} and $\Delta S^{\ddagger} = +15.9 \pm 2.0$ cal K^{-1} mol^{-1}, and when LL = tmd $\Delta H^{\ddagger} = 26.0 \pm 0.4$ kcal mol^{-1} and $\Delta S^{\ddagger} = +14.9 \pm 1.2$ cal K^{-1} mol^{-1}. The acid hydrolysis reactions were also studied (Chapter 5, ref. 56).

Acid and base hydrolyses of *cis*-$[Co(tmd)_2(RNH_2)Cl]^{2+}$ ions (R = H, Me, Et, Pr^n, Bu^n, Bu^i, or $PhCH_2$) proceed at *ca.* 10^2 times the rate for the corresponding *cis*-$[Co(en)_2(RNH_2)Cl]^{2+}$ ions owing to a reduction in E_a by *ca.* 2.4 kcal mol^{-1}. The ability of tmd molecules to twist more readily than en molecules in the trigonal-bipyramidal five co-ordinate transition state is invoked to account for this rate difference. The acid hydrolysis reactions are considered in Chapter 5 (ref. 48).[6]

The S_N1cb mechanism does not fit the data obtained for the base hydrolysis of (+)-*cis*-$[Co(en)_2(NH_3)(X)]^{n+}$ ions (X = Br^-, DMSO, or TMP).[7] At 25 °C and I = 1.0 M, $10^{-2}k_{OH} = 2.35$ and 2.5 M^{-1} s^{-1} for X = DMSO and TMP respectively, and when S = DMSO it was established that 100% Co—O bond fission is involved. The ratio of *cis*/*trans*-$[Co(en)_2(NH_3)(OH)]^{2+}$ products is constant (77% *trans* : 23% *cis*) for all three leaving groups, X, but optical retention in this *cis*-product varies with X (78, 83.5, and 85% retention for X = Br, DMSO, and TMP respectively). In the presence of azide ion, the relative amounts of *cis*- and *trans*-$[Co(en)_2(NH_3)N_3]^{2+}$ ion formed are independent of the concentration of N_3^- ion used (66% *cis*, 34% *trans*), but retention in the *cis*-azido-product

[2] W. L. Reynolds and S. Hafezi, *Inorg. Chem.*, 1978, **17**, 1819.
[3] N. K. Mohanty and R. K. Nanda, *Indian J. Chem.*, 1978, **55**, 1008.
[4] L. S. Bark, M. B. Davies, and M. C. Powell, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1661.
[5] Y. Ito and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 1083.
[6] B. M. Oulaghan and D. A. House, *Inorg. Chem.*, 1978, **17**, 2197.
[7] D. A. Buckingham, C. R. Clark, and T. W. Lewis, *Inorg. Chem.*, 1979, **18**, 1985.

again varies with X (73.5, 83, and 85% for X = Br^-, DMSO, and TMP). Marginally more azido-products are formed (*ca.* 3%) when X = Br^- than when X = DMSO or TMP. An ion-pair scheme (Scheme 2) is proposed in which CoY

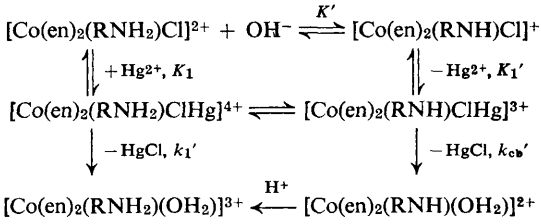


Scheme 2

represents various species of general formula $[Co(en)_2(NH_3)Y]^{n+}$. With this scheme, the product ratio, $R = k_{N_3}K_{N_3}/(k_{H_2O} + k'_{H_2O}K_{N_3}[N_3^-])$, and water rather than OH^- ion is involved in the rate-determining step.[7] Scheme 2 is similar to Scheme 1 with ion-pair formation preceding conjugate-base formation. The importance of ion-pairs is also stressed for the base hydrolysis of (+)-*cis*-$[Co(en)_2X(gly)]^+$ ions (X = Cl or Br).[8]

Rate data at 25 °C for the two successive steps in the base hydrolysis of *trans*-$[Co(en)_2(NCS)_2]^+$ ions are reported to be $10^3k_1 = 3.27\ M^{-1}\ s^{-1}$ ($\Delta H_1^{\ddagger} = 35.7 \pm 0.9$ kcal mol^{-1}, $\Delta S_1^{\ddagger} = 50.0 \pm 3.7$ cal $K^{-1}\ mol^{-1}$) and $10^3k_2 = 0.48 \pm 0.17\ M^{-1}\ s^{-1}$ ($\Delta H_2^{\ddagger} = 36.5 \pm 2.4$ kcal mol^{-1}, $\Delta S_2^{\ddagger} = 48.9 \pm 8.2$ cal $K^{-1}\ mol^{-1}$). The equilibrium constant for the second step involving $[Co(en)_2(NCS)(OH)]^+$ ion was estimated to be 1.98×10^{-2} with $\Delta H^\circ = 12.8 \pm 1.1$ kcal mol^{-1} and $\Delta S^\circ = 35.3 \pm 4.3$ cal $K^{-1}\ mol^{-1}$.[9]

Base hydrolysis of *cis*-$[Co(en)_2(RNH_2)Cl]^{2+}$ ions (R = Ph or *m*- or *p*-MeC_6H_4) has been studied in the presence of Hg^{2+} ions, and Scheme 3 is proposed;



Scheme 3

Rate = $k_2[Hg^{II}][Co(en)_2(RNH_2Cl)^{2+}]$, where $k_2 = k_1'K_1 + k_{cb}'K_1'K'[OH^-]$. Electrophilic catalysis by Hg^{2+} is more effective under basic conditions than under acidic conditions.[10] The results are shown in Table 1.

Table 1 *Rate data associated with Scheme* 3 *at* 25 °C (*data from ref.* 10)

R	$10^2k_1'K_1$/ $M^{-1}\ s^{-1}$	$10^{-10}k_{cb}'K_1'K'$/ $M^{-2}\ s^{-1}$	$10^6k_1/s^{-1}$	$10^{-6}k_{cb}K$/ $M^{-1}\ s^{-1}$
Ph	8.39	1.79	7.01	1.15
p-MeC_6H_4	9.15	5.78	6.97	1.96
m-MeC_6H_4	10.02	4.17	6.43	1.12

[8] C. J. Boreham, D. A. Buckingham and C. R. Clark, *Inorg. Chem.*, 1979, **18**, 1990.
[9] J. Zsakó, S. Jitian, Cs. Várhelyi, and M. Lungu, *Rev. Roum. Chim.*, 1979, **24**, 257.
[10] P. D. Ford and K. B. Nolan, *Inorg. Chim. Acta*, 1979, **35**, L377.

A comparison of the rates of aquation, Hg^{II}-assisted aquation, and base hydrolysis of *trans*-$[Co(en)_2Cl(RCH_2CO_2)]^+$ ions (R = H, Cl, Br, I, CN, or NH_2/NH_3^+) is shown in Table 6 of Chapter 5.[11] Electronegative substituents (R) enhance the acidity of the amine (en) protons, which increases the base hydrolysis rates. The products of base hydrolysis are $71 \pm 5\%$ *trans*- and $29 \pm 5\%$ *cis*-$[Co(en)_2(H_2O)(RCH_2CO_2)]^{2+}$. For *trans*-$[Co(en)_2Cl(RCO_2)]^+$ ions studied between pH 9.0 and 9.8, the second-order rate constants for loss of Cl^- ion are 40, 9.5, and 3.8 $M^{-1}\,s^{-1}$ and the *trans* : *cis* product ratios are 50 : 50, 58 : 42, and 66 : 34 for R = H, Et, and Bu^t respectively.[12] The rates and stereochemistry are sensitive to the nature of the *trans*-substituents, steric hindrance favouring the *trans*-product.

At 25 °C, the second-order rate constant for the base hydrolysis of *cis*-$[Co(en)_2(NH_2R)Br]^{2+}$ ions ($I = 0.1$ M $NaClO_4$) is 82 $M^{-1}\,s^{-1}$ for a range of groups R (R = Me, Et, Pr, Bu, cyclopentyl, or cyclohexyl). However, when R = cyclopropyl or 2,2-dimethoxyethyl, the rate increases owing to steric acceleration in the ionization step of the S_N1cb mechanism. Also, with RNH_2 replaced by α- or ω-amino-alkanols, specific hydrogen-bonding leads to an increase in the rate of base hydrolysis.[13] For *cis*-$[Co(en)_2(HL)Cl]^{2+}$ ion (HL = imidazole) between pH 8.20 and 9.74, at 25 °C and $I = 0.1$ M, $k_{OH} = 29 \pm 3$ $M^{-1}\,s^{-1}$, $\Delta H^* = 22$ kcal mol^{-1}, and $\Delta S^* = 21$ cal $K^{-1}\,mol^{-1}$. The pK_a of the co-ordinated imidazole is 10.5, and above pH 9.9 $[Co(en)_2(L)Cl]^+$ ion is involved in the base hydrolysis. At very high pH, evidence for deprotonated en was also found.[14] Similar studies of *cis*-$[Co(en)_2(HL)Cl]^{2+}$ ion (HL = benzimidazole) show that the predominant species between pH 9.2 and 9.9 is the $[Co(en)_2(L)Cl]^+$ ion.[15].

Studies of *cis*-$[Co(en)_2(HL)Br]^{2+}$ ion (HL = 2-aminothiazole) in acetate buffers reveal a pseudo-first-order rate constant, k_{obs}, for loss of Br^- ion of the form: $k_{obs} = k_1 + k_2K/[H^+] + k_3'[OAc^-]$. K is the equilibrium constant for *cis*-$[Co(en)_2(L)Br]^+$ formation (involving loss of an NH_2 proton) and k_1 and k_2 are the rate constants for loss of Br^- from *cis*-$[Co(en)_2(HL)Br]^{2+}$ and its conjugate base respectively.[16] At 45 °C the rate constants were found to be $10^4k_1 = 2.95 \pm 0.04$ s^{-1}, $10^9k_2K = 5.18 \pm 0.5$ M s^{-1}, and $10^4k_3' = 4.75 \pm 0.25$ $M^{-1}\,s^{-1}$.

Three isomers of $[Co(cyclam)Cl_2]^+$ ion, having *N*-configurations *trans-RSSR*, *trans-RRRR*(*SSSS*), and *cis-RRRR*(*SSSS*), have been investigated in anucleophilic buffers between pH 6 and 8, with $I = 0.05$ M ($NaNO_3$). The structure of the new *transRRRR*(*SSSS*)-isomer is shown in Chapter 5 (p. 176). At 25 °C, the rate data are $10^{-4}k_{OH}/M^{-1}\,s^{-1} = 6.5$, 15.7, and 230, ΔH^*/kcal $mol^{-1} = 10.7$, 11.3, and 9.3, and ΔS^*/cal $K^{-1}\,mol^{-1} = 0$, +2, and +2 for the three respective isomers. Although the *trans-RRRR*(*SSSS*) isomer aquates 10^3 times more rapidly than the *trans-RSSR* form, the base hydrolysis is only about twice as fast at 25 °C. If we represent the conjugate-base mechanism by Scheme 4

[11] K. B. Nolan and A. A. Soudi, *J. Chem. Res.* (*S*), 1979, 130.
[12] P. D. Ford and K. B. Nolan, *J. Chem. Res.* (*S*), 1979, 220.
[13] R. W. Hay and D. P. Piplani, *J. Chem. Soc., Dalton Trans.*, 1978, 556.
[14] R. W. Hay, M. Jajik, and P. R. Norman, *J. Chem. Soc., Dalton Trans.*, 1979, 636.
[15] A. C. Dash and S. K. Mohapatra, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1596.
[16] A. C. Dash and S. K. Mohapatra, *Indian J. Chem., Sect. A*, 1977, **15**, 871.

$$\text{RNHCl} + \text{OH}^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{RNCl} + \text{H}_2\text{O}$$

$$\text{RNCl} \xrightarrow{k_2} \text{RN}^+ + \text{Cl}^- \xrightarrow[+\text{H}_2\text{O}]{\text{rapid}} \text{RNOH} + \text{Cl}^-$$

Scheme 4

[RNH=Co(cyclam)Cl], then $k_{OH}=k_1k_2/(k_{-1}+k_2)$. The *trans-RSSR* isomer was shown previously to be the first case, where k_{-1} and k_2 are comparable in magnitude, and curvature in the Eyring plots below 20 °C confirms this behaviour.[17] The results of studies of H/D exchange which are now underway should help to establish a firm mechanistic picture.

Rate data are reported for the loss of an 'in-plane' NH_3 molecule from base hydrolysis of $[Co(tren)(NH_3)_2]^{3+}$ (A) and two isomers of $[Co(Metren)(NH_3)_2]^{2+}$ [Metren=$MeNHCH_2CH_2N(CH_2CH_2NH_2)_2$] having the structures shown in Chapter 5 [(B)=(8) and (C)=(6) with X=NH_3]. The following mechanism is proposed which is analogous to Scheme 2:

$$\text{Complex} + \text{OH}^- \overset{K_{ip}}{\rightleftharpoons} \text{Complex,OH}^- \overset{K}{\rightleftharpoons} (\text{Conjugate base}) \xrightarrow{k} \text{products}$$

With this scheme, $k_{obs}=kKK_{ip}[OH^-]/\{1+K_{ip}[OH^-](1+K)\}$. Plots of k_{obs} *versus* $[OH^-]$ are curved, and for (C) complete formation of the conjugate base is involved at high $[OH^-]$ and the limiting value of k_{obs} is equal to k. However, for (A) and (B) the amine protons are not sufficiently acidic, so that complete conjugate-base formation is not involved and the limiting values of k_{obs} at high $[OH^-]$ are equated to kK in the above scheme. At 25 °C, the limiting rate constants at high $[OH^-]$ are 42, 0.65, and 0.018 s^{-1} for (A), (B), and (C) respectively.[18] The analogous $[Co(Metren)(NH_3)X]^{2+}$ ions (X=Cl, Br, or N_3) have also been investigated (Chapter 5, ref. 58).

Base hydrolysis of $[Co(tren)(CO_3)]^+$ ion is a slow process, with 10^3k_{OH}= 3.6 M^{-1} s^{-1}, $\Delta H^{\ddagger}=17.2\pm1.9$ kcal mol^{-1}, and $\Delta S^{\ddagger}=-12\pm6$ cal K^{-1} mol^{-1}. $[Co(tren)(OH)(OCO_2)]^+$ ion is the first-formed product which loses CO_2 very slowly under basic conditions ($10^6k_{OH}=8.2$ M^{-1} s^{-1}, $\Delta H^{\ddagger}=24.7\pm1.2$ kcal mol^{-1}, $\Delta S^{\ddagger}=1.0\pm4.0$ cal K^{-1} mol^{-1}), but upon acidification the usual rapid loss of CO_2 occurs from the immediately formed $[Co(tren)(OH_2)(HCO_2)]^{2+}$ ion: $k=1.19$ s^{-1}, $\Delta H^{\ddagger}=14.3\pm0.4$ kcal mol^{-1}, and $\Delta S^{\ddagger}=-10.2\pm1.2$ cal K^{-1} mol^{-1}. Co—O bond fission is involved in the rate-determining steps of the base hydrolyses.[19]

Studies of base hydrolyses in liquid ammonia and ethane-1,2-diamine have appeared.[20-22] The ammoniation of *cis*- and *trans*-$[Co(en)_2Cl_2]^+$ gives $[Co(en)_2(NH_3)_2]^{3+}$ as described in Chapter 5 (ref. 55). In liquid ammonia the pK_as of the en molecules of the *trans*- and *cis*-dichloro-isomers are 7.84 at 7.71 respectively at 208.2 K. Ammoniation of $[M(en)_2Cl_2]^+$ ions proceeds with retention of con-

[17] J. Lichtig and M. L. Tobe, *Inorg. Chem.*, 1978, **17**, 2442.
[18] D. A. Buckingham, C. R. Clark, and T. W. Lewis, *Inorg. Chem.*, 1979, **18**, 2041.
[19] T. P. Dasgupta and G. M. Harris, *Inorg. Chem.*, 1978, **17**, 3123.
[20] S. Balt, J. Breman, and W. de Kieviet, *J. Inorg. Nucl. Chem.*, 1979, **41**, 331.
[21] S. Balt, M. W. G. de Bolster, and H. J. Gamelkoorn, *Inorg. Chim. Acta*, 1979, **35**, L329.
[22] H. Ogino and J. C. Bailar, *Inorg. Chem.*, 1978, **17**, 1118.

figuration.[22] Base hydrolysis of $[Co(NH_3)_5(NH_2R)]^{3+}$ ions (R = H, Me, Et, Pr^n, or Pr^i) in solutions of en have a pseudo-first-order rate constant, $k_{obs} = k_1K_{cb}[(enH)^+ClO_4^-]^{-1}$, where K_{cb} is the conjugate-base formation constant.[21] Values of ΔH^* fall in the range 32—34 kcal mol^{-1}, and ΔS^* in the range 26—36 cal K^{-1} mol^{-1}.

Studies of the base hydrolysis of co-ordinated amino-acid esters were considered in Chapter 5 (refs. 57, 70).

2 Other Oxidation State III Studies

Base hydrolysis of $[Cr(bipy)_3]^{3+}$ ion has been investigated in 1.0 M [NaCl] between pH 6 and 14. *cis*-$[Cr(bipy)_2(OH)_2]^+$ ion is the product, and $k_{obs} = [OH^-]/(B + A[OH^-]) + C[OH^-] + D[OH^-]^2$ (*A*, *B*, *C*, and *D* are constants). An S_N2 mechanism involving attack by H_2O or OH^- ion at the metal centre is proposed, and the term involving $[OH^-]^2$ is accounted for by invoking attack by OH^- ion at the rapidly formed ion-pair, $\{[Cr(bipy)_3]^{3+}, OH^-\}$.[23]

An S_N1cb mechanism is proposed for the base hydrolysis (loss of first Cl^-) of *trans*-$[Ru(L)_4Cl_2]^+$ ions [$(L)_4 = (NH_3)_4$, $(en)_2$, 2,3,2-tet, or cyclam]. The results are collected in Table 2. The reactions proceed with retention of configuration, and the rates increase with increased chelation. The *cis*-$[Ru(en)_2Cl_2]^+$ ion

Table 2 *Rate data at* 25 °C *for the base hydrolysis of* trans-$[Ru(L)_4Cl_2]^+$ *ions (data from ref.* 24)

L_4	$k_{OH}/M^{-1}\ s^{-1}$	ΔH^*/kcal mol^{-1}	ΔS^*/cal K^{-1} mol^{-1}
$(NH_3)_4$	6.1×10^{-3}	23.5	9.5
$(en)_2$	0.60	28.0	35
2,3,2-tet	72	26.0	35
cyclam	110	25.5	35

s much more labile than the *trans*-isomer, the reaction of the *cis*-species being too fast to measure in 10^{-4} M $[OH^-]$ at 0 °C. The *σ-trans*-effect of the amido-groups formed during the conjugate-base mechanism accounts most readily for the observed reactivity trend, with the tendency for trigonal-bipyramidal intermediates excluded in view of the stereoretentive nature of the reactions. The increase in the nephelauxetic effect of cyclam > 2,3,2-tet > en > NH_3 is expected to enhance the *σ-trans*-effect of the deprotonated nitrogen donor atom and hence to enhance the rate of base hydrolysis.[24]

An S_N1cb mechamism is also favoured for the stereoretentive base hydrolysis of *trans*-$[Rh(cyclam)XY]^+$ ions (X, Y = Cl, Br, or I). The results are collected in Table 3. The *trans*-effect of I^- ion is evident, with ΔH^* for loss of Cl^- 6.1 kcal mol^{-1} less with I^- rather than Br^- or Cl^- *trans* to the leaving group. Variations in the values of ΔH^* (rather than k_{OH} at a particular temperature) indicate that Rh^{III} is a class (*b*) or 'soft' metal ion. At 25 °C, the relative rates of base hydrolysis of *trans*-$[M(cyclam)Cl_2]^+$ ions are Co^{III} ($k_{OH} = 6.7 \times 10^4\ M^{-1}\ s^{-1}$, $\Delta H^* = 13.4$ kcal mol^{-1}) $\gg Cr^{III}$ ($k_{OH} = 1.3\ M^{-1}\ s^{-1}$) $\gg Rh^{III}$ ($k_{OH} = 3.8 \times 10^{-8}\ M^{-1}\ s^{-1}$). The

[23] M. A. Jamieson, N. Serpone, and M. Maestri, *Inorg. Chem.*, 1978, **17**, 2432.
[24] C. K. Poon and D. A. Isabirye, *J. Chem. Soc., Dalton Trans.*, 1978, 740.

Table 3 *Rate constants at* 55 °C *and activation parameters for the base hydrolysis of* trans-[Rh(cyclam)XY]$^+$ *ions* (*data from ref.* 25)

X	Y	10^5k_{OH}/M^{-1} s^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
I	I	753±13	33.9±0.1	34.9±0.2
I	Br	256±4	30.8±0.2	23.2±0.4
I	Cl	121±4	29.2±0.3	17.0±0.5
Br	Br	13.8±0.4	35.4±0.2	31.5±0.4
Br	Cl	3.59±0.04	35.3±0.1	28.5±0.2
Cl	Cl	0.750±0.004	35.3±0.2	25.1±0.7

basicity of co-ordinated cyclam is expected to vary with M in the order Cr^{III} > Co^{III} > Rh^{III}, and the low reactivity of the Rh^{III} complexes is attributed partly to the low acidity and partly to the larger crystal-field activation energy.[25]

Rate data for the base hydrolysis of *trans*-[Rh(LL′)Cl_2]$^+$ ions (LL′ = a range of substituted ethane-1,2-diamine molecules) are collected in Table 4. In general, $k_{obs} = k_1 + k_2[OH^-]$ from studies in up to 1 M [OH^-], with $k_2 = 0$ when LL′ = tmeda. This is consistent with the S_N1cb mechanism since there are no acidic protons when LL′ = tmeda.[26]

Table 4 *Rate data for the hydrolysis of* trans-[Rh(LL′)$_2$$Cl_2$]$^+$ *ions in basic media*: $k_{obs} = k_1 + k_2[OH^-]$ (*data from ref.* 26)

LL′	10^5k_1/ s^{-1}[a]	$\Delta H^{\ddagger}_1$/ kcal mol^{-1}	$\Delta S^{\ddagger}_1$ cal K^{-1} mol^{-1}	10^5k_2/ M^{-1} s^{-1}	$\Delta H^{\ddagger}_2$/ kcal mol^{-1}	$\Delta S^{\ddagger}_2$/cal K^{-1} mol^{-1}
en	4.88	27.8±0.4	0.2±1.0	7.26	33.5±0.6	17.0±1.2
$Me_2NCH_2CH_2NH_2$	2.51	28.0±0.5	−0.7±1.2	221	29.5±0.1	12.6±0.2
$Me_2NCH_2CH_2NMe_2$[b]	70.0	25.5±0.2	−1.2±0.2			

[a] 80 °C; some data are also reported for LL′ = $MeNHCH_2CH_2NH_2$, $MeNHCH_2CH_2NHMe$, and $Me_2NCH_2CH_2NHMe$. [b] tmeda.

3 Other Oxidation States

The pseudo-first-order rate constant (k_{obs}) for the base hydrolysis of amino-carboxylato-complexes of V^V, Mo^{VI}, and W^{VI} vary with [OH^-] according to the general equation $k_{obs} = (k_1 + k_2K_0[OH^-]^n)/(1 + K_0[OH^-]^n)$ with $n = 2$ for V^V, and $n = 1$ for Mo^{VI} and W^{VI}, where K_0 is the outer-sphere association constant and k_1 and k_2 are the rate constants for reaction of the rapidly formed ion-pair with H_2O and OH^- ion respectively. Complexes with ida^{2-}, $edda^{2-}$, nta^{3-}, and $edta^{4-}$ ions were investigated, and non-bonded carboxylate arms were found to increase values of k_1 and k_2 by factors of 10^2—10^3. An analytic procedure has been proposed, based on these reactions, which allows concentrations of V^V, Mo^{VI}, and W^{VI} to be estimated to an accuracy of *ca.* 5% at molarities in the region of 10^{-5} M.[27]

[25] H. L. Chung and E. J. Bounsall, *Can. J. Chem.*, 1978, **56**, 709.
[26] M. P. Hancock, B. T. Heaton, and D. H. Vaughan, *J. Chem. Soc., Dalton Trans.*, 1979, 761.
[27] K. Zare, J. Lagrange, and P. Lagrange, *Inorg. Chem.*, 1979, **18**, 568; *Bull. Soc. Chim. Fr., Part I*, 1978, 7.

Several studies of the base hydrolyses of polyanions of V^{V} and W^{VI} have appeared.[28–31] The $[V_{10}O_{28}]^{6-}$ ion was investigated between pH 6 and 12.5. At low pH $[V_{10}O_{28}H]^{5-}$ is formed and at high pH $[V_{10}O_{29}H]^{7-}$, the former species being less reactive and the latter more reactive.[28] For the $[W_6O_{21}H]^{5-}$ ion, stopped-flow studies reveal a rate law of the form: Rate $=(k_{H_2O}+k_{OH}[OH^-])[W_6O_{21}H^{5-}]$. At 25 °C in 2 M [NaCl], $k_{H_2O}=1.6\pm0.6\ s^{-1}$ and $k_{OH}=2022\pm113\ M^{-1}\ s^{-1}$, with $\Delta H^{\ddagger}=6.45\pm0.4$ kcal mol^{-1} and $\Delta S^{\ddagger}=-23.9\pm1.6$ cal K^{-1} mol^{-1}. An S_N2 mechanism is proposed as found for $[Cr_2O_7]^{2-}$, $[Mo_7O_{24}]^{6-}$, and $[V_{10}O_{28}]^{6-}$ ions.[29]

Three stages were detected during the base hydrolysis of $[SiW_{12}O_{40}]^{4-}$ ion. Two intermediates, $[SiW_{11}O_{39}]^{8-}$ and $[SiW_9O_{34}]^{10-}$, were detected and the final products are $[SiO_4]^{2-}$ and $[WO_4]^{2-}$ ions. The reactions were investigated in 1.0 M [MCl] (M = Li, Na, or K) and dependences on the choice of M observed. For the first two stages, $k_{obs}=k_{H_2O}+k_{OH}[OH^-]$, k_{OH} decreasing with M in the order K > Na > Li. The third stage involves the formation of large ion-aggregates and a strong dependence on cation concentration. Comparison of the activation parameters with those for the base hydrolysis of other approximately spherical polyanions shows that $\Delta H^{\ddagger}$ increases as the overall charge on the polyanion increases.[30] Similar studies of $[PW_{12}O_{40}]^{3-}$, $[BW_{12}O_{40}]^{5-}$, and $[H_2W_{12}O_{40}]^{6-}$ ions have appeared.[31]

Base hydrolysis of *trans*-$[Pt(NH_3)_4(OH)(SO_4)]^+$ ion gives *cis*- and *trans*-$[Pt(NH_3)_4(OH)_2]^{2+}$ with $k_{obs}=(a+b/[H^+])/(c+[H^+])$. The mechanism is uncertain at the present time.[32]

[28] F. Corigliano and S. di Pasquale, *J. Chem. Soc., Dalton Trans.*, 1978, 1329.
[29] J. P. Collin, F. Kloos, P. Lagrange, and J. P. Schwing, *Nouv. J. Chim.*, 1979, **2**, 39.
[30] D. L. Kepert and J. H. Kyle, *J. Chem. Soc., Dalton Trans.*, 1978, 137.
[31] D. L. Kepert and J. H. Kyle, *J. Chem. Soc., Dalton Trans.*, 1978, 1781.
[32] R. C. Johnson and C. G. Widmer, *Inorg. Chem.*, 1979, **18**, 2027.

7

Octahedral Complexes: Formation

BY J. BURGESS AND P. MOORE

Kinetics and mechanisms of complex formation form the major subject of an extensive and liberally referenced (836 citations) review of formation and ligand exchange.[1] The effects of pressure on kinetics of complex formation[2] and high-pressure stopped-flow techniques[3] have been reviewed in conference reports. The interpretation of high-pressure laser Raman results relating to ion association and complex formation in the Mg^{2+}–SO_4^{2-} system has been the subject of an exchange of views.[4] Information about ion association in the Eigen–Wilkins mechanism for complex formation is more often obtained from ultrasonic measurements. Recent papers in this area deal with solutions of manganese sulphate,[5] magnesium sulphate, and magnesium chloride.[6] Analogous information has been obtained by precise conductimetric measurements on magnesium sulphate solutions,[7] complex permittivity measurements on solutions of nickel salts,[8] and a newly described coagulation method applied to magnesium and lanthanum sulphate solutions.[9] This last method is based on determining critical coagulation concentrations for negatively charged silver iodide colloids. Effects of ionic strength[10] and of pressure[11] on the pre-association step of complex formation have also been described for a range of metal(II) cations. All of these references are consistent with the Eigen–Wilkins mechanism for formation reactions between labile metal ions and 'normal' ligands.

[1] D. W. Margerum, G. R. Cayley, D. C. Weatherburn, and G. K. Pagenkopf, in 'Coordination Chemistry, Volume 2', ed. A. E. Martell, ACS Monograph No. 174, 1978, pp. 1—220.
[2] H. Kelm and D. A. Palmer, *NATO Adv. Study Inst. Ser., Ser. C.* 1978, **C41**, 281; D. A. Palmer and H. Kelm, *ibid.*, p. 421, 435 (*Chem. Abs.*, 1979, **90**, 61 774, 61 910, 61 776); A. Jost, *Chem. Abs.*, 1979, **90**, 175 297.
[3] K. Heremans, J. Snauwaert, and J. Rijkenberg, *Chem. Abs.*, 1979, **90**, 175 337.
[4] F. H. Fisher, *J. Phys. Chem.*, 1978, **82**, 495; W. A. Adams, A. R. Davis, and R. M. Chatterjee, *ibid.*, p. 496.
[5] M. Akagün, *Acustica*, 1978, **39**, 344 (*Chem. Abs.*, 1978, **89**, 66 282).
[6] Chen-Tung Chen, Lee-Sea Chen, and F. J. Millero, *J. Acoust. Soc. Am.*, 1978, **63**, 1795 (*Chem. Abs.*, 1978, **89**, 118 099).
[7] A. D. Pethybridge and S. S. Taba, *Faraday Discuss. Chem. Soc.*, 1977, No. 64, p. 274.
[8] E. A. S. Cavell and S. Petrucci, *J. Chem. Soc., Faraday Trans. 2*, 1978, **74**, 1019.
[9] N. Kallay and I. Krznaric, *Indian J. Chem., Sect. A*, 1978, **16**, 713 (*Chem. Abs.*, 1979, **90**, 13 035).
[10] K. G. Ashurst and R. D. Hancock, *Natl. Inst. Metall., Rep. S. Afr., Rep.*, 1977, 1914 (*Chem. Abs.*, 1978, **88**, 127 114); K. S. Johnson and R. M. Pythowicz, *Am. J. Sci.*, 1978, **278**, 1428 (*Chem. Abs.*, 1979, **90**, 44 667).
[11] K. Shimizu, N. Tsuchihashi, and Y. Kondo, *Rev. Phys. Chem. Jpn.*, 1977, **47**, 80 (*Chem. Abs.*, 1978, **88**, 111 369).

1 Oxidation State II

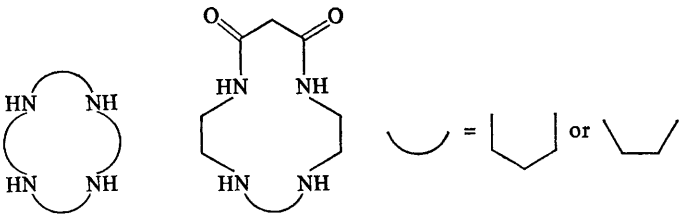
Nickel(II) (d^8).—The mechanism of complex formation for some metal(II) cations is now so well established, at least for simple ligands, that such reactions, particularly of nickel(II), are used to probe solvent and salt effects on kinetic patterns. Many of these studies are therefore dealt with in the Chapter on medium effects (Part II, Chapter 13). They include the reactions of nickel(II)[12] and of magnesium(II)[13] with chloride in aqueous alcohols, of nickel(II) with imidazole in aqueous ethanol,[14] with malonate in fructose–water solutions,[15] with thiocyanate in methanol–DMSO mixtures,[15] and with murexide or pada in various micellar media,[16] and of several metal(II) cations with fluoride in aqueous salt solutions.[17] In general, medium effects on observed rate constants (k_f) for complex formation operate on the pre-association step (K_{os}) rather than on the interchange process (k_i).[18] The Eigen–Wilkins mechanism operates in all these media; it has also been shown to operate for the bidentate ligand Et_2dtc in DMSO,[19] and even at the surface of a mercury electrode.[20]

An example of a straightforward kinetic study of complex formation in aqueous solution is provided by that of nickel(II) with 4,4′-, 5,5′-, and 6,6′-dimethyl-2,2′-bipyridyl.[21] The kinetics of reaction of nickel(II) with acetylacetone, in water and in aqueous methanol, indicate that only the enol form of the ligand reacts.[22] This conclusion may be contrasted with reactions of copper(II), iron(III), and dioxouranium(VI), where both enol and keto forms of acetylacetone are believed to react with the cation. The rate enhancement compared with normal ligands observed in the reaction of nickel(II) with 2-picolylmethylamine has been assigned to the operation of an internal conjugate base mechanism. It is noteworthy that the monoprotonated form of the ligand reacts with nickel(II) at the normal rate.[23] Ultrasonic studies of the kinetic patterns for reactions of nickel(II) with amino-acids reveal relaxation frequencies that are not readily attributable to one or

[12] S. V. Gorbachev, E. G. Timofeeva, and G. I. Tisenko, *Russ. J. Phys. Chem.*, 1978, **52**, 663.
[13] V. Abaraviciute, B. Kuksas, and R. Savickas, *Akust. Zh.*, 1978, **24**, 801 (*Chem. Abs.*, 1979, **90**, 62 070).
[14] V. A. Shormanov, Yu. S. Koryagin, and G. A. Krestov, *Koord. Khim.*, 1979, **5**, 251 (*Chem. Abs.* 1979, **90**, 175 480); see also *Chem. Abs.*, 1979, **90**, 44 425.
[15] M. Delsignore, D. Saar, and S. Petrucci, *Adv. Mol. Relaxn. Interact. Processes*, 1978, **13**, 13, 249 (*Chem. Abs.*, 1979, **90**, 12 896).
[16] T. Okubo and N. Ise, *Polym. Bull. (Berlin)*, 1978, **1**, 109 (*Chem. Abs.*, 1979, **90**, 44 419); J. Holzwarth, W. Knoche, and B. H. Robinson, *Ber. Bunsenges. Phys. Chem.*, 1978, **82**, 1001; B. H. Robinson, A. D. James, and D. C. Steytler, *Chem. Abs.*, 1979, **90**, 44 460; *J. Chem. Soc., Faraday Trans. 1*, 1978, **74**, 2625; M. Fischer, W. Knoche, B. H. Robinson, and J. H. M. Wedderburn, *ibid.*, 1979, **75**, 119; B. H. Robinson, D. C. Steytler, and R. D. Tack, *ibid.*, p. 481.
[17] V. V. Blokhin, L. A. Kul'vinova, Yu. A. Makashev, V. E. Mironov, and V. V Shurukhin, *Chem. Abs.*, 1979, **90**, 77 263.
[18] J. F. Coetzee, *Chem. Abs.*, 1979, **90**, 44 458.
[19] P. J. Nichols and M. W. Grant, *Aust. J. Chem.*, 1978, **31**, 2581.
[20] O. E. Ruvinskii and V. N. Sirko, *Elektrokhimiya*, 1978, **14**, 1043 (*Chem. Abs.*, 1978, **89**, 137 465).
[21] D. Pacheco, A. R. De Romero, J. D. Medina, V. De Santis, and J. L. Calderon, *J. Inorg. Nucl. Chem.*, 1979, **41**, 839.
[22] M. J. Hynes and B. D. O'Regan, *J. Chem. Soc., Dalton Trans.*, 1979, 162; and references therein.
[23] C. D. Hubbard and W. Palaitis, *J. Coord. Chem.*, 1979, **9**, 107.

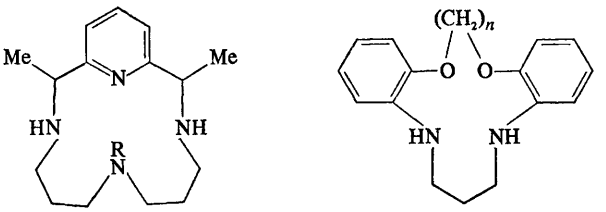
other step in the Eigen–Wilkins mechanism. Values of τ^{-1} of greater than 3×10^7 s^{-1} are too fast for the interchange step (k_1), too slow for the initial pre-association equilibrium. Rather they seem to apply to equilibrium formation and dissociation of intramolecular hydrogen bonds within the amino-acid ligands; these relaxation frequencies depend neither on the concentration of the nickel(II) nor on that of the amino-acid. Rate constants for this hydrogen-bond breaking range from 28×10^7 s^{-1} for glycine down to 3×10^7 s^{-1} for 6-aminohexanoic acid.[24]

A general review of macrocyclic ligands contains some kinetic data, including illustrations of the large effect of ring size variation on rates of formation of nickel(II) complexes with tetra-aza-ligands.[25] Less dramatic changes are, of course, observed when ring size variation is restricted to the six possible combinations of di- and tri-methylene bridges in the group of ligands (1). Kinetic parameters have been reported for formation of the nickel(II), cobalt(II), copper(II), and zinc(II) complexes of these ligands.[26] Ring-size effects are also involved in relative[26] reactivities of the macrocycles (2) with copper(II), though here the



(1) (2)

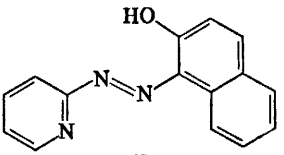
main kinetic interest lies in comparison of the reactivities of these ligands with those of non-dione analogues.[27] The related macrocycles (3; R = H or Me) react somewhat more slowly than most 14-membered tetra-aza-cyclic ligands, presumably because the pyridyl unit introduces a degree of rigidity.[28] Reorganization of the half-co-ordinated ligand is an important feature of the formation kinetics for the reaction of nickel(II) with the macrocycles (4).[29]



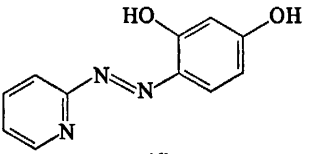
(3) (4) n = 2 or 3

[24] S. Harada, K. Higashi, K. Tamura, M. Hiraishi, and T. Yasunaga, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 2596.
[25] D. H. Busch. *Acc. Chem. Res.*, 1978, **11**, 392.
[26] A. P. Leugger, L. Hertli, and T. A. Kaden, *Helv. Chim. Acta*, 1978, **61**, 2296.
[27] M. Kodama and E. Kimura, *J. Chem. Soc., Dalton Trans.*, 1979, 325.
[28] P. Schultz-Grunow and T. A. Kaden, *Helv. Chim. Acta*, 1978, **61**, 2291.
[29] A. Ekstrom, L. F. Lindoy, H. C. Lip, R. J. Smith, H. J. Goodwin, M. McPartlin, and P. A. Tasker, *J. Chem. Soc., Dalton Trans.*, 1979, 1027.

Cobalt(II) (d^7).—The reaction of cobalt(II) with pan (5) is slightly slower than that with par (6), allegedly owing to the greater bulk of the pan ligand.[30] Several complex formation reactions show complicated kinetic patterns due to parallel redox processes. This is true for the cobalt(II) reactions mentioned above[30]



(5)

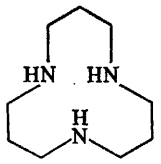


(6)

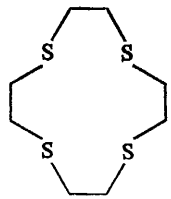
and for reaction of cobalt(II) with pyridine-2-aldoxime.[31] Previous reports on this latter reaction[32] indicated slow substitution at Co^{2+}aq, which is surprising. The present study shows that this slow process is a redox reaction subsequent to fast substitution at the cobalt(II) centre.[31] Reactions of several first-row transition metal 2+ cations with the carbonate radical, CO_3H, are also of course complicated by its strong oxidizing power. However, the respective formation kinetics can be extracted, and conform to the normal mechanism.[33]

The reaction of cobalt(II) with azide and mercaptoacetic acid has been studied.[34] The rate law suggests equilibrium formation of CoN_3^+ followed by slow reaction with mercaptoacetate.

Copper(II) (d^9).—Ring-size effects, studied for tetra-aza-ligands as mentioned above,[25-27] have also been investigated for formation reactions of copper(II) with triazacyclo-nonane, -decane, and -dodecane (7). Here bimolecular rate constants decrease as ring size increases, from 2.4×10^6 M^{-1} s^{-1} for the first-named to 23 M^{-1} s^{-1} for the last.[35] Reactivities of macrocyclic and open-chain analogues have been compared for kinetics of formation of polythiaether complexes of copper(II). The lowest rate is reported for the reaction with the smallest macrocycle, (8), the highest rate with the least-hindered open-chain ligand, $Me_2S(CH_2)_2$-$S(CH_2)_3S(CH_2)_2SMe_2$.[36]



(7)



(8)

[30] K. Mochizuki, T. Imamura, T. Ito, and M. Fujimoto, *Bull. Chem. Soc. Jpn.*. 1978, **51**, 1743.
[31] G. Bazsa, H. G. Shinouda, and M. T. Beck, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1665.
[32] M. W. Blackmore and R. J. Magee, *J. Inorg. Nucl. Chem.*, 1969, **31**, 2859.
[33] V. W. Cope, M. Z. Hoffman, and Schoen-nan Chen, *J. Phys. Chem.*, 1978, **82**, 2665.
[34] R. Abu-Eittah and G. Arafa, *Indian J. Chem., Sect. A*, 1978, **16**, 315.
[35] T. J. Riedo and T. A. Kaden, *Helv. Chim. Acta*, 1979, **62**, 1089.
[36] L. L. Diaddario, L. L. Zimmer, T. E. Jones, L. S. W. L. Sokol, R. B. Cruz, E. L. Yee, L. A. Ochrymowycz, and D. B. Rorabacher, *J. Am. Chem. Soc.*, 1979, **101**, 3511.

Iron(II) (d^6).—Reactions of $[Fe^{II}(CN)_5(OH_2)]^{3-}$ anions with ligands, closely related to solvolysis and ligand replacement reactions dealt with elsewhere in this volume, also come into this category of formation reactions. Reactivity–ligand field correlations have been discussed for reactions with imidazole, glycine, and L-histidine; in these the site of bonding to the iron has been established for the last two named.[37] In reactions with cyanopyridines the incoming ligand bonds to the iron initially through the nitrogen of the pyridine or the nitrogen of the cyanide; isomerization of the less stable isomer to the thermodynamically stable isomer follows. Rates and activation parameters were determined for these reactions. Kinetic parameters have also been reported for the reactions with benzonitrile and with *o*-, *m*-, and *p*-dicyanobenzenes,[38] and for the reaction with 4-aminopyridine.[39]

Ruthenium(II) (d^6).—Reactions of *trans*-$[Ru(NH_3)_4(SO_3)(OH_2)]$ with imidazole and related ligands[40] and of $[Ru(edta)(OH_2)]^{2-}$ with pyrazine and other ligands[41] have been studied. The first of these illustrates yet again the strong *trans*-effect of co-ordinated sulphite. The second reaction exhibits marked catalysis by ruthenium(III).

Zinc(II) (d^{10}).—Ultrasonic studies have provided rate constants for reactions of zinc(II) with glycine ($k_f = 5.9 \times 10^7\ M^{-1}\ s^{-1}$ at 25 °C) and three other amino-acids in aqueous solutions.[42] Reaction of aquozinc(II) with pada is slightly slower, with $k_f = 6.4 \times 10^6\ M^{-1}\ s^{-1}$ at 25 °C.[43] Kinetics of ternary complex formation have been reported for reactions of $[ZnL]^+_{aq}$ ($L = OH^-$, OAc^-, NCS^-, N_3^-, or F^-) with 1,10-phenanthroline.[44]

Cadmium(II) (d^{10}).—Ligand substituent effects have been explored for the reaction of cadmium(II) with a series of tetraphenylporphines, in acetate medium. Rates vary by over 100 times over the series studied; the activation energy for formation of the tetra-*o*-methoxy-derivative is over 9.5 kcal mol^{-1} less than that for the tetra-*o*-chloro-compound.[45]

2 Oxidation State III

Cobalt(III) (d^6).—The volumes of activation for the anation of $[Co(CN)_5(OH_2)]^{2-}$ ion (Chapter 5, Table 1) and for the aquation of $[Co(CN)_5X]^{3-}$ ions (X = anion) are entirely in accord with the extreme *D*-mechanism.[46] High-pressure studies of the anation of $[M(NH_3)_5(OH_2)]^{3+}$ ions (M = Co, Rh, or Cr) gave the ΔV^* values shown in Table 1. These results, together with those for the corresponding aquation reactions enable values for ΔV° to be estimated, and the values obtained

[37] H. E. Toma, J. M. Martins, and E. Giesbrecht, *J. Chem. Soc., Dalton Trans.*, 1978, 1610.
[38] A. P. Szecsy, S. S. Miller, and A. Haim, *Inorg. Chim. Acta*, 1978, **28**, 189.
[39] N. V. Hrepic and J. M. Malin, *Inorg. Chem.*, 1979, **18**, 409.
[40] G. M. Brown, J. E. Sutton, and H. Taube, *J. Am. Chem. Soc.*, 1978, **100**, 2767.
[41] T. Matsubara and C. Creutz, *J. Am. Chem. Soc.*, 1978, **100**, 6255.
[42] S. Harada, Y. Uchida, M. Hiraishi, H. L. Kuo, and T. Yasunaga, *Inorg. Chem.* 1978, **17**, 3371.
[43] B. H. Robinson and N. C. White, *J. Chem. Soc., Faraday Trans. 1*, 1978, **74**, 2625.
[44] S. Yamada, K. Ohsumi, and M. Tanaka, *Inorg. Chem.*, 1978, **17**, 2790.
[45] O. I. Koifman, B. D. Berezin, L. P. Shormanova, and E. M. Kuvshinova, *Koord. Khim.*, 1978, **4**, 1494 (*Chem. Abs.*, 1979, **90**, 29 648).
[46] D. A. Palmer and H. Kelm, *Z. Anorg. Allgem. Chem.*, 1979, **450**, 50.

Table 1 *Volumes of activation for the anation of* $[M(NH_3)_5(OH_2)]_3^+$ *ions by* X^{n-} *ions and the aquation of* $[Co(NH_3)_5X]^{(3-n)+}$ *ions (data from ref.* 47)

M	X^{n-}	I/M	T/°C	$\Delta V_{an}^{\ddagger}$/cm^3 mol^{-1}	$\Delta V_{aq}^{\ddagger}$/cm^3 mol^{-1}
Co^{III}	Cl^-	2.0	60	$+1.4\pm0.8$	-8.2 ± 1.6
	SO_4^{2-}	2.0	60	$+2.3\pm1.8$	-7.9 ± 0.3
Rh^{III}	Cl^-	2.0	60	$+3.0\pm0.7$	-14.5 ± 4.6
Cr^{III}	NCS^-	1.0	50	-4.9 ± 0.6	
	NCS^-	0.3	50	-2.4 ± 1.3	-8.6 ± 1.0 [a]

[a] 80°C.

compare reasonably well with those from equilibrium studies. No evidence for ion-pairing with the incoming anion could be found at the high ionic strengths used (plots of k_{obs} *versus* $[X^{n-}]$ were linear), even for the reaction with sulphate ion. It is estimated that for SO_4^{2-} ion the ion-pair formation constant must be less than 0.33 M^{-1} at $I=2.0$ M. The values of $\Delta V^{\ddagger}$ for the anation reactions are interpreted in terms of an I_d mechanism for Co^{III} and Rh^{III} and an I_a mechanism for Cr^{III}. The result for Rh^{III} contrasts with that obtained for water exchange with $[Rh(NH_3)_5(OH_2)]^{3+}$ ion ($\Delta V^{\ddagger}=-4.1\pm0.4$ cm^3 mol^{-1} at 308.2 K) which was interpreted by Swaddle and Stranks in terms of an I_a mechanism.[47] Sykes and co-workers have also presented evidence for an I_d mechanism for substitution reactions of $[Cr(NH_3)_5(OH_2)]^{3+}$ ion, based on the small variation in anation rates for a range of nucleophiles.[48]

Substitution reactions of $[Co(NH_3)_5S]^{3+}$ ions (S = H_2O or DMSO) with Cl^-, py, and $(EtO)_3PO$[49] and with $[SeO_3]^{2-}$ ion[50] have been reported. The reaction with $[SeO_3]^{2-}$ ion gives linkage isomers, the *Se*-bonded complex being formed when S = DMSO, whereas the *O*-bonded isomer is formed, without Co—O bond cleavage, when S = H_2O.[50] The latter reaction can be regarded as nucleophilic attack by the co-ordinated H_2O at the Se^{IV} centre. A similar study involves the reaction of $[Co(CN)_5(OH_2/OH)]^{2-,3-}$ ions with $[HSeO_3]^-$ ion.[51] From studies between pH 2 and 12 and $I=1.0$ M [$NaClO_4$], at 25 °C, $k_{obs}=k_1[HSeO_3]/(1+k_2'[H^+])$, where $k_1=47.0\pm1.5$ M^{-1} s^{-1} and $10^{-6}k_2'=2.45\pm0.17$ M^{-1}. These reactions can be regarded alternatively as electrophilic attack by Se^{IV} at the co-ordinated oxygen atom. $[Co(NH_3)_5(OCOMe)]^{2+}$ ion can also be formed by electrophilic attack by dicyclohexylcarbodi-imide (RN=C=NR) at $[Co(NH_3)_5(OH_2)]^{3+}$ ion in acetic acid.[52]

Reaction of $[Co(NH_3)_5X]^{n+}$ ions (X = H_2O, NH_3, Cl^-, Br^-, NO_3^-, CO_3^{2-}, NO_2^-, ONO^-, CN^-, or N_3^-) with HF has been investigated.[53] Only when X = NH_3, Cl^-, Br^-, or CN^- is $[Co(NH_3)_5F]^{2+}$ ion not formed. In the presence of HCl, F^- ion is displaced to give $[Co(NH_3)_5Cl]^{2+}$ ion. The *O*-bonded NO_3^-, CO_3^{2-}, and NO_2^- complexes react *via* an aqua-intermediate as expected. $[Co(NH_3)_5N_3]^{2+}$ ion gives $[Co(NH_3)_5(N_3H)]^{3+}$.

[47] R. van Eldik, D. A. Palmer, and H. Kelm, *Inorg. Chem.*, 1979, **18**, 1520.
[48] T. Ramasami and A. G. Sykes, *Inorg. Chem.*, 1976, **15**, 2885.
[49] R. C. Paul, O. D. Sharma, and J. C. Bhatia, *Indian J. Chem., Sect. A*, 1977, **15**, 966.
[50] R. C. Elder and P. E. Ellis, *Inorg. Chem.*, 1978, **17**, 870.
[51] K. R. Ashley and Y. Jan, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1099.
[52] L. M. Jackman, R. M. Scott, and J. F. Dormish, *Inorg. Chem.*, 1979, **18**, 2023.
[53] M. F. A. Dove, *J. Fluorine Chem.*, 1978, **11**, 317.

A comparison of the relative *trans*-effects of *S*-bonded sulphite and sulphinate ions (X) in $[Co(NH_3)_5X]^{n+}$ ions was described in Chapter 5 (ref. 29). Anation by NCS^- ion was studied and a *D*-mechanism established. Data for the anation of *trans*-$[Co(en)_2(SO_3)(OH_2)]^+$ ion are collected in Table 2. These results are inter-

Table 2 *Rates and equilibrium constants at* 25 °C *for the reaction of trans*-$[Co(en)_2(SO_3)(OH_2)]^+$ *ion with anions* X^{n-} *(data from ref.* 54)

X^{n-}	$S_2O_3^{2-}$	NCS^-	NO_2^-	N_3^-	$[Fe(CN)_6]^{3-}$	HN_3	NH_3	imidazole
$10^{-3}k_f$/ $M^{-1}\,s^{-1}$	1.27	0.275	0.206	0.240	1.72	0.014	0.067	0.052
K_{eq}/M^{-1}	180	2500	1000	290		<1.2	3.0	260

preted in terms of an I_d rather than a *D*-mechanism.[54] A second group has studied the anation of *trans*-$[Co(LL)_2(SO_3)(OH)]$ (LL = en or tmd) and the results were interpreted in terms of a *D*-mechanism (Scheme 1). Values of $k_f = k_1k_2/k_{-1}$ and

$$[Co(LL)_2(SO_3)(OH)] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Co(LL)_2(SO_3)]^+ + OH^-$$

$$k_{-2} \Big\uparrow \Big\downarrow k_2 + X^{n-}$$

$$[Co(LL)_2(SO_3)X]^{(1-n)+}$$

Scheme 1

$k_d = k_{-2}$ are collected in Table 3, together with the equilibrium constants from kinetic studies ($K_{kin} = k_f/k_d$) and equilibrium studies (K_{thermo}).[55] A *D*-mechanism is also favoured for the reaction of $[Co(LL)(NO_2)_4]^-$ ions (LL = en or tmd) with NH_3, py, N_3^-, or NCS^- ions involving substitution of one NO_2^- ion.[56] The relative

Table 3 *Rate and equilibrium data for the formation of trans*-$[Co(LL)_2(SO_3)X]^{(3-n)+}$ *ions at* 25 °C *and* $I = 1.0$ M *(data from ref.* 55)

LL = en X^{n-}	$10^2k_f/s^{-1}$	$10^5k_d/s^{-1}$	10^2K_{kin}	10^2K_{thermo}
N_3^-	3.62 ± 0.23	55 600 ± 1600	6.51 ± 0.60	1.61 ± 0.09
NO_2^-	1.34 ± 0.05	8 210 ± 410	16.3 ± 1.4	17.5 ± 0.3
NCS^-	2.53 ± 0.14	4 000 ± 890	63 ± 18	10.6 ± 0.3
CN^-	1.33 ± 0.05	2.41 ± 0.23		55 200 ± 2900
SO_3^{2-}	4.09 ± 0.05	111 000 ± 500	36.8 ± 2.1	36.8
LL = tmd				
N_3^-	45.5 ± 2.0	$(6.75 \pm 0.15) \times 10^5$	6.74 ± 0.45	3.63 ± 0.19
NO_2^-	25.1 ± 0.3	$(8.10 \pm 0.20) \times 10^4$	31.0 ± 1.1	39.0 ± 0.3
NCS^-	28.9 ± 1.2	$(1.00 \pm 0.07) \times 10^5$	28.9 ± 3.2	48.6 ± 0.5
CN^-	44.8 ± 4.4	$(3.6 \pm 1.6) \times 10^2$	12 400 ± 6700	11 200 ± 200
SO_3^{2-}	33.1 ± 2.0	$(1.41 \pm 0.05) \times 10^5$	23.5 ± 2.3	11.5 ± 0.6

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[55] Y. Ito, A. Terada, and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 2898.
[56] Y. Ito and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 2321.

nucleophilicity of ligands towards the five-co-ordinate intermediate $[Co(LL)(NO_2)_3]$ was found to be $OH^- \gg N_3^- > NO_2^- > MeCO_2^- > NCS^- \gg H_2O > Cl^-$, I^-.

Formation of the mono- and di-chloro-complexes of $[Co(en)(OH_2)_4]^{3+}$ ion (pK_a *ca.* 3.7) has been investigated.[57] The stability constants are $K_1 = 16 \pm 3$ at pH 1 and $I = 0.3$—0.5 M, and $K_2 = 1.2 \pm 0.3$ at pH 0.5 and $I = 1.4$ M. Formation of the monochloro-complex is rate determining, with $k_{obs} = k[Cl^-][H^+]^{-1}$. At 25 °C, $I = 1.0$ M $[Cl^-]$, and $[H^+] = 0.4$ M, $10^5 k_{obs} = 7.88$ s^{-1}, $\Delta H^* = 28.8$ kcal mol^{-1}, and $\Delta S^* = 18.5$ cal K^{-1} mol^{-1}.

The catalytic effect of nitrate ion on the rate of the reaction between *cis*-$[Co(en)_2(OH)_2]^{3+}$ and Hox^-/H_2ox has been investigated.[58] The nitrate ion is believed to catalyse the formation of a stereoretentive five-co-ordinate intermediate, $[Co(en)_2(OH_2)]^{3+}$. The uncatalysed reaction proceeds with the usual I_d mechanism, and the ion-pair formation constants (K) and interchange rate constants (k) were obtained for the reactions of both Hox^- ion and H_2ox. At 323.2 K and $I = 1.0$ M $[ClO_4^-]$, $K = 1.0 \pm 0.3$ and 4.4 ± 1.5 for H_2ox and Hox^- respectively. The interchange rate constants and activation parameters were essentially the same for both pathways: $10^5 k = 5.9 \pm 1.8$ s^{-1}, $\Delta H^* = 27.2 \pm 1.5$ kcal mol^{-1}, and $\Delta S^* = 6.1 \pm 4.5$ cal K^{-1} mol^{-1}.

A similar mechanism was observed for the reaction of *cis*-$[Co(en)_2(OH_2)(NH_3)]^{3+}$ and salicylate (HL^-) ions.[59] $k_{obs} = kK[HL^-]/(1 + K[HL^-])$. At 25 °C, $K = 2.3 \pm 0.3$ M^{-1} and $10^7 k = 78$ s^{-1}, the interchange rate constant being very close to the solvent exchange rate constant ($10^6 k_{ex} = 1.1$ s^{-1}). The reaction is stereoretentive.

Formation of $[Co(LL)_3]^{3+}$ ion (LL = biguanidine) from *cis*-$[Co(LL)_2(H_2O)_2]^{3+}$ and *cis*-$[Co(LL)_2(H_2O)(OH)]^{2+}$ ions is characterized by ΔH^*/kcal mol^{-1} $= 19.8 \pm 1.1$ and 20.2 ± 0.8, and ΔS^*/cal K^{-1} mol^{-1} $= -3.4 \pm 1.6$ and -3.5 ± 1.3 respectively.[60]

Formation of *trans*-$[Co(dmg)_2(Me)L]$ from the reaction of a range of N- and P-donor ligands, L, with *trans*-$[Co(dmg)_2(Me)L^1]$ (L^1 = 4-CN-py or Ph_3P) in dichloromethane solution proceeds with a *D*-mechanism. Displacement of L^1 from *trans*-$[Co(dmg)_2(L^1)X]$ (L^1 = 4-CN-py, Ph_3P, or 4-Bu-py) was also studied, and the *trans*-effect of ligands X found to be *p*-$SO_2C_6H_4Me_3 < CHBr_2 \leqslant SCPh_3 < CH_2Br < p\text{-}C_6H_4Br < p\text{-}C_6H_4OMe < Ph < p\text{-}CH_2C_6H_4CN < Me \lessdot CH_2Ph <$ Et. The results are collected in Table 4. The discriminating ability of the five-co-ordinate intermediates $[Co(dmg)_2X]$ is quite small (reactivity ratios in the range 1.2—5.4).[61]

Thermodynamic and kinetic data are reported for the addition of pyridine to the five-co-ordinate species (9) (X = Me, Ph, or Et, $R^1 = C_2H_4$ or *o*-C_6H_4, R^2 = Me or H, R^3 = H or CO_2Et, R^4 = Me or OEt, or $R^3 + R^4$ = benzo) and (10) ($R^1 = C_2H_4$, *o*-C_6H_4, $R^2 = CO_2Et$ or COMe).[62]

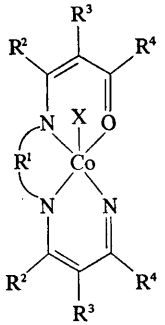
Reaction of the water-soluble Co^{III}-porphyrin $[Co(L)]^{5+}$ L = tetrakis-(*N*-methyl-4-pyridyl)porphine] with azide ion and 1,1,3,3-tetramethyl-2-thiourea extends

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[58] R. van Eldik and G. M. Harris, *Inorg. Chem.*, 1979, **18**, 1997.
[59] A. C. Dash and B. Mohanty, *J. Inorg. Nucl. Chem.*, 1979, **14**, 1053.
[60] B. Chakravarty and A. K. Sil, *Indian J. Chem., Sect. A*, 1978, **16**, 312.
[61] R. C. Stewart and L. G. Marzilli, *J. Am. Chem. Soc.*, 1978, **100**, 817.
[62] E. G. Jaeger and P. Renner, *Z. Chem.*, 1978, **18**, 193.

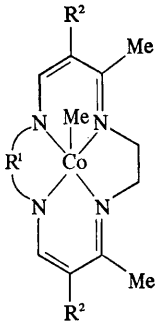
Table 4 *Observed rate constants at* 25 °C *in dichloromethane solution for the displacement of ligand* L *from* trans-$[Co(dmg)_2(L)X]$, *by excess* Bu^n_3P *unless specified*

L = 4-*cyanopyridine*					
X	$SO_2C_6H_4Ne^a$	$CHBr_2$	CH_2Br	C_6H_4Br	C_6H_4OMe
$10^4k/s^{-1}$	2.0	5.2	27	100	160
X	Ph	$CH_2C_6H_4CN$	Me	$PO(OMe)_2$	
$10^4k/s^{-1}$	290	450	570	100[b]	
$L = Ph_3P$					
X	$SCPh_3$	Ph	Me	$PO(OMe)_2$	
$10^4k/s^{-2}$	7.3	740	800	260[b]	
L = 4-t-*butylpyridine*					
X	Me	CH_2Ph	Et	$PO(OMe)_2$	
$10^4k/s^{-1}$	13.2	86	400	2.7[b, c]	
X	PO(OMe)	$PhPO(Ph)_2$			
$10^4k/s^{-1}$	33[b,c]	36[b,c]			

[a] Displacement by $(MeO)_3P$. [b] Extrapolated. [c] In benzene solution.



(9)



(10)

earlier investigations of the reactions with thiocyanate ion and pyridine. The thiourea ligand has about the same influence on the rate of addition of a second ligand as does thiocyanate ion, and these have a much larger effect than N_3^- ion.[63]

Neutral detergents (*e.g.* 2% Triton X 100) increase the equilibrium formation constants and rates of thiocyanate anation of Co^{III}-porphyrins in aqueous media by a factor of less than two.[64]

Reaction of *trans*-$[Co(en)_2Cl_2]^+$ with excess $(RO)_2CHCH_2NH_2$ (L; R = Me or Et) gives *cis*-$[Co(en)_2(L)Cl]^{2+}$, Treatment with HCl then forms *cis*-$[Co(en)_2\{ROC(OH)HCH_2NH_2\}Cl]Cl_2$ which, when heated *in vacuo* at 100 °C, gives $[Co(en)_2(NH_2CH_2CHO)]Cl_3$ and ROH. Rate data were obtained for the solvolysis of $[Co(en)_2(L)Cl]^{2+}$ ions in HCl.[65]

[63] R. F. Pasternak, B. S. Gillies, and J. P. Stramsted, *Bioinorg. Chem.*, 1978, **8**, 33.
[64] G. N. Williams and P. Hambright, *Inorg. Chem.*, 1978, **17**, 2687.
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Reactions of 1,2,3-$[Co(L^1)_2(L^2)]$ and 1,2,6-$[CoL^1_3]$ ($L^1 = NH_2CH_2CH_2O^-$, L^2 = glycinate or alinate ions) with glycinate ion have been investigated. Isomerization to 1,2,3-isomers was observed.[66]

Reaction of $[Co(L)_3]$ [$L = S_2P(OMe)_2$] with $Ph_2PCH_2CH_2PPh_2$ (dppe) has been studied by spectrophotometry and conductivity measurements in dichloromethane solution. Two steps were identified:[67]

$$[Co(L)_3] + dppe \longrightarrow [Co(L)_2(dppe)]^+ + L^-$$

$$[Co(L)_2(dppe)]^+ + L^- \longrightarrow [Co(L)\{S_2PO(OMe)\}(dppe)] + P(OMe)_2S(SMe)$$

For the first ligand displacement step, $\Delta H^* = 14.3 \pm 1.0$ kcal mol^{-1} and $\Delta S^* = -17 \pm 3$ cal K^{-1} mol^{-1}. The second step involves nucleophilic attack by the displaced ligand L^- at the P—O—C carbon atom of co-ordinated L^-.

Chromium(III) (d^3).—For a discussion of ΔV^* values for the anation of $[M(NH_3)_5(OH_2)]^{3+}$ ions (M = Co^{III}, Rh^{III}, or Cr^{III}), see the section on Co^{III} formations. Studies of the reaction of *trans*-$[Cr(H_2O)_4Cl_2]^+$ ion with high concentrations of HCl/LiCl are complicated by the approximate dependence of the activity of HCl on $[HCl]^2$, which would explain previous studies which showed a third-order rate law.[68] Plots of k_{obs} *versus* a_{HCl} are linear with a $k_{obs} = k_1\ a_{HCl} + k_{-1}$. Activation parameters associated with k_1 and k_{-1} are $\Delta H^*(k_1) = 24$ kcal mol^{-1}, $\Delta H^*(k_{-1}) = 24$ kcal mol^{-1}, $\Delta S^*(k_1) = -3.8$ cal K^{-1} mol^{-1}, and $\Delta S^*(k_{-1}) = +5.2$ cal K^{-1} mol^{-1}.

Reactions of $[Cr(H_2O)_6]^{3+}$ ion with $[P_3O_9]^{3-}$ (trimetaphosphate ion) and $[P_4O_{12}]^{4-}$ ions have been compared.[69,70] For the latter reaction,[70] the activation parameters are $\Delta H^* = 18.8$ kcal mol^{-1} and $\Delta S^* = -17.9$ cal K^{-1} mol^{-1}. Formation of Cr^{III} phosphates is also reported from studies of the reactions of $[Cr(H_2O)_4(LL)]^+$ ions (LL = mal[71] or ox[72]) with H_3PO_4.

The reaction of $[Cr(H_2O)_6]^{3+}$ ion with bipy is a second-order process, independent of pH in the range 4.0—4.8. An S_N2 mechanism is proposed.[73] A series of papers has appeared from the same group dealing with the reactions of $[Cr(H_2O)_6]^{3+}$ ion with anthranilic,[74] salicylic,[75] *p*-hydroxybenzoic,[76] and phthalic acids.[77] An I_a mechanism involving various anions of the respective acids is proposed. For example, the variation of k_{obs} with $[H^+]$ for the reactions with anthranilic and

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[71] N. R. Anipindi, V. A. Ramam, and M. N. Sastri, *Indian J. Chem., Sect. A*, 1977, **15**, 1021.
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p-hydroxybenzoic acids (HL) is of the form $k_{obs}=k_{an}K_IK_a[HL]/([H^+]+K_a+K_IK_a[HL])$:

$$HL \overset{K_a}{\rightleftharpoons} L^- + H^+$$

$$[Cr(H_2O)_6]^{3+} + L^- \overset{K_I}{\rightleftharpoons} [Cr(H_2O)_6]^{3+},L^- \text{ (ion pair)}$$

$$\text{ion pair} \xrightarrow{k_{an}} [Cr(H_2O)_5L]^{2+} + H_2O$$

For HL = *p*-hydroxybenzoic and anthranilic acid, $\Delta H^*(k_{an})=25$ and 23 kcal mol^{-1}, $\Delta S^*(k_{an})=6.0$ and -0.2 cal K^{-1} mol^{-1}, $\Delta H^\circ(K_I)=-12.4$ and -9.7 kcal mol^{-1}, $\Delta S^\circ(K_I)=-38$ and -29 cal K^{-1} mol^{-1} respectively. The other reactions are all very similar, with dianions involved in some cases.

A comparison of the rates of reaction of $[Cr(H_2O)_6]^{3+}$ and $[Cr(H_2O)_5(DMF)]^{3+}$ ions with edta has been made. The equilibrium constant for the formation of $[Cr(H_2O)_5(DMF)]^{3+}$ is 0.21 ± 0.01 M^{-1}, and the second-order rate constant for its reaction with edta is 7.9×10^{-2} M^{-1} s^{-1}, compared with a value of 1.5×10^{-5} M^{-1} s^{-1} observed for the reaction with $[Cr(H_2O)_6]^{3+}$ ion.[78]

Several groups have studied the catalytic effect of H_2O_2 on the formation of $[Cr(edta)]^-$ ion.[79–81] The reaction of $[Cr(H_2O)_6]^{3+}$ with edta in the presence of H_2O_2 is very complex and involves both Cr^{IV} and Cr^V species, which disproportionate. Decomposition of H_2O_2 with the liberation of O_2 is also observed. A simplified scheme is as follows ($k_2 > k_3k_1 \approx k_4$):[79]

$$Cr^{III} \xrightarrow[H_2O_2]{k_1} Cr^{IV} \xrightarrow{k_2} Cr^{IV}(edta) \underset{k_4}{\overset{k_3}{\rightleftharpoons}} Cr^{III}(edta)$$

The catalytic effect of H_2O_2 on the reactions of edta with $[Cr(mal)_3]^{3-}$ and *cis*-$[Cr(mal)_2(H_2O)_2]^-$ ions is also reported.[80]

For the reaction of $[Cr(H_2O)_6]^{3+}$ with edta in the presence of either Fe^{II} and H_2O_2 or $[S_2O_8]^{2-}$ and Fe^{II}, the following mechanisms are proposed:[81]

$$Cr^{III}aq + OH\cdot \xrightarrow{(edta)} [Cr^{IV}(edta)] + OH^-$$

$$H_2O_2 + [Cr^{IV}(edta)] \longrightarrow [Cr^{III}(edta)(H_2O)]^- + HO_2\cdot$$

$$[Fe^{III}(edta)] + HO_2\cdot \longrightarrow [Fe^{II}(edta)] + H^+ + O_2$$

$$S_2O_8^{2-} + [Fe^{II}(edta)] \longrightarrow SO_4\cdot^- + SO_4^{2-} + [Fe^{III}(edta)]$$

$$Cr^{III}_{aq} + SO_4\cdot^- \xrightarrow{edta} [Cr^{IV}(edta)] + SO_4^{2-}$$

$$[Cr^{IV}(edta)] + Cr^{III}_{aq} \longrightarrow [Cr(edta)(H_2O)]^- + Cr^{IV}$$

Sulphite ion is a better catalyst than nitrite ion for the reaction of $[Cr(ox)(H_2O)_4]^+$ ion with edta. Spectral evidence for the involvement of rapidly formed $[Cr(ONO)(ox)(H_2O)_3]$ and $[Cr(OSO_2H)(ox)(H_2O)_3]$ is presented.[82]

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[79] M. T. Beck and Z. Tóth, *Magy. Kem. Foly.*, 1979, **85**, 5; *Bull. Chem. Soc. Jpn.*, 1979, **52**, 598.
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For the reaction of $[Cr(NH_3)_6]^{3+}$ ion with edta (H_2L^{2-}), a rate law of the form $Rate = (k_1[H_3O^+] + k_2K[H_2L^{2-}])[Cr(NH_3)_6^{3+}]$ is observed.[83] The reaction of $[Cr(ox)(H_2O)_4]^+$ ion with $[H_2PO_2]^-$ ion was also investigated by the same group.[84] From studies between pH 3.7 and 4.9, $Rate = kK[Cr(ox)(H_2O)_4^+][H_2PO_2^-]/[H^+]$.

An I_a mechanism is proposed for the reaction of *cis*-$[Cr(mal)_2(OH)_2]^-$ ion with bipy and phen. The activation parameters are very similar to those obtained previously for the analogous reactions of *cis*-$[Cr(ox)_2(OH_2)_2]^-$ ion.[85]

Anation of *cis*-$[Cr(ox)(en)(OH_2)_2]^+$ ion by oxalate ion has been investigated between pH 2 and 5; $k_{obs} = k_1K_c[H^+]([H^+] + K_2'[ox^{2-}])/\{K_2'([H^+] + K_{al}) + K_c([H^+] + K_2')[ox^{2-}]\}$, where K_2' and K_{al} are the acid dissociation constants of an associated Hox^- ion and the aqua-ligands respectively, K_c is the outer-sphere association constant with ox^{2-} ion, and k_1 is the interchange rate constant ($10^3k_1 = 1.44 \pm 0.05\ s^{-1}$, $\Delta H^{\ddagger} = 18.1 \pm 0.4$ kcal mol^{-1}, $\Delta S^{\ddagger} = -10.7 \pm 1.4$ cal K^{-1} mol^{-1}).

The *cis*-$[Cr(en)_2(OH_2)F]^{2+}$ ion has been resolved with bromocamphor-π-sulphonate ion, and anation with NCS^- and F^- ions in methanol is reported to proceed with retention of configuration.[87]

Formation of Δ,Λ-$[(en)_2Cr$-$\mu(RCO_2)(OH)$-$Cr(en)_2]^{4+}$ ions (R = Me, H, $H_3\overset{+}{N}CH_2$, or NH_2CH_2) from reactions of the μ-dihydroxo-species with RCO_2H was considered in Chapter 5 (ref. 107).

Manganese(III) (d^4).—A kinetic and thermodynamic study of the reaction of Mn^{III} with cdta (cyclohexane-1,2-diamine-*NNN'N'*-tetra-acetate) ion has been reported.[88] The inverse stability constant is 1.4×10^{-24} M^{-1}.

Iron(III) (d^5).—Complexes of Fe^{III} can be either high-spin ($t_{2g}^3e_g^{*2}$) when they are fairly labile, or low-spin (t_{2g}^5) when they are inert. The labile systems are considered first.

A temperature-jump method has been used to obtain equilibrium constants and rate constants for the formation of mono- and bis-complexes of $[Fe(H_2O)_6]^{3+}$ with Cl^- ion. For the mono-species, the interchange process involving the ion-pair $[Fe(H_2O)_6]^{3+}$, Cl^- (outer-sphere formation constant 1.1 M^{-1}) is characterized by $k_f = 21.8$ M^{-1} s^{-1} and $k_d = 3.7$ s^{-1} at 25 °C ($I = 2.6$ M). The equilibrium formation constant (k_f/k_d) is 5.9 M^{-1}. For the bis-species, k_f is calculated to be 324 M^{-1} s^{-1} from the measured dissociation rate constant, $k_d = 185$ s^{-1} ($K_2 = 1.75$ M^{-1}).[89]

A high-pressure laser temperature-jump technique has been used to investigate the reaction between $[Fe(H_2O)_6]^{3+}$ and Br^- ions at pressures of up to 2.76 kbar (Scheme 2). For the formation reaction $\Delta V^{\ddagger}(k_1) = -19 \pm 4$ cm^3 mol^{-1} at $I = 2.0$ M and 25 °C, and an I_a mechanism is proposed. For the overall reaction involving $[Fe(H_2O)_6]^{3+}$ and Br^-, $\Delta V^{\ddagger}(k_1K_1) = -8 \pm 4$ cm^3 mol^{-1}. Values were reported previously for Cl^- (-4.5 ± 1.1 cm^3 mol^{-1}) and NCS^- (an average value of 0 ± 5 cm^3 mol^{-1}). The variation in the rate constants (k_1K_1) for reactions of

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[88] V. V. Lapkin and N. I. Pechurova, *Chem. Abs.*, 1978, 136 565.
[89] U. Strahm, R. C. Patel, and E. Matijevic, *J. Phys. Chem.*, 1979, **83**, 1689.

$$\begin{array}{ccccc} Fe^{3+} + Br^- & \overset{K_1}{\rightleftharpoons} & Fe^{3+},Br^- & \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} & FeBr^{2+} \\ \Big\Updownarrow K_a & & \Big\Updownarrow K_b & & \Big\Updownarrow K_c \\ Fe(OH)^{2+} + Br^- & \overset{K_2}{\rightleftharpoons} & Fe(OH)^{2+},Br^- & \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} & Fe(OH)Br^+ \end{array}$$

Scheme 2

$[Fe(H_2O)_6]^{3+}$ with these three ions (at 25 °C, $k_1K_1/M^{-1}\,s^{-1} = 122$, 4.8, and 1.6 for NCS^-, Cl^-, and Br^- ions respectively) is as expected for an I_a mechanism. In contrast, the reactions involving the hydroxo-species, $[Fe(H_2O)_5(OH)]^{2+}$ ion, are believed to proceed with an I_d mechanism.[90]

The effect of varying ionic strength and the anions NO_3^-, ClO_4^-, SO_4^{2-}, and Cl^- on the rate of formation of $[Fe(NCS)]^{2+}$ ion has been investigated by a stopped-flow method,[91] and the catalysed formation of $[Fe(NCS)]^{2+}$ has been investigated in the presence of aliphatic carboxylic acids (involving $[Fe(HL)(NCS)]^+$ ions where $HL = RCO_2H$; R = H, Me, or Pr) by temperature-jump.[92] The latter reactions involve a fast formation of $[Fe(OH)(HL)(NCS)]^+$ ions, followed by a slower loss of HL from this first formal species. A mechanism analogous to that proposed by Rorabacher (ICB effect) is suggested.[92]

Two steps are apparent in the reaction between $[Fe(H_2O)_6]^{3+}$ and $[Fe(CN)_5CO]^{3-}$ ions.[93] Rapid formation of the violet $[(H_2O)_5FeNCFe(CN)_4(CO)]$ is followed, after an induction period, by a slower polymerization reaction. For the rapid reaction, the ion-pair formation constant is estimated to be $660 \pm 60\ M^{-1}$ and the interchange rate constant $27 \pm 8\ s^{-1}$ at 25 °C and $I = 0.1$ M.

A stopped-flow method has been used to study the reactions of the $[Fe(H_2O)_6]^{3+}$ ion with the α-hydroxy-carboxylic acids glycolic, DL-lactic, DL-malic, and benzilic acids. The main pathway involves reactions of $[Fe(H_2O)_5(OH)]^{2+}$ ion with HL, and an I_d mechanism is proposed.[94] A similar study involves reactions with acetohydroxamic acid, hydroxyproline hydroxamic acid, tryptophane hydroxamic acid, and histidine hydroxamic acid.[95] The second-order rate constants at 25 °C fall in the range $(1.14—5.90) \times 10^3\ M^{-1}\,s^{-1}$.

A spin change is involved in the formation of low-spin bis(imidazole) complexes of the type *trans*-$[Fe(L)(X)_2]^+$ (L = protoporphyrin IX dimethyl ester, X = imidazole or *N*-propyl- or *N*-methyl-imidazole) from reactions of high-spin [Fe(L)Cl] with X.[96,97] High-spin six-co-ordinate intermediates of the type [Fe(L)Cl(X)] are involved, and slightly different mechanisms are proposed for the reactions with the unsubstituted and *N*-methyl-imidazoles studied. Imidazole reacts more rapidly and a mechanism is proposed involving assisted loss of Cl^- through hydrogen-bonding with imidazole $\{k_{obs} = k_1K[X]^2/(1 + K[X])\}$:

[90] B. B. Hasinoff, *Can. J. Chem.*, 1979, **57**, 77.
[91] B. Banas and M. Wronska, *Pol. J. Chem.*, 1978, **52**, 239.
[92] B. S. Prabhananda, *J. Inorg. Chem.*, 1978, **40**, 525.
[93] H. E. Tomas and L. A. A. Oliveira, *Inorg. Chim. Acta*, 1979, **33**, L143.
[94] E. Mentasti, *Inorg. Chem.*, 1979, **18**, 1512.
[95] N. Kujundzic and M. Pribanic, *J. Inorg. Nucl. Chem.*, 1978, **40**, 729.
[96] W. W. Fiske and D. A. Sweigart, *Inorg. Chim. Acta*, 1979, **36**, L429.
[97] D. Burdige and D. A. Sweigart, *Inorg. Chim. Acta*, 1978, **28**, L131.

$$[Fe(L)Cl] + X \overset{K}{\rightleftharpoons} [Fe(L)Cl(X)]$$

$$[Fe(L)Cl(X)] + X \xrightarrow{k_1} [Fe(L)X_2]^+,Cl^- \text{ (assisted)}$$

For the reaction with *N*-methylimidazole the proposed mechanism, after the rapid first step (equilibrium constant K), is as follows $\{k_{obs} = k_1K[X]/(1 + K[X])\}$:

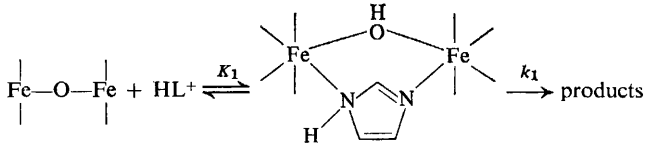
$$[Fe(L)Cl(X)] \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [Fe(L)X]^+,Cl^- \text{ (unassisted)}$$

$$[Fe(L)X]^+,Cl^- + X \xrightarrow{k_3} [Fe(L)X_2],Cl^-$$

For the reaction with *N*-methylimidazole, $k_1 = 8.1 \pm 0.7\ s^{-1}$ and $K = 2.6 \pm 0.3\ M^{-1}$ at 25 °C. The high-spin six-co-ordinate intermediate was not detected spectrally when X = imidazole,[96] only when X = *N*-propylimidazole[97] or *N*-methylimidazole.[96]

^1H N.m.r. has been used to study the binding of CN^- ion, imidazole, and both ligands to ferriprotoporphyrin IX Cl (haemin) in deuterio-DMSO solution. Two steps were detected in the binding of CN^- ion, the previously unknown monocyano-adduct being formed first ($10^{-4}K_1 = 1.9 \pm 0.3\ M^{-1}$, $10^{-3}K_2 = 1.1 \pm 0.2\ M^{-1}$), whereas the reaction with imidazole goes in a single step ($10^{-4}\ \beta_2 = ca.\ 6\ M^{-2}$ at 25 °C). The monocyano-complex is low-spin whereas the monoimidazole adduct is high-spin. Exchange rates between the various species is slow on the n.m.r. time-scale ($k_{ex} < 160\ s^{-1}$ at 65 °C).[98]

Reactions of imidazole with two μ-oxo-dimer species $[Fe(L)]_2O$ [L = tetrakis-(*p*-sulphophenyl)porphinate (TPPS) or tetrakis-(*p*-trimethylammoniumphenyl)-porphinate (TAPP)] have been compared. At 30 °C and $I = 0.1$ M [$NaNO_3$], the TPPS complex reacts at least 40 times as fast as the TAPP complex. A mechanism involving the reaction of protonated imidazole (HL^+) to give the μ-hydroxo-μ-imidazole adduct of structure (11) is proposed:



(11)

Values of k_1 and K_1 are $7 \pm 2\ s^{-1}$ and $-47 \pm 9\ M^{-1}$ when L = TPPS, and $k_1 = 3 \pm 0.1\ s^{-1}$ and $K_1 = 5.6 \pm 0.5\ M^{-1}$ when L = TAPP. The rate difference resides primarily in the effects of charge.[99]

Dissociative substitution reactions involving low-spin *trans*-[Fe(cyclam)-(NCS)X]$^+$ ions were considered in Chapter 5 (ref. 130).

Rate data for the formation of $[Fe(CN)_5(NH_2Ph)]^{2-}$ ion from $[Fe(CN)_5(H_2O)]^{2-}$ ion have also been reported.[100]

[98] J. T. Wang, H. J. Yeh, and D. F. Johnson, *J. Am. Chem. Soc.*, 1978, **100**, 2400.
[99] A. N. Thompson and M. Krishnamurthy, *Inorg. Chim. Acta*, 1979, **34**, 145.
[100] V. V. Bechkarev, V. L. Ivasenko, and V. P. Lapatinskii, *Chem. Abs.*, 1979, **90**, 128 200.

Ruthenium(III) (d^5).—Rate data for the following equilibria are collected in Table 17 of Chapter 5:[101,102]

$$[Ru(edta)(OH_2)]^- + L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Ru(edta)L]^{n-} + H_2O$$

These reactions are significantly more rapid than other Ru^{III} substitutions because of assistance by the un-co-ordinated carboxylate arm of the quinquedentate edta.

Anation of *trans*-$[Ru(NH_3)_4(L)(OH_2)]^{3+}$ ion (L = isonicotinamide) by Cl^- or Br^- ions is a simple second-order process, whereas for the reaction with I^- ion reduction to Ru^{II} is involved and $k_{obs} = k_1[I^-]^{5/2}[I_3^-]^{1/2} + k_2[I^-]^2$. The first term is accounted for by the following mechanism:

$$2Ru^{III}(OH_2) + 3I^- \rightleftharpoons 2Ru^{II}(OH_2) + I_3^-, K_3$$

$$2Ru^{II}(OH_2) + I^- \longrightarrow Ru^{II}I + H_2O, k_4$$

$$2Ru^{II}I + I_3^- \rightleftharpoons 2Ru^{III}I + 3I^-, K_5$$

$k_1 = k_4K_3^{1/2}$ with $k_4 = 0.20 \pm 0.04$ M^{-1} s^{-1} and $10^4K_3 = 2.0$ M^{-2}. The second term in the expression for k_{obs} (rate constant k_2) is more obscure, but it is suggested that substitution coupled with electron transfer is involved.[103]

Rates of formation and dissociation of mono- and bis-adducts of the oxime complexes *trans*-$[Ru^{III}(L)_2(H_2O)_2]^+$ (HL = α-furyl-mono-oxime or -dioxime) have been determined.[104]

Rhodium(III) (d^6).—In a very interesting paper, the case has been made for studying anation reactions at low, variable concentrations of added anion and ionic strengths rather than at the high constant ionic strengths which most workers prefer to use. Anation of $[Rh(NH_3)_5(OH)_2]^{3+}$ ion by Cl^- was studied at low variable I values ($I < 0.3$ M), with $0.01 < [Cl^-]/M < 0.3$. Activity corrections were made, using the Davies equation (with an adjustable parameter), and ion-pairing was studied spectrophotometrically (15—40 °C) and potentiometrically at 25 °C. Perchlorate ions and chloride ions form ion-pairs with the same ease, the ion-pair formation constant at low ionic strength being 26.5 ± 0.8 for $+3/-1$ ions of this type. An interchange mechanism was confirmed, with the interchange rate constant extrapolated to $I = 0$ characterized by $\Delta H^* = 26.2$ kcal mol^{-1} and $\Delta S^* = 3.3$ cal K^{-1} mol^{-1}. This compares with a value of $\Delta H^* = 25$ kcal mol^{-1} reported previously. A comparison of this interchange rate constant with the solvent-exchange rate indicates that bond making is not very important in the transition state, *i.e.* the mechanism is nearer to I_d than to I_a. However, other values of the interchange rates at $I = 0$ are required before a distinction between I_a and I_d mechanisms is made in this way.[105]

The alternative approach of using high, constant ionic strengths is typified by the anation studies of $[M(NH_3)_5(OH_2)]^{3+}$ ions made at high pressures and $I = 2.0$ M

[101] T. Matsubara and C. Creutz, *Inorg. Chem.*, 1979, **18**, 1956; *J. Am. Chem. Soc.*, 1978, **100**, 6255.
[102] Y. Yoshino, T. Uehiro, and M. Saito, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 1060.
[103] D. E. Richardson and H. Taube, *Inorg. Chem.*, 1979, **18**, 549.
[104] V. M. Savostina, O. A. Shpigun, N. V. Klimova, I. Y. Kolotyrkina, and V. M. Peshkova, *Chem. Abs.*, 1979, **90**, 128 332.
[105] M. J. Pavelich, S. M. Maxey, and C. Pfaff, *Inorg. Chem.*, 1978, **17**, 564.

($M = Co^{III}$ or Rh^{III}) or $I = 1.0$ M ($M = Cr^{III}$).[105] Under these conditions, no evidence could be found for ion-pairing with the incoming anion (Cl^- or SO_4^{2-} for $M = Co^{III}$ or Cl^- for $M = Rh^{III}$), and the value of $\Delta V^* = +3.0 \pm 0.7$ cm^3 mol^{-1} for the Cl^- anation of the Rh^{III} complex was interpreted in terms of an I_d mechanism. The negative ΔV^* value for solvent exchange with $[Rh(NH_3)_5(OH_2)]^{3+}$ reported previously (ΔV^* *ca.* -4 cm^3 mol^{-1}) was discussed. Values of ΔV^* for the Cl^- ion anation of $[RhCl_5(OH_2)]^{2-}$ and *cis*-$[RhCl_4(OH_2)_2]^-$ ions are 15.7 ± 6.5 and 14.7 ± 1.6 cm^3 mol^{-1} respectively, and these significantly positive ΔV^* values are a good indication of a dissociative mechanism for these reactions between ions of like charge.[106]

Formation of $[Rh(HL)_3]^{3-}$ ion from the reaction of $[Rh(H_2O)_6]^{3+}$ with unithiol (H_3L) has been studied. Acetic acid accelerates the reaction through the formation of acetato-complexes.[107]

The formation of *mer*-$[Rh(L)(L')(RNH_2)Cl_2]^+$ ion from the reaction of *trans*-$[Rh(L)_2Cl_2]^+$ ion with RNH_2 (L = *N,As*-bonded *o*-dimethylaminophenyldimethylarsine, and L′ is the same ligand co-ordinated only through the As-donor atom) was described in Chapter 5 (ref. 151).

Iridium(III) (d^6).—An activation energy of 30.9 kcal mol^{-1} is reported for the reaction of $[Ir(H_2O)_6]^{3+}$ ion with 2-(2-thiazolylazo)-5-(diethylamino)phenol. $MeCO_2^-$ and $EtCO_2^-$ ions accelerate the formation rate by labilizing the aquo-ligands.[108]

The rates of reaction of chloroaqua-complexes of Ir^{III} with the oximes α-furyldioxime, α-furylmono-oxime, and 5-nitro-2-oximethiophenone aldehyde increase with the oxime donor atoms in the order, $O,O \ll N,N < O,S < S,N$. The 1:1 complexes are formed faster than the 1:2 species, the bis-complexes requiring a higher ligand concentration for complete formation.[109]

N.m.r. evidence for the formation of covalent hydrates of the type $[Ir(bipy)_2(bipy.H_2O)]^{3+}$ (and analogous Ru^{III} species)[111] has been presented.[110]

3 Oxidation State IV

Titanium(IV) (d^0).—A stopped-flow method has been used to study the reaction of Ti^{IV} with substituted salicylic acids (salicylic, β-resorcylic, and 5-nitro- and 5-amino-salicylic acids),[112] and with diantipyrylmethane (L).[113] Formation of mono-, bis-, and tris-complexes of L were investigated with structures $[Ti(OH)_2L]^{2+}$, $[Ti(OH)_2L_2]^{2+}$, and $[TiL_3]^{4+}$. The last reaction, involving the formation of the tris-complex, is the slowest step involved.

[106] K. F. Hyde, H. Kelm, and D. A. Palmer, *Inorg. Chem.*, 1978, **17**, 1647.
[107] E. A. Klimkovich, B. M. Machul'skii, and Y. U. Usatenko, *Chem. Abs.*, 1979, **90**, 29 605.
[108] T. I. Shuru'ova and V. M. Ivanov, *Zh. Neorg. Khim.*, 1978, **23**, 2135.
[109] V. M. Savostina, O. A. Shpigun, V. A. Parmerova, and L. A. Bubchikova, *Chem. Abs.*, 1978, **89**, 136 427; *Koord. Khim.*, 1978, **4**, 604.
[110] R. D. Gillard, R. J. Lancashire, and P. A. Williams, *J. Chem. Soc., Dalton Trans.*, 1979, 190.
[111] J. A. A. Sagüés, R. D. Gillard, R. J. Lancashire, and P. A. Williams, *J. Chem. Soc., Dalton Trans.*, 1979, 193.
[112] V. T. Novikov, V. P. Lapatinskii, L. A. Chernova, and V. L. Ivasenka, *Chem. Abs.*, 1979, **90**, 142 613.
[113] A. Y. Nazarenko, *Chem. Abs.*, 1978, **89**, 12 700.

Formation of peroxotitanium(IV) has also been investigated by a stopped-flow method in strongly acidic ($HClO_4$, HCl, and H_2SO_4) solutions.[114] Cryoscopy indicates that a monomer complex is formed, and ion-exchange studies show a charge of +1. The highest rate of formation was observed in H_2SO_4 solution, and in 0.05 M [H_2SO_4] at 25 °C the second-order rate constant is 346 M^{-1} s^{-1}.

Vanadium(IV) (d^1).—Replacement of the basal water molecules (in a *cis*-position to V=O) in [VO(L)(H_2O)] [L=(2-pyridylmethyl)iminodiacetate ion] by X^-= NCS^- and N_3^- ions has been investigated by the stopped-flow method:[115] $k_{obs}=k_d+k_f[X^-]$, where k_d and k_f are the dissociation and formation rate constants respectively. The results are shown in Table 19 of Chapter 5. Values of ΔS^* associated with k_f are significantly negative, and an associative mechanism seems likely for these reactions.

Molybdenum(IV) (d^2).—A number of groups have studied Mo^{IV} formation from the disproportionation of Mo^V dimers into $Mo^{IV}+Mo^{VI}$. Reaction of [LMo^V-O-$\mu(O)_2$-$Mo^VOL]^{2-}$ ion (L=cysteine) with excess O_2 in phosphate buffers at pH 6.5 is characterized by the mechanism shown in Scheme 3, in which 10^3k_1=

$$[Mo^V_2O_4(L)_2]^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Mo^{IV}O(L)]^{2-} + [Mo^{VI}O(L)]$$

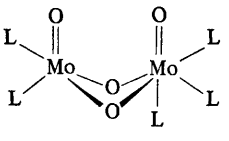
$$k_2 \downarrow O_2, 2H^+$$

$$[Mo^{VI}O(L)(H_2O_2)]$$

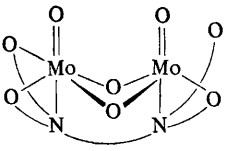
Scheme 3

1.5 ± 0.2 s^{-1} and $k_{-1}k_2^{-1}=0.9\pm0.2$ at 25 °C.[116] In the presence of excess O_2, $k_{obs}=k_1k_2[O_2]/(k_{-1}[Mo^{VI}]+k_2[O_2])$.

Reaction of $[Mo^V_2O_4(L)_2]^{n-}$ (L=cysteine, histidine, citric acid, $[HP_3O_{10}]^{4-}$, H_2O, or $edta^{4-}$) with cyanide ion in aqueous solution gives $[MoO_4]^{2-}$ and $[Mo^{VI}(O)(OH)(CN)_4]^{3-}$ ions. The reactions are first-order in complex and hydroxide ion, and complexes with structure (12) react at about the same rate (at 25 °C, k/M^{-1} $s^{-1}=150$ when L=histidine, citric acid, or $[HP_3O_{10}]^{4-}$ ion, and 77 when L=cysteine). A mechanism involving nucleophilic attack by OH^- to give an intermediate or transition state with a single μ-oxo-bridge is proposed. The edta complex is considerably more robust ($k=0.02$ M^{-1} s^{-1} at 25 °C) and this extra stability is attributed to the bridging of the two Mo^V ions by the edta backbone (13).[117]



(12)



(13)

[114] M. Veber and L. J. Csanyi, *Acta Phys. Chem.*, 1977, **23**, 297.
[115] M. Nishizawa and K. Saito, *Inorg. Chem.*, 1978, **17**, 3676.
[116] T. M. Tam and J. H. Swinehart, *Inorg. Chem.*, 1979, **18**, 975.
[117] P. R. Robinson and C. R. Landis, *Inorg. Chim. Acta*, 1979, **33**, 63.

Rate data for the disproportionation of the μ-oxo-dimers $[O\{Mo^{V}O(L)_2\}_2]$ to $[Mo^{IV}OL_2]$ and $[Mo^{VI}O_2L_2]$ and for the reverse recombination reaction are collected in Table 5. The reactions were studied by a concentration-jump, stopped-flow method.[118]

Intermediate formation of $[Mo(NCS)_6]^{2-}$ occurs in the oxidation of $[Mo(NCS)_6]^{3-}$ with $[IrCl_6]^{2-}$. It is proposed that $[Mo(NCS)_6]^{2-}$ changes co-ordination number by addition of one or two H_2O molecules, and that this species then aquates to a pentathiocyanato product in a kinetically followable step. The aquation reaction was investigated by the stopped-flow method in aqueous HCl, and $k_{obs}=(k_1[H^+]+k_2K_a)/(K_a+[H^+])$; at 25 °C, $K_a=0.06\pm0.03$ M, $k_1=2.96\pm0.3$ s^{-1}, and $k_2=17.4\pm3.8$ s^{-1}. Formation of $[Mo(NCS)_6(OH_2)_n]^{2-}$ ion ($n=1$ or 2) accommodates the observed pH dependence, where k_1 and k_2 are identified as reactions of the aqua-adduct and its conjugate base (hydroxo-complex) respectively.[119] Rapid disproportionation of two non-equivalent Mo^{IV} species to Mo^{III} and Mo^{V} follows.

Manganese(IV) (d^3).—For the disproportionation of $[Mn^{III}(CN)_6]^{3-}$ ion to $[Mn^{IV}(CN)_6]^{2-}$ and $[Mn(H_2O)_6]^{2+}$, the following mechanism is proposed:[120]

$$[Mn(CN)_6]^{3-} + 6H_3O^+ \longrightarrow [Mn(H_2O)_6]^{3+} + 6HCN$$

$$[Mn(CN)_6]^{3-} + [Mn(H_2O)_6]^{3+} \longrightarrow [Mn(H_2O)_6]^{2+} + [Mn(CN)_6]^{2-}$$

Iridium(IV) (d^5).—Effects of temperature, pH, and Cl^- on the rates of formation of chloro-complexes of Ir^{IV} have been investigated.[121]

Platinum(IV) (d^6).—The reaction of *trans*-$[Pt(CN)_4Br(OH_2)]^-$ and Br^- ions has been extended to higher $[Br^-]$ and the pseudo-first-order rate constant was found to vary as follows (p, q, r, and s are constants): $k_{obs}=p[Br^-]^2/(1+q[Br^-])+r[Br^-]^3/(1+s[Br^-])$. The following mechanism involving reductive elimination followed by oxidative addition (reoa) is proposed:

$$Br^- + BrPt^{IV}OH_2 \underset{\text{rapid}}{\overset{K}{\rightleftharpoons}} Br\cdots BrPt^{IV}OH_2$$

$$Br\cdots BrPt^{IV}OH_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Br{-}Br\cdots BrPt^{II}\cdots OH_2$$

$$Br{-}Br\cdots Pt^{II}\cdots OH_2 + Br^- \xrightarrow{k_2} Br^- + BrPt^{IV}Br$$

$$Br^- + Br\cdots BrPt^{IV}OH_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Br_3\cdots Pt^{II} + OH_2$$

$$Br_3\cdots Pt^{II} + Br^- \xrightarrow{k_4} 2Br^- + BrPt^{IV}Br$$

Provided $K[Br^-]\ll 1$, this mechanism leads to the expression $k_{obs}=k_1K\{(k_2/k_{-1})[Br^-]^2/(1+(k_2/k_{-1})[Br^-]\}+k_3K(k_4/k_{-3})[Br^-]^3/\{1+(k_4/k_{-3})[Br^-]\}$. The second term contributes *ca.* 50% to k_{obs} even at low $[Br^-]$. There is spectroscopic evidence

[118] T. Matsuda, K. Tanaka, and T. Tanaka, *Inorg. Chem.*, 1979, **18**, 454.
[119] A. B. Soares, R. S. Taylor, and A. G. Sykes, *Inorg. Chem.*, 1978, **17**, 496.
[120] G. Trageser and H. H. Eysel, *Inorg. Chim. Acta*, 1978, **26**, L56.
[121] A. T. Pilipenko, E. P. Parkomenko, and N. F. Falendysh, *Chem. Abs.*, 1979, **90**, 29 647.

Table 5 *Rates and activation parameters at* 25 °C *for the equilibria* $[Mo^{V}_{2}O_{3}L^{4}] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Mo^{IV}OL_2]+[MoO_2L_2]$ *in* 1,2-*dichloroethane solution* (*data from ref.* 118)

L	k_1/s^{-1}	$\Delta H_1^{\ddagger}$/kcal mol^{-1}	$\Delta S_1^{\ddagger}$/cal K^{-1} mol^{-1}	$10^{-2}k_{-1}/M^{-1}\ s^{-1}$	$\Delta H_{-1}^{\ddagger}$/kcal mol^{-1}	$\Delta S_{-1}^{\ddagger}$/cal K^{-1} mol^{-1}	$10^{3}K/M^{a}$
Et_2NCS_2	2.93	17.0	0.1	14.7	5.1	−27.0	2.0
Et_2NSSe	3.78	18.8	7.3	9.0	3.8	−32.5	4.2
Et_2NCSe_2	10.8	12.8	−10.9	8.3	6.9	−22.5	13.0

[a] Equilibrium constants: $\Delta H°$/kcal mol^{-1} = 12, 15, and 6; $\Delta S°$/cal K^{-1} mol^{-1} = 28, 40, and 11.3 for L = Et_2NCS_2, Et_2NSSe, and Et_2NCSe_2 respectively.

for the formation of the charge-transfer complexes, and the Br_2 must remain attached to the Pt^{II} in the above scheme.[122]

For the reaction of *trans*-$[Pt(en)_2Br_2]^{2+}$ with CN^- ion, the usual Pt^{II} catalysis is involved, and formation of *trans*-$[Pt(en_2BrCN]^{2+}$ ion is characterized by $k_{obs}=k_0+k_2[CN]+k_3[CN^-][Pt(en)_2{}^{2+}]$. An overall value of $\Delta H^{\ddagger}=9.5\pm 0.5$ kcal mol^{-1} is reported.[123]

4 Oxidation State V

Vanadium(V) (d^0).—Reaction of V^V (HVO_3) with the metal ion indicator 1-(2-pyridylazo)-2-naphthol (pan) has been studied by a stopped-flow method in the presence of charged micelle-forming compounds such as tetradecyldimethylbenzylammonium chloride (A) and hexadecylpyridinium chloride (B). In a solution of pan in (A), it is believed that pan is in the neighbourhood of the charged micelle surface and aligns its chelating group with that surface. The reaction in the presence of (B) is faster than in the presence of (A).[124]

A novel high-pressure stopped-flow study of the reaction of $[VO_2(nta)]^{2-}$ ion with H_2O_2 has been reported.[125] From studies between pH 2.2 and 4.2, $k_{obs}=(k_1+k_2[H^+])[H_2O_2]$, and, at 25 °C and $I=1.0$ M, $k_1=7.41$ M^{-1} s^{-1}, $10^{-4}k_2=1.86$ M^{-2} s^{-1}, and $\Delta V^{\ddagger}(k_1)=-3.3\pm 0.6$ cm^3 mol^{-1}. The negative $\Delta V^{\ddagger}$ value is consistent with an associative mechanism.

5 Oxidation State VI

Chromium(VI) (d^0).—Formation of $[CrO(O_2)_2(OH_2)]$ (blue peroxychromic acid) was discussed together with the acid dissociation kinetics in Chapter 5 (ref. 170).

Molybdenum(VI) (d^0).—The published structural information on Mo^{VI} polyanions has been analysed and a mechanism for their formation proposed.[126] The mechanism involves successive additions of protonated octahedra for low condensation reactions (fast processes) and structural rearrangements for higher condensations. The presence of cations with small ionic radii leads to the formation of higher condensations (*e.g.* $[Mo_{36}O_{112}]^{8-}$) with loosely packed structures, whereas in the presence of tetra-alkylammonium salts polyanions of low condensation are rapidly formed. The structures of all of the polyanions are based on tetrameric units similar to those found in Nb^V, Ta^V, and W^{VI} polyanions.

Some kinetic data have been obtained for the formation of a red complex on reaction of Mo^{VI} with NCS^- ion in HCl or H_2SO_4 solution.[127]

Tungsten(VI) (d^0).—Acidification of 10^{-3} M $Na_2[WO_4]$ in a stopped-flow experiment shows that $[H_8W_6O_{24}]^{4-}$ is formed as a transient intermediate *ca.* 500 ms after mixing, and this decomposes to a mixture of $[HW_6O_{21}]^{5-}$ and $[(HW_6O_{20})_n]^{3n-}$. The transient $[H_8W_6O_{24}]^{4-}$ ion is stabilized for hours in solutions of Me_4NCl.[128]

[122] C. P. J. Vuik and A. J. Poë, *Inorg. Chim. Acta*, 1979, **34**, 129.
[123] A. V. Babkov, R. A. Omarova, and A. I. Busev, *Koord. Khim.*, 1978, **4**, 1262.
[124] H. Kohara, *Chem. Abs.*, 1978, **88**, 198 348.
[125] S. Funahashi, K. Ishihara, and M. Tanaka, *Inorg. Chim. Acta*, 1979, **35**, L351.
[126] A. Goiffon and B. Spinner, *Bull. Soc. Chim. Fr., Part I*, 1977, 1081.
[127] M. R. S. Grade and J. M. Anes, *Chem. Abs.*, 1979, **91**, 9973.
[128] D. L. Kepert and J. H. Kyle, *J. Chem. Soc., Dalton Trans.*, 1978, 133.

8

Octahedral Complexes: Exchange and Replacement Processes Involving Solvated and Ligated Metal Ions

BY J. BURGESS

1 Solvated Metal Ions: Exchange with Solvent

This chapter starts with one of the simplest types of substitution process. The very simplicity of solvent exchange, and the fact that reagent and solvent are identical, have created problems in mechanism diagnosis. The most useful criterion to have emerged in the past few years for establishing mechanisms of solvent exchange is that of activation volume. A recent conference report includes a discussion of this topic;[1] recent papers give the relevant experimental background to high-pressure n.m.r. determination of activation volumes.[2,3] Correlation of activation enthalpies with solvent basicity parameters has also been discussed in relation to mechanisms of solvent exchange.[4]

Kinetic results for solvent exchange at solvento-metal cations are summarized in the Table.[5–16] In addition to these quantitative results, the rate of water exchange at zinc(II) has been estimated from a variety of complex formation kinetic results to lie between $10^{7.3}$ and $10^{7.9}$ s^{-1} at 25 °C.[17] Qualitative information relevant to DMSO exchange at ruthenium(II)[18] and at dioxouranium(VI)[19] is available from n.m.r. spectra and fluorescence studies respectively.

[1] T. W. Swaddle, *Chem. Abs.*, 1979, **90**, 142 639.
[2] H. Vanni, W. L. Earl, and A. E. Merbach, *J. Magn. Resonance*, 1978, **29**, 11; W. L. Earl, H. Vanni, and A. E. Merbach, *ibid.*, 1978, **30**, 571.
[3] H. Kelm and D. A. Palmer, *NATO Adv. Study Inst. Ser., Ser. C*, 1978, **C41**, 281; D. A. Palmer and H. Kelm, *ibid.*, p. 435 (*Chem. Abs.*, 1979, **90**, 61 774, 61 776).
[4] O. W. Kolling, *Trans. Kansas Acad. Sci.*, 1978, **81**, 303 (*Chem. Abs.*, 1979, **90**, 210 784).
[5] D. L. Pisaniello and S. F. Lincoln, *Aust. J. Chem.*, 1979, **32**, 715.
[6] F. L. Dickert, *Ber. Bunsenges. Phys. Chem.*, 1979, **83**, 593.
[7] D. L. Pisaniello, S. F. Lincoln, and E. H. Williams, *Inorg. Chim. Acta*, 1978, **31**, 237.
[8] E. von Goldammer and W. Kreysch, *Ber. Bunsenges. Phys. Chem.*, 1978, **82**, 463.
[9] J.-C. Boubel, J. Brondeau, and J.-J. Delpuech, *Adv. Mol. Relax. Interact. Processes*, 1977, **11**, 323 (*Chem. Abs.*, 1978, **88**, 80 035).
[10] P. J. Nichols and M. W. Grant, *Aust. J. Chem.*, 1978, **31**, 2581.
[11] K. E. Newman, F. K. Meyer, and A. E. Merbach, *J. Am. Chem. Soc.*, 1979, **101**, 1470.
[12] J.-C. Boubel. J.-J. Delpuech, and A. Peguy, *Mol. Phys.*, 1977, **34**, 1093.
[13] R. P. Bowen, G. J. Honan, S. F. Lincoln, T. M. Spotswood, and E. H. Williams, *Inorg. Chim. Acta*, 1979. **33**, 235.
[14] G. J. Honan, S. F. Lincoln, and E. H. Williams, *J. Chem. Soc., Dalton Trans.*, 1979, 320.
[15] G. J. Honan, S. F. Lincoln, and E. H. Williams, *Inorg. Chem.*, 1978, **17**, 1855.
[16] D. L. Pisaniello, S. F. Lincoln, and E. H. Williams, *J. Chem. Soc., Chem. Commun.*, 1978, 1047.
[17] S. Yamada, K. Ohsumi, and M. Tanaka, *Inorg. Chem.*, 1978, **17**, 2790.
[18] A. R. Davies, F. W. B. Einstein, N. P. Farrell, B. R. James, and R. S. McMillan, *Inorg. Chem.*, 1978, **17**, 1965.
[19] Yu. E. Nikitin, Yu. I. Murinov, D. D. Afonichev, G. S. Parshin, and V. P. Kazakov, *Radiokhimiya*, 1978, **20**, 244 (*Chem. Abs.*, 1978, **89**, 31 456).

Table *Kinetic parameters for solvent exchange at metal cations; rate constants (at temperature/*K *stated) are in* s^{-1}, *activation enthalpies in* kcal mol^{-1}, *activation entropies in* cal K^{-1} mol^{-1}, *and activation volumes in* cm^3 mol^{-1} *(at* 298 K). *The nucleus monitored (n.m.r.) is also indicated*

	DMSO	MeCN	DMF	Acetone	TMU	HMPA	TMP
Mg^{2+}			$k_{215}=23.5$ $\Delta H^{\ddagger}=18.6$ $\Delta S^{\ddagger}=+35$ (^{1}H) (ref. 5)	$\tau_{289}^{-1}=2.8\times10^5$ $\Delta H^{\ddagger}=12$ $\Delta S^{\ddagger}=+6.2$ (^{13}C) (ref. 6)			$k_{225}=683$ $\Delta H^{\ddagger}=12.3$ $\Delta S^{\ddagger}=+9.4$ (^{31}P) (ref. 7)
Mn^{2+}	$k_{298}=2.7\times10^6$ $\Delta H^{\ddagger}=8.9$[a] $\Delta S^{\ddagger}=+0.7$ (^{1}H; ^{13}C) (ref. 9)						
Ni^{2+}	$k_{298}=9.8\times10^3$[b] $\Delta H^{\ddagger}=12$ [b] $\Delta S^{\ddagger}=0$ [b] (^{13}C) (ref. 10)	$k_{289}=2840$ $\Delta H^{\ddagger}=15.4$ $\Delta S^{\ddagger}=+8.9$ $\Delta V^{\ddagger}=+9.6$[c] (^{1}H) (ref. 11)		$\tau_{298}^{-1}=1.3\times10^5$ $\Delta H^{\ddagger}=16.2$ $\Delta S^{\ddagger}=+18.6$ (^{13}C) (ref. 6)		$\Delta H^{\ddagger}=3.6$ (^{31}P) (ref. 12)	
						Dissoc. path / Assoc. path	
UO_2^{2+}			$k_{220}=199$ $\Delta H^{\ddagger}=7.7$ $\Delta S^{\ddagger}=-12.8$ (^{1}H) (ref. 13)		$k_{273}=73$ $\Delta H^{\ddagger}=19.1$ $\Delta S^{\ddagger}=+20.4$ (^{1}H) (ref. 14)	$k_{273}=12.5$ / $k_{273}=173$ [d] $\Delta H^{\ddagger}=3.4$ / $\Delta H^{\ddagger}=5.4$ $\Delta S^{\ddagger}=-41.5$ / $\Delta S^{\ddagger}=-29$ (^{1}H) (ref. 15)	
Sc^{3+}							$k_{300}=66$ $\Delta H^{\ddagger}=7.1$ $\Delta S^{\ddagger}=-27$ (^{1}H; ^{31}P) (ref. 16)

[a] The value of 3.4 kcal mol^{-1} for the activation energy for DMSO exchange at Mn^{2+} (ref. 8) is admitted to be unexpectedly low. [b] *Cf.* 11×10^3, 12.2, and +1.2 respectively (J.-C. Boubelet and J.-J. Delpuech, *Mol. Phys.*, 1974, **27**, 113). [c] $\Delta\beta^{\ddagger}$ is negligibly small. [d] M^{-1} s^{-1}.

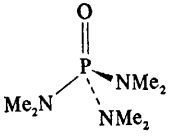
Mechanisms of solvent exchange in the systems included in the Table have been established or suggested from the kinetic parameters and from variation in exchange rates with solvent composition in solvent mixtures containing the solvent in question and a non-co-ordinating 'inert' co-solvent. Examples of the latter approach include exchange of trimethyl phosphate at magnesium(II), with CD_2Cl_2 or $(CD_3)_2CO$ as inert co-solvent,[7] and DMF at dioxouranium(VI), with CD_2Cl_2 as inert co-solvent.[13] Exchange at magnesium(II),[5,7] nickel(II),[11] and dioxouranium(VI)[13,14] is in general dissociative. The only exception appears to involve the powerful donor hexamethylphosphoramide, the kinetics of whose exchange at dioxouranium(VI) indicate parallel associative and dissociative paths.[15] Exchange of trimethyl phosphate at magnesium(II) may be S_N1(lim), or D, in mechanism,[7] as may exchange of DMF at iron(III).[20] There appears to be an isokinetic relationship for solvent exchange at magnesium(II);[5-7] the non-inclusion of methanol in this plot suggests that there may be some error in published kinetic parameters for this solvent. There are sometimes marked disagreements between published values of activation enthalpies and entropies from different sources for a given cation–solvent system. A striking example is that of DMSO exchange at nickel(II).[21] In such circumstances it is important that the full Swift and Connick equations be used to obtain the activation parameters; all approximations should be eschewed.[11]

Kinetic parameters have been reported for solvent exchange at several ternary complexes. Many investigations concern nickel(II); solvents include methanol,[22] DMF,[23] acetonitrile,[23,24] DMSO,[25] and tris(dimethylamino)phosphine oxide.[26] Kinetics of DMF exchange at $[M(NH_3)_5(DMF)]^{3+}$ (M = Co or Rh)[27] and of acetonitrile at $[SbCl_5(MeCN)]$[28] have also been described. Again the mechanisms are usually dissociative, though the activation volume for DMF exchange with the $[Rh(NH_3)_5(DMF)]^{3+}$ cation suggests a predominantly associative mechanism here.[27]

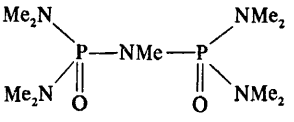
2 Ligated Metal Ions: Ligand Exchange

Several ligand exchange reactions are closely related to the solvent exchange reactions referred to in the previous section, in that the ligands concerned are related to frequently studied solvent molecules. Examples of such ligands include pyridine *N*-oxide [exchange at nickel(II) in D_2O],[29] tris-dimethylaminophosphine oxide (1) [exchange at nickel(II) again],[30] and the bidentate nipa (2).[31] For the last-named ligand exchange is extremely slow compared with unidentate solvent

[20] R. Schmid and V. N. Sapunov, *Int. J. Chem. Kinet.*, 1979, **11**, 1.
[21] See, *e.g.*, J. Burgess, 'Metal Ions in Solution,' Ellis Horwood, Chichester, 1978, Chapter 11.
[22] F. L. Dickert, *Z. Phys. Chem. (Frankfurt am Main)*, 1977, **106**, 155.
[23] L. L. Rusnak, E. S. Yang, and R. B. Jordan, *Inorg. Chem.*, 1978, **17**, 1810.
[24] N. Herron and P. Moore, *J. Chem. Soc., Dalton Trans.*, 1979, 441.
[25] C. L. Watkins and M. E. Harris, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1769.
[26] J.-C. Boubel, J.-J. Delpuech, and A. Peguy, *J. Chem. Soc., Dalton Trans.*, 1978, 1506.
[27] S. T. D. Lo, M. J. Sisley, and T. W. Swaddle, *Can. J. Chem.*, 1978, **56**, 2609.
[28] R. Good, D. R. Zbinden, J. E. Kessler, and A. E. Merbach, *Inorg. Chim. Acta Lett.*, 1978, **28**, L155.
[29] J. C. Ronfard-Haret and C. Chachaty, *J. Phys. Chem.*, 1978, **82**, 1541.
[30] J.-C. Boubel, J.-J. Delpuech, and A. Peguy, *J. Chem. Soc., Dalton Trans.*, 1978, 1506.
[31] P. R. Rubini, L. Rodehüser, and J.-J. Delpuech, *Z. Naturforsch.*, 1978, **33b**, 684.



(1)



(2)

analogues. Kinetics of ligand exchange involving nipa have been studied for several metal ions.[32] Rate constants and activation parameters are reported for exchange at Mg^{2+}, Ca^{2+}, Sr^{2+}, and even Li^{+}. Reaction is too slow to monitor for Al^{3+}, Ga^{3+}, In^{3+} or Be^{2+} even at 120 °C. N.m.r. spectroscopy is the ubiquitous tool for use in this area of kinetics. It was used in the foregoing examples, and in studying serine exchange at copper(II) and establishing fast exchange of $SiMe_3$ at cadmium(II).[33]

The rate law, rate constants, and activation parameters have been obtained for exchange of trifluoroacetate with its dinuclear molybdenum(II) complex $[Mo_2(O_2CCF_3)_4]$. The results are discussed with particular reference to related dimolybdenum and dirhenium metal–metal-bonded compounds.[34] A preliminary report on copper(II) exchange with copper(II)–salen complexes gives evidence to support the hypothesis of the intermediacy of dinuclear species.[35]

N.m.r. studies of ligand exchange involving aminopolycarboxylate ligands include those of egta at calcium(II)[36] and of edta at magnesium(II), calcium(II), and strontium(II).[37] The relative importance of dissociative and associative (*i.e. via* an L—M—L intermediate) paths has been assessed, and the reactivities of variously protonated and deprotonated forms of the ligands and the complexes have been considered.

Several papers have dealt with exchange reactions of bis-Schiff base–copper(II) complexes, which may be classed as octahedral, tetragonal, or square-planar according to taste and bias. Substituent effects have been established for Cu^{2+} exchange with bis-salicylaldiminato-complexes;[38] sufficiently large substituents lead to distortions towards tetrahedral geometry around the copper and thus to faster exchange.[38, 39] Ligand exchange in complexes of this type containing nitrosyl groups can be monitored by e.s.r. spectroscopy.[40] Kinetics of amine exchange with copper(II)–Schiff base complexes have been studied as part of an investigation into factors controlling stabilities;[41] amine exchange occurs with

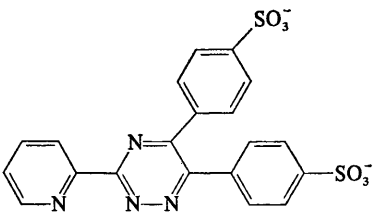
[32] A. A. Popel', A. V. Zakharov, I. I. Evgen'eva, and L. V. Vasil'eva, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1978, **23**, 1351.
[33] L. Rösch and G. Alnau, *Angew. Chem. Int. Ed. Engl.*, 1979, **18**, 60.
[34] K. Teramoto, Y. Sasaki, K. Migita, M. Iwaizumi, and K. Saito, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 446.
[35] G. Köhler and H. Elias, *Inorg. Chim. Acta Lett.*, 1979, **34**, L215.
[36] P. Mirti, *J. Inorg. Nucl. Chem.*, 1979, **41**, 323.
[37] P. Mirti, *J. Inorg. Nucl. Chem.*, 1978, **40**, 833.
[38] H. Winkler, K. J. Wannowius, and H. Elias, *Z. Phys. Chem.* (*Frankfurt am Main*), 1977, **107**, 57.
[39] G. R. Dukes and S. R. Lovelady, *J. Chem. Soc., Chem. Commun.*, 1978, 583.
[40] S. S. Eaton and G. R. Eaton, *Inorg. Nucl. Chem. Lett.*, 1979, **15**, 29.
[41] P. Nagy and R. Herzfeld, *Szegedi Tanarkepzo Foiskola Tud. Kozl.*, 1976, 33 (*Chem. Abs.*, 1978, **89**, 95 828).

free Schiff base after rate-determining loss of Schiff-base ligand from the metal ion.[42]

3 Ligated Metal Ions: Ligand Replacement

One of the most active areas remains that of displacement of di-imine ligands from low-spin iron(II) complexes by such nucleophiles as cyanide or hydroxide. Argument continues as to whether the mechanisms of such reactions involve initial attack at the iron or at the co-ordinated ligand (giving a Meisenheimer-type intermediate). Discussion of this subject is split between this and the next section.

Stereochemical studies of the reaction of cyanide with tris-1,10-phenanthroline-iron(II)[43] indicate inversion resulting from cyanide attack on the iron atom. Recent stereochemical studies on the analogous 3-methyl-1,10-phenanthroline complex, which contains a useful additional stereochemical marker in the methyl group, lead to the same mechanistic conclusions.[44] Volumes of activation for hydroxide and for cyanide attack at the $[Fe(bipy)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$ cations lie between $+19$ and $+22$ cm^3 mol^{-1}. These values are surprising for an associative mechanism, no matter where the attack takes place.* The authors favour an interpretation in which ion-pairs play a central role,[45] as in the Eigen–Wilkins mechanism for complex formation. However, solvation effects may be large here, as both hydroxide and cyanide will be heavily hydrated. Desolvation of these anions could produce a significant positive contribution to the overall activation volume for an associative mechanism. The resolution of this ion-pairing question lies in principle in experiments on negatively charged complexes, but, as mentioned elsewhere, the kinetic patterns for the obvious candidate, $[Fe(fz)_3]^{4-}$ [fz = (3)] are not straightforward. Ion-pairs are important in photochemical attack of thio-cyanate at $[Ru(bipy)_3]^{2+}$. Here there is no question of attack of the relatively weak nucleophile NCS^- at the co-ordinated ligand.[46]



(3)

* High-pressure stopped-flow studies on the reaction of 2,4,6-trinitroanisole with methoxide indicate an activation volume of -7.2 cm^3 mol^{-1} for formation of the Meisenheimer complex in this system (N. Takisawa, M. Sasaki, F. Amita, and J. Osugi, *Chem. Lett.*, 1979, 671).

[42] R. Herzfeld and P. Nagy, *Magy. Kem. Lapja*, 1977, **32**, 588 (*Chem. Abs.*, 1978, **89**, 49 481.
[43] R. D. Archer and D. D. Dollberg, *Inorg. Chem.*, 1974, **13**, 1551.
[44] R. D. Archer, personal communication.
[45] G. A. Lawrance, D. R. Stranks, and S. Suvachittanont, *Inorg. Chem.*, 1979, **18**, 82.
[46] P. E. Hoggard and G. B. Porter, *J. Am. Chem. Soc.*, 1978, **100**, 1457.

The effect of the nature of various di-imine ligands in reactivity has been studied for reaction with hydroxide[47] and with cyanide.[48] In the latter investigation the effects of ligand denticity were probed by employing a series of Schiff-base ligands with denticities between two and six. Kinetic parameters for the reaction of the $[Fe(5\text{-Br-phen})_3]^{2+}$ cation with cyanide in aqueous solution have been reported;[49] kinetics of reactions of di-imine–iron(II) complexes with cyanide have also been studied in ethylene carbonate– and propylene carbonate–water mixtures.[50] Effects of solvent variation on reactivity have been dissected into initial-state and transition-state components for the reaction of $[Fe(phen)_3]^{2+}$ with hydroxide in methanol– and in acetone–water mixtures[51] (*cf.* p. 294).

Some years ago it was claimed that the $[Fe(fz)_3]^{4-}$ anion reacted with oxalate by a bimolecular mechanism.[52] Nucleophilic attack of oxalate at metal or ligand here seemed equally unlikely, and a reinvestigation of this reaction, with a parallel study of reactions of this complex with edta and related ligands, indicates a dissociative mechanism, with ligand competition causing the observed kinetic pattern.[53]

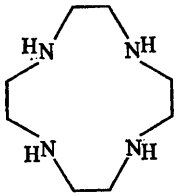
The 4-aminopyridine ligand is easily and quickly displaced from $[Fe(CN)_5(4\text{-}NH_2\text{-py})]^{3-}$ by, for instance, 2-methylpyrazine. Weak iron–nitrogen bonding in this complex anion is consistent with the exceptionally low wavelength of the metal-to-ligand charge-transfer band.[54] Substitution at complexes of this type[55] is generally thought to proceed by a *D* mechanism, though some authors entertain the possibility of an I_d mechanism, at least in certain cases.[56] The latest evidence purporting to support an I_d mechanism is not, however, entirely convincing (see p. 287). The first step in the oxidation of $[Fe^{II}(CN)_5(CO)]^{3-}$ by iron(III) is a substitution step to give a mixed-valence intermediate $[Fe^{II}(CO)(CN)_5Fe^{III}]$. Similar mechanisms may be involved in the formation of such species as Prussian Blue and Turnbull's Blue.[57]

Kinetic data have been extracted by a complete lineshape analysis for rates of exchange of imidazole and its 1- and 2-methyl derivatives at the $[Fe(LLLL)(X\text{-imid})]^{2+}$ cations (LLLL = 2,3,9,10-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-1,3,8,10-tetraene). Reaction rates for these *D* substitutions are determined by electronic rather than by steric factors.[58]

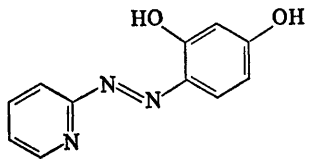
Several papers deal with ligand replacement (by edta and related ligands) in copper(II) complexes. The role and structure of mixed-ligand intermediates in the displacement of trigly or glycinamide by edta or cydta have been discussed.

[47] M. J. Blandamer, J. Burgess, P. Cookson, D. L. Roberts, P. Wellings, F. M. Mekhail, and P. Askalani, *J. Chem. Soc., Dalton Trans.*, 1978, 996.
[48] M. J. Blandamer, J. Burgess, R. I. Haines, F. M. Mekhail, and P. Askalani, *J. Chem. Soc., Dalton Trans.*, 1978, 1001.
[49] J. Burgess and F. M. Mekhail, *Transition Met. Chem.*, 1978, **3**, 162.
[50] M. J. Blandamer, J. Burgess, S. J. Hamshere, and F. M. Mekhail, *Transition Met. Chem.*, 1979, **4**, 77.
[51] M. J. Blandamer, J. Burgess, and D. L. Roberts, *J. Chem. Soc., Dalton Trans.*, 1978, 1086.
[52] V. V. S. E. Dutt and H. A. Mottola, *Anal. Chem.*, 1977, **49**, 319.
[53] J. Burgess and M. V. Twigg, *Transition Met. Chem.*, 1978, **3**, 88.
[54] N. V. Hrepic and J. M. Malin, *Inorg. Chem.*, 1979, **18**, 409.
[55] See also, *e.g.*, A. P. Szecsy, *Diss. Abs. Int. B*, 1979, **39**, 3323 (*Chem. Abs.*, 1979, **90**, 110 641).
[56] I. Murati, D. Pavlović, A. Šustra, and S. Ašperger, *J. Chem. Soc., Dalton Trans.*, 1978, 500.
[57] H. E. Toma and L. A. A. Oliveira, *Inorg. Nucl. Chem. Lett.*, 1979, **33**, L143.
[58] C. E. Holloway, D. V. Stynes, and C. P. J. Vuik, *J. Chem. Soc., Dalton Trans.*, 1979, 124.

Differences between results with edta and cydta are attributed to steric factors.[59] Both steric and proton-transfer barriers lead to slow reaction of [Cu^{II}(trigly)] with the macrocyclic ligand 1,4,7,10-tetra-azacyclododecane (4).[60] A mixed-ligand intermediate is involved in the replacement of par (5) by cydta in [Cu^{II}-(par)]. Reaction rates are modified in the presence of such anions as acetate,



(4)



(5)

azide, or halides owing to equilibria involving the generation of significant amounts of complexes [Cu^{II}(par)L]$^-$.[61] The rate law and rate constants have been determined for the displacement of 4-(4,5-dimethyl-2-thiazolylazo)-2-methylresorcinol (dmtamr) from its copper(II) complex by cydta, in order to assess the likely usefulness of dmtamr as a metallochromic indicator in cydta titrations of various metal ions.[62]

Ligand replacements for which kinetic data have been reported include [Ni(dgen)]$^{2+}$ plus edta (parallel dissociative and associative paths),[63] [Pb(edta)] plus *R*-(−)-pdta,[64] polyether complexes of lead(II) plus nitrogen macrocycles,[65] metal(II)-oxine complexes plus edta,[66] and a variety of analogous reactions involving lanthanide and actinide complexes (see Chapter 10). Kinetic data are also available for ligand exchange between trien and tetren complexes of cadmium(II) and the edta complex of copper(II).[67]

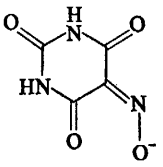
Earlier kinetic results on the displacement of ttha from nickel(II) by cyanide[68] have been reinterpreted in terms of a slightly different reaction scheme.[69] A tentative mechanism has been proposed to explain kinetic observations on the displacement of quadridentate α-amine oximes from copper(II); the first step is rapid but reversible attack by the cyanide.[70]

Rate constants for various ligand replacement reactions in the system of equation (1) have been determined for use in calculating stability constants for

$$[Ni(en)_2]^{2+} + 4CN^- \rightleftharpoons [Ni(CN)_4]^{2-} + 2en \qquad (1)$$

[59] J. M. T. Raycheba, G. R. Dukes, and D. W. Margerum, *Inorg. Chem.*, 1978, **17**, 2449.
[60] M. Kodama and E. Kimura, *Inorg. Chem.*, 1978, **17**, 3716.
[61] M. Tabata and M. Tanaka, *Inorg. Chem.*, 1978, **17**, 2779.
[62] C. Sanchez Pedreno, *Quim. Anal.*, 1977, **31**, 249 (*Chem. Abs.*, 1978, **89**, 118 418).
[63] R. Pearson and G. K. Pagenkopf, *Inorg. Chem.*, 1978, **17**, 1799.
[64] J. D. Carr, *Inorg. Chem.*, 1978, **17**, 1095.
[65] M. Kodama and E. Kimura, *Inorg. Chem.*, 1978, **17**, 2446.
[66] K. Haraguchi, K. Nakagawa, and S. Ito, *J. Inorg. Nucl. Chem.*, 1979, **41**, 379.
[67] T. Katsuyama and T. Kumai, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 1072.
[68] V. Stara and M. Kopanica, *Collect. Czech. Chem. Commun.*, 1972, **37**, 2882.
[69] K. Kumar and P. C. Nigam, *J. Coord. Chem.*, 1979, **9**, 139.
[70] R. K. Murmann and B. Monzyk, *Inorg. Chem.*, 1978, **17**, 2461.

sundry ternary complexes which are intermediates in this system.[71] Although the displacement of one violurato-ligand (6) from $[Ru(viol)_3]^-$ by nitrite follows a second-order rate law, the rate-determining step is thought, on stereochemical



(6)

and kinetic grounds, to be dissociative breaking of one ruthenium(II)–ligand bond.[72] Rate constants have been determined for reactions of three tetra-μ-carboxylatorhodium(II) compounds with pyridine, picolinic acid, niacin, and isonicotinic acid.[73]

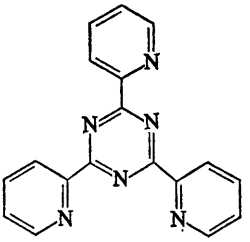
4 Ligated Metal Ions: Attack at Co-ordinated Ligand

As intimated at the beginning of the previous section, discussion of the mechanisms of reactions of nucleophiles with iron(II)–di-imine complexes continues to flourish. The main question is whether nucleophiles such as hydroxide, methoxide, or cyanide[74] attack at the central metal atom or at the co-ordinated di-imine ligand. The original assumption of direct attack at iron in complexes of the $[Fe(phen)_3]^{2+}$ type was questioned several years ago.[75] Since then a considerable body of evidence has been presented in support of initial attack at the ligand but a body of opinion remains that is sceptical of such a mechanism.

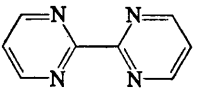
There are advantages in working with ruthenium(II) complexes rather than with the less inert iron(II) complexes. Hydroxide attack at the $[Fe(tptz)_2]^{2+}$ cation, where tptz is the triazine ligand (7), results in complete decomposition of the complex, but reaction of the $[Ru(tptz)_2]^{2+}$ cation with hydroxide involves an initial reversible step,[76] with very slow subsequent decomposition to metal ion and free tptz. This initial reversible step is thought to produce the ligand-substituted intermediate $[Ru(tptzOH)(tptz)]^+$; the analogous intermediate for iron can have only a transient existence.[77]* The kinetics of hydroxide attack at the tris-2,2′-bipyrimidine [bipym (8)] complexes of iron(II) and of ruthenium(II) have been established. Nucleophilic attack at the co-ordinated ligand in the ruthenium compound is indicated by the observed cleavage of a bipym ligand. There is kinetic evidence for attack of hydroxide at the ligand for the iron complex too.

* Rate laws, rate constants, activation parameters, and enthalpies and entropies of reaction have been determined for hydroxide attack at the bis-tptz complexes of cobalt(II) and of nickel(II) (P. A. Williams, *Transition Met. Chem.*, 1979, **4**, 24).

[71] K. Kumar and P. C. Nigam, *Indian J. Chem., Sect. A*, 1978, **16**, 518.
[72] C. Bremard, G. Nowogrocki, and S. Sueur, *Inorg. Chem.*, 1978, **17**, 3220.
[73] J. L. Bear, R. A. Howard, and J. E. Korn, *Inorg. Chim. Acta*, 1979, **32**, 123.
[74] M. T. Beck, *J. Indian Chem. Soc.*, 1977, **54**, 19.
[75] R. D. Gillard, *Inorg. Chim. Acta*, 1974, **11**, L21; *Coord. Chem. Rev.*, 1975, **16**, 67.
[76] V. M. S. Gil, R. D. Gillard, P. A. Williams, R. S. Vagg, and E. C. Watton, *Transition Met. Chem.*, 1979, **4**, 14.
[77] R. D. Gillard and P. A. Williams, *Transition Met. Chem.*, 1978, **3**, 334.



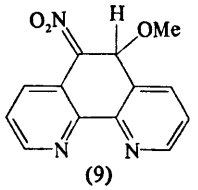
(7)



(8)

These 2,2′-bipyrimidine complexes are relatively unstable, and attack by azide and thiocyanate, not established for, *e.g.*, the $[Fe(bipy)_3]^{2+}$ cation, has been observed for the $[Fe(bipym)_3]^{2+}$ cation.[78] The ferrozine [fz=(3)] complex $[Fe(fz)_3]^{4-}$ is very stable and one of the most inert di-imine–iron(II) complexes. There is here ample time to demonstrate the rapid formation of an intermediate, and to follow the decay of the $[Fe(fz)_3]^{4-}$ and the intermediate by conventional spectroscopic techniques. The use of aqueous methanol as solvent proved advantageous, as this increased the chemical potential of the hydroxide ion and thence increased formation of the intermediate. The 4− charge on the complex here, in contrast to the great majority of di-imine complexes studied, rules out significant ion-pairing between complex and hydroxide.[79]

Attack of methoxide (in DMSO to maximize its chemical potential) at 5-nitro-1,10-phenanthroline, free and co-ordinated to iron(II) and ruthenium(II), has been demonstrated by 220 MHz ^1H n.m.r. spectroscopy. The Meisenheimer-compound from the free ligand is stable for days in a sealed tube; its n.m.r. spectrum shows the methoxide to be at the 6-position, *ortho-* to the nitro-group (9). Attack



(9)

at co-ordinated 5-nitro-1,10-phenanthroline is also believed to occur at the 6-position.[80] The ^{13}C n.m.r. spectrum of so-called $[Ir(phen)_2(unidentate\ phen)(OH)]^{2+}$ has been run,[81] but unfortunately not interpreted. It is therefore not clear whether this cation contains unidentate phen or whether the hydroxide is substituted in the co-ordinated phen. In the case of the reaction of the $[Fe(5\text{-}NO_2\text{-}phen)_3]^{2+}$ cation with cyanide it has proved possible to precipitate the

[78] R. D. Gillard, R. J. Lancashire, and P. A. Williams, *Transition Met. Chem.*, 1979, **4**, 115.
[79] M. J. Blandamer, J. Burgess, and P. Wellings, *Transition Met. Chem.*, 1979, **4**, 95.
[80] D. W. W. Anderson, P. Roberts, M. V. Twigg, and M. B. Williams, *Inorg. Chim. Acta Lett.*, 1979, **34**, L281.
[81] J. L. Kahl, K. Hanck, and K. DeArmond, *J. Inorg. Nucl. Chem.*, 1979, **41**, 495.

intermediate *en route* to $[Fe(5\text{-}NO_2\text{-}phen)_2(CN)_2]$.[82,83] Spectroscopic studies[82] and other evidence[83] are consistent with cyanide being attached to the co-ordinated ligand in this intermediate, though there is some disagreement over its exact nature.

5 Exchange of Central Metal Atom

Recent kinetic studies of metal ion exchanges include those of europium(III) with its cydta complex[84] and of various lanthanides(III) with their respective dtpa complexes.[85] Kinetic studies of metal ion replacement include reactions of nta, edda, heedta, egta, cydta, and dtpa complexes of zinc(II) with copper(II),[86] of edta nedta, cydta, and dtpa complexes of lead(II) with cobalt(II),[87] of the edta complex of nickel(II) with indium(III),[88] and of ttha complexes of cadmium(II) with lanthanides(III).[89] There are again several systems mainly concerned with 3+ and 4+ ions, for example those involving edta and dtpa complexes of lanthanides.[90] In systems containing ions of high charge, it seems to be easier to demonstrate the existence of dinuclear intermediates of the type invoked in 'associative' (*cf.* above) pathways.

[82] R. D. Gillard and P. A. Williams, *Transition Met. Chem.*, 1977, **2**, 247.
[83] J. Burgess and R. I. Haines, *J. Chem. Soc., Dalton Trans.*, 1978, 1447.
[84] W. D'Olieslager and A. Oeyen, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1565.
[85] A. J. Mahmood, *J. Bangladesh Acad. Sci.*, 1977, **1**, 103.
[86] E. Mentasti and E. Pelizzetti, *Inorg. Chem.*, 1978, **17**, 3133.
[87] T. Nozaki and M. Sakamoto, *Nippon Kagaku Zasshi*, 1978, 639 (*Chem. Abs.*, 1978, **89**, 12 703).
[88] T. Takahashi, *Fukushima Kogyo Koto Semmon Gakko Kiyo*, 1976, 39 (*Chem. Abs.*, 1978, **89**, 169 784).
[89] Y. Masuda, T. Nakamori, and E. Sekido, *Nippon Kagaku Kaishi*, 1978, 204 (*Chem. Abs.*, 1978, **88**, 127 125).
[90] T. V. Ternovaya, V. P. Shelest, and N. A. Kostromina, *Russ. J. Inorg. Chem.* (*Engl. Transl.*) 1978, **23**, 1650.

9

Octahedral Complexes: Isomerization and Racemization

BY P. MOORE

1 Complexes of Cobalt(III), Rhodium(III), Iridium(III) and Chromium(III)

Three studies involving intramolecular linkage isomerizations of the unidentate NO_2^-, NCS^-, and $MeCO_2^{2-}$ ions have appeared.[1-3]

Volumes of activation for reaction (1) are -6.7 ± 0.4, -7.4 ± 0.4, and -5.9 ± 0.6 cm^3 mol^{-1} for M = Co^{III}, Rh^{III}, and Ir^{III} respectively. The partial

$$[M(NH_3)_5ONO]^{2+} \longrightarrow [M(NH_3)_5NO_2]^{2+} \quad (1)$$

molar volumes of the nitrito- and nitro-Co^{III} complexes are 82.3 ± 1.4 and 69.4 ± 0.1 cm^3 mol^{-1}, and an intramolecular mechanism, established many years ago by tracer experiments, also fits with the volume profile diagram.[1]

Activation parameters established for reaction (2) in aqueous acidic solution, and in DMSO solution, are ΔH^*/kcal mol^{-1} = 25.0 and 25.5, ΔS^*/cal K^{-1}

$$[Co(NH_3)_5SCN]^{2+} \longrightarrow [Co(NH_3)_5NCS]^{2+} \quad (2)$$

mol^{-1} = 3.4 and 0.5, and ΔV^*/cm^3 mol^{-1} = -5.3 ± 0.8 and -1.0 ± 1.2 respectively. These results are also consistent with an intramolecular mechanism and exclude the possibility of formation of an intimate ion-pair in the transition state. It is postulated that a labile intermediate is formed in which the cobalt ion interacts with a filled π-orbital spread over the whole thiocyanate ligand, possibly with some back-bonding involved too.[2]

Reaction of $[Co(NH_3)_5(^{18}OH)]^{2+}$ ion with acetyl perchlorate in trimethyl phosphate solution gives $[Co(NH_3)_5(^{18}OCOMe)]^{2+}$ ion. However, in more polar solvents isomerization to the $[Co(NH_3)_5(OC^{18}OMe)]^{2+}$ ion occurs, and during purification (by recrystallization) it is necessary to avoid polar solvents like H_2O to prevent the linkage isomerization. At room temperature 32% rearrangement occurs in the solid phase after 90 days.[3]

Activation parameters, ΔV^*, ΔH^*, and ΔS^* for the isomerization of *trans*-$[Co(en)_2(OCOMe)(OH_2)]^{2+}$ ion under different conditions are collected in Table 1.[4] Previous high-pressure studies[5] of the *trans* → *cis* isomerizations of

[1] M. Mares, D. A. Palmer, and H. Kelm, *Inorg. Chim. Acta*, 1978, **27**, 153.
[2] D. A. Palmer, R. van Eldik, and H. Kelm, *Inorg. Chim. Acta*, 1978, **30**, 83.
[3] L. M. Jackman, J. F. Dormish, R. M. Scott, R. H. Portman, and R. D. Minard, *Inorg. Chem.*, 1979, **18**, 1503.
[4] G. A. Lawrance and S. Suvachittanant, *J. Coord. Chem.*, 1979, **9**, 13.
[5] P. L. Kendall, G. A. Lawrance, and D. R. Stranks, *Inorg. Chem.*, 1978, **17**, 1166.

Table 1 *Activation parameters* [a] *at 25 °C for the isomerization of* trans-$[Co(en)_2(OCOMe)(OH_2)]^{2+}$ *ion in different media (data from ref.* 4)

Conditions	$\Delta V^{\ddagger}$/cm^3 mol^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
0.05 M $HClO_4$	7.9±0.3	28	14.6
0.05 M $HClO_4$ + 0.95 M $NaClO_4$	6.5±0.4	27	11.0
1.0 M $HClO_4$	5.6±0.6	27	11.2

[a] $\Delta\beta^{\ddagger} \approx 0$ in the high-pressure work.

$[Cr(mal)_2(OH_2)_2]^-$ and $[Cr(ox)_2(OH_2)]^-$ ions gave $\Delta V^{\ddagger} = +8.9$ and -16.6 cm^3 mol^{-1} respectively, and despite the markedly different values of $\Delta V^{\ddagger}$ all of these results can be interpreted in terms of dissociative mechanisms. In the case of $[Cr(ox)_2(OH_2)_2]^-$ ion ($\Delta V^{\ddagger} = -16.6$ cm^3 mol^{-1}, $\Delta\beta^{\ddagger} = -1.8$ cm^3 mol^{-1} kbar^{-1}), opening of one end of a chelate oxalate ion is proposed, with solvent electrostriction by the released, negatively charged carboxylate ion accounting for the negative $\Delta V^{\ddagger}$ value. For $[Cr(mal)_2(OH_2)_2]^-$ ion ($\Delta V^{\ddagger} = +8.9$ cm^3 mol^{-1}, $\Delta\beta^{\ddagger} \approx 0$), dissociative interchange of an aqua-ligand is proposed (I_d mechanism), and this mechanism is also postulated for the $[Co(en)_2(OCOMe)(OH_2)]^{3+}$ ion.[4]

The widely held view that complexes of the type *cis*-$[Co(en)_2(X)Y]^{n+}$ aquate with retention of configuration must be modified in the light of a more recent study.[6] The complexes (X = Y = Cl^- or Br^-; X = Cl^- or Br^-, Y = OH^-; X = Cl^-, Br^-, or DMSO, Y = N_3^-) were resolved, and their aquation reactions studied spectrophotometrically and polarimetrically in dilute $HClO_4$ at 25 °C. All were found to aquate with significant stereochemical change (15—30%) but with the chiral *cis*-product always fully active. The product stereochemistries and rates of isomerization and racemization are collected in Tables 3 and 4 of Chapter 5. The Hg^{II}-, NO^+- (azido-complexes), and Cl_2-induced (DMSO complex) reactions were also investigated and the conclusion reached that for (+)-*cis*-$[Co(en)_2(X)Y]^{n+}$ ions the steric course of the spontaneous and induced aquation reactions is essentially the same and independent of the nature of the leaving group.

Ligand-field irradiation of *cis*-*β*-$[Co(L)Cl_2]^+$ and *cis*-*β*-$[Co(L)Cl(OH_2)]^{2+}$ ions gives *trans*-$[Co(L)Cl(OH_2)]^{2+}$ ion (L = 2,3,2-tet) as the only photoproduct ($10^3\Phi = 8.3$ and 5.3 respectively). However, photolysis of *cis*-*β*-$[Rh(L)Cl_2]^+$ gives both *cis*-*β*-$[Rh(L)Cl(OH_2)]^{2+}$ and *trans*-$[Rh(L)Cl(OH_2)]^{2+}$ ions (1:3 ratio) with a total quantum yield for Cl^- loss of 0.26. The *cis*-*β*-$[Rh(L)Cl(OH_2)]^{2+}$ ion photoisomerizes to the *trans*-product with $\Phi = 0.13$. In comparison with the analogous complexes of trien, the increased photoisomerization when L = 2,3,2-tet is justified in terms of a dissociative mechanism.[7]

The *trans*-*R*,*R*,*R*,*R*(*S*,*S*,*S*,*S*)-$[Co(cyclam)Cl_2]^+$ ion aquates to give 75% *trans*- and 25% *cis*-$[Co(cyclam)Cl(OH_2)]^{2+}$ ion ($10^3 k_{aq} = 1.75$ s^{-1} at $I = 1.0$ M $[NO_3^-]$, 10^{-2} M $[H^+]$, $\Delta H^{\ddagger} = 24.2 \pm 0.5$ kcal mol^{-1}, $\Delta S^{\ddagger} = +9.9 \pm 1.6$ cal K^{-1} mol^{-1}), and then isomerizes to 100% *cis*-complex with $10^2 k_i = 1.3$ s^{-1} at 25 °C, $\Delta H_{i}^{\ddagger} = 25.8$ kcal mol^{-1}, and $\Delta S_i^{\ddagger} = +19.3$ cal K^{-1} mol^{-1}. The cyclam configuratio is maintained throughout.[8]

[6] W. G. Jackson and A. M. Sargeson, *Inorg. Chem.*, 1978, **17**, 1348.
[7] E. Martins, E. B. Kaplan, and P. S. Sheridan, *Inorg. Chem.*, 1979, **18**, 2195.
[8] C. J. Cooksey and M. L. Tobe, *Inorg. Chem.*, 1978, **17**, 1558.

Rate data at 25 °C for the inversion of Λ-[Co(L)$_3$] [L=(−)-1-*N*-(α-phenylethyl)dithiocarbamate] in CH_2Cl_2 and CS_2 solution are $10^5k/s^{-1}=21$ and 8.5, $\Delta H^{\ddagger}$/kcal mol^{-1} = 19.2 and 19.0, and $\Delta S^{\ddagger}$/cal K^{-1} mol^{-1} = −9.4 and −10.6 respectively. Because of the long flexible tail in these molecules, a minimum of steric interaction occurs when the tails of all three ligands are wrapped around the molecule in the same sense. This is shown in Figure 1, where the (−)-ligand

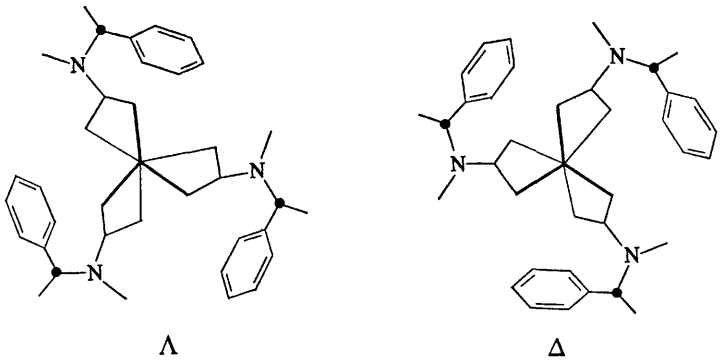


Figure 1

is depicted. In both the Λ- and Δ-forms the tails are arranged with right-hand chirality. For this reason, synthesis of these complexes starting with the (−)- and (+)-ligands gives Λ-[Co(−)-L$_3$] and Λ-[Co(+)-L$_3$] respectively.[9]

Rate data for the *mer* → *fac* isomerization of *trans*-[Co(dien)(L)(OH$_2$)$_2$]$^{3+}$ ions [L=H$_2$O, NH$_3$, py, or RNH$_2$ (R=PhCH$_2$, cyclohexylmethyl, or cyclohexyl)] and [Co(dien)(LL)(OH$_2$)]$^{3+}$ ions [LL=(NH$_3$)$_2$, 1,3-pn, or 1,2-pn (pn=propylenediamine)] are collected in Table 2.[10] The reactions were only studied over a narrow, 15 K, temperature range. The rate of *fac* → *mer* isomerization of *trans*-[Co(dien)(OH$_2$)$_3$]$^{3+}$ ion was also investigated in HClO$_4$ solution and found to be accelerated by addition of NO_3^- ion: $10^4k_{obs}/s^{-1}=3.1+17.1[NO_3^-]$ at

Table 2 *Rate data at* 25 °C, I=1.0 M (0.95 M [HNO$_3$]) *for the* mer → fac-*isomerization of* trans-[Co(dien)(L)(OH$_2$)$_2$]$^{3+}$ *and* [Co(dien)(LL)(OH$_2$)]$^{3+}$ *ions (data from ref.* 10)

L *or* LL	10^7 k/s^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1} [a]	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
H_2O	2470	26	+10
NH_3	16 200	22.5	+7
py	4650	33	+17.4
$PhCH_2NH_2$	13 700	22.5	+3.2
Cyclohexylmethylamine	25 300	22	+1.9
Cyclohexylamine	46 000	22.5	+6
$(NH_3)_2$	9.7	27	+4.1
$NH_2(CH_2)_3NH_2$	71.7	25	−0.24
$NH_2CH(Me)CH_2NH_2$	1.7	30	+9.3

[a] Reported E_a − 0.6 kcal mol^{-1}.

[9] R. A. Haines and S. M. F. Chan, *Inorg. Chem.*, 1979, **18**, 1495.
[10] D. A. House, *Inorg. Chim. Acta*, 1978, **30**, 281.

40 °C and $I = 1.0$ M. Formation of $[Co(dien)(ONO_2)(OH_2)_2]^{2+}$ ion as an intermediate of increased reactivity is postulated to account for the effect of nitrate ion. For the other reactions, a mechanism involving loss of H_2O to give a trigonal-bipyramidal transition state is postulated. The rate varies with the nature of the group in a *trans*-position with respect to the leaving water molecule (H_2O is observed to be far better than NH_3 as a *trans*-labilizing group with $\Delta H^{\ddagger}$ 3.6—7.2 kcal mol^{-1} lower), and also with the type of chelate ring system [*e.g.* (dien)(NH_3) or $(en)_2$]. The (dien)(NH_3) combinations isomerize more rapidly than *trans*-$(en)_2$ systems, with strained *mer*-dien more easily moving into a *fac*-position in the trigonal-bipyramidal transition state.[10]

The $(-)_D$-*u-fac*-$[Co(L)_2]^{3+}$ ion (L = di-2-aminoethyl sulphide) is stable in acidic solution, but in the presence of charcoal as a catalyst (involving trace Co^{II} formation) racemization occurs at 10^{-2} M $[H^+]$ without any detectable decomposition. A mechanism involving Co—S bond dissociation is proposed.[11] Similar studies are reported for $[Co(dien)L]^{3+}$ [L = Medien = $NH_2CH_2CH_2$-$N(Me)CH_2CH_2NH_2$] and $[Co(dien)_2]^{3+}$ ions. Three possible geometric isomers are shown in Figure 2. In homogeneous solution the *s-fac*- and *u-fac*-isomers of

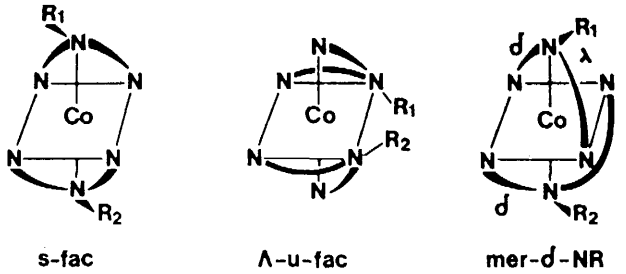


Figure 2

$[Co(dien)(L)]^{3+}$ ion after 2 days at 90 °C give an equilibrium mixture of *s-fac*:*u-fac*:*mer* = 81:10:9. The *u-fac*- and *mer*-isomers can be isolated by Sephadex cation-exchange column chromatography and identified by ^{13}C n.m.r. $[Co(dien)L]^{3+}$ ion in the presence of catalytic charcoal gives seven complexes. After 4 h at 80 °C, these are $[Co(dien)_2]^{3+}$ (*s-fac*:*u-fac*:*mer* = 5:23:19), $[Co(dien)(L)]^{3+}$ (*s-fac* and *u-fac*), and $[Co(L)_2]^{3+}$ (*s-fac* plus a little non-separable *mer*) in the ratio 23:4:26. The charcoal induces complete ligand dissociation and intermolecular exchange, whereas the homogeneous reactions proceed intramolecularly. At least two and probably three intramolecular rearrangement processes are postulated for the homogeneous reactions. Some pathways involve Co—N bond fission to give transient five-co-ordinate intermediates, but twist mechanisms *via* trigonal-prismatic transition states are also considered. Base catalysis involving conjugate-base formation was also observed.[12] Six isomers of $[Co(L)L^1]^{3+}$ ion (HL = D- and L-aspartic acid, HL^1 = L-histidine) have also been prepared and the kinetics of their isomerization reactions studied at 80 °C.[13]

[11] A. Hammershoei and E. Larsen, *Acta Chem. Scand., Ser. A*, 1978, **32**, 485.
[12] G. H. Searle, R. F. Keene, and S. F. Lincoln, *Inorg. Chem.*, 1978, **11**, 2362.
[13] M. Watabe, H. Yano, and S. Yoshikawa, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 61.

When L = L- and D-aspartate, $\Delta H^{\ddagger} = ca.$ 60 kcal mol^{-1} and 43 kcal mol^{-1} respectively.[14] The reactions are base-catalysed, and in acidic solutions or organic solvents the rates are slower or isomerization is not observed.

Four complex ions of general formula $[Cr(NH_3)_x(H_2O)_{4-x}Cl_2]^+$ have been investigated (x = *mer*-3, *cis*-2, *trans*-2, or 1), all of which contain *trans*-dichloro configurations. Isomerizations to *cis*-dichloro species and aquation reactions were observed, kinetic data for the latter process being obtained by following the release of Cl^- ions with an ion-specific electrode.[15]

The $[Cr(L)_n(en)_{3-n}]^{3+}$ ions have been prepared (L = 2,2′-bipyridyl *NN*′-dioxide) and the $[CrL_3]^{3+}$ ion observed to racemize spontaneously in the dark by an intramolecular twist mechanism. The rate data are compared with those for analogous reactions of $[Cr(phen)_3]^{3+}$ and $[Cr(ox)_3]^{3-}$ ions in Table 3.[16]

Table 3 *Comparison of rate data for the racemization of* $[Cr(L)_3]^{3+/3-}$ *ions (data from ref.* 16)

L	pH	T/°C	10^4k/s^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
2,2′-bipyridyl *NN*′-dioxide	2[a]	26.9	1.4	19.2	−12
phen	6	25.0	0.005	24	−11
ox^{2-}	7	18.2	1.75	15.8	−24

[a] $I = ca.$ 0.02 M.

2 Other Metal Complexes

The effect of different counteranions, X^-, on the rate of racemization of $[Ni(phen)_3]^{2+}$ ion has been investigated in H_2O–Bu^{t}OH mixtures. When the mole fraction of Bu^{t}OH is greater than 0.5, X^- ions accelerate the racemization rate in the order $ClO_4^- < I^- < Br^- < Cl^-$. Attack by X^- at the metal ion rather than the 2- or 4-positions of phen (analogous to the Gillard mechanism) is postulated to be involved, primarily because Cl^- ion is a better accelerating anion than I^- ion and the reverse behaviour would be expected if attack at the aromatic ring were involved.[17]

Rate data from ^{1}H n.m.r. investigations of the intramolecular rearrangement processes involving a number of β-diketonate complexes of V^{III} are collected in Table 4. An unambiguous distinction between twist and bond-rupture mechanisms could not be established.[18] The V^{III} complexes rearrange significantly faster than the analogous Al^{III} species and at rates comparable to those of Mn^{III} and Ga^{III}.

Two groups report n.m.r. studies of configurational rearrangements of *cis*- and *trans*-$[Ti^{IV}(LL)_2X_2]$.[19–22] When LL = 2,4-dimethylpentane-2,4-diolate or

[14] M. Watabe, K. Kurosu, and S. Yoshikawa, *Chem. Abs.*, 1979, **91**, 45 044.
[15] L. Moensted and O. Moensted, *Acta Chem. Scand., Ser. A*, 1978, **32**, 917.
[16] H. Kanna, K. Kashiwabara, and J. Fujita, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 761.
[17] M. Yamamoto, T. Fujiwara, and Y. Yamamoto, *Inorg. Nucl. Chem. Lett.*, 1979, **15**, 37.
[18] A. J. C. Nixon and D. R. Eaton, *Can. J. Chem.*, 1978, **56**, 1005, 1012.
[19] N. Baggett, D. S. P. Poolton, and W. B. Jennings, *J. Chem. Soc., Dalton Trans.*, 1979, 1128.
[20] D. G. Bickley and N. Serpone, *Inorg. Chim. Acta*, 1978, **28**, 169.
[21] D. G. Bickley and N. Serpone, *Inorg. Chim. Acta*, 1979, **32**, 217.
[22] D. G. Bickley and N. Serpone, *Inorg. Chem.*, 1979, **18**, 2200.

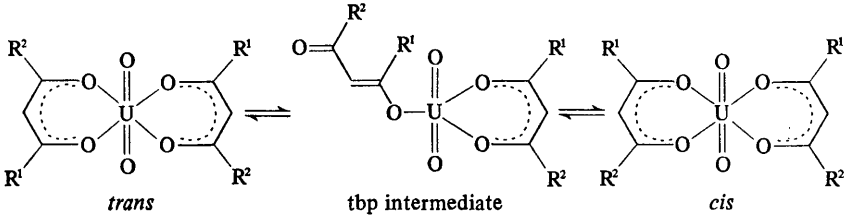
Table 4 *Rates and activation parameters at* 25 °C *for the rearrangement processes of vanadium*(III) *β-diketonates in various solvents (data from ref.* 18)

Complex[a]	*Solvent*	k/s^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
[V(tfac$_3$)]	$CDCl_3$	8.9	18.0	6.3
	PhCl	9.2	16.5	1.3
	CCl_4	10.9	16.4	1.3
	Me_2CO	13.3	15.9	−0.1
[V(hfac)$_2$(tfac)]	$CDCl_3$	103	12.7	−10.0
[V(hfac)$_2$(acac)]	$CDCl_3$	86	11·8	−9.6
	PhCl	105	11.3	−11.2
	CCl_4	110	7.2	−21.0
	Me_2CO	790	5.3	−28.1
	MeCN	565		
	CH_2Cl_2	~30		
	C_6H_6	~40		
[V(acac)$_2$(hfac)]	$CDCl_3$	40		
	PhCl	23		
[V(triac)$_2$(acac)]	$CDCl_3$	28	10.1	−18.0
[V(dibm)$_3$]	$CDCl_3$	19	14.9	−2.7

[a] tfac$^-$ = 1,1,1-trifluoropentane-2,4-dionate ion; hfac$^-$ = 1,1,1,5,5,5-hexafluoropentane-2,4, dionate ion; triac$^-$ = 3-acetylpentane-2,4-dionate ion; dibm$^-$ = 2,6-dimethylheptane-3,5-dionate ion.

2,3-dimethylbutane-2,3-diolate ion and X = isopropoxide ion, the rates of coalescence of the diolate *gem*-dimethyl resonances (degenerate enantiomerization, rate constant k_1) and the rate of dionate methyl site exchange (k_2) were obtained. The k_1/k_2 ratio is not very solvent dependent but varies from 2.0 to 1.0 with changes in the diolate ligands. Values of $\Delta G^{\ddagger}$ range from 11.9 to 16.2 kcal mol^{-1}, and a non-rupture trigonal-twist mechanism is postulated. Coalescence of the pentanedionate and acetyl methyl resonances in the spectrum of bis-(3-acetylpentane-2,4-dionato)(2,4-dimethylpentane-2,4-diolate)titanium(IV) occurs at 196 °C and involves Ti–O bond rupture ($\Delta G^{\ddagger}$ 25 kcal mol^{-1}).[19] A twist mechanism is also favoured for $[M(LL)_2X_2]$ when $M = Ti^{IV}$, LL = anion of di-isobutylmethane (dibm) or dipivaloylmethane (dpm) and X = F, Cl, or Br, and when $M = Sn^{IV}$ or Ge^{IV} and LL = dibm. When $M = Ti^{IV}$ and X = Cl, the rates vary in the order acac < dibm < dpm, and for $[Ti(dbm)_2X_2]$ the rates vary with X in the order Cl < Br ~ F.[20] For *cis*-$[Ti(acac)_2(OR)_2]$ (R = Ph, 2-Pr^i-C_6H_4, or 2,6-Pr$^i_2$-C_6H_3), rates and activation parameters were determined and a twist mechanism favoured with some contribution from five-co-ordinate intermediates.[21] In the case of *cis*-$[Ti(LL)_2(OR)_2]$ (LL = acac$^-$, 8-hydroxyquinolate, or 8-hydroxyquinaldinate, R = 2,6-Pr$^i_2$-C_6H_3), values of $\Delta H^{\ddagger}$/kcal mol^{-1} are 6.3 ± 1.7, 14.7 ± 0.8, and 21.2 ± 1.3 and $\Delta S^{\ddagger}$/cal K^{-1} mol^{-1} are -36.5 ± 5.7, -9.7 ± 2.2, and $+2.2 \pm 3.3$ respectively for inversion in *m*-dichlorobenzene solution. The acac methyl group exchange is characterized by $\Delta H^{\ddagger} = 13.8 \pm 0.3$ kcal mol^{-1} and $\Delta S^{\ddagger} = -10.6 \pm 1.0$ cal K^{-1} mol^{-1}. Unlike the acac complexes, those of 8-hydroxyquinoline and 8-hydroxyquinaldinate rearrange *via* Ti—N bond rupture.[22]

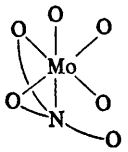
The kinetics of the *cis*⇌*trans* isomerization of $[UO_2L_2]$ (L = benzoylacetylacetone) have been investigated in $CDCl_3$ solution by ^1H n.m.r. (Scheme 1;



Scheme 1

$R^1 = Ph$, $R^2 = Me$).[23] A mechanism involving bond rupture to give a trigonal-bipyramidal intermediate is postulated, and at 25 °C, $k = 24.5\ s^{-1}$, $\Delta H^{\ddagger} = 4.9 \pm 0.3$ kcal mol^{-1}, and $\Delta S^{\ddagger} = +35.2 \pm 1.1$ cal K^{-1} mol^{-1}.

The *fac*-[$Mo^{III}O_3$ (nta)]$^{3-}$ ion containing an un-co-ordinated carboxylate arm (1) is observed to undergo exchange between free and bound carboxylate groups with $\Delta H^{\ddagger} = 16.4 \pm 0.9$ kcal mol^{-1} and $\Delta S^{\ddagger} = 5 \pm 1$ cal K^{-1} mol^{-1} at 25 °C in 3:1 CH_2Cl_2:MeOH solution. Water accelerates the rate of intramolecular exchange by assisting Mo—N bound cleavage. The analogous W^{VI} complexes with aminocarboxylates are significantly less labile.[24]



(1)

[23] A. Vasilescu and T. Oncescu, *Rev. Roum. Chim.*, 1978, **23**, 1055.
[24] K. F. Miller and R. A. D. Wentworth, *Inorg. Chem.*, 1978, **17**, 2769.

10

Complexes with Co-ordination Number Greater than Six

BY P. MOORE

1 Lanthanides: Ligand Exchange

Intermolecular exchange of $[M(nta)_2]^{3-}$ ions (M = La, Ce, Pr, Nd, Sm, Eu, Tm, Yb, Lu, or Y) with excess nta has been investigated by ^1H n.m.r. as a function of pH. Three kinetic pathways were observed:

$$[M(nta)_2]^{3-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [M(nta)] + nta^{3-} \quad (1)$$

$$[M(nta)_2]^{3-} + {}^*nta^{3-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [M(nta)({}^*nta)]^{3-} + nta^{3-} \quad (2)$$

$$[M(nta)_2]^{3-} + H^+ \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [M(nta)] + Hnta^{2-} \quad (3)$$

Values of k_{-3} are nearly constant for all M (2×10^3—6×10^3 M^{-1} s^{-1}) and *ca.* 10^4 smaller than values of k_{-1}. An I_d mechanism is proposed for pathway (1) (rate constant k_{-1}) but pathway (3) may either involve an I_d mechanism or a slow H^+-migration from the partially bonded $Hnta^{2-}$. Pathway (2) involves progressive chelation of the entering ligand and simultaneous dechelation of the leaving ligand.[1]

The stability constants of the ternary complexes formed between $[Eu(edta)]^-$ ion and ida^{2-}, $Meida^{2-}$, and nta^{3-} ions are log K = 4.28, 4.33, and 5.05 respectively. The $[Ln(edta)(ida)]^{3-}$ ions show maximum stability in the middle of the lanthanide series: log K = 3.27 (Pr), 4.28 (Eu), and 2.67 (Yb). Reactions of $[Ln(edta)]^-$ ions with excess nta^{3-} ion also involve the formation of $[Ln(nta)_2]^{3-}$, $[Ln(edta)_2]^{5-}$, and $[Ln_2(edta)_3]^{6-}$ ions. Ligand exchange reactions were investigated and the pseudo-first-order rate constants are collected in Table 1. Exchange of ida^{2-} with $[Pr(edta)(ida)]^{3-}$ ion was too fast to measure.[2]

Table 1 *Pseudo-first-order rate constants* (s^{-1}) *for ligand exchange between excess* L *and* $[M(edta)L]^{n-}$ *ions at* 25 °C (*data from ref.* 5)

Ligand	ida	Meida	nta
M			
Eu	210 ± 20	250 ± 20	25 ± 8
Yb	119 ± 20		31 ± 8

[1] Y. Gfeller and A. E. Merbach, *Inorg. Chim. Acta*, 1978, **29**, 217.
[2] R. V. Southwood-Jones and A. E. Merbach, *Inorg. Chim. Acta*, 1978, **30**, 135.

Parallel associative and dissociative pathways are reported for the reactions of [Eu(L)] and [Ho(L)] (L = methylthymol blue) with edta in ammonium acetate buffers.[3]

Reactions of excited Tb^{3+} ($^5D_4$) and Dy^{3+} ($^4F_{9/2}$) with the anions of salicylic acid and 5-sulphosalicylic acid have been investigated in H_2O and MeOH by luminescence kinetics.[4] The anions are reported to be bidentate in H_2O and unidentate in MeOH.

The chelate adducts formed between the lanthanide shift reagent [Eu(fod)$_3$] and [Co(β-diketonates)$_3$] have relatively long lifetimes for dissociation (*ca.* 10^{-2} s).[5]

2 Lanthanides: Metal Exchange

For the exchange of M = Ce^{III}, Eu^{III}, Tb^{III}, or Tm^{III} with the respective $[ML]^{2-}$ ions (L = $dtpa^{5-}$) between pH 4.2 and 6.8 in acetate buffers, the rate law is reported to be[6]

$$\text{Rate} = (k_1[M] + k_2[H^+][M] + k_3[H^+] + k_4[H^+]^2 + k_5[H^+]^3)[ML^{2-}]$$

Exchanges of Eu^{III} with [Eu(cdta)]$^-$ (cdta^{4-} = *trans*-cyclohexane-1,2-diamine-*NNN'N'*-tetra-acetate ion) in acetate buffer[7] and of La^{III}, Pr^{III}, Sm^{III}, Gd^{III}, and Er^{III} with [Ce(edta)]$^-$ at pH 6—7 have also been studied. For the latter reactions formation of $[Ce(edta)Ln]^{2+}$ bridge-species by co-ordination of Ln^{III} with one of the carboxylate groups of the co-ordinated edta is involved.[8]

3 Actinides

Rate data for the exchange of solvents (L) with $[U^{VI}O_2L_5]^{4+}$ and $[UO_2L^4(X)]^{n+}$ ions (L = H_2O, X = DMSO, Cl^-, or Br^-) are collected in Table 2.[9–14] These data are considered further in Chapter 8. Exchange of tri-n-butyl phosphate (L) with $[UO_2(NO_3)_2L_2]$ has also been investigated in MeCN solution; the reaction is catalysed by H_2O and MeOH and inhibited by added nitrate ion.[15] The catalytic effect of water and amines has also been investigated in benzene solution.[16]

Rate constants for the reaction of $[UO_2(OH_2)_5]^{2+}$ ion with the keto and enol forms of acac are reported to be 3.58 ± 0.40 and 5330 ± 940 M^{-1} s^{-1} respectively at 25 °C.[17]

[3] E. A. Anastasieva, O. I. Davydova, L. V. Krasukhina, and T. V. Mal'kova, *Chem. Abs.*, 1978, **89**, 66 029.
[4] V. P. Gruzdev and V. L. Ermolaev, *Zh. Neorg. Khim.*, 1978, **23**, 1509.
[5] L. F. Lindoy and H. W. Louie, *J. Am. Chem. Soc.*, 1979, **101**, 841.
[6] A. J. Mahmood, *Chem. Abs.*, 1979, **90**, 93 061.
[7] W. d'Olieslager and A. Oeyen, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1565.
[8] E. Brucher and I. Banyai, *Acta Chim. Acad. Sci. Hung.*, 1977, **95**, 147.
[9] Y. Ikeda, S. Soya, H. Fukutami, and H. Tomiyasu, *J. Inorg. Nucl. Chem.*, 1979, **41**, 1333.
[10] G. J. Honan, S. F. Lincoln, E. H. Williams, and T. M. Spotswood, *J. Chem. Soc., Dalton Trans.*, 1979, 1220.
[11] G. J. Honan, S. F. Lincoln, and E. H. Williams, *J. Chem. Soc., Dalton Trans.*, 1979, 320.
[12] R. P. Bowen, G. J. Honan, S. F. Lincoln, T. W. Spotswood, and E. H. Williams, *J. Chem. Soc., Dalton Trans.*, 1979, **33**, 235.
[13] G. J. Honan and S. F. Lincoln, *J. Solution Chem.*, 1978, **7**, 443.
[14] G. J. Honan, S. F. Lincoln, and E. H. Williams, *Inorg. Chem.*, 1978, **17**, 1855.
[15] B. Cohen, S. Weiss, and Y. Egozy, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1059.
[16] N. Mazurek, Y. Egozy, and S. Weiss, *J. Inorg. Nucl. Chem.*, 1979, **41**, 1023.
[17] M. J. Hynes and B. D. O'Regan, *Chem. Abs.*, 1978, **89**, 12 735.

Table 2 *Rate data for the exchange of solvents* (L) *with* $[U^{VI}O_2L_5]^{2+}$ *and* $[UO_2L_4(X)]^{n+}$ *ions*

L	X	*Solvent*	k/s^{-1} (T/°C)	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	*Ref.*
H_2O	H_2O	H_2O–acetone [a]	299 (−70)	9.9	2.1	9
H_2O	DMSO	H_2O–acetone [a]	455 (−70)	6.0	−16.2	9
H_2O	Cl^-	H_2O–acetone [a]	163 (−70)	6.1	−17.6	9
H_2O	Br^-	H_2O–acetone [a]	265 (−70)	6.7	−13.5	9
MeCONHMe		CD_3CN	336 (0)	13	+0.8	10
$(Me_2N)_2CO$		Cl_2CD_2 [b]	73 (0)	19	+20	11
Me_2NCHO		CD_2Cl_2	199 (−50)	7.6	−12.8	12
Me_2SO		$(CD_3)_2CO$	273 (−13)	9.3	−11.4	13
$(Me_2N)_3PO$ [c]		CD_2Cl_2	k_1 = 12.5 (0) [d]	3.4	−41	14
$(Me_2N)_3PO$		CD_2Cl_2	k_2 = 173 (0) [d]	5.3	−29	14

[a] $[UO_2]^{2+}$:H_2O:[$^2H_6$]acetone 1:13.0:93.6. [b] Rate data very similar in CD_3CN. [c] $[UO_2L_4]^{2+}$. [d] Rate = $4(k_1 + k_2[L])$ $[UO_2L_4^{2+}]$.

Some indication of the relative labilities of Th^{IV}, U^{IV}, Np^{IV}, and Pu^{IV} complexes comes from studies of the acid-catalysed dissociations of $[ML]^-$ ions ($L = dtpa^{5-}$) in the presence of the anion of arsenazo(III) (A):

$$[ML]^- + nH^+ + mA \longrightarrow [MA_m] + H_nL^{5-n}$$

At 25 °C, $k/M^{-3}\,s^{-1} = 1640 \pm 400$, 2.32 ± 0.59, 0.275 ± 0.055, and 0.056 ± 0.005 for Th^{IV}, U^{IV}, Np^{IV}, and Pu^{IV} respectively.[18]

A stopped-flow study of the reaction of aqueous Am^{3+} ion with $cdta^{4-}$ (L^{4-}) to give $[Am(L)]^-$ ion indicates the formation of a relatively long-lived intermediate in which chelation of three of the carboxylate groups of $cdta^{4-}$ has occurred, to give $[Am(H_nL)]^{n-4}$, which subsequently deprotonates to give the final product. Formation of the Am—N bond is postulated to be rate-determining.[19]

Polarographic and voltammetric studies of the disproportionation of U^V in the presence of the complexing anions sulphate, citrate, tartrate, and oxalate have been reported.[20]

Exchange of radiocyanide (HCN) with $K_4[W(CN)^8]$ was found [21] to be zero-order in free HCN, and the first-order rate constant is characterized by $\Delta H^{\ddagger} = 31.72$ kcal mol^{-1}, $\Delta S^{\ddagger} = 5.45$ cal K^{-1} mol^{-1}.

4 Fluxional Systems

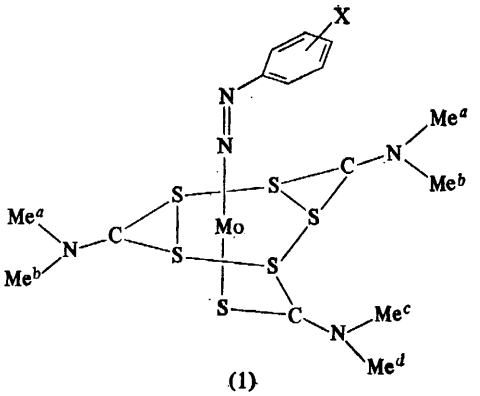
The seven-co-ordinate $[W(CO)_3(L)_2]$ (L = dimethyldithiocarbamate ion) shows three ^{13}C n.m.r. resonances at 163 K. On raising the temperature, two of these resonances coalesce independently of the third ($\Delta G^{\ddagger} = 8.1$ kcal mol^{-1}) and at still higher temperatures all three resonances merge ($\Delta G^{\ddagger} = 9.0$ kcal mol^{-1}). Both processes involve intramolecular isomerism.[22] A series of seven-co-ordinate complexes of the type $[Mo(N_2R)(S_2CNMe_2)_3]$ [R = aryl; (1)] are also fluxional, and the activation parameters for the dynamic process which is observed are collected in Table 3. Simultaneous collapse of all of the methyl resonances is involved. A good correlation between the logarithm of the observed

Table 3 *Activation parameters at* 25 °C *for the simultaneous fluxional rearrangement of all three bidentate dithiacarbamate ligands of* $[Mo(N_2R)(S_2CNMe_2)_3]$ (1) *in nitrobenzene solution (data from ref.* 26)

Aryl group R *substituent* X	$\Delta G^{\ddagger}$/kcal mol^{-1} [a]	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1} [b]
p-OMe	17.5	−2.6
*p*Me	17.6	+4.1
H	17.7	+2.4
p-Cl	18	+16.4
m-NO_2	18.4	+4.3
p-NO_2	18.5	+1.9

[a] ±0.05 kcal mol^{-1}. [b] ±7.2 cal K^{-1} mol^{-1}.

[18] A. V. Stepanov and M. A. Nemtsova, *Chem. Abs.*, 1978, **89**, 136 430.
[19] J. C. Sullivan, K. L. Nash, and G. R. Choppin, *Inorg. Chem.*, 1978, **17**, 337.
[20] J. Kuta and L. Pospisil, *Electrochim. Acta*, 1979, **22**, 1109.
[21] M. Zielinski, *Pol. J. Chem.*, 1978, **52**, 1507.
[22] J. L. Templeton, *Adv. Chem. Series*, 1979, No. 173.



(1)

rate constant and the Hammett substituent parameter, σ, is reported.[23] The seven-co-ordinate peroxo-complexes $[Nb^{V}(O_2)Cl_3(L)]^-$ (L = diketonate ion) unlike $[NbOCl_3(L)]^-$ are stereochemically rigid. The complexes $[W^{VI}O_2F_2(L)]$ are also rigid molecules.[24]

A number of fluxional eight-co-ordinate complexes of the type $[ML_4]$ [M = U^{IV} or Th^{IV}, L = dipivaloylmethanate or dibenzoylmethanate;[25] M = Zr^{IV}, Hf^{IV}, Ce^{IV}, or Th^{IV}, L = β-diketonates;[26] or M = Ti^{IV} or Zr^{IV}, L = R_2NCOS (R = Me, Et, or Pr^i)[27]] have been investigated by n.m.r. methods. The monothiocarbamate complexes of Ti^{IV} and Zr^{IV} with R = Me show four equal-intensity low-temperature ^{1}H n.m.r. *N*-Me resonances, as expected for a dodecahedral all-*cis*-structure in which the four sulphur atoms are on one side and the four oxygen atoms are on the other side of the molecule. Two dynamic processes can be resolved from the n.m.r. spectra, a low-temperature process involving intramolecular metal-centred rearrangement, and a high-temperature process involving C—N bond rotation.[27] By working in freons between −170 and −115 K, the ^{1}H and ^{19}F n.m.r. spectra of $[ML_4]$ and $[ML_2(NO_3)_2]$ (L = β-diketonate) species can be frozen out. Some rate data for Zr^{IV} complexes are collected in Table 4. ^{19}F Spectra of $[Zr(CF_3COCHCOMe)_4]$ show the presence of more than one isomer.

Table 4 *Rate data for the intramolecular rearrangements of eight-co-ordinate* Zr^{IV} *β-diketonate complexes* $[Zr(L)_4]$ *(data from ref.* 29)

L_4	k/s^{-1} *at* −125 °C	ΔH^*/kcal mol^{-1}	ΔS^*/cal K^{-1} mol^{-1}
$(acac)_4$	200	4.1±0.3	−18.7±2.5
$(acac)_2(NO_3)_2$	290	4.5±0.3	−15.2±2.5
$(Bu^tCOCHCOMe)_4$	6.8	5.5±0.5	−16.2±2.9

[23] E. O. Bishop, G. Butler, J. Chatt, J. R. Dilworth, G. J. Leigh, and D. Orchard, *J. Chem. Soc., Dalton Trans.*, 1978, 1654.
[24] J. Y. Calves, J. E. Guerchais, R. Kergoat, and N. Kheddar, *Inorg. Chim. Acta*, 1979, **33**, 95.
[25] C. Kiener, G. Folcher, G. Langlet, P. Rigny, and J. Virlet, *Nouv. J. Chim.*, 1979, **3**, 99.
[26] R. C. Fay and J. K. Howie, *J. Am. Chem. Soc.*, 1979, **101**, 1115.
[27] S. L. Hawthorne, A. H. Bruder, and R. C. Fay, *Inorg. Chem.*, 1978, **17**, 2114.

$[M(acac)_4]$ (M = Zr or Hf) appear to have square-antiprismatic geometries in solution. Rearrangements are believed to occur without bond rupture, but 1-bond dissociation cannot be ruled out.[26]

Reviews dealing with aspects of the stereochemistry of six-, seven-, and eight-co-ordinate complexes have appeared.[28,29]

[28] D. L. Kepert, *Prog. Inorg. Chem.*, 1977, **23**, 1; 1977, **23**, 67; 1978, **24**, 179.
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11

Compounds of Main Group Elements (Group III and Higher)

BY G. STEDMAN

The coverage and style of treatment are essentially the same as in the corresponding section of Volume 6.

1 Group III

Boron.—This section considers tetrahedral anions and related species, boron–hydrogen compounds, and boron–oxygen compounds. The effect of solvent on the hydrogen isotope exchange reaction, and also the hydrolysis, of $[BN_3CN]^-$ in H_2O–DMSO has been studied.[1] A mechanism involving H_2BH_2CN is favoured. The hydrolysis of $[BH(NC_4H_4)_2CN]^-$ occurs in acid and in basic media, and is much more rapid than the hydrolysis of $[BH_3CN]^-$.[2] Permutational analysis of reaction (1) leads to the suggestion[3] that the BH_5 species is a rigid C_5 species,

$$[BH_4]^- + H^+ \longrightarrow BH_5 \longrightarrow BH_3 + H_2 \qquad (1)$$

involving an H_2 subunit; this latter point also emerged from earlier MO calculations. The reaction of $NaBH_4$ and H_2SO_4 under anhydrous conditions may involve a trigonal-bipyramidal species with an axial–equatorial loss of H_2. The reaction of $NaBH_4$ with HF under anhydrous conditions involves a non-rigid BH_5 species. The reduction of $[TeO_3]^{2-}$ by $[BH_4]^-$ in acid and in alkaline media probably involves $[BH_3OH]^-$ and $[BH(OH)_3]^-$ as active boron species.[4] The hydrolysis products of $[BH_4]^-$ are also involved in the reaction of potassium permanganate with sodium borohydride.[5] Further studies of the hydrolysis of $[BF_4]^-$ have appeared.[6]

A rather elegant study of the decomposition of $[B_3H_8]^-$ in aqueous acidic methanol at -78 °C gives rate law (2), and leads to the formation of a species formulated as $[B_3H_7 \cdot OH_2]$ and H_2. On warming the solution to

$$-d[B_3H_8^-]/dt = k[B_3H_8^-][H^+] \qquad (2)$$

[1] M. M. Kreevoy and E. H. Baughmann, *Finn. Chem. Lett.*, 1978, **35** (*Chem. Abs.*, 1978, **88**, 126 942).
[2] B. Győri, J. Emri, and L. Szilági, *J. Organomet. Chem.*, 1978, **152**, 13.
[3] R. Willem, *J. Chem. Soc., Dalton Trans.*, 1979, 33.
[4] E. S. Kotelevets, V. S. Khan, and E. N. Marinova, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1978, **23**, 374.
[5] V. S. Khan and V. F. Martynova, *Zh. Neorg. Khim.*, 1978, **23**, 680 (*Chem. Abs.*, 1978, **88**, 181 734).
[6] V. S. Plakhotnik and S. M. Slizkii, *Russ. J. Phys. Chem.* (*Engl. Transl.*), 1978, **52**, 290; V. N. Plakhotnik, L. V. Boguslavskaya, and V. V. Varekii, *Kinet. Katal.*, 1977, **15**, 41 (*Chem. Abs.*, 1978, **88**, 177 768).

-45 °C, complete hydrolysis to boric acid and H_2 occurs at a rate independent of acidity ($[H^+] \leqslant 1.5$ M). At higher acidities there is evidence for acid catalysis of the hydrolysis reaction. When alkali is added to a solution of the intermediate at -78 °C a species $[B_3H_7OH]^-$ is formed, which at -65 °C disproportionates as in reaction (3). A mechanism involving successive attacks

$$[B_3H_7OH]^- + 2[OH]^- + H_2O \longrightarrow 2[BH_4]^- + [B(OH)_4]^- \qquad (3)$$

by hydroxide ion at the most positive boron is one possible hypothesis to explain the results.[7] The acid-catalysed methanolysis of $Na(Me_2N)\cdot 2BH_3$ can be followed by ^{11}B n.m.r., and the solutions give signals due to μ-$Me_2N\cdot B_2H_5$, $HB(OMe)_2$, and $B(OMe)_3$, together with another peak which may be due to an intermediate $Me_2NH\cdot BH_2OMe$.[8] The mechanism suggested is

$$2MeOH + \mu\text{-}Me_2N\cdot B_2H_5 \longrightarrow MeOH\cdot BH_3 + Me_2NBH_2\cdot HOMe$$

$$Me_2NBH_2\cdot HOMe \longrightarrow Me_2NH\cdot BH_2OMe$$

The reaction between Me_2DNBH_3 and Cl_2 to form Me_2HNBH_2Cl and $MeDNBH_2Cl$ is thought[9] to involve a 'hot' product Me_2DNBH_2Cl which can lose DCl to form Me_2NBH_2, which then recombines with either HCl or DCl.

The cleavage of $[Me_2SnB_{10}H_{12}]$ by bromine occurs by a stepwise cleavage of B–Sn–B three-centre bonds.[10] The isomerization of 1-ClB_5H_8 or 2-ClB_5H_8 in toluene solutions is catalysed by diethyl ether and follows simple second-order kinetics. A 1:1 complex is involved, and it is considered that a boron cage rearrangement is more likely than a mechanism involving cleavage of a B—Cl bond.[11] In the preparation of methyl-substituted boranes by cleavage of bridge systems with ammonia, followed by protonation with liquid hydrogen chloride, a directive effect seems to be operative in the cleavage reaction, the boron atom furthest from the methyl group being split off.[12] Hydrogen exchange between $[BEtH_3]^-$ and BEt_3 in THF involves a hydrogen-bridged diboron species, and there is rapid exchange between monoboron and diboron species. The rate is sensitive to steric effects due to the alkyl groups.[13] Molecular orbital calculations for the energy of various geometries of $[B_8H_8]^{2-}$ have been carried out in order to throw light on the fluxional behaviour of this ion. Explanations based on a stable D_{4d} structure are discounted.[14] Spontaneous isomerization of $[B_{11}H_{11}]^{2-}$ at -70 °C has been observed to occur rapidly on the n.m.r. time-scale, and MO calculations have revealed a possible low-energy pathway.[15] Calculations on possible fluxional processes for $[B_3H_8]^-$ and B_5H_{11} have been reported.[16]

[7] W. L. Jolly, J. W. Reed, and F. T. Wang, *Inorg. Chem.*, 1979, **18**, 377.
[8] C. Balulescu and P. C. Keller., *Inorg. Chem.*, 1978, **17**, 3707.
[9] W. H. Myers and G. E. Ryschkewitsch, *Inorg. Chem.*, 1978, **17**, 1157.
[10] T. J. Dupont, R. E. Loffredo, R. C. Haltiwanger, C. A. Turner, and A. D. Norman, *Inorg. Chem.*, 1978, **17**, 2062.
[11] D. F. Gaines and J. L. Walsh, *Inorg. Chem.*, 1978, **17**, 806.
[12] I. S. Jaworiwsky, J. R. Long, L. Barton, and S. G. Shore, *Inorg. Chem.*, 1979, **18**, 56.
[13] C. A. Brown, *J. Organomet. Chem.*, 1978, **156**, C17.
[14] D. A. Kleier and W. N. Lipscomb, *Inorg. Chem.*, 1979, **18**, 1312.
[15] D. A. Kleier, D. A. Dixon, and W. N. Lipscomb, *Inorg. Chem.*, 1978, **17**, 166.
[16] I. M. Pepperberg, D. A. Dixon, W. N. Lipscomb, and T. A. Halgren, *Inorg. Chem.*, 1978, **17**, 587.

An n.m.r. study of $B(OMe)_3$ in methanol shows fast methyl exchange, with $k(MeOH)/k(MeOD) = 1$. Reaction is catalysed by both acids and bases.[17] The decomposition of the *N*-nitrosohydroxylamine-*N*-sulphonate anion to nitrous oxide and sulphate ion is catalysed by boric acid:

$$-d[SN_2O_5^{2-}]/dt = \{k_1[H^+] + k_2[H^+][B(OH)_3]\}[SN_2O_5^{2-}]$$

The boron acts as a Lewis acid towards the nitroso-group, while a hydroxy-group interacts with the SO_3 giving rise to five-co-ordinate sulphur.[18] This has been made the basis of an analytical method for boron.[19] The kinetics of complexation between boric acid and salicylate ions substituted in the 5-position-have been measured.[20] The rate law takes the form (4).

$$k = k_b + k_s[H_3BO_3] \quad (4)$$

Finally, a kinetic study of the protodeboronation of ferroceneboronic acid $[FcB(OH)_2]$ in sulphuric acid is noted. This occurs by an S_E2 mechanism.[21]

Aluminium.—An increasing amount of attention is being devoted to kinetic and mechanistic studies of aluminium chemistry. A full account has appeared[22] of the substitution of DMSO in $[Al(DMSO)_6]^{3+}$ by pyridine, bipyridyl, terpyridyl, phenanthroline, and t-butylamine in nitromethane solution. The outer-sphere association constants appear to be rather large. Steric effects are suggested as the cause of the rather slow ring-closure steps for bipyridyl and terpyridyl. Proton n.m.r. has been used to study a number of metal acetylacetonates in trifluoroacetic acid, and early conclusions[23] about the mechanism of ligand exchange in the aluminium(III) complex have been modified. It is now suggested[24] that the breaking of the first Al—O bond is rate determining, not fission of the second Al—O bond as was previously proposed. The intramolecular rearrangement of aluminium β-diketonate complexes is considered to occur by a twisting mechanism rather than a bond-rupture process.

A variety of papers on substitution reactions at aluminium(III) in aqueous media have appeared. Complexation with 5-nitrosalicylic acid has been studied[25] and compared with related studies involving other salicylic acid derivatives. It seems possible that the substitution process may be associative in character. There has been an investigation[26] of the kinetics and equilibria of the reactions with Semi-xylenol Orange and Semi-methylthymol Blue. The latter two reactions involve a pre-equilibrium step, followed by a substitution stage in which several outer-sphere water molecules are removed. The relative reactivities of three different reaction pathways are $[H_3L]^- + [AlOH]^{2+} > [H_2L]^{2-} + [AlOH]^{2+} > [H_2L]^{2-} + Al^{3+}$. The kinetics of complexation of aluminium(III) with fluoride are

[17] W. C. Hutton and T. I. Crowell, *J. Am. Chem. Soc.*, 1978, **100**, 6904.
[18] J. L. Palmer and R. W. Coughlin, *J. Catal.*, 1978, **53**, 345.
[19] J. C. Gijsbers and J. G. Kloosterboer, *Anal. Chem.*, 1978, **50**, 455.
[20] A. Queen, L. Davies, and A. Con, *Can. J. Chem.*, 1979, **57**, 920.
[21] B. Floris and G. Illuminati, *J. Organomet. Chem.*, 1978, **150**, 101.
[22] A. J. Brown, O. W. Howarth, P. Moore, and W. J. E. Parr, *J. Chem. Soc., Dalton Trans.*, 1978, 1776.
[23] K. Saito and K. Masuda, *Bull. Chem. Soc. Jpn.*, 1968, **41**, 384; *ibid.*, 1970, **43**, 119.
[24] A. J. C. Nixon and D. R. Eaton, *Can. J. Chem.*, 1978, **56**, 1928.
[25] B. Perlmutter-Hayman and E. Tapuhi, *Inorg. Chem.*, 1979, **18**, 875.
[26] S. Murakami, *J. Inorg. Nucl. Chem.*, 1979, **41**, 209.

interpreted[27] by an Eigen–Wilkins type mechanism, involving association of HF with Al^{3+}. Ultrasonic techniques have been used to study the formation of complexes between the sulphate ion and aluminium(III) and scandium(III). The proposed mechanism[28] involves the removal of successive solvent molecules (S) from a solvent-separated ion pair. The rate of interconversion,

$$M^{3+} + [SO_4]^{2-} \rightleftharpoons M^{3+}(S)_2[SO_4]^{2-} \rightleftharpoons M^{3+}(S)[SO_4]^{2-} \rightleftharpoons [MSO_4]^{+}$$

of the two outer-sphere complexes is greater by a factor of twenty for scandium than for aluminium, somewhat surprising in view of the similarity of charge and ionic radius. Pressure-jump studies of solutions of aluminium(III) acetate have also been published.[29]

Some further work on polymeric aluminium(III) species has appeared. The reactions of $[Al(OH)_6]^{3-}$, $[Al_2(OH)_{10}]^{4-}$, and $[Al_4(OH)_{16}]^{4-}$ with ferron (8-hydroxy-7-iodo-5-quinolinesulphonic acid) at pH 5 were studied.[30] The differences in rate were ascribed to differing reactivities of the hydroxyl bridges. ^{27}Al N.m.r. is finding increasing use as a tool, and it has been used to study hydrolytic polycondensation equilibria,[31] and also to investigate the kinetics and mechanism of the reaction of $[Al_2(OH)_5Cl]$ with hydrochloric acid.[32]

The rate of extraction of aluminium(III) from aqueous mineral acid by di-(2-ethylhexyl)phosphoric acid (DEHPA) has been measured[33] and found to follow rate law (5).

$$\text{Rate} = k[Al^{III}][\text{DEHPA}][H^+]^{-1} \qquad (5)$$

Reaction (6) appears[34] to involve a dimeric aluminium species with bridging alkoxy and chlorine groups, which decomposes by liberation of a carbonium ion from the alkoxy bridge.

$$(ROAlCl_2)_n + (MeAlCl_2)_2 \longrightarrow \text{>Al—O—Al<} + \text{hydrocarbon} \qquad (6)$$

Theoretical calculations have been reported of the reorganization energy of AlH_3,[35] and of the Berry co-ordinate for pseudorotation in $[Al(OH)_5]^{2-}$.[36]

Gallium.—The species $[Ga(BH_4)Me_2]$ is suggested to be $[Me_2Ga(\mu\text{-}H)_2BH_2]$, although there is ready exchange of hydrogen and methyl between the gallium and boron centres. The $[Ga(\mu\text{-}H)_2B]$ fragment is more susceptible to attack by

[27] V. V. Blokhin, L. A. Kulvinova, Yu. A. Makashev, and V. E. Mironov, *Zh. Neorg. Khim.*, 1979, **24**, 239 (*Chem. Abs.*, 1979, **90**, 110 657).
[28] A. Bonsen, W. Knoche, W. Berger, K. Giese, and S. Petrucci, *Ber. Bunsenges. Phys. Chem.*, 1978, **82**, 678.
[29] M. Hiraishi, S. Harada, and T. Yasunaga, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 2317.
[30] W. Gessner and B. Koedderitzsch, *Z. Chem.*, 1978, **18**, 370.
[31] M. A. Fedotov, O. P. Krivoruchko, and R. A. Buyanov, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1978, **23**, 1282.
[32] M. S. Henty and A. Prescott, *J. Chem. Res.* (*S*), 1978, 427.
[33] T. Sato, T. Yoshino, T. Nakamura, and T. Kudo, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1571; *ibid.*, 1979, **41**, 731.
[34] W. Kosinska, K. Z. Ardecka, A. Kunicki, M. Boleslawski, and S. Pasynkiewicz, *J. Organomet. Chem.*, 1978, **153**, 281.
[35] A. Okninski and S. Pasynkiewicz, *Inorg. Chim. Acta*, 1978, **28**, L125.
[36] R. J. Hill, G. V. Gibbs, and R. C. Peterson, *Aust. J. Chem.*, 1979, **32**, 231.

protonic agents than is the Me_2Ga group.[37] The kinetics of decomposition of Ga_2Br_6 in aqueous solution at high temperature have been measured.[38]

Thallium.—A review of organothallium chemistry contains a section on kinetics and mechanism.[39] The reaction of $RTlX_2$ ($X = MeCO_2$ or Pr^iCO_2) with Me_4Sn involves[40] the free ion $RTlX^+$ as reactant.

$$RTlX_2 + Me_4Sn \longrightarrow RMeTlX + Me_3SnX$$

The oxidation of the hydrazinium ion by Tl^{3+} probably involves substitution of hydrazine for water in the hydrated thallium(III) species.[41] The kinetics of complex formation between thallium(III) and 4-(2-pyridylazo)resorcinol in aqueous solutions have been studied. Two pathways have been identified, involving Tl^{3+} and $[TlOH]^{2+}$ reacting with the protonated ligand. The similarity in rate to that of the corresponding reaction of thallium(III) with Semi-xylenol Orange indicates that the rate is controlled by loss of water from the hydrated thallium cation.[42]

2 Group IV

Carbon. A stability constant for $[(CN)_3]^-$ has been measured;[43] there is a rapid formation of this species from $[CN]^- + (CN)_2$, followed by a slower decomposition to organic products. The oxidation of cyanide ion by ozone in aqueous solution has been reported.[44]

$$O_3 + 2[CN]^- \longrightarrow 2[CNO]^- + 0.5O_2$$

$$\text{Rate} = k[O_3][CN^-]^2$$

Ab initio MO–LCAO–SCF methods have been applied to the formation of the bicarbonate ion from carbon dioxide and hydroxide ion. It is concluded that in the gas phase there should be no barrier to reaction, and that in solution solvation of the hydroxide ion *reduces* reactivity. The authors speculate[45] that the high activity of carbonic anhydrase may be due to an unsolvated hydroxide in Zn—OH in a hydrophobic environment.

Silicon.—The sterochemistry for nucleophilic substitution at silicon has continued to receive detailed study. The hydrolysis of chlorosilanes in weakly polar solvents is catalysed by nucleophiles such as HMPA, DMSO, and DMF.[46] Reaction involves retention of configuration at silicon,[47] with nucleophilic attack by water on a five-co-ordinate silicon species. Stable 1 : 1 adducts of HMPA and Me_3SiX have been isolated, which are thought to have the structure

[37] A. J. Downs and P. D. P. Thomas, *J. Chem. Soc., Dalton Trans.*, 1978, 809.
[38] L. F. Kozin, R. G. Sarmurzina, V. F. Vozdvizhenskii, and W. M. Mishchenko, *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.*, 1977, **25**, 38 (*Chem. Abs.*, 1978, **88**, 42 158).
[39] H. Kurosawa, *J. Organomet. Chem.*, 1978, **158**, 221.
[40] I. F. Gun'kin, K. P. Butin, I. P. Beletskaya, and A. O. Reutov, *Bull. Acad. Sci. USSR*, 1978, **27**, 879.
[41] K. S. Gupta, *J. Inorg. Nucl. Chem.*, 1977, **39**, 2093.
[42] R. Funada, T. Imamura, and M. Fujimoto, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 1535.
[43] M. T. Beck, V. Gaspar, and D. P. Goel, *Inorg. Chim. Acta*, 1979, **33**, L147.
[44] S. A. Kashtanov, V. I. Matrozov, A. M. Stepanov, and B. A. Tregubov, *Ukr. Khim. Zh. (Russ. Ed.)*, 1978, **44**, 1286 (*Chem. Abs.*, 1979, **90**, 110 623).
[45] B. Jönsson, G. Karlström, and H. Wennerström, *J. Am. Chem. Soc.*, 1978, **100**, 1658.
[46] R. J. P. Corriu, G. Dabosi, and M. Martineau, *J. Organomet. Chem.*, 1978, **150**, 27.
[47] R. J. P. Corriu, G. Dabosi, and M. Martineau, *J. Organomet. Chem.*, 1978, **154**, 33.

$[(Me_2N)_3P(O)SiMe_3]^+X^-$; these may be the type of intermediate involved in HMPA-catalysed racemization of optically active triorganosilanes.[48] The effect of the leaving group on the sterochemistry of substitutions at silicon has been reported,[49] and there have been kinetic and stereochemical studies of the reaction between organolithium reagents and fluoro- and methoxy-silanes.[50] A full account has appeared of the studies that showed that reagents that give 1,2-addition to α-enones react with optically active silicon compounds to give retention of configuration whereas those that favour 1,4 addition give inversion.[51] Experiments on the reaction of chiral NpPhMeSiCOMe with alkoxides (Np = naphthyl) shows that the rearrangement pathway involves a stereospecific migration of Np or Ph in the five-co-ordinate intermediate from silicon to the carbonyl group. Migration by Np and Ph occurs to *different* faces of the $\rangle CO$ group.[52]

The hydroxide ion-catalysed cleavage of the Si—H bond in pentamethyl- and tetramethyl-disiloxane in moist ethanol follows simple second-order kinetics.[53] Solvent effects on the alkali-catalysed hydrolysis of organosilicon hydrides are interpreted as showing that a hydrogen-bonded trimer $(H_2O)_3$ is involved.[54] Heterogeneous catalysis of the alcoholysis of the Si—H bond has been observed with a range of salts, *viz.* KNCS, HCO_2K, KF, CsF, and $MeCO_2Cs$; co-ordination by the anion at silicon to form an intermediate species is suggested.[55] A very unusual reaction occurs between organosilicon hydrides and $[Ph_3C]^+[AsF_6]^-$ in dichloromethane. Hydride transfer occurs, with the formation of a positively charged silicon intermediate. This is converted into a neutral intermediate, which then reacts to form a fluorosilane.[56] Cleavage of silicon compounds by halogens,

$$H_2O + 2XY + 2PhSiMe_3 \longrightarrow (Me_3Si)_2O + 2H^+ + 2Y^- + 2PhX$$

has been investigated in some detail.[57] Various rate laws have been observed. For some systems reaction stops at about 50% completion, possibly because of the formation of a complex between the halide ion product and the halogen. The polarity of the halogen appears to be a very important factor in determining reactivity. Thus for the second-order pathway BrCl is much more reactive than Br_2 or Cl_2 whereas for the third-order pathway ICI is much more reactive than IBr or Br_2:

$$\text{Rate} = k[PhSiMe_3][hal] \qquad hal = BrCl, Cl_2$$

$$\text{Rate} = k^1[PhSiMe_3][hal]^2 \qquad hal = ICI, IBr$$

$$\text{Rate} = k[PhSiMe_3][hal] + k^1[PhSiMe_3][hal]^2 \qquad hal = Br_2$$

[48] J. Chojnowski, M. Cypryk, and J. Michalski, *J. Organomet. Chem.*, 1978, **161**, C31.
[49] R. J. P. Corriu, J. M. Fernandez, and C. Guerin, *J. Organomet. Chem.*, 1978, **152**, 25.
[50] R. J. P. Corriu, J. M. Fernandez, and C. Guerin, *J. Organomet. Chem.*, 1978, **152**, 21.
[51] R. J. P. Corriu and C. Guerin, *J. Organomet. Chem.*, 1978, **144**, 165.
[52] A. G. Brook, T. J. D. Vandersar, and W. Limburg, *Can. J. Chem.*, 1978, **56**, 2758.
[53] J. J. Tondeur, G. Vandendunghen, and M. Xhigne, *Reaction Kinet. Catal. Lett.*, 1977, **7**, 327.
[54] O. W. Steward, A. G. Lutkus, and J. B. Greenshields, *J. Organomet. Chem.*, 1978, **144**, 147.
[55] J. Boyer, R. J. P. Corriu, P. Perz, and C. Reye, *J. Organomet. Chem.*, 1978, **157**, 153.
[56] J. Chojnowski, L. Wilczek, and W. Fortuniak, *J. Organomet. Chem.*, 1977, **135**, 13.
[57] J. R. Chipperfield, R. Z. Fernandez, and D. E. Webster, *J. Chem. Soc., Perkin Trans. II*, 1979, 117.

For reaction (7) simple second-order kinetics are observed.[58]

$$SiCl_3I + ICl \longrightarrow SiCl_4 + I_2 \quad (7)$$

A kinetic study of the electrophilic cleavage of the Si—Ar bond by HBr has been reported.[59] The kinetics of cleavage of the Si—S bond have been studied in the hydrolysis of compounds of the type $(RO)_3SiSH$ and R_3SiSH, to yield the corresponding Si—OH species and H_2S.[60]

The photolysis of $Me_3SiMePhSiSiMe_3$ and $Me_3SiPhMeSiSiPhMeSiMe_3$ in DMSO has been studied in some detail.[61] One pathway involves loss of PhMeSi, which then reacts with DMSO to yield phenyl methyl silanone,

$$PhMeSi + Me_2SO \longrightarrow PhMeSiO + Me_2S$$

which can be trapped. The other pathway by which reaction can occur involves nucleophilic attack by the oxygen of DMSO on the silicon of a PhMeSi group, with migration of a phenyl group to an adjacent silicon atom:

$$Me_3SiMePhSiSiMePhSiMe_3 + Me_2SO \longrightarrow Me_3SiSiMePh_2 + MeSi(O)SiMe_3 + Me_2S$$

The reaction of SiH_3PH_2 with NH_3 to form PH_3, $(SiH_3)_2NH$, and $(SiH_3)_3N$ has been studied, together with subsequent elimination reactions that lead to a series of silazane oligomers and polymers. The mechanisms for these exchange and redistribution reactions have been discussed.[62]

The condensation reactions of mono-, di-, and tri-silicic acid in aqueous acid solution can be followed by use of ^{29}Si n.m.r. spectroscopy. Hydrolysis reactions occur along with condensation reactions.[63] The kinetics of reaction of molybdic acid and condensed silicic acids have been examined. Three steps have been observed when cyclic silicates have been used: (i) complex formation between silicic acid and molybdic acid, (ii) cleavage of the Si—O—Si linkage, and (iii) formation of the molybdosilicic acid.[64] For open-chain silicic acids only two stages are observed. A series of highly selective interconversions of cyclosiloxanes can be carried out in polar solvents such as organonitrocompounds, using electrophilic catalysts such as zinc chloride or ferric chloride. Intermediates such as $MePhSiClOSiMe_2OSiPhMeOSiMe_2ZnCl$ are postulated.[65] The cleavage of the Si—O bond in $Me_3SiOOSiMe_3$ by anions (A^-) in propan-2-ol has been studied kinetically:[66]

$$Me_3SiOOSiMe_3 + A^- \longrightarrow Me_3SiA + [OOSiMe_3]^-$$

Hindered rotation in $Bu^t_2HSiSiHBu^t_2$ has been studied by ^1H and ^{13}C n.m.r. spectroscopy and provides an example of an intramolecular process. The marked difference to the behaviour of the corresponding carbon compound is ascribed to the increased length of the central bond.[67] Hindered rotation in the

[58] D. Hass, D. Ludewig, and S. Goldstein, *Z. Chem.*, 1978, **18**, 349.
[59] E. Hengge and H. Eberhardt, *Monatsh. Chem.*, 1979, **110**, 39.
[60] A. Herman, B. Becker, and W. Wojnowski, *Z. Anorg. Allg. Chem.*, 1979, **450**, 178.
[61] H. Okinoshima and W. P. Weber, *J. Organomet. Chem.*, 1978, **155**, 165.
[62] A. D. Norman and W. L. Jolly, *Inorg. Chem.*, 1979, **18**, 1594.
[63] D. Hoebbel, G. Garzó, G. Engelhardt, and A. Till, *Z. Anorg. Allg. Chem.*, 1979, **450**, 5.
[64] H. Stade, *Z. Anorg. Allg. Chem.*, 1978, **446**, 5; *ibid.*, 1978, **441**, 29.
[65] D. E. Spielvogel and C. L. Frye, *J. Organomet. Chem.*, 1978, **161**, 165.
[66] G. A. Razuvaev, V. A. Yablokov, A. V. Ganyushkin, N. V. Yablokova, and G. S. Kalinina, *J. Organomet. Chem.*, 1979, **165**, 281.
[67] D. A. Stanislawski, A. C. Buchanan, and R. West, *J. Am. Chem. Soc.*, 1978, **100**, 7791.

tetra-alkyldisilanes and the corresponding diphosphanes is remarkably similar, and it is concluded that there is no need to invoke special electronic effects to explain the latter.[68]

Germanium.—Previous work on the decomposition of $[GeH_3CO_2]^-$ in neutral and in alkaline solution has been followed by a study of the decomposition in aqueous acid. The products include carbon monoxide, a little monogermane, and a solid of approximate composition $GeH_{0.6}$. The rate law is relatively simple:

$$\text{Rate} = k[H^+][GeH_3CO_2H]$$

The species GeH_2 is suggested as an intermediate, and the mechanism proposed[69] is

$$GeH_3CO_2H + H^+ \longrightarrow [GeH_3]^+ + CO_2 + H_2$$

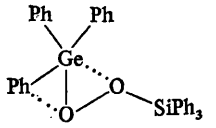
$$GeH_3^+ \rightleftharpoons GeH_2 + H^+$$

$$GeH_2 \longrightarrow GeH_4 + GeH_{0.6}$$

The situation is more complex than represented above; in strongly acid solution the formation of carbon monoxide is quantitative, but the yield of $GeH_4 + GeH_{0.6}$ is not. Instead $[GeH_3]^+$ is formed in solution. Ligand exchange between $[Ge(acac)_3]^+$ and ^{14}C-labelled acetylacetone has been studied[70] in TCE, $MeNO_2$, or MeCN solution:

$$\text{Rate} = k[H_2O][Ge(acac)_3^+]$$

The effect of added acid or base and the magnitude of the H/D isotope effect suggest that the rate-controlling step is governed by the ease of proton transfer between the leaving and the incoming ligand in an intermediate. The mechanism is different to that used to describe the racemization of $[Ge(acac)_3]^+$ The complex $[Ge(bzbz)_3]^+$ has been prepared and resolved. The kinetics of racemization and of exchange with the ^{14}C-labelled ligand in acetonitrile have been examined. The racemization is thought to occur by a mechanism involving solvent-assisted breaking of one Ge—O bond, leaving a 'dangling' ligand. However, a twist mechanism does not seem to have been completely excluded. The relatively slow rate of ligand exchange compared with the case of $[Ge(acac)_3]^+$ is attributed to steric effects.[71] The isomerization of $Ph_3GeOOSiPh_3$ to $Ph_2(PhO)GeOSiPh_3$ is catalysed by $[CN]^-$, and is suggested[72] to involve (1).



(1)

[68] S. G. Baxter, D. A. Dougherty, J. P. Hummel, J. F. Blount, and K. Mislow, *J. Am. Chem. Soc.*, 1978, **100**, 7795.

[69] D. J. Yang, *Report*, 1977, LBL-6290 (*Energy Res. Abs.*, 1978, **3**, 4555; *Chem. Abs.*, 1978, **88**, 177 783); D. J. Yang and W. L. Jolly, *Inorg. Chem.*, 1978, **17**, 621.

[70] A. Nagasawa and K. Saito, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 2015.

[71] F. B. Ueno, A. Nagasawa, and K. Saito, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 1363.

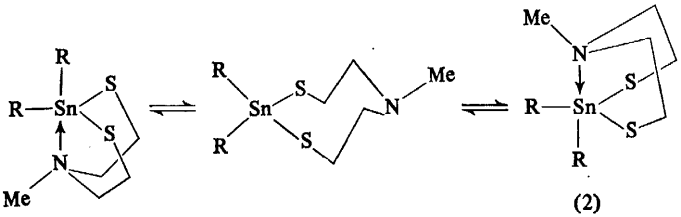
[72] V. A. Yablokov, G. S. Kalinina, M. V. Yablokova, T. A. Basalgina, N. S. Vyazankin, and G. A. Razuvaev, *J. Organomet. Chem.*, 1978, **153**, 25.

Tin.—A review on the chemistry of compounds containing the Sn—N bond contains some mechanistic material.[73] The formation of Ph_2SnL_2 from Ph_2SnCl_2 and L (L = a substituted 8-quinolate ion) has been studied kinetically in DMSO solution. Different rate laws are observed for the parent compound (8) and its 2-methyl derivative (9). Steric effects are suspected as the cause of the difference.[74]

$$\text{Rate} = (k_1 + k_2[\text{HL}]^2)[Ph_2SnCl_2] \quad (8)$$

$$\text{Rate} = (k_3 + k_4[\text{HL}])[Ph_2SnCl_2] \quad (9)$$

The solvolysis and substitution reactions of $[(2\text{-Mepy})_2SnCl_4]$, $[(3\text{-Mepy})_2SnCl_4]$, $[(4\text{-Mepy})_2SnCl_4]$, $[(\text{quinoline})_2SnCl_4]$, and $[(\text{isoquinoline})_2SnCl_4]$ in $(EtO)_3PO$ have been studied.[75] Exchange between Me_3SnCl and Me_3SnSPh has been studied by ^1H n.m.r., and the rate found to *decrease* with increase of temperature; mechanisms involving five- and eight-membered cyclic transition states are favoured.[76] Intramolecular mobility of ligand in five-co-ordinate tin, *N*-methyl-5,5-dialkyldiptychthia-azastannolidenes (2), occurs by a dissociation–inversion



(2)

mechanism.[77] Acid-catalysed cleavage reactions of vinyl and allyl tin compounds have been reported.[78] An S_E2 ion-pair mechanism is proposed for the reaction of some $RSnMe_3$ compounds with electron-withdrawing substituents (R = 9-Me-fluorenyl, indenyl, or PhC≡C) with halogens. In solvents of low polarity optically active indenyl derivatives racemize slowly, but the addition of HMPA increases this rate, probably occurring when $R^-[SnMe_3]^+$ reverts to the covalent form. In polar solvents a significant degree of dissociation occurs.[79]

Lead.—Exchange reactions involving polyamine-*N*-polyacetate complexes of lead(II) continue to be studied. An investigation of the substitution of lead(II) by cobalt(II) has been reported,[80] and there has been a re-interpretation of earlier data on ligand-exchange kinetics between $[Pb^{II}(\text{edta})]$ and *R*-(−)-pdta.[81] Rates

[73] Yu. I. Dergunov, V. F. Gerega, and O. S. D. Yachkovskaya, *Russ. Chem. Rev.* (*Engl. Transl.*), 1977, **46**, 1132.
[74] D. F. Martin and B. S. Jurmark, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1493; D. F. Martin and R. D. Walton, *J. Organomet. Chem.*, 1966, **5**, 57.
[75] R. C. Paul, D. D. Sharma, and J. C. Bhatia, *Indian J. Chem., Sect. A*, 1978, **16**, 334 (*Chem. Abs.*, 1978, **89**, 118 462).
[76] E. D. Korniets, L. A. Fedorov, E. I. Fedin, and D. N. Kratsov, *Bull. Acad. Sci. USSR*, 1977, **26**, 1401.
[77] C. Mugge, K. Jurkschat, A. T. Tzschach, and A. Zschunke, *J. Organomet. Chem.*, 1979, **164**, 135.
[78] V. Peruzzo, G. Plazzogna, and D. Marton, *Inorg. Chim. Acta*, 1978, **30**, 145; G. Plazzogna, V. Peruzzo, and G. Rossetto, *Inorg. Chim. Acta*, 1978, **31**, L395.
[79] I. P. Beletskaya, A. N. Kashin, and O. A. Reutov, *J. Organomet. Chem.*, 1978, **155**, 51.
[80] T. Nozaki and M. Sakamoto, *Nippon Kagaku Kaishi*, 1978, 639 (*Chem. Abs.*, 1978, **89**, 12 703).
[81] J. D. Carr, *Inorg. Chem.*, 1978, **17**, 1095.

of complexation of Pb^{2+} by 15-crown-5 and 18-crown-6 ethers in aqueous solution have been examined by ultrasonic methods (Sr^{2+}, Ba^{2+}, and Hg^{2+} were also studied). A two-stage mechanism is preferred involving a conformational change in the crown ether, followed by a rate-determining step involving loss of co-ordinated water. A plot of rate against (charge/radius) gave a common line for cations with a noble gas configuration, but higher rates for Pb^{2+}, Hg^{2+}, Ag^{+}, and Tl^{+}. These ions give rates that show a distinct dependence upon the nature of the ligand, and the rate-determining step may involve the loss of more than one co-ordinated water molecule.[82] A number of studies of the interaction of metal cations with organosulphur compounds have appeared in recent years. The reaction of thioacetamide with Pb^{2+} (and also Cd^{2+} and Co^{2+}) in aqueous acetate buffer has been shown to involve the formation of 1:1 metal thioacetamide complexes, followed by a rate-determining step involving a conjugate

$$MeCSNH_2 + M^{2+} \longrightarrow MS + MeCN + 2H^{+}$$

base of the complex. The relative reactivities are $Pb^{II} > Cd^{II} > Co^{II}$, and are consistent with HSAB theory.[83] There has been a study of the cleavage of Pb_2Ar_6 by hydrogen chloride in dioxan, in chloroform, and in 20% methanol–80% benzene. Simple second-order kinetics were observed, and for substituted phenyl groups the reactivity sequence is *p*-OMe > *p*-Me > *m*-Me > H > *p*-Cl > *m*-Cl. There was little or no isotope effect when DCl was used in place of HCl. A four-centre transition state is proposed, with Pb—Cl and C—H bond formation more advanced than the fission of the H—Cl and Pb—C bonds.[84]

3 Group V

Nitrogen.—A more detailed report has now appeared on the kinetics of aromatic nitration of toluene by nitric acid in 77.3 and 78.45% w/w sulphuric acid, which supersedes an earlier account.[85] Activation energies for the hydration of $[NO_2]^{+}$ are reported as 10.5 ± 4.0 and 12.0 ± 4.0 kcal mol^{-1} for the two sulphuric acid concentrations respectively. The kinetics of nitration of reactive aromatics in sulphuric acid, perchloric acid, and methanesulphonic acid have been studied by another group.[86] They have worked in the region where the kinetic order in [ArH] lies between 0 and 1, and have obtained rate constants for the formation of the nitronium ion. Plots of $d(\log k)/d(-H_0)$ give slopes close to unity, and the authors argue that the mechanism involves general acid catalysis.

$$[B—H]^{+} + HONO_2 \longrightarrow B + H_2O + [NO_2]^{+}$$

The ionization ratio $[NO_2^{+}]/[HNO_3]$ for nitric acid in 80—96% sulphuric acid has been studied by Raman spectroscopy[87] and a pK_a of -15.2 evaluated. Measurements based on u.v. spectra ($pK_a = -15.3$) are generally consistent with

[82] L. J. Rodriguez, G. W. Liesegang, M. M. Farrow, N. Purdie, and E. M. Eyring, *J. Phys. Chem.*, 1978, **82**, 647.
[83] O. M. Peeters, N. M. Blaton, and C. J. de Ranter, *J. Chem. Soc., Perkin Trans. II*, 1978, 23.
[84] V. G. Kumar Das, Ng Seik Weng, and L. H. Gan, *J. Organomet. Chem.*, 1978, **157**, 219.
[85] G. F. Sheats and A. N. Strachan, *Can. J. Chem.*, 1978, **56**, 1280.
[86] R. B. Moodie, K. Schofield, and P. G. Taylor, *J. Chem. Soc., Perkin Trans. II*, 1979, 133.
[87] N. C. Marziano, P. G. Traverso, A de Santise, and M. Sampoli, *J. Chem. Soc., Chem. Commun.*, 1978, 873.

the Raman value, though there are problems with the quantitative interpretation of the u.v. data. Two other studies in nitric acid–sulphuric acid mixtures may be mentioned. The reaction with formic acid shows oscillatory behaviour in gas evolution.[88] A new mechanism for the nitrous acid-catalysed reaction of dimethylaniline with nitric acid in 85% sulphuric acid has been postulated, involving a radical–cation pair intermediate:[89]

$$[PhNMe_2H]^+ + [NO]^+ \xrightarrow{\text{slow}} [PhNMe_2 \cdot {}^+NO] \xrightarrow[\text{fast}]{\text{nitrate}} \text{products}$$

A kinetic study of hydrogen isotope exchange between the nitrogen pole of aromatic amines and acid solvents shows that this process is also catalysed by $[NO]^+$, and gives the same rate law and rate constants to the above reaction. A similar intermediate is suspected.

A full account has now appeared[90] of the kinetics of the reaction of sulphamic acid with nitric acid mentioned in Volume 5, but the details of the mechanism are

$$NH_2SO_3H + HNO_3 \longrightarrow H_2SO_4 + N_2O + H_2O$$

still unresolved. A ^{15}N study of the reaction confirms[91] the earlier views that nitramide (nitroamine) is probably the precursor of most of the nitrous oxide formed in the decomposition. However, it is suggested that at lower temperatures than those used in the kinetic studies there may also be a pathway involving nitroxyl as an intermediate, which dimerizes to form nitrous oxide.

Nitroxyl is a species that has often been postulated as an intermediate in reaction of nitrogen compounds. It has recently been proposed that there may be two different forms of nitroxyl, with different reactivities. This conclusion arises[92] from a study of the reactions of nitroxyl in the present of hydroxylamine:

$$2HNO \longrightarrow N_2O + H_2O$$

$$HNO + NH_2OH \longrightarrow N_2 + 2H_2O$$

The nitroxyl species formed in the decomposition of trioxodinitrate (Angeli's Salt),

$$[HN_2O_3]^- \longrightarrow HNO + [NO_2]^-$$

gives a different proportion of dinitrogen to nitrous oxide to the nitroxyl formed in the reaction of nitric oxide with hydroxylamine:

$$NO + NH_2OH \longrightarrow HNO + NHOH$$

$$[NO]^- + NH_2OH \longrightarrow N_2 + [OH]^- + H_2O$$

$$NO + NHOH \longrightarrow [HONH{-}NO] \longrightarrow N_2O + H_2O$$

It is suggested that the two different forms may be due to different electron states of nitroxyl, rather than the reaction of different tautomers HNO and NOH.

Some interesting work has appeared on the reaction mechanisms of nitrosyl

[88] C. J. G. Raw, J. Frierdich, F. Perrino, and G. Jex, *J. Chem. Phys.*, 1978, **82**, 1952.
[89] J. C. Giffney and J. H. Ridd, *J. Chem. Soc., Perkin Trans. II*, 1979, 618.
[90] M. N. Hughes, J. R. Lusty, and H. L. Wallis, *J. Chem. Soc., Dalton Trans.*, 1978, 530.
[91] L. S. Dzelkalns and F. T. Bonner, *Inorg. Chem.*, 1978, **17**, 3710.
[92] F. T. Bonner, L. S. Dzelkalns, and J. A. Bonucci, *Inorg. Chem.*, 1978, **17**, 2487.

compounds. *Ab initio* calculations have been made[93] on a relatively new species, nitrosyl cyanide, and its decomposition reactions:

$$N_2 + CO \longleftarrow ONCN \longrightarrow NO + CN$$

A particularly interesting study concerns[94] the reactivity of N_2O_4 and N_2O_3. There has long been speculation about the possible role of the isomeric species $ONONO_2$ in the reactions of O_2NNO_2, and of ONONO in the reactions of O_2NNO. There has been evidence from matrix-isolation studies that such species can exist, but now these have been postulated as the reactive forms in the reaction of gaseous oxides of nitrogen with secondary amines in aqueous solution. There are unexpectedly large amounts of *N*-nitrosation in the reaction of gaseous N_2O_4 with piperidine in 0.1 M sodium hydroxide. It is suggested that the $ONONO_2$ isomer is formed when the nitrogen(IV) oxide dissolves in the aqueous solution, and that this nitrosates before hydrolysis by alkali. A similar result is observed for reaction of a gaseous mixture of $NO + NO_2$ (N_2O_3) with piperidine in aqueous alkali, and this may indicate ONONO as an active species. The results imply that the hydrolyses of N_2O_4 and N_2O_3 in aqueous solution are not catalysed by alkali. These observations are worth a good deal of attention; certainly electrophilic *N*-nitrosation in alkaline solution is most unusual. A more familiar type of *N*-nitrosation of substituted anilines by nitrosyl chloride and nitrosyl bromide has been reported.[95] The formation of nitrosyl halides from nitric oxide and the halogens is one of the classic reactions studied by kineticists, and has long been the standard example of third-order kinetics in gas-phase reactions These processes have now been studied in non-aqueous solvents, and follow a rate law similar to that observed in the gas phase:

$$d[NOX]/dt = k_f[NO]^2[X_2] - k_b[NOX]^2$$

$$2NO + X_2 \rightleftharpoons 2\,NOX$$

Values of k_f are 2.79×10^6, 2.75×10^3, and 8.83×10^5 $M^{-2}\,s^{-1}$ for reaction in carbon tetrachloride at 25 °C for X = O, Cl, and Br respectively.[96] The value of k_f increases on going from carbon tetrachloride to glacial acetic acid. Another study[97] somewhat similar to this concerns the kinetics of the thermal decomposition of nitryl chloride in 1-chloroperfluoroheptane. There are two parallel processes, (10) and (11). Some nitrosyl chloride is formed as a by-product in the

$$2ClNO_2 \longrightarrow 2NO_2 + Cl_2 \qquad (10)$$

$$2ClNO_2 \longrightarrow 2ClNO + O_2 \qquad (11)$$

first of these reactions (10). This nitrosyl chloride can have a significant effect on the kinetics and mechanism of reaction,[98] and this is summarized below.

$$ClNO + ClNO_2 \longrightarrow NO + Cl_2 + NO_2 \quad \text{slow}$$

$$NO + ClNO_2 \longrightarrow ClNO + NO_2 \quad \text{fast}$$

[93] B. G. Gowenlock and L. Radom, *Aust. J. Chem.*, 1978, **31**, 2349.
[94] B. C. Challis and S. A. Kyrtopoulos, *J. Chem. Soc., Perkin Trans. II*, 1978, 1296.
[95] M. R. Crampton, J. T. Thompson, and D. L. H. Williams, *J. Chem. Soc., Perkin Trans. II*, 1979, 18.
[96] W. C. Nottingham, *Diss. Abs. Int. B.* 1978, **38**, 5409 (*Chem. Abs.*, 1978, **89**, 31 482).
[97] H. D. Knauth and H. Martin, *Z. Naturforsch.*, 1978, **33a**, 1037.
[98] H. D. Knauth, H. Martin, and H. Schlapkohl, *Z. Naturforsch.*, 1978, **33a**, 1048.

Several other reactions of nitrogen–oxygen compounds have been studied mechanistically. There is an account of the oxidation of nitrite ion to nitrate ion by hypochlorite in aqueous basic solution (pH 11) and by chlorite in mildly acid aqueous solution (pH 5). The rate laws are similar,

$$-\mathrm{d}[NO_2^-]/\mathrm{d}t = k[H^+]^2[ClO^-][NO_2^-]$$
$$-\mathrm{d}[NO_2^-]/\mathrm{d}t = k'[H^+]^2[ClO_2^-][NO_2^-]$$

and it is stated[99] that the reaction mechanisms seem to be identical on the basis of the kinetic expressions and the activation energies. The alkaline hydrolysis of alkyl nitrates has been investigated, including an ^{18}O tracer study. Exclusive N—O bond fission is observed.[100] A study of the reaction of nitrous acid with $[Co(en)_2Cl(NH_2OH)]^{2+}$ shows a complex dependence upon acidity. For $[H^+] > 0.1$ M rate law (12) is observed, whereas at lower acidities (13) is found. When the corresponding complex of *O*-methylhydroxylamine is prepared the

$$\text{Rate} = k[H^+][HNO_2][Co(en)_2Cl(NH_2OH)^+] \quad (12)$$
$$\text{Rate} = k'[H^+]^{-1}[HNO_2][Co(en)_2Cl(NH_2OH)^+] \quad (13)$$

reactivity towards nitrous acid is very much reduced.[101] Rate law (12) is the form characteristic of an electrophilic nitrosation reaction, and a pathway of the type (14) seems possible, similar to that observed for the nitrosation of free hydroxylamine. The mechanism of oxidation of the free hyponitrite ion by dinitrogen tetroxide has been discussed, together with the corresponding reaction of Angeli's Salt (disodium trioxodinitrate). Reaction is suggested[102] to involve attack by the nitrosonium ion at an oxygen centre.

$$Co(NH_2OH) \longrightarrow CoNH{-}ONO \longrightarrow Co(\text{hyponitrite}) \begin{matrix} \nearrow N_2O \\ \searrow N_2 \end{matrix} \quad (14)$$

One of the most striking properties of hydrazine is the high nucleophilic reactivity, an example of the α-effect. *Ab initio* SCF calculations have been carried out for a number of nucleophiles (including hydrazine), some of which show the α-effect. For the group as a whole there was no general correlation between nucleophilic reactivity and the properties of the HOMO; however, the α-effect nucleophiles did possess an antisymmetric, antibonding HOMO, and electrons in this orbital are expected to be readily polarized by an approaching electrophile. The calculations are held strongly to support Ingold's view of α-nucleophilicity.[103] The reduction of cobalt(III) carbonate complexes by hydrazine appears to involve a rate-determining nucleophilic substitution by hydrazine.[104]

[99] T. Nagaishi. S. Nozaki, T. Kaneda, M. Matsumoto, S. Yoshinaga, H. Nakamura, S. Arieda, and L. Nakamori, *Kyushu Sangyo Duigaku Kogakubu Kenkyu Hokoku*, 1977, **14**, 4 (*Chem. Abs.*, 1978, **89**, 186 639).

[100] S. Oae, N. Asai, and K. Fujimori, *J. Chem. Soc., Perkin Trans. II*, 1978, 571.

[101] M. N. Hughes, K. Shrimanker, and P. E. Wimbledon, *J. Chem. Soc., Dalton Trans.*, 1978, 1634.

[102] H. Schultheiss and E. Fluck, *Z. Anorg. Allg. Chem.*, 1977, **437**, 47.

[103] M. M. Heaton, *J. Am. Chem. Soc.*, 1978, **100**, 2004.

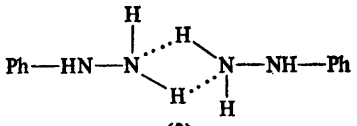
[104] S. P. Tanner, *Inorg. Chem.*, 1978, **17**, 600.

Similarly the reduction of iodine by hydrazine appears to involve the latter species acting as a nucleophile:[105]

$$I_2 + N_2H_4 \rightleftharpoons [N_2H_4I]^+ + I^-$$

$$[N_2H_4I]^+ \rightleftharpoons \text{products}$$

Proton transfer between salicylic acid and tetra-alkylhydrazines has been studied[106] in DMSO. The rates are remarkably low, and give a Brønsted coefficient of -1.16. Proton exchange in liquid phenylhydrazine occurs much more readily at the NH_2 than at the NH group. A transition state of type (3) is suggested.[107]



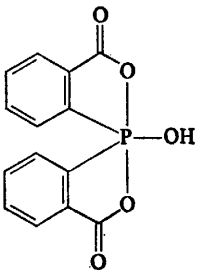
(3)

There has been a good deal of activity in the field of di-imide chemistry recently, including claims to have observed *cis*-HN=NH.[108] A recent report of the isolation of *cis*-MeN=NH has appeared. The i.r. spectrum has been measured, and on the basis of a vibrational assignment of the spectrum the authors question whether in fact *cis*-HN=NH has yet been observed.[109] The group who reported the observation of *cis*-HN=NH have investigated the acid-catalysed decomposition of di-imide; reaction proceeds *via* a dimerization reaction, forming ammonium azide as the end product.[110] Theoretical calculations of the pathways by which *cis*- and *trans*-di-imide can act as reducing agents towards ethene have been published.[111] Another species which has often been postulated as an intermediate in reactions of nitrogen–hydrogen compounds, triazene (H_3N_3), has been observed[112] in pulse radiolysis studies of aqueous solutions of hydrazine. The conjugate acid and base species, $[H_4N_3]^+$ and $[H_2N_3]^-$ (or $[H_3N_3OH]^-$), have also been observed and pK values obtained. The kinetics of decomposition of triazene have been measured in this study, and the rates show a complex dependence on pH. The base-catalysed decomposition of nitroamine has been studied in 80% w/w DMSO–H_2O. The mechanism is essentially the same as in water.[113] Finally we note that a mechanism has been proposed for the reaction of urea with sulphuric acid.[114]

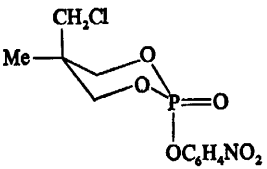
Phosphorus.—Reactions of oxoanions and related species, phosphorus–oxygen–nitrogen compounds, phosphazanes, and other components and intramolecular processes are considered in this section.

[105] S. E. King, J. N. Cooper, and R. D. Crawford, *Inorg. Chem.*, 1978, **17**, 3306.
[106] S. F. Nelsen, P. J. Kinlen, and D. H. Evans, *J. Am. Chem. Soc.*, 1979, **101**, 1875.
[107] I. Yavari and J. D. Roberts *J. Am. Chem. Soc.*, 1978, **100**, 4662.
[108] N. Wiberg, G. Fischer, and H. Bachhuber, *Angew. Chem. Int. Ed. Engl.*, 1977, **16**, 780.
[109] N. C. Craig, M. A. Kliewer, and N. C. Shah, *J. Am. Chem. Soc.*, 1979, **101**, 2480.
[110] N. Wiberg, H. W. Haering, and S. K. Vasisht, *Z. Naturforsch.*, 1979, **34b**, 356.
[111] D. J. Pasto and D. M. Chipman, *J. Am. Chem. Soc.*, 1979, **101**, 2290.
[112] J. W. Sutherland, *J. Phys. Chem.*, 1979, **83**, 789.
[113] P. de Maria and A. Fini, *J. Solution Chem.*, 1977, **6**, 727.
[114] A. R. Butler and C. Glidewell, *J. Chem. Res.* (*S*), 1978, 239.

A review has appeared[115] on the kinetics of hydrolysis of phosphate esters. Hydroxyphosphoranes have long been postulated as intermediates in the hydrolysis of esters of oxoacids of phosphorus. Compound (4), which is a possible model for such species, has been synthesized.[116] Nucleophilic substitution at *cis*- and *trans*-isomers of (5) (X=*p*-$NO_2C_6H_4$) by nucleophilic oxoanions in aprotic solvents gives complex results. The degree of retention/inversion is strongly dependent upon the cation, and on the solvent. The inversion process involves an S_N2 tbp-type transition state, while the retention process is suggested to involve the addition of an ion pair across the P=O bond to form a square-pyramidal species.[117]



(4)



(5)

The hydrolysis of dimethyl aroylphosphonates proceeds by initial hydration of the carbonyl group, followed by an alkali-catalysed step involving cleavage of a P—C bond:[118]

$$ArCOP(O)(OMe)_2 + H_2O \rightleftharpoons ArC(OH)_2P(O)(OMe)_2$$

$$ArC(OH)_2P(O)(OMe)_2 + [OH]^- \rightleftharpoons ArC(O^-)(OH)P(O)(OMe)_2$$

$$ArC(O^-)(OH)P(O)(OMe)_2 \longrightarrow ArCOOH + HP(O)(OMe)_2$$

The acid-catalysed hydrolysis of $PhCOP(O)(OEt)_2$ is also thought to proceed by a mechanism involving carbonyl addition of water.[119] There is ^{18}O evidence for a phosphorane intermediate in the hydrolysis of $MeP(O)(OPh)_2$.[120] The hydrolysis of $P(O)(NH_2)_3$ in acetate buffers has been examined.[121] Studies of micellar catalysts of the dephosphorylation of *p*-$NO_2C_6H_4OP(O)(OPh)_2$ have been reported.[122] The formation of phosphate esters from $P(O)Cl_3$ and *p*-octylphenol in kerosene solution has been reported.[123] The formation and hydrolysis of condensed phosphate species has always been a topic of interest, and there is

115 V. E. Bel'skii, *Russ. Chem. Rev.* (*Engl. Transl.*), 1977, **46**, 828.
116 Y. Segall and I. Granoth, *J. Am. Chem. Soc.*, 1978, **100**, 5130.
117 M. Bauman and W. S. W. Wadsworth, jun., *J. Am. Chem. Soc.*, 1978, **100**, 6388.
118 R. Kluger and J. Chin, *J. Am. Chem. Soc.*, 1978, **100**, 7382.
119 K. S. Narayanan and K. D. Berlin, *J. Am. Chem. Soc.*, 1979, **101**, 109.
120 I. Sigal and F. Westheimer, *J. Am. Chem. Soc.*, 1979, **101**, 752.
121 N. Kumagai, M. Uemura, and H. Mase, *Nippon Kagaku Kaishi*, 1978, 535 (*Chem. Abs.*, 1978, **89**, 12 674).
122 C. A. Bunton, G. Cerichelli, Y. Ihara, and L. Sepulveda, *J. Am. Chem. Soc.*, 1979, **101**, 2429.
123 C. K. Yun, C. K. Choi, J. S. Chung, and Y. M. Koo, *Inorg. Nucl. Chem. Lett.*, 1978, **14**, 405.

an account[124] of the use of ^{31}P n.m.r. to investigate the hydrolysis of condensed phosphates in aqueous sodium silicate solution. $Na_3P_3O_9$ hydrolyses by the route (15) whereas $Na_4P_4O_{12}$ hydrolyses at a lower rate by reaction (16).

$$[P_3O_9]^{3-} + 2[OH]^- \longrightarrow [P_3O_{10}]^{5-} + H_2O \quad (15)$$

$$[P_4O_{12}]^{4-} + 2[OH]^- \longrightarrow [P_4O_{13}]^{6-} + H_2O \quad (16)$$

The hydrolysis of the imido-derivative of the trimetaphosphate anion, $Na_3O_6P_3(NH)_3$ has been examined[125] in acid and alkaline solution. In 1 M hydrochloric acid hydrolysis to di-imidotrimetaphosphate and then to imido-trimetaphosphate occurs by successive substitution of NH by O, but without any ring opening. There have also been ^{17}O studies of the exchange of water with molybdophosphovanadic heteropolyanions.[126]

The reaction of orthophosphorous acid, H_3PO_3, with vanadium(v) in the presence of silver(I) yields a rate law that is zero-order with respect to the concentration of vanadium(v). This is not thought to involve a rate-determining formation of the tautomer $P(OH)_3$ from $HP(O)(OH)_2$, but instead a mechanism involving the formation of complexes between H_3PO_3 and vanadium(v) is favoured.[127] Phosphite esters are involved in the Arbusov reaction, and there has been work on the mechanism of the reactions between trimethyl phosphite and α-halogenoacetophenones.[128]

A review has been published, containing some kinetic material on the reaction of compounds containing the $\rangle$P—S— group with alkyl halides.[129] An intermediate has been detected[130] in the reaction of aniline with α-$P_4S_3I_2$:

$$3PhNH_2 + \alpha\text{-}P_4S_3I_2 \longrightarrow 2PhNH_3I + P_4S_3(NHPh)_2$$

$$P_4S_3(NHPh)_2 \longrightarrow P_4S_3(NPh) + PhNH_2$$

The use of P_4S_{10} as a mild reducing agent for converting sulphoxides into sulphides appears[131] to involve a rate-determining nucleophilic attack by the oxygen in the S→O bond at phosphorus in P_4S_{10}. Phosphonium intermediates have been detected[132] in the reaction of phosphorus thionesters, $\rangle$P(S)OR, with chlorine or sulphuryl chloride. The alkaline hydrolysis of trolene, a commonly used insecticide, has been examined:[133]

$$(MeO)_2P(S)OAr \longrightarrow (MeO)_2P(S)OH + HOAr$$

Ar = 2,4,5-trichlorophenyl

Mechanisms have been proposed for the reactions of phosphorus(v) halides with sulphuric acid, chlorosulphonic acid, fluorosulphonic acid, and 25% and

[124] A. Porzel, E. Roensch, B. Thomas, and H. Scheler, *Z. Chem.*, 1978, **18**, 340.
[125] L. Meznik, J. Novosad, and K. Dostal, *Collect. Czech. Chem. Commun.*, 1978. **43**, 2846.
[126] M. N. Fedotov and R. I. Maksimovskaya, *Dokl. Akad. Nauk SSSR*, 1978, **240**, 128 (*Chem. Abs.*, 1978, **89**, 118 422).
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[133] E. V. Zakharov and V. A. Kharmats, *Russ. J. Phys. Chem. (Engl. Transl.)*, 1977, **51**, 640.

65% oleum on the basis of a ^{31}P n.m.r. study.[134] This work has been extended to the phosphorus(III) halides.[135]

The reaction of $P_4N_4Cl_8$ with *N*-methylaniline involves predominately a non-geminal substitution pathway,[136] whereas the reaction of 1-propenyl-lithium or 2-propenyl-lithium with $P_3N_3F_6$ occurs by geminal substitution.[137] This latter result was not expected on the basis of either polar or steric effects, and it is suggested that the first substitution modifies the properties of the substituted phosphorus so that the 3*d* orbitals no longer effectively overlap with the lone pair on the nitrogen. Ammonolysis of *N*-methyl-*N*-(diethoxyphosphorylamido)chlorocyclotriphosphazatrienes yields products with geminal amino-groups,[138] $P_3N_3Cl_3[NMeP(O)(OEt)_2](NH_2)_2$ and $P_3N_3Cl_2[NMeP(O)(OEt)_2]_2(NH_2)_2$. Geminal substitution in $(NPCl_2)_2NSOF$, $(NPCl_2)NSOPh$, and *trans*-$NPCl_2(NSOPh)_2$ by thiocyanate ion is observed.[139] The reaction of *cis*-$NPCl_2(NSOCl)_2$ with dimethylamine gives four isomeric products $N_3PS_2O_2Cl_3NMe_2$, and a second substitution produces three isomeric products. The position of substitution is strongly dependent upon solvent; an S_N2 mechanism is proposed for these reactions in diethyl ether and an S_N1 process in acetonitrile.[140] A study of the rates of monoamination of $P_3N_3Cl_6$ by a wide range of amines has been reported.[141] A two-step mechanism, involving the formation and decomposition of a five-co-ordinate phosphorus intermediate is favoured. The role of steric effects on the rate of reaction is discussed in some detail. The authors have also described[142] a method for the determination of *cis*- and *trans*-configurations in 2,4,6,6-tetrachloro-2,4-Ar(dialkylamino)cyclotriphosphazenes based upon ^{19}F n.m.r., which may be useful in mechanistic studies of the substitution reactions of the phosphazanes.

The reaction of 2,4-dinitrophenyl dihydrogen phosphate, $ArPH_2$, and the salts $[ArPH]^-[R_4N]^+$, $[ArPH]^-[R^1{}_3NH]^+$, $[ArP]^{2-}[R_4N]^+[R^1{}_3NH]^+$, and $[ArP]^{2-}[R^1{}_3NH]^+$ ($R^1{}_3N = Pr^i{}_2EtN$, $R_4N = Bu^n{}_4N$) has been studied[143] in protic and aprotic solvents in the presence and absence of alcohols or water. The acid $ArPH_2$ and the monoanion $[ArPH]^-$ react *via* an arylphosphorane five-co-ordinate intermediate, whereas the dianion $[ArP]^{2-}$ reacts by a pathway generating monomeric metaphosphate $[PO_3]^-$. An analysis of substituent effects on the kinetics of hydrolysis of quaternary phosphonium salts in aqueous methanol is considered to support a mechanism involving an R_4POH adduct (as proposed by Ingold in 1929):[144]

$$[R_4P]^+ + [OH]^- \longrightarrow R_4POH \longrightarrow R_3PO + RH$$

[134] K. B. Dillon, M. P. Nisbet, and T. C. Waddington, *J. Chem. Soc., Dalton Trans.*, 1978, 1455.
[135] K. B. Dillon, M. P. Nisbet, and T. C. Waddington, *J. Chem. Soc., Dalton Trans.*, 1979, 883.
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[142] Z. Biran and J. M. E. Goldschmidt, *J. Chem. Soc., Dalton Trans.*, 1979, 1017.
[143] F. Ramirez and J. F. Marecek, *J. Am. Chem. Soc.*, 1979, **101**, 1460.
[144] B. Siegel, *J. Am. Chem. Soc.*, 1979, **101**, 2265.

Ideas on the mechanism of hydrolysis reaction of silicon compounds have been suggested to be applicable to the hydrolysis of phosphates and phosphonates.[145] Kinetic evidence has been presented for analogies between the mechanism of hydrolysis of menthyl chloro(phenyl)phosphonate and the mechanism of hydrolysis of chlorosilanes.[146] Two intermediates have been detected in the chlorination of $PhP(SiMe_3)_2$ to $PhPCl_2$ by $COCl_2$.[147] Scrambling reactions in tetra-alkyl- and tetra-aryl-diphosphanes have been studied by ^{31}P, ^{1}H, and ^{13}C n.m.r.[148] Kinetic parameters for the opening and reclosing of spirophosphoranes containing a P—H bond have been measured using ^{31}P n.m.r.[149]

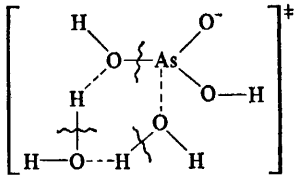
Theoretical calculations on PH_5 indicate[150] a much smaller energy barrier for the Berry Pseudorotation mechanism than for the Turnstile Rotation mechanism. It is predicted that the Turnstile mechanism will be most favoured with bulky and electropositive ligands on the system. The barrier to fluorine exchange in CF_3MePF_3 has been measured by low-temperature n.m.r.; when this is combined with barrier data in other substituted fluorophosphorus compounds it suggests that in $(CF_3)_2PF_3$ the free energy of activation for fluorine exchange will be around 1—3 kcal mol^{-1}. A comparison of $(CF_3)_3PMe_2$ with CF_3MePF_3 has led to the suggestion that the exchange process for chlorine is different to that for fluorine.[151] The averaging of CF_3 group environments in $(CF_3)_3MePY$, (Y = F, Cl, OMe, SMe, or NMe_2) by n.m.r. gives $\Delta G^{\ddagger}$ values $F < Cl < OMe < SMe < NMe_2$. $(CF_3)_3PMe_2$ does not show fluxional behaviour up to 90 °C. A multiple-step pathway consisting of sequential Berry-type processes is proposed.[152] N.m.r. studies suggest[153] an intramolecular fluorine transfer process between $F_5PCH_2PF(NMe_2)_2$ and $F_4PCH_2P(F)_2(NMe_2)_2$. Fluxional behaviour has been observed in PF_2NHPF_4.[154]

Arsenic.—^{17}O N.m.r. studies of aqueous solutions of sodium arsenite (0.6—4.1 M) indicate[155] a pathway for exchange involving $[AsO(OH)]^-$. Two parallel reactions are observed, one first order and one second order in arsenite concentration. For the first-order process a very negative entropy change, $\Delta S^{\ddagger} = -29$ cal K^{-1} mol^{-1}, is interpreted as showing that two water molecules are involved (6), whereas the second-order process is thought to be a reversible dehydration:

$$2[AsO(OH)_2]^- \rightleftharpoons H_2O + [As_2O_3(OH)_2]^{2-}$$

The mechanism of reduction of arsenic(III) by hypophosphorous acid in hydrochloric acid involves a substitution process, with the formation of bridged species

[145] R. J. P. Corriu, C. Guérin, and G. Guiraud, *J. Chem. Soc., Chem. Commun.*, 1979, 8.
[146] R. J. P. Corriu, G. F. Lanneau, and D. Leclercq, *J. Organomet. Chem.*, 1978, **153**, C1.
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[152] R. G. Cavell, J. A. Gibson, and K. I. The, *Inorg. Chem.*, 1978, **17**, 2880.
[153] A. H. Cowley and R. C.-Y. Lee, *Inorg. Chem.*, 1979, **18**, 60.
[154] D. W. H. Rankin and J. G. Wright, *J. Chem. Soc., Dalton Trans.*, 1979, 1070.
[155] W. C. Copenhafer and P. H. Rieger, *J. Am. Chem. Soc.*, 1978, **100**, 3776.



(6)

between $As(OH)_2Cl$, $As(OH)Cl_2$, and $AsCl_3$ and the tautomeric form of H_3PO_2.[156] A kinetic study involving the enzyme-catalysed arsenolysis of D-glyceraldehyde-3-phosphate by arsenic(V) has been used as an analytical method for arsenic.[157] The variation of the n.m.r. spectrum of the spiroarsanes $PhAs(O_2C_2Me_4)_2$ and $HOAs(O_2C_2H_4)_2$ has shown that they lie on the Berry co-ordinate between the trigonal-bipyramidal and the square-pyramidal geometries. The implication of this in the interpretation of the n.m.r. spectra of spiroarsanes has been discussed.[158]

Antimony.—Acetic anhydride usually acts as an electrophilic acylating agent, but in the reaction with $Sb(OR)_3$ the variation of rate with the nature of the alkyl group leads to the conclusion that antimony is the electrophilic centre, and that it attacks the 'ether' oxygen of acetic anhydride:[159]

$$Sb(OR)_3 + nAc_2O \longrightarrow (RO)_{3-n}Sb(OAc)_n + nROAc$$

A rather thorough investigation of the complex formed between MeCN and SbF_5 in non-aqueous solvents has been carried out using i.r., Raman, and ^{13}C, ^{121}Sb, and ^1H n.m.r. spectroscopy. The breakdown of the complex occurs by a dissociative mechanism.[160]

Bismuth.—Rate and equilibrium studies of the hydrolysis of Bi^{3+} by d.c. polarography have been reported.[161]

4 Group VI

Oxygen.—A kinetic study of the decomposition of triethyloxonium salts, $[OEt_3]A$ ($[A]^- = [BF_4]^-$, $[PF_6]^-$, or $[SbF_6]^-$) in methylene chloride has been studied. The decomposition is strongly affected by the presence of EtOEt or dioxan. The mechanism is suggested to involve a four-centre transition state.[162]

Sulphur.—*Ab initio* calculations indicate[163] that a weak $[R_3S_3]^-$ complex is an intermediate in the exchange reaction between R^1SSR^2 and $[R^3S]^-$. The calculations indicate a linear species, with the charge located on the peripheral sulphur

[156] M. B. Muratbekov, B. A. Berenzhanov, E. S. Bugenov, M. Burkitbaev, and S. A. Ermekova, *Kinet. Katal.*, 1978, **19**, 1085 (*Chem. Abs.*, 1978, **89**, 169 778).
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[163] J. A. Pappas, *J. Chem. Soc., Perkin Trans. II*, 1979, 67.

atoms. The kinetics of solvolysis of $(HS)_2CS$, (MeS)(HS)CS, and (EtO)(HS)CS have been studied in aqueous mineral acid.[164]

It is known that an *O*-bonded sulphite ion catalyses ligand replacement in chromium(III) complexes. It has been shown[165] that sulphite also catalyses the exchange of ^{18}O between water and $[Cr(H_2O)_6]^{3+}$, the rate varying with the ratio $[HSO_3^-]/[H^+]$. Transient species have been observed in the flash photolyses of $[S_2O_3]^{2-}$, and the kinetics of decay measured.[166] Similar studies on $[SeO_3]^{2-}$, $[SeO_4]^{2-}$, and $[TeO_3]^{2-}$ have been carried out.[167–169] The acid and alkaline hydrolysis of sodium dithionate has been studied kinetically and the following rate law established:

$$-d[S_2O_6^{2-}]/dt = (k_a[H^+] + k_{aq} + k_b[OH^-][Na^+])[S_2O_6^{2-}]$$

Rate-determining reactions between $[NaS_2O_6]^-$ and $[OH]^-$, and $[S_2O_6]^{2-}$ and $[H^+]$ are suggested.[170] There is a report of the kinetics of formation and decomposition of the higher polythionic acids.[171] The acid-catalysed hydrolysis of methyl toluene-*p*-sulphenate, ArS(OMe), has been studied in moist organic solvents:[172]

$$H^+ + H_2O + ArS(OMe) \longrightarrow MeOH + ArS(OH) \longrightarrow ArSS(OAr)$$

$$H^+ + ArSS(OAr) + ArS(OMe) \longrightarrow ArSS(Ar)S(OAr)$$

$$H_2O + ArSS(Ar)S(OAr) \longrightarrow ArSSAr + ArSO_2H$$

$$ArSO_2H + ArSOMe \longrightarrow ArSSO_2Ar + MeOH$$

$$ArSS(Ar)S(OAr) + MeOH \longrightarrow ArSSAr + ArS(O)OMe$$

The same workers have also studied the racemization of (+)-methyl *p*-tolyl sulphoxide in acetic acid and in nitrobenzene; reaction is catalysed by the chloride ion, and a chlorsulphonium ion is suggested as an intermediate.[173] The racemization can occur[174] by the reaction

$$Cl^- + [ArSMeCl]^+ \rightleftharpoons ArSMe + Cl_2$$

A study of the reaction of chlorosulphonic acid with aromatics has appeared.[175] The first step is a sulphonation, followed by conversion of the sulphonic acid into a sulphonyl chloride.

[164] V. A. Kremer, L. A. Zatuchnaya, and V. A. Kaminskaya, *Deposited Doc.*, 1976, VINITI, 2741 (*Chem. Abs.*, 1979, **90**, 29 663).
[165] F. Monacelli, *Gazz. Chim. Ital.*, 1977, **107**, 525.
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[170] T. Sato, K. Aida, T. Komatsubara, and T. Okabe, *Nippon Kagaku Kaishi*, 1978, 1221 (*Chem. Abs.*, 1978, **89**, 186 586).
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[172] E. Ciuffarin, S. Gambarotta, M. Isola, and L. Senatore. *J. Chem. Soc., Perkin Trans. II*, 1978, 554.
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[174] E. Ciuffarin, S. Gambarotta, M. Isola, and L. Senatore, *J. Chem. Res.* (*S*), 1978, 272.
[175] F. Cavagna, T. Grewer, O. Jaenicke, and H. Zeininger, *Chem.-Ing.-Tech.*, 1978, **50**, 51 (*Chem. Abs.*, 1978, **88**, 111 157).

The formation of disulphides from sulphenyl chloride occurs by a radical mechanism, and the kinetics of the homolytic dissociation have been investigated using radical traps:[176]

$$ArSCl \rightleftharpoons ArS\cdot + Cl\cdot \rightleftharpoons \tfrac{1}{2}ArSSAr + \tfrac{1}{2}Cl_2$$

The rate is strongly dependent upon solvent, and increasing solvent nucleophilicity leads to a marked increase in rate.

Until recently nucleophilic substitution at S_4N_4 derivatives was not a known process but the products of reaction of $S_4N_4O_2$ with sodium methoxide in methanol have now been isolated and found[177] to be $[S_4N_4O_2OMe]^-Na^+$. Studies of the deprotonation of $S_4N_4H_4$, the reaction of S_4N_4 with potassium in $MeOCH_2CH_2OMe$, and the electrochemical reduction of S_4N_4 in ethanol all lead to the conclusion[178] that $[S_3N_3]^-$ plays a central role in the chemistry of S_4N_4. Reaction of S_4N_4 with liquid ammonia, secondary amines, or cyanide ion can lead to the formation of $[S_4N_5]^-$. Two new thiazyl halides, $S_4N_4F_2$ and $S_4N_4Cl_2$, are primary intermediates in the fluorination and chlorination of S_4N_4 respectively.[179] A study of the hydrolysis of PhNHSCMe, thioacetanilide, shows that reaction in dilute sulphuric acid proceeds as follows:

$$H_2O + PhNHSCMe \longrightarrow H_2S + PhNHOCMe \longrightarrow H_2S + PhNH_2 + MeCO_2H$$

In more concentrated sulphuric acid C—N bond cleavage occurs. The C—S cleavage reaction,

$$PhNHSCMe \longrightarrow PhNH_2 + MeCSOH$$

involves a neutral tetrahedral intermediate, whereas the C—N cleavage reaction involve an amino-protonated tetrahedral intermediate.[180] There has been a study of the hydrolysis of RRNC(S)Cl and related derivatives.[181] The catalytic activity of *N*-benzylthiourea in the iodine–azide reaction has been studied.[182]

A new five-co-ordinate species, $CH_2{=}SF_4$, has been isolated which gives ^{19}F and ^1H n.m.r. spectra compatible with a Berry pseudorotation.[183]

Selenium.—The reaction between $PhSeO_2H$ and thiols occurs in two distinct stages over the pH range 0.2—10 in aqueous dioxan:

$$PhSeO_2H + 3RSH \longrightarrow PhSeSR + RSSR$$

$$PhSeO_2H + RSH \longrightarrow PhSe(O)SR + H_2O \qquad \text{stage 1}$$

$$PhSe(O)SR + 2RSH \longrightarrow PhSeSR + RSSR + H_2O \qquad \text{stage 2}$$

Each stage has its own distinct and different rate/pH profile. For acidic solution, at pH < 2 stage 1 involves reaction between $[PhSeO_2H_2]^+$ and RSH, from

[176] V. A. Ignatov and N. V. Zhorkin, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1978, **21**, 956 (*Chem. Abs.*, 1978, **89**, 169 758).
[177] H. W. Roesky, M. Witt, B. Krebs, and H. J. Korte, *Angew. Chem. Int. Ed. Engl.*, 1979. **18**, 415.
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[179] L. Zbořilová and P. Gebauer, *Z. Anorg. Allg. Chem.*, 1979, **448**, 5.
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[182] H. Müller, L. Beyer, Ch. Müller, and Ch. Schröter, *Z. Anorg. Allg. Chem.*, 1978, **446**, 216,
[183] G. Kleemann and K. Seppelt, *Angew. Chem. Int. Ed. Engl.*, 1978, **17**, 516.

pH 2.5 to 4.5 reaction between $PhSeO_2H$ and RSH, and at pH > 5 reaction between $PhSeO_2H$ and $[RS]^-$. The second stage can involve two different pathways:[184]

$$PhSe(O)SR + [RS]^- \longrightarrow RSSR + [PhSeO]^- \xrightarrow[\text{fast}]{RSH} PhSeSR + OH^-$$

$$PhSe(OH)SR]^+ + RSH \longrightarrow [RSSRH]^+ + PhSeOH \xrightarrow[\text{fast}]{RSH} PhSeSR + H_2O$$

A kinetic study of selenium(IV) catalysis of the conversion of *p*-hydrazinobenzenesulphonic acid to *p*-diazobenzenesulphonic acid has been made the basis of an analytical method for selenium(IV).[185]

Tellurium.—The electrochemical oxidation of the telluroycanate ion in acetonitrile produces tellurocyanogen *via* the ion $[(TeCN)_3]^-$ as an intermediate; $(TeCN)_2$ decomposes to give $Te + (CN)_2$.[186]

5 Group VII

Fluorine.—In 1926 it was reported[187] that passage of fluorine through an aqueous solution of a sulphate produced a powerful oxidizing species that disappeared on standing. This work has been confirmed,[188] and the 'ephemeral oxidant' identified as fluoroxysulphate, $[SO_4F]^-$. Some kinetic observations on the stability of the solution are reported. The reaction of hypofluorous acid with water, bisulphate ion, and $[Cr(NH_3)_5N_3]^{2+}$ has been studied[189] using ^{18}O as a tracer. The reaction involves oxygen transfer with the formation of HOO*H, $[O_3SOO^*H]^-$, and $[Cr(NH_3)_5NO^*]^{2+}$.

Chlorine.—The reaction of hypochlorous acid with hydrogen peroxide follows the rate law

$$\text{Rate} = k[HOCl][H^+][Cl^-]$$

This is thought to involve the same rate-determining stage as a number of other reactions.[190] A previously unknown species ClONO has been observed to be formed in the heterogeneous reaction between ClNO and Cl_2O.[191] It slowly isomerizes to $ClNO_2$. A detailed study of electrophilic chlorination of a range of metal acetylacetonate complexes by an S_E2 reaction of *N*-chlorosuccinimide in CD_3OD, $CDCl_3$ and C_6D_6 has been reported.[192] This is another elegant example of the application of stopped-flow, pulse Fourier-transform ^1H n.m.r.

Bromine.—The reaction mechanisms of a relatively new species, the perbromate ion, are currently under investigation. The redox reactions with a number of reductants have been studied,[193] and in reactions with sulphite and arsenite it

[184] J. L. Kice and T. W. S. Lee, *J. Am. Chem. Soc.*, 1978, **100**, 5094.
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[193] E. H. Appelman, U. K. Klaning, and R. C. Thompson, *J. Am. Chem. Soc.*, 1979, **101**, 929.

appears that oxygen transfer occurs. It is suggested that this may be general for reaction with two-equivalent reducing agents. A kinetic study of the iron(II)-induced oxidation of iodide by perbromate has been carried out, and the method used as the basis for an analytical procedure for edta and related chelating agents.[194] Another investigation[195] of the chemistry of a somewhat unfamiliar species is a study of the reaction of $[BrO_2]^-$ with I^-, $[SO_3]^{2-}$, $[HCOO]^-$, and $[S_2O_3]^{2-}$. There is a general similarity with the reactions of $[ClO_2]^-$. The rates all show a dependence on hydroxide ion concentration of the form $k = k_1 + k_2[OH^-]^{-1}$. Several papers have appeared on the reactions of bromine. The hydrolysis in aqueous solutions of bromide and chloride ions has been studied; rate constants are given in the Table.[196]

Table *Rate constants of the forward and back reactions occurring in aqueous solutions of bromine at* 20 °C

Reaction	*System*	$k_f/M^{-1}\,s^{-1}$	k_b/s^{-1}
$H^+ + [Br_2OH]^- \rightleftharpoons Br_2 + H_2O$	Br_2–Br^-–H_2O	1.33×10^{10}	91.8
$H^+ + [Br_2OH]^- \rightleftharpoons Br_2 + H_2O$	Br_2–Cl^-–H_2O	1.33×10^{10}	91.8
$H^+ + [BrClOH]^- \rightleftharpoons BrCl + H_2O$	Br_2–Cl^-–H_2O	4.2×10^8	2.9×10^5
$HBrO + Br^- \rightleftharpoons [Br_2OH]^-$	Br_2–Cl^-–H_2O	1.7×10^8	8×10^7
$HBrO + Cl^- \rightleftharpoons [BrClOH]^-$	Br_2–Cl^-–H_2O	7×10^5	1.5×10^5
$[Br_2Cl]^- + HBrO \rightleftharpoons Br_2 + [BrClOH]^-$	Br_2–Cl^-–H_2O	5×10^8	1.5×10^{8a}

[a] $M^{-1}\,s^{-1}$.

The oxidation of iodide by bromine has been reported[197] and a mechanism suggested:

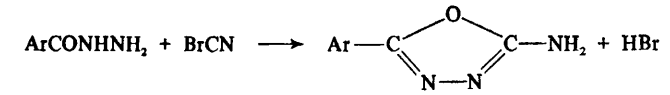
$$Br_2 + I^- \longrightarrow IBr + Br^-$$

$$IBr + H_2O \longrightarrow IOH + H^+ + Br^-$$

$$H^+ + I^- + IOH \longrightarrow I_2 + H_2O$$

The reaction of bromine and thiocyanate ion to form cyanogen bromide has been made the basis of an analytical method.[198]

Polarographic studies of the kinetics of the reaction of BrCN and ClCN with hydroxide ion have been reported.[199] There has also been a kinetic study of the reaction leading to (7).[200]



(7)

[194] L. A. Lazarou and T. P. Hadjiioannou, *Anal. Chem.*, 1979, **51**, 790.
[195] C. L. Lee and M. W. Lister, *Can. J. Chem.*, 1979, **57**, 1524.
[196] A. G. Ivanchenko, M. N. Vargaftik, L. A. Katsman, V. I. Ksenzenko, and S. M. Gutiontov, *Bull. Acad. Sci. USSR*, **26**, 1571.
[197] T. S. Rao, S. I. Mali, and V. T. Dangat, *Z. Phys. Chem. (Leipzig)*, 1979, **260**, 31.
[198] J. B. Landis, M. Rebec, and H. L. Pardue, *Anal. Chem.*, 1977, **49**, 785.
[199] F. Ludovic and M. Dronca, *Rev. Chim. (Bucharest)*, 1977, **28**, 1148 (*Chem. Abs.*, 1978, **88**, 159 117).
[200] C. R. Kramer, *Z. Phys. Chem. (Leipzig)*, 1978, **259**, 1100.

6 Group VIII

Xenon.—Several studies have been reported by Russian workers on the reactions of xenon difluoride in aqueous solution. The oxidation of phenol to *p*-benzoquinone is suggested[201] to involve an intermediate in the hydrolysis of xenon difluoride, possibly xenon monoxide. The rate of disappearance of xenon difluoride in the presence of phenol is the same as the rate of hydrolysis in the absence of the latter. A competition method has been used to study the role of this postulated intermediate.[202] The kinetics of reaction of xenon difluoride with 2,3,6,6-tetramethylpiperidin-1-oxyl have been studied.[203] In a review of recent developments in the chemistry of some electronegative elements there is a brief summary of fluxional behaviour in the proposed tetramer of XeF_6 in solution.[204]

[201] A. A. Goncharov and Yu. N. Kozlov, *Russ. J. Phys. Chem.* (*Engl. Transl.*), 1978, **52**, 539.
[202] A. A. Goncharov, Yu. N. Kozlov, and A. Purmalis, *Zh. Fiz. Khim.*, 1978, **52**, 2870 (*Chem. Abs.* 1979, **90**, 61 849).
[203] V. A. Golubev, N. N. Salmina, B. L. Korsunskii, N. N. Alenikov, and F. I. Dubovitskii. *Bull. Acad. Sci. USSR*, 1978, **27**, 672.
[204] K. Seppelt, *Acc. Chem. Res.*, 1979, **12**, 211

12
Organometallic Substitution Reactions

BY A. J. DEEMING

1 Carbon Monoxide Replacement in Mononuclear Metal Carbonyls

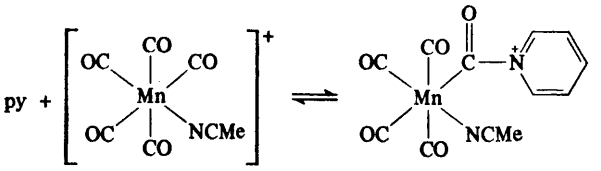
Thermal Substitution.—Carbonyl substitutions in Group VI metal carbonyls occur predominantly by dissociative pathways, associative pathways also contributing when the more nucleophilic incoming ligands are considered. The kinetics of the reaction of $[W(CO)_3(CS)(phen)]$ with ligands L (phosphines or phosphites) to give $[W(CO)_2(CS)L(phen)]$ show first- and second-order terms:[1]

$$\text{Rate} = (k_1 + k_2[L])[\text{complex}]$$

The k_1 term dominates at the higher temperatures and is about 140 times greater than for $[W(CO)_4(phen)]$ under the same conditions. This results from a decrease in activation energy supposedly originating from the better π-acceptor properties of CS compared with CO, leading to M—CO bond weakening.

The labilizing effects of ligands on CO substitution has been considered theoretically.[2] The carbonyls of $[Mn(CO)_6]^+$ are less labile than those of $[Mn(CO)_5X]$ (X = H, Br, or COMe) although ground-state bonding considerations would lead to the opposite expectation. Furthermore the *cis*-CO groups of $[Mn(CO)_5X]$ are more labile than the *trans*. Calculations indicate that steric relaxation in the five-co-ordinate intermediate contributes significantly to the differences in activation energies for CO dissociation because the transition state is close to the intermediate. Stabilization of square-pyramidal $[Mn(CO)_5]^+$ by increasing the angle between the axial and equatorial CO groups above 90° is less than for $[Mn(CO)_4X]$ and for this species the stabilization is greatest for X in an equatorial position. Relaxation of the bond lengths or MCO angles was not allowed for, but nonetheless the treatment provides a rationale for the labilizing effect of ligands which are weaker π-acids than CO. These effects have been applied in interpreting the base catalysis of carbonyl substitution.[3] Second-order kinetic terms found for good incoming nucleophiles L might result from bimolecular association of L with carbon atoms of CO. The complex $[Mn(CO)_5(MeCN)]^+$ is much more rapidly substituted by py to give $[Mn(CO)_3py_3]^+$ than by PPh_3 and a pre-equilibrium involving (1) has been proposed. The RCO group generated would be a good *cis*-labilizing group for the reasons stated above.[2] Labilizing effects of several orders of magnitude are possible so that even though the acid–base adduct is not detectable it could be present in sufficient concentration for a

[1] R. A. Pickering and R. J. Angelici, *Inorg. Chem.*, 1978, **17**, 2035.
[2] D. L. Lichtenberger and T. L. Brown, *J. Am. Chem. Soc.*, 1978, **100**, 366.
[3] T. L. Brown and P. A. Bellus, *Inorg. Chem.*, 1978, **17**, 3726.

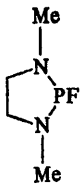


(1)

marked kinetic effect. Small concentrations of iron carbonyl anions catalyse the substitution of $[Fe(CO)_5]$ by tertiary phosphines and phosphites (L) to give exclusively $[Fe(CO)_4L]$ without the usual admixture with $[Fe(CO)_3L_2]$, but whether this is a case of base catalysis is unknown.[4]

The association of acids as well as bases with CO can greatly influence the rate of CO substitution. Thus $Na[HFe(CO)_4]$ readily exchanges with ^{13}CO whereas the exchange for $[PPN][HFe(CO)_4]$ [PPN = $N(PPh_3)_2$] is slow, and addition of $NaBPh_4$ to the PPN salt increases the rate of exchange.[5] Both salts are substantially ion-paired under the reaction conditions but, whereas C_{3v} symmetry is maintained for the anion in the PPN salt in solution as in the crystal, specific Na–OC(equatorial) interactions presumably account for the higher reactivity of the Na salt. Interestingly the Na salt is 20 times more reactive with O_2 than the PPN salt at room temperature, which accounts among other things for the use of $[PPN]^+$ in synthetic work.

The complex $[Fe(FL)(CO)_4]$ prepared from the ligand FL (2) reacts with PF_5 to give $[Fe(L)(CO)_4][PF_6]$.[6] The cationic complex undergoes intermolecular CO



(2)

transfer fast enough to lead to n.m.r. coalescences with loss of ^{31}P–^{13}C coupling and also statistically exchanges with free ^{13}CO within 30 min at 25 °C. The enthalpy of activation $\Delta H^{\ddagger}$ (15.7 kcal mol^{-1}) may be compared with 42.7 kcal mol^{-1} for CO exchange in $[Fe(CO)_4(PPh_3)]$. Reduced M—C bond strengths in cations are probably insufficient to account for the marked increase in rate and it has been suggested that a 16-electron intermediate is stabilized by co-ordination through both P and N.

Substitution of two CO ligands each of $[Ni(CO)_4]$, $[Co(NO)(CO)_3]$, and $[Fe(NO)_2(CO)_2]$ by reaction with bidentate diarsine ligands or phen has been

[4] S. B. Butts and D. F. Shriver, *J. Organomet. Chem.*, 1979, **169**, 191.
[5] M. Y. Darensbourg, D. J. Darensbourg, and H. L. C. Barros, *Inorg. Chem.*, 1978, **17**, 297.
[6] D. W. Bennett and R. W. Parry, *J. Am. Chem. Soc.*, 1979, **101**, 755.

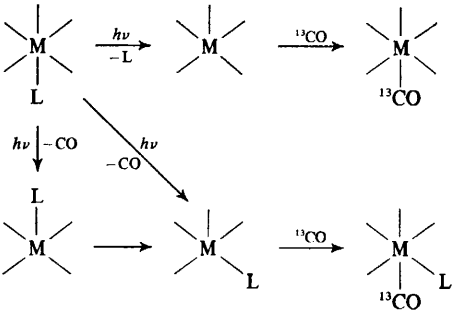
studied kinetically.[7] For the nitrosyl complexes an initial CO substitution leads to a kinetically unobservable ring closure. Rate = $(k_1+k_2[L])$[complex], with k_2 dominating with good nucleophiles in poorly co-ordinating solvents. However, k_1 varies greatly with solvent unlike k_2, and associative pathways are suggested for both pathways. With $[Ni(CO)_4]$ kinetic data are analysed in terms of two consecutive first-order reactions, the first giving $[Ni(CO)_3L]$ and the second being ring closure. The mechanism is believed to be

$$[Ni(CO)_4] \rightleftharpoons [Ni(CO)_3] + CO \quad \left.\begin{array}{l} \\ [Ni(CO)_3] + L \xrightarrow{\text{fast}} [Ni(CO)_3L] \end{array}\right\} \text{First reaction}$$

$$[Ni(CO)_3L] \longrightarrow [Ni(CO)_2L] + CO \quad \text{Second reaction}$$

Photosubstitution.—The primary process in the photosubstitution of $[Cr(CO)_6]$ and of $[W(CO)_6]$ by pyridine has been studied, in particular to account for the quantum deficit (for example, $\Phi_A = 0.66 \pm 0.05$ for $[py] = 2.4 \times 10^{-3}$ M and $[Cr(CO)_6] = 3.5 \times 10^{-4}$ M; 292 nm irradiation in cyclohexane).[8] Results in viscous solvents eliminated cage recombination as a possibility, and excited singlet to excited triplet intersystem crossing was shown to occur with unit efficiency so that the triplet state must dissociate and the deficit is due to a radiationless decay which competes with dissociation.

Substitution of both L (pyridine or piperidine) or ^{12}CO by ^{13}CO occurs on irradiating $[M(CO)_5L]$ (M = Cr, Mo, or W) at 366 or 313 nm.[9] The relative quantum yields of these two reactions are very dependent upon M, amine substitution having the higher quantum yield for both Mo and W but both reactions having approximately the same quantum yield for Cr. Substitution of CO leads specifically to *cis*-$[M(CO)_4(^{13}CO)L]$. Assuming that $[Cr(CO)_4L]$ and $[Cr(CO)_5]$, have similar rates of ^{13}CO capture, the route *via* the C_{4v} intermediate is only possible if the rate constant for C_{4v} to C_s rearrangement is greater than 3×10^4 s^{-1} (Scheme 1). Otherwise the *trans*-product would have been detected. This point could be tested by photosubstitution of the yet unavailable *trans*-$[M(CO)_4(^{13}CO)L]$ by ^{12}CO.



Scheme 1

[7] B. J. Plankey and J. V. Rund, *Inorg. Chem.*, 1979, **18**, 957.
[8] J. Nasielski and A. Colas, *Inorg. Chem.*, 1978, **17**, 237.
[9] D. J. Darensbourg and M. A. Murphy, *Inorg. Chem.*, 1978, **17**, 884.

The rate of the slow thermal substitution of CO by $P(OPh)_3$ (L) in $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(\eta^1\text{-}C_5H_5)]$ is barely enhanced by near-u.v. irradiation unless catalytic amounts of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2$ are present. A radical-chain mechanism is proposed:[10]

$$[FeCp(CO)_2]_2 \xrightarrow{h\nu} 2[FeCp(CO)_2\cdot]$$

$$[FeCp(CO)_2\cdot] + L \longrightarrow [FeCp(CO)L\cdot] + CO$$

$$[FeCp(CO)L\cdot] + [FeCp(CO)_2(\eta^1\text{-}Cp)] \longrightarrow [FeCp(CO)_2\cdot] + [FeCp(CO)L(\eta^1\text{-}Cp)]$$

The fast substitution of the 17-electron species $[FeCp(CO)_2\cdot]$ is well grounded, but the homolytic displacement at $\eta^1\text{-}C_5H_5$ is the key propagation step to establish. Evidence for this came from a crossover experiment using an equimolar mixture of $[FeCp(CO)_2(\eta^1\text{-}Cp)]$ and $[Fe(CO)_2(\eta^5\text{-}MeC_5H_4)]_2$ which underwent intermolecular scrambling between cyclopentadienyl and methylcyclopentadienyl ligands on irradiation. The substitution of $[WH(C_5H_5)(CO)_3]$ by PPh_3 in benzene has been reported earlier to be a second-order reaction, but recently very irreproducible rates were found for this reaction in the dark in heptane.[11] The addition of benzoyl peroxide and other species gave marked rate enhancement. Photolysis in the presence of a little $[W(C_5H_5)(CO)_3]_2$ gave quantum yields >1000 consistent with a photo-induced radical chain mechanism involving the propagation steps shown. This corresponds directly to the mechanism in the iron

$$[WCp(CO)_3\cdot] + PPh_3 \longrightarrow [WCp(CO)_2(PPh_3)\cdot] + CO$$

$$[WCp(CO)_2(PPh_3)\cdot] + [WHCp(CO)_3] \longrightarrow [WCp(CO)_3\cdot] + [WHCp(CO)_2(PPh_3)]$$

case above[10] except that there is a homolytic displacement at a metal hydride instead of η^1-cyclopentadienyl. The corresponding Mo complex is substituted 10^6 times more rapidly than the W one.

2 Replacement of Other Ligands in Mononuclear Metal Carbonyls

Thermal Substitution.—The substitutions of tertiary phosphines L in the complex *cis*-$[Mo(CO)_4L_2]$ by CO occur by dissociative mechanisms, the CO entering

$$cis\text{-}[Mo(CO)_4L_2] + {}^{13}CO \longrightarrow cis\text{-}[Mo(CO)_4({}^{13}CO)L] + L$$

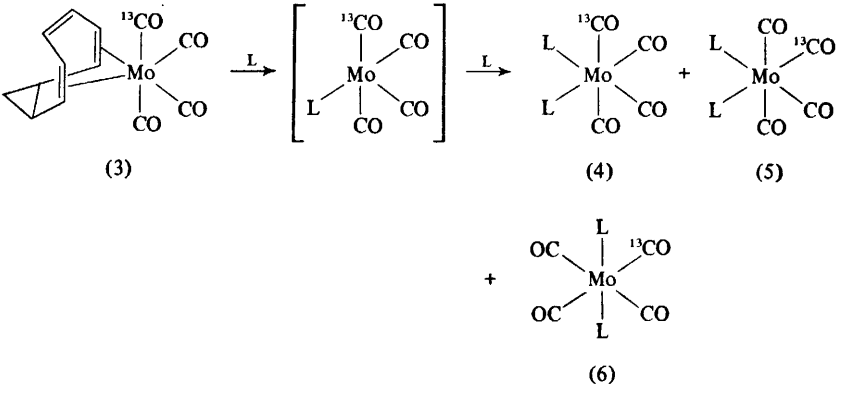
cis to the remaining ligand L.[12] The substitution rates increase markedly with increasing bulk of L (first-order $k = < 1.0 \times 10^{-6}$ s^{-1} for PMe_2Ph but 6.4×10^{-2} s^{-1} for $PPhCy_2$), and in mixed complexes *cis*-$[M(CO)_4LL']$ the larger phosphine enhances the rate of dissociation of the smaller. Rate data are also given for PPh_3 replacement in the *trans*-isomer and for *cis–trans* isomerization, both slower than PPh_3 replacement in the *cis*-isomer (Table 1). Thus the intermediate $[Mo(CO)_4(PPh_3)]$ (C_s-isomer) formed from *cis*-$[Mo(CO)_4(PPh_3)_2]$ has a higher energy barrier for reaction with PPh_3 to give the *trans*-isomer than to re-form the *cis*-isomer. This C_s-isomer is stereochemically rigid during its solution lifetime. The stereochemical rigidity of co-ordinatively unsaturated species has also been examined in the reactions of $[Mo(\eta^4\text{-}C_9H_{10})({}^{13}CO)(CO)_3]$ (3) formed by stereo-

[10] B. D. Fabian and J. A. Labinger, *J. Am. Chem. Soc.*, 1979, **101**, 2239.
[11] N. W. Hoffman and T. L. Brown, *Inorg. Chem.*, 1978, **17**, 613.
[12] D. J. Darensbourg and A. H. Graves, *Inorg. Chem.*, 1979, **18**, 1257.

Table 1 *Activation parameters for* PPh_3 *substitution by* CO *and for* cis–trans *isomerization of* $[Mo(CO)_4(PPh_3)_2]$

	k(70 °C)/s^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
cis-isomer	31.6	29.7	14.2
trans-isomer	0.47	22.9	−14.0
cis to *trans*	0.674	23.6	−11.1

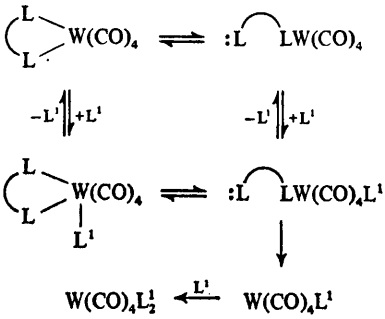
specific addition of ^{13}CO to $[Mo(\eta^6\text{-}C_9H_{10})(CO)_3]$. The replacement of the organic ligand is too rapid for an easy kinetic treatment but the rate is dependent upon the nature and the concentration of the tertiary phosphine or phosphite (L).[13] A reversible chelate ring opening probably leads to a five-co-ordinate species that is stereochemically rigid during its solution lifetime since (4) is formed exclusively except where $L = P(OMe)_3$, which gave predominantly (6)



in a mixture with (4) and (5). A combination of small size and electronic properties similar to CO is required for stereochemical non-rigidity in the intermediate and $[Mo(CO)_5]$ itself is non-rigid. Since *fac*- and *mer*-$[Mo(diphos)L(CO)_3]$ can be made by reaction of L [PPh_3 or $P(OPr^i)_3$] with *fac*-[Mo(diphos)(cyclohexylamine)$(CO)_3$] or with $[Mo(diphos)(CO)_4]$ respectively, the intermediate [Mo(diphos)$(CO)_3$] cannot be rapidly dynamic. The kinetics of *fac* to *mer* isomerization have shown that in the equilibrium between the intermediates, [Mo(diphos)$(CO)_3$], the form with both P-attachments in the base of the square pyramid is thermodynamically favoured even though the *mer*-isomer has the favourable six-co-ordinate geometry.[14]

Both dissociative and associative pathways have been found for the substitution of $[W(CO)_4(MeSCH_2CH_2SMe)]$ by $P(OPr^i)_3$ (associative path predominating)[15] or of $[W(CO)_4(diamine)]$ [diamine = $Me_2N(CH_2)_2NMe_2$ or $Me_2N(CH_2)_3NMe_2$] with phosphines or phosphites (dissociative path predominating).[16] A kinetic analysis is consistent with the mechanism in Scheme 2. In one case the inter-

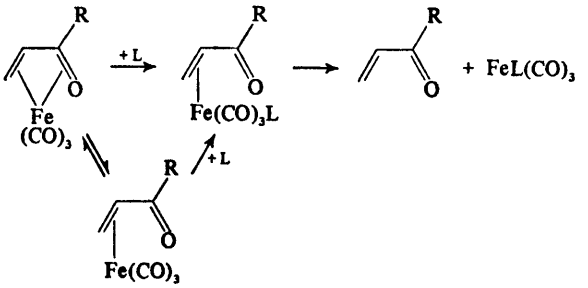
[13] D. J. Darensbourg and A. Salzer, *J. Am. Chem. Soc.*, 1978, **100**, 4119.
[14] J.-C. Rousche and G. R. Dobson, *Inorg. Chim. Acta*, 1978, **28**, L139.
[15] G. R. Dobson and Honours Science 102–2, *J. Coord. Chem.*, 1978, **7**, 253.
[16] G. R. Dobson and A. Moradi-Araghi, *Inorg. Chim. Acta*, 1978, **31**, 263.



Scheme 2

mediate *cis*-[W{$Me_2N(CH_2)_3NMe_2$}{$P(OCH_2)_3CMe$}$(CO)_4$] with unidentate diamine was isolated.

Associative and dissociative paths have also been established from studies of the kinetics of reactions of [$Fe(CO)_3$(η^4-dienone)] with tertiary phosphines and now for polyenes,[17] which is a very useful route to [$Fe(CO)_3$(polyene)] complexes. Both paths as shown in Scheme 3 lead to an initial dissociation of the organic carbonyl, and the rate constants for the unimolecular path increase with increasing donor ability of group R (Ph < H < Me) where the incoming polyene is cyclohepta-1,3,5-triene (L).



Scheme 3

The mechanism of the metathesis reaction of the new vanadium hydride $[V(C_5H_5)H(CO)_3]^-$ with alkyl halides is a free-radical chain process involving $[V(C_5H_5)(CO)_3]^{\cdot -}$ based on normally applied criteria such as the similar rates for primary, secondary, and tertiary R and the formation of completely racemic

$$[V(C_5H_5)H(CO)_3]^- + RX \xrightarrow{\text{THF, 25 °C}} [V(C_5H_5)(CO)_3X]^- + RH$$

$PhCHDCH_3$ from optically active $PhCHBrCH_3$ and the vanadium deuteride.[18] The propagation steps in the metathesis are

$$[V(C_5H_5)(CO)_3]^{\cdot -} + RX \longrightarrow [V(C_5H_5)(CO)_3X]^- + R\cdot$$

$$R\cdot + [V(C_5H_5)(CO)_3H]^- \longrightarrow [V(C_5H_5)(CO)_3]^{\cdot -} + RH$$

[17] J. A. S. Howell and P. M. Burkinshaw, *J. Organomet. Chem.*, 1978, **152**, C5.
[18] R. J. Kinney, W. D. Jones, and R. G. Bergman, *J. Am. Chem. Soc.*, 1978, **100**, 7902.

From the known rate of ring closure of hex-1-enyl radical to cyclopentylmethyl radical and the observed low yield of methylcyclopentane by this route, the rate of the hydrogen transfer step must be *ca.* 2×10^7 M^{-1} s^{-1}, even greater than for the corresponding reaction for Bu^n_3SnH. There is evidence that $[Mo(C_5H_5)_2H_2]$ reacts with alkyl halides by a related radical-chain mechanism.[19]

Photosubstitution.—In the photosubstitution of py and substituted pyridine ligands (L) by a diphosphine as shown, the quantum yields are very dependent

$$cis\text{-}[W(CO)_4L_2] + cis\text{-}Ph_2PCH{=}CHPPh_2 \xrightarrow{436\ nm} [W(CO)_4(Ph_2PCH{=}CHPPh_2)] + 2L$$

upon whether the lowest-energy electronic transition is ligand-field (*e.g.* L = 3,4-dimethylpyridine, $\Phi = 0.37$) or W → L charge-transfer in character (*e.g.* L = 4-formylpyridine, $\Phi = 0.0007$).[20] The primary photochemical process is L dissociation and the charge-transfer excited state is essentially unreactive. Quantum yields are also very dependent upon the cation for anionic carbonyls (see Table 2).[21] Counterion effects are small in aqueous media, but effects can be large in media of low dielectric constant. This could be an example of the effect of specific cation–oxygen interactions with small cations like Li^+. An unidentified white product accounts for most of the anion consumed in the presence of $AsPh_4^+$.

Table 2 *Quantum yields for substitution of* $[W(CO)_5Br]^-$ *by* CO (436 nm, 7 °C, CO-*saturated* $CHCl_3$)

Cation	Φ^a	Φ^b
Li^+	0.094	0.094
NEt_4^+	0.0034	0.0034
$AsPh_4^+$	0.014	0.002

[a] Disappearance of $[W(CO)_5Br]^-$. [b] Formation of $[W(CO)_6]$.

Photosubstitution of $[Mo(CO)_5(PPh_3)]$ leads to CO loss ($\Phi_{366\ nm} = 0.58$) in preference to PPh_3 loss ($\Phi_{366\ nm} = 0.11$). The equilibrium of *cis*- and *trans*-$[Mo(CO)_4(PPh_3)_2]$ leads to a photochemical stationary state in favour of the thermodynamically less stable *cis*-isomer, and evidence is given for a facile conversion of the unsaturated C_{4v}-isomer of $[Mo(CO)_4(PPh_3)]$ into the C_s-isomer, substantiating observations made on thermal reactions.[22]

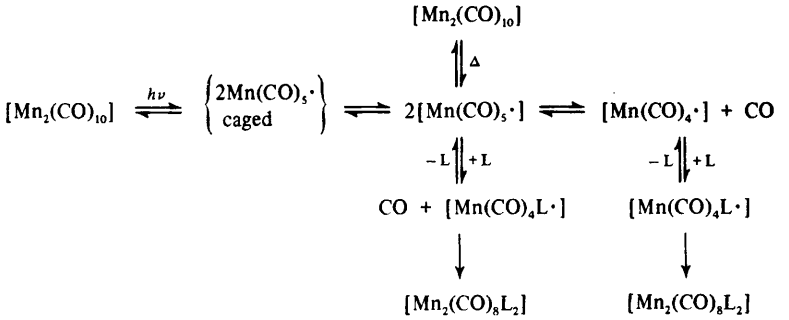
3 Substitution Reactions and Cluster Breakdown of Polynuclear Metal Carbonyls

Dinuclear Carbonyls.—Substitution reactions of $[Mn_2(CO)_{10}]$ do not occur by CO dissociation or by associative reaction with incoming ligand, but by thermal or photochemical formation of $[Mn(CO)_5\cdot]$. Rapid substitution of metal carbonyl radicals has been frequently noted but the mechanisms of these substitutions are

[19] A. Nakamura, *J. Organomet. Chem.*, 1979, **164**, 183.
[20] H. B. Abrahamson and M. S. Wrighton, *Inorg. Chem.*, 1978, **17**, 3385.
[21] R. M. Dahlgren and J. I. Zink, *J. Chem. Soc., Chem. Commun.*, 1978, 863.
[22] D. J. Darensbourg and M. A. Murphy, *J. Am. Chem. Soc.*, 1978, **100**, 463.

still unclear, certain authors citing evidence for dissociative routes,[23] others for associative;[24] the two routes are indicated in Scheme 4.

For $[Mn_2(CO)_{10}] = 4 \times 10^{-4}$ M, the quantum yield to give mainly disubstituted product is independent of the nature and concentration of the reacting phosphine or phosphite L ($\Phi = 0.9$ at 350 nm), but added CO can reduce the value to 0.6—0.7.[23] This can be accounted for if $[Mn(CO)_5\cdot]$ undergoes rapid CO loss; however, if the substitution of $[Mn(CO)_5\cdot]$ is associative CO must be able to



Scheme 4

replace L from $[Mn(CO)_4L\cdot]$. Although the drop in Φ with CO present can be accommodated by both mechanisms, the very high values for the rate of the associative pathway appear unacceptable to the authors,[23] especially as 19 electron intermediates are required. The high quantum yield requires $[Mn(CO)_5\cdot]$ radicals to be substituted very rapidly indeed since the rate constant for their recombination is almost diffusion-controlled ($2k = 1.2 \times 10^9$ M^{-1} s^{-1}).[25] The detailed kinetics of the thermal conversion of $[Mn_2(CO)_8(PPh_3)_2]$ into $[Mn_2(CO)_8(PPh_3)\{P(OPh)_3\}]$ on reaction with $P(OPh)_3$ in cyclohexane have been interpreted on the other hand by a pathway comparable with that in Scheme 4 but with associative substitution of $[Mn(CO)_4(PPh_3)\cdot]$ followed by preferential recombination of unlike radicals.[24] E.s.r. evidence is given for the long-lived radicals of type $[Mn(CO)_3L_2\cdot]$ formed by extended treatment of $[Mn_2(CO)_8(PBu_3)_2]$ or $[Mn_2(CO)_7\{P(OEt)_3\}_3]$ with an excess of the ligands.[26] The spectrum of $[Mn(CO)_3(PBu_3)_2\cdot]$ was interpreted to show a square-pyramidal geometry with *trans*-equatorial phosphines, so that radical recombination seems sterically prevented. The radical $[Mn(CO)_5\cdot]$ is also formed by pulse radiolysis of ethanolic solutions of $[Mn_2(CO)_{10}]$ or $[Mn(CO)_5X]$ (X = Br or I). Rates of reaction of e^-(solv) with these compounds, of recombination of $[Mn(CO)_5\cdot]$ radicals, and of their reaction with O_2 were measured.[25] $[Mn(CO)_5\cdot]$ has an absorption maximum at 830 nm ($\varepsilon_{830} = 800 \pm 80$ M^{-1} cm^{-1}) and the route for its formation was shown to be

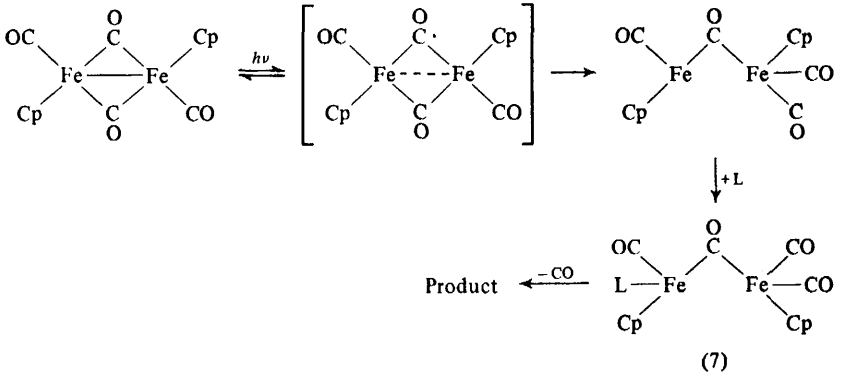
$$e^-(solv) + [Mn_2(CO)_{10}] \longrightarrow [Mn_2(CO)_{10}]^- \xrightarrow{\text{fast}} [Mn(CO)_5\cdot] + [Mn(CO)_5]^-$$

[23] D. R. Kidd and T. L. Brown, *J. Am. Chem. Soc.*, 1978, **100**, 4095.
[24] J. P. Fawcett, R. A. Jackson, and A. Poë, *J. Chem. Soc., Dalton Trans.*, 1978, 789.
[25] W. L. Waltz, O. Hackelberg, L. M. Dorfman, and A. Wojcicki, *J. Am. Chem. Soc.*, 1978, **100**, 7259.
[26] D. R. Kidd, C. P. Cheng, and T. L. Brown, *J. Am. Chem. Soc*, 1978, **100**, 4103.

By forming $[Mn(CO)_5^{\bullet}]$ and $[Re(CO)_5^{\bullet}]$ on irradiation of molecular beams it has been confirmed that photodissociation at 300 nm involves only M—M cleavage.[27] Activation enthalpies for homolytic bond fission ΔH_{hf}^{*} of mono- and di-substituted derivatives of $[Mn_2(CO)_{10}]$ have been obtained from the kinetics of substitution or reaction with O_2.[28] These are in the order $L = CO \sim P(OMe)_3 \sim P(OPh)_3 > PEt_3 \geqslant PBu_3 \sim AsPh_3 > PPh_3 > PCy_3$ for $[Mn_2(CO)_8L_2]$. Correlations have been made between these kinetic bond strengths and the ligand cone angle as well as the frequency of the $\sigma \rightarrow \sigma^*$ transition thought to be responsible for photochemical M—M fission. Steric effects dominate fission rates, and whereas many ligands have a linear correlation between ΔH_{hf}^{*} and $\nu(\sigma \rightarrow \sigma^*)$ bulky ligands give particularly low ΔH_{hf}^{*} values interpreted in terms of residual steric effects. These only operate as the Mn—Mn bond extends during homolysis: *i.e.* they are not ground-state effects.

The mixed dimers $[(C_5H_5)(CO)_3M{-}Co(CO)_4]$ or $[(C_5H_5)(CO)_3M{-}Fe(CO)_2(C_5H_5)]$ (M = Mo or W) photolyse in CCl_4 with $\Phi_{366\,nm}$ in the range 0.3—0.5.[29] Cleavage of M—M bonds occurs to give corresponding chloro-derivatives, except for Co which gives $[Co_2(CO)_8]$. The order of reactivity of the generated metal radicals towards Cl-atom abstraction is $[(C_5H_5)W(CO)_3] > [(C_5H_5)Mo(CO)_3] > [(C_5H_5)Fe(CO)_2] > [Co(CO)_4]$.

Dimeric compounds with bridging CO do not necessarily give mononuclear radicals on photolysis. Scheme 5 shows the route established for photosubstitution of $[Fe_2(C_5H_5)(CO)_4]$ by PPh_3 or $P(OPr^i)_3$.[30] The main evidence is that



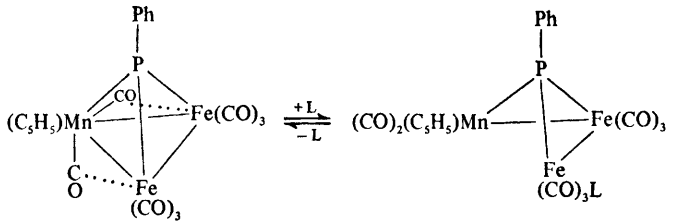
(7)

Scheme 5

irradiation at −78 °C gave the yellow intermediate (7) which has $\nu(CO) = 1720\ cm^{-1}$, is e.s.r. silent, and does not show a $\nu(\sigma \rightarrow \sigma^*)$ absorption. Thus instead of M—M cleavage to give two 17 electron fragments, the integrity of the dimer is maintained with 16 and 18 electron metal centres. This allows a rapid uptake of ligand at the unsaturated centre. Higher clusters could behave in this way because the metal atoms are of necessity bridged.

[27] A. Freedman and R. Bersohn, *J. Am. Chem. Soc.*, 1978, **100**, 4116.
[28] R. A. Jackson and A. Poë, *Inorg. Chem.*, 1978, **17**, 997.
[29] H. B. Abrahamson and M. S. Wrighton, *Inorg. Chem.*, 1978, **17**, 1003.
[30] D. R. Tyler, M. A. Schmidt, and H. B. Gray, *J. Am. Chem. Soc.*, 1979, **101**, 2753

Higher-nuclearity Carbonyls.—Interest has centred recently on factors that allow facile incorporation of ligands into clusters, especially where this can occur by addition, since a knowledge of these could lead to a rational search for cluster catalysis. Direct addition of ligands can occur if multiple M—M bonds can be reduced or single M—M bonds cleaved, if the mode of bonding of other ligands can be modified (*e.g.* linear to bent NO co-ordination, or μ^3- to μ^2-ligand conversion), or if CO can be displaced by thermal, photochemical, or chemical means (with Me_3NO, for example).[31] The rates of CO addition to the triply M—M bonded compounds $[M(C_5Me_5)(CO)_2]_2$ are in the order Mo > W > Cr,[32] and a simple case of reversible ligand addition (L = CO or PPh_3) with M—M cleavage has been studied kinetically (Scheme 6).[33] The addition of PPh_3 is



Scheme 6

second order with low activation enthalpy, implying an associative mechanism with simultaneous M—M cleavage, whereas the reverse reaction is first order in complex with $\Delta H^* = 28$ kcal mol^{-1}. The overall cluster opening is exothermic ($\Delta H = -19.3$ kcal mol^{-1}). The carbonylation of $[Co_4(CO)_{12}]$ is similar in that the initial reversible step is believed to be bimolecular addition of CO with Co—Co breaking.[34] The reaction is first order in $[Co_4(CO)_{12}]$ but varies from first order in CO at low pressures and high temperatures to second order at high pressures (up to 120 atm) and low temperatures. There is kinetic evidence that $[Co_4(CO)_{13}]$ can undergo bimolecular attack by CO or a unimolecular isomerization, both of which lead eventually to $[Co_2(CO)_8]$. There is a mechanistic relation between ligand additions at clusters which lead to substitution or cluster breakdown. The kinetics of conversion of $[Co_4(CO)_{11}L]$ (L = trimethyl phosphite) into $[Co_4(CO)_{10}L_2]$ and of this into $[Co_4(CO)_9L_3]$ by reaction with L have been measured.[35] Both conversions have important rate terms dependent upon phosphite concentration which might be identified with association.

The replacement of CO in $[FeCo_2(CO)_9S]$ by ^{14}CO or other ligands L occurs by two paths: $-d[complex]/dt = \{k_1 + k_2[L]\}[complex]$.[36] The k_1 path is negligible except for very weakly nucleophilic ligands like CO or $AsPh_3$ and, since k_2 is strongly dependent upon the nucleophile, it is thought that bond forming in reaching the transition state is important. However, nothing can be

[31] B. F. G. Johnson, J. Lewis, and D. Pippard, *J. Organomet. Chem.*, 1978, **160**, 263.
[32] R. B. King, M. Z. Iqbal, and A. D. King, *J. Organomet. Chem.*, 1979, **171**, 53.
[33] G. Huttner, J. Schneider, H.-D. Müller, G. Mohr, J. von Seyerl, and L. Wohlfahrt, *Angew. Chem. Int. Ed. Engl.*, 1979, **18**, 76.
[34] G. Bor, U. K. Dietler, P. Pino, and A. Poë, *J. Organomet. Chem.*, 1978, **154**, 301.
[35] D. J. Darensbourg and M. J. Incorvia, *J. Organomet. Chem.*, 1979, **171**, 89.
[36] R. Rosetti, G. Gervasio, P. L. Stanghellini, *J. Chem. Soc., Dalton Trans.*, 1978, 222.

said about the structures of the adducts or whether M–CO or M–M cleavage is associated with the addition.

Reactions of $[Ru_3(CO)_{12}]$ with tertiary phosphines can lead to substituted derivatives of $[Ru_3(CO)_{12}]$ or $[Ru(CO)_5]$. The substitution of $[Ru_3(CO)_{11}L]$ ($L = PPh_3$) by L gives $[Ru_3(CO)_{10}L_2]$ which can be further substituted to give $[Ru_3(CO)_9L_3]$. Whereas $[Ru_3(CO)_{12}]$ is both associatively and dissociatively substituted, $[Ru_3(CO)_{11}L]$ only follows a dissociative path but, since the lability is about 60 times greater, an associative path of unchanged rate would not have been detected. Incorporation of a second PPh_3 further increases the lability by 30%. The kinetics and mechanisms are, however, complex.[37] More extended treatment of the trisubstituted cluster with ligand leads to cluster breakdown and for PBu_3 the reaction is essentially quantitative:

$$[Ru_3(CO)_9(PBu_3)_3] + 3PBu_3 \longrightarrow 3[Ru(CO)_3(PBu_3)_2]$$

Three routes have been identified from the kinetics where the phosphorus ligand is PBu_3, PPh_3, or $P(OPh)_3$.[38] A rate-determining loss of L is suppressed with sufficient of the ligand present, but rate-determining loss of CO and a process involving rate-determining fragmentation independent of [CO] or [L] operate. The CO dissociation path is believed to be

$$[Ru_3(CO)_9L_3] \rightleftharpoons [Ru_3(CO)_8L_3] + CO$$
$$[Ru_3(CO)_8L_3] \rightleftharpoons [Ru_3(CO)_8L_3]^*$$
$$[Ru_3(CO)_8L_3]^* \longrightarrow \text{products}$$

The natures of the two octacarbonyl species have been discussed.

4 Substitutions Involving Co-ordinated Alkenes

Kinetic data are given for the reactions shown.[39]

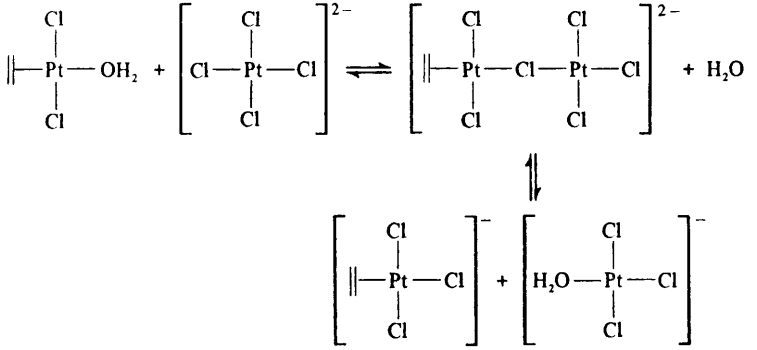
$$[PtCl_4]^{2-} + \text{alkene} \longrightarrow [PtCl_3(\text{alkene})]^- + Cl^-$$
$$[PtCl_3(H_2O)]^- + \text{alkene} \longrightarrow [PtCl_3(\text{alkene})]^- + H_2O$$
$$\text{or } [PtCl_2(H_2O)(\text{alkene})] + Cl^-$$

Activation parameters have been determined for both reactions where ethylene is incorporated, with data for the first reaction where the alkene is *cis*- or *trans*-but-2-ene or $CH_2{=}CHCH_2X$ ($X = NH_3^+$, OH, SO_3^-, or H). There are rather undramatic effects on the rate constants on varying the substituents. The complex $[PtCl_2(H_2O)(C_2H_4)]^-$ is a catalyst for the aquation of $[PtCl_4]^{2-}$ to give $[PtCl_3(H_2O)]^-$, the rate law for which is $-d[PtCl_4^{2-}]/dt = \{k_0 + k_{cat}[PtCl_2(H_2O)(C_2H_4)]\}[PtCl_4^{2-}]$. The uncatalysed rate constant $k_0 = (3.8 \pm 0.1) \times 10^{-5}\ s^{-1}$, in agreement with an earlier value, and $k_{cat} = (4.2 \pm 0.1) \times 10^{-2}\ M^{-1}\ s^{-1}$. The proposed mechanism is as shown in Scheme 7, with aquation of Zeise's anion occurring too rapidly to affect the kinetics.[40] Asymmetric induction has been observed in the reaction:

$$[PtCl(\text{L-am})(C_2H_4)] + \textit{trans}\text{-MeCH}{=}\text{CHMe} \longrightarrow [PtCl(\text{L-am})(\text{MeCH}{=}\text{CHMe})] + C_2H_4$$

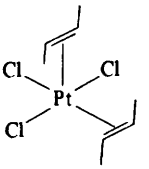
(L-am = various L-aminocarboxylates)

[37] S. K. Malik and A. Poë, *Inorg. Chem.*, 1978, **17**, 1484.
[38] S. K. Malik and A. Poë, *Inorg. Chem.*, 1979, **18**, 1241.
[39] M. Green and C. J. Wilson, *J. Chem. Res.* (*S*), 1978, 175.
[40] M. Green and M. G. Swanwick, *J. Chem. Soc., Dalton Trans.*, 1978, 158.

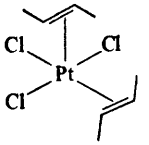


Scheme 7

There is an initial fast increase in c.d. strength, which reflects the more rapid formation of the *S,S*-butene complex than of the *R,R*-butene one. Subsequently the C_2H_4 liberated catalyses the attainment of equilibrium between the isomeric products in which the *R,R*-butene isomer predominates.[41] Related to this is the exchange of *trans*-but-2-ene with $[PtCl_3(S,S\text{-}trans\text{-but-2-ene})]^-$. The rate of exchange determined by use of ^{14}C-labelled alkene was compared with the rate of racemization determined from the drop in c.d. strength. Since the racemization is about 8 times slower than substitution, the substitution must occur with preferential retention.[42] There is apparently less steric hinderance in the formation of (8) than of (9) as the intermediate, and clearly both alkenes must be co-ordinated at some stage to give the effect.



(8)



(9)

[41] Y. Terai, H. Kido, K. Kashiwabara, and K. Saito, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 3245.
[42] Y. Terai and K. Saito, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 503.

13

Effects of Medium on Substitution Reactions

BY J. BURGESS

1 Introduction

Inorganic kineticists with an interest in solvent medium effects have not been generously supplied with reviews recently. Solvent paths and solvento-intermediates in substitution at square-planar centres have been discussed in a well referenced review.[1] Unfortunately, another fully referenced and undoubtedly important review, on solvent properties of significance in determining reactivity in substitution at nickel(II), has appeared in a periodical access to which may prove difficult for many readers.[2] The contents of another, more general, review of solvent effects on kinetics, which includes discussion of appropriate physical models, may prove equally elusive.[3]

In the present Report we shall deal with solvent effects and with salt effects, including effects of polyelectrolytes and of micellar agents. The emphasis will be on substitution at inorganic centres, but related references of relevance will also be mentioned.

2 Solvent Effects

General.—A simple application of the use of mixed solvent series is in examining the dependence of rate on concentration of one component. Attempts have been made to distinguish between the operation of a simple one-step *D* mechanism or of a reaction sequence involving an aquo-intermediate for substitution at complex anions $[Fe(CN)_5L]^{3-}$ by reducing the concentration of solvent water by the addition of substances such as sorbitol, glucose, sucrose, glycerol, or ethylene glycol. The modest decrease in rate as the water concentration decreases was taken to indicate the intermediacy of $[Fe(CN)_5(OH_2)]^{3-}$,[4] but the authors' discussion takes little account of the effects of addition of these polyhydroxylic solvents on the structure, as opposed simply to the concentration, of the water (*cf.* section on solvent structure below).

Nitromethane has been used as a diluent in establishing the rate law for exchange of dimethyl sulphoxide at aluminium(III),[5] and the variation of rate

[1] R. J. Mureinik, *Coord. Chem. Rev.*, 1978, **25**, 1.
[2] J. F. Coetzee, D. Frollini, C. G. Karakatsanis, E. J. Subak, and K. Umemoto, *Chem. Abs.*, 1978, **89**, 49 428.
[3] J. B. Czerminski and T. M. Krygowski, *Wiad. Chem.*, 1978 **32**, 259 (*Chem. Abs.*, 1978, **89**, 66 102).
[4] I. Murati, D. Pavlović, A. Šustra, and S. Ašperger, *J. Chem. Soc., Dalton Trans.*, 1978, 500.
[5] A. J. Brown, O. W. Howarth, P. Moore, and W. J. E. Parr, *J. Chem. Soc., Dalton Trans.*, 1978, 1776.

with DMSO concentration, using acetone or benzene as diluents, has been interpreted in terms of a *D* mechanism for substitution at phthalocyanine complexes $[Fe(pc)L_2]$ (L = imidazole or 4-aminopyridine).[6] The use of water as a diluent has been exemplified by studies of the equilibrium of equation (1). Here the dependence of rates on DMSO indicates that $[Ni(LLLL)(DMSO)]^{2+}$, containing

$$[Ni(LLLL)(DMSO)_2]^{2+} \rightleftharpoons [Ni(LLLL)]^{2+} + 2\,DMSO \qquad (1)$$

five-co-ordinate nickel, is a transient but significant intermediate.[7] Rate trends in DMSO–water mixtures have also proved useful in elucidating the mechanism of hydrolysis of the $[BH_3CN]^-$ anion. Trends in exchange and hydrolysis rates support the postulate that H_2BH_2CN is a common intermediate.[8]

Simpler uses of mixed solvents include the use of appropriate mixtures of methanol and water so that sufficiently low temperatures may be attained to obtain evidence for the intermediacy of $B_3H_7OH_2$ in acid hydrolysis of the $[B_3H_8]^-$ anion,[9] of glycerol and water so that sufficiently high temperatures may be reached for acceptably rapid formation of the $[Ru(tptz)_2]^{3+}$ cation,[10] and of ethanol and water so that both components of the chromium(III) + 2,2′-bipyridyl reaction may be dissolved.[11]

Isotope Effects.—The trend in the ratio of isotope exchange to hydrolysis rates for the $[BH_3(CN)]^-$ anion in DMSO–water mixtures supports the postulate of an H_2BH_2CN intermediate common to both reactions.[8] The observation that rates of base hydrolysis of phosphonium salts are about twice as large in D_2O as in H_2O suggests that P—C bond-breaking and hydrogen removal are not synchronous.[12] Oxygen exchange with molybdate and with tungstate in basic aqueous media, *i.e.* with the simple $[MoO_4]^{2-}$ and $[WO_4]^{2-}$ anions, follows a two-term rate law corresponding to parallel spontaneous and hydroxide-catalysed paths. Isotope (H/D) effects on the former path have been interpreted in terms of a mechanism of solvent-assisted dissociation of the leaving oxygen.[13] Isotope effects, and solvent dependence of rates, both from stopped-flow pulsed Fourier-transform n.m.r. experiments,[14] indicate an S_E2 mechanism for the reaction of *N*-chlorosuccinimide with a series of acetylacetone complexes $[M(acac)_3]$.[15]

Physical Properties of Solvent.—Two physical properties of solvents of direct concern to kineticists are dielectric constant (relative permittivity) and viscosity. Dependences of rates on dielectric constants have been established for substitution of $PhNH_2$ at the $[Fe(CN)_5(OH_2)]^{3-}$ anion[16] and for the bromide–bromate

[6] J. G. Jones and M. V. Twigg, *J. Chem. Soc., Dalton Trans.*, 1978, 1709.
[7] Y. Masuda, T. Ito, N. Yoshida, and M. Fujimoto, *Chem. Lett.*, 1979, 565.
[8] M. M. Kreevoy and E. H. Baughman, *Finn. Chem. Lett.*, 1978, 35 (*Chem. Abs.*, 1978, **88**, 126 942).
[9] W. L. Jolly, J. W. Reed, and F. T. Wang, *Inorg. Chem.*, 1979, **18**, 377.
[10] Y. Sasaki, *Anal. Chim. Acta*, 1978, **98**, 335.
[11] J. N. Mandel and G. S. De, *Indian J. Chem., Sect. A*, 1978, **16**, 580.
[12] G. Aksnes, *Phosphorus Sulphur*, 1977, **3**, 227.
[13] H. von Felten, B. Wernli, H. Gamsjäger, and P. Baertschi, *J. Chem. Soc., Dalton Trans.*, 1978, 496.
[14] C. A. Fyfe, M. Cocivera, and S. W. H. Damji, *Acc. Chem. Res.*, 1978, **11**, 277.
[15] A. J. Brown, O. W. Howarth, and P. Moore, *J. Am. Chem. Soc.*, 1978, **100**, 713.
[16] V. V. Bochkarev, V. L. Ivasenko, and V. P. Lopatinskii, *VINITI Dep. Doc.* 135–77, 1977 (*Chem. Abs.*, 1979, **90**, 128 200).

reaction.[17] In the latter case the observed dependence was used to estimate the radius of the (solvated) transition state. Solvent viscosity is thought not to be important in determining reactivity trends in cyanide attack at $[Fe(CN)_5L]^{3-}$ anions with L = nitrosobenzene or 3-cyanopyridine,[4] but the inverse correlation of rates with viscosities for photosolvation of the *trans*-$[Cr(NCS)_4(NH_3)_2]^-$ anion in several solvents and in glycerol–water mixtures suggests that solvent orientation may be an important factor in determining reaction rates here.[18] The changeover from chemical activation to diffusion activation for complex formation in increasingly viscous media has been discussed in earlier Reports.[19] The most recent contribution in this area demonstrates the expected trend to diffusion activation on cooling glycerol–water solvent mixtures; the reaction involved here is that of myoglobin with carbon monoxide.[20]

An equation correlating reaction rates for acid- and base-catalysed organic reactions with the pK_w and water concentrations in dioxan–water mixtures, equation (2), may prove of value in inorganic contexts.[21]

$$\log k_{obs} - pK_w = n[H_2O] + \text{constant} \qquad (2)$$

The very different basicities of water and of ammonia lead to different reactivity patterns for S_N1cb base hydrolyses of cobalt(III) compounds. The latest contribution in this area has been a study of base hydrolysis of a series of complexes $[Co(NH_3)_5(RNH_2)]^{3+}$ in liquid ethylenediamine.[22] The basicity or solvating power of the solvent determines the form of the rate law for substitutions at copper(II)–Schiff base complexes. The term corresponding to solvolysis is, of course, only significant for solvents with an affinity for copper(II).[23]

Empirical Solvent Parameters.—The interest in relating reactivity trends to selected empirical solvent parameters, either for mechanism diagnosis or merely for tidiness, continues. However, the fashion has swung to Gutmann's (enthalpy-based) donor numbers, *DN*,[24] with the occasional mention of the complementary acceptor number, *AN*.[25] Thus $\Delta H^{\ddagger}$ for solvent exchange at iron(II) and at nickel(II) has been found to correlate with 'enthalpy-based measures of solvent basicity', *i.e.* *DN*.[26] On the other hand, the observation of equal activation enthalpies for exchange of DMF and of acetonitrile at nickel(II), both in the form of the hexasolvento-cation and as a mixed Schiff-base solvento-cation, is not as expected from *DN* values.[27] Quantum yields for photosolvolysis of the *trans*-$[Cr(NCS)_2(en)_2]^+$ cation correlate linearly with *DN* values, indicating the operation of an S_N2 mechanism here.[18] The increase in racemization rate of the $[Ni(phen)_3]^{2+}$ cation with increase in solvent *DN* has been attributed to the

[17] M. S. Subhani, *Rev. Roum. Chim.*, 1978, **23**, 719.
[18] M. Cusumano and C. H. Langford, *Inorg. Chem.*, 1978, **17**, 2222.
[19] See p. 263 of Volume 5 of this Report.
[20] B. B. Hasinoff, *J. Phys. Chem.*, 1978, **82**, 2630.
[21] M. M. Elsemongy, *J. Indian Chem. Soc.*, 1978, **55**, 245.
[22] S. Balt, M. W. G. de Bolster, and H. J. Gamelkoorn, *Inorg. Chim. Acta Lett.*, 1979, **35**, L329.
[23] H. Voss, K. J. Wannowius, and H. Elias, *Inorg. Chem.*, 1979, **18**, 1454.
[24] V. Gutmann, *Fortschr. Chem. Forsch.*, 1972, **27**, 59.
[25] W. Mayer, V. Gutmann, and W. Gerger, *Monatsh. Chem.*, 1975, **106**, 1235.
[26] O. W. Kolling, *Trans. Kansas Acad. Sci.*, 1978, **81**, 303 (*Chem. Abs.*, 1979, **90**, 210 784).
[27] L. L. Rusnak, E. S. Yang, and R. B. Jordan, *Inorg. Chem.*, 1978, **17**, 1810.

intermediacy of solvento-intermediates.[28] Covalent hydrate formation (*cf.* Chapter 8 of this part) may be involved in 1,2-dichloroethane–water mixtures. Rates of exchange of acetylacetone with $[VO(acac)_2]$ decrease as the *DN* of solvent added to dichloroethane increases. Here competition between one end of the acac ligand and the solvent is invoked.[29] A general equation for correlating rates with solvent *DN* and *AN* values[30] has been developed further for application to dipolar aprotic solvents.[31] Deviations from these equations are ascribed to specific solvent structural effects (see below). One system where correlation of rates with *DN* values was not successful involved photochemistry of dithizone complexes of mercury(II), cadmium(II), and zinc(II). Here correlation with Hildebrand's δ_S was also bad, with Kosower's *Z* somewhat less bad.[32] The results of attempts to correlate reactivities with *DN* and *AN* values for substitution at palladium(II) were also disappointing.[33] Here explanations of reactivity trends in terms of transfer chemical potentials for initial and transition states were more attractive (see below).

Examples of Grunwald–Winstein treatments of reactivity trends have become rare in inorganic chemistry. Some more information has been presented on such plots for aquation of $[M(NH_3)_5Br]^{2+}$ cations with M = Cr or Co in aqueous alcohols.[34] The variation of rate constant with solvent *Y* value for the isomerization of a chlorophenylacetylene complex of platinum to its chloro-phenylalkynyl form, equation (3), is so small that an intramolecular mechanism is indicated.[35]

$$[Pt(\eta^2\text{-PhC}{\equiv}\text{CCl})(PPh_3)_2] \longrightarrow [PtCl(C{\equiv}CPh)(PPh_3)_2] \qquad (3)$$

A few more solvent *Y* values have recently become available,[36] including a value for the toluene–water interface![37]

Rates of solvolysis of *trans*-$[Co(dmgH)_2(RNH_2)X]$ (R = H, Me, Et, or Bu, X = Cl, Br, or I) in alcohols, acetonitrile, DMF, and DMSO do not correlate well with solvent dielectric constants, but do correlate with the respective solvent E_T values.[38]

A detailed analysis of reactions of amines, phosphines, and sulphides with alkyl halides in terms of four equations involving various empirical solvent parameters may well prove of value to inorganic kineticists as well as the organic chemists to whom this paper is primarily addressed.[39]

[28] M. Yamamoto, T. Fujiwara, and Y. Yamamoto, *Inorg. Nucl. Chem. Lett.*, 1979, **15**, 37.
[29] M. Nishizawa and K. Saito, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 483; see also *Chem. Abs.*, 1978, **88**, 79 826.
[30] U. Mayer, *Monatsh. Chem.*, 1978, **109**, 421.
[31] U. Mayer, *Monatsh. Chem.*, 1978, **109**, 775.
[32] C. Geosling, A. W. Adamson, and A. R. Gutierrez, *Inorg. Chim. Acta*, 1978, **29**, 279.
[33] S. Balt and J. Meuldijk, *Z. Naturforsch.*, 1979, **34b**, 843.
[34] V. Holba and O. Grancicova, *Collect. Czech. Chem. Commun.*, 1979, **44**, 495.
[35] J. Burgess, M. E. Howden, R. D. W. Kemmitt, and N. S. Sridhara, *J. Chem. Soc., Dalton Trans.*, 1978, 1577.
[36] T. W. Bentley, C. T. Bowen, W. Parker, and C. I. F. Watt, *J. Am. Chem. Soc.*, 1979, **101**, 2486.
[37] S. L. Regen and J. J. Besse, *J. Am. Chem. Soc.*, 1978, **100**, 7117.
[38] N. M. Samus', Nguen Tkhan' Khong, and I. A. Fridman, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1978, **23**, 549.
[39] F. Quemeneur and B. Barion, *J. Chem. Res.*, 1979, (*S*) 188, (*M*) 2357.

Solvation and Solvent Structure.—A review of various models for water structure, dealing especially with the shell model and its recent modifications and improvements, is fundamental to the interpretation of kinetic patterns in water, in binary aqueous mixtures, and in aqueous salt solutions.[40] The effects of alcohols on water structure are reflected in the kinetics of racemization of (+)-$[Co(phen)_3]^{3+}$ in t-butyl alcohol–water mixtures,[41] and in the reaction of Ni^{2+} with chloride in aqueous methanol and aqueous ethanol.[42] In the latter case, the effect of the nickel chloride on the structure of the binary aqueous solvent mixtures is apparent. The structure of the solvation shell around Ni^{2+} in nickel chloride solutions has been probed by *X*-ray[43] and neutron[44] scattering techniques. Similar studies have been described for solutions of magnesium nitrate[45] and of iron(III) nitrate.[46] In the latter, there appear to be six water molecules in the primary solvation shell, twelve in the secondary shell. Investigations of copper(II) and aluminium(III) salt solutions have demonstrated the importance of solvent replacement in the secondary solvation shell in determining quadrupolar relaxation. An equation has been derived for calculating the frequency of ligand exchange in the secondary solvation shell of Al^{3+}.[47] The exclusively dipolar mechanism for longitudinal relaxation of manganese allows one to probe, by suitable n.m.r. means, molecular reorientation processes in Mn^{2+}-containing solutions. In DMSO, the mean time for interaction between a secondary solvation molecule and the primary solvation shell of the Mn^{2+} is *ca.* 4×10^{-12} s (at 25 °C); the residence time for DMSO in the primary solvation shell is *ca.* 10^{-6} s.[48] Reorientation times in secondary solvation shells have been shown to be important in photosolvation of the *trans*-$[Cr(NCS)_4(NH_3)_2]^-$ anion.[18] Similar solvent cage effects seem to be important in determining reactivities in the surprisingly slow isomerization of the $[Ni(2,3,2\text{-tet})(DMSO)_2]^{2+}$ cation[49] and in pyrophosphate hydrolysis.[50] In the latter system, hydrophobic DMSO shells around the pyrophosphate anions are thought to hinder the approach of the attacking water. Solute–solvent hydrogen-bonding interactions, and the differing effects of added alcohols or acetone on these, are invoked to explain the different reactivity trends for $[Cr(NCS)_4L_2]^-$ anions (with L = ammonia[51] or benzylamine[52]) in alcohol–water and acetone–water solvent mixtures.

[40] H. A. Scheraga, *Acc. Chem. Res.*, 1979, **12**, 7.
[41] M. Yamamoto, Y. Uwate, and Y. Yamamoto, *Inorg. Nucl. Chem. Lett.*, 1976, **12**, 713.
[42] S. V. Gorbachev, E. G. Timofeeva, and G. I. Tisenko, *Russ. J. Phys. Chem.* (*Engl. Transl.*), 1978, **52**, 663.
[43] R. Caminiti, G. Licheri, G. Piccaluga, and G. Pinna, *Faraday Discuss. Chem. Soc.*, 1977, No. 64, 62.
[44] G. W. Neilson and J. E. Enderby, *J. Phys. C*, 1978, **11**, L625.
[45] R. Caminiti, G. Licheri, G. Piccaluga, and G. Pinna, *Chem. Phys. Lett.*, 1979, **61**, 45.
[46] R. Caminiti and M. Magini, *Chem. Phys. Lett.*, 1979, **61**, 40.
[47] M. M. Zaripov, *J. Struct. Chem.*, 1978, **19**, 636.
[48] J. C. Boubel, J. Brondeau, and J.-J. Delpuech, *Adv. Mol. Relaxation Interaction Processes*, 1977, **11**, 323.
[49] D. F. Cook and E. D. McKenzie, *Inorg. Chim. Acta*, 1978, **29**, 193.
[50] A. Z. Muradov, N. V. Volkova, L. S. Mushketik, and A. A. Yasnikov, *Dopov. Akad. Nauk Ukr. RSR, Ser. B: Geol., Khim. Biol. Nauki*, 1979, 123 (*Chem. Abs.*, 1979, **90**, 210 695).
[51] P. Kita and R. Kostrzewska-Zeidler, *Pol. J. Chem.*, 1978, **52**, 187 (*Chem. Abs.*, 1978, **88**, 159 194).
[52] J. Zsakó, C. Várhelyi, D. Oprescu, and I. Ganescu, *Acta Chim. Acad. Sci. Hung.*, 1978, **97**, 159 (*Chem. Abs.*, 1978, **89**, 186 625).

Solvent effects on reactivity in the Eigen–Wilkins mechanism for complex formation normally operate on the initial association equilibrium (K_{os}) rather than on the interchange rate constant (k_i). The effects of various solvent properties on K_{os} have been reviewed,[53] and Fuoss has presented a new modification of his ion-pairing model and equation to improve applicability to small ions in polar solvents.[54] Solvation and solvent structural effects on K_{os} and on k_i have been described and discussed for such formation reactions as Mg^{2+} plus chloride in aqueous alcohols (MeOH, EtOH, PrOH),[55] Ni^{2+} plus imidazole in aqueous ethanol,[56] and Be^{2+} plus sulphate in aqueous DMSO.[57,58] Poor solvation of sulphate at high proportions of DMSO leads to large values for K_{os} for this last reaction. The kinetics of reaction between Nd^{3+} or Gd^{3+} and chloride, in aqueous methanol, have been interpreted in terms of a change in co-ordination number associated with complex formation.[59] It seems unlikely that solvation numbers of the lanthanide(III) cations change along the 4*f* series,[60] so the current hypothesis is that additional solvent molecules are lost in the complexation step for formation of chloro-complexes of Nd^{3+} or Gd^{3+}, but not in the case of, *e.g.*, Er^{3+}. This picture is expected to vary with the nature both of the ligand and of the solvent medium.[59] Rates of formation of cyclic and linear polythiaether complexes of Cu^{2+} vary much more with solvent composition than do their dissociation rates, at least in methanol–water mixtures. Various rate comparison and stability constant considerations indicate that solvation effects are not dominant in the macrocyclic effect for these polythiaether ligands.[61] Mercury(II)-catalysed aquation of chloro-transition metal complexes shows a similar kinetic pattern to the above Eigen–Wilkins formation mechanism, with an initial equilibrium formation of a dinuclear intermediate followed by slow breakdown of this intermediate. Solvent effects on both steps have been probed for the catalysed aquation of the $[Rh(NH_3)_5Cl]^{2+}$ cation in aqueous ethanol.[62]

Systems in which specific solvent structural effects do not seem to affect kinetic patterns include the reactions of Ni^{2+} with malonate in aqueous *d*-fructose,[63] some substitutions at $[Fe(CN)_5L]^{n-}$ anions,[4] and aquation of the $[Cr(NH_3)_5Br]^{2+}$ cation in several series of alcohol–water mixtures.[34] Deviations from a newly proposed correlation of rates with solvent *DN* and *AN* values (*cf.* above, refs. 24 and 25) have been used as a probe for specific solvent structural effects.[30,31] Ethylene carbonate and propylene carbonate have no structure

[53] J. F. Coetzee, *Chem. Abs.*, 1979, **90**, 44 458.
[54] R. M. Fuoss, *J. Am. Chem. Soc.*, 1978, **100**, 5576.
[55] V. Abaraviciute, B. Kuksao, and R. Savickas, *Akust. Zh.*, 1978, **24**, 801 (*Chem. Abs.*, 1979, **90**, 62 070).
[56] V. A. Shormanov, Yu. S. Koryagin, and G. A. Krestov, *Koord. Khim.*, 1979, **5**, 251 (*Chem. Abs.*, 1979, **90**, 175 480); *Chem. Abs.*, 1979, **90**, 44 425.
[57] R. Lachmann, I. Wagner, D. H. Devia, and H. Strehlow, *Ber. Bunsenges. Phys. Chem.*, 1978, **82**, 492.
[58] D. H. Devia and H. Strehlow, *Ber. Bunsenges. Phys. Chem.*, 1979, **83**, 627.
[59] H. B. Silber, D. Bouler, and T. White, *J. Phys. Chem.*, 1978, **82**, 775.
[60] G. Geier and U. Karlen, *Helv. Chim. Acta*, 1971, **54**, 135; S. S. Yun and J. L. Bear, *J. Inorg. Nucl. Chem.*, 1975, **37**, 1757.
[61] L. L. Diaddario, L. L. Zimmer, T. E. Jones, L. S. W. L. Sokol, R. B. Cruz, E. L. Yee, L. A. Ochrymowycz, and D. B. Rorabacher, *J. Am. Chem. Soc.*, 1979, **101**, 3511.
[62] S. F. Chan and L. Chang, *Chem. Abs.*, 1979, **90**, 157 707.
[63] M. Delsignore, D. Saar, and S. Petrucci, *Adv. Mol. Relaxation Interaction Processes*, 1978, **13**, 249.

forming properties. Therefore kinetic studies of various substitution reactions of cobalt(III), chromium(III), iron(II), and platinum(II) complexes in aqueous solvent mixtures containing these co-solvents[64] form a useful complement to kinetic studies in, *e.g.*, alcohol–water mixtures when one is attempting to assess the importance of solvent structure in determining reactivity.

In most of the investigations mentioned so far in this section involving solvent mixtures it is likely that the primary solvation shell does not vary with solvent composition. However, there are occasions when variation of reactivity with solvent mixture composition is attributed to changes in primary solvation shell composition, as in the case of reaction of Ni^{2+} with ammonia in aqueous methanol.[65] In the reaction of Be^{2+} with sulphate in aqueous DMSO, there is strong n.m.r. evidence for variation in primary solvation shell composition.[58] In the reaction of Co^{2+} with tetraphenylporphine in acetic acid–water the kinetics also reflect the presence of varying amounts of mixed solvates.[66] By way of contrast, in reactions of copper(II) with polythiaethers in methanol–water mixtures only Cu_{aq}^{2+} reacts; mixed solvates are claimed to be of negligible reactivity.[61] In the reaction of chromium(III) with edta in methanol– and ethanol–water mixtures, variation in pK for the Cr^{3+} has an effect on the formation rates, but the individual rate constants for the reactions of Cr^{3+} and of $CrOH^{2+}$ with the ligand seem to be practically independent of solvent composition.[67]

In isomerization, racemization, and ligand-exchange reactions of β-diketone complexes, solvents affect reactivity both in solvation changes at the complex and the leaving β-diketone, and in the possibility of competition between (donor) solvent and free ligand-oxygen in one-end-off intermediates. This has already been mentioned in the earlier section on solvent parameters (see above), for acetylacetone exchange with $[VO(acac)_2]$.[29] Other cases where solvent competition effects appear to suggest a one-end-off intermediate include the reaction of $[Fe(acac)_3]$ with 2-thenoyltrifluoroacetonate[68] and racemization of the $[Ge(bzbz)_3]^+$ cation.[69] Small solvent effects seem to indicate an intramolecular mechanism for rearrangement of $[Al(acac)_3]$,[70] for *fac* → *mer* isomerization of the $[Mn(CO)_3(dpm)Cl]^+$ cation,[71] and for *cis* ⇌ *trans* isomerization of $[M(CO)_2(LL)]$ (M = Cr, Mo, or W, LL = a chelating diphosphine ligand).[72] Relatively small solvent effects on rates and activation parameters for rearrangement of $[V(tfac)_3]$ and $[V(hfac)_2(acac)]$ do not permit an unequivocal choice between one-end-off and intramolecular twist mechanisms.[73] Solvent effects on the reaction of $[M(acac)_3]$ complexes (M = Co, Rh, Ir, Al, or Ga) with *N*-chlorosuccinimide tie in with the established picture of solvation for acetylacetone

[64] M. J. Blandamer, J. Burgess, S. J. Hamshere, and F. M. Mekhail, *Transition Met. Chem.*, 1979, **4**, 77.
[65] W. J. MacKellar and D. B. Rorabacher, *J. Am. Chem. Soc.*, 1971, **93**, 4379.
[66] O. A. Golubchikov, B. D. Berezin, L. P. Shormanova, and N. N. Gridina, *Russ. J. Inorg. Chem. (Engl. Transl)*, 1978, **23**, 56.
[67] M. Kimura and J. Shirai, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1085.
[68] T. Sekine, H. Honda, M. Kokiso, and T. Tosaka, *Bull. Chem. Soc., Jpn.*, 1979, **52**, 1046.
[69] F. B. Ueno, A. Nagasawa, and K. Saito, *Bull. Chem., Soc. Jpn.*, 1979, **52**, 1363.
[70] A. J. C. Nixon and D. R. Eaton, *Can. J. Chem.*, 1978, **56**, 1928.
[71] A. M. Bond, B. S. Grabaric, and Z. Grabaric, *Inorg. Chem.*, 1978, **17**, 1013.
[72] A. M. Bond, B. S. Grabaric, and J. J. Jackowski, *Inorg. Chem.*, 1978, **17**, 2153.
[73] A. J. C. Nixon and D. R. Eaton, *Can. J. Chem.*, 1978, **56**, 1005.

chelates.[15] The rate constant for the reaction of Ni^{2+} with acetylacetone varies surprisingly little on going from water to aqueous methanol with $x_{MeOH}=0.8$.[74]

Kinetic studies in mixtures of organic solvents remain rare, but there have been three in recent months. These include the reaction of nickel(II) with thiocyanate in methanol–DMSO mixtures,[63] DMSO exchange at Al^{3+} in mixtures of this solvent with nitromethane,[5] and solvolysis of iron(II)–phthalocyanine complexes in DMSO–acetone or –benzene mixtures.[6]

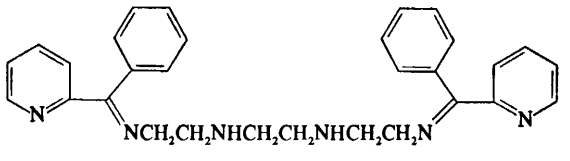
Relative Importance of Initial- and Transition-state Effects.—Kinetic measurements indicate differences between initial-state and transition-state properties. If solvent effects on the initial state can be established by appropriate thermodynamic measurements and assumptions, then solvent effects on the transition state can be deduced. Such dissections of solvent effects on reactivity trends for reactions of transition-metal complexes have recently been reviewed.[75] A more general review of medium effects on initial and transition states concentrates on organic examples, discussing the use of thermodynamic transfer functions and pointing out the possible complication of the structure of the transition state changing as the composition of the medium changes.[76] Indeed a discussion of the kinetics of the reaction of the $[BH_4]^-$ anion with H^+ suggests that the transition states in water and in anhydrous sulphuric acid differ.[77] Transition state transfer activity coefficients[78] have also been discussed, with particular reference to acid-catalysed reactions.[79]

The first inorganic reactions for which solvent effects on reactivities were analysed into initial-state and transition-state contributions were those of tetraalkyltin compounds with mercury(II) halides.[80] There has been some subsequent disagreement over activation parameters for such reactions of tetramethyltin, and these have now been redetermined.[81] For transfer from methanol to acetonitrile, the decreases in ΔG^* and ΔH^* are mostly due to increases in the initial-state values. For transfer from methanol to DMSO the decreases in ΔG^* and ΔH^* are dominated by very large decreases in transition-state values.

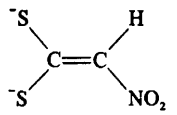
The necessity of introducing extrathermodynamic assumptions in order to estimate transfer parameters for individual ions introduces a degree of uncertainty into initial state–transition state analyses for reactions involving ionic species. This has been illustrated for the reaction of the $[Fe(phen)_3]^{2+}$ cation with hydroxide in methanol–water mixtures. However, despite the uncertainties it is quite clear that in this system, and for the same reaction in acetone–water mixtures, solvation of the $[Fe(phen)_3]^{2+}$ reactant or moiety is the dominant factor, at any rate in water-rich solvent mixtures.[82] The pattern for this reaction, and for analogous reactions of related low-spin iron(II) complexes, closely resembles that for base

[74] M. J. Hynes and B. D. O'Regan, *J. Chem. Soc., Dalton Trans.*, 1979, 162.
[75] M. J. Blandamer and J. Burgess, *Pure Appl. Chem.*, 1979, **51**, 2087.
[76] E. Buncel and H. Wilson, *Acc. Chem. Res.*, 1979, **12**, 42.
[77] R. Willem, *J. Chem. Soc., Dalton Trans.*, 1979, 33.
[78] *Pure Appl. Chem.*, 1978, **50**, 587.
[79] K. Yates and T. A. Modro, *Acc. Chem. Res.*, 1978, **11**, 190.
[80] See pp. 112–113 of Volume 1 of this Report.
[81] M. H. Abraham, J. Andonian-Haftvan, and M. R. Sedaghat-Herati, *J. Organomet. Chem.*, 1979, **172**, 31.
[82] M. J. Blandamer, J. Burgess, and D. L. Roberts, *J. Chem. Soc., Dalton Trans.*, 1978, 1086.

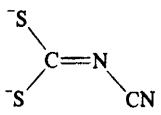
hydrolysis of methyl iodide rather than that for, say, base hydrolysis of esters.[83] From comparative kinetic studies of sexadentate Schiff-base (1) and tris-2,2′-bipyridyl complexes of iron(II) with cyanide, it appears that initial state–transition state solvation differences are less important for the former.[84] Reactions of these iron(II)–di-imine complexes with hydroxide or with cyanide increase greatly in rate on adding, for instance, an alcohol or DMSO to the aqueous system. In contrast, cyanide attack at square-planar platinum(II) or palladium(II) complexes of the dithia-ligands ned (2) and cdc (3) takes place much more slowly in methanol than in water.[85] This reactivity difference can hardly be ascribed to solvation of the cyanide, whose chemical potential must increase greatly on transfer from water into methanol. Cyanide and hydroxide attack at di-imine complexes of iron(II), and of ruthenium(II), is thought, at least in some quarters,[86] to take place *via* initial attack at the co-ordinated ligand. For the reaction of hydroxide with $[Ru(tptz)_2]^{2+}$ [tptz=(4)], comparison of activation entropy with reaction entropy



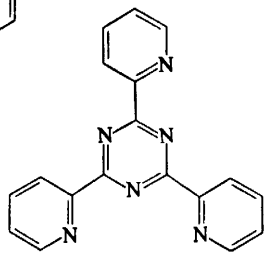
(1)



(2)



(3)

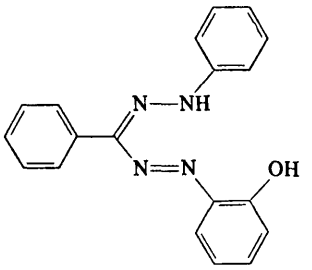


(4)

suggests that solvation effects are not particularly significant in transition-state formation for generation of the ligand-substituted species.[87] In the peroxodisulphate oxidation of $[Fe(bipy)_2(CN)_2]$, studied in methanol–water mixtures containing up to 40% methanol, transition-state effects are very much bigger than initial-state effects. Indeed ΔG_{tr}(initial state) values are very close to zero, since the chemical potential of the peroxodisulphate increases and that of the iron(II) complex decreases to nearly the same extent as the amount of methanol is increased. Therefore the observed marked decrease in rate constant, by about 40 times on going from water to 40% methanol, is attributable almost entirely to transition-state destabilization.[88]

[83] M. J. Blandamer, J. Burgess, P. Cookson, D. L. Roberts, P. Wellings, F. M. Mekhail, and P. Askalani, *J. Chem. Soc., Dalton Trans.*, 1978, 996.
[84] M. J. Blandamer, J. Burgess, R. I. Haines, F. M. Mekhail, and P. Askalani, *J. Chem. Soc., Dalton Trans.*, 1978, 1001.
[85] M. J. Hynes and P. F. Brannick, *Proc. R. Irish Acad.*, 1977, **77B** 479; *J. Chem. Soc., Dalton Trans.*, 1977, 2281.
[86] R. D. Gillard, *Inorg. Chim. Acta Lett.*, 1974, **11**, L21; *Coord. Chem. Rev.*, 1975, **16**, 67; J. Burgess and R. I. Haines, *J. Chem. Soc., Dalton Trans.*, 1978, 1447.
[87] R. D. Gillard and P. A. Williams, *Transition Met. Chem.*, 1978, **3**, 334.
[88] M. J. Blandamer, J. Burgess, and R. I. Haines, *J. Chem. Soc., Chem. Commun.*, 1978, 963.

The type of analysis discussed in the preceding paragraph with particular respect to d^6 iron(II) complexes has also been attempted for d^8 palladium(II)[33] and gold(III)[89] substitutions. In the case of the reactions of [Pd(fo)L], where H_2fo is the formazan (5) and L = ammonia or pyridine, with thiocyanate, thiourea, or triphenylphosphine, a kinetic–thermodynamic analysis shows Gibbs free



(5)

energies of transfer of the initial and transition states to be similar in most cases, for transfer from methanol to acetone, dioxan, acetonitrile, and DMSO. In other words, solvation changes on going from the initial to the transition state are generally small. The few exceptions noted may involve specific solvent structural effects.[33] The reaction of the $[Au(Et_4dien)Cl]^{2+}$ cation with hydrazoic acid involves a large cation and an uncharged molecule, so again relatively small solvation changes will be expected on going from the initial to the transition state. The kinetics observed are consistent with this expectation, but a full kinetic–thermodynamic analysis is here precluded by the hazards which may be involved in establishing transfer parameters for hydrazoic acid.[89]

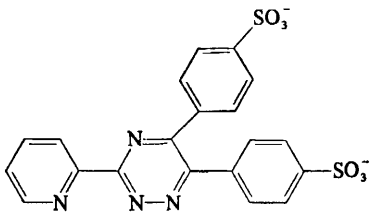
The large increase in rate and decrease in activation energy for base hydrolysis of the tetraphenylphosphonium cation as the proportion of the organic component increases in THF–water mixtures is attributed to a combination of initial-state desolvation and transition-state stabilization. It is claimed that something like 13 water molecules have to be removed from the solvation shell in going from the initial to the transition state.[90] The results from this study are discussed in relation to those from earlier studies involving the co-solvents acetone, dioxan, and DMSO.[12,90]

Reactivity trends for *D* substitution at $[Fe(CN)_5L]^{n-}$ anions will depend on solvent effects on the starting anion and on the separating moieties $[Fe(CN)_5]^{3-}$ and L ($L^{\pm}$) in the transition state. The activation parameters determined for a series of anions of this type with L = ammonia, amine, or aniline have been held to indicate the importance of transfer of the leaving group L to the solvent,[91] an importance seemingly not recognized in some other studies.[4] Small differences in reactivity between various complexes with $L = NH_2(CH_2)_nNH_2$ or $NH_2(CH_2)_nNH_3^+$, $3 \leqslant n \leqslant 6$, have also been attributed to solvation effects at the

[89] M. J. Blandamer, J. Burgess, S. J. Hamshere, and P. Wellings, *Transition Met. Chem.*, 1979, **4**, 161.
[90] F. Y. Khalil and G. Aksnes, *Can. J. Chem.*, 1978, **56**, 1933.
[91] N. E. Katz, P. J. Aymonino, M. A. Blesa, and J. A. Olabe, *Inorg. Chem.*, 1978, **17**, 556.

ligand L (L^+).[92] In this investigation the solvent composition was not varied, as it had previously been suggested that solvation effects at $[Fe(CN)_5]^{3-}$ are large,[93] and would probably swamp L (L^+) variation effects. In fact reactions of this type should prove very interesting for a full initial state–transition state analysis over a range of binary aqueous solvent mixtures, as it should be possible to establish transfer parameters for the $[Fe(CN)_5L]^{n-}$ anion of the initial state, for the transition state $[Fe(CN)_5 \cdots L]^{+n-}$, and, using free L and perhaps $[Fe(CN)_6]^{3-}$ as model for $[Fe(CN)_5]^{3-}$, the transition-state components. Thence it might prove possible to estimate the degree of separation of leaving ligand from metal ion in the transition state, which could be compared with the estimates from activation volume determinations.[94]

The increase in chemical potential, arising from less favourable solvation, of many simple anions on transfer from water into binary aqueous mixtures or into organic solvents has been much utilized in preparative and kinetic organic chemistry, and is also relevant to several recent inorganic kinetic and mechanistic studies. Thus the higher chemical potential of hydroxide in aqueous methanol leads to increased reactivity for $[Fe(fz)_3]^{4-}$ [fz = ferrozine (6)] with hydroxide *via*



(6)

increasing extent of formation of the co-ordinated-ligand intermediate (*cf.* above).[95] Similar comments apply to the reaction of the 5-nitro-1,10-phenanthroline complexes of iron(II) and ruthenium(II) with methoxide in DMSO.[96] The importance of ion-pairing in aquation of iron(II)–di-imine complexes in water is small and of arguable kinetic importance (*cf.* Section 3 below), but the concentration of ion-pairs with chloride or sulphate is much larger in DMSO, with important kinetic consequences (*cf.* Section 3 below).[97] The increasing chemical potential of sulphate as the proportion of DMSO increases in aqueous mixtures also affects rates in the beryllium(II) + sulphate reaction, *via* increasing K_{os} for the first stage in the Eigen–Wilkins mechanism.[58] Variation in the chemical potential of the chloride ion is presumably an important factor in determining the marked solvent dependence of rate for the forward reaction

[92] N. E. Katz, M. A. Blesa, J. A. Olabe, and P. J. Aymonino, *J. Chem. Soc., Dalton Trans.*, 1978, 1603.
[93] M. J. Blandamer, J. Burgess, and R. I. Haines, *J. Chem. Soc., Dalton Trans.*, 1976, 1293.
[94] J. Burgess, R. I. Haines, D. R. Stranks, and T. E. Sullivan, *J. Chem. Soc., Dalton Trans.*, 1977, 1460.
[95] M. J. Blandamer, J. Burgess, and P. Wellings, *Transition Met. Chem.*, 1979, **4**, 95.
[96] D. W. W. Anderson, P. Roberts, M. V. Twigg, and M. B. Williams, *Inorg. Chim. Acta Lett.*, 1979, **34**, L281.
[97] D. J. Farrington, J. G. Jones, and M. V. Twigg, *J. Chem. Soc., Dalton Trans.*, 1979, 221.

of equilibrium (4).[98] Similar considerations will apply to redox reactions as well

$$[CoCl_3(solvent)]^- + Cl^- \rightleftharpoons [CoCl_4]^{2-} + solvent \quad (4)$$

as to the above substitution examples. Thus variations in the chemical potentials of Fe^{2+}, Fe^{3+}, and $FeOH^{2+}$ will contribute to the observed decrease in the iron(II)–iron(III) electron exchange rate in aqueous HMPA as x_{HMPA} increases (at low x_{HMPA}).[99] Rates of reduction by solvated electrons will also depend on solvation energies for the electron;[100] indeed solvation free energies for the electron have been estimated in water, methanol, and DMF.[101]

In aquation of the cations $[M(NH_3)_5Br]^{2+}$ (M = Cr or Co) in alcohol–water mixtures, solvent composition variation has much more effect on $\Delta S^{\ddagger}$ than on $\Delta H^{\ddagger}$. This is attributed to solvation-shell ordering effects in the transition state.[34] Enhancement of reactivity in the reaction of cobalt(II) with chlorophyllic acid in methanol on addition of lithium nitrate is attributed to inhibition of transition-state solvation.[102] The effective radius of a transition state can be guessed from the variation of rate constant with dielectric constant. This approach has been used for the bromide–bromate reaction.[17] In contrast to this concentration of attention on the transition state, it may be noted that it is the stabilization of the reactant in relation to water structure that is thought to control the variation of the racemization rate of the (+)-$[Co(phen)_3]^{3+}$ cation in t-butyl alcohol–water mixtures.[41]

3 Salt Effects

The dependence of rate on ionic strength has been used as part of the evidence in confirming the operation of the I_d mechanism for the reaction of Ni^{2+} with Et_2dtc^- in DMSO,[103] and in supporting the assumption of an S_N2 mechanism for the reaction of Cr^{3+} with 2,2′-bipyridyl in aqueous ethanol.[11] In the latter case there is little variation of rate with ionic strength as bipy is uncharged. A more dramatic example is provided by the reaction of Zn^{2+} with pada, where good agreement has been obtained between rate constants derived from *T*-jump experiments at very high ionic strength[104] and dye laser photochemical relaxation experiments at low ionic strength.[105] The activation energy for the formation of $MnSO_4$ from Mn^{2+} and SO_4^{2-} decreases from about 8.4 to about 6.0 kcal mol^{-1} as the concentration of manganese(II) sulphate increases from zero to 2 M.[106] Periodate oxidation of co-ordinated thiocyanate, in $[M(NH_3)_5(NCS)]^{2+}$ (M = Cr or Co), shows the expected dependence of rate on ionic strength, though the measured activation entropy is negative and thus not according to expectation for a reaction between ions of opposite charge.[107]

[98] R. Schmid, W. Tschebull, and V. Gutmann, *Rev. Chim. Minérale*, 1978, **15**, 23.
[99] G. Wada, S. Nakago, and Y. Abe, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 1381
[100] A. M. Afanassiev, K. Okazaki, and G. R. Freeman, *J. Phys. Chem.*, 1979, **83**, 1244.
[101] H. Imai and K. Yamashita, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 3103.
[102] B. D. Berezin, N. I. Volkova, and E. B. Karavaeva, *Chem. Abs.*, 1978, **88**, 159 146.
[103] P. J. Nichols and M. W. Grant, *Aust. J. Chem.*, 1978, **31**, 2581.
[104] G. R. Cayley and D. N. Hague, *Trans. Faraday Soc.*, 1971, **67**, 786.
[105] B. H. Robinson and N. C. White, *J. Chem. Soc., Faraday Trans. I*, 1978, **74**, 2625.
[106] M. Akagün, *Acustica*, 1978, **39**, 344.
[107] V. Holba and O. Volarova, *Collect. Czech. Chem. Commun.*, 1978, **43**, 574.

In contrast to these classical treatments of salt effects, many kinetic studies show significant specific effects, often attributable to such phenomena as ion-pairing or ion effects on solvent structure. Chloride ions have a large accelerating effect on racemization of the $[Ni(phen)_3]^{2+}$ cation in t-butyl alcohol–water mixtures ($x_{Bu^tOH} > ca.$ 0.5),[28] and on solvolysis of the $[Fe(phen)_3]^{2+}$ cation in DMSO.[97] Ions such as bromide or sulphate have much smaller effects on the latter reaction, and perchlorate actually retards the racemization. Ion-pairing is also thought to be the cause of the relatively small effects of chlorides of alkali metals and alkaline-earth metals on aquation rates for the $[Fe(bipy)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$ cations in aqueous solution.[108] Tetra-alkylammonium halides have a larger effect on aquation of the $[Fe(bipy)_3]^{2+}$ cation[109] and, more dramatically, on aquation of the $[Fe(5\text{-}NO_2phen)_3]^{2+}$ cation[110] in aqueous solution. Salt effects on the aquation of the $[Fe(5\text{-}NO_2phen)_3]^{2+}$ cation in binary aqueous mixtures have now been studied, for the co-solvents t-butyl alcohol, acetone, acetonitrile, and DMSO. The observed resultants of salt and co-solvent effects suggest that in most of the solvent systems studied salt effects are determined by ion size rather than by hydration characteristics, though both size and solvation seem to be significant for the t-butyl alcohol–water mixtures.[111]

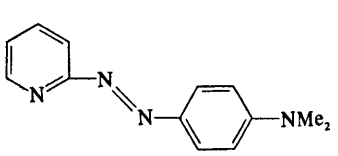
Effects of added salts on the Belousov–Zhabotinskii oscillating reaction have also been attributed to solvent structural factors, through the influence of the cations (Li^+, Na^+, K^+, Me_4N^+) on the water structure.[112] Specific effects of added salts on transition states have been proposed for the reactions of cobalt(II) with chlorophyllic acid (in methanol)[102] and the conversion of β- into α-dodecamolybdosilicate.[113] In the former case added lithium nitrate is thought to inhibit solvation of the transition state, but in the latter added ions are believed actually to enter the transition state. Salt effects on the kinetics and mechanism of formation of monofluoro-complexes of a range of M^{2+} and Al^{3+} cations in aqueous media are described in a conference report comprehensible only to readers of Russian.[114]

4 Micellar Effects

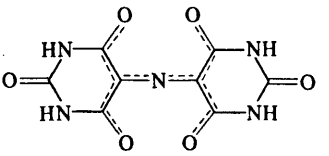
These have formed the subject of a general review[115] and of an issue of *Berichte der Bunsengesellschaft für Physikalische Chemie*;[116] specifically inorganic applications have also been briefly reviewed in a paper which attempts a correlation using the Poisson–Boltzmann equation applied to a parallel-rod cell model.[117] In these general reviews organic systems, and both redox and substitution reactions of inorganic species, are covered.

[108] A. P. Chagas, M. Tubino, and E. J. S. Vichi, *Inorg. Chim. Acta Lett.*, 1978, **28**, L137.
[109] S. Raman, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1073.
[110] M. J. Blandamer, J. Burgess, and S. H. Morris, *J. Chem. Soc., Dalton Trans.*, 1975, 2118.
[111] N. F. Ashford, M. J. Blandamer, J. Burgess, D. Laycock, M. Waters, P. Wellings, R. Woodhead, and F. M. Mekhail, *J. Chem. Soc., Dalton Trans.*, 1979, 869.
[112] L. Treindl and S. Drojáková, *Collect. Czech. Chem. Commun.*, 1978, **43**, 1561.
[113] T. Fujinaga, M. Koyama, and T. Hori, *Bull. Inst. Chem. Res., Kyoto Univ.*, 1977, **55**, 482 (*Chem. Abs.*, 1978, **89**, 49 506).
[114] V. V. Blokhin, L. A. Kul'vinova, Yu. A. Makashev, V. E. Mironov, and V. V. Shurukhin, *Chem. Abs.*, 1979, **90**, 77 263.
[115] C. A. Bunton, *Catal. Rev. Sci. Eng.*, 1979, **20**, 1 (*Chem. Abs.*, 1979, **90**, 210 664).
[116] *Ber. Bunsenges. Phys. Chem.*, 1978, **82**, 931–1015.
[117] M. Ishikawa, *J. Phys. Chem.*, 1979, **83**, 1576.

There has been much activity in the area of micellar and polyelectrolyte effects on formation of nickel(II) complexes, especially of pada (7) and murexide (8). An earlier investigation[118] of the effects of sodium dodecyl sulphate on the reaction with pada has been extended.[119, 120] The use of relaxation techniques



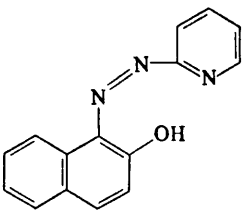
(7)



(8)

complements the original stopped-flow techniques, especially for the particularly fast reactions in the region of the critical micelle concentration (c.m.c.).[121] Conductance and spectrophotometric stopped-flow experiments give consistent results for the reaction with murexide; sodium polyethylene sulphonate retards this reaction greatly.[122] The Ni^{2+} is partitioned between bulk solvent and the charged micelle surface. The formation rate constant is affected little by added sodium dodecyl sulphate until a concentration in the region of the c.m.c. is reached, whereafter the rate drops dramatically. It is suggested that complex formation kinetics of this type may prove a useful probe into micellar systems and their mode of operation.[123] Rates for dissociation of nickel(II)–murexide, and for water exchange at, and displacement from, nickel(II) in Aerosol-OT-stabilized water pools in heptane (a reversed micelle system) are very similar to those in pure water.[120, 124]

Replacement of pan (9) in $[Cu(pan)]^+$ by edta anions occurs in two stages, with a transient $[(pan)Cu(edta)]^{n-}$ intermediate. The overall process is accelerated by cationic surfactants, which act as concentrators of the anionic edta. However, dodecyl sulphate inhibits strongly, because of strong repulsion between this



(9)

[118] A. D. James and B. H. Robinson, *J. Chem. Soc., Faraday Trans. I*, 1978, **74**, 10.
[119] J. Holzwarth, W. Knoche, and B. H. Robinson, *Ber. Bunsenges. Phys. Chem.*, 1978, **82**, 1001.
[120] B. H. Robinson, A. D. James, and D. C. Steytler, *Chem. Abs.*, 1979, **90**, 44 460.
[121] B. H. Robinson and N. C. White, *J. Chem. Soc., Faraday Trans. I*, 1978, **74**, 2625.
[122] T. Okubo and N. Ise, *Polym. Bull. (Berlin)*, 1978, **1**, 109 (*Chem. Abs.*, 1979, **90**, 44 419).
[123] M. Fischer, W. Knoche, B. H. Robinson, and J. H. M. Wedderburn, *J. Chem. Soc., Faraday Trans. I*, 1979, **75**, 119.
[124] B. H. Robinson, D. C. Steytler, and R. D. Tack, *J. Chem. Soc., Faraday Trans., I*, 1979, **75**, 481.

surfactant and the negatively charged edta ligand. This prevents the edta approaching the $[Cu(pan)]^+$, which is solubilized in the micelle surface.[125]

In many respects micellar effects on redox reactions parallel those on substitution reactions.[116,117] Thus the effects of cetyltrimethylammonium bromide on the reaction between the $[Mn(cydta)]^-$ anion and $[Co(edta)]^{2-}$ or $[Co(cydta)]^{2-}$ complement the $[Cu(pan)]^+$ + edta system mentioned in the previous paragraph.[126] Other micellar redox systems include two involving the ever popular $[Ru(bipy)_3]^{2+}$ cation as electron acceptor, from $[Mo(CN)_8]^{4-}$ (ref. 127) and methylphenothiazine.[128] Finally, an ingenious extension involves the incorporation of the micelle group, in this case a dodecylcarboxamide substitutent, into the di-imine ligand of the $[Ru(bipy)_3]^{2+}$ cation.[129]

[125] H. Kohara, *Kitakyushu Kogyo Koto Semmon Gakko Kenkyu Hokoku*, 1979, **12**, 57, 63 (*Chem. Abs.*, 1979, **90**, 175 332, 175 510).
[126] A. A. Bhalekar and J. B. F. N. Engberts, *J. Am. Chem. Soc.*, 1978, **100**, 5914.
[127] E. Pelizzetti and E. Pramauro, *Inorg. Chem.*, 1979, **18**, 882.
[128] M. Maestri, P. P. Infelta, and M. Graetzel, *J. Chem. Phys.*, 1978, **69**, 1522.
[129] Y. Tsutsui, K. Takuma, T. Nishijima, and T. Matsuo, *Chem. Lett.*, 1979, 617

Part III

BIOINORGANIC STUDIES

By

A. G. LAPPIN

1 Introduction

In this part, an attempt has been made to extend the range and depth of coverage over previous volumes. Emphasis is placed on reactions of metalloproteins at the expense of model processes, which are to some extent covered in other chapters. A great deal of selectivity has been applied to the material. The work included generally has a high mechanistic content and relates to well defined and well characterized systems. Studies on proteins which are currently fashionable among 'inorganic chemists' are given priority. The Report is divided into a number of sections but some licence has been used in the interpretation of the headings. For example, electron transfer reactions of haemoglobin and myoglobin are discussed in Section 3 under the heading of redox reactions in biological systems rather than in Section 8. Redox studies of metal peptide complexes are on the other hand discussed briefly in Section 2. Review articles and books on specific topics are noted in the relevant sections though, on a more general note, titles in the series 'Metal Ions in Biological Systems' on the chemistry of iron[1] and the interaction of metal ions with nucleotides[2] have appeared. A series of books on the porphyrins[3] has also been published.

2 Metal–ion Transport and Complexation

Crown Ethers, Cryptates, and Sepulchrates.—The results of an ultrasonic absorption study[4] of the complexation of bivalent metal ions with 18-crown-6 and 15-crown-5 are consistent with a two-step mechanism,

$$L \rightleftharpoons L^*$$

$$M^{2+} + L^* \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ML^{*2+}$$

in which a rapid conformational equilibrium of the crown ether L is sufficiently rapid and lies well in favour of L* to avoid coupling to the subsequent metal ion binding step. The rates of formation of the complexes, k_1 (Table 1), are similar

Table 1 *Complexation and dissociation rates of metal ions with biologically important ligands at* 25 °C

Reaction	*I*/M	k_f/M^{-1} s^{-1}	k_b/s^{-1}	*Ref.*
Sr^{2+}+15-crown-5		6.5×10^7	7.3×10^5	4
Ba^{2+}		1.2×10^8	2.3×10^6	4
Pb^{2+}		3.2×10^8	4.6×10^6	4
Hg^{2+}		1.6×10^8	3.3×10^6	4
Sr^{2+}+18-crown-6		7.7×10^7	1.5×10^5	4
Ba^{2+}		1.3×10^8	1.7×10^4	4
Pb^{2+}		3.3×10^8	1.8×10^4	4
Hg^{2+}		4.0×10^8	1.5×10^6	4
Li^++(1a) (211)	0	4.8×10^5	4.4×10^{-3}	6

[1] 'Metal Ions in Biological Systems', ed. H. Siegel, Vol. 7, Marcel Dekker, New York, 1978.
[2] 'Metal Ions in Biological Systems', ed. H. Siegel, Vol. 8, Marcel Dekker, New York, 1979.
[3] 'The Porphyrins', ed. D. Dolphin, Vols. 1—7, Academic Press, New York, 1978.
[4] L. J. Rodriguez, G. W. Liesegang, M. M. Farrow, N. Purdie, and E. M. Eyring, *J. Phys. Chem.*, 1978, **82**, 647.

Table 1—*continued*

Reaction	*I*/M	k_f/M^{-1} s^{-1}	k_b/s^{-1}	*Ref.*
Na^+	0	3.1×10^6	2.50	6
Li^++(1b) (221)	0	1.8×10^7	7.5×10	6
Na^+	0	1.7×10^8	2.35	6
K^+	0	3.8×10^8	1.09	6
Rb^+	0	4.1×10^8	7.5×10	6
Cs^+	0	$\sim5.0\times10^8$	$\sim2.3\times10^4$	6
Li^++(1c) (222)	0		$>3.0\times10^2$	6
Na^+	0	2.7×10^8	2.87	6
K^+	0	4.7×10^8	1.8×10^{-2}	6
Rb^++(1c) (222)	0	7.6×10^8	8.0×10^{-1}	6
Cs^++(1c) (222)	0	$\sim9.0\times10^8$	$\sim4.0\times10^4$	6
Ni^{2+} [a]+$[HP_2O_7]^{3-}$	0.1	5.3×10^5	170	10
Ni^{2+} [a] +$[HP_3O_{10}]^{4-}$	0.1	1.4×10^6	55	10
Ni^{2+} [a]+CDP^{3-}	0.1	5.7×10^5	190	10
Ni^{2+} [a]+CTP^{4-}	0.1	1.3×10^6	51	10
Ni^{2+} [a]+ADP^{3-}	0.1	5.2×10^5	170	11
Ni^{2+} [a]+ATP^{4-}	0.1	1.4×10^6	55	11
Ni^{2+} [a]+$NiCDP^-$	0.1	3.2×10^4	800	10
Ni^{2+} [a]+$NiCTP^{2-}$	0.1	1.4×10^5	875	10
Ni^{2+} [a]+$NiADP^-$	0.1	3.2×10^4	800	11
Ni^{2+} [a]+$NiATP^{2-}$	0.1	1.4×10^5	875	11
Ni^{2+}+HLys	0.1	4.2×10^3	4.9×10^{-2}	22
Ni^{2+}+HOrn	0.1	2.2×10^3	4.1×10^{-2}	22
Co^{2+}+HLys	0.1	6.0×10^5	8.8×10^1	22
Co^{2+}+HOrn	0.1	6.5×10^5	1.5×10^2	22
$[Ni(HLys)]^{2+}$+HLys	0.1	4.7×10^3	2.8×10^{-1}	22
$[Ni(HOrn)]^{2+}$+HOrn	0.1	1.0×10^4	9.8×10^{-1}	22
$[Co(HLys)]^{2+}$+HLys	0.1	1.0×10^6	5.8×10^2	22
$[Co(HOrn)]^{2+}$+HOrn	0.1	3.2×10^6	2.6×10^3	22

[a] 15 °C.

for both ligands studied with each metal ion and are consistent with rate-determining water loss at the metal, and the dissociation rates k_{-1} reflect the strain in the two ring systems.

The complexing behaviour of crown ethers towards acetonitrile has been used[5] to enhance the rate of hydrolysis of *trans*-$[Co(en)_2(NO_2)(MeCN)]^{2+}$. Weak pre-association of the crown ether with metal-bound acetonitrile is followed by a rate-determining interchange. The overall second-order rate constant is 8.7×10^{-4} M^{-1} s^{-1} at 20 °C for 18-crown-6 and about half that value for 15-crown-5.

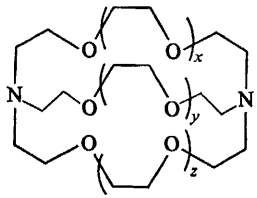
Kinetic behaviour of the alkali-metal ions with cryptands (1) has been investigated[6] by pH jump in methanol.

$$M(1)^+ \underset{k_f}{\overset{k_b}{\rightleftharpoons}} M^+ + (1)$$

$$(1) + H^+ \overset{k_H}{\rightleftharpoons} (1)H^+$$

[5] G. L. Blackmer, M. D. Nordyke, T. M. Vickrey, R. A. Bartsch, and R. A. Holwerda, *Inorg. Chem.*, 1978, **17**, 3310.

[6] B. G. Cox, H. Schneider, and J. Stroka, *J. Am. Chem. Soc.*, 1978, **100**, 4746.



(1) a; $x = 1$, $y = z = 0$ (2, 1, 1)
b; $x = y = 1$, $z = 0$ (2, 2, 1)
c; $x = y = z = 1$ (2, 2, 2)

Dissociation rates k_D were obtained at high acidity where k_H is fast and were corrected for ionic strength using a Debye–Hückel equation. The results show that the cryptate selectivity results mainly from k_D and that the transition state for the reaction has little interaction between the metal and the cryptand to differentiate between metals. Rates k_f increase with increasing cavity size. The thermodynamics of cryptand formation in water and methanol have also been used[7] to calculate the free energy and enthalpy of transfer of the free ions between the two media.

Proton transfer reactions of the cryptands are important in elucidating the conformational changes between *exo*-forms, where the nitrogen lone pairs are pointing into the solution, and *endo*-forms which can bind metal ions and where the nitrogen lone pairs point into the cryptand cavity. Two studies have been reported[8,9] and the rate for the proton transfer,

$$H_2O + (1) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (1)H^+ + OH^-$$

k_{-1}, is three to seven orders of magnitude lower than the corresponding rate for aliphatic amines,[8] suggesting that the site of protonation is within the ligand cavity.

Phosphates and Nucleotides.—Reactions of nickel(II) with inorganic phosphates[10] are consistent with an I_d mechanism with outer-sphere complex formation constants of 34 and 80 M^{-1} for $[HP_2O_7]^{3-}$ and $[HP_3O_{10}]^{4-}$ respectively and an interchange rate of 1.6×10^4 s^{-1} at 15 °C. Kinetic parameters for the corresponding cytidine nucleotide phosphates CDP^{3-} and CTP^{4-} are almost identical but additional steps, the formation of 2:1 metal:ligand complexes, again by an I_d mechanism, are proposed to explain the kinetic behaviour at high reagent concentrations:

$$Ni^{2+} + L^{n-} \rightleftharpoons NiL^{(n-2)-}$$

$$NiL^{(n-2)-} + Ni^{2+} \rightleftharpoons Ni_2L^{(n-4)-}$$

Additional kinetic complications with the adenine derivatives ADP^{3-} and ATP^{4-} can be accounted for[11] by the inclusion of an isomerization step in which

[7] J. Gutknecht, H. Schneider, and J. Stroka, *Inorg. Chem.*, 1978, **17**, 3326.
[8] B. G. Cox, D. Knop, and H. Schneider, *J. Am. Chem. Soc.*, 1978, **100**, 6002.
[9] R. Pizer, *J. Am. Chem. Soc.*, 1978, **100**, 4239.
[10] C. M. Frey and J. E. Stuehr, *J. Am. Chem. Soc.*, 1978, **100**, 134.
[11] C. M. Frey and J. E. Stuehr, *J. Am. Chem. Soc.*, 1978, **100**, 139.

there is an interaction

$$NiL^{(n-2)-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NiL^{(n-2)-*}$$

between the adenine base and the nickel(II) ion. The rate constants k_1 for ADP^{3-} and ATP^{4-} are 4.50×10^2 and 1.0×10^3 s^{-1}, suggesting that the interaction is inner sphere rather than through a water-bridged hydrogen-bonded species. The similarities in the rate constants for 1 : 1 complex formation are consistent with little or no participation from the nucleotide bases but subsequent interactions involve the cytidine and adenine. An interaction of the N-7 nitrogen of ATP^{4-} was also detected in a re-investigation[12] of the magnetic resonance properties of solutions containing manganese(II) and ATP^{4-} at pH 4.0. The role of outer-sphere complex formation is emphasized in a study[13] of the effects of pH and temperature of the exchange of ATP^{4-} and manganese(II). Four solvent molecules are bound[14] to $[Mn(ADP)]^-$ in aqueous solution consistent with two bound phosphate oxygens or one phosphate oxygen and an adenine nitrogen. Complexation of a second molecule of ADP^{3-} gives a complex which may be formulated $[Mn(ADP)_2(H_2O)_3]^{4-}$, suggesting that the second ADP is bound as a result of stacking interactions. Solvent exchange rates for nucleotide phosphate complexes are in the range $5.0—7.6 \times 10^7$ s^{-1} and are not significantly different from the value for $[Mn(H_2O)_6]^{2+}$, which is 2.2×10^7 s^{-1} at 25 °C. It is concluded that phosphate binds to the metal ion by an interaction that is mainly ionic.

Manganese(II) binds weakly ($K < 10^3$ M^{-1}) to a bovine heart protein kinase.[15] On addition of ADP^{3-} and a peptide substrate two enhanced binding sites ($K \approx 1 \times 10^5$ and 2×10^4 M^{-1}) are formed. The stronger binding site, which is catalytically active in peptide phosphorylation, involves an enzyme–ADP–metal complex and is blocked by the inert probe $[Co(NH_3)_4ATP]$. The weaker binding site inhibits phosphorylation and involves protein binding. There are many reports[16–19] of the use of inert metal–ATP complexes to investigate phosphorylation mechanisms and the subject has been reviewed.[20]

Selective hydrolysis of ATP^{4-} to give ADP^{3-} and inorganic phosphate is catalysed[21] by cobalt(III) complexes that have available co-ordination sites. The most effective complexes have three potential co-ordination sites, and a study of the reaction with $[Co(dien)Cl_3]$ reveals a maximum rate when the Co^{III} : ATP ratio is 3 : 2. A co-operative interaction between two complexes is proposed.

Amino-acids and Peptides.—The ω-monoprotonated forms of lysine and ornithine are reactive[22] in the formation of complexes with nickel(II) and cobalt(II).

[12] R. Basosi, N. Niccolai, E. Tiezzi, and G. Valensin, *J. Am. Chem. Soc.*, 1978, **100**, 8047.
[13] E. Gaggelli, F. Laschi, and N. Niccolai, *J. Chem. Soc., Faraday Trans. I*, 1978, **74**, 2154.
[14] M. S. Zetter, G. Y.-S. Lo, H. W. Dodgen, and J. P. Hunt, *J. Am. Chem. Soc.*, 1978, **100**, 4430.
[15] R. N. Armstrong, H. Kondo, J. Granof, E. T. Kaiser, and A. S. Mildvan, *Biochemistry*, 1979, **18**, 1230.
[16] T. M. Li, R. L. Switzer, and A. S. Mildvan, *Arch. Biochem. Biophys.*, 1979, **193**, 1.
[17] T. M. Li, A. S. Mildvan, and R. L. Switzer, *J. Biol. Chem.*, 1978, **253**, 3918.
[18] R. K. Gupta and J. L. Benovic, *J. Biol. Chem.*, 1978, **253**, 8878.
[19] J. Granof, M. M. Werber, and A. Danchin, *Bioinorg. Chem.*, 1978, **9**, 81.
[20] J. I. Legg, *Coord. Chem. Rev.*, 1978, **25**, 103.
[21] S. Suzuki, T. Higashiyama, and A. Nakahara, *Bioinorg. Chem.*, 1978, **8**, 277.
[22] K. Kustin and J. L. McClean, *J. Phys. Chem.*, 1978, **82**, 2549.

Water exchange at the metal ion rather than ring closure, as might be expected with the α-protonated zwitterion, is rate determining, though for nickel(II) the rates are lower than expected owing to screening by the protonated amine. Bis-complex formation is more rapid than mono-complex formation, suggesting that the ligand labilizes the co-ordinated water.

A detailed analysis[23] of the effect of copper(II) on the amine proton exchange rate of glycine is complicated by the high rate of glycine exchange in the bis-glycine complex $[Cu(G)_2]$. This allows the determination of the rates of processes between the diamagnetic and paramagnetic environment and a value of 1.0×10^8 M^{-1} s^{-1} was obtained for the exchange rate constant. Dissociation of glycine from $[Cu(G)_3]^-$ proceeds with a rate constant of 6×10^7 s^{-1} at 25 °C.

Displacement of triclycine (G_3) from $[CuH_{-2}G_3]^-$ by macrocyclic tetra-amine ligands (Table 2), is much slower[24] than the corresponding process with trien.[25] The proposed mechanism involves initial binding at the carboxyl site followed by proton transfer to the adjacent peptide link, thus weakening the copper(II)–peptide bond. The rate with $[CuH_{-2}G_3]^-$ is 4×10^3 higher than the rate with $[Cu(edta)]^{2-}$, which has no proton acceptor site and requires nucleophilic displacement by the macrocycle.

Table 2 *Reactions of copper peptide complexes with nucleophiles at* 25 °C, $I = 0.1$ M

	Reaction	k/M^{-1} s^{-1}	*Ref.*
$[Cu(H_{-2}G_3)]^-$	+ 12-ane$(N_4)H^+$	2.5×10^2	24
	+ 12-ane$(N_4)H_2^{2+}$	2.7×10^2	24
	+ 15-ane$(N_4)H^+$	3.0×10^2	24
	+ 15-ane$(N_4)H_2^{2+}$	1.4×10^2	24
	+ trien	1.1×10^7	25
	+ trienH^+	5.1×10^6	25
	+ trienH_2^{2+}	1.2×10^5	25
$[Cu(H_{-1}Ga)_2]$	+ trien	1.4×10^4	26
	+ trienH^+	5.3×10^3	26
	+ trienH_2^{2+}	5.0×10^2	26
$[Cu(H_{-1}G_3)_2]^{2-}$	+ trien	$< 10^2$	26

Rate constants for the nucleophilic attack by trien on copper(II)–peptide complexes follow the order $[Cu(H_{-2}G_3)]^- \gg [Cu(H_{-1}Ga)_2] \gg [Cu(H_{-1}G_3)_2]^{2-}$, where Ga is glycinamide.[26] The rate for the bis-triglycine complex is anomalous in that the others follow the expected order paralleling the decrease in ligand-field stabilization of the complexes and it is proposed that axial co-ordination of the triglycine carboxylate groups prevents nucleophilic attack. Rearrangement of the complex to $[Cu(H_{-1}G_3)(G_3)]^-$ which contains only one deprotonated peptide nitrogen is a prerequisite to reaction.

Dissociation of triglycine from palladium(II) proceeds[27] by an initial rapid breaking of the carboxyl–palladium bond followed by sequential protonation and cleavage of the metal–peptide linkages at rates of 23.4 and 2.7 s^{-1} at 25 °C.

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Loss of the terminal amine is very slow and is catalysed by chloride ion, and a value of 6.68×10^{-3} s^{-1} was obtained in 0.4 M Cl^-.

Tervalent copper[28] and nickel[29] are involved in the autoxidation reactions of $[Cu(H_{-3}G_4)]^{2-}$ and $[Ni(H_{-3}G_4)]^{2-}$ respectively. In the case of nickel, decomposition of $[Ni(H_{-3}G_4)]^-$ proceeds by decarboxylation of the terminal carboxy-group adjacent to the peptide nitrogen.[29,30] With copper,[28] decomposition of $[Cu(H_{-3}G_4)]^-$ proceeds through a carbon-centred free radical produced by abstraction of a hydrogen atom from the peptide backbone. Bulky carbon substituents assist the stabilization of the higher-oxidation state ions, and a study of the stabilities of leucyl tripeptide complexes with copper(II) and nickel(II) has been reported.[31] Copper(III) and nickel(III) tripeptide complexes of α-aminoisobutyric acid are thermally stable but are readily decomposed by photochemical pathways.[32] Resonance Raman and other studies with copper(III) peptide complexes have also been reported.[33–37]

3 Redox Reactions in Biological Systems

Cytochromes.—A review article on the properties and reactions of cytochromes of the higher plants and algae has been published.[38]

Cytochrome c. Redox reactions of cytochrome *c* with inorganic and organic reagents and with other metalloproteins continue to provide a source of interest. The reactions between cytochrome *c*(II) and a number of copper(II) complexes of 1,10-phenanthroline and its derivatives show simple second-order kinetics[39,40] and the derived rate constants are given in Table 3. Reaction rates show only a small dependence on pH, consistent with haem edge outer-sphere electron transfer, and thermodynamic parameters reflect reaction between two similarly charged species. A structural barrier to electron transfer in the copper complexes prevents meaningful application of Marcus theory but a comparison of the results with cyt *c*(II) and $[Co(phen)_3]^{2+}$ as reductants suggests that the former protein shows similar electron-transfer behaviour to low molecular weight complexes.

Changes in solvation caused by specific ion binding at some distance from the haem edge are proposed[41] to explain the effect of changing the ionic medium on the oxidation of horse heart cytochrome *c*(II) by $[Fe(CN)_6]^{3-}$ at pH 7.0. Binding constants vary from 3 M^{-1} for phosphate to 7 M^{-1} and 18 M^{-1} for chloride and

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Table 3 *Rate constants and thermodynamic parameters for electron-transfer reactions of proteins in aqueous solution at 25 °C*

Reaction	pH	*I*/M	k/M^{-1} s^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	*Ref.*
Cyt *c*(II)[a] + $[Cu(dmp)_2]^{2+}$	6.1	0.1	1.00×10^{6}	3.8	−18.4	39
$[Cu(phen)_2]^{2+}$	6.1	0.1	2.72×10^{1}	13.9	−7.9	39
$[Cu(phen)]^{2+}$	6.1	0.1	4			39
$[Cu(phen)_3]^{2+}$	6.1	0.1	0.20			39
$[Cu(5\text{-}NO_2phen)_2]^{2+}$	6.1	0.1	1.57×10^{2}	11.0	−11.9	39
$[Fe(CN)_6]^{3-}$	7.0	0.1	7.10×10^{6}			41
$[Fe(CN)_6]^{3-}$	7.0[b]	0.2	3.10×10^{6}			41
$[Fe(CN)_6]^{3-}$	7.0	0.1	2.30×10^{7}			55
$[Co(phen)_3]^{3+}$	7.0	0.1	1.50×10^{3}	11.3	−6.2	55
TFA cyt*c*(II)[a] + $[Fe(CN)_6]^{3-}$	7.0	0.1	1.20×10^{6}			55
$[Co(phen)_3]^{3+}$	7.0	0.1	1.67×10^{4}	10.5	−3.9	55
Cyt *c*(III)[c] + ^{Co}Cyt *c*(II)	7.0	0.1	8.30×10^{3}	2.3	−33	42
$[Fe(edta)]^{-}$	7.0	0.1	4.60×10^{1}	4.2	−36	42
$S_2O_4^{2-}$	8.0	0.1	1.50×10^{4}	0.8	−31	45
SO_2^{-}	8.0	0.1	3.90×10^{7}	0.0	−23	45
ascorbate^{2-}	—	0.1	1.00×10^{4}			47
Cyt *c*(III)[a] + ascorbate^{2-}	—	0.1	3.10×10^{5}			47
ascorbic acid	8.0	0.1	450			48
ascorbic acid	7.2	0.1	64			48
glutathione [d]	7.5	1.0	3.48			52
glutathione [d]	7.5	1.0	10.6			52
cyt c_{553}	7.0	0.1	3.96×10^{4}	−0.6	−7	54
$[Fe(edta)]^{-}$	9.0	0.1	2.05×10^{4}			55
TFA cyt *c*(III)[a] + $Fe(edta)^{-}$	7.0	0.1	5.10×10^{3}	3.9	−28	55
^{Co}Cyt *c*(III)[c] + PM	7.0	0.1	2.90×10^{4}	6.3	−18	42
$S_2O_4^{2-}$	8.0	0.1	2.60	7.2	−31	45
SO_2^{-}	8.0	0.1	5.60×10^{3}	6.0	−22	45
Cyt c_{551}(III)[e] + ascorbate^{2-}	—	0.1	2.90×10^{4}			47
Mb(III)Im + SO_2^{-}	8.2	0.5	8.80×10^{7}			79
$Mb(III)Im^{-}$ + SO_2^{-}	8.2	0.5	1.50×10^{6}			79

Table 3—*continued*

Reaction	pH	*I*/M	k/M^{-1} s^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	*Ref.*
Mb(III)(1-MeIm)+SO_2^-	8.2	0.5	2.0×10^8			79
Mb(III)(2-MeIm)+SO_2^-	8.2	0.5	2.0×10^6			79
Mb(III)(4-NO_2Im)+SO_2^-	8.2	0.5	8.0×10^6			79
Mb(III) (2-Me-5-NO_2Im)+SO_2^-	8.2	0.5	8.8×10^6			79
Mb(III)py +SO_2^-	8.2	0.5	2.9×10^8			79
Mb(III)2-pic+SO_2^-	8.2	0.5	3.1×10^7			79
Mb(III)3-pic+SO_2^-	8.2	0.5	2.6×10^8			79
Mb(III)4-pic+SO_2^-	8.2	0.5	2.8×10^8			79
Mb(III)H_2O+SO_2^-	8.2	0.5	4.5×10^6			79
Mb(III)H_2O+$S_2O_4^{2-}$	—	0.5	52			80
Mb(III)H_2O+SO_2^-	—	0.5	1.1×10^6			80
Hb(III)+[Fe(edta)]$^{2-}$	7.0	0.2	29	5.5	−33	81
Hb(III)+[Fe(cydta)]$^{2-}$	—	0.2	0.3			82
Hb(III)H^++[Fe(cydta)]$^{2-}$	—	0.2	18.4			82
Hb(II)$^{\alpha}$+[Fe(cydta)]$^{2-}$	—	0.2	0.56			82
Hb(III)$^{\alpha}H^+$+[Fe(cydta)]$^{2-}$	—	0.2	9.7			82
Hb(III)$^{\beta}$+[Fe(cydta)]$^{2-}$	—	0.2	0.55			82
Hb(III)$^{\beta}H^+$+[Fe(cydta)]$^{2-}$	—	0.2	19.4			82
Hb(III)+ascorbate	7.0	0.1	3.05×10^{-2}			84
Hb(III)$^{\beta}$+ascorbate	7.0	0.1	1.94×10^{-2}			84
Hr(III)(III)^{f}+SO_2^-	8.2	0.2	4.70×10^5			99
Hr(III)(III)^{g}+SO_2^-	8.2	0.2	1.30×10^5			99
Hr(III)(III)^{h}+SO_2^-	8.2	0.2	1.10×10^6			99
Hr(III)(III)^{f}+Mb(II)	6.3	0.2	5.60			100
Hr(III)(III)^{g}+Mb(II)	6.3	0.2	0.25			100
Hr(III)(III)^{h}+Mb(II)	6.3	0.2	2.00			100
Hr(III)(III)^{g}+Mb(II)O_2	6.3	0.2	0.06			100
Fd(III)(II)^{i}+[Co(NH_3)$_6$]$^{3+}$	8.0	0.1	1.90×10^4	18.7	23.8	102
Fd(III)(II)^{j}+[Co(NH_3)$_6$]$^{3+}$	8.0	0.1	1.60×10^4			102
Fd(III)(II)^{k}+[Co(en)$_3$]$^{3+}$	8.0	0.1	1.60×10^3	21.0	26.4	102
Fd(III)(II)^{i}+[Co(NH_3)$_5$Cl]$^{2+}$	8.0	0.1	4.10×10^5	8.4	−4.6	102

Fd(III)(II)^{k} + $[Co(NH_3)_5(C_2O_4)]^+$	8.0	0.1	5.70×10^3	8.0	−14.6	102
Fd(III)(II)^{k} + $[Co(dmg)(PhNH_2)_2]^+$	8.0	0.1	7.40×10^5	6.7	−9.2	102
Fd(III)(II)^{k} + $[Co(edta)]^-$	8.0	0.1	7.20×10^3	5.2	−23.4	102
ACu(II)^{e} + ascorbate^{2-}	—	0.1	1.00×10^4			47
ACu(II)^{e} + cyt c_{553}	7.0	0.1	1.43×10^7			54
ACu(II)^{l} + cyt c_{553}	7.0	0.1	5.23×10^5	−1.6	−15	54
ACu(II)^{e} + cyt c_{553}	7.0	0.1	2.11×10^6	−1.9	−12	54
ACu(II)^{e} + cyt c_{551}	7.0	0.1	2.90×10^6	−0.5	−3	54
ACu(II)^{e} + $[Fe(CN)_6]^{4-}$	7.0	0.1	65.70			125
ACu(II)^{e} + $[Fe(CN)_6]^{4-}$	5.0	0.1	1.80×10^3			125
ACu(I)^{e} + $[Co(phen)_3]^{3+}$	9.0	0.1	1.11×10^4			125
ACu(I)^{e} + $[Co(phen)_3]^{3+}$	6.0	0.1	2.43×10^3			125
ACu(I)^{e} + $[Co(DPSphen)_3]^{3-}$	7.5	0.1				125
ACu(I)^{e} + $[Fe(CN)_6]^{3-}$	6.0	0.1	1.82×10^4			125
ACu(I)^{e} + $[Fe(CN)_6]^{3-}$	9.0	0.1	4.90×10^3			125
PCu(II)^{m} + cyt c_{553}	7.0	0.1	4.00×10^5	−1.5	−4	54
PCu(II)^{n} + cyt c_{553}	7.0	0.1	7.36×10^5	−1.7	−5	54
PCu(II)^{i} + $[Fe(CN)_6]^{4-}$	7.5	0.1	1.90×10^4	6.3	−17.5	122
PCu(II)^{i} + $[Ru(NH_3)_5py]$	7.5	0.1	1.10×10^6	9.7	1.6	122
PCu(I)^{i} + $[Co(phen)_3]^{3+}$	7.5	0.1	3.0×10^3	14.3	6.0	122
PCu(I)^{i} + $[Fe(CN)_6]^{3-}$	7.5	0.1	9.40×10^4	−3.3	−47	122
PCu(I)^{i} + $[Co(DPSphen)_3]^{3-}$	7.5	0.1	1.90×10^2	9.0	−18	123
$StCu^{I}$ + $[Co(edta)]^-$	10.0	0.5	8.90	11.3	−16	126
+ $[Co(pdta)]^-$	7.0	0.5	17.90	8.5	−24	127
+ $[Co(cydta)]^-$	7.0	0.5	17.00	8.7	−24	127
Cyt *c* peroxidase^{e} + cyt c_{551}(II)^{e}	6.0	0.01	1.34×10^4			145
Cyt *c* peroxidase^{e} + cyt c_{555}(II)	6.0	0.01	9.60×10^3			145
Cyt *c* peroxidase^{e} + cyt c_{550}(II)	6.0	0.01	1.13×10^4			145
Cyt *c* peroxidase^{e} + ACu^{I}	6.0	0.01	1.26×10^4			145
Cyt *c* peroxidase^{e} + cyt c_{551}(II)$^{-o}$	6.0	0.01	1.29×10^4			145
Cyt *c* peroxidase^{e} + cyt *c*(II)^{a}	6.0	0.01	6.20×10^3			145
LCu(II) + H_2Q	7.0	0.5	4.5×10^2			161
LCu(II) + H_2Q-Me	7.0	0.5	4.49×10^2			161
LCu(II) + H_2Q-Bu^{t}	7.0	0.5	1.54×10^2			161

Table 3—*continued*

Reaction	pH	*I*/M	k/M^{-1} s^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	*Ref.*
LCu(II) + H_2Q-OH	7.0	0.5	2.7×10^4			161
LCu(II) + H_2Q-Cl	7.0	0.5	4.3×10^3			161
LCu(II) + H_2Q-CO_2^-	7.0	0.5	2.2×10^0			161
LCu(II) + H_2Q-SO_3^-	7.0	0.5	4.02×10^1			161

[a] Horse heart. [b] pD = 7.4 in D_2O. [c] Bovine heart. [d] Two conformers. [e] *Pseudomonas aeruginosa*. [f] *Themiste pyroides*. [g] *Phasocolopsis gouldii*. [h] *Themiste pyroides* monomer. [i] Parlsey. [j] Spinach. [k] *Alcaligenes faecalis*. [l] *Alcaligenes* spp. [m] Bean. [n] *Scenecdemus*. [o] *Pseudomonas fluorescens*.

potassium ion ($I=0.2$ M, 24 °C), whereas for picrate there is evidence for a stronger hydrophobic interaction (500 M^{-1} at $I=0.05$ M, 24 °C), close to the haem edge at phenylalanine-82, and for binding of a second picrate ion.

Non-adiabatic multiphonon electron tunnelling theory[42] has been used to interpret kinetic data on a number of redox reactions of cytochrome *c* and yields a self-exchange rate constant for the protein of 1.7×10^4 M^{-1} s^{-1} ($\Delta H^* = 4.9$ kcal mol^{-1}; $\Delta S^* = -23$ cal K^{-1} mol^{-1}) in good agreement with experimental values at high ionic strength of 1×10^4 M^{-1} s^{-1} ($\Delta H^* = 7.0$ kcal mol^{-1}; $\Delta S^* = -18$ cal K^{-1} mol^{-1}). Whereas Marcus theory based on a variety of cross reactions gives no consistent self-exchange rate constant for cytochrome *c*, the electron tunnelling theory can be used to calculate cross-reaction rate constants to within a factor of two for most reactions studied. Reduction of cyt *c*(III) by its cobalt(II)-substituted derivative ^{Co}cyt *c*(II) proceeds at a second-order rate of 8.3×10^3 M^{-1} s^{-1} at 25 °C over the pH range 4.5—10.[43] The calculated rate constant of 9.6×10^3 M^{-1} s^{-1} is in good agreement with experiment and gives some credence to the calculated self-exchange rate constant for ^{Co}cyt *c* of 5.1×10^{-3} M^{-1} s^{-1}. This must be compared with the Marcus value (1.6×10^{-4} M^{-1} s^{-1}) but unfortunately no definitive experimental value exists ($< 1.33 \times 10^2$ M^{-1} s^{-1}) to distinguish between the adiabatic and non-adiabatic tunnelling mechanisms.

The rate-determining step in the reduction of methaemoglobin by ^{Co}cyt *c*(II), catalysed by phenazine monosulphite (PM) is the reduction of the mediator with $k_1 = 2.9 \times 10^4$ M^{-1} s^{-1} at 25 °C ($I=0.1$ M, pH 7.0):

$$^{Co}\text{cyt } c(\text{II}) + \text{PM} \overset{k_1}{\rightleftharpoons} {}^{Co}\text{cyt } c(\text{III}) + \text{PM}^0$$

$$\text{Hb(III)} + \text{PM}^0 \rightleftharpoons \text{Hb(II)} + \text{PM}$$

Rates for a series of mediators increase with decreasing reduction potential of the mediator until it is less than the potential of the Hb(III)/(II) couple.

Reduction of ^{Co}cyt *c*(III) by dithionite is biphasic,[45] consisting of a rapid reaction of SO_2^- and a slower phase due to $S_2O_4^{2-}$. Both reactions show a maximum rate at pH 9.3, indicating that the form of ^{Co}cyt *c*(III) with lysine-79 co-ordinated axially to the metal ion is more reactive than with methionine-80 co-ordinated. The reactions are outer-sphere, and good agreement in rate constants and thermodynamic parameters is found with values calculated using non-adiabatic tunnelling theory. Comparison of the results for ^{Co}cyt *c*(III) and cyt *c*(III) suggest that the lower reactivity of the former reagent is due in part to stronger vibronic-coupling parameters for redox reactions.

A model based on electron tunnelling from radicals produced by hydrogen abstraction on the surface of the protein to the haem centre has been used[46] to explain absorbance changes in the reactions of cyt *c*(III) with H· and OH· radicals. Although alternative mechanisms such as electron hop cannot be ruled out the tunnelling model gives a fairly good explanation of the indirect reduction and a frequency factor for the tunnelling process of $10^{11.5}$ s^{-1} was derived.

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Strong pH dependencies of the rates of reduction of a number of cytochromes *c* and the blue copper protein azurin by ascorbic acid are interpreted[47] in terms of reaction of the ascorbate anion rather than highly reactive deprotonated forms of the proteins since it is unlikely that all the proteins would act in a similar fashion. The second-order rate constants for the ascorbate^{2-} anion increase with increasing positive charge on the protein consistent with an outer-sphere mechanism. This is confirmed by cyt *c*(III) where the rate of reduction by ascorbate exceeds the limiting rate of substitution of methionine-80 by imidazole at pH 9.0 ($I=0.1$ M, 21 °C), 8 s^{-1}. Activation parameters are similar to those of other outer-sphere reactions between proteins and small-molecule redox agents.

Liposomes reduce the rate of reduction of cytochrome *c* by ascorbate at low ionic strength (<0.01 M) by two orders of magnitude compared with the reaction in the absence of liposomes or at high ionic strength where electrostatic interactions disrupt the lipid vesicles.[48] On the other hand, with 2-amino-4-hydroxy-6,7-dimethyl-5,6,7,8-tetrahydropteridine, $DMPH_4$, which is neutral at pH 7, the rate is increased by the liposome binding. Monophasic kinetics are observed throughout consistent with a rapid equilibrium between bound and free cytochrome *c*, and a value for the binding constant of 2.1×10^5 M^{-1} was derived. The unusual behaviour with $DMPH_4$ suggests that cytochrome *c* undergoes a conformational change on binding which makes the haem edge more accessible.

Stopped-flow circular dichroism studies[49] of the reduction of cyt *c*(III) by dithionite (5×10^{-3} M) at pH 10 reveal a rapid decay ($k=200$ s^{-1}) in the c.d. signal at 402 nm with synchronous formation of a transient at 413 nm. Subsequent decay of the transient to the cyt *c*(II) spectrum proceeds with a rate constant of 17 s^{-1} at 28 °C. The results are interpreted in terms of reduction of lysine-79-bonded cyt *c*(III) to the transient followed by ligand exchange to give the methionine-80-bonded cyt *c*(II), which is stable at this pH. Reduction of cyt *c*(III) by ferroprotoporphyrin[50] at pH 7.0 shows similar behaviour with a transient c.d. signal at 417 nm representing conformationally unstable cyt *c*(II) which decays with a rate constant of 7.1 s^{-1} at 28 °C. No characteristic intermediate is detected in the reverse reaction and it is suggested that this 'microscopic irreversibility' may be important for the transfer of electrons in one direction by biological molecules.

Biphasic kinetic behaviour in the reduction of cyt *c*(III) by glutathione, which has the potential to recognize different protein forms, suggests[51,52] the existence of two cyt *c*(III) conformers which may be interconverted by protonation ($pK_a \approx 7$) followed by a slow conformational change. Transient glutathione–cyt *c*(III) complexes were detected at the 339 nm isosbestic and the retention of the 695 nm absorption indicates that the site of complexation is not close to the haem iron. Decay of the transient at 339 nm is consistent with slow disulphide formation.

[47] A. L. Al Ayash and M. T. Wilson, *Biochem. J.*, 1979, **177**, 641.
[48] J. B. Cannon and T. E. Erman, *Biochem. Biophys. Res. Commun.*, 1978, **84**, 254.
[49] I. Tabushi, K. Yamamura, and T. Nishiya, *Tetrahedron Lett.*, 1978, 4921.
[50] I. Tabushi, K. Yamamura, and T. Nishiya, *J. Am. Chem. Soc.*, 1979, **101**, 2785.
[51] N. Kujundzic and J. Everse, *Biochem. Biophys. Res. Commun.*, 1978, **82**, 1211.
[52] J. Everse and N. Kujundzic, *Biochemistry*, 1978, **18**, 2668.

Reduction[53] of cyt *c*(III) by O_2^- is not catalysed by copper ions at pH < 8. The reaction of copper(I)–formate complexes (0.1 M [formate]) with cyt *c*(III) at pH 6.7 is too slow (1.5×10^3 M^{-1} s^{-1}) to allow copper to compete with cyt *c*(III) for O_2^-.

Marcus theory has been used to interpret the reactions of cytochromes *c* and blue copper proteins.[54] For thirteen protein–protein electron-transfer reactions, the data can be fitted with the self-exchange rate constants of 2.8×10^8 M^{-1} s^{-1} for cyt c_{553}, 4.6×10^7 M^{-1} s^{-1} for cyt c_{551}, and 1.5×10^2 M^{-1} s^{-1} for cyt *c* at 25 °C and pH 7 ($I = 0.1$ M). These results indicate little if any selectivity between the redox partners (and that the same mechanism is operating no matter what the redox partner, in contrast to studies with small molecule reagents). The large difference in exchange rate between cyt *c* and the other two proteins may be due to a less open haem crevice and the high positive charge of the former reagent. The use of cyt *c* derivatives in which all 19 lysine residues are bound as their trifluoroacetate (TFA) adducts allows a test of the coulombic contributions to relative Marcus theory.[55] Activation parameters for reduction of TFA cyt *c*(III) by $[Fe(edta)]^{2-}$ ($\Delta H^* = 3.9$ kcal mol^{-1}; $\Delta S^* = -28$ cal K^{-1} mol^{-1} at 25 °C, pH 7.0, and $I = 0.1$ M) are similar to those for the native protein with the lysines deprotonated at pH 9.0 ($\Delta H^* = 4.8$ kcal mol^{-1}; $\Delta S^* = -24$ cal K^{-1} mol^{-1} at 25 °C, $I = 0.1$ M). The Franck–Condon barrier in the reduced cytochrome is likewise little affected since rate and activation parameters for reaction with the positively charged $[Co(phen)_3]^{3+}$ are similar for the native protein and its TFA adduct. Correction for the electrostatic interactions gave the same reactivity pattern, $[Co(phen)_3]^{3+}$, $[Fe(CN)_6]^{3-} > [Fe(edta)]^{2-}$, for the TFA cyt *c* self-exchange rate constant as for the native protein, confirming that this rate is dependent on non-adiabaticity and non-electrostatic work terms and is independent of electrostatic interaction.

Preparation[56,57] of a number of cyt *c*(II) derivatives in which a single lysine is bound to 4-chloro-3,5-dinitrobenzoate has enabled[58] the mapping of the binding domain of cyt *c* oxidase. At pH 7.8, oxygen uptake studies suggest two adjacent cyt *c*(II) binding sites on the oxidase, one in which the redox turnover is faster than dissociation and a second which would allow cyt *c* to serve as an electron shuttle between oxidase assemblies. The effect of the lysine derivatives on the kinetics pinpoints the domain of interaction on cyt *c*(II) as centred at a hydrophobic surface, residues 81—83, adjacent to lysines-13 and -72 with lysines-87, -8, and -27, which have a smaller effect, on the periphery. This domain includes the upper half of the exposed haem edge, the probable site of electron transfer. Similar results have been found with methylated lysine derivatives.[59] Further studies reveal that the effect of the lysine derivatives is apparent not only in limiting protein–protein binding interactions but also, through sterically induced

[53] Y. Ilan, Y. A. Ilan, and G. Czapski, *Biochim. Biophys. Acta*, 1978, **503**, 399.
[54] S. Wherland and I. Pecht, *Biochemistry*, 1978, **17**, 2585.
[55] R. A. Holwerda, R. A. Read, R. A. Scott, S. Wherland, H. B. Gray, and F. Millett, *J. Am. Chem. Soc.*, 1978, **100**, 5028.
[56] D. L. Brautigan, S. Ferguson-Miller, and E. Margoliash, *J. Biol. Chem.*, 1978, **253**, 130.
[57] D. L. Brautigan, S. Ferguson-Miller, G. E. Tarr, and E. Margoliash, *J. Biol. Chem.*, 1978, **253**, 140.
[58] S. Ferguson-Miller, D. L. Brautigan, and E. Margoliash, *J. Biol. Chem.*, 1978, **253**, 149.
[59] R. Rieder and H. R. Bosshard, *J. Biol. Chem.*, 1978, **253**, 6045.

changes in alignment, in the rates of electron transfer.[60] The haem crevice is also implicated in the binding domains of cytochrome *c* peroxidase[61] and succinate–cytochrome *c* reductase.[62, 63] In the latter study,[63] since the rate of dissociation of the cyt *c*–cyt *c* oxidase complex is lower than the rate of electron transfer in mitochondria, a cyt *c* oxidase–cyt *c* reductase complex is proposed with a continuous binding site for the haem edge domain of cyt *c*. Lysine derivatives have also been used with a molybdenum dimer reductant.[64]

Reactions of a number of cytochromes *c* with cytochrome *c* oxidase have been examined[65] to establish a common mechanism and allow comparisons of reactivities. The mechanism, involving two cytochrome *c* binding sites on the oxidase with electron transfer between cyt *c* and an oxidase molecule that is already complexed with one molecule of cyt *c*, is the simplest of several possibilities. Comparisons of rate data pinpoint protein–protein binding as the dominant parameter in reactivity and that charge location rather than net charge controls binding.

The surface charge distribution in tuna ferricytochrome *c* has been used[66] to calculate the electric potential field outside the molecule at pH 7.5. Small, negatively charged molecules are attracted to the protein and on following the field lines have a greater probability of finding the haem edge. The importance of the cytochrome *c* dipole with its positive end near alanine-83 in aligning the haem edge of the protein with cyt *c* oxidase is also of note since the centre of the binding domain is the phenylalanine-82 residue.

Studies of the complex acid-denaturing kinetics of cytochrome *c* reveal[67, 68] that the reduced forms are substantially more stable towards unfolding than the oxidized forms. This is related to the strength of the iron–methionine bond. It is unlikely that protein unfolding has a physiological role in electron transfer.[67] Differences in the fragment exchange behaviour of cyt *c*(II) and cyt *c*(III) suggest that the dynamic conformation of the protein changes markedly on oxidation or reduction.[69] The activation parameters for the unfolding process, $\Delta H^{\ddagger} = 44$ kcal mol^{-1}, $\Delta S^{\ddagger} = 65$ cal K^{-1} mol^{-1} at 25 °C, indicate a balance between an entropic term favouring the unfolded form and an enthalpic term favouring the folded state.

Cytochrome c_3. Reductions of cytochrome c_3 from *Desulfovibrio vulgaris*, which contains four haem *c* molecules with axially bound histidine residues, covalently attached to a single peptide chain, have been reported.[70] Reactions with CO_2^-

[60] S. Ferguson-Miller, D. L. Brautigan, B. Chance, A. Waring, and E. Margoliash, *Biochemistry*, 1979, **17**, 2246.
[61] C. H. Kang, D. L. Brautigan, N. Osheroff, and E. Margoliash, *J. Biol. Chem.*, 1978, **253**, 6502.
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[63] A. J. Ahmed, H. T. Smith, M. B. Smith, and F. S. Millett, *Biochemistry*, 1978, **17**, 2479.
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[66] W. H. Koppenol, C. A. J. Vroonland, and R. Braams, *Biochim. Biophys. Acta*, 1978, **503**, 499.
[67] H. R. Drew and R. E. Dickinson, *J. Biol. Chem.*, 1978, **253**, 8420.
[68] G. McLendon and M. Smith, *J. Biol. Chem.*, 1978, **253**, 4004.
[69] R. R. Hautgan and H. Tanivchi, *J. Biol. Chem.*, 1978, **253**, 5373.
[70] V. Favandon, C. Ferradini, J. Pucheault, L. Gilles, and J. LeGall, *Biochem. Biophys. Res. Commun.*, 1978, **84**, 435.

radical and dithionite, where the active species is SO_2^-, are biphasic, suggesting the presence of two pairs of equivalent haem residues and that intramolecular electron exchange between the pairs is slow ($< 2\ s^{-1}$). On the other hand n.m.r. results with the partially reduced cytochrome indicate relatively fast electron exchange which must take place by an intermolecular mechanism. All four haem centres are kinetically equivalent on reduction by the solvated electron.

Cytochrome f. Superoxide reduces *Raphanus sativus* cytochrome *f* with a second-order rate constant of $6 \times 10^6\ M^{-1}\ s^{-1}$ at pH 7.8 and 28 °C, which is an order of magnitude higher than the rate of the corresponding reaction with cytochrome *c*.[71] Autoreduction of cytochrome *f* has a pH-dependent first-order rate of $2 \times 10^{-3}\ s^{-1}$ at 30 °C (pH 7.8), which suggests that the electron donor is the protein itself. Inhibition by *p*-chloromercuriobenzoate is consistent with a sulphydryl donor which is more reactive in its deprotonated form.

Cytochrome o. Cytochrome *o* from *Vitreoscilla* has a dimeric structure with monomeric units consisting of two identical peptide chains, each with a single haem. Carbon monoxide binds only to the reduced form in a co-operative manner whereas CN^- binds both oxidized and reduced forms and shows no co-operativity.[72, 73] Co-operativity between the subunits has also been detected in dithionite reduction[74] and various intermediates in the aerial oxidation process have been detected.[75]

Cytochrome P-450 Low temperatures have been used to examine[76] the sequence of oxygen reduction and hydroxylation in bacterial cyt P-450. Anaerobic reduction of cyt P-450, with camphor (RH) as substrate, by putidaredoxin (put) proceeds through an intermediate complex which is formed with a second-order rate constant of $3.5 \times 10^5\ M^{-1}\ s^{-1}$ extrapolated to 25 °C (0.1 M phosphate, pH 7.0) and assuming that the ratio of forward to back electron-transfer rate constants, k_2/k_{-2}, is 0.4:

$$\text{put} + \text{cyt P-450(III)RH} \underset{}{\overset{k_1}{\rightleftharpoons}} \text{put–cyt P-450(III)RH} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{put}^{\cdot}\text{–cyt P-450(II) RH}$$

$$\Downarrow$$

$$\text{put}^{\cdot} + \text{cyt P-450(II)RH}$$

Oxygenation of the reduced cyt P-450(II)RH complex allows a second electron transfer from put which triggers camphor hydroxylation.

Reduction of cyt P-450(III) by pyridinyl radicals is faster without camphor as substrate than with,[77] despite an increase in the reduction potential from -340 mV to -170 mV. This trend suggests that redox is dependent on the accessibility of the haem pocket to the radical. The order is reversed with 1-methyl-3-carbamidopyridinium radical, which is thought to react by a different mechanism.

[71] K. Tanaka, M.-A. Takahashi, and K. Asada, *J. Biol. Chem.*, 1978, **253**, 7397.
[72] B. Tyree and D. A. Webster, *J. Biol. Chem.*, 1978, **253**, 6988.
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[74] B. Tyree and D. A. Webster, *J. Biol. Chem.*, 1978, **253**, 7635.
[75] B. Tyree and D. A. Webster, *J. Biol. Chem.*, 1979, **254**, 176.
[76] G. H. B. Hoa, G. Begard, P. Debye, and I. C. Gunsalus, *Biochemistry*, 1978, **17**, 2835.
[77] P. Debye, E. J. Land, R. Santus, and A. J. Swallow, *Biochem. Biophys. Res. Commun.*, 1979, **86**, 953.

Myoglobin and Haemoglobin.—The observation[78] that the rate of reduction of a horse heart metmyoglobin Mb(III) imidazole adduct by dithionite exceeds the rate of ligand dissociation from the iron centre has prompted a study[79] with Mb(III) imidazole and pyridine derivatives (see Table 3). The general mechanism,

$$\text{Mb(III)L} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Mb(III)(OH}_2\text{)} + \text{L}$$

$$\text{Mb(III)(OH}_2\text{)} + \text{SO}_2^- \xrightarrow{k_2} \text{Mb(II)(OH}_2\text{)}$$

$$\text{Mb(III)L} + \text{SO}_2^- \xrightarrow{k_3} \text{Mb(II)(OH}_2\text{)} + \text{L}$$

with the k_2 term dominant, suggests electron transfer through the ligand, L, and with imidazole derivatives the relative order of the rates k_3, 1-Me-Im > Im ≫ 2-Me-Im, correlates with the rate of deuterium exchange, consistent with nucleophilic attack by SO_2^- on the ligand. Rates of reduction of the pyridine derivatives exceed the rate, $k_2 = 4.5 \times 10^6$ M^{-1} s^{-1} at 25 °C, for reduction of the product of ligand dissociation.

Reduction of sperm whale myoglobin involves[80] reactions of both SO_2^- and $S_2O_4^{2-}$ with second-order rate constants 1.1×10^6 M^{-1} s^{-1} and 52 M^{-1} s^{-1} at 25 °C, $I = 0.50$ M. The pH dependence of the reaction indicates that ionization of the iron-co-ordinated water molecule inactivates the protein to reduction. Whereas reaction with SO_2^- is faster than the rate of anation and must be outer-sphere, either inner-sphere or outer-sphere mechanisms are possible with $S_2O_4^{2-}$. However, since H_2O is lost as an iron ligand on reduction, an outer-sphere process in which the Fe—O bond is stretched is proposed. Reduction of cyanometmyoglobin, Mb(III)CN, with dithionite is biphasic with initial rapid electron transfer followed by cyanide dissociation from deoxy-Mb(II) with a rate constant of 0.23 s^{-1}.

The hydrophilic reductant $[Fe(edta)]^{2-}$ is a useful reagent for determining[81] the accessibility of the active sites of Mb(III) and methaemoglobin, Hb(III). Relative Marcus analysis reveals greater reactivity of Mb over Hb and comparison of protein self-exchange rate constants obtained with $[Fe(edta)]^{2-}$ and $[Fe(cydta)]^{2-}$ suggests steric inhibition with the latter reagent. The $[Fe(cydta)]^{2-/-}$ couple has been used[82] to compare the redox activities of Hb and two derivatives Hb^{α} and Hb^{β} which have respectively the metal centres in the α -and β-chains in the reduced form. The protein reductions can be described by the mechanism

$$\text{Hb(III)H}^+ \rightleftharpoons \text{Hb(III)} + \text{H}^+ \quad \text{p}K_a\ 7\text{—}8$$

$$\text{Hb(III)H}^+ + [\text{Fe(cydta)}]^{2-} \xrightarrow{k_1}$$

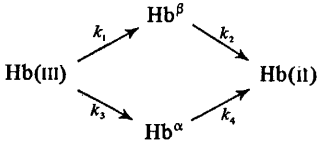
$$\text{Hb(III)} + [\text{Fe(cydta)}]^{2-} \xrightarrow{k_2}$$

involving ionization of the haem co-ordinated water molecule, and the protonated *T*-form is more reactive than the deprotonated *R*-form because it resembles

[78] E. Olivar, D. J. A. de Waal, and R. G. Wilkins, *J. Biol. Chem.*, 1977, **252**, 4038.
[79] D. R. Eaton and R. G. Wilkins, *J. Biol. Chem.*, 1978, **253**, 908.
[80] M. Itzkowitz and A. Haim, *Bioinorg. Chem.*, 1978, **9**, 323.
[81] A. G. Mauk and H. B. Gray, *Biochem. Biophys. Res. Commun.*, 1979, **86**, 206.
[82] T. Yamada, C. P. Marini, and J. C. Cassatt, *Biochemistry*, 1978, **17**, 231.

deoxy-Hb. A similar scheme is proposed for the protein oxidation reactions. Reduction of Hb(III) proceeds *via* initial attack on the β-chain followed by the α-, possibly with fast conformational acceleration.

An intermediate Hb^{β} is detected in the reduction of met-Hb(III) by ascorbate at pH 7.0 (Scheme 1).[83] The detailed mechanism[84] reveals k_1, k_2 as the principal



Scheme 1

reduction pathway with $k_1 = 3.05 \times 10^{-2}\,M^{-1}s^{-1}$ and $k_2 = 1.94 \times 10^{-2}\,M^{-1}s^{-1}$ (25 °C, $I = 0.1$ M). Inositol hexakisphosphate, which affects the quaternary structure, including $R \rightarrow T$ state conversion, accelerates k_1 by a factor of 10 whereas k_2 is unaffected. Reduction by NADH-cytochrome b_5 reductase takes place[85] by a similar mechanism where inositol hexakisphosphate affects k_1 and k_4, both β-chain reactions, suggesting a local structural modification of the protein. An axial inner-sphere process in which the rate is determined by the steric accessibility of the iron is proposed[86] for the oxidation of the haem proteins Hb(III), Mb(III), and cytochromes *c* by alkyl halides in aqueous solution at pH 7.4. The rates of conversion of oxyhaemoglobin, $Hb(II)O_2$, into Hb(III) by organic reductants (Table 4) follow the ease of hydrogen abstraction from the substrate by

Table 4 *Rate constants for the conversion of oxyhaemoglobin to methaemoglobin in aqueous solution at* 25 °C

Reductant	pH	*I*/M	$k/M^{-1}\,s^{-1}$	*Ref.*
$PhNHNH_2$	7.4	0.1	45	87
Cyclohexa-1,4-diene	7.4	0.1	0.9	87
Hydroquinone	7.4	0.1	8.4×10^{-2}	87
Benzhydrol	7.4	0.1	7.9×10^{-2}	87
2-Methylcyclopentane-1,3-dione	7.4	0.1	2.6×10^{-2}	87
Acetylacetone	7.4	0.1	2.8×10^{-3}	87
Benzaldehyde	7.4	0.1	2.1×10^{-3}	87
Malononitrile	7.4	0.1	1.4×10^{-4}	87
Cr^{2+}	7.4	0.1	7.0×10^{3}	87
H_2NNH_2	7.4	0.1	0.3	87
$[Fe(CN)_6]^{4-}$	7.4	0.1	0.15	87
Fe^{2+}	7.4	0.1	33	87
$[Fe(CN)_5(OH_2)]^{3-}$ [a]	7.2	0.05	480	88
$[Fe(CN)_6]^{4-}$ [a]	7.2	0.05	0.08	88
Solvated e^-	7.0	0.1	1.4×10^{9}	89

[a] 20 °C.

[83] A. Tomoda, M. Takeshita, and Y. Yoneyama, *J. Biol. Chem.*, 1978, **253**, 7415.
[84] A. Tomoda, A. Tsuji, S. Matsukawa, M. Takeshita, and Y. Yoneyama, *J. Biol. Chem.*, 1978, **253**, 7420.
[85] A. Tomoda, T. Yubisui, A. Tsuji, and Y. Yoneyama, *J. Biol. Chem.*, 1979, **254**, 3119.
[86] E. W. Bartnicki, N. O. Belser, and C. E. Castro, *Biochemistry*, 1978, **17**, 5582.

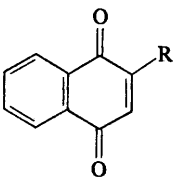
iron(II)-bound oxygen.[87] Although in most cases the final product is deoxy-Hb(II), met-Hb(III) was detected spectrophotometrically or by the addition of CN^-. With

$$Hb(II)O_2 + RH \longrightarrow Hb(III) + H_2O_2 + R\cdot$$
$$Hb(III) + R\cdot \longrightarrow Hb(II) + R$$

hydroquinone and the inorganic reductants Cr^{2+} and $[Fe(CN)_6]^{4-}$ the reaction terminated at the met stage. The reagent $[Fe(CN)_5(OH_2)]^{3-}$ is much more effective[88] in its reaction with $Hb(II)O_2$ than is $[Fe(CN)_6]^{4-}$. In the presence of catalase to prevent interference from H_2O_2 produced in the reaction, second-order rate constants are $8\ M^{-1}\ s^{-1}$ and $1.3 \times 10^{-3}\ M^{-1}\ s^{-1}$ respectively with protein products $Hb(III)(OH_2)$ and Hb(III)CN. The rate difference suggests formation of a μ-peroxo-bridged intermediate for the $[Fe(CN)_5(OH_2)]^{3-}$ reaction with the peroxo-group leaving as a ligand of $Fe(CN)_5$. The reactions are monophasic and there is no indication of rate differences for the α- and β-chains.

A pulse radiolysis study[89] of the reduction of Hb(III) and its derivatives $Hb(III)F^-$, $Hb(III)O_2$, $Hb(III)N_3^-$, and $Hb(III)CN^-$ by the solvated electron reveals a very rapid electron transfer, $8—16 \times 10^9\ M^{-1}\ s^{-1}$ followed by spin-state relaxation of the iron(II). No relaxation is noted for the CN^- derivative because CN^- remains bound on reduction, but with the others the similarity in relaxation rates, $60—70 \times 10^3\ s^{-1}$, is consistent with loss of the axial group before the spin-state transition. A mechanism in which the distal histidine is the primary electron acceptor and donates the electron to iron(III) by an inner-sphere mechanism is proposed. The spin-state transition takes place on dissociation of the co-ordinated histidine.

Reduction of $Hb(II)O_2$ by menadione,[90] vitamin K_3 (2), involves an e.p.r.-detectable semiquinone radical as intermediate. The reaction rate is reduced by catalase but is enhanced by superoxide dismutase which prevents the reverse of the reaction between O_2 and the menadione radical.



(2)

Leghaemoglobin, LHb(II), is a monomeric protein with a high oxygen affinity. It reacts[91] with H_2O_2 to form LHb(IV) in a single two-electron step with a rate constant of $2.24 \times 10^4\ M^{-1}\ s^{-1}$ at pH 7.0 and 20 °C. LHb(III) reacts only slowly with H_2O_2. The oxidized protein exists[92] in a stable low-spin iron(III)–ligand

[87] C. E. Castro, R. S. Wade, and N. O. Belser, *Biochemistry*, 1978, **17**, 225.
[88] S. Kavanishi and W. S. Caughey, *Biochem. Biophys. Res. Commun.*, 1979, **88**, 1203.
[89] A. Raap, J. W. van Leevwen, H. S. Rollema, and S. H. de Bruin, *Eur. J. Biochem.*, 1978, **88**, 555.
[90] C. C. Winterbourn, J. K. French, and R. F. C. Claridge, *Biochem. J.*, 1979, **179**, 665.
[91] I. Aviram, B. A. Wittenberg, and J. B. Wittenberg, *J. Biol. Chem.*, 1978, **253**, 5685.
[92] J. B. Wittenberg, *J. Biol. Chem.*, 1978, **253**, 5690.

radical form in basic media, but at pH 5 or less changes to a transient species which resembles an iron(IV) porphyrin. The two forms are interconvertible in borate buffer on lowering the temperature, and a similar observation[93] has been made in a study of hydrogen peroxidized myoglobin. Autoxidation kinetics for myoglobin have also been reported.[94]

Haemerythrin.—The iron binding site in haemerythrin, Hr, is dinuclear[95] with one metal ion bound to histidines-73, -77, and -101. The other is bound to histidines-25 and -54 and tyrosine-109 with glutamic acid-58[96] and aspartic acid-106 as bridging ligands. Substrate oxygen is bound asymmetrically[97] as peroxide in the same manner as azide and thiocyanate.[98]

Reduction of the octameric metHr(III)(III) by $S_2O_4^{2-}$ is biphasic,[99] consisting of a rapid electron-transfer step dependent on $[S_2O_4^{2-}]^{1/2}$ and a slower reaction independent of $[S_2O_4^{2-}]$. The initial phase is interpreted in terms of reaction of the protein with $SO_2^{\bullet-}$ to give a semi-met intermediate which contains Fe^{III}-Fe^{II} units and this is followed by disproportionation-controlled reduction to the deoxy-form. A similar mechanism is proposed for the monomeric metmyo-Hr(III)(III) form of the protein. Dissociation of N_3^- is required before reduction of $Hr(III)(III)N_3^-$.

When deoxymyoglobin, Mb(II), is used as reductant,[100] the reactions are much slower, with reduction of the first iron(III) of a pair as the rate-determining step followed by rapid reduction of the second iron(III). It is suggested that electrons are introduced through histidine-73, which is *ca.* 2 Å from the protein surface, and that the first electron is transferred to the more deeply buried iron(III). Application of Marcus theory to the reactions yields self-exchange rates for Hr from *Themiste pyroides* and *Phasocolopsis gouldii* of 10^{-3} and 10^{-5} M^{-1} s^{-1} respectively at 25 °C. As with dithionite, $Hr(III)(III)N_3^-$ is unreactive but oxymyoglobin, $Mb(II)O_2$, reduces haemerythrin to give met-Mb(III).

Iron–Sulphur Proteins.—A review article[101] on the properties of iron–sulphur protein found in chloroplast membranes has been published. The oxidations[102] of dithionite-reduced parsley and spinach two-iron ferredoxins, Fd(III)(II), with cobalt(III) complexes are independent of pH over the range 7.0—9.0. A change in the order of reaction for the tripositive reagents $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$ from one to zero with increasing concentration is ascribed to association with the negatively charged protein followed by rate-determining electron transfer:

$$Fd(III),(II) + Co(III) \overset{K}{\rightleftharpoons} Fd(III)(II), Co(III)$$

$$Fd(III)(II),Co(III) \xrightarrow{k_{et}} Fd(III)(III) + Co(II)$$

[93] J. B. Wittenberg, *J. Biol. Chem.*, 1978, **253**, 5694.
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[101] R. Malkin and A. J. Bearden, *Coord. Chem. Rev.*, 1979, **28**, 1.
[102] F. A. Armstrong and A. G. Sykes, *J. Am. Chem. Soc.*, 1978, **100**, 7710.

Association constants, K, for the parsley (998 M^{-1}) and spinach (993 M^{-1}) proteins are very similar with $[Co(NH_3)_6]^{3+}$ as oxidant and the value for $[Co(en)_3]^{3+}$ is 597 M^{-1} with parsley at 25 °C. A more complex alternative mechanism in which association produces an inactive complex cannot be ruled out but is considered unlikely since changing the ionic strength does not affect the limiting rate. Of a series of cobalt(III) complexes, only those with 3+ and 2+ charges exhibit association behaviour in the available concentration ranges but the thermodynamic parameters for overall electron transfer, Kk_{et} (Table 3) show a trend with the charge on the complex, suggesting that electrostatic and solvation effects are important.

Redox-inactive $[Cr(NH_3)_6]^{3+}$ binds to reduced parsley ferredoxin with an association constant of 476 M^{-1} at the same site as $[Co(NH_3)_6]^{3-}$, $[Co(NH_3)_5Cl]^{2+}$, and $[Co(NH_3)_5(C_2O_4)]^{+}$, thus inhibiting oxidation of the protein.[103] Binding has no effect on the rate with $[Co(acac)_3]$ but causes acceleration with the negatively charged $[Co(edta)]^{-}$. It is unlikely that $[Cr(NH_3)_6]^{3+}$ has an effect on the redox potential of the iron system but it is suggested that $[Co(acac)_3]$ and $[Co(edta)]^{-}$ bind at different sites from the positively charged oxidants.

The rate of reduction of cytochrome *c* by the cobalt-substituted analogue of rubredoxin is a factor of 2.25 lower than the rate with rubredoxin itself.[104] Both proteins mediate the reduction of cytochrome *c* in the presence of NADH and the decrease in the rate is attributed to the decreased efficiency in oxidation of cobalt(II) compared with iron(II). Reduction of cytochrome *c* by NADPH is catalysed[105] by an adrenodoxin reductase–adrenodoxin complex in which the rate-determining step is electron transfer from the flavin (FAD) of the reductase to the Fe_2S_2 centre of adrenodoxin. The pH dependence of the rate shows a pK_a of 6.75, with the high-pH form 27.5 times more reactive than the low-pH form. Both NADPH reduction of the complex and cytochrome *c* oxidation of the complex were faster than the catalytic rate. Catalytic roles of four iron–sulphur centres in trimethylene dihydrogenase[106] and ferredoxin nitrite reductase[107] have also been examined. Synthetic analogues of four iron ferredoxins have also attracted much attention.[108–110]

Copper Blue Proteins.—The present understanding of the chemistry of the copper blue electron-transfer proteins has taken a significant step forward with the publication of molecular structures for azurin[111] and plastocyanin.[112]

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[112] P. M. Colman, H. C. Freeman, J. M. Guss, M. Murata, V. A. Norris, J. A. M. Ramshaw, and M. P. Venkatappa, *Nature*, 1978, **272**, 319.

Together with EXAFS,[113] n.m.r.,[114,115] resonance Raman,[116,117] metal-ion substitution,[118] and model studies,[119,120] a great deal of information on the structural characterization of the proteins is now available. A study[121] of the redox thermodynamics of *Ps. aeruginosa* azurin, bean plastocyanin, and *Rhus vernicifera* stellacyanin gives reduction potentials for the three proteins of 330, 347, and 184 mV respectively, in good agreement with previous values. Entropy changes suggest that the hydrophobicity of the metal centre increases in the order stellacyanin < plastocyanin < azurin and correlate well with the kinetic accessibility of the proteins.

Cross reactions of plastocyanins and azurins from various sources with cytochromes can be fitted[54] to the Marcus equation using constant self-exchange rate constants of 6.6×10^2 M^{-1} s^{-1} for the plastocyanins, 9.9×10^5 M^{-1} s^{-1} for *Ps. aeruginosa* azurin, and 2.6×10^5 M^{-1} s^{-1} for the other azurins at 25 °C, pH 7.0, and 0.5 M phosphate buffer. This contrasts with the large variation in self-exchange rate constants for the proteins evaluated from reactions with small-molecule inorganic reagents where kinetic accessibility of the copper centre is important. The results suggest that there is no selectivity in the protein–protein reactions and that they take place by a common mechanism.

A mechanism involving protein–complex association prior to electron transfer has been proposed to explain deviations from first-order behaviour in the oxidations and reductions of parsley and spinach plastocyanins[122,123] and *Ps. aeruginosa* azurin[124,125] with inorganic reagents. The oxidations of reduced plastocyanin by $[Co(phen)_3]^{3+}$ and $[Fe(CN)_6]^{3-}$ have a pH dependence indicative[122] of redox-inactive protonated forms of the protein with pK_a values 6.1 and 5.7 respectively. For the reaction with $[Co(phen)_3]^{3+}$,

$$PCu^{I} + [Co(phen)_3]^{3+} \overset{K}{\rightleftharpoons} PCu^{I}, [Co(phen)_3]^{3+}$$

$$PCu^{I},[Co(phen)_3]^{3+} \xrightarrow{k} PCu^{II} + Co^{II}$$

this was shown[123] to be due to a reduction in the association constant K, caused by protonation affecting the binding site of the inorganic ion rather than a reduction in k, the electron-transfer rate constant, as might be expected if protonation at a copper(I) ligand were to occur. The corresponding reaction with the cobalt complex of 4,7-diphenylsulphonate-1,10-phenanthroline, $[Co(DPSphen)_3]^{3-}$, is much slower and is independent of pH. Experiments in which $[Fe(CN)_6]^{3-}$ reacts with PCu^{I} which is complexed to $[Co(DPSphen)_3]^{3-}$ indicate

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[114] H. A. O. Hill and B. E. Smith, *Biochem. Biophys. Res. Commun.*, 1978, **81**, 1201.
[115] E. L. Ulrich and J. L. Markley, *Coord. Chem. Rev.*, 1978, **27**, 109.
[116] N. S. Ferris, W. H. Woodruff, D. B. Rorabacher, T. E. Jones, and L. A. Ochrymowycz, *J. Am. Chem. Soc.*, 1978, **100**, 5939.
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[118] D. L. Tennent and D. R. McMillin, *J. Am. Chem. Soc.*, 1979, **101**, 2307.
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[122] M. G. Segal and A. G. Sykes, *J. Am. Chem. Soc.*, 1978, **100**, 4585.
[123] A. G. Lappin, M. G. Segal. D. C. Weatherburn, and A. G. Sykes, *J. Am. Chem. Soc.*, 1979, **101**, 2297.

that electron transfers to the two negatively charged reagents occur through different sites on the protein surface. It is concluded that the pH dependences of the redox potentials of the protein evaluated with different reagents are likely to be different. By way of a contrast, although the reduction of PCu^{II} by $[Fe(CN)_6]^{4-}$ involves pre-association, the reaction has little or no pH dependence.

Similar results are noted[124,125] for azurin where, for the reduced protein ACu^{I}, different binding sites with pK_a values 7.6 ($[Co(phen)_3]^{3+}$), 7.1 ($[Fe(CN)_6]^{3-}$), and no pH dependence ($[Co(4,7\text{-}DPSphen)_3]^{3-}$) are reported. No dramatic switch-off in reactivity, as with plastocyanin, is noted, however, and the trend in the rates with protonation reflects that expected for the effect of electrostatic attraction on substrate binding. The pK_a of 7.1 for $[Fe(CN)_6]^{3-}$ reaction is shifted to pK_a 6.1 for $[Fe(CN)_6]^{4-}$ reduction of ACu^{II} and, by comparing the kinetic pK_a values with those obtained by n.m.r.,[115] tentative assignments to histidines-35 and -83, which are not bound to the copper ion, are made.

A list of association constants, K, and limiting electron-transfer rate constants, k, for reactions of proteins with small molecule inorganic reagents is presented in Table 5. In general the thermodynamic parameters evaluated for the association constants show a trend depending on the charge on the inorganic complex, implying some electrostatic involvement in the binding, whereas activation entropy for electron transfer is negative and is not consistent with electron transfer within a compact assembly. Reduction of azurin(II) by ascorbate ion has also been reported.[47]

Pre-association and limiting electron-transfer behaviour is also observed[126] in the oxidation of stellacyanan, St(I), by $[Co(edta)]^-$ at pH 7.0. The large negative entropy of activation for electron transfer is interpreted as indicative of a non-adiabatic mechanism. When binding of $[Co(edta)]^-$ to the protein is prevented, either at pH 10.0 or by the addition of $edta^{4-}$ to block the reactive site, electron transfer takes place through an alternative adiabatic pathway. Under these conditions a Marcus self-exchange rate constant of $3 \times 10^5\ M^{-1}\ s^{-1}$ was evaluated, in good agreement with other studies.

No association was detected[127] in the comparable reactions of $[Co(pdta)]^-$ and $[Co(cydta)]^-$ where the bulky alkyl substituents prevent precursor complex formation by hydrogen-bonding to the reduced protein. The similarity in rate constants and activation parameters for the two reagents suggests that efficiency of electron transfer from stellacyanin is governed by the approach of a carboxylate from the ligand to the copper centre rather than the alkylated backbone.

4 Peroxidase, Oxidase, and Superoxide Dismutase

Horseradish Peroxidase.—Chlorine dioxide, ClO_2, is formed by the disproportionation of chlorite ClO_2^- catalysed by HRP,

$$4HClO_2 \longrightarrow 3ClO_2 + Cl^- + 2H_2O$$

[124] A. G. Lappin, M. G. Segal, D. C. Weatherburn, and A. G. Sykes, *J. Chem. Soc., Chem. Commun.*, 1979. 38.
[125] A. G. Lappin, M. G. Segal, D. C. Weatherburn, R. A. Henderson, and A. G. Sykes, *J. Am. Chem. Soc.*, 1979, **101**, 2302.
[126] G. S. Yoneda and R. A. Holwerda, *Bioinorg. Chem.*, 1978, **8**, 139.
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Table 5 *Association constants, electron-transfer rate constants, thermodynamic and activation parameters for reactions of proteins with inorganic complexes at* 25 °C, $I = 0.1$ M

Reaction	pH	K/M^{-1}	ΔH/ kcal mol^{-1}	ΔS cal K^{-1} mol^{-1}	k/s^{-1}	$\Delta H^{\ddagger}$ kcal mol^{-1}	$\Delta S^{\ddagger}$ cal K^{-1} mol^{-1}	*Ref.*
Fd(III)(II)[a] + $[Co(NH_3)_6]^{3+}$	8.0	998	10.2	47.9	19.2	8.5	−24.1	102
Fd(III)(II)[b] + $[Co(NH_3)_6]^{3+}$	8.0	993			15.9			102
Fd(III)(II)[a] + $[Co(en)_3]^{3+}$	8.0	597	11.0	49.5	2.7	10.0	−23.1	102
Fd(III)(II)[a] + $[Co(NH_3)_5Cl]^{2+}$	8.0	194	2.6	19.2	2300	5.8	−23.8	102
PCu^{I}[a] + $[Co(phen)_3]^{3+}$	7.5	167	10.0	45	17.9	4.3	−39	122
PCu^{I}[b] + $[Co(phen)_3]^{3+}$	7.5	389			16.7			122
PCu^{I}[a] + $[Co(DPSphen)_3]^{3-}$	7.5	4600	−4.2	2.7	0.041	13.2	−20.6	123
PCu^{II}[a] + $[Fe(CN)_6]^{4-}$	7.5	110	−5.1	−7.8	170	11.4	−9.7	122
ACu^{I} + $[Co(phen)_3]^{3+}$	9.1	457	−1.2	8.1	21.3	14.3	−4.5	125
ACu^{I} + $[Co(DPSphen)_3]^{3-}$	7.0	2750	−3.7	3.3	0.21	10.7	−25.9	125
ACu^{II} + $[Fe(CN)_6]^{4-}$	5.2	290			7.3			125
$StCu^{I}$ + $[Co(edta)]^{-}$	7.0[c]	149	−1.2	6	0.169	1.8	−56	126
LCu^{II} + H_2Q-OH	7.0[c]	1.00×10^3			27.1			161
LCu^{II} + H_2Q-Cl	7.0[c]	1.37×10^2			31.6			161
LCu^{II} + H_2Q-CO_2^{-}	7.0[c]	2.84×10^1			0.253			161

[a] Parsley. [b] Spinach. [c] $I = 0.5$ M.

and acts as a chlorinating agent for monochlorodimedone. The disproportionation was studied[128] in the absence of dimedone and yielded the first example of direct oxidation of HRP to HRP(II). The pH dependence of the reaction suggests that $HClO_2$ is the reactive oxidant with a second-order rate constant (Table 6) of 8×10^8 M^{-1} s^{-1} at 20 °C, $I = 0.1$ M. Mechanisms in which HRP(I) is formed and is rapidly reduced are also consistent with the experimental data. In a second paper[129] it is noted that HRP(II) is formed only at high pH in this reaction and the chemistry of HRP(II) is consistent with an acid–base equilibrium with a pK_a of *ca.* 8.6. The acidic form is unstable relative to the basic form and only the former can be oxidized to HRP(I) by H_2O_2.

Table 6 *Reactions of peroxidase compounds at* 25 °C

Reaction	pH	*I*/M	k/M^{-1} s^{-1}	*Ref.*
HRP + $HClO_2$ [a]	—	0.1	8.0×10^8	128
HRP + N_3^- [b]	5.0		6.8×10^6	130
HRP + CN^-	—	0.11	1.06×10^5	131, 132
HRP + H_2O_2	—	0.11	1.55×10^7	131, 132
HRP + H^+ [a,c]	—	0.2	1.0×10^{10}	133
HRP + H^+ [a,d]	—	0.2	1.5×10^{10}	133
HRP(II)H + $[Fe(CN)_6]^{4-}$	—	0.11	1.4×10^4	131
HRP(II) + IAA [a,c]	4.4	0.05	1.5×10^3	136
HRP(II) + IAA [a,d]	4.4	0.05	1.2×10^4	136
HRP(I)H + $[Fe(CN)_6]^{4-}$	—	0.11	1.4×10^7	131
HRP(I) + $[Fe(CN)_6]^{4-}$	—	0.11	5.2×10^5	131
HRP(I) + $[Fe(CN)_6]^{4-}$	5.0	0	1.6×10^9	134
HRP(I) + I^-	5.0	0	6.6×10^5	134
HRP(I)H + L-tyrosine H_2	—	0.01	4.5×10^3	135
HRP(I) + L-tyrosine H_2	—	0.01	4.8×10^4	135
HRP(I) + L-tyrosine H	—	0.01	4.0×10^5	136
HRP(I) + IAA [a,c]	4.4	0.05	6.8×10^3	136
HRP(I) + IAA [a,d]	4.4	0.05	2.0×10^6	136
TPH + H_2O_2 [e]	—	0.11	1.17×10^7	140
TPH_2 + H_2O_2 [f]	—	0.11	6.0×10^5	140
TPH + H_2O_2 [f]	—	0.11	1.6×10^6	140
TP + $PhCH_2CO_3H$ [e]	—	0.11	3.0×10^6	141
TP + $PhCH_2CO_3H$ [f]	—	0.11	1.1×10^6	141
TP + $PhCH_2CO_3^-$ [f]	—	0.11	4.0×10^4	141

[a] 20 °C. [b] 23 °C. [c] Isoenzyme A. [d] Isoenzyme C. [e] Turnip peroxidase P_1. [f] Turnip peroxidase P_7.

Azide binding to HRP is fast compared with normal haemoproteins,

$$HRP + N_3^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HRP(N_3)$$

with $k_1 = 6.8 \times 10^6$ M^{-1} s^{-1} at pH 5.0, 23 °C.[130] While the dissociation rate is independent of pH, $(2.0—3.5) \times 10^5$ s^{-1}, the formation rate is sensitive to protonation of a group on the distal side of the haem which leads to more facile incorporation of N_3^-. Reactions of HRP with HCN and H_2O_2 show similar pH

[128] W. D. Hewson and L. P. Hager, *J. Biol. Chem.*, 1979, **254**, 3175.
[129] W. D. Hewson and L. P. Hager, *J. Biol. Chem.*, 1979, **254**, 3182.
[130] I. Morishima, S. Ogawa, T. Yonezawa, H. Nakatani, K. Hiromi, T. Sano, and T. Yasunaga, *Biochem. Biophys. Res. Commun.*, 1978, **83**, 724.

dependencies and are inhibited by protonation of a group with pK_a 4.15 which is thought to be a propionate side-chain of the haem. A deuterium isotope effect of 1.6 is noted only with the H_2O_2 reaction [HRP(I) formation], suggesting a mechanism in which a proton is abstracted from H_2O_2 by the propionate group to give the HO_2^- nucleophile. The alkaline form of HRP is formed on deprotonation with pK_a 10.9[131] and is less unreactive towards CN^- binding and HRP(I) formation. Two studies of the acid–alkaline conversion of HRP have been reported.[132,133] There is general agreement in the results with the neutral isoenzyme, which was studied by both groups, and explanations based on the deprotonation of water co-ordinated in the sixth position of the iron(III) co-ordination sphere and inhibited by hydrogen-bonding or electrostatic effects are proposed. In alkaline conditions the dependence of the rate of HRP(I) formation on increasing $[H_2O_2]$ changes from first to zero order,[132] consistent with substrate–HRP complex formation:

$$H_2O_2 + HRP \overset{K}{\rightleftharpoons} H_2O_2\text{–}HRP \xrightarrow{k_d} HRP(I)$$

The dependence of k_d on pH is complex and requires the presence of two ionizable groups. No kinetic isotope effects are noted in the $[Fe(CN)_6]^{4-}$ reductions of HRP(I) and HRP(II), which are affected by protonation of groups on the proteins with pK_a values of 5.2 and 8.6 respectively.

The effects of electrostatic interactions on the reactions between HRP(I) and I^- and $[Fe(CN)_6]^{4-}$ have been investigated by extrapolating[134] ionic-strength dependent rate data to zero ionic strength as a function of pH. Protein charges evaluated by Debye–Hückel equations are always lower than total calculated charges, and for I^- the pH dependence of the rate is not solely due to electrostatic interactions but also to titration of a catalytically important group. Similarly the $[Fe(CN)_6]^{4-}$ rates do not correlate with the net charge on the enzyme at all values of pH. The high ionic strengths used in most studies swamp most of the electrostatic interactions.

An enzyme–substrate complex has been detected[135] in the oxidative dimerization of L-(−)-tyrosine by HRP(I) to give HRP(II). The pH dependence of the reaction reveals an enzyme protonation at pK_a 5.42 with a less reactive protonated form. The hydroperoxide of indole-3-acetic acid (IAA) is important[136] in the autoxidation of IAA catalysed by HRP. Formation of HRP(I) by reaction with the hydroperoxide is easier for the neutral isoenzyme than for the acidic species at pH 4.4 and this determines the catalytic activity. HRP(II) is detected as an intermediate in the reaction and it reacts with IAA to form radicals. The involvement of both HRP(I) and HRP(II) is proposed[137] in the autoxidation of 2-nitropropane to acetone and HNO_2, catalysed by HRP.

[131] H. B. Dunford, W. D. Hewson, and H. Steiner, *Can. J. Chem.*, 1978, **56**, 2844.
[132] D. Job and H. B. Dunford, *Can. J. Chem.*, 1978, **56**, 1327.
[133] T. Araiso and I. Yamazaki, *Biochemistry*, 1978, **17**, 942.
[134] H. Steiner and H. B. Dunford, *Eur. J. Biochem.*, 1978, **82**, 543.
[135] I. Ralston and H. B. Dunford, *Can. J. Biochem.*, 1978, **56**, 1115.
[136] R. Nakajima and I. Yamazaki, *J. Biol. Chem.*, 1979, **254**, 872.
[137] J. De Rycher and B. Halliwell, *Biochem. J.*, 1978, **175**, 601.

N.m.r. investigations[138] of HRP(I) and HRP(II) reveal that the former is high-spin iron(IV) with an associated radical, which may be an amino-acid close to the iron rather than the porphyrin ring. The sixth ligand is not H_2O but is a group with pK_a 5.6, probably a histidine. This contrasts with the $PFe^{IV}{=}O$ structure proposed previously where P is the porphyrin. The HRP(II) has iron(IV) in its low-spin configuration. Substitution of the protohaemin chromophore for deuterohaemin in HRP(I) changes the ground state of the iron from $^2A_{2u}$ to $^2A_{1u}$ and causes a 75% reduction in peroxidase activity.[139] The protein, however, has no catalase activity even though catalase has a $^2A_{1u}$ ground state, which suggests that the amino-acid structure has an important role to play in enzyme activity.

Turnip Peroxidases.—Compound (I) formation has been investigated[140] for two turnip peroxidase isoenzymes. Acidic isoenzyme P_1 has a low reduction potential and high peroxidase activity whereas basic isoenzyme P_7 has low peroxidase activity. Both isoenzymes show evidence for intermediate complex formation in their reactions with H_2O_2 at high pH. Examination of the acidity dependencies reveal that protonation occurs on P_1 at pK_a 3.72 and 10.00 whereas on P_7 protonation occurs at pK_a 2.5, 4.0, and 9.03. For both isoenzymes the protein forms at the extremes of the acidity range are unreactive to compound (I) formation and cyanide binding. Compound (I) formation using peroxybenzoic acids reveals[141] that reactions of the un-ionized acids compose the major pathway, but with P_7 reactions of the ionized species are also detected. The rates depend on the acid pK_a values and the higher reactivities of the un-ionized species reflect hydrophobic substrate binding.

Lactoperoxidase.—Added iodide ion affects[142] the rates of oxidation of the antithyroid drugs methylthiouracil and methylmercaptoimidazole by lactoperoxidase by binding to the protein with a stability constant of *ca.* 2×10^5 M^{-1} at 25 °C. No iodide oxidation takes place but the increases in rate suggest that the ion is effective in regulating the relative rates of substrate oxidation. Singlet oxygen is produced[143] in the reaction of lactoperoxidase with H_2O_2 in the presence of Br^- ion. Lactoperoxidase catalyses the oxidation of SCN^- by hydrogen peroxide but the reaction products oxidize protein sulphydryl groups. A likely intermediate, $OSCN^-$, was detected[144] in the reaction and addition of this reagent and $(SCN)_2$ to lactoperoxidase was shown to cause sulphydryl oxidation.

Cytochrome *c* Peroxidase.—*Pseudomonas* cytochrome *c* peroxidase catalyses the peroxidatic oxidation of *c*-type cytochromes and azurin and must be in its reduced form before steady-state velocities are attained.[145] The rates of one-electron reduction of the protein by a variety of reagents have been determined at pH 6.0,

[138] I. Morishima and S. Ogawa, *J. Am. Chem. Soc.*, 1978, **100**, 7125.
[139] R. K. DiNello and D. Dolphin, *Biochem. Biophys. Res. Commun.*, 1979, **86**, 190.
[140] D. Job and H. B. Dunford, *Can. J. Biochem.*, 1978, **56**, 702.
[141] D. Job and P. Jones, *Eur. J. Biochem.*, 1978, **86**, 565.
[142] J. L. Michot, J. Nunez, M. L. Johnson, G. Irace, and H. Edelhoch, *J. Biol. Chem.*, 1979, **254**, 2205.
[143] J. Piatt and P. J. O'Brien, *Eur. J. Biochem.*, 1979, **93**, 323.
[144] T. M. Aune and E. L. Thomas, *Biochemistry*, 1978, **17**, 1005.
[145] M. Ronnberg and N. Ellfolk, *Biochim. Biophys. Acta*, 1978, **504**, 60.

$I = 0.01$ M, and 25 °C. The reactions are first order in oxidant concentrations and second-order rate constants are presented in Table 3.

Cytochrome *c* Oxidase.—A review[146] of cytochrome *c* oxidase literature from 1974 to 1978 has been published. Cytochrome oxidases have four redox centres which generally act in pairs. *Pseudomonas aeruginosa* cyt c_{551} oxidase functions as a nitrate reductase but has terminal oxidase properties and consists of two subunits each of which contains haem *c* and haem d_1. Oxidation of the ascorbate-reduced protein by molecular oxygen[147] is triphasic but only the first phase is dependent on O_2 with a second-order rate constant of 3.3×10^4 M^{-1} s^{-1} at 25 °C, pH 7.0, 0.1 M phosphate. A study of the reaction intermediates reveals that only haem *c* is oxidized in the initial phase though the spectrum of haem d_1 is affected. Further changes in the spectrum of haem d_1 ($k = 1.0$ s^{-1}) are followed by a slow conformational change ($k = 0.1$ s^{-1}) around this chromophore. A similar conformational change is detected[148] in the oxidation by $[Fe(CN)_6]^{3-}$ under nitrogen. Initial oxidation of haem c_1 occurs at a rate of *ca* 10^5 M^{-1} s^{-1} and is unaffected by CO binding whereas oxidation of haem d_1 is an order of magnitude slower and is completely inhibited by CO binding. The cyanide ion binds to both haem *c* and haem d_1 components of fully oxidized cyt c_{551} at very similar rates, 0.2 M^{-1} s^{-1} at 25 °C and pH 7.0. Ascorbate reduction of haem *c* is inhibited by cyanide binding[149] and in the reduced protein only haem d_1 binds the ion.

Cytochrome *c* oxidase for higher organisms contains two haem chromophores at different reduction potentials, *a* and a_3, each with an associated copper centre, Cu_A and Cu_B respectively. The sequence of reduction of molecular oxygen by fully reduced, membrane-bound cytochrome *c* oxidase has been deduced[150,151] using dual-wavelength multichannel spectroscopy at low temperature. Initial binding of O_2 is followed by formation of superoxide and oxidation of haem a_3. Subsequent reactions include internal electron transfer from haem *a* and Cu_B with formation of peroxide. Ferricyanide pretreatment[152] oxidizes only haem *a* and its associated copper and the initial interaction with O_2 again produces superoxide and oxidized haem a_3.

Binding of carbon monoxide to cytochrome *c* oxidase has also been examined[153] and activation parameters are consistent with initial bridging between the haem centre and its associated copper followed by rearrangement to form the carbonmonoxyhaem. The number of CO molecules bound to cyt *c* oxidase is affected by the presence of ATP which suggests[154] that electron transfer through the oxidase can be controlled by changing the oxygen affinity.[155]

[146] M. Erecinska and D. F. Wilson, *Arch. Biochem. Biophys.*, 1978, **188**, 1.
[147] C. Greenwood, D. Barber, S. R. Parr, E. Antonini, M. Brunori, and A. Colosimo, *Biochem. J.*, 1978, **173**, 11.
[148] D. Barber, S. R. Parr, and C. Greenwood, *Biochem. J.*, 1978, **173**, 681.
[149] D. Barber, S. R. Parr, and C. Greenwood, *Biochem. J.*, 1978, **175**, 239.
[150] G. M. Clore and E. M. Chance, *Biochem. J.*, 1978, **173**, 799.
[151] G. M. Clore and E. M. Chance, *Biochem. J.*, 1979, **177**, 613.
[152] G. M. Clore and E. M. Chance, *Biochem. J.*, 1978, **173**, 811.
[153] G. M. Clore and E. M. Chance, *Biochem. J.*, 1978, **175**, 709.
[154] H. J. Harman and M. Sharrock, *Biochim. Biophys. Acta*, 1978, **503**, 56.
[155] H. J. Harman and M. K. F. Wikström, *Biochim. Biophys. Acta*, 1978, **503**, 67.

One-electron reduced cyt *c* oxidase oxidizes[156] cyt *c*(II) with a second-order rate of 5×10^6 M^{-1} s^{-1} at pH 7.4 and 25 °C. The presence of CO inhibits the reaction but the catalytic activity of the enzyme in the presence of oxygen is the same as the resting or fully reduced species. A rapid initial reaction with oxygen with a second-order rate constant of 1×10^8 M^{-1} s^{-1} has been measured.[156, 157] The interaction between cytochrome *c* and cytochrome *c* oxidase is mainly electrostatic in nature between lysine residues on cytochrome *c* and carboxyl residues on the oxidase.[158] This allows the use of a peptide coupling agent to determine that the cytochrome *c* binding site on cytochrome *c* oxidase lies in subunit IV. Cytochrome oxidase can be resolved into two components,[159, 160] one of which is an electron-transport complex; the other shows non-specific ion-transport properties and is buried in the enzyme, completely inaccessible to surface probes. It may be that, in cytochrome oxidase, electron transport is coupled to cation movement.

Copper Oxidases.—The reductions of *Rhus vernicifera* laccase, LCu(II), by hydroquinone derivatives involve[161] a mechanism in which pre-equilibrium enzyme–substrate complex formation is followed by rate-limiting electron transfer:

$$\text{LCu(II)} + \text{H}_2\text{Q} \overset{K}{\rightleftharpoons} \text{LCu(II)}\cdot\text{H}_2\text{Q}$$

$$\text{LCu(II)}\cdot\text{H}_2\text{Q} \xrightarrow{k} \text{LCu(I)} + \text{HQ}\cdot$$

Substituents on the hydroquinone with lone pairs enhance the binding (Table 5) and allow bidentate co-ordination of the hydroquinone. It is proposed that the phenolate oxygen is co-ordinated by type 2 copper whereas the lone-pair substituent is associated with the type 3 dinuclear reduction centre. Binding is also affected by bulky substituents and by the distance between the two co-ordinating groups. Electron transfer is controlled by protein activation rather than by the ease of activation of the hydroquinones.

The type 3 chromophore of laccase, which is normally considered to act as a co-operative two-electron centre, has been shown[162] to undergo one-electron reduction with strong reductants. It is suggested that the two-electron behaviour is the exception rather than the rule. The type 3 centre has similar magnetic properties to the chromophore in oxyhaemocyanin.[163] Photoirradiation at 330 nm, the type 3 absorption, at low temperature leads to reduction of type 1 centre and production of a biradical.[164] The process is reversible on warming to room

[156] S. Rosen, *Biochim. Biophys. Acta*, 1978, **503**, 389.
[157] L. C. Petersen, *Eur. J. Biochem.*, 1978, **85**, 339.
[158] C. H. A. Seiter, R. Margalit, and R. A. Perreault, *Biochem. Biophys. Res. Commun.*, 1979, **86**, 473.
[159] M. Fry, H. V. Zande, and D. E. Green, *Proc. Natl. Acad. Sci. USA*, 1978, **75**, 5908.
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[161] R. A. Holwerda, J. D. Clemmer, G. S. Yoneda, and B. J. McKerley, *Bioinorg. Chem.*, 1978, **8**, 255.
[162] O. Farver, M. Goldberg, S. Wherland, and I. Pecht, *Proc. Natl. Acad. Sci. USA*, 1978. **75**, 5245.
[163] D. M. Dooley, R. A. Scott, S. Ellinghaus, E. I. Solomon, and H. B. Gray, *Proc. Natl. Acad. Sci. USA*, 1978, **75**, 3019.
[164] Y. Henry and J. Peisach, *J. Biol. Chem.*, 1978, **253**, 7751.

temperature, demonstrating that there is direct energy transfer between the two centres.

Anaerobic reduction[165] of ascorbate oxidase, AO_{ox}, by ascorbate ion is an eight-electron process. Initial reduction of the type 1 centre is reversed as the type 3 centre is reduced and it is suggested that type 1 copper is close to the substrate binding site and that type 3 is involved in the interaction with molecular oxygen. Azide, which can bind to type 2 copper, has no effect on the reduction process. A potentially catalytically active intermediate is formed[166] in the reaction between ascorbate oxidase and hydrogen peroxide at pH 7.6, 0.01 M phosphate, and 25 °C:

$$AO_{red} + H_2O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AO{\cdot}H_2O_2$$

Formation and dissociation rate constants are 58.5 $M^{-1}\,s^{-1}$ and $1.75 \times 10^{-3}\,s^{-1}$ respectively and the complex decays over a matter of hours. Although both O_2 and ascorbate binding to the protein are independent of pH, a functional group with pK_a 7.8 must be protonated for catalytic activity and it is suggested that this protonation occurs in a reaction intermediate. It is proposed that types 1 and 2 copper are electron-accepting sites and that both electrons are transferred simultaneously to type 3. The two electrons and a proton possibly, from a tyrosine residue with pK_a 7.8, are transferred to O_2 to form HO_2^- as a catalytic intermediate.

Ceruloplasmin can act as a scavenger for O_2^-.[167] The type 2 binding site of the protein has either three or four nitrogen donors which are magnetically equivalent and can bind two fluoride ions suggesting that the ligands in the axial positions are readily exchanged.[168] Photoreduction of the protein[169] has a maximum quantum yield at 400 nm which corresponds to tyrosyl–copper(II) charge transfer. The two type 1 centres are reduced at different rates, with no type 2 reduction.

The mechanism of action of galactose oxidase involves oxidation of the alcohol to the aldehyde by a copper(III) form of the enzyme which is reduced to copper(I). Reoxidation involves a copper(II)–superoxide intermediate.[170]

Four atoms of copper have been found[171] for each tetrameric unit of dopamine-β-mono-oxygenase and the reduced enzyme requires the presence of additional reductant for hydroxylase activity.[172] The deaminating enzyme benzylamine oxidase consists of two subunits[173] and has two tightly bound, but well separated,

[165] L. Avigliano, G. Rotilio, S. Urbanelli, B. Mondovi, and A. Finazzi-Agro, *Arch. Biochem. Biophys.*, 1978, **815**, 419.
[166] R. E. Strothkamp and C. R. Dawson, *Biochem. Biophys. Res. Commun.*, 1978, **85**, 655.
[167] I. M. Goldstein, H. B. Kaplan, H. S. Edelson, and G. Weissman, *J. Biol. Chem.*, 1979, **254**, 4040.
[168] J. H. Dawson, D. M. Dooley, and H. B. Gray, *Proc. Natl. Acad. Sci. USA*, 1978, **75**, 4078.
[169] M. Herve, A. Garnier, L. Tosi, and M. Steinbuch, *Biochem. Biophys. Res. Commun.*, 1978, **80**, 797.
[170] G. A. Hamilton, P. K. Adolf, J. de Jersey, G. C. DuBois, G. R. Dyrkacz, and R. D. Libby, *J. Am. Chem. Soc.*, 1978, **100**, 1899.
[171] T. Skotland and T. L. Jones, *Eur. J. Biochem.*, 1979, **94**, 145.
[172] T. Skotland, T. L. Jones, and T. Flatmark, *Biochem. Biophys. Res. Commun.*, 1978, **84**, 83.
[173] J. Grant, I. Kelly, P. Knowles, J. Olsson, and G. Pettersson, *Biochem. Biophys. Res. Commun.*, 1978, **83**, 1216.

chemically distinct copper(II) sites and one catalytically active carboxyl grouping.[174] The copper does not act as an electron sink in the catalytic cycle and only one site is apparently involved. Both copper ions have two water molecules, axial and equatorial, which undergo fast exchange but only the equatorial water molecule is displaced by CN^- and N_3^-, which also inhibit O_2 binding. A mechanism in which the copper acts as a template for amine transfer to the carboxyl and as an activator for molecular oxygen is proposed.[174] The stereochemistry of the oxidation of dopamine has been examined.[175]

Dinuclear models for type 3 copper which undergo reversible two-electron[176,177] and irreversible reduction[178] have been reported. The latter compound forms an adduct with ascorbate which shows intense charge-transfer absorption, but ascorbate does not reduce the copper(II) dimer.

Superoxide Dismutase.—Reduction of superoxide dismutase (SOD) adds an electron to the copper site, leaving the zinc unchanged. *X*-Ray absorption data suggest[179] that the copper site loses symmetry on reduction, consistent with an oxygen ligand or tetrahedral distortion of the four histidine imidazole ligands. Magnetic resonance results[180] reveal that the histidines are arranged in a roughly planar configuration and that one axial position is occupied by a ligand from the protein whereas the other position has H_2O which undergoes rapid exchange, $1.6 \times 10^5\ s^{-1}$, independent of pH at pH $\geqslant$ 12. It is suggested that the protons on this molecule are used in the dismutase reaction

$$2H^+ + O_2^- \longrightarrow H_2O_2 + O_2$$

which is independent of pH in the range 5—10. On increasing the pH, histidine-61, which bridges the copper and zinc, is replaced on copper by co-ordinated water.

Wheat germ SOD can be dissociated[181] into inactivated monomeric units by sodium dodecyl sulphate with a first-order rate of $7.8 \times 10^{-5}\ s^{-1}$ at 25 °C. The process is reversible with two first-order formation reactions which are consistent with refolding of the monomer, rate constant $3.3 \times 10^{-3}\ s^{-1}$, and reassociation to dimer, $2.3 \times 10^6\ s^{-1}$. Approximately half of the SOD activity is restored after the first phase, implying that the monomeric form can be catalytically active. Binding of Cu^{2+} to Zn-apobovine SOD is dependent[182] on pH and is consistent with initial binding to the active site ligands,

$$Cu + \text{Zn-SOD} \overset{\text{fast}}{\rightleftharpoons} \text{Cu,Zn-SOD} \overset{\text{slow}}{\longrightarrow} \text{SOD}$$

followed by slow rearrangement of the site around the metal.

174 R. Barker, N. Boden, G. Caley, S. C. Charlton, R. Henson, M. C. Holmes, I. D. Kelly, and P. F. Knowles, *Biochem. J.*, **1979**, **177**, 289.
175 M. C. Summers, R. Markovic, and J. P. Klinman, *Biochemistry*, 1969, **18**, 1979.
176 D. E. Fenton, R. R. Schroeder, and R. L. Lintvedt, *J. Am. Chem. Soc.*, 1978, **100**, 1931.
177 D. E. Fenton and R. L. Lintvedt, *J. Am. Chem. Soc.*, 1978, **100**, 6367.
178 J. J. Grzybowski, P. H. Merrell, and F. L. Urbach, *Inorg. Chem.*, 1978, **17**, 3078.
179 W. E. Blumberg, J. Peisach, P. Eisenberger, and J. A. Fee, *Biochemistry*, 1978, **17**, 1842.
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181 A. Rigo, F. Marmocchi, D. Cocco, P. Viglino, and G. Rotilio, *Biochemistry*, 1978, **17**, 534.
182 A. Rigo, P. Viglino, M. Bonori, D. Cocco, L. Calabrese ,and G. Rotilio, *Biochem. J.*, 1978, **169**, 277.

5 Coenzyme B_{12} and Cobaloxime Chemistry

Coenzyme B_{12}.—Coenzyme B_{12} catalyses a number of important rearrangement reactions. A rearrangement of butenylcobaloximes (Scheme 2) with a half-life of

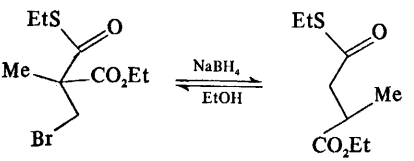


Scheme 2

ca. 100 min at 53 °C in $CDCl_3$ is explained[183] in terms of a bimolecular homolytic displacement involving attack of [Co^{II}(dmgH)$_2$py] at the terminal unsaturated carbon and formation of a three-membered carbon ring. This suggests that 1,2-rearrangements catalysed by coenzyme B_{12} proceed by homolytic Co—C bond cleavage to give B_{12r} and the carbon-centred radical, followed by remote attack at an unsaturated carbon–carbon bond. A similar mechanism is proposed in the vitamin B_{12}-dependent catalysis by dioldehydratase where propionamide side-chains on the corrin ring facilitate homolytic Co–C bond cleavage and contribute to the stabilization of the radical intermediates.[184] Proton transfer from propane-1,2-diol is involved[185] in the inactivation of dioldehydratase by glycerol, and an intermediate, likely to be 5′-deoxyadenosine, of adenosylcobalamin with three equivalent hydrogens is proposed. The stereochemistry of the reaction has been investigated[186] with butane-2,3-diols where only the *meso*-isomer can act as substrate and inactivator of the enzyme. The *dl*- and *d*-isomers do not induce Co—C bond cleavage.

The cobalt(II) form of coenzyme B_{12a}, B_{12r}, has been detected[187] in the coenzyme B_{12}-dependent ethanolamine ammonialyase catalysed reaction. Binding of adenosylcobalamin to the protein causes a slow conformational change and the reactions of 2-amino-alcohols proceed by formation of an enzyme–substrate complex followed by radical and cobalt(II) formation and finally disappearance of the cobalt(II). Rate differences with 2-aminoethanol and L-2-aminopropanol arise mainly in this latter step.

The carbon skeletal rearrangement shown in Scheme 3 is catalysed[188] by coenzyme B_{12} in a mechanism which involves heterolytic Co—C bond cleavage



Scheme 3

[183] A. Bury, M. R. Ashcroft, and M. D. Johnson, *J. Am. Chem. Soc.*, 1978, **100**, 3217.
[184] T. Toraya, E. Krodel, A. S. Mildvan, and R. H. Abeles, *Biochemistry*, 1979, **18**, 417.
[185] W. W. Bachovchii, K. W. Moore, and J. H. Richards, *Biochemistry*, 1978, **17**, 2218.
[186] K. W. Moore and J. H. Richards, *Biochem. Biophys. Res. Commun.*, 1979, **87**, 1052.
[187] M. R. Holloway, H. A. White, K. N. Joblin, A. W. Johnson, M. F. Lappert, and O. C. Wallis, *Eur. J. Biochem.*, 1978, **82**, 143.
[188] A. I. Scott, J. Kang, D. Dalton, and S. K. Chung, *J. Am. Chem. Soc.*, 1978, **100**, 3603.

and formation of a carbanion. There is, however, no certainty that rearrangement takes place in this anionic species.

Photo-homolytic cleavage of Co—C bonds has been studied for Vitamin B_{12}[189] and cobalt(III) complexes with tetra-aza-14-membered macrocyclic ligands.[190] In the latter study, the rate of recombination of the radical with cobalt(II) is *ca.* $10^8\ M^{-1}\ s^{-1}$ at 25 °C. The cobalt(III) complexes have a low energy threshold to photolysis, > 540 nm.

Different decomposition mechanisms[191] for the products of the reaction between $Co^{II}Me_6$[14]-diene-N_4, $Co^{II}L$, and carbon-centred aliphatic alcohol radicals suggest an explanation for the inhibition of diol dehydratase by N_2O.

$$Co^{III}LCH_2OH \longrightarrow Co^{I}L + CH_2O \quad (1)$$

$$Co^{III}LCH(OH)CH_2OH \longrightarrow Co^{III}LCH_2CHO + H_2O \quad (2)$$

$$Co^{III}LCH_2CHO \xrightarrow{H^+} Co^{III}L + CH_3CHO$$

If process (1) occurs in parallel with process (2) in the dehydration of ethylene glycol, then the B_{12s} form of the enzyme, containing Co^I, which reacts rapidly with N_2O, is formed.

A disagreement[192,193] about the rate of reaction between B_{12s} and B_{12a} has been resolved.[194] In the acidic region below pH 7.8, reaction is rapid with a rate constant of *ca.* $1.8 \times 10^8\ M^{-1}\ s^{-1}$ at 25 °C whereas above pH 7.8, where the aquocobalamin B_{12a} is deprotonated to form hydroxycobalamin B_{12b}, the rates are substantially lower, *ca.* $10^4\ M^{-1}\ s^{-1}$.

Oxidation of B_{12r} by the dibromide radical proceeds[195] by an inner-sphere mechanism with a rate constant of $3.4 \times 10^9\ M^{-1}\ s^{-1}$ at 22 °C and pH 4.5. The product is a Co^{III}–Br_2 complex in which Br—Br bond cleavage is rapid, $1 \times 10^4\ s^{-1}$, and which is followed by aquation with a rate constant of $6.4 \times 10^2\ s^{-1}$.

The mechanism of hydrogen evolution from hydridocobaloxime [HCo(dmgH)$_2$(PBu^n_3)] involves[196] two pathways representing reactions of different protonated forms of the complex:

$$[HCo(dmgH)_2(PBu^n_3)] + H^+ \rightleftharpoons [HCo(dmgH)(dmgH_2)(PBu^n_3)]^+$$

The unprotonated forms react by a bimolecular step with rate constant $1.7 \times 10^4\ M^{-1}\ s^{-1}$ at 25 °C in 40% MeOH–H_2O. Reaction of the acid form is unimolecular with a rate constant $1.6 \times 10^{-3}\ s^{-1}$ involving two-electron oxidation of the metal from cobalt(I) to cobalt(III). This requires a rapid reaction between cobalt(I) and cobalt(III) to give the cobalt(II) product. Methylcobalamin is also involved in methane biosynthesis.[197]

[189] I. P. Rudakova, T. E. Ershova, A. B. Belikov, and A. M. Yurkevich, *J. Chem. Soc., Chem. Commun.*, 1978, 592.
[190] C. Y. Mok and J. F. Endicott, *J. Am. Chem. Soc.*, 1978, **100**, 123.
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[196] T. H. Chao and J. H. Espenson, *J. Am. Chem. Soc.*, 1978, **100**, 129.
[197] G. N. Schrauzer, J. H. Grate, and R. N. Katz, *Bioinorg. Chem.*, 1978, **8**, 1.

Cyclic voltammetric studies[198] reveal that methylcobinamide can be reduced by one electron to a Co^{I}–CH_3 species which rapidly dissociates with a rate constant of *ca.* 2.5×10^3 s^{-1} at 19 °C in DMF–propanol solvent. Methylcobalamin is more reactive, with a dissociation rate of 1.2×10^3 s^{-1} at −30 °C. Redox between vitamin B_{12a} and B_{12r} is affected[199] by the presence or absence of axially bound benzimidazole base. This allows the determination of base-on, base-off rates by cyclic voltammetry. Values of 44 s^{-1} and 0.18 s^{-1} are reported for B_{12a}. The redox process is also affected by whether the cobalamin is in its aquo or its hydroxo form.

Transmethylation by Cobalamins.—Two mechanisms of methyl transfer from cobalamins are found, a homolytic process with metals that have reduction potentials less than 0.50 V and an electrophilic (carbanion heterolytic) process for metals with potentials greater than 0.85 V. The $Pt^{IV/II}$ couple is 0.76 V and both oxidation states are required for methylation.[200] A mechanism is proposed in which $[PtCl_4]^{2-}$ binds through the propionamide and acetamide side-chains of the corrin thereby promoting formation of the 'base on' form and activating the Co–C bond. The methylation step involves $[PtCl_6]^{2-}$ either in a redox switch where two electrons are abstracted from bound Pt^{II} followed by methyl transfer to the then bound Pt^{IV} or by direct electrophilic attack by $[PtCl_6]^{2-}$.

An electrophilic attack mechanism is proposed[201] for the transmethylation reactions of organometallic complexes by methylcobalamin. Reaction rates show first-order dependences on methylcobalamin and the organometallic concentrations with second-order rate constants varying from 6.9×10^{-2} M^{-1} s^{-1} for MeHgOAc to 4.5×10^{-5} M^{-1} s^{-1} for Me_2SnOAc at 25 °C, pH 4.55, and ionic strength 0.1 M. Oxidative alkylations of Sn^{II} in the presence of iron(III) and with catalytic amounts of alkylcobalamin show[202] a rate law of the form

$$\text{Rate} = k_{\text{alkyl}}[Sn^{II}][\text{alkylcobalamin}]$$

with rate constants $k_{\text{methyl}} = 1.4$ M^{-1} s^{-1} and $k_{\text{ethyl}} = 3.3 \times 10^{-2}$ M^{-1} s^{-1} at pH 1.0 and 20 °C. The proposed mechanism involves reaction of Sn^{III} with vitamin B_{12a}:

$$Sn^{III} + B_{12a}\text{-alkyl} \longrightarrow Sn^{IV}\text{-alkyl} + B_{12r}$$

Cobalamin and Cobaloxime Substitution Reactions.—The substitution kinetics of vitamin B_{12a} with 8-azaguanine and 6-mercaptopurine have been investigated[203] in aqueous media at 25 °C and ionic strength 0.1 M. The complex pH dependences are interpreted in terms of reactions of the 'base on' aquocobalamin with protonated and deprotonated forms of the ligands. Rate constants are listed in Table 7 and are consistent with a dissociative interchange mechanism. A similar mechanism is likely[204] in the substitution reaction of cyanocobalamin with $[Fe(CN)_6]^{4-}$. Both 'base on' and 'base off' forms of the coenzyme are reactive.

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[204] Y. Sulfab and M. S. El-Ezaby, *Inorg. Chim. Acta*, 1978, **26**, 177.

Table 7 *Rate constants for substitution reactions of cobalamin and cobaloxime complexes at* 25 °C *in aqueous solution*

Reaction	*I*/M	k_1/M^{-1} s^{-1}	k_1 /s^{-1}	*Ref.*
[(bzm)Co^{III}(OH$_2$)][a] + 8-azaguanine H	0.1	40	18.4	203
+ 8-azaguanine$^-$	0.1	800	1.4×10^{-2}	203
+ 6-mercaptopurine H	0.1	62	2.0×10^{-2}	203
+ 6-mercaptopurine$^-$	0.1	220	8.8×10^{-4}	203
[(bzm)Co^{III}(CN)][b] + [Fe(CN)$_6$]$^{4-}$	1.0	2.37×10^{4}		204
[(H$_2$O)Co^{III}(CN)][b] + [Fe(CN)$_6$]$^{4-}$	1.0	1.23×10^{5}		204
[EtCo^{III}(dmgH)$_2$(OH$_2$)] + NEt(OMe)$_2$	1.0	8.09×10^{1}	1.33×10^{-1}	205
[(PhCH$_2$CH$_2$)Co^{III}(dmgH)$_2$(OH$_2$)] + NEt(OMe)$_2$	1.0	5.11×10^{1}	7.15×10^{-2}	205
[MeCo^{III}(dmgH)$_2$(OH$_2$)] + NEt(OMe)$_2$	1.0	5.09	5.91×10^{-3}	205
[{NC(CH$_2$)$_3$}Co^{III}(dmgH)$_2$(OH$_2$)] + NEt(OMe)$_2$	1.0	1.30	1.23×10^{-2}	205
[(MeOCH$_2$CH$_2$)Co^{III}(dmgH)$_2$(OH$_2$)] + NEt(OMe)$_2$	1.0	9.40	8.87×10^{-3}	205
[(PhOCH$_2$CH$_2$)Co^{III}(dmgH)$_2$(OH$_2$)] + NEt(OMe)$_2$	1.0	7.24	8.00×10^{-3}	205
[(MeCH=CH)Co^{III}(dmgH)$_2$(OH$_2$)] + NEt(OMe)$_2$	1.0	1.38	1.33×10^{-3}	205
[{MeO$_2$C(CH$_2$)$_2$}Co^{III}(dmgH)$_2$(OH$_2$)] + NEt(OMe)$_2$	1.0	1.15×10^{1}	1.21×10^{-2}	205
[PhCo^{III}(dmgH)$_2$(OH$_2$)] + NEt(OMe)$_2$	1.0	6.21×10^{-1}	4.54×10^{-4}	205
[(CF$_3$CH$_2$)Co^{III}(dmgH)$_2$(OH$_2$)] + NEt(OMe)$_2$	1.0	2.69×10^{-2}	9.49×10^{-6}	205
[(MeO$_2$CCH$_2$)Co^{III}(dmgH)$_2$(OH$_2$)] + NEt(OMe)$_2$	1.0	2.71×10^{-2}	4.57×10^{-6}	205
[(HO$_2$CCH$_2$)Co^{III}(dmgH)$_2$(OH$_2$)] + py	1.0	5.64×10^{-1}	9.19×10^{-5}	206
[{HO$_2$C(CH$_2$)$_2$}Co^{III}(dmgH)$_2$(OH)] + py	1.0	7.23×10^{2}	4.12×10^{-1}	206

[a] Vitamin B$_{12a}$. [b] Cyanocobalamin.

Substitution of the *trans* aquo-ligand in alkylcobaloximes, $[RCo(dmgH)_2(H_2O)]$, by dimethoxyethylamine[205] and pyridine[206] is considered to proceed by a limiting dissociative or *D* mechanism. Linear free-energy relationships allow calculation[205] of the six–five-co-ordinate equilibrium for the complexes from which the rate of attack of dimethoxyethylamine on the five-co-ordinate species can be evaluated. It is concluded that the transition state for this process occurs early in the reaction with only around 20% bond formation. A *D* mechanism is also preferred in a study[207] of the *trans* labilizing effect of anionic ligands X on the substitution reactions of $[XCo(dmgH)_2L]$, where L is cyanopyridine or triphenylphosphine. In dichloromethane at 25 °C, the reaction rates are independent of both the concentrations and the natures of the incoming ligands. Inhibition studies suggest a highly reactive five-co-ordinate intermediate $[XCo(dmgH)_2]$ which reacts indiscriminately with either incoming or outgoing ligand. The *trans* effect of X (alkyl, alkyl halide, aryl, *etc.*) was found to reflect ground-state Co—L bond weakening for good *trans* activators.

6 Metal–Porphyrin Complexes

Metal Porphyrin Formation.—The rate of formation of cationic porphyrin complexes of copper(II) is dependent on the basicity of the ligand.[208] Tetra-(4-*N*,*N*′,*N*″-trimethylanilinium)porphyrin, H_2TAP, reacts with a second-order rate constant of 6.2 $M^{-1}\,s^{-1}$, almost thirty times faster than the corresponding process for the less basic tetra-(4-*N*-methylpyridinium) porphyrin, TMpyP, with a rate constant of 0.23 $M^{-1}\,s^{-1}$ at 25 °C, $I=0.1$ M. The rate for 5-(4-pyridyl)-10,15,20-triphenylporphyrin is 9.1×10^{-3} $M^{-1}\,s^{-1}$ at 25 °C in the presence of 1.5% sodium dodecyl sulphate micelles which solubilize the ligand.[209] Amine ligands enhance[210] the rate of formation of copper(II)–tetraphenylporphyrin (TPP), and a mechanism involving copper–amine complexes is proposed. Rate acceleration is observed only with unidentate amines, and chelates such as ethylenediamine have an inhibiting effect.

Basic conditions were used to solubilize haematoporphyrin IX for a study[211] of the complexation of Zn^{2+}. Three reactive zinc species were detected, $Zn(OH)_2$, $[Zn(OH)_3]^-$, and $[Zn(OH)_4]^{2-}$, with rate constants 10.3, 2.5, and 0.125 $M^{-1}\,s^{-1}$ respectively, at 25 °C, $I=0.3$ M, decreasing with increasing hydroxylation. Porphyrin exchange[212] between cadmium(II) and zinc(II) in pyridine solution in the presence of 0.5 M H_2O involves a Cd–P–Zn activated complex since the exchange rates are orders of magnitude higher than the rate of incorporation of zinc into the free porphyrin, H_2P.

Substitution Reactions.—Similar kinetic behaviour is observed[213] in the dissociation reactions of the cationic $[Fe^{III}_2(TMpyP)_2O]$ and the $[Fe^{III}_2(TPPS)_2O]$

[205] K. L. Brown and A. W. Awtrey, *Inorg. Chem.*, 1978, **17**, 111.
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[212] J. Reid and P. Hambright, *Inorg. Chim. Acta*, 1979, **33**, 435.
[213] F. L. Harris and D. L. Toppen, *Inorg. Chem.*, 1978, **17**, 71.

μ-oxo-dimers [TPPS = tetra-(4-sulphophenyl)porphyrin]. A mechanism involving pre-equilibrium protonation, and dissociation of the μ-hydroxy-dimer with rate constants 0.155 and 2.69 s^{-1} for the TMpyP and TPPS species, at 25 °C and 0.1 M ionic strength is proposed. The difference in the protonation constants, pK_a 5.9 and 8.5 respectively, is consistent with the difference in the overall charge on the complexes. Dissociation kinetics have also been investigated[214] for co-proferrihaem. The co-proporphyrin chromophore has additional propionate side-chains compared with protoporphyrin or deuteroporphyrin which interact to cause a decrease in the dimer association constant.

In mixed dichloromethane–nitromethane solvent at 25 °C, the formation of $[Fe^{III}(TPP)(ImH)_2]$ from $[Fe^{III}_2(TPP)_2O]$ involves[215] an imidazole μ-oxo-dimer complex with an association constant K of 220 M^{-1}:

$$[Fe_2(TPP)_2O] + ImH \overset{K}{\rightleftharpoons} [Fe_2(TPP)_2O(ImH)]$$

Kinetic ambiguity between the subsequent reactions,

$$[Fe_2(TPP)_2O(ImH)] \xrightarrow{k_1}$$

$$[Fe_2(TPP)_2O(ImH)] + ImH_2^+ \xrightarrow{k_2}$$

with $k_1 = 1.0\ s^{-1}$ and $k_2 = 5500\ M^{-1}\ s^{-1}$ (Table 8) and a mechanism in which the μ-oxo-imidazole complex is unreactive cannot be resolved. Similar kinetic

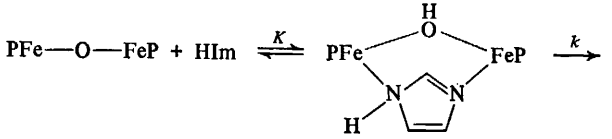
Table 8 *Rate constants for substitution reactions of metal porphyrin complexes at* 25 °C *in aqueous solution*

Reaction	*I*/M	$k/M^{-1}\ s^{-1}$	*Ref.*
$[Fe^{III}PPIX] + Im$	0.04	2.3×10^4	217
+ 1-MeIm	0.04	4.2×10^4	217
$[HOCr^{III}TPPS] + Im$	0.2	74	218
$[Co^{III}TMpyP] + SCN^-$	—	2.1	219
$[Co^{III}TPPS] + SCN^-$	—	157	219
$[Co^{III}MPDME] + SCN^-$	*a*	333	219
$[Co^{III}DPDME] + SCN^-$	*a*	238	219
$[Co^{III}TPPS] + SCN^-$	*a*	200	219
$[Co^{III}TMpyP] + SCN^-$	*a*	3.0	219
$[Co^{III}TMpyP] + SCN^-$	0.5	2.1	220
+ py	0.5	0.7	220
+ tmtu	0.5	1.1	220
$+ N_3^-$	0.5	1.7	220
$+ HN_3$	0.5	0.3	220
$[HOCo^{III}TMpyP] + SCN^-$	0.5	110	220
+ py	0.5	220	220
$[HOCo^{III}TMpyP] +$ tmtu	0.5	120	220
$+ N_3^-$	0.5	85	220
$[NCSCo^{III}TMpyP] + SCN^-$	0.5	3.0×10^3	220
$[pyCo^{III}TMpyP] +$ py	0.5	2.8	220
$[tmtuCo^{III}TMpyP] +$ tmtu	0.5	3.7×10^4	220
$[N_3Co^{III}TMpyP] + N_3^-$	0.5	7.2×10^2	220

[a] 2.5% Triton X.

[214] S. B. Brown and H. Hatzikonstantinou, *Biochim. Biophys. Acta*, 1978, **544**, 407.
[215] D. Ostfeld and J. A. Colfax, *Inorg. Chem.*, 1978, **17**, 1796.

behaviour in the reactions of $[Fe^{III}_2(TPPS)_2O]$ and $[Fe^{III}_2(TAP)_2O]$ at 30 °C in 0.1 M $NaNO_3$ is interpreted[216] in terms of a μ-imidazole, μ-hydroxy dimer adduct with cleavage of the adduct in the rate-determining step (Scheme 4).



Scheme 4

Adduct formation results in a more positive charge and hence the association constant K and rate constant k are larger for TPPS, 47 M^{-1} and 7 s^{-1}, than for TAP, 5.6 M^{-1} and 1.3 s^{-1}.

The kinetics of formation of bis-imidazole complexes of monomeric iron(III) porphyrins have been investigated:[217]

$$[FeP(H_2O)] + 2Im \rightleftharpoons [(Im)_2FeP] + H_2O$$

For the tetraphenylporphyrin complex, the rate law involves a complex formation term dependent on $[Im]^2$, suggesting that the rate-limiting step is the addition of the second imidazole group with a third-order rate constant of 3.8×10^5 $M^{-2}\,s^{-1}$ for imidazole and of 1.8×10^5 $M^{-2}\,s^{-1}$ for its 1-methyl derivative at 25 °C and 0.04 M ionic strength. However, for the complex with protoporphyrin IX, $[Fe^{III}PPIX]$, the formation rate term shows limiting first-order behaviour at high imidazole concentrations, allowing rate terms for formation of the mono-imidazole complex to be evaluated as 2.3×10^4 $M^{-1}\,s^{-1}$ for imidazole and 4.2×10^4 $M^{-1}\,s^{-1}$ for 1-methylimidazole. This difference in mechanism can be explained if the high-spin–low-spin change occurs after the addition of the second ligand in $[Fe^{III}PPIX]$ but before the second addition in $[Fe^{III}TPP]^{3+}$.

The pH dependence of the rate of reaction between imidazole and $[Cr^{III}(TPPS)]$ reveals[218] that the reactive metal species in mono-complex formation has a hydroxy-group *trans* to the aquo leaving group:

$$[HOPCrOH_2] + ImH \xrightarrow{k_1} [HOPCrImH] + H_2O$$

The hydroxy-group is a good *trans* activator, and a rate constant of 74 $M^{-1}\,s^{-1}$ was evaluated for the process at 25 °C and ionic strength 0.2 M. A second imidazole adds by a D mechanism after rapid tautomerization to produce a deprotonated imidazole ligand and an aquo leaving group:

$$[HOPCrImH] \rightleftharpoons [H_2OPCrIm] \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [PCrIm] + H_2O$$

$$[PCrIm] + ImH \xrightarrow{k_3} [HImPCrIm] \xrightarrow[\text{fast}]{H^+} [HImPCrImH]$$

[216] A. N. Thompson and M. Krishnamurthy, *Inorg. Chim. Acta*, 1979, **34**, 145.
[217] R. F. Pasternack, B. S. Gillies, and J. R. Stahlbush, *J. Am. Chem. Soc.*, 1978, **100**, 2613.
[218] M. Krishnamurthy, *Inorg. Chim. Acta*, 1978, **26**, 137.

Rate constants 2.0×10^{-2} s^{-1} and 0.32 for k_2 and k_{-2}/k_3 respectively were evaluated and the scheme is consistent with slower reaction when the poorer *trans* activator, Im^-, is present.

Addition of 2.5% Triton X to solubilize porphyrin complexes causes less than a factor of two increase in the rates of thiocyanate anation compared with the reaction in aqueous solution.[219] This allows comparisons to be made with a range of porphyrin complexes of cobalt(III) with differing porphyrin basicity without the complications due to the peripheral charge effects normally found with water-soluble ligands. Reaction rates show a *cis* effect which is dependent on the porphyrin basicity rather than the peripheral charge, consistent with the presence of more labile cobalt(II) character with porphyrins of high basicity. An I_d mechanism is proposed[220] for the anation of water-soluble [Co^{III}(TMpyP) with azide and tetramethylthiourea, tmtu. Pathways involving the bis-aquo- and the aquo-hydroxy-forms of the complex are detected but [Co^{III}(TMpyP)$(OH)_2$] is unreactive. Formation of the bis-azide and tmtu complexes shows a dependence of the rate on the *trans* labilizing effect of the first ligand and a comparison with the reactions of thiocyanate reveals that thiocyanate is sulphur-bonded in the complex.

Redox Reactions.—Reduction of [Co^{III}(TPPS)] by Cr^{2+} follows a two-term rate law with an observed rate constant[221] $k_{obs} = \{173 + (2.0/[H^+])\}[Cr^{II}]$. The first term is interpreted as outer-sphere reduction of the bis-aquo-Co^{III}(TPPS) complex but ambiguity exists for the $[H^+]^{-1}$ term between an inner-sphere axial hydroxo-bridged mechanism or an inner-sphere process where the Cr^{2+} binds to a peripheral sulphonate. Some chromium(III) is found in the product but no more is incorporated if this is recycled with chromium(II), suggesting tha the axial mechanism is operating. Consistent with this is a smaller $[H^+]^{-1}$ term in the reduction of the chromium(III)-bound complex. An axial inner-sphere hydroxo-bridged mechanism is the sole detectable[222] pathway in the chromous reduction of iron(III) meso- and deutero-porphyrin IX dimethyl esters, [Fe^{III}-MPDME] and [Fe^{III}DPDME] in the presence of 2% triton X-100. Rate constants 1.7×10^5 and 5.5×10^5 M^{-1} s^{-1} were evaluated for the two complexes at 25 °C and 0.5 M ionic strength.

Outer-sphere reduction[223] of [Fe^{III}(TMpyP)(OH_2)] and [Fe^{III}(TMpyP)-(OH_2)OH] by $[Ru(NH_3)_6]^{2+}$, with second-order rate constants 1.6×10^5 and 5.1×10^6 M^{-1} s^{-1} at 25 °C, $I = 0.5$ M, allows calculation of the Marcus self-exchange rate constants for the two species. The five-co-ordinate high-spin aquo-complex has a self-exchange rate of 1.2×10^6 M^{-1} s^{-1} whereas for the low-spin hydroxy-species the exchange rate exceeds 10^9 M^{-1} s^{-1}, consistent with a lower Franck–Condon barrier in reduction to low-spin iron(II) for the latter complex.

Pulse radiolysis reduction of [Fe^{III}PPIX] in the presence of sodium dodecyl sulphate micelles at high pH is followed by absorbance changes which are

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ascribed[224] to protonation of the iron(II)–porphyrin hydroxy-product. These changes are absent at pH 4.0 where the iron(III) complex is protonated. In a study[225] of the superoxide dismutase activity of iron complexes, [Fe^{III}TMpyP] was found to be particularly effective and the rate of reduction by superoxide was evaluated as 3×10^7 M^{-1} s^{-1} at pH 10.1. The reaction is likely to be outer-sphere though the rapid axial ligand exchange of high-spin iron(III) porphyrin complexes does not allow an inner-sphere mechanism to be ruled out. Hydrogen peroxide formed in the reaction destroys the complex but this can be prevented by the addition of catalase.

Simultaneous two-electron transfer from ascorbate to [Fe^{III}_2(TMpyP)$_2$O] dimer is proposed[226] to explain the complex kinetic behaviour of the reaction. Rate constants for the fully protonated, H_2A and monoprotonated, HA^-, forms of the reductant were evaluated to be 283 M^{-1} s^{-1} and 4 M^{-1} s^{-1} at 25 °C, I=0.1 M. The data do not, however, allow a distinction to be drawn between electron transfer at the bridging oxygen, terminal water, or porphyrin periphery. In the presence of histidine,[227] the major species is [Fe^{III}(TMpyP)(his)$_2$], which is reduced by ascorbate in an inner-sphere pathway involving protonation and dissociation of one of the axial histidine ligands. The rate constant for histidine dissociation, 25.2 s^{-1}, is remarkably similar to the rate of dissociation of methionine-80, 60 s^{-1}, in the ascorbate reduction of cytochrome *c*. Autoreduction of [Fe^{III}TPP] in the presence of piperidine proceeds[228] by proton abstraction from co-ordinated piperidine as shown by a large isotope effect in the reaction. Electron transfer produces iron(II) and a nitrogen radical.

An outer-sphere mechanism involving a 1:1 iron(II)–porphyrin–oxygen π-complex is proposed[229] to explain the oxidation of low-spin six-co-ordinate iron(II) porphyrins with axial amine ligands in amine solvents. Acid catalysis is explained by protonation of the π-bound oxygen with electron transfer giving iron(III) and the $HO_2\cdot$ radical in the rate-determining step. In aqueous media, oxidation of [Fe^{II}(TPPS)(Im)$_2$] is inhibited by Im, suggesting dissociation of an axial ligand and an inner-sphere electron transfer. An inner-sphere mechanism is also proposed[230] for the reaction of [Mn^{II}(TPPS)$(OH_2)_2$].

A dependence of the rate of reduction of Co^{II}, Fe^{II}, and Mg^{II} complexes of TPP by 2,5-di-t-butylbenzoquinone radical in THF on the metal ion suggests[231] a mechanism in which electron transfer takes place through the metal ion and is then redistributed to the porphyrin ring. Changes in geometry at the metal centre provide a barrier to reduction, which would otherwise be expected to be diffusion controlled.

[224] E. L. Evers, G. G. Jayson, and A. J. Swallow, *J. Chem. Soc., Faraday Trans. I*, 1978, **74**, 418.
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7 Molybdenum-containing Enzymes and Related Molybdenum Chemistry

Nitrogenase.—A review of the recent chemistry of nitrogen fixation has appeared.[232] The iron protein of nitrogenase from *Clostridium pasteurianum* acts as a one-electron redox system in the sequence [233]

electron donor ⟶ iron protein (Fe) ⟶ iron–molybdenum protein (Fe–Mo) ⟶ N_2

where the electron donor is dithionite and shows behaviour consistent with an Fe_4S_4* centre. For the nitrogenase system in *Azobacter vinelandii*, the redox behaviour is sensitive to the ratio of (Fe) to (Fe–Mo) which are associated in the catalytic cycle.[234] Both 1 : 1 and 2 : 1 complexes are fully active as electron transfer units but an excess of (Fe–Mo) protein causes inhibition. Association of the two proteins is a rapid process with a second-order rate constant[235] of *ca.* 10^8 M^{-1} s^{-1}, which implies a dissociation rate of *ca.* 10 s^{-1}. Since this is more rapid than the turnover rate of 6.4 s^{-1}, it is concluded that the proteins can dissociate after each electron transfer. Similar conclusions[236] are reached for nitrogenase and nitrogenase reductase.

Two binding sites for acetylene have been detected[237] by e.p.r. studies on the (Fe–Mo) protein of nitrogenase from *Klebsiella pneumoniae*. The reduction product, ethylene, has a single site and only the stronger acetylene site with an association constant in excess of 6×10^4 M^{-1} at pH 7.4 and 10 °C is catalytically active. Binding of acetylene or carbon monoxide at the second site results in a dead-end complex.

The (Fe–Mo) protein catalyses acetylene reduction in the presence of $NaBH_4$ with an activity about 8% of that shown by nitrogenase itself.[238] This supports the suggestion that the Fe–Mo cofactor is the active site of nitrogenase at which N_2 is bound and is subsequently reduced. Evidence from EXAFS studies also suggests[239] that the Fe–Mo site in the cofactor is very similar to the site in the intact protein. Considerable success in the assignment of ligand types in model molybdenum complexes[240] has led to the proposal[241] that the molybdenum in the co-factor has primarily S ligation and that whereas there appears to be no Mo=O bond in the semi-reduced resting state, on aerial oxidation of the protein features ascribed to the Mo=O chromophore are observed. An interaction of the molybdenum with Fe is also proposed and it is suggested that the site contains an Mo–Fe–S cluster.

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Thiol extrusion of the FeS centres from *Azobacter vinelandii* and *Clostridium pasteurianum* with alkyl fluorothiols allows identification of at least two Fe_4S_4* and one Fe_2S_2* cluster in the (Fe–Mo) protein.[242] A cluster model in which two Fe_4S_4* units are bridged through a corner iron on each cube by a $Mo^{IV}S_4$ unit is proposed[243] for the active site of the (Fe–Mo) cofactor. Molecular nitrogen binds axially to the central molybdenum and is π-bonded to the iron in the cubes. This weakens and activates the N≡N bond and electrons are injected stepwise *via* the two iron–sulphur cubes with successive protonation at the terminal N. This latter point is consistent with a report[244] that N—NH_2 is important in nitrogen fixation.

The synthesis of Mo–Fe–S clusters as models for the active site of the enzyme has been possible.[245–247] The clusters consist of two $MoFe_3S_4$ cubes bridged through the molybdenum corners by three S atoms but cannot be true analogues because they differ in the Fe:S:Mo ratio. Mononuclear Mo^V complexes of cysteinyl peptide ligands have also been reported.[248]

In its reactions with alkyl nitriles, nitrogenase shows some chemical selectivity whereas, in general, Mo-thiol models do not. The use of glutathione instead of cysteine increases selectivity in the models and this has prompted a study[249] of the catalytic activity of molybdenum complexes with reduced insulin. A total of four oxomolybdate ions can be bound by cysteinyl sulphur co-ordination to a single peptide chain, and in the reduction of acetylene two mechanisms are proposed: a single Mo site producing ethylene and, at higher molybdenum concentration, a dinuclear Mo_2 site producing ethane, to explain the decreasing C_2H_4:C_2H_6 ratio with increasing Mo concentration. Both nitriles and acetylenes show evidence for steric hindrance, and since the complex catalyses[250] the borohydride reduction of N_2 to NH_3 it reaffirms that substrate reductions of nitrogenase are typical of mononuclear Mo active sites and that Fe–S or Mo–Fe–S clusters are not required. The authors suggest that the nitrogenase active site is in a partially obstructed pocket in which N_2H_4 is continuously generated and is subsequently reduced and is therefore not detected to any extent in the reaction. Iron–sulphur clusters could be close to the Mo site but need not form a Mo–Fe–S cluster.

The active site of nitrogenase may involve a cycle between Mo^{VI} and Mo^{IV} during catalysis. Reversible binding of acetylene in the molybdenum(IV) complex $[OMo(S_2CNEt_2)_2]$ is a prerequisite to borohydride reduction to ethylene. It is

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[250] B. J. Weathers, J. H. Grate, N. A. Strampach, and G. N. Schrauzer, *J. Am. Chem. Soc.*, 1979, **101**, 925.

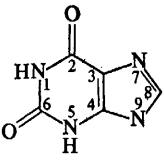
significant that ethylene does not bind to the complex and it is suggested[251] that this may serve as a nitrogenase model. The first step in the alkylation of molybdenum-bound N_2 from the complex $[Mo(N_2)_2(dppe)_2]$ (dppe = Ph_2PCH_2-CH_2PPh_2) is loss of a nitrogen molecule with a rate constant of *ca.* 1×10^{-4} s^{-1} at 20 °C in THF.[252] Subsequent attack by alkyl halide, RX, with Mo—X bond formation and R—X bond cleavage gives the reactive alkyl radical which can bind to co-ordinated nitrogen. Flash photolysis of the corresponding tungsten complex gives $[W(dppe)_2]$, which reacts with two molecules of N_2 in consecutive steps.[253] In the presence of 2-bromobutane, attack by the alkyl halide occurs only after addition of the first N_2 molecule, thereby lending support to the above mechanism. Reduction of $[Mo(N_2)_2(dppe)_2]$ by HBF_4 in THF results in formation of the N—NH_2 complex which can be trapped by reaction with a carbonyl R^1R^2CO to give the N—N=CR^1R^2 complex.[254] Photolysis of $[Mo_2X_8]^{4-}$ (X = Br or Cl) in HX results[255] in a ligand–metal charge-transfer excited state which reacts with water to give $[Mo_2X_8H]^{3-}$. Decomposition of the Mo—H intermediate results in production of H_2.

The labilizing effect of Mo—S—Mo bridges is noted[256] in a study of the thiocyanate complexation with $[Mo_2S_2O_2(C_2O_4)_2(H_2O)_2]^{2-}$. Complex formation occurs with a rate of 2.1×10^5 M^{-1} s^{-1} at 25 °C, 1.0 M ionic strength compared with 5×10^3 M^{-1} s^{-1} for $[Mo_2O_4(C_2O_4)_2(H_2O)_2]^{2-}$, the oxygen-bridged complex.[257] Dissociation rates show a similar trend.

Xanthine Oxidase.—A study[258] of the magnetic interaction between Mo^V and the FeS* clusters of the resting II form of xanthine oxidase reveals that there is no correlation between the extent of interaction and electron-transfer behaviour. It is suggested that the two centres are between 20 and 25 Å apart. Electron transfer between the distant Fe—S* and Mo centres and the flavin centre of the oxidase, which is *ca.* 20 Å from the closest paramagnetic species,[259] is rapid ($\geqslant 10^2$ s^{-1}). No absorbance changes corresponding to electron transfer were observed in a *T*-jump study, suggesting that electron transfer is temperature independent and is unlikely to involve a change in protein structure. Electron transfer through hydrophobic channels or by a quantum mechanical tunnelling process is the most likely mechanism.

Xanthine (3) can fit into the active site of xanthine oxidase in two orientations, only one of which is catalytically active.[260] Only the active complex is formed with

[251] E. A. Maatta, R. A. D. Wentworth, W. E. Newton, J. W. McDonald, and G. D. Watt, *J. Am. Chem. Soc.*, 1978, **100**, 1320.
[252] J. Chatt, R. A. Head, G. J. Leigh, and C. J. Pickett, *J. Chem. Soc., Dalton Trans.*, 1978, 1638.
[253] R. J. W. Thomas, G. S. Lawrence, and A. A. Diamantis, *Inorg. Chim. Acta*, 1978, **30**, L353.
[254] M. Hidai, Y. Mizobe, M. Sato, T. Kodama, and Y. Uchida, *J. Am. Chem. Soc.*, 1978, **100**, 5740.
[255] W. C. Trugler, D. K. Erwin, G. L. Geoffroy, and H. B. Gray, *J. Am. Chem. Soc.*, 1978, **100**, 1160.
[256] F. A. Armstrong, T. Shibahara, and A. G. Sykes, *Inorg. Chem.*, 1978, **17**, 189.
[257] G. R. Cayley and A. G. Sykes, *Inorg. Chem.*, 1976, **15**, 2882.
[258] D. J. Lowe and R. C. Bray, *Biochem. J.*, 1978, **169**, 471.
[259] J. R. Fischer and J. K. Hurst, *Bioinorg. Chem.*, 1978, **9**, 181.
[260] R. C. Bray, M. J. Barber, and D. J. Lowe, *Biochem. J.*, 1978, **17**, 653.



(3)

1-methylxanthine as substrate. The substrate binds at the anion site, directly to molybdenum through N-9, and a proton is transferred from C-8 to a position where coupling to the molybdenum(v) formed during turnover is observed.[261] A kinetic study of this process has been reported. The proton exchanges with solvent D_2O with a rate constant of 27 s^{-1} at pH 8.2 and 12 °C using 1-methylxanthine as substrate, and reduction of Mo^V to Mo^{IV} occurs with a rate constant of 1.3 s^{-1}. A similar process is noted with the cyanide-ion treated desulphoxanthine oxidase where an exchange rate with solvent D_2O of 0.4 s^{-1} was evaluated. By assuming diffusion-controlled proton transfer, pK_a values of *ca.* 8[262] and 10 for the native and desulpho proteins are consistent with experimental data. It is suggested[263] that the protonation process can be represented as

$$\text{Enz—Mo=X} + \text{H}^+ \rightleftharpoons \text{Enz—Mo—X—H}$$

where X is S or O. On deprotonation, Mo^V is oxidized to Mo^{VI} by internal electron transfer to the Fe—S* centre. A concerted attack on xanthine by a nucleophile in the active centre of the oxidase yields a covalent intermediate which breaks down to give the reaction products.[264]

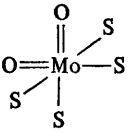
A study[265] of the molybdenum centre of the protein using EXAFS reveals that in the oxidized state the co-ordination of the metal ion involves two *cis*-M=O bonds each with a *trans* sulphur donor. A third sulphur donor, more distant and possibly from a methionine, is also proposed and there is some evidence for a distant amine donor at which protonation can occur to cause coupling to the molybdenum(v) detected during turnover. The Mo^V e.p.r. signal from the oxidase is similar to a signal from a model Mo^V oxo-compound in which there is planar S,N,N,S co-ordination.[266] Thiol extrusion of the FeS* centres in xanthine oxidase using *p*-trifluoromethylbenzenethiol reveals[267] that the eight iron atoms in the proton are arranged in four Fe_2S_2* centres.

Xanthine dehydrogenase, which is similar to xanthine oxidase, can accept six electrons on reduction. Electron transfer from the substrates xanthine and NADH is triphasic[268] with initial rapid two-electron transfer to Mo^{VI} followed by slower two-electron reduction of the flavin and subsequent one-electron addition to each of a pair of Fe_4S_4* centres. The latter two processes have rate

[261] S. Gutteridge, S. J. Tanner, and R. C. Bray, *Biochem. J.*, 1978, **175**, 869.
[262] A. D. Tsopanakis, S. J. Tanner, and R. C. Bray, *Biochem. J.*, 1978, **175**, 879.
[263] S. Gutteridge, S. J. Tanner, and R. C. Bray, *Biochem. J.*, 1978, **175**, 887.
[264] R. C. Bray, S. Gutteridge, D. A. Stotter, and S. J. Tanner, *Biochem. J.*, 1979, **177**, 357.
[265] T. D. Tullius, D. M. Kurtz, S. D. Conradson, and K. O. Hodgson, *J. Am. Chem. Soc.*, 1979, **101**, 2776.
[266] J. T. Spence, M. Minelli, P. Kroneck, M. I. Scullane, and N. D. Chasteen, *J. Am. Chem. Soc.*, 1978, **100**, 8002.
[267] D. M. Kurtz, G. B. Wong, and R. H. Holm, *J. Am. Chem. Soc.*, 1978, **100**, 6777.
[268] I. N. Fhaslain, M. J. Hynes, and M. P. Coughlan, *Biochem. J.*, 1978, **171**, 83.

constants of 21.4 and 0.091 s^{-1} for xanthine and 114.4 and 0.77 s^{-1} for NADH respectively at pH 7.8 and 25 °C.

Sulphite Oxidase.—The molybdenum site of sulphite oxidase has been investigated[269] by EXAFS in its IV, V, and VI oxidation states. The highest oxidation level has two *cis*-M=O bonds with strong *cis*-S donors which are *trans* to each other. Two further S donors are also proposed at longer distances (4). Similar co-ordination has been achieved[270] in a model complex with a quadridentate ligand and shows similar EXAFS behaviour.



(4)

Nitrate Reductase.—Reduction of nitrate by molybdenum(V) complexes of the type $[MoOCl_3L]$ and $[MoOClL^1{}_2]$, where L and L^1 are neutral or anionic bidentate ligands, proceeds[271] by rate-determining loss of Cl^- in DMF at 25 °C:

$$[MoOClL_2] \underset{}{\overset{k_1}{\rightleftharpoons}} [MoOL_2] + Cl^-$$

$$[MoOL_2] + NO_3^- \longrightarrow [MoO(NO_3)L_2]$$

$$[MoO(NO_3)L_2] \longrightarrow [Mo^{V}O_2L_2] + NO_2$$

Rate constants, k_1, for L = phen and bipy are 4.45×10^{-3} s^{-1} and 2.39×10^{-3} s^{-1} respectively and subsequent steps involve inner-sphere co-ordination of nitrate and one-electron transfer. This is suggested as a model for nitrate reductase with disproportionation of the NO_2 produced as the final step:

$$2NO_2 + H_2O \longrightarrow NO_3^- + NO_2^- + 2H^+$$

These complexes have unusual e.p.r. properties which have hitherto been considered to indicate sulphur co-ordination in model compounds and in flavoproteins.[272]

8 Oxygen Transport Proteins

Haemoglobin and Myoglobin.—Protein structure can exert control of co-operativity in ligand binding to deoxyhaemoglobin, Hb(II), either directly in small conformational changes caused by diffusion of the substrate from the protein surface to the haem centre or indirectly in conformational changes induced by substrate binding to the metal.[273] The use of transition-state theory and Hammond's postulate has enabled conclusions about the dependence of co-operativity on substrate to be drawn from kinetic data on substrate binding to

[269] S. P. Cramer, H. B. Gray, and K. V. Rajagopalan, *J. Am. Chem. Soc.*, 1979, **101**, 2772.
[270] J. M. Berg, K. O. Hodgson, S. P. Cramer, J. L. Carbin, A. Elsberry, N. Parijadath, and E. I. Steifel, *J. Am. Chem. Soc.*, 1979, **101**, 2774.
[271] R. D. Taylor, P. G. Todd, N. D. Chasteen, and J. T. Spence, *Inorg. Chem.*, 1979, **18**, 44.
[272] C. A. McAuliffe and B. J. Sayle, *Bioinorg. Chem.*, 1978, **8**, 431.
[273] A. Szabo, *Proc. Natl. Acad. Sci. USA*, 1978, **75**, 2108.

isolated α- and β-Hb(II) chains (Table 9). Faster binding reactions, k_{on}, have more reactant-like transition states and are insensitive to indirect conformational changes. Hence, in these cases, co-operativity is largely determined by k_{off}. The lower the rate, the more product-like the transition state and the greater the involvement of indirect conformational changes, although with CO and the more bulky isocyanides direct conformational controls (steric factors) may also be operative.

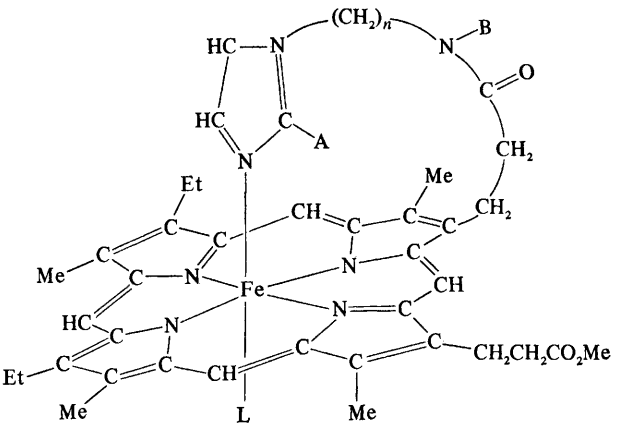
Table 9 *Formation rate constants for mammalian haemoglobin complexes with small molecules in aqueous solution at* 25 °C

Reaction	pH	$k_{on}/M^{-1}\,s^{-1}$	*Ref.*
Hb[a] + NO	7.0	2.5×10^{7}	273
O_2		5.0×10^{7}	273
CO		4.0×10^{6}	273
EtNC		3.0×10^{5}	273
BuNC		2.3×10^{5}	273
Pr^{i}NC		5.0×10^{4}	273
Bu^{t}NC	7.0	5.0×10^{3}	273
Hb(III)(II)αCO + CO	6.0	$3—5\times10^{6}$	291
Hb(III)(II)βCO + CO	6.0	4×10^{6}	291
Hb(II)(II)αCO + CO	6.0	4×10^{6}	291
+ CO	6.0	3×10^{5}	291
Hb(II)(II)βCO + CO	6.0	4×10^{6}	291
+ CO	6.0	3.5×10^{5}	291
Hb(III)$_3$(II) + CO	6.2	4.1×10^{6}	292
Hb(III)$_3$(II)[b] + CO	6.2	1.1×10^{5}	293
Hb(III)$_3$(II) + CO	6.8	5.1×10^{6}	293
Hb(III)$_3$(II)[b] + CO	6.8	1.0×10^{6}	293
Hb(III)$_3$(II) + CO	8.9	1.1×10^{7}	293
Hb(III)$_3$(II)[b] + CO	8.9	1.3×10^{7}	293
Hb(III)$_3$(II) + O_2	6.8	2.3×10^{7}	293
Hb(III)$_3$(II)[b] + O_2	6.8	9.8×10^{6}	293
Hb(III)$_3$(II) + O_2	6.8	2.2×10^{7}	293
Hb(III)$_3$(II)[b] + O_2	6.8	2.4×10^{7}	293

[a] Isolated α- and β-chains. [b] In presence of IHP.

Structural changes which occur on ligand binding to Hb(II) have been studied[274] by comparisons of crystal structures of Hb(II), Hb(II)CO, and Hb(III). Similar changes are found with the latter two structures which both have ligands in their sixth co-ordination positions. Co-operativity in Hb(II) is in part due to a quaternary structural change from a low-affinity *T*-state in which the iron(II) lies below the haem plane and is tightly bound to the proximal histidine to a high-affinity *R*-state in which the metal ion lies in the haem plane with weaker binding to the proximal base. Model studies with porphyrin ligands which have built in proximal bases with varying amounts of strain have had some success[275—277] in mimicking *R*- and *T*-state behaviour (5) (Table 10). Shortening the chelate ring

[274] J. Baldwin and C. Cliothia, *J. Mol. Biol.*, 1979, **129**, 175.
[275] J. Geibel, J. Cannon, D. Campbell, and T. G. Traylor, *J. Am. Chem. Soc.*, 1978, **100**, 3575.
[276] D. K. White, J. B. Cannon, and T. G. Traylor, *J. Am. Chem. Soc.*, 1979, **101**, 2443.
[277] V. S. Sharma, J. F. Geibel, and H. M. Ranney, *Proc. Natl. Acad. Sci. USA*, 1978, **75**, 3747.



(5) $Fe^{II}LN(B)(CH_2)_nN$

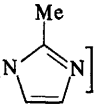
or providing steric strain in the base causes tension and induces *T*-type behaviour.[275] Although the rate of CO binding with these *T*-type models is higher than with the *R*-type models, in contrast to haemoglobin, this is ascribed to a change in mechanism from direct association, thought to be *ca.* 10^5 M^{-1} s^{-1} for *T*-state models, to base elimination. In the haem proteins, the rigid structure causes a local high concentration of base, thereby preventing the dissociative mechanism. Non-equivalence between the α- and β-chains of Hb can also be rationalized[277] if it is dependent on differences in tension of the proximal bases. With O_2, the bent FeOO grouping is sensitive to increased proximal tension by electronic and steric interactions with the porphyrin ring whereas these interactions are less significant with the linear FeCO grouping. In addition, for CO binding in Hb(II) there are steric interactions from distal residues.

An alternative explanation of the effect of the proximal base in determining *R* and *T* behaviour relies on strong hydrogen-bonding to the N-1 proton of imidazole which in effect causes deprotonation. Deprotonation of the imidazole base does have an effect on the binding rate of CO on Fe^{II}TPP complexes in toluene but this is in the opposite sense to what might be expected.[278,279] It is unlikely that this mechanism is operative but the effect could be explained by relatively small changes in the state of protonation.

The roles of the distal residues histidine and valine on substrate binding have also been investigated.[280] They help maintain restraint in the *T*-state and prevent iron(II) oxidation. Neither residue has an effect on the bent FeOO chromophore but the distal histidine interacts with linearly bound CO.

[278] B. B. Wayland, L. F. Mehne, and J. Swartz, *J. Am. Chem. Soc.*, 1978, **100**, 2379.
[279] J. C. Swartz, M. A. Stanford, J. M. Moy, B. M. Hoffman, and J. S. Valentine, *J. Am. Chem. Soc.*, 1979, **101**, 3396.
[280] P. W. Tucker, S. E. V. Phillips, M. F. Perutz, R. Houtchens, and W. S. Caughey, *Proc. Natl. Acad. Sci. USA*, 1978, **75**, 1076.

Table 10 *Rate constants for substitution reactions of haemoglobin model complexes at* 20 °C *in aqueous solution at* pH 7.3

Reaction		$k_{on}/M^{-1}\,s^{-1}$	k_{off}/s^{-1}	*Ref.*
$[Fe^{II}LO(CH_2)_2N$ 	+CO	2.3×10^{7}	4.4×10^{-2} [a]	275, 277
	$+O_2$	4.9×10^{7}	160	275, 277
$[Fe^{II}LNH(CH_2)_3N$ 	+CO	1.2×10^{8}		275
$[Fe^{II}LNH(CH_2)_3N$ 	+CO	1.1×10^{7}	1.9×10^{-2} [a]	275, 277
	$+O_2$	2.2×10^{7}	23	275, 277
	+NO	8×10^{7}		277
$[Fe^{II}LNH(CH_2)_4N$ 	+CO	1.5×10^{7}	2.4×10^{-2} [a]	275, 277
	$+O_2$	2.9×10^{7}	24	275, 277
$[Fe^{II}LNH(CH_2)_3py]$	+CO	1.2×10^{7}	3.5×10^{-2} [a]	277
	$+O_2$	1.7×10^{7}	380	277
$[Fe^{II}TPP]+CO$ [b]		5.8×10^{8}		279
$[Fe^{II}TPP(Im)]+CO$ [b]		1.1×10^{7}		279
$[Fe^{II}TPP(Im^{-})]+CO$ [b]		3.4×10^{4}		279
$[Fe^{II}DPD(Im^{-})]+CO$ [b]		1.0×10^{5}		279

[a] pH 7.0. [b] Toluene, 21 °C.

Iron(II) porphyrins, like iron(II) phthalocyanin,[281] interact reversibly with O_2 in aqueous solution but subsequently dimerize and are oxidized to iron(III). Sterically hindered *ortho*-analylamide derivatives of iron(II) porphyrins, the 'picket fence' porphyrins, prevent dimerization and hence oxidation and serve as models for the high-affinity *R*-state of Hb(II). Using as the proximal base 2-methylimidazole, which has a steric interaction with the porphyrin ring and holds the iron in its unliganded position below the ring, a low-affinity *T*-form of the complex can be produced.[282, 283] In the crystalline state, picket fence porphyrins show co-operativity very similar to that shown by haemoglobin in mechanistic and quantitative detail.[284]

[281] C. Ercolani, F. Monacelli, and G. Rossi, *Inorg. Chem.*, 1979, **18**, 712.
[282] G. B. Jameson, F. S. Molinaro, J. A. Ibers, J. P. Collman, J. I. Brauman, E. Rose, and K. S. Suslick, *J. Am. Chem. Soc.*, 1978, **100**, 6769.
[283] J. P. Collman, J. I. Brauman, D. M. Doxsee, T. R. Halbert, and K. S. Suslick, *Proc. Natl. Acad. Sci. USA*, 1978, **75**, 564.
[284] J. P. Collman, J. I. Brauman, E. Rose, and K. S. Suslick, *Proc. Natl. Acad. Sci. USA*, 1978, **75**, 1052.

A stochastic model has been applied[285] to the diffusion of O_2 through myoglobin where binding is governed by multiple barriers. The theory is applicable even at high substrate concentrations where there may be more than one O_2 molecule in the protein and where linear rate equations break down. An increase in the rate of proton exchange for tritium at pH 7.4 in oxyhaemoglobin, Hb(II)O_2, suggests[286] greater solvent accessibility compared with Hb(III)CN, which shows a normal response. A corresponding decrease in the solvent accessibility of the deoxy-form at the same pH with a difference around 17 protons between oxy- and deoxy-forms points to a pH-induced conformational change in which there is a rearrangement of the strongly bound water at the interfaces between the α- and β-subunits.

The high-affinity *R*- and low-affinity *T*-states of fish haemoglobins are readily interconverted by changes in pH.[287, 288] At pH < 6 and 20 °C, chain heterogeneity is detected in the reactions of the *T*-state with CO while under more alkaline conditions, pH > 8.5, reactions of the *R*-state are monophasic. Experiments at intermediate pH are readily accounted for by a conformational stability constant which varies from 4×10^7 at pH 6.0 to 8 at pH 8.5. Light increases CO dissociation from both *R*- and *T*-states.[289] The effects of pH on tadpole haemoglobin have also been investigated.[290]

Binding of CO to the products of reduction of partially reduced met-Hb(III) derivatives has been examined.[291] Reductions of one haem centre in Hb$^{\alpha}$CO and Hb$^{\beta}$CO (met forms with CO bound to the reduced α- and β-chains respectively) lead to species which react rapidly with CO, showing *R*-type behaviour. Reductions of both haem centres at pH 6 yield species exhibiting biphasic CO binding behaviour suggesting the presence of both *R*- and *T*-states but giving no evidence for chain heterogeneity. The kinetics of CO binding to singly reduced met-Hb(III), where the reduction site is presumed to be distributed between α- and β-chains, yield a binding rate at pH 6.2 which is similar to that of the *R*-conformers of other deoxy-Hb species.[292] In the presence of inosine hexaphosphate (IHP), which induces a conformational change producing the *T*-state, the rate is decreased by a factor of 40. Increasing the pH to > 8.0 in the presence of IHP re-forms the *R*-state,[293] and though the origin of this transition is not fully understood it is not connected with the spin-state change on ionization of bound water in Hb(III). Co-operativity in the consecutive binding[294] of two substrates on the α-chains of Hb$^{\alpha}$ is most pronounced with O_2 as substrate although two conformational changes in the iron(III) β-chain were detected after the binding of each of the two CO molecules.

[285] N. Alberding, H. Franenfelder, and P. Hanggi, *Proc. Natl. Acad. Sci. USA*, 1978, **75**, 26.
[286] B. E. Hedhind, P. E. Halloway, B. E. Halloway, E. S. Benson, and A. Rosenberg, *J. Biol. Chem.*, 1978, **253**, 3702.
[287] W. A. Saffran and Q. H. Gibson, *J. Biol. Chem.*, 1978, **253**, 3171.
[288] W. A. Saffran and Q. H. Gibson, *J. Biol. Chem.*, 1979, **254**, 1666.
[289] S. J. Torkelson and Q. H. Gibson, *J. Biol. Chem.*, 1978, **253**, 7331.
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[291] H. S. Rollema, A. Raap, and S. H. DeBruin, *Eur. J. Biochem.*, 1978, **83**, 313.
[292] K. Ho, M. H. Klapper, and L. M. Dortman, *J. Biol. Chem.*, 1978, **253**, 238.
[293] Y. A. Ilan, A. Samuni, M. Chevion, and G. Czapski, *J. Biol. Chem.*, 1978, **253**, 82.
[294] N. Makino, Y. Sugita, and T. Nakamura, *J. Biol. Chem.*, 1979, **254**, 2353.

Spin label studies reveal[295] that the extent of deoxygenation of Hb shows no preference in the α- and β-chains. The presence of IHP, however, causes deviations which imply that the α-subunit exhibits preferential binding. Inosine hexaphosphate can stabilize[296] Hb with asparagine-102 replaced by threonine in a form with a deoxy-quaternary structure (*T*-state) even when bound with CO. The protein has a low CO affinity and is almost devoid of co-operativity with a second-order binding rate of 1.03×10^5 M^{-1} s^{-1}. There is no evidence for significant chain non-equivalence. Kinetic data on Hb with a serine in place of tryptophan in the α,β contact region have also been reported.[297]

The reactions of apo-Hb with CO complexes of protoferrohaem, FePCO, involve initial interaction at a hydrophobic region on the protein surface after which the protein folds around the haem:[198]

$$\text{Apo-Hb} + \text{FePCO} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{complex} \xrightarrow{k_2} \text{HbCO}$$

Rates, k_1k_2/k_{-1} ,for the negatively charged haem and neutral haem dimethyl ester are 6×10^7 and 1×10^7 M^{-1} s^{-1} respectively and are similarly affected by the presence of IHP, indicative of an induced protein conformational change rather than an electrostatic interaction. The CO and O_2 binding properties of Hb reconstituted with proto-, meso-, and deutero-ferrohaem derivatives have also been reported.[299]

Dissociation of NO from Hb shows co-operativity similar to the corresponding reaction with O_2 and is biphasic in the presence of IHP, indicating *T* (k_{off} = 10^5 s^{-1}) and *R* ($k_{off} = 10^3$ s^{-1}) forms.[300] The rate differences are ascribed to weakening of the proximal Fe—N bond in the *R* to *T* transition which allows movement of the iron into the haem plane and stronger bonding to the substrate. Steric interactions on the distal side affect only CO. Whereas binding kinetics of NO to Hb are rapid and unco-operative,[301, 302] the corresponding reactions with the isostructural Mn-substituted Hb are slow and co-operative, similar to the Hb interaction with CO.[302] A comparison of the two reactions with NO suggests that the influence of *T*-state structure in ^{Mn}Hb is exerted after the initial metal–ligand encounter since NO can reach the manganese ion about 700 times faster than it is bound.

Molecular tunnelling processes have been detected[303] in the recombination of HbCO after flash photolysis at low temperature (< 10 K) and attempts to analyse the data using non-adiabatic molecular group transfer theory have met with reasonable success. At higher temperatures, (< 20 K) a non-exponential Arrhenius pathway is detected suggesting a distribution of activation enthalpies depend-

[295] T. Asakura and P.-W. Lau, *Proc. Natl. Acad. Sci. USA*, 1978, **75**, 5462.
[296] C. L. Castillo, S. Ogawa, and J. M. Salhany, *Arch. Biochem. Biophys.*, 1978, **185**, 504.
[297] J. Sasaki, T. Imamura, T. Yanase, D. H. Atha, A. Riggs, J. Bonaventura, and C. Bonaventura, *J. Biol. Chem.*, 1978, **253**, 87.
[298] A. H. Chu and E. Bucci, *J. Biol. Chem.*, 1979, **254**, 3772.
[299] G. Falcioni, E. Fioretti, G. Giordina, I. Ariani, F. Ascoli, and M. Brunori, *Biochemistry*, 1978, **17**, 1229.
[300] V. S. Sharma and H. M. Rannay, *J. Biol. Chem.*, 1978, **253**, 6467.
[301] F. Taketa, W. E. Antholine, and J. Y. Chen, *J. Biol. Chem.*, 1978, **253**, 5448.
[302] Q. H. Gibson and B. M. Hoffman, *J. Biol. Chem.*, 1979, **254**, 4691.
[303] J. Jortner and J. Ulstrup, *FEBS Lett.*, 1979, **99**, 1.

ent on protein conformation.[304] Whereas the rate at these low temperatures is determined mainly by the tension in the proximal histidine and by changes in the iron spin state,[303, 304] at higher temperatures the opening of a hole in the protein to allow access by the substrate to the metal site, involving widespread conformational changes, becomes important.[304]

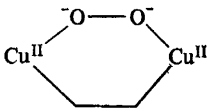
The very fast reactions following laser photolysis of HbCO have been detected[305] on the picosecond time-scale, revealing a dissociation rate process with a rate constant of 8.9×10^{10} s^{-1}, which is of the order of a vibration period. On this time-scale, the CO is not necessarily removed from the protein cavity. On the nanosecond time-scale, recombination phenomena have been interpreted[306] in terms of a direct recombination process which is enhanced at low temperatures where the CO cannot escape the cavity, rather than as a tertiary structural change. CARS experiments suggest[307] that the iron undergoes an out of the haem-plane displacement within 6 ns of CO dissociation. Spin-state changes in aquomethaemoglobin have also been examined using *T*-jump,[308, 309] and the spin transitions in $Hb(III)N_3^-$ and $Mb(III)N_3^-$ induced by IHP binding have been reported.[310] A study of the kinetics of the diffusion-controlled reaction of Hb with CO in glycerol–water mixtures of high viscosity has been published.[311]

Haemocyanin.—Haemocyanin is a very large protein with 7—8 molecular oxygen binding domains each of *ca.* 50 000 molecular weight. The protein from *Murex fulvescens* can be fractionated into two subunits that are functionally similar but structurally different.[312] Both subunits show biphasic oxygen dissociation rates of *ca.* 60 s^{-1} (30%) and 16 s^{-1} (70%) at pH 8.9 where the rates show a maximum. Six subunits of 750 000 molecular weight are found[313] in *Penaeus setiferus*, and a kinetic study of the allosteric effectors H^+, which decreases O_2 affinity, and Ca^{2+} and Cl^-, which increase affinity, has been reported. In order to explain co-operative factors, a three-state model involving low-affinity T_6, high-affinity R_6, and intermediate T_3R_3 forms is required. For *Helix pomatia*, which has twenty subunits of molecular weight 50 000, each with an oxygen binding site, a two-state model suffices.[314] At pH 8.2 and 20 °C, the *T*-state has binding and dissociation rate constants of 1.3×10^6 M^{-1} s^{-1} and 300 s^{-1} respectively and the rate of the allosteric change $T \rightarrow R$ is 15—120 s^{-1}, which is slower than the binding rate for the *R*-form.[315] Studies on the subunit

[304] N. Alberding, S. S. Chan, L. Eisenten, H. Franenfelder, D. Good, I. C. Gunsalus, T. M. Norlund, M. F. Perutz, A. H. Reynolds, and L. B. Sorensen, *Biochemistry*, 1978, **17**, 43.
[305] L. J. Noe, W. G. Eisert, and D. M. Rentzepis, *Proc. Natl. Acad. Sci. USA*, 1979, **75**, 573.
[306] D. A. Duddell, R. J. Morris, and J. T. Richards, *J. Chem. Soc., Chem. Commun.*, 1979, 75.
[307] R. F. Dallinger, J. R. Nestor, and T. G. Spiro, *J. Am. Chem. Soc.*, 1978, **100**, 6251.
[308] A. Bracht, B. R. Eufinger, A. Redhardt, and J. Schlitter, *Biochem. Biophys. Res. Commun.*, 1979, **86**, 585.
[309] U. Dreyer and G. Ugenfritz, *Biochem. Biophys. Res. Commun.*, 1979, **87**, 1011.
[310] M. F. Perutz, J. K. M. Sanders, D. H. Chenery, R. W. Noble, R. K. Pennelly, L. W.-M. Fung, C. Ho, I. Giannini, D. Porschke, and H. Winkler, *Biochemistry*, 1978, **17**, 3640.
[311] B. B. Hasinoff, *Arch. Biochem. Biophys.*, 1978, **191**, 110.
[312] M. Brouwer, M. Ryan, J. Bonaventura, and C. Bonaventura, *Biochemistry*, 1978, **17**, 2810.
[313] M. Brouwer, C. Bonaventura, and J. Bonaventura, *Biochemistry*, 1978, **17**, 2148.
[314] L. Zolla, H. A. Kuiper, P. Vecchini, E. Antonini, and M. Brunori, *Eur. J. Biochem.*, 1978, **87**, 407.
[315] R. van Driel, H. A. Kuiper, E. Antonini, and M. Brumori, *J. Mol. Biol.*, 1978, **121**, 431.

confirm that no protons are taken up when oxygen binds to either *T*- or *R*-state.[316]

The oxygen binding site of the protein contains two copper atoms which can be oxidized by H_2O_2 to give the diamagnetic met form.[317] The half-met enzyme is prepared by nitrite oxidation[318] and is paramagnetic ($Cu^{II}\cdots Cu^{I}$) with one unpaired electron on copper(II) in a D_{4h} site. The other copper is in a copper(I) state *ca.* 6 Å distant. Small inorganic ligands such as CN^-, NO_2^-, N_3^-, and $MeCO_2^-$ can bind to the half-met and the met-apo[319] form where the copper(I) has been removed. Removal of these small ligands is more difficult in the half-met enzyme, which suggests that copper(I) plays a part in the binding, possibly by way of a bridge. This is confirmed by electronic spectroscopy[320] with the azide complex to which a further azide ion can also be bound. Studies on methaemocyanin suggest[321] the presence of an endogenous bridge between the copper(II) ions, and a model for oxyhaemocyanin in which two tetragonal copper(II) ions are bound both by an exogenous peroxide (O_2^{2-}) and by an endogenous protein ligand is proposed.[322] The peroxide is bound end to end rather than perpendicular to the copper–copper distance (6). The ligand bridging behaviour is adequately



(6)

described by this model.[323] Ligands that force the copper atoms more than 5 Å apart break the endogenous bridge and expose a second ligand binding site. Thioacetamide binds to haemocyanin reversibly and displaces molecular oxygen by causing a conformational change which modifies the O_2 binding site.[324] The binding site is close to the surface of the protein.[325]

Haemocyaninin model complexes including a dinuclear 'face to face' inclusion complex in which copper(II) ions are bound by one oxygen, two nitrogen, and two sulphur donors in a macrobicyclic ligand have been reported.[326] A mononuclear five-co-ordinate complex of copper(I) with two imidazole ligands

[316] H. A. Kuiper, M. Brunori, and E. Antonini, *Biochem. Biophys. Res. Commun.*, 1978, **82**, 1062.
[317] P. E. McMahill and H. S. Musa, *Biochem. Biophys. Res. Commun.*, 1978, **84**, 749.
[318] R. S. Himmelwright, N. C. Eickman, and E. I. Solomon, *Biochem. Biophys. Res. Commun.*, 1978, **81**, 237.
[319] R. S. Himmelwright, N. C. Eickman, and E. I. Solomon, *Biochem. Biophys. Res. Commun.*, 1978, **81**, 243.
[320] R. S. Himmelwright, N. C. Eickman, and E. I. Solomon, *Biochem. Biophys. Res. Commun.*, 1978, **84**, 300.
[321] R. S. Himmelwright, N. C. Eickman, and E. I. Solomon, *Biochem. Biophys. Res. Commun.*, 1979, **86**, 628.
[322] N. C. Eickman, R. S. Himmelwright, and E. I. Solomon, *Proc. Natl. Acad. Sci. USA*, 1979, **76**, 2094.
[323] R. S. Himmelwright, N. C. Eickman, and E. I. Solomon, *J. Am. Chem. Soc.*, 1979, **101**, 1576.
[324] J. M. Guo, C. Chang, N. C. Li, and K. T. Douglas, *Biochemistry*, 1978, **17**, 452.
[325] N. Shaklai, A. Gafni, and E. Daniel, *Biochemistry*, 1978, **17**, 4438.
[326] R. Louis, Y. Agnus, and R. Weiss, *J. Am. Chem. Soc.*, 1978, **100**, 3604.

binds O_2 reversibly as a copper(II)–O_2^- complex which is paramagnetic. Peroxide bridging between two copper(I) units in a diamagnetic structure is also detected.[327]

9 Metal-catalysed Non-redox Processes

Zinc Enzymes.—The similarities in the active-site geometries of zinc enzymes have been examined.[328] In all cases the metal ion is bonded by three protein ligands, one of which is histidine, and H_2O in a distorted tetrahedral arrangement. The substrate may bind either by displacing the water molecule or at a fifth co-ordination site. A group with the function to abstract a proton from water was found to be in a constant spatial arrangement with respect to the zinc. Tetrahedral models for zinc active sites with ligands containing three imidazole donors have been prepared.[329] The spectroscopic and thermodynamic properties of the complexes, however, suggest that the geometry is not quite right to provide a good mimic for carbonic anhydrase.

Carboxypeptidase.—The formation of a diazo-derivative of tyrosine-248 of carboxypeptidase A (CPA) with *p*-arsanilic acid provides a probe into the active centre of the enzyme. However, a conformational change on diazo-coupling to tyrosine-248 makes tyrosine-198 accessible to nitration.[330] Circular dichroism studies[331] of the diazo-enzyme with the inhibitor *β*-phenylpropionate reveal four substrate binding sites, three of which overlap. The substrate 3,3-diphenylpropanoate activates the CPA-catalysed hydrolysis of benzoylglycyl-L-phenylalanine but inhibits ester hydrolysis of benzoylglycyl-*O*-phenylalanine non-competitively.[332] The similarity of the activation and inhibition constants for the two processes suggests that 3,3-diphenylpropanoate binds at a single modifier apolar site near phenylalanine-279, tyrosine-198, and the guadinium of argenine-71 and close to the peptide and ester substrate binding sites. Both competitive and non-competitive inhibition of peptide hydrolysis is shown by 3-phenylpropanoate[333] and it is proposed that the carboxyl of the inhibitor binds to the zinc atom, giving the correct spatial arrangement to allow the phenyl side-chain to slide into the apolar pocket between phenylalanine-279 and tyrosine-198. Although this does not interfere with peptide binding, it does prevent catalysis by an inner-sphere mechanism in which the peptide carbonyl is co-ordinated to the zinc. Competitive inhibition results with esters which are suggested to bind through the zinc atom. Discrete steps in the interaction of arsanilazo-CPA with hydrolysis products or substrates which hydrolyse slowly have been detected using *T*-jump.[334] A mechanism involving diffusion-controlled enzyme–substrate complex formation followed by a conformational change before hydrolysis is

[327] M. G. Simmons and L. J. Wilson, *J. Chem. Soc., Chem. Commun.*, 1978, 634.
[328] P. Argos, R. M. Garavito, W. Eventoff, M. G. Rossman, and C. I. Branden, *J. Mol. Biol.*, 1978, **126**, 141.
[329] C. C. Tang, D. Davalian, P. Huang, and R. Breslow, *J. Am. Chem. Soc.*, 1978, **100**, 3918.
[330] L. Cueni and J. F. Riordan, *Biochemistry*, 1978, **17**, 1834.
[331] G. M. Alter and B. L. Vallee, *Biochemistry*, 1978, **17**, 2212.
[332] J. F. Sebastian and W.-Y. Lo, *Can. J. Biochem.*, 1978, **56**, 329.
[333] R. Poorman, M. Kuo, D. I. Johnson, S. Liu, and J. F. Sebastian, *Can. J. Biochem.*, 1979, **57**, 357.
[334] L. W. Harrison and B. L. Vallee, *Biochemistry*, 1978, **17**, 4359.

proposed. By studying the interaction with glycyl-L-phenylaniline and with the product L-phenylalanine, a complete kinetic picture can be built up as in Scheme 5, with K_1 and K_5 2.1×10^4 M^{-1} and 9.9×10^3 M^{-1} respectively, k_3, the hydrolysis

$$\text{CPA} + \text{Gly-L-Phe} \overset{k_1}{\rightleftharpoons} \text{CPA,Gly-L-Phe} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \{\text{CPA,Gly-L-Phe}\} \xrightarrow{k_3} \{\text{CPA,L-Phe}\}$$

$$\{\text{CPA,L-Phe}\} \underset{k_4}{\overset{k_{-4}}{\rightleftharpoons}} \text{CPA} + \text{L-Phe} \overset{K_5}{\rightleftharpoons} \text{CPA,L-Phe}$$

Scheme 5

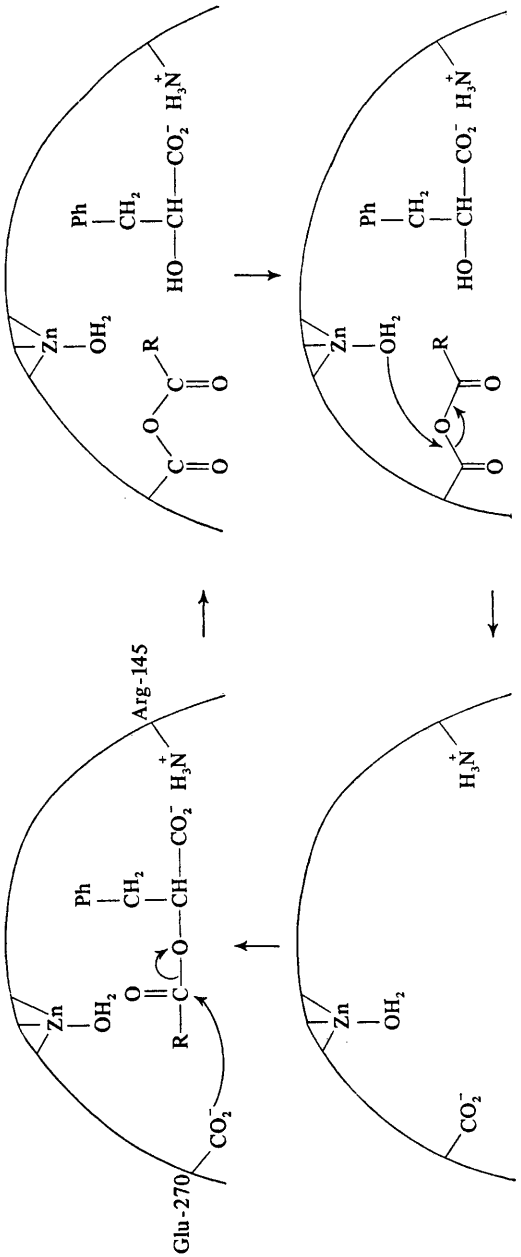
rate constant 1.0×10^{-2} s^{-1}, and the other constants 3.25×10^3 s^{-1} (k_2), 1.0×10^3 s^{-1} (k_{-2}), 1.75×10^3 s^{-1} (k_4), and 1.16×10^3 s^{-1} (k_{-4}) at 25 °C, pH 8.0, and 0.5 M ionic strength.

Nitration of the active-site tyrosine residues by $C(NO_2)_4$ is faster in the Zn-reconstituted enzyme than in the native enzyme, implying that there are micro-environmental changes between the two forms.[335] The nitration reactivity can be correlated with the length of time the protein resides in the apo-state.

The role of the metal ion in ester hydrolysis catalysed by CPA has been examined with both Zn^{2+}- and Co^{2+}-substituted enzymes.[336] When the terminal carboxyl of the substrate is electrostatically linked to argenine-145 and the aromatic side-chain lies in a hydrophobic pocket, the only residues close enough to the substrate to enter catalysis are glutamate-270, tyrosine-248, the metal ion, and its associated water. Low-temperature studies aid the elucidation of the mechanism. Between −25 and −45 °C in ethylene glycol–water mixtures two kinetically discrete processes are detected, the slower of which corresponds to the catalytic rate constant. The faster reaction is interpreted as deacylation of a mixed anhydride acyl–enzyme intermediate formed by nucleophilic attack by glutamate-270 on the substrate (Scheme 6). Differences in the acidity dependences of the catalytic rate constant with the metal ions Zn^{2+} (pK_a 6.1) and Co^{2+} (pK_a 4.9) suggest that ionization of the metal-bound water molecule occurs and is involved in the decay of the anhydride. The catalytic rate constant shows an isotope effect in D_2O.

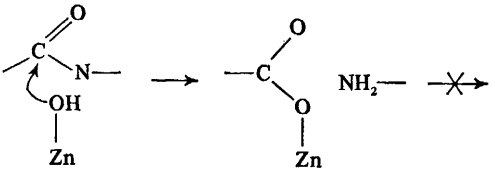
Oxidation of the Co^{2+}-substituted CPA by *m*-chloroperbenzoic acid results in the clean formation[337] of the Co^{3+} substitution-inert species which has a half-life of *ca.* 30 min at 25 °C. The spectrum is consistent with a tetrahedral environment with histidines-69 and -196, glutamate-72, and a water molecule as donors. Peptide substrate Gly-Gly-Gly-L-Phe binds to the enzyme but is not hydrolysed, showing that a metal carbonyl mechanism, in which the substrate carbonyl is activated by inner-sphere binding to the metal ion and displacing co-ordinated water, is operating. Subsequent nucleophilic attack by glutamate-270 at the carbonyl is proposed (Scheme 7). The alternative inner-sphere mechanism, Scheme 8, involving a metal anhydride, would result in a single turnover which

[335] M. Zisapel, *Biochem. Biophys. Res. Commun.*, 1978, **81**, 28.
[336] M. W. Makinen, L. C. Kuo, J. J. Dymowski, and S. Jaffer, *J. Biol. Chem.*, 1979, **254**, 356.
[337] H. E. Van Wert and B. L. Vallee, *Biochemistry*, 1978, **17**, 3385.



Scheme 6

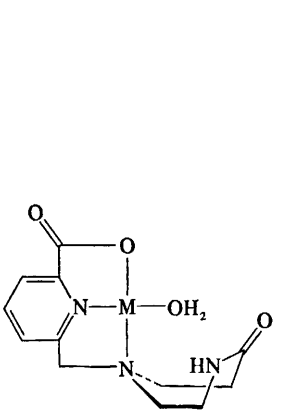
Scheme 7



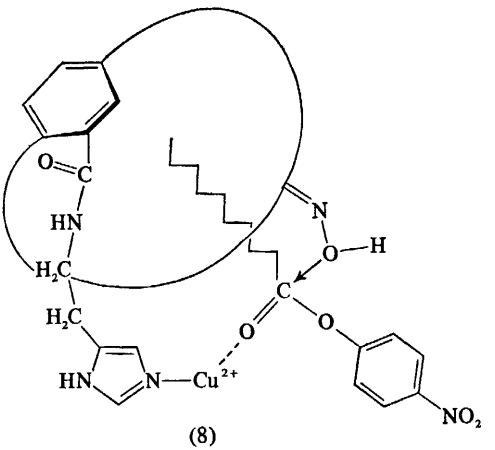
Scheme 8

is not observed. Corresponding conclusions with the ester substrate Gly-Gly-Gly-L-OPhe were not possible since niether binding nor hydrolysis was detected.

Rapid amide hydrolysis by copper and zinc complexes of a ligand which mimics[338] the carboxypeptidase active site (7) has been observed. The metal is held perpendicular to the amide plane, and at pH 7.6 and 50 °C hydrolysis occurs 2×10^5 times faster in the presence of zinc than in its absence. Copper is a more potent catalyst. A metal-dependent pK_a ($\geqslant 8.5$ for Zn^{2+} and 7.6 for Cu^{2+}) is consistent with a mechanism in which the amide carbonyl is attacked by a co-ordinated hydroxyl nucleophile. A more sophisticated model[339] with a [20]paracylcophane which has a nucleophilic and a metal binding site attached (8) catalyses the hydrolysis of *p*-nitrophenyl hexadecanoate. The mechanism



(7)



(8)

involves substrate binding in the hydrophobic cleft and nucleophilic attack by the oxime nitrogen. The binding constant of 9.1×10^4 M^{-1} in 11% ethanol, 1% dioxan at pH 8.2 and 40 °C is not affected by the absence of the metal ion, copper, which functions by interacting with the ester carbonyl and activating the bond to nucleophilic attack. The catalysis rate constant is 8.7×10^{-3} s^{-1}.

The kinetics of substitution of bivalent metal ions into the metal ion site of apo-CPA have been investigated.[340] Although the complex pH dependence was not analysed, the rates (Table 11) are as high as those for formation of the

[338] J. T. Groves and R. M. Dias, *J. Am. Chem. Soc.*, 1979, **101**, 1033.
[339] Y. Murakami, Y. Aoyama, M. Kida, and J.-i. Kikuchi, *J. Chem. Soc., Chem. Commun.*, 1978, 494.
[340] E. J. Billo, K. K. Brito, and R. G. Wilkins, *Bioinorg. Chem.*, 1978, **8**, 461.

Table 11 *Rate constants for substitution reactions of metal ions with apocarboxypeptidase A in aqueous solution at* 25 °C, pH 7.0, *and* 1.0 M *ionic strength*[340]

Reaction	$k_1/M^{-1}\,s^{-1}$	k_{-1}/s^{-1}
apoCPA + Mn^{2+}	1.7×10^5	—
Co^{2+}	3.0×10^4	8×10^{-3}
Ni^{2+}	5.0×10^3	3×10^{-5}
Zn^{2+}	7.0×10^5	4×10^{-4}
Cd^{2+}	9.0×10^5	—

corresponding metal ion complexes of 1,10-phenanthroline, suggesting considerable flexibility in the protein binding site. This contrasts with results for carbonic anhydrase where the rates are lower and exhibit a greater range, consistent with a more rigid binding site.

Carbonic Anhydrase. The dehydration of bicarbonate catalysed by human[341] and spinach[342] carbonic anhydrase, CA, has been reported:

$$HCO_3^- + H_3O^+ \rightleftharpoons 2H_2O + CO_2$$

In *N*-methylimidazole buffer at 25 °C and 0.01 M ionic strength, the spinach reaction involves enzyme–substrate complex formation with an association constant of 29 M^{-1} that is independent of pH. On the other hand the catalysis constant shows a variation with pH with dehydrase activity dependent on protonation of a titratable group with pK_a 7.7. The catalysis rate constant for the acidic form is $1.4\times10^5\ s^{-1}$.

Bovine erythrocyte CA shows both oxonase and esterase activity with dimethyl 2,4-dinitrophenyl phosphate and 2,4-dinitrophenyl acetate respectively.[343] Both processes show similar pH dependencies with pK_a values of 7.37 (oxonase) and 7.53 (esterase) and maximum activity in the basic form. Inhibition by acetazolamide at pH 8.95 yields the same inhibition constant for both reactions, implying involvement of the active-site zinc to the same extent in both processes. Methyl and ethyl pyruvate are susceptible to hydrolysis,

$$MeCOCO_2R + H_2O \longrightarrow MeCOCO_2H + ROH$$

and to hydration,

$$MeCOCO_2R + H_2O \longrightarrow MeC(OH)_2CO_2R$$

and both processes are catalysed by bovine CA.[344] This allows examination of the dual function of the enzyme on the same substrate. The reactions have similar pH dependencies with pK_a values of *ca.* 7, but the substrate binding constants for hydration, 2.6 M^{-1} for methyl pyruvate, are smaller than the corresponding values for hydrolysis, 6.7 M^{-1} for the same substrate at 25 °C, pH 6.5, and ionic strength 3.5 M. This and different inhibition constants for acetazolamide for the two processes suggest that different modes of substrate binding and hence different courses of enzyme action are involved.

[341] I. Simonsson, B.-H. Jonsson, and S. Lindskog, *Eur. J. Biochem.*, 1979, **93**, 409.
[342] Y. Pocker and R. R. Miksch, *Biochemistry*, 1978, **17**, 1119.
[343] Y. Pocker and S. Sarkanen, *Biochemistry*, 1978, **17**, 1110.
[344] Y. Pocker, J. E. Meany, B. C. Davis, J. Arrigoni, and J. E. Stein, *J. Am. Chem. Soc.*, 1978, **100**, 2883.

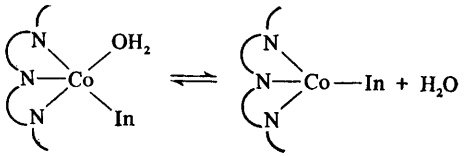
Inhibition of bovine CA by 5-methyl-1,10-phenanthroline[345] and aniline[346] involves direct tertiary co-ordination to the zinc ion. With the latter reagent, however, ^1H n.m.r. relaxation of metal-bound water is unchanged on aniline co-ordination suggesting either that a histidine ligand is replaced or that a fifth co-ordination site is available. By contrast, methanol binds at a hydrophobic region *ca.* 6 Å from the metal site and shows non-competitive inhibition of *p*-nitrophenyl acetate hydrolysis activity.[346]

Carboxymethylation of histidine-200 in human CAB provides an n.m.r. probe into the active site of the enzyme.[347] Two pK_a values of 7.2 and 9.9 are noted,[348] the lowest of which is ascribed to ionization of the histidine. Around pH 8, n.m.r. relaxation data show[347] that the residue is immobile and the abnormal chemical shift implies carboxyl co-ordination to the zinc ion which is 6 Å distant. The second pK_a is consistent with dissociation of the carboxyl and formation of a zinc hydroxy-species.

Addition of oxyhaemoglobin to CA causes[349] a decrease in the CO_2 self-exchange rate and an increase in the hydration activity measured by ^{18}O tracer studies of exchange between CO_2 molecules and CO_2/H_2O respectively at 25 °C. This is explained in terms of proton transfer from HbO_2 to the active CA site by way of a complex[350] with a stability constant between 10^5 and 10^7 M^{-1}.

A number of proton exchange studies of Co^{II}-substituted CA have been reported. Buffer[351] shifts the kinetic pK_a value derived from ^1H relaxation studies on bovine CA from pH 8 (unbuffered) to pH 7, which is the value derived from spectroscopic measurements. This is interpreted in terms of an exchanging proton in unbuffered solution which controls access to the cobalt(II) but is not bound to it. In a further study,[352] it is asserted that at high pH, where a co-ordinated water molecule is ionized, unless there is a fifth aquo-ligand, the exchanging water cannot be bound to the metal. Correction of the solvent relaxation behaviour[353] for diamagnetic effects allows two pK_a values of 6.11 and 8.5 to be determined for bovine CA with a maximum relaxation rate in the basic form. The metal ions in cobalt(II) bovine CA and its derivatives with a number of inhibitors, In, are pseudotetrahedral and proton relaxation can be interpreted[354] in terms of exchangeable protons on metal co-ordinated water over the pH range 6—9. Electronic spectra reveal that some inhibitors such as NCO^- replace co-ordinated water whereas others such as NCS^- take up a fifth co-ordination site. It is apparent that there is a finely balanced equilibrium, as shown in Scheme 9, which is dependent on hydrogen-bonding and other factors around the metal ion site.

[345] Y. Kidani and J. Hirose, *Biochem. Biophys. Res. Commun.*, 1978, **82**, 506.
[346] J. O. C. Westerik, B. Sarkar, R. Deslauriers, and I. C. P. Smith, *J. Biol Chem.*, 1978, **253**, 8499.
[347] P. K. Jellers, W. McI. Sutherland, and R. G. Kalifah, *Biochemistry*, 1978, **17**, 1305.
[348] A. J. M. S. Winterkamp, I. M. Armitage, J. H. Prestegard, J. Slomski, and J. E. Coleman, *Biochemistry*, 1978, **17**, 3730.
[349] D. N. Silverman, C. Tu, and G. C. Wynns, *J. Biol. Chem.*, 1978, **253**, 2563.
[350] D. N. Silverman, L. Backman, and C. Tu, *J. Biol. Chem.*, 1979, **254**, 2588.
[351] M. E. Fabry, *J. Biol. Chem.*, 1978, **253**, 3568.
[352] G. S. Jacob, R. D. Brown, and S. H. Koenig, *Biochem. Biophys. Res. Commun.*, 1978, **82**, 203.
[353] J. W. Wells, S. I. Sandel, and S. H. Koenig, *Biochemistry*, 1979, **18**, 1989.
[354] I. Bertini, G. Canti, C. Luchinat, and A. Scozzafava, *J. Am. Chem. Soc.*, 1978, **100**, 4873.



Scheme 9

Oxidation of cobalt(II) bovine CA by H_2O_2 is inhibited[355] by specific inhibitors of CA, suggesting an inner-sphere mechanism. Reduction of the resultant cobalt(III)-substituted enzyme by dithionite also proceeds by an inner-sphere process and the rates of binding of CN^- and N_3^- to the cobalt(III) enzyme have been determined as 6.0×10^{-2} and 7.0×10^{-2} M^{-1} s^{-1} respectively, faster than those of low-spin cobalt(III) inorganic complexes. The cobalt(III) in the carbonic anhydrase is octahedral.

Dissociation of Zn^{2+} from CA is slow[356] with a half-life of *ca.* 3 years at pH 7.0 and 4 °C. It is enhanced by lowering the pH and by the presence of chelating agents such as 1,10-phenanthroline. The denaturing mechanism involves protonation of nitrogen on the imidazole side-chains of one of the co-ordinating histidine ligands, 93, 95, or 118, and a second protonation with a pK_a of *ca.* 7.7 has an effect. It is evident that the metal has both labile and inert characteristics, the latter due to the rigidity of the enzyme binding site.

Other Zinc Enzymes. Studies aimed at elucidating the mechanism of dimeric alcohol dehydrogenase enzymes have also been reported. Cobalt(II) can replace zinc(II) at the two catalytic and non-catalytic sites in the liver enzyme, LADH.[357] Reduction of pyridinealdehyde derivatives by the yeast enzyme has been examined.[358] In acetonitrile solution, reduction by NADH analogues is catalysed by metal ions and mechanistic studies of the reaction have been carried out.[359,360] Biomimetic studies of zinc-catalysed carbonyl reduction have also been reported.[361]

Concanavalin A.—The interactions of metal ions with the transition-metal S1, and calcium-ion, S2, binding sites of concanavalin A have attracted some attention. Each protomer of molecular weight 27 000 has one S1 and one S2 site and the protein exists in a dimeric form, pH < 5.5, and tetrameric form, pH > 7.0. Metal ion binding has been studied using the fluorescence quenching of 4-methylumbelliferyl-α-D-mannopyranoside (MUM), a sugar residue which binds to the protein in its various metallated forms:[362]

$$M^{2+} + \text{apoConA} \underset{}{\overset{k_1}{\rightleftharpoons}} {}^{M^{2+}}\text{ConA}$$

$${}^{M^{2+}}\text{ConA} + \text{MUM} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} {}^{M^{2+}}\text{ConA MUM}$$

355 H. Shinar and G. Navon, *Eur. J. Biochem.*, 1979, **93**, 313.
356 A. Y. Romans, M. E. Graicken, C. H. Lochmüller, and R. W. Henken, *Bioinorg. Chem.*, 1978, **9**, 217.
357 A. J. Sytkowski and B. L. Vallee, *Biochemistry*, 1978, **17**, 2850.
358 M. Hughes and R. H. Prince, *J. Inorg. Nucl. Chem.*, 1978, **40**, 719.
359 M. Hughes and R. H. Prince, *J. Inorg. Nucl. Chem.*, 1978, **40**, 703.
360 M. Hughes, R. H. Prince, and P. Wyeth, *J. Inorg. Nucl. Chem.*, 1978, **40**, 713.
361 R. A. Hood and R. H. Prince, *J. Chem. Soc., Chem. Commun.*, 1979, 163.
362 P. C. Harrington and R. G. Wilkins, *Biochemistry*, 1978, **17**, 4245.

At pH 6.4 and 7.2, binding of both Mn^{2+} and Ca^{2+}, k_1, was faster than sugar binding, k_2, with a lower limit of 5×10^4 M^{-1} s^{-1}. However, at pH 5.0, metal binding was rate determining with $k_2 = 1.2 \times 10^3$ M^{-1} s^{-1} and $k_{-2} \leqslant 0.5$ s^{-1} for Mn^{2+} ($I = 1.0$, 25 °C). Calcium binding to the apo-protein was slower and with very small fluorescence changes but reaction of Ca^{2+} with $^{Mn^{2+}}$ConA was examined in detail and the mechanism

$$Ca^{2+} + {}^{Mn^{2+}}ConA \underset{}{\overset{K}{\rightleftharpoons}} {}^{Ca^{2+}Mn^{2+}}ConA \xrightarrow{k} {}^{Ca^{2+}Mn^{2+}}ConAL$$

is consistent with a rapid association to give a labile metallated protein $^{Ca^{2+}Mn^{2+}}$ConA followed by a conformational change which locks the metal binding site with kinetic parameters $K = 3.5 \times 10^2$ M^{-1} and $k = 0.026$ s^{-1} at 25 °C. Sugar binding in the labile intermediate is comparable to that in $^{Mn^{2+}}$ConA and much lower than in the native locked form. Binding of Mn^{2+} to monomeric $^{Ca^{2+}}$ConA has been examined over the pH range 5—7 by e.p.r. and n.m.r. line-broadening techniques.[363] Approximately half the manganese is bound within one second and the rate law for disappearance of the remaining free manganese,

$$\text{Rate} = k[{}^{Ca^{2+}}ConA_{monomer}][Mn^{2+}]^2$$

measured from e.p.r. studies, is consistent with solvent-exchange studies only if the rate-determining step involves reaction of a $^{Ca^{2+}}ConA_{dimer}$–Mn^{2+} complex with Mn^{2+}. Both methods indicate a maximum in the rate at pH 5.5 with a fourth-order rate constant of 7.8×10^{11} M^{-3} s^{-1}. A large positive entropy of activation implicates a conformational change, possibly of the unlocked to locked forms, in the reaction.

Polarographic studies[364] reveal that the rate of the unlocked to locked conformational change is 9.5×10^{-3} s^{-1} at 25 °C ($I = 0.1$ M, pH 5.6), with $\Delta H^{\ddagger} = 25.4$ kcal mol^{-1} and $\Delta S^{\ddagger} = 17$ cal K^{-1} mol^{-1}, and is independent of whether the metal ion in the S1 site is Zn^{2+}, Co^{2+}, or Mn^{2+}. The latter ion is the only transition metal which induces the conformational change in the absence of Ca^{2+}, revealing that ion size is important in filling S2. Further studies show that the conformational change can occur in the absence of Ca^{2+} at rates dependent on the metal ion and on pH.[365, 366] All locked forms bind MUM equally well and the binding of MUM to an apo-form in the locked conformation has also been examined.

The structural changes which occur on metal binding to ConA have been examined[367] by *X*-ray crystallography. Significant differences are confined to the metal binding site, and the *cis*-peptide link between alanine-207 and aspartic acid-208 in the native, locked protein is found to be *trans* in the unlocked apo-form.

[363] G. M. Alter and J. A. Magnuson, *Biochemistry*, 1979, **18**, 29.
[364] A. D. Sherry, A. E. Buck, and C. A. Peterson, *Biochemistry*, 1978, **17**, 2169.
[365] C. A. Stark and A. D. Sherry, *Biochem. Biophys. Res. Commun.*, 1979, **87**, 598.
[366] S. H. Koenig, C. F. Brewer, and R. D. Brown, *Biochemistry*, 1978, **17**, 4251.
[367] G. N. Reeke, J. W. Becker, and G. M. Edelman, *Proc. Natl. Acad. Sci. USA*, 1978, **75**, 2286.

Kinetic studies[368] of the dimer–tetramer equilibrium in native ConA at pH 7.2 and 23 °C ($I = 0.5$ M NaCl),

$$2\text{ConA}_{\text{dimer}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{ConA}_{\text{tetramer}}$$

yield rate constants and activation parameters, $k_1 = 215\ \text{M}^{-1}\ \text{s}^{-1}$ ($\Delta H^* = 40$ kcal mol^{-1}, $\Delta S^* = 90$ cal K^{-1} mol^{-1}) and $k_{-1} = 3.1 \times 10^{-4}\ \text{s}^{-1}$ ($\Delta H^* = 7$ kcal mol^{-1}, $\Delta S^* = 47$ cal K^{-1} mol^{-1}). The large positive entropy contribution suggests that the dimers associate through an extensive hydrophobic interaction.

[368] M. Huet and J.-M. Claverie, *Biochemistry*, 1978, **17**, 237.

Part IV

ORGANOMETALLIC COMPOUNDS

By

A. J. DEEMING

1

Intramolecular Exchanges and Isomerizations

BY A. J. DEEMING

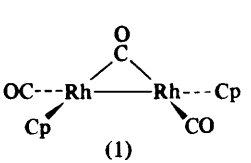
1 Metal Carbonyls

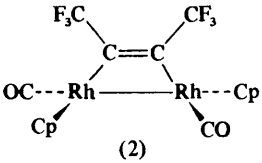
Mononuclear Compounds.—The *cis*- and *trans*-isomers of $[Mo(CO)_4(PBu^n_3)_2]$ interconvert without incorporation of ^{13}CO or other ligands to give a mixture containing *ca.* 85% *trans*, and the activation energy is *ca.* 5 kcal less than for dissociative loss of CO from analogous phosphine complexes; hence the reaction is intramolecular.[1] Use of *mer*-$[Mo(CO)_3(^{13}CO)(PBu^n_3)_2]$ showed that axial–equatorial CO site exchange in the *cis*-isomer did not precede formation of the *trans*-isomer. A trigonal twist mechanism is likely. The rates of *cis–trans* isomerization have been measured for the complexes $[M(CO)_2(diphos)_2]$ [M = Cr, Mo, or W, diphos = $Ph_2P(CH_2)_nPPh_2$, $n = 1$, 2, or 3] and in the corresponding 17-electron compound formed by a one-electron oxidation. The rates are essentially independent of [diphos], [CO], or the solvent, and again an intramolecular mechanism might operate.[2] The dynamic n.m.r. behaviour of the protonated complexes $[MoH(CO)_2(diphos]_2]^+$ indicates an intramolecular hydrogen migration. The H atom is capping a face of an octahedron and migrates to other faces above the plane of the four P atoms, leading to exchange of P atoms, or to faces below the P_4 plane, leading to exchange of the two CO groups. These migrations amount to interconversions of monocapped octahedra *via* pentagonal-bipyramidal intermediates or transition states.[3] Dynamic behaviour is also found for $[MoX(CO)_2(diphos)_2]^+$ and $[TaX(CO)_2(diphos)_2]$ (X = halide), although these adopt monocapped trigonal-prismatic structures.[4] The increase in $\Delta G^{\ddagger}$ with increasing steric hindrance points to an intramolecular process, as do the low $\Delta S^{\ddagger}$ values. Various polytopal rearrangements are considered but not discriminated experimentally.

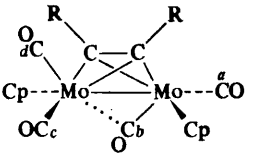
Dinuclear Compounds.—The CO site exchange in $[Rh_2C_5H_5)_2(CO)_3]$ (1) was earlier thought to occur by the well-known pairwise bridge-closing and -opening mechanism which would require an intermediate with three bridging CO groups. Since $[Rh_2(C_5H_5)_2(CO)_2(PMe_2Ph)]$ also shows coalescence of the ^{13}CO signals at similar temperatures and, since PMe_2Ph does not migrate, the mechanism must be either a direct 1 : 1 bridge–terminal CO site exchange or, less likely, a process requiring an unsymmetrical non-bridged intermediate. CO exchange

[1] D. J. Darensbourg, *Inorg. Chem.*, 1979, **18**, 14.
[2] A. M. Bond, B. S. Grabaric, and J. J. Jackowski, *Inorg. Chem.*, 1978, **17**, 2153.
[3] S. Datta, B. Dezube, J. K. Kouba, and S. S. Wreford, *J. Am. Chem. Soc.*, 1978, **100**, 4404.
[4] L. D. Brown, S. Datta, J. K. Kouba, L. K. Smith, and S. S. Wreford, *Inorg. Chem.*, 1978, **17**, 729.

generates a time-averaged plane of symmetry since the diastereotopic Me groups are exchanged.[5] The pairwise bridge-closing and -opening mechanism does fit observations on the related compound (2). The CO groups of the *trans*-isomer migrate rapidly between Rh atoms, giving a ^{13}CO n.m.r. triplet at room temperature but a doublet at -40 °C. Pairwise bridge closing is not possible in the *cis*-isomer, which is consequently static.[6] The Mo_2C_2 skeleton of (3) is rigid

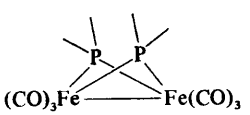

(1)

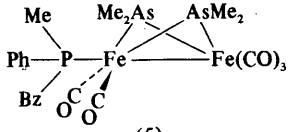

(2)

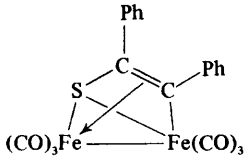

(3)

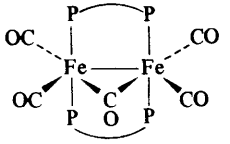
but a rapid process generates time-averaged C_2 symmetry. The semi-bridged CO site is successively occupied by carbonyls *c* and *b*, but there is no CO transfer between metal atoms. At higher temperatures further coalescences take place as time-averaged C_{2v} symmetry is achieved. This requires a rotation of terminal ligands about the Mo—Mo axis.[7] The complex $[Ru_2(C_5H_5)_2(CO)_3(CNR)]$ gives *cis*- and *trans*-isomers in solution with both bridged and terminal isocyanide ligands, which rapidly exchange by established mechanisms.[8]

The complex $[Fe_2CO)_6(\mu\text{-}POCH_2CMe_2CH_2O)_2]$ has the framework (4) and undergoes two intramolecular processes, flipping of the organic rings and a slower flipping of the butterfly Fe_2P_2 framework.[9] In related but substituted compounds such as (5) there is a rapid localized axial–equatorial CO exchange within the $Fe(CO)_3$ group and a slower butterfly flipping. The diastereotopic CO groups next to the chiral tertiary phosphine exchange at the same rate and probably by the same process as the methyl exchange, and both are best accounted for by the


(4)


(5)

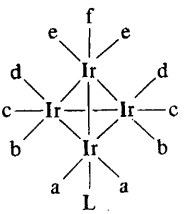

(6)


(7)

[5] J. Evans, B. F. G. Johnson, J. Lewis, T. W. Matheson, and J. R. Norton, *J. Chem. Soc., Dalton Trans.*, 1978, 626.
[6] R. S. Dickson, C. Mok, and G. Pain, *J. Organomet. Chem.*, 1979, **166**, 385.
[7] W. I. Bailey, M. H. Chisholm, F. A. Cotton, and L. A. Rankel, *J. Am. Chem. Soc.*, 1978, **100**, 5764.
[8] J. A. S. Howell and A. J. Rowan, *J. Organomet. Chem.*, 1979, **165**, C33.
[9] C. M. Bartish and C. S. Kraihanzel, *Inorg. Chem.*, 1978, **17**, 735.

butterfly mechanism.[10] The complex (6) undergoes rapid interchange of the σ-Fe—C bond between the metal atoms.[11] Complex (7), which contains the diphosphite $(EtO)_2POP(OEt)_2$, undergoes a process in which all five CO groups circumnavigate the iron atoms in the equatorial plane so that a μ-CO is located alternately on opposite sides of the molecule. This was deduced from the simultaneous collapse of the individual ^{13}CO n.m.r. signals.[12]

Polynuclear Carbonyls.—The mechanisms of metal cluster rearrangements has been reviewed again.[13] The treatment of the fluxional behaviour of cluster carbonyls in terms of motions of a metal atom polyhedron within an outer polyhedron of CO ligands, which may itself be reorganized, has been developed. In applying this approach to $[M_4(CO)_{12}]$ clusters, the different patterns of CO-scrambling seem to arise from the different ways the metal tetrahedron can be successively arranged in an icosahedron of ligands which may rearrange into a cubo-octahedron.[14] Variable-temperature ^{13}C n.m.r. spectra of a range of polynuclear carbonyls (some already communicated) have been gathered together for discussion.[5] Included are $[Rh_2(C_5H_5)_2(CO)_3]$, $[Co_2(CO)_8]$, $[Co_4(CO)_{12}]$, $[Rh_4(CO)_{12}]$, $[RhCo_3(CO)_{12}]$, $[Co_4(PhMe)(CO)_9]$, tertiary phosphine substituted derivatives of these and $[Rh_6(CO)_{15}I]^-$. The fluxional behaviour of $[Rh_4(CO)_{12}]$ has been discussed in terms of the rotation of a Rh_4 tetrahedron within a carbonyl icosahedron with an intermediate with no μ-CO of *T* symmetry rather than the older view of there being an equilibrium between a C_{3v} ground state and a T_d structure of higher energy, like the ground-state structure of $[Ir_4(CO)_{12}]$.[5] Most substituted derivatives of $[Ir_4(CO)_{12}]$ contain bridging CO except for $[Ir_4(CO)_{11}(CNBu^t)]$, the *X*-ray structure (8) of which shows it to have been



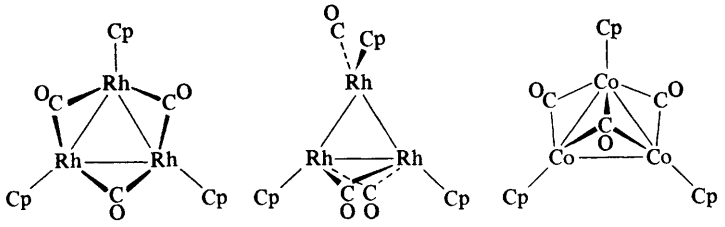
(8)

derived directly from that of the parent. The ^{13}C n.m.r. spectrum shows six carbonyl signals (a—f) at −84 °C but broadening and coalescences involve all but the signal due to f. This is entirely consistent with the mechanism of exchange *via* the $[Rh_4(CO)_{12}]$-type structure since the *trans* relation of f with the isocyanide is maintained with this mechanism.[15] There has been much written about the solution structure of $[Co_4(CO)_{12}]$ but further evidence is presented for the crystal

[10] T. C. Flood, F. J. DiSanti, and K. D. Campbell, *Inorg. Chem.*, 1978, **17**, 1643.
[11] J. P. Hickey, J. C. Huffman and L. J. Todd, *Inorg. Chim. Acta*, 1978, **28**, 77.
[12] F. A. Cotton, R. J. Haines, B. E. Hanson, and J. C. Sekutowski, *Inorg. Chem.*, 1978, **17**, 2010.
[13] E. Band and E. L. Muetterties, *Chem. Rev.*, 1978, 639.
[14] B. F. G. Johnson and R. E. Benfield, *J. Chem. Soc., Dalton Trans.*, 1978, 1554.
[15] J. R. Shapley, G. F. Stuntz, M. R. Churchill, and J. P. Hutchinson, *J. Chem. Soc., Chem. Commun.*, 1979, 219.

structure (C_{3v}) persisting in solution rather than the adoption of the D_{2d} structure. The ^{13}C n.m.r. signals should be with intensity ratio 1:1:1:1 (C_{3v}) or 1:1:1 (D_{2d}). The signals certainly appear to be of the form 1:1:1, but these coalesce on warming because of a dynamic process, presumably like that for Rh, to give a single resonance. The average chemical shift is only in the correct position for signals in ratio 1:1:2, so that the C_{3v} structure must be present with accidental coincidence of two absorptions. The reason for the incorrect intensity ratio is unknown.[16]

The trinuclear complex $[Rh_3(C_5H_5)_3(CO)_3]$ has C_{3v} and C_s isomers which are not readily interconverted, so that the dynamic behaviour for the C_s isomer (10)

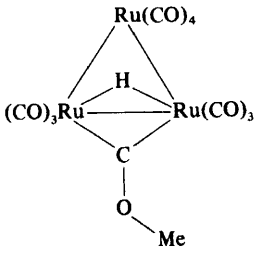


cannot involve the non-bridged C_{3v} isomer (9).[17] Equilibria between structures of types (10) and (11) (found for Co but not detected for Rh) is rapid at -125 °C allowing CO groups to move around the Rh_3 triangle to create averaged C_{3v} symmetry without CO groups moving between opposite faces. This gives ^{13}C n.m.r. quartets in the ratio 1:2. At higher temperatures a single quartet results from a similar (10) $\rightleftharpoons$ (11) equilibrium but by a different set of CO movements allowing CO groups to migrate over both faces (averaged D_{3h} symmetry). Localized CO exchange within an $M(CO)_3$ unit of a cluster is common and now evidence is given for a localized exchange in an $M(CO)_4$ unit in compounds of type $[Os_3HX(CO)_{10}]$.[18] This might also operate in $[Os_3(CO)_{12}]$, *i.e.* axial–equatorial site exchange without CO migration between atoms.

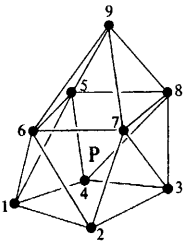
In complex (12), formed by methylation of $[Ru_3H(CO)_{11}]^-$, four separate dynamic exchange processes have been identified.[19] In order of decreasing rate these are rotation about the C—OMe bond to generate a plane of symmetry, localized $Ru(CO)_4$ exchange, localized $Ru(CO)_3$ exchange, and total exchange in some unknown way.

Increasingly large clusters are now being studied for dynamic n.m.r. behaviour and two recent examples are $[Rh_9(P)(CO)_{21}]^{2-}$ and $[Rh_{17}(S)_2(CO)_{32}]^{3-}$. The nine Rh atoms in the capped square antiprism (13) shown fall into three sets in ratio 4:4:1, so the symmetrical ten-line ^{31}P n.m.r. multiplet indicates a rare example of a dynamic metal framework exchanging all the Rh atoms about the

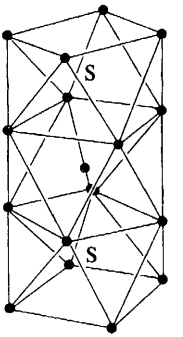
[16] S. Aime, L. Milone, D. Osella, and A. Poli, *Inorg. Chim. Acta*, 1978, **30**, 45.
[17] R. J. Lawson and J. R. Shapley, *Inorg. Chem.*, 1978, **17**, 772.
[18] E. G. Bryan, A. Forster, B. F. G. Johnson, J. Lewis, and T. W. Matheson, *J. Chem. Soc., Dalton Trans.*, 1978, 196.
[19] B. F. G. Johnson, J. Lewis, A. G. Orpen, P. R. Raithby, and G. Süss, *J. Organomet. Chem.*, 1979, **173**, 187.



(12)



(13)

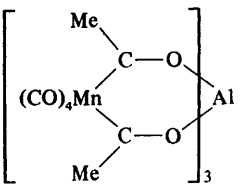


(14)

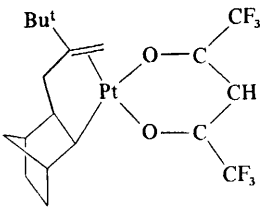
P atom.[20] Cleavage of bond 7—8, atoms 3, 7, 9, and 8 becoming the square basal plane, formation of the 2—4 bond, atom 1 becoming the apical atom, is a simple mechanism for this exchange. The ^{13}C n.m.r. spectrum shows that exchanges occur within the outer carbonyl shell. In the larger cluster $[Rh_{17}(S)_2(CO)_{32}]^{3-}$ the skeleton (14) is rigid but CO migrations are identified.[21] There are four terminal and four bridging CO groups associated with each of the four layers of external metal atoms. Only for the inner layers is the rapid interchange of bridging for terminal CO groups observed, so that these CO groups travel round the perimeter of the cluster. The 100% natural abundance of ^{103}Rh ($I=\frac{1}{2}$) is a most fortunate aid to an understanding of cluster behaviour, and rhodium clusters will remain the most thoroughly studied in this respect.

2 Oxygen-bound Ligands

The kinetics of isomerization of complexes of type [Al(β-diketonato)$_3$] were studied earlier and now isomerization involving the *cis*- and *trans*-isomers of a related complex (15) has been studied.[22] The *trans* (C_1) isomer on dissolving in CCl_4 is converted into an equilibrium mixture with the *cis* (C_3) isomer; the rates of isomerization and the equilibrium positions have been determined. The intramolecular process relates kinetically to similar processes involving classical β-diketonato-ligands.



(15)



(16)

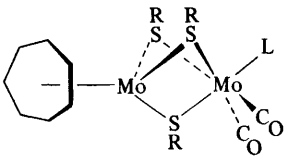
[20] J. L. Vidal, W. E. Walker, R. L. Pruett, and R. C. Schoening, *Inorg. Chem.*, 1979, **18**, 129.
[21] J. L. Vidal, R. C. Schoening, R. L. Pruett, and R. A. Fiato, *Inorg. Chem.*, 1979, **18**, 1821.
[22] C. M. Lukehart and G. P. Torrence, *Inorg. Chem.*, 1978, **17**, 253.

Most mechanisms of four-co-ordinate Pt^{II} and Pd^{II} complexes involve expansion of the co-ordination shell. This appears not to be so for the site exchange of the CF_3 substituents of complexes such as (16). Since rapid exchange occurs in dry hexane, there seems to be an intramolecular mechanism, either with tetrahedral or three-co-ordinate Pd^{II} as the intermediate, neither of which are to be expected normally. If η^3-allyl ligands are used, η^1-allyls are not involved and three-co-ordinate complexes with unidentate β-diketonato-ligands are invoked. This behaviour depends upon having a good *trans*-labilizing group (such as a σ-carbon ligand) and a good leaving group such as the fluorinated diketone.[23]

3 Sulphur- or Selenium-bound Ligands

The complex $[Rh(\eta\text{-}C_5Me_5)(S_2CNMe_2)_2]$ contains uni- and bi-dentate dithiocarbamato-ligands. The kinetics of exchange of these ligands in this and related Rh and Ir complexes have been studied by variable-temperature ^1H n.m.r.[24] The reaction is intramolecular and the positive ΔS^* values indicate a dissociative mechanism, expected perhaps for an 18-electron complex. The complex $[Pt(Se_2CNBu^i_2)_2(PR_3)]$ also contains uni- and bi-dentate (diselenocarbamato) ligands and their exchange has been studied by ^{77}Se n.m.r.; as above the exchange is intramolecular.[25]

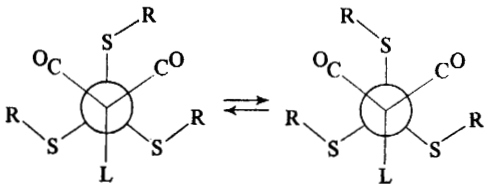
For the dinuclear complexes such as $[Ru_2(SR)_2(CO)_2(C_5H_5)_2]$ isomerism results from the different dispositions of the CO, C_5H_5, and R groups about the Ru_2S_2 ring. Isomers with relative *cis* and *trans* arrangements of C_5H_5 ligand only very slowly interconvert so that reversible opening of the four-membered ring cannot account for the rapid isomerism involving inversion at sulphur.[26] The kinetics of inversion at sulphur could also be measured by dynamic n.m.r. for $[Cr(CO)_5(MeSCHMePh)]$ since the chiral centre rendered the two possible Me positions diastereotopic. Inversion at sulphur occurs faster than ligand exchange.[27] In the complex (17) a fast dynamic process retains the *trans* relations



(17)

between SR and CO or L (tertiary phosphorus) ligands and collapses the three Bu^t(R) signals into two of intensity, ratio 1:2.[28] The equilibrium shown (Scheme 1) accounts for this, with higher barriers for inversion at S when $L = P(OMe)_3$

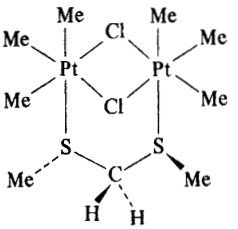
[23] C. J. Mays and J. Powell, *Inorg. Chim. Acta*, 1978, **26**, L21.
[24] D. R. Robertson and T. A. Stephenson, *J. Chem. Soc., Dalton Trans.*, 1978, 486.
[25] J. P. Fackler and W.-H. Pan, *J. Am. Chem. Soc.*, 1979, **101**, 1607.
[26] S. D. Killops and S. A. R. Knox, *J. Chem. Soc., Dalton Trans.*, 1978, 1260.
[27] J. H. Eekhof, H. Hogeveen, R. M. Kellogg, and E. Klei, *J. Organomet. Chem.*, 1978, **161**, 183.
[28] I. B. Benson, S. A. R. Knox, P. J. Naish, and A. J. Welch, *J. Chem. Soc., Chem Commun.*, 1978, 878.



Scheme 1

than when L is more basic ($PMePh_2$, PMe_2Ph, or PMe_3). The greater build-up of electron density at the *trans*-Mo—S bond is expected to favour a more closely planar geometry at the S atom and a lower inversion barrier.

A change in the pattern of ^{195}Pt to Me coupling with temperature has been used to identify a dynamic process in complex (18).[29,30] Between −95 and

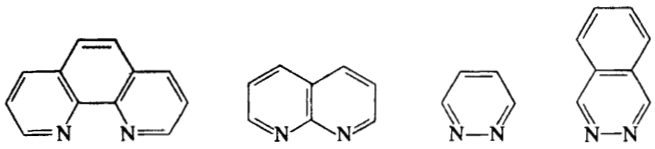


(18)

−20 °C both inversion of the six-membered SCSPtClPt ring and inversion of configuration at the S atom lead to n.m.r. coalescences, but above 0 °C the normal 1:4:1 signal of the SMe groups transforms into a 1:8:18:8:1 quintet as the S atoms average their contacts with the two Pt atoms. At even higher temperatures, all six Pt—Me group signals have coalesced. Dissociation–recombination mechanisms are needed, it seems, to account for the high-temperature coalescences.

4 Nitrogen-bound Ligands

The structures and rates of interchange of nitrogen atoms in $[PtCl(PEt_3)_2L]BF_4$, where L is one of the diaza-compounds (19)—(22) have been determined. With 1,10-phenanthroline (19) the rate of intramolecular exchange was too rapid to freeze out on an n.m.r. time-scale and with 1,8-naphthyridine (20) the coalescence

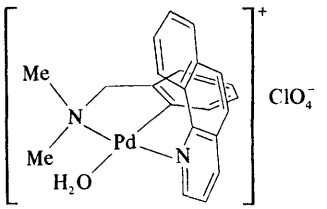


(19) (20) (21) (22)

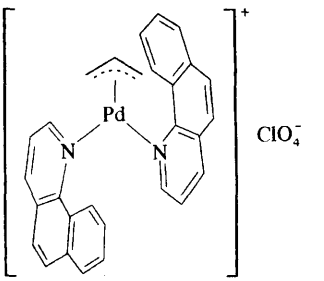
[29] E. W. Abel, A. R. Khan, K. Kite, K. G. Orrell, and V. Šik, *J. Organomet. Chem.*, 1978, **145**, C18.

[30] E. W. Abel, A. R. Khan, K. Kite, K. G. Orrell, and V. Šik, *J. Chem. Soc., Chem. Commun.*, 1979, 126.

temperature was easily achieved, but with pyridazine (21) and phthalazine (22) the rate was very low, the nitrogen atoms only interchanging at elevated temperatures by a dissociative mechanism.[31–33] The rates depend on whether the angle between the lone pairs allows Pt—N bond formation as the original Pt—N bond is cleaved. Dynamic n.m.r. behaviour of $[Pd(C_6H_4CH_2NMe_2)(H_2O)L]ClO_4$ (23) involves a first-order racemization which was followed by the coalescence of the NMe n.m.r. signals.[34] The lack of interchange of free with co-ordinated L and



(23)



(24)

the non-dynamic behaviour of the corresponding nitrato-complex among other observations led to a proposed mechanism involving the unimolecular dissociation of H_2O, the rotation of the heterocyclic ligand through the co-ordination plane, and the re-co-ordination of H_2O. From the observed effect of adding water to the solvent acetone it was suggested that ion-paired form of (23) underwent more rapid racemization. The interchange of the non-equivalent nitrogen ligands in (24) occurs at the same rate as the interchange of the η^3-allyl termini,[35] and *via* a similar mechanism, in this case involving the dissociation of one of the nitrogen ligands before the remaining one can rotate through the co-ordination plane.

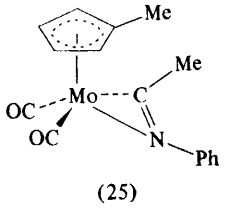
The nitrosyl complex $[Ir(\eta^3\text{-allyl})(NO)(PPh_3)_2]^+$ gives isomers with bent and linear M—N—O respectively. The $[PF_6]^-$ salt has the linear form [ν(NO) = 1763 cm^{-1}] and the $[BF_4]^-$ salt the bent form [ν(NO) = 1631 cm^{-1}] in the crystals, but both forms are present in CH_2Cl_2 solution.[36] However, a single set of n.m.r. signals was obtained and, after the η^1–η^3 allyl exchange process was frozen out at −17 °C, further cooling gave as yet uninterpretable changes in the spectrum. It is likely that −83 °C is still insufficiently low to freeze out the exchange of the two isomers and this is the first evidence that bent to linear M—NO conversion can occur rapidly; this is of significance to associative mechanisms for metal nitrosyls.

The ^{13}C n.m.r. spectrum of (25) shows coalescence of the *C*O signals with associated pairwise coalescence of the methylcyclopentadienyl signals on increas-

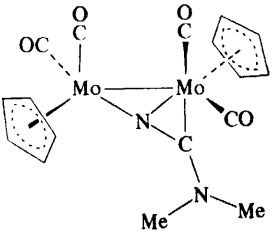
[31] G. W. Bushnell and K. R. Dixon, *Can. J. Chem.*, 1978, **56**, 878.
[32] J. B. Brandon, M. Collins, and K. R. Dixon, *Can. J. Chem.*, 1978, **56**, 950.
[33] G. W. Bushnell, K. R. Dixon, and M. A. Khan, *Can. J. Chem.*, 1978, **56**, 450.
[34] A. J. Deeming and I. P. Rothwell, *J. Chem. Soc., Dalton Trans.*, 1978, 1497.
[35] A. J. Deeming and I. P. Rothwell, *Inorg. Chim. Acta*, 1978, **31**, 271.
[36] M. W. Schoonover, E. C. Baker, and R. Eisenberg, *J. Am. Chem. Soc.*, 1979, **101**, 1880.

ing the temperature from 0 to 65 °C. Interchange of the CO ligands would not create the observed time-averaged plane of symmetry so that rapid iminoacyl movement is necessary. Since there is little solvent effect on the rate, a η^1-iminoacyl intermediate is unlikely, but rather there is a direct rotation of the η^2-iminoacyl ligand about the ligand–metal axis.[37]

Averaging of the ends of the η^3-allyl in [Pd(η^3-allyl)Cl($PhCH_2NHCH{=}NCH_2Ph$)] is not synchronous with the averaging of the benzyl signals in the n.m.r. spectrum. Two $PhCH_2$ signals are present even when the allylic protons are rapidly exchanging, and an exchange of free with co-ordinated nitrogen ligands best explains their exchange.[38]



(25)



(26)

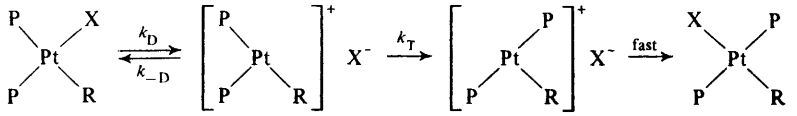
The four non-equivalent CO ligands, the two C_5H_5 groups, and the two NMe groups of compound (26) exchange at the same rate, as shown by appropriate ^1H and ^{13}C n.m.r. coalescences. Motions that could interchange the bonding of the Me_2NCN ligand between the Mo atoms (enantiomerization) need not exchange all four CO ligands, but if there is only a pairwise exchange a separate process of similar energy must exchange the two CO groups at each Mo atom.[39]

5 Phosphorus-bound Ligands

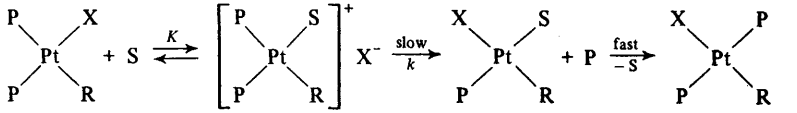
The *X*-ray structure of $[RhH(PPh_3)_3].Me_2NH.THF$ shows the hydride to have a distorted square-planar structure and the ^{31}P n.m.r. spectrum at −86 °C is consistent with this C_{2v} geometry. A non-dissociative mechanism exchanges the three PPh_3 ligands and a tetrahedral intermediate (C_{3v}) was proposed.[40] The complex $[RhMe(PPh_3)_3]$ was reported to be tetrahedral on the basis of the equal coupling of the three ^{31}P nuclei to the CH_3 group but it is probably also a dynamic square-planar compound. $[RhCl(PPh_3)_3]$ is square planar but non-dynamic. The mechanism of the *cis–trans* isomerism of $[PtRX(PEt_3)_2]$ (R = alkyl or substituted aryl, X = halide) has again been discussed in the light of an alternative suggestion to the originally proposed dissociative route.[41] The main evidence for the dissociative mechanism (Scheme 2) is that rates of solvolysis are greatly reduced by steric crowding while the rate of isomerization is little affected.

[37] R. D. Adams and D. F. Chodosh, *Inorg. Chem.*, 1978, **17**, 41.
[38] T. Boschi, U. Belluco, T. Toniolo, R. Favez, and R. Roulet, *Inorg. Chim. Acta*, 1979, **34**, 37.
[39] M. H. Chisholm, F. A. Cotton, M. W. Extine, and L. A. Rankel, *J. Am. Chem. Soc.*, 1978, **100**, 807.
[40] S. H. Strauss, S. E. Diamond, F. Mares, and D. F. Shriver, *Inorg. Chem.*, 1978, **17**, 3064.
[41] R. Romeo, *Inorg. Chem.*, 1978, **17**, 2040.

Dissociative mechanism:



Associative mechanism:

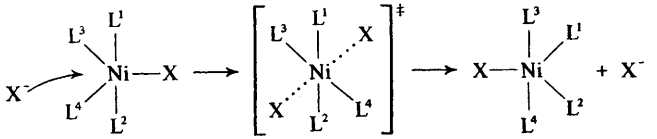


(P = PEt_3, S = solvent)

Scheme 2

Furthermore the large positive values of ΔH^* and ΔS^* for isomerization are to be contrasted with the low ΔH^* and large negative ΔS^* for solvolysis. The associative mechanism (Scheme 2) does not predict the observed rate behaviour and it is difficult to see why small amounts of X^- should lead to facile removal of the strongly bound PEt_3. The balance of evidence seems to favour the dissociative mechanism which is not expected unless there are strongly *trans*-labilizing ligands present (see also ref. 23).

^{31}P N.m.r. has been used to study P-site exchange in the trigonal-bipyramidal complexes $[NiX_2L_3]$ (X = CN, Cl, Br, or I), $[NiXL_4]X$ (X = Cl, Br, or I) and $[NiL_5](BF_4)_2$, where $L = PMe_3$,[42–44] and each is believed to have a different mechanism. Axial–equatorial interchange for $[NiL_5]^{2+}$ is intramolecular and rapid ($\Delta G^* = 6.2 \pm 0.2$ kcal mol^{-1}) and a Berry pseudorotation is likely. A similar mechanism operates for $[NiXL_4](BF_4)$ with $\Delta G^* = 6.6$ (Cl), 7.8 (Br), and 8.2 (I) kcal mol^{-1}, and it is expected that the iodide should be slowest for pseudorotation. However, the rate of exchange for $[NiXL_4]X$ is much greater and first order in both complex and halide concentrations in the order X = Cl < Br < I. An I_a mechanism with a 20-electron transition state is suggested (Scheme 3), but for NiX_2L_3 rates are lower and a *D* mechanism is proposed.



Scheme 3

6 Carbon-bound Ligands

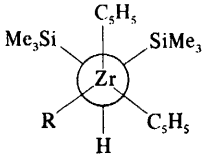
σ-Bonded Carbon Compounds.—T_1 Measurements have been made and used to estimate the barriers to rotation about CH_3—transition metal bonds. These

[42] M. Dartiguenave, Y. Dartiguenave, A. Gleizes, C. Saint-Joly, J. Galy, P. Meier, and A. E. Merbach, *Inorg. Chem.*, 1978, **17**, 3505.

[43] P. Meier, A. E. Merbach, M. Dartiguenave, and Y. Dartiguenave, *J. Chem. Soc., Chem. Commun.*, 1979, 49.

[44] P. Meier, A. E. Merbach, M. Dartiguenave, and Y. Dartiguenave, *Inorg. Chem.*, 1979, **18**, 610.

barriers to rotation are significantly high: *cis*-$[Os(CO)_4Me_2]$, 4.4 ± 0.7; $[Fe(C_5H_5)(CO)_2Me]$, 5.4 ± 2; $[Mo(C_5H_5)(CO)_3Me]$, >6; and $[Zr(C_5H_5)_2Me_2]$ >6 kcal mol^{-1}.[45] The barriers increase with increased steric congestion and approach values for which ^1H n.m.r. spectra could be 'frozen-out'. Indeed, with crowded alkyls n.m.r. spectra have been frozen-out, and since $[Zr(C_5H_5)_2R\{CH(SiMe_3)_2\}]$ adopts the low-symmetry configuration (27) at low temperatures, it has been



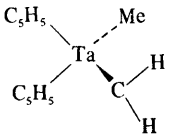
(27)

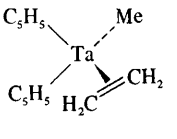
possible to obtain rotation barriers from coalescence of either the Me_3Si or C_5H_5 n.m.r. signals.[46] Rotational barriers (ΔG^*) in the range 11.6—15.3 kcal mol^{-1} depending upon R were obtained, so that presumably the value for $[Zr(C_5H_5)_2Me_2]$ is between 6 and 11.6 kcal mol^{-1}, and the reason for the large barriers for the $CH(SiMe_3)_2$ complex is largely steric. Two ν(CO) absorptions are found for $[Pt(C_5H_5)Me_2(COMe)]$ in the solid and in solution but a single set of ^1H n.m.r. signals, indicating a rapid interconversion of conformers by rotation about the Pt—acyl bond.[47]

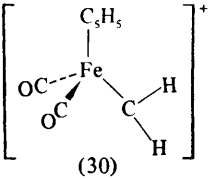
The complex $[Ag_2Li_2(C_6H_4CH_2NMe_2)_4]$ contains the *ortho*-substituted aryl forming a three-centre, two-electron bridge between Ag and Li and with nitrogen atoms bonded to Li. This is a chiral arrangement and the CH_2 nuclei are diastereotopic as are the NMe_2 groups. Exchange of the diastereotopic groups as observed by coalescences the ^1H n.m.r. between -60 and $+110$ °C. NMe_2 groups exchange more rapidly than the CH_2 atoms by N-dissociation, inversion at N, and rotation about N—C before re-co-ordination of N. A slower process leading to CH_2 exchange requires rotation at the aryl–metal linkage, the first reported example of this.[48]

Carbene Complexes.—There is considerable variation in the barriers to rotation about M—CR_2 bonds. The ^1H n.m.r. spectrum of $[Ta(C_5H_5)_2(CH_2)Me]$ (28) contains an AB quartet for the CH_2 group up to the decomposition temperature (95 °C), which requires the rotational barrier $\Delta G^* \geqslant 20$ kcal mol^{-1}. The CH_2 group is oriented as shown to allow considerable π-electron transfer to the CH_2 group, which has nucleophilic character as a consequence. There is no metal π-orbital of suitably low energy available in the orientation perpendicular to this so the rotational barrier is large, as in the corresponding C_2H_4 compound (29), which in adopting the conformation shown uses the same available metal π-orbital.[49] Bulky substituents on the carbene cause a small rotation out of the

[45] R. F. Jordan, E. Tsang, and J. R. Norton, *J. Organomet. Chem.*, 1978, **149**, C53.
[46] J. Jeffery, M. F. Lappert, N. Tuyet Luong-Thi, J. L. Atwood, and W. E. Hunter, *J. Chem. Soc., Chem. Commun.*, 1978, 1081.
[47] A. Shaver, *Can. J. Chem.*, 1978, **56**, 2281.
[48] G. van Koten and J. G. Noltes, *J. Organomet. Chem.*, 1979, **171**, C39.
[49] R. R. Schrock and P. R. Sharp. *J. Am. Chem. Soc.*, 1978, **100**, 2389.


(28)


(29)


(30)

perpendicular orientation and reduce the rotational barrier $\Delta G^{\ddagger}$ (Table 1),[50] and it is believed that these observations are related.

Table 1 *Angles ϕ rotated about the* M—CR_2 *bond from the perpendicular orientation (solid state) and rotational barriers for this bond*

Complex	ϕ/°	$\Delta G^{\ddagger}$ (±0.2)/kcal mol^{-1}
$[Ta(C_5H_5)_2(CH_2)(CH_3)]$	0	20
$[Ta(C_5H_5)_2(CHPh)(CH_2Ph)]$	−5.7	19.2
$[Ta(C_5H_5)_2(CHCMe_3)Cl]$	10.3	16.8

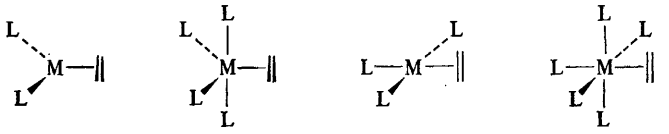
Calculations on $[Fe(C_5H_5)(CO)_2(CH_2)]^+$ (30) (only isolated for substituted carbenes) show that there are suitable metal π-orbitals perpendicularly disposed and although the orientation shown is favoured the calculated rotational barrier is only 6.2 kcal mol^{-1}, but this has not been determined experimentally.[51] The carbene complexes $[Fe(C_5H_5)(CO)L(RNHCNHMe)]^+$ (L = MeNC or tertiary phosphines) undergo intramolecular isomerization but this involves rotation about C—N rather than Fe—C bonds, and the rotational barriers (16.7—17.9 kcal mol^{-1}) are essentially independent of L and R.[52]

η^2-Alkene and η^2-alkyne Complexes.—There is well established evidence that an η^2-alkene can only change to co-ordination through the opposite ligand face by dissociation and recombination and not by any low-energy intramolecular rotation. Thus dissociation is required for racemization of *trans*-1,2-disubstituted ethene, for example. However, rotation about the metal–alkene axis allows intramolecular changes, sometimes very rapid but sometimes too slow to lead to n.m.r. line-broadening.

Intermolecular exchange between free and co-ordinated ethyl methacrylate (ema) in $[Ni(PMe_2Ph)_2(ema)]$ gives n.m.r. coalescence between free and co-ordinated ema signals and also coalescence in the ^{31}P spectrum and the derived kinetic form is consistent with an S_N2 mechanism.[53] With other tertiary phosphines used with larger cone-angles, the rate is much lower (no coalescence) and unfavourable steric crowding in the associated state, $[Ni(PR_3)_2(ema)_2]$, might be responsible; cone-angles are: PMe_2Ph, 127°; PEt_3, 132°; $PEtPh_2$, 141°; and PPh_3, 145°.

[50] R. R. Schrock, L. W. Messerle, C. D. Wood, and L. J. Guggenberger, *J. Am. Chem. Soc.*, 1978, **100**, 3793.
[51] B. E. R. Schilling, R. Hoffmann, and D. L. Lichtenberger, *J. Am. Chem. Soc.*, 1979, **101**, 585.
[52] B. V. Johnson, D. P. Sturtzel, and J. E. Shade, *J. Organomet. Chem.*, 1978, **154**, 89.
[53] T. Yamamoto, J. Ishizu, S. Komiya, Y. Nakamura, and A. Yamamoto, *J. Organomet. Chem.*, 1979, **171**, 103.

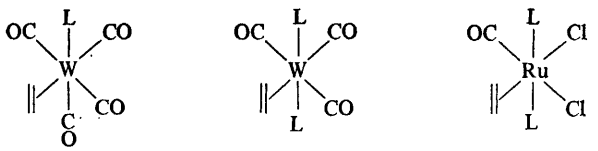
Intramolecular alkene rotation depends very much on the metal and its co-ordination geometry as well as on alkene substituents, as born out by theoretical and experimental studies. Calculations on $[Ni(CO)_2(C_2H_4)]$ and $[Ni(PH_3)_2(C_2H_4)]$ give large rotational barriers (23.6—33.7 kcal mol^{-1} depending upon the angle through which the H atoms are bent back) and, in agreement with simple ideas, the barrier is due to the greater bonding interaction involving the C_2H_4 π^*-orbital in geometry (31) compared with the perpendicular C_2H_4 orientation.[54] Both (31) and (32) should have strong preferences for the orientations shown and high rotational barriers; however, (33) and (34) have similar or equal energy metal π-orbitals for whichever perpendicular C_2H_4 orientation is adopted and so barriers should be low. Qualitatively calculations agree with experimental results.



(31) (32) (33) (34)

Calculations on *trans*-$[MoL_4(C_2H_4)_2]$ (L = CO or PH_3) have shown that the two C_2H_4 ligands will be preferentially aligned mutually perpendicular and parallel to *trans*-L—Mo—L axes. The calculated rotational barrier of 16 kcal mol^{-1} is to be compared with 15.3 kcal mol^{-1} obtained experimentally for a related phosphine complex.[55] Alkenes certainly do line up with the L—M—L axes, and *cis*-$[W(CO)_4L(alkene)]$ (L = $AsMe_3$ or PMe_3) and *mer*-$[W(CO)_3(PMe_3)_2(alkene)]$ adopt configurations (35) and (36) respectively. CO is a better π-acceptor than $AsMe_3$ or PMe_3 and in the orientations shown maximum overlap of metal orbitals with the alkene π^*-orbital is achieved. With $CH_2{=}C(CO_2Me)_2$ and *cis*- or *trans*-$MeO_2CCH{=}CHCO_2Me$ rotational barriers were obtained from n.m.r. coalescences.[56] In $[RuCl_2(CO)(C_2H_4)(PMe_2Ph)_2]$ (37) the C_2H_4 also aligns with the P—Ru—P axis in the crystal, but rotation is so rapid at −40 °C that a single sharp triplet is obtained for C_2H_4 in the ^1H n.m.r. spectrum. Coupling to ^{31}P shows that the rapid H-exchange is intramolecular and the low barrier to rotation must reflect the lower π-basicity of Ru^{II} compared with Mo^0 or W^0.[57]

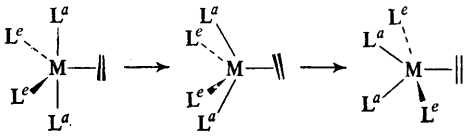
For five-co-ordinate alkene complexes (32) the calculated barrier for simple rotation about the M—C_2H_4 axis is more than twice the barrier obtained if



(35) (36) (37)

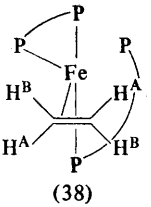
[54] T. A. Albright, R. Hoffmann, J. C. Thibeault, and D. L. Thorn, *J. Am. Chem. Soc.*, 1979, **101**, 3801.
[55] C. Bachmann, J. Demuynck, and A. Veillard, *J. Am. Chem. Soc.*, 1978, **100**, 2366.
[56] U. Koemm, C. G. Kreiter, and H. Strack, *J. Organomet. Chem.*, 1978, **148**, 179.
[57] L. D. Brown, C. F. J. Barnard, J. A. Daniels, R. J. Mawby, and J. A. Ibers, *Inorg. Chem.*, 1978, **17**, 2932.

LML angles are allowed to change as the rotation proceeds. The net result is that alkene rotation and Berry pseudorotation are strongly coupled (Scheme 4)

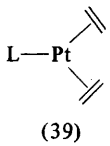


Scheme 4

so that a 90° alkene rotation leads to the initial geometry.[54] Studies on $[Co(Bu^tNC)_4(tcne)]X$ (tcne = tetracyanoethylene) and related compounds are consistent with this mechanism.[58] Interestingly E_a and $\Delta S^{\ddagger}$ are fairly insensitive to the nature of the isocyanide but very sensitive to X in CH_2Cl_2 solution, in which ion-pairing is important. For the complex above $E_a = 13.0$ ($X = ClO_4$), 16.1 ($X = PF_6$), and 18.5 ($X = BPh_4$) kcal mol^{-1}, the activation energy increasing with increasing bulk of the counter-anion. The ^1H n.m.r. spectrum of the complex $[Fe(C_2H_4)(Me_2PCH_2CH_2PMe_2)_2]$ at −25 °C shows four methyl signals and an AA′BB′ C_2H_4 signal (plus ^{31}P coupling) consistent with geometry (38), but a single Me signal and a C_2H_4 quintet at 80 °C after coalescence of these signals. For a rigid FeP_4 arrangement alkene rotation would not exchange H^A and H^B, but the mechanism in Scheme 4 leads to the observed exchanges.[59] For $RCH{=}CH_2$ rotational barriers are in the order $R = Me < H < CO_2Me < CN$, which correlates with the increasing strength of the Fe—alkene bonding (in particular the π-component).



(38)



(39)

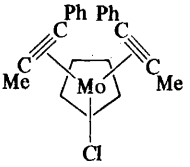
The importance of electronic effects on rotational barriers is best assessed in alkene complexes of low co-ordination number, and $[Pt(C_2H_4)_2L]$ (L = tertiary phosphine or arsine) with the planar arrangement (39) is a good example. Table 2 shows how $\Delta G^{\ddagger}$ for rotation varies with L; the most basic phosphines (small or bulky) give the highest values. Furthermore replacement of one C_2H_4 by C_2F_4 leads to a decrease in the barrier for the remaining C_2H_4. These effects are entirely consistent with the barrier increasing with increasing π-basicity of Pt.[60] Rotational barriers for $[W(C_5H_5)(CO)_2(C_2H_4)Me]$ and the corresponding indenyl complex are the same.[61]

[58] K. Sato, K. Kawakami, and T. Tanaka, *Inorg. Chem.*, 1979, **18**, 1532.
[59] C. A. Tolman, S. D. Ittel, A. D. English, and J. P. Jesson, *J. Am. Chem. Soc.*, 1978, **100**, 4080.
[60] N. C. Harrison, M. Murray, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1978, 1337.
[61] H. G. Alt, J. A. Schwärzle, and C. G. Kreiter, *J. Organomet. Chem.*, 1978, **153**, C7.

Table 2 ΔG^* *at coalescence for alkene rotation in the complexes* $[Pt(C_2H_4)_2L]$

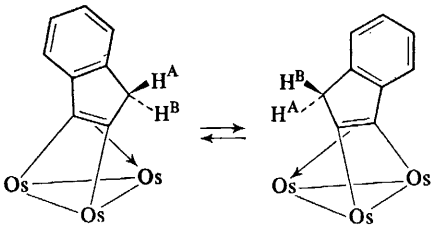
L	PMe_3	PMe_2Ph	$PMePh_2$	PPh_3	PCy_3
ΔG^*/kcal mol^{-1}	13.0	12.4	12.2	10.2	12.8

In $[Mo(C_5H_5)Cl(PhC{\equiv}CMe)_2]$ the rotations of the alkynes are not independent.[62] Compound (40) gives two *cis*-isomers, one of which is illustrated, and a *trans*-isomer which interconvert by alkyne rotation, but the rates of interchange of the *trans*- with the *cis*-isomers are not the same so that the rate of rotation of one alkyne is sensitive to the orientation of the other.



(40)

The rotation of the μ^3-indyne ligand derived from indene in the cluster $[H_2Os_3(C_9H_6)(CO)_9]$ with respect to the Os_3 triangle has been described. Although such rotations had been indicated by earlier results, the exchange of H^A with H^B clearly shows that the rotation interconverting (41) and (42) is associated with a flipping of the organic ligands so that the opposite faces are successively involved in the η^2-bond (Scheme 5).[63] The non-equivalent hydride ligands exchange faster



(41) (42)

Scheme 5

than H^A with H^B, presumably by an independent route. A theoretical treatment to establish the preferred configurations of μ^3-ligands such as alkynes or $C{=}CH_2$ in trinuclear clusters and the barriers to their rotation has been carried out.[64]

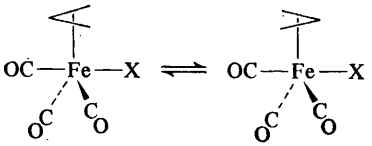
η^1–η^3 Conversions of Allyl Complexes.—The direct thermal decarbonylation of $[Mn(CO)_5(\eta^1\text{-crotyl})]$ gives $[Mn(CO)_4(\eta^3\text{-crotyl})]$ with the η^3-ligand in the *syn*-configuration irrespective of whether the initial η^1-crotyl contained a *cis* or a *trans* double bond. However, using $[Ir(diphos)_2]Cl$ as the decarbonylation agent to allow the use of milder conditions, it was shown that *cis*-η^1-crotyl gave *anti*-

[62] J. W. Faller and H. H. Murray, *J. Organomet. Chem.*, 1979, **172**, 171.
[63] A. J. Deeming, *J. Organomet. Chem.*, 1978, **150**, 123.
[64] B. E. R. Schilling and R. Hoffmann, *J. Am. Chem. Soc.*, 1979, **101**, 3456.

η^3-crotyl and *trans*-η^1-crotyl gave *syn*-η^3-crotyl, so that the conversion can be carried out with retention of configuration.[65]

Both η^1- and η^3-allyl complexes of Pt^{II} are accessible and their interchange is readily facilitated by loss or gain of various ligands.[66] $[Pd(C_5H_5)(2\text{-methylallyl})(PR_3)]$ exists in two isomeric forms rapidly interconverting to give coalesced n.m.r. signals at room temperature. At $-60\,^{\circ}C$ separate n.m.r. signals were obtained for the major isomer, which is the 18-electron complex with η^1-allyl and η^5-C_5H_5, and for the minor 16-electron isomer having η^3-allyl and η^1-C_5H_5.[67] This is an unusual case of simultaneous η^1–η^3 and η^5–η^1 ligand interconversions as a rapid intramolecular process.

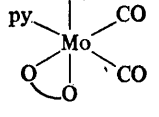
Exchange Involving η^3- but not η^1-Allyl Ligands.—Several papers have appeared describing intramolecular rotation of η^3-allyl groups with respect to the other stationary ligands or the combined movement of η^3-allyl and other ligands, both occurring without the *syn–anti* hydrogen exchange which characterizes η^1–η^3 interconversions.[68–71] In solutions at low temperatures the *endo*-isomer (43) of $[FeX(C_3H_5)(CO)_3]$ predominates in a mixture with the *exo*-isomer (44) (Scheme 6). Spin saturation can be transferred from the *anti*-protons of (44) to the *anti*-



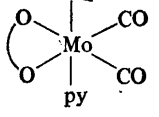
(43) (44)

Scheme 6

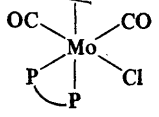
protons of (43) without affecting the *syn*-protons of (43). Thus they are interconverting, but not *via* η^1-allyl intermediates, and the simplest motion to accomplish this is an allyl rotation.[68] For $[MoCl(\eta^3\text{-}C_3H_5)(CO)(diphos)]$ a similar allyl rotation is also observed.[69] However, simple rotation about the M—allyl axis will not lead to the observed n.m.r. coalescences in $[Mo(\eta^3\text{-}C_3H_5)(acac)(CO)_2(py)]$, isomers (45) and (46),[70] and in $[MoCl(\eta^3\text{-}C_3H_5)(CO)_2(Ph_2PCH_2CH_2PPh_2)]$ (47).[71] The intramolecular interchange of the major isomer (45) with



(45)



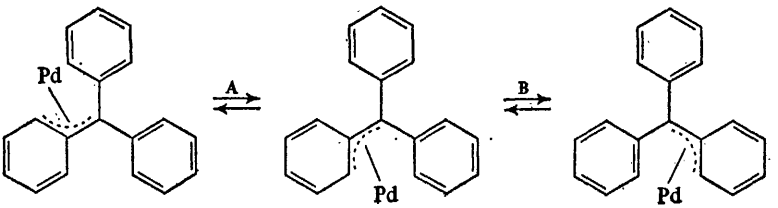
(46)



(47)

[65] N. N. Druz, V. I. Klepikova, M. I. Lobach, and V. A. Kormer, *J. Organomet. Chem.*, 1978, **162**, 343.
[66] G. Carturan, A. Scrivanti, U. Belluco, and F. Moriandi, *Inorg. Chim. Acta*, 1978, **27**, 37.
[67] H. Werner and A. Kühn, *Angew. Chem. Int. Ed. Engl.*, 1979, **18**, 416.
[68] J. W. Faller and M. A. Adams, *J. Organomet. Chem.*, 1979, **170**, 71.
[69] J. W. Faller and D. A. Haitko, *J. Organomet. Chem.*, 1978, **149**, C19.
[70] B. J. Brisdon and A. A. Woolf, *J. Chem. Soc., Dalton Trans.*, 1978, 291.
[71] J. W. Faller, D. A. Haitko, R. D. Adams, and D. F. Chodosh, *J. Am. Chem. Soc.*, 1979, **101**, 865.

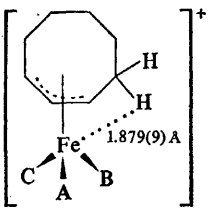
the minor (46) leads to n.m.r. coalescences while for (47) exchange of the ends of the allyl occurs, and both require stereochemical non-rigidity of the octahedral geometry. A Bailar twist mechanism could interconvert (45) and (46) and also seems to be necessary for (47), but barriers of *ca.* 11 kcal mol^{-1} are very low for such motions.



Scheme 7

The η^3-allyl complex [Pd(acac)(CPh_3)] (Scheme 7) undergoes three distinct dynamic processes leading to n.m.r. coalescences which are, in decreasing order of rate, process (A), process (B), and a process (C) leading to the interchange of the non-equivalent ends of the acetylacetonato-ligand which remain distinct during (A) and (B).[72] The rate of (C) is slightly concentration dependent, unlike (A) and (B), and the process is probably not intramolecular.

The cyclo-octenyl complex [Fe(η^3-C_8H_{13}){$P(OMe)_3$}$_3$]$^+$ (48) is a very interesting (formally 16-electron) compound which achieves co-ordinative saturation by a two-electron donation from a filled σ-(sp^3)C—H bond of a CH_2 group next to the η^3-allyl.[73,74] This lowers the symmetry, so that three separate ^{31}P signals are expected for the phosphites A, B, and C. A very fast process leading to an AB_2 spectrum interchanges B with C as the Fe–H interaction oscillates between the two adjacent CH_2 sites to generate a time-averaged plane of symmetry. A slower process exchanges A, B, and C. The corresponding 17-electron paramagnetic complex formed by a one-electron (Na–Hg) reduction is similarly dynamic but so rapidly so that the two processes are characterized by appropriate coalescences in the e.s.r. spectrum.[75] For the oscillation $k = 10^{10}$ s^{-1} at room

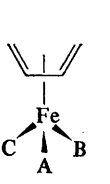


(48)

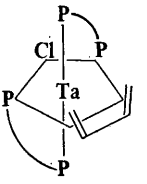
[72] B. E. Mann, A. Keasey, A. Sonodo, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1979, 338.
[73] S. D. Ittel, F. A. Van-Catledge, C. A. Tolman, and J. P. Jesson, *J. Am. Chem. Soc.*, 1978, **100**, 1317.
[74] J. M. Williams, R. K. Brown, A. J. Schultz, G. D. Stucky, and S. D. Ittel, *J. Am. Chem. Soc.*, 1978, **100**, 7407.
[75] S. D. Ittel, P. J. Krusic, and P. Meakin, *J. Am. Chem. Soc.*, 1978, **100**, 3264.

temperature ($E_a = 4.0$ kcal mol^{-1}) and for the rotation $k = 2 \times 10^8$ s^{-1} ($E_a = 5.1$ kcal mol^{-1}). The rotation (A, B, and C exchange) in the cation has $E_a = 14.4$ kcal mol^{-1}.

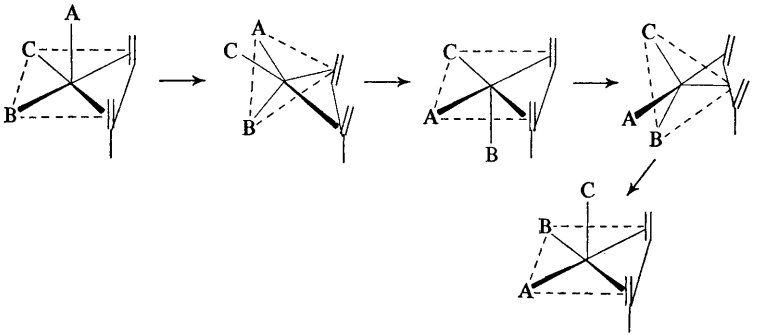
η^4-Diene Complexes.—Intramolecular exchange has been studied in complexes of form [M(η^4-diene)L_3],[76–78] the variable-temperature $^{31}P\{^1H\}$ n.m.r. work on [Fe(isoprene){P(OMe)$_3$}$_3$] (49) being the most complete study.[77] The observed lineshapes for the coalescence of the three ^{31}P signals were compared with those calculated for various permutations of phosphites A, B, and C. The observed and calculated spectra can only be reconciled for a cyclical exchange of the phosphite ligands, which of course amounts to a rotation of the diene. Regarding (49) as a square pyramid with A in the axial site, two Berry pseudorotations *via* trigonal bipyramids would give the same permutation of ligands (Scheme 8). Two alternative descriptions of the same ligand permutations are described for the complex (50), [TaCl(η^4-naphthalene)($Me_2PCH_2CH_2PMe_2$)$_2$], which can be regarded as a



(49)



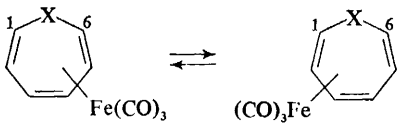
(50)



Scheme 8

pentagonal bipyramid. ^{31}P Coalescences can be interpreted in terms of a naphthalene rotation or a pentagonal bipyramid transverse through a monocapped trigonal prism.[79] The complex [Cr(diene)(CO)$_4$] is fluxional when the diene is butadiene but not when it is cyclo-octa-1,5-diene.[80]

[76] M. Bressan, R. Ettorre, and P. Rigo, *J. Organomet. Chem.*, 1978, **144**, 215.
[77] F. A. Van-Catledge, S. D. Ittel, and J. P. Jesson, *J. Organomet. Chem.*, 1979, **168**, C25.
[78] H. Behrens, G. Thiele, A. Pürzer, P. Würstl, and M. Moll, *J. Organomet. Chem.*, 1978, **160**, 255.
[79] J. O. Albright, S. Datta, B. Bezube, J. K. Kouba, D. S. Marynick, S. S. Wreford, and B. M. Foxman, *J. Am. Chem. Soc.*, 1979, **101**, 611.
[80] C. G. Kreiter and Özkar, *J. Organomet. Chem.*, 1978, **152**, C13.



X = CO or CH_2

Scheme 9

The diene complexes in Scheme 9 exist in the enantiomeric forms shown. Irradiation with circularly polarized light (380—500 nm) leads[81] to selective destruction of one enantiomer to give the observed rotation $\alpha_D = +(0.012 \pm 0.002)°$ after 3% destruction, which gives an estimated specific rotation for the pure enantiomer of *ca.* 700°. To observe the effect at all the equilibrium in Scheme 9 must be very slow. Where $X = CH_2$ there is no n.m.r. line-broadening up to 100 °C, consistent with a slow equilibrium, but spin saturation could be transferred from site 1 to site 6, consistent with the 1,3-shift occurring at a significant rate.[82]

Other Polyene or Polyenyl Complexes.—The complex $[Mo(\eta^1\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)(NO)(S_2CNR_2)]$ (R = Me or Bu^n) undergoes three independent fluxional processes: rotation about the C—N bond of the sulphur ligand, 1,2-shifts of the η^1-C_5H_5 ligand, and a slower interchange between the C_5H_5 ligands. It has been unambiguously shown by spin-saturation transfer methods that 1,2-shifts are faster than 1,3-shifts in the η^1-ligand, confirming earlier work.[83] Exchange between the three CO groups of $[Fe(CO)_3(dienyl)]^+$ (containing a substituted pentadienyl) has been thoroughly examined by lineshape analysis of the coalescing ^{13}C n.m.r. signals and measured barriers to $Fe(CO)_3$ rotation agree closely with those derived from extended Hückel calculations.[84] The complexes $[M(\eta^6\text{-cyclo-octatetraene})(CO)_3]$ (M = Cr or W) have been well studied; earlier work showed the simultaneous collapse of all the CH signals consistent with ring-whizzing by random or 1,3-shifts. Use of spin-saturation transfer methods, however, has shown that spin-saturation transfer is not random but rather a combination of 1,2- and 1,3-shifts is required to fit the observations. Ring-whizzing and ring exchange have been studied for two related polyene complexes, $[Fe(\eta^4\text{-}C_8H_8)(\eta^6\text{-}C_8H_8)]$ (C_8H_8 = cyclo-octatetraene)[86] and $[Ru(\eta^4\text{-}C_6Me_6)(\eta^6\text{-}C_6Me_6)]$.[87] In the iron complex, whizzing of the η^4-ring occurs rapidly ($\Delta G^{\ddagger} = 5.4$ kcal mol^{-1}), ring interchange more slowly ($\Delta G^{\ddagger} = 10.9$ kcal mol^{-1}), while shifts in the η^6-ring occur more slowly if at all. The four types of CH in the η^6-ring retain their differentiation in the transition state, which leads to η^4–η^6 ring interchange. The ring interchange in the Ru complex appears to involve

[81] S. Litman, A. Gedanken, Z. Goldschmidt, and Y. Bakal, *J. Chem. Soc., Chem. Commun.*, 1978, 983.
[82] K. J. Kavel and M. Brookhart, *J. Am. Chem. Soc.*, 1978, **100**, 1619.
[83] M. M. Hunt, W. G. Kitu, B. E. Mann, and J. A. McCleverty, *J. Chem. Soc., Dalton Trans.*, 1978, 467.
[84] P. A. Dodosh, D. G. Gresham, D. J. Kowalski, C. P. Lillya, and E. S. Magyar, *Inorg. Chem.*, 1978, **17**, 1775.
[85] J. A. Gibson and B. E. Mann, *J. Chem. Soc., Dalton Trans.*, 1979, 1021.
[86] B. E. Mann, *J. Chem. Soc., Dalton Trans.*, 1978, 1761.
[87] M. Y. Darensbourg and E. L. Muetterties, *J. Am. Chem. Soc.*, 1978, **100**, 7425.

the 16-electron intermediate $[Ru(\eta^4\text{-}C_6Me_6)_2]$. The rate of localized exchange in the η^4-ring is enhanced and the rate for the slower η^4–η^6 ring interchange to a smaller extent on adding $AlMe_3$ to the solution. The effect is dependent upon $[AlMe_3]$ but the mechanism is not understood.

N.m.r. line-broadening effects are observed to result from rapid electron transfer between $[Cr(arene)_2]$ and the paramagnetic $[Cr(arene)_2]^+$, from which k(exchange) is calculated to be about 3×10^8 M^{-1} s^{-1}. The rate is insensitive to the degree of methylation of the arene.[88]

[88] Ch. Elschenbroich and U. Zenneck, *J. Organomet. Chem.*, 1978, **160**, 125.

2

Metal–Carbon Bond Formation and Cleavage, Including Oxidative Addition and Reductive Elimination

BY A. J. DEEMING

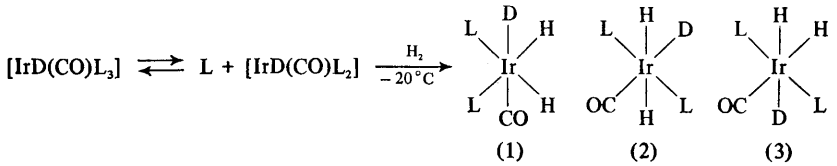
Metal-to-carbon σ-bonds may be formed and cleaved by various reactions, of which oxidative addition and reductive elimination are only one aspect. Oxidative addition involves various mechanisms and extends beyond organometallic chemistry so that reactions not involving M—C bonds will also be included here.

1 Oxidative Addition and Reductive Elimination

Factors affecting oxidative addition/reductive elimination equilibria have been discussed. Enthalpies of addition have been measured[1,2] and decreasingly exothermic additions found to be in the order $Cl_2 > Br_2 > I_2 >$ *ortho*-tetrachloro-1,2-benzoquinone > HBr > HCl > $CF_3C{\equiv}CCF_3$ > tetracyanoethylene > $O_2 > C_2F_4$-$H_2 > MeO_2CC{\equiv}CCO_2Me > C_2H_4 > SO_2 \sim CO$ for the additions of these molecules to $[IrCl(CO)(PPh_3)_2]$. In general, the enthalpies of addition to Ir are 50% greater than to Rh, and for $[IrX(CO)(PR_3)_2]$ the additions are increasingly exothermic in the order F < Cl < Br < I, while the influence of PR_3 must be considered in terms of steric as well as electronic factors (for example, by using Tolman's σ and v values, respectively). Photoelectron spectra of tertiary phosphines have given vertical ionization potentials for the lone pairs and contrary to normal belief these are greater for alkyl- than for aryl-phosphines (PMe_3 8.58, PMe_2Ph 8.37, $PMePh_2$ 8.07, and PPh_3 8.1 eV),[3] the reverse order to that expected from their basicities (pK_a for conjugate acids: PMe_3 7.85, PMe_2Ph 6.25, $PMePh_2$ 4.65, PPh_3 3.05).[4] It is argued that the greater rates and equilibrium constants for the oxidative addition to PMe_3 compared with PPh_3 compounds must be of steric rather than electronic origin, on the basis of vertical ionization potentials.[3] However, vertical ionization potentials of PR_3 may be unreliable when their influence on the nucleophilic/basic metal centre is assessed since changes in the CPC angles and other relaxation effects on co-ordination are not taken into account.[4]

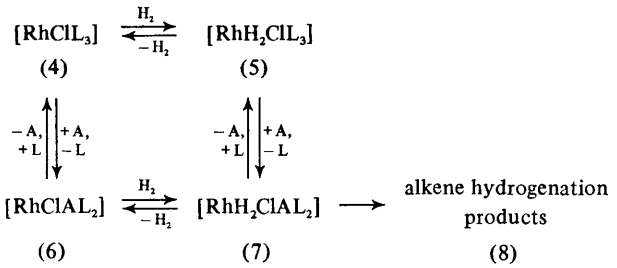
[1] N. E. Burke, A. Singhal, M. J. Hintz, J. A. Ley, H. Hui, L. R. Smith, and D. M. Blake, *J. Am. Chem. Soc.*, 1979, **101**, 74.
[2] R. S. Drago, M. S. Nozari, R. J. Klinger, and G. S. Chamberlain, *Inorg. Chem.*, 1979, **18**, 1254.
[3] J. Behan, R. A. W. Johnstone, and R. J. Puddephatt, *J. Chem. Soc., Chem. Commun.*, 1978, 444.
[4] B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1979, 104.

Hydrogen.—A justified generalization, it seems, is that H_2 only adds readily to co-ordinatively unsaturated complexes in a *cis* manner and *via* a three-centred MH_2 transition state. However, H_2 reacts with $[IrH(CO)L_2]$ ($L = PPh_3$), formed in a dissociative pre-equilibrium from $[IrH(CO)L_3]$, to give *fac-* and *mer-*$[IrH_3(CO)L_2]$, and deuterium labelling has indicated *trans* addition;[5] see Scheme 1. *trans* Addition in forming (2) is not necessary if there is an intramolecular conversion of (3) into (2), but this was not shown.



Scheme 1

The addition of H_2 to $[RhCl(alkene)L_2]$ ($L = PPh_3$) has been studied by stopped-flow methods, where alkene A = styrene or acrylonitrile, and leads to alkene hydrogenation products.[6,7] Constants K_{67} and k_{78} (Scheme 2) were abstracted



Scheme 2

from kinetic data. The equilibrium constant K_{67} is greater for styrene (3.2×10^3 M) than for acrylonitrile (3.5×10^2 M), while for these alkenes, respectively, $k_{78} = 2.7$ and $0.5\ s^{-1}$. The less electron-withdrawing alkene leads to a higher equilibrium constant for the oxidative addition and a lower value for alkene incorporation (K_{46}), as expected from simple considerations.

The reductive elimination of H_2 has been studied mechanistically in a few cases. The protonation of $[CoH\{P(OR)_3\}_4]$ gives $[CoH_2\{P(OR)_3\}_4]^+$, which exchanges H_2 with D_2 without formation of HD, so that an oxidative addition/reductive elimination pathway is proposed.[8] The reaction of the dihydride cation with phosphite is also believed to occur *via* a preliminary reductive elimination

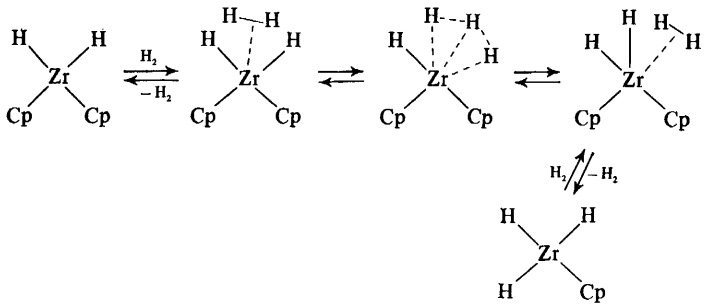
[5] J. F. Harrod, G. Hamer, and W. Yorke, *J. Am. Chem. Soc.*, 1979, **101**, 3987.
[6] Y. Ohtani, A. Yamagishi, and M. Fujimoto, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 69.
[7] Y. Ohtani, A. Yamagishi, and M. Fujimoto, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 2562.
[8] E. L. Muetterties and P. L. Watson, *J. Am. Chem. Soc.*, 1978, **100**, 6978.

of H_2 (P = trialkyl phosphite) [see equations (1) and (2)]. At 30 °C $k_1 = 4.2 \times 10^{-5}$

$$[CoH_2P_4]^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2 + [CoP_4]^+ \quad (1)$$

$$[CoP_4]^+ + P \xrightarrow{k_2} [CoP_5]^+ \quad (2)$$

s^{-1} for $P = P(OMe)_3$, which is at least 10^3 times faster than the reductive elimination of methane from $[CoHMe\{P(OMe)_3\}_4]^+$, which could be a general difference between the elimination of alkanes compared with hydrogen. The elimination of H_2 from $[MoH_2(C_5H_5)_2]$ is more complicated. Thermally, the dihydride reacts with CO (1 atm, 80 °C, 24 h) to give $[Mo(CO)(C_5H_5)_2]$, $[Mo(C_5H_7)(C_5H_5)(CO)_2]$, and $[MoH(C_5H_5)_2(CO)]^+[Mo(C_5H_5)(CO)_2]^-$, from which it is clear that H_2 elimination competes with H_2 transfer to C_5H_5.[9] Photochemically, a concerted H_2 elimination gives the reactive intermediate $[Mo(C_5H_5)_2]$, which gives simple adducts with CO, PPh_3, or C_2H_2, but in the absence of the ligands $[Mo(C_5H_5)_2]$ reacts with $[MoH_2(C_5H_5)_2]$ to release more H_2. The photochemistry of this system has been considered in some detail.[10] In contrast, $[ZrH_2(C_5H_5)_2]$ reacts by associative paths, as in its rapid exchange with D_2 at −78 °C to give $[ZrHD(C_5H_5)_2]$ and HD. MO calculations for various possible intermediates indicate (Scheme 3) that the H—H bond of the incoming molecule is cleaved as a new



Scheme 3

H—H bond is being formed.[11] This avoids the need to give $[ZrH_4(C_5H_5)_2]$ by oxidative addition. The related hydrogenolysis of Zr—Me of $[ZrHMe(C_5H_5)_2]$ has been treated similarly.

Reductive elimination of H_2 as shown below occurs by two parallel pathways, one first-order and the other second-order in complex concentration. The first-

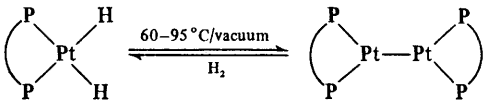
$$2[HCo^{III}(dmgH)_2(PBu_3)] \rightleftharpoons H_2 + 2[Co^{II}(dmgH)_2(PBu_3)]$$

order path is also first-order in $[H^+]$ after allowing for the acid–base equilibrium involving protonation/deprotonation of oxime oxygen atoms, while the other

[9] M. A. Adams, K. Folting, J. C. Huffman, and K. G. Caulton, *J. Organomet. Chem.*, 1979, **164**, C29.
[10] G. L. Geoffroy and M. G. Bradley, *Inorg. Chem.*, 1978, **17**, 2410.
[11] H. H. Brintzinger, *J. Organomet. Chem.*, 1979, **171**, 337.

path shows no $[H^+]$ dependence. The paths are identified with heterolytic and homolytic cleavage of Co—H, respectively.[12]

The reversible reaction in Scheme 4 is believed to occur *via* the 14-electron



Scheme 4

mononuclear intermediate Pt(diphos), where the diphosphine ligand is Bu^tPh-$PCH_2CH_2PBu^tPh$, for example.[13] With bulky unidentate phosphines mononuclear PtL_2 complexes are known but with these the H_2 adduct, but probably not the addition, is *trans*.

Oxygen.—Oxygen adducts of square-planar d^8-complexes are best described as octahedral peroxo d^6-complexes. Early determinations of O—O lengths in adducts of Ir^I (1.30—1.63 Å) led to the idea that the electronic structure of the co-ordinated O_2 was extremely dependent upon the electron density at the metal as controlled by the other ligands. The bond-length range is in fact much smaller (1.45—1.50 Å) so that all adducts of Ir^I and Rh^I are peroxo species. An examination of the kinetic and mechanistic details of the addition indicates that there is no chemically significant intermediate in the formation of the peroxo derivative of $[M(Ph_2PCH_2CH_2PPh_2)_2]^+$ (M = Co, Rh, or Ir),[14] *i.e.* there is no evidence against a direct single-step sideways O_2 addition.

However, reactions subsequent to the addition may be important. The kinetics of the reaction of $[RhCl(CO)L_2]$ $[L = PPh_2(OBu^i)]$ with O_2 in dimethylacetamide (DMA) are consistent with the mechanism given in Scheme 5. The overall

$$[RhCl(CO)L_2] \underset{k_{-1},+L}{\overset{k_1,-L}{\rightleftharpoons}} \text{solvated species } Rh^I \xrightarrow{k_2,+O_2} \text{products}$$

Scheme 5

stoicheiometry is given in equation (3). There is a first-order rate dependence on

$$4[RhCl(CO)L_2] + 5O_2 \xrightarrow[DMA]{60\ ^\circ C} [Rh_4Cl_4(CO)_4(O_2)_2L_2] + 6L{=}O \qquad (3)$$

$[O_2]$ at low pressures with the order falling and approaching zero on an increase in pressure to about 700 Torr. This was shown to be consistent with the rate law as derived from the mechanism in Scheme 5: $-d[O_2]/dt = k_1k_2[Rh^I][O_2]/(k_{-1}[L] + k_2[O_2])$.[15]

Halogens.—The chlorination of $[PdCl_4]^{2-}$ in aqueous solution involves a rapid oxidation followed by a slow replacement of co-ordinated chloride by solvent.[16]

[12] T.-H. Chao and J. H. Espenson, *J. Am. Chem. Soc.*, 1978, **100**, 129.
[13] T. Yoshida, T. Yamagata, T. H. Tulip, J. A. Ibers, and S. Otsuka, *J. Am. Chem. Soc.*, 1978, **100**, 2063.
[14] L. Vaska, R. C. Patel, and R. Brady, *Inorg. Chim. Acta*, 1978, **30**, 239.
[15] W. R. Cullen, B. R. James, and G. Strukul, *Inorg. Chem.*, 1978, **17**, 484.
[16] R. J. Mureinik and E. Pross, *J. Coord. Chem.*, 1978, **8**, 127.

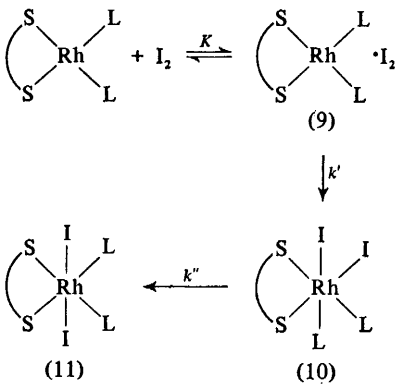
The oxidation reaction is first-order in both complex and chlorine. The dependence on $[Cl^-]$ at high chloride concentrations leads to the mechanistic interpretation given in equations (4) and (5). The authors believe that the final step

$$[PdCl_4]^{2-} + 2Cl^- \rightleftharpoons [PdCl_6]^{4-} \quad (4)$$

$$[PdCl_6]^{4-} + Cl_2 \longrightarrow [PdCl_6]^{2-} + 2Cl^- \quad (5)$$

shown is an outer-sphere electron-transfer process. At low chloride concentrations the kinetics would not be easily interpreted because of the partial conversion of chlorine into HOCl and the presence of aquo-palladium(II) species.

In the reaction of I_2 with the dimethyldithiocarbamato complex $[Rh(S_2CNMe_2)L_2]$ (L = 2,4,6-trimethylphenyl isocyanide) three species of stoicheiometry $[RhI_2(S_2CNMe_2)L_2]$ appear to be involved (Scheme 6).[17] The first is



Scheme 6

believed to be a charge-transfer adduct (9) formed in a pre-equilibrium and, since stopped-flow kinetics were measured with an excess of I_2 present, is formed essentially completely in the early stages. The observed first-order rate constant for formation of the *cis* adduct (10) is given by $k_{obs} = Kk'[I_2]/(1 + K[I_2])$, which reduces to $k_{obs} = k'$ since $K[I_2] \gg 1$. The formation of (10) ($t_{1/2} = 3$ ms at 10 °C) is complete before significant isomerization to the *trans*-isomer (11) ($t_{1/2}$ for isomerization = 3 s at 10 °C). In the study of the I_2 addition to $[RhL_4]ClO_4$ (L = 2,4,6-trimethylphenyl isocyanide) the stopped-flow kinetics have again been interpreted in terms of an intermediate *cis*-adduct.[18] The visible spectrum of the intermediate is close to that of the product *trans*-$[RhI_2L_4]ClO_4$ so it is unlikely to be a charge-transfer adduct.

The cleavage of metal–metal bonds by Br_2 is a form of oxidative addition. The reactions of tertiary-phosphine-substituted derivatives of $[M_2(CO)_{10}]$ ($M_2 = Mn_2$, MnRe, or Re_2) with Br_2 are kinetically complicated, with orders of reaction in bromine as high as three.[19] This could be a consequence of rapid pre-association with Br_2 prior to the slow oxidation step, and in the case of

[17] R. Kuwae, T. Tanaka, and K. Kawakami, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 437.
[18] R. Kuwae and T. Tanaka, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 1067.
[19] G. Kramer, J. Patterson, and A. Poë, *J. Chem. Soc., Dalton Trans.*, 1979, 1165.

$[Mn_2(CO)_8(PEt_2Ph)_2]$ there is kinetic evidence for this. An electrophilic attachment of Br_2 at CO oxygen atoms is suggested.

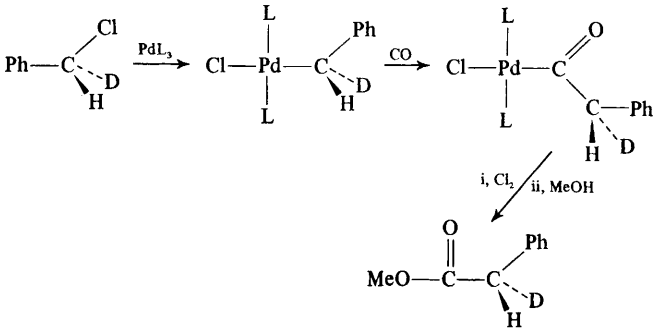
Sulphonyl Halides.—The rate of oxidative addition of RSO_2Cl to Vaska-type compounds $[IrX(CO)L_2]$ is given by $-d[Ir^I]/dt = k_2[Ir^I][RSO_2Cl]$. Rates decrease in the orders $I^- > Br^- > Cl^-$ for X^- and $PMePh_2 > P(4\text{-}MeC_6H_4)_3 > PPh_3 > P(OPh)_3$ for L, which is to be expected for a nucleophilic metal centre.[20] However, the order of rate dependence on the nature of the sulphonyl chloride is $4\text{-}MeC_6H_4SO_2Cl > PhSO_2Cl > 4\text{-}ClC_6H_4SO_2Cl$, which is interestingly the reverse trend of that found for the oxidative addition of aryl azides or aryl thiols. The mechanism is unknown although it appears not to involve radicals.

Alkyl, Aryl, and Allyl Halides.—The normal MeI oxidative addition products of square-planar d^8-complexes contain Me ligands. Thus at room temperature $[Fe(PMe_3)_4]$ in pentane reacts with MeI to give $[FeMeI(PMe_3)_4]$, but reaction in ether at $-30\,^\circ C$ gives the isomer $[FeHI(PMe_3)_3(PMe_2Et)]$. The deuteriated species $[Fe\{P(CD_3)_3\}_4]$ under the low-temperature conditions reacts with CH_3I to give $[FeDI\{P(CD_3)_3\}_3\{P(CD_3)_2(CD_2CH_3)\}]$, and this appears to indicate that at low temperatures the Fe^{II} tautomer (13) in the equilibrium in equation (6)

$$\underset{(12)}{[Fe(PMe_3)_4]} \rightleftharpoons \underset{(13)}{[FeH(PMe_3)_3(CH_2PMe_2)]} \qquad (6)$$

reacts preferentially at carbon with MeI.[21] The product formed at room temperature is not formed by rearrangement of the adduct of (13) but by direct addition at (12).

The optically active benzyl halide PhCHDCl reacts with $[Pd(PEt_3)_3]$ to give $[Pd(PhCHD)Cl(PEt_3)_2]$ with net (72%) inversion of configuration at carbon as established by the reaction sequence in Scheme 7, in which the stereochemistry

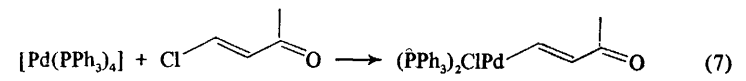


Scheme 7

of the benzyl chloride and ester can be related, CO insertion being assumed to occur with retention.[22] Inversion is consistent with an S_N2 mechanism, but this alone would not account for the lost activity. This loss was shown not to be

[20] M. Kubota, C. J. Curtis, and T. G. Chappell, *Inorg. Chim. Acta*, 1978, **27**, 261.
[21] H. H. Karsh, *Chem. Ber.*, 1978, **111**, 1650.
[22] Y. Becker and J. K. Stille, *J. Am. Chem. Soc.*, 1978, **100**, 838.

caused by a nucleophilic exchange in the neutral σ-benzyl complex nor by a σ–π rearrangement, which does occur, but stereospecifically with retention at carbon.[23] Oxidative addition of vinyl chlorides occurs with retention of configuration about the double bond in the example shown in equation (7).[24]



(7)

Earlier work on the reactions of vinyl halides with tertiary phosphine platinum(0) compounds showed that complexes such as [Pt(η^2-vinyl halide)$(PPh_3)_2$] are formed initially, and the kinetics and mechanism of the oxidative addition (isomerization) were examined. Corresponding work on halogenoalkynes has now been carried out.[25] Thus when *cis*-[$PtCl_2(PPh_3)_2$] is reduced with hydrazine in the presence of PhC≡CX ($X^- = Br^-$ or I^-) the product obtained is [PtX(C≡CPh)$(PPh_3)_2$]. However, with PhC≡CCl the intermediate substitution product [Pt(η^2-PhC≡CCl)$(PPh_3)_2$] could be isolated and its internal oxidative addition examined mechanistically [see equation (8)].

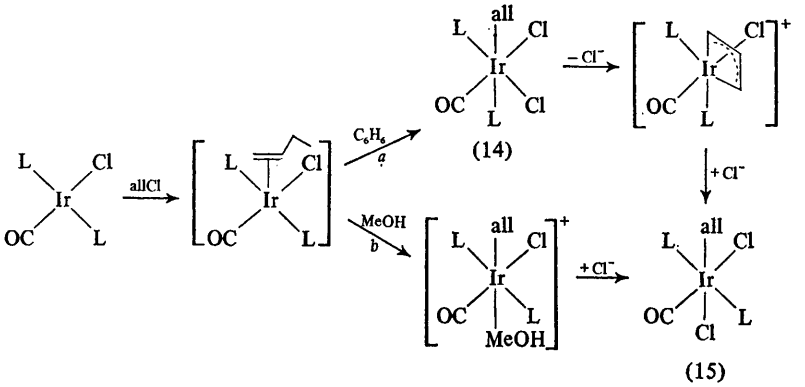
$$[Pt(\eta^2\text{-PhC}{\equiv}CCl)(PPh_3)_2] \longrightarrow \textit{cis}\text{-} + \textit{trans}\text{-}[PtCl(C{\equiv}CPh)(PPh_3)_2] \quad (8)$$

In the different solvents used the *cis*:*trans* product ratio varies and, although first-order kinetics operate over more than three half-lives, initial rates only were used. The first-order rate constants are fairly insensitive to the nature of the alcoholic solvent. Unlike the corresponding isomerization of [Pt(η^2-$Cl_2C{=}CCl_2$)$(PPh_3)_2$], which apparently occurs by an S_N1 chloride loss and recombination, the chloroalkyne complex isomerizes by an intramolecular pathway more like that found for [Pt(η^2-BrFC=CF_2)$(AsPh_3)_2$]. These deductions are based on the observed solvent dependence of the rates.

Oxidative addition of unsaturated halides is also believed to involve η^2-co-ordination prior to C—X cleavage in other cases.[26,27] Allyl chloride reacts 10^4 times faster with [IrCl(CO)$(PMe_2Ph)_2$] than MeI, a larger factor than expected for normal nucleophilic substitution of these compounds.[27] A modified S_N2 mechanism is proposed with somewhat different routes in MeOH and C_6H_6 to account for the different isomers formed as shown in Scheme 8.

Rates of addition in the order $CH_2{=}CHCH_2Cl > CH_2{=}CHCHMeCl > CH_2{=}CMeCH_2Cl \sim MeCH{=}CHCH_2Cl$ are consistent with prior η^2-co-ordination. There is *cis* addition in benzene, whereas in methanol it is believed that Cl^- is lost but displaces a co-ordinated solvent molecule in the final stage. Isomer (14) gives isomer (15) in methanol, $CHCl_3$, MeCN, and even slowly in benzene but at measured rates too low for it to be an intermediate in the oxidative addition in methanol. Furthermore, allyl bromide adds stereospecifically *trans* to [IrCl(CO)$(PMe_2Ph)_2$] if the isomer of type (15) is formed by route *a*, but mixed isomers were obtained by route *b*. Bromide ion released in this route

[23] Y. Becker and J. K. Stille, *J. Am. Chem. Soc.*, 1978, **100**, 845.
[24] M. Onishi, H. Yamamoto, and K. Hiraki, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 1856.
[25] J. Burgess, M. E. Howden, R. D. W. Kemmitt, and N. S. Sridhara, *J. Chem. Soc., Dalton Trans.*, 1978, 1577.
[26] J.-C. Rousche and G. R. Dobson, *J. Organomet. Chem.*, 1978, **150**, 239.
[27] R. G. Pearson and A. T. Poulos, *Inorg. Chim. Acta*, 1979, **34**, 67.



Scheme 8

would exchange with unreacted starting complex. The total racemization of optically active CH_2=CH—CHMeCl in the oxidative addition remains unexplained. A related mechanism is suggested for the reaction of [Mo(phen)-$(CO)_4$] with allyl bromide [equations (9) and (10)] although the evidence is fragile because there is a rate-determining CO loss from the tetracarbonyl.[26] This accounts for allyl bromide addition and thermal substitution by phosphorus ligands both having similar kinetics. Generally, $-d[Mo(phen)(CO)_4]/dt = (k_1 + k_2[X])[Mo(phen)(CO)_4]$ where X= allyl bromide, PR_3, or $P(OR)_3$. In 1,2-dichloroethane $k_2 = 0$ but the THF solution there is a small second-order contribution to the rate.

$$[Mo(phen)(CO)_4] \overset{-CO}{\rightleftharpoons} [Mo(phen)(CO)_3] \xrightarrow[\text{fast}]{\text{allyl bromide}} [Mo(\eta^2\text{-}CH_2{=}CHCH_2Br)(phen)(CO)_3] \quad (9)$$

$$[Mo(\eta^2\text{-}CH_2{=}CHCH_2Br)(phen)(CO)_3] \xrightarrow{\text{fast}} [MoBr(\eta^3\text{-}C_3H_5)(phen)(CO)_2] + CO \quad (10)$$

The kinetics of the related oxidative addition of allyl halides (allY) to *fac*-$[MX(phen)(CO)_3]^-$ (M = Mo or W) have not been measured but the product is $[MX(\eta^3\text{-all})(phen)(CO)_2]$ and Y^-.[28] This would support the loss of halide to solution from the η^2-allyl halide in the oxidation step rather than its transfer directly to the metal atom.

Reactions of halocarbons RX, including allyl bromide, with *cis*-$[M(CO)_2(dmpe)_2]$ (M = Cr or Mo, dmpe = $Me_2PCH_2CH_2PMe_2$) do not give alkyl complexes but *cis*-$[MX(CO)_2(dmpe)_2]X$ or *trans*-$[MoH(CO)_2(dmpe)_2]X$.[29] Various forms of evidence, including e.s.r. spectroscopy, have been used to support an outer-sphere electron transfer from complex to RX to give a paramagnetic M^I intermediate. Rates have been measured in certain cases and, for $RX = CCl_4$, $-d[Mo(CO)_2(dmpe)_2]/dt = k[Mo(CO)_2(dmpe)][CCl_4]$, which corresponds to the formation of the intermediate *trans*-$[Mo(CO)_2(dmpe)_2]^+$, and

[28] B. J. Brisdon, D. A. Edwards, and J. W. White, *J. Organomet. Chem.*, 1978, **156**, 427.
[29] J. A. Connor and P. I. Riley, *J. Chem. Soc., Dalton Trans.*, 1979, 1318.

similar second-order kinetics are observed for the subsequent conversion of this into *cis*-[MoCl(CO)$_2$(dmpe)$_2$]Cl. The rates of oxidative addition of halocarbons RX to [PtMe$_2$(dipy)] to give *trans*-[PtRXMe$_2$(dipy)] are, not unexpectedly, in the order RX = $CCl_4 > CH_3Cl > CH_2Cl > CHCl_3$.[30]

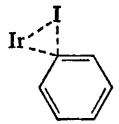
Oxidative addition of simple alkyl halides (MeI, benzyl halides, *etc.*) to [IrCl(CO)(PPh$_3$)$_2$] are second order, but aryl iodides react very much more slowly (moderate rates only at about 150 °C) and by a two-term rate law: $-d[Ir^I]/dt = (k_1 + k_2[ArI])[Ir^I]$ with $k_2 = k'/[PPh_3]$.[31] The mechanism illustrated in equations (11)—(13) is consistent with the rate law if $K \ll [PPh_3]$ (L = triarylphosphine, S = solvent):

$$[IrCl(CO)L_2] + S \rightleftharpoons [IrCl(CO)L(S)] + L \quad (11)$$

$$[IrCl(CO)L(S)] + ArI \longrightarrow [IrClI(Ar)(CO)L(S)] \quad (12)$$

$$[IrClI(Ar)(CO)L(S)] + L \longrightarrow [IrClI(Ar)(CO)L_2] + S \quad (13)$$

This is the first observed behaviour of the type for Vaska's compound, and the higher k_2 values for the less basic phosphines are also unusual and a consequence of the L dissociation mechanism. The linear free-energy relation between k_2 and the Hammett σ_p parameter for substituents on ArI ($\rho = +0.6$) implies an essentially non-polar transition state such as (16).



(16)

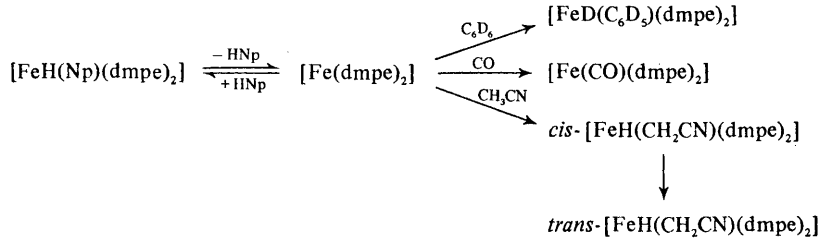
Hydrogen Halides.—Addition of DCl to [PtH(PEt$_3$)$_3$]$^+$ at −80 °C gives the *trans*-adduct, but above −60 °C reductive elimination occurs to regenerate platinum(II) complexes with [HPEt$_3$]$^+$ and [DPEt$_3$]$^+$ among the products. However, a similar low-temperature addition of DCl to *trans*-[PtH(CN)(PEt$_3$)$_2$] gives an isomeric mixture of [PtHD(CN)Cl(PEt$_3$)$_2$] containing H *trans* to both Cl and CN. Either the addition is non-stereospecific or there is rapid H–D scrambling.[32] The kinetics of HCl addition to [IrCl(cod)L] and to [Ir(cod)L$_2$]$^+$ [cod = cycloocta-1,5-diene, L = PPh$_2$(OMe) or PMePh$_2$] have been studied.[33] An analysis of the data reveals that Cl$^-$ adds to the iridium(I) in both cases before H$^+$; see equation (14), for example. Other reported observations were reconsidered in

$$[IrCl(cod)L] + Cl^- \rightleftharpoons [IrCl_2(cod)L]^- \xrightarrow{H^+} [IrHCl_2(cod)L] \quad (14)$$

terms of an initial halide co-ordination, and the authors believe that this may have general implications to the mechanisms of oxidative addition reactions.

[30] J. Kuyper, *Inorg. Chem.*, 1978, **17**, 77.
[31] R. J. Mureinik, M. Weitzberg, and J. Blum, *Inorg. Chem.*, 1979, **18**, 915.
[32] I. M. Blacklaws, L. C. Brown, E. A. Ebsworth, and F. J. S. Reed, *J. Chem. Soc., Dalton Trans.*, 1978, 877.
[33] T. V. Ashworth, J. E. Singleton, D. J. A. de Waal, W. J. Louw, E. Singleton, and E. van der Stok, *J. Chem. Soc., Dalton Trans.*, 1978, 340.

With C—H Bond Cleavage.—The complexes [MH(2-naphthyl)($Me_2PCH_2CH_2PMe_2$)$_2$] (M = Fe, Ru, or Os), abbreviated to [MH(Np)(dmpe)$_2$], readily eliminate naphthalene to give a co-ordinatively unsaturated d^8-intermediate, which rapidly co-ordinates to free ligand, if this is available, or undergoes oxidative addition with C—H cleavage (Scheme 9).[34–36] Most of the oxidative addition reactions



Scheme 9

have the same rate and are first-order in complex; $k(M=Ru) = (3.7 \pm 0.5) \times 10^{-4}$ s^{-1} at 25 °C and $(1.7 \pm 0.17) \times 10^{-3}$ s^{-1} at 40 °C. This rate-determining reductive elimination of naphthalene becomes increasingly slow in the order Fe ≫ Ru ≫ Os.

In the oxidative addition of acetonitrile the formation of the *cis*-product is inhibited by added HNp, whereas the rate of the *cis–trans* isomerization is independent of HNp concentration. The formation of the *cis*-isomer in the oxidative addition is consistent with a three-centred MCH transition state like the MH_2 transition state in the oxidative addition of H_2. There is no evidence yet for the stereochemistry at carbon during sp^3 C—H cleavage by oxidative addition in this or any other system, although there is earlier evidence for retention of configuration in the reverse reductive elimination supposedly occurring in the [$RhCl(PPh_3)_3$]-catalysed decarbonylation of aldehydes. Retention is required by the generally accepted mechanism. The complex [FeH(Np)(dmpe)$_2$] reacts with HCN or HCl by different routes since the reactions are much faster than unimolecular HNp loss would allow, and DCl gives [2-D]naphthalene.

The cleavage of sp^3 C—H bonds by oxidative addition only occurs with fairly acidic molecules, and others have argued that this is an unpromising route to the activation of normal saturated alkanes.[37] The reductive elimination of methane from [$PtHMeP_2$] (P = tertiary phosphine) has the stoicheiometries shown in equations (15) and (16) in the absence or presence of added L (*e.g.* PPh_3 or

$$3[PtHMeP_2] \longrightarrow 3CH_4 + 2[PtP_3] + Pt \quad (15)$$

$$[PtHMeP_2] + L \longrightarrow CH_4 + [PtP_2L] \quad (16)$$

PhC≡CPh), respectively. The rates are the same in both cases and are given by $-d[PtHMeP_2]/dt = k[PtHMeP_2]$ where $k = (4.5 \pm 0.5) \times 10^{-4}$ s^{-1} at −25 °C.[37] A

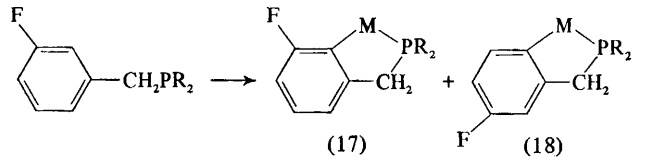
[34] C. A. Tolman, S. D. Ittel, A. D. English, and J. P. Jesson, *J. Am. Chem. Soc.*, 1978, **100**, 4080.
[35] S. D. Ittel, C. A. Tolman, A. D. English, and J. P. Jesson, *J. Am. Chem. Soc.*, 1978, **100**, 7577.
[36] C. A. Tolman, S. D. Ittel, A. D. English, and J. P. Jesson, *J. Am. Chem. Soc.*, 1979, **101**, 1742.
[37] L. Abis, A. Sen, and J. Halpern, *J. Am. Chem. Soc.*, 1978, **100**, 2915.

mixture of $[PtH(CH_3)P_2]$ and $[PtD(CD_3)P_2]$ gave only CH_4 and CD_4, and $[PtH(CD_3)P_2]$ and $[PtD(CH_3)P_2]$ gave only CHD_3 and CH_3D, with $k_H/k_D = 3.3 \pm 0.3$ (for these different isotopes bound to Pt). Results support an intramolecular reaction with rate-determining C–H bond formation as the Pt–C and Pt—H bonds are cleaved [see equation (17)]. Although PtP_2 is very reactive

$$cis\text{-}[PtHMeP_2] \xrightarrow{-CH_4} PtP_2 \xrightarrow{\text{fast}} \text{products} \qquad (17)$$

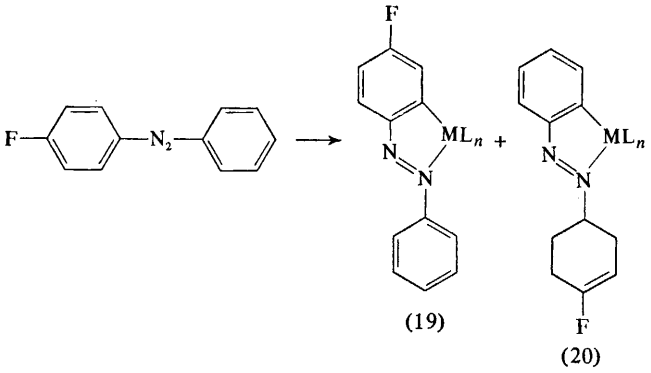
towards oxidative addition, this reaction goes readily to completion so that oxidative addition of CH_4 to PtP_2 is precluded thermodynamically. Decreasing values of k are found for PR_3 in the order $R = 4\text{-}ClC_6H_4 > Ph > 4\text{-}MeC_6H_4 > 4\text{-}MeOC_6H_4$, electron-withdrawing groups favouring the reductive elimination as expected, and for the alkyl group at Pt in the order $Ph > Et > Me > CH_2CH{=}CH_2$.

There are many examples of sp^3, sp^2, or sp C—H bond cleavage in transition-metal compounds, especially if a five-membered chelate ring is formed. From the determined sites of metallation certain metals (*e.g.* Pd^{II} and possibly Pt^{II}) behave as electrophiles, while Mn^I, Ir^I, and Rh^I behave as nucleophiles. For example, $3\text{-}FC_6H_4CH_2PR_2$ has been shown to give the product ratio (17):(18) = 80:20 with Ir^I or Rh^I, but (18) is formed totally with Pd^{II} (Scheme 10).[38]



Scheme 10

Similarly, with 2-, 3-, or 4-substituted $XC_6H_4N{=}NAr$ (Ar = Ph or C_6F_5) the observed site of metallation shows that Pd^{II} is an electrophile, but Mn^I as $[MnMe(CO)_5]$ is a nucleophile. Substituent effects are, however, small. For example, with manganese the ratio (19):(20) = 67:33, but for palladium (19):(20) = 40:60 (Scheme 11).[39] This could indicate that there is little change in electron



Scheme 11

[38] S. Hietkamp, D. J. Stufkens, and K. Vrieze, *J. Organomet. Chem.*, 1979, **168**, 351.
[39] M. I. Bruce, B. L. Goodall, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1978, 687.

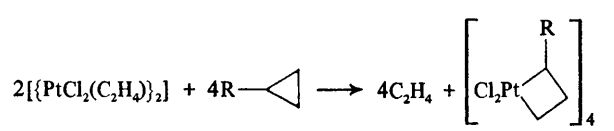
density at the aromatic ring on forming the transition state in these metallations.

It is clear from the nature of the products that in these metallation reactions Ir^I and Rh^I undergo oxidative addition, but with $[MnMe(CO)_5]$ the loss of CH_4 means that oxidative addition, if it occurs, is followed by reductive elimination. The mechanistic details of these reactions remain obscure.

Oxidative addition with cleavage of H—H, C—H, and Si—H bonds requires a co-ordinatively unsaturated metal species such as four-co-ordinate d^8-complexes. Thus, although nucleophilic anions such as $[Mn(CO)_5]^-$ react readily with alkyl halides, the reaction with $HSiPh_3$ is photoinduced.[40] Irradiation gives $[Mn(CO)_4]^-$, which can then undergo oxidative addition leading to *cis*-$[MnH(SiPh_3)(CO)_4]^-$.

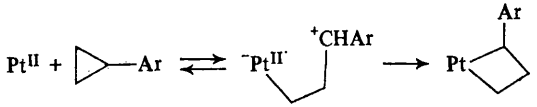
Factors affecting simple reductive elimination *versus* other forms of elimination (*e.g.* α), especially with respect to dihydrides, dialkyls, and mixed alkylhydrides (which eliminate fastest) of mono- and di-nuclear osmium complexes, have been discussed. In compounds such as $[OsHMe(CO)_4]$ or $[OsMe_2(CO)_4]$ simple reductive elimination does not occur; for example, a mixture of $[OsH(CD_3)(CO)_4]$ and $[OsD(CH_3)(CO)_4]$ gave CH_4, CH_3D, CD_3H, and CD_4, and a dinuclear mechanism is proposed.[41]

With C—C Bond Cleavage.—Oxidative addition of this sort only occurs with strained ring compounds, and metal insertions into cyclopropane rings have been reviewed.[42] The oxidative additions of arylcyclopropanes to $[\{PtCl_2(C_2H_4)\}_2]$, which exists as $[PtCl_2(C_2H_4)(THF)]$ in tetrahydrofuran, are first-order in both reactants [equation (18)].[43] In THF solution, in which the most detailed



(18)

kinetics were measured, both the starting material and product, which are dimeric and tetrameric respectively when isolated, seem to be monomeric with co-ordinated solvent. Rates increase with solvent polarity: CH_3CN, $CHCl_3$ > acetone > THF ≫ 1,4-dioxan. This and the negative ΔS^* values (*e.g.* −14 cal K^{-1} mol^{-1} for PhC_3H_5 in THF) indicate that a dipolar or partially dipolar transition state is involved; for 4-XC_6H_4-substituted cyclopropanes rates are in the order X = EtO ≫ Me > H. Co-ordination of the arylcyclopropane prior to C—C cleavage probably occurs and the mechanism in Scheme 12 has been

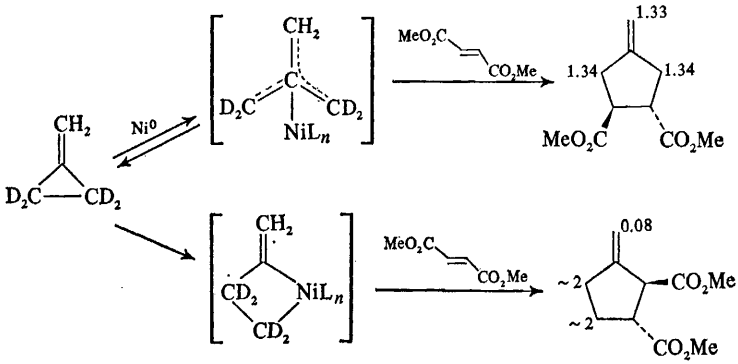


Scheme 12

[40] R. A. Faltynek and M. S. Wrighton, *J. Am. Chem. Soc.*, 1978, **100**, 2701.
[41] J. R. Norton, *Acc. Chem. Res.*, 1979, **12**, 139.
[42] S. Savel, *Acc. Chem. Res.*, 1978, **11**, 204.
[43] R. J. Al-Essa, R. J. Puddephatt, M. A. Quyser, and C. F. H. Tipper, *J. Organomet. Chem.*, 1978, **150**, 295.

suggested, except that the intermediate can only be partially dipolar since there is no isomerization of 1,2-disubstituted cyclopropanes.

In other cases cyclopropane ringopening by oxidative addition to give a metallocyclobutane leads eventually to other derived species. For example, phenylcyclopropane reacts with $[IrCl(N_2)(PPh_3)_2]$ to give the hydrido η^3-allyl complex $[IrHCl(\eta^3\text{-}PhCHCHCH_2)(PPh_3)_2]$, established by *X*-ray diffraction.[44,45] This is probably formed by rearrangement of $[IrCl(PhCHCH_2CH_2)(PPh_3)_2]$. The oxidative addition of methylenecyclopropane to [Ni(acrylonitrile)$_2$] occurs by cleavage of either of the ring C—C bonds as established by using the ring-deuteriated compound. In Scheme 13 the number of deuterium



Scheme 13

atoms in each site of the products is shown and strongly supports these intermediates,[46] formed in both cases by oxidative addition to nickel(0).

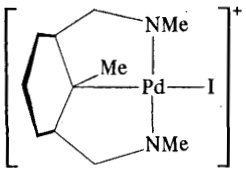
The mechanism of reductive elimination with C—C bond formation has been studied for $[Ni(CN)PhP_2]$, where $P = PEt_3$[47] or PCy_3 (tricyclohexylphosphine).[48] The thermal decomposition of $[Ni(CN)Ph(PCy_3)_2]$ gives very little PhCN, but with an excess of $P(OEt)_3$ this is formed quantitatively by a reaction, first-order in both complex and triethyl phosphite. An associative reaction with reductive elimination from the five-co-ordinate intermediate is most likely since there is no rate retardation by added PCy_3, and the rate characteristics are very like those of bimolecular substitution, which, of course, requires the formation of a very similar intermediate. For the reaction of $P(OEt)_3$ with $[Ni(CN)Ph(PEt_3)_2]$ competitive substitution of phosphine by phosphite and reductive elimination need to be considered to account for the kinetics; in this case added PEt_3 does lead to rate retardation. Nonetheless, reductive elimination from a five-co-ordinate species still seems to operate.

2 Carbon–Hydrogen Bond Cleavage by Electrophilic Metals

There is evidence that palladium(II) is an electrophile in its cyclometallation

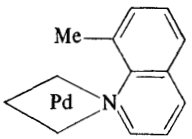
[44] T. H. Tulip and J. A. Ibers, *J. Am. Chem. Soc.*, 1978, **100**, 3252.
[45] T. H. Tulip and J. A. Ibers, *J. Am. Chem. Soc.*, 1979, **101**, 4201.
[46] R. Noyori, M. Yamakawa, and H. Takaya, *Tetrahedron Lett.*, 1978, 4823.
[47] G. Favero, M. Gaddi, A. Morvillo, and A. Turco, *J. Organomet. Chem.*, 1978, **149**, 395.
[48] G. Favero, A. Morvillo, and A. Turco, *J. Organomet. Chem.*, 1978, **162**, 99.

reactions,[39] and Parshall has suggested that in the case of aromatic metallations the Pd initially co-ordinates through nitrogen and then at one face of the arene ring prior to *ortho*-C—H cleavage. The palladations of $PhCH_2NMe_2$ and PhN=NPh are examples. A crystal structure of the MeI adduct of an aryl platinum complex shows an unusual Pt—C bond that seems to model closely the initial stages of cyclopalladation where there is facial attack at the ring (21).[49]

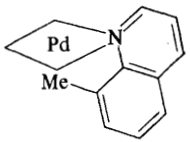


(21)

The initial Pt—C interaction is trapped because of the poor leaving properties of Me^+. The authors, however, think that this is like the final stages of reductive elimination. The palladation of benzo[*h*]quinoline cannot occur by facial attack. Stable Pd^{II} complexes of this ligand and 8-methylquinoline have destabilizing Pd—H interactions above the co-ordination plane,[50] and it appears that factors allowing or favouring the movement of the CH group into the co-ordination plane also favour cyclometallation, which presumably then requires configuration (23) rather than (22).[51] This is consistent with palladium acting as an electrophile, but the intimate mechanisms are still unknown.

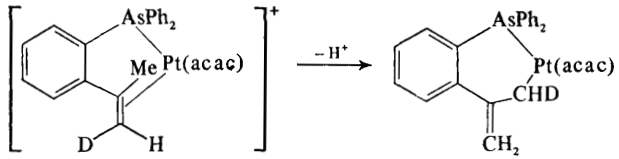


(22)



(23)

The formation of Pt—C σ-bonds by deprotonation of 2-vinylphenylarsines can occur at allylic or vinylic sites, and in each case the C atom σ-bonded to Pt in the product was bonded to Pt in the starting material [equations (19) and (20)]. In one case the C=C bond shifts, but not the other.[52]



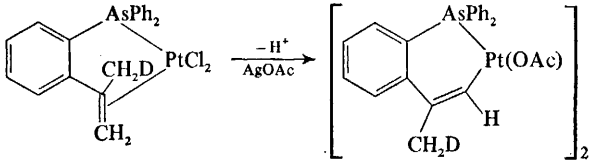
(19)

[49] G. van Koten, K. Timmer, J. G. Noltes, and A. L. Spek, *J. Chem. Soc., Dalton Trans.*, 1978, 250.

[50] A. J. Deeming, I. P. Rothwell, M. B. Hursthouse, and L. New, *J. Chem. Soc., Dalton Trans.*, 1978, 1490.

[51] A. J. Deeming and I. P. Rothwell, *J. Chem. Soc., Chem. Commun.*, 1978, 344.

[52] M. K. Cooper, P. J. Guerney, H. J. Goodwin, and M. McPartlin, *J. Chem. Soc., Chem. Commun.*, 1978, 861.



(20)

3 Cleavage of Metal–Carbon Bonds by Electrophiles

This can occur by initial electrophilic attack at the metal followed by reductive elimination, by outer-sphere electron transfer from the metal followed by nucleophilic displacement at carbon, by direct attack at carbon (or the M—C bond), or, finally, by attack at some other site such as a C=C bond. This topic has been reviewed.[53]

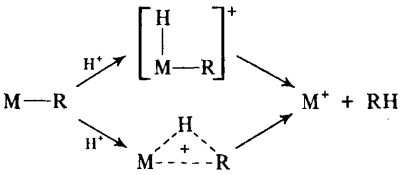
The acidolysis of alkyl or aryl platinum(II) complexes involves at least two mechanisms, the oxidative addition/reductive elimination route or direct protonation of the Pt—C bond. The reactions in equations (21)—(23) have been studied mechanistically:

$$[PtH(CH_2CN)(PPh_3)_2] + HCl \xrightarrow{\text{ref. 54}} [PtHCl(PPh_3)_2] + CH_3CN \quad (21)$$

$$[PtAr_2(PEt_3)_2] + HCl \xrightarrow{\text{ref. 55}} [PtArCl(PEt_3)_2] + ArH \quad (22)$$

$$[PtArMe(PEt_3)_2] + HCl \xrightarrow{\text{ref. 56}} [PtArCl(PEt_3)_2] + CH_4 \quad (23)$$

Generally, rates $= (k_2[H^+] + k_3[H^+][Cl^-])$ [complex]. If k_3 is not zero, as in the cyanomethyl case, an oxidative addition mechanism operates. Protonation leads to $[PtH_2(CH_2CN)(PPh_3)_2(solvent)]^+$, which slowly and directly eliminates CH_3CN (k_2 pathway), or Cl^- replaces the co-ordinated solvent before doing so (k_3 pathway). In the other two examples $k_3 = 0$ and there are quite large kinetic isotope effects ($k_H/k_D = 6$); this is given as clear evidence for direct rate-determining addition at the Pt—C bond without oxidative addition. Perhaps there is a continuum of behaviour between the extremes illustrated in Scheme 14, but this is unknown.



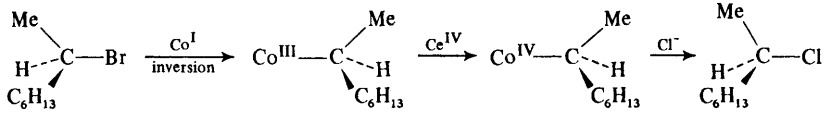
Scheme 14

[53] M. D. Johnson, *Acc. Chem. Res.*, 1978, **11**, 57.
[54] P. Uguagliati, R. A. Michelin, U. Belluco, and R. Ros, *J. Organomet. Chem.*, 1979, **169**, 115.
[55] R. Romeo, D. Minniti, S. Lanza, P. Uguagliati, and U. Belluco, *Inorg. Chem.*, 1978, **17**, 2813.
[56] R. Romeo, D. Minniti, and S. Lanza, *J. Organomet. Chem.*, 1979, **165**, C36.

Further evidence has been given for complete retention of configuration about the C=C bond in the acidolysis of vinyl palladium complexes,[57] but whether oxidative addition occurs or not is unknown.

The gas-phase reaction of $[MnMe(CO)_5]$ with proton donors BH^+ leads to the ions $[Mn(CO)_5]^+$ and $[MnHMe(CO)_5]^+$. The ion $[MnHMe(CO)_5]^+$ is only observed with bases B having lower proton affinity than those giving $[Mn(CO)_5]^+$.[58] Thus protonation can occur at the Mn—Me bond leading directly to methane with little or no activation energy, while protonation at Mn gives the kinetically stable protonated alkyl complex.

Halogen cleavage of alkylcobaloximes such as sec-octylcobaloximes occurs generally with net inversion of stereochemistry at carbon. Two mechanisms have been discussed: an S_E2(inversion) attack of X_2 at carbon or a one-electron transfer from cobalt(III) to X_2 to give an alkylcobalt(IV) species, which undergoes S_N2 displacement at carbon by X^- formed in the oxidation step. Oxidation of alkylcobaloximes by Ce^{IV} does give alkylcobalt(IV) compounds, which are stable at low temperatures, and now it has been reconfirmed that these react with Cl^- to give alkyl chlorides with $90 \pm 10\%$ inversion at carbon, consistent with an S_N2 displacement (Scheme 15).[59] The first-order dependence of the disappearance



Scheme 15

of Co^{IV} on $[Co^{IV}]$ when there is a large excess of Cl^- rules out disproportionation leading to decomposition, as with the corresponding Et complex. Oxidation followed by S_N2 displacement at carbon does not adequately account for the reactions of alkylcobaloximes with ICl.[60] Although there is a partial net inversion, both alkyl iodides and chlorides are formed, whereas S_N2 displacement would only give the chloride. The mechanism in equations (24) and (25) is

$$R—Co^{III} + ICl \longrightarrow R—Co^{IV} + ICl^{\cdot -} \quad (24)$$

$$ICl^{\cdot -} \longrightarrow I^{\cdot} + Cl^- \quad (25)$$

argued to be consistent with the products and their stereochemistry. The alkylcobalt(IV) species undergoes S_H2 attack by $I^{\cdot}$ (inversion) rather than S_N2 with Cl^-, but there could also be homolysis to give alkyl radicals that combine with $I^{\cdot}$ (racemization).

Chemical ($CuCl_2.2H_2O$) or electrochemical oxidation of $[FeR(\eta^5\text{-}C_5H_5)(CO)_2]$ (R = Me, $PhCH_2$, or $PhCH_2CH_2$) with an excess of Cl^- gave $[FeCl(\eta^5\text{-}C_5H_5)(CO)_2]$ and RCl. If this reaction proceeds through $[FeR(\eta^5\text{-}C_5H_5)(CO)_2]^+$, and there is electrochemical evidence for a one-electron oxidation, then

[57] M. D. Frysuk and B. Bosnich, *J. Am. Chem. Soc.*, 1979, **101**, 3043.
[58] A. E. Stevens and J. L. Beauchamp, *J. Am. Chem. Soc.*, 1979, **101**, 245.
[59] R. H. Magnuson, J. Halpern, I. Ya. Levitin, and M. E. Vol'pin, *J. Chem. Soc., Chem. Commun.*, 1978, 44.
[60] J. P. Kitchin and D. A. Widdowson, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1384.

the subsequent reaction with Cl^- follows a different course from that with cobaloximes. Use of *threo*-PhCHDCHD-iron complex gave PhCHDCHDCl with predominant retention, as found in the chlorination of the same complex.[61]

The stereochemistries of the compounds PhCHDCHDX formed by halogenation of *cis-threo*-[PhCHDCHDMn$(CO)_4(PEt_3)$] in both polar and non-polar solvents have been determined for $X^- = Cl^-$, Br^-, or I^-.[62,63] For $X^- = Cl^-$ there is predominant inversion in non-polar solvents with the extent of inversion falling with rising solvent polarity. Iodination on the other hand gives predominant retention in most solvents. Although the kinetics are not given, the stereochemistries were interpreted in terms of S_E2(inversion), S_E2(retention), and what is described as S_E(oxidation) processes; the latter involves a one-electron oxidation to $[Mn^{II}R(CO)_4(PEt_3)]X$ or a two-electron oxidation to $[Mn^{II}R(CO)_4(PEt_3)X]X$ as the first step. Two or more mechanisms result, it seems, from the similar energies of the Mn—C bonding orbital and the 'non-bonding' *d*-orbitals, attack occurring at either.

Mercury(II) chloride reacts with $[FeR(C_5H_5)(CO)_2]$ and *trans*-$[WR(C_5H_5)(CO)_2(PEt_3)]$ (R = *threo*-PhCHDCHD) to give mainly *threo*-[RHgCl] and the corresponding chloro transition-metal compound.[64] This result and earlier kinetic data (for Fe) are consistent with an oxidative addition to give $[FeR(HgCl)(C_5H_5)(CO)_2][HgCl_3]$, which undergoes reductive elimination with retention. A classical S_E2 mechanism is ruled out mainly by the small dependence of the reaction rate on the bulk of the primary alkyl group. With *cis*-$[MnR(CO)_4(PEt_3)]$ there is net inversion of configuration at carbon, and an S_E2(inversion) mechanism is proposed.

[61] W. Rogers, J. A. Page, and M. C. Baird, *J. Organomet. Chem.*, 1978, **156**, C37.
[62] D. Dong, B. K. Hunter, and M. C. Baird, *J. Chem. Soc., Chem. Commun.*, 1978, 11.
[63] D. Dong and M. C. Baird, *J. Organomet. Chem.*, 1979, **172**, 467.
[64] D. Dong, D. A. Slack, and M. C. Baird, *Inorg. Chem.*, 1979, **18**, 188.

3
Insertion Reactions

BY A. J. DEEMING

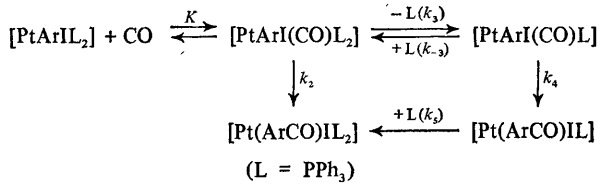
1 Carbon Monoxide Insertion

The kinetics of the carbonylation and decarbonylation reactions in the manganese system

$$[MoR(CO)_5] + CO \rightleftharpoons [Mn(RCO)(CO)_5]$$

have been measured and the influence of group R discussed.[1] Decarbonylations at 80 °C in benzene are first order, with rates varying over about an order of magnitude, decreasing in the order R = cyclohexylmethyl ($k \geqslant 250 \times 10^{-5}$ s^{-1}) > Me > $PhCH_2$ > $MeOCH_2$ > EtO_2C > MeCO > $PhCH_2CO$ > CF_3 ($k = 2.8 \times 10^{-5}$). If the formation of $[Mn(RCO)(CO)_4]$ were rate-determining, electron-withdrawing groups should have given increased rates of CO loss, so perhaps the conversion of $[Mn(RCO)(CO)_4]$ into $[Mn(R)(CO)_4]$ is kinetically significant. In the carbonylation of $[Mn(CH_2R)(CO)_5]$ or $[Fe(CH_2R)(CO)_4]^-$ there is a linear free-energy relationship between log k and the Taft σ^* values for the group RCH_2 over the σ^* range −0.13 to 0.215 but not > 0.215. The slope ρ^* is −8.8 and −8.7 in the two cases, electron-withdrawing groups giving enormously lower rates. The CO insertion into M—H, M—COMe, M—CHO, or M—CH_2OH, each possibly involved in Fischer–Tropsch chemistry, are either very slow or still to be observed and this can be rationalized in terms of σ^* values, although thermodynamic as well as kinetic reasons could prevent certain of these insertions.

trans-$[PtArI(PPh_3)_2]$ inserts CO by dissociative and migration routes *via* five-co-ordinate Pt^{II} carbonyl intermediates (Scheme 1). Values for Kk_3 and Kk_2 were

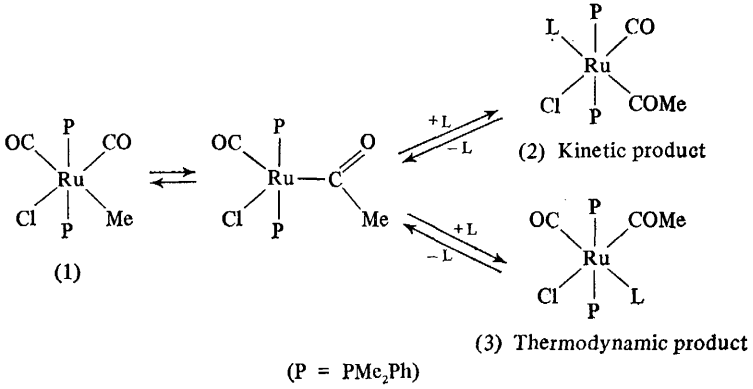


Scheme 1

abstracted from the kinetics so the ratio of dissociative to migration rates (k_3/k_2), but not their absolute values, was established. Electron-withdrawing substituents on the phenyl group give lower k_3/k_2 ratios.[2] An interesting system is described

[1] J. N. Cawse, R. A. Fiato, and R. L. Pruett, *J. Organomet. Chem.*, 1979, **172**, 405.
[2] N. Sugito, J. V. Minkiewicz, and R. F. Heck, *Inorg. Chem.*, 1978, **17**, 2809.

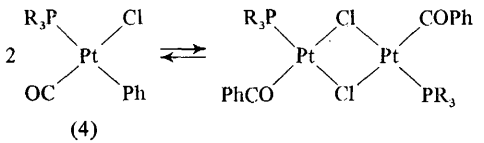
for which rapid alkyl/acyl interconversions can lead to n.m.r. coalescences.[3] In the formation of (2; L=CO) (Scheme 2) the incoming ligand enters *trans* to the



Scheme 2

highly *trans*-directing acyl group, which is also *trans*-labilizing so that coalescence of Me and MeCO n.m.r. signals of (1) and (2) resulting from their rapid exchange is observed. When L=PMe$_2$Ph, the unique phosphine exchanges with free phosphine, an increasing concentration of which suppresses the broadening of the MeCO signals which results from Me/MeCO ligand exchange. Whereas the equilibrium between (1) and (2) is rapid, that between (1) and the thermodynamically stable isomer (3) is not.

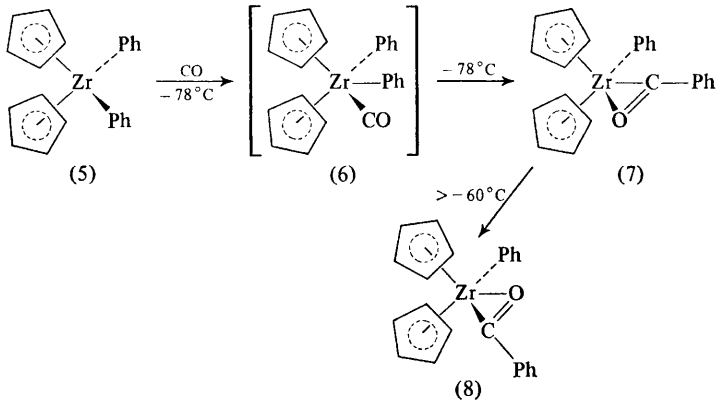
Of the three possible geometric isomers of [PtPhCl(CO)(PR$_3$)], each of which has been characterized, only the one (4) shown in Scheme 3 is in equilibrium with



Scheme 3

the corresponding benzoyl complex.[4,5] The *cis* arrangement of Ph and CO and the position of Ph *trans* to a good *trans*-labilizing group seem to be necessary for insertion. The equilibrium positions correlate with the rates of alkyl migrations as determined in other systems, *i.e.* there is decreasing acyl present in the order Et > Ph > Me > PhCH$_2$. Geometric requirements for facile CO insertion have been examined for [Zr(C$_5$H$_5$)$_2$Ph$_2$]. The CO group does not enter centrally as sometimes envisaged but as shown in Scheme 4. The kinetically controlled η^2-acyl (7) must be formed *via* the intermediate (6). Above −60 °C a first-order isomerization to the thermodynamically more stable isomer (8) occurs.[6]

[3] C. F. J. Barnard, J. A. Daniels, and R. J. Mawby, *J. Chem. Soc., Dalton Trans.*, 1979, 1331.
[4] G. K. Anderson and R. J. Cross, *J. Chem. Soc., Chem. Commun.*, 1978, 819.
[5] G. K. Anderson and R. J. Cross, *J. Chem. Soc., Dalton Trans.*, 1979, 1246.
[6] G. Erker and F. Rosenfeldt, *Angew. Chem. Int. Ed. Engl.*, 1978, **17**, 605.



Scheme 4

A keen point of interest is whether or under what conditions CO insertion into M—H bonds can occur and a report that $[Zr(C_5H_5)_2HCl]$ reacts with CO to give $[(C_5H_5)_2ClZr—CH_2—O—ZrCl(C_5H_5)_2]$ is an interesting example.[7] Criteria established for CO insertions with Mn or Fe do not apply to the early transition metals where the hydrides are more nucleophilic and products stabilized (as with η^2-acyls) by strong M—O bonds. Formyl complexes of the middle to late transition metals have not been formed by CO insertion but by hydride addition at CO or by reaction of metal carbonyl anions with formylacetic anhydride, for example. With $[Mn(CO)_5]^-$ the latter compound gives $[Mn_2(CO)_{10}]$, and $H^{13}CO—O—COMe$ has been used to establish the course of this reaction.[8] Thus 60–80% of the ^{13}C is incorporated into $[Mn_2(CO)_{10}]$, almost certainly *via* $[Mn(H^{13}CO)(CO)_5]$ which readily decarbonylates to $[MnH(CO)_4(^{13}CO)]$ and hence to the parent carbonyl.

The decomposition of $[Mn(HCO)(CO)_5]$ must have $k \geqslant 1.2 \times 10^{-2}$ s^{-1} at 20 °C compared with $k = 2 \times 10^{-4}$ s^{-1} at 14 °C for $[Mn_2(CO)_9(CHO)]^-$; the anion is kinetically more inert and this seems to be a general phenomenon. Insertion of CO into M—H bonds is not the only, or possibly the main, route to CO reduction by transition-metal hydrides. The complex $[Co_2(CO)_8]$ in benzene catalyses benzene reduction as well as CO reduction to methanol, methyl formate, *etc.* with CO–H_2 at 300 atm and 200 °C.[9] Pseudo-first-order rate constants defined by $d[\text{product}]/dt = k[CoH(CO)_4]$ are 1.6×10^{-5} and 5.6×10^{-6} s^{-1} for methanol and methyl formate respectively. The endothermic abstraction of H atoms from $[HCo(CO)_4]$ by CO ($\Delta H^\circ = 40.0 \pm 1.7$ kcal mol^{-1}),

$$[HCo(CO)_4] + CO \longrightarrow HCO\cdot + \cdot Co(CO)_4$$

is proposed as a key step in the reduction and is compatible with the observed activation enthalpy for formation of reduction products; $\Delta H^* = 40.7 \pm 6\%$ kcal

[7] G. Fachinetti, C. Floriani, A. Roselli, and S. Pucci, *J. Chem. Soc., Chem. Commun.*, 1978, 269.
[8] R. A. Fiato, J. L. Vidal, and R. L. Pruett, *J. Organomet. Chem.*, 1979, **172**, C4.
[9] J. W. Raithke and H. M. Feder, *J. Am. Chem. Soc.*, 1978, **100**, 3623.

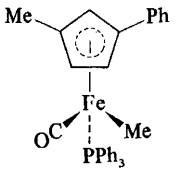
mol^{-1}. A reduction mechanism of this sort would seem to require H—M bond strengths not much greater than 58 kcal mol^{-1}, as observed for $[HCo(CO)_4]$.

Decarbonylation of metal acyls can lead to isomerized alkyl complexes. Thus $[IrCl(CO)(cyclo\text{-}octene)_2]_2$ reacts with RCOCl to give $[IrRCl_2(CO)_2]_2$, in which R may have isomerized, but this results from subsequent reversible β-eliminations rather than from the decarbonylation step itself.[10]

An MO treatment of the CO insertion reaction has been carried out to evaluate the geometric aspects of the conversion of $[MnMe(CO)_5]$ into $[Mn(MeCO)(CO)_4]$. Other aspects of CO insertion have also been tackled, *i.e.* the possible involvement of dinuclear mechanisms, solvent effects, which can be considerable, possible CHO formation from the hydride, size effects of the migrating group, the effect of the other ligands, *etc.*[11] The treatment does not seem to require any fundamental modification of empirically derived views of the reaction.

2 Sulphur Dioxide Insertion

Earlier results showing that SO_2 insertion into transition metal–alkyl bonds occurs with inversion at carbon have been confirmed using $[Fe(C_5H_5)(CO)_5R]$, *cis*-$[Mn(CO)_4(PEt_3)R]$, and *trans*-$[W(C_5H_5)(CO)_2(PEt_3)R]$ (R = *threo*-PhCHDCHD).[12] Furthermore, using compound (9), it has been shown that SO_2 insertion to give the $MeSO_2$ complex occurs with 95% stereospecificity in CH_2Cl_2 and with 79% stereospecificity in neat SO_2.[13] The absolute configuration of the

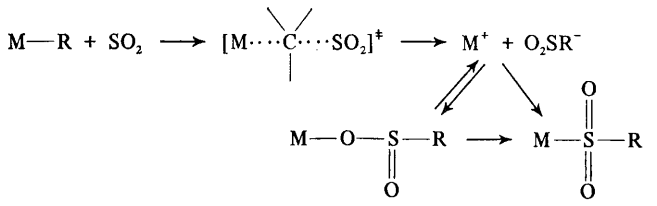


(9)

corresponding $Me_2CHCH_2SO_2$ complex has been determined by *X*-ray anomalous dispersion techniques showing that there is retention of configuration at iron.[14] SO_2-insertion into the Ti—Me bond of $[Ti(C_5H_5)(C_5H_4CHMePh)Me(C_6F_5)]$ also occurs stereospecifically at Ti and probably with retention.[15]

These observations together with earlier kinetic data have been interpreted in terms of the mechanism in Scheme 5. An electrophilic displacement at carbon leads to the ion-pair $M^+O_2SR^-$ with inversion at carbon. Furthermore the 16-electron cation M^+, for example $[Fe(C_5H_5)(CO)(PPh_3)]^+$, must be non-planar and hence chiral. It is not entirely clear to what extent the configuration of the cation is maintained by ion-pair formation, since the partial epimerization in neat SO_2 is attributed to a partial dissociation of the ion-pair. It seems best explained

[10] M. A. Bennett, R. Charles, and T. R. B. Mitchell, *J. Am. Chem. Soc.*, 1978, **100**, 2737.
[11] H. Berke and R. Hoffmann, *J. Am. Chem. Soc.*, 1978, **100**, 7224.
[12] D. Dong, D. A. Slack, and M. C. Baird, *J. Organomet. Chem.*, 1978, **153**, 219.
[13] T. G. Attig, R. G. Teller, S.-M. Wu, R. Bau, and A. Wojcicki, *J. Am. Chem. Soc.*, 1979, **101**, 619.
[14] S. L. Miles, D. L. Miles, R. Bau, and T. C. Flood, *J. Am. Chem. Soc.*, 1978, **100**, 7278.
[15] A. Dormand, C. Moise, A. Dahchour, and J. Tirouflet, *J. Organomet. Chem.*, 1979, **168**, C53.



Scheme 5

by the barrier to inversion being higher in the ion-pair, since calculations indicate that the 16-electron compound is most favourably non-planar and that this does not require ion-pairing.

An alternative mechanism might operate with organocobaloximes, and possibly other systems as well.[16] Evidence is given for a radical-chain mechanism with initiation by C—Co rupture or adventitious Co^{II} impurities with the following propagation steps:

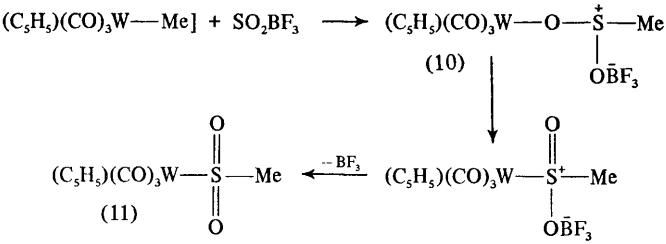
$$\left.\begin{aligned} M\cdot + SO_2 &\longrightarrow MSO_2\cdot \\ MSO_2\cdot + RM &\longrightarrow MSO_2R + M\cdot \end{aligned}\right\}$$

and/or

$$\left.\begin{aligned} R\cdot + SO_2 &\longrightarrow RSO_2\cdot \\ RSO_2\cdot + RM &\longrightarrow MSO_2R + R\cdot \end{aligned}\right\}$$

The transfer of alkyl groups between metal atoms was established in mixed Co and Rh systems. The insertion reaction is markedly photocatalysed, the rates are variable, there are induction periods, and Co^{II} catalyses the reaction. These observations support the radical nature of the reaction.

Boron trifluoride in SO_2 leads to SO_2 insertion rates for $[W(C_5H_5)(CO)_3R]$ ($R = Me$ or $PhCH_2$) up to 2×10^4 times faster than without BF_3 present.[17] This is not a catalytic effect since the product (10) contains BF_3. This slowly isomerizes (Scheme 6) and then can give (11) by loss of BF_3. The actual reagent is believed to be $O{=}\overset{+}{S}{-}O\bar{B}F_3$, which is more electrophilic than SO_2.



Scheme 6

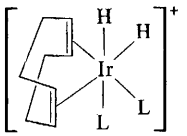
[16] A. E. Crease and M. D. Johnson, *J. Am. Chem. Soc.*, 1978, **100**, 8013.
[17] R. G. Severson and A. Wojcicki, *J. Am. Chem. Soc.*, 1979, **101**, 877.

3 Alkene and Alkyne Insertion

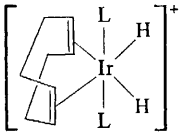
The kinetics have been measured for the insertion of acrylonitrile into the Pt—H bond of the 3-cyanopropyl hydrido-complex (12) (L = PPh_3). The rate is first order

$$\underset{(12)}{\textit{trans}\text{-}[PtH(C_3H_6CN)L_2]} + CH_2{=}CHCN \longrightarrow \underset{(13)}{\textit{cis}\text{-}[Pt(C_3H_6CN)(CH_2CH_2CN)L_2]}$$

in both (12) and acrylonitrile and is suppressed by added L. The replacement of L by alkene in a rapid pre-equilibrium is apparently followed by a slower insertion reaction. Evidence for five-co-ordinate species in this system was obtained by addition of L to (12) to give an equilibrium containing $[PtH(C_3H_6CN)L_3]$ ($K = 70 \pm 10\ M^{-1}$ at $-130\ °C$).[18] It is commonly believed that the system M(C=C)H must be planar for alkene insertion and some evidence for this is that complex (14) undergoes alkene insertion, leading to cyclo-octene, at least 40 times faster than (15).[19,20] Both have mutually *cis*-alkenes and hydrides but only (14) has this planar arrangement.



(14)



(15)

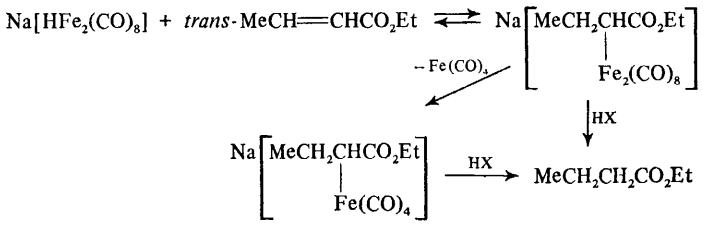
The insertion–β-elimination equilibrium between (16) and (17) is reported to be sufficiently rapid for n.m.r. line-broadening; broad ^1H n.m.r. signals for Rh*H* and C_2H_4 are observed at room temperature which sharpen to the expected

$$\underset{(16)\ (18\text{-electron})}{[Rh(C_5H_5)H(C_2H_4)(PMe_3)]^+} \rightleftharpoons \underset{(17)\ (16\text{-electron})}{[Rh(C_5H_5)(Et)(PMe_3)]^+}$$

double doublet for Rh*H* ($\delta -10.5$) and two multiplets for C_2H_4 (δ 3.0 and 3.5) at $-20\ °C$. Since the other resonances are sharp at both temperatures, the rapid equilibrium shown probably accounts for the observations. One would not normally expect such behaviour except where, as here, 16- and 18-electron systems are both readily accessible.[21]

Attempting to establish the mechanism of the reaction of $[HFe_2(CO)_8]^-$ with activated alkenes, it was shown that the reaction is first order in alkene and hydride, that there is a regiospecific reversible insertion step (D-exchange studies), and that there is an inverse isotope effect ($k_D/k_H = 3.5$) for change of hydride for deuteride. There is good evidence that the reversible insertion step occurs with the dimer and without CO dissociation, unlike the corresponding reaction with $[HFe(CO)_4]^-$ which requires a preliminary loss of CO. The subsequent competitive breakdown into mononuclear species and acidolysis are slow steps (Scheme 7).[22]

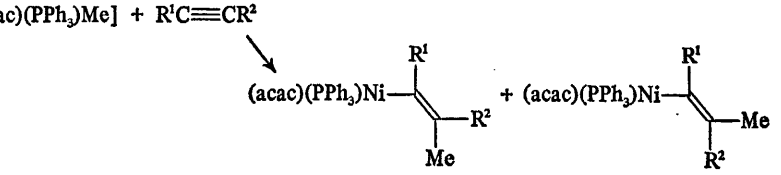
[18] R. Ros, R. A. Michelin, R. Bataillard, and R. Roulet, *J. Organomet. Chem.*, 1979, **165**, 107.
[19] R. H. Crabtree, H. Felkin, T. Khan, and G. E. Morris, *J. Organomet. Chem.*, 1978, **144**, C15.
[20] R. H. Crabtree, H. Felkin, T. Fillebeen-Khan, and G. E. Morris, *J. Organomet. Chem.*, 1979, **168**, 183.
[21] H. Werner and R. Feser, *Angew. Chem. Int. Ed. Engl.*, 1979, **18**, 157.
[22] J. P. Collman, R. G. Finke, P. L. Matlock, R. Wahren, R. G. Komoto, and J. I. Brauman, *J. Am. Chem. Soc.*, 1978, **100**, 1119.



Scheme 7

There has been an MO examination of the pathways for C_2H_4 insertion into $[PtHCl(PH_3)_2]$, and the H-transfer to co-ordinated C_2H_4 in three-, four-, and five-co-ordinate species in various geometries was examined.[23] The most favourable arrangement proved to be a four-co-ordinate complex with *cis* H and C_2H_4, leading directly to the ethyl complex. The C_2H_4 is perpendicular to the square plane in the ground state for steric reasons, it seems, but with low-energy requirements to rotate into the plane prior to H-migration. It is perhaps surprising that no easy route through a five-co-ordinate intermediate was found as this would lead directly to the square-planar 16-electron product which has been frequently invoked as the mechanism in the past.

cis-Addition of M—H or M—R across alkynes is normally observed but there are several cases of *trans*-addition.[24, 25] Care must be taken in interpreting the stereochemistry of the insertion reaction in terms of the stereochemistry of the product even if this has been shown to be kinetically controlled. [Ni(acac)-(PPh_3)Me] reacts with PhC≡CPh to give exclusively the *trans*-product but with PhC≡CMe exclusively the *cis*-product (Scheme 8), whereas if the products are



Scheme 8

allowed to reach equilibrium a mixture of *cis*- and *trans*-compounds is obtained in each case.[25] The rate of insertion decreases with increasing $[PPh_3]$ and the insertion takes place for [Ni(acac)Me(alkyne)] probably with *cis* geometry. Rapid PPh_3-catalysed *cis-trans* equilibrium in the intermediate [Ni(acac)(vinyl)] leads to the observed stereochemistries in the product formed by PPh_3 addition. If this interpretation is correct, it leaves unresolved the nature of the mechanism for the *cis–trans* isomerization.

Although insertion into M—C bonds should occur intramolecularly this need not be so for M—H bonds. Alkynes react with $[PdH(NO_3)(PR_3)_2]$ to give

[23] D. L. Thorn and R. Hoffmann, *J. Am. Chem. Soc.*, 1978, **100**, 2079.
[24] N. C. Rice and J. D. Oliver, *J. Organomet. Chem.*, 1978, **145**, 121.
[25] J. M. Huggins and R. G. Bergman, *J. Am. Chem. Soc.*, 1979, **101**, 4410.

[Pd(alkenyl)(NO_3)L_2] either directly *via* [PdH(alkyne)L_2]$^+$ or by protonation of [Pd(alkyne)L_2].[26] Zero-valent Pt^0 complexes are obtained in the corresponding reaction with Pt and these may be protonated to give Pt^{II} alkenyl complexes. However, evidence that the H atom remains bound to Pd throughout until it is finally transferred to the alkyne came from the observed formation of the alkenyl compound even in the presence of 'proton sponge'. In other cases deprotonation to give Pt^0 followed by protonation is proposed.[27]

[26] H. C. Clark and C. R. Milne, *J. Organomet. Chem.*, 1978, **161**, 51.
[27] T. G. Attig, *Inorg. Chem.*, 1978, **17**, 3097.

4
Ligand Reactions

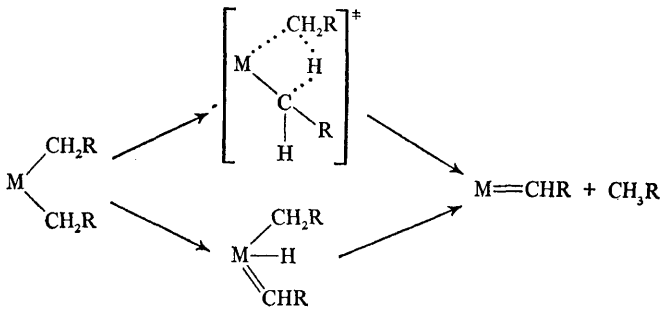
BY A. J. DEEMING

1 α-Elimination Reactions

Two important modes of decomposition of transition-metal alkyls are α- and β-elimination, while intramolecular reductive elimination, oxidative addition (*e.g.* γ-elimination), and homolytic M—C bond fission are other pathways available. The formation of alkylidene complexes by α-elimination has been reviewed.[1] The mechanism of α-elimination has received some attention recently but is not well worked out. The thermal decomposition of pentabenzyltantalum has the following stoicheiometry, although the nature of the Ta product is obscure:

$$2[Ta(CH_2Ph)_5] \longrightarrow 5PhCH_3 + [Ta_2(CHPh)_5]$$

The observed first-order rate constant for decomposition is independent of the initial concentration and experiments to distinguish an intramolecular mechanism from a free-radical chain reaction rule out the former.[2] It is rather more difficult to establish whether the α-H atom is transferred to Ta initially or directly to the more basic axial alkyl group (Scheme 1).

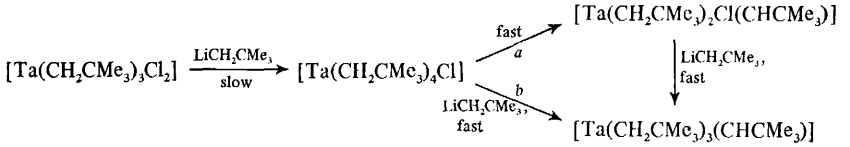


Scheme 1

The complex $[Ta(CH_2CMe_3)_3Cl_2]$ reacts with $LiCH_2CMe_3$ to give $[Ta(CH_2CMe_3)_4Cl]$ by a slow rate-determining step and hence by a faster reaction to $[Ta(CH_2CMe_3)_3(CHCMe_3)]$.[3] Using CD_2CMe_3 as the group in both reagents,

[1] R. R. Schrock, *Acc. Chem. Res.*, 1979, **12**, 98.
[2] V. Malatesta, K. U. Ingold, and R. R. Schrock, *J. Organomet. Chem.*, 1978, **152**, C53.
[3] R. R. Schrock and J. D. Fellmann, *J. Am. Chem. Soc.*, 1978, **100**, 3359.

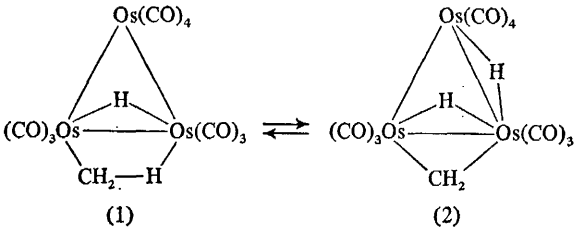
mainly CD_3CMe_3 was obtained so that the α-D is transferred to give neopentane but there is evidence that $[Ta(CH_2CMe_3)_5]$ is not involved in these reactions. Of the two routes in Scheme 2 it seems that both may operate, (*a*) being favoured in non-polar solvents.



Scheme 2

The kinetics of the decomposition of $[Ta(C_5H_5)(CH_2CMe_3)_2Cl_2]$ (existing as rapidly interconverting *cis*- and *trans*-isomers) show first-order behaviour.[4] $[Ta(C_5H_5)(CHCMe_3)Cl_2]$ (>95%) is formed in the dark at < 30 °C but more of other products under other conditions. A mixture of CH_2CMe_3 and CD_2CMe_3 complexes gave almost exclusively CH_3CMe_3 and CD_3CMe_3 in the early stages before significant intermolecular ligand transfer had taken place, indicating an intramolecular path. The ratio $k_H/k_D = 6 \pm 1$ was determined by use of the $CHDCMe_3$ complex. There is evidence that only the *cis*-isomer is active so that the leaving alkyl group must be *cis* to the incipient alkylidene, and a concerted H-transfer to the alkyl is therefore preferred.

In other examples, however, H-atom transfer from the α-carbon to the metal atom does occur. The clearest case is shown in Scheme 3. The equilibrium is fast

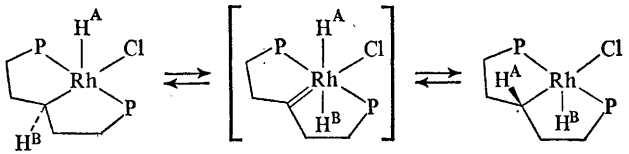


Scheme 3

enough ($k \approx 10^{-3}$ s^{-1} at 14 °C) for spin-saturation transfer methods to be used. The CH_3 group has three different H environments rapidly interchanging. Since one H is in a bridging site between C and Os, very little rearrangement is required for the α-elimination. Interestingly there is a very marked equilibrium isotope effect favouring D bound to Os or in a bridging site between C and Os.[5,6] The ability to form a bonding H—M interaction prior to α-C—H cleavage might be a property of polynuclear metal compounds, but rapidly reversible α-elimination also occurs with mononuclear compounds. Complex (3), derived from

[4] C. D. Wood, S. J. McLain, and R. R. Schrock, *J. Am. Chem. Soc.*, 1979, **101**, 3210.
[5] R. B. Calvert, J. R. Shapley, A. J. Schultz, J. M. Williams, S. L. Suib, and G. D. Stucky, *J. Am. Chem. Soc.*, 1978, **100**, 6240.
[6] R. B. Calvert and J. R. Shapley, *J. Am. Chem. Soc.*, 1978, **100**, 7726.

$Bu^t_2P(CH_2)_5PBu^t_2$ and $RhCl_3.3H_2O$, undergoes the rapid equilibrium shown in Scheme 4 so that the ^{103}Rh resonance, from $^1H\{^{31}P,^{103}Rh\}$ INDOR measure-



(3) (4)

Scheme 4

ments, is a 1:2:1 triplet due to coupling to H^A and H^B, which are effectively equivalent.[7] Co-ordinative unsaturation seems necessary for this process to be rapid and notably (3) and (1) are unsaturated, unless one regards the two electrons in the σ-C—H bond of (1) as saturating the complex. Furthermore, if H^B in (3) is replaced by Me the complex is non-dynamic.

Reversible H-transfer between metal and α-carbon atoms is also required in the loss of ethylene from $[(C_5H_5)_2WMe(CH_2CH_2PMe_2Ph)]^+$ to give $[(C_5H_5)_2WH(CH_2PMe_2Ph)]^+$ and hence by isomerization to $[(C_5H_5)_2WMe(PMe_2Ph)]^+$. If the original complex contains the CD_3 group it generates the new CD_3 complex in >97% isotopic purity by this route, and a reversible 1,2-H shift equilibrium between the 16-electron intermediate $[(C_5H_5)_2WMe]^+$ and the 18-electron $[(C_5H_5)_2WH(CH_2)]^+$ is necessary to account for this behaviour.

In Scheme 2 α-elimination at the neopentyl complex is shown, but neopentyl complexes may also undergo γ-elimination. Thus $[Pt\{P(C_2D_5)_3\}_2(CH_2CMe_3)_2]$ (5) decomposes at 157 °C in cyclohexane to (8) (80%) and neopentane.[9] Reaction of (8) with DCl confirmed that γ-C—H cleavage had occurred and since the corresponding CD_2CMe_3 complex gives CHD_2CMe_3 the γ-H must be transferred to the neopentyl group lost. The empirical rate law below is consistent with Scheme 5

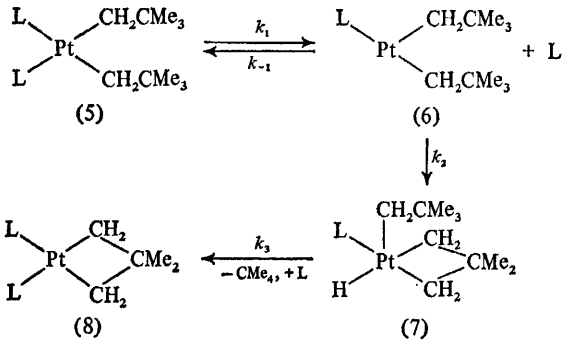
$$d[(5)]/dt = k_{obs}[(5)][L]^{-1} \quad (L = \text{triethylphosphine})$$

if either the oxidative addition (k_2) or reductive elimination (k_3) is rate-limiting. Indeed (5) was shown to undergo exchange with free L at lower temperatures (100 °C) at rates independent of [L]. Both the exchange and the γ-elimination seem to involve dissociation behaviour.

2 Other H-Transfer Reactions

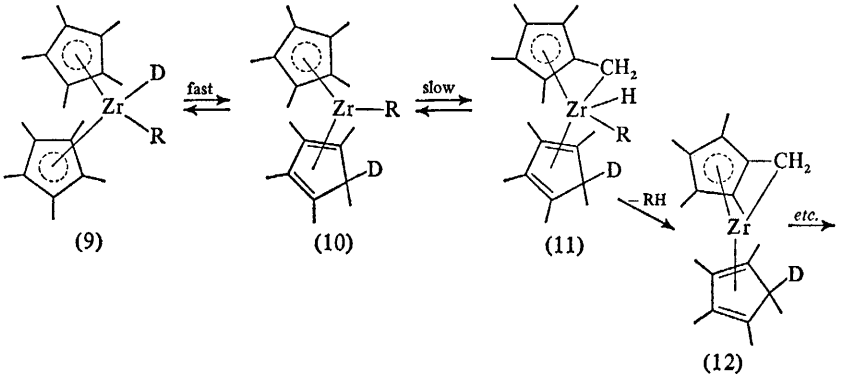
What appears from the stoicheiometry to be a simple reductive elimination is not. Thus, although thermolysis of $[Zr(C_5Me_5)_2H(CH_2CHMe_2)]$ gives isobutane by a first-order reaction, $[Zr(C_5Me_5)_2D(CH_2CDMe_2)]$ gives CH_3CDMe_2, and CDH_2CDMe_2 is formed when the pentamethylcyclopentadienyl ligands are fully deuteriated. Furthermore there is no kinetic isotope effect for deuteriation at the isobutyl or hydride ligands but the rate constant drops from $(7.2 \pm 0.5) \times 10^{-5}$ s^{-1}

[7] C. Crocker, R. J. Erringham, W. S. McDonald, K. J. Odell, B. L. Shaw, and R. J. Goodfellow, *J. Chem. Soc., Chem. Commun.*, 1979, 498.
[8] N. J. Cooper and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1979, 1121.
[9] P. Foley and G. M. Whitesides, *J. Am. Chem. Soc.*, 1979, **101**, 2732.



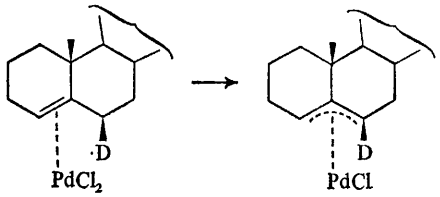
Scheme 5

to $(3.8 \pm 0.5) \times 10^{-5}\ s^{-1}$ (74 °C) on deuteriation of the C_5Me_5 ligand. A mechanism consistent with these observations is shown in Scheme 6, the conversion of (10) into (11) being rate-limiting.[10]



Scheme 6

The H-transfer in the formation of [(η^3-allyl)PdCl] from [(η^2-alkene)$PdCl_2$] is stereospecific with the H atom *syn* to Pd being lost, possibly as H^+ to an adjacent Cl ligand (Scheme 7). k_H/k_D (> 3.5) was believed to be too large for H-atom



Scheme 7

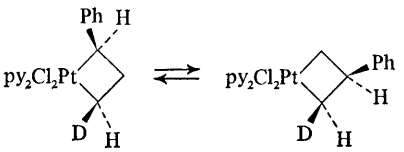
[10] D. R. McAlister, D. K. Erwin, and J. E. Bercaw, *J. Am. Chem. Soc.*, 1978, **100**, 5966.

transfer to Pd, but this is not incontravertible evidence.[11] In the steroid-4-en-3-one series, either the *syn*- or the *anti*-H atoms may be lost and it seems that deprotonation may occur with Pd co-ordination at the ketone instead of the alkene function.[12]

Complete deuteriation of the toluene methyl group in $[Mo(SMe)_2(\eta^6\text{-toluene})]_2$ takes place in D_2O–Na_3PO_4 buffer (pD = 11) and the stabilization of the benzyl anion by co-ordination to the Mo atom is believed to be the driving force.[13] Loss of OH^- from [Fe(cyclohexadienyl)(η^5-$C_5H_4CHMeOH$)] leads to intramolecular H-transfer, possibly *via* the Fe atom from cyclohexadienyl to the other ligand to form $[Fe(\eta^6\text{-}C_6H_6)(\eta^5\text{-}C_5H_4CH_2Me)]^+$ as established by labelling experiments.[14]

3 Carbon Skeleton Rearrangements

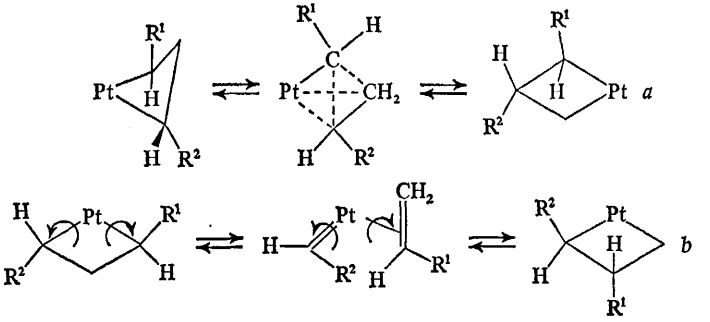
Metallocycloalkanes.—Recently accumulated evidence requires the alkene metathesis reaction to involve the interconversion of mixed carbene–alkene complexes with metallocyclobutanes. With Pt, a highly stereospecific rearrangement of a four-membered ring is observed and work on the mechanism is reported. In the reaction in Scheme 8[15] and with diphenyl-substituted rings[16] the inter-



Scheme 8

conversion retains the configurations at the respective carbon atoms, *i.e.* there is no *cis–trans* isomerization. This appears to be against a carbene–alkene intermediate, such as $[L_nPt(CHD)(PhCH{=}CH_2)]$, since reformation of the ring after rotation about the Pt—alkene bond would change the configurations. The involvement of cyclopropane intermediates is also discounted, and mechanisms in Scheme 9 are discussed. Route (*a*)[16] is perhaps indistinguishable from (*b*)[15] which, although involving the carbene–alkene intermediate, requires the totally specific rotations shown; independent ligand rotations in the intermediate are not possible. Short transannular distances in four-membered rings containing Pt[17] are related to the sort of interaction necessary and best visualized in description (*a*) in Scheme 9. The kinetics of approach to equilibrium of the

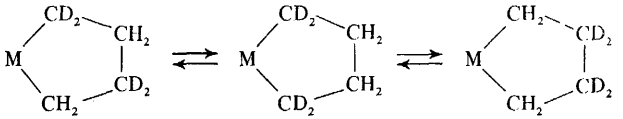
[11] I. J. Harvie and F. J. McQuillin, *J. Chem. Soc., Chem. Commun.*, 1978, 747.
[12] K. Henderson and F. J. McQuillin, *J. Chem. Soc., Chem. Commun.*, 1978, 15.
[13] W. E. Silverthorn, C. Couldwell, and K. Prout, *J. Chem. Soc., Chem. Commun.*, 1978, 1009.
[14] M. M. Khan and W. E. Watts, *J. Chem. Soc., Perkin Trans. I*, 1979, 1879.
[15] C. P. Casey, D. M. Scheck, and A. J. Shusterman, *J. Am. Chem. Soc.*, 1979, **101**, 4233.
[16] R. J. Al-Essa, R. J. Puddephatt, M. A. Quyser, and C. F. H. Tipper, *Inorg. Chim. Acta*, 1979, **34**, L187.
[17] D. A. Clarke, R. D. W. Kemmitt, M. A. Mazid, M. D. Schilling, and D. R. Russell, *J. Chem. Soc., Chem. Commun.*, 1978, 744.



Scheme 9

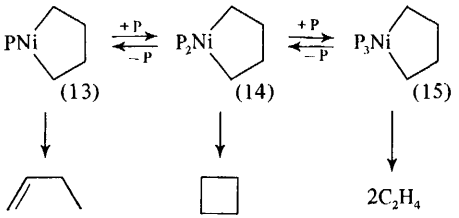
reaction in Scheme 8 are first order with k_{obs} proportional to $[py]^{-1}$. Dissociation of py precedes the rearrangement.[18, 19]

Rearrangements of five-membered metallocycles are also of mechanistic interest. For instance, nickelacyclopentanes may break down to cyclobutane, ethylene, or butenes depending upon circumstances. The deuteriated compounds in Scheme 10 [M = $Ni(PPh_3)_3$ or $Ti(C_5H_5)_2$] undergo the specific rearrangements



Scheme 10

shown which must be *via* the bis(ethylene) complexes and without H-transfer.[20] The co-ordination number of the metal seems to be of prime importance in determining the mode of reaction, and Scheme 11 (P = tertiary phosphine) sum-



Scheme 11

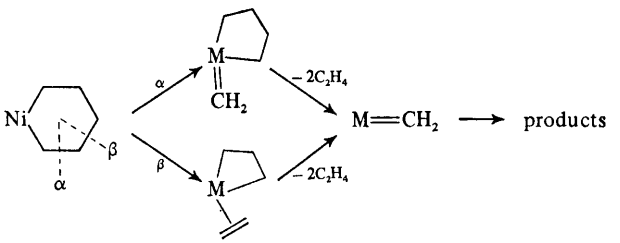
marizes behaviour observed with nickelapentanes, and perhaps unexpectedly C—C rupture occurs in the molecule of highest co-ordination number.[21] Where P = P(cyclohexyl)$_3$, only the three-co-ordinate species exists in solution and

[18] R. J. Al-Essa, R. J. Puddephatt, C. F. H. Tipper, and P. J. Thompson, *J. Organomet. Chem.*, 1979, **157**, C40.
[19] R. J. Al-Essa, R. J. Puddephatt, M. A. Quyser, and C. F. H. Tipper, *J. Am. Chem. Soc.*, 1979, **101**, 364.
[20] R. H. Grubbs and A. Miyashita, *J. Am. Chem. Soc.*, 1978, **100**, 1300.
[21] R. H. Grubbs, A. Miyashita, M. Liu, and P. Burk, *J. Am. Chem. Soc.*, 1978, **100**, 2418.

butenes exclusively are formed on decomposition, and correspondingly where $P_2 = Ph_2PCH_2CH_2PPh_2$ exclusively cyclobutane is formed. However, when $P = PPh_3$, the product ratio depends upon $[PPh_3]$ and with an excess of PPh_3 the complex present is (15) and ethylene only is formed by a reaction first order in complex concentration. Compound (15; $P = PPh_3$) dissolved in solution in the absence of added P gives cyclobutane (70%), C_2H_4 (5%), and butenes (25%), presumably *via* (14), (15), and (13) respectively.[21] This nickel system has been developed to give the first example of catalytic dimerization of ethylene to cyclobutane.[22] Orbital symmetry arguments have been used to show that the decomposition of (14) or the square-pyramidal isomer of (15) to give cyclobutane is allowed but that to give ethylene is forbidden. The reverse is true for the trigonal-bipyramidal isomer of (15), which presumably then is the isomer present.[23] Apparently the decomposition of (13) to give butenes involves a β-elimination and this is consistent with the conclusion that, for Pt at least, the reverse alkene insertion reaction occurs preferentially for the four-co-ordinate hydrido-alkene complex leading to the three-co-ordinate Pt alkyl complex.[24]

Reversible fragmentations just like those in Scheme 10 are also described for metallaindanes of Zr, in this case allowing the replacement of two carbon atoms of the metallocycle by two new carbon atoms of an incoming alkene. The rate of reaction is independent of the structure and concentration of the incoming alkene and a unimolecular ring opening seems likely.[25]

The decomposition of larger six-membered metallocycles such as $[(PPh_3)_3NiCH_2CH_2CH_2CH_2CH_2]$ gives methane and ethylene as well as cyclopentane and pentenes. Scission of both the α-C—C and β-C—C bonds explains these products (Scheme 12). Deuteriation at the α-carbon atoms was confirmed by the formation of co-ordinated CD_2 since this could be trapped by cyclohexene to give the corresponding deuteriated norcarane.[26]

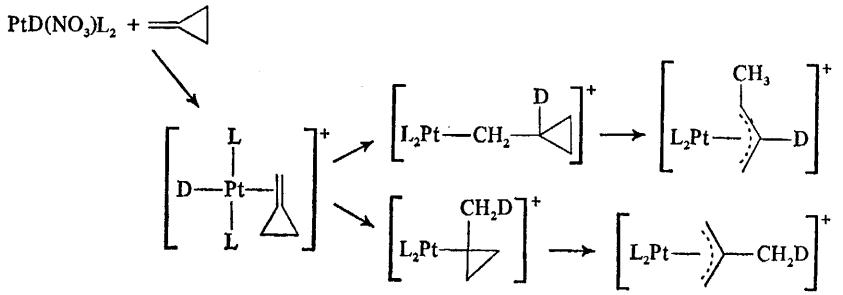


Scheme 12

Other Carbon Rearrangements.—The ring opening of [PtCl(1-^{2}H-cyclopropyl)-$(PMe_2Ph)_2$] on treatment with $AgNO_3$–KPF_6 gave the η^3-allyl complex [Pt(η^3-$CH_2CDCH_2)(PMe_2Ph)_2]PF_6$ quite stereospecifically without any H-transfer.

[22] R. H. Grubbs and A. Miyashita, *J. Am. Chem. Soc.*, 1978, **100**, 7416.
[23] P. S. Braterman, *J. Chem. Soc., Chem. Commun.*, 1979, 70.
[24] D. L. Thorn and R. Hoffmann, *J. Am. Chem. Soc.*, 1978, **100**, 2079.
[25] G. Erker and K. Kropp, *J. Am. Chem. Soc.*, 1979, **101**, 3659.
[26] R. H. Grubbs and A. Miyashita, *J. Am. Chem. Soc.*, 1978, **100**, 7418.

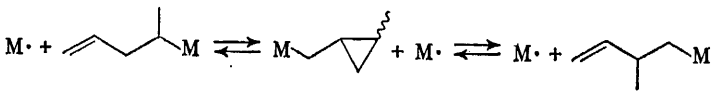
Specific cleavage of the C—C bond most removed from the metal is necessary to account for this.[27] Three-membered ring opening also occurs on reaction of methylenecyclopropane with Pt^{II} hydrides to give η^3-allyl complexes and again deuteriation studies have shown high specificity. The route in Scheme 13 (L = PPh_3) is consistent with the isotopic distribution in the isomeric η^3-allyl products.[28]



Scheme 13

The ethylidene complex $[Ta(C_5H_5)_2(CHMe)Me]$ interestingly does not isomerize to $[Ta(C_5H_5)_5(C_2H_4)Me]$ under conditions where which this would certainly be stable, but instead carbene insertion (*cf.* CO insertion) occurs to give $[Ta(C_5H_5)_2(CHMe_2)]$ which is not observed but readily gives $[Ta(C_5H_5)_2(H)(MeCH{=}CH_2)]$ by β-elimination. Rotation about the Ta—alkene bond is slow, *i.e. endo–exo* interconversion is slow, and although one isomer is formed initially, followed by slow isomerization, it could not be established whether the *endo*- or the *exo*-isomer was formed first. The insertion–β-elimination mechanism requires the *exo*-isomer to be the kinetic product.

Carbon skeleton rearrangements in but-3-enyl cobaloximes have been shown to involve the homolytic displacement reaction (Scheme 14). The corresponding

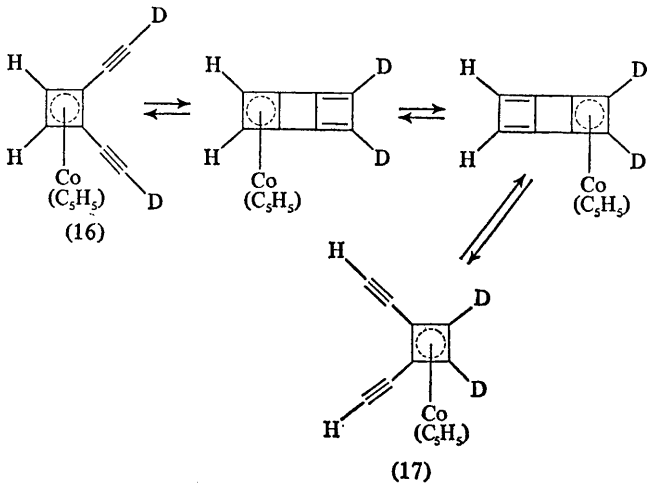


Scheme 14

displacement reaction with $CCl_3{}^{\bullet}$ is well characterized while in this case $Co^{II}(M^{\bullet})$ catalyses the exchange, by the displacement shown. In the case of the 1,2-dimethylbut-3-enyl complex, difficulty was found in obtaining the acyclic compound free from the cyclopropylmethyl complex as the rearrangement occurred on attempted purification. Experiments showed that free organic radicals or Co^{I} are not involved.[30] Various known rearrangements catalysed by coenzyme B_{12} have been discussed in terms of related mechanisms with cyclopropane intermediates.

[27] R. L. Phillips and R. J. Puddephatt, *J. Chem. Soc., Dalton Trans.*, 1978, 1732.
[28] R. L. Phillips and R. J. Puddephatt, *J. Chem. Soc., Dalton Trans.*, 1978, 1736.
[29] P. R. Sharp and R. R. Schrock, *J. Organomet. Chem.*, 1979, **171**, 43.
[30] A. Bury, M. R. Ashcroft, and M. D. Johnson, *J. Am. Chem. Soc.*, 1978, **100**, 3217.

Certain cobalt cyclobutadiene complexes with acetylenic substituents rearrange on vacuum distillation through a hot tube (525 °C) and two mechanisms have been considered. The one in Scheme 15 involves a [2+2] cycloaddition so that



Scheme 15

the cobalt can slide between the C_4 rings of the intermediate followed by a retro-[2+2] reaction. Alternatively the C_4 ring could open to give two co-ordinated diynes so that the cobalt could slide between these groups prior to ring closure. Compound (16) isomerizes specifically by a pairwise exchange to give a 1:1 mixture of (16) and (17), no other isotopic distribution being formed. This supports the intramolecular mechanism in Scheme 15 although other bonding patterns within the intermediate are feasible.[31]

4 Nucleophilic Additions

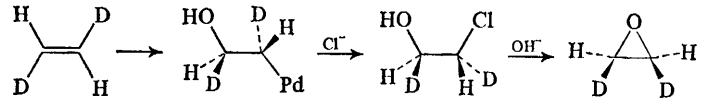
Additions at Monoenes.—Results obtained recently have led to a reappraisal of the mechanism of the Wacker process (the $[PdCl_4]^{2-}$–$CuCl_2$-catalysed oxidation of ethylene to acetaldehyde). A key feature of the originally proposed mechanism, largely deduced from the kinetic form of the reaction (below) is the formation of

$$d[CH_3CHO]/dt = k[C_2H_4][PdCl_4^{2-}]/[H^+][Cl^-]^2$$

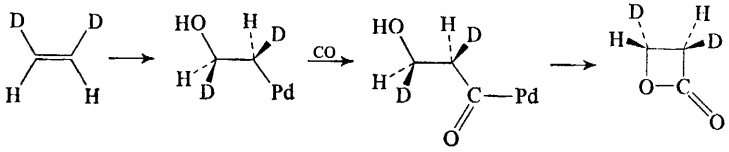
cis-$[PdCl_2(OH)(C_2H_4)]^-$ by pre-equilibria followed by rate-determining intramolecular *cis*-transfer of OH^- to give a β-hydroxyethyl complex, which rapidly gives acetaldehyde. The stereochemistry of the addition cannot be deduced from any study of the product, but two studies[32–34] have relied on intercepting the β-hydroxyethyl intermediate formed under Wacker conditions to give products

[31] J. R. Fritch and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, 1978, **100**, 3643.
[32] J.-E. Bäckvall, B. Åkermark, and S. O. Ljunggren, *J. Am. Chem. Soc.*, 1979, **101**, 2411.
[33] J. K. Stille and R. Divakaruni, *J. Am. Chem. Soc.*, 1978, **100**, 1303.
[34] J. K. Stille and R. Divakaruni, *J. Organomet. Chem.*, 1979, **169**, 239.

from which the stereochemistry of addition can be deduced. The addition is clearly *trans*; see Schemes 16 and 17. The conclusions assume that the displace-



Scheme 16



Scheme 17

ment by Cl^- at the primary alkyl group occurs by an S_N2 path[32] (Scheme 16) or that CO insertion is with retention of configuration at carbon[33,34] (Scheme 17). The kinetics have been reinterpreted in the light of these results. A direct rate-determining attack of OH^- from the solution at $[PdCl_2(C_2H_4)(H_2O)]$ is not possible since rates in excess of that controlled by diffusion would be required by the measured or estimated pre-equilibrium constants. (Some of these equilibrium constants have been recently readjusted.[35]) It is agreed now[32,34] that the key hydroxypalladation step is a pre-equilibrium with the rate-determining step being the subsequent loss of Cl^- to form a three-co-ordinate intermediate:

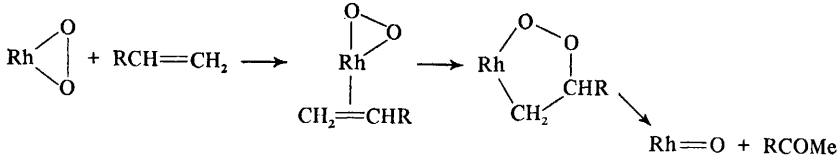
$$H_2O + [PdCl_2(C_2H_4)(H_2O)] \rightleftharpoons [H_2\overset{+}{O}{-}CH_2CH_2\overset{-}{P}dCl_2)H_2O)]$$

$$[H_2\overset{+}{O}{-}CH_2CH_2\overset{-}{P}dCl_2(H_2O)] + H_2O \rightleftharpoons [HOCH_2CH_2PdCl_2(H_2O)]^- + H_3O^+$$

$$[HOCH_2CH_2PdCl_2(H_2O)]^- \xrightarrow{\text{slow}} [HOCH_2CH_2PdCl(H_2O)] + Cl^-$$

The formation of a three-co-ordinate species before a fast β-elimination fits in well with other recent observations.

The oxidation of alkenes to ketones can occur by routes other than hydroxymetallation. Oct-1-ene is converted into octan-2-one using $[Rh(O_2)(AsPh_3)_4]ClO_4$ and using 70% enriched ^{18}O in the complex there is 70% ^{18}O in the octan-2-one,[36a] which is accounted for by the mechanism in Scheme 18. Similar conclusions are made from a related study using $[RhCl(PPh_3)_3]$.[36b]



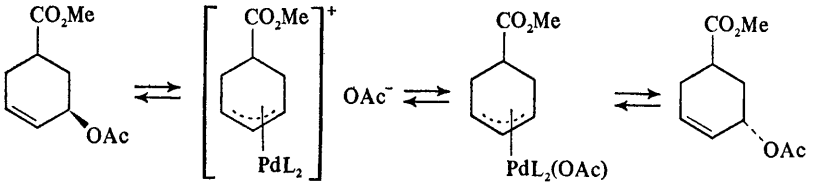
Scheme 18

[35] R. N. Pandey and P. M. Henry, *Can. J. Chem.*, 1979, **57**, 982.

[36] (*a*) F. Igersheim and H. Mimoun, *J. Chem. Soc., Chem. Commun.*, 1978, 559; (*b*) R. Tang, F. Mares, N. Neary, and D. E. Smith, *ibid.*, 1979, 274.

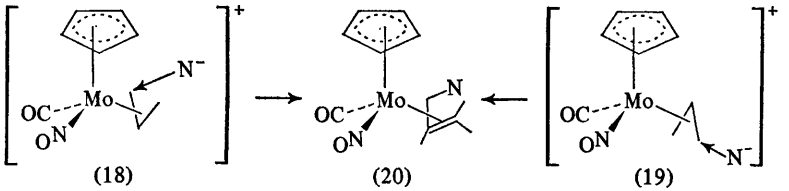
Nucleophiles other than OH^- also give stereospecific additions at alkenes. The acetylacetonate ion adds to co-ordinated *cis*- or *trans*-$C_2H_2D_2$ in $[Pd(C_5H_5)(PPh_3)(CHD{=}CHD)]^+$ to give $[Pd(C_5H_5)(PPh_3)\{CHDCHDCH(COMe)_2\}]$ by *trans*-addition,[37] and the overall *cis*-diamination of alkenes has been achieved by *trans*-aminopalladation of alkenes followed by oxidative amination in which the amine displaces the oxidized palladium by an S_N2 displacement so that there is inversion at the Pd-bound carbon atom. Other carbon-centred nucleophiles (aryl, alkyl, or methoxycarbonyl) had previously been shown to add *cis* to alkenes, presumably by prior co-ordination at the metal.

Additions at η^3-Allyls.—Treatment of 1,3-dienes with $[PdCl_2(PhCN)_2]$ in the presence of Me_2NH generates η^3-allyl complexes by amine addition at a terminal carbon atom of the diene. Subsequent treatment with $AgBF_4$ or PPh_3 in the presence of amine gave the 1,4-diaminated product. The diaminated product from cyclohexa-1,3-diene is >94% *cis* so that the initial nucleophilic addition of amine and Pd across the diene is *trans* and the nucleophilic addition at the η^3-allyl must occur at the face opposite to the co-ordinated palladium.[39] This *exo*-addition is the normal mode of attack,[40] but reversible *exo*- and *endo*-nucleophilic additions must occur to account for the isomerization shown in Scheme 19, which is catalysed by PdL_4 ($L = PPh_3$).[41]



Scheme 19

There is remarkable stereospecificity in nucleophilic additions at the η^3-allyl groups of the isomeric compounds (18) and (19) (Scheme 20). The barrier to *endo–exo* isomerization is high so that they may be separately prepared and nucleophilic additions at each studied. Nucleophilic attack at the different ends of the allyl group in (18) would give different diastereomeric forms of the alkene



Scheme 20

[37] H. Kurosawa and N. Asada, *Tetrahedron Lett.*, 1979, 255.
[38] J.-E. Bäckvall, *Tetrahedron Lett.*, 1978, 163.
[39] B. Åkermark, J.-E. Bäckvall, A. Löwenborg, and K. Zetterberg, *J. Organomet. Chem.*, 1979, **166**, C33.
[40] A. V. Rivera and G. Sheldrick, *Acta Crystallogr.*, 1978, **B34**, 3374.
[41] B. M. Trost, T. R. Verhoeven, and J. M. Fortunak, *Tetrahedron Lett.*, 1979, 2301.

complex. (The Mo atom is asymmetric and co-ordination of a monosubstituted alkene through its opposite faces gives different diastereomers). The interesting result is that (18) and (19) give one and the same diastereomer (20) resulting from attack at the allyl end *trans* to NO for the *endo*-isomer (18) but *cis* to NO for the *exo*-isomer (19). The barrier to rotation about the alkene–Mo bond in (20) is 15 kcal mol^{-1} so that, although (18) and (19) give different orientations of (20) originally, these rapidly equilibriate.[42] A theoretical interpretation of these results has been attempted.[43]

The kinetics of the *exo*-PPh_3 addition at the η^3-allyl function of $[Co(C_5H_5)$-(1,2,3,5,6-η^5-cyclo-octadienyl)]$^+$ have been measured. With an excess of PPh_3 present the observed first-order rate constant for the approach to equilibrium is given by $k_{obs} = k_1[PPh_3] + k_{-1}$ so that rate constants and activation parameters for forward and reverse reactions are obtained. The mechanism is a simple addition, the rate of which is at least 65 times less than that at the 1,2,3,4,5-η^5-cycloheptadienyl analogue.[44]

At Other Hydrocarbon Ligands.—Additions at η^4-, η^5-, η^6-, and η^7-ligands are reported for various nucleophiles. All additions seem to be at the face of the ligand removed from the metal atom. Fluoride ions add when these are 'bare' (KF–18-crown-6-ether–MeCN),[45] and so do acetone (as $MeCOCH_2^-$)[46] and iodide,[47] and even the ring atoms of aromatics (*e.g.* $PhNMe_2$) may be sufficiently nucleophilic,[48] but tertiary phosphines have been mostly studied. The addition of tertiary phosphines at $[Fe(CO)_3$(cyclohexadienyl)]$^+$ is first order in both reagents and there is a marked rate dependence upon the basicity of the phosphine, suggesting important bond making to form the transition state.[49] The k_1 and k_{-1} values have been determined for PBu_3 addition to η^6-arenes to give η^5-dienyl complexes (Scheme 21). The dependence of k_1 on the arene relates as

$$[Mn(arene)(CO)_3]^+ + PBu_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Mn(arene \cdot PBu_3)(CO)_3]^+$$

$$\xrightarrow{h\nu} [Mn(arene)(CO)_2(PBu_3)]^+$$

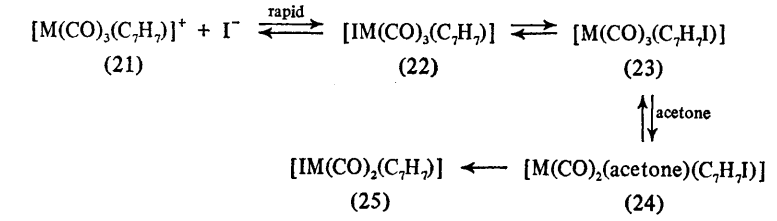
Scheme 21

expected to its electrophilicity with decreasing rates in the order $C_6H_5Cl \geqslant$ 4-$MeC_6H_4Cl > C_6H_6 > C_6H_5Me >$ 4-$C_6H_4Me_2$, and as with other PR_3 additions $\Delta H^{\ddagger}$ is relatively small and $\Delta S^{\ddagger}$ large and negative. The rates of nucleophilic addition at carbon are quite similar for Mn and Re complexes, but with MeCN

[42] R. D. Adams, D. F. Chodosh, J. W. Faller, and A. M. Rosan, *J. Am. Chem. Soc.*, 1979, **101**, 2570.
[43] B. E. R. Schilling, R. Hoffmann, and J. W. Faller, *J. Am. Chem. Soc.*, 1979, **101**, 592.
[44] L. A. P. Kane-Maguire, P. D. Mouncher, and A. Salzer, *J. Organomet. Chem.*, 1979, **168**, C42.
[45] B. F. G. Johnson, K. D. Karlin, J. Lewis, and D. G. Parker, *J. Organomet. Chem.*, 1978, **157**, C67.
[46] C. White, S. J. Thompson, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1978, 1305.
[47] P. Powell, L. J. Russell, E. Styles, A. J. Brown, O. W. Howarth, and P. Moore, *J. Organomet. Chem.*, 1978, **149**, C1.
[48] G. R. John and L. A. P. Kane-Maguire, *J. Chem. Soc., Dalton Trans.*, 1979, 1196.
[49] G. R. John and L. A. P. Kane-Maguire, *J. Chem. Soc., Dalton Trans.*, 1979, 873.

the attack is at the metal atom to displace the arene, but in this case the reaction is much faster for Re than Mn.[50] Relative electrophilicities of carbon atoms at 20 °C as gathered together from various studies are $[(C_7H_8)Mn(CO)_3]^+$ 10^4, $[(C_7H_9)Co(C_5H_5)]^+$ 1.5×10^3, $[(C_4H_4)Fe(CO)_4(NO)]^+$ 10^3, $[(C_6H_7)Fe(CO)_3]^+$ 150, $[(2\text{-}MeOC_6H_6)Fe(CO)_3]^+$ 30, $[(C_7H_7)Cr(CO)_3]^+$ 30, $[(C_7H_9)Fe(CO)_3]^+$ 4, and $[(C_6H_6)Mn(CO)_3]^+$ 1.[44,51]

Flow ^1H n.m.r. and stopped-flow spectrophotometry have been applied to the reaction of the tropylium complex $[M(CO)_3(C_7H_7)]^+$ (M = Mo or W) with iodide and three intermediates eventually leading to the CO substitution product have been observed (Scheme 22). The initial attack is surprisingly at the metal in view



Scheme 22

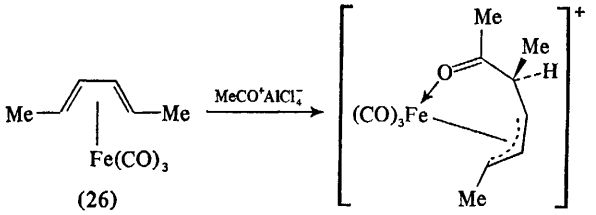
of all the above work indicating attack at carbon. Attack at the saturated complex in this way would require a η^7 to η^5 conversion of the C_7H_7 ligand. Complex (23), containing a C—I bond, exists as isomers (93:7 ratio), which are believed to be the *exo*- and *endo*-products.[47]

Nucleophilic addition of carbanions (as LiR) at $[Cr(arene)(CO)_3]$ gives the corresponding Meisenheimer complex $[(Cr(arene{\cdot}R)(CO)_3]^-$ from which the substituted arene is freed by oxidation. The regioselectivity of such reactions using substituted arenes has been examined and the site of attack correlates tolerably well with the LUMO coefficients as estimated for the free arene, the effect of the metal being ignored in this crude analysis.[52] Estimations have been made of the frontier electron densities at metal, carbonyl carbon, and ring carbon atoms in neutral compounds of type $[M(polyene)(CO)_3]$ where M(polyene) = $Ni(C_2H_4)$, $Co(C_3H_5)$, through to $Cr(C_6H_6)$, so as to predict the site of nucleophilic attack. In no case is attack at the ring predicted, while depending upon the molecule attack occurs at M or CO.[53]

5 Electrophilic Additions

Friedel–Crafts acylation ($RCOCl$–$AlCl_3$–CH_2Cl_2, 25 °C) of compounds of type $[Fe(diene)(CO)_3]$ has been shown to occur by *endo*-addition of RCO^+ (as its ion-pair with $[AlCl_4]^-$) at carbon. Simple substitution products are obtained because of the stabilization of the intermediate cation by iron. The *X*-ray structure (PF_6^- salt) of the intermediate formed as in Scheme 23 confirms the geometry

[50] L. A. P. Kane-Maguire and D. A. Sweigart, *Inorg. Chem.*, 1979, **18**, 700.
[51] D. M. Birney, A. M. Crane, and D. A. Sweigart, *J. Organomet. Chem.*, 1978, **152**, 187.
[52] M. F. Semmelhack, G. R. Clark, R. Farina, and M. Saeman, *J. Am. Chem. Soc.*, 1979, **101**, 217.
[53] D. A. Brown, J. P. Chester, and N. J. Fitzpatrick, *J. Organomet. Chem.*, 1978, **155**, C21.



(26) (27)

Scheme 23

of attack and that a co-ordinatively saturated intermediate is possible because of co-ordination of the ketonic carbonyl.[54] Relative partial rate factors for acylation of various substituted diene complexes are reported; substituent effects are small. Acetylation rates relative to benzene (conditions as above) are C_6H_6 1.0, toluene 140, acetylferrocene 190 (0 °C), $[Fe(C_4H_6)(CO)_3]$ 3850, $[Fe(4\text{-}BrC_6H_4C_4H_5)(CO)_3]$ 4700, $[Fe(2\text{-}MeC_4H_5)(CO)_3]$ 4770, $[Fe(1\text{-}MeC_4H_5)(CO)_3]$ 7300, $[Fe(PhC_4H_5)(CO)_3]$ $\sim 1.2 \times 10^5$, ferrocene 3.3×10^6 (0 °C). Evidence points to a rate-determining electrophilic addition at carbon although attack at metal followed by transfer to carbon is not easy to eliminate as a possibility.[55]

Protonation of $[Fe(diene)L_3]$ [L = $P(OMe)_3$] to give $[Fe(allyl)L_3]^+$ corresponds with acetylation to give compounds of type (27) except that there is no obvious donor group present to convert the 16-electron into an 18-electron cation. In these circumstances it appears that electrons from a σ-C—H bond are involved in co-ordination as shown in Part IV, Chapter 1, for compound (48).[56,57] This could be regarded as containing a three-centre, two-electron M—H—C bridge and to lie somewhere along the reaction path between $[Fe(allyl)L_3]^+$ and $[FeH(diene)L_3]^+$. Evidence, often circumstantial, supports the idea that protonation at $[Fe(diene)L_3]$ occurs initially at Fe followed by H-transfer to carbon.

[54] G. A. Sim and D. I. Woodhouse, *Acta Crystallogr*, 1979, **B35**, 1477.
[55] R. E. Graf and C. P. Lillya, *J. Organomet. Chem.*, 1979, **166**, 53.
[56] S. D. Ittel, F. A. Van-Catledge, C. A. Tolman, and J. P. Jesson, *J. Am. Chem. Soc.*, 1978, **100**, 1317.
[57] J. M. Williams, R. K. Brown, A. J. Schultz, G. D. Stucky, and S. D. Ittel, *J. Am. Chem. Soc.*, 1978, **100**, 7407.

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