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The electric current in organic chemistry

Edgar Fahs Smith

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THE ELECTRIC CURRENT IN ORGANIC CHEMISTRY.

AN

ADDRESS

BY

EDGAR F.ahs SMITH

VICE PRESIDENT, AND CHAIRMAN OF SECTION C

BEFORE THE

SECTION OF CHEMISTRY

AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE

BOSTON MEETING

FIFTIETH ANNIVERSARY

AUGUST, 1898.

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ADDRESS

BY

EDGAR F. SMITH,

VICE PRESIDENT, AND CHAIRMAN OF SECTION C.

THE ELECTRIC CURRENT IN ORGANIC CHEMISTRY.

It is now almost a century since Volta, the Italian physicist, wrote the following words:

"I have made experiments, showing the transmission of the electric fluid . . . I have applied different metals to all sorts of animal bodies . . . even to such substances as paper, leather, linen (well saturated with water), as well as to water itself . . . . The metals are not only conductors of electricity, but they also excite it, and this is a grand discovery!"

Yes, it was, indeed, a "grand discovery," for it led to further investigation with the final demonstration that animal and metal electricity were identical. What is more, it unquestionably opened the way to the construction of the battery bearing the name of this honored investigator, who, however, little dreamed of the splendid achievements which were to follow the introduction into chemistry of the form of energy, made so readily accessible by his battery and its numerous subsequent modifications; for history tells us that he failed to observe the decomposition which arose upon immersing the terminals of one of his cells into water. That was to remain for the keener vision of Nicholson and Carlisle.

The chemical phenomena, exhibiting themselves constantly to Volta while experimenting with his battery, were to him absolutely devoid of interest, yet they continued to crowd to the front

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and eventually attracted the attention of a brilliant coterie of investigators, whose discoveries could never have come in their most shadowy forms to Volta in his wildest dreams! In evidence of this I need merely mention the electrolytic decomposition of water, just alluded to, by Nicholson and Carlisle; the deposition of the metals lead and silver (probably the beginning of electro-chemical analysis); the remarkably mysterious and quiet passage of oxygen from the end of the silver terminal over to the zinc terminal where it appeared as gas—all observed by Cruikshank; the discovery by Davy that the current set free hydrogen and oxygen from water in the proportion in which they united to form the parent substance; the conclusion reached by Ritter that reduction invariably took place at one pole while oxidation occurred at the other; the evolution of Grothuss' theory in regard to the decomposition of liquids generally by the current—a theory highly suggestive in various directions (thus, the esterification theory of Williamson is based upon the same idea of alternate decompositions and reformations); the magnificent conquests made by Davy, culminating in the isolation of the interesting and valuable alkali metals, sodium and potassium; giving to the chemical world not only two new elements, but also inciting students the world over to research in wide reaching fields —a discovery pronounced by Ostwald to be "the close of the first act of the electrochemical drama," and yet what wonderful progress had been made through the application of the new agent! But richer discoveries were to follow. Recall the labors of Berzelius and Hisinger upon which was founded a theory now almost forgotten; and in its day a retarder, in some measure, of the proper understanding of simple chemical combinations. But it was helpful and contributed at least a mass of facts, applied later successfully in the solution of various chemical problems. And as we advance I must not fail to mention Becquerel, de la Rive and Pfaff, who contributed much of lasting value during the controversy waged by the adherents of opposing schools in regard to the origin of the current, in the midst of whom appeared the immortal Faraday, fixing the relation between the electrical magnitudes and the combining numbers of chemistry; really taking the initial steps in the foundation of the quantitative period of electrochemistry. I must not, however, dwell too long upon the many observations made by him. Let suffice the mere mention of his identification of machine and Volta electricity; his declaration concerning electrochemical decomposition that "the effect is produced by an internal corpuscular action, exerted according to the direction of the electric current, and that it is due to a force either superadded to or giving direction to the ordinary chemical affinity of the bodies present;" his suggestion, after wrestling with the nomenclature of that day prevalent in electrochemistry, of the terms anode, kathode, electrode, ion, etc., etc.; his efforts to measure electricity when he wrote "that the decomposing action of the current is constant for a constant quantity of electricity," and following this thought constructed an instrument which, "being interposed in the course of the current, used in any particular experiment, should serve at pleasure either as a comparative standard of effect, or as a positive measurer of this subtile agent." Again, having repeated all his earlier experiments with the most varying conditions, he wrote "variations in the intensity . . . . produced no difference as to the equal action of large and small electrodes;" and when he had completed his volta-electrometers they were so arranged that "after the current had passed through one it should divide into two parts; these after traversing each one of the remaining instruments should reunite. The sum of decomposition in the two latter vessels was always equal to the decomposition in the former vessel . . . . exactly the same quantity of water was decomposed in all the solutions by the same quantity of electricity." When the current acted upon caustic soda or potash, magnesium sulphate or sodium sulphate, just as much hydrogen and oxygen were evolved from them as from the diluted sulphuric acid with which they had been compared. And his final declaration in regard to water "that when subjected to the influence of the electric current, a quantity of it is decomposed exactly proportional to the quantity of electricity which had passed." Nor can I refrain from a brief allusion to the electrolysis of molten salts, also conducted by Faraday. You all remember the experiment he performed with lead chloride. The weighed platinum wire kathode was introduced into the molten salt; "a button of alloy could be observed gradually forming and increasing in size." In time the experiment was interrupted, when it was discovered that the "positive electrode had lost just as much lead as the negative had gained, ... the equivalent number, by comparison with the result in the volta-electrometer, being **103.5**." Some one has said and I think we all will echo the sentiment, that "the data communicated by Faraday as the result of his years of observation of the action of the electric current upon chemical compounds, are among the most important in the history of electrochemistry." They form the basis of all the quantitative laws which have been developed in this special field. They merit place side by side with the law of combining weights.

Equally important, perhaps, both from a theoretical and practical standpoint have been the results recently won by the introduction of the current into the field of pure chemistry through the persistent efforts of untiring investigators. Mark how, in the diffusion of solids in their solvents, van't Hoff perceived a similarity to the expansion of gases; how he succeeded in measuring that diffusive, expansive force, bearing the name osmotic pressure; then note the astonishing consequences of this discovery. The simple relation between gas volume, attending pressure and temperature had led Avogadro to promulgate his hypothesis in regard to molecules — a thought considered by all of us as a fundamental in our science. This hypothesis van't Hoff made bold to apply to solutions and there resulted a theory for solutions analogous to that previously wrought out for gases. To-day molecular weight determinations are made almost daily in our research laboratories as an indirect consequence of this deduction. Indeed, the laws governing osmotic pressure, when applied in the most varied forms, remained satisfactory except with solutions of salts, bases and acids. Their osmotic pressure was far beyond what could be expected from the theory of van't Hoff. How was this to be explained? The answer came from Arrhenius (1887): the departure from the law is due to dissociation, and most astonishing of all is that the dissociation of bodies in their solvents occurs only in the case of those which conduct the electric current, *i. e.* with electrolytes. Compounds not dissociated in aqueous solution — which adhere to the law of osmotic pressure — do not conduct the electric current. There remained but a step to the assumption that the products of dissociation, in aqueous solution, were identical with the substances termed ions, which in electrolysis appear at the electrodes. A logical query, consequent upon this declaration, was:

Are, for example, free potassium and free chlorine present in an aqueous solution of potassium chloride? Let me read you Ostwald's well-known reply to this question:

"What actually exists in the solution are single potassium atoms with enormous electrical charges. We do not know what these charges are in reality, but this we know — that the chemical properties of substances are greatly altered by electrical charges. On the other hand what we know as free potassium is a solid substance whose molecules consist of potassium atoms not charged with electricity at all . . . . As soon as the potassium atoms in solution lose their charge, as they do, for example, when led by an electric current to a platinum wire, where they can give up their electricity, potassium with its ordinary properties is at once produced."

A further consequence of osmosis and that of free ions in solution is Nernst's theory in regard to the electric current in the voltaic cell — the little instrument sent into the world a century ago, from which have come such epoch-making results, so that one cannot help but be profoundly impressed with the time-honored words — "despise not the day of small things."

However, it is not alone in the field of pure chemistry that helpful and interesting consequences of the introduction of the "subtile agent" are found. The patient, careful analyst, as he struggles to unravel the problems Nature has placed before him, will ever hold sacred the name and memory of our own Dr. Gibbs who, in 1865, first called the attention of the chemical world to that simple yet beautiful and extremely satisfactory determination of copper in the electrolytic way, which proved the incentive to further study in this direction; so that at present twenty-one metals lend themselves to electrolytic determination from solutions of the most varied character, and in the same manner at least one hundred and twenty separations have been made, all of which for accuracy, neatness and rapidity leave little to be desired.

In the commercial manufacture of potassium chlorate, potassium persulphate, caustic, iodoform, etc., etc., those who seek to apply the principles of chemistry in the establishment of industries of national import, have found in the current a most fruitful aid, the full consequences of which are yet untold.

But it was not to any one of these I especially desired to direct your attention. As indicated by my subject I had in mind another thought and, craving your further indulgence, I shall at once proceed to a new chapter in this historic résumé of electrochemistry.

You are all familiar with the classic experiment made fifty years ago (1848) by Kolbe. I refer to the electrolysis of concentrated solutions of potassium acetate and valerate. You remember that this was the first investigation of its kind in the domain of organic chemistry. The results were most interesting and were thought to have shed a new light upon and given deeper insight into the constitution of compounds. In the case of potassium acetate the course of the decomposition was considered as being fully represented by the resulting products:

$$\begin{array}{l}
\overbrace{CH_3.\,CO_2}^{+}\;\overbrace{K\qquad H\,OH}^{-}\qquad\overbrace{CH_3\qquad CO^2}^{+}\quad\overbrace{KOH + H}^{-}\\
\qquad\qquad\qquad + \qquad\qquad = \quad | \quad + \qquad\quad + \\
CH_3.\,CO_2\,K\qquad H\,OH\qquad CH_3\qquad CO_2\qquad KOH\qquad H
\end{array}$$

It was held to be a very simple decomposition.

Kekulé in 1864 gave to the world facts gathered by him in the electrolysis of dibasic acids, *e. g.*, succinic, fumaric, maleïc, and brom-maleïc acids. The first gave hydrogen and ethylene, together with carbon dioxide; the two isomeric acids gave acetylene, while brom-maleïc acid was thought to have yielded brom-acetylene. In 1866 Brester subjected various aliphatic bodies to electrolysis, but obtained nothing new. Aarland next followed with his study of the three isomerides—citraconic, itaconic and mesaconic acids, or the allylene dicarboxylic acids as they may also be termed. Aarland expected that when these three bodies were subjected to electrolysis they would yield three isomeric allylenes. He also purposed testing the suggestion of Carstanjen that six isomeric allylenes really existed. Without entering into details I may say that itaconic acid was electrolyzed with ease; its gaseous products were allylene and carbon dioxide. The residue contained acrylic and mesaconic acids. The resulting allylene was completely absorbed by bromine, but not by an ammoniacal silver nitrate solution. Citraconic acid yielded allylene, containing hydrogen exchangeable for metal and acrylic and mesaconic acids. Similar products were discovered in the electrolysis of potassium mesaconate.

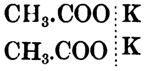
Mesaconic and citraconic acids bearing the same relation to one another as fumaric acid sustains to maleïc acid, of course yielded allylene, $CH_3C \equiv CH$, whereas itaconic acid was resolved by the current into symmetrical allene, $CH_2 = C = CH_2$.

As we search farther we shall learn that, under the influence of the electric current, butyric acid was observed to give hexane, valeric acid, octane, caproic acid, decane, etc. Oxalic acid was completely changed to carbon dioxide and water. Malonic acid was resolved into the same components, but the dissociation proceeded less rapidly. Upon electrolyzing an alkaline solution of sodium succinate, Bourgoin observed ethylene and acetylene in addition to the customary gas products. Free malic acid was decomposed very slowly; its alkali salts yielded carbon dioxide, monoxide, oxygen, aldehyde and acetic acid. Tartaric acid was broken down into acetic acid. Lactic and sarcolactic acids, in neutral solution, gave acetaldehyde, while in alkaline solution, owing to the condensing power of the alkali, aldol or crotonaldehyde appeared. Glyceric acid was resolved into formaldehyde, carbon dioxide, monoxide and water. In the case of the electrolysis of β-hydroxy-acids the rule seems to have been oxidation; the possibility of condensation, however, was not excluded. Formaldehyde was obtained in very appreciable quantities in the electrolysis of a concentrated solution of glycollic acid, whereas in dilute solution the products were carbon dioxide, carbon monoxide and very little formaldehyde.

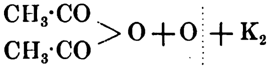
Let us pause a few moments and consider how these decompositions have possibly occurred. Kolbe considered the course of the action as very evident. The equation previously given represents his idea, "the acetic acid in the field of the galvanic action is oxidized by the oxygen so that it is resolved into carbon dioxide and methyl, both of which appear at the positive pole, while only hydrogen is formed at the negative electrode."

Kolbe, Kekulé and others regarded the decomposition of the organic acid as a secondary reaction. The oxygen, arising in the water-decomposition, they considered exerted an oxidizing effect upon the acid. Bourgoin's researches upon the electrolysis of organic acids were very extensive, and it was the opinion of this investigator that the most important phase in their electrolysis was the production of intermediate anhydrides of the acids. These, Bourgoin thought, then parted with oxygen, and secondary products were formed. In this latter class he included the passage of the anhydride into the acid by water absorption, as well as the oxidation of the acids by the oxygen released from the acid.

These ideas represented by symbols would appear as follows:

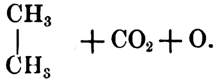
1. 

$$\begin{matrix} CH_3.COO \vdots K \\ CH_3.COO \vdots K \end{matrix}$$

2. 

$$\left.\begin{matrix} CH_3\cdot CO \\ CH_3\cdot CO \end{matrix}\right> O + O \vdots + K_2$$

or

3. 

$$\begin{matrix} CH_3 \\ | \\ CH_3 \end{matrix} + CO_2 + O.$$

But, we continue to ask, are an anhydride and oxygen formed before the hydrocarbon is produced? If so, does the oxygen then decompose the anhydride with the formation of the hydrocarbon and carbon dioxide? We are not alone in this inquiry, but Löb has endeavored to find an answer in the experimental way. To do this, he electrolyzed phthalic acid, dissolved in alcohol (a little sulphuric acid was added to increase the conductivity) with a feeble current. The latter was allowed to act for several hours and there resulted an almost quantitative yield of phthalic anhydride. It is not surprising that this chemist inclines to the view of an intermediate anhydride formation, but he wisely says that this is only demonstrable with acids, whose anhydrides are very stable.

In dealing with the electrolysis of free acids we can scarcely assert that breaking-down occurs, because the acid reappears as such at the positive electrode. Graphically represented we should have:

$$(1) \qquad 2CH_3.COOH = 2CH_3.COO + H_2$$
$$2CH_3.COO + H_2O = 2CH_3.COOH + O$$

or

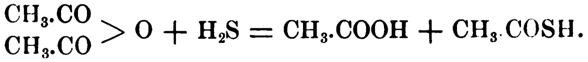
$$2CH_3.COOH = 2CH_3.COO + H_2$$
$$2CH_3.COO = (CH_3.CO)_2.O + O$$
$$(CH_3.CO)_2O + H_2O = 2CH_3.COOH.$$

The first equation shows that oxygen comes from the water, while in the second it has its origin in the intermediate anhydride formation. But let us follow Löb and with him substitute hydrogen sulphide for water, then the equations just written would appear thus:

$$2CH_3.COOH = 2CH_3.COO + H_2$$
$$2CH_3.COO + H_2S = 2CH_3.COOH + S$$

or

$$2CH_3.COOH = 2CH_3.COO + H_2$$
$$2CH_3.COO = (CH_3.CO)_2O + O$$



$$\begin{matrix} CH_3.CO \\ CH_3.CO \end{matrix} > O + H_2S = CH_3.COOH + CH_3.COSH.$$

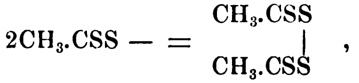
What do these teach us?

1. If an intermediate anhydride is not formed then the original acid will be regenerated and sulphur will separate.

2. If the anhydride is produced an evolution of oxygen will take place, and a molecule of a thio-acid will be obtained for every molecule of the ordinary acid.

An experiment was performed to test these ideas. Very pure acetic acid was reduced to a low temperature and in this condition saturated with hydrogen sulphide. It was electrolyzed, the gas being still conducted into the solution. Not a particle of sulphur separated at the anode, and the solution contained thio-acetic acid.

Two experiments, therefore, indicated the formation of an intermediate anhydride. However, other views are prevalent. Thus, Schall entertains the opinion that a peroxide is first produced in the electrolytic decompositions of the class we are considering. He electrolyzed the alkali salts of dithio-acids and obtained persulphides of the acids:



$$2CH_3.CSS - = \begin{array}{c} CH_3.CSS \\ | \\ CH_3.CSS \end{array},$$

and then the action ceased. It may be because the persulphides are so much more stable than the corresponding peroxides. Schall apparently has been confirmed and indeed antedated in his views, for Bunge in 1870 subjected thio-acetic acid and thio-benzoic acid to electrolysis and obtained acetyl disulphide and benzoyl disulphide, "facts which," the author remarks, "justify the conclusion that the compound group separating in the electrolysis of the thio-acids, at the anode, is liberated as a complex."

Hamonet conducted an extensive series of experiments with the alkali salts of the fatty acids. Inasmuch as he worked upon a much larger scale than his predecessors his conclusions are entitled to thoughtful consideration. They are in substance:

1. The equation, expressing the decomposition of salts of the fatty acids, as introduced by Kolbe, cannot be regarded as correct. Frequently, paraffin hydrocarbons are not obtained, or at least in very small amounts.

2. The olefines predominate in this decomposition.

3. An alcohol with n-carbon atoms is invariably formed if the acid contains $n + 1C$, and its structure is not always what we might expect.

So much for the acids. Plainly this particular line of inquiry needs and deserves further attention from the investigator.

The changes induced in organic substances by the electric current are, as a rule, so complex that their study is surrounded by vastly more and greater difficulties than obtain in the electrolysis of inorganic bodies. Von Miller, recognizing this feature, has adopted means of continuously exposing and withdrawing electrolyzed products from the field of action. In this manner he has striven to obtain a more complete picture of what actually occurs under the influence of the current. In the electrolysis of a mixture of potassium acetate and potassium glycollate the product was ethyl alcohol:

$$\begin{matrix} CH_3.COOK \\ CH_2.OH.COOK \end{matrix} = K_2 + 2CO_2 + CH_3.CH_2OH$$

True, the quantity of alcohol was not great, but its formation was certainly very significant. Through the instrumentality of the current even iodine and the nitro-group have been introduced into organic derivatives. Thus, the electrolysis of potassium propionate, in the presence of potassium iodide, yielded ethyl iodide, and that of sodium propionate and sodium nitrite, nitroethane.

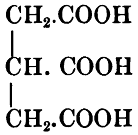
Brown and Walker, keeping in view the fact that Kolbe had synthesized hydrocarbons by electrolyzing fatty acids and the additional knowledge that ester groups are electrolytically inactive (first observed by Guthrie), effected some most interesting electrosyntheses, an outline of which is all that I can now give you. They reasoned in this way: If the mono-esters of dicarboxylic acids are electrolyzed, carbon dioxide will be eliminated, and a diester of some higher dicarboxylic acid will be formed:

$$2\ C_2H_5.OOC.CH_2.COOK = C_2H_5.OOC{\cdot}CH_2.CH_2COOC_2H_5 + 2CO_2.$$

The experiment was performed with potassium ethyl malonate. The concentrated solution of this salt was introduced into a platinum crucible, which served as the kathode. A heavy platinum wire, in spiral form, constituted the anode. The current density approached three hundred amperes per square decimeter. A yield of sixty per cent of the theoretically required succinic ester was obtained. They further synthesized adipic acid and sebasic acid. In all of these syntheses secondary changes were noticed, so that it is in no wise surprising that the reaction of Brown and Walker was not entirely successful with the ester salts of unsaturated dicarboxylic acids, in which an ethylene union is present.

The ester potassium salts of phthalic acid, of benzyl malonic acid and the salts of oxyacids, such as malic, proved unavailable for synthetic purposes.

I must not omit mention of a rather interesting result, recently communicated by v. Miller and Hofer. As observed, these chemists have entered quite largely into the study of the electrolysis of what may be termed mixtures. They have applied the new method to tricarballylic acid with the view of determining constitution. This acid, as you are all aware, is tribasic:



$$\begin{array}{l} \mathrm{CH_2.COOH} \\ | \\ \mathrm{CH.\ COOH} \\ | \\ \mathrm{CH_2.COOH} \end{array}$$

From it we can obtain two different mono-esters, two di-esters, and one tri-ester. Quoting von Miller and Hofer freely I shall say that there is no ordinary chemical procedure which will determine, for example, the position of the ester groups in the diesters. So these investigators set about and saponified the triester one-third; they then mixed the potassium salt of the resulting diester with potassium acetate and subjected the mixture to electrolysis. Large quantities of ethyl succinic ester were formed, a proof of the presence of the unsymmetrical diester in the saponification product, for the symmetrical diester would have yielded methyl glutaric ester. The authors went farther. They had obtained a diester acid, constitution unknown, while preparing the triester. The potassium salt of this diester acid they mixed with potassium acetate and electrolyzed as before. The product again gave ethyl succinic ester, showing that the original body was the unsymmetrical diester. These are the first examples of electrosyntheses being used to determine constitution, which could not be arrived at in any other way.

Mulliken has also brought to light a new class of electrosyntheses. He has directed his investigation mainly to bodies containing a —CH_2— or —CH— group, in union with more negative groups. We know that such substances contain hydrogen, which can be replaced by metals. Their sodium salts in alcoholic solution conduct themselves like electrolytes; they break down into sodium and a complex anion—the carbonaceous residue. "The products obtained in all the electrosyntheses, thus far made, are the same one would expect to be formed by the action of iodine on the sodium or silver compounds of the substances electrolyzed:

$$\underset{\text{Sodium diethyl malonate}}{2C_7H_{11}O_4Na} + 2\,I = 2NaI + \underset{\text{Ethyl ethane-tetracarboxylate}}{C_2H_2(CO_2C_2H_5)_4}$$

$$2C_7H_{11}O_4Na\ (\text{electrolyzed}) = 2Na + C_2H_2\,(CO_2C_2H_5)_4."$$

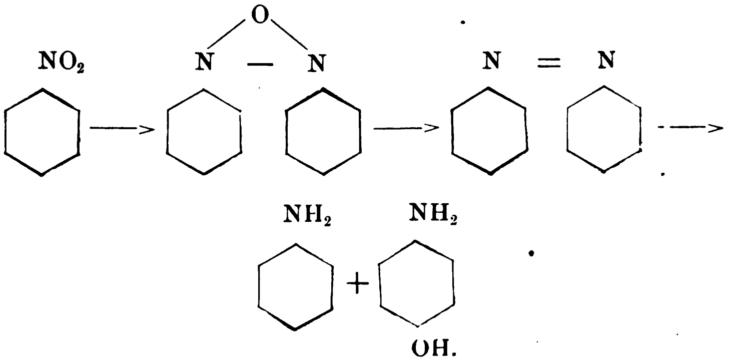
Weems has continued this line of investigation and from his results has felt justified in concluding that the electrosyntheses effected from malonic ester, methin-tricarboxylic ester, acetylacetone and acetoacetic ester are best explained as the result of the direct union of the anions. "Pairing of anions has been shown to be of particularly common occurrence in the electrolysis of sodium compounds of derivatives of malonic ether." Such pairing has been observed in certain examples of the aceto-acetic ester type, but it can scarcely be said to be general. Pairing of anions does not take place in the electrolysis of compounds like acetamide, benzamide, succinimide and phthalimide. The same holds with their sodium and mercury salts.

A very recent synthesis is that of dinitrohexane, a result of the electrolysis of potassium nitroisopropane.

Let us take a cursory glance at the deportment of the alcohols, when exposed to the current. Methyl and ethyl alcohol have been electrolyzed with electrodes of platinum and electrodes of other substances, with and without diaphragms. The results have been of the most varied character. In aqueous sulphuric acid solution methyl alcohol gave methyl formate, acetic acid, and methyl acetate. Formic aldehyde was not observed. Methane was produced when the electrolyzed solution contained potassium carbonate. Ethyl alcohol, in sulphuric acid solution, gave acetic acid, formic ester and ethyl sulphuric acid. Chlorinated acetic acids were obtained when hydrochloric acid was substituted for sulphuric acid. Glycol, in sulphuric acid, gave trioxymethylene, glyceric acid, formic acid and an isomeric glucose. Glycerol yielded formic and acetic acids, together with glyceraldehyde. Chloral hydrate, in presence of sulphuric acid, with a diaphragmed cell yielded chlorine and acetaldehyde. The hexahydric alcohols and sugars gave products similar to those obtained from glycerol. Thus, grape sugar was resolved into carbon dioxide, carbon monoxide, trioxymethylene, and saccharic acid.

Now turn with me to the aromatic series. It is here that stable nitro-derivatives flourish, so to speak, and in the reducing side of the current chemists possess a means of attacking these bodies most energetically. Let us take nitrobenzene as the particular subject for consideration. That this yields azobenzene, when it is reduced in an alkaline solution, and aniline in an acid solution, are well established facts. Does this hold true when the electric current is the agent of reduction?

The reply to this inquiry divides itself. In an alkaline solution azobenzene and hydrazobenzene are formed. In an acid solution the picture is different from that which is generally supposed to represent the course of the reduction, for Gattermann found p-amidophenol. The explanation given for the presence of this body is that when the current reduces nitrobenzene the first product is phenylhydroxylamine, $C_6H_5NH.OH$, and that the sulphuric acid present rearranges this compound into p-amidophenol. Aniline was invariably found with the latter body. This led Elbs to subject the process to a more careful and critical study. Gattermann considered that the sulphuric acid figures very seriously in the reduction. Indeed, he thought that it played a triple role, as it conducted the current, occasioned the molecular rearrangement, and served as the solvent. The question, which naturally suggested itself to the inquiring mind was, could the quantity of this reagent in any manner modify the course of the reaction? Could it affect the yield of the several substances? So it was proposed to substitute acetic acid of varying concentration. The yield grew larger but that of the aniline increased with the increased amount of p-amidophenol. Evidently, then, aniline could not be considered in this reduction, by the current, as a secondary, but rather as a normal product. A kathode of lead was substituted for that of platinum, and strangely enough the quantity of aniline became greater. Was it possible that the aniline was due to a secondary reduction of the p-amidophenol? Or are the lead electrodes responsible for the direct reduction of nitrobenzene to aniline? Experiments, made to test the first point, demonstrated that p-amidophenol, when operated upon with the conditions as before, was not reduced to aniline. After much search it was found that p-amidophenol and aniline were produced in equal proportions with platinum electrodes, by prolonging the period of action. Therefore, it must have been the spongy lead which effected the reduction of the nitrobenzene to aniline. Gattermann remained firm in his view that nitrobenzene was first reduced to phenylhydroxylamine, which in turn became p-amidophenol, and contended that the latter ought to be obtained entirely free from aniline. However, azoxybenzene had also been detected in the reduction mass, and naturally the thought followed that possibly the p-amidophenol was derived from it. The equation which I add will explain this reasoning:

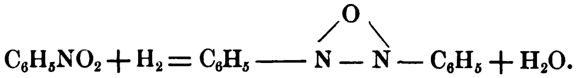


Observe, by adopting this idea of the reduction we can plainly comprehend the presence of both aniline and p-amidophenol. Experiment alone could decide whether this was the true course. Accordingly nitrobenzene and azoxybenzene were electrolyzed under similar conditions. The first gave an abundant yield of p-amidophenol, while scarcely any of it was obtained from the azoxybenzene. The evidence, therefore, strongly favored Gattermann's original conception, viz.: that the p-amidophenol had its origin in the phenylhydroxylamine—the intermediate product. The question continued to interest chemists to such a degree that Löb suspended nitrobenzene in fuming hydrochloric acid or in alcoholic hydrochloric acid, or in mixtures of hydrochloric acid and acetic acid, and reduced it electrolytically. The products were p- and o-chloranilines. The corresponding bromanilines were obtained when hydrobromic acid was used. Löb and Gattermann concluded then that the reduction was correctly represented in the following equations:

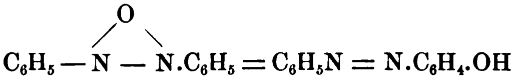
1. $C_6H_5NO_2 + 4H + HCl = C_6H_5NHCl + 2H_2O,$
2. $C_6H_5NHCl = C_6H_4Cl\ NH_2$

o-and p-aniline.

While with Elbs the course of reduction would be represented in this manner:

1. 

$$C_6H_5NO_2 + H_2 = C_6H_5 - \overset{O}{N - N} - C_6H_5 + H_2O.$$

2. 

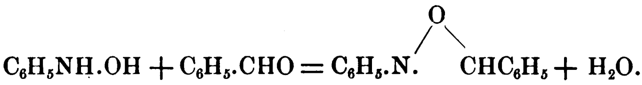
$$C_6H_5 - \overset{O}{N - N}.C_6H_5 = C_6H_5N = N.C_6H_4.OH$$

3. $C_6H_5{-}N = N.C_6H_4OH + 2HCl = C_6H_5NHCl + HClNC_6H_4OH$

$$= \underset{a}{\underline{C_6H_4ClNH}} + \underset{b}{\underline{C_6H_3(OH)Cl.NH_2}}$$

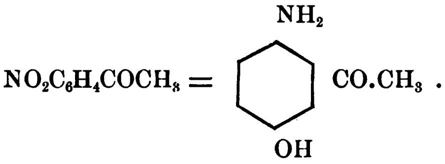
A second body (b) chloramidophenol should be produced if the view of Elbs was correct. It was, however, at no time discovered in the reaction mass, thus affording additional evidence of the correctness of the first idea. It is not necessary for me to submit all the evidence pointing to the presence of the extremely unstable intermediate compound C_6H_5NHCl, which rearranged itself into the chloranilines. Enough to know that it is very convincing and has been further corroborated by the isolation of the body $C_6H_5NCl.CO.CH_3$, observed by Bender.

Gattermann, seeking further support for his views, introduced benzaldehyde into the reduction mixture at the very outstart. He obtained benzylidene hydroxylamine, a condensation product previously prepared by Bamberger upon mixing benzaldehyde and phenylhydroxylamine:



$$C_6H_5NH.OH + C_6H_5.CHO = C_6H_5.N\overset{O}{\diagup\diagdown}CHC_6H_5 + H_2O.$$

Further, o-nitrotoluene and benzaldehyde gave benzylidene-o-tolyl hydroxylamine, and m- and p-nitrotoluenes the corresponding bodies, thus completely establishing the point under discussion. The reduction of nitro ketones gave the expected derivatives of p-amidophenol, *e. g.*, m-nitroacetophenone yielded amido-oxyacetophenone—



Similar results were realized with m-nitrobenzophenone and with m-nitrophenyl-p-tolyl ketone.

Time forbids more than mere mention of Löb's reduction of the three nitrobenzoic acids and the theory he has proposed in explanation of their reduction; the hydrogenizing of pyridine with the production of piperidine; the obtainment of pipecoline from picoline; the probable reduction of all the higher homologues of pyridine; the conversion of quinoline into its tetrahydride and a trimolecular dihydroquinoline; that of quinaldine to its tetrahydride and a trimolecular dihydroquinaldine; Noyes and Dorrance's reduction of nitro-bodies containing substituents in the para-position, as well as the reduction of p-nitro-benzoic acid in acid solution by Noyes and Clements; Ahrens' efforts to reduce nitriles to primary amines; the conversion of eugenol into isoeugenol and the electrolytic oxidation of the latter to vanilline; Elbs' oxidation of p-nitrotoluene to p-nitrobenzyl alcohol; that of nitrosopiperidine to dipiperidyl; that of the toluene sulphonamides to benzoic sulphinides with the formation of saccharin, and finally the reduction of certain oxy-acids to dyes of great value.

My story is now told and it only remains for me to acknowledge my deep indebtedness to the various writers upon electrochemistry, whose thoughts and words I have freely drawn upon and utilized in preparing this very incomplete sketch of what must be regarded as merely the beginnings of the electrolysis of organic bodies. I feel, however, that you will grant that they have been most fruitful, and are indeed highly suggestive. It would be presumption on my part to suggest, for I am satisfied many new thoughts have come to you in listening to, as they have to me in preparing, this review, and to them will be added many more if we will but experiment in the field now opening to us.

I know of no more fitting conclusion to these imperfect and fragmentary paragraphs, than the words of Michael Faraday, truly a father of electrochemistry, who said:

"It is the great beauty of our science . . . that advancement in it, whether in degree great or small, instead of exhausting the subjects of research, opens the doors to future and more abundant knowledge, overflowing with beauty and utility to those who will be at the . . . . pains of undertaking its experimental investigation."

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