# ELECTROCHEMISTRY

OF

# ORGANIC COMPOTJNT

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BY

DR. WALTIIER LOB

*Privatdocent in the University of Bonn*

AUTHORIZED TRANSLATION FROM THE AUTHOR'S ENLARGED AND REVISED THIRD EDITION

## ELECTROLYSIS AND ELEOTROSYNTHESIS

OF

## ORGANIC COMPOUNDS

II. W. F. LOJiENZ, A.M., Pii.I).

*Graduate of the University of Berlin*

*Formerly* Instructor *of Organic Glwmtetrii in the University of J^nnttylvania*

*Z^ramlalor of Lawar-Cohriti "Urinary Analysis^* etc,

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CHAPTER II.



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OF

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A survey of the great number of organic electrochemical investigations shows a very unequal distribution of scientific labor among the separate parts of the extensive domain. The electrolytic reactions have been by far most thoroughly investigated, particularly the reduction processes. Oxidation and substitution reactions have more rarely been the subject of successful researches.

Pyrogenic decompositions and syntheses of organic substances produced by the induction spark, the electric arc, or highly heated conductors of the first class have been numerously mentioned. However, we are just beginning to obtain scientific results in this line of work. It has already been mentioned that our knowledge of the action of the glow and convective. discharge on carbon compounds is extremely insignificant.

The varied properties of organic bodies explain this unequal treatment and the result. The reduction of carbon compounds occurs usually at certain reducible groups in the molecule without destroying this latter. The whole molecule is usually exposed to the action of the electrolytic oxygen. The final product of a reduction is closely related chemically to the material started out with; the end result of an oxidation is often the complete combustion of the molecule. Quite a number of possibilities exist between a slight attack by oxygen upon and the complete destruction of a compound by oxidation. A realization of these, if at all possible, depends upon most painstaking observations of fixed experimental conditions, which are often difficult to determine. Hence oxidation processes are much more complicated than reduction processes, and usually less profitable. These same points of view also apply to electrolytic substitution, which, being an anodic process, is often only with difficulty protected from the oxidizing action of the current.

The relatively great sensitiveness of most carbon, compounds to high temperatures confined electrothermic decompositions and syntheses of organic bodies to a small area, so long as the heat was derived from the induction spark, or the electric arc. Electrical energy has, however, proved itself a convenient medium for investigating the behavior of sensitive substances at relatively high temperatures, ever since metallic wires, or carbon filaments, have been used as sources of heat which can be easily regulated by increasing or decreasing the current pressure.

The properties of electric energy as well as those of the carbon compounds require special forms of experiment for organic electrochemistry. These differ entirely from the purely chemical art of experimentation, i.e., partially new experimental methodics are necessary. The more it was possible to recognize the important points in the course of an electrochemical process the clearer the viewpoints became regarding the choice of the most suitable conditions for experiment. *The* endeavor theoretically to represent and unite the numerous observations went hand in hand with the experimental development. Theoretical considerations led to new experimental conditions and new problems. The theory becomes closely associated, by certain requirements, not only with the subject « of the experiment but also with its arrangement. A description of organic electrochemistry must fully recognize theory and methodics as well as the chemical results.

Depending upon the forms in which electrical energy is employed in organic chemistry, we can distinguish three processes, electrolytic, electrothermic, and electric-discharge reactions. A threefold division into theory, methodics and experimental results, hence, naturally follows for the disposition of each of the three resulting chapters.

It may be remarked, particularly in regard to the description of the methods, that only the necessary and important data are mentioned here. The author does not intend to give a practical guide for making experiments. Only original investigations or special text-books [1] can serve such a purpose. It is the object of the respective descriptions in this book to discuss the general. principles and to lead the reader to a clear understanding and a correct interpretation of the various methods.

[1] See, for instance, Oettel, Electrochemical Experiments, 1897 (translated by E. F. Smith); also Oettel, Practical Exercises in Electrochemistry, 1897 (translated by E. F. Smith, Phila.); Elbs, Experiments for the Electrolytical Preparation of Chemical Preparations, Halle, 1902.

# PART I.

## *ELECTROLYTIC PROCESSES.*

## CHAPTER I.

## THEORETICS.

### 1. FORMS OF REACTION.

Two possibilities must be distinguished in the electrolysis of organic bodies. The carbon compound is either an electrolyte, i.e., a salt, base, or acid, or it is a non-electrolyte.

In the first case the compound itself furnishes the ions which condition the conductivity. The work of electrolysis than consists in the transportation of these ions to the anode and cathode, and it is a secondary question whether these ions are liberated molecularly or atornically, or whether they react with one another, or with the substance still present in the solution, or with the solvent.

Of the organic ions the anions are almost exclusively taken into consideration, since organic cations, like the organic ammonium ions, have been little investigated as to their behavior in electrolysis. The actual liberation of the ions cannot'be observed, because when deprived of their electrical state they cannot exist. On the contrary, the anions oftea react with one another after their discharge. Thus eithey a union of several anions occurs or, far oftener, more complicated transpositions and decompositions accompany these reactions.

An example of the first kind of decomposition is furnished by the electrolysis of potassiumr xanthate[1]:

$$2\,C_2H_5OCSSK = 2\,C_2H_5OCSS' + 2\,K\backslash$$
$$2\,C_2H_5OCSS = C_2H_5OCSS\text{-}SSCOC_2H_5.$$

In this case two anions unite to form xanthic disulphide. On the other hand, in the electrolysis of sodium acetate, .the anions are united, but carbonic acid is simultaneously split off:

$$2\,CH_3COO = C_2H_6 + 2CO_2.$$

The anions of the fatty acids show this behavior to a greater or less degree under certain current conditions.

But if the organic compound does not conduct the current, other ions must be present for accomplishing the electrolysis. For this purpose usually an inorganic acid, base, or salt—corresponding organic compounds can of course also be used—is dissolved in the solution. Then, primarily, the passage .of the current does not at all affect the organic non-electrolyte. Only the ions are driven to the electrodes where they can discharge themselves. At the instant, however, when the discharge occurs, the r&le of the organic body begins. If it cannot react with the discharged ions it remains unchanged, and is not affected by the action of the electrolysis. This possibility will naturally not be considered in the present discussion. The fact to be observed is, that the carbon compound reacts with the discharged ions—it then becomes a *depolarizer.*

Many organic acids, bases, and salts can act as depolarizers when ions are discharged which react easily with them. For example, p-nitrobenzoic acid in alkaline solution is reduced smoothly to p-azobenzoic acid. The sodium ions which are discharged react so rapidly with the nitro-group that the nitrobenzoic acid does not behave as an electrolyte but essentially as a depolarizer, particularly since the ions of the sodium

[1] Schall, Ztschr. f. Elektrochemie 3, 83 (1896).

lution take care of the conductivity. Organic elec-
also furnish the ions which act upon an organic
Thus, if an acid is electrolysed in absolute alcohol
cnetiincs formed:

RCOO +$C_2$H/)H - IICOO$C_2H_5$ + OH.

the alcohol is at the same time a solvent and a

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tie depolarizer is reduced by the electrolysis.

hydroxide solution take care of the conductivity. Organic electrolytes can also furnish the ions which act upon an organic depolarizer. Thus, if an acid is electrolyzed in absolute alcohol an ester is some times formed:

$$RCGO -fC_2H_5OH =RCOOC_2H_54\sim OH.$$

In this case the alcohol is at the same time a solvent and a depolarizer.

We therefore divide the phenomena of electrolysis of carbon compounds into two classes: Either the organic bodies themselves act as electrolytes—the effect of the electrolysis is the discharge and the eventual additional reaction of their ions at the electrodes (primary reactions)—or they are depolarizers (secondary reactions).

The latter class is by far the larger. It can agaia be subdivided into two groups, the cathodic and the anodic depolarizers. It is very seldom that a body acts simultaneously as a cathodic arid anodic depolarizer. More often a cathodic (or anodic) depolarizer, by reacting with the cations (or anions), acquires the faculty of now depolarizing anodically (or cathodically). Thus, for example, an easily reducible body may be changed by cathodic reduction into one easily oxidized, i.e. accessible to the action of the anions. However, it is more conducive to clearness to adhere to the division into cathodic and anodic depolarizers and to determine the nature of the possible reactions.

Cathodic Depolarizers.—Hydrogen and metal ions pass to the cathode-—if we take no account of the small and unimportant number of organic cations. Hydrogen and metals can withdraw oxygen, i.e. deoxidize; and the hydrogen can also be added directly to the compound. Such bodies that can yield oxygen or take up hydrogen, or do both simultaneously, are called *reducible* compounds. They themselves are hence oxidizers whose characteristic property it is to destroy positive discharges. The reaction at the cathode is called reduction. Every cathodic depolarizer is reduced by the electrolysis.

The reduction of nitrobenzene to nitrosobenzene furnishes an example of deoxidation:,

$$C_6H_5N0_2 + 2H = C_6H_5NO + H_20.$$

In the conversion of azobenzene to hydrozobenzene an addition of hydrogen takes place:

$$C_6H_5N \gg NC_6H_5 \; H\sim 2H = C_6H_5NH - NHC_6H_5.$$

A withdrawal of oxygen and addition of hydrogen occurs simultaneously in the reduction of nitrobenzene to phenylhydroxylamine:

**Anodic Depolarizers.** — The conditions are somewhat more complicated at the anode. All the anodic depolarizers are oxidizable; it is true, even reducing substances which destroy the negative charges-. But the reaction-picture is more varied at the anode than at the cathode — due to the individual variety of the anions. If the action consists merely in a withdrawal of hydrogen and an addition of oxygen, or both, it is called oxidation.

Examples of such oxidations are the conversion of hydrazobenzene into azobenzene :

$$C_6H_5NH - NH - C_6H_5 + 0 = C_6H_5N - NC_6H_5 + H_20;$$

the conversion of benzene into hydroqumone by a direct addition of oxygen :

the production of nitrobenzoic acid from nitrotoluene by the addition of oxygen and withdrawal of hydrogen:

$$N0_2C_6H_4CH_3 \; 4\text{-}3 \; 0 = N0_2C_6H_4COOH + H_20.$$

Discharged ions, like the halogens, are also often added directly",
to an organic, unsaturated body. An additfon ••<}
parable with the addition of hydrogen at the cathode,

$$\begin{matrix} CH & & CHBr_2 \\ & +4Er = & 3fi \\ & & CHBr_2 \end{matrix}$$

or , a substitution takes place, i.e. an anion — simple or compound — replaces ari element or group of elements of the depolarizer ; — e.g. in the electrolysis of acetone in hydrochloric acid:

$$CH_3COCH_3+2\,C1=CH_2C1COCH_3+HC1.$$

Possibly the anion itself undergoes changes before it acts upon the depolarizer, so that the organic compound can no-longer be spoken of as a true depolarizer for the anion but only for its decomposition products. Thus, in the presence of a base, the anion $CH_3COO$ would behave in such a manner that, after it was split up into ethane and carbonic acid, only the latter would react with the base. However, such a reaction can no longer be regarded as an electrochemical one.

It seems particularly difficult to determine in a simple way the nature of an electrolytic reaction where there are so many possible ways for a reaction to take place. We shall see later on, however, that, by a proper consideration of the subject, a definition is obtained.

Another form of reaction occurs in the electrolysis of organic-compounds.. While it cannot be regarded as purely electrical,, no more so than the preceding one, it appears only in a utDizable-way among the peculiarities of the electrical method. The-product resulting primarily, or secondarily, can. occur first int an unstable modification, and can then rapidly undergo further-changes. I shall here only refer to the intermediate formation of phenylhydroxylamine in the reduction of nitrobenzene in concentrated sulphuric acid, which, as is well known, immediately rearranges itself into amidophenol: •

Gattenmum [1] has shown that the unstable modification can be isolated by adding benzuldehyde to the original electrolytic fluid. The aldehyde reads more rapidly with the intermediate product phenylhydroxylumine than the sulphuric acid can act to effect a molecular rearrangement.

Intermediate phases of elee.trioul oxidation and reduction can similarly be isolated by adding to the electrolytes various substances which react more rapidly with the phase than the oxidation or reduction (regulable by the current conditions) can take place. This artifice, utilized by Lob[2] and Ilaber.,[3] makes it possible to obtain theoretically important insights into the successive and often very transitory conditions of complicated processes.

## 2. PHOPKRTIKB OF Ku'XrmoLVTio PitoeKbSKs.

The electrolytic method .possesses a number of properties which markedly distinguish it from all other chemical methods. In the first place* the current produces the effect which the chemical method can accomplish only through the agency of certain materials, such an load peroxide, chromic acid, etc., in the case of oxidations, and xinc, stannous chloride, iron, etc., in the presence of acids or alkalies in reductions. This effect is solely produced by ion-discharges, forces which are ultimately derived from a source of electrical energy, i.e. water power or coal.

A consumption of energy replaces a consumption of material. The economic ratio of thctno, which is of great practical importance, depends upon the factors controlling the prices of , material and energy.

In such proeeHHOB which require, even in electrolysis, the prenonco of certain subst uncos endowed with characteristic* oxidizing and reducing proportion as a necessary component in the react ion, the actual material consumption is nevertheless very incousidombh[1]. Tho. mibstancoH hi question, for instance

f,

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the metallic salts, need only be present in the electrolyte in very trifling quantity, since, after accomplishing their purpose they are regenerated, by the, current and can be reused for accomplishing innumerable reactions. In this case, also, only the question of energy need be considered.

Moreover, the electrochemical method allows the confining of the reaction to a certain space within the chemical system. The reaction occurs only in the immediate neighborhood of the electrode,—thus the reactions of the ions themselves take place on the electrode surface at the instant of their discharge,, those of the depolarizers in proportion to the quantity coming in contact with the electrode surface, either by diffusion or stirring. The extent of the space in which the reaction occurs therefore depends upon the extent of the electrode surface; it can be considered as an extremely thin layer which is in intimate contact with the electrode. In this layer the reaction processes occur in accordance with .the known laws of reaction kinetics, i.e. their velocity depends upon the concentration of the active molecules. These are, however, the ions just discharged, either alone, when they react with one another, or simultaneously with the molecules of the depolarizer. The concentration of the latter is independent of the electrical conditions, but the concentration of the ions IKS determined by the intensity of the current, according to Faraday's law.

### 3. SIGNIFICANCE OF THE VELOCITY OF REACTION.

The electrically feasible reaction conditions are (1) the extent of the reaction space and (2) the quantity of reactive ions in the latter, i.e. the concentration of the ions can be regulated in a purely electrical way and within the broadest limits. The highest dilutions can be realized just as well with weak currents and large electrode surfaces as the highest concentrations with strong currents and small surfaces. That most important factor of reaction kinetics, the *reaction velocity,* is thus determinatively influenced by these concentrations. The importance of the reaction velocity is especially f undamental for the course of the reaction; for in the majority of cases it is a case of processes vying with one another, the reaction velocities of which determine the preponderance, and hence the result, of the one or the other process.

The last remark, that competitive reactions occur almost always, needs a brief explanation. One reaction possibility is electrolytically always present—the liberation of the ions in a molecular state on the electrode. This liberation is a reaction which must not be confounded with the discharge which precedes it. The discharge takes place in accordance with Faraday's law, and since the discharged ions—they are either atoms or "unsaturated" groups formed by dissociation—cannot exist, they react with a certain but unknown velocity. They thus combine to form molecules or complexes, and the stable end-products are liberated in conformity with Faraday's law, the quantity separated being proportional to the discharge. But if a depolarizer is present, the discharged ions have the opportunity to react- with it instead of being set free. The depolarization reaction also takes place with a certain velocity. The two velocities, however, are decisive for the partitive ratio between an ionic liberation and a reaction with the depolarizer. Herein lies the importance of reaction velocities in electrolytic processes.

The question follows: How can we regulate *ad libitum* these velocities, i.e. usually make the reaction with the depolarizer the most predominating one? Apparently this is only possible within the bounds set by the chemical nature of the active molecules—by a shifting of concentrations in the reaction space, which can be regulated on the one hand by the variation in the quantity of the depolarizer, and on the other hand by the concentration of the discharged ions and the size of the reaction space, i.e. the electrode surface. The velocity of liberation is also increased by increasing the current strength, upon which the prevailing concentration of the discharged ions in the unit of time depends, likewise by decreasing the electrode surface, which has the same effect as the increase in concentration. It will therefore be the experimental problem to choose the current strength, electrode dimension, and depolarizer quantity in such a manner as to produce the desired effect.

* The ratio of the current strength to the electrode surface is called current density. This latter and the quantity of the depolarizer therefore are decisive factors in electrolysis.

## 4. REACTION VELOCITY AND SPECIFIC EFFECT OF REDUCING AND OXIDIZING AGENTS.

These conditions can only give an insight into the quantitative course of an electrolysis. The qualitative course of the reaction is conditioned by the chemical forces of affinity specific of the single elements or compounds and characteristic of the reacting masses.

In the majority of the electrolyses of organic bodies the circumstances are very much simplified by the fact that it is only a question of two different forms of reaction, viz. reduction and oxidation. The limits within which a reduction can take place at all are already given in the case of a cathodic depolarizer by its nature, no matter which reducing agent is employed. For instance, only nitrosobenzene, phenylhydroxylamine and aniline need be considered in the reduction of nitrobenzene, and the chemical nature of the reducing ions cannot enlarge these boundaries. Since the single reduction phases are quantitatively related to one another, the one following being always the direct reduction product of the preceding one, arid since the obtainable phase depends solely upon the more or less strong reduction, the special efficacy of the various reducing agents presents itself as a quantitative order which can be repeated at will. The individual properties of the reducing agencies become mutually comparable in a quantitative way. For instance, if nitrobenzene is reduced to aniline with copper and sodium hydrate, but, using zinc and sodium hydrate solution, only to azobenzene, the specific action of the copper and zinc is shown qualitatively, but the quantitative connection exists also at the same time that copper is a stronger reducing agent than zinc, i.e. a qualitatively equal agent.

The effects producible by choosing a suitable reducing agent can also be obtained electrically. The important problem arising in electrolysis is to convert the qualitative phenomena into quantitative ones, and to find a uniform measure for the changing effects. Naturally, the above applies in like manner to an oxidizing agent.

As we have already seen, the current density is the regulator of the electrically obtainable concentration conditions for the discharged ions, and thereby becomes codeterminative of the velocity of reaction. The obtainable phase of an oxidation or reduction is intimately related to the velocity of reaction, for as soon as the reaction velocity of the liberation of reducing or oxidizing ions greatly exceeds the reduction or oxidation velocity with the depolarizer, the reduction or oxidation stops. Thus the obtainable phase, i.e. the quality of the reaction, occurs also as a function of the reaction velocity.

## 5. ELECTRODE POTENTIAL AND REACTION MECHANISM.

The question touched upon above can be more fully defined as follows: Do we know of a factor which includes both the concentration conditions at the electrodes—the functions of the current density and depolarizer concentration—and also takes into consideration the individual character of the active masses,[1] i.e. the ions of the depolarizer? The answer is affirmative. All these influences are contained in the electrode potential.

This claim becomes intelligible if we consider more carefully the nature of the electrode material. It is necessary to choose a certain theory among the various ones which have been proposed—with more or less justification—on the electrical mechanism of reaction. I select that one which seems to me to have the best foundation. The fundamental idea of this theory has been derived from Tafel.[2] Its general usefulness

[1] The nature and the efficacy of the electrode metal are included in the term of "active masses", the ions. This will be shown below.
[2] Ztschr. f. phys. Chemie 34, 199 (1900).

I * have explained in conjunction with R. W. Moore. The whole idea will bo hero predicated and developed.

Without laying too much stress upon the most modern view, that of regarding electricity atomieally by means of the idea, of electrons, all known phenomena justify us in dealing with positive and negative electrical quantities as with chemically active masses, and applying to them the principles of reaction kinetics.

The ions are accordingly chemical compounds, so to speak, of atoms and electrons.

The process in an electrolysis is the following: The ions migrate to the electrodes, the cations to the cathode and the unions to the anode*. This takes place as soon an they come within such proximity of the electrodes that a neutralisation of the electricity can occur. *Wo,* are justified in assuming that this phenomenon takes place on the border line between, the metal and the* solution in such a manner that the ions touch the electrode, strike* against it, but without being on the, electrode; the discharge of the* ions will occur in an extremely thin layer immediately above the surface of the electrode. In the case of elementary ions, this discharging process yields free elementary atoms of great affinity; complex ions give very reactive* groupH which are unnaturated and possess "free" valencen, mid hence are very prone to react further.

The .supposition of such a discharge which, precedes, the deposition is not arbitrary, but necessary. The supposition that the discharge does not take place on the electrodes but at the latter, Heornn at firot Home what arbitrary. However, the behavior of attackable cathodes proves conclusively that the discharge cannot occur on the electrode. We also arrive at formulas which conform to the observations, if we suppose that the discharged but not yet liberated ions obey the laws of osmotic pressure, i.e. the laws governing gases. Thin fact clear, and agrees with our knowledge of the matter, if the discharged ions are in a liquid layer, no matter how thin

**. *L* phyH. Chomio** 47, 418 (1004).

this may be. It is very difficult to understand, if the ions discharge themselves upon the metal surface. We would then be compelled to assume that the solution of any atoms in solid metals obeyed the laws of gases, an assumption which is very improbable and leads, especially in anodic phenomena, to impossible consequences.

The gist of this view is the strict division of the electrode process into the ionic discharge, by which the ions are transferred into the atomistic or unsaturated (very reactable) state, and into the molecular separation of the discharged ions. This second process takes place with a certain velocity the true value of which is unknown to us. It is in general so rapid that discharge and separation appear to us to occur simultaneously. The discharge takes place according to Faraday's law; likewise the separation, after a stationary equilibrium prevails between the discharged ions, the atoms or unsaturated groups, and the separation products.

We can write the first process as a cathodic reaction:

the second as

$$2K=K_2,$$

whereby the second equation may be perhaps reversible, as above mentioned. Accordingly, apparent divergences from Faraday's laws may occur at the beginning of the electrolysis.

If we also assume the first equation as reversible, the participation of the electrolytic osmotic pressure would follow from simple reaction-kinetic considerations.

The second equation is of more interest here. It takes place evidently with a finite velocity so that other velocities can compete with it. This last is afforded by the reaction of the discharged ions with the depolarizer. When this velocity is far the most important one a separation of ions cannot be observed; as is the case with many oxidations and reductions.

Chemical work, with which a certain amount of heat and external work (increase in volume, overcoming pressure) is

often associated, is done at tli « 1 r
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the product of potential :IL»! t*^
The quantity of electricity i^m-^ry f : . ,^< t
gram-equivalent of ion? I< ctlway- :L ! -,.:..
drawn from Faraday's hnvs. Th»T< ft n C % I / -\
plished by a gram-equivuleu <»f \n\ -n i.» , t. - ^
work, external work and |XK<il»ly Li}* rat. ! ^ J ;
portional to the elect rot le poifiituil. If iL* , \
consists only of a chemical reaction, h :i « l.-i:.^ :
energy of the reacting system, the { « u-i/Li : ^-<
be determinative for the value *if* the T.\ '1 . ! *
It is, of course, an entirely iliflt Ts'iif «f*»-*i :.
chemical products are formed. Tlie cLki..n.i'i
character of the reacting bodie< rcir.i^ :ir? 5 ._'
known fact that the end- product uf a n..i ::.»:, -j.
of the value of the energy change t:tkii/z ph. - - >
always more or less related to the r.iar.rLil- <:,.**
The sequence of these considerations i< tli.*t t',j; ,'
can produce only like *dynamic* etfeets.

If the potential is expressed by the Xernst for

in which f i is the concentration of the dischar^N : " \ •* A' f (L obeying the laws of gases, seek to re~entfT tin «>j.'tr >.*• '•"*"• a certain pressure—the electrolytic iviiit^tk* [,r*^>;j»'" ..', : . is the concentration of the ions? in the eltH*tro!y*t , : t- • :y evident that the potential must contain, apart fr»'Li Mr 'i:** concentration of the electrolyte, all infliieiict s »vlii^L aifir:i:!" the concentration of the discharged ion? ,rj\ T!ie>i* i/!1 ; :*•• ^ are, primarily, the current density whoso «izt rr«:u^;^ fin* number of the ions discharged in a unit of tpiit* at a uv^.1 electrode surface, hence regulating its coneentniti M: ^ <»o:* !- arity, the reactions of the IOBS Tvith one another and \v.th tin depolarizer. For variations in the concc ntration of tii** \idue *d* occur through both processes and, since the velocity of the reaction of the discharged ions with the depolarizer also depends upon its chemical nature and concentration, these two last-mentioned factors are also embraced by the potential.

A more thorough knowledge of these relations is gained by a consideration of the typical electrode processes. ,

## 6. ELECTRODE PROCESSES!

### A. Cathodic Processes.

#### *a. Unattackable and Attackable Cathodes.*

In organic chemistry only those cathode processes are of importance which occur with the reduction of an organic depolarizer. This reduction is done by the ions discharged at the cathode. The chemical nature of these -ions can be very variable and, conjointly therewith, the reduction can occur in a variable manner.

In acid solution—assuming the depolarizer to be a non-electrolyte—hydrogen ions will occur, and in alkaline solutions alkali ions, and by making suitable additions any desired kind of ions can be brought into action at the cathode; thus any metal ions may be set free. The metal ions are either added directly to the electrolyte in the form of a metallic salt or hydroxide, or they are derived from the cathode metal itself, in case the cathode is " attackable", and pass from this into the electrolyte.

The various reduction processes can be brought about simply if the cathode metal is primarily considered and a distinction is made between attackable and uriattackable cathodes. The former are such as give no active ions in the presence of the respective electrolyte and depolarizer, so that only the cations of the electrolyte can be shown to be discharged by the current. Attackable cathodes are those which send traceable quantities of ions into the electrolyte during the passage of the current, or in its absence. Naturally, only those attackable cathodes which can yield reducing ions are of interest here.

Since some investigators seer^ to believe that every redtietion must be referred to the action of hydrogen, let it be emphatically pointed out here that, besides many chemical phenomena, the fact that it is immaterial whether the reduction is made at an attackable cathode or by the addition of the ions of this cathode metal to the electrolyte at an unattackable electrode proves the reducing capacity of the metal. In both cases similar results are obtained. But if ions of attackable metals tiro added, this metal is not deposited on an unattackable electrode so long as sufficient quantities of the depolarizer are present and the velocity of depolarization sufficiently outweighs the velocity of discharge. Although the cathode metal, say platinum, always remains the same, an effect occurs nevertheless, similar to that which would be obtained at a cathode composed of the attackable metal in the electrolyte. The conclusion follows necessarily that these metal ions in the electrolyte, and not the hydrogen atoms, determine the reducing action by their separation on or in the electrode.

Wo can hence consider conjointly the case of attackable electrodes with that of the presence of metal ions in the electrolyte at unattackable electrodes, and contrast this with the reduction by hydrogen at unattackable electrodes.

For the latter we will suppose that the hydrogen atoms discharge themselves in the cathode boundary surface, and that these discharged ions' have two reaction possibilities at their disposal. They are either separated molecularly on the cathode, or they reduce the depolarizer. The reduction, velocities of both processes are determinative for the ratio of division. If the reduction takes place far more quickly than the formation of hydrogen molecules, practically no hydrogen will be evolved. The velocity of hydrogen formation is hence of importance in the utilization of the current action for reduction. It depends to a great degree upon the chemical nature and surface condition of the cathode, arid is very likely related to the catalytic nature of the metal These phenomena will be considered conjointly under the discussion on " excess potential/'

Ions are sent off from attackable cathodes immediately into the electrolyte, so that the relations in the latter are qualitalively the same && when metal ions are aclciecl directly to the electrolyte. The metal employed as cathode is hence immaterial for trie effect so far as it has not actually reacted with the electrolyte, and can often be replaced by an unattackable cathode.

Under these conditions the metal ions play the role of hydrogen atoms, as above explained. They discharge themselves in the cathode boundary surface and, depending upon their reaction velocities, affect the reduction of the depolarizer and the metallic deposition. With a great reduction velocity, therefore, no metal whatever is deposited on the cathode so long as sufficient quantities of the depolarizer are present.[1]

An important result of these considerations, and one which confirms the observations, is the knowledge obtained that *dlions, which reduce when, discharged, are again converted by this reduction •performance info the ionic state and are -not at all separated.*

### *b. Excess Potential and the Reduction Action.*

Although the evolution of hydrogen by galvanic action at platinized platinum, electrodes is a well-nigh reversible phenomenon, it proves irreversible at all other cathodes.

To convert, in a given electrolyte, a gram-equivalent of hydrogen from **the** ionic into the molecular state at atmospheric pressure, the same amount of work, which is, of course, dependent upon the beginning and end condition, is always required. But the electrical work is different at different electrodes and, since the same quantity of electricity is combined with a gram-equivalent of hydrogen, the potential of hydrogen evolution is different with the individual metals. Naturally, with the equality of the initial and final state the surplus of the electrical work performed must be compensated by an equivalent gain in work. Calorific phenomena probably accompany the increase in required work necessary for the hydrogen evolution; the results of experimental work on this subject, however, are not yet at our disposal. *Excess potential* is the excess of the discharge potential of hydrogen over the potential value of a

[1] D. R. P. I17GO7 (1900) of C. F. Boehringer u. Sohne; Lob and Moore, Ztschr. f. phys. Chemle 47, 418 (1904).

ydrogen electrode in the corresponding electrolyte. The uantity of heat produced by the excess potential can be very Dnsiderable. If we designate the absolute potential of the ^versible hydrogen evolution by a, and the value of the excess otentia! by *e,* then the electrical work in the separation of a ram-equivalent of gaseous hydrogen in the first case is

nd in the second

$$Ai=96540(a+e).$$

ince the total work in both cases must be equal, there results., , as assumed, a production of a quantity of heat *q* occurs, the guation

$$96540a=96540(a-fe)-g,$$

r

$$g=96540s.$$

or mercury *e* is=0.78 volt, from which *q*= 18026 cal. results.

[96540 coul. X1 volt = 23110 cal.]

According to Caspar!,[1] these excess potentials have the )Uowing values with individual metals:

| | | |
|---|---|---|
| At platinized platinum ...................... | 0.005 | volt, |
| "' bright platinum........................... | 0.09 | '' |
| " nickel .......................................... | 0.21 | " |
| " copper ........................................ | 0.23 | " |
| ".tin ............................................... | 0.53 | " |
| " lead ............................................ | 0.64 | " |
| " zinc ............................................ | 0.70 | c ı |
| " mercury ...................................... | 0.78 | ı'c |

ernst, who introduced the conception of excess potential into ie science of electrochemistry, accepts as the cause of these lenomena the varying solubility of hydrogen in the metals.

. f. phys. Chem. 30, 89 (1899V

Since the energy **erf** rcHlurlmn djl-nds HtlHly u,Hm th« hdght of the cathode potential, f h.> hip «T f I,.* i-xn-ss potential is the stronger the former must IM*. so IOIIR ah hydrogen is the reducing agent. , · t t ,

A great nurrilx'r of lads af,w « with thin rune-option. The assumptions repcnnling tlw fWtriral miudion inodianism, according to wlii<"» flic* ilfcrhnrp- of hydro^n ions rniwt be distinctly (listing ^MI<|C| frnlfl lhl/Ir li;nl«'lilll!ir w*iKinilion, loud to the same coiu'Iusiotts. Tin* rfwttofi velocity c»f molecular formation from th«' iliM-iiarpMl hy«ln.jrMi icms Is lc»wm>d at metals with exc»cw [Hifpniial, H» thai the fiivimon ImUveen molecular formation and rnhirtin^ «>f fl«* poiariwT turns in favor of the ln/M<*r. Thin retanlali^n i»f liyclnipen evolution is shown in the hitfh'T f»i»teiitiaL in the excenn vulla^c. With a high excess voltage in the «ii*ehanrinE ^pac-e H«rcing(»r concentrations of c Uncharged reactive hy«lrdgen *nm* ran accumulate, so that the reiltirtiiw f«f Inwlie^ rechu-ibli* with difiiculty, which doc*s no! f»rwr it! phit iiit»"ii platinum electrodes, succeeds at zinc or rnerrury i'«tln«les.

Since in the fuiuhiiiM'tital views *n* »*pumtion <>f hydrogen in or upon the c*ath<Mle «!i«^ not enter into Hit* rjtiestion, the close connection of thin wpurution with tin- Hoittbility of Itydroogen in the mot.nlH cannot In* eiineetveil. In thin eitse it is more plausible **to** think of flw rrarfioit luring mtuiytically influenced by tlic.* rnetnl. ArroniiiiKly, tin* pktlnizcd platinum would be the **naotal** which accelerate the reaction

2/7 •-'//..-.»

The higher the c*xceHH jwttfiiflal the ^nmller the* catalytic acceleration of the rxMtcfion, :iit«l henre the htniiifer tht* concurrent reduction.

[1] S. Tafel, **Ztscltr. f. phy»» Hutu** III, »*» flfWtj; Lnii, 7.1-dir f, Kkkir«-chemie 7, 320, 3S:i (HlCMI'l^lIi; f r«'1ift, fj«i'iir I **Kl**k!rf**h«mi»»** t, **042** (1903).

[2] E. Miiller giv<%« n **htifiitar «^p!mmti«4t, l*nf fUff"* t«*t ion** tlie **catalytic** action, which is Herf* parfiritliiilv rfnlil*nH/wI ^fwltr f, aiw>rg, (1n*m, 20, 1 (1901).

The Idea of excess potential is useful in applying the process of separating a certain kind of ions at unattackable cathodes. For reduction it has up to the present only been proved for hydrogen; it is nevertheless possible that the separation potential of every ion changes with the nature of the electrode, .since the opportunity for the reaction of discharged ions being catalytically influenced to form stable molecules is always present. E. Miiller [1] and Coehn [2] have shown that the excess potential phenomenon also occurs in anodic processes.

The generally disseminated idea, however, that the *excess potential of hydrogen* also plays a part in the case of attackable •cathodes is untenable. With metals which furnish reducing ions—and each cation is capable of reducing—hydrogen does not take part, or at least plays only a secondary role. The specific reducing actions of copper, zinc, tin, and lead cathodes .are not to be explained by the excess potential of hydrogen, Since attackability is also a function of the electrolyte, the rule of excess voltage may be applicable in one case and not in another. For example, Tafel[3] could explain the strong reducing action of a lead cathode in sulphuric-acid solution by the high excess potential of the lead, while the same metal is attackable in alkaline electrolytes and yields reducing ions, whereby the hydrogen action seems excluded.[4]

*c. Concerning Substances Reducible with Difficulty.*

Besides the discussion on the strong depolarizers thus far •considered, it will be well to make a few special remarks on substances reducible with difficulty. The insight into the theoretical relations here existing has not yet been cleared up, and is much more difficult than in the ease of the substances which consume practically all the cations which are discharged. However, it is not at all necessary to add special views to those already generally developed. They suffice for the present

[1] Jahrb. f. Elektrpchemie VIII, 292; Ztschr. f. anorg. **Chem.'26,**1 (1901)
[2] Ztschr. f. Elektrochemie 9, 642 (1903).
[8] Ztschr. f, phys. Chemie 34,199 (1900).
[4] C1 Ldb and Moore, Ztschr. f. phys. Chem. **46,** 427 (1904).

in explaining tli<- 1 !u»n«)ii»'na urrtirrhig ISITP, and we may sibly get along ^v lh a iuiiflfnii infrpn'talinn. The importance of r<**lC ,,,,,, iriti(·s I(II tlll· nilllw llf ,,vc,ry cal action req*^*rr ^ ^ ^ <ixlll:ni:itillll of UlC· of the influences < in ʎl«. rf.ii«>.. .,f tin- n-acticm to that fundament al therefore, be we'll In em.n.ler the*, ml! ticular side and to a-k what relaticw <i<» the electrical factors bear to the rotation velnrity, nntl in what niainuT do they act on the lattc*r. It aj*pai>' tliut the rHtirii^ ,u·t;lon ()f difficultly redvKTil»l<* sul*1awt* :it uimtlarkable c-uthodc-K takoft place different! \% <lclH-iiiliiiK ^ijHin tin- mati'rial of iho latter. This diversity **cran** 1«* rxplaini'd l»y utiftlujil nuluftion velocities. The l^er clc»li^MtI UJMIM tin* <Htnn*ntration of tin* reacting substances which H« far »*< the ion:-' al«mi' to lx» taken into consideration an* ri»fici*rn«Ml b? regulated liy tlie current strength, the c*l«'iuicat rr>-i*ifance itf tin* hyutcin, I.e. the nature of the fneiHuni, sun I l*y catalytic*. iuiiucnm< which, with the choice* cil* snitahli* ct»utiitiMrtH. are to lie iwerilml to the .electrode metitl. The ineaMirnhle cli*ctrical factor, the potential, comprises **si** part nf llii^nr am! it ist of consequence to thxiH know !h«* itetcnnining the potential in s\ic*li u ttmnner fl»* rtniiiirliciii with the reaction velocity rc^fnainH clear.

mm

Substances .reiiurllilf* **ilillinilîv an*** tnrli trifling polarising value, - In HIP oW unessentially lowers[1] the cu ' jmft*iitLiI **whii-h warn** mined for the i>nn* rlrHrnlyli* been fully invc·*Mtignti*fl tiy 1

In the COBO <if of rriiucgd In aeid solution at priM^ticmlly the consump^ tion of hydrojaccm by llti* *m* quantity of hyclrr>gi*ti liy iin* *m* that

1? m'

[1] With caffeine? ntu! in an in potential occurs **«utt** CMV the Influence of ttit? fiitlimli* «»tlin erf Substances Reducible

always takes place into hydrogen consumed !•> <**< '•• * ; and hydrogen evolved molmilarly a* a «r:» - ^ T lr • preceding explanations, it is dourly evidri.t th i t * potential must play a decisive* part in all tb »• r . . > forms an expression for the above- mention* ^ f n i t " '" » in proportion to the reaction velocities H v» »••<> , • velocity of formation of molecular h\dnw» •' ^ " » ' influenced catalytically by the- electrode materi.d, ^ • ' the excess potential of the eledrode in J*UP> :»»*id *u'i," * depolarizer will be decisive* for the reduction «•»<»• ! "*, j * that the catalytic property is not ini»li!i«"l by H" * '» : The latter, under similar expenm«[9]iital 1'itiifSiUNii , j*,-i i i [8] no catalytic acceleration of the mlitHtoit if * h *«MV " always with a similar velocity with tb[1] I i \ * l i * » f * ^ I change in the division ratio between hydmfHi <-v«*hiM"?. * duction is only determined l>y a chnitp* in %vk«*tH nj f t , - * ' Naumann's [l] experiments aKn»c[v] with t hi ;, II*' !«« *u * • I f * 1,1* velocity with which catTeinc* in reduce* I at l[f]*»itl r»tiiM»li 4* i upon the cathode potential in pure arid, Th«* i* * i 'i « ^j * J* [f] • the more energetically the higher Ilie e\ci«» . l»nf*'i<fi !t n acid. This rule does, not apply when tin* e,ttli«i<S»[4] in* i -J [ti] ally iniluences the actual velocity of i * ' «l i u MMH i > t - v , between hydrogen and tho depolarizer Thn%* ?ilf* lu* i M ', more quickly at mercury than at lead rlt-Hfi, it i( ^?j.. both metals possess the name[1] cathode p*»teiifi-d *^i th excess potential in pure acid. The* v««!oe$ty *if *M I,^*M- evolution of hydrogen can al«o b* n taid^d l*y tl-« } «>* ** LI the caffeine molecules, as t!ie caffeine* moifrtilt • t«* u » n « - illustration, increase the chemical re.^taric** in «Ja[i] ! » • ! » » $ ' the electrode surface. In this ease Uw i XI*^A ptif ^t<t ul n^ ? » and with it the cathode potential, At flu* w*> t$n;i depolarizing action of the caffeine* HH«|U lu Itrni-r t{,« *, * »r potential. If the first action— with fjiitiniiin/ *,j i a?* —is the stronger, an increase in pnteiitint h at lit f r,K;,.f » , , spite of the addition of caffeine. By f u w

[1] Sen note on. 21.,

of caffeine, the potrntial is finally <.;m**d to drop % stronger depolarizing eflVc-tSK This phriif>mi»m>H nfrurs ;tt lead but not at mercury cttUic»l"s^N««W«"»^- I» the I;UHT rase* only the depolarizing action nf raiiVtiir isdimvn; this is pfrhap* dopon-ent upon the diO'i'ivnf surfan* rnnditinns nf tanl and mercury.

The cathode* lt<»ti*ntial i» dHi*nimn*d nn th*» nm* hand by the electrolytic' <^inntii- prr.-. un nf ihi <.;<ihnd<'f i.(»,? by the quantity of hy< Ir«*krl'» \U»ifh i »'vul\xl i*Ii'c!n»lyiirjilly at uimt-' tackable catho«!*v in ih*- unit nf <iiu... With thb Isyftn^n, the ions discharsc*cl in thr hnun*i;iry lavt-r, uhii-h unii»» to form molecular hy<In*tr**n, ;MV in i'»l.'iilil*rwui. Thi «*lertn*lyti« .osmotic prossun* i-, th<-n«jnri', iu<it«p* u<t*'Ht »*f ib i[Uantity of hydrogen ust»<l l»y t!i»' «l*«l»i*l iri/iT, Mun-nMT, fin* poii'iitial is determined by thi' «'«»nrfnii,Mti»tn »l fin* iiyilmui'ii i*»ns in the .electrolyte, \vhir-h I'^nr^nir iti»t'i i-u/ hi* lalj'ii a- «*onsJant when strong :i<-M *iti* ?i.t"j.

The coiiclu^l«Hi 'ii!»»'Ai » }n«n»*i I*v XjiiUiiatin» It* In* drawn "from theses coir i»l«'!ati*m- ! ;irr* U«M Jnlln\\inj5- \t ifii*rc»ury cathodes, \v-ho.-f «*\rf - ptf^fjlh! i !>f*t iiillipiiri'fi hy the* caffeine, the* c*;it<^»»J»» pittMnhal in»i f •** «*i*ijtij l it-i-If nf c*vc»ry .moment during f i^ft H"lM'ti'»n »** IJ »»nlv ihr fh**'frnlyfii' i*\alu-tion of hydrof5**ii firriiH*"} an»l tin* rnrniit rfiii4iiiii*d in /\w reduction of tli«* i ali-Mm* «lrl imt inihimi'M if hfijjhf At lead •electrodes, H</\\v*\«t, ?l^** t^if{i»^ii» liMfrntij»)-» ar? alttjiy** MI»II»-what higher fliifinji th«* iniction thun in tin* ^aiiu* i*I«*Hro« lytic hydrog^ti ^v?4iili*>n in th«* jaw* arid, jinn* (!»*« in«*r«»a<t* in •excess potentiul rati^*«l IA ih«* rn*-!^*iit»* i* add«*d to it,

It is cvi<h*iif 'from ji tfiit'i»lii;iii*iii nf flii">* variously pw ••sible influeiK*i*Hf ^fn-ii ?*• lh»* rh;uiv«* in *)<" «*tf<*^ jtnffntin 'Caused by tin* >l**jrt4ni»*r» tin* rnf ilitr artiun nf ib* iiii4it upon the vc*l€ic*if v l«itli nf lip* itiiiifinibr tfttftiiifpitt nf liydrngH .•and the reaction l#'tiv****ij liydr^'H tin* d»fjft4iiirf*r -llni' the value of tin* i/ifliiuli* P riiiifllltiriiii*i! hy a MWH O

[1]Naumannf in lii^ tiiu*«*rf4tf<*ft» fit*^ «i**tl'*r «)i^hiitt^it v brti, contains the hyf »«»f }<*'•»., tiifit tip* ti,ilf«i«< **f<*im»ti<'f*** ?tti4 fir **ntl*Mii«m** «»ae •tions are of the HHIn*< *t*

moments which can be independent of one another. Hence the reduction effect can vary even with equal potentials at different electrodes, which is true, for example, with caffeine at lead and mercury cathodes.[1]

## B. Anodic Processes.

A theoretical insight into this part of the electrolysis of organic compounds is much less clear than in the ease of ciitho< lie-processes.

The pure action of oxygen is in every way comparable with that of hydrogen. Only a greater variety is hens possibly because ozone as well as oxygen can be formed. At platinum electrodes, for instance, the formation of oxygen occurs at 1 .OS volts as measured with a hydrogen electrode at zero value, and that of ozone at 1.67 volts. Moreover, the great susceptibility of the carbon compounds towards oxygen, as already alluded to, which may easily lead to their complete destruction,, and the great number of oxidation phases to which each molecule may in a greater or less degree be subject, render difficult an insight into the electrical oxygen actions.

It has already been mentioned that the excess potential phenomenon occurs also with the oxidation phenomena. Thus it is possible to conyert p-nitrotoluene into p-nitroboriHoic acid at' lead-peroxide anodes, while at platinum anodes only the alcohol is formed. It still seems inexplicable how thin peculiar action of the anode material takes place. The simplest yet sufficient .explanation is to assume that the anode in capable of influencing catalytically the oxidation process an well as the* formation of molecular oxygen. If the first process is accelerated and the second retarded, we obtain the excess potential by which the evolution of oxygen occurs only at a higher potential. Inversely, the oxygen and ozone formation can be made reversible, and the oxidizing action decreased.

A further complicating moment in electrolytic oxidations, as opposed to reductions, is the variety of possible ionic

[1]Tafel and Schmitz, Ztschr. 1 Elektrochemie $8_r$ 281 (1002),

moments which can be independent of one another. Hence the reduction effect can vary even with equal potentials at different oloetnxles, which is true, for example, with caffeine at loud and mercury cathodes.[1]

**B. Anodic Processes.**

A theoretical insight into this part of the electrolysis of organic compounds is much loss clear than in the case of cathodic processes.

The pun* action of oxygen is in every way comparable with that of hydrogen. Only a greater variety is here possible, because ozone us well as oxygon can be formed. At platinum electrodes, for instance, the formation of oxygon occurs at 1.08 volts as measured with a hydrogen electrode* at zero value, and that of ozone at 1.07 volts. Moreover, the great susceptibility of the carbon compounds towards oxygen, as already alluded to, which may easily lead to their complete destruction, and the grout number of oxidation phases to which each molecule may in a greater or less degree be subject, render difficult an insight into the electrical oxygen, actions.

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A further complicating moment in electrolytic oxidations, HHoppoMni to rodwtionH, ia the* variety of possible ionic actions,

[1] **TaM** ami S , Xtsebr, **f. Eloktrochomio** *H,* **281** (1002).

While the process at the cathode always ends finally in withdrawal of oxygen or in taking up of hydrogen, the number of possible reactions at the anode—aside from solution-phenomena, which are without interest here—is a much greater one. For, each ion which is capable of substituting can pass into the reactive state at the anode and produce reactions which ^cannot be numbered with the real oxidations. In the first place numerous substitutions can occur in difficultly oxidizable bodies, especially aromatic compounds, for instance the chlorination of phenols and phthalei'ns, nitration of acids, diazotizing of amines, etc. Substitution and oxidation processes often occur simultaneously, as in the electrolytic formation of iodoform from alcohol.

A great many more individual varieties of reactions must be taken into consideration in anodic processes. However, the same fundamental law holds good for each of the separate possible processes as with the reductions, in that the energy of the action of the anion is determined by the anode potential. Thus 0. Dony Renault,[1] carefully observing limited anode potentials in the electrical oxidation of the alcohol, could .obtain acetaldehyde or acetic acid at will.

The reason for the prominence of reduction processes as apposed to the less prominent electrical oxidations has already been given. Besides the complexity of the phenomena, it •must be taken into consideration that the oxygen evolved at platinum anodes has a low potential. The action of an oxidizer depends upon the oxidation potential with which the oxygen attacks the depolarizer. Even though the oxidation potential can, within certain limits, be varied by the anode potential, for instance by the material of the anode, it nevertheless does not attain the value of the strong chemical oxidizers, as for example chromic acid or permanganic acid. This follows from the small activity of electrolytic oxygen in regard to separate bodies.

Since it is not possible always to obtain the entirely iiidi-

[1] Ztschr. f. Elektrochemie 6, 533 (1900).

vielual action of these two bodies on organic -cc^ipqUTiels with the aid of eled.rolytically evolved oxygen,, it Beemed advisable, to use the chemical oxidizers, which have already been mentioned, in the electrolytic cell. This was done by employing the electrical process only for the regeneration of the chromic or permanganic acids which, an such, oxidize organic bodies in a purely chemical way, being themselves converted thereby into lower stages of oxidation. The advantage of such a method lies in a saving of both the oxidising acids, because, on account of the regeneration to their highest state of oxidation, very small quantities suffice* to oxidize unlimited quantities of organic bodies. This oxidation process is hence* both a secondary and a chemical one*. Nevertheless, it possesses the essential features of an electrochemical process, the substance being replaced l>y the energy.

Attackable anodes, which are brought into solution by the unions of the electrolyte[1], are[1], of ne> value[1], or only of a wholly secondary one, in the elect rolysls of organic compounds. But in Hid* eases where, by reason of the attackubility, oxidizing nubBtancoH arc formed on the; anode, the latter can assume the function** of an oxygen carrier. Thus, if a lead anodo is superficially coated with load peroxide, thin latter offoota the oxidation, being in turn reduced but always regenerated by the current. But if a lead-peroxide anode, prepared in this manner, aetB merely by means of its excess potential for the clisrliarged oxygen, without reacting directly with the elepohtrmvr, if naturally exercises only the functions of an unattackablc anode*.

Finally may be mentioned the purely catalytic action of the electrodes upon the reaction products produced by the eled.rolynis, a sphere of phenomena which lies outside* the purely" electrical relation**. This is the ease, for instaneie, in the decomposition of hydrogen peroxide* by electrical oxidation at platinum anodes into water artel oxygon. But even the electrical conditions can te modified by such reaction^ if change** in the concentration relations of the predominating ions are combined with them.

## 7. THEORY OF THE REACTION VELOCITY IN ELECTROLYTIC PROCESSES.

The ease with which the reaction conditions can be controlled makes electrolytic processes especially adapted for studying the laws of reaction, particularly those of reaction velocities. The dependence of the reacting agents upon the current strength, according to Faraday's laws, makes* it possible to vary *ad libitum* the temporal total course of a reaction within wide limits—a possibility which in purely chemical operations, by changing the conditions of pressure and temperature, exists to a far less extent.

Attempts have not been lacking to regard electrical processes from a reaction-kinetic point of view, and to use them directly for determining reaction velocities. Even though these experiments are based naturally upon single simple examples—mostly reduction experiments — their theoretical results have, especially for physicochemical speculations of organic reactions, such general importance that the reasoning: involved in the most important theories will briefly be outlined here.

### *a. The Diffusion Theory.*

Since, according to the preceding descriptions, the reaction space of electrolytic processes consists of an extremely thin layer in contact with the electrode—the contact surface of electrolyte and electrode—these processes can generally be regarded as reactions in heterogeneous systems. Nernst[1] lias proposed a theory for such systems, which has been tested experimentally by Brunner.[2] The principle of this theory consists in basing the reaction velocities on th& diffusion velocity.

The equilibrium between two phases at their boundary surface must be produced with extremely great rapidity,,

[1] Ztschr. f. phys. Cheinie 47, 52 (1904). See also the earlier investigation: Noyes and Whitney, ibid. 23, 689 (1897)

[2] Ztschr. f. phys. Chem. 47, 58 (1904)

otherwise infinitely great, or at least very great, forces would develop between the extremely close points between which the reaction occurs. Those would, however, bring about the equilibrium practically instantly. In such a case the reaction velocity is conditioned by the velocity with which the mobile components reach the border-line of the phases, i.e. by the diffusion velocity.

The contact surface[1], of both phases will now actually possess a thin but measurable layer of the thickness *8,* within which the whole diffusion process occurs.

If we designate the concentration of the diffusing substance at the surface of the fixed phase by (7, its concentration in the solution by *c,* its diffusion constant by *D,* and the surface* of the solid body by *F,* then in the period *dt* the quantity of substance

will diffuse to the contact surface and immediately react. The speed of reaction becomes

(h nJ^Z£
dt x d '

If wo consider that *0* possesses an extremely small and negligible value, on account of the csquilibirum which occurs, instantly, the following equation results:

dx DF
dt**.F'C"

The speed of reaction is proportional to the concentration of the* diffusing mibstanee.

In applying these results to electrochemical reactions there is to be added, only the condition that the concentration of the reacting substance in the immediate vicinity of the electrode munt always possess a very small- value, which can easily be attained by choosing a suitable current tension. Then the reaction velocity will depend only upon the quantity of the substance reaching the electrode. Electrolytic transference must be considered as well as the diffusion, if ions are involved.

Since the quantity of the discharged ions depends upon the current strength, it represents a measure of the reaction velocity, if (1) side reactions are excluded — for instance, if no ions are discharged without reacting — and (2) the current strength chosen is not so small that the reaction velocity possesses a higher value than the discharging velocity of the ions regulated by the intensity.

In other words: The current strength is then only a direct measure of the reaction velocity, if the maximum current strength at which all the liberated ions are just able to react is employed. The production of this condition can be easily recognized experimentally by the fact that the least increase of this maximum intensity leads to side reactions, most frequently to a molecular separation of the discharged ions.

Before the Nernst theory was proposed, H. Goldschmidt [1] had already employed this idea for studying the relation between reaction velocity and concentration of aromatic nitro-bodies.

If the maximum current strength at which 110 hydrogen is yet evolved, is designated by $J_{mj}$ the concentration of the body to be reduced by C, the experimental equation resulted

$C^*$ is the concentration of a cross-section, i.e. the reaction takes place directly at the electrode surface. If we suppose that the adjustment of the equilibrium takes place there with •extreme rapidity, according to Nernst, then the reaction velocity will have to be based solely on the diffusion velocity, and will, therefore, be directly proportional to the concentration of the depolarizer in the electrolyte. The theory hence demands the formula

T ' __ TT mrt
$J_m$ — J\. -0.

[1] Ztschr. f. Elektrochemie, 7, 263 (1900).

The lack of conformity has not yet been explained. Perhaps the supposition of a very rapid attainment of the equilibrium at the electrode does not apply to the reduction of nitrobenzene; which abounds in phases,

The results of Akerberg[1] concerning the velocity of the •electrolytic decomposition of oxalic acid in the presence of sulphuric acid agree better with the theoretic requirements. So long as the proportion of oxalic acid is considerable, the decomposition takes place according to Faraday's laws/ i.e. without evolution of oxygen. But if the solution has reached a certain dilution, the electrolysis occurs—independently of the* current density—accompanied by an evolution of oxygen proportional to the concentration of the oxalic acid in the solution. The decomposition of the oxalic acid then takes place in the; same proportion as new oxalic acid diffuses from the* okictrolyto to the electrode* boundary surface. Consequently, according t;o Nernst's theory, the electrolytic oxidation velocity henceforth becomes a diffusion velocity.

The hypothesis of the latter Is always the instantaneous equilibrium at the contact surface of heterogeneous phases; hut. the fulfillment of this condition is not to be accepted forthwith, particularly in the case of many organic processes which —for instance, the reduction of nitre-bodies—are able to give a whole series of intermediate phases up to the final equilibrium.

The influence of the electrode material upon the velocity of reaction decides particularly against its significance in all cases as a diffusion velocity.

Finally, to view electrolytic processes as heterogeneous systetriH does not seem at all sound, according to the description of the electrochemical reaction mechanism given in our introduction. If the first proceas, in accordance with the given ^position, is the diacharge in the electrode boundary surface, and if the second is the separation on the electrode or the

f. anorg. Ohemic $!, 161 (1002). Bee also Brurmer, Reaction 'V«tk>citl« in Heterogeneous Systems, p. 52, Thesis, Gflttingen, 1003. Of. fito Luther arid Brittle^ 2tnchr. f. phy». Ohemie 45, 216 (1903), reaction of the ions present in the boundary surface with the-depolarizer, hence in the fluid system, then the actual reaction takes place in a homogeneous system. The typical influence of the reacting ions will then show itself in the velocity constant of this reaction; likewise, if the ions are derived from the latter, the typical effect of the electrode metal will be seen. A sharp distinction will then exist between the discharge, which can occur with an extremely great velocity, and the actual chemical reaction with the depolarizer, the velocity of which will be measurable and distinctly individualistic. In this case the velocity of diffusion alone cannot represent the velocity of reaction.

With the aid of other ideas concerning the electrical reaction mechanism, particularly the reduction mechanism, Haber and Russ[1] arrive at the same interpretation . They advance the proposition: " The . reducing phase Is formed at the cathode with an immeasurably great velocity constant, but the velocity with which it acts chemically on the depolarizer depends upon the latter's peculiarities and is often measurably small/ ;

By a " reducing phase" is meant hydrogen or any metal phase which is supposed to stand in a dynamic equilibrium with it, so that the action of the different cathode materials can be taken as equal, a condition which can be experimentally obtained by the choice of a cathode potential which remains always the same.

### 6. *Osmotic Theory of Electrical Reduction.*

Haber [2]. was the first to publish a theory of electrical reduction which is in many points free from the limiting conditions of the diffusion theory. Later, conjointly with Russ,[3] he brought it to the form given below.

[1] Ztschr. f. phys. Chemie 47, 263 (1004).
[2] Ibid. 32, 193 (1900).
[8] Ibid. 47, 263 (1904).

The sphere of validity of this theory, in conformity with the experimental material, extends to the use of unattackable cathodes at current strengths which, in contradistinction to those chosen by Goldschmidt, lie considerably below those necessary for developing hydrogen. The conditions are hereby simplified, because, on the one hand, the reduction must proceed exactly according to Faraday's laws, and, on the other hand, it can be regarded as being always accomplished by the same agent, hydrogen. This latter hypothesis, since it permits the assumption that the reducing agent obeys the laws of gases, is extremely weighty for the theory. Herewith is assumed that the hydrogen is present in the electrode surface with the concentration *CH*- If we want to assume the replacement of the hydrogen by a metal, the latter must also be regarded as obeying the laws of gases. It hence suffices to deduce the theory only for hydrogen as a reducing agent. If *CH* be the concentration of the hydrogen atoms at the cathode, then the potential *E,* according to Nernst's osmotic formula, is

***Off***

in which *R* is the gas constant, and *T* the absolute temperature. If the hydrogen in the cathode now reacts with the depolarizer *M,* for instance according to the equation

the speed of reduction is

or, neglecting the subtractive member,

*dt*

According to the above-mentioned hypotheses, we can ^directly substitute the current strength / for the speed, which is proportional to it,

~~dt ==klJf

1 = C^2_H or, more simply, 77777- = @^2H>

/V wJW"

'M

If this value is introduced into the potential equation,

there results

RT. J

6r if $C_H$- is considered as constant, and the constant *kf* is placed in the formula as subtractive member,

•pm r

E =-7r-ln79—const.

^ ^M

The relations were now tested for the constant / in an alcoholic nitrobenzene solution; as a result the formula can also be written in the following manner:

const. ;

furthermore, lor constant nitrobenzene concentration,

V KT, T

E «-rt-lnj — const.,

and finally for constant cathode potential, the relation

r*------- = const.

So far as a logarithmic connection between *E* on the one hand, and / and $C_M$ on the other resulted, the theory is verifled by the observation. However, the constant factor before the logarithm was not found at $\frac{RT}{\cdot}$•—. It always possessed a larger and somewhat variable value.

Haber and Russ[1] therefore changed the original formula to

$$E = x\,(\text{-T}; \text{— ln -77-''} \text{— const.}).$$

This expression was substantiated by experience when the influences of diffusion were avoided as much as possible. The factor $x$ appears as a function of the electrode condition

It would lead too far to enlarge upon the meanings of the factor $x$ which were discussed by Haber arid Russ.[2]

### *c. Nummary of the Theories.*

Tho two theories of Nernst and Haber above mentioned seem to contradict one another in important points. The electrical speed of reaction in the diffusion theory (Nernst) is directly a speed of diffusion; Haber's formula holds good only in case the diffusion is excluded as much as possible.

The contradiction is only an apparent one, and the difference between the theories lies in the hypotheses. The measurement of the speeds of reaction depends upon the conditions of the experiment. If the reaction between two components of reaction actually takes place instantaneously, we can vary the time of reaction entirely at will by the period of time during which we add *one* of the components. If the latter is used up with immeasurable rapidity, the measured velocity of reaction muflt naturally always remain proportional to the added quantity of the reaction components. The Nernst theory is based on relations in which this subsequent delivery "*m* effected only by the diffusion, the reacting agent furnished by the current being

[1] ZtMhr. f phy*. Chamie 47, 204 (1004).

[2] Cf, atari; *Hum,* Concerning Reaction Accelerations and Reaction Retardations in Electric Reductions and Oxidations. Ztschr. f. phys. Chemie 44, 641 (1003) Hoe also the chapter on electrode material

kept at the electrode by the potential relations in an infinitesimal concentration as opposed to the external concentration. Since the reaction can only proceed further if new quantities of the agent reach the electrode, and this subsequent delivery can be brought about only by transference and diffusion, the first conclusion drawn is that these two factors determine the current strength. The current can reach the electrode only by means of ions. Since, moreover, the measurable velocity of reaction is regulated by the current strength, it follows further that this velocity of reaction is also regulated by the effects of diffusion and transference. It is mentioned in Ackerberg's experiments what'the ratios are in the presence of a depolarizer. The theory holds good if the measurable speed of reaction, which need not be identical with the actual velocity, is artificially made a diffusion velocity. The considerations of Haber suppose that the ions and depolarizer are in such great concentrations at the electrode that the ions derived from the great surplus bring about the reaction in accordance with the current strength—*independently* of that which is subsequently delivered by diffusion. The relations of Haber are therefore valid only in such cases where impoverished phenomena are excluded at the cathode. Those of Nernst are true only in such where complete impoverishment exists, i.e., where almost zero concentration of the depolarizer is created at the direct border line of reaction. For the reaction can progress only in this case in the same proportion as the depolarizer enters by diffusion into the reaction layer.

We easily obtain results having the advantage of better proof, if we base the reaction-kinetic speculations upon the views developed on the reaction mechanism, according to which the discharge of the ions at the electrode is strictly to be distinguished from the separation on the electrode or the reaction with the depolarizer. This kind of proof is naturally of greater significance for the Haber than for the Nernst deductions. For even if the whole reaction, according to our supposition, takes place in the fluid phase, i.e. in a homogeneous system, the principles of the reaction can practically be applicable in heterogeneous systems. In the localization of the discharging space in the immediate vicinity of the electrode, the layer in which the discharged ions are present may be considered as an extremely thin film which behaves as a heterogeneous formation towards the electrolyte. The concentration of the discharged ions in this film is undoubtedly extremely small at the great velocity of reaction with which they separate or react. Thus the progress of the reaction depends upon the velocity with which diffusion and transference conduct new ions to this film. If the concentration of the depolarizer is strong, only the last-mentioned factors will influence the reaction velocity; if it *w* weak, the quantity of the depolarizer, which is supplied by diffusion, plays an important part.

Our views, that the laws of gases can actually be applied to the concentration of the discharged ions, form a desirable confirmation of Haber's relations. For the discharged ions, which are not in or upon the electrode but in the solution, must haw an osmotic; pressure proportional to the concentration in the discharging space, i.e. the current strength, according to Habor'8 conditions. The validity of the laws of gases, if we suppose a solid solution of the ions in the electrode, is difficult to explain, particularly if the case is one of metal ions whicli reach the cathode and there produce reduction effects. The deductions of Haber remain unchanged formally, but their sphere of validity appears enlarged, however, since under the necessarily limited conditions the behavior of attackable cathodes becomes also theoretically representable. A repetition of thoso (Inductions, however,will not be given here.

The theoretical treatment of the physicochemical material, which organic, chemistry places HO abundantly at our command, is yet in its initial state. Not only do the many obscure points incite to a continuation of the work, but the few results and the numerous problems rather justify the opinion that the phenomena of organic electrolysis are especially adapted to carry the teachings of physical chemistry into the domain of organic chemistry.

# CHAPTER II.

## METHODICS.

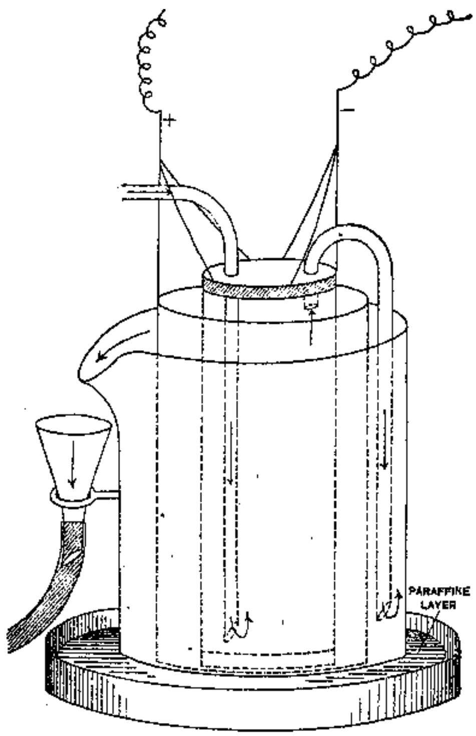
IT is assumed that the reader is familiar with the general arrangements of electrochemical experiments. In the following pages only those particulars will receive attention which are of special importance in the electrolysis of organic compounds. The arrangement which permits the observation of the decisive potentials, and their control and maintenance at a' constant, is particularly important. Of importance are certain electrolyzing apparatus suitable for particular purposes, and also arrangements for stirring, which often decisively influence the course of an experiment.

### 1. THE CELLS.

Cells of the most varied constructions, depending upon the problem in hand, are required. The conductivity of the electrolyte, the necessity of collecting gases, the separation of the cathode and anode chambers, regulation of the temperature, the variation of the size of the electrode, all demand certain requirements and arrangements.

Of course, the comprehensiveness of the experiment is also of great importance. However, only the conditions which enter into the question of scientific investigations are of interest here. We shall, therefore, waive the repetition of the technical arrangements for organic electrochemical processes.

In the simplest case it suffices to immerse the two electrodes always in a certain position in a glass vessel, and usually parallel to one another. The vessel is closed with a hermetically fitting stopper when gases are to be collected. Three be -obtained by putting in glass or porcelain worms through, which a continuous current of water is conducted. Metallic worms must only be used if they are to serve at the same time as electrodes. Otherwise they act in an undesirable manner as intermediate conductors in the electrolysis. Often it is impor-




FIG, 1.—Arrangement for Cooling the Electrodes.

tant to keep the electrodes cool, since their surfaces limit the .actual reaction space.

Cooling of the electrodes is done either by using worm electrodes, as above mentioned, or, if this is made impossible by the-nature and form of the electrodes, by choosing hollow, cylindrical electrodes,—through which water is passed,—and of perforations are required in the stopper, one for a glass tube,, urul the other two for the electrodes, the latter being sealed in. A little mercury closes the circuit. Changes in temperature are obtained by outwardly heating or cooling the vessel. Stirring is caused by the eleetrolytically evolvod gases.

The current conditions can be varied in the most different ways. By a choice* of concentrations, or by additions, the conductivity can bo increased or diminished; also by raising or lowering the voltage. The height of the electromotive force developed in the coll determines the current strength; the ratio of the hitter to the electrode surfaces gives the current density, and to the volume of the electrolytes, the current concentrations.[1]

This simplest form of arrangement seldom suffices; usually a separation of the cathode and anode spaces is required. This is oftonest obtained by the use of a diaphragm, or by connecting, with a siphon arrangement, two separate vessels,—one containing then anode and the other the cathode fluid; this latter method is more rarely used, however, because the resistance is liable to become too great. Porous earthenware cylinders or plates arc* usually employed as diaphragms. Diaphragms, which often answer well, are sometimes made of gypsum, pressed asbestus (only utili^able in alkalies [2])r porous cement, and parchment paper. So-called " acid-proof[5>] diaphragms are also used. Cylindrical vessels arc[1], simply placed • in the \viderjluier vessel, and plates arc* fitted in tightly, or cemented simpler method is to make the cell of two separate part if fit ting upon ono another. Between these the diaphragm platn is tightly wedged with screws by means of a ruMxT ring or a caoutchouc frame. The Wehrlin [3] cell is made in thin fashion. Cooling and Btirring in eleetrolytical experiments-are of Bpi*c*5i.il Importance, Aside from the external cooling of the ('Uwtrolyfe, u constant temperature of the latter can

•Tufal, XtHchr. f. phyi*. <!hom. 34, 201 (1900).
[1] Ix'Sibinc, KtHchr. f. Kl«kfcrf»ch«mi« 7, 290 (1901).
* Ibid, 3, 4aiCIH07),

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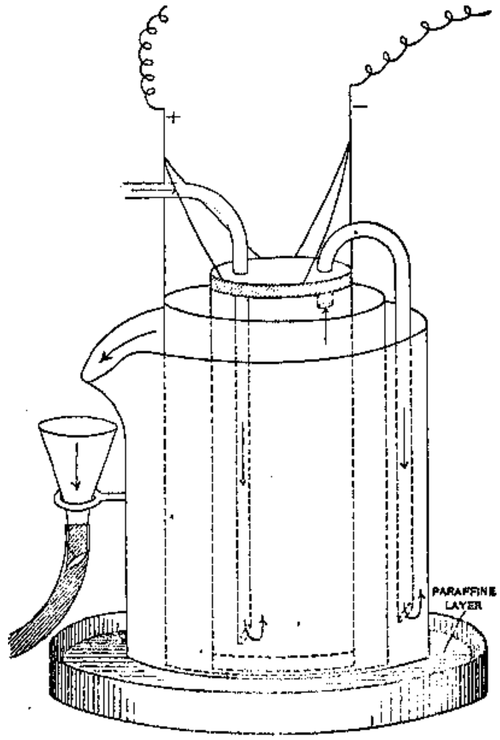


FIG. 1.—Arrangement for Cooling the Electrodes.

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It is evident from the drawings that, by choosing suitable diaphragms, the reaction chambers can be closed from without.

In using earthenware cylinders, the reaction fluid—anodic or cathoclic—is most suitably placed in the earthenware cylinder, especially if the gases arc* to be determined.

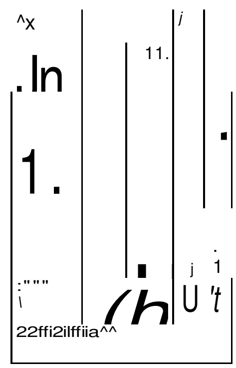
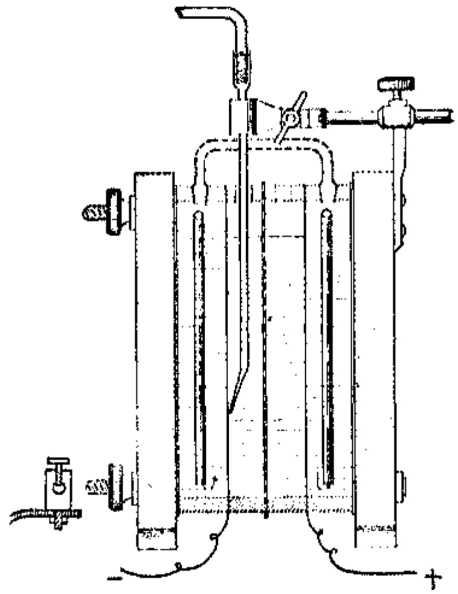


FIG. 2. Tafel'n Electrolytic Cell.



Fio. 3,—Wcjhrlin'B (toll.

Gas or mechanical stirrera are made UHC», of for ntirring the* electrolytes Mechanical stirrem, however, are ernpbyed only if the e»le»ctre)lytiei ganc*H arc* to be investigated, unless the.wi suffice for the stirring, as Is the case in experiments with high current strengths. By permitting the base of the stirresr to dip into mercury,[3] the? mechanical stirring can easily be arranged in a manner so as to obtain a herrnetieul se»uL

[1] **Ztschr. f. Kicktrr>chernie 2, «(W5 (1890).**

[3] **Her.** cl **deutffch. chcin. Clwwlliich.** *$&>* 222,1 **(HKK».**

'Ldb^tschr, **f, Elektrochcmic 7, 117** (HKK)); **KtMchr.** f, phya Chf*rnii* S4, 647 **(1900).**

The gas-tight electrode stirrers are based on the same principle. They have the advantage of using the electrodes themselves,—which may have any shape,—for stirring. A

troae sun&ue mo ^^«^— -r—/. -TM- TM^^ A0 ^ great; importance in a series of reactions, for instance in the simultane-

fine division of the components is thus assured on the electrode surface the (reaction space). This matter is of great im-

•__ - ,-^wrt« r\-f vckor»'firinQ "f

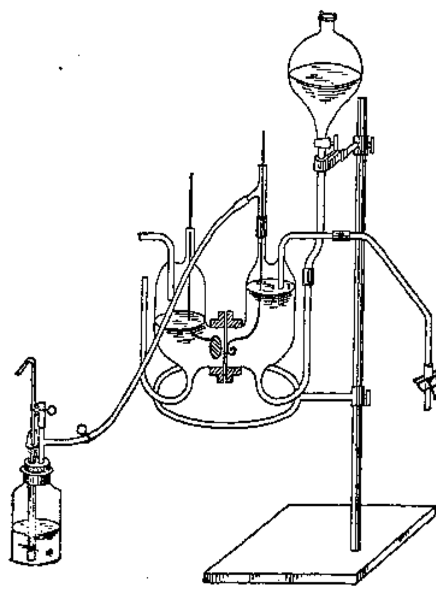


FIG. 4.—Electrolytic Cell (Hofer's)

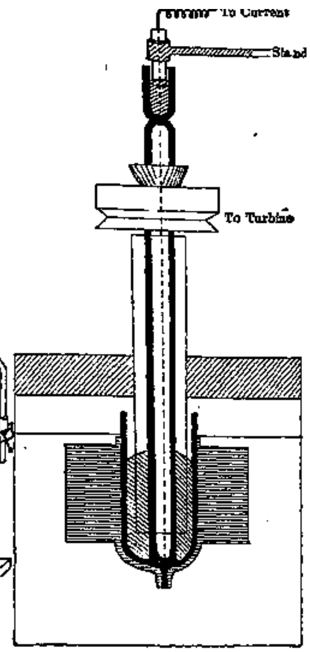



FIG. 5.—Gas-tight Electrode Stirrer.

ous reduction of two nitro-bodjies to a mixed azo-body, or in the electrolytic preparation of azo-dyes, etc. (See Fig. 5.) The current is conducted through mercury, which is poured into the glass tube in which the electrode is sealed.

## 2. ARRANGEMENT OF EXPERIMENTS AND MEASUREMENTS OF POTENTIAL.

The typical arrangement for an electrical decomposition is that in which the main current flows through an ammeter and the cell, and the* terminals of a voltmeter, in branch circuit, are connected directly to two points at the electrodes.

The potential of the electrode at which the respective reaction takes place is of decisive importance on the course of the electrolysis; it may be the cathode or anode potential or sometimes both. The potential *difference* between the electrodes, which is influenced by many contingencies, such as the resistance of the diaphragm, etc., is, on the contrary, generally without importance for the reaction. The voltmeter shows the consumption of electrical energy only in combination with the ammeter.

The potential of an electrode is determined in combination with a second constant electrode which does not belong to the actual electrolytic system. This subsidiary or standard electrode, whose* potential is either arbitrarily taken as zero or has a certain absolute value, is connected by a siphon with the liquid surrounding the experimental electrode. The electromotive force of this galvanic combination is then measured by one of the well-known methods, with a galvanometer or capillary electrometer. If the potential difference of the standard electrode is correctly subtracted from the obtained value, the difference in potential of the reaction electrode, based on the agreed-upon zeroi value of the potential, is obtained.

Two subsidiary or standard electrodes are in use, the calomel electrode of Oswald[1] and the hydrogen electrode of Nernst.[2] The former, consisting of a combination of mercury covered with rnorcurous chloride* an depolarizer and immersed in a solution of Vio a-potassium-chloride solution, has, according to the best rneasuromeritH, an absolute potential of 0.013 volt-4-0.0008 (t°~18), in the nonse that mercury is positive, tin* solution negative*. The standard hydrogen electrode

r, FJiyMicoch^micfti McuimiromentH, p. 383, Leipzig, 1902.
*Ztnehr. f. KtoktrochVmie 4, 377 (1898); 7, 253 (1900); see also Wilsfc, JStMchr, f, l>hy«. (*h«*m, #5, 291 (1000); (Mwald-Wilwnore, Ztachr. f. phy*. Ch«n. 30, 91 (1901).

consists of a platinum sheet charged with hydrogen in a normal electrolyte, i.e. normal as to the hydrogen ions. In preparing the hydrogen electrode, the sheet platinum (or palladium) is arranged so as to lie half in the electrolyte and half in hydrogen gas, and the saturated state is maintained by having a constant current of hydrogen pass through the electrolyte. The half of the electrode not in the electrolyte must thus be surrounded during the entire time of the experiment by an atmosphere of hydrogen. Nernst gives the hydrogen electrode the arbitrary value 0.

Depending upon the form of the cell, the connection with the standard cell can be made by means of a siphon or other method. Of • course the electrolyte of the normal electrode must not react appreciably with that of the experimental cell, and in most cases it will be of value to separate both, by a suitably adjusted diaphragm.

The problems to which the measurement of the electrode potential gives rise are manifold.

The task is often to determine at what potential a reaction begins; in other words, what discharge potential the separated or reacting ion possesses in the presence of the depolarizer. The determination of this value is most simply made by measuring the decomposition potential.[1] This method is based upon the fact that a permanent decomposition of an electrolyte can only take place by using a certain electromotive force which is just able to overcome that of the polarization. If we begin to polarize with a small electromotive force, the current cannot at first permanently pass the cell. Only when the electromotive force exceeds the value of the polarization does the sudden deflection—the "'rebound'[7] of a galvanometer enclosed in the circuit for observation—phow the passage of the current, revealing the decomposition value of the electrolyte. If in a coordinate system the electromotive forces are considered as abscissas, the current strengths or deflection factors of the galvanometer as ordinates, then curves are obtained which show

JLe Blanc, Ztschr. f. phys. Chem. 8, 299 (1891); 12, 333 (1893).

characteristic breaks at the decomposition values. If the electrode at which the reaction is expected to occur is combined with a normal electrode, and the difference in potential at the work-electrode is observed for increasing current strengths, it will be found that at a certain value of the latter, a sudden passage of the current, which appears as a break in the curve, occurs. This break i's characteristic for the beginning of any kind of reaction, whether it be that of the separation of ions or their reaction with the depolarizer. When several kinds of ions are separated or react at different electromotive forces,[1] these* breaks can repeat themselves in the curve.

The simplest method of determining the beginning or non-occurrence of a reaction consists in measuring the discharge potential of the cations or aruons before and after the addition of the depolarizer which is to be acted upon. A change in potential at the addition shows the beginning of the reaction.

It is of especial importance to know the potential interval within which one or several distinct reactions take place. The determination of this depends upon the change in potential which the presence of a depolarizer produces as opposed to an electrolyte containing no depolarizer. For example, if it is desired to learn if chlorine derivatives of phenol can be prepared at the anode by electrolysis of a hydrochloric-acid solution of phenol, then the point of decomposition of the chlorine ion, in combination with the hydrogen electrode, is found at Uil volts in a 1/i n-hydrochloric-acid solution. If phenol is uddfid to this solution, the break in the curve occurs already at 0.9 volt.[2] Therefore the span in potential, within which the reaction for the formation of chlorine derivatives of phenol rriunt take place, lies between 0.9 arid 1.8 volts. In thin manner l)ony~H£nault, among others, determined the dtwompoHition potential of the OH ions, in combination with the* hydrogen electrode, in. dilute sulphuric-acid solution both without and with the addition of ethyl alcohol. He found

/... »H. dh^ BweTibid 6,1KJ0898).'

"i *Cf. Dony-H^nnult, Ztsehr, f. Klektrochemie 6, 533 (1900).

in the first case that the discharge potential was at 1.66 volts, in the second case at about 1.2-1.3 volts. Either acetaldehyde or acetic acid can be formed by the action of hydroxyl ions upon alcohol. A measurement of the decomposition potential of the hydroxyl ions in dilute sulphuric acid and in the presence of acetaldehyde did not perceptibly lower the potential. The acetaldehyde, under the existing circumstances, does not act as a depolarizer, so that, if the potential during electrolysis is kept between 1.3-1.6 volts, an almost

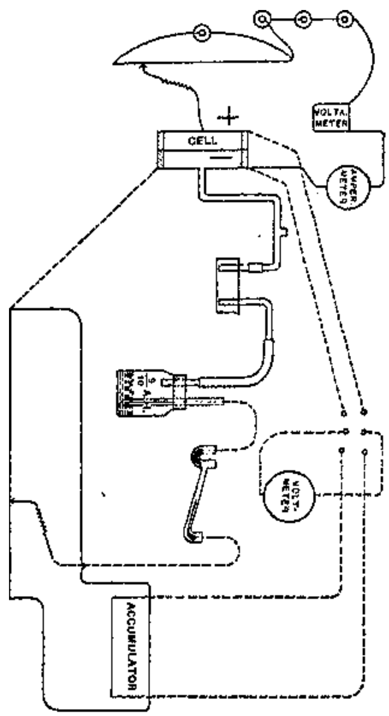



FIG. 6.—Arrangement of Experiment (Ilaber).

quantitative yield of acetaldehyde must be obtained. The experiments completely verified this theoretical deduction.

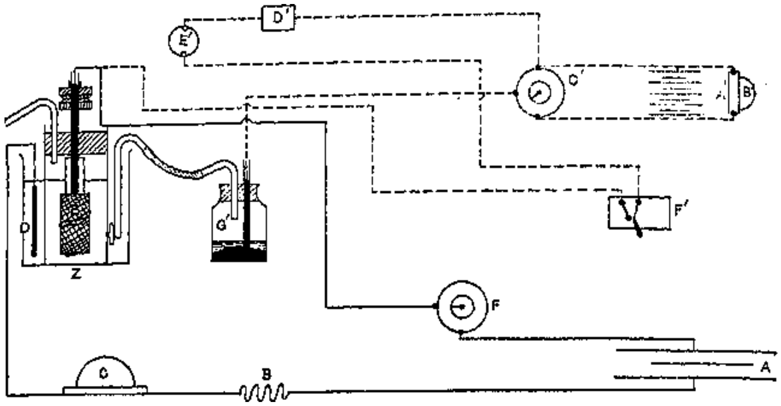
The second problem, which often occurs, is to keep this potential at a certain value, or within certain limits. This is accomplished by setting the cell, which consists of the work-electrode and the normal electrode, at the desired tension by choosing the suitable polarizing current strength—according to the compensation method,—and by taking care that the tension existing between the work electrode and the standard electrode retains the value of the compensating potential by varying the current strength, as may become necessary during the course of the. experiment. Haber[l] has I used this method of procedure for limited potentials, and Lob and Moore[2] employed it for an entirely distinct constant' potential during prolonged electrolyses, Figs. 6 and 7 are ' sketches of the arrangements of their experiments. The requirements for the reduction of nitrobenzene, as expressed in the theoretical part of this book, were proved by these experiments,—namely, that, by reason of the necessary limitations, only the cathode potential is decisive for the obtainable reduction phase.

If in simpler cases, which are naturally rarer in organic electrolysis, the only point is to keep the total decomposition tension between the electrodes below a certain value, then it will suffice to employ suitably small electromotive forces, or such limited by branching.

Finally, the measurement of single electrode potentials is of importance *m* itself for obtaining the depolarizing values, i.e., the potential differences of an. electrolyte in connection with a certain electrode with or without a depolarizer. It is evident that these depolarizer values are characteristic quantities for the chemical nature of the depolarizer, and are very closely related to the constitution and configuration of the molecule. Introductory experiments on this question for nitro- and nitroso-bodies have been made by Panchaud de Bottens.[8] Lob and 11
Moore [4] have also measured the depolarizing values for nitrobenzene at different electrodes and current strengths. It was

, i Ztschr. f. Elektrochemie 4, 507 (1898).
*Ztschr. f. physik. Chena. 47, 432 (1904).
Ztschr. f. Elektrochemie 8, 305, 332 (1902).
*Ber. d 5. Internat. Kongr. f. angew. Chemie, Berlin, 1903, 4, 656.

found that they- generally became smaller with increasing current strengths. Single electrode metals, however, show peculiarities which suggest the occurrence of variable reactions. Besides the usual method of arrangement mentioned at the beginning of this chapter, in which the current derived from any suitable source of electricity passes through the cell, the apparatus can often be suitably simplified—especially for electrical reductions—by employing Lob reaction cells[1]




Main Current: ----—— *A,* Current Source, £ Rheostat, C Ammeter, *D* Anode, *E* Cathode, *F* Plate Kettintance, % Experimental (Jell.
Measuring Current: ...........A'Compensation Accumulators, *ft*[1] JProciHion Voltmeter, C'Plate Resistance, ***I)'*** Ballast IlemAtance, *JK*[f] Galvanometer, *f''* Instantaneous Cutout, *O* Standard Electrode.

FIG. 7.—Ldb's Experimental Arrangement

or short-circuiting cells. Cells can be constructed, which do away with the primary-current production in laboratory work, based upon the fact, already used by Iloyer[2] in the reduction of oxalic acid, that a reaction producible by the current can inversely serve as a part of a suitably constructed electric cell. If, for instance, nitrobenzene is dissolved in concentrated sulphuric acid, the solution poured into an earthen ware cylinder, a piece of platinum dipped in the latter and the

[1] Ber. d. deutsch. chem. Geseilsch. 29, 1390 (1806).
[2]Compt. rend. 69, 1374 (1869); see also **Lapeyri&re,** Tommasi, Trait6 d'Elecbcochimie 724,720 (1899).

cylinder with its contents placed in another vessel containing dilute sulphuric acid in which is immersed a piece of amalgamated zinc, we have nn electric cell or battery. On making a metallic contact between the zinc and platinum with a binding-screw, quite a considerable; current circulates even at a low tension since the resistance is small. After a few hours the contents of the earthenware cylinder solidifies, forming a pasty mass of amidophonol sulphate*. Such systems can be prepared in very many suitable forms, particularly in such a manner that heat, or pressure, etc., can be applied during the operation.

## 3. THE ELECTRODES.

The nature of the electrodes is of great importance for the course of electrolytic processes. The material is not only decisive for the effect, as already fully discussed, but the nature of the surface and the.*, previous treatment of the electrodes can decidedly influence the; course of the electrolysis. In the first place it is obvious that the size of the surface wetted by the electrolyte is codeterminative for the potential and current density, and even on this account its smoothness or roughness form decisive factors; but its form, and the mutual position of both, electrodes, must also be taken into consideration, for on these; depend the distribution of the lines of force on the surface. In general, the data em the current densities and of the potentials refer to mean values; actually both are usually unlike at different points of the surface, since the number of the discharging current lines is an uneven one.

If *IH,* the»re*fore, often to be recommended, especially in aeerurate potential measurements, to "'touch over " the surface. Ilalxr [1] d<x»ft this by shaping the siphon end of the standard'| • electrode into a capillary tube, which he conducts along the \ electrode surface. If the object is to obtain tolerably equal current doriBiticB without this accurate checking of the resuits, the relative! size arid position of both electrodes must

[1] Ztechr. f. phya. Chemto **8£,** 209 (1900).

be taken into consideration. They may be chosen of similar dimensions and like form, and hung parallel in the bath. A better way is to choose concentric arrangements such as mentioned by Lob[1] and Tafel.[2] These electrodes consist of concentric cylinders between which the electrolysis takes place.

It has already been mentioned, in the discussion on the excess potential phenomenon, in what manner the nature of the- electrode potential is of importance for the potential, leaving out of the question the changed dimensions. The evolution of hydrogen is well-nigh reversible at platinized platinum (0.005 volt excess potential); at bright.(polished) platinum it is already 0.09 volt. This influence possibly occurs in a similar manner with,all electrode materials. Tafel,[3] by reducing difficultly reducible substances in sulphuric-acid solution, was able to obtain good results only at a lead cathode, the surface* of which was coated with a layer of spongy lead. Such a surface can easily be prepared by first coating the electrode anodically with a thin film of lead peroxide and then reducing this cathodically. Simultaneously a solution of the foreign metals in the surface coat is brought about by the anodic process and a *pure* lead surface obtained by reduction. Tafel, by a great number of examples, has likewise demonstrated how important it is to have a pure cathode. Even traces of impurities can decisively modify the effect. The simplest supposition is that the velocity of separation of the discharged ions is catalytically influenced by the traces of impurities. This assumption agrees best with the experimental results. Indeed, if the reduction energy is lowered by the impurities, we must conclude that an accelerated catalytical action of the hydrogen formation occurs; this agrees with the observation of Tafel. that, with a constant-current source and outer resistance, a disturbance of the reduction goes hand in hand with an increase ot the current, or, what is the same thing, a lowering of the potential difference at the cathode.

[1] Ztschr. f. Elektrochemie 2, 665 (1896).
[2] Ber. d. deutsch. chem. Gesellsch. **33,** 2223 (1900).
[3] Ztschr. f. phys. Chem. **34,** 187 (1900).

Lob and Moore'[1] have obtained the suitable surface constitution and purity of the cathode in a different manner from "Tafel. They start with a carefully platinized platinum gauze electrode? and coat this electrolytically with the desired metal by electrolysing a pure salt solution under suitable conditions. They thus succeeded, even with attackable cathodes, in obtaining quite constant cathode potentials for a long period.

Russ[2] has observed a peculiar influence of the pretrcatment ' of the electrodes. If strong currents are sent through the cell for a longer period, so that an energetic evolution of hydrogen occurs in the presence of a depolarizer, the cathode potential soon drops, even if the current remains constant, and the evolution of hydrogen ceases. The original potential and renewed hydrogen evolution, after a short interruption of the current, reoccurs when the current is again turned on. Hence,, the electrodes depolarize butter after being charged with hydrogen than without the latter. The extent of this influence varies with different metals.

[1] i. c.
[2] ZtHchr. f. phy» Chem. 44, 041 (1903).

# CHAPTER III.

## ELECTROLYSIS OF ALIPHATIC COMPOUNDS.

ORGANIC compounds which are decomposed in solution by a direct current can be divided into those that behave as electrolytes and those that act merely as depolarizers. This division is not, however, altogether appropriate, because both effects often occur simultaneously, so that a strict carrying out of this disposition is not possible without arbitrariness and numerous repetitions. The classification into oxidation and reduction processes, which proved practical in the theoretical part, would also be serviceable in the presentation of the experimental data, even though anodic and cathodic effects are sometimes observed side by side, or successively, in an electrolysis. However, the advantages of the latter division are combined with the greatest possible survey of the material if this is arranged only in accordance with the chemical, character of the substances which serve as the starting-point. The sequence of the latter is prescribed by the familiar arrangement employed in text-books on organic chemistry. Moreover, the property of depolarizing, anodically or cathodipally, depends upon the nature of the materials which serve as the starting-point, each group of bodies exhibiting a fixity in its electrochemical behavior, whereby an almost separate grouping of the oxidation and reduction processes naturally follows.

### 1. CAEBON AND HYDROCARBONS.

#### Carbon.

Carbon, the characteristic element of all organic com pounds, is, as such, also the primal product in the eleetrosynthesis of organic substances. The well-investigated electro-thermie processes of carbide formation on the one hand, and, on the other, the little explained phenomena of the electrolytic solution of carbon by the action of the anode current, form the introduction to these syntheses. That this solution occurs when carbon is used as the anode in an acid electrolyte, has been repeatedly observed; likewise the frequently occurring presence[1] of carbon in the cathode precipitate in galvanic metal-deposition luts also been rioted. In the electrolysis of dilute sulphuric aeid, using carbon electrodes, Bartoli and Papasogli[1] had found that the anode carbon is attacked, which was shown by the appearance of carbon mon- and dioxide. Coehn[2] then demonstrated that carbon goes into solution under suitable conditions, coloring the sulphuric acid; as a constituent part of the cation it wanders to the cathode arid deposits itself, like a metal, as a conductive[1], coating upon the platinum cathode. The nature* of the solution (carbon hydroxide?) and of the precipitate has not yet been explained. Coehn[3] was able, however, to prove that the solution of the carbon conforms to Faraday's law arid leads to the expected electrochemical equivalerit $\frac{12}{j} \approx 3$.

*Hydrocarbons.*

The great chemical resistibility of aliphatic hydrocarbons and the aggregate state of their members poor in carbon make thorn appear as unsuitable material for electrolytical experiments. Only the addition-reactions of unsaturated hydrocarbons offer an experimental field. Thin has riot yet been developed. These reactions are cathodic in the addition of hydrogen, and anodic in the addition of halogens, etc. The fact that such hydrocarbons occur in the decomposition of aliphatic acids gives us an indication as to their behavior, which will be mentioned at the proper place.

. chtm. 14, 90; IB, 401 (1885); Comp. rend. 102. 303 (1886).

[2] ZtHchr. f, Klektrochemfo 2, 640, 010 (1896).

•Ibid $S_r$ 424 (1807),

Acetylene is the only hydrocarbon which has been used as a primal material.

**Acetylene.** — Coehn and Billitzcr[1] have subjected acetylene to the action of the oxidizing current in alkaline and acicl solution with limited anode potential The discharging potential of oxygen, which is in the neighborhood of 1.7 volts in a pure potassium-hydroxide solution, is lowered by acetylene to 1.22 volts. At this potential a reaction begins. It **is** possible in the same experiment to convert the process into a quantitative one, if the tension is kept between **1.22** and 1.6 volts, a potential at which a second reaction begins, as shown by the sudden jump in the current strength. At 1.35 volts formic acid is produced exclusively, according to the following equation:

$$C_2H_2 + 6\ OH - 2\ H_20 + 2\ HCOOIL$$

In sulphuric-acid solution the process proceeds differently. By conducting acetylene into sulphuric acid, aldehyde is first produced. This causes a depolarization of about 0.19 volt. A quantitative oxidation of the aldehyde to acetic add occurs if the tension remains below the discharging tension of oxygen:

$$,\ CH_3CHO + 2\ OH - CHaCOOH + H_2O.$$

Nothing is as yet known regarding the reduction of acetylene and the addition of halogens.

### 2. NITRO-DERTVATIVES OP HYDROCARBONS.

The reduction of aliphatic nitro-hycirocarbons in dilute alcoholic sulphuric-acid solution has been accomplished by Pierron.[2] The /J-alkyl-hydroxylamines are obtained at platinum anodes and at a'temperature of *15°-20P:*

$$RNO_S+4H- RNHOH+HaO,$$

[1] Ztschr. f. Elektrochemie *7,* 681 (1901).
[2] Bull, soc, chim. [3] **21,** 780 (1809).

and at 70°-75° the amines:

$$RNOo+611 - RNH_2 + 2H_20.$$

Nitromethane thus yields either methylhydroxylamine or methylamine. When concentrated hydrochloric or sulphuric acid in used, hydroxylarninc and formaldehyde are formed, i,e. the decomposition products of an oxime which was probably formed first:

$$CII_3N0_2+2H«CH_2 : NOH + II_2O = NH_2OH + CH_30.$$

Under similar conditions *nitroethane* is converted into /?-ethylhydroxylarnine or othylamine; and 7^-*nitropropane* int<& /?-n-propylhydroxy lamina or n-propylamine.

### 3. HYDROXYL COMPOUNDS.

Oxidation products are principally to be expected with the aliphatic hydroxyl compounds as the lowest stage of oxidation. In fact, hydrogen is evolved unused, even if the cathode and anode are not separated by diaphragms, while the oxygen is-absorbed.

Methyl Alcohol.—We are indebted to Renard,[1] Almeida and Dehc'rain,[2] Jaillard,[3] Habermann [4] and Cdnnell [&] for numerous experiments on the electrolysis of methyl alcohol.

The results obtained with methyl alcohol can be summed up MS follows: Hydrogen being evolved, the oxidation products-formed arc*:

1. In aqueous sulphuric-acid solution: Methyl formate, methylal, methyl acetate, acetic acid, and methyl-sulphuric add, a little carbon dioxide and monoxide, but no formic aldehyde*.

* Compt. rend, 80, 105, 230 (1875).
[2] Ibid. **51,** 214 (1865).
[s] Ibid. 68, 203 (1863).
*Monatnch. 7,2590886).
•Pogg. Ann, *n,* 487 (1835).

Renard considers the formation of acetic acid as ;due to reciprocal action between the alcohol and carbon monoxide:

$$CHsOH + CO = CH_3 - COOH.$$

Jahn [1] thinks the formation must be traceable to the presence of ethyl alcohol.

2. In aqueous solution, on addition of potassium acetate (Habermann): Besides carbon dioxide and carbon monoxide, methane and potassium methyl-carbonate.

3. Without a solvent, by itself or with the addition of a little alkali: Chiefly potassium carbonate; also hydrogen, oxygen, carbon monoxide, and carbon dioxide.

While these experiments, which were carried out without giving a theoretical insight into the nature of the electrochemical reaction, yielded almost all the possible oxidation products in the oxidation of methyl alcohol, Klbs arid Brunner [2] have discovered a method which gives 80% of the current yield in formaldehyde. This is exactly the substance which could not be proven present up to that time among the electrolytic oxidation products of methyl alcohol. Elbs and Brunner electrolysed an aqueous solution of 160 g. methyl alcohol and 49 to 98 g. sulphuric acid in a litre. They employed a bright platinum anode in an earthenware cylinder, using a current density of 3.75 amp.'and a temperature of 30°. Only traces of formic acid and carbonic acid and a little carbon monoxide, aside from the 80 per cent, of formaldehyde, were formed. Plating the platinum anode with platinum decreased the yield of formaldehyde at the expense of the carbon dioxide. With an anode of lead peroxide the carbon dioxide exceeded the aldehyde.

Dony-H6nault,[3] by measuring the depolarizing action of the alcohol in 3 n-sulphuric acid, found no indications of the

[1] Jahn, Grandriss d. Elektrochemie 201 (1894).
[2] Ztschr, 1 Elektrochemie 0, 604 (1900).
[8] Ibid.,533 (1900).

production of formaldehyde, and also obtained a negative result in an (.experiment.

The significance of all the conditions, for instance the acid concentration, plainly follows from the different results of the liist-namod investigators.

Ethyl Alcohol.—In the case of this alcohol the more important results have been obtained by the investigators above mentioned. Schonbein [1] and Becquerel,[2] and Bartoli and Papasogli[3] also later carried out some investigations on the same subject. The results of the researches are, in general, that the final products formed are the following:

1. In sulphuric acid solution: Aldehyde, acetic ester, formic ester, ethylidene oxyethyl ether [ CHs—CH< Xn TJ 1
\ \UU2-tl ,5/
(Renartl), and ethyl-sulphuric acid.

2. Almeida and DelwSrain state that in the electrolysis of a nitric-acid solution they observed, in addition to these oxidation products, carbonaceous derivatives of ammonia at the negative pole.

3. In hydrochloric-acid solution[4] chlor-acetic acids occur, in addition to the corresponding oxidation products (Riche [5]).

Habermann, on electrolysing the alcohol in alkaline solution, obtained, besides carbon dioxide, an aldehyde resin (Liidersdorf and Connel [6]) from which he isolated a body closely related to cinnarnic aldehyde. In aqueous solution, on the addition of potassium acetate, the alcohol was split up into ethane, potassium ethyl-carbonate, carbon dioxide, and acetic ester.

Jaillard[7] and Riche[8] proved the formation of aldehyde in sulphuric- and acetic-acid solution. In hydrochloric-acid solu-

[1] ToinmaHi, Truit.6 d'Klcetrochirme 726 (1889).
[3]Compt. r«nd. 81, 1002 (1875) et al. places of Compt rend.; Tommasi, d'KIectrochimie 726 (1889).
'**Wiedcm.** Beibliiiter 7, 121 (1882).
[4] Fogg. Ann. 19,77 (1830).
•TornmaKi, Trait/* d'Eleetroehimie 728 (1889),
[9] Pogg. Ann. **30,** 487; Phil Mag 18, 47.
Utampt. rend. 58, 203 (1804).
[8] Tommasi, Trait^ d'Kloctrochimie 728 (1889).

tion Liidersdorf[1] obtained ester like compounds containing chlorine. Dony-Henault[2] and Elbs and Brunner[3] have shown how to obtain certain products, depending upon definite conditions. While the former directed his aim to the anode potential; the latter sought to determine precisely the chemical factors which influence the reaction.

Dony-Henault observed that alcohol is oxidized in sulphuric-acid solution already at an anode potential of 1.3 volts, .as measured in connection with the hydrogen electrode- The oxidation of acetaldehyde, on the contrary, requires a potential of 1.66 volts to convert the aldehyde into acetic acid. Hence, the alcohol can be oxidized only to aldehyde between 1.3 and 1.66 volts. The experiment proved that, when a platinized platinum electrode is employed, only acetaldehyde is formed, and this quantitatively. The aldehyde yield decreases at a higher potential, the acid content of the electrolytes increases, and, at the same time, ethyl-sulphuric acid can be detected, as already shown by Ilenarcl. Dony-Henault ascribes the formation of this acid to the discharge of the SCVions. According to Elbs, a purely chemical action of the sulphuric acid (which becomes concentrated at the anode) on the alcohol is the more probable.

Elbs and Brunner electrolysed an aqueous solution containing 5 g.-molecule equivalents of alcohol and **0.5-1** g.-molecule equivalent of sulphuric acid. They obtained acetaldehyde, acetic acid, and carbon dioxide, but no carbon monoxide. Acetic acid is the principal product at a bright (polished) platinum electrode. It is formed with a current yield of over 80%, the yield of aldehyde amounting to about only one twentieth of the weight of the acetic acid,

*lodoform from Ethyl Alcohol*—Chloroform and bromoform cannot be prepared eieetrolytically from alcohol (Elbs and Herz[4]). This is contrary to the claims of the I). II. P. No.

[1] Pogg. Ann. 19,77 (1830).
[2] **Ztsehr. f. Elektrochomie 0, 533 (1900).**
[3] Ibid 6, 604 (1900)
[4] Ibid. 4, 118 (1807),

29771 (1884). Coughlin [1] has .substantially verified the results of Elbs in the case of bromoforrn. He obtained only small quantities of this body which can be easily prepared electrolytically from acotone. The* formation of iodoform, on the contrary, takes place smoothly. It is obtained technically according to the above-mentioned patent. Elbs and Herz have established the following conditions for this reaction. The course of the reaction is illustrated by the equation:

$$10\,I + H_20 = CHI_3 + C0_2 + 7\,HI.$$

The electrolysis is best performed as follows: A solution of 13-15 g. calcined soda and 10 g. potassium iodide in 100 cc. water and 20 cc. alcohol is placed in a porous earthenware cylinder with platinum anode. The cathode, of nickel, is surrounded by a strong solution of sodium hydroxide. The electrolysis is carried out at a temperature of 70° C., with a current density at the anode of 1 amp. *per* 100 sq. cm., arid is continued for 2-3 hours. After several hours the iodoform crystallizes out, the current yield being from 60-70 per cent. The chief by-product remaining in the mother liquor is sodium iodate.

The reduction of the iodoform by the electrolytically generated hydrogen is insignificant, according to the observations of Forster and Mewes.[2]

This behavior permits the discarding of the earthenware cylinder. It suffices to envelop the cathodes with parchment paper, whereby the resistance and the consumption of electrical energy is considerably diminished. The diffusion of the free alkali hydroxide away fromtho cathode necessitates the continuous introduction of carbonic-acid gas, because caustic alkali prevents the formation of iodoform, while carbonate promotes it. When using the covered cathodes, 20 g. calcined soda, 20 g. potassium iodide, and 50 cc. alcohol in 200 cc. water are electrolysed at a temperature of 50°-70°, a current of carbonic-acid gas .being conducted into the solution between anode and

[1] Am. Ctosm. Journ. 27, 63 (1901).
[2] »tochr. f. Klektwxshflmie 4, 268 (1897),

cathode. The current density at the platinum anode can be from 1 to 3 amp., at the platinum cathode 4 to 8 amp., for 100 sq. cm.[1] The current yield is about 80%. A series of secondary reactions, which are not mentioned in the above equation, occur in this process. The hydriodic acid reacts with the soda, liberating carbonic acid and forming sodium iodide, which in turn is subject to decomposition. The iodine is converted at the anode into hypoiodite which converts the alcohol by oxidation and substitution into iodoform. Alkali-iodate is also formed by oxidation of the hypoiodite.

The reaction is the same as that involved in the usual chemical preparation of iodoform, whereby a colorless solution of hypoiodite (obtained by dissolving iodine in a sufficient quantity of potassium-hydroxide solution) is made to react with alcohol. The decomposition potential of potassium iodide, investigated by Dony-Henault,[2] shows that the iodine as such does not act on the alcohol, but only after its conversion into hypoiodite. The iodine ions are set free at the same anode potential no matter if alcohol is added or not. The alcohol does not act as a depolarizer towards the iodine ion; the electrical iodoform synthesis is a typical secondary process.

*Preparation of Chloral.*—Chloral is obtained according to a process[3] devised by the Chemische Fabrik auf Aktien (vorrn. E. Schering), if alcohol is permitted to flow into the anode chamber of the cell during the electrolysis of a potassium-chloride solution. Glucose, starch, and sugar thus also yield chloral

Incidentally it may also be mentioned that Sand and Singer [4] have prepared alcohols electrolytically by reducing the mercuric-iodide compounds of alcohols. The cathode is a large sheet of platinum which is immersed in the solution of

[1] Elba, tFbungsbeispiele fur die elektrolytische Darstellung chemischer Praparate (Halle, 1902), 95.

[2] Ztschr. f. Elektrochemie 7, 57 (1900).

[3] Elektrochem. Ztschr. 1, 70 (1894).

[4] Ber. d. deutsch. chem. Gesellsch. 35, 3179 (1902).

the iodide in a 10% potassium-hydroxide solution:

$$IHgCH_2 \bullet CHaOH + 2\,H = Hg + HI + C_2H_5OH.$$

Propyl Alcohol. — n-Propyl alcohol offers a considerably greater resistance to electrical oxidation than methyl or ethyl alcohol, according to experiments made by Elbs and Brunner.[1] Propionic acid is formed as the principal product, with a current- yield of over 90%, at bright (polished) and platinized platinum anodes, as well as at lead peroxide anodes when the alcohol is electrolysed in sulphuric-acid solution. A little propionic aldehyde also occurs at lower current densities. The formation of carbon mon- and dioxides is likewise very insignificant.

Isopropyl Alcohol, under conditions similar to the above electrolysis of n-propyl alcohol, decomposes in accordance with the equations:

I. CHaCHCOHJCHa+O-CHaCOCHs+HaO;
II. $CH_3COCH3+30=CH_3COOH+HCOOH$;
III. $HCOOH + 0\text{-}C0_3+H_20$.

Acetone, acetic acid, formic acid, and carbonic acid are formed. The oxidation takes place more easily than in the case of the primary alcohols, and yields up to 70% acetone, which, however, is readily oxidized further. In alkaline electrolytes the alcohols are converted at the anode into complicated condensation products of the aldehydes.

Isoamyl Alcohol. — The amyl alcohol produced during fermentation was likewise exposed by Elbs and Brunner to the anodic current action in sulphuric-acid solution. It is converted into isovaleric acid with a current yield of about 80%. Some carbonic acid also formed, but isovaleric aldehyde was not present under the chosen conditions.

GlycoL — Of diatomic alcohols only glycol seems to have been the subject of investigation. Renard [2] observed in the

[1] Ztschr. f. Elektrochemie 6, 608 (1900).

[2] *Aim.* chim. phys. [5] 17, 303, 313 (1879); Compt. rend. 81, 188 (1875), **82,** 562 (1870} .

electrolysis of a sulphuric-acid solution of glycol, besides the formation of hydrogen, carbon mon- and dioxide, arid oxygen, that trioxymethylene, glycolic acid, formic acid, arid a substance isomeric with-glucose were present in the solution.

In phosphoric-acid solution the results arc* similar.

Glycerin.—Ilenard[l] also investigated the behavior of glycerin. In the electrolysis of a dilute sulphuric-acid solution he obtained besides the gases, hydrogen, oxygen, carbon monoxide and dioxide,—trioxymcthyleno, formic acid, acetic acid, glyceric aldehyde, arid a body to whose barium compound he gave the formula (CsHaO^Ba (glyceric acid?). Further electrolysis of *glyc&ric aldehyde* gave the ordinary oxidation products, and, as in the case of glycol, a substance closely related to ordinary glucose. Stone and McCoy[2] found similar results in acid solution.

Bartoli and Papasogli[3] repeated these experiments, varying the material of the electrodes, and obtained the following results:

Carbon anode and platinum cathode gave trioxymethylene, formic acid, glyceric acid, a substance similar to glucose, and a resin.

Graphite and platinum electrodes yielded the same products, but a larger per cent of formic acid was formed on using the latter. Mellogen was formed at the positive electrode.

Experiments on the electrolysis of glycerin in alkaline solution were made by Werther,[4] Itcnard,[5] Voigt,[6] and Stone and McCoy.[7] As principal products there* resulted acrolem and acrylic acid, besides glyceric aldehyde or its condensation products, and glyceric acid, graphitic acid, formic acid and, according to Voigt, also propionic acid.

[1] Compt. rend, 81, 188 (1«75), 82, 562 (1876).
[2] Amer. Chem. Journ. 15, 666 (1803),
[8] Gam chim. **18,** 287 (1883).
[4] Journ, prakt, Chem, 88, 161 (1868).
[6] Compt. rend. 82, 562 (1876).
[8] Ztschr. f. angew. Chcmie 107 (1894).
[7] Amer. Chem.* Journ. **15,** 656 (1893).

;*§

Mannite.—This hexatornic alcohol has been investigated by Renard.[1] Bizzarini and Campani[2] have published the results of an investigation on erythrite.

In the elcctrolyzed. fluid from mannite Renard obtained formic acid, trioxymethylene, oxalic acid, a sugar isomeric with glucose, and an acid, $C_6H_8O_8$, which he regarded as the aldehyde of saccharic acid. He could not detect mannonic acid. Erythrite is oxidized to a great extent.

## 4. DERIVATIVES OF THE ALCOHOLS.

Mercaptans. — Bunge[3] electrolysed the alkali salts of ethyl and methyl rnercaptans and observed the formation of disulphides at the positive pole. In the case of the sulpho-compounds, however, the free acids were generated.

Methyl-Sulphuric Acid.—This acid, investigated by Renard,[4] yielded hydrogen at the negative pole, while formic acid, carbon dioxide, carbon monoxide, and trioxymethylene, besides free sulphuric acid, were found at the positive pole.

Potassium Trichlonnethyl-Sulphate.—This compound, electrolyzed by Bunge/ gave hydrogen and alkali at the negative pole; and at the positive pole oxygen, carbonic-acid gas, chlorine, sulphuric acid, and perchloric acid.

Potassium Trichlonnethylsulphonate.—This salt was electrolyzed by Kolbe [6] in neutral concentrated aqueous solution and gave the following results:

The solution became strongly acid and contained free hydrochloric and sulphuric acids. Hydrogen was gradually evolved at the negative pole, After the decomposition was complete the solution contained potassium perchlorate, which was also observed in the case of potassium trichlormethyl-sulphate.

[1] Ann. chim. phys. [5] 17, 289, 316 (1879).
[2] Gaza, chim. **13,** 490 (1883).
[8] Her. d. deutsch. chenx. Gesellseh. B, 295, 911 (1870).
[4] Ann, chim. phys. [5] 17, 289 (1879).
[6] Ber. d, deutsch. chenx Geseilsch. 3, 911 (1870).
[1] Joum. prakt. Chan. 62, 311 (18,54).

Ethyl-Sulphuric Acid.—Ethyl-sulphuric acid, on being subjected to electrolysis gave, according to Renard,[1] at the negative pole hydrogen, and at the positive pole acetic acid, some formic acid, aldehyde, and sulphuric acid. In concentrated solution a greater proportion of acetic acid was formed. The potassium salt on electrolysis breaks up, according to Hittorf,[2] into the ions K- and $-OSO_2-OC_2H_5$.

By using a diaphragm, Guthrie [3] obtained aldehyde and carbonic acid at the anode.

Ethyl-Phosphoric Acid yielded Renard[1] carbonic acid, aldehyde, and free phosphoric acid.

Potassium Isoamyl-Sulphate, according to Guthrie,[3] is decomposed into oxygen, valeric acid, and sulphuric acid, while

Potassium Isoamyl-Phosphate is split up into valeric acid and phosphoric acid.

Potassium Isethionate breaks up (Bunge [4]) into hydrogen and free acid.

## 5. ALDEHYDES, KETONES, AND THEIR DERIVATIVES.

### (a) *Aldehydes.*

Aldehydes occur as oxidation products of primary alcohols. They are readily converted into acids and give, when reduced, primary alcohols. The ketones, the oxidation products of secondary alcohols, are oxidized with difficulty. They can only be converted into acids by simultaneously splitting up the carbon chain. On being reduced they are again converted into secondary alcohols. This behavior is also apparent upon electrolysis; however, the reaction becomes more complicated as the molecule becomes more complex by an enlargement of the carbon chain and the entrance of substituents. Extensive decompositions then occur readily and the decomposition prod-

[1] Ann. chim. phys. [5] 17, 289 (1879).
[2] Pogg. Ann. 106, 530 (1859).
[8] Lieb. Ann. 99, 64 (1856).
[4] Ber. d. deutsch chern. Gesellsch. 3, 911 (1870).

ucts, which are, naturally, often neither aldehydes or ketones; are changed further in accordance with their individual nature. Aldehydes and ketones (like the alcohols) are non-electrolytes, and act merely as depolarizers. The acids, however, which are formed by the reaction, often play a decisive part in the current conductivity, so that more thorough experiments are required in many cases to fully learn the conditions electrically dominating.

The fact that aldehydes occur among the reaction products of the alcohol electrolyses is perhaps the reason why they have rarely been chosen as the starting-point in special experiments. Considering the important role the aldehydes play as intermediate members of syntheses, the treatment of this subject would be highly remunerative, particularly 'with the aid of potential adjustments at certain values. More attention has recently been given to work on the ketones.

Derivatives of Formaldehyde and Acetaldehyde.—According to Tafel and Pfeffermann,[1] the phenylhydrazones of aldehydes are readily converted into amines by reduction in sulphuric-acid solution at a lead cathode. Thus *ethylidene phenylhydrazine* yields about 60% of the theoretical percentage of pure ethylamine salt. The decomposition of *glyoxime* is more complicated. Besides ammonia and glyoxal and a small quantity of an acid (glyoxylic acid ?) there is formed as the principal product the crystalline sulphate of a base, $C_2H_8O_2N_2$, the nature of which could not be determined with certainty. Ethylenediamine is not formed. Nor was a diamine obtained from *methylglyoxime.*

The condensation products of aldehydes with ammonia or amido-eompounds are easily reduced to amines in sulphuric-acid solution at lead cathodes. Thus *hexamethylenetetramine* yields methylamine (Knudson [2]); *ethylideneimine,* ethylamine; the base from acetaldehyde and ethylamine, diethylamine. Aromatic aldehydes behave similarly. The Farbwerke vorm. Meister,

[1] Her. d. deutsch. Gesellsch. 35,1510 (1902).
[2] D. R. P. No, 143197(1902).

Lucius and Br lining [1] obtain the same effect in neutral or ammoniacal solution of the condensation products of fatty aldehydes with ammonia.

*Chloral Hydrate.* — Tommasi [2] electrolysed a sulphuric-acid solution of chloral hydrate and was able to detect the presence of hydrochloric acid. On using diaphragms an abundance of chlorine was evolved at the anode, and acetalhedyde collected at the cathode.

Grape Sugar. — This sugar (investigated by Renard [3]) on being subjected to the action of the current broke up into carbon mon- and dioxide, formic acid, trioxymethylene, and saccharic acid. O'Brien Gunn[4] mentions that the aqueous glucose solution is converted by cathode reduction into mannite:

Cane Sugar. — On electrolyzing a concentrated solution of cane sugar, Brester [5] found that the solution turns strongly acid and acquires reducing properties, very little carbon dioxide being evolved. He was unable to determine the nature of the substance which he isolated by distillation, and which was free from formic and acetic acids. Continued electrolysis produced further oxidation.

The same author made some experiments on the electrolysis of dextrine, gum arabic, and collodion, but obtained no noteworthy results.

The general impression gained from these investigations is one of successive oxidation. The electrolytic oxygen gradually oxidizes the substances, the final product being carbon dioxide. Intermediate products are formed during the electrolysis, their quantity varying with the duration of the electrolysis. In following out these processes it. is of especial importance immediately to withdraw the electrolyzed liquid from the action

[1] D. R. P. No. 148054 (1903).
[2] Tommasi, Trait6 (TElectrochimie 741 (1889).
[3] Ann. chim. phya [5] **17,** 289 (1879).
[4] D. R. P. No. 140318(1900).
[5] Bull. soc. chim. 8, 23 (1866).

of the current, in the manner practiced by Miller and Hofer,[1] by allowing the solution to flow slowly over the electrodes. Experiments of this nature ha^e not yet been made here.

Ulsch[2] has made some observations on the complete electrochemical oxidation of cane sugar to carbonic acid and water. In a sulphuric acid of 1.15 sp. gr.; with the addition of manganese sulphate as an oxygen-carrier, about 98% of the theoretically calculated amount of carbonic acid is obtained. The oxidation at 40°-SO° in barium-hydrate solution is also fairly complete, but not directly to carbonic acid; oxalate appears also to be formed.

The apparently successful attempts at electrical purification of sugar juice, for which a large number of patents[3] have been taken out, may be briefly mentioned here. The gist of the various methods lies, on the one hand, in the destruction of the impurities by oxidation at the anode, and, on the other hand, in the production of precipitates which carry down colored organic substances and facilitate crystallization of the sugar'by eliminating these impurities.

*I. Ketones.*

Acetone.—Friedel,[4] by electrolyzing a sulphuric-acid solution of acetone, obtained carbonic acid, acetic acid, and formic acid. Mulder [5] and Riche [6] were able to isolate *mono-* and *dichloracetone* from the hydrochloric-acid electrolyte, and *monobromacetone* from a hydrobromic-acid solution.

These older investigations are supplemented by more recent researches with more exact results.

According to a process patented by E. Merck,[7] acetone is

[1] Ber. d. deutsch. chem. Gesellsch. 27, 461 (1894).

[3]Ztschr. f. Elektrochemie 5, 539 (1899).

[3] Ibid. 1, 251 (1894), 3, 16 (1896); Jahrb. d Elektrochemie 8, 322 (1896), 8, 628 (1901).

«Lieb. Ann. 112, &76 (1859).

[5] Jahresb. f. Chernie 339 (1859).

• Compt. rend. 49, 176 (1859).

[7]D. R P. No. 113719 (1899).

reduced in acid and alkaline solution at a lead cathode to isopropyl alcohol and pinacone. The yields of the latter, however, are better in acid solution. About 40 parts of isopropyl alcohol and 20 parts of pinacone are obtained from 100 parts of acetone, if a sulphuric-acid electrolyte is employed. The reactions take place according to the equations:

1. $CH_3COCH_3 + 2H = OH_3CH(()H)CH_3$,

2. $2CH_3COCH_3 + 2H$ -CH

The claims of the patent were verified by Klbs.[1] Elbs and Brand[2] publish the following details: In a 10% sodium-hydroxide solution the reduction of acetone at a loud cathode proceeds even with a low current density, hydrogen being continually liberated. The yield of isopropyl alcohol and pinacone is small; and the by-products are mosityloxide, phorone, and other condensation products. About 120 g. pure isopropyl alcohol arid GO g. pinacone hydrate worfc obtained in dilute sulphuric-acid solution from 300 g. acetone, load cathodes being; also used in this ease. At mercury cathodes the reduction of acetone leads to a smooth conversion into isopropyl alcohol (Tafel[3]), without appreciable quantities of pinacone being formed. The cathode electrolyte was 40% sulphuric acid. The experiments were made by keeping the solution cool with ice.

Richard [4] reverts to the attempts of Mulder arid Riche to prepare halogen compounds of acetone. These substitution processes occur, of course, at the anode. With a low anode current density and in concentrated hydrochloric-acid solution (3 vol. acetone to 2 vol. hydrochloric acid) rnonoehloraeetone is produced, the fluid being ice-cooled, and unattackable elec-

[1] Ztschr. f. Blektrochemie 7, 644 (1901). Bee also Bibs and Schmitz, Journ. f. prakt. Chem. 51, 891 (1895).

[3] Ztschr. f. Elektrochemie 8, *78$* (1902).

[8] Ibid, 288 (1902).

[4] Compt. rend, **133,** 878 (1901).

trades without diaphragms employed. Monobromacetone is obtained in a similar manner, but a diaphragm and a somewhat higher temperature (35°-40°) are advantageous in its preparation.

*Chloroform.*—Tceple * has verified the claims of Schering's[2] patent as to the preparation of chloroform from acetone. The solution of the problem consisted simply in electrolyzing a solution of a chloride in the presence of acetone under conditions that would continuously give the greatest possible yield of hypochlorite. The most important conditions for this purpose are a temperature below 25°, a solution containing no alkali, or as little as possible, a high current density at the cathode, and a comparatively low one at the anode (Oettel, Forstcr, etc). Teeple gives the following details: In an ordinary cylinder of 150-200 cc. capacity place 100 cc. water, 20 g. sodium chloride, and 4 cc. acetone; a platinum cylinder serves as anode, and a platinum wire as cathode; close the vessel with a cork connected with a reflux condenser; cool the apparatus with running water and electrolyze, passing in a slow stream of chlorine as needed to neutralize the alkali; anode current density about 6 amp. per sq. dm. or less. After 8 to 10 frours a layer of chloroform may be removed from the bottom of the electrolyte.

The electrolysis of a calcium-chloride solution in the presence of acetone would be the best method of forming chloroform if the high resistance due to the deposits forming on the cathode could be overcome in some way.

*Bromoform.*—As already mentioned, bromoform is not formed from alcohol under the conditions which are suitable for the preparation of iodoform. It is possible, however, to convert acetone quantitatively into bromoform (Coughlin[3]), if acetone arid potassium bromide are subjected in aqueous solution at 25° to the anodic current action and soda is gradually added. A diaphragm is used. More thorough experiments on this

[1] Journ. Amer. Cliena. Soc. 2C, 536 (1904).
[2] D. R. P. 29771 (1884).
[2] Am. Chem. Joum. 27, 63 (1902).

method were carried out by Miiller and Loebe.[1] They showed that the diaphragm becomes unnecessary if a strong current of carbonic-acid gas is passed through the electrolytes kept at 15°-17°. They thus obtained a current yield of 90.2% bromoform. With a lower yield, oxidation and further bromination occurs besides the formation of bromoform. This latter takes place in stoichiometrical proportions according to the equation

$$CH_3COCH_3 + 6Br + H_2O = CHBr_3 + CH_3COOH + 3HBr,$$

or in the form of an ionic equation,

$$3Br' + 6\oplus + H_2O + CH_3COCH_3 = CHBr_3 + CH_3COOH + 3H'.$$

This formula is not intended to show that the acetone acts directly as a depolarizer of the bromine ion. The reaction mechanism has not yet been completely elucidated.

*Iodoform*[2] *from Acetone.*—Teeple[3] mentions a method by which almost the theoretical yield of iodoform can be obtained by the electrolysis of a potassium-iodide solution in the presence of acetone. No diaphragm is required, the essential feature being the gradual addition of a substance like hydrochloric acid, hydriodic acid, or, better, iodine, to neutralize the excess of potassium hydroxide as fast as it is formed. The temperature is kept below 25°, and the electrolyte thoroughly stirred; in fact the same current conditions should be observed as in the case of chloroform above mentioned, the aim in this case also being to maintain the conditions always favorable for the production of a maximum amount of hypoiodite.

Oxidation of Ketoximes.—According to an investigation made by J. Schmidt,[4] ketoximes, on electrolysis in dilute sulphuric-acid solution, are decomposed in such a way that pseudonitroles are formed besides other nitroso-compounds. If *acetoxime* is oxidized at a temperature not over 10° in a 2%

[1] Ztschr. f. Elektrochemie **10,** 409 (1904).
[2] See also p. 60.
[3] Journ. Amer. diem. Soc. **26,** 170 (1904).
[4] Ber. d. deutsch. chem. Gesellsch. **33,** 871 (1900).

sulphuric-acid solution, using a platinum anode, and an earthenware cell as diaphragm, the anode fluid is soon colored blue; at the same time a white crystalline substance is precipitated upon the anode. This substance is propylpseudonitrole,,

[2] This was formed perhaps in the following;

manner :

$$4(CH_3)_2C:NOH + 3N_2O_4 = 4(OH_3)_2C<;Q^2 + 2H_2O + 2NO.$$

A part of the aeetoxime will split up upon electrolysis, oxides[1] of nitrogen being given off, and these latter in the nascent state will convert any unchanged aeetoxime into propylpseudonitrole. A blue nitroso-compouncl can be isolated from the anode solution. A diaphragm is unnecessary in these experiments. *Diethylketoxime* and *methylethylketoxime* behave just like aeetoxime.

Isopropylamine is formed in the reduction of aeetoxime in sulphuric-acid solution at a lead cathode (Tafel and Pfeffermann [1]). This process is a general one. The electrolytic reduction of ketoximes leads, like that of the aldoximes and phenylhydrazones, to the final formation of amines. About 66% of the theoretically possible quantity of isopropylamine is formed from aeetoxime; *acetonphenylhydrazone* gives about the same yield.

*Glyoxime,* OHN = CH:CH:NOH, under similar conditions, yields, as the chief product (about 60% yield) a substance whose reactions probably characterize it as /?-ethyleriedihydroxylamine :

$$\begin{array}{lcl} CH:NOH & & CH_2NHOH \\ | & Hh\ 2H_3\ - & | \\ CH\text{-}.NOH & & CHaNHOH. \end{array}$$

The electrolyte also contains ammonia, glyoxal, and small quantities of acid (glyoxalic acid).

[J] Ber. d. deutsch, chem. Gesellsch. 35, 1510 (1902); see also D. R. R. No. 141346 (1902).

*Isonitrosoacetone.* — Ahrens and Meissner [1] electrolyzed isonitrosoacetone, $CH_3COCHNOH$, in sulphuric-acid solution to obtain amidoacetone. However, a poor yield of dimethylpyrazine, CeHgMg (ketine) was obtained.

Methylethylketone. — This substance, reduced at a lead cathode in the same manner as acetone by Elbs and Brand,[2] gives very unfavorable results in alkaline solution. In sulphuric-acid solution, although the yield is insufficient, there were obtained the modification of methylethylpinacone melting at 50°,

r<TT nw
$OH_3$v /Utl$_3$
>C(OH)-C(OH)<
C$_2$H/ $^X C_2H_5$,

and secondary butyl alcohol, $CH_3CH(OH)\text{-}CH_2\text{-}CH_3$.

Acetylacetone.— This is said to pass, in alcoholic solution, into tetracetylethane (Mulliken [3]):

$CH_3$ - *CO,* $CH_8$C(X /CO - $CH_8$
2 >$CH_2$= >CH~CH< +$H_2$.
CHs-CO/ $CH_3$CCK XIO-CHs

The substance therefore breaks up into H" and (CHaCO^CH';
the anions unite at the anode to the resulting compound.

Acetylacetondioxime, in a 30% sulphuric acid at a lead cathode, is converted into dimethylpyrazolidine and 2.4-diaminopentane (Tafel and Pfeffermann [4]).

| | | |
|---|---|---|
| | $CH_3$ | |
| C:N-OH | CH-NH | CH-NHa |
| | $CH_2$ | $H_2$ |
| C:N-OH | CH-NH | CH-NHa |
| CHs | CH3 | |
| Acetylacetonedioxime. | Dimethylpyrazolidine. | Diaminoptotane. |

Pyrazolidine is the chief product.

[1] Ber. d. deutsch. chem. Gescllsch. **30,** 532 (1897).
[2] Ztschr. f. Elektrochemie 8, 786 (1902).
[3] Amer. Chem. Journ. **15,** 323 (1893).
[4] Ber. d. deutsch. chem. GesellscL **30,** 219 (1903).

## 6. ACIDS.

While the substances thus far discussed are active only as depolarizers, but not as electrolytes, the conditions are different in the case of acids and their salts. These are primarily electrolytes ; their ions take care of the current conductivity and are first separated or brought into reaction at the electrodes. In general, hydrogen ions are discharged at the cathode when acids form the electrolyte, and metal ions in the case of salts; acid-radical ions are discharged at the anode. The latter have the form RCOO and are subject to a series of reaction possibilities. By reacting with water the acid is again regenerated, oxygen being evolved*

$$RCOO + H_2O = RCOOH + OH.$$

Often, however, two anions unite, carbon dioxide being split off:

$$2RCOO == R_2 + 2CO_2,$$

wherein, if R is a hydrocarbon radical, like methyl, ethyl, etc., hydrocarbons are formed having double the number of carbon atoms contained in the radicals united with the carboxyl group. Thus ethane is synthecized from acetic acid. This simple form of reaction is often not the predominating one, which will be explained more fully under the separate substances.

An acid can often develop acid properties at other than the carboxyl groups, e.g. hydroxyl and methylene groups. In that case there must occur the corresponding ions which are able to direct the reaction in entirely different channels from those mentioned. Thus, as is well known, the methylene group placed between two carboxyl or ester groups is capable of forming salts. Such salts as, for instance, sodium cliethylmalonic ester, behave, on electrolysis, in a manner analogous to that of the salts of carboxylic acids. By determining their conductivities, Ehrenfeld [1] has recently proved that the

[1] Ztschr. f. Elektrochemie 9, 335 (1903).

methylene groups of succinic acid, malonic acid, and glutaric acid are capable of forming hydrogen ions.

The first successful experiments in the electrolysis of aliphatic carboxylic acids were made by Kolbe.[1] These experiments are supplemented by the researches of Kekule,[2] Brown and Walker,[3] Mulliken,[4] and Weems,[5] who amplified our knowledge regarding this subject which, still further investigated in the most varied directions by a number of investigators, has yielded valuable results.

Carbonic Acid. — Carbonic acid deserves mention here because it can be converted electrolytically into formic acid. Royer [6] observed its formation at zinc and zinc-amalgam electrodes in the electrical reduction of carbonic acid dissolved in water, a current of the gas being conducted through the latter during electrolysis. Klobukow [7] was likewise able to prove the presence of formic acid in water which was electrolysed and through which a current of carbonic-acid gas was passed.

Lieben [8] has made extensive experiments on the reductivity of carbonic acid. He obtained formic acid as the sole reduction product of carbonic acid. The supposition of Bach [9] that formaldehyde must also be formed is false. The formation of formaldehyde was never proved. Quite recently Coehn and Jahn[10] have shown that formic acid is the only tangible reduction product. They succeeded in obtaining quantitative current yields, using carefully prepared amalgated zinc electrodes, as already previously employed by Royer, and using a cold saturated potassium-sulphate solution as electrolyte. According to Constam and Hansen,[11] potassium

[1] Lieb. Ann. **69,** 257 (1849), 113/244 (1860).
[2] Ibid. **131,** 79 (1864).
[3] Ibid. **261,** 107 (1891), **274,** 41 (1893).
[4] Amer. Chem. Journ. 15, 523 (1893).
[5] Ibid. 16,569 (1894).
[6] Compt. rend. **70,** 731 (1870).
[7] Joum. 1 prakt. Chem. [2] **34,** 126 (1887).
[8] Monatshefte f. Chem. 16, 211 (1895), 18, 582 (1897).
[9] Compt. rend. 126, 479 (1898).
[10] Ber. d. deutsch. chem. Gesellsch. **S7,** 2836 (1904).
[11] Ztschr. f. Elektrochem. 3, 137 (1896), 3, 445 (1897).

percarbonate is formed when a saturated solution, of potassium carbonate is electrolysed at -10° to -15°, particularly at a high current density, the anions $KC0_3$ uniting *-when* set free:

KO$_X$

O>

$K_2C_20_6$= |

o

\\ *)CO*

*~KO/*

The potassium salt is precipitated as a blue powder. It has not been possible to isolate other salts and free percarbonic acid. The experiments of Salzer,[1] however, indicate that the free acid may' occur perhaps intermediately. He proved the presence of active oxygen in a solution of potassium bicarbonate through which was passed a continuous current of carbonic-acid gas.

1. MOWOBA.SIC ACIDS, $C_nH_2$?i02.

Formic Acid. — This acid and its salts have "been the subjects of thorough electrolytic investigations. These were carried out chiefly by Brester,[2] Renard [3] and Bourgoin,[4] Bartoli and Papasogli,[5] Jahn,[6] etc.

The progress of the decomposition is accompanied by the evolution of carbon dioxide and oxygen at the positive pole and hydrogen at the negative pole. The quantitative relations of the decomposition products vary with the concentration of the solution and the density of the current. The reactions occur according to the following equations -

HCOOH=HCOO-fH,

2HCOO -h$H_20$=2HCOOHH-0,

\+ OH=$H_20$+$C0_2$.

[1] Ztschr. f. Elektrocten. 8, 902 (1902).
[2] Ztsclir. f. Chem. 60 (1866).
[8] Ann. chirn. phys. [5] 17, 289 (1878)
* Ibid. [4] M, 157 (1868).
[6] Gazz. chim. lfc, *22,* 28 (1883).
[9] Wied. Ann. (N, 3?.) 37,408 (1889).

It is therefore theoretically impossible to effect the complete decomposition of the formic acid present. In the electrolysis of sodium formate, carbon dioxide and formic acid are in fact always formed at the positive pole and hydrogen and sodium hydroxide at the negative pole.

A splitting up of the anions HCOO into H and 002 at the anode does not occur, since the oxidizing hydroxyl ions split off the hydrogen as water (Hofer and Moest[x]). The discussion of the other salts is unnecessary since their behavior is quite analogous.

The dependence of the decomposition of formic acid upon the conditions of the experiment has been investigated by Petersen [2] and Salzer.[3]

Petersen found that, if the solution was concentrated, the current strength exercised only a trifling influence on the decomposition phenomena in the electrolysis of sodium formate. According to Salzer's researches, formic acid in sulphuric-acid solution cannot completely suppress the evolution of oxygen at a platinized anode. Sodium formate is for the most part converted into carbonate; in neutral solution small quantities of percarbonate are also formed.

*Formic ester* in sulphuric-acid solution is attacked only with difficulty in the cathode chamber (Tafel and Friedrichs [4]); acetic ester, cyanacetic ester, and phenylacetic ester, it may be remarked here, are not attacked at $11.

## Acetic Acids.

Acetic Acid.—Glacial acetic acid is a poor conductor of electricity. According to Lapschin and Tichanowitsch,[5] its decomposition when effected by 900 Bunsen elements yields at the anode carbon mon- and dioxide, and at the cathode carbon

[1] Lieb. Ann. **323,** 284 (1902).
[2] Ztschr. f. phys. Chem. **33,** 106 (1900).
[3] Ztschr. f. Elektrochemie 8, 893 (1902).
* Ber. d. deutsch. chem. Gesellsch. 37, 3187 (1904).
[5] Neue Peters. Acad. Bull. 4, 81 (1861).

and a small quantity of a gas the nature of which was not established.

Bourgoin,[1] on electrolysing the dilute acid, observed hydrogen. at the negative pole and oxygen, carbon dioxide, and traces of carbon monoxide at the positive pole.

The reactions involved in the decomposition of the *alkali salts* are more interesting. Kolbe,[2] on decomposing a concentrated solution of potassium acetate, obtained a hydrocarbon in addition to other decomposition products. According to the idea then prevailing, acetic acid underwent oxidation in the sense that it was thereby changed into carbon dioxide and methyl, both of which appeared at the positive pole, while at the negative pole only hydrogen was evolved, and a part of the methyl was oxidized to methyl oxide. The hydrocarbon evolved was in fact ethane, which always accompanies the decomposition of potassium-acetate solutions, while the other decomposition products formed vary with the density of the electric current and the temperature of the solutions. Thus Kolbe identified methyl ether and methyl acetate in the solution, while Bourgoin observed no decomposition products other than carbon monoxide and dioxide. Jahn,[3] who employed currents of very low electrode density, obtained by the electrolysis of an almost saturated solution of sodium acetate only carbon dioxide, ethane, and hydrogen. The formation of ethane can be explained by assuming either the direct oxidation of the acetic acid.,

or the decomposition of the anion,

1 Ann. chirn. phys. [4] 14, 157 (1868).
2 Lieb. Ann. 69. 279 (1849).
Crundriss d. Eleteochemie (1895), 292.

Kekul6 [1] advanced a theory based upon the phenomena of decomposition, 'and from this deduced certain formulae which make it possible to predict the nature of the products resulting from the electrolysis of monobasic and dibasic acids of the fatty-acid series. Since, however, the reaction is influenced by the slightest variation of conditions, his formula hold good only in the case of the decomposition of perfectly pure substances, a condition seldom met with in practice.

Lob[2] is in favor of accepting in certain cases the theory advanced by Kekul<§, who sought by experiments to prove the intermediate formation of the anhydride, while Schall[3] assumes the formation of an acid superoxide:

$$2RCOO - \begin{matrix} R-COO \\ R-COO \end{matrix}$$

$$\begin{matrix} R-COO \\ R-COO \end{matrix} = R.R + 2CO_2.$$

This conclusion is drawn from the observed fact that the dithionic acids, on the electrolysis of their alkali salts, actually give acid supersulphides which correspond with the superoxides:

R-CSS—+R-CSS— -R-cm.

R-CSS/'

In contrast to the acid superoxides, the acid supersulphides are stable compounds.

Bourgoin draws the following conclusions from his experiments : He considers the intermediate anhydride formation as the most important process in the electrolysis of organic acids; this brings about the secondary oxidation processes, oxygen being given off. He also considers as secondary reactions. the transition from the acid anhydride to the hydrate with the taking up of water, and the oxidation, of acids by the oxygen clerived from the acid itself. This explanation agrees

^ieb. Ann. 131,70 (1864).
* Ztschr. f. Electrochemie 3, 43 (1896).
[8] Ibid. 3, 83 (1896).

with the fact that water is a weak electrolyte and serves principally as a dissociating medium. The typical processes in the electrolysis of acetic acid are hence the following:
Electrolytic decomposition:

$$2CH_3COOK = {CH_3CO \atop CH_3CO} > O + O + 2K.$$

Characteristic oxidation:

$$\left. {CH_3-CO \atop CH_3-CO} \right> O + O = 2CO_2 + C_2H_6$$

Kolbe and Kampf,[1] on electrolyzing a concentrated potassium-acetate solution, obtained at the anode acetic methyl ester, formic methyl ester, ethane, ethylene, and carbon dioxide; and at the cathode hydrogen and potassium hydroxide. In an alkaline solution of the salt Bourgoiri[2] obtained, amongst other products, sodium formate (by reduction of the carbonic acid); but so far as hydrocarbons were -concerned he could only prove the presence of ethane and ethylene.

Besides the alkali salts, the copper, lead, manganese, and uranium saUs were subjected to electrolysis by Dupre,[3] Wiecle-mann,[4] Despretz,[5] and Smith.[6] The metals were precipitated on the cathode, a portion of the manganese and lead in the form of superoxides.

Elbs,[7] by the electrolysis of lead diacetate in glacial-acetic-acid solution, obtained at the anode crystallized lead tetracetate:

$$2(CH_3COO)_2Pb = Pb + (CH_3COO)_4Pb.$$

Fused potassium acetate, according to the experiments of Lassar-Cohn,[8] yields at the cathode methane, hydrogen, and

[1] Journ. prakt. Chcm. [2] 4, 46 (1871).
[2] Ann. cliim. phys. [4] 14, 157 (1808).
[3] Arch. d. scienc. phys. et. nat (Geneva) 85, 998 (1871).
[4] Poggend. Ann. 104, 162 (1858).
[5] Compt. rend. 45, 449 (1857).
[6] Amer. Chem. Journ. 7, 329 (1885). Electrochemical Analysis (Smith), p. 94.
[7] Ztschr. f. ELefctrochemie 3, 70 (1896).
[8] Lieb. Ann. 251, 358 (1889).

carbon; at the anode carbon dioxide. This result has recently been substantiated by Berl,[1] who also proved by special experiments that this decomposition is the result of the action of the potassium, set free cathodically, on the fused potassium acetate.

Very careful and comprehensive experiments on the electrolysis of the alkali salts of organic acids have very recently been made by Petersen.[2] The latter made exact analyses of the gases occurring at the electrodes and thereby obtained an insight into the quantitative course of the reactions, and determined their nature.

Petersen[3] was enabled to wholly confirm the earlier statements regarding the electrolysis of acetic acid by Murray,[4] who investigated the influence of the concentration, current strength, and temperature upon the course of the electrolysis and found, like earlier investigators, carbonic acid, oxygen, hydrogen, ethane, and methyl acetate. Murray disputes only the occurrence of ethylene which Kolbe and Kampf declare they found.

Petersen, however, clearly proved the presence of the latter in small quantities, and expressed the decomposition of acetic acid by the following equations:

I. $2CH_3COOH - 2CH_8COO$ -f- $H_2$.

II. $2CH_3COO+H_2O-2CH_3COOH+O$.

III. $2CH_3COO-C_2H_6+2CO_2$.

IV. $2CH_3COO-CH_3COOCH_3+CO_2$.

V.

In general, equations I and III predominate; V is always only traceable.

Hofer and Moest [6] report upon the formation of alcohols in the electrolysis of salts of fatty acids.

[1] Ber. d. deutsch. chem. Geaellsch. **37,** 325 (1904).
[2] Ztschr. f. phys. Chem. **33,** 90, 295, 698 (1900).
[3] Ibid. 108 (1900).
[4] Journ. of the Chen. Soc. **61,** 10 (1892).
[6] Lieb. Ann. **323,** 284 (1902). D. R. P. No. 138442 (1901).

They found that copious quantities of methyl alcohol, but no perchloric acid esters, were produced by the electrolysis of a mixture of sodium, acetate and sodium perchlorate. The reaction takes place in the same manner as in the case of some homologues of acetic acid, and it was found that aa addition of alkali sulphate or carbonate acts like the perchlorate.

The general nature of the reaction is that the carboxyl group is replaced by hydroxyl, so that an alcohol is formed having one carbon atom less than the acid ; thus methyl alcohol is obtained from acetic acid :

$$CH_3COO+OH=CH_3OH+C0_2.$$

The hydroxyl ion can be derived from the water, or be formed **in.** the regeneration of the inorganic acid acting as electrolyte:

$$C10_44\text{-}HOH=HC10_4\text{-f-}OH.$$

The formation of methyl alcohol can hence be formulated as follows:

If the electrolysis is carried out between platinum electrodes without diaphragms but with continual stirring, up to 90% of the theoretical. yield of methyl alcohol can be obtained from acetic a,cid and the above-mentioned inorganic salts.

The method can -also be employed in the preparation of formaldehyde, since the methyl alcohol on further oxidation is converted into formaldehyde (see p. 58).

Quite recently FSrster and Piguet [1] have investigated the electrolysis of potassium acetate, using various anodes. In the earlier experiments polished platinum had served as the anode. Indium, gives the same results as platinum; with iron and palladium anodes, however, not a trace of ethane is formed, but essentially aa evolution of oxygen occurs besides the oxidation of the acetic acid to carbon dioxide. At platinized platinum electrodes there occurs, depending upon the current tension, either an evolution of oxygen and oxidation to carbonic acid (no ethane being formed), or ethane is produced, with

[1] Ztschr. f. Elektrocheniie 10, 729 (1904).

very little evolution of oxygen and a very considerable oxidation of the acetic acid to carbon mon- and dioxide,

Forster and Piguet recognize three processes:

1. Evolution of oxygen.
2. Oxidation of the acetic ester formed to carbon dioxide or carbon monoxide.
3. Formation of ethane.

They find that the anode potential determines the effect. The first reaction, which occurs predominatingly at iron and palladium electrodes, requires the lowest potential. With platinized platinum electrodes the potential lies higher; the oxidation action can exceed the evolution of oxygen; and with a particularly high potential, which is obtained by prepolarizing the platinized anode,[1] ethane is produced. With polished platinum and iridium anodes the potential is still higher than with prepolarized platinized platinum anodes. Thus the production of ethane predominates over the oxidation of acetic ester. Regular fluctuations of the anode potential, which often occur in electrolysis, seem to point to the formation of transition resistances by intermediately occurring phases of poor conductivity (acetic acid, acetic anhydride).

The presence of free alkali is always injurious to the production of ethane. The evolution of oxygen at platinized platinum increases with increasing alkalinity and decreases at polished anodes, while the oxidation of acetic ester increases.

Hofer and Moest[2] call attention to the great part which the production of the methyl alcohol demands in the oxidation effects, and which Forster and Piguet have neglected to point out. They formulate the principal processes in the following manner:

1. $CH_3COO' + CH_3COO' + \oplus 2 = C_2H_6 + 2CO_2,$

2. $CH_3COO' + OH' + \oplus 2 = CH_3OH + CO_2,$

3. $CH_3COO' + CH_3COO' + \oplus 2 = CH_3COOCH_3 + CO_2.$

[1] S. Friessner, Zeitschr. f. Elektrochem. 10, 270 (1904).

[2] Ztschr. f. Elektrochem, 10, 833 (1904).

An impartial decision has not yet been given as to whether the ethane production depends upon a direct union of the anions or upon the oxidation of an intermediate product, like acetic acid, acetic anhydride, or acetyl superoxide.

*Monochloracetic Acid*, according to Kolbe,[1] is reduced to acetic acid, hydrochloric acid being split off; at the same time free chlorine is evolved (Bunge [2]).

*Sodium Dichloracetate* yields, besides carbon mon~ and dioxide and oxygen, a very easily decomposable oil containing chlorine, whose natur& has not yet been made clear. (Troeger and Ewers.[3])

4

*Trichlor acetic Acid* was electrolysed by Elbs and Kratz [4] as sodium or zinc trichloracetate. Trichlor acetic trichlormethyl ester was formed:

$$2CCl_3COO = CCl_3COOCCl_3 + 2CO_2.$$

*Potassium Cyanacetate.*—With this Moore [5] obtained at the positive pole carbon dioxide, besides traces of nitrogen and ethylene cyanide; at the negative pole hydrogen and potassium hydroxide, bodies analogous to those obtained in the decomposition of sodium acetate.

*Thioacetic Acid.*—On electrolysis this gives acetyl disulphide at the anode (Bunge [6]):

$$2CH_3COSH = \begin{matrix} CH_3COS \\ | \\ CH_3COS \end{matrix} + H_2.$$

[1] Lieb. Ann. 69, 279 (1849).
[2] Jorn. russ. chem. Gesellsch. 1, 690 (1892); see also Troeger and Ewers, Journ. f. prakt. Chem. 58, 121 (1898).
[3] Journ. f. prakt. Chem. 58, 121 (1898).
[4] Ibid. [2] 55, 502 (1897).
[5] Ber. d. deutsch. chem. Gesellsch. 4, 519 (1871).
[8] Ibid. 3, 297 (1870).

## Propionic Acids.

Propionic Acid. — The electrolysis of a concentrated solution of sodium propionate was carried out by Jahn [1] and, when density of the currents employed was not too great, yielded hydrogen, ethylene, and carbon dioxide, but little butane, the quantity of which further decreased when the electrolyte was diluted. This result Petersen [2] confirmed. The evolution of oxygen increases as the butane yield decreases. The amount of ethylene increases with increased dilution up to a maximum, which is reached at a concentration of the electrolyte corresponding to about 14% potassium propionate. On further dilution it again decreases. Petersen [2] also found that ethyl propionate is always produced, corresponding to the analogous process in the case of acetic acid. He expresses the course of the electrolysis by the following equations:

```
T 9P
1. ^\J2
TT or* XT rv~\r\ i XT r\ or* TT rv~^r\TT i r\
11. ^L^lisvAJU + liovJ = JU2ri5L'UL)JLl -f U.

IV 9P
JL V . -ijvy o
V 2C
]
```

Miller and Hofer'[3] have been successful in introducing iodine into propionic acid by electrolysing an aqueous solution of sodium propionate and potassium iodide.

Ethyl alcohol can be obtained in small quantity from sodium propionate and sodium perchlorate in concentrated solution (Hofer and Moest[4]) in the same manner as methyl alcohol and formaldehyde are formed from acetic acid and perchlorate:

[1] Wied. Ann. (N. F.) 37, 430 (1889); see also Bunge: Chezn. Centralblatt 1, 382 (1890).

[2] Ztschr. f. phys. Chem. **33,** 110 (1900).

[8] Her. d. deutsch. chem. Gesellsch. 28, 2436 (1895).

[4] Lieb. Ann. **323,** 284 (1902).

Acetaldehyde is formed as the oxidation product of the latter.

*Sodium a-Dichlorpropionate* behaves analogously to sodium trichloracetate (Troeger and Ewers*). There is formed, besides carbonic acid and oxygen, the crystalline a-dichlorpropionic a-dichlorethyl ester:

$$2CH_3CCl_2COO = CH_3CCl_2COOCCl_2CH_3 + CO_2.$$

*Sodium fl-iodopropionate,* according to the last-named investigators, yields a little iodoform besides iodine; the gases formed are principally carbonic acid. Carbon monoxide and oxygen occur only in small quantity.

### Butyric Acids.

Butyric Acids.—The two butyric acids -were eiectrolyzed by Bunge.[2] With isobutyrie acid it was not possible to obtain hexane, but the normal acid yielded some butane besides larger quantities of propylene.

Careful and reliable investigations on the electrolysis of the potassium salts of *butyric and isobutyric acids* have been published by M. P. Hamonet.[3] His apparatus consisted of a copper beaker **23** cm. high and 8 cm. in diameter, which served as the cathode. *A* porous earthenware cell, which contained the anode and was closed with a three-hole stopper, stood in the beaker. The perforations in the stopper held a thermometer, a gas-delivery tube, and the electric conductor leading to the anode. The anode used in some experiments ivas a platinum wire 1 mm. in diameter and 2 m. in length; in others a platinum cylinder **14** cm. high and 2.5 cm. in diameter. This variation of current density was, however, of second&ry importance. Solutions of the potassium salts having a specific gravity of 1.08-1.19 were used as the electrolyte. Current strengths of 4-5 amp. were reached with a difference of potential at the poles of 6-9 volts. The electrolysis was continued **2-3** hours,

[1] Journ. f. prakt. Chem. 58,121 (1893).
[2] Journ. f. russ. pliys. Gesellsch. **21,** 525 (1889).
[3] Coinp. rend. 125,252 (1895).

the solution being kept cool. The following results were obtained :

*Potassium Butyrate,*

$$CH_3\text{-}CH_2.CH_2.COOK,$$

yielded 225 g. propylene bromide ($CH_3$-CHBr-$CH_2$Br), corresponding to 47 g. propylene ($CH_2$~CH==$CH_2$); 18 gr. isopropyl alcohol (CHa-CHOH-CHs); 4.5 g. butyric isopropyl ester (CH,v$CH_2$-CIl2-COOCH($CH_3$)2); and 4.5 g. complicated products, which became resinous when the ester was saponified by boiling with alkali hydroxide. Hexane (CH3-CH2-$CH_2$-$CH_2$ •$CH_2$-$CH_3$), and propyl alcohol ($CH_8$-$CH_2$-$CH_2$OH) could not be detected. They could, therefore, have been formed only in trifling quantity.

The very remarkable formation of isopropyl alcohol can only be explained by assuming the hydration of propylene or the molecular rearrangement of the group CHsCH^CHs -.

*Potassium Isobutyrate,*

$$(CH_8)_2{:}CH.COOK$$

This salt gave 300 g. propylene bromide ($CH_3$ • CHBr - $CH_2$Br) equivalent to 62. g propylene ($CH_3$-CH:$CH_2$); 26 g. isopropyl alcohol, $(CH3)_2$:CH-OH; over 12 g. isobutyric isopropyl ester, $(CH_3)_2$:CH.COO-CH:$(CH_3)_2$; and 6 g. of an oil having a pepper-like odor and boiling at 130°~150°.

In this case also the paraffin isohexane (CHa) 2: CH - CH: $(CH_3)_2$ was not formed.

Hamonet draws the following conclusions from these results:

1. The equation

$$2C_nH_{2n+}l \cdot COO - C_2nH_4n_+2 + 2C0_2,$$

representing the reaction in the electrolysis of the alkali salts of the fatty acids, which since the experiments of Kolbe has been almost universally accepted, can no longer claim to represent the truth in the case, since no or almost no paraffins result from this operation.

2. The olefine $C_nH_{2?t}$ sometimes predominates among the products formed by the electrolysis of the alkali salts of the fatty acids;

**CnHsn+lCOOK**

The general nature of the reactions is represented by the following equation:

3. An alcohol with *n* carbon atoms is always formed if the acid contains (n-f-1) carbon atoms. The structure of the alcohol is not always that which is expected. Frequently more than a third of the energy of the current is expended in the formation of the alcohol. Whether the alcohol is generated by the saponification of the ester present, according to the equation

$$2C_nH_{2n+}i - COO = C_nH_{2n+1} - COOCnIWi + C0$$

or whether it is formed by the hydration of the defines,, $C_nH_{2u}+H_2O = C_wH_{2w+}iOH$, is still uncertain. (Compare the explanation of Hofer and Moest, p. 84.)

A more thorough investigation of the substances resulting from the electrolysis of compounds possessing higher molecular weights is yet wanting.

Petersen [l] was able to obtain n-hexane and propyl butyrate in small quantity from butyric acid; from isobutyric acid he got diisopropyl (isohexane) in addition to the products observed by Hamonet.

If butyric acid is electrolysed with perchlorate, according to the procedure of Hofer and Moest$_7$[2] hexane is the preponderating product; there are also obtained propyl alcohol and its oxidation product, propionic aldehyde:

$$CHaCHflCHaCOO + OH - CH_3CH_2CH_2OH + C0_2.$$

i Bull. d. 1'Acad. roy. deDanemark (1897) 397; Ztschr/f phys. Chem. 3& 115 (1900).

Isobutyric acid yields, accordingly, isopropyl alcohol and :acetone.

*Trichlorbutyric Acid.*—According to Troeger and Ewers,[1] a tetrachlorhexyleneglycol is formed at the anode from sodium #a/?-trichlorbutyrate. The authors assume the following equations from this process:

i. 2CH3 • CHOI-ca2 coo =

CH3 • CHC1 • CC12 ™ CC12 - CHOI - CH8 + 2CO,;

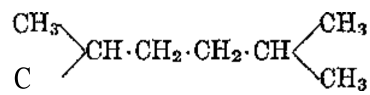
II. CH.3 • CHOI - CC12 ™ CC1* • OHC1 • CH» + 2H,0

. = CHsCHOH - CC12 - CC12 • CHOI! - CH* + 2HCI.

i Accordingly, a hexachlorhcxane would be first formed in •a normal manner, C02 being split off; secondarily, the two very mobile /^-chlorine atoms would be torn away by water, hydrochloric acid and tetrachlorhexyleneglycol resulting.

## Valeric Acids.

Valeric Acids.—Kolbe[2] electrolyzed the potassium salt of *isovaleric add* in concentrated aqueous solution and obtained *&8* chief product octane (dissobutane):



Besides this there appeared as decomposition products hydrogen, carbonic acid, butylene, and the butyl ester of valeric acid.

Brester,[3] who performed his experiments under different conditions, obtained at the anode a gaseous mixture of carbon dioxide, butylene, and oxygen.

Petersen [4] subjected the behavior of both acids to a thorough investigation. He established the formation of normal octane .and butyl valerate in the decomposition of *n-valeric acid;* among

[1] Journ. f. prakt. Chem. 59, 404 (1899).
[2] Lieb. Ann. 69, 257 (1849).
[8] Jahresb. f. Chern. 86 (1859), 757 (1866),
[4] Ztsehr. f. phys. Chem. **33**V 295' (1900).

the evolved gases butylene and also hydrogen and oxygen were found. A small quantity of butyl alcohol, which was further oxidized to butyric aldehyde, was also formed by the saponification of butyl valerate.

The oil which is formed in the electrolysis of potassium isovalerate is composed of diisobutyl and triniethylniethyl isovalerate, besides a small quantity of isobutyl isovalerate and isobutyrie aldehyde. By saponification of the ester, trimethylcarbinol accompanied by a trifling quantity of isobutyl alcohol is found in the solution.

/5-butylene and isobutylene could be detected in the evolved gases.

Petersen adduces the following equations of reactions as the predominating ones:

I. $2(CH_3)_2$:CH.CH2-OOOH-2(CH3)2:CB:.$CH_3$.COO+$H_2$;.

II. $2(CH_3)$2:CH.$CH_2$.COO-+$H_2$0

=$2(CH_3)_2$:CH.$CE_2$-COOH+O;

III. $2(CH_3)$2:CH'$CH_2$-COO

IV. $2(CH_3)$2:CH-$CH_2$-COO

V. $2(CH_3)_2$:CH.$CH_2$-C0040

To the above may be added the following equations of minor importance:

VI. $(CH_3)_2$:CH.$CH_2$-COO-C.$(CH_3)$34-$H_2$0 -

VII.

= $(CH_8)$ 2 :CH-$CH_2$COOH + $(CH_3)_2$ :CH «$CH_2$OH;

VIII. $(CH_3)_2$:CH.$CH_2$OH-hO=$(CH_3)_2$:CH.COH-f$H_2$0.

Even this complicated scheme cannot claim to be complete. Probably some entirely different reactions which have thus far not been elucidated, occur also. Considerable differences between the yields theoretically expected aad those actually obtained point to such, a supposition.

Trimethylacetic Acid *(Pivalic acid)* — the third of the valeric acids — has also been investigated by Petersen. It yields trimethylcarbinol and probably hexamethylethane, besides an isomeric body, and also two isomeric butylenes, isobutylene predominating with perhaps also /3-butylene. Aldehyde is not formed ; neither is an ester formed.

The principal processes taking place are the following:

I. $2C(CH_3)3COOH = 2C(CH_3)_3COO + H_2$;
II. $2C(CH_3)3COO + H_20 - 2C(CH_3)_3COOH + 0$;
III. $2C(CH_3)_3COO - C(CH_3)_3 - C(CH_3)_3 - l - 2C0_2$;
IV.

The trimethylcarbinol, a secondary product, is probably formed [1] by the addition of water to the isobutylene.

The electrolysis of these three isomeric acids affords thus •considerable qualitative differences in the results. Summing up the whole matter, it can be said that the electrolysis of a valeric acid gives octane, butyl valerate, butylene, butyl alcohol, and butyric aldehyde.

1. The normal valeric acid yields normal compounds exclusively.

2. Isovaleric acid gives diisobutane, triniothylmothyl isovalerate, and trimethylcarbinol, also a little isobutyl isovalerate, isobutyl alcohol, and isobutyric aldehyde, and, finally, two isomeric butylenes, isobutylene and /9-butylenc.

The products resulting from the electrolysis of trimethylacetic acid have been summarised above.

The fourth isomeric valeric acid (active), *ethylmethylacetia acid,* has not yet been investigated.

n-Caproic Acid. — A concentrated solution of the potassium salt gave decane, and traces of the amyl ester of caproic acid, both of which are normal ' decomposition products. The electrolyses were made by Brazier and Gossleth,[2] and by Wurtz.[3]

[1] Ztschr. f. phys. Chemie **33,** 710 (1900),
[2] Licb. Ann. 75, **265** (1850).
[3] Ann. chim. phys. [3] **44,** 291 (1855).

The electrolytic relations in the decomposition of caproic acid were investigated by Rohland,[1] who electrolyzed the alkali .salt. He obtained normal decane, CioH22.

Petersen [2] investigated the electrolysis of potassium caproate on a larger scale. The oil which separated during the passage of the current consisted of normal decane, a little amyl caproate and arnyl alcohol, a trifling quantity of amylene^ and an aldehyde, probably $CH_3(CH_2)_3COH$. The greater quantity of the amylenes formed during the electrolysis was found in the gaseous mixture; isopropylethylene, (CEsJsCHCHrCH^ was probably present with the normal .amylene, $CH_3CH_2CH_2CH:CH_2$.

n-Heptylic Acid, *Oenanthylic Acid.*—The normal acid was electrolyzed by Erazier and Gossleth,[3] under conditions similar to those for caproic acid, and gave *two* hydrocarbons^ Ci2H26 and Ci2H24, in addition to hydrogen, potassium carbonate, and acid potassium carbonate.

On electrolysing a concentrated solution of potassium n-heptylate, Eohland[4] obtained, besides dodecane, C^B^e, a small quantity of a mixture of unsaturated hydrocarbons of the series *CJtisn* boiling at 145°.

n-Caprylic Acid.—Rohland[5] electrolyzed a concentrated potassium-salt solution of this acid and obtained the hydrocarbon tetradecane, CuHso-

Pelargonic Acid, under similar conditions, gives the hydrocarhcn dioctyl.

The formation of defines, in the electrolysis of aliphatic monocarboxylic aeids, depends, perhaps, not apon an oxidation process,

[1] 2feselir. f. Elektrochemie 4, 120 (1S&7).
[2] 2fcschr. f. ph^s. Ch&n. 53, 317 (1900).
[3] lieb. Ana. 75, 265 (1850).
[4] Ztschr. f. Elektrochemie 4,120 (18^7).
•1, c.

but upon a mutual reaction of the anions, analogously to that which causes the formation of saturated hydrocarbons:

II. 2CJWlCOO -CnH2n

The occurrence of secondary or tertiary alcohols depends presumably upon the addition of water to the olefines :

According to Petersen,[1] the equations expressing the general decomposition of aliphatic acids are the following:

I. 2C3nH$_{2n+}$iCOOH-20^^+1000+H$_2$;
IL 2CnH$_{2n+}$iCOO+H$_2$0=2CnH$_{2n+1}$COOH-hO;
III. 2CnH$_{2n+1}$COO-C$_{2n}$H$_4$n$_+$2+2C0$_2$;
IV. 2C»H2n$_+$iCOO -CnH$_2$»$_+$iCOOCnH$_2$n$_+$i +C0$_2$;
V. 2CnH$_{2n+}$iCOO-CnH$_{2n+}$iCOOH+CnH$_2$n+C0$_2$;
**VI. C$_n$H$_{2n}$ + H$_2$0 -CnH$_{2n+}$iOH;** ) Secondary
**VII.** CnH$_{2n}$+CnH$_{2n+}$iCOOH=CnH2n^lCOOCnH$_{2n+1}$. f tertiary.

Of the unsaturated monocarboxylic acids, *undecylenic acid* and *olelc acid* have been investigated by Rohland.[2] Both yielded, on electrolyzing their potassium salts in aqueous solution, a mixture of unsaturated hydrocarbons, the nature of which was not determined.

Electrolysis of Mixtures.—Wurtz [3] was the first to conceive the extremely fruitful idea in electrosynthesis of making syntheses of substances with mixed radicals by electrolyzing two components. After discovering Ms hydrocarbon synthesis, which depends upon the action of sodium upon alkyl iodides, and the use of the method in the preparation of "mixed radicals " from two different alkyl iodides, he also tried to obtain

[1] Ztschr. f. phys. Chem. SS, 720 (1900).
[2] l.c.
[8] Arm. chim. phys. [3] 44, 275 (1855); Jahresb. f. Chem. 1855, 575.

mixed hydrocarbons by electrolyzing the salts of fatty acids, using Kolbe's hydrocarbon synthesis:

$$RiCOO+R_2COO = RiR_2+2C0_2.$$

The successful results of these experiments prompted various investigators to select, as the materials for the starting-point of their electrolysis, mixtures of substances whose electrolytic intermediate products could mutually react, v. Miller and Hofer made use of these forms of reactions in the fatty-acid series for accomplishing the syntheses of acids. Lob in a similar manner prepared mixed azo-compouncls in the aromatic series. The following are the experiments made by Wurtz:

*Potassium acetate* and *potassium cenanihylate* yield trifling quantities of heptane (methylcaproyl, Wurtz):

$$CH_3COO\ 4\text{-}\ COO - (CH_2)\ 5 \bullet CH_3 = CH_3 - (CH_2)_5 - CH_3\ 4\text{-}2C0_2.$$

*Potassium valerate* and *potassium cenanthylate* give the expected mixed hydrocarbon, a decane, as chief product (butylcaproyl, Wurtz):

$$(GH_8)\ 2{:}\ CH \bullet CH_2 \bullet COO + COO - (CH_a)\ 5 \bullet CH_3$$

There are formed also a little octane, dodecane, and unsaturated hydrocarbons.

In the following discussion the description of the electrolysis of mixtures is given under the heading of the highest hydrocarbon component, since the reaction in electrolysis depends upon the nature of the components of the mixtures; thus the behavior of each separate component will then have been previously described.

## II. Monobasic Alcohol- and Ketonic Acids.

### *a. Alcohol- (Hydroxy-) Acids.*

While the acid anions of the unsubstituted aliphatic monocarboxylic acids react preponderatingly by splitting off carbonic acid, without further oxidation of the radical united to the carboxyl group, the anion of the hydroxy-acids is regularly oxidized further. The extent of the oxidizing action depends, among other circumstances, to a great extent upon the concentration. For example, glycollic acid in concentrated solutions is oxidized almost completely to formaldehyde, and to a less extent to formic acid and carbonic acid. By increasing the dilution carbon monoxide occurs in place of formaldehyde.[1]

TT ^TT r\tJfr^/~\r~\ i 0/™\TT r*r\ \ r^r\ i 0TT f~\
11. UH2OHUUU + oOli =LU + oU2"roll2U.

The substitution of methyl for hydroxyl does not affect the easy oxidability. It is evident from the theoretical explanations given in the first chapter that the changes in concentration are of importance for the course of the reaction only in so far as they influence the anode potential. By artificially keeping the latter constant, the products must remain the same, being independent of the conditions of concentration. In general, the following rules can be adduced for the electrolysis of oxy-acids (chiefly worked out by Miller and Hofer,[2] and Hamonet[3]):

a-Oxy-acids are converted by electrolysis in concentrated solution into aldehydes or ketones. If the solution is more highly diluted, the compound is oxidized to carbon monoxide.

/9-Oxy-acids behave more like acetic acid; they are, at least partially, converted into glycols, or their others:

I. $2OH.C_nH_mCOO-OH.C_wH«.C_nH_w.OH+2CO_2$;
II. $2RO-CJU3OO-RO-C_WH_W \cdot G_nBU-OR+2CO_2$.

In the case of dioxy-acids the oxidation affects both hydroxyl groups, the intermediate CHOH-groups being oxidized to carbon mon- or dioxide.

[1] Ber. d. deutsch. chern. Gesellsch. 27, 461 (1894).
[2] Ibid.
[8] Compt. rend. 132, 259 (1901).

The experiments of Miller and Hofer were made by passing the electrolyte in a slow stream through the cell (Apparatus, Fig. 4, p. 44). This made it possible to find decomposition products which would otherwise have been changed by further electrolysis; a more complete expression of the course of the decomposition was thus obtained. It is to be regretted that the researches do not mention the necessary data regarding the electrical conditions.

Glycollic Acid. — If a solution of 30 g. sodium glycollate in 38 cc. water is electrolysed with a current strength of 1 amp., there are formed chiefly carbonic acid and formaldehyde, besides a little carbon monoxide, formic acid, and oxygen (Miller and Hofer[1]). Walker[2] obtained aldehyde in the electrolysis of the sodium salt of *ethyl glycollic ether.*

Methoxylglycollic Acid. — The electrolysis of its sodium salt was made by the same authors[3] and yielded formaldehyde, methylal, formic acid, and carbonic acid; in dilute solution also carbon monoxide and a little methyl alcohol.

A mixture of potassium glycollate and potassium acetate unites at the positive pole to form ethyl alcohol (Miller and Hofer[4]); some acetaldehyde is also formed by further oxidation:

$$CH_2(OH)COO + CH_3COO = CH_3CH_2(OH) + 2CO_2.$$

### Oxypropionic Acids.

Ordinary Lactic Acid. — As Kolbe[5] had already discovered, the concentrated solution of the potassium salt gave carbon dioxide and acetic aldehyde. The investigators above mentioned also observed the presence of some formic acid. When the solution surrounding the positive pole was kept slightly

[1] Ber. d. deutsch. chem. Gesellsch. 27, 467 (1894).
[2] Journ. Chem. Soc. 65, 1278 (1896).
[3] Ber. d. deutsch. chem. Gesellsch. 27, 469 (1894).
[4] Ibid. 28, 2437 (1895).
[5] Lieb. Ann. 113, 214 (1860).

alkaline, aldol and crotonic aldehyde were formed instead of acetic aldehyde.

Sarcolactic Acid.— When the solution surrounding the positive pole was kept neutral, a concentrated solution of the sodium salt yielded acetic aldehyde and carbon dioxide.

Hydracrylic Acid (Ethylenelactic Acid = /?-oxypropionic Acid) . — Resin and a little formic acid were found present in the electrolyte surrounding the positive pole.

The potassium salt of the alcoholic amyl ether of this acid, the /?~amyloxypropionic acid, was electrolysed by Hamonet.[1] It gave about 50 per cent of the theoretical yield of 1.4-butandioldiamyl ether (diamyl ether of butylene glycol) .

$$2C_5HnO\text{-}CH_2\text{-}CH_2COO$$

Glyceric Acid (Dioxypropionic Acid). — This acid decomposes into carbon mon- and dioxide, formaldehyde, and formic acid (Miller and Hofer).

### Oxy butyric Acids.

a-Oxybutyric Acid ($CH_8$-C3H2-CHOH-COOH).— This substance was converted into carbon dioxide, propionic aldehyde, and some formic acid (Miller and Hofer) .

a-Oxyisobutyric Acid (($CH_3$)2:CHOH-COOH).— This compound, investigated in the same manner, was found to be partially oxidized at the anode to acetone. Much carbonic acid and a little carbon monoxide is also evolved.

. ^-Oxybutyric Acid ($CH_3$-CH(OH)-$CH_2$.COOH).— From this acid were obtained in the positive electrolyte crotonic aldehyde • and a little formic acid, also resinous substances. Considerable quantities of carbonic acid, also a little carbon monoxide and unsaturatecl hydrocarbons, are formed. The small quantities of saturated hydrocarbons are derived probably from impurities in the acid (presence of acetic acid) . " ^ r~ "^ t " ,p> *>

r-0xybtityric Acid ($CH_2OH - CH_2 \cdot CH_2 \cdot COOH$) .— I&monet * electrolyzed the alkali salt of ^-isoamyloxybutyric acid in order to obtain symmetrical hexylene glycol, or its diamyl ether. The desired reaction did not take place :

$$2C_5Ci iOCH_2 - CH_2 - CH_2 \cdot COO$$

$$=C_5Hn - OCE_2 -$$

/9-Methylglyceric Acid (a-/?-Dioxybutyric Acid (M. Pt. 74-75°)=$CH_3$-CHOH.CHOH.COOH).—When the potassium salt of this acid is electrolyzed (Pissarshewski[2]) it breaks up into carbon mon- and dioxide, formaldehyde, formic acid, acetaldehyde, acetic acid, and another substance having the property of reducing Fehling's 'solution. This latter compound was not isolated.

/?-Methylglycidic Acid, 0<; /CH-COOH | XJH-CHs behaves similarly.

## 6. *Ketonic Acids.*

Pyroracemic and Isevulinic acid, i.e., an *a*- and a f-ketonic acid are the only monobasic ketonic acids which have been electrolyzed. The electrolysis of a representative of a /?-ketonic acid, acetoacetic acid, could not be carried out, on account of the instability of the free acid and its salts. The reactions take place partly in a manner similar to those occurring in the decomposition of acetic acid; the anions unite to form a diketone, carbonic acid being split off; and partly in a further oxidation to acetic acid, with the occurrence of carbon mon- and dioxides.

[1] Compt. rend. 136, 96 (1903).
[2] Ztschr. d. russ. chem. phys. Gesellsch. **29,** 289, 338 (1897).

Pyroracemic Acid. — Potassium pyroracemate gives (Hofer)-* chiefly acetic acid and also a little diacetyl:

$$=CH_3COOH+CO_2;$$

$$\text{II. } 2CH_3\text{-}CO\text{-}COO = CH_3 \cdot CO \cdot CO\text{-}CH_3 + 2CO_2,$$

Rockwell 2 found at %he anode some acetaldehyde, and at the cathode the normal reduction product of pyroracemie acid, i.e. a-lactic acid:

$$CH_8\text{-}CO.COOH+H2\text{-}CH_3\text{-}CHOH\text{-}COOH;$$

also some propionic acid, probably formed by further reduction. Lsevulinic Acid. — This acid is much better adapted for the synthesis of the corresponding diketone -than, is pyroracemie acid. Hofer,[3] on electrolyzing the potassium salt of the acid* obtained about 50% of the theoretically expected quantity of 2.7-octandion:

$$2CH_3\text{-}CO\text{-}CH2\text{-}OH_2\text{-}COO$$

Considerable quantities of acetic acid are also formed, and some carbon monoxide is produced by the oxidation of the methylene groups.

Acetoacetic Acid. — If the sodium compound of acetoacetie ester (Weems[4]) in alcoholic solution is electrolyzed, there is formed diacetylsuccinic ester:

$$2\begin{matrix}COCH_8\\|\\CHNa\\|\\COOC_2H_6\end{matrix} = 2\begin{matrix}COCH_3\\|\\CH\\|\\COOC_2H_6\end{matrix} + 2\,Na$$

$$2\begin{matrix}COCH_3\\|\\CH\\|\\COOC_2H_5\end{matrix} = \begin{matrix}C2H_5OOC\text{-}CH.CH.COOC_2H5\\H_3CCO\ \ COCH_8.\end{matrix}$$

» Ber. d. deutsch. chem. Gesellsch. 33, 650 (1900).

* Journ. Amer. Chem. Soc, 24, 719 (1902).

[s]l. c.

Amer. Chem. Journ. 16, 569 (1894).

Pyroracemic Acid. — Potassium pyroracemate gives (Hofer) - chiefly acetic acid and also a little diacetyl:

$$II.\ 2CH_3 - CO - COO = CH_3 \cdot CO * CO \cdot CH_3 + 2CO_2,$$

Rockwell [2] found at %he anode some acetaldehyde, and at the cathode the normal reduction product of pyroraceirie acid, i.e. a-lactic acid:

$$CH_3.CO\text{-}COOH4\text{-}H_2=CH_3\text{-}CHOH.COOH;$$

also some propionic acid, probably formed by further reduction.

Laevulinic Acid. — This acicl is much better adapted for the synthesis of the corresponding diketone -than is pyroracemic acid. Hofer,[3] on electrolyzing the potassium salt of the acid* obtained about 50% of the theoretically expected quantity of 2,7-octandion:

$$2CH_8\text{-}CO\text{-}CH_2\text{-}CH2\text{-}COO$$

Considerable quantities of acetic acid are also formed, and some carbon monoxide is produced by the oxidation of the rnethylene groups.

Acetoacetic Acid.—If the sodium compound of acetoacetic ester (Weems[4]) in alcoholic solution is electrolyzed, there is formed diacetylsuccinic ester:

" $COCH_3$ $COCH_3$

2/~ITT"\T-. <T)/"'ITJ" I O "\Tr»
OJuLisa ~ £ UJti ~r^ IN a

$COOC_2H_5$ $COOC_2H_5$

$$\begin{array}{ll} COCH_3 & \\ 2CH & = C_2H_5OOC\text{-}CH\text{-}CH\text{-}COOC_2H_5 \\ COOC_2H_S & \quad H_3CCO\ COCH_3. \end{array}$$

[1] Ber. d. deutsch. chem. Gesellsch. **33,** 650 (1900).
[2] Joura. Amer. Chem. Soc. **24,** 719 (1902).
»1. c.
Amer. Chem. Joum. 16, 569 (1894).

According to Tafel and Friedrichs,[1] acetoacetic ester can be easily reduced in sulphuric-acid solution. This reduction evidently extends to the carbox-ethyl group because a molecule of the ester requires almost six atoms of hydrogen.

*Acetylmalonic Add,* $CH_3$-00-CH:(OOOH)2, and *Acetone-dicarboxylic Acid,* CO: $(CH_2COOH)_2$, do not permit their anions to unite (Weems[2]).

In connection with his investigation of ketonic acids, Hofer [3] has used the electrosynthetic reaction, previously discovered with Miller/ which consists in electrolyzing potassium salts of organic acids in mixture with potassium acetate and other lower fatty acids. The general nature of the reaction is that the two anions unite, as in Kolbe?s synthesis, carbonic acid being split off, e.g.,

$$R-CO-COO + Ri-COO-R-CO-Ri+2CO_2.$$

*Potassium Pyroracemate* and *Potassium Acetate* thus yield acetone as the chief product:

$$CH_3OOCOO+CH_3COO -CH_8COCH_3+2C02.$$

Some acetic methyl ester and traces of diacetyl are also formed.

*Potassium Pyroracemate* and *Potassium Butyrate* unite to form methylpropylketorxe:

$$CH_3-CO-COO+CH_3-CH_2.CH_2-COO = CH_3-CO-CH_2.CH_2.CH_3+2CO_2.$$

Some diacetyl is also formed in this case, with trifling quantities of esters of butyric acid, and larger quantities of hydrocarbons, chiefly hexane and decane. The hexane was formed from the butyric acid, the decane from caproic acid, an impurity in the butyric acid.

[1] Ber. d deutsch. chem. Gesellsch, **37,** 3188 (1904).
»l. c.
[3] Her. d. deutsch. chem. Gesellsch. **S3,** 650 (1900).
[4] Ibid. 28, 2427 (1895).

*Potassium*
gously, methy

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*Potassium*
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$CH_3 - CO \cdot CH$

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ester groups, according to an experiment of Guthrie,[1] are electrolytically inactive; the mono-esters of dibasic acids behave like monobasic acids, i.e. carbon dioxide is split off and di-esters of higher dibasic acids are formed, saponification converting the esters into the free dibasic acids:

$$2ROOC(CH_2)_xCOO = ROOC(CH_2)_x - (CH_2)_xCOOR + 2CO_2.$$

Thus the diethyl ester of succinic acid is formed from ethyl potassium malonate:

$$2C_2H_5OOCCH_2COO - C_2H_5OOCCH_2CH_2COOC_2H_5 + 2CO_2.$$

Von Miller and Hofer[2] broadened the possibility of the electro-syntheses of dibasic acids by borrowing an idea of Wurtz and using the results of Brown and Walker. Wurtz,[3] as already mentioned, had electrolysed mixtures of two fatty-acid salts* and accomplished the union of the different radicals to form the corresponding hydrocarbons. In the same manner, von Miller and Hofer electrolyzecl mixtures of fatty-acid salts and mono-esters of dicarboxylic acids. Hereby the esters of mono-carboxylic acids containing a higher number of carbon atoms are formed. **If,** for instance, a mixture of potassium acetate and potassium ethyl succinate is subjected to electrolysis, butyric ethyl ester is formed, according to the following equation:

$$CH_3COO + COOCH_2CH_2COOC_2H_5 = CH_3CH_2CH_2COOC_2H_5 + 2CO_2.$$

If the two carboxyl groups of dibasic acids are esterifiecl, such a di ester can behave as an acid only when methylene groups possessing a decidedly acid character are present. Mulliken[4] and Weems[5] investigated such compounds. The sodium

[1] Lieb. Ann. 99, 65, 1856.
[2] Ber. d. deutsch. chem. Gesellsch.' 28, 2427 (1895).
[3] Jaheresber. d. Chem, 575 (1855).
[4] Amer. Chem. Joum. 15, 323 (1893).
[5] Ibid 16/569 (1894).

compounds of diethyl esters of dibasic acids in particular frequently behave in a manner analogous to that of the carboxylic acids, the anions uniting. The same compounds are thus obtained as are formed by the elimination of sodium by iodine. Thus sodium diethylmalonic ester gives ethanetetracarboxylie ester;

$COOC_2H_5$   $COOC_2H5$

oJ w

2CHNa = 2CH~ + 2Na

it

$300_2H_5$   $COOC_2H_5$

$COOC_2H_5$   $COOC_3H_5$   $COOC_2H_5$ S

·J \- 2 CH» = CH ----------------------------CH

A $I_5$   $COOC_2H_5$   $COOCaHs$.

If the methylene groups of dicarboxylic acids contain electrolytically sensitive radicals, the reaction picture is shifted, as will be touched upon in the special cases.

Oxalic Acid.—The deportment of the saturated solution of the free acid on electrolysis was determined by Brester,[1] Bourgoin,[2] Balbiano and Alessi,[3] Bunge,[4] and Renarcl.[5] The general result was that oxygen and carbon dioxide were obtained at the anode and hydrogen at the cathode. It is possible to completely oxidize oxalic acid to carbon dioxide. On this property depends the great importance of oxalic acid in quantitative electrolytic analysis, into which it has been introduced by Classen.[6]

The ability of ammonium oxalate to form soluble double salts with many difficultly soluble or insoluble metallic salts is in accord with the favorable conduct of the acid on eleetroly-

[1] Jahresb. f. Chem. 87 (1866).
[2] Compt. rend. 67, 97 (1868).
[8] Gazz. chim. **12,** 190 (1882); Ber. d. deutsch. chem. Gesellsch. 15, 2236 (1882).
[4] Ber. d. deutsch. chem. Gesellsch. 9, 78 (1876),
[5] Ann. chim. phys. [5] **17,** 289 (1878).
[8] Classen, Quan. Analysis by Electrolysis (Wiley & Sons, N. Y.).

pis, by whk'b operation it may bo entirely removed from the solution in the form of gas.

The redwing effects off the current on oxalie acid were also observed. Tims on electrolysing both the free acid and its sodium salt Balbluno arid Alessi were able to prove the presence of Klyrollir acid. Tafel and Friedrichs [1] obtained a good yield of giyo.xylir arid hy reducing oxalic acid in sulphuric-acid solution at lead or mercury cathodes. Oxalic ester and oxal-acetic ester are easily reduced also.

The oxidation is not complete if the electrolysis is conducted in th*' cold solution, carbon monoxide as well as carbon dioxide being then formed at lite positive polo.

The decomposition reactions of oxalates are entirely analogous to those of I he free arid. In alkaline solution the oxidation proceeds more rapidly than in neutral solution because of the letter {•oMilwtivity of the alkalies.

Xatiintlk* ethyl potassium oxalate cannot react in accordance with the scheme of the Brown and Walker's syntheKI*H. When it was electrolysed both investigators[2] observed tin* pre.sewe of ethytene. This unsaturated hydrocarbon was very likely derived from the. enter group.

h'tenson[3] iuu* fonimlated the following equations of decomposition:

L

!L

III. $f(!C)0)_2$-$2C()_2$;

IV.

tbfii on the* c»loctroly«is of oxalic acid must be sup-
t by tlio«» regarding itB rtuluction to glycollic acid,
«c*ici, and th« reduction to formic acid (Royer[4]),

[1] l.lrtr, d. dmiUeh. chcm. Ckswollacli. 37, 3180 (1004).

[2] *Lwh. Aim.* 274, 70 (1893).

[3] Zuwhr. f. ptiys. Chem. S^l, 098 (1000).

[4] Compt. rentl §9,1374 (1869), 70,731 (1870).

which is brought about when using oxalic acid in place of nitric acid in a Grove coll.

A scries of n%seur<:hus. concerning the relation between the oxidation of oxalic acid and the electrical conditions have been made. Oettel[1] discovered that the current consumption required for an oxidation proems is greater when a smaller current density is used than when a higher density is employed. Ackerberg[2] determined that the* oxidation, which is trifling at a polished platinum anode, is quantitative under the same conditions at a platinized anode. Salzer[3] investigated the electrolysis of oxalic, acid, as to the tension conditions and oxidation action, in sulphuric-acid and in aqueous solutions at polished (bright) and platinized anodes.

Malonic Acid, -Thin acid waft investigated by Bourgoin.[4] In a concentrated solution of slrupy consistency it, like oxalic acid, is only slowly oxidized to carbon dioxide, with evolution of oxygon. A strongly concentrated solution of the unaltered acid is found surrounding the positive electrode, even after an electrolysis of long duration. On electrolysis of the sodium salt carbon monoxide[1] is also present in the gaseous mixture evolved. The proportions of the various gases, carbon rnon- and dioxide, and oxygen, remain fairly constant during the period of electrolysis (85.8%, 9.7%, 4.5%).

In alkaline solution the decomposition products are the same as in neutral solution, only the proportions of the individual gases being different, and varying according to the duration of the electrolysis.

Miller,[6] on electrolyzing znalonates, was able to detect a trifling quantity of ethylene.

Petersen [6] verified this fact- He formulated the following reactions:

1 Ztqchr. f. Elektrochemie 1, 90 (IHOI),
2 Ztachr. 1 anorg. Chen, **SI,** Id! (1002).
8 Ztschr. f. Elektrochemie 8, 807 (1002).
* Ann. ohim. phys. [1] 14,157 (1857); Bull d. i. soc. cMm. S3, 417 (1889).
5 Joum. 1 prakt. Chemie **127,** 328 (1870).
« Ztschr. f. phys, Cheraio **33,** 7CM) (1000).

II. CI $I_a$
III. 2(JII
IV. CIl2

in which, hovrovor, III is inconsiderable.

The Brown- Walkor [1] method has been found to be of ex- <-«-»llont scrvico in the electrolysis of the potassium salts of the mono-esters of makmie acid. The formation of the cliethyl cst.or of sweinic acid from ethyl potassium malonate has already IK»OII mentioned (p. 103).

If the* othyl potassium salts of substituted acids are chosen as the starting-point ., it is possible to obtain (lisubstituted acids, according to the above reactions.

^

1. *Ethyl potassium methylmalonate* yields the two symmetrical (limethylsuccinic acids having the melting-points 193° and 121°. , '|

2. *Ethyl potmwium ethylmalonate* yields the corresponding *symmetrical didkylxumnic* ocwis, with the melting-points 192° and 130°.

3. *Ethyl pota«wium dimethylmalonate* affords *tetramethyl-tsuecinic acid.*

4. From *ethyl potassium (Hethylmalonate* a substance having the conipoKitioti Ci-iHgeO^ and which differs from the expected tetniothyl-HUCciaic acid by (^H^ was obtained. The nature of this body has not yet teen determined.

Hyclrobromic acid splits off alcohol, the com which has perhaps the furfurarie formula

**O:O O:O**

**being** formed.

All **thofics** reactions do not take place smoothly, but are accompanied by secondary reactions, principally oxidations,

***n.* c.**

nr,



which are limited as much as possible by working with strong concentrated solutions and low temperatures. Moreover, the formation of esters also is always possible according to the equation

$$2\,CH_3.C()() - cn»c()()CH_3 + cc>_2;$$

and, finally, the formation of imsut united esters may take place analogously to the formation of othylcne from propionie acid:

$$2\,C_2H_{fi}COO <= C_2I\,U + C0_2 + C_2H_5COOH.$$

Thus it was possible to isolate *methylacrylic acid* by the electrolysis of *ethyl potassium diiudhylm (donate:*

$2\,C_2 - C_2 1\,I_{fi}$

[1] Amer. Ohem. Joum. IS, 323 (1803).
[2] Ibid. IS, 569 (1804).
[8] Ber. d. deutsch. ehana. Gosellsch. 28, S438 (1895).

In the same way *ethylcrotome arid* is formed from the *ethyl potassium salt* of *diethylmalonic acid.*

Mulliken,[1] on electrolysing *sodium malonic diethyl ester* in alcoholic solution, obtained *ethanetelrdcarboxylic ester,* as already mentioned. Weems,[2] on elcctrolyzing the corresponding compound of *methylmalonie. acid,* obtained *dimetliylethanetetracarboxylic ester,* whereas *ethylmalonic ester* gave *diethylethanetetror carboxylic ester.*

The method of von Miller/[1] electrolysing *potassium ethylmalonate* with *potassium salts of aliphaiic carboxylic acids,* also .gives satisfactory results. If *potassium acetate* is chosen as the second component of the electrolytic mixture, propionie •ethyl ester is formed; and likewise by using *potassium pro pionate* or *potassium butyrate* we obtain butyric ethyl ester or valeric ethyl ester respectively.

Nitromalonic Acid.—According to Ulpiani and Gasparini,[1] a hydro-alcoholic solution of nitromalonic ethyl ester does not conduct the current, but an aqueous solution of the ammonium salt does. According to this the ester appears as a true nitro-compound:

$$\begin{array}{l} COOC_2H_5 \\ CHN0_2 \quad , \\ COOC_2H_5 \end{array}$$

but its ammonium salt, on the contrary, as an isnitro-salt:

$$\begin{array}{l} COOC_2H_5 \\ C = NOONH_4. \\ COOC_2H_5 \end{array}$$

The electrolysis of this latter does not give the free isonitro acid at the anode, but the *dinitroethanetetracarboxylic ester:*

$$2\ \begin{array}{l} CNOO \\ (X)OC_2H_5 \end{array} = (COOC_2H_5)2C(N0_2)C(N02)(COOC_2H_5)2.$$

The ammonium salt of *nitromalonamide* yields at the anode, only free nitromalonamide, whereas *julminuric acid* (nitrocyan-acetaniick'),CN-CH(N02)-0^jjjj, on electrolysis of its ammonium salt, gives a new reaction product which has not yet been investigated,

Succinic Acid.—Bourgoin [2] and KekuM [3] found that the free acid underwent oxidation with difficulty, only a small quantity of carbon monoxide in addition to some oxygen and carbon dioxide being formed.

The neutral sodium salt gave the same products, as did also the alkaline solution of this salt, except that in the latter experiment the formation of carbon monoxide predominated. If, however, four molecular equivalents of sodium succinate were

* **Gazg.** chim, $2, II, 235 (1902); Ztschr. f. Elektrochemie 9, 477 (1903).
[9] Ann, de chim. et phys. (4) **14,** 157 (1866).
»Lieb. Ann. 1*1,84(1864).

treated with one equivalent of sodium hydroxide, ethylene and a little acetylene could also be detected. Kolbe [1] states that methyl oxide is also formed; Bourgoin, however, was unable to confirm this statement.

Clarke and Smith, [2] on oxidizing succinic acid in alkaline solution, obtained, besides oxygen, carbon mon- and dioxide, ethylene, methane, tartar ic acid, and oxalic acid.

Petersen[3] was unable to detect either carbon monoxide or acetylene in a slightly acid electrolytic solution of potassium succinate. The following equations essentially express the course of the electrolysis:

$$\text{I. } C_2H_4(COOH)_2 = C_2H_4(COO)_2 + H_2;$$
$$\text{II. } C_2H_4(COO)_2 + H_20 - C_2H_4(COOH)_2 + 0\ ;$$
$$\text{III. } (C_2H_4)(COO)_2\text{-}0_2H_4 + 2$$

Small variations in the conditions of the experiment, as well as in the degree of acidity, the temperature, arid the kind and size of the electrodes, exert a great influence on the course of the electrolysis.

According to the method of Brown and Walker,[4] adipic diethyl ester is formed from ethyl potassium succinate :

$$2(CH_2)2 \begin{matrix} COOC_2H_5 \\ 300 \end{matrix} \qquad \bullet(CH_2)_4 \begin{matrix} \\ COOC_2H_5 \end{matrix}$$

Fairly large quantities of propionic and acrylic esters are also formed, probably by the reaction

$$2COOCH_2CH_2COOC_2H5 \quad .\ \text{-}\ CH_3 \qquad {}_2 : CHCOOC_2H_5 + 2C0_2.$$

[1] Lieb. Ann. **113,** 244 (1800).
[3] Joura. Amer. Ghem. 8oc. **21,** 907 (1899).
[8] Ztschr. f. physik. Chem. **Si,** 701 (1900).
*l.c.

Bouveault[1] claims that the yield of adipic acid is better on electrolysing the methyl ester-salt in methyl-alcoholic solution. He obtained a yield of 80% by using a mercury cathode and a hollow platinum spiral anode, through which a current of cold water was passed. The acid succinic methyl ester occurs as the principal by-product, also a neutral methyl ester of a tribasic acid which was not investigated.

Sodium succinate and sodium* perchlorate, electrolyzed by Hofer and Moest,[2] gave hydracrylic acid as the chief product, besides acetaldehyde, acetic acid, methyl alcohol, and formic acid. The splitting off of carbonic acid and the introduction of the hydroxyl group occurs only at one carboxyl group:

$$\begin{matrix} CH_2\text{-}COO \\ CH_2\text{-}COOH \end{matrix} + OH = \begin{matrix} CH_2\text{-}OH \\ | \\ CH_2\text{-}COOH \end{matrix} + CO_2.$$

Von Miller and Hofer[3] have also carried out the principle of the electrolysis of mixtures, discussed under malonic acid, using potassium ethyl succinate, and submitting the latter to electrolysis at the anode with potassium salts of monocarboxylic acids. They thus obtained on the addition of *potassium acetate* about 69% of the theoretical quantity of butyric ethyl ester:

$$CH_3 \cdot COO + COO \cdot CH_2 - CH_2 \cdot COOC_2H_5 = CH_3 \cdot CH_2 - CH_2 - COOC_2H_5 + 2CO_2.$$

- Incidentally a yield of about 22% of adipic ester was obtained.

The synthesis of valeric ethyl ester from potassium ethyl succinate and *sodium propionate* was accomplished in the same way:

$$CH_3 \cdot CH_2 \cdot COO + COO(CH_2)_2COOC_2H_5 = CH_3(CH_2)_3COOC_2H_5 + 2CO_2.$$

[1] Bull. soc. chim. **29,** 1038, 1043 (1903).
[2] Lieb. Ann. **S23,** 284 (1902).
[3] Ber. d. deutsch. chem. Gesellsch. 28,2431 (1895).

Furthermore, by using a mixture of potassium ethyl sumn and *potassium isobutyrale,* isobutylucHir rstcr was obtained:

(CH3)2 :CHCOO + COO(CI W '*< H K'

Vanzetti and Coppacloro[1] have oxtpndi'd tl»» von Mil Hofer method to the olro.trolysis of a mix! wo of /•//*/// */uttu mdonate* and e%/ *jmtamtnn snccinntr.* [r]**riv*y** ohtaincMt a p«w»r yield of the desired glut uric diefhvl ester:

COOC2H5 • CHo • COO -f (^00 . ( 'II, . ('! f , - ( '( H H y I,
I.vt'Ha-CIL.-CHyCOCHyf;, i 2('0a.

Moreover, suecinic diethyl f*st(»r \va.s formal from thi* iti acid, and adipic diethyl entcT from the* sttmttif acid.

*Pyrotartttric J( n'tl^*

Glutaric Acid *(Normal ryrntartnri*' And).-* ......... Thc» n'suIlM obtained by Rehoul and Bourgoiit[2] an* thr followium: A part of the acid remains unrhangfil, while n small part *IB* decomposed according to the* following equal ion:

A hydrocarbon **of** the* **compos! t ion |** C'l1^, ***/Mlz*** C[f]ff/ **not ol>-**tained; nor was an olefme **formed.**

Similar observations were* ramie in the* **!*foetroly#i&** of sium glutarate, also in **alkaline flotation.** *

Petersen[3] expresses **the** **of** tho **by the** following equations:

[1] Atti R. Accad. del Ltneei 12, If, 2«!l f HICI3),

[3] Bull. soc. chim. 27, 545 (1877) ; *CmnpL* wnd. HI, 12*11, *mm*

[3] Ztschr. f. phys. ehem. IS, 703

•

×

x rr ×

The strong aldehyde reaction of flic* olfofrolytp, uffpr the experiment was finished, indicates that the* primary alcohol is partially oxidized further to propionir altli'liyrlf. or that the propylene can yield propylew* ox do through (hi* influence of the anodic oxygen, and, by molecular w*arranj?einent, the a dehyde :

Oils Cir« OH.1
CH + 0 = 011 \ - ( ' I I 2
$CH_2$ $CI1_2$/

Ethylmalonic Acid.— The Ix'havior of ethyl potassium ethylmalonate has already been im»nfione<l in flu* di^cuHsion of malonic acid. The potassium «alt, in it 20[r],' slightly acid solution, yields propyleno (Peterwri [1])j «nil probably, like* pyrotartaric acid, primary and sc[i]eonclary propyl alrohol.

Adipic Acid.— The ethyl potiiHBitiin will- tfonvcrfwl into the sebacic diethyl ester by Brown and Wnlkor[1]:

$C000_2Hs$
$2(CH_2)_4$ «
COO

Pimelic Acid. — In the flame? rnunncT$_y$ th<» iiii*f]iyl of n-decanedicarboxylic acid is formed from tiif* salt of pimelic acid (Komppa,[2] aho Walker ami Liiffim!f*n [3]). n-Pentenecarboxylic ethyl ester occurs us a by-prodtjct at tlia anode:

I. $COOC_2H_5$ COOCaH*
$2(CH_2)_5$ $-(CH_2)i_D$ $+2f!C)_2$;
CO $COOC_2H_5$

II $COOC_2H_5$ OOOCalU
. $2(CH_2)_5$ $«(CH,)_3$
COO CH
$CH_a$

"1. c.
[2]Ber. d. deutsch. chem. 14, 9W
[8] Journ, Chem. Soc. 70,1197 (IJ0I)

[redacted]

**Acids.**

estigations of K
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the maleate.
ution of the alk
ocarbon isomeri
formula $CH_2=C$

along with tliis compound, sonic propylcne was forme

11( a portion of the acid was always regenerated.

Citraconic Acid.- . *'flu**- concentrated solution of t i n salt likewise* elect rolywd by Aarland,[1] yielded, In^ides carbon, $C_3$ILi, small traces of acrylic and inesaconie aei

Mesaconic Acid, under similar conditions, IIP .stiir ^ives 1 hydrocarbon and traces of acrylic and itnconic arids.

The unsutumtcd acids, on electrolysis, consequentl; s. lik« to give no synthetic products at all. The aromatic ;n phthalic and Ixjiizyhnalonir acid. Mum- similarly.

## V. Polybasic Acids.

Malic Acid.—The electrolysis of malic acid was effected l»y Bourgoin[2] and Bresteiv[1] Bnlli list* frei- acid, which is hut sli»\vly decomposed, and the neutnil alkali salt, p:w* the same prinluct.s carbon dioxide and *it* little carlnm nif»hf»xio!n and oxypeii. After the completion of the p\l»rrimcnt I lie solut"u»n contained some aldehyde and acetic acid. Von Miller and Ilofei"[1] al^o found crotonaldc»hydc».

Tartaric Acid (I)extr<H-c»t:iry).--The free ucid is partially oxidized (Bourgoin[5] and Ki*kuli[fl]i to carb(»n flioxiflc and carbon monoxide, while the solution contains awt'ic itri«l Neutral pottisaium turtntte principally car I ion dioxidt* besides a little carl>on monoxiile an«l oxygen, ncid p«ifiiK4itiii tartrate being at the wmw* tiitit* depciHifed. In alkaline sc»hitionrt the same gases carry with tlicin truces of ethane, the formation of which is due to potasHiuniiU"i»tnli*f wliicli is foutul pres«*nt in the solution at the end of the openifion; alno some ethylene. Von Miller and Ilofcr[7] ohtiiinrul from a coitccntrated Rtlutiou of potassium tartrate* eiirtion moil- and dioxitleH mid

[1] Journ. prakt. (1u«n, (2] 7, 112 MH7»>,
[2] Bull. see. chim. [2] 0, 427 (IHtiH).
[3] Ibid. 8, 23 (1867),
[4] Ber. d. doutach. chem, «7f 470
[8] Compt. rend. 05, 11.44 uoc. chim. (2] II, 4CIS
[e] Lieb. Ann. 131, 88 (ISIM),
[7] **Ber. d. deutseh. chem. «7, 470**

with a little formaldehyde and formic acid, but no acetic acid and ethylene as affirmed by Bourgoin. The ethyl ester behaves in a like manner.

Racemic Acid. — The same investigators found that *racemic acid,* on electrolysis of the sodium salt in aqueous solution, gives carbon mon- and dioxides and an aldehyde which was not further investigated.

Ethyltartaric Acid. — This gave the same gases, but any other substances which may have been formed were not identified.

Methanetricarboxylic Acid. — Mulliken[1] employed the method, which has already been discussed (p. 104), in the electrolysis of the sodium salt of the triethyl ester of this acid and obtained othanchoxacarboxylic ester, besides some malonic ester. Further oxidation caused the formation of sodium bicarbonate:

$$2(COOC_2H_6)_3C = (COOC_2H_5)_3C\text{-}C(COOC_2H_5)_3.$$

Tricarballylic Acid. — The potassium salt of the diester of this acid wus subjected by von. Miller[2] to the Brown-Walker reaction, but without success. The ester-acid was in part regenerated. When potassium acetate, however, was added to the anode solution the expected reaction occurred; ethylsuecinic ester was produced:

$CH_2\,COOC_2H_5$

I COOC$_2$H$_5$

$CH_2\text{-}COO$

The peculiar fact that the di-esters of tricarballylic acid, when electrolysed by themselves, do not afford the expected synthetical reaction, while the electrolysis of a mixture of the acid with potassium acetate gives these synthetic products, was made use of by von Miller with several aromatic acids which had previously proven unsuitable for synthesis when used alone (see these).

[1] Am. Chem. Journ. 15, 323 (1893)
[2] Ztsch. f. Elektrochemie 4, 55 (1897).

Aconitic Acid. — On electrolyzing a concentrated; strongly alkaline solution of the potassium salt, Berthelot [1] observed oxygen, carbon monoxide, and a little acetylene at the anode.

Marie[2] was able to convert aconitic acid into tricar ballylic acid at a mercury cathode surrounded with a solution of the acid half neutralized with sodium hydrate. Sixty per cent of the theoretical yield was obtained :

$$\begin{array}{lll} CH\text{-}COOH & & CH_2\text{-}COOH \\ C\text{-}COOH & +2H & CH\text{-}COOH \\ CH_2\text{-}COOH & & CH_2\text{-}COOH. \end{array}$$

## 7. AMINES, ACID AMIDES, IMIDES, AND NITRILES.

The literature on these subjects is very scarce. Little is known regarding the electrolysis of amines, whose anodic behavior would probably be very interesting. They are stable at the cathode, and can be obtained electrolytically by reduction of the nitriles. Weems [3] has electrolysed acid amides in the form of their sodium or mercury compounds. He obtained only the unchanged material used as the starting-point.

Tetrajnethylammonitim Hydrate. — Palmaer [4] electrolyzed a solution of the hydrate in liquid ammonia in a Dewar vessel at about — 41°. Deep-blue rings having the color of a solution of sodium in liquid ammonia appeared at the cathode when the circuit was closed. A solution of free tetramethylammoniurn is probably formed, which could not be isolated. The chloride behaves like tetramethylammonium hydrate.

Tetraethylammonium Chloride. — Goecke [5] has investigated the behavior of the iodide of this compound in aqueous solution. He found at the anode tetraethylammonium triiodide :

[1] Compare Bourgoin, Bull. soc. chim. [2] 9, 103 (1868).
[2] Compt. rend. **136,** 1331 (1903).
[3] Am. Chem. Journ. **16,** 569 (1894).
* Ztschr. f . Elektrochenu 8, 729 (1902).
[5] Ibid. 10,250 (1904).

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**A motlrrati* yirltl iff jH p-tolylsuccinimide in U*V ,' M** I- niiUnr

**CH.»-(U**

\\MYJ I-Hlli i

Acelylpyrroliclone ran In* i* 50',' <' HSilplsurir a«'i<i flafrl an-[1]

/N'riMlI;! + 21!;* V* 11-, II. M.

Hydrocyanic Acid. In uljVyn

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Sodium On **I*'r?i^

this **salt for n |>n»|ittifn^i j««n«»»l** 1'Mtli" MI'«*} •!*»' f^n>ri!i »i

[1] !.c.

[3] Aw rlilm |»hv«« 7H, IMS 'l>tJl <

[1] JahntMb. f. CliHrt IHu'i, Ii«fi

* Tnw HI ui*i, Tr «il/ rf I'll **<*t** r**I«iitii«' 7y>

§Jtrtin», f }trnUt. rliniiP* Si, 1 1 » flHj'ts

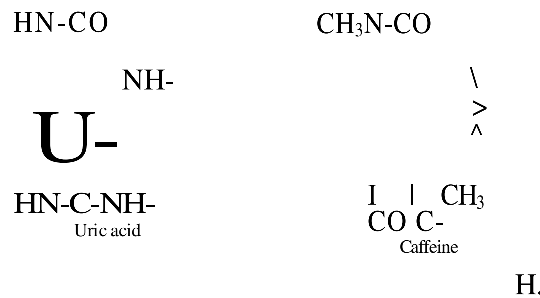
•Fjlff l*,tl Xo 7126 aHHUj; |>ft

i f. riiifii, *ihm,* *mi*

E. Fischer claims that the members of the uric-acid group can be considered as derived from purin, a parent substance:

```
           (6)
(1)  N = CH;
           I    (7)
(2)  CH(5)C-NH\
                  >CH.
(3)  N - C-N
         (4) (9)
```

Accordingly, uric acid appears as 2, 6, 8-trioxypurin, **arid** caffeine as 1, 3, 7-trimethyl-2, 6-dioxypurin:



Uric acid    Caffeine

In the electrolytical reduction of the investigated purin derivatives, it appeared that the oxygen in position (6) of the purin nucleus is the only one that can be eliminated for hydrogen. But an addition of hydrogen occurs also without ii loss of oxygen; this happens in the conversion of uric acid into tetrahydrouric acid. Further particulars will be mentioned under the individual substances.

Parabanic Acid, the urei'de of oxalic acid and oxidation product of uric acid obtained by the action of nitric acid, is converted into hydantoi'n and ethyl urea (Tafel and Reindl[1]).

Methyluracyl, the reaction product of acetoacetic ester and urea (water and alcohol being eliminated)^ can be easily reduced in sulphuric-acid solution (Tafel and Weinschenk[2]). Methyl-trimethylene urea is formed, also a considerable quantity of 1.3-diaminobutane:

[1] Ber. d. deutsch. chem. GeseDseh. 34, 3286 (1901).
[2] Ibid. 33, 3378 (1900).

•>'» <--fH:, NU -CJH-CH;,

I. n» <'H 1l, (!() ('H2 .f.n80

MI <>(f Nil (HI;,

N'H HI-CH,

. <*'» HI. i H,0 _,,cO2.

N f H3--(!IIs

Barbituric AcW, ,\fnlnn;/l I'm/. W.MS invest igut.o<! by the Hani" an! IIMI- {* iik«-wi?a- jrivc-s two products, syl hydroiinwsl

gi ami triHii'thyli'in' urea:

MI CO XII -(JHa

J i. CO Cfi^L'ili » co (';na+nao;

MI Co XH co

XII CO XH-.C!Ia

II, CO I'Hri4H3 CO CH-I-2H-/l

XII CO Nfl-CIIu

'J1i<- JMtfivcilihility «»f uuiiutty) iircu inio friwictftrlcwe urea t:*k«'jj itM-niiUt'Ctioit m-itfifhw ti"*> r>inj»o-';(l»ilitv <»fUi«' rvHiruI tireuH *lain* 'iiiriiiin , rujii rvirltoiitc aHil uffonU ft Kitiiftlc method of MItt.iihiiip J,.'J 'IJ,iJi»iiiftj<r<>j«trtt' from ntiil'nijf iichl in the name, ucmit'-r u • Mi i)i.'iruir«thutniie is proiittrci! frotn methyl uracyl:

xn *nij* Nrtz off,

CO riljiHaf) - <IH»KJOa.

MI nia N!ra-oir2

IMnltirfc AcW, *Tfrrlrttnjfi* £/rm.— Tufel and Jleiiull ' rr<ciu<w<! iiJtt) Stic*' ntiii oht;»ined *M* <-hii*f redact bn product Iiydro-umryl, sS^i «»«(»« JrimethyleiH' urea nrtd oxytrimethylenn ?iro«,:

[1] Ifcr «J «

NH-CO NH-$CH_2$

I. CO CHOH+$3H_2$=CO $CH_2$+$2H_2$0;

NH-CO NH-CO

NH-CO NH-$CH_2$

II. CO CHOH + $5H_2$ = CO $CH_2$+$3H_2$0;

NH-CO NH-$CH_2$

NH-CO NH-$CH_2$

III. CO CHOH+$4H_2$ = CO CHOH+$2H_2$0.

NH-CO NH-$CH_2$

Uramil is the reduction product of violuric acid, which is the isonitroso-compound of barbituric acid:

NH-CO

CO CH-$NH_2$.

NH-CO

It is easily reducible, ammonia being split off, and forms hydro-uracyl[1] as the solely erystallizable body. The same product is derived in considerable quantity in the electrolytic reduction of Alloxan, *Mesoxalyl Urea.* There are also produced in this reduction alloxantin, which is difficulty soluble and can only slowly be reduced further, and large quantities of non-crystallizable gummy substances:

NH-CO NH-$CH_2$

I. CO CO+$4H_2$=CO $CH_2$+$2H_2$0;

NH-CO NH-CO

NH-CO NH-CO CO-NH

II. 2CO CO+$H_2$=CO 0 CO + $H_2$O.

NH-CO NH-CO CO-NH

Alloxantin

[1] Ber. d. deutsch. chem. Gesellsck. **S4,** 3290 (1901).

Uric Acid. The reduction of uric *mid* can IK* conducted in HitHi a way lli;it if taken place principally according to the following t'f jtiatif m (TafeP;:

<V,iM>:i\4 Hill -CWiAjXi l-H/i

Tafel ealln thf resulting product puron, and given it tli(» follmvint!; ffiriiiiilji;

XII I'll,

n> ru \it
!
MI ni NII- n).

It i? fWiuni nliiiu i »*\r!»j^iv«*Iy in the reduction of uric acid in j* T.V ' ulphuiir *Ht'l I* ;it *IM V1 and uith *lil^h* cuirrent con-ei'iiffifiHii, A jftrt tif flu* punm i/i inolc^nilnrly rc*n,rntngc*d ;j|?«*:i'i^ at J'J ! V» !»tr!iiifil4 mi i^ciiitf*rk* suhstunnc*, isopuron* li» fn;*'tiir*' *»1 fh*' litliT IIIIH not yrt b'eii i»xpluin<*d, Tetra-h* IiMnri«' af)*t aiid i^npurnrt iin» formed in KC)% nulphuricj acid at *'in* at,'i with ;i l«ito**r rtim*nt wneerifritfiorL

1'ir i^rKfti****^ *%'iii b* rxpn.'HHc»il iiy t!ie following equations:

MS 0»
I, «'«* r \||
MI « MI
i •, i ,t
MJ <'»
II. r«» r Ml
.\H r Mr
XII CIIj
!
XII CO

Nil-(U12

X1I--(;II-N»-
I*iif«t*

X>C;CM-I[20;
VH/

or

- v
j >00.
00 -NIK

CH-NH

Si, JWH (mil).

The structure of the last-mentioned acid has not yet been determined with certainty.[1]

Strange to state, the methylated uric acids, when reduced, do yield purons which (excepting tetramethylpuron) can be molecularly rearranged into isomeric isopurons, but the corresponding hydrated uric acids are not produced (Tafel[2]).

3-Methyluric Acids.—The two isomeric and structurally identical 3-methyluric acids, the 5- and £-acids, give 3-methylpurons. These latter are extremely similar, but show differences in solubility which point to the possibility of an isomerisrn. A certain quantity of isopurons was already formed during electrolysis by the rearranging action of the 60-70% sulphuric acid used as electrolyte:

```
     NH-CO                      NH~CH2

     CO    C-NHv                CO   CH-NHv
      |    ||       >CO+3H2 =    |    |        >CO+H2O.
CH3N - C-NH/              CH3N - CH-NH/
```

i.3-Dimethyluric Acid. — The reduction to 1.3-dimethylpuron takes place very slowly in a 75% sulphuric acid solution. The molecular rearrangement to isopuron is also very slow.

3.9-Dimethyluric Acid gives similarly a 3.9-dimethylpuron which, if heated in a 10% sodium-hydrate solution, smoothly rearranges itself to form the iso-compound. The electrolytical effect is hence a normal one:

```
     NH-CO                      NH-CH2

      CO   C  -NHx              CO   CH~NHx
      |    ||        >CO+3H2-   |    |         >CO+H2O.
CH3N  -C  -N  /                 N   -CH-N  /
            CH3                 CH3      CH3
```

7.9-Dimethyluric Acid gives correspondingly a 7.9-dimethyl-purcm-

[1] Ber. d. deutsch. chem. GeseUsch. 34, 1181 (1901).
[2] Ibid., 279 (1901).

^** m it 3& 2?* *•* s»- ** sr £r si* £• «2 *•*
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ija*.* ? 3 5 -4 5-5 *<

p. rr

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»^* O C- *» »S- -^'
I.,5 2.^ * i" ~
"» ag ^ s. g -* ,.
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quantity. The reaction takes place in accordance with the following equation:

```
                                   NH-CH2
   NH-CO
   CO   C-NHx                      CO   C-
    1    ||        >CH+2H2                              CH+HaO.
   NH-C-     W                     NH-C-
     Xanthine                        Desoxyxanthine
```

The latter compound is therefore to be regarded as 2-oxy-1.6-dihydropurin. These experiments were made by Tafel and Ach.[1] 4

3-Metliylxantliine gives analogously 3-methyldesoxyxanthine or 3-methyl-2-oxy-1.6-dihydropurin (Tafel and Weinschenk[2]), and

Heteroxanthine, 7-Methylxanthine, yields desoxyheteroxanthine, or 7-methyl-2-oxy-1.6-dihydropurin:

```
    NH-CO                NH-CH2
I    CO   C-NH-
     !    ||             CO   C-NHx
  CH3N  -C-  N-                              >.4-2Ha-    I     il
                                                     >CH+H20
NH-CO                                                       .
I   I                    CH3N   -C-N  '

                                    NH-CH2
        |    |  CH3                 ||     CH
        CO   C-Nx                   CO ~C-
        |    ||    >CH+2H2=  |      ||     ,,
        NH-C-N^                     NH-C-N^
```

EF desoxy-compounds are suitably oxidized, they lose two atoms of hydrogen and pass into oxypurins. 3-Methyldesoxyxanthine is thus converted into 3-methyl-2-oxypurin:

```
      N=CH
   CO C-NH\
   I   II     >H,
   CH3N-C-   W
```

[1] Ber. d. deutsoh. chem. GeseUsch. **34,** 1165 (1901).
[3] Ibid. **33,** 3369 (1900).

and desoxyheteroxanthine gives the corresponding 7-methyl-2-oxypurin. These • oxidation products furnish the proof of the constitution of desoxy-compounds. The constitution for some of the members had been determined by E. Fischer through synthesis.

Theobromine, or 3.7-Dimethylxanthine, was reduced by Tafel [1] *in* 50% sulphuric acid. He obtained desoxytheobromine, or 3.7-dimethyl-2-oxy-1.6-dihydropurin:

NH-$CH_2$<br>
| | $CH_3$<br>
CO C-Nv<br>
H.<br>
I II<br>
$CH_3$N - C-

3.7-Dimethyl-2~oxypurin is formed on oxidation with an excess of silver acetate.

Caffeine, or 1.3.7-Trimethylxanthine, was reduced in 50% sulphuric acid to desoxy caff erne by Tafel and Baillie,[2] while they were investigating the reduction of acylamines to alkylamines. In a later investigation[3] they showed that desoxycaffe'ine is to be designated as 1.3.7-trimethyl-2-oxy-1.6-dihydropurin:

$CH_3$N-$CH_2$<br>
| | $CH_3$<br>
CO C-Nv<br>
CH.

By oxidising it with lead peroxide, 3.7-dimethyl-2-oxy-purin-1-rnethylhydroxide is obtained:

OH<br>
CEkN-CH<br>
| | $CH_3$<br>
CO C-

[1] Ber. d, deutsch. chem. Gesellsck. **32,** 3194 (1899).
[2] Ibid, 686(1899).
* Ibid., 3206 (1899).

This is a compound which corresponds to the 3-methyl-2-oxypurin obtained from 3-methyldesoxyxanthine. Its strongly basic properties are conditioned by the methyl group in position (1). It may be here mentioned that Tafel has worked out his valuable method chiefly by the use of caffeine. The corresponding investigation has already been considered (p. 24 and p. 52).

Guanine, 2-amino-6~oxypurin, when electrolytically reduced in a 60% sulphuric acicl, is converted into desoxyguanine, a base containing no oxygen (Tafel and Ach [1]):

NH-CO NH-$CH_2$

$NH_2C$ C-NH- $NH_2C$
\CH+$2H_2$ = CH+$H_20$.
v

Desoxyguanine, 2-amino-1.6-dihydropurin, is easily oxidized to 2-aminopurin : ;

$NH_2C$ C-NH-
[U VV — IN JO.N.
II II > H.
N - C - *W*

This substance is isomeric with adenine and is vef/ sta% i lar to it. Nitrous acid converts it into 2-oxypurin, an isomer of hypoxanthine.

The firm of C. F. Boehringer & Sohne (Waldhof-Mannheim) has patented [2] TafePs process for reducing xanthine bases.

9. DERIVATIVES OF CARBONIC ACID CONTAINING SULPHUR.

Potassium Xanthate.—C. Schall[3] ^ obtained; by the electrolysis of potassium xanthate in aqueous solution and with

[1] Ber. d. deutsch. chem. Gesellsch. S4; 1170 (1901). '

[2] See especially D. R. P. No. 108577 (1808): Process for the preparation of xanthines containing less oxygen by means of the electrolytic reduction in .acid solution of alkylated xanthines.

[8] Zeitschr. f. Elektrochemie 2, 475 (1896); 8, 83 (1897).

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%1 fiiiM

O'J pIllH HI f4J

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1CI ») ;)UVH«friV .-In K!.<A'tn,JL r|| J

# CHAPTER IV.

## THE ELECTROLYSIS OF AROMATIC COMPOUNDS.

IN the aliphatic series the carboxylic acids furnish the principal material of electrolysis. This is due to the reactiveness of their anions, which readily split off carbonic acid, thus affording manifold syntheses. In the aromatic series, however, the nitro-compounds are the more interesting, on account of their easy reducibility and the importance of their reduction products. The facts which give to electrochemical reduction pre-eminence over oxidation have already been explained in the introduction (p. 2).

Single oxidation processes have, however, also become important. Besides the oxidability of easily oxidizable substances, for instance aniline, or easily oxidizable groups like methyl, the peculiar reaction which seems to occur very frequently in the electrical oxidation in sulphuric acid, and which consists of the entrance of oxygen into the benzene nucleus, must be emphasized. Hydrocarbons, phenols, quinones, and azo-compounds seem to behave alike in this respect.

Electrolytic substitutions furnish a further general point of view.

Although the substitution processes afforded by the action of the primarily discharged anion of an inorganic salt upon an organic body are to be included among the simpler reactions, the results obtained so far in this domain have been very scanty, especially in regard to aromatic substances. The above-mentioned investigations of Elbs and Hertz, as well as those of Forster and Mewes on the electrolytic preparation of iodofonn, can serve as an indication that many interesting and reitu.ment~ tive problems yet await solution in this field.

## 1. HYDROCARBONS.

Benzene.—Renard,[1] by the anodical action of the current in.an alcohol-sulphuric-acid solution of benzene with plntinum anodes, obtained a body melting at 171° which Gattowmtm and Friedrichs[2] recognized later as hydroquinone. The la/tter is also formed (Kernpf[3]) if a mixture of benzene and n 1 ()',,'• sulphuric acid is eloctrolyzod at lead-peroxide anodes rind lend or zinc cathodes. Quinone is first produced at the anode with the aid of the lead peroxide. It is then reduced at the enthodo to hydroquinone.

The process very likely occurs in the same way at a plntinum anode. Hydroquinone itself, when oxidized electrolyticully, yields only traces of quinone (Liebermann[4]), quinhydronc* being the chief product.

However, it is not impossible that at platinum miod<»[s] a direct introduction of hydroxyl groups into the l:>c»nssonn nucleus, i.e. a primary formation of hydroquinone*? taken place, especially if concentrated sulphuric acid is clioson JIB the electrolyte. Chemical as well as -electrochemical *vxjK»riences indicate this. Thus, by means of persulphuric iteid or its salts, obtained by the electrolysis of sulphuric acid or its salts, nitrophenol can be directly converted into nitrohydroquirione, salicylic acid into hydroquinonecarboxylie acid, anthraquinone into alizarin, and this latter into alissuriii-bcirdeaux and alizarin-cyanine.

It may be here mentioned that oxygen can thus "bo c*ledrolytical'ly introduced into azobenzene. Heilpern,[6] by eleciroiyr/lng azobenzene in concentrated sulphuric acid, obtained totruoxy-

[1] Compt. rend. 91, 175 (1880).
[2] Ber. d. deutsch. chem. Gesellsch. 27, 1942 (1894).
[3] D. R. P. No. 117251 (1899).
*Ztschr. f. Eiektrochemie 2, 497 (1896).
[5] Ibid. 4, 89 (1879).

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azobenzene, a fast dye, soluble in concentrated sulphuric acid with a cherry-red color and resistant to the action of light and acicls.

Toluene.—According to Renard,[1] this compound, by electrolytic oxidation in alcoholic-sulphuric acid, forms benzaldehyde and phenose, $C6H_6(OH)_6$(?). According to Puls,[2] there are produced in the same electrolyte, using a diaphragm and a platinum anode, benzaldehyde, benzoic acid, benzoic ethyl ester, and, as chief product, p-sulphobenzoic acid. Under the same conditions, Merzbacher and Smith[3] had obtained a poor yield of benzoic ethyl ester.

Law and Mollwo Perkin [4] report on the electrolytic oxidation of toluene, the three *xylenes, mesitylene,* and *pseudocumene.* In a sulphuric-acid-acetqne solution of toluene they obtained a little benzaldehyde and perhaps benzyl alcohol. The electrolysis of an emulsion of toluene and dilute sulphuric acid leads to a complete combustion of the toluene to carbonic acid and water.

4 The three xylenes, electrolyzecl in acetone and dilute sulphuric acid, yield principally the three toluic aldehydes, rn-Xylene, even when sodium acetate and acetic acid are employed as electrolyte, gives the m-toluic aldehyde.

Pseudocumene, in the presence of acetone and sulphuric acid, gives apparently a mixture of the three isorneric dimethylbenzaldehy'des. Analogously, mesitylene is oxidized to mesitylenic aldehyde.

Naphthalene.—This substance, electrolysed by Panchaud de Bottens [5] in a sulphuric-acid-acetane solution at platinum and lead anodes, gives, besides a brown by-product, principally a little a-naphthoquinone. In glacial-acetic-sulphuric acid traces of phthalic acid are formed at platinum electrodes.

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* Compt. rend. 91, 175 (18SO).
[2] Chem. Ztg. **25,** 263 (1901).
[8] Journ. Am. Chem. Soc. 22, 723 (1900).
[4] Trans, of the Faraday Soc. I (25/10, 1904).
[6] Ztschr. f. Elektrochemie 8, 673 (1902).

### 2. NITRO- AND NITROSO-COMPOUNDS.

Of all organic substances which have been tested as to their behavior towards the action of the electric current, aromatic nitro-compounds have received the most accurate treatment and attained the greatest importance. The reason for this lies, on the one hand, in the fact that the nitro-group, being extremely reducible, reacts only at the cathode, whereby the end-products are closely and simply related to the product started with; and, on the other hand, in the variety of the reduction phases which the nitro-group can develop, depending upon the conditions of the experiment.

It thus happens that the class of nitro-bodies not only affords the greatest number of important results and smooth reactions, and thereby is of great importance technically and for the manufacturing side of organic chemistry, but it also offers the suitable starting-point for the treatment of general and special theoretical questions. So far as these are of a general nature, treating of the relation of the reaction velocity to the reduction velocity and referring to the importance of the cathode material, they have already been discussed in the first chapter. The theoretical relations, which are of importance only for the reduction of nitro-bodies, will be briefly considered here. They can be divided into purely chemical and electrochemical ones. The former, which obtain in every method for the reduction of nitro-bodies, deserve mention because they were first understood in closest connection with the *electrical* reduction; they refer to chemically possible reduction phases and their gradation. The latter encompass the dependence of the chemical results upon the electrical conditions of experiment and the special r61es of the separate decisive factors.

The importance, thus shown, of our knowledge of the electrical reduction of nitrobenzene in regard to the practical and theoretical exploitation of the electrolysis of organic substances makes it desirable to first give a short historical survey of the development of the views and the importance of the separate observations.[1]

*a. General Observations on the Reduction of Nitro-compounds.*

Hiiussermann [2] reduced *nitrobenzene* and *nitrotoluenes* both in alkaline and acid solution, the former with iron, the latter with platinum, electrodes. By reduction in alkaline solution, he obtained as principal product *hydrazobenzene* and *hydrazotoluene* respectively; in sulphuric-acid solution he got from nitrobenzene, as chief products, *benzidine sulphate* and *azoxybenzene,* besides an easily changeable body which was not further determined. o-Nitrotoluene [3] under like conditions gave *o~toluidine sulphate,* besides small quantities of *o-toluidine;* p-nitrotoluene yielded principally p-toluidirie.

Elbs, on the contrary, obtained entirely different results when he electrolytically reduced p-nitrotoluene and nitrobenzene in acid and in alkaline solution with other cathode metals. There were formed in the reduction of nitrobenzene in alkaline solution at a lead or mercury cathode varying quantities of *azoxy-* arid *azobenzene,* the former mostly preponderating. *p-Nitrotoluene* behaves similarly if reduced in the same manner, —*p-azoxy-* and *p-azotoluene* being produced. The reduction takes place much more slowly and less completely in this case than when nitrobenzene is used. Hausserrnann observed the same with o-nitrotoluene. o-Nitrophenol behaves quite differently; the chief product is o-amidophenol, besides red and brown substances which could not be obtained pure. In the reduction of nitrobenzene in sulphuric-acid solution Elbs employed a zinc cathode and obtained chiefly *aniline.*

Elbs[4] draws the following conclusion: " Without considering the other conditions of experiment, the kind of metal

[1] This classification (a) has been partially taken from the dissertation of my pupil Jos. Schmitt: " Concerning the Importance of the Cathode Material in the Electrolytic Reduction of m~ and ]>-Nitrotoluene/' Bonn, 1904.

[2] Chem. Ztg. 17, 129, 206 (1893).

[3] Ibid, 209 (1893).

employed as electrode seems to exert an important influence, since Haussermann obtained benzidine and azoxybenzene from nitrobenzene at a platinum electrode/' Gattermann and Koppert,[1] by electrolytically reducing nitrobenzene in concentrated sulphuric acid with the addition of a few drops of water, obtained other results. After several hours' electrolysis the contents of the earthenware cell, which contained the reduction fluid together with a platinum cathode, solidifies, forming a colorless mass of crystals of p-amidophenol sulphate, which was permeated by a blue-green liquid.

After these observations, Gattermann and his pupils[2] continued their investigation on the reduction of aromatic nitro-bodies to amiclophenol derivatives. They thus examined mono- and dinitrohydrocarbons, nitroamines, nitrocarboxylic and nitrosulphonic acids, also the esters of the acids. After the reaction had been successfully tested in over 40 cases it was adjudged to be of general applicability.

The important result of these experiments is that nearly all nitro-bodies with an unoccupied para-position are converted by electrolytic reduction in concentrated sulphuric acid into p-amidophenol derivatives, i.e. not only is the nitro-group reduced completely to the amido-group, but in most cases the hydrogen atom in p-position to the amido-group is simultaneously substituted by the hydroxyl group.

A short time after the publication of the interesting experiments of Gattermann, A. A. Noyes and A. A. Clement[3] made known their studies on the electrolytic reduction of nitrobenzene in sulphuric-acid solution.

Noyes and Clement used concentrated sulphuric acid of L84 to 1.94 sp. gr. as a solvent for nitrobenzene. Gattermann and Koppert had treated the sulphuric-acid solution before the reduction with a few drops of water. Noyes and Clement obtained from 50 g. nitrobenzene at platinum electrodes 30 g. anhydrous p-amidophenol-o-sulphonic acid, cor-

[1] Chem, Ztg. **17,** 210 (1893).
* Ber. d. deutseh. chem. Gesellsck **26,**1844,2810 (1893); **27,**1927 (1894).
[8] Ibid. **20,** 990 (1893).

responding to a yield of 40 per cent, of the theoretically possible quantity.

Three years later Elbs [1] reverted to the experiments of Gattermann. On repeating the. same he obtained, indeed, the same results, but simultaneously observed that considerable quantities of aniline are always formed besides the p-amidophenol. When Elbs used glacial acetic acid as a diluent of the sulphuric acid he found a considerable increase in the yield of p-amidophenol, but the yield of aniline kept apace of that of the latter. If he used a lead in place of a platinum cathode, the reduction was accelerated, being favorable to the aniline formation at the expense of the p-amidophenol.

Lob[2] found a reaction analogous to that of Gattermann when he reduced nitrobenzene in hydrochloric-acid solution or suspension, using platinum electrodes.

In this process there is formed as chief product a mixture of o- and p-chlor aniline. The formation of this can be explained thus : The primarily formed phenylhydroxylamine reacts with the hydrochloric acid, simultaneously rearranging itself:

$$= C_6H_5NHC1 + H_2O.$$

The same mechanism of molecular rearrangement must be assumed in Gatterrnann's reaction:

Direct proof of the correctness of this view was produced by Gattermann[3] on adding benzaldehyde to the solution of nitrobenzene in sulphuric acid. Benzylidenephenylhydroxylamine is formed:

$$CeH5NHOH+OHOC6H5-C6H_5-\overset{/O\backslash}{N— HC}-C_6H_5;$$

[1] Ztschr. f. Elektrochemie 2, 472 (1896).
* Ber. d, deutsch. chem. Gesellsch. **29,** 1804 (1896).
[8] Ibid,, 3034, 3037, 3040 (1896).

i.e. the condensation product of phenylhydroxylamine with benzaldehyde.

A similar influence of the cathode material, as observed by Elbs in replacing the platinum electrode by a lead cathode in sulphuric-acid solution, was found by Lob [1] when he used a lead cathode in hydrochloric-acid solution. No chloraniline was formed, aniline being produced almost exclusively.

Further observations concerning the influence of the cathode material in reductions were made by Lob [2] in his studies on the electrolytic preparation of benzidine. His results are briefly the following:

1. Platinum and nickel electrodes behave alike in the experiments to reduce nitrobenzene in acid solution to benzidine. Carbon cathodes, on[s] the contrary, give only little benzidine; zinc and amalgamated zinc electrodes yield no, or extremely little, benzidine, while aniline, as already previously observed by Elbs, results as the principal product.

2. Mercury, nickel, copper, zinc, lead, iron, brass, and zinc amalgam were tried as electrode material in respect to their reduction behavior in the reduction of azobenzene to benzidine in alcohol-sulphuric—acid solution. It was shown that the furthest utilizable reduction was obtained with mercury; the usefulness of the other metals was determined to be in the following order: Lead, sheet nickel, nickel-wire gauze, copper, zinc, iron, and brass.

3. In the reduction experiments of nitrobenzene to azobenzene in alkaline-alcoholic solution mercury electrodes prove good; however, nickel-wire—gauze electrodes give excellent results. This had been already shown by Elbs.[3]

4. The same is true in the reduction of nitrobenzene to azoxybenzene igt an alkaline aqueous suspension.

Finally, the employment of a strong hydrochloric acid and a tin cathode, or an unattackable cathode with addition of

[1] Ztschr. f. Elektrochemie 4, 430 (1898).
[2] Ibid 7, 337, 597 (1900-1901).
[8] Ibid. 5, 108 (1898).

stannous chloride, was ascertained to constitute a condition for the reduction of azoxybenzene and azoben0< * to benzidine.

The practical results of all these investigations for t reduction of nitrobenzene ancl its reduction phases are the following:

At attackable electrodes, like zinc, lead, and tin, the tion generally proceeds further than at unattackable electro <1< such as platinum, nickel, and mercury. The attempts utilize technically these properties of the cathode metals $ a series of nitro-bodies led to important patents.

Thus Boehringer & Sohne[1] (Mannheim) patented a proc*< by which, when employing tin-cathodes (or cathodes of otlh indifferent metals with an addition of a small quantity of tin salt), fatty or aromatic mtro-compouncis, dissolved suspended in aqueous or hydro-alcoholic hydrochloric ac*3 can be reduced' in almost theoretical yields to the correspori ing amines.

In hydrochloric-acid solution, as already mentioned, chic anilines are produced q,t platinum electrodes.

According to another patent[2] of the same firm, cop fH lead, iron, chromium, and mercury can be used instead of I i if these metals are added in the form of their salts or as a fine:? divided powder to the cathode electrolyte.

After the publication of these patents Elbs and Silbermaii I reported that if a lead cathode in sulphuric acid is employ* the same results are attained. It proved to be true that order to obtain the best yields of aniline diluted alcohol serv as a better diluent for the sulphuric acid than the glacial aec*i acid formerly employed. Zinc behaves in sulphuric-acid tions like lead; however, the precipitation of difficultly ble zinc double salts is a hindrance. Elbs likewise obtain 90 per cent of the theoretical yield of toluidines from o- ;uu

[1] D. R. P. No. 116942 (1899).
[2] D. R. P. No. 117007 (1900).
[3] Ztschr. 1 Elektrochemie 7, 589 (1901).

m-nitrotoluene; the yield from p-nitrotoluene was a few per cent. less.

A supplementary patent of Boehringer & Sohne [1] extends the process of the D. R. P. No. 116942 to the reduction of azo-bodies to amines.

The patent claim is as follows: "Process for the reduction of azo-bodies to the corresponding amines; consisting in reducing azo-bodies in acid solution by simultaneously conducting a constant electric current either with a tin cathode, or with an indifferent cathode and the addition of a tin salt or pulverized metallic tin.[7;]

In a later patent[2] C. F. Boehringer & Sohne point out that the nitre-compounds in acid solution can not only be reduced to amines with such metals as easily evolve hydrogen with dilute acids, but also with copper. This fact offers particular technical advantages, because copper can be most easily and completely regenerated electrolytica ly from the liquors. While in the above-mentioned methods the reduction to the amines is made in acid solution, C. F. Boehringer & Sohne have obtained a patent[3] according to which it is also possible to reduce nitro-bodies to the corresponding amines in alkaline and alkali-salt suspension, if a copper cathode with or without the addition of copper powder is employed.

According to an investigation by Elbs and Brand,[4] the addition of copper powder is absolutely necessary for obtaining the desired effect.

In 1899 the Farbenfabriken vorm. Friedr Bayer & Co.[5] (Elberfeld) patented a process for electrolytically preparing azo- and hydrazo-eompounds. The method is characterized by the fact that the nitro-body to be reduced is held suspended in the alkaline cathode liquid, and is reduced during continuous vigor-

*D. R. P. No. 121835 (1900). See also the English Pat: No. 19879 (1901).

[2]D. B. P. No. 127815 (1901),

[3]D. R. R No. 130742 (1901)..

* Xtschr. f. Elektrochemie 8, 789 (1902).

*D. R. P. No. 121899(1899).

ous stirring and the addition of a metallic oxide solution of zinc, tin, or lead.

This method was then extended by a supplementary patent,[1] according to which the reduction of aromatic nitro-bodies is carried out in aqueous alkaline suspension instead of in the presence of alkali-soluble oxides of the heavy metals and the use of such metal cathodes the oxides of which are soluble in alkalies.

It is very evident, from all these observations, what influence the cathode material exercises on the obtainable reduction phase of nitrobenzene and its derivatives. There is no lack of attempts to explain this influence. The expressed opinions can be grouped under three points of view:

1. The specific action of the cathode metal is a purely chemical function.

2. It is a purely electric function, and depends upon the potential values obtainable on the various metals.

3. A summation of electrical and chemical influences occurs.

Elbs [2] defends the first view. He explains the aniline forrna-tion at lead and zinc cathodes in sulphuric-acid solution in the following manner:

" We will have to suppose that the lead sponge occurring at the lead cathode reduces the nitrobenzene to aniline. Mentioriable quantities of lead sulphate cannot be found, since this is continually reconverted to lead sponge by the freed hydrogen ions. This process is analogous to the one previously published "by me[3] in which a hydro-alcoholic solution of nitrobenzene acidified with sulphuric acid gives aniline when a zinc cathode is used. Considerable quantities of zinc sulphate do not occur. At a platinum cathode, under the same conditions, no aniline is formed, but azoxybenzene and hyclrazobenzene or benzidine form. This has been confirmed by Haussermann." [4]

The explanation attempted by Elbs agrees in general with

[1] D. R. P. No. 121900 (1899).
[2] Ztschr. f. Elektrochemie 2, 474 (1896).
[8] Chem. Ztg. 17, 209 (1893).
[4] Ibid., 129 (1893).

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lead cathode is primarily reduced almost exclusively to hyclroxylamine, which can only with great difficulty be changed elcctrolytically into ammonia. At copper electrodes ammonia exclusively is formed. Since nitric acid cannot be reduced to hydroxylamine to any appreciable extent chemically by copper, nor electrically at copper electrodes, Tafel supposes that an intermediate product is formed in the electrolysis of nitric acid; possibly dihydroxylamine Nil (OH) 2 possesses the property of being chemically reduced by copper to ammonia. Thus the reduction to hydroxylamine would be a purely electrical process, while the formation of ammonia at copper electrodes depends on a combination of electrical and chemical reductions.

Two important results can be derived from all these investigations: The certain insight into the course of the reduction of the single phases and the clear knowledge of the importance of the cathode potential.

Since the decisive relations have been worked "out with the simplest representative of a nitro-body, nitrobenzene, the necessary data on this substance will be discussed first, arid these data will be supplemented so far as necessary under the derivatives of nitrobenzene.

### *b. The Reduction of Nitrobenzene.*

#### I. Chemical Relations.

The course of electrical reduction, like that of purely chemical reduction, depends decisively upon whether the reduction is carried out in an alkaline or acid solution. But these relations are of a positive nature in electrolysis only so long as they are not compensated by the electrical factors, such as cathode material and potential. To avoid a complication, it is necessary to limit the considerations primarily to unattackable cathodes and to take no account of an adjustment to certain and constant cathode potentials, and to exclude a secondary interference of the solvent, for instance by molecular rearrangements. In.. this general comprehension of the problem it can be said that the weU-knawn chemical rule reoccurs in electrolytical reduction; viz., in acid solution the f«»nnati'»n of aniline ^ favored, in alkaline solution thai «<f axi»xy=- and ;*/."hfn/,»'n",

Lob / has. tried to explain these farts nn th«* ba.*-i- »*f the electrolytic dissoriat»on theory. He enij»ha.,-i/r-- f!t«- faet that in alkaline solution sodium inn-, in arid vuiuH'in hvdr«c»-n ions, lend chiefly tci efferf. reduction. In th«' biUrr »'a>»- ?hi»

i[ tion of hydra xo~ and nmido-cnjupout scale. Kven if these* considerations sit ion thai in alkaline elect rt»lyfe>. i; marily the reducing agent, are Hm; Bci^rii unsuitable as a ba-sis of a jr«*i because Ihiber has proved by th^i p!, in\ the typically alkaline reduc-fioii product,*, ;*/osy- nnd a/o- !>en%ene, possess a sec'ondary chanicter, -do not I*«IM.nj*; lo tlie normal coursr* of n*ac!ion. but are first fWiwd by the mn-d(»ns:iti(»ns of iifinjiul r**dnction phu-Ne^. Siiif* l!al*«»r lin^ also shown that, the primary reduction jirf«iiipf^ its alKalinr* and aci«l electn»lyfes art* flu* .suiiits the ilivergf^M*!*^ in tin* results ran be explained only by the rewtion veloci-ties with \vlilfli the iii!*!itiii!if*d f«iiiiif*ii«itiniiH ficrur, HI iliiit in this the influence of llie ion* shown itself.

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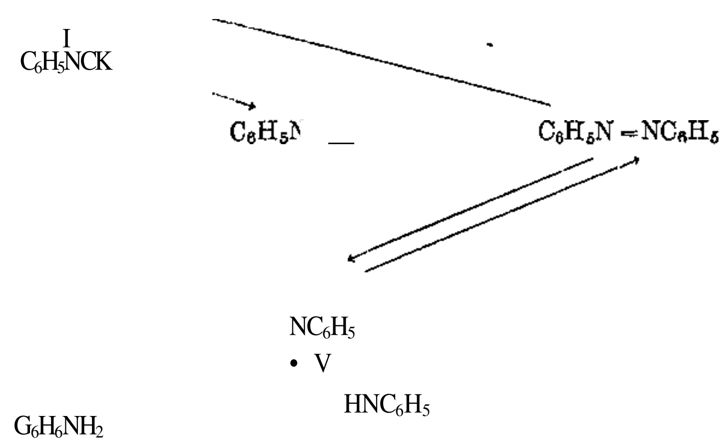
**ail HHWH;;** **f**

in the first instance the condensation of nitrosobenzene with phenylhydroxylamine to azoxybenzene, which is further reducible to hydrazobenzene; also the reaction of the hydrazobenzene thus produced with unchanged nitro- or nitrosobenzene to azobenzene, which is likewise a primary source of hydrazobenzene; then the rearrangement of the latter to benzidine, that of phenylhydroxylamine to amidophenol or its derivatives, and finally the .capability of phenylhydroxylamine to yield azobenzene in alcoholic-alkaline solution with the splitting off of water

The different processes occur in varying proportions quantitatively or qualitatively, depending upon the nature of the electrolyte and of the cathode material, and upon the current conditions.

The following reduction and reaction scheme can be given in support of Haber's descriptions for the electrolytic processes:




Azoxybenzene is therefore formed by condensation of nitrosobenzene and phenylhydroxylamine. This reaction, like the production of azobenzene, takes place very rapidly under the influence of sodium ions; the ready occurrence of both of these substances ia alkaline solution is thus easily explained. Azobenzene is mostly produced by a condensation of nitro-

A splitting off of water, especially in alcoholic-alkaline solution, readily converts phenylhydroxylamine into azobenzene:

$$2C_6H_5NHOH - 2H_2O = C_6H_5N = NC_6H_5.$$

Azobenzene, like azoxybenzene, can also pass into hydrazobenzene, and further to aniline. In acid solution the molecular rearrangements readily occur: Phenylhydroxylamine to amidophenol, and hydrazobenzene to benzidine and diphenyline. If the problem is to obtain certain reduction phases, the task will be to determine those conditions of experiment which will reduce as far as possible the velocity of all competing reactions. Thus, if we designate all processes which deviate from the straight reduction path nitrobenzene→nitrosobenzene→phenylhydroxylamine→aniline—as secondary condensations and secondary rearrangements, the following conditions will, for example, be presented as suitable for the preparation of aniline: Very high reduction velocity, combined with very low condensation velocity (avoidance of azoxybenzene and azobenzene) and very trifling rearrangement velocity (avoidance of amidophenol).

In like manner the conditions are to be varied according to the object in view: to obtain azoxybenzene the reduction velocity must be lowered, and the condensation velocity increased. The means by which we can accomplish at will this or that reaction will more accurately be explained under the individual reduction phases.

II. Significance **of** the Electrical Relations.

It is evident that the whole connection between experimental conditions and the obtainable reduction phase is regulated by the reaction velocities of the competing processes. The possibility of the formation of each reduction product is always present in the reduction of nitrobenzene; only those products, however, can become the principal products which are so rapidly produced that the other possible processes cannot find time to take place to any appreciable extent. Thus only aniline will be principally produced if the intermediately occurring phenylhydroxylamine is not rearranged more quickly than the reduction takes place. Inversely, to obtain arnidophenol, the rearrangement velocity must be so increased that the reduction velocity of phenylhydroxylamine will be trifling.

The point is to determine the factors upon which the velocity of reaction leading to the separate phases depends.

This question can be divided and simplified'. It is, therefore, apparent that a whole series of circumstances must be decisive. The nature of the cathode will regulate the actual reduction speed (p. 11 et seq.), either by furnishing the reducing ions, or by influencing catalytically the reaction between the discharged ions and the depolarizer; or by both injfluences making themselves felt simultaneously. The concentration of the acid influences the velocity of rearrangement, either of that of the phenylhydroxylamine or of the hydrazobenzene. The nature and concentration of the alkali, arid the presence or absence of alcohol, determines the velocity of the condensations or of the splitting off of water from phenylhydroxylamine, and these relations mutually permeate one another. If the problem can thus be subdivided into individual problems, it can also be considerably simplified by the form of the interrogation: Is there *one* factor in which all these relations are decisively expressed; is there one quantity which determines clearly the velocities of the possible reactions ?

The answer, under certain limitations, is an affirmative one. The value of the* cathode potential wholly includes all single[4] factors--a certain value of the cathode potential corresponds to a wholly certain reduction product, IP* matter if it occurs primarily or secondarily. To emphasize only th»' /////• important point -so long as a hotly acts as a depolarizer it arts codefenninnfivcly on the value of the potential. If its depolarizing propeily is destroyed hy rearrangements, or hv condensations which hart* iif^tliiiig to ilu ilin*<»ily with the clcc'lnra.! process, tjjis reaction must express itself in tin* vahi(» of tin* potential. Of <f*»urse a rertitin phasr rannof l>c» protluctMl tuiiier .ill rotiilitif»ns, for instaun*, nf optional concent rat ions of the electrolyte; tliis ^Jiown itsi-lf in tin* fact, that it in not then possible to ohfuin tin* jwttential conditioning this phas**- the potential always remain.** the fuea.^ lire for lite* possihle efffcf. However, these considerations an* only true provisionally in the C»M* \vhere the reialirm in which the potential stand* to the current strength «tiif1 to the concentration of flu* depolarizer is a l'*'riwiti**nt one, which can c\'isilv IK* fulfilled by a nuitahle clioicn* i»f f*ondif ions. Kxcej>tioim to the rule* and the of the excrptioiiH will I*c exl«lns!ii*(l preni'fitly,

I*HC* in iictf always uuule of I hi[1]- iifj{0*fUnit fuct in prai'fice; the existing chemical i*\piit'iief*;% th** ^irnpticttv <*f Ili»* e\j*»»riinents often render if le;»/i}»Jf to produce fit*- »l*'*tr»'d »1Ji*ct with certainty hy ohs«»rvinK a s<'rt«*< uf «^r4ly con>rnH«'«{ run*ditioni4 such as ciiiireiifrafitiii, teiuj»»Tatur**. *»!«»«*!r«^l>* ttmterial, and current di'tiHity hut Hiwe rfinfliiloii'/ the-n hav*» only the effect of liuiiting the {ififniliiil ft* tip* valuer wre^-siry for ohtitiniiig the n*Hu!f. lfk* flrfi*ritiifii*tsrtfi of this ri4ufi*iii required some tinii% and i*vf*u to-day flp* i*iiiiiti*rli««i lrfw»*fn potential and midioit vc»IcM?ity in mil rct'ogmmi liy ali iiivr*«"tigators*[1]

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Haber [1] deserves the credit of having determined the importance of the potential at unattackable cathodes in the reduction of nitrobenzene. Later Lob and Moore[2] experimentally proved for a whole series of cathode metals and additions that with equal cathode potentials the results are always qualitatively and quantitatively the same; but if the potential is neglected the most varied products result. But the potential is only a measure for the reduction energy if the total current work is essentially employed for the reduction process, and if greater quantities of it are not used up for accomplishing certain other work at the electrodes. Cases in which this occurs have been observed by Russ/[3] and by Haber and Iluss.[4] They tried to explain these, as touched upon in the first chapter. It appears, namely, that the electric energy necessary for a certain fixation of the potential of the cathode often depends not only upon the chemical material of the cathode, but also upon its surface and its previous treatment. Retarding or accelerating influences can occur at the electrode; a pre-polarization especially can convert it into an active labile condition, whose cause—perhaps the formation of a gas film absorbed by the electrode—has not yet been explained. If the renewal of such a gas film, or more generally speaking, the restoration of the changeable electrode conditions, demands appreciable quantities of the total work, the potential^ can no longer serve solely as an expression for the chemical changes at the cathode.

Lob arid Moore have experimentally proven the decisive importance of the potential in the reduction of nitrobenzene; the electrodes investigated by them were riot seriously affected

Elektrochcmie 10, 579 (1904). In reality it is a question of competitive reaction velocities which must find their expression in the potential.

[1] Ztschr. f. Elektrochemie 4, 511 (1898); Ztschr. f. phys. Chemie 32, 193 (1900).

[3] Ztschr. f. phys. Chemie 47, 418 (1904).

[3] Ibid. 44, 041 (1903).

* Ibid. 47, 257 (1904).

by the last-mentioned influences. The results of their investigation are the following:

In the reduction of nitrobenzene in a 2% aqueous sodium.-hydroxide solution, according to previous publications, azoxy—benzene is formed at platinum and nickel electrodes, azobenzeno at lead, tin, and zinc cathodes, and aniline at copper cathodes, especially in the presence of copper powder. It was found that, in an unchangeable experimental arrangement, a cathoclo potential of 1.8 volts, as measured in connection with the deed-normal electrode, could be carried out with all the chosen cathodes and additions. At this constant potential, by using different metals and adding various metallic hydroxides, the whole reduction was carried out and the nature and quantity of the reduction products determined in each case. It turned out that the emphasized differences in the results disappeared arid that, with an equal potential of all cathodes, similar yields of azoxybenzene and aniline and traces of azobenzene resulted. The cathodes were of platinum, copper, copper and • copper* powder, tin, platinum with addition of stannous hydroxide^ zinc, platinum with addition of zinc hydroxide, lead, platinum with addition of lead hydroxide, and nickel. The yields of azoxybenzene varied from 41-65%; of aniline 23-53%.

Considering the trifling quantity of the product started with which had to be chosen in order to at all carry out the experiments, and considering the difficulty with which **a,n** accurate quantitative separation and determination of tlxe reduction products could be carried out, the proposition thett can be laid down as a sure result of the above is that the *cathode potential -is the measure for the reduction energy for nitrobenzerz^ when a 2% sodium-hydroxide solution is employed as electrolyte.*

Another investigation may here be mentioned which™—chiefly carried out with nitro-bodies—contains ideas which become of general importance and can perhaps furnish a new* physicochemical method for determining constitutions.

Panchaud de Bottens[1] has determined the drop in potential

[1] Ztschr. f. Elektrochemie 8, 305, S32 (1902).

to which a hydrogen electrode is subject on the addition of bodies of the aromatic series. Tnese"" depolarizing values/' when, measured under exactly similar circumstances, are a function of the chemical nature of the depolarizer and are closely related to their composition and constitution. It might be of particular interest to choose an oxygen electrode in place of a hydrogen electrode, since perhaps all organic substances .show a depolarizing value when measured by the former. The results are tile-following:

The depolarization of a hydrogen electrode in the presence of a reducible body was investigated, fifty-three aromatic bodies being thus examined: Nitroso-, nitro- and nitrosamine-, isodiazo- and diazonium-bodies. The investigation of the depolarization was made by taking into consideration its course in time and in connection with the concentration.

1. The reduction energy of hydrogen at platinized platinum electrodes can be given in comparison with reducible bodies as " depolarization value " in volts.

2. Analogously constituted bodies have analogous depolarization values.

3. Different groups of depolarization values correspond to differently constituted groups of bodies.

4. The absolute valued of the classes of bodies investigated in acid solution ($^{n}/i$ $H_2SO_4$ or $^{n}/i$ $CH_3COOH$) are the following:

a. Nitroso-eompounds = 0.64 —0.5 volt,
*b.* Mononitro-compounds = 0.33 —0.23 volt,
*c.* Nitrosamines and isodiazohydrates = 0.16 -0.09 volt^
*d.* Diazoriium compounds = 0.47-0.37 volt,
*e.* Isodiazotates, normal diazo-compounds, do not depolarize.

5. Regular laws have not resulted in the case of isomera within a group.

6. In acid solution, in the case of isomers of nitro-disubstitution products, the ortho-position proved to be the one which depolarized the hydrogen electrode the most.

7. The method for the determination of the depolarization value shows in the case of the two investigated isodiazohydrates (isodiazobenzenehydrate and p-nitroisodiazobenzenehydrate) that they belong to the nitrosamines.

### III. Presentation of the Reduction Phases of Nitrobenzene.

An idea of the electrolytic behavior of nitrobenzene is best obtained by the use of the reduction scheme, by carrying out the experiments according to the chief products occurring in the reductions. For after the first observations of Kendall,[1] Elbs,[2] Hiiussermann,[3] and Lob,[4]—who all taught and showed the variety of obtainable products that it is possible to bring about electrolytically at almost every reduction stage—a desire predominated to find out the conditions which make possible and favor the preponderating formation of a certain substance. The primary reduction products are nitrosobenzene, phenylhydroxylamine and aniline. Secondary substances, i.e. those produced by chemical action, are azoxybenzene and azobenzene, which in turn can give hydrazobenzene or benzidine and aniline. Phenylhydroxylamine can pass into amidophenol and also undergo other rearrangements and condensations. The possibility of causing at will certain phases to yield the chief products of reduction is of great importance for the manufacturing and technical side of the electrolysis of nitrobenzene. The following is known concerning the formation of the separate reduction stages:

**Nitrosobenzene.**—It **is** natural that so good a depolarizer as nitrosobenzene is at the cathode cannot be separated as such under the conditions of a continuous reduction. Haber,[5] ,by adding a-naphthol and hydroxylamine to the electrolyte in alkaline solution, could, however, prove the presence of nitrosobenzene in the form of its characteristic condensation product,

[1] B. R. P No. 21131 (1883).
[2] Chem. Ztg. 17, 209 (1893).
[8] Ibid., 129, 209 (1893).
[4] Ztschr. f. Elektrochemie 3, 471 (1897).
[5] Ibid. 4, 511 (1898).

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the great reactivity of the body, which reactivity exposes it, •even during the electrolysis, to further reactions. In alkaline •solution it is chiefly the condensation of phenylhyclroxylamine with its predecessor in the reduction, nitrosobenzene, to azoxybenzene; or in alcoholic-alkaline solution the condensation of two molecules to azobenzene. In acid solution the rearrangement phenomena caused by the acids are chiefly important. Owing to the dependence of the rearrangement velocity upon the acid concentration, concentrated acids are best suited for the purpose. The nature of the acid is often decisive for the rearrangement products.

Amidophenol.—On reducing nitrobenzene in concentrated sulphuric acid, Noyes and Clement[1] obtained p-amidophenolsulphonic acid. Gattermann and Koppert,[2] by using nitrobenzenesulphonic acid in tolerably concentrated sulphuric acid, got p-amidophenol sulphate. Gattermann,[3] on varying the experimental conditions, also employing concentrated sulphuric acid, obtained para-amidophenol directly from nitrobenzene. He explains the latter's formation by assuming the intermediate production of phenylhyclroxylamine, which in further reduction rearranges itself into the end-product.

$$C_6H_5N0_2 4- 2H_2 = C_6H_6NHOH -1- H_20,$$
$$C_6H_6NH(OH) = NH_2C_6H_4OH.$$

Some o-amidophenol is formed besides the p-compound.

Chloraniline.—Lob [4] has found that p- arid o-chloraniline •are obtained by the electrolytic reduction of nitrobenzene suspended in fuming hydrochloric acid, nitrobenzene dissolved in alcoholic hydrochloric acid, and nitrobenzene dissolved in mixtures of hydrochloric and acetic acids. With hydrobromic acid the corresponding *bromanilines* are formed.

[1] Ber. d. deutsch. chem. Gesellsch. **26,** 990 (1893).
*Chem. Ztg. 17, 210 (1893).
[8] Ber. d. d&itsch. chem. Gesellsch. **26,** 1844 (1893).
[4] Ztschr. f. Elektrochemie 8, 46 (1896); Ber. d. deutsch. chem. Gesellsch. 29, 1894 (1896).

The reaction takes place as shown in the following equations:

2. CeHsNHOH + HCl-CeHsNHCl + HaO.

3. $C_6H_5NHC1={}^{0}3C1C_6H4NH2$.

The phenylchloramine formed by the action of hydrochloric acid on phenylhydroxylamine changes by molecular rearrangement into o- and p-chloraniline.

Condensation Products with Aldehydes. — Gattermann[1] has obtained direct proof of the intermediate formation of phenylhydroxylamine in the preparation of amidophenol by adding benzaldehyde to the solution at the beginning of the electrolysis. He was thus able to isolate a condensation product of phenylhydroxylamine with benzaldehyde. In this way he obtained from nitrobenzene *benzyUdene-phenylhydroxylamine,*

The presence of formaldehyde in the eleptrolytic reduction of nitre-compounds produces an effect entirely different from that caused by the addition of benzaldehyde. The phenomena occurring in this case have been thoroughly investigated by Lob.[2]

The fundamental object of his researches differs from that of Gattermann, in that Lob undertakes to establish the separate phases of the reduction of the nitro-group. * This he accomplishes by the addition of formaldehyde to the electrolyte under varying conditions, and as a result the intermediate products, at the moment of their formation, combine with formaldehyde, producing condensation compounds which do not undergo further decomposition. By regulating the potential or density of the current the reaction can at

[1] Ber. d. deutsch. chem. Gesellsch. **29,.** 3040 (1896).
[2] Ztschr. 1 Elektrochemie 4, 428 (1898).

will be checked at a perfectly definite phase ol tion.

In the electrolysis of nitrobenzene by this in were formed:

1. *p-Anhydrohydroxylaminebenzyl alcohol,*

$$CH_3OH$$

which may also be directly prepared by the ac* maldehyde on phenylhydroxylamine.

2. Methylenedi-p-anhydroamidobenzyl alcohol,

a reaction product of formaldehyde and aniline.

3. Anhydro-p-amidobenzyl alcohol,[1]

$$\left[ C_6H_4 < \begin{matrix} CH_2 \\ | \\ NH \end{matrix} \right]$$

which can be likewise obtained by the action of fn upon aniline.

Azoxybenzene.—This substance was recognized ago in the investigations of Elbs;[2] Haussermann,[3] IS as one of the reduction products occurring both and alkaline electrolytic reduction of nltrohc*rix berger and Haber then explained its format ion I densation of phenylhydroxylamine and nitroHobmz by electrolyzing nitrobenzene suspended **in** clilii alkaline or alkaline-salt solutions at unattaekabl

[1] Ber. d. deutsch chem. Gesellsch. 81, 2037 (1898).
[2] Chem. Ztg. 17,209 (1893).
[3] Ibid., 129 (1893).
*D. R. P; No. 79731 (1894).
[8] Ztschr. f. Elektrochemie 7, 335 (1900); Ztschr. f. phy»v C (1900).

(platinum, nickel, mercury), succeeded in finding a method which gives a good material- and current-yield of azoxybenzene almost free from other reduction products. In this case the unattackable cathode plays a leading part, aside from the use of aqueous electrolytes. The choice of attackable cathodes modifies the process very considerably, the nature of the metal producing individual effects.

Azobenzene. — Alcoholic-alkaline solutions act differently from aqueous-alkaline electrolytes. Even if unattackable electrodes are employed with the former, the process can be regulated so as to give very good yields of azobenzene. This was demonstrated by Elbs and Kopp.[1] Two concurrent processes determine presumably the azobenzene formation, firstly, the splitting off of water from two molecules of phenylhydroxylamine produced by the influence of the alcoholic-alkaline solution; secondly, the reaction of hydrazobenzene (resulting from the azoxyberizene formed secondarily) with unchanged nitrobenzene or nitrosobenzene. That the latter reaction occurs is shown by the fact that, if the electrolysis is prematurely interrupted, azoxyberizene and azobenzene and hydrazobenzene are always present. When alcoholic electrolytes were employed It proved advantageous to substitute for the free alkali sodium acetate which, on account of its easy solubility in alcohol, its good conductivity and trifling action on the diaphragm, possesses considerable advantages over sodium hydroxide. These processes are not technically valuable on account of the employment of alcohol.

Bayer & Co.[2] seek to avoid this latter inconvenience by reducing nitrobenzene, suspended in aqueous alkaline or alkali-salt solutions, in the presence of such metallic cathodes, or the addition of such metallic salts, whose oxides are soluble in caustic alkali,—for instance lead, zinc, tin, or their salts. The yields of azobenzene obtained by this method are said to be

[1] Ztschr. f. Elektrochemie 5, 108 (1898); D. R. P. No. 100233, 100234 (1898).

[2] D. R. P. No. 121899 and 121900 (1899).

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theory azobenzene is a condensation product of hydrazobenzene and nitre- or nitrosobenzene.

Benzidine.—That nitrobenzene, by electrolytical reduction in acid solution, can directly yield benzidine, was first proved by Hiiussermann,[1] who used sulphuric acid. Lob [2] later proved the same to be true for hydrochloric-, acetic-, and formic-acid electrolytes. However, several reactions predominate in this direct acid reduction, which prevent the carrying out of the reaction up to hydrazobenzene, or the formation of benzidine. Phcnylhydroxylamine may particularly be mentioned in this connection. In alcoholic-acid solution it is partly rearranged to amidophenol or its ethers, and partly reduced to aniline. Azoxybenzene, in acid solution, is the starting-point in the benzidine formation; however, in this case, the combining velocity of nitrosobenzene and phenylhydroxylamine is not very great, so that the latter is to a very considerable extent subject to the more rapidly acting influence of the acid.

Besides azoxybenzene, azobenzene also gives hydrazobenzene, as already mentioned, e.g. in acid solution benzidine results. Azobenzene, however, is formed only in very small quantity.

Lob,[3] convinced of the futility of thus being able to obtain a good yield of benzidine by a direct reduction of nitrobenzene in acid solution, sought to carry out the benzidine process by a careful realization of the conditions theoretically required—primary preparation of azoxy- or azobenzene in the best quantitative yields, i.e. in electrolytes, containing alkali or alkali-salt, then reducing thfese products in acid solution. Two processes / thus resulted. In the first one the electrolytic reduction was carried out to azobenzene in alcoholic-alkaline solution, then the cathode solution was acidified with sulphuric acid, and the further reduction and molecular rearrangement combined in one operation. The second process, which was

* Chem. 2Jtg. 77, 108 (1893).

[2] Ztschr. f. Elektrochemie S, 471 (1897); Ber. d. deutsch. chem. Gesellsch. **29,** 1894 (1896).

[8] £tschr. 1 Elektrochemie 7, 320, 333, 597 (1900-1901).

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later Elbs and Silberjnann [1] also obtained 90 per cent of the theoretical yield of aniline with the aid of a lead cathode.

We are indebted to C. F. Boehringer & Sohne[2] for the comprehensive exploitation of the influence of cathode material in the preparation of aniline. They have patented the results of their experiments. The importance of the decisive conditions of the experiments, as in those of Elbs and Silbermann and of Lob, lies in the increase of the reduction velocity of phcnylhydroxylaminc to aniline, so that competing rearrangement and condensation reactions are given no time to occur. Almost quantitative yields of aniline are obtained. The nature of the process consists in reducing the nitrobenzene in acid solution, or suspension, *by* means of indifferent electrodes and with the addition of a tin, copper, iron, chromium, lead, or mercury salt, or the corresponding metal in a finely divided state.

The metal employed, or the corresponding degree of quantivalence of the metal ion, is regenerated by the current, depending upon the greater or less electrolytic ismotic pressure of the metal. Cathodes of tin can also be employed instead of the tin salt.

It may be mentioned incidentally, that according to investigations by Holier[3] a strong odor of phenylisocyanide, CeHsN —C, occurs in the electrolysis of nitrobenzene in alcoholic-alkaline solution and without a diaphragm. But a separation of the carbylairiine could not be made. Homologues of nitrobenzene, when electrolyzed under analogous conditions, also yield isonitrile.

### *c. Substitution Products of Nitrobenzene.*

#### *I.* General Laws governing Substitution.

The reduction scheme sketched by Haber for the reduction of nitrobenzene also holds true for the substitution products of nitrobenzene in so far as the formation of their reduction phases can be coordinated to the same reduction, condensation, or molecular rearrangement processes. But the decisive influ-

[1] Ztschr. f. Elektrochemie 7, 589 (1901).
*D. R. P. No. 116942 (1899); 117007 (1900).
*Ztschr. f. Elektrochemie 5, 463 (1898).

once of (he subsf itucnts manifests it-elf in varioir. H;IV1% ff} the first place, the experimental condition.- deirnuined f<*r tin* preparation of certain reduction stag's of ni!roln-n/»'ij»- tin nut obtain for Its derivatives, at fi*ast nnly in a liiiiif^-u imnn'-r. The position and nature of the HtlHif tsnif "-• al-» <>n»Mi hindir the preparation of single phases, In nihi-r \\nriix; ib* r»'ar-

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Nevertheless .[v]t»ine reacti<ije- are known which pn*"=**«>.M ;i certitiii general applicability. *I*hi[v]* i[1]" tru«* »*s ^iiiff^rujiiiiir;- reduction in concentrated sulphuric acid, whii'li iiivr"- ino>-!ly nniidoj)h(*nols, if the ortho- or para-pt>siti«iu i-, unnci*upiiM|, Only [i-nilrotoliieiif* and the nitroaldehydeH form «*\rt[4]jf!i«.ii$'% whicli will lie dixMjsse*!.

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**to the :**

**NO**

**XII**

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Since the tendency to form quinone derivatives is lacking in m-nitraniline, the nitroso- and hydroxylamine phase can unite normally to the. azo-body.

For the same reason perhaps the exclusive formation of o- arid p-amidophenol occurs:

/NO JSTOE

CTT / vr* TT&

gJuL4< —> V^gll^A

/NHOH .NOH

or $C_6H_4$<; ^$C_6H_4$^ +$H_20$.

\OH %Q

These quinone derivatives, by further reduction, can produce only amidophenols. If the quinone formation is prevented from taking place, for instance by esterifying the hydroxyl-group, the normal reaction to azoxy-bodies occurs, o- and p-Nitroanisol pass smoothly into azoxy- or azo-derivatives. The acylizing of the arnido-group in the case of o- and p-nitroamines hinders likewise the quinone, and, therewith the arnine, formation. The azoxy-body is smoothly formed, thus:

'NO HOHN\r

X^OCeHs '

CoHs

$C_6H_5$CCK

But the alkylization does not prevent the formation of quinone and therefore the reduction to the amido-phase:

/NO

$C_6H_4$<

\$NHC_6H_5$

/NHOH

or $C_8H$< -^$C_6H_4$C +$H_2O$.

\$NHC_6H_5$ $^X NC_6H_5$

Elbs sums up in the following manner the rules which apply to the electrochemical reduction of aromatic mononitro-bodies in alkaline solution. Hereby it must be taken into consideration that the primarily formed azoxy-body, under the conditions chosen by Elbs, leads to the azo-body.

1. Nitrobenzene and its homologues give azo-bodies; amines do not occur, or only in traces.

2. Halogenized nitrobenzenes and their homologues yield azo-compounds; difficulties occasionally occurring are caused by the alkaline cathode fluid attacking the halogen made mobile by the nitro-group, or inversely the nitro-group made mobile by several halogen atoms.

3. Mtrobenzene-m-sulphonic acid and its homologues give azo-bodies.

4. Mtrobenzenecarboxylic acids yield azo-compounds, but only the o-acids behave differently.[1]

5. m- and p-Nitroacid-nitriles yield azo-bodies, with or without a partial saponification, depending upon the conditions of the experiment.

6. m-Nitraniline and its homologues give azo-bodies, but o-and p-nitraniline and its homologues, on the contrary, give diamines.

The same rule obtains for the secondary and tertiary amines derived from the three nitranilines.

7. Acylized nitranilines (acidnitroamides) and their homologues give azo-bodies, no matter which position the nitro-group occupies in regard to the acylized amido-group. The cathode fluid must be kept approximately neutral during reduction, otherwise the acid amides are saponified if the solution becomes considerably alkaline.

8. o- and p-Nitrophenols give amidophenols.

9. Nitrophenol ethers give azo-bodies, no matter what position the nitro-group occupies.

These rules do not hold true for dinitro-bodies.

The experiences gained in the electrolysis of nitrobenzene concerning the influences of the cathode material have also obtained in great measure, with the substituted nitrohydrocarbons. The general result can be summed up in the statement that at unattackable cathodes, such as platinum, nickel,

[1] Lob, Ztschr. f. Elektrochemie 2, 532 (1896).

T



and mercury, in aqueous-alkaline solution azoxy-bodies[1] are produced, and at attackable cathodes, such as lead or copper, azo-, hydrazo-,[2] and even amido-compounds are formed. The latter are obtained by the method of C. F. Bohringer & Sohne,[3] using a copper cathode, or an unattackable cathode with addition of copper powder. o-Toluidine, m-phenylenediamine from m-nitraniline, and a-naphthylamine, in addition to aniline, were prepared in good yields by this method.

In alcoholic solution this difference does not occur so distinctly; it is also easy to reduce to the hydrazo-phase at unattackable electrodes.

The influence of the cathode' metal is much more manifest when acid electrolytes are employed than in alkaline reduction. In alkaline solution at copper electrodes, if we except the last-mentioned process, the rapidly occurring condensation of the first reduction phases—of the nitroso- and hydroxylamine body—always leads immediately to the azoxy-body and makes this appear to be the typical product of the alkaline reduction, which can in turn be further reduced. In acid solution this condensation takes place so slowly that the molecular rearrangement of the hydroxylamine and its further reduction to amine has time to take place alongside the formation of the azoxy-bocly and the reduction of the latter to the hydrozo-compound or benzidine.[4]

The increased reactivity of the whole molecule or single groups, which is often associated with the entrance of nitro-groups, is also apparent in the capability of some nitro-bodies to be relatively easily oxidized. The little that is known is appended to the description of the behavior of the individual members. The characteristic features of the oxidation processes in question have been explained in the first chapter (p. 27 et seq.)-

[1] Ztschr. f. Elektrochemie 7, 335 (1900).
[2] D. R. P. No. 121899 and 121900 (1899).
[8] D. R. P. No. 130742 (1901).
[4] Cf. Haussermann, Chem. Ztg. 17, 209 (1893).

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FJectrolyxed in alcoholic-alkaline solution, according to thi* directions of Klbs, in-ascot oluenc is almost quantitatively produced; the further current' action gives ni-hydniHololuene (Holtde[1]).

hub and Schwitt- electrolysed jn-nitro(oluene in alkaline-aqueous susjrt'iision. employing various cathode* metals in order to determine their influence. The other conditions of the experiments were the* same. w-Axoxytoluene, which is to* a small extent converted info hydrascofoluene, and m-toluidine an* produced. The yields vary, depending upon the nat.ure of the eathod**: the reduction was weakest at nickel cathodes, i.e., il hardly passed beyond flu* axoxy-pha.se; aJ. xinc, copl»cr$_t$ aiul cop)XT in the presence «if <-(»p|HT powder, I lie yield of nmlne incn*ases in the given series of the metals, while that of ascoxytoiuene decreases. The following table shows these relations. Five grams m-nitrotoiucne gave:

| | | | |
|---|---|---|---|
| **Nirki-i.** | | | |
| Kiitr, . | 2. *V2* | | I.lfi |
| | I.3H | II 1 | I.f»K |

Pif*rrc»ii»[:i] by oxi<ii?Jtig electrolytU'ully m-nitrotoliu*ne under the* ronditioriH *4*lvmm* for flu* o-iitlrotci!«i»ne$_f$ obtained about 20 JKT conf. ni-nitrolx*fixal(lf*hyfl(*.

p-NItrot01tt«Be-•••—• In «lilutf» milpliurlcHicid Holutiou, HUUHHIT-nutnn[4] cilitniiied {>tninifliiii* IIH th« chief product; Ciutfer-iiiitiiti Kop{nTt,* by refiiicing in concentrated Huijihuric

p. f, K!f*ltr*r!ti'r«i^I$_f$ 322

[§]Ili*f» 4 **flout** !i$_4$ 20, 2S1CI CmilS); I). It 1», No.

fcftf *| **J

f.iiififl S**X *«! 'If '<le

'fJSfj 'fl|S *|^|p«*»f) im»jj tf«jte|ts4ft p M;*tf |

r1Lf

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^fJ^I {f1.111

jMlli *ttl|iff!jfi| <| Jil faUjWIJll li«l||t:HU.t|MtCM If JHW OHIp

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JO *llfllllfli'lj!j«l *UtUI *p1Mj M»xMoi> 'ill)

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of p,)p[H! SI

l.U1J

*liniLioj .if|| ShiiAi'n pin?

SI

OZI

The excess of formaldehyde present in the Iiqui<l a^ain acts on the tnluidine, so that ;i mixture of dimet hylioluidine and trintej hylehetritoluidine results.

In alcoholic-alkaline Dilution Klbs,[1] Klbs and Knpp,[2] a.nd Lob [:l] obtained p-azof oluenc. If the elect rolvsis is prematurely interrupted, the electrolyte contains large quantities of p-a/o\ytolu«'jjc; on prolonged electrolysis p-hydra/*(»t<)Itu»n<* is quantitatively prod wed, areording to the prongs of Mlhs.

Ldli and Srhinitf [J] invest i^a.fed f!ie, behavior of p-nitro-foliii'ne in alkaline-aqitfotis suspen.sior» at di(Ter<»nt. <'a.thodes. The result is similar to that obtained in (lie ra.se of m»ni(n> toluene, hut f!i«' azoxy-body was always coiitaiiiinated with ,«onie a/*(M'ciiiipf*und. Five grains p-nif.rofoluenc* following:

| | Vi»*M in | Tnlui/liw, |
|---|---|---|
| Zinc*, ,, | 2, IIII | 0,c»7 |
| < V f|»f !!T, nfi*I | 3UO | C). HH |
| | !, 70 | |

If the I'jirreiit yieidn ribfriiiied under Miiiiilitr (jonditioiiH from in- and p»iiifrot«iliiei«f» lire fompiired with one* another, it is found thai i1r f^eoinpoiiiid H iiion* ca.siiy reduetble than the m-liod, Tin* ifiiitrnee nf the po/itioii of lite methyl group **thus** in mui both in the flieiniral teHitlt and tho reHiHtanai! ri*fliii[f]ing ag^fifa

/ by eli HI ruly tlrully *imldhm*^ f)-nitrotoltic*rM» in it of rciin»nfr:«feii iiN*fr and «i!phutic *iwuln* at a large* platinum HIKII!I% rditnintntl {^iiilroliitii^yl alcohol,— ^urnait yield Md 41) |ii*r cc*nt,

/,!«. 17, am MH»3); /44rbr f, F4
f Kl<4frirlii*iiii«4 I If)

[4] ItrnL 10, 7M flfK
[1] liiwi g» r*^2

If the electrolysis is carried out in 80% sulphuric acid, "both p-nitrobenzaldehycle and the alcohol are obtained (Labhardt and Zschoche [x]).

C. F. Boehringer &*S6hne[2] add 0.1 part by weight per litre of manganese sulphate to the anode electrolyte,—a mixture of sulphuric and acetic acids,—and obtain smoothly p-nitrobenzoic acid at a lead-peroxide anode.

### NITROXYLENES.

Nitro-p-xylene, reduced in concentrated sulphuric acid, gives the corresponding amidoxylenol (Gattermann and Heider[3]):

$$C_6H_2; \begin{array}{ll} CH_8 & (1) \\ 'NH_2 & (2) \\ CHa & (4) \\ OH & (5) \end{array}$$

Gattermann,[4] by adding benzaldehyde during the reduction, obtained the benzylidene-derivative

$$(CH_3)2C_6H_3N \text{ -CECeEg.}$$
$$\backslash O /$$

p-Nitro-o-xylene was reduced by Elbs and Kopp[6] in alcoholic alkaline solution with addition of sodium acetate. They obtained good yields of azoxy-, azo- and hydrazoxylene.

p-Mtro-m-xylene, when treated similarly gives analogous products.[6]

Elbs and his pupils[6] obtained in the same manner the corresponding azoxy-, azo- and hydrazo-bodies from *o-nitrobenzylqniUne, p-nitrobenzylaniline, nitrotolylaminophenylmethane,* NH2CeH4CH2 • C6H3CHsN02, and *m-nitroleucomalachite green* [(CEaJaNCGE^CE-06^^62; but the last-mentioned substance was not reduced to the azo-phase.

[1] Ztschr. f. Elektrochemie 8, 93 (1902).
[2] D. R. P. No. 117129 (1900).
[8] Ber. d. deutsch. chem. Gesellsch. 27,1930 (1894).
[4] Ibid. **29,** 3040 (1896).
[5] Ztschr. f. Elektrochemie 5, 110 (1898).
[8] Ibid. 7, 136 (1900).

m-Dinitrobenzene, on reduction in concentrated sulphuric acid, is converted into o-p-diamidophenol (Gattermann and Abresch [1]).

o-p-Dinitrotoluene (2.4) is analogously reduced to 2.4.5-diamidocresoL Sachs and Kempf[2] oxidized this substance electrolytically in sulphuric acid solution at a lead anode and obtained a medium *yield* dinitrobenzoic acid.

*2 - 4-* 6-Trinitrotoluene gives analogously trinitrobenzoic acid.

p-Dinitrostilbene. While carrying out some experiments on the dye "'sun yellow/[7] which is obtained by warming p-nitrotoluenesulphonic acid with sodium hydroxide, Elbs and Kremann[3] worked on the etectrochemical reduction of several stilbene derivatives.

They obtained the following results: *p-Dinitrostilbene,* reduced in alkaline solution, gives p-azoxystilbene; in hydrochloric-acid solution with addition of stannous chloride (method of C. F. Boehringer & Sohne), p-diaminostilbene.

o-Mtrodiphenyl and *p-nitrodiphenyl* in alkaline electrolytes give the azoxy-derivativos (Elbs); p-nitrodiphenyl also gives inconsiderable quantities of p-amidodiphenyl, while in alcoholic-sulphuric acid at platinum and lead cathodes it is easily reduced to p-amidodiphenyl (Fichtc and Sulzberger [4]).

2.2-Dinitrodiphenyl was reduced by Wohlfahrt;[5] in accordance with Elb's process, and gave a very good yield of phenazone, while in hydrochloric-acid electrolyte with the addition of stannous chloride hydrophenazone hydrochloride was formed.

/N«N-

The method of Wohlfahrt has been extended by Ullniann and Dieterle [6] to several o-dinitrodiphenyl derivatives. The

[1] Ber. d. deutsch. chem. Gesellsch. 26, 1848 (1893).
[2] Ibid. **35,** 2712 (1902).
[8] Ztschr. 1 Elektrochemie 9, 416 (1903).
[4] Ber. d. deutsch. chem. Gesellsch. **37,** 881 (1904).
[6] Journ. f. prakt. Chem. [2] 65, 295 (1902).
[8] Ber. d. deutsch. chem. Gesellsch. **37,** 23 (1904).

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(2,5)nitrobenzene (by-products: p-dichloraniline and chloraminophenol ($ClOHC_6H_3NH_2$, o-bromnitrobenzene, m-brom-
5 2 1
nitrobenzene, p-bromnitrobenzene, m-iodonitrobenzene, p-iodonitrobenzene, o-chlor-m-nitrotoluene (by-products: o-chlor-m-toluidine), o-chlor-p-nitrotoluene, p-chlor-o-nitrotoluene, p-chlor-m-nitrotoluene (by-products: o-chlor-m-toluidine and o-amino-m-cresol).

Gattermann's reaction also proceeds smoothly with the halogen derivatives, if the para-position to the nitro-group is not occupied.

p-Chlornitrobenzene, on account of the mobility of its chlorine atom, is converted in concentrated sulphuric acid into p-amidophenol (Noyes and Dorrance [1]).

m-Bromnitrobenzene gave a good yield of bromamidophenol (Gattermann and Heider[2]).

p-Brom-o-nitrotoluene gives the bromamidocresol.

CD
NH$_2$ (2),
(4)'
^Br (5)
\OH

p-Brom-m-nitrotoluene yields analogously the bromamido-cresol.

/CH$_3$ (1)
$C_6H_2$/>NH$_2$ (3)
<Br (4)'
\OH (6)

IV. Nitrophenols.

o-Nitrophenol, reduced electrolytically, gives a good yield of o-amidophenol both in alkaline-aqueous solution at platinum cathodes (Lob[3]) and in alcoholic potassium-hydroxide solution at lead or mercury cathodes (Elbs [4]).

*o~Nitroanisol,* electrolyzed under the same conditions as

[1] Ber. d. deutsch. chem. Gesellsch. 28, 2349 (1895).
[2] Ibid. 27,1931 (1894).
[3] Ztschr. f. Elektrochemie 2, 533 (1896).
[4] Jouna. f. prakt. Chemie. **43,** 39 (1891).

mentioned under o-nitrophenol, gives o-azoxyanisol, o-azoanisol, and o-hydrazoanisol (Häussermann,[1] Elbs and Rohde[2]). It differs, therefore, from the above compound in this respect. *o-Nitrophenetol* behaves similarly.

**m-Nitrophenol,** on being reduced, does not afford an opportunity for the quinone formation, and gives, hence, in alkaline solution m-azophenol. In alcoholic-sulphuric acid solution and at a lead cathode it is reduced to m-amidophenolsulphonic acid (Klappert[3]).

**p-Nitrophenol** behaves like the ortho-compound. According to Elbs,[4] a good yield of p-amidophenol is produced in alkaline solution. Its ethers *p-nitroanisol* and *p-nitrophenetol* behave normally; they give chiefly the azoxy-derivatives, also some p-anisidine and phenetidine respectively.

Intermediate phases of the reduction can be separated in the case of o- and p-nitrophenol, if a concentrated solution of aniline hydrochl[illegible] is used as electrolyte (Löb[5]). Compli-cated condensati[illegible] products are obtained. It seems that the nitrosophenols pr[illegible]rily formed react in the form of quinone-oximes with an[illegible]

p-Nitrophen[illegible] us gives as principal prod[illegible] et dianilido-[illegible]nce which is also produced [illegible]n the reduc-[illegible]l, besides a blue induline-[illegible]ke dyestuff. [illegible] reaction has not yet been [illegible]plained. [illegible] on reduction in alcoholic-alk[illegible] line solution, [illegible]nol (Elbs[6]).

**Nrriioi'itKNYi,** KTHKHH,

Heveral representatives of this class of compounds wore investigated as to their behavior in alkaline reduction (llaus-sermarm and Schmidt [l]). These* Investigators confirmed the rules which Klb established for nitrophenyl ethers.

o-Nitrophenyl ether, p-Nitrophenyl ether are smoothly converted intu axoxyphenyl ethers.

p-Nitrophenyl-p-tolyl ether gives similarly the p-uHoxy-j»hi*nyl"p-t ol\ 1 ft her.

Hydroxyquinone-p-nitrodiphenyl ether yields p~a,%oxydiphenyl filler,

p-An»iriophenyl p-tolyl eiher is smoothly formed from p-nitrophenyl-p-tolyl ether in hydnrhloric-acid susp(»nsiou with a till cutlioiir,

V. Nitraniiines.

o-NitraniIine$_f$ when electrolysed in alkaline solution (Klhs and Holide [2]i yieldn sniootlily o-phenyl<[i]H*diamin<^ wltilc[4] the iiiti'nn«*<liat«*ly refiirriug nitroso- or hydroxyl'imine-phasc*^ similar to tlm^* in the jKsrries, readily rearrange* th(»jtus(;lvc»H into ijiiiiiioin* *ii*rivativeH,

m-Kilraniilne lK*lmvi*H dtflwfttly, Tliis Hiibstttriw, by c»l<»c-trol\>i>* in mi alkaline elertrolytr, given a good yield of m-ciiam-inoii/tiib'iixeiif* i'KlbM ami Kopp,[i] and Lclh [''J])$_f$ also u little u^oxy-eompfiiitpl rind true* M of in-plienvlenedhmine. TIu* rc*dtjciion can al.-o Hi* <*;»rrietl of it to the hvinixo-IiaHi*, jrn-Nitranilinc?

Koh<le [n] Jri^ tnvesfigatnl the inlhienn* of methyl groupn in flu* :tini«i^-|(roiip> in alkit lini* redt

or the }iviln»7,o»body. [7] reduced it in

[1] fii r ft ih'titwh. rlwtti. Omillsc'li, 91, 87<W (IfKli),
[?]7f^iir f, Mi*ktroc*lt«tmi«f 7$_t$ H-l, 3-111 (HKK)).
[1] ibiii, r». mi
* lliiil -!S
» |«JT «l d«'Ul'<rh rliHti, (^^*H»u*h S!B, IH-IO
f, Eli4f twfififilf* 7$_t$ 32K$_f$ :i;iK (1IMKI)
f, iiiiic«iw$_t$ rinitii* 107 CtHltf).

mitrafnl xulpliurir *nn*l* ami thus r-Miiv»T!i'.| if into i.^.j. dhiiHliyl tlininiiinplirnol.

///-A *itrtMHlitttt'tlif/ltrnlttiir* ran !»• ronvrrtrpl l,v f ;.;j fsT. murm's prnn-ss into iu-|»-.|ini'*Hjyl.|i:ijni.!..|.i»,-j,Ml • Ahiv-.-,.^r

*ut-Xilfuwvtlttliinrlinr* MKIY»'S lik»- fa- itif r^im^li* !;,M]in».. If is convert p« I in alk;tliii(M-Jir!rolyti<y in?o«liHi.-f!,>] jn-Ii.-unH^ axolK'iixrni*, nr -Iiyilra/olM-n/i'iji*.

p-Nitranilinc, l»y rpiliiriiiijj in rniiri.i,fr;if.-il MjlphuH,. ;,ri,|. yii'lii an ajiiiilfijilniin! |*.r;iisr tin- ji- j,.,^ij i,,u J, i^rujli.-il' yc's ami Domtiic'i^ mint,,! it ,,, j^Jirtiiiiilnl-M,/.-,^1 ,^ JH roil

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Th<* Irliaviiir of *fi-AHnHwnlww* riunv inrMmtally Ir **IIW^ltiiilifMi hiTf. Tills *ui*taiin. |,y fli-rtriJv^H ill ari«| s-ululjr,,,** with a iin mtlioii,% **or** mlttitifj!, of ^aiiiiMiiMri,l,,rii|i.. J, . , , f ,

of

in alkaliii- «*liitif foriiiaiinn fr«m,

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*nil*

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*Hinc,* by elect rolytical reduction in concentrated sulphuric and, is converted into the important inter-inedint f product of dycst tiff manufacture, p-aniido-ni-oxy-diethylaaiiinc.

Col I/ -OH

[1] gives the name compound.

lln* nitrotolwdinrs \vh«»n rc'du<$(»d (»l(»ctrolytically in acid and alkaline solution lH»hav<[i] like* th<* nitranilincs. The position. of th«( in*'thyl gr«mp inuHt, of rour.so, bc» bonu* in inind.

**p~Nitro-o-toluidine is** ^onvortcul by Gutt(*nimnirs proccBS[2] into <iiaiuid(»W'i-'ol:

NHa (2) i $U_2$- r / Nil- (2) **'Hta:-. NHs (4) NOH (f,).

lii this r:i*' tin* hyclroxyl group occupioH the o-position in n*HjH'H. to iti*[4] tirlginal nltro-grcntp,

hi ulkalitH* rffinrtloit {»4oliiyk*iic»cliniiilnf! is produced (Klbn).[3]

o-Nitro-p-toiuidina in Hiilpliuric*. acid solution givtw tlic «ikfiiif!«>pri'*Hol IIH f.>-nitr<H)-toh.ad5m>, tho liydroxyl group

I IP* pnni-pfwition to tin* original nitro-group,

lip* I'lfftrical mlfidiwi in an alkaline* clootrolyto leads to !i yii*!«l of o-toIuyh»nf*(Jiamino. If tho n*<luction is carru**! out in nolutiort, *m-nitro~p~toluidine* arid *rn*witro-* iiili>M% «j* |K« Hup|xifl(!(i, are eonvc»rted **into** assoxy-,

**hyilra2ltH*onil'HMHl«lH.**

m-NItrodto«t%I-p-t01iiidift0 **dimcithylbenzimidazolo (Pinnow [4])**

[1] I), 1C F S%>, HHI2JJ
* Il*«r 4 dtfiitxrti cl»r»iii CJiw*Il^Ii» ill, IH/K) (IK03).
[1] f, ElAtrfii*liiwili^ **7, 14JJ (HKKI).**
* **Jwurn.** f, **«,** S« (WIl); **Oft** **570** (1902).

$CH_3$

N

N-CH
$CH_3$

and dimethyltoluylenediamine. The reaction is carried out in Lob's short-circuit cell (p. 50). An addition of graphite powder accelerates the reaction, which probably is mainly caused by the intermediately occurring nitroso-compound splitting off water, and thus yielding the diinethylbenzimidazole,

-
\N($CH_3$)

-N

N-CH
$CH_3$

m-Nitrodimethyl-o-toluidine. — This substance, reduced in alkaline electrolytes, gives tetramethyl-m-dituaido-p-azotoluene.

andtetramethyl-m-diarnido-p-hydrazotoluene.

VI. Nitro-derivatives of Biphenylamine and Amidotripheny 1m ethane.

p-Nitrodiphenylamine, by reduction in alcoholic-alkaline solution according to Elbs[7] method, gives a good yidd of p-aniido-diphenylamine (Rohde[1]); the primary production of quirione probably prevents the formation of the azoxy-compound :

/$NO_2$ NHOH .NH

NH— $C_6H_6$ —$C_6H_4$

$NH_2$

$NHC_6H_5$

Benzoyl-p-nitrodiphenylamine cannot yield a qiuaonedi-

[1] Ztschr, f. Elektroehemie 7, 320 (1900).

imido-derivat ive. Benzoyl-p-axoxydiphonyliimino as well as the azo-com pound an* hence produced if u saponification of tin* beuxoyl group by the free alkali is prevented by neutralising with acetic acid, or if ammonium acetute is employed in plan* of tin* sodium acetate in the cathode fluid.

p-Nitrodiamidotriphenylmethane, on electrolytic reduction in concentrated sulphuric acid by a method of the (Josollsc.haft. fin* ('hem. Industrie in Basel [1] can be. converted into p-rosaniliue. The method Is of geiu-ral applic-ubility : earbinoles XIl-^j C^f<J!,| - (VMIiH-j result in the reduction of nilro-louc.o-bodii's of the type N<)a - ClsILr- •CMIIlo. (In these • formula! it <-it (i) df*notes ar«»inulic^ nuliciils with primary, secondary, or tcrtia.i\y amid<^r<>up.s ^r with hyilroxyl-groups.)

Thus is formed p-nitrc»-bitter-alm()n<l-oil-gr(utn from *j)-nitro-tHrttwrt It i/ltl i<itn!thttriitltt'tH/tttirih-(irw.*
Besiiles fin* mentioned products nerving an *klw* .starting-point, I here w« »rr* also use* 1 *it-tnlroilinundu-u-ditolyl-niclhunv, p-nitrotctra,-ifu'tii/l-nH'tfiant')* and other analogous compounds,

### VIL Nitroaldehydes and Nitroketones.

Kaufnuutri and Hof[2] nubjc'cttul *m*-to reduction in alkaline-alcoholic solution and thus ohtainiui *nwMti\wiM<Av* acid HH the principal product and iiKixobenxyi alcohol an u secondary product. Hince the* yiehl cif lilt* latter in extremely small when compared with that of the Conner, the autliors USHUHWM! that there occurred a, further do-Hfrurtive action of thi* alkali on the* prirruirtly form<*<! nitrobenssyl tilriilio! in Hiicli a way that 8 moli»culeH of the alcohol give* 1 molepule jixoxyf^'fiicyl alcoiiol and »J molcrtileH a.S5oxyfx'nBoie acliL Th**M* rfiibhtaiiceH are then convert c^cl l>y the* further action of flu* rum*nt into the* eon*eHponding u'/o-compountl, thiiH *liiwtMnK* fctii«deffilily the quantity ratio of the* primarily formed aci<l in cumpiirwon with the* alcohol (nc*e p. 1X8). By Ihw n*ncfion further Lob[3] wan li'<l to a ByntheBtH of !«fK*uitipmi!id«; tlic*w» will be mentioned later. If

[1] 1), l i , N«*. M«07 MHttt). C Vtn. XtK. 20, 242
r, f,

nitroaldehydes are reduced in sulphuric-acid solution, either the free aldehydephenylhydroxylamines, or their condensation products with unchanged nitroaldehycle, i.e., nitrobenzylidene-aldehyde-phenylhydroxylamines, are formed, *m-* and *p-Nitrobenzaldehyde* were investigated. The formation of these bodies is expressed by the following equations:

$$\text{I. } C_6H_4<{}^{xCHO} + 2H_2 = C_6H_4<{}^{xCHO}_{xNHOH}$$

$$\text{II. } C_6H_4<_{\backslash NHOH} + OHCC_6H_4NO_2 == H_20$$

$$+ C_6H_4<{}^{/CHO}_{\backslash N\text{ -- }CHC_6H_4NO_2.}\ /0\backslash$$

On further reduction the process can again repeat itself, so that similar higher molecular compounds are formed. The nitro-benzylidenealdehydophenylhydroxylamines are produced from the two mentioned aldehydes. If the p-nitrobenzaldehyde is reduced beyond the compound mentioned in the equation, the n-p-formylphenyl ether of p-azoxybenzaldoxirne is formed (Always [1]), as shown in the following equations:

•N0$_2$ /N0$_2$
o n YJ / i /i"pr _P TJ /
_ ZL/6-o-4s$_v$ \CHO ~r TtJci —• veJnL-iN. $^X$CH - NC$_6$H$_4$CBIO,
\O/

/N0$_2$
II. 2C$_6$H$_4$<
X!H—NC$_6$H$_4$CHO+6H
\O/
/.

III

NC$_6$H$_4$CHO
C$_6$H$_4$

0 +3H$_2$0.
sl.\

NC$_6$H$_4$CHO
[/ /U^
X3H—:

[1] Ber. d. deutsch. chern. GcseEsch. **29,** 3037 (1896); 3ft, 23 (1903); Ztsehr f. Elekfcrochemie 3, 373 (1897).

In the reduction of aromatic nitroketones in concentrated sulphuric acid the normal reaction, i.e.7 the formation of p-amidophenol derivatives, occurs (Gattermann *).

m-Mtroacetophenone gives amidooxyacetophenone.

m-Mtrobenzophenone and m-nitropheayl-p-tolylketone give analogous bodies.

In alkaline-alcoholic solution Elbs and Wogrinz [2] obtained m-azoxy- and m-azoacetophenone from m-nitroacetophenone. The reduction to the hydrazophase was only partially successful.

By using a copper cathode with addition of copper sulphate, in place of the previously employed nickel gauze cathode, a good yield of m-aminoacetophenone is obtained in sulphuric-acid solution; in alkaline solution a poor yield results.

m-Nitrobenzophenone, on electrolysis in alkaline solution at ordinary temperature, gives an almost quantitative yield of iH-azoxybenzophenone; when reduced at the boiling temperature, a good yield of m-azobcnzophenone is obtained, while in sulphuric-acid solution m-aminobenzophenone readily results. In the above processes the carbonyl group apparently does not participate in the reduction of the nitroketones.

### VIII. Nitrobenzenecarboxylic Acids.

**Nitrobenzoic** Acids.—The m~ and p-acids, by reduction in alkaline solution, are smoothly and almost quantitatively converted into the corresponding azo-acids, while the o-acid, according to Lob's [3] researches, under similar conditions yields o-azoxy- and o-hydrazobenzoic acid and complex blue decomposition products. This deportment is of particular interest because the o-acid also occupies an exclusive position in the *chemical* reduction, and similar experiences seem to repeat themselves with the nitrobenzenesulphonic acids (Gattermann [4]).

In dilute sulphuric acid Hostmaim[6] converted o-nitro-

[1] Ber. d. deutsch. chem. Gesellsch. **29,** 3034 (1896).
[2] Ztschr. f. Elektrochemie 9, 428 (1903).
[8] Ibid. 2, 532 (1896).
* Ibid. 10,581 (1904).
[5] Chem. Ztg. **17,** 1099 (1893).

benzoic acid into o-azo-, hydraxoberixoic acid and untlirani acid.

In concentrated sulphuric; acid oyxanthranilir arid,

/(.'<)( )H (1j
Colls–. N!$I_2$ (2),
\OH (5)

is produced by (he* method oif (latte'rrnann,[1] from flu* * » r f i acid; l-3-(kimidosalieylie acid Ls formed from the* metu-aei*

p-Nitrobenxoic acid, according *to* Clement and N<*y*' gives the p-urnidophenolsulphonie acid when electndywl very concentrated sulphuric acid.

The *(h* and *m-nilrobMizoir,* es-ter.v, on electrolysis, dep* themselves like the free acids (('Jattcrnmrm). Tiie latter iiiv^ tigutor,[8] by pn^puring the l)enzylicleni* fom|K»ijud hy the ii^t method, proved the* intermediate formation of the Jiy ainint* phane in the* reduction of the nt-ncid,

The experiments ofHcliall and Klein [4] concerning the tion of riitrolx*nxene from o-nitrofK*nxoir* acM arc cjuife ing. If a solution of soda in molten o-nitrol>cnzoi<*aci<i (ntrl«-*i acid escapes during the* solution process, so (hat a snluti of the sodium salt in the acid itself is obtained) is electrolys* at 200° and at platinum electrodes, rc'lutively large* i}iiiinfi! of nitrobenizc^ne are prexluceti; at the* name time* a gun in rvolv at the* anode (OOja?). During an electre^lysis last>ing etnr* two hours, with 0,8 to 1 amp., about 1 <*c, was obtained. T experiments were .made with the expectation erf reaction, among the aromatic acids similar to Koll»f»X Alt In »ti in the case of the aliphatic adds a limit hydrex?arlK>n is by the union of two unions with splitting off of acid, for instance,

[1] **Ber. d, deutuch. chem.** Oamjikch, **'26,** *tit,*
[2] **Am. Chem.** Journ. **16,** 511 **(1894).**
[1] **Her. d. dcutaeh. ehem.** Ge«fll«Ii. 2t»
* Ztschr. f. Elektrocheraii! I, **266 (1898),**

-Nitrocinnamic

ihonitrocinnami

The ethyl, ester leads to the same cuimutrin-.....either by saponifioation of the nitro-esl^r befon* tin* r<Mlurtinn. '»r by the splitting off of alcohol from the intermediately aiiiiclooxyciiiiuauie ester.

a-Nitrophthalic Acid \vns ronverted by KIbs' [l] method into azo- and and hydrafcophthalie a.eid; traei%s of a-aminoj»hlliaiir acid were also produced.

/J-Nitrophthalic Acid behaves similarly.

Mtroisophthalic Acid.^ This substance, hy eleelrcilylii[8] r«*-(luctiou in concent nitcM,! sulphuric arid, according t«» ftait »*r-maim,[2] is converted into the* sulphate of oxyainidoL-ojilif lialir acid. *Nitroterephthatw acid* gives an ainiilooxy I fTeplit halir aciil.

m-Nitrobenzonitrile can be[1] converted hy Klhs* rm*f ii'«!» depcaiding upon tin* conditions of the exjtf'riwi'nt, cif hrr \viflinut saponification into ni-a!5olx»n/.onitril«t or with Haponificatinn into in-a55oxyb(?nxaniid<* and in-a/*olH*nx:uni<lt,

p-Nitrobenzonitrile gives juuilogously axo- and a/.oxyuiiriU* or azo- and azoxybenza,mide.

**IX. Nit robenzt'nesul phonic**

Those[1] sulphonic aeicis which huvc the* S(');iII.groiip In th«* m-position to the* nitrogroup, havi* hr*rn p'trtictiiarh for. » • -tigated. Under tli<[k] conditions choM*n In Iilh^« \\n*\ \i«'J<i universally azo- aiul Iiydni7,o-hndif^t llin^ *nitruli* n,'t H* m-sulphonic acid, o-witmtoluene-iwulithtiftlc ncttl, p-nitntttiiw* /^ ***-sulphonic add* arc convcrtc<l into the rcirr«*Hjicindiitg axcr- «»i hydrazo-compounclH.

p-Nitrobenzenesulphonic Acid nlj*o in*havf*H nornmllv nn electrolytic reduction in slightly nlkiiliiiii* solution at cathodes (Elba and Wohlfahrt [5]j; it yields HZCH, or hv*l

[1] Ztsehr. f. Ei«ktroch(*mic 7, 113 (HlfMl)
[3] Bcr. d. dcmtflch, chf»m. C*i*«41irli, 0lt lK
•Ztachr. f. ElektrDcheraic 7, 143 OtiOO).
[4] Ibid. 7, 142 (ICMKI).
[s] Ibid. 8, 780 (1002)

acid. In tin[4] case of the o-nitro-acid, on the contrary, the, reduction is far from normal; complicated products and o-aminosulphonic acid are chiefly produced.

p-Nitrotoluenesulphonic Acid. 'The (lescllschaft f. diem. Industrie of Basel [!] prepares orange <lyes by using as cathode* fliiiil nn alkaline solution of the yellow condensation products of *t~nit.rtrfttltti'twxiiljiht>nir und.*

tik

f(*,g. a mixture of axoxystilbenedisulphonic acid, a^ostilbencv disulphonic arid, and dinitrcistilbenc*disul phonic, acidj. The reduction, however, must not be continued until amido-eorn-potmds result.

Klbs and Kremann" have likewise inveHtigatcMl th(» el(*ctr<v chemical behavior of the dye **sun yellow*' fonnec] in alkaline solution of the p-fiitrotctltif*ncHulphomc aeid, and found the following:

1. "Sun yellow" consists chiefly of jMi^>xyHtilbcnodiHul~phonic aciil.

*2.* Ifediiffd in alkiiliui* solution it yield; as end product, I>-axot«*lu(*ni**lij4ulphonic acid,

.'{. Iii nci«l Mil sit kin with addition of ntannoUH chlorido there lire* ffiniied |Mliainino.stiIliene(li.sulphoni« acid and p-lolui-

Hit* lollnu'ing may be remarked concerning the reduction in-ncii! /oiutioti; Aironling ti» HiiiiHwrmann/[1] rnet-anilic acid IK ^bfjiiiieii from *m*iutnthvnzenehul[thmie* acid in dilute ri^ a**id; in concent rated acid JM-

iven mrnilarly 2 -4-5-ttnano-

**a<** id,

[1] fug. Frit . **No.** **(IKttty.**
Zfwbr, I, Eli!ktrwlw*»iie % 410 **(1 003).**

**[1] !k?r. *I (IctitJtch. d«tm. (k» . S7, HWH (1804).**

p-Dinitrostilbenedisulplionic Acid (according to Elb^ Kremann[1]), like *p-azostilbenesulphonic acid,* yields in **ii^*** solution p-azotoluenedisulphonic acid, while in acid so'! with the addition of stannous chloride the end-product diaminodibenzyldisulphonic acid.

p-Binitrodibenzyldisulphonic Acid yields in-alkaline s< ^ [1] p-azodibenzyldisulphonic acid; in acid solution, in the pr* '•' of-stannous chloride, p-diaminodibenzyldisulphonic acid-

### X. Other Reductions of Nitro-compounds.

Lob [2] has utilized the possibility of conducting the red*J in alkaline solution up to the azo-phase for accompli^! * i direct electrosynthesis of mixed azo-bodies and azo-dyes.

The components of the desired compounds are redu*"* equimolecular proportions under conditions which make p«« the union of the two radicals during the azo-phase. By 11 of this method azo-compourids in which the • substitute o* in any desirable position to the azo-bond; and which **i*r<** obtainable by the Griess method, can be prepared.

Thus m-nitrobenzaldehyde, which in alkaline sc.*i gives equal molecules, of m-nitrobenzoic acid and m-nitrol * alcohol, yields as chief product m-m-azobenzoic-acid-t M * alcohol,

$$m\text{-}COOHC_6H_4N{=}NC_6H_4CH_2OH,$$

i

and as secondary products m-azobenzoic acid and m-azof * alcohol.

Kaufmann and Hof[3] (p. 181) had subjected m-nitrrj aldehyde to reduction in alkaline solution, but they <li« observe the occurrence of the mixed azo-compound; thcj* i only the azo-alcahol and the azo-acid7 and explained tit** yield of the former by the behavior of the m-nitrobenzyl n 1 towards alkalies, as shown in the equation:

[2] Ber. d. deutsch. chem Gesellsch. 31,2201 (1898); Ztschr. f. Elektr** 15, 456 (1899).

[8] Chem. Ztg. **20,** 242 (1896).

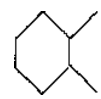
*itrobenzenesulp*
und in the for
un be crystal
lizing the el
ng the solutio
ne is formed f
oiling at 185°
mpounds are
tives of the
very favorable.
r [2] have found
erted into phen
alkaline soluti

There result from
o-Mtrobenzeneazophenol, phenolphentriazole; from
o-Mtrobenzeneazosalicylic acid, salicylic-acid-phentriazole,

/
/\N=NC6H3< X
\/N02 COOH; 3

and from

o-Nitrobenzeneazo-a-naphthol, a-naphtholphentriazole :



## XI. Nitro-Derivatives of the Naphthalene, Anthracene, and Phenanthrene Series.

Since only the nitro-group is subject to reduction by the cathodic action of the current on nitro-compounds, nothing new can here be added regarding the possible reduction phases. The conditions which with the benzene derivatives lead to certain stages, cannot always be directly applied to these substances; this is due to the influence which the whole molecule possesses over the reaction velocity of the separate processes. This deportment is especially shown by the nitro-derivatives of the anthracene series. Nevertheless, some of the more general conditions also obtain here; for instance, nitronaphthalene derivatives in acid electrolytes at attackable cathodes, according to the process of Boehringer & Sohne,[1] are also easily reduced to amines. Gattermann's method has also been serviceable in the preparation of amidonaphthols.

a-Mtronaphthalene,[2] in aqueous acetone solution was reduced by Voigt to nitrosostyrol besides a little naphthylamine. The latter is quantitatively obtained if #-nitronaphthalene is

[1] D. R. P. No. 116942 (1899); 117007 (1900)
[2] Ztschr. f. angew. Chemie (1894) 108.

reduced in a hydrochloric-acid electrolyte with an attackable cathode, or with addition of salts of the latter.[1]

a^i-Mtronaphthalene-as-sulphonic acid was converted by Voigt [2] into hydrazonaphthidenesulphonic acid and some naphthylaniine. Gattermanri [3] obtained by Ms method the aminonaphtholsulphonic acid in a normal manner. Analogously behave

#i-Mtronaph.thalene-/?3- and /3$_4$-stilplionic acids and the disulphonic acids (/?2, *fa,* and *p<$£* of a-Nitronaphthalenc.[4]

(aia$_4$)Dinitronaphthalene (according to a patent of the Badisclie Anilin- u. Sodafabrik) alone, or mixed with *(a* 1.0:2) *dinitronaphthalene j* gives in concentrated sulphuric-acid solution a product which, by heating with dilute acids, can- readily be converted into naphthazarin.[6]

*aia%-* and *aia^-* Dinitronaphthalene, if reduced according to Tafel, in a mixture of acetic and sulphuric acid with prepared lead cathodes, gives the 1-6- and 1 • 8-naphthylenediamincs (Holler [6]).

a-Mtro-/9-naphthyl ethyl ether, .—This naphthol ether, unlike the nitrophenol ethers, gives a-amido-/9-naphthyl ethyl ether as end-product of the alkaline reduction (Rhode[7]).

o-Nitroanthraquiaone has been reduced by Moller [8] in alcoholic-sulphuric acid arid in slightly alkaline solution to o-amidoanthraquinonc. By electrical oxidation in concentrated sulphuric acid there is formed, according to Weizrnarm,[9] nitro-oxyanthraquinonc; with alternating currents alizarinamide was produced; and in the presence of glycerin, mannit, etc., blue arid

[1] D. R. P. No. 116942 (1899); 117007 (1900)
[2] Ztschr. f. angew. Chemie. 1894, 108.
* Her. d. deutsch. chem. Gesellsch. 26, 1852 (1893).
*I>. II. P. No. 81621 (1893).
[8]D, R. P. No. 79400 (1894).
[6] Elektrochem. Ztschr. 10, 199, 222 (1903-1904).
[7] Ztschr. f. Blektrochemie 7, 340 (1900).
[8] Ibid., 741, 797 (1901).
[9] Fr. P. No. 265292 (1897).

green reduction products resulted. The action of the cathodic current on

i • 2-Dinitroantnraquinone and i • 5-Dinitroanthraquinone in a solution of glacial acetic acid with addition of sulphuric acid produces diamidoanthraquinones;[1] the yield, however, is poor. The employment of lead cathodes, as shown by Tafel, may perhaps increase the latter.

According to experiments of the Badische Anilin- u. Soda-fabrik,[2] a dinitroanthraquinone dissolved in fuming sulphuric acid is changed by electrolytic reduction to blue mordant dyes.

Dinitroantlirarufindisulplionic Acid and Dinitrochrysazindisulphonic Acid.—These substances are easily reduced electrolytically in sulphuric-acid solution to diamidoanthrarufmdisulphonic acid and diamidochrysazindisulphonic acid.[3]

p-Nitrophenanthrene has been converted by Schmidt and Strobel[4] into 9-azoxyphenanthrene by Elbs' process.

2-Nitrophenanthrenequinone in acid solution at lead cathodes gives 2-aminophenanthrenequinone (Holier).

2 -y-Dinitrophenanthrenequinone is converted in acid solution into 2 • 7-diamidophenanthrenequinone (Holier).

## XII. Nitroso- and Nitro-Derivatives of the Pyridine and QuinoHne Ser es.

Nitrosopiperidine, on electrolytic reduction in sulphuric-acid solution (Ahrens [5]), gives piperylhydrazine, piperidine, and ammonia; at the anode there are formed at the same time a diamine, CioHis^; of the fatty acid series, and two isomeric amidovaleric acids, besides hydrochloric acid and piperidine. Under similar conditions

Nitroso-a-pipecoline gives a-methylpiperylhydrazine, a-pipecoline and ammonia at the cathode, and at the anode a

[1] Elektrochem. Ztschr. **10,** 199, 222 (1903-1904).
[2] D. R. P. No. 92800, 92998 (1896).
[8] D. R. P. No. 105501 (1898).
[4] Ber. d. deutsch. chem. Gesellsch. **36,** 2512 (1903).
[6] Ztschr. f. Elektrochemie 2, 578 (1896); Ber. d. deutsch. Gesellsch **30, £33** (1897); **31,** 2272 (1898).

diamine and an amidocaproic acid. In the same manner the other nitroso-derivatives of homologous piparidines on electrical reduction give corresponding piperylhydrazines. Ahrens and Sollmann[1] similarly prepared from
Mtroso-/?-pipecoline the /?-pipecolylhydrazinc; from
Nitroso-^-pipecoline the f-pipecolylhydrazine; from
Nitroso-a-a-lupetidine the a-a-dirnethylpiperylhydrazine; from

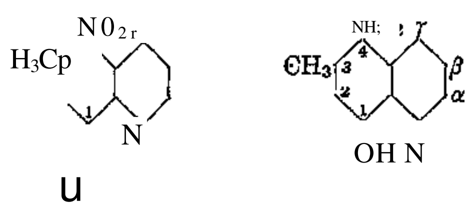
Nitrosoaldehydecopellidine the aldehydecopcllidinehydrazine; and from

Nitroso-s-trimethylpiperidine the s-trimethylpiperylhydrazine.

Nitrosotetrahydroquinoline. —- Concerning the experiments of Ahrens and Widera [2] on the oxidation of nitroso-derivatives of pyridine and quinoline there is yet to be mentioned the smooth conversion of nitrosotetrahydroquinoline into tetrahydroquinoline. The nitroso-group is found as nitric acid in the anode fluid.

4-NitroquinoUne and i-o-Nitroquinoline, reduced in concentrated sulphuric acid, give 1.4-oxyamidoquinoline and 1.4-amidooxy quinoline (Gattermann [3]),

4-Nitro-3-toluquinoline gives likewise a 4-amido-l-oxy-3-toluquinoline •




## 3. AMINO-DERIVATIVES,

Aniline.—Rotondi [4] electrolysed aniline in an ammoniaeal solution. After a period of three days, during which hydrogen was continually evolved at the negative pole and a tarry sub-

[1] Chem. Ztschr. 2, 414 (1003).
[2] Her. d. deutsch. chem/Geeellsch. 81, 2276 (1898).
[3] Ibid. 27,1939(1804).
[4] JTahresh. f. Chemie, 1884, 270.

III

stance was deposited at the positive pole, Rotondi interrupted the electrolysis and was able, with more or less certainty, to establish the following processes :

1. The formation of diazo-compounds :

$$C_6H_5NH_2(HN0_3) -hHN0_2=C_6H_5N_2N03 +2H_20.$$

2. The formation of diazoamido-compounds :

$$2C_6H_5NH_2 + HN0_2 = CeHsNzNHOeHs + 2H_20.$$

$$C_6H_5N_2N0_3 + C_6H_5NH_2 = CeBU^NE - C_6H_5 + HN0_3.$$

3. The formation of azo-compounds by direct oxidation of aniline :

$$2C6H_6NH_2 -\{-20 = 2H_2$$

4. The formation of amidoazo-compounds by molecular rearrangement of diazoamido-compounds. The nitrous acid and nitric acid were oxidation products of the ammonia which was added.

C. F. Boehringer & Sohne add a manganese salt to the electrolyte [1] in the presence of a strongly dissociating acid and thus smoothly oxidize aniline to quinone.

The fact that aromatic amines are often directly convertible by oxidation into dyes, early directed attention to the electrolytic oxidation of amines for the direct preparation of dyes. The investigations of Goppelsroder,[2] which were carried out some time ago, have primarily this end in view.

GoppelsroderTias compiled the technical results in a small pamphlet: " Farbelektrochemische Mitteilungen " (Mulilhausen, 1889). They may be briefly mentioned here.

If a galvanic current is conducted through acid or neutral aqueous solutions of aniline, there is formed at the positive

[1] D. R. P. No. 117129 (1900).

[2] Dringler, Polytechn. Journ. 221, 75; 223, 317, 634; 234, 92, 209 (1876)-1877). Cf. also: Concerning the Preparation of Dyes, and their Simultaneous Formation and Fixation in the Fibers with the Aid of Electrolysis, Goppelsroder, Reichenberg, 1885.

pole, besides other coloring matters, aniline black, C24H2iN4Cl. Under similar conditions dyes are obtained at the positive pole from the salts of *toluidine, me«hylaniline, diphenylamme ƒ ditolylamine,* and *phenyltolylamine.*

On electrolysis of a mixture of anthraquinone and caustic potash Goppelsrocler obtained alizarine.

The numerous experiments which led to the formation of dyes at the anode, when aniline, toluidine, mothylaniline, diphenylandne, *methyldiphenylamine* and *naphlhylamine* or their salts were electrolyzecl, have, however, not been scientifically investigated and, hence, still remain unsolved. The same holds true of Goppelsroder's investigations concerning the oxidation of phenol and anthraquinone. The most important discovery is the fact that aniline salts smoothly yield aniline black at the anode; the naphthylamine salts give naphthylamine-violet.[1]

Voigt,[2] by the electrolytic oxidation of suitable mixtures of bases, prepared rosaniline, chrysaniline, safranine, and p-leucaniline. His object in these researches was the same as that of Goppelsrocler; namely, the preparation directly in the bath of the important dyes of the aniline scries.

[1] The following literary data will serve as a guide:
*Research* 1.* Preparation of aniline black.
*Research* 2.f Electrolysis of aniline with excess of aniline.
Electrolysis of toluidine.
Electrolysis of mixtures of aniline with toluidine igomcrs.
*Research* 3.J Electrolysis of aniline and toluidine salts in the presence of potassium nitrate, nitrite, or chlorate in aqueous solution.
*Research* 4.§ Electrolysis of the salts of methylaniline.
Electrolysis of the salts of diphenylamme.
Electrolysis of the salts of methyldiphenylamine.
Electrolysis of phenol.
Electrolysis of the salts of naphthylamine.
*Research* 5-‖ Conversion of anthraquinone into alizarine by th© electrolysis of a mixture of anthraquinone and potassium hydroxide.

[2] Ztsch. f. angew. Chemie, 1894, p. 107.

* Dingier, Polytechm. Jotirn. 221, 75 (1670).
† *Ibid.* 233,317 (1877).
‡ *Ibid.* 223, 634(1877).
§ *Ibid.* 224, 92 (1877).
‖ *Ibid.* 224, 209 (1877).

If electrolytic oxygen is permitted to act upon aniline in concentrated acetic-acid solution, acetanilide is formed (Voigt); by using a dilute solution, however, amidohydroquinone is obtained.

These investigations have not been satisfactorily concluded, which is also the case with those of Foelsing,[1] who, by the oxidation of p-phenylenediamine and benzene-p-phenylene-diamine, obtained indigo-blue dyes.

According to Lob's[2] experiments (see p. 176) by electrolytic reduction of nitro-compounds in a solution of fuming hydrochloric acid in an excess of an aromatic amine, incluline-like dyes—not identical with the known induline dyes—are obtained. Szarvasy,[3] however, by anodic electrolysis of molten aniline' hydrochloride, obtained electrolytically the indulines themselves. If a mixture of aniline and aniline hydrochloride is electrolyzed at 70°~90°, there is obtained a rich yield of azophenine, the known intermediate product of the indulines. By electrolysis of the pure molten salt at about 150°-300°, induline, anilidoinduline, and induline 6 B, besides the intermediate products of the induline formation, could be detected as products of the anodic oxidation. The oxidizing agent in these processes, which were carried out without an oxygen-containing electrolyte, was chlorine, which probably first produces azo-compounds that react further in the molten mass with aniline hydrochloride.

The interesting research of Votocek, Zenisek [4] and Sebor [5] may also be referred to in this connection. This permits the Sandmeyer-Gattermann reaction (substitution of the diazo-group by chlorine and bromine) to be carried out electrolytically. For this purpose the diazotized "solution of the amine is electrolyzed —for instance 50 g. aniline, 120 g. HC1, 38.5 g. $NaN0_2$—between copper electrodes with addition of cuprous chloride or copper sulphate. At the end of the experiment (ceasing of the nitrogen

[1] Ztschr. f. Elektrochemie 2, 30 (1895).
[2] Ibid. 6, 441 (1900).
[3] Ibid. 6,403 (1900).
[4] Ibid. 5, 485 (1899).
[6] Ibid. 7, 877 (1901).

evolution) 64% chlorbenzene and 10% azobenzene could be isolated. This process could be used successfully for obtaining brombenzene by addition of copper sulphate and potassium bromide, also for p-chlortoluene and 0-chlornaphthalene. The method is not applicable for preparing fluorbenzene and a-chlornaphthalene.

The direct diazotization and preparation of *azo-dyes* in one electrochemical process was discovered by Lob.[1] His method—an anodic process—is based on the following principle:

As is well known, azo-dyes are generally prepared by cliazotizing the amine in acid solution or suspension at a low temperature and then bringing together the diazotizecl solution with the usually alkaline solution of the components to be joined.

The same 'effect can be reached electrochemically, if amine, nitrite; and the coupling components of the compound desired are simultaneously exposed in a neutral or sometimes alkaline electrolyte to the anodic action of the current at an unattackable electrode.

The first stage of the process consists undoubtedly in the action of the discharged N02 ions on the amine, as-shown in the equation

$$RNH_2 + N0_2 \rightarrow RN - NOH + OH.$$

However, if an amine alone is subjected to the anodic current action in the presence of the nitrite, complicated products result; besides the action of the N02 ions upon the amido-group and the typical decomposition of the diazo-body by the electrolyte, substitution and oxidation processes seem to occur.

It is therefore necessary to add components to the electrolyte already before the electrolysis, which react so rapidly with the intermediately occurring cliazo-bodies that the latter is withdrawn from the other disturbing influences.

Phenols are particularly suited as addition substances for fixing the diazo-bodies. Experiments have shown that the coupling of the diazo-compound with the acid component takes

[1] Ztschr. f. Elektrociiemie 1ft, 237 (1904).

place much more rapidly than its decomposition by the mentioned influences. In the presence of phenols the formation, of the azo-dyes can therefore be made the predominating one. It is very evident that in this process amines are not applicable as components for coupling purposes, because they are themselves subject to the action of the nitrite ions; and other complicated reactions.

The experiments are generally conducted by putting the aqueous solution, or suspension, of amine, coupling component—preferably in the form of a soluble salt—and nitrite, in equimolecular proportions, in the anode chamber, which is suitably separated from the cathode chamber by a diaphragm. Platinum is the best anode material; any suitable metal can serve as cathode. The current conditions chosen may vary greatly—from 50-600 amp. per square meter of anode surface. It is very important that the anode fluid be stirred during the whole experiment.

An increase in temperature is sometimes beneficial, but is generally unfavorable for the yield and purity of the dyes. An artificial lowering of the temperature, which is necessary for the chemical diazotizing process, is never required. Several examples are classified in the following table:

| | | | | | |
|---|---|---|---|---|---|
| Anode solutions : | Sodium Sulphanilate<br>0-Naphthol<br>Sodium<br>Nitrite<br>Water<br>s | Benzidine<br>Naphthionate<br>Sodium Nitrite<br>[illegible]<br>Sodium<br>Hydroxide | Dianisidine<br>/?-Naphthol<br>Sodium<br>[illegible]<br>Water | Benzidine<br>Sodium<br>Salicylate<br>Sodium<br>Nitrite<br>Water | Sodium.<br>1.4-NaphthyI-aminesulphonate.<br>/9-Naphthol<br>Sodium<br>Nitrite<br>Water |
| Results : | Orange II | Congo | Dianisidine-blue | Chrvsamine " G | Rocceline |

Dimethylaniline, electrolyzed in sulphuric-acid solution at platinum electrodes in the presence of some chromic acid, gives tetramethylbenzidine. In this case the oxidizer is chromic acid; the current action consists only in the generation of the latter (Lob *).

Triamidotriplienylmethane. — The Farbwerken vorm. Meister, Lucius, & Briining,[2] by electrolytically oxidizing those substances which are formed in the treatment of the hydrochloric-acid salts of homologues of triamidotriphenylmethane with fuming sulphuric acid in the presence or absence of sulphur, succeeded in preparing blue, basic triphenylmethane dyes.

## 4. PHENOLS.

Phenol. — Bunge,[3] Bartoli and Papasoli [4] submitted phenol to the action of the electric current. Bunge observed that the decomposition of potassium phenolate was analogous to that of an acid or a salt ; the potassium phenolate was split up into K (cation) and CeHsO (anion), the latter combining with water to form phenol, with the liberation of oxygen. Bartoli and Papasogli, on electrolyzing solutions of phenol in potassium and sodium hydroxide, and using electrodes of coke, graphite, and platinum, obtained an acid having the composition CrHeO^t, which melted at 93°, reduced ammoniacal silver solution and Fehling's solution on being heated, and when in aqueous solution was not precipitated by acids. When, however, retort coke was used as the positive electrode, an extensive decomposition of the phenol occurred and a resin was formed.

On subjecting a neutral potassium phenolate solution to the action of the electric current they were able to isolate a compound, Ce5H48022, soluble in alkali and precipitated from such solutions by mineral acids. This latter compound on being oxidized with nitric acid formed picric acid. When allowed to remain in solution in the presence of dilute acids for a pro-

[1] Ztschr. 1 Elektrochemie 7, 603 (1901).
[2] D. R. P. No. 100556 (1897).
[8] Ber. d. deutsch. chem. GeseUsch. S, 296 (1870).
z. chim. 14, 103 (1884).

longed period, it underwent decomposition according to the following equation:

The electrolysis of neutral sodium-phenolate solution gave an acid having the formula C29H2o08, which likewise is decomposed on boiling with dilute acids:

= C iy

The compound C^HioOs is soluble in alcohol, melts at 75°, and is isomeric with the hydroquinone ether obtained by Etard from chlorchromic acid and phenol. It has tne composition

The relations which exist between the potential and the pressure with which a discharged ion, like chlorine, bromine, or iodine reacts with phenol nave been determined by Zehrlant[1] with the following results:

The substitution of chlorine in phenol in dilute acid solution does not take place, nor does that of bromine, since the oxidation begins earlier, at a lower potential, than the halogen discharge. Iodine also does not act on phenol in acid solution. A bromination can, however, be obtained if, on the one hand, the potential for the beginning of the oxidation is raised by decreasing the oxygen- or hydroxyl-ionic concentration; on tlie other hand, the discharge potential of bromine is lowered by increasing the bromine concentration i.e., if concentrated hydrobromic acid (multiple normal) is employed, bromination occurs.

Thymol.—In alkaline solution halogen substitution takes place very rapidly with phenols. This fact has led to the

. f. Elektrochemie 7, 501 (1901).

electrolytic preparation of dithymoldiiodidc, the antiseptic *aristol,* as made by Messinger and Vortmann[1] by the electrolysis of an alkaline solution of thymol with the addition of potassium iodide.

Directions for the preparation of a whole series of iodides of phenols are mentioned in the same patent papers; e.g., from *fi-naphthol, phenol, resorcin, salicylic acid, crexolinic acid, carva-crol, p-isobutylphenol, o-m-p-isobutylcre$ol, etc.*

Nosophen, a tetraiodophenolphthalcin, from phenolphtha-lei'n (Classen arid Lob [2]), is obtained in like mariner.

With these methods of preparation there corresponds a simi-lar process, which the Societe chimique cles usines clu llhonc anc. Gilliard, Monnet et Cartier patented in Germany,[3] for the clec-trolytic preparation of cosine arid other halogen derivatives of the fluorescein group. The solutions of the fluorescei'ns in alkali-hydroxide or in alkali-carbonate solution serve as anode fluids. The halogens, such as chlorine or bromine, are introduced into the anode compartment, whereby salts of the halogen acids form and simultaneous halogermtion of the fluorescent occurs.

Since the salts are again decomposed by the current, with splitting off of the halogen, which in turn reacts on tho fluores-cei'ns, the quantitative—very important for bromine and iodine—utilization of the halogen can take place. The well-known eosins are said to be obtained in excellent yields and in a high state of purity.

*Phenylmercaptan.* —Bunge,[4] who had obtained othyldi-sulphide from ethyl meraiptan (see p. (55), also investigated phenylmercaptan. Phenyldisulphido, (GoH$) 282, was formed from phenylmercaptan at the positive pole.

Hydroquinone.—If an acid hydroquinone solution with addition of a manganese salt, according to the process of 0. P. Boehringer & Sohne,[6] is electrolysed, quinone is smoothly pro-

[J]D. R, P. No. 64405 (1891).
[2] Ber. d. deutsch. chern. Gcscllsch. 28, 1603 (1895).
[3] D. It P. No. 108838 (1899).
[4] Ber d. deutsch. chem. Gesellsch. S, 911 (1870).
[5]D. R. P. No. 117129 (1000).

duced. But if a weak sulphuric-acid solution without addition is electrolyzed, quinonehydrone **is** precipitated at the anode (Liebmann [x]) .

Resorcin. — Alefeld and Vaubel,[2] by electrolytic oxidation, have obtained dyes of different shades from resorcin and other Lydroxyl derivatives of the aromatic series, such, as gallic acid, tarinic acid; fhiorescems and eosins. An investigation of the dyes was not made.

Pyrogallol (pyrogallic acid).— According to A. G. Perkin and F. M. Perkin,[3] purpurogallin CnEgOs, can readily be obtained by electrochemical oxidation of pyrogallol in dilute sulphuric acid with addition of sodium sulphate at a platinum-iridhini anode.

Gallic Acid behaves likewise. Purpurogallincarboxylic acid, CnHrOsCOOH, is probably obtained.

Eugenol. — The firm v. Heyden Nchfg.[4] obtains vanillin electrolytically from eugenol. The latter is rearranged by alkalies into isoeugenol and then oxidized electrolytically in alkaline solution:

$$C_6H_3\begin{cases}OH \\ OCH_3 \\ CH_2CH{=}CH_2\end{cases} \rightarrow \ aeOCEs\begin{cases}OH \\ \\ CH«CHCH_3\end{cases}$$

Eugenol — Isaeugenol

$$- \begin{cases} \\ CH{=}CHCH_3\end{cases} +30 \quad \begin{cases}OH \\ \\ CHO\end{cases} +CH_3C300H.$$

Isoeugenol

5. ALCOHOLS, ALDEHYDES, EEJTONES, ANI> QUINONBS.

These classes of bodies, owing to their peculiarity in being both reducible and oxidizable, present many interesting phenomena respecting their electrolytic behavior. Since every

[1] Ztschr. f. Elektroehemie 2, 497 (1896).
[2] Chemu Ztg. 22, 297 (1898).
* Proceed. Chem. Soc. 19, 58 (1903).
[4] D. R.P. KTo. 92007 (1895).

electrolytic cell performs both functions at both electrodes, the problem presents itself to apply both of these effects of the current to one and the same substance. We shall see that this possibility has actually been realized in individual cases.

Salicin, saligenin-glucose, by the action of the enzymes ptyalin and emulsion, is known to split up into glucose and saligenin (i.e. o-oxybenzyl, e.g. salicyl alcohol) . On boiling with dilute acids the same decomposition occurs, but saligenin is resinified to saliretin. Tichanowitz [1] and Hostmann [2] found that salicin on electrolysis splits up into glucose and salicyl alcohol, the latter being partially oxidized to salicylic aldehyde and salicylic acid.

Benzaldehyde. — Kauffmann,[3] by electrolyzing benzaldehyde in a 12-15% solution of potassium bisulphite, obtained at the cathode a mixture of hydrobenzom and isohyclrobenzi'on. According to his statements,[4] an alcoholic solution of sodium hydroxide is more suitable for the reaction than the aqueous solution of bisulphite. Other aldehydes and ketones show & behavior similar to that of benzaldehyde, as will be explained under the individual substances.

Tafel and Pfeffermann [5] have discovered a useful method for preparing amines. They electrolytically "reduce oximes and phenylhydrazones in sulphuric-acid solution. Thus

*BenzyKdenephenylhydrazone,* the condensation product of benzaldehyde and phenylhydrazine, gives 43 per cent, of the theoretical yield of benzyl amine, besides some aniline:

$$C_6H_5CH = NNHC_6H_5 + 4H \rightarrow C_6H_5CH_2NH_2 + C_6H_5NH_2.$$

*Bendaldoxime,* by reduction, is split up, yielding 69 per cent. of the theoretically possible quantity of benzylamine:

$$C_6H_5CH = NOH + 4H \rightarrow C_6H_5CH_2NH_2 + H_2O.$$

[1] Chem. Centralb. 613 (1861).
[2] Chem. Ztg. **17,**1099 (1893).
[3] Ztschr. f. Elektrochemie 2, 365 (1893)
* Ibid. 4, 461 (1898).
[5] Ber. d. deutsch. chem. GesellscK 35,1510 (1902).

Salicylaldehydephenylhydrazone, by electrolytical oxidation in alkaline solution at a platinum anode can be converted into salicyl-a-osazone (Biltz[1]).

$$20EC_6H_4CH = NNHC_6H_5 4- 0$$
$$OHCeH\hat{}CCeBUOH$$
$$\text{II} \quad \| \qquad\qquad + H_20.$$
$$C_5H_5HNN \; NNHCeHs$$

Acetophenone, Cells • CO -$CH_3$. — Acetophenone yields acetophenonepinacone,

$$\begin{array}{ccc} CeHsv & & /CeHs \\ & >C(OH)\text{-}C(OH)< & \\ CR/ & & {}^XCH_3 \end{array}$$

if reduced in alcoholic sodium hydroxide (Kauffmann [2]) . Elbs and Brand[3] employed an alcoholic-alkaline solution and lead cathodes; electrolyzing at the boiling temperature, they also obtained acetophenonepinacone and a moderate yield of methylphenyl carbinol:

$$C_6H_5CH(OH)CH_3.$$

In sulphuric-acid solution and at lead cathodes the same substances are produced in almost equal yields.

*Acetophenoneoxime,* investigated by Tafel and Pfeffermann[4] in the same way as benzaldoxime, gives phenylethylamine sulphate :

$$\begin{array}{ll} v & \\ >C = NOH \; 4\text{-}4H \rightarrow & >CHNH_2 \; 4\text{-}H_20. \\ & / \end{array}$$

**Benzophenone,** on being reduced in alkaline solution at lead cathodes (Elbs and Brand[5]), gives benzhydrol almost quantitatively,

[1] Lieb. Am. 305, 167 (1899).
[2] Ztschr. f. Elektrochemie 4, 461 (1898).
[3] Ibid. 8, 784 (1902).
[4] Lc.

f[1] TT
5\CHOH,

while in sulphuric-acid solution the reduction becomes more complicated. If the warm solution is electrolyzed with a moderate current density, there occurs as chief product /?-benzpinacoline, which is to be regarded as a molecular rearrangement product of the primarily formed benzophenonepinacone with splitting off of water:

C5\C(OH)—C(OH)/ 6
S \f^T C65 I

With a very small current density and at a low temperature (0°-2°) the yield of /9-benzpinacoline is trifling, benzhydrol and diphenyl me thane being chiefly produced.

If the alcohol and sulphuric acid are replaced by acetone and phosphoric acid respectively, and the electrolysis is carried out with a high current density and with a warm solution, there will be formed, by the action of phosphoric acid with simultaneous splitting off of water, a-benzpinacoline, the rearrangement product of benzophenonepinacone:

C(OH)—C(OH)< / $^XC_6H_5$ C6115\ $C_6H_5$ ,/C~ \P Csf $^XC_6H_5$.

*Benzophenoneoxime.* — This substance, on electrolysis in a 60% sulphuric acid at lead and mercury electrodes — the latter being preferred on account of the difficultly soluble sulphate which i$ formed — is reduced to benzhydrylamine (Tafel and Pfeffermann -

NOH +4H CHNH$_2$ +H$_2$0.

Elbs and Brand[2] also investigated the following ketones:

Lc. n.c.

Phenyl-p-tolylketone, by alkaline reduction, gives almost quantitatively phenyl-p-tolylcarbinol :

The same product, together with phenyl-p-tolylpinacone, is produced in sulphuric-acid solution at a low current density and temperature. With a higher current density and temperature the formation of carbinol is trifling, and a good yield of phenyltolylpinacone is obtained :

$C_6H_5$-C(OH)$C_6H_4$CH3

$C_6H_B$-C(OH)C6$H_4$CH3.

Phenyl-m-xylylketone. — The reaction product of the alkaline reduction is a liquid modification of phenyl-rn-xylylcarbinol; but in sulphuric-acid-acetone solution at the boiling temperature phenyl-m-xylylpinacone is- obtained. The yield of the latter is 40-50 per cent, of that theoretically possible.

Phenyl-a-naphthylketone. — A satisfactory yield of phenyl-a-naphthylcarbinol is obtained in alkaline electrolytes; in acid solution only phenyl-a-naphthyl-/?-pinacoline,

results. This is due to the fact that phenylnaphthylpinacone is very sensitive towards acids; thus only its conversion product is obtained above,

The same is true in acid solution of

p-Ethoxybenzophenone, which yields p-ethoxybenz-/?-pinacoline :

6 4 >CCOC

$C_2H_5OC_6H_4$

p-Oxybenzophenone.—While this ketone is not reducible in alkaline electrolytes, the normal reduction product, p-oxybenzpinacone, is produced in alcoholic-sulphuric acid:

$$C_6H_5C(OH)C_6H_4OH$$

$$C_6H_5C(OH)C_6H_4OH.$$

p-Oxybenzophenonebenzoate.—This substance is reduced to the carbinol in sodium-acetate solution. To prevent saponification during reduction, the free alkali must be continually neutralized with acetic acid.

Phthalyl-p-aminobenzophenone.—This compound, by reduction in sulphuric-acid solution, gives a poor yield of pinacone.

Elbs and Brand sum up the results of their investigation as follows:

1. The electrochemical reduction of ketones in alkaline solution at lead cathodes gives the same products as the chemical reduction with sodium amalgafn or with zinc dust and alkali; the process is in many cases suitable for the preparation of benzhydrols.

2. The electrochemical reduction of ketones in acid solution (dilute sulphuric or phosphoric acid) at lead cathodes leads to pinacones; if these are sensitive towards acids, the corresponding *a* or /? pinacolines are obtained in their stead. For this reason the electrochemical process is not so generally applicable for the preparation of aromatic pinacones as the method employing glacial acetic acid and zinc dust, which has been worked out by Elbs and Schmidt;[1] but the electrochemical reduction is more energetic than that with zinc dust and glacial acetic acid. Fatty ketones are reduced like the aromatic ketones, with the difference that fatty and fatty-aromatic ketones give simultaneously alcohols and pinacones, whereas pure aromatic ketones yield chiefly only pinacones.

Tetramethyldiamidobenzophenone, Michler's ketone, according to Kauffmann,[2] when electrolytically reduced in alcoholic

[1] Journ. f. prakt. Chem. 51, 591 (1895).
[2] Ztschr. f. Elektrochemie 4, 461 (1898).

sodium-hydroxide solution, gives the corresponding benzhydrol:

$$CO\left\langle\begin{matrix}C_6H_4N(CH_3)_2\\C_6H_4N(CH_3)_2\end{matrix}\right. + 2H = CHOH\left\langle\begin{matrix}C_6H_4N(CH_3)_2\\C_6H_4N(CH_3)_2\end{matrix}\right.$$

Elbs and Brand [1] obtained the same result.

^Escherich and Moest [2] made an extensive investigation with the object of preparing electrolytically tetra-alkylated diamido-benzhydrols. They discovered that, by observing certain experimental conditions, the reduction can at will be directed to the hydrol or the pinacone. This is particularly true with Michler's ketone. We can thus obtain chiefly pinacone, for instance, by employing copper cathodes in a dilute sulphuric-acid solution; nickel cathodes, under the same conditions, yield about equal quantities of pinacone and hydrol, wnile by using lead cathodes and mercury cathodes, hydrol is chiefly produced. Moreover, the pinacone reaction occurs the more easily the more concentrated the solution is of the acid. Because of the resistibility of the resulting reduction products towards anodic oxygen, separate electrode chambers are not required.

Since

**Tetramethyldiamidodiphenylmethane,**

$$(CH_3)_2NC_6H_4v$$
$$(CH_3)_2NC_6H$$

on electrolytic oxidation in dilute sulphuric acid at a lead anode also readily yields the hydrol, the oxidizing action of the current can also be employed, besides the reducing action, in the preparation of the hydrol, if a mixture of tetramethyldianiidodiphenylmethane and .tetramethyldiainidobenzQ-phenone in molecular proportion is electrolyzed. Escherich and Moest actually obtained a very good yield of the hydrol, — without an evolution of gas, — at the cathode and anode.

Dibenzylketone. — Elbs and Brand[3] have published a short

[1] Ztschr. f. Elektrochemie 8, 786 (1902).
[2] Ibid. 8, 849 (1902); D. R. P. No. 133896 (1901).
Ztschr. f. Elektrochemie 8, 784 (1902).

note on this substance. The reduction seems to take place like that of other ketones; but the nature of the oily reaction-product was not determined.

Benzile.— The aromatic diketone benzile, CeHsCO • CO • $CeH_5$, gives peculiar results (Kauffmann [1]). By reduction in an alkaline alcoholic solution a whole series of bodies is formedyi.e., benzoic acid, benzilic acid, tetraphenylerythrite:

$C_6H_5$-CHOH

$C_6H_5$-COH

$C_6H_5$-COH

$C_6H_5$-CHOH,

and a substance, $C_28H_260a$, containing one less atom of oxygen, which has probably the constitution

$C_6H_5$-CHOH

$C_6H_5$-COH

CeHs-CHOE.

Tetraphenylerythrite is also formed by the direct reduction of benzoin.

Benzoin. — Benzile, by reduction in dilute alcoholic sodium hydroxide and in alcoholic sulphuric acid, according to James,[2] can inversely be converted into benzoin. Oxidation of benzoin in alkaline and sulphuric-acid solution gives a poor yield of benzoic acid. In alcoholic hydrochloric acid, especially at a high current density, benzile is formed.

Anthraquinone. — The first researches concerning the electrolysis of this substance were made by Goppelsroder (see p. 194), who, by suspending anthraquinine in potassium hydroxide,

[1] Ztschr. f. Elektrochemie 4, 461 (1898).
[2] Journ. Am. Chem. Soc. 21, 889 (1899).

suspected reduction products, such as oxyanthranol or hydroanthroquinone, among the substances deposited on the cathode electrode. If the current is sent through a mixture of anthraquinone and molten alkali, oxyanthraquinone first, then alizarate, and then purpurate, is supposed to be formed. These experiments, however, require to be repeated with greater exactitude.

According to Weizmann,[1] anthraquinone, dissolved in concentrated sulphuric acid, is converted by electrolytic oxidation into monoxy-, dioxy-, and trioxyanthraquinone. An addition of oxalic acid to the sulphuric acid is suitable for obtaining dioxyanthraquinone. A nitrooxyanthraquinone, which is convertible by electrical reduction into amidoalizarin, is similarly obtained from *mononitroanthraquinone.*[2] The amidoalizarin can be directly obtained from nitroanthraquinone if its solution is electrolysed with an alternating current. The sulphonic-acid derivatives of anthraquinone behave like anthraquinone.

The phenomena occurring with these oxidations were later more accurately investigated by Perlin.[3] From anthraquinone in 92% sulphuric acid 90 to 96% dioxyanthraquinones and a small quantity of monoanthraquinones were obtained. Besides *a-* and /9-monooxyanthraquinone, quinizarin, alizarin, and purpurin could be isolated. If the anthraquinone-sulphuric acid solution is employed as cathode fluid, anthranols, anthrones, and hydroanthranols are formed. If the sulphuric-acid concentration of the anode solution is increased, there are formed sulphurated oxyanthraquinones.

*a-Mononitroanthraquinonej* under like conditions, gives a nitrooxyanthraquinone besides a mixture of di- and trioxyanthraquinone.

*Dibromanthraquinone* gives violet crystals, perhaps a tetriiroxydibromanthraquinone.

**Phenanthrenequinone,** according to Perlin, is electrolytically oxidized in concentrated sulphuric-acid solution to a mixture of mono- and trioxyphenanthrenequinone.

[1] F. P. No. 265291 (1897).
[2] F. P. No. 265292 (1897).
*Diss. Berlin, March, 1899.

All these oxidation processes illustrate the possibility already mentioned (p. 132) of introducing oxygen electrolytically into the benzene nucleus.

### 6. ACIDS.

The electrolysis of aromatic acids by no means offers results which are comparable to those obtained by the electrolysis of aliphatic acids. In so far as the aromatic acids, or their salts, act as electrolytes, a regeneration of the acid from the anion RCOO and water, with evolution of oxygen, occurs almost exclusively. A splitting off of carbonic acid, which makes possible the manifold reactions of aliphatic acids, almost never occurs here. The results obtained with aromatic acids are, therefore, only of a more general interest so far as the acids, by substitutions in the benzene nucleus, can act as cathodic or anodic depolarizers, and can in this way exert reduction and oxidation effects.

Benzole Acid.—Benzole acid and its salts were examined by several investigators, first by Matteuci,[1] then by Brester,[2] but most thoroughly by Bourgoin.[3]

The result of all these investigations is to show that here no secondary reactions take place, as was observed in the case of the fatty acids, but that the only effect of the current is to produce a separation into hydrogen (or metal) and the acid radical, the latter regenerating the acid at the positive pole.

In an alkaline solution it is possible to so increase the oxidation that the benzole acid is destroyed. The decomposition products which thefi appear at the anode are carbon dioxide, carbon monoxide, and sometimes acetylene. The odor of bitter almonds is also frequently observed.

A thorough investigation was made by L6b,[4] who employed a current having a potential of 6-7 volts and a current density of 15-20 amp. per sq. cm. and obtained a small quantity of

[1] Bull. soc. chim. 10, 209 (1868).
[2] Jahresb. f. Chem. (1866), 87.
[3] BuU. soc. chim. 9, 431 (1867).
[4] Ztschr. f. Elektrochemie, 2, 663; 3, 3 (1896).

a substance containing sodium, but the chemical nature of which has not yet been determined. There is formed besides this compound a small quantity of benzaldehyde, as well as acetylene and carbon monoxide. Under no circumstances do diphenyl or other hydrocarbons occur; nor do fatty acids appear, which is otherwise generally the case in an extensive oxidation of this character.

According to the investigations of Schall,[1] diphenyl does, however, occur if a solution of sodium benzoate in molten benzoic acid is electrolyzed at 100 volts between silver electrodes.

*Benzoic Esters.*—Tafel and Friedrichs,[2] by conducting the electrolysis in alcoholic-aqueous sulpnuric acid at lead or mercury cathodes, obtained methyl benzyl ether and the ethyl benzyl ether from benzoic methyl and benzoic ethyl esters respectively. Mettler,[3] by a similar arrangement, obtained chiefly benzyl alcohoi and some benzyl methyl ether from benzoic methyl ester.

The *esters* of *monochlor- and brombenzow acids* also yield the corresponding ethers and alcohols.

TMobenzoic Acid.—On electrolyzing this acid Bunge[4] obtained the bisulphide of benzoyl.

Sulphobenzoic Acid.—This acid, according to the statements of the same investigator, is not changed by the current.

Phthalic Acid.—Bourgoin[5] states that the electrolysis of this acid and of its neutral or alkaline salts resulted in the formation of the unchanged acid at the positive pole. The appearance of small quantities of carbon dioxide and carbon monoxide, however, was an evidence that a small portion of the acid had undergone oxidation.

The potassium salt of the mono-ethyl ester of phthalic acid, when electrolyzed by Brown and Walker,[6] became dark-colored, and a resinous substance was .formed, but the isolation of any

[1] Ztschr. f. Elektrochemie 6, 102 (1899),
[2] Ber. d. deutsch. chem. Gesellsch. 87, 3182 (1904).
[3] Ibid. £7, 3692 (1904).
[4] Ibid. 3, 296 (1870).
[6] Jahresb. 1 Chem. 631 (1871).
[6] Lieb. Ann. 274, 67 (1893).

new electrolytic product was not possible. *Phthalic esters,* according to Tafel and Friedrichs,[1] can be readily reduced in the presence of sulphuric acid at lead or mercury cathodes.

Phenylacetic Acid. — This acid, electrolyzed in the form of its potassium salt by Slawik,[2] yielded free phenylacetic acid.

p-Toluic Acid. — According to an incomplete research by Labhardt and Zschoche,[3] p-toluic acid in alkaline solution -at polished platinum anodes is oxidized to terephthalic acid :

COOH

COOH JOOH.

p-Toluenesulphonic Acid. — This acid gives at platinum and lead electrodes a poor yield of p-sulphobenzoic acid (Sebor[4]).

Cinnamic Acid. — Cinnamic acid, investigated by Brester,[5] showed a similar behavior in the electrolysis of both the free acid and the neutral solutions of its salts. Lob [6] has reported an accidental observation on the formation of *bromstyrene* by electrolysis of cinnamic acid in the presence of potassium bromide.

In acid solution Marie[7] converted cinnamic acid almost quantitatively into hydrocinnamic acid.

Benzylmalonic Acid. — When this acid in the form of its ethyl-potassium salt was submitted to electrolysis by Brown and Walker [8] it exhibited a bejiavior materially different from that of malonic acid. The solution became dark-colored, but contained no new compound. If oxidation occurred; it was a complete oxidation into carbon dioxide and carbon monoxide, such as has been observed in the case of unsaturated acids.

However, when v. Miller [9] electrolyzed the ethyl-potassium

[1] l. c.
[2] Ber. d. deutsch. chem. Gesellsch. 7, 1051 (1874).
[8] Ztschr. f. Elektrochemie 8, 93 (1902).
[4] Ibid. 9,370 (1903).
[5] Jahresb. 1 Chem. 87 (1866).
[9] Ztschr. f. Elektrochemie 3, 46 (1896).
[7] Compt. rend. 136, 1331 (1903).
[8] Lieb. Ann. 274,67(1893).
[8] Ztschr. f. Elektrochemie 4, 57 (1897).

salt of this acid in the presence of *potassium acetate,* not only a'-methylhydrociimamie ester,

$$C_6H_5CH_2CH<\begin{matrix}COOC_2H_5\\ CH_3\end{matrix}$$

but also dibenzylsuccinic ester,

$$\begin{matrix}C_6H_5 - CH_2 - CH - COOC_2H_5\\ C_6H_5 - CH_2 - CH - COOC_2H_5,\end{matrix}$$

was produced, as was to be expected according to the Brown-Walker reaction. There are also present the normal by-products of the electrolysis of such kind of acids, in this case hydrocinnamic acid and cinnamic acid. On repeating these experiments, Hauser[1] was also able to isolate propylbenzene, the formation of which was brought about by the electrolysis of hydrocinnamic ester—readily formed from the material started with—and potassium acetate.

The electrolysis of the ester-salt of benzylmalonic acid with *potassium butyrate* and *caproate* takes place just as with potassium acetate. Good yields of propylhydrocinnamic ester and amylhydrocinnamic ester, besides dibenzylsuccinic ester and cinnamic and hydrocinnamic esters, are obtained.

Dibenzylacetic Acid. — This substance, on electrolysis of its potassium salt, and a mixture of this salt with fatty acid salts, gives no tangible products.

Salicylic Acid.—The formation of yellow mordant dyes, which are obtained by the electrolytic oxidation of aromatic oxycarboxylic acids in sulphuric-acid solution (Badische Anilin- u. Sodafabrik[2]), seems to be based on the frequently mentioned introduction of oxygen into the benzene nucleus. The materials serving as starting-point, aside from salicylic acid, were symmetrical *m-dioxybenzoic* acidf *gallic add, tannin, gallaminic acid, esters of the adds, m- and p-oxybenzoic acid, and other oxy-acids.*

[1] Dissertation Munich (1901).
[3]D. R. P. No. 85390 (1895).

The electrolytic introduction of halogens into salicylic acid has been mentioned under phenols (p. 201).

Von Miller and Hofer [1] have applied their method for the electrolysis of organic oxy-acids to several aromatic acids containing substituents; these experiments may briefly be mentioned here.

Plienyl-/?-lactic Acid. — This acid gives at the anode benzaldehyde, besides resinous bodies.

Mandelic Acid. — This substance yielded at the anode chiefly carbonic acid, a little carbon monoxide, and also benzaldehyde. The same body was formed in the electrolysis of *phenyl-glyceric acid.*

Suip&oanthranilic Acid. — This substance, according to a patent [2] of Kalle & Co., can be converted into anthranilic acid if electrolyzed in neutral or slightly acid solution at a mercury cathode.

### 7. ACID AMIDES AND NITRILES.

According to the investigations of Baillie and Tafel,[3] the reduction of acid amides in sulphuric-acid solution at lead cathodes leads to amines, as shown in the equation:

$$RCONH_2 + 4H = ECH_2 - NH_2 + H_20.$$

Benzamide yields only a little benzylamine; benzaldhyde, which probably contained benzyl alcohol, was also formed. In a similar manner

Bimethylbenzamide gives dimethylbenzylamine;
Acetanilide gives ethylaniline ;
Acetyl-o-toluidine gives ethyl-o-toluidine; and
Succinanil gives phenylpyrrolidone:

$CH_2$—OCX $\quad\quad$ $CH_2$— OC
I $\quad$ $>NC_6H_5+4H =$ | $\quad$ ;,
$CH_2$—OCX $\quad\quad$ $CH_2$~CH

[1] Ber. d. deutsch. chera. Gesellsch. 27, 461 (1894).
[2] D. K. P. No. 146716 (1902).
[8] Ber. d. deutsch. chem. Gesellsch. 32, 68 (1899).

(The same reaction in the aliphatic series, p. 119, in the pyridine and quinoline series, p. 218.)

o-Toluenesulphonamide (o-Toluenesulphamide).—According to a patent of F. v. Heyden Naehfolger,[1] benzoylsulphonimides can be prepared by the electrolytic oxidation of toluenesulphonamides in alkaline, or earthy-alkaline solution; for example* o-benzoylsulphonimide (benzoic sulphimide), or sacharin, from o-toluenesulphonamide:

$$C_6H_4<^{SO_2 \cdot NH_2}_{CH_3} + 3O = C_6H_4<^{SO_2}_{CO}>NH + 2H_2O.$$

The p-nitro-substitution products of o-toluenesulphcnamide- are said to behave similarly.

Just as amines are easily obtained by reduction of nitriles- with sodium amalgam or sodium and alcohol, so this reaction can be carried out electrolytically (p. 121).

Benzonitrile.—Ahrens,[2] by electrolytic reduction of this substance in dilute 'sulphuric acid at a platinum cathode^ obtained benzylamine; in like manner,

Benzylcyanide gave the corresponding phenylethylamine.

### 8. THE INDIGO REDUCTION.

The reduction of indigo by electrolytic hydrogen in alkaline suspension, the fluid being warmed, has already been carried. out by Fr. Goppelsroder[3] and v. "Wartha.[4] Mullerus [5] easily reduced indigosulphonic acid.

Thorough studies regarding the process of the reduction of indigo by the electric current have recently been made by A. Binz,[6] and Binz and Hagenbach[7]; these show that most probably zinc and not hydrogen plays the chief part in the reduction. Thus when indigo is electrolytically reduced in

[1] D. R. P. No. .85491 (1895).

[2] Ztsdhr. 1 Elektrochemie 3, 100 (1896).

[3] Preparation and Fixation of Dyes with the Aid of Electrolysis, Reichenberg, 1885.

[4] Chan. Ztg. 8, No. 25 (1884).

[5] Ibid. 17,1454 (1893).

[6] Ztschr. 1 Elektrochemie 5, 5, 103 (1898); 9, 599 (1903).

[7] Ibid. $, 261 (1899).

alkaline solution, almost no formation of indigo-white occurs,, but if alkaline-zinc solutions and zinc cathodes are employed a smooth reduction (formation of the vat) takes place.

Binz concludes further that the conversion of indigo into indigo-white depends upon a withdrawal of oxygen and not upon the taking up of hydrogen, as hitherto supposed. The phenomena observed in the reduction of indigo agree with the views regarding the behavior of attackable cathodes, as mentioned in the introduction (p. 18). The reducing agent is the discharged zinc-ions, whose separation on the cathode and whose reaction with the depolarizer indigo occurs in a proportion which depends upon the velocities of the two processes. The cathode potential appears as a measure for the reduction energy,, whose value is naturally determined by the chemical nature of the zinc, and cannot forthwith be attainable by any other reducing agent such as hydrogen. In this respect we can say with Binz that the indigo reduction is based upon the direct action of the metal.

Without entering upon the subject of the electrolytic preparation of reducing substances which are useful for vat formation, such as hydrosulphites, a process[1] of the Farbwerke-Meister, Lucius and Briining in Hochst may here be mentioned by which sulphite solutions are electrolyzed at higher temperatures in the presence of indigo. Hereby the sulphites are converted into hydrosulphites, which accomplish the reduction of indigo, the sulphites being regenerated. The latter are again continually reduced. In alkaline electrolytes a vat is immediately formed and in acid solutions solid indigo-white is precipitated. The current density and cathode material can at wil] be chosen within wider limits.

## 9. PYEIDINE DERIVATIVES AND ALKALOIDS.

The pyridine ring is easily reducible. Hydropyridines are formed from pyridine and its derivatives, and piperidines by complete hydration. Quinoline and acridine are also easily converted into hydro-compounds.

[1] D. H. P. No. 139567 (1902).

These reductions can easily be obtained with the electric current under suitable conditions; the alkaloids, which have a pyridine nucleus, also behave analogously.

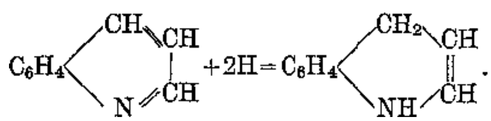
Pyridine. — Ahrens [l] accomplished the electrolytic reduction of *pyridine* and the derivatives of pyridine, and obtained piperidine from pyridine, and a-pipecoline from *a-picoline.* In these electrolyses lead cathodes and 10% solutions of sulphuric acid were employed.

If strong sulphuric acid and a platinum cathode are used there is formed a substance containing nitrogen and sulphur, the chemical nature of which has not yet been determined.

Benzoylpiperidine. — On the occasion of their experiments regarding the reduction of acicl amides, Baillie and Tafel,[2] by electrolytical reduction in sulphuric acid at a lead cathode, converted benzoylpipericline into benzylpiperidine and obtained a yield of 77 per cent, of the latter compound.

Quinoline was electrolyzed by Ahrens [3] in a 10% sulphuric acid. The cathode was of lead, and the anode of platinum. An apparent!}[7] tri-molecular hydroquinone $(CgH_9N)3$ was chiefly formed at the cathode, besides small quantities of hydroquinoline $(C_9H_9N)2$ and tetraliydroqumoline, $C_9HiiN_2$.

According to a later patent of E. Merck,[4] if quinoline is electrolyzed in dilute sulphuric acid containing for 1 equivalent of the base at least 4 equivalents of the acid, and free from metallic salts, a good yield of dihydroquinoline is obtained.




Acetyltetrahydroqttinoline. — As in the case of benzoyipiperidine, Baillie and Tafel [5] were able to reduce this compound, and obtained a good yield of ethyl tetrahydroquinoline.

[l] Ztschr. 1 Elektrochemie 2, 577, 580 (1898) ; also D. R P. No. 90308 (1896).
[2] Rer. d. deutsch. chem. Gesellsch. 32, 74 (1899).
[5] Ztschr. f. Elektrochemie 2, 580 (1893).
[4] D. R. P. No. 104664 (1898).
[6] Berd. deutsch chem. Gesellsch. 32, 74 (1899).

Quinaldine (a-methylquinoline), according to the process of Ahrens,[1] can be converted into dihydroquinaldine, CioHioNH, and tetrahydroquinaldine, $Ci_0Hi_3N$.

The nitroso- and nitro-derivatives of the pyridine and quinoline series have already been discussed (see p. 192).

The *coca-alkaloids,* like cocaine, atropine, etc., contain perhaps a combination of a piperidine ring with a pyrrolidine ring. This combination is also expressed in their behavior in electrolysis. At present the following is known.

Atropine, CirHtaNOs.—From the neutral sulphate of atropine crystallized atropine is gradually precipitated at the cathode, while at the anode carbon dioxide, carbon monoxide, oxygen, and nitrogen are evolved. The acid sulphate behaves in a similar manner, but the evolution of nitrogen w[r]as not observed (Bourgoin[2]).

Atropine is decomposed by baryta water into tropic acid and Tropine.

—CH—CH2

$CH_3N$ CHOH=$C_8Hi_SNO$.

CH2—CH—CH2

This substance? on electrolysis in alkaline and acid solution at lead electrodes, and at a low temperature, is converted into tropin one.[3]

CH2—CH—CH2

$CH_3N$ CO

CH2—CH—CH2.

A good yield of this substance is obtained. *Pseudotropine* behaves in the same manner.

[1] Ztschr. f. Elektrochemie 2, 580 (1896).
[2] Bull. soc. chim. 12, 400 (1869).
[8] D. R. D. No. 118607 (1900).

Tropinone.—This compound can inversely be easily reduced to pure tropine. The chem. Fabrik vorm. E. Sobering[1] employs as electrolyte an aqueous ammoniacal ammonium sulphate solution.

E. Merck,[2] by electrolysis of a slightly alkaline solution, obtains, besides tropine, pseudotropine. The yield is 50 per cent. of the tropinone employed.

### Opium **Bases.**

Opium. — If opium is subjected to the action of the electric current, morphine ($Ci_7Hi_9NO(OH)_2$) goes to the cathode and ineconic acid (oxypyronediearboxylie acid) to the anode (Lassaigne).[3]

Morphine, CiyH^NOs -fH$_2$0. — Pommerehne,[4] by the electrolysis of a solution of morphine acidified with sulphuric acid, obtained after a few days crystals of oxydimorphine sulphate at the anode. The solution became dark-colored.

Codeine (methylmorphine) $Ci_7H_{17}NO(OH)0 \cdot CH_3$. — On electrolysis of the neutral sulphate hydrogen is evolved, codeine is precipitated, and the solution turns brown (Bourgoin [5]).

The acid sulphate undergoes more complete decomposition, and carbon dioxide, carbon monoxide, oxygen, and nitrogen are split off.

Cotarnine, C^HisNC^ — This compound is converted quantitatively by the electrolytic hydrogen into pure hydrocotarnine (Brandon and Wolffenstein [6]) :

Hydrastimne, CuHisNOs, which does not, indeed, belong to the opium bases, may nevertheless be mentioned here. This substance is similarly converted into hydrohydrastinine, Cn

[1] D. R. D. No. 96362 (1898).
[2] D. R. D. No. 115517 (1900).
[3] Tommasi, Trait4 d'Electrochimie 788 (1889).
[4] Arch. Pharm. **2S5,** 364 (1897).
[5] Bull. soc. chim. **12,** 400 (1869).
[6] Ber. d. deutsch. chem. GeselLsch. 81, 1577 (1898); D. R, P. No. 94949

### Quina- and Strychnos Bases.

Quinine, $C_{20}H_{24}N_2O_2$.—Although the neutral sulphate is a Tery poor conductor, the acid sulphate is readily decomposed into carbon dioxide, carbon monoxide, and nitrogen. The color of the solution changes to a dark brown.

Besides the last-named gases, the above-mentioned alkaloids split off various other products, principally complicated nitrogen-containing compounds (Bourgoin[1]).

Pommerehne,[2] by electrolysis of a sulphuric-acid quinine solution, obtained a green resinous mass, which is perhaps identical with thalleioquin (?).

*Quinine, cinclwnine* (CigB^^O), and *cinchonidine* ($C_{19}H_{22}N_2O$), on electrolysis at lead cathodes in a 50% sulphuric-acid solution, are converted into non-crystallizable tetrahydro-bodies (Tafel and Naumann[3]).

Strychnine, $C_{21}H_{22}N_2O_2$.—The neutral sulphate suffers but little change. The solution becomes slightly colored, hydrogen and oxygen are given off, and crystals of strychnine collect at the cathode.

The acid sulphate behaves in a like manner, except that in its case the formation of carbon dioxide and carbon monoxide, as well as oxygen and nitrogen, shows that a part of the substance undergoes complete decomposition. In strongly acid solutions the splitting off of nitrogen does not occur (Bourgoin [4]).

Tafel and Naumann [5] have made more thorough investigations regarding the electrolytic reduction of strychnine in strong sulphuric acid solution at lead cathodes. According to Tafel's researches, strychnine is to be regarded as a cyclical acid anilide of the formula:

$$(C_{20}H_{22}ON)<\begin{matrix}CO\\ N\end{matrix}.$$

[1] Bull. soc. chim. **12,** 400 (1869).

[2] l. c.

[3] Ber. d. deutsch. chem. Gesellsch. **34,** 3299 (1901).

[4] Bull. soc. chim. **12,** 400 (1869).

[5] Lieb. Ann. 301, 291 (1898); Ber. d. deutsch. chem. Gesellsch. **34** 3291 (1901).

The water-soluble tetrahydrostryelinine is first formed:

3H2OH
(C2oH22ON) '

which by further reduction is converted ink) strychnidine:

(C20H22ON)

.
N

The quantity of the former preponderates at a low temperature. On the other hand, the higher the temperature the greater the quantity of strychnidine formed.

Brucine, C2sH26N204. — A solution of the neutral sulphate turns red and the sulphate is decomposed. Hydrogen is evolved . at the negative pole, but the brucine completely absorbs the oxygen at the positive pole (Bourgoin).

The acid salt is very energetically decomposed, becoming first red and then brown. At the anode carbonic-acid gas, carbon monoxide, oxygen, and nitrogen escape (Bourgoin[1]).

Besides the gases mentioned, the above alkaloids break up into other products, principally complex compounds containing nitrogen.

According to Tafel's and NaumannV investigations, brucine behaves like strychnine in so far as that by reduction under similar conditions tetrahydrobrucine is produced; however, to obtain the crystalline product the temperature must not exceed 15°. But a body corresponding to strychnidine was not found among the products of the electrolytic reduction of brucine.

If we give brucine the following formula (Moufang and Tafel*):

CO

[1] 1. c.
M. c.
[3] Lieb. Am. **804*24** (1898).

then tetrahydrobrucine has most probably the formula :

$$CH_2OH$$

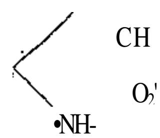
Brucidine, corresponding to strychnidine, is formed from tetrahydrobrucine if this is heated to 200°, water being split off:

Sv

$$[C_{20}H_{20}(OCH_3)_2ONK \begin{matrix} /CH_2 \\ X_N \end{matrix} \cdot$$

Morpholone. — Lees and Shedden [1] have investigated the electrolytic reduction of pheno- and naphthomorpholones in sulphuric-acid solution. Morpholines are produced only as by-products, the morpholone ring being for the most part broken up.

**Phenomorpholone,**




gives as end-products of the reduction acetyl-o-aminophenol,

$$C_6H_4<\begin{matrix} OH \\ NHCOCH_3, \end{matrix}$$

also ethyl-o-aminophenol,

$$C_6H_4<\begin{matrix} OH \\ N \end{matrix}$$

and also isoacetyl-o-aminophenol,

$$C_6H<\begin{matrix} OH \\ \wedge \end{matrix}$$

[1] Proceed. Chem. Soc. **19,132** (1903); Journ. Chem. Soc. 83, 750 (1903)

**n-Methylphenomorpholone,**

$C_6H_4<$

$CH_3$

gives, besides n-acetylmethyl-o-aminophenol,

OH
/$COCH_3$
<
X$CH_3$

and n-methylethyl-o-aminophenol,

/OH
$C_6H_4<$ /$CH_aCH_3$,
\

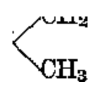
also n-methylpiienomorpholine,

$C_6H$.

3

C
H

n-Methyl-/?-naphthomorpholone gives n-methylethyl-a-amino-/?-naphthol:



and n-methyl-/?-naphthomorpholine:

°\
I
C $CH_2$
H
2
/

'<«»

frj

## 10. THE CAMPHOR GROUP.

Camphor.—This substance, as shown by the synthesis car-
Tied out by Romppa,[1] has certainly the formula proposed by Bredt:

$CH_3$

$CH_2$----- CH ----- CH2

Being a ketohe it can be reduced to the secondary alcohol >borneol:

$CH_3$
$CH_2$---------C------- CH(OH)

$CH_2$-

This reduction has been carried out electrolytically by Tafel Schmitz [2] in sulphuric-acid solution at mercury catnodes. They obtain thus about 45 per cent, of the theoretically possible yield, with a maximum current consumption of 38 per cent. .At lead cathodes no satisfactory reduction can be effected.

W'.

m

Camphoric Acid,

$CH_3$
CHo -- C --- COOH *

$CH_2$---- CH -- COOH

is the oxidation product of camphor with nitric acid.

Brown and Walker[3] also electroylzed (see p. 102) the .sodium-ethyl salt of camphoric acid and obtained two esters "-which they were able to separate by means of fractional dis-

[1] Ber. d. deutsch. chem. Oesellsch. 86, 4332 (1903).
[2] Ztschr. f. Elektrochemie 8, 288 (1902).
*Lieb. Ann. 274, 71(1893).

tillation. One of these (boiling-point 212°-213°) on being; saponified yielded an unsaturated monobasic acid, CoH^O^ *cwnpMytic add;* the other having a higher boiling-point (240°-242°), was the neutral ester of a diabasic acid, CisHscAi, to which Walker gave the name of *camphothetic acid.* These experiments are of great importance, because they prove t he-dibasic nature of camphoric acid, a fact which was doubted by Friedel.

Walker and Henderson [1] found, moreover, that upon electrolysis of concentrated aqueous solutions of the ethyl-potassium salt of *allocamphoric acid* there are formed as chief products the ethyl esters of a dibasic acid, CieE and of a monobasic acid, CgHisCOOH:

1. $2C_8H_{14}<$ xCOOCsHs / XCOO $-2C0_2 + C_{16}H_{28}<$ /COOCaHs / $^XCOOC_2H_5$

2. 2CgHi4<' xCOOC$_2$H$_5$ / N COO = CsHi4<T XCOOH

It has been found on further investigation [2] that besides the strongly dextrorotary unsaturated acid designated as *allocampholytic acid,* CgH^COOH, an isomeric acid is formed which, although slightly dextrorotary as obtained, is perhaps even laevorotary in an entirely pure condition. The latter on being" heated to 200° splits off carbon dioxide and yields a hydrocarbon, CsHi4, which boils at 120-122° and appears to be identical with *laurolene,*

$CH_2$-CR

1 ,

;y CH2—

made from camphoric acid.

A ketonic acid, $C_8Hi_3O$-COOH, melting-point 228°, is also-found as an additional product of the electrolysis of potassium

[1] Journ. Chem. Soc. **67,** 337 (1895).
[2] Ibid. 69, 748(1897).

alloeamphoric ethyl ester. The authors concluded from their observations that camphoric acid contains the group

H

H-O

-O/H

V\COOH

-C-COOH,

a deduction which had, of course, to be later modified.

According to later experiments of Walker and Cormack,[1] it-is possible to obtain isolauronolic acid by eleetrolyzing the methyl-ester-potassium salt of camphoric acid:

$$2C_8H_{14}<{}^{COOCH_3}_{COO-} = C_8H_{14}<{}^{COOCH_3}_{COOH} + CO_2 + C_8H_{13}COOCH_3.$$

The free optically inactive isolauronolic acid,

CH₂—CCOOH
‖
CH₃C
CH₂—C
\
CH₃

was obtained from the latter ester. The electrolytic reaction occurs hence in a normal direction.

Camphoric-acid imide,

$$\begin{array}{l} \quad\;\; CH_3 \\ CH_2—C——CO\backslash \\ \qquad\qquad\qquad\quad >NH \\ CH_2—CH—CO/ \end{array}$$

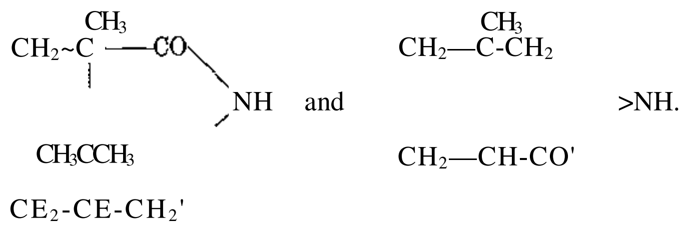
was reduced in sulphuric-acid solution at a prepared lead cathode. The experiment was made by Tafel and Eckstein,[2] in connection with their investigations concerning the electro-

[1] Proceed. Chem. Soc. 16, 58 (1900).

[2] Ber. d. deutsch. chem. GeseUsch. M, 3274 (1901); see also D. R. P No. 126196 (1900).

lytic reduction of succinimide (p. 119). Just as succinimide, by replacement of one of the two oxygen atoms by two hydrogen atoms, is converted into pyrrolidone and, by complete elimination of the oxygen, into pyrrolidine—although only to a very slight extent—so camphoric-acid imide gives two perfectly-analogous products, camphidone and camphidine.

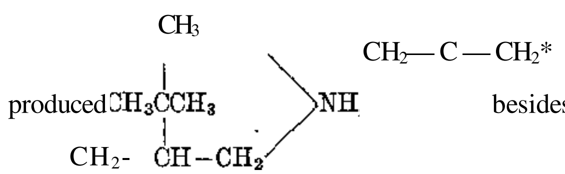
Camphidone occurs in two isomeric modifications, separable in the form of the picrates, α-camphidone and β-camphidone:



Which one of these is the α- and which the β-camphidone remains undecided.

Camphidine,

is always produced



besides camphidones, and can be readily separated from these, since it possesses a decidedly basic character.

As the camphidones are extremely resistant towards further reduction, they form no intermediate phase in the camphidine formation. We must suppose that only those acid-imide molecules, both of whose carboxylic groups are by accident *simultaneously* attacked by the reducing agent, are changed into camphidine. Or, a carbinol-like intermediate product, in which the second carboxylic group—in contradistinction to that of camphidone—is electrolytically attackable, is already formed during the transition from camphoric-acid imide to the camphidone.

## 11. ELECTROLYSIS OF BLOOD AND ALBUMEN.

Blood.[1]—The defibrinated blood of a dog was submitted to electrolysis by Becquerel. He made use of platinum electrodes and a current furnished by a battery of three Daniell cells. At the negative pole he observed the following phenomena:

The blood became brown and alkaline, and contained neither white nor red corpuscles; it possessed the property of gradually dissolving blood-corpuscles and had the odor of putrid meat.

At the positive pole uridecomposeci and partially decomposed blood-corpuscles were present in large quantities. The fluid gave a precipitate of albumen with nitric acid, mercuric chloride and lead acetate.

Albumen.[2]—When an albumen solution was electrolysed by Dumas and Prevost$_7$ under conditions similar to those used by Becquerel for blood, the alkali metal went to the negative pole, hydrogen was evolved, and acetic and phosphoric acids appeared at the positive pole. The result of this is that the albumen is coagulated at the negative pole (by the alkali present), while at the positive pole the solution remains clear.

As Lassaigne has shown, pure albumen in aqueous solution is a non-conductor of electricity; the addition of salts or acids is therefore necessary in its electrolysis.

The Pharmaceutical Institute of L. W. Gans of Frankfurt[3] has made known a process for electrochemically preparing fluorine-substitution products of albumens. The latter are suspended, or dissolved in a dilute aqueous solution of hydrofluoric acid or salts of this acicl, and subjected at a platinum electrode to the anode current action. The discharged fluorine reacts with the albumen, forming substitution products.

[1] Tommasi, Trait6 d'Electrochimie 800 (1889),
[2] I.e.
[S] D. R. P. No. 116881 (1898).

## CHAPTER V.

### ELECTROLYSIS WITH ALTERNATING CURRENTS.

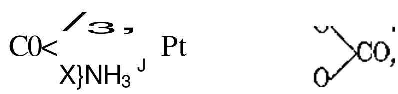
IF the polarity of the current is not allowed to change too rapidly, it is possible, since oxidation and reduction occur successively at each pole, to accomplish electrolyses with alternating currents. Experiments with this end in view have been made *by* Drechsel.[1] Dehydration is a case of simultaneous reduction and oxidation. The supposition that in living organisms carbamide is produced from ammonium carbamate by the splitting off of water prompted Drechsel to make experiments in this direction. When an aqueous solution of ammonium carbamate is electrolysed with a current from a battery of 4-6 Grove cells, and platinum electrodes used, carbamide is obtained independently of the electrode material when alternating currents are employed. The reactions are supposed to be either

I. $NH_2COONH_4 + O = NH_2COONH_2 + H_2O$;
II. $NH_2COONH_2 + 2H = NH_2CONH_2 + H_2O$,

or

II.

The observation that the platinum electrodes were strongly attacked, with the formation of platinum salts, caused Gerdes [2] to investigate the platinum bases. As the principal product he found a compound to which he gave the following formula :



[1] Journ. prakt. Chem. **22,** 476 (1880); Ber. d. deutsch. chem. Gesellsch. 18,2436 (1880).

[2] Journ. prakt. Chem. **26,** 257 (1882); see also Inaug-Dissert., Leipzig 1882.

and the chloride of which is said to have the composition

ClNE3N / s a
>Pt< Ptam-2E20.
C1NH/ XNH3NH3CF "

Gercles also examined the nitrate and sulphate of this base.

In the course of further researches [1] Drechsel found that when alkaline solutions were used platinum "was present in the electrolysed fluid. Copper when used as electrode showed a similar behavior; lead was less attacked, gold but very slightly, and palladium not at all.

The formation of *phenylsulphuric acid* in living organisms is supposed, like carbamide, to be the result of dehydration. Taking this into consideration, Drechsel carried out the following experiment:

A saturated solution of aeicl magnesium carbonate was mixed with an equal volume of a solution of magnesium sulphate and the mixture was saturated with commercial carbolic acid.

When this solution was electrolyzed for thirty hours with alternating currents, using platinum electrodes, then the following products were obtained :

1. /–Diphenol.
2. Pyroeateclin.
3. Hydroquinone.
4. Phenylsulphuric acid.
5. Oxalic acid.
6. Formic acid.
7. Succinic acid.
8. Malonic acid (?).
9. n- Valeric acid (?).
10. n-Butyric acid (?).
11. Some cyclohexanone,[2] CsHioO.

According to Drechsel the formation of the phenol ester of sulphuric acid is probably represented by the following equations:

I. $C_6H_5OHH$- $KOS0_3H$ +0 - $C_6H_6OOS0_3H+H_20$.

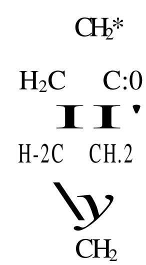
Later Drechsel [2] electrolyzed *normal caproic add* with alternating currents. The electrolytic solution contained, in a vol-

[1] Joum, prakt. Chera. 29, 229 (1884).
[2] Ibid. *M,* 135 (1886).

ume of 3 liters, 200 g. of caproic acid as magnesium salt and was nearly saturated with acid magnesium carbonate. Platinum electrodes were used. At the end of the experiment the following compounds could be identified in the solution:

1. Valeric acid.
2. Butyric acid.
3. Oxalic acid.
4. Succinic acid.
5. Adipic acid.
6. Oxycaproic acid.
7. Glutaric acid.

In a still later research on the electrolysis of *phenol* with alternating currents Drechsel[1] detected phenylsulphuric acid, dioxybenzenes, a number of acids of the fatty acid series, and in addition to these an oil which he identified as hydrophenoketone,



and whose phenylhydrazine compound he was able to isolate. Drechsel regards hydrophenoketone as the origin of the fatty compounds formed. By the direct addition of water to this compound caproic acid results, and this then breaks up into the acids and other decomposition products mentioned above.

Some of the above acids have been mentioned as decomposition products of phenol in the investigation cited on the electrolysis of phenol.

[1] Journ. pract. Chem. 38, 65 (1888).

# CHAPTER VI.

## ELECTRIC ENDOSMOSE.

BY electric endosmose or cataphoresis is meant the often observed phenomenon of the migration or flow of a fluid, under the influence of potential differences, through the diaphragm separating the cathode and anode chambers. This flow or transportation of fluid always occurs in a certain direction, either to the anode or to the cathode, depending upon the nature of the substances and the diaphragm; it has no connection with the electrical phenomena following Faraday's laws. If the rigid d'aphragm is replaced by fine suspensions which act like a movable diaphragm, the fluid remains at rest, but the suspended particles migrate, i.e., are urged in the fluid towards[1] the electrode. This directed movement depends undoubtedly upon a polar charge of the suspended particles contrary to that of the water. Since the organic colloids, like the colloid solutions of albumen, carbohydrates, haemoglobin, indigo, and of natural dyes, act as an extremely fine suspension, cataphoresis also possesses great importance for organic substances, as to their suspension, coagulation and sedimentation phenomena. The scientific treatment of this field has begun. Bredig[1] mentions' that the direction of albumen depends upon the chemical composition of the fluid; for instance, whether the aqueous medium is alkaline or acid.

Electric endosmose is of technical importance for the[4] dehydration of organic, finely suspended substances containing[1] very much water, for example, the drying of peat, according,

[1] **Ztschr. f. Elektrochemie 9, 739 (1903).**

to the experiments of Schwerin.[1] The peat, at a tension of 4 to 5 volts per centimeter peat layer, migrates to the anode and is deposited on the latter in a firm coat, while at the cathode the water becomes clear. Aqueous dye-pastes behave similarly. The technical purification of albumens by cataphoresis is also said to be feasible.

Another field in which cataphoresis, or the convective conduction as the process is also called, has apparently already become of great importance, is the tanning industry.

If the skin to be tanned is brought between the cathode and anode in a dilute tannic-acid solution, a migration of the colloidally dissolved tannic acid takes place through the skin from the positive to the negative electrode. By a regular slow change of the "current direction the tannic-acid solution can be pressed into the pores of the skin and thus a considerable saving in time is accomplished.[2]

*Note.*—It has been known for a long time that many finely divided bodies suspended in water, as gold, copper, graphite, silica, feldspar, sulphur, lycopodium, etc., as well as minute drops of liquids, such as 682 and oil of turpentine, and bubbles of oxygen, marsh-gas, etc., show cataphoresis phenomena. All these are urged in water towards the positive electrode, but in oil of turpentine the direction is reversed except in the case of particles of sulphur; the direction is also reversed for silica in carbon disulphide. The earlier experiments along these lines on solid particles contained in fluids of high resistance were made by Faraday, Jiirgensen, Quincke, etc.—Translator.

[1] Ztschr. f. Elektrochemie 9, 739 (1903); D. R. P. No. 131932 (1901).
[2] S. Foelsing, Jahrb. d. Elektrochemie 2, 269 (1895).

# PART II.

## *ELECTROTHERMIC PROCESSES AND THE SILENT ELECTRIC DISCHARGE.*

## CHAPTER I.

### THEORETICS AND METHODICS.

#### 1. THEOBETICS.

ACCORDING to Ohm's law the strength or intensity of the electric current, i.e. the quantity of electricity which is conducted by an electric conductor or a system of conductors in a given time, is directly proportional to the effective electromotive force, and inversely proportional to the resistance of the current field:

$$w$$

where $i$ is the current strength, $e$ the electromotive force or the tension, and $w$ the resistance. The work which electrical energy can perform in a current field is expressed by the product of the electromotive force existing in this field and the current strength

where $A$ denotes the work to be done.

Substances are known which interpose a more or less strong resistance to the passage of the current, and such whose resistance is so great that practically no passage of the current takes place. The former are called, conductors of electricity; the latter non-conductors or insulators. The conductors themselves are in turn again subdivided into two sharply defined classes; those which conduct the current without being materially changed, i.e. the passage of electricity produces no change in the chemical composition of the substance, and those—presenting a remarkable contrast to the former—in which the passage of electricity results in the chemical decomposition of the substance of the conductor at points where the electric current enters and leaves the body, i.e. Ranges of the substance occur. To the former class of conductors belong all metals and carbon, the conductors of the first class; to the latter the bases, acids, and salts in solution, particularly aqueous solution, or in a molten, and also, under certain conditions, in a solid,[1] state. They form conductors of the second class, or electrolytes.

Ohm's law is equally applicable to both classes. The work which the current can do, however, depends upon the nature of the conductor. If the circuit is completely metallic and closed, the total electric energy can be converted into heat; but if the circuit contains an electrolyte, a large part of the electric energy is used up in the production of chemical ,and physical effects which occur w[r]hen the circuit is closed.

To determine in a simple way the connection of the electric •energy with the calorific energy caused by it, an electric circuit can be closed by a metallic wire placed in a calorimeter, .and the current measured calorifically by the heat effects produced by the different electromotive forces and intensities. The result of such measurements is the equivalence of the heat occurring in the conductor with the electric energy, hence with the product of electromotive force into the electric quantity

$$Q = kei,$$

where $Q$ denotes the heat generated in the wire. The factor $k$ is the electrical equivalent of heat, which permits a numerical

-[1] See Nemst, on "solid electrolytes/' Zeit. f. Elektrocheinie 6, 41-43 (1899).

comparison of the two forms of energy. It follows, that

0.239 cal = 1 voltxl coulomb.

If we introduce from Ohm's law tJtie factor *iw* for the electromotive force *e,* then

The amount of heat generated in a given time varies directly as the product of the resistance of the conductor into the square of the current strength. This relation is called *Joule's*[1] *law,* named after its discoverer. The heat which is thus derived only from the current quantities, but not from chemical changes, is also called *Joule's heat.*

If, besides the metallic connections, an electrolyte is included in the closed circuit, a part of the electric energy is used up in chemical work. The electrical energy is then transformed in various ways,—in all parts of the current 'field heat is developed proportional to the resistance of each separate part and the square of the current strength, but chemical work and material changes and disarrangements in the electrolyte are also accomplished.

In utilizing the heat produced by the current for reactions of organic bodies, only those systems are taken into account in which the current, by forming a spark discharge or luminous arc, is forced either to pass through gases or vapors with high resistance, or to heat wires or filaments to high temperatures. While the extremely high temperatures, which can be attained by means of the voltaic arc in the electric furnace, have through Moissan's investigations become of great importance for mineral chemistry, it is a peculiarity of organic substances, whose conditions of existence, with few exceptions, are connected with relatively low temperatures, and are mostly quite sensitive, that the methods applicable here must allow a fuller scope in temperature than is accorded by the spark discharge or luminous arc. RuhmkorfPs coils, and less often frictional electric machines,

[1] Phil. May 19, 260 (1841).

are usually employed for giving sparks. The resistance furnaces, in which a tube of carbon is heated by the current, seem more suited for carrying out pyrogenic reactions of carbon compounds. Both heating methods have already been used. Lepsius [1] has employed the luminous arc for decomposing gases and demonstrating volumetric proportions, also for preparing water gas. Bredig[2] made some qualitative tests on the behavior of separate organic fluids towards the luminous arc, while Hofmann and Buff[3] have also investigated the effect of electrically incandescent platinum and iron wires on some gases and vapors. Legler,[4] in his experiments on the incomplete combustion of ether, also employed electrically heated platinum. Moreover, Haber,[5] by making the heated conductor (of platinum, platinum-iridium, or carbon) tube-shaped and conducting the current of gas through the hollow centre in which was placed a glass or porcelain tube, perfected the principle of resistance ovens for the chemical investigations of gases. But these investigations did not lead to an extensive use of these- electrical methods for obtaining pyrogenic reactions with organic bodies. Most of the material of such reactions has so far been collected with the spark discharge between metallic electrodes; of late years numerous experiments on the pyrogenic reactions of organic bodies have been undertaken with electrically incandescent wires or filaments.

## 2. THE REACTION TEMPERATURES.

Before taking up the subject of the individual results, some remarks on the attainable temperatures, the possibility of their variation, their measurement and calculation will be made.

No very accurate measurements of the temperatures occurring in the spark discharged are available, great difficulties

[1] Ber. d. deutsch. chem. Gesellsch. 23, 1418, 1637, 1642 (1890).

[2] Ztschr. f. Elektrochemie 4, 514 (1898).

[3] Lieb. Ann. 113, 129 (1860).

[4] Ibid. 217, 381 (1883); Ber d. deutsch. chem. Gesellsch. 18, 3350 (1885).

[5] Experimental Investigations on the Decomposition and Combustion of Hydrocarbons (Munich, 1896) 43.

being encountered in their determination. Calorific methods are best suited for investigating the temperature of the luminous arc, or the radiant energy is employed for learning the temperature. In the latter case a bolometer or photometer is used.

According to Violle,[1] the temperature of the positive carbon point and of the carbon particles in the voltaic arc equals the evaporation temperature of carbon. This was determined by breaking off the incandescent tip of the carbon and dropping it into a calorimeter. One gram carbon requires 1600 cal. to heat it from 0° up to its evaporation temperature. As 300 cal. are necessary to heat it from 0° to 1000°, 1300 cal. remain for raising the temperature from 1000° to 3°, if *x* is the evaporation temperature of carbon. If we take the specific heat of carbon at 0.52, then 1300 cal. represent 2500° more, so tliat the evaporation temperature of carbon, *x*/ and the hottest parts of the luminous arc, equal 3500$^0$.[2]

Langley, Paschen, Violle, and Le Chatelier[2] sought to determine the temperature of the heated body by means of the radiant intensity.

The use of the thermopile in the form of Le Chatelier [7]s[3] platinum, platinum-rhodium thermocouple, a so-called pyrometer, has obtained especial importance. This can be used to measure temperatures up to 1700$^0$.[4] The electromotive force is measured either by one of the well-known methods, or else direct reading precision-voltmeters (or galvanometers), whose scales are divided both into millivolts and into the corresponding degrees Celsius or Fahrenheit, are employed. The determination of the

[1] Cpmpt. rend. 115, 1273 (1892); 119, 949 (1894).

[2] Bams, Die physik. Behandlung und die Messung hoher Temperaturen, Leipzig, 1892; also Bredig, Uber die Ghemie der extremen Temperaturen, Leipzig, 1901.

[3] Le Chatelier et Boudouard, Mesure des temperatures elevens, Paris, 1900. Le Chatelier, Compt. rend. 114, 470 (1892) etc. Holborn u. Wien. Ann. 56, 360 (1895); 59, 213 (1896); Holborn u. Day, Wied. Ann. C8, 820 "(1899), etc.

[4] Wanner's Optical Pyrometer indicates up to 4000° C. See Journ. Am. Chem. Soc., 1904.

temperature from the electromotive force is based upon the fact that on heating the joint where the platinum wire is fused to the platinum-rhodium wire, an electromotive force of about one millivolt for every 100° C. is produced. The ratio of the electromotive force to the temperature of the fused joint is accurately determined by the Physik-tech. Reichsanstalt, and the result accompanies the calibrated pyrometer. The data always refer to an arrangement whereby the connections between the thermocouple and the conducting wires are at 0°, while the fused joint of the couple is placed in the space whose temperature is to be measured.

The resistance thermometer[1] is extremely convenient for measuring wide ranges of temperature. The electric resistance of pure metals increases with the temperature about 0.4% per degree (C.); but the temperature coefficient for different metals and also for different temperature intervals is by no means constant.[2] If the temperature coefficient is known, for accurate purposes the resistance during the experiment can be measured with a "Wheatstone bridge; for less accurate measurements it will often be sufficient to determine the tension of the incandescent wire and the intensity in the current circuit, and to calculate the resistance according to Ohm's law. Care must, however, be taken that the conducting wires connected with the wire whose temperature is being investigated are practically without resistance. For showing the dependence of the resistance upon the temperature an equation of the following form usually suffices:

or

The values a, 6, and c, or *a,* /?, and *f* are given in the tables.

Pyrogenic reactions, whose course remains the same within

* Holborn and Wien, Wied. Ann. 56, 383 (1895); **59,** 213 (1896). Callendar, Phil. Mag. **32,** 104 (1891). *

[2] Landolt-Bornstein, Physik.-Chemische Tabellen.

larger temperature intervals, permit of a further simplification, naturally at the cost of accuracy. If we make

in which the range of the respective temperature must be considered in the choice of *a,* then

$QL'W_0$

*a* is for iron about 0.0045, for nickel 0.0036; for platinum 0.0033, and for platinum-indium (20% iriduini) 0.00105, all metals in wire shape. Tliis approximate determination is convenient, even if pyrogenic reactions are brought about *by* the wire itself, whereby an accurate determination of reaction temperature often becomes illusory for the most .various reasons.[1]

### 3. ARRANGEMENTS.

Little can be said about the arrangements to be chosen for the pyrogenic reactions of organic bodies. Both the spark discharge and the luminous arc can be produced in fluids or molten substances. Lob,[2] in decompositions with, the luminous arc, employed a small flask with three tubulures, about the shape aad size of the boiling-vessel employed in Beckmann/s method for determining molecular weights. Each of the two side tubes of equal dimensions supports a thin carbon rod passed through the perforation of a tightly fitting stopper, so that the electrodes in the inside of the vessel are at an angle to one another. The centre tubulure supports a return condenser to which is attached an arrangement for collecting the generated gases. By regulating the "volume of the liquid in the decomposition flask the luminous arc can at will be produced in the liquid or its vapor. In the latter case the substance is heated to boiling and the circuit closed as soon as the air in the apparatus is displaced by the vapor.

[1] LOb, Ztschr. f. Elektrochemde 7, 903 (1901).
[2] Ber, d. deutsch. chern. Gesellsch. **34,** 915 (1901).

The degree of decomposition by the voltaic arc depends of course, to a great extent upon the chemical nature of the liquids and vapors in which the luminous arc is produced- While ether, methyl alcohol, ethyl alcohol, glacial acetic acid, and other aliphatic fluids and their vapors are subject to decompositions with very trifling charring, and give products which are chemically closely related to the products started with, benzene, toluene, nitrobenzene, aniline, naphthalene, phenol, and other members of the aromatic series are destroyed, and considerable charring results.

For this reason the method worked out and employed by Lob,[1] replacing the luminous arc by metallic and carbon resistances, proves in general to be more suitable for the purpose of obtaining pyrogenic reactions of organic substances.

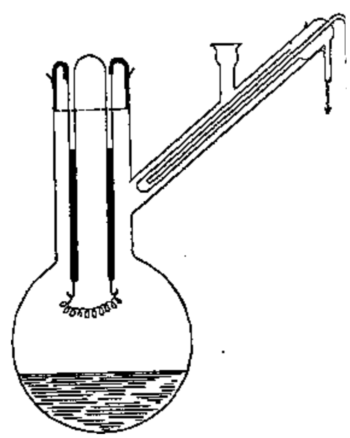


FIG. 8.—Eleetropyrogenizer.

A round flask with a long neck is closed with a thrice-perforated stopper. Two small glass tubes with strong platinum hooks sealed in the lower ends are passed through the two side perforations; a little mercury forms the connection between the hooks and the conducting wires leading in. Or, strong wires bent into hooks at one end are directly stuck through the stopper, which can be done without injuring the tight fit. The incandescent wire, a metallic wire of about 0.2 mm. diameter, is fastened to the hooks by wrapping it around or hooking it on. A return condenser is placed in the centre perforation. Lob, when making decompositions in a perfectly air-tight apparatus and under diminished pressure, replaces the stopper by a ground-glass stopper in which the

[1] L6b, Ztschr. 1 Elektrochemie 7, 904 (1901); 10, 505 (1904).

small tubes with platinum hooks are sealed in. The return condenser, which serves as an internal cooling apparatus, is attached to the side; another glass tube sealed in the wall of the flask (not shown in the figure) serves for admitting air, or for the passage of other gases for special purposes (see Fig. 8). This apparatus is particularly adapted for pyrogenic reactions of high-boiling substances in a partial vacuum. The substance is placed in the round bulb. Direct heating converts it into vapor, which, after the air has been removed, is permanently in contact with the incandescent wire.

# CHAPTER II.

## THE SPARK DISCHARGE AND THE VOLTAIC ARC.

### 1. THE SPARK DISCHARGE.

It is well known that most of the gaseous hydrocarbons of the aliphatic series when exploded with an excess of oxygen are converted into the end-products of combustion, carbonic acid and water. This fact is made use of in quantitative gas analysis. The combustion is often not complete; intermediate products can be obtained if we start with hydrocarbon derivatives instead of the hydrocarbons themselves.

Berthelot gave a comprehensive exposition of the results known at that time on the effect of the spark discharge upon the formation and decomposition of carbonic acid and hydrocarbons and the herewith occurring equilibrium phenomena (Berthelot, Essai de M<§canique Chimique II, 336-362, Paris, 1879).

Methane.—The induction sparks decompose this substance into carbon and hydrogen (Hofmann [1] and Buff), which fact Dalton had already observed.

Berthelot[2] obtained hydrogen, carbon and acetylene. If the latter is continually gotten rid of, the greater part of methane can be converted into acetylene,'otherwise the latter is decomposed and changed in a complex manner.

Methane is also produced by the reaction of carbon monoxide with hydrogen under the influence of the induction spark

[1] Lieb. Ann. 113,129 (1860).
[2] Ibid. 123,211 (1862).

(Brodie [a]), a fact which, explains the formation of hydrocyanic aeid from carbon monoxide, hydrogen, and nitrogen, as will be mentioned further on.

Ethylene is decomposed "by the spark discharge into its elements (Dalton, Hofmann, and Buff[2]). According to Wilde,[3] acetylene is first formed, and is then decomposed into its elements. Besides, according to Thenard and Berthelot,[4] a fluid and solid product are produced.

W. G. Mixter [5] has. recently investigated the combustion phenomena of several hydrocarbons by means of a weak electric spark discharge, and has proven among other things that ethylene can also yield acetic acid besides carbonic acid. The pressure under -which the gases react is important for the course of the experiment. Mixter sought to determine the relative reaction -velocities as compared with, that of an oxyhydrogen mixture, under equal conditions.

Acrolem, $CH_2$:CH-$CHO_J$ according to E. von Meyer,[6] is formed when ethylene with an excess of oxygen is exploded in a eudiometer.

Formic Acid.—Wilde [7] found that the action of the electric spark on gaseous mixtures of oxygen and alcohol, hydrogen and carbon dioxide, and methane and carbon dioxide, produced formic acid. In the first and last mentioned of these mixtures *acetic add* is also formed.

Acetylene.—The spark acts, as already mentioned, by reason of its high temperature which, according to Berthelot,[8] is sufficient to produce acetylene from a mixture of carbon disulphide and hydrogen, sulphur being precipitated.

[1] Lieb. Ann. 1G9, 270 (1873).
[2] Ibid. 113,129(1860).
[3] Ztschr. f. Cheniie 2, 735 (1866).
[4] Tralt<§ de M<§caiique chirnique II, 350 (1879).
[8] Ann. Joum. of Sc. [4] 4, 51 (1897); Jotirn. Chem. Soc. **73,** 246 (1898); Proceed. Chem. Soc. 39 (1898).
• JOUTH. f. prakt. Cheniie [2] 10, 113 (1874).
[7] Bull. soc. cliixn. [2] 5,267 (1866).
• [8] Tommasi Trait 6* d'Eleetrochimie 715 (1879).

Hydrocyanic Acid. — Berthelot[1] obtained this substance by passing the electric spark through a mixture of acetylene and nitrogen. The acid is in fact frequently produced in far-reaching decompositions by the electric spark; thus from a mixture of ethylene or aniline vapor with nitrogen (Berthelot[x]), from a mixture of acetylene with nitric oxide (Huntington[2]), •ammonia with benzene, or ether and nitrogen (Perkin[3]), etc. The reactions are also in a certain sense reversible. Hydrocyanic acid is readily split up by the current (Gay-Lussac [4]), and in the presence of hydrogen (Berthelot [5]), into acetylene and nitrogen.

The union of acetylene and nitrogen to hydrocyanic acid takes place rather smoothly if the easy decomposability of acetylene is lessened by dilution with hydrogen, as was already done by Berthelot.[6] His experiments were recently again taken up by Gruszkiewicz.[7] The electrodes were blackened by a deposition of carbon except with a maximum content of acetylene of 5 per cent, by volume (composition of tne gas mixture-: 5 per cent, acetylene, 5 per cent, nitrogen and 90 per cent, hydrogen).

Gruszkiewicz obtained better results by using a mixture of carbon monoxide, hydrogen, and nitrogen. He found that the proportion of the components was essentially decisive for the yield and the reaction velocity. A mixture approximately corresponding in composition to that of water gas, Dowson gas, generator gas, etc., gave encouraging results. Thus, if 3 liters of a gas mixture of 54.62 per cent. CO, 24.88 per cent. N£, and 20.50 per cent. $H_2$ were permitted to flow for an hour through the space through which the sparks were discharged, then about 12 cc. hydrocyanic acid were obtained. Carbon dioxide, like carbon monoxide, is reduced by hydrogen in the spark dis-

[1] Bull. soc. chim. [2] 13, 107 (1869).
[2] D. R. P. No. 93852 (1895).
[8] Jahresb. f. Chemie. 399 (1870).
* Ann. chim. phys. 78, 245 (1811); Gilberts Ann. 1811.
[8] Bull. soc. chim. [2] **13,** 107 (1869).
[6] Trait£ de MScanique chimique II, 355 (1879).
[7] Ztschr. f. Elektrochemie 9, 83 (1903).

charge, and changed, by uniting with nitrogen, into hydrocyanic acid. The reaction can be shown in the equation,

$$2CO+3H_2 4- N_2 = 2HCN + 2H_20;$$

or,

$$2CO+6H_2=2CH_4+2H_20$$

$$2CEU+N_2«2HCN+3H_2.$$

Cyanogen shows the same easy decomposability as hydrocyanic acid. Both Berthelot[1] and Hofmann and Buff[2] observed that cyanogen, was decomposed into its elements by the action of the electric spark. The least trace of water in the gas caused the formation of hydrocyanic acid and acetylene.

The observation of Morrens,[3] who claimed to have obtained cyanogen in an atmosphere of nitrogen by passing the induction spark between two carbon electrodes, is therefore incorrect. The decomposition of cyanogen by the action of the electric spark has, moreover, been noted by Davy, and by Andrews andTait.[4]

Ethyl Alcohol.—In an atmosphere of ethyl-alcohol vapors, M. Quet[5] and Perrot [6] obtained, besides some carbon, a substance which exploded on being heated, the chemical nature of which they were unable to determine. The liquid became acid but Perrot found that no water was formed in the decomposition of the alcohol; he was also unable to prove the presence of carbonic acid gas. Melly [7] and Lommel[8] made similar experiments, the latter employed a Holtz machine. The gas escaping in the decomposition of the alcohol probably contains acetylene and ethylene.

Ethyl Ether.—According to Wilde's[9] experiments, ethyl ether, under reduced pressure, also yields ethylene besides other

[1] Compt. rend. 82, 1360 (1876).
[2] Lieb. Ann. IIS, 129 (1860).
[3] Compt. rend. 48, 342 (1859).
[4] Journ. Chom. Soc. 13, 344 (1861).
[1] Compt. rend. 46, 903 (1858).
[8] Ibid 46, 180 (1858); 47, 351 (1859).
[7] Tommasi, Trait6 d'Electrochimie, 724 (1879).
[8] Ibid, 725 (1879).
[8] Ztschr. f. Chemie 2, 735 (1866).

gases, and a deposition of carbon. Truchot[1] observed methane and hydrogen besides the ethylene. Perrot,[2] by the action of bromine upon the gases obtained by the action of the electric spark, was able to isolate a liquid, $C_3H_5Br_3$, boiling at 135°-140°, and isomeric with tribromhydrin. Klobukow,[3] by heating ether vapor to 250°-300° and passing the spark through the latter, obtained carbon monoxide, hydrogen, methane, ethylene, and acetylene.

Acetone.—Wilde[4] investigated the action of the electric spark on acetone vapor in a Torricelli vacuum. Acetylene was formed in the gas mixture and carbon was deposited on the sides of the vessel.

Formic Acid, on the contrary, does not yield acetylene (Wilde). Nor could he prove the presence of this gas in the decomposition of *acetic acid.*

Methylamine.—The electric spark, when passed through methylamine vapor by Hofmann and Buff,[5] gave primarily hydrogen and methylamine hydrocyanide; further action brought about complete decomposition, tarry substances being deposited.

Trimethylamine was investigated by the same authors. It also is completely broken up, tarry products being formed.

Ethylamine.—Hofmann and Buff obtained tar-like products and a non-alkaline gas having an odor like that of ethyl cyanide.

The experiments carried out on the behavior of compounds of the aromatic series when subjected to the electric spark have so far given very few results.

Benzene.—Destrem[6] investigated the action of the induction spark between two platinum points on benzene, and obtained a gas mixture of acetylene and hydrogen, while the liquid contained diphenyl and a crystalline substance which was not closely investigated. Benzene vapor, under reduced pressure,

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1 Compt. rend. 84, 714 (1877).
2 Ibid. **46,** 180 (1858).
3 Journ. f. prakt. chemie [2] **34,** 126 (1886).
4 Bull. soc. chim. [2] 5, 267 (1866).
5 Lieb. Ann. **113,** 129 (1860).
6 Bull. soc. chim. **42,** 267 (1884).

is decomposed by the electric spark, likewise producing acetylene (Wilde[2]).

Toluene. — Destrem[1] obtained from toluene, as from benzene, acetylene, and hydrogen. The liquid contained, besides. diphenyl, a solid substance which was not further investigated.

Naphthalene. — Wilde[2] also investigated the behavior of naphthalene vapor under reduced pressure when subjected to the action of the induction spark. He obtained a gas mixture, containing acetylene.

Aniline. — Destrem[3] investigated the action of the electric spark from an induction apparatus on aniline vapor, and observed a decomposition into acetylene, hydrogen, hydrocyanic acid, and nitrogen.

Pyrogenic reactions of organic compounds with the "'electric: flame/' (flaming discharge) as produced at a lower tension and higher intensity than required for the production of the spark (at about 2000-4000 volts and 0.05-0.15 amp.) have not yet been carried out.

According to the investigations of W. Muthmann and EL Hofer,[4] interesting results are also to be expected in its application to organic compounds.

## 2. THE VOLTAIC ARC.

As already mentioned in the introduction, the enormously high temperature of the luminous arc is only applicable in certain cases to organic compounds.

Several reactions have, however, become of fundamental, theoretical and practical importance; for instance, Berthelot's acetylene synthesis, the preparation of carbides, and some other processes.

[1] Bull. soc. chim. **42,** 267 (1884).
[2] Ibid. 5, 267 (1866). '
•1. c., see also Jahresb. f. Chem. 272 (1884).
[4] Ber. d. deutsch. chem.Gesellsch. **36,** 438 (1903).

Acetylene.—Berthelot[1] showed that carbon and hydrogen combined to acetylene on passing the voltaic arc over carbon points in an atmosphere of hydrogen. The synthesis of acetylene from its elements first made possible the complete synthesis of a whole series of organic compounds. Acetylene, as is well known, is produced by the decomposition of many organic compounds at high temperatures. Bredig[2] thus obtained acetylene, besides other hydrocarbons, when he produced the luminous arc in liquid petroleum.

The Metal Carbides.—These are of great technical and scientific importance. They have been repeatedly and thoroughly described, hence a reference to various works upon this subject will suffice here.[3]

Bolton[4] succeeded in combining *chlorine and carbon.* He employed the voltaic arc between carbon electrodes in an atmosphere of chlorine. Perchlorethane is principally produced; hexachlorbenzene is formed in lesser quantity. As both of these chlor-hydrocarbons are produced by the complete chlorinatlon of carbon tetrachloride, Bolton assumes their intermediate existence; the intermediate occurrence of gaseous or fluid compounds like perchlorethylene does not seem improbable. Bromine and iodine appear to react analogously (Bolton[4]); experiments with the latter halogens yet await a scientific treatment. They would undoubtedly prove remunerative.

Lob [5] has made several other decompositions by means of the voltaic arc between carbon points. These were carried out with the following vapors and liquids:

Methyl Alcohol yields formic acid, and also about 39 per cent, methane, 45 per cent, hydrogen, small quantities of carbonic

[1]Ann. chim. phys. [4] 13, 143 (1868); see also Berthelot: EssaideMecanique CMmique II, 332-336 (1879).

[2] Ztschr. f. Elektrochemie 4, 514 (1898).

[3]Moissan, The Electric Furnace, Ahrens: Die Metallkarbide (Sammlung chemisch-technischer Vortrage), Stuttgart, 1896, Haber: Grundriss der technlscher Elektrochemie, Miinchen und Leipzig, 1898. See also," Recent literature on carbides," Journ. Am. Chem. Sac. 1904, p. 200.—Trans.

[4] Ztschr. f. Elektrochemie 8, 165 (1902); 9, 209 (1903).

[5] Ber. d. deutsch. chem. Gesellsch. 34, 9l5 (1901).

acid carbon monoxide, and acetylene. Formaldehyde is not formed.

Glacial Acetic Acid yields about 35 per cent, carbon monoxide, 26 per cent, hydrogen, 15.5 per cent, carbonic acid, and 12 per cent, saturated and 7 per cent, unsaturated hydrocarbons.

Benzene.—The benzene is colored brown and is considerably charred; no substance could be isolated from the liquid. The escaping gas consists of 86-90 per cent, hydrogen as well as small quantities of saturated and unsaturated hydrocarbons.

Fapfrthalene likewise yields chiefly hydrogen, the residue being greatly charred.

Cyanogen is completely decomposed by the voltaic arc, as shown by Hofmann and Buff.[1]

Cyanides.—The attempts to prepare cyanides by the direct or indirect" union of nitrogen and carbon must be mentioned here; they are of importance particularly for the problem of utilizing atmospheric nitrogen. Since the reactions take place at a high temperature, we can also make use of electrically produced heat, as suggested by Readmann;[2] but in his process—a mixture of oxides or carbonates of alkalies, or earthy alkalies, with carbon is heated in the voltaic arc between two carbon points in the presence of nitrogen—electrolysis occurs as'an important factor. The conditions are similar in his attempts, undertaken with Gilmour,[3] to prepare potassium ferrocyanide.

[1] Lieb. Ann. 113, 129 (1860).
[2] Eng. Pat. No. 6621 (1894).
[3] Eng. Pat. No. 24116 (1892).

# CHAPTER III.

## THE UTILIZATION OF CURRENT HEAT IN SOLID CONDUCTORS.

Methane. — Davy decomposed methane with an electrically incandescent platinum wire into carbon and hydrogen, an effect which was also later obtained by Hofmann and Buff[1] with an electrically incandescent iron spiral.

Ethylene, according to the last named investigators, [1] likewise breaks down, under similar conditions, into its elements.

Cyanogen. — Cyanogen also is completely split up by an incandescent iron wire into carbon and nitrogen.

Haber [2] has made some experiments regarding the decomposition of several hydrocarbons in the electric furnace. The gas current was conducted through a glass or porcelain tube which was placed in an electrically heated tube of platinum, platinum-iridium, or carbon.

Hexane. — No considerable decomposition of hexane vapor occurs at about 600°; at 800°-940°, however, there were produced the following percentages of gases, based on 100 per cent. of the vaporized hydrocarbon :

| | |
|---|---|
| Methane ............. | 27.77% |
| Olefines (ethylene). ... | 22. 14% |
| Acetylene ............ | 1. 00% |
| Hydrogen ..... ...... | 2.44% |
| Benzene ............. | 6. 76-10% |
| Carbon .............. | 3.27% |
| Tar ............... . . | 29.22% |

[1] Lieb. Ann. **113,** 129 (1860).

[2] Experimental-Untersuchungen über Zersetzung und Verbrennung von Kohlenwasserstoffen, 43-77 Munich (1896).

At a still higher temperature hexane is for the greater part converted into its elements.

Trimethylethylene is split up at 930°-940° in the following manner. From 100 per cent, of material started with there were obtained.

| | |
|---|---|
| Methane | 27.72% . |
| Ethylene | 8.10% |
| Hydrogen | 1.76% |
| Gaseous by-products. .. . | 4.46% |
| Acetylene | 0.30% |
| Carbon | 5.09% |
| Benzene | 8.00-13.41% |
| Tar | 33.71-39.12% |

The above figures represent percentages by weight. At 1000° trimethylethylene is also extensively decomposed.

Ethyl Ether.—For obtaining a slow combustion of the ether, Legler[1] passed a mixture of ether vapor and air over an electrically incandescent platinum wire and obtained a mixture of formic acid, acetic acid, formaldehyde, acetaldehyde, and hexaoxymethylene peroxide (CH^O^Oa+SE^O.

Lob has recently carried out a great number of pyrogenic reactions and syntheses, employing the already • described arrangement (p. 242) with electrically incandescent metallic wires and carbon filaments.

Methyl Alcohol.[2]—On employing a cherry-red incandescent iron wire, this substance yielded, besides formic acid and a little trioxymethylene, a gas mixture containing about 72 per cent, hydrogen, 20 per cent, carbon monoxide, 6.5 per cent, methane, and traces of carbon dioxide. The figures represent percentages by volume, the same as below.

Chloroform.[3]—This compound, when brought into contact with an incandescent wire of iron, nickel, platinum,, or platinum-iridium heated to 850°-950°, is decomposed, there being formed perchlorbenzene (10%), perchlorethane (12%), and perchlor-

[1] Ber. d. deutsch. chem. Gesellsch. 18, 3350 (1885).
[2] Ibid. 34, 917 (1901).
[3] Ztschr. 1 Elektrochemie 7, 903 (1901).

ethylene (30%). The figures refer to percentages by volume based on the original material. Much hydrochloric acid is also produced, and, after the passage of the gases through water, a small quantity of carbon monoxide. If a mixture of chloroform with water is subjected to a similar pyrogenic decomposition, a good deal of carbon monoxide is evolved. Its formation is to be explained by the intermediate presence of dichlormethylene.

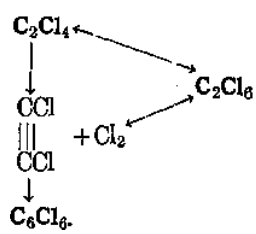
Ctiloroform and Aniline.[1] — The vapors of these two substances, blown with steam against the incandescent metallic wire, unite chiefly to triphenylguanidine, while decomposition products of chloroform alone, perchlorbenzene, perchlorethane and perchlorethylene, are present in considerably smaller quantities. The formation of triphenylguanidine is easily understood by supposing that dichlormethylene is intermediately produced. Phenylisocyanide is primarily formed from this substance and aniline; the isocyanide- immediately takes up chlorine, which is derived from the accompanying process, 3C2CU = Cede + SCk, and unites further with the excess of aniline to triphenylguanidine :

**II.**

**III.** $C6H_6NCCl2+2CiH_aNH_2$«$C6H5NC(HNC6H_5)2+2Ha$.

On the basis of these experiments Lob arranges the following scheme for the pyrogenic chloroform decomposition, which affords a complete expression of all the observed phenomena :

$$CCl_3H \dashrightarrow CCl_2+HCl$$

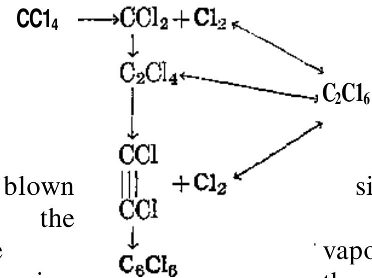



[1] Ztschr. f. Elektrochemie 7, 903 (1901).

The arrows show the direction and the possible reversibility of the reactions; stable end-products are printed in heavy type.

Carbon Tetrachloride.[1] —This compound, when decomposed' alone by an arrangement similar to that used for chloroform, gives off great quantities of chlorine; perchlorbenzene, perchlorethane (in very trifling quantity), and perchlorethylene are also produced. The presence of water in this case also increases the yield of carbon monoxide. Aniline leads to triphenylguanidine, some resin being also formed.

The scheme of decomposition for tetrachlormethane is the following:




If air is blown simultaneously with the tetrachlormethane vapors against the incandescent wire, there is produced phosgene, which is probably formed by direct oxidation of dichlpr-methylene :

Perchlorethylene[2] yields a gas mixture of chlorine and a little carbon monoxide, and also phosgene in the presence of air. The residue in the flask consists principally of perchlorbenzene besides traces of perchlorethane. Addition of water considerably increases the quantity of carbon monoxide.

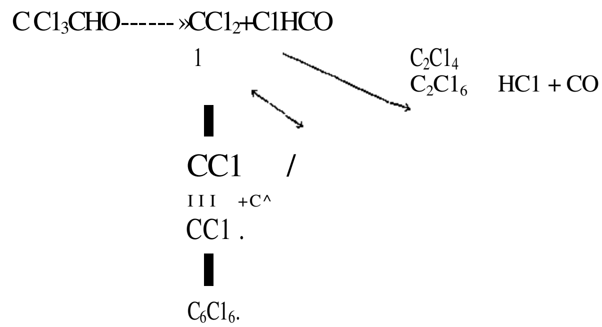
**Chloral Hydrate,[3] when subjected to pyrogenic decomposi-**

te.

[2] l. c.

[3] Ztschr. f. Elektroehemie 10, 504 (1904).

tion alone or mixed with water vapors, breaks up in the same manner. The reactions are expressed in the following scheme:




Besides the products observed in the decomposition of chloroform, carbon monoxide also occurs as a direct decomposition product of the unstable formylchloride.

Trichloracetic Acid is completely decomposed at higher temperatures into gases; Joist[1] could detect hydrochloric acid, chlorine, carbon monoxide, and carbon dioxide, besides traces of phosgene. The decomposition takes place, perhaps with the aid of moisture, as shown in the equation:

$$2CCl_3COOH + H_2O = Cl_2 + 4HCl + 3CO + CO_2.$$

Phosgene is formed secondarily from chlorine and carbon monoxide.

Acetyl Chloride breaks up (Joist[1]) completely into approximately equal volumes hydrochloric acid, carbon monoxide, and unsaturated hydrocarbons (mostly ethylene). The reaction is expressed in the equation:

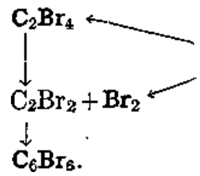
$$2CH_3COCl = 2HCl + 2CO + C_2H_4.$$

Bromoform splits off hydrobromic acid and some free bromine, and yields as chief product perbromethylene, also perbrom benzene (Joist[1]). Hexabromethane occurs only in traces; this was to be expected on account of its easy decomposability into bromine and perbromethylene. Some carbon monoxide

[1] The experiments have not yet been published. Bonn (1904).

escapes. If the bromoform vapors are mixed with aqueous vapors the products remain the same; but no gas is evolved, and the water contains, besides hydrobromic acid, small quantities of formic acid. The following expresses the decomposition:

$$CBr_3H \longrightarrow CBr_2 + HBr$$



*I*

Presence of water determines the reaction:

$$CBr_2 + 2H_2O = HCOOH + 2HBr,$$

while with chloroform the reaction is

$$CCl_2 + H_2O = CO + 2HCl,$$

carbon monoxide being produced.

Benzene, as is well known, is easily converted at high temperatures into diphenyl and complex hydrocarbons. Lob's[1] method is very well suited for preparing diphenyl on a small scale. Metallic wires serve the same purpose as carbon filaments. Diphenylbenzene occurs as a by-product in small quantity.

Nitrobenzene, blown in vapor form against the incandescent wire, decomposes violently, sometimes explosively, producing a charred mass and large quantities of nitric oxide. The reaction is moderated by diluting the vapors with aqueous vapor, but the obtainable products are so complex that their determination has not yet been accomplished (Lob [2]).

[1] Ztschr. f. Elektrochemie 8, 777 (1902)'.

[2] Ber. d, deutsch. chem. Gesellsch. 34, 918 (1901); Ztschr. f. Elektrochemie 8, 775 (1902).

o-Nitrotoluene. — Although the pure vapors of o-nitrotoluene behave like those of nitrobenzene, o-nitrotoluene diluted with aqueous vapors yields anthranilic acid, in addition to a little o-cresol and salicylic acid and considerable resinous substances (Lob [x]). It is possible that anthranil is primarily formed from o-nitrotoluene, water being split off; the anthranil is then converted into anthranilic acid by the highly heated steam, just as by boiling with alkalies:

$$C_6H_4 < \begin{matrix} NO_2 \\ CH_3 \end{matrix} \quad -C_6$$

The presence of salicylic acid must evidently be referred to the action of the hot aqueous vapors upon anthranilic acid:

$$C_6H_4 < \begin{matrix} NH_2 \\ COOH \end{matrix} \quad H_2O \qquad \begin{matrix} OH \\ OOH \end{matrix} + NH_3.$$

Slight traces of ammonia could be detected. The o-cresol was evidently formed from o-nitrotoluene and aqueous vapor, with splitting off of nitrous acid.

The material of the glower is mostly without any influence on the reaction. Platinum, platinum-indium, nickel, iron and carbon gave qualitatively equal results; only copper wires are not applicable for the preparation of anthranilic acid. They primarily cause a reduction to o-toluidine and then complete combustion is brought about by the copper oxide which is formed.

Aniline.[2]— This compound is colored brown, ammonia is split off and some gas evolved. Diphenylamine and carbazole could be isolated.

Diphenylamine.[2] — On conducting the. vapors of this sub-. stance mixed with those of chloroform over metallic glowers,

[1] Ztschr. f. Elektrochemie 8, 776 (1902).

[2] Ber. d. deutsch. chem. Gesellsch. **34,** 918 (1901); Ztschr. f. Elektroefcemie 7, 913 (1901).

diphenylamine combines with chloroform and gives a small yield of acridine.

Benzyl Chloride, *benzol chloride* and *benzotrichloride,* when subjected like chloroform to pyrogenic decomposition, behave quite like the latter compound; a dissociation into hydrochloric acid, or chlorine and phenylmethylene, or chlorphenylmethylene, seems to occur first (Lob[1]).

Benzal Chloride gives smoothly stilbene, with splitting off of hydrochloric acid:

$$2C_6H_5CH_2Cl \rightarrow 2C_6H_5-CH + 2HCl$$
$$\downarrow$$
$$C_6H_5\cdot CH:CH\cdot C_6H_5.$$

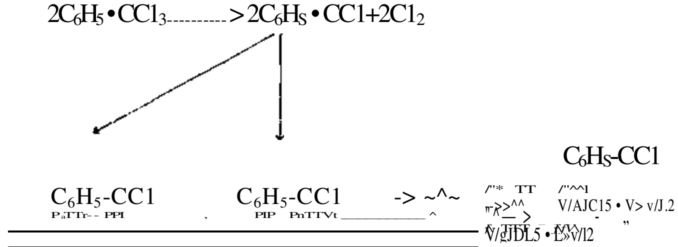
Benzal chloride also splits off hydrochloric acid, but no chlorine; a mixture of $\alpha$- and $\beta$-tolane dichlorides results:

$$2C_6H_5\cdot CHCl_2 \rightarrow 2C_6H_5\cdot CCl + 2HCl$$

$$C_6H_5-CCl \qquad\qquad C_6H_5-CCl$$
$$\qquad\qquad\qquad\qquad ClC-C_6H_5$$

Benzotrichloride at first gives off chlorine, which does not, however, escape, but is absorbed by a part of the primarily formed tolane-dichlorides; these are thereby converted into tolanetrichloride and tetrachloride.

$$2C_6H_5\cdot CCl_3 \rightarrow 2C_6H_5\cdot CCl + 2Cl_2$$




[1]Ber. d. deutsch. chem. Gesellsch. 36, 3059 (1903); Ztschr. f. Elektrochemie 9, 903 (1903).

If a mixture of benzotrichloride and water is subjected to pyrogenic decomposition, the yield of tolane dichlorides, tri- and tetrachlorides is very small, although these substances do not entirely disappear. Benzaldehyde and benzoic acid become the chief products. The benzaldehyde is apparently the reaction product of chlorphenylmethylene with water, and the benzoic acid the oxidation product of the benzaldehyde by the intermediately occurring chlorine. Benzalchloride, in the presence of water, gives benzaldehyde; no benzoic acid is formed.

# CHAPTER IV.

## THE SILENT ELECTRIC DISCHARGE AND THE ACTION OF TESLA-CTJRRENTS.

### I. THE SILENT ELECTRIC DISCHARGE.

WHILE the action of the induction spark upon organic bodies, gases and vapors is undoubtedly a thermic process., in the silent electric discharge the electric energy plays a more important part, either as such or in the form of radiant energy. In this case we are dealing with a constant passage of an electric current through gases. Even if the theory of the conduction in gases is still in its primitive stages, many phenomena already point to ionic formations or electron effects. The silent electric discharge takes place continuously between two conductors separated by a dielectric such as glass, or gases, if the potential difference of the two conductors exceeds a certain value.

In rarefied gases the discharge is accompanied by luminous appearances (glow discharges), which are often suited for investigations in spectrum analysis; under ordinary pressure and in daylight the gases do not glow; but in the dark and with a sufficiently high tension, even without rarefaction, the glow occurs.

The rise in temperature during the discharge is trifling; therefore reactions which are brought about by the latter's influence often assume a different role than those produced by the induction spark. In the latter case stable compounds are produced, which is very natural, considering the high temperature. The formation of labile, often endothermic substances, is incited by the silent electric discharge. These substances are easily decomposed by stronger calefaction. The great value of these reactions for simple syntheses—as employed by nature in plants for producing the labile compounds, which serve as plant nourishment, from the most stable products started with—lies in this property. This problem is extremely important. The synthesis of substances important for nature—the carbohydrates, albumens—in the laboratory with our usual chemical resources is only a first step in the realm of actual synthesis. This will only be found when we can follow the paths which nature herself chooses in preparing her products. Her methods are undoubtedly much simpler than the artificial, chemical processes that we must make use of in reaching the same goal. The whole primary material upon which we can base the formation of the most various substances of organic nature is the atmosphere—are carbonic acid, oxygen, nitrogen, and water. The synthesis of complex substances from these materials is known to take place under the influence of light rays and the absorption of energy. Such a transformation of a system of lower energy into one of higher energy usually occurs only at high temperatures. The silent electric discharge occupies a prominent place among the forms of energy which, like light, favor endothermic reactions at ordinary temperatures.

Berthelot,[1] in pointing to the nature of the reactions occurring under its influence, which are particularly similar to those of plants, advanced the following views: In clear weather there exists between two strata of air only one metre apart a potential difference of 20-30 volts which, in rainy weather, can increase to about 500 volts. Reactions can already take place under the influence of such tensions; thus at 7 volts a fixation of nitrogen by carbohydrates can already occur; the decomposition of carbonic acid requires higher tensions.

Opportunities for reactions on the surfaces of plants, by the formation of potential differences, are likewise continually present. In other words, Berthelot ascribes a leading part in natural syntheses to atmospheric tensions, which can neutralize one another in the form of invisible discharges (convective discharges) through thin strata of air acting like dielectrics.

[1] Compt. rend. 131, 772 (1900).

Even if this hypothesis does not seem to be scientifically well founded, it is nevertheless suitable for showing the importance of this but little investigated domain.

We still know nothing of the consumption of energy in the reactions produced by the silent electric discharge. The spent energy can be easily determined by employing certain current conditions; it is difficult to calculate experimentally the utilized energy; this is due to the insignificance of the obtained reactions and the simultaneously occurring heat quantities.

The fact that Faraday's law is not applicable shows that the reactions which are. caused by the discharge are not of a purely electrochemical nature. The chemical effect is usually larger than can be accounted for by the minimum quantities of electricity. As shown by the kind of reactions, thermic effects are also unlikely, although an influence of the temperature produced by the discharge is always manifest. The supposition is more probable that the invisible electric discharge, in which cathode and ultra-violet rays are present, introduces into the system great quantities of kinetic energy by the movement of electrons; this energy is then transformed into chemical energy. This kinetic energy would then have to be equivalent to the heat of formation of the occurring substances, taking into account the part directly converted into heat. Bichat and Guntz[1] have shown by a simple example, that of ozone, that the heat developed in the induction tube and calorimetrically measured, plus the heat of formation of the produced ozone, is equal to the calorific equivalent of the spent electrical energy.

The actual efficiency of ozonizers is extremely small. With the best ozone apparatus and under the most favorable circumstances only about 15 per cent, of the total energy can be utilized for the chemical reaction.

### a. Arrangements.

The well known and variously shaped small ozonizers of Berthelot and Siemens are generally satisfactory for scientific

[1] Aim. chim. phys. [6] 19, 131 (1890).

experiments. According to a recommendation of Losanitsch and Jovitschitsch the apparatus are suitably called " electrizers." The principle employed in their construction is always the same. An air space or chamber, chosen as narrow as possible, exists between two conductors, either metals or electrolytes, which axe connected with the terminals of an induction coiL


FIG. 9.

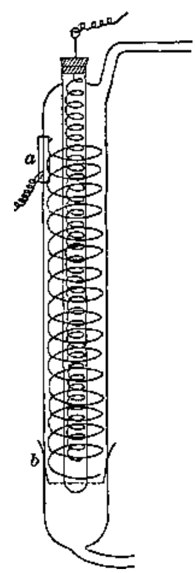



FIG. 10.

The metals serving as electrodes are in most cases separated — electrolytes of course always — from the discharging chamber by thin glass walls. Suitable small tubes attached to the apparatus afford means of ingress and egress for the gases or vapors to be acted upon. The space between the walls in the discharging chamber is of great influence (A. de Hemptinne *).

Some apparatus used by myself in experiments as yet unfinished may be mentioned here. The difference from former

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constructions exists (in Fig. 9) in the constant production of the vapors in a flask with a ground-glass neck made to fit one end of the induction tube; the flask contains the reaction fluid. This apparatus has an arrangement for cooling the vapors and one for working under diminished pressure. In Fig. 10 the apparatus can be taken apart at the ground-glass connection &• in such a way that liquids, solids, and electrodes of various* materials, especially for investigating catalytic effects, can-be brought into it. The current connections with the outer-coat is made in Fig. 10 by means of a* platinum loop a, fused into the side of the tube, in which is hooked the spiral electrode, of any kind of metal wire.

Special attention in these experiments must be paid to the-interrupter (rheotome*); platinum, and mercury circuit-breakers and electrolytic ones are applicable. The former possesses the disadvantage of great wear and tear, and in prolonged experiments requires frequent regulation. If kept clean, the-mercury circuit-breaker is very convenient. The Wehnelt circuit-breaker interrupts high current strengths very exactly, and, when suitably made, can be used both with alternating and direct currents. To save the consumption of platinum I construct the electrolytic interrupters by placing in front of a large carbon plate the point of a nickel wire 2 mm. thick as active electrode in a 2-3% sodium-hydroxide solution. Glass worms regulate the temperature with high current strengths. This simple and cheap arrangement has proven serviceable.

### b. Chemical Results.

The action of the silent electric discharge upon organic compounds takes its starting point in the observation that *oxygen* under its influence is polymerized to ozone. Although the work done in this field, which until recently was chiefly carried on by the French school, has not yet shown great practical results, we need not doubt that these phenomena deserve

[1] See also Leitfaden des Rontgenverfahrens, published by Dessauer and Wiesner, Berlin, 1903.

the greatest interest and are closely related^ as already emphasized, to the fundamental questions of synthesis in general. Besides the experiments on the behavior of organic vapors, the observations which have been made on the synthesis of simple organic compounds from carbonic acid and carbon monoxide—substances which we are not accustomed to regard as organic—are of particular interest. The results so far obtained are mentioned below. We are mostly indebted to Berthelot's investigations along this line of work.

### *I. Carbonic . Acid and Carbon Monoxide.*

Carbonic Acid. — Berthelot [1] observed the decomposition into carbon monoxide and oxygen. The reaction is reversible, an equilibrium occurs, in which, however, the partially ozonized oxygen converts carbon monoxide into carbonic acid and a solid carbon suboxide, CUOs, which Brodie [2] had already formerly observed. Carbon dioxide, under a pressure of 3-10 mm. mercury, splits up very rapidly and up to 70 per cent, into carbon monoxide and oxygen (Norman Collie [3]).

Carbonic acid, in the presence of., water, is converted into formic acid and oxygen (Losaftitsch and Jovitschitsch [4]) ; the latter, partially ozonized, produces hydrogen peroxide.

Lob [5] showed that moist carbon dioxide also always yields carbon monoxide and only the latter forms the starting point for formic acid. The following reactions occur:

2. $CO + H_2 0\text{-}HCOOH$,
3. $3\ 0_2 = 2\ 0_3$,
4.

[1] Essai de Me*canique chimique II, 377 (1879).
[2] London R. Soc. Proceed. **21,** 245 (1873); Lieb. Ann. 169, 270 (1873).
Uoum. of the Chem. Soc. 465, 1063 (1901).
* Ber. d. deutsch. chem. GeseUsch. 30,135 (1879).
[5] Sitzungsberichte d. niederrheinischen Gesellschaft fur Natur- u. Heilkunde (1903).

Carbonic acid and hydrogen, according to the experiments of Losanitsch and Jovitschitsch,[1] also unite to form formic acid.

Carbon Monoxide. — Considering the easy decomposability of carbonic acid with splitting off of carbon monoxide, the latter 's behavior is particularly interesting. According to Berthelot[2] it breaks up into carbonic acid and the above-mentioned suboxide:

Moist carbon monoxide, according to the concordant results of Losanitsch [1] and Jovitschitsch, of Lob [3], and of Hemptinne,[4] yields formic acid. There are also always formed some carbonic acid (Maquenne,[5] and Hemptinne) and hydrogen (Maquenne). The dimensions of the "'electrizer," particularly the distance of the walls between which the discharge occurs, are of special influence on the result (Hemptinne) .

The influence of the experimental conditions is shown in the action of the silent discharge upon a mixture of carbon monoxide and hydrogen. Thenard, Brodie, and Berthelot [&] found a solid body (X^HsOs)™; Berthelot also observed a little carbon dioxide, acetylene, and an olefine-like hydrocarbon. Losa.nitsch and Jovitschitsch [7] obtained formaldehyde and its polymers; Hemptinne observed an oily liquid, without being able to say anything definite regarding the formation of formaldehyde.

At any rate all these experiments are worthy of the most thorough study. If the assertion of Phipson [8] is correct, that in plants hydrogen peroxide first produces formaldehyde from. the carbonic acid ($C0_2$-f ^C^CT^O + Os), the possibility of

[1] J.c.
[2] Essai de M£canique chimique II, 379 (1879).
[3] See note 5 on page 266.
[4] Bull, de 1'Acad. roy. de Belg [3] **34,** 269 (1897).
[5] Bull. soc. ohixn. [2] **89,** 308 (1883).
[8] Essai de M6canique chimique II, 382 (1879).
[7] l.c.
[8] Chem. News, **50,** 37, 288 (1884).

the formation of sugar by polymerization is at once given. The well-known Bayer theory, of the formation of sugar in plants, in connection with the above-mentioned view of Berthelot on the importance of atmospheric tensions for the chemical reactions of plants thus obtains new essential, and experimentally accessible, facts.

Recent investigations of Berthelot[1] deserve the greatest-attention exactly in this connection. He found:

1. Carbon monoxide and carbon dioxide condense with an excess of hydrogen to carbohydrates ;

$$n(CO_2 + 2H_2) = \qquad + nH_2O.$$

2. If only a little hydrogen is present, complicated compounds rich in oxygen result.

3. In a mixture of carbon monoxide, carbon dioxide, hydrogen, and nitrogen, the discharge produces nitrogen containing compounds having the formula :

$$(COH_3N)_n, \quad \text{or} \quad (COH_3N)_n + nH_2O,$$

which are comparable with hydrocyanic acid, and the compounds of the carbamide and xanthine groups.

With an excess of carbon monoxide Berthelot finds substances which seem related to parabanic acid. If water occurs in the reactions, ammonium nitrite is present.

Berthelot's observations are confirmed by the experiments of A. Slosse,[2] who, by subjecting a mixture of 1 volume carbon monoxide and 2 volumes hydrogen to the induction action in an ozonizer, obtained a crystalline, fermentable sugar which could have been formed from formaldehyde and methyl alcohol — both of which can be shown to be present — by the further action of the discharge :

$$_2 = CH_2O;$$
$$_2 = CH_3OH.$$

[1] Compt. rend. 126, 609 (1898).
[2] Bull, de l'Acad. roy. de Belg. **35,** 547 (1898).

Berthelot has published a paper[1] on the apparatus employed in his experiments, the methods of the quantitative determinations, the influence of the conditions on the reaction velocity, and the dependence of the results upon the duration of the experiment. The latter is particularly important for the theoretical interpretation of the results. Simple, binary compounds are primarily formed which are secondarily polymerized to complex compounds — similarly as in physiological processes, in which the assimilated substances, after being split up into simpler substances for the purpose of nutrition, are again united to complicated compounds.[2]

Losanitsch and Jovitschitsch,[3] by the action of the silent electric discharge upon a mixture of carbon monoxide with other gases, have also accomplished the following syntheses. They obtained:

1. From *carbon monoxide* and *hydrogen sulphide :* Formaldehyde and sulphur, and thioformaldehyde and its polymers respectively, besides water,

$$HCOH + H_2S - HOSH + H_20.$$

2. From *carbon monoxide* and *hydrochloric acid:* The unstable f ormylchloride :

$$CO+HC1-HCOC1.$$

3. From *carbon disulphide* and *hydrogen :* Hydrogen sulphide and carbon monosulphide :

4. From *hydrogen sulphide* and *carbon monoxide:* Carbon oxysulphide and carbon monosulphide:

$$CS_2+CO-COS+CS. \quad *$$

[1] Compt. rend. 126, 561 (1898); **131,** 772 (1900).

[2] 1. c.

[8] Ber. d. deutsch. .cliem. Gesellsch. **30,** 135 (1897).

In the further description of the results obtained in the



5. From *carbon monoxide* and *ammonia:* Formamide:

realm of silent discharges we will first consider the behavior of

According to Slosse,[1] 1 vol. CO and 2 vols. $NH_3$ give a crystalline substance resembling urea.

6. From *nitrogen* and *water:* Ammonium nitrite:

single organic substances, then that of mixtures.

## *//. Hydrocarbons.*

Methane. — Aliphatic hydrocarbons, exposed to the action of a high-tension discharge, yield hydrogen, a little acetylene, which in the course of the experiment can again disappear by polymerization, and polymerized hydrocarbons. From methane Berthelot [2] obtained the last-mentioned gases, a resinous hydrocarbon, and traces of a fluid possessing a turpentine odor. He found — in percentages by volume — from 100 $CH_4$: 105.2 $H_2$> 4.4 CBU, a solid hydrocarbon of the empirical formula CioHig.

*Methane* and *oxygen,* according to Maquenne,[3] yield formaldehyde besides considerable formic acid.

*Methane* and *carbon monoxide,* according to Losanitsch and Jovitschitsch/ unite to acetaldehyde and its condensation and polymerization products; according to Hemptinne,[5] aldehydic substances.

*Methane* and *carbonic acid* condense (Thenard and Berthelot[2]) to an insoluble carbohydrate; Berthelot observed the presence of a trace of butyric acid. The residual ga'ses contained a little acetylene and considerable carbon monoxide.

[1] Bull, de l'Acad. roy. de Belg. 35, 547 (1898).
[2] Compt. read. 82, 1360 (1876); TraitS de Mecanique Chimique II, 379 (1879). See also Compt. rend. 126, 561 (1898).
[8] Bull. soc. chim. **37,** 298 J1882).
[4] Ber. d. deutsch. chem. Gesellsch. 30, 135 (1897).
[5] Bull, de TAcad. roy. de Belg. [3] **34,** 275 (1897).

*Methane* and *nitrogen* in the mixture 100 $CH_4$-f 100 $N_2$ give 117.7 $H_2$, 3.4 $CH_4$, 74 $N_2$, and a solid body having approximately the composition, $C_8Hi_2N''_4$ (Berthelot [1]).

Ethane. — From pure ethane Berthelot, at the beginning of the experiment, obtained (1. c.) a little acetylene and ethylene besides a resinous hydrocarbon. He found at the end of the experiment, from 100 $C_2H_4$i 107.8 $H_{2;}$ 0.7 $CH_4$, $Ci_0Hi_8$. The unsaturated hydrocarbons had become polymerized.

*Ethane* and *carbon monoxide* yielded Hemptinne (1. c.) chiefly acetaldehyde, also some acetone:

*Ethane* and *nitrogen.* — There were obtained from 100 $C_2H_6$ + 100 $N_2$ (Berthelot) : 98.2 $H_2$, 3.0 $CH_4$, 73.5 $N_2$, $Ci_6H_{32}N_4$.

Ethylene.— 100 $C_2H_4$ gave 25.15 $H_2$, 4.35 $C_2H_6$ $(C_8Hi_4)_{ra}$ (Berthelot). In former experiments Berthelot had obtained a fluid ($C_2$oHi6.e) already observed by Th^nard.

*Ethylene* and *nitrogen.* — 100 $C_2H_4$ + 100 $N_2$ gave 28.6 $H_2$, 0.4 $C_2H_{6;}$ 62.2 $N_2$, $Ci_6H_{32}N_4$.

Propylene.— 100 parts yielded: 34.2 $H_2$, 0.7 $CH_4$, $Ci_6H_{26}$.

*Propylene* and *nitrogen.* — 100 CaHe + lOO $N_2$ gave 17.8 $H_{2;}$ 60.5 $N_{2j}$ $Ci_5H_{28}N_4$. '

Trimethylene.— 100 $C_3H_6$ -» 37.3 He, 1.4 $CH_4$, $Ci_5H_{26}$.

*Trimethylene* and *nitrogen.* — 100 $C_3H_6$ + 100 $N_2$~»41.4$H_2$, 1.6 $CH_4$, 61.4 $N_2$, $Oi_5H_{26}N_4$.

Acetylene.— 100 $C_2H_2$ -> 1.8 $H_2$, 0.8 $C_2$ $H_4$, 0.08 $C_2H_{6;}$ and an explosive substance. In the presence of hydrogen this substance is partially absorbed by the acetylene.

*Acetylene* and *nitrogen.* — 100 $C_2H_2$4-100$N_2$ gave no hydrogen and no hydrocarbon, but 88.6 $N_2$ and a solid substance, Ci6Hi6$N_2$.

AUylene.— 100 $C_3H_4$-»3 $H_2$, $(C_{16}Hi_9)_2$.

*Allylene* and *nitrogen.* — 100 $C_3H_4$ + 100 $H_2$ -> 82.2 $N_2$, $Ci_5H_{20}N_2$.

In the experiments of Berthelot the gas analyses refer to the residual gas volume after the discharge has acted on the

gaseous mixture for 24 hours. The high molecular formulae give approximately the composition of the solid condensation products.

Berthelot[1] thus summarizes his experiences as to these reactions:

1. The limit hydrocarbons *$G_n$~H.2n+2* lose 2 atoms of hydrogen per molecule. Solid hydrocarbons, most probably of a cyclical nature, are formed as polymerization products.

2. The olefines CnEfen also polymerize with loss of hydrogen. The solid products hereby formed, (CJ3$_2$Jm — H$_2$, in which *m* equals 4 or 5, or a multiple of these values, remind one of the camphenes, so far as their composition is concerned. They certainly belong to the cyclical hydrocarbons.

3. The acetylene hydrocarbons, *Cn3.2n-2,* polymerize without loss of hydrogen.

4. All hydrocarbons take up nitrogen, forming probably cyclical polyamines; methane and ethylene hydrocarbons seem to give tetramines; and acetylene hydrocarbons, diamines.

Benzene gave Hemptinne[2] resinous substances, several hydrocarbons, a little acetylene, and hydrogen.

*Benzene* and *hydrogen* easily unite under the influence of the discharge. Berthelot[3] found that 1 cc. benzene takes up 250 cc. hydrogen, i.e., about 2 equivalents, forming a solid polymeric hydrocarbon (CeH^n.

*Benzene* and *nitrogen,* according to Jterthelot,[4] form a polymeric condensation product, one part by weight of benzene taking up about 0.12 part by weight of nitrogen. The substance, on being heated, splits off ammonia and seems to be a diphenylenediamine. Recently Berthelot [5] has found that *argon* is also absorbed by aromatic compounds, especially by mercury phenide, forming a mercurargon phenide. Mercury metMde, on the contrary, does not absorb argon, but if nitrogen

[1] See also Jahrb. d. Elektrochemie of Nernst and Borchers, V, 202 et seq, (1899).

[2] Ztschr. f. phys. Chemie **25,** 298 (1898)

[3] Compt. rend. 82, 1360 (1876).,

[4] Ann. chim. phys. 1J, 35 (1897).

[5] Compt. rend. **129,** 71, 378 (1899).

is simultaneously present, it condenses with this to a condensation product of approximately the formula $C_{20}H_{34}N_5$.

Turpentine ($C_{20}H_{16}$) unites with about 2.5 equivalents of hydrogen to a solid polymeric body.[1]

### *III. Alcohols.*

Methyl Alcohol.—According to Maquenne,[2] the vapor of methyl alcohol is decomposed by the silent discharge chiefly into methane and carbon monoxide; some hydrogen, ethylene, and acetylene and very little carbonic acid are also produced. The quantity of hydrogen increases with increasing pressure (from 3-100 mm. mercury pressure), that of the other products decreases:

| Pressure. - | 3 mm. | 100 mm. |
|---|---|---|
| CO ..................... | 24 3 | 19 6 |
| $CO_2$ | 0 0 | 0 0 |
| [illegible] | 4 3 | 0 9 |
| [illegible] | 51 0 | 30 7 |
| [illegible] | 20 4 | 42 8 |
| | | |

A decomposition is caused by a high temperature similar to that produced by the discharge.

A.'Hemptinne subjected a large number of substances to rapid electric oscillations in an arrangement which, according to the method of Lecher,[3] permitted an investigation of the influence of various wave lengths.[4] He found that methyl alcohol[5] at 15 mm. pressure and with weak oscillations gave:

| | |
|---|---|
| Undecomposed alcohol......................... | 2.0% |
| Carbonic acid..................................... | 4.2% |
| Carbon monoxide .......... ..................... | 30.4% |
| Hydrogen.......................................... | 30.5% |
| Methane (and other hydrocarbons). .. | 32.9% |

[1] Trait^ de M6canique chimique II, 382 (1879).
[2] Bull. soc. chim. [2]37,298 (1882); 40,60 (1883).
[3] Wied. Ann. **41,** 850 (1890).
[4] Ztschr. f. phys. Chem, 22, 358 (1897).
[5] Ibid. **25,** 284 (1898).

I

Stronger oscillations produced about the same effects. Hemptinne suggests the following three problematical equations for explaining the reaction:

the oxygen acts in turn upon the methane and forms $CO_2$, CO, and $H_2O$, while methane itself simultaneously breaks up into hydrogen and other hydrocarbons. /

The following processes seem to him less likely:

$$\text{II. } CH_3OH = CO + 2H_2,$$

because the solid reaction product of hydrogen and carbon monoxide, which Berthelot found, is not present, and:

IIL

with subsequent polymerization, since here the formation of large quantities of methane is difficult to explain.

Owing to the present existing difficulty of explaining the complex action of electric oscillations, I should like to here refer, but only by way of suggestion, to a further possibility which takes account of the polymerizing influence of the oscillations. It is imaginable that primarily two or several molecules of methyl alcohol become associated and yield a product which is broken up during the progress of the experiment. The decomposition products thus formed are then further effected by the influence of the oscillations. The total equation would then be the following:

As some carbon dioxide is always formed from carbon monoxide and water, such a breaking up of the molecules would agree with the analytical results of Hemptinne.

**Ethyl Alcohol.** — Maquenne [1] obtained a gas which possessed

[1] soc. chim, [2] **37,** 298 (1882); 40, 61 (1883).

a strong aldehydic odor, and contained hydrogen, ethane, ethylene, acetylene, carbon monoxide, and carbon dioxide. He determined the following results for various pressures:

| Pressure. | 2 mm. | 110 mm. |
|---|---|---|
| $CO_2$ | 2.2 | 0.0 |
| CO | 11.0 | [illegible] |
| CnH«~f OnH/1 | 14.0 | 14.8 |
| [illegible] | 30.1 | 19.8 |
| [illegible] | 42.6 | 65.4 |
| | | |

Hemptinne[1] found:

Undecomposed alcohol .......................... ". 3%
Carbon dioxide....................................... 2%
" monoxide ........................, ____ 22%
Hydrogen............................................. 25%
Ethane and methane ............................ ,

To prove the supposition of a decomposition: = C2He + 0, Hemptinne added some phosphorus to the vapors, for immediately binding the oxygen occurring intermediately ^ He actually found a decrease in carbon monoxide and the hydrocarbons and a considerable increase in the quantity of hydrogen. Carbon dioxide was not present. On the contrary, if oxygon is added directly to the alcohol vapor, the quantities of carbon mon- and dioxide and of the hydrocarbons increase considerably, while the quantity of hydrogen decreases. These phenomena, of course, do not prove the primary process, C2H50H = C2He+0, which is altogether unlikely. For the chief change occurs in the proportion of hydrogen to hydrocarbon (without P: 20% $H_2$, 62.5% $C_2H_6$ + $CH_4$; with P: 65% $H_2$,' 27% C2H0 + CH4); it points to the influence of the medium upon the reaction velocity and the equilibrium, but does not permit a decision as to the course of the reaction. The explanation of these processes occurring with simple substances still requires a great deal of experimental work.

Absolute, fluid alcohol, according to Berthelot,[1] breaks up slowly with evolution of hydrogen and ethane. Aldehyde is simultaneously produced and a complex hydrocarbon having perhaps the composition CJEan-

Hemptinne[2] also investigated the following alcohols:

Propyl Alcohol.—Result:

| | |
|---|---|
| Undecomposed alcohol | 2% |
| Carbon monoxide | 16% |
| Hydrogen | 37% |
| Propane, ethane, and methane | 45% |

Isopropyl Alcohol breaks up, under similar conditions, in almost exactly the same way as the normal alcohol.

Allyl Alcohol was .exposed for only a minute to electric oscillations; it yielded:

| | |
|---|---|
| Undecomposed alcohol | 35% |
| Hydrocarbons, CnBfen | 35% |
| Carbon monoxide | 10% |
| Hydrogen, and other hydrocarbons | 20% |

Glycerin.—The gaseous products formed are carbon dioxide, carbon monoxide, and hydrogen.

Glycol gives carbon dioxide, carbon monoxide, hydrogen, and methane.

Phenol is decomposed, splitting off a gasc omposed of carbon mon- and dioxide and hydrogen.

## *IV. Aldehydes and Ketones.*

Aldehydes and ketones were also investigated by Hemptinne.[2]

Acetaldehyde gives carbon monoxide, hydrogen, and methane.

Paraldehyde.—The gaseous products formed are carbonic acid,

[1] Compt. rend. 126, 693 (1898). »l. c.

hydrocarbons ($C_nH_2n$), carbon monoxide, hydrogen, and methane.

Propylaldehyde breaks up in a different manner than the isomeric allyl alcohol. The gas, separated from the aldehyde, contained carbonic acid, methane, and ethane, hydrocarbons, $C_nH_27i$, carbon monoxide, and hydrogen.

Acetone, likewise isomeric with allyl alcohol, gives the same products as propyl aldehyde. As the quantity of carbon monoxide does not decrease in the presence of phosphorus, Hemptinne concludes that the following decomposition process occurs :

According to Maquenne [1] acetone vapor is decomposed by the electric discharge into hydrogen, ethane, and carbon monoxide, a small quantity of acetylene and carbon dioxide being also formed. The quantity ratios are less dependent upon the pressure than in the case of methyl and ethyl alcohol :

| Pressure. | Trifling. | 100 mm. |
|---|---|---|
| (XL | 1 1 | 0 6 |
| CO .............................. | 37.5 | 42.1 |
| OJL | 4 3 | 2 9 |
| $C_2H_6$ .............................. | 32 4 | 30 0 |
| ρ | 24 7 | 24 4 |
| | | |

Glyoxal breaks up into carbonic acid, hydrocarbons ($C_nH_2J$, and hydrogen.

*V. Acids and Esters.*

Formic Acid.—Maquenne[2] has investigated the action of the discharge upon formic-acid vapor under various pressures. He found carbon monoxide, carbonic acid, and hydrogen. With increasing pressure (2-100 mrn. mercury) the quantity of carbon monoxide decreases, while the quantities of carbonic

[1] BuU. soc. chim. [2] 40, 63 (1883).
[2] Ibid. 39, 306 (1883).

acid and hydrogen increase correspondingly. Hemptmne [1] obtained similar results.

*Formic Methyl Ester* yielded the following gases (Maquenne [2]) :

| | |
|---|---|
| Carbon dioxide | 8.1% |
| " monoxide | 46.8% |
| Ethylonc | 0.5% |
| Methane | 20.6% |
| Hydrogen | 24.0% |

*Formic Ethyl Ester* gives (Hemptinne) :

| | |
|---|---|
| Carbon dioxide | 13% |
| "' monoxide | 42% |
| Hydrogen | 25% |
| Ethane and methane | 20% |

Acetic Acid.— Besides hydrogen, carbon mon- and dioxides, Maquenne [3] also obtained methane, ethylene, and acetylene, With increasing pressure he found an increase in hydrogen and carbon monoxide, a decrease in-carbonic acid and hydrocarbons. Hemptinne observed similar results with his experimental arrangement. He accepts the following as the primary decomposition process, corresponding to that of the alcohols :

Hemptinne does this to explain the presence of large quantities of ethylene.

Acetic Methyl **Ester,** according to Hemptinne, breaks up quantitatively almost in the same manner as the isomeric formic ethyl ester:

| | |
|---|---|
| Carbon dioxide | 11% |
| " monoxide | 47% |
| Hydrogen | 20% |
| Ethane and methane | 22% |

[1] l. c.
[2] Bull. soc. chim. [2] 40, 64 (1883).
[3] Ibid. **39,** 306 (1883).

Propionic Acid gives carbonic acid, hydrocarbons ($C_nH_{2n}$), carbon monoxide, hydrogen, and saturated hydrocarbons.

Glyceric Acid.—Although glycerin did not yield any hydrocarbons, there were obtained, on using glyceric acid, besides carbon mon- and dioxides and hydrogen, about 20% methane.

Glycoffic Add.—This acid, $CH_2OHCOOH$, breaks up smoothly into hydrogen (70%) and carbonic acid (30%).

Oxalic Acid splits off carbonic acid, carbon monoxide, and hydrogen.

Benzoic Acid gives the same products. Hemptinne, who has investigated the last-mentioned acids, draws the conclusion from his observations that the molecule is burst by the influence of the electric vibrations, whereby isomeric substances often give the same bodies, and sometimes various decomposition products.

## *VI. Concerning the Binding of Nitrogen to Organic Substances.*

### (Berthelot's Investigations.)

#### Alcohols and Nitrogen.[1]

Berthelot subjected weighed quantities of the alcohols and certain volumes of nitrogen to the action of the silent electric discharge. In most cases the action was limited to 24 hours (when it was continued for a longer period, an absorption of nitrogen no longer occurred). He obtained the following results

Methyl Alcohol. — 0.0515 g. and 11.5 cc. $N_2$ were used. Composition of the resulting gas: $H_2$—18.5 cc., CO^O.9 cc., absorbed nitrogen: 9.4 cc.

These values correspond to the process:

a body of the composition $C_4H_{12}N_2O_4$ or $[C_2H(OH)NH_2 + H_2O]_2$ must therefore have been formed. This formula points to the formation of an amidine or its hydrate.

[1] Compt. rend. 126, 616 (1898).

The alcohol is also decomposed by itself, which could be proved by experiments of short duration in which no notable absorption of nitrogen had taken place. According to the gas analyses, the decomposition of the alcohol occurs as shown in the equations:

$$2CH_3OH = CH_4 + C0_2 + 2H_2,$$

$$CH_3OH = CO + 2H_2.$$

(Cf. the experiments of Hemptinne, p. 274.)

The other alcohols behave analogously.

Ethyl Alcohol. — There were employed 0.056 g. and 19.1 cc. $N_2$. Gas obtained: $H_2$ = 26.8 cc., $C0_2$ = 0.2 cc., $N_2$ = 8.2 cc.; absorbed nitrogen, 10.9 cc.

These values represent the reaction

from which (taking into consideration the alcohol decomposed without absorption of nitrogen) the formation of an amidine of the formula

$$C_4H_8N_20_2 = [C_2H(OH)\ NH_2]_2$$

results.

Normal Propyl Alcohol. — Employed 0.082 g. and 19.6 cc. nitrogen. Gas obtained: $H_2$=23.4 cc., $C0_2$=2.0 cc.; 00 = 0.2 cc., N2=7.4 cc.; absorbed nitrogen, 12.2 cc.

Process: $C_3H_7OH$-$H_2$-f K,

from which the formation of the amidine,

$$[C_3H_2(NH_2)H_20]_2 \quad \text{or} \quad [C_3H_3(OH)NH_2]_2,$$

is inferred.

Isopropyl Alcohol shows the same ratios as the normal alcohol.

AHyl Alcohol.— Employed: 0.150 ^g. and 23.5 cc. $N_2$~ 1|
Residual gas: H2 = 6.8 cc., N2 = 4.3 cc. Absorbed nitrogen^ ii
19.2 cc.

Process: $3C_3H_5OH4\text{-}N_2\text{--}fH$,

from which is inferred the formation of the amidine, £

Phenol and pyrocatecMn readily absorb nitrogen; *pyrogallol^ hydroquinone,* and *resorcin* absorb the gas quite slowly.

Ethers and Nitrogen.[1]

Ethylene Oxide. — 100 cc. $C2H_40$ and 115.5 cc. $N_2$ giver $H_2$=5.5 cc., $C2H_6$ = 0.4cc., N2=10.1 cc. Absorbed nitrogen 105.9 c.c. The formation of a body,

is inferred; It could be considered as an isomer of a hydrate of cyanamide. 1',!^

Methyl Ether.—100 cc. $(CH_3)_20$ and 127.9 cc. $lsT_2$ give- $H_2$ = S6 cc., N2 = 65.6 cc. Absorbed nitrogen: 62.3 cc.

The ratio of the elements which react is the following:

$$(CH_3)_20\text{-}1.72H\text{-}fl.25N.$$

The proportions are similar to those of the isomeric ethyl alcohol, but in the case of methyl ether they indicate a mixture.

Ethyl Ether.—100 cc. $(C_2H_5)0$ and 141 cc. $N_2$ give:: H2 = 174.2 cc.; $N_2$=44.6 cc. Absorbed nitrogen: 96.4 cc.

Ratio of the reacting elements:

$$(C_2H_5)0\text{--}\sim 3.58H+N_2.$$

Ethyl ether therefore gives off twice as much hydrogen and absorbs twice as much nitrogen as methyl ether; which seems to point to a fixed ratio between the nitrogen compounds farmed and the molecular weight of the compounds started with.

### Aldehydes, Ketoaes, and Nitrogen.[1]

Acetaldehyde.—Employed: 24 cc. $CH_3CHO$ and 22.8 cc. $N_2$. Based on 100 cc. aldehyde, there were obtained at the end of the reaction: $H_2$ = 25.8 cc.; $H_2$ = 59.6 cc. Absorbed nitro-.gen: 35.4 cc.

The ratio of the reacting elements is expressed by the formula

$$C_2H_{3.5}ON_{0.35}.$$

The ratio also remains constant with an excess of nitrogen, .and leads to the reaction product

which, judging from its marked basic character, seems to contain amido-groups.

Ethylene oxide, isomeric with this aldehyde, combines with iive times as much nitrogen.

Propyl Aldehyde.—A large excess of nitrogen being present, there were formed, based on 100 cc. $C2H_5CHO$ vapor: $112^s$ 43.6 cc., $C0_2$+C0 = 4 cc. Absorbed nitrogen: 66.7 cc.

These quantities correspond to a product CgHieN^a, in which there are likewise supposed to be several amido-groups.

Acetone.—By employing an excess of nitrogen, there were formed, based upon 100 cc. $CH_3COCH_3$ vapor: $H_2$ = 33.3 cc, Absorbed nitrogen: 89 cc.

These relations are expressed by the formula

$$[C_3H(OH)(NH_2)_2]_n.$$

Allyl alcohol, which is isomeric with acetone, absorbs only one third as much nitrogen as acetone takes up and only half that taken up by propyl aldehyde.

Methylal.—With an excess of nitrogen there are formed from 100 cc, $CH_2(OCH_3)_2$: $H_2$=71.1 cc., $C0_2$ = 4.4 cc., CO=2.2 cc. Absorbed nitrogen: 128.9 cc.

[1] Compt. rend. **12G>** 671 (1898).

Berthelot seems to refer the calculated composition of the reduction product

$$6H_20$$

to polyamines having many hydroxyl groups and derived from. the type $(CHN)_{n;}$ i-e., bodies which were obtained by him from carbon monoxide, hydrogen, and nitrogen by means of the silent electric discharge.

The following experiments could not be carried out to the-end of the reaction on account of the trifling vapor tension of the materials started with.

Aldol takes up large quantities of nitrogen, giving off trifling; amounts of hydrogen; *paraldehyde* behaves similarly. *Trioxy-methijlene,* on the contrary, and *formaldehyde* solution absorb nitrogen only very slowly.

Camphor takes up nitrogen, forming a basic body.

Benzaldehyde, benzoin, cinnamic aldehyde, salicylic aldehyde^ furfurol, and quinone, under the influence of the discharge, absorb nitrogen more or less rapidly.

Glucose, cellulose (paper), and dextrine[1] can slowly take up nitrogen; likewise the humus substances obtained by the action. of concentrated hydrochloric acid upon sugar.

### Acids and Nitrogen.[2]

Formic Acid. — Since formic acid is easily split up by the silent electric discharge into carbon mon- and dioxides and hydrogen^ a noticeable absorption of nitrogen does not occur, but *formic methyl ester,* although being likewise fundamentally broken. up, takes up larger quantities of nitrogen.

Acetic Acid. — This acid absorbs nitrogen, forming trifling; quantities of ammonia and a product which, according to the analyses of the gases obtained by the discharge, is said to have the composition of an amine or amide (Berthelot). The be-havior of *acetic methyl ester* gives results which call to mind.

[1] Essai de Mfemique chimique II, 388 (1879).
[2] Compt. rend. **126,** 681 (1898).

those of acetic acid and methyl alcohol when each substance is subjected by itself to reaction with nitrogen.

Other acids investigated were:

Propionic acid, crotonic acid, benzole acid, succinic acid, malei'c and fumaric acid, phthalic acid, camphoric acid, glycollic acid, lactic acid, malic acid, tartaric acid, the oxybenzoic acids, pyroracemic acid, laevulinic acid, dehydracetic acid, and aceto-acetic acid (or its esters).

All these substances (with the exception of fumaric and phthalic acid, which, under the experimental conditions, do not absorb nitrogen) take up more or less readily varying quantities of nitrogen. The m-oxybenzoic acid absorbs considerably less easily than its isomers.

### Nitrogen Compounds and Mtrogen.[1]

Methylamine. — Hydrogen and nitrogen are split off, a solid product with alkaline reaction, and probably possessing the composition of hexamethylenetetramine, being formed.

Bimethylamine absorbs nitrogen, splitting off water in ratios that likewise indicate the formation of hexamethylenetetramine.

Trimethylamine. — This substance, by absorbing a correspondingly greater quantity of nitrogen, also seems to lead to the same compound.

Ethylamine does not react with nitrogen, but it gives -off ,a quantity of hydrogen which indicates the formation of a body homologous to hexamethylenetetramine.

Normal Propylamine absorbs nitrogen and gives off hydro-:gen. The course of the reaction indicates the formation of tetramines, which are derived from methyl- and ethylamine.

Iso-Propylamine shows the same behavior as the normal compound.

Allylamine develops hydrogen, but neither absorbs nor splits off nitrogen. The reaction product has a strong odor of piperidine and perhaps the composition CgHigNs or C^HsoISU.

[1] Compt. rend. 126, 775 (1898).

Aniline, Methylaniline, Benzylamine, the Toluidines, Pyridine, and Piperidine take up nitrogen. Experimental, essential facts for determining the nature of the resulting products are lacking.

Ethylenediamine.—The volume of this compound is rapidly increased by the action of the silent electric discharge. Hydrogen is primarily developed, with some ammonia, nitrogen, and methane or ethane. Absorption of nitrogen and ammonia soon occurs, and hydrogen is split off. In the second stage the formation of condensation products (polyamines) presumably predominates, while in the first period the decomposition of the material started with prevails.

Propylenediamine behaves precisely like ethylenediamine,

Phenylenediamine (m- and p-), Benzidine and Nicotine absorb very little nitrogen.

Acetamide and Glycocoll absorb little nitrogen, and the quantity of the latter seems to depend upon the nitrogen absorption capacity of the respective acids.

Sulphocarbamide remains unchanged.

Nitriles (acetonitrile, benzonitrile, tolunitrile, benzyl cyanide) absorb nitrogen, the last three by direct addition without giving off another element, while acetonitrile gives hydrogen and some methane.

Aldoxkne (CHs-CHrN-OH) combines with nitrogen and splits off water.

Phenylhydrazine is slightly decomposed, splitting off hydrogen and nitrogen.

Mtrometliane is fundamentally broken up, presumably by internal oxidation, and with formation of condensed products; hydrogen, oxygen, carbonic acid, and nitrogen are developed.

Nitroethane, unlike the last-mentioned compound, absorbs nitrogen. The behavior of nitromethane corresponds to that of formic acid, and that of nitroethane to that of acetic acid.

Nitrobenzene takes up little nitrogen.

« The following substances were also investigated:

Pyrrol, Indol, Indigotin, Azobenzene, and Albumens, all absorbing nitrogen.

t "

Ttdophene. — This compound under the influence of the electric discharge absorbs as much as 8.6 per cent of its own weight of nitrogen, $(C_4H_4S)_2N$ being formed (Berthelot).[1]

The following conclusions can be drawn from Berthelot 's observations :

1. All the investigated alcohols fix nitrogen, forming amido-like substances.

2. The aliphatic alcohols thereby lose hydrogen (excepting allyl alcohol), an atom of nitrogen replacing a molecule of hydrogen.

3. The loss of hydrogen is related to the behavior of the hydrocarbons, which form the basis of the alcohols, when the former are subjected to the same conditions.

4. Phenols bind nitrogen in varying proportions, but without giving off hydrogen.

5. The isomeric aliphatic alcohols behave alike. They thus differ from the three dihydroxybenzenes.

6. All aldehydes bind nitrogen by forming condensation products. Amines or amides are produced. These are closely related to the ammonia derivatives of the aldehydes, particularly the glycosins, glyoxalines, and polyamines containing little hydrogen.

7. Organic acids, just like the alcohols, aldehydes, and hydrocarbons, generally combine with nitrogen, but no hydrogen, or but very little, is split off. Only phthalic acid and fumaric (contrary to maleic) acid do not absorb nitrogen.

8. Most of the investigated nitrogenous compounds absorb an additional quantity of nitrogen, and polyamines, polyamides, and condensation products seem to be produced. Exceptions, which do not show this behavior of absorbing nitrogen, are: ethylamine, allylamine, phenylhydrazine, sulphocarbamide, ethylenediamine, and propylenediamine. Methylamine and nitromethane even give off nitrogen; this is probably due to the low percentage of carbon.

9. Aliphatic nitrogen-containing compounds in taking up

[1] Ann. chim. phys. 11, 35 (1897).

nitrogen lose about as much hydrogen as their corresponding hydrocarbons and alcohols. Compounds are produced whose cyclic character becomes more pronounced with an increasing number of carbon atoms in the original molecules. Exceptions to this rule are compounds rich in oxygen, like nitroethane and glycocoll.

10. Cyclical compounds in absorbing nitrogen do not give off hydrogen any more than cyclical hydrocarbons and phenols. Piperidine, on the contrary, being a hydrated compound, loses hydrogen in absorbing nitrogen, just like aliphatic substances.

11. All compounds taking up nitrogen by simple addition—without giving off hydrogen—i.e., hydrocarbons, alcohols, aldehydes, acids, and bases, when subjected to the influence of the silent discharge, yield substances which behave like amides or amines. Since the formation of these substances cannot, of course, be based upon a substitution of NH2, NH, or *N* in place of hydrogen, we must ascribe cyclic constitutions to the products obtained.

12. The following table shows a comparison of polyamines formed from hydrocarbons, alcohols, and bases by reaction with nitrogen through the influence of the discharge. The formulae of the reaction products are not rational ones, but merely arranged in such a way that the quantities of the separate elements in the molecule always refer to four nitrogen atoms. This is done to express, in a comparable manner, the atomic relations between the elements in the polyamines.

**Composition of Polyamines formed from**

| | Hydro-carbons. | Alcohols. | Bases. | | |
|---|---|---|---|---|---|
| | | | Primary. | Secondary. | Tertiary. |
| Methane Series | | | | $C_aH_{18}H_4$ | |
| Ethane Series | | | | | |
| Propane Series | | | | | |
| Allyl Series | | | | | |

The following relations result from the tables:

For an equal weight of nitrogen the condensation of the hydrocarbon residue combined with the nitrogen increases in the transition from derivatives of hydrocarbons to those of the .alcohols, excepting the polyamines resulting from the methane series. This is very evident if the composition of the mentioned hydrocarbon residues is referred to an equal number of carbon atoms. The same increase is found if we pass from the derivatives of the alcohols to those of the primary bases; excepting the compounds of the ethane series. This condensation is twice as large with the products from diamines as with those from monamines.

## 2. BEHAVIOR OF VAPORS TOWARDS TESLA CURRENTS.

A few remarks may be made here concerning observations in a realm which promises to become especially important for theoretical organic chemistry. It has been known for some time that highly rarefied gases or vapors, when subjected to the action of highly tensioned electric vibrations, become luminous. Eemptinne,[1] by using Tesla currents and organic substances, has recently taken up the subject of the relation between luminosity and chemical action and the dependence of the phenomena upon the pressure. He found that the luminosity of the various substances in the arrangement of Tesla is dependent upon the pressure. A perceptible decomposition occurs from the beginning of the luminosity. A connection exists between the pressure at which the light effects of organic substances begin and their molecular weights; but these relations have not yet been sufficiently explained.

H. Kaufmann[2] has made extensive investigations concern-

[1] ^tschr. f. phys. Chemie 22, 358; 23, 483 (1897); Bull, de l'Acad roy de Betg. **11,** 775 (1902).

[2] Ztschr. f. physik. Chem. 2^, 719 (1898); 27, 519 (1898); 28, 673 (1899); Ber. d. deutsch. chem. Gesellsch. 33, 1725 (1900); 34, 682 (1901); 35, 473, .3668 (1902); 36, 561 (1903).

ing the luminosity of organic vapors under the influence of Tesla currents at atmospheric pressure. He was thus enabled to formulate a series of remarkable laws.

His experiments were arranged in the following manner:

The electric field in which the vapors are excited to luminosity is produced by a Tesla transformer, on the inside of a somewhat wide test-tube which has been converted into an ozonizer. The outer layer, 5 cm. high and consisting of thin sheet copper, is wrapped half way up around the test-tube; the outer layer has a narrow vertical slit for conveniently observing the inside of the tube. The inner coat, of mercury or tin, is placed in a small, narrow glass tube, which is kept rigid and exactly in the axis of the test-tube by a stopper closing the latter. The stopper also supports a return-condenser arrangement, usually a rising tube. The substances to be investigated are placed in a solid or liquid state in the test-tube, and the whole tube is then filled with vapor by vigorous boiling.

Some unimportant changes in the arrangement, such as lowering the layers, etc., are made with very difficultly volatile substances and such that readily char.

The luminous phenomena in these ozonizers occur in the shape of more or less wide, colored bands of light, mostly in a horizontal and radial direction. Non-luminous vapors either remain wholly dark or become,—this is oftener the case,—interspersed with green-colored sparks. The sparks very rapidly decompose the vapors, precipitating carbonaceous substances; the luminosity itself, on the contrary, produces only extremely trifling changes in the substances.

The color of the luminous effects, in the majority of cases, is violet, with numerous gradations between blue and red, rarely yellow and green.

The hitherto observed regularities refer to the vapors emitting the first-mentioned colors. We shall emphasize only a few points among the great number of observations:

1. Aromatic substances usually possess an extraordinarily higher luminosity than aliphatic compounds. However, simple .aromatic hydrocarbons like benzene, its homologues and benzene

derivatives, possessing two or more nuclei linked by aliphatic? residues, are either non-luminous or only slightly so. But hydrocarbons containing two or more directly linked benzene nuclei like diphenyl, carbazol, and condensed nuclei like naphthalene, anthracene, and phenanthrene show a brilliant violet luminosity.

2. Substituents exert a powerful influence upon the light effects. The introduction of several hydroxyl groups into aromatic hydrocarbons of one nucleus produces luminous effects which do not occur with only one hydroxyl group in the molecule. The ammo-group always excites luminosity even in mono-nuclear hydrocarbons. The effect of the amino-group often enforces that of the hydroxyl group, thus aminophenols produce luminous effects which are often very intense.

3. Acetyl, benzylidene, nitro-groups, the halogens, chlorine, and bromine, and the carboxyl group, on the contrary, considerably decrease the luminosity, sometimes completely.

Kaufmann seeks to employ these facts for obtaining an insight into the ring system of benzene. Instead of using the term "constitution/' he uses that of "condition," and shows that in the luminous compounds the benzene nucleus is in an unstable condition, one in, which it is disposed to change into a quinone-like structure. The condition of the benzene nucleus, determined by the chemical behavior of the ring, changes from substance to substance in the greatest variety. These conditions have possibilities which are represented by the Kekule, the diagonal (Glaus and Korner), and the Dewar formula with only one para-bond. The condition characterized in the first formula, according to Baeyer's investigations, is found in phloroglucin; the diagonal formula agrees excellently for phthalie acid; and the Dewar formula, for instance, for dimethyl-p-phenylenediamine.

The conditions for most of the benzene derivatives differ from these three limiting conditions and assume[1] mostly an intermediate position which approximates more or less that of the one or other limiting condition, The luminosity caused by the action of Tesla currents indicates that the ring of the respective substance exists in Dewar's condition; the stronger the luminosity the more pronounced the latter must be.

The one para-bond in Dewar's ring is unstable, and is characterized by the fact that it can easily be broken down, by oxidizers; it thus differs from the three para-bonds of the two other f ormute.

4. In the aliphatic series Tesla currents are absorbed and •converted into light by the vapors of aldehydes and ketones; the carbonyl group is the sole carrier of the luminosity. The latter disappears with derivatives of aldehydes and ketones which do not have the carbonyl group. The luminosity decreases: Firstly, with increasing number of carbon atoms (introcluction of methyl groups); secondly, with the entrance of a •earboxethyl group; and thirdly, especially in the presence of a phenyl residue (benzaldehyde, acetophenone, etc., show no luminous effects). Ring ketones without a double bond between carbon atoms can be luminous; such with double bonds cannot.

Kaufmann explains the luminosity of aldehydes and ketones by the supposition that the carbonyl group, the carrier of the luminous effects in those substances" can occur in various states •or conditions, like the benzene nucleus. Only such bodies which have the atoms of the carbonyl group loosely bound &nd in a reactive state can show luminosity. Reactability and luminosity run parallel. The latter is, hence, present in .aldehydes and ketones, but not in acids, acid anhydrides, esters, and amides, all of which contain the same group but in a condition of extremely trifling reactability; or, we can say, the .atoms of this group are firmly bound.

The luminosity of vapors under the influence of Tesla oscillations is undoubtedly closely related to the constitution of the substances. It also seems true that a continuous transition from the non-luminous to the luminous vapors takes place, so that only quantitative, but no substantial, differences exist between the conditions characterized by the luminosity. In order to-obtain a better understanding of the relations, it is necessary to measure these phenomena and, on the basis of quantitative determinations, to seek determinative connections, just as, for instance, has been done in the case of the conductivity **of** 'electrolytes. , . ,

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