ELECTROSYNTHESES IN THE SERIES OF DIBASIC ACIDS.

by

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HISTORICAL.

Kolbe may be regarded as the pioneer of electrolytic synthesis, his discoveries resulting as a natural consequence of his investigations of the effects of the electric current upon solutions of organic substances. When he published "Contributions to the Knowledge of Conjugated Compounds" (A. 54, 145) in the year 1845 he seems to have regarded the application of electrolysis to such solutions merely as a means of submitting the dissolved substance to the reducing influence of hydrogen at the moment of its liberation and it is not until the year 1849 that we find Kolbe regarding the electric current as an agent for chemical synthesis.

During the prosecution of his researches upon the activity of hydrogen and oxygen when liberated in the galvanic circuit, he subjected acetic acid to the action of the electric current. Starting from the hypothesis that acetic acid was a conjugated compound of oxalic acid and the conjunct methyl, he expected that electrolysis would effect a separation of the conjuncts and that, with the simultaneous decomposition of water, carbonic acid and marsh gas would/

would be obtained.

Since results proved the decomposition to be other than anticipated Kolbe commenced a series of experiments upon the homologues of acetic acid and examined in detail the products of electrolysis. Perhaps the most interesting and important discovery was that the products of electrolysis varied with varying concentration of the electrolyte. A dilute aqueous solution of potassium acetate when subjected to the influence of the electric current is decomposed with the formation of oxygen and free acetic acid at the anode, while at the cathode hydrogen escapes and potassium hydroxide is formed in solution: Faraday's Reaction. On the other hand when a concentrated solution is electrolysed under similar conditions, while the cathode products remain unchanged, that at the anode is now a gaseous mixture consisting for the most part of carbon dioxide and ethane; Kolbe's First Reaction. A second reaction proceeds simultaneously, but to a limited extent, resulting in the formation of ethyl acetate. Kolbe found that this reaction occurred to a much greater extent during the electrolysis of potassium valerate, considerable quantities of the butyl ester of the acid being obtained, and that in addition to the hydrocarbon "valyl", analogous to ethane, an odorous gas was evolved/

evolved along with the carbonic acid. This was subsequently proved to exhibit the composition of olefiant gas but to have double its specific gravity (its composition being $C_4 H_8$). Hence came the interesting discovery that unsaturated compounds may be obtained by the electrolytic decomposition of a saturated organic substance. The results of Kolbe's investigations may be summarised as follows. He identified and investigated three distinct types of reactions which might occur when an organic acid (R' COOH) or salt of the fatty series is subjected to the electric current, these reactions leading to the isolation of the acid, a saturated hydrocarbon of the type R' R', an unsaturated hydrocarbon R' minus H or an ester R' COOR' according to the conditions under which the experiment was conducted.

Crum Brown and Walker (Trans. Soc. Edin. 36, 211) extended these syntheses to dibasic acids, the hydrogen of one carboxyl group being replaced by an alkyl group R' and that of the other by a potassium atom. Since Guthrie had previously proved that an ester group plays no part in electrolysis they expected decomposition at the anode to take place as represented by the following equation.-

2 R'OOC.R". COOK = R'OOC.R".R". COOR' + 2 CO_2

R" being an alkylene group.

That the highest expectation was fully realised is proved by the fact that, by means of electrolysis followed by saponification and acidification, they were able to pass from succinic acid to adipic acid, thence to sebacic acid and finally to n. hexadecadicarboxylic acid, a new acid of the oxalic series. Another achievement was the synthesis of suberic acid from glutaric acid, the subsequent electrolysis of the potassium ethyl salt of the product yielding another acid, n. dodecadicarboxylic acid. Thus the electric current may be regarded as an agent whereby the oxalic acid series may be ascended synthetically. In the following year the same authors published another paper (Trans. Soc. Edin. 37, 361) which showed that this method of synthesis could be extended by submitting to electrolysis the potassium alkyl salts of saturated dibasic acids with side chains. From ethyl potassium methyl malonate they effected the synthesis of two acids of the composition $C_6 H_{10} O_4$ and by investigating their properties, including the electrical conductivity, found these to be identical with anti and para symmetrical dimethyl succinic acids. Similarly ethyl potassium ethyl malonate yielded two isomeric acids $C_8 H_{14} O_4$ which were found to be identical with para symmetrical diethyl succinic acid and anti symmetrical/

symmetrical diethyl succinic acid. Numerous interesting products of secondary reactions were also isolated; for example, dimethyl malonic acid yielded a considerable quantity of methyl acrylic acid and diethyl malonic acid gave a remarkably large yield of ethyl crotonic acid.

When other investigators extended their researches to the electrolysis of the alkali salts of oxy, keto, and oxyamino acids it was found that salts of the aliphatic α -oxy-acids were oxidised at the anode, the anion H R COH.COO' being first decomposed into carbon dioxide and H R COH - , oxidation then taking place as follows.-

$$2\ H\ R\ COH - + O = 2\ R\ CHO + H_2O.$$

Moreover the aldehyde so formed may be further oxidised with the evolution of carbon monoxide; this change does not occur so readily but it may be promoted by dilution and also by the intermediate formation of an aldehydic acid as in the case of tartaric acid electrolysis. β - oxy-acids follow Kolbe's reaction, potassium β -amyloxypropionate giving 1:4 butanediol as represented by the equation

$$2\ C_5H_{11}OCH_2CH_2COO' = C_5H_{11}O(CH_2)_4OC_5H_{11} + 2\ CO_2$$

In/

In contrast to oxy-acids the α and γ ketocarboxy-acids give Kolbés reaction yielding diketones, but if the potassium salt is in high concentration it is oxidised anodically. An example of diketone formation is obtained from the electrolysis of a solution of the potassium salt of pyruvic acid, diacetyl being obtained. In a similar way the potassium salt of levulinic acid yields 2.7 octadion. The alkali salts of polyoxycarboxy acids behave quite differently, oxidation occurs on electrolysis and the degradation to an aldehyde containing one carbon less than the original carboxy-acid can be effected. This knowledge has been utilised in the synthetic production of certain sugars, d-arabinose being obtained by the electrolysis of the potassium salt of d.gluconic acid; l-erythose resulting from the electrolysis of the alkali salts of arabonic acid.

In an analogous manner a mixture of oxy- and amino- aldehydes, with one carbon less than the electrolyte, has been obtained by the electrolysis of an oxyamino-acid. The following two equations show the extent of oxidation.-

(a)

$$HO.CH_2.CH.NH_2.COO' + OH' + 2\oplus = HO.CH_2.CHO + CO_2 + NH_3$$

and/

and simultaneously

(b)

$$HO.CH_2.CH \cdot NH_2 \cdot COO' + OH' + 2\oplus = OHC.CH_2 \cdot NH_2 + CO_2 + H_2O$$

Wurtz, working with mixtures, successfully synthesised hydrocarbons by electrolysing a solution containing the potassium salts of two aliphatic carboxylic acids and subsequently effected the synthesis of a monocarboxylic acid by reacting upon a mixture containing the potassium salts of an aliphatic acid and a dicarboxylic acid ester.

In modern times efforts are continually being made to extend the boundaries of electrolytic synthesis and to so regulate it that it may be of universal application. Compounds containing two carboxyl or two keto groups attached to the same methylene grouping give, with sodium in alcoholic solution, salt-like bodies which can be regarded as formed by the substitution of sodium for a hydrogen atom in the methylene group; these salts yield on electrolysis in aqueous alcoholic solution two residues which combine at the anode to form high molecular compounds, the case of sodium malonic ester being represented as follows:-

$$2\ CH\ (COO\ C_2H_5)_2' = \begin{matrix} CH\ (COO\ C_2H_5)_2 \\ | \\ CH\ (COO\ C_2H_5)_2 \end{matrix}$$

ethane tetracarboxylic ester being obtained. This however may not be regarded as another example of Kolbe's reaction, it belongs to that anodic process leading to the polymerisation of anions.

Murray (J. C. S. 61, 10) states systematically the various factors which influence the nature of the ultimate products of electrolysis: he shows that the Faraday reaction is promoted by dilution, while the Kolbe reaction prevails with a highly concentrated electrolyte and that, in addition, current strength, variation in the size of the anode, temperature, affect the yield; increase of current, decrease of anode surface and lowering of temperature all favouring Kolbe's reaction. He also proved that the presence either of an acid or an alkali, even in a comparatively small quantity, reduces the yield of ethane during the electrolysis of a potassium acetate solution.

Scientists have advanced various hypotheses to explain electrolytic syntheses and from these attempted theories two schools have developed. Kolbe himself may be regarded as the founder of one of these although his ideas have been modified and extended by Bourgoin, John, Bunge, Fichter and Krummenacher who put forward a chemical explanation for/

for these electrolytic phenomena the nucleus around which their thoughts and theories revolve being the extraordinary oxidising power that Kolbe proved to be possessed by a platinum anode. They consider the formation of ethane to be due to the intermediate formation of the anhydride which is then oxidised by the anodic oxygen to give ethane and carbon dioxide, the reaction being similar to that observed by Schutzenberger when he oxidised acetic anhydride by means of barium peroxide. Foerster and Piquet also incline to the possibility of the transient separation of intermediate products at the anode. The second school led by Crum Brown and Walker base their explanations on the hypothesis of electrolytic dissociation. When an aqueous solution of an acid is electrolysed a migration of the ions in solution occurs, the electro-positive hydrogen or metal going towards the negative electrode, the cathode, while the electro-negative residue goes to the positive electrode, the anode. At the respective electrodes these ions give up their electrical charges and become chemically free. This discharge of ions on their reaching the electrode of opposite charge explains all electrolytic reactions, for the ions freed from their charges are, in general incapable of existing as such, hence subsequent chemical changes occur/

occur resulting in the formation of more stable compounds. But besides being able to unite with each other the ions may suffer decomposition into simpler compounds; they may react on the solvent, become oxidised or reduced. Hence while this school does not refute oxidation during electrolysis it stipulates that the oxidation is the oxidation of ions and not of an intermediate product like an anhydride or an acid and that those complicated secondary reactions which usually accompany the primary change are due to the presence of large and easily oxidisable groups. These ideas are supported by Murray who regards the oxidation theory as a highly improbable and circuitous explanation. Moreover the latter theory does not afford a ready explanation of ester formation.
In support of his views Jahn assumed that the more condensed the oxygen produced the more complete would be the oxidation and therefore that the use of a small anode would reduce the yield of ethane. He succeeded in proving this to be the case but his experimental details were rough and unreliable and his results were completely overthrown by Crum Brown and Walker in the year 1890, who conducted a series of careful experiments proving conclusively that a large anode decreased the yield of ethane. They thus strengthened their/

their hypothesis that electrolytic reactions are ionic and that when the discharged ions are spread over a wide area they have not the same opportunity of reacting with each other and are consequently forced to attack the water, the organic acid in this case being regenerated and neutralised by the potassium hydroxide produced at the cathode. Fichter and Krummenacher vigorously oppose the ionic hypothesis; they argue that it is too mechanical, it fails to account for the formation of unsaturated hydrocarbons and the experimental conditions under which Kolbe's synthesis of hydrocarbons is possible are exactly those under which electrochemical oxidation is specially promoted, a smooth platinum or smooth iridium anode being required. Since such an anode, possessing a high overvoltage is necessary for the evolution of oxygen, they maintain that oxidation is the basis of all electrochemical reactions and that there is an indissoluble union between the complete oxidation of acetic acid and the hydrocarbon synthesis.

While the above statements are based upon facts they do not lead to a theory which oxidation enthusiasts believe to be contrapositive to the theory of electrolytic dissociation which does not deny/

deny oxidation although it states that the oxidation is that of ions and not of intermediate compounds. Indeed, Jahn's oxidation theory rests on a doubtful foundation for, as Murray states, acetic acid is not easily oxidised by electrolytic oxygen, a solution containing 10% sulphuric acid and 10% acetic acid giving on electrolysis less than .5% of carbon dioxide in the evolved gases. On the other hand if the view taken be that it is the acetions themselves which suffer oxidation* to carbon dioxide, it can be supported by numerous experimental results and, in addition, most of the subsidiary secondary reactions which occur can be clearly explained.

* Oxidation is here used in its wide sense of the loss of a negative charge or the gain of a positive one.

e.g. $Fe^{\cdot\cdot} \rightarrow Fe^{\cdot\cdot\cdot}$ in $FeSO_4 \longrightarrow Fe_2(SO_4)_3$

$K^{\cdot} \rightarrow K^{\cdot\cdot}$ in $K_2MnO_4 \longrightarrow KMnO_4$

$2\,(CH_3COO)' \rightarrow 2\,CH_3$ in $CH_3COO' \rightarrow CH_3 + 2\,CO_2$

CH_3COO'

PREPARATION OF SUBERIC ACID AND AZELAIC ACID FROM CASTOR OIL.

Markownikoff (Ber. 26, 3089) states that if 200 grammes of castor oil be oxidised by 400 grammes of nitric acid (specific gravity 1.25) azelaic acid can be obtained. Care must be taken to add the nitric acid in small portions as a brisk reaction ensues at ordinary temperatures, but if this precaution be taken the author affirms that once the first violent frothing is over the mixture can be heated, under a reflux condenser, on a sandbath until the reaction is complete. He obtained azelaic acid crystals in this way, his yield being 13%.

On attempting to obtain suberic acid and azelaic acid by the above method, the present author found that many alterations, involving additional precautions, had to be made as the reaction was excessively violent and at times quite uncontrollable. Oxidation proceeded quite quietly when the nitric acid was first introduced into the flask (fitted with a mechanical stirrer) and then one gramme of a catalyst, potassium nitrite, and a few pieces of porous tile added, the castor oil being finally run in/

in in small quantities. When all the oil had been added the flask and its contents were heated for half an hour on a sandbath after which the oil was repeatedly extracted with considerable quantities of hot water. These solutions were then concentrated until a white powder began to separate out; this was filtered off and the filtrate again concentrated, the process being repeated until precipitation of solid ceased. The total yield was 40 grammes. Titration of the product of oxidation with standard sodium hydroxide, free of carbon dioxide, showed it to consist of azelaic acid and suberic acid, the proportion present in the mixture being roughly one part of azelaic to two parts of suberic.

Experiment proved that a better yield was obtained by first hydrolysing and acidifying the castor oil and then oxidising the product obtained.

SEPARATION OF THE TWO ACIDS.

The method employed by Markownikoff was found to be both tedious and unsatisfactory while the following scheme gave a speedy and efficient separation. Advantage being taken of the comparatively great solubility of azelaic acid in ether at 15°C. compared with that of suberic acid in the same/

same medium (solubility of azelaic 2.7 per 100, that of suberic 0.8 per 100), enough ether was taken to dissolve the whole of the azelaic acid in the mixture and leave the suberic acid undissolved, the quantity required being ascertained by calculation based upon the solubilities of the acids and the results of titration. Owing to the inflammable nature of ether and the proportionately large amount required to effect the separation (100 c.c. of ether for 10 gm. of mixed acids) the mixture was treated in batches of 50 grammes. Solution was promoted by means of a mechanical stirrer and precautions taken to prevent loss of ether by evaporation, the wide neck of the containing bottle being fitted with a cork through which passed, in addition to the stirrer, a safety tube loosely plugged with cotton wool. After being continuously stirred for one and a half hours the contents of the bottle were filtered through a Buchner funnel and the ether distilled off from the filtrate. The residue of distillation was found to be impure azelaic acid, a weighed quantity being titrated with standard barium hydroxide and the amount of suberic acid present obtained by calculation. Water was then added to this impure acid, the quantity being just sufficient to keep the suberic acid/

acid present in solution at room temperature: finally heat was applied by means of a steam bath until complete solution occurred and the solution was then set aside to cool slowly. Large glistening flakey crystals separated and these were found to be azelaic acid in an almost pure condition, their melting point being 102°C. - 104° C. The acid was further purified by recrystallisation from benzene and the melting point again determined: the acid now melted sharply and suddenly at 106°C.

The crude suberic acid (melting point 130°C. - 135°C.) left in the Buchner funnel was purified by boiling it with benzene and so removing the last traces of azelaic acid which is extremely soluble in hot benzene while suberic acid is practically insoluble. The purified product melted at 139°C. In this way, from 200 grammes of the mixture 106 grammes of suberic acid and 64 grammes of azelaic acid were obtained in an absolutely pure crystalline condition.

This work was done in the spring of the year 1919 before the recent publication of a paper by Stosius and Wiesler. (Biochemische Zeitschrift 1920). These chemists obtained azelaic acid by the oxidation of ricinoleic acid in alkaline solution, the oxidising/

oxidising agent used being potassium permanganate. According to their own statement azelaic acid is thus obtained but only in small yield and in an impure condition. While oxidation by means of nitric acid as conducted by the present author does not produce a magnificent yield of azelaic acid and suberic acid, these are obtained in a perfectly pure condition.

Day, Kon and Stevenson (J. C. S. May 1920) also obtained these acids by the oxidation of castor oil on a large scale with nitric acid, but their experiments have the disadvantage of being extremely lengthy and cumbersome, moreover their laborious processes only afforded an extremely low yield.

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THE ELECTROSYNTHESIS OF *n*-HEPTANE DICARBOXYLIC ACID AND ITS SUBSEQUENT IDENTIFICATION WITH THE AZELAIC ACID OBTAINED FROM CASTOR OIL.

Preparation of diethyl suberic ester:-

60 grammes of suberic acid were introduced into a flask containing 500 cubic centimetres of absolute alcohol and hydrochloric acid gas was then passed in from a Kipp for one hour, the contents being subsequently boiled on a water bath for four hours and left standing overnight. After distilling off the alcohol, the ester was repeatedly washed with water to remove any traces of hydrochloric acid. (It was found necessary to add ether in order to effect a sharp separation into two layers).
On drying the solution and distilling off the ether 65 grammes of pure ester were obtained.

Preparation of potassium ethyl salt.

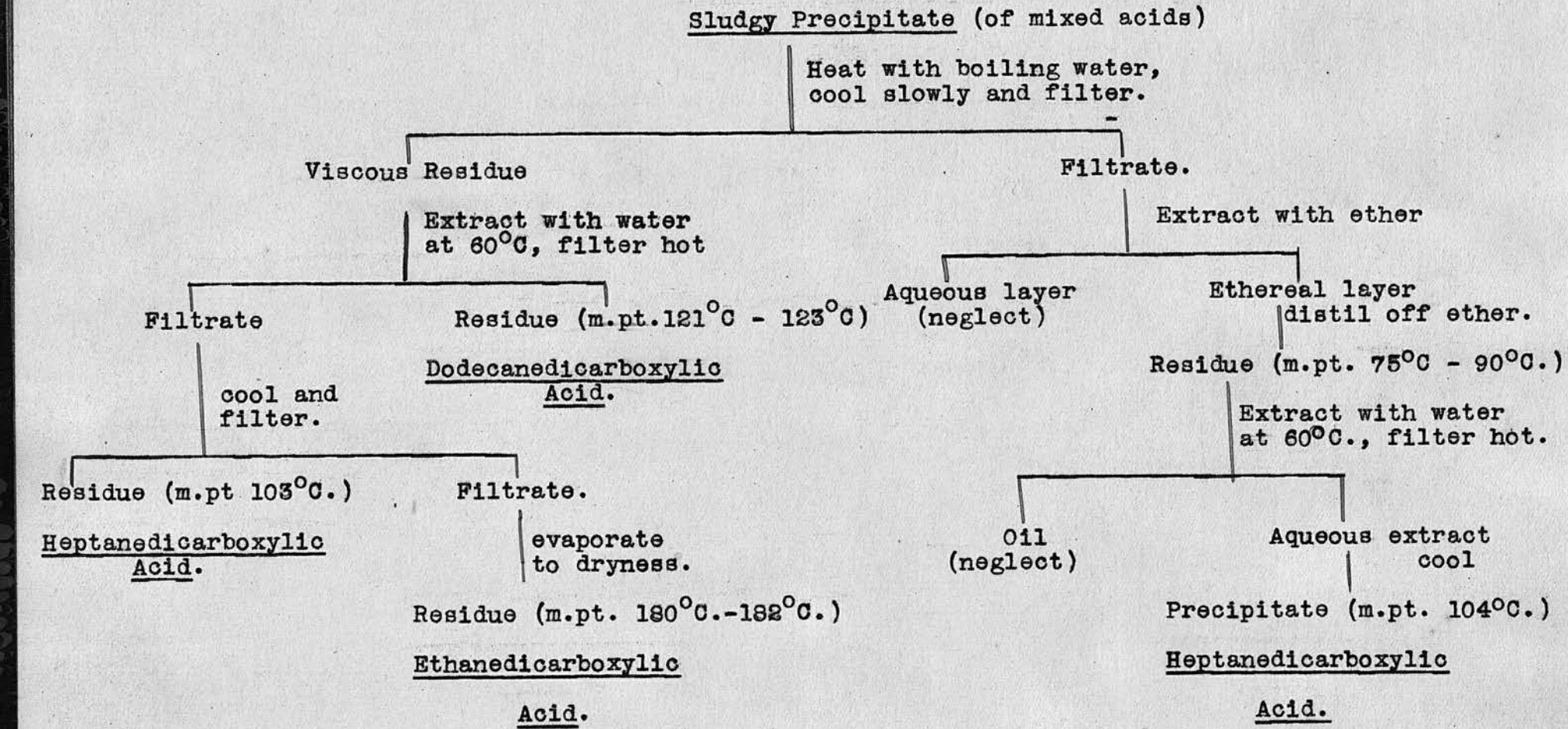
The diethyl ester (50 gms.) thus prepared was dissolved in rectified spirits (1100 c.c.) and half saponified at room temperature by treatment with the calculated quantity of potassium hydroxide in four successive portions; the aqueous extract was finally concentrated to a 50% solution on the water bath.

Half saponification of diethyl malonic ester.

Diethyl malonate (100 gms.) obtained from monochloracetic acid by Noyes' method was half saponified in one stage by dissolving it in half a litre of alcohol and slowly adding a solution consisting of 40 grammes of potassium hydroxide sticks in half a litre of alcohol. The hygroscopic potassium ethyl salt of malonic acid so formed was then dissolved in an equal weight of water.

Electrolysis: The two 50% solutions were added together, the proportions taken being such that the mixture contained three molecular proportions of malonate to one of suberate. Electrolysis was conducted in a platinum crucible 5 centimetres high and 4 centimetres in diameter, which served as a cathode, the anode being a stout platinum wire spiral which dipped into the crucible, the distance between it and the crucible being approximately .5 centimetre. The reason for this choice of anode was that a great current density could be obtained on account of the relatively small surface area, hence the discharged anions would be closely packed and tend to react with each other and not with the water used as solvent, the former reaction being that/

that required for the successful synthesis of new dicarboxylic esters. In the experiment conducted the current averaged 1.7 amperes and 7.5 volts and the temperature was controlled so that it never rose above 15° C: this was accomplished by means of a continuous stream of cold water which encircled the crucible during the reaction. The mixture (20 cc.) was electrolysed for two hours and the yellow oil (4 cc.) which formed on the surface of the electrolyte was removed; successive experiments were conducted and in all 22 grammes of the pale yellow oil were obtained. This was subjected to steam distillation in order to remove any low boiling esters of monobasic acids which might be present: subsequent saponification and acidification of the residual oil produced a sludgy precipitate. Acting upon the hypothesis that this contained *n*- ethanedicarboxylic acid, $COOH\,(CH_2)_2\,COOH$, *n*-heptanedicarboxylic acid $COOH\,(CH_2)_7\,COOH$ and *n*-dodecanedicarboxylic acid $COOH\,(CH_2)_{12}\,COOH$, a scheme was devised for the separation and isolation of *n*-heptanedicarboxylic acid. The following chart indicates the general scheme adopted.-


Sludgy Precipitate (of mixed acids)
Heat with boiling water, cool slowly and filter.
Viscous Residue
Filtrate.
Extract with water at 60°C, filter hot
Extract with ether
Filtrate
Residue (m.pt.121°C - 123°C)
Aqueous layer (neglect)
Ethereal layer
distil off ether.
Dodecanedicarboxylic Acid.
Residue (m.pt. 75°C - 90°C.)
cool and filter.
Extract with water at 60°C., filter hot.
Residue (m.pt 103°C.)
Filtrate.
Heptanedicarboxylic Acid.
evaporate to dryness.
Oil (neglect)
Aqueous extract cool
Residue (m.pt. 180°C.-182°C.)
Precipitate (m.pt. 104°C.)
Ethanedicarboxylic Acid.
Heptanedicarboxylic Acid.

Special note should be made of the method of separating a mixture of organic compounds by treating it with water at a definite temperature. Since the solubility of the dicarboxylic acids decreases with increase of molecular weight, it seemed reasonable in the present research to assume that the acid of greatest molecular weight could be separated from the mixture by dissolving out the remaining two acids by means of water at a definite temperature.
The validity of the theoretical hypothesis was proved, for on treating the mixture with water at 60°C. dodecanedicarboxylic acid was isolated in practically a pure state: further separation of the constituents was effected by allowing the hot filtrate to cool slowly, white crystals melting at 103° C. being precipitated. On evaporating the mother liquid to dryness another compound was obtained whose melting point (180° C. - 182° C.) indicated its identity as impure succinic acid.

The product melting at 103°C, which from its mode of formation may be called *n*-heptanedicarboxylic acid, was recrystallised from benzene and the melting point of the purified product was noted to be 106°C. It yielded the following results on analysis.

Titration: 6.3 cc. of .0979 N caustic soda were required to neutralise .0579 gm. of the synthetic acid. Theoretically 6.28 cc. of .0979 N caustic soda are required to neutralise .0579 gm. of COOH $(CH_2)_7$ COOH.

Combustion: .1056 gm. of the synthetic acid gave .0805 gm. H_2O and .2225 gm. CO_2

$\therefore$ H = 8.49% C = 57.46%

$C_9 H_{16} O_4$ requires H = 8.51% C = 57.45%

All these results point to the identity of n heptanedicarboxylic acid and azelaic acid; this identity was confirmed by a mixed melting point determination, the azelaic acid used being that obtained by the oxidation of castor oil.
This electrosynthesis of azelaic acid proves conclusively its straight chain structure, a fact which was previously indicated by its chemical synthesis by Haworth and Perkin (J.C.S. 1894).

THE ELECTROSYNTHESIS OF N-TETRADACANEDICARBOXYLIC ACID.

Preparation of the Potassium ethyl salt of azelaic acid:-

Azelaic acid, (62 gms.) obtained by oxidation of castor oil, was first converted into the diethyl ester the same method being adopted as that used in the preparation of diethyl suberate. The diethyl salt (68 gms.) obtained was then dissolved in 25 times its own weight of rectified spirits and half saponified in stages, any trace of the normal potassium salt being removed by taking advantage of the fact that it is insoluble in absolute alcohol while the half ester is soluble. The resulting aqueous solution of potassium ethyl azelate was concentrated to the consistency of a fine syrup.

Electrolysis: The apparatus employed was exactly the same as in the case of the azelaic acid synthesis, 20 cubic centimetres of the syrup being treated at a time. Here the current averaged 2 amperes and the voltage 20. In this case, in addition to the layer of yellow oil which formed on the surface during electrolysis,/

electrolysis, a white solid separated and ether had to be added in order to maintain current conduction. This white solid was found to be potassium carbonate, the source of this being the reaction between the anodic carbon dioxide and the potassium hydroxide formed by the liberation of potassium at the cathode. The oily layer, consisting of impure esters, was extracted with ether, dried, and the ether distilled off; the residue weighing 23 grammes, was then steam distilled until no more oil was carried over. In this way most of the impurities were removed. A greasy solid remained in the distilling flask but on drying this on porous tile and then recrystallising from methyl alcohol a pure white powder (17 gms.) was obtained which melted at 39°C.

Combustion:

·1483 gm. ester gave ·1471 gm. H_2O
and ·3826 gm. CO_2
H = 11·02% and C = 70·33%

(2) ·1489 gm. ester gave ·1487 gm. H_2O
and ·3826 gm. CO_2
H = 11·11% and C = 70·15%

$C_{20}H_{38}O_4$ requires H = 11·11% and C = 70·19%

Hence the diethyl ester of tetradecane - dicarboxylic acid has been synthesised and, from the method/

method of synthesis, since azelaic acid has been proved to possess a straight chain structure, this is a normal ester.

Saponification: The synthetic ester (3 gms.) was boiled on the water-bath with caustic soda (2 gms) and an excess of methyl alcohol. Saponification occurred almost immediately. When the alcohol was distilled off and the residue extracted with water complete solution occurred showing that all the ester had been converted into the sodium salt. On acidification a gelatinous product was obtained which had to be isolated by extraction with ether. Recrystallisation from boiling ether yielded a white powder (1·8 gms.) of melting point 124°C. Analysis yielded the following results.

Titration: ·0515 gm. acid required 3·1cc of ·1180N $Ba(OH)_2$ but

·0515 gm. $CooH\ (CH_2)_{14}\ CooH$ requires 3·05cc.

Combustion:

·1458 gm. acid gave ·1375 gm. H_2O and ·3583 gm. $C\ O_2$

H = 10·47% and C = 67·02%

$C_{16}H_{30}O_4$ requires H = 10·49%; C = 67·13%.

The synthetic acid is therefore n tetradecane-dicarboxylic acid and its formation therefore fills up the gap in the series of the even members of the synthetic dicarboxylic acids.

The synthesis was completed in March 1919 before the publication of the paper (1920) "Über die electrosynthesische Darstellung der Tetradecamethylene dicarbonsaure" which was the work of Stosius and Weisler. These authors also successfully isolated the acid by a method differing only in detail from that described in the present thesis. They pointed to its identity with Bougalt's Thapsic acid (C. r. 150) by means of analysis conducted according to Pregl's micro-analytic method.

The identity of the n-tetradecanedicarboxylic acid prepared in the present research with that of the Thapsic Acid obtained by Canzoneri (Gazetta Chemica 13, 514) was proved beyond doubt by the results obtained from the preparation of two derivatives. First, the anhydride of the synthetic acid was obtained by boiling a small quantity of the latter with excess of acetic anhydride. On subsequent cooling and dilution with water an oil separated which rapidly solidified

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This impure solid was then recrystallised from ligroin and dried in a vacuum dessicator; the melting point of the pure product was found to be 71°C. Further confirmation of the identity of the synthetic and the natural acids was acquired by preparing the anilide and determining its melting point.

In this preparation the synthetic acid was heated with excess of aniline in a sealed tube at a temperature of 180°C. The present author found that the time stated by Canzoneri was not sufficient to ensure complete conversion, a much better result being obtained by boiling for 4 hours then allowing the experiment to stand overnight and finally boiling for another 4 hours. The most satisfactory method of isolating the anilide was found to be that of extracting the contents of the tube with ether, dilute hydrochloric acid being added to dissolve out the excess of aniline. On subsequently drying the ethereal layer and distilling off the ether the anilide was obtained as a pale violet powder which on recrystallisation from alcohol was found to melt at 163°C. Since the melting point of either derivative coincides with that obtained by Canzoneri from the corresponding derivative of Thapsic acid there is no doubt whatever about the identity of the two acids.

IDENTIFICATION OF THE LOW BOILING ESTER.

The oily aqueous distillate collected during steam distillation was extracted with ether and the extract subjected to fractional distillation. As a large proportion distilled between 210°C and 212°C it was collected separately and a series of qualitative tests applied in order to classify the compound. On hydrolysis it was found to decolourise potassium permanganate in aqueous solution, the original substance therefore can be relegated to the class of unsaturated esters. Its boiling point was found by the Smith method to be 210°C. These results suggested the possible identity of this substance as n heptene-carboxylic ester.

Combustion:

(1) ·1614 gm. ester gave ·1557 gm. H_2O and ·4168 gm. CO_2

H = 10·71% ; C = 70·44%.

(2) ·1760 gm. ester gave ·1665 gm. H_2O and ·4556 gm. CO_2

H = 10·51%; C = 70·61%

$C_9H_{16}O_2$: $CH_2=CH(CH_2)_5COOC_2H_5$ requires

H = 10·59% and C = 70·60%

These/

These results are in accordance with the supposition that the ester is n heptenecarboxylic ester, a normal product of the electrolysis.

LIMITS OF APPLICABILITY OF THIS METHOD OF ELECTROSYNTHESIS.

The many syntheses already achieved show that electrolytic synthesis is applicable to most if not all members of the malonic acid series; moreover, the synthesis of azelaic acid as described in the present thesis shows that the electric current can be utilised for the building up of new compounds not only from a single substance in solution but also from a mixture of two half esters of fatty dibasic acids. This opens up the way to the electrolytic synthesis of the odd members of the dibasic acid series.

Up to the present day it has not been possible to apply this method to unsatured dibasic acids. Shields (J.C.S. 59,737) made un unsuccessful attempted synthesis from hydrogen ethyl maleate. It would appear that from unsaturated acids containing the ethylene union between two carbon atoms, one of which is combined to a carboxyl group whose hydrogen is replaced by a metal, no synthetic products are formed by electrolysis, only simple substances being obtained and that these may be regarded as oxidation products of the anion.

An/

An attempt was next made to ascertain whether an unsaturated half ester containing the ethylene grouping further removed from the carboxyl group could not be made the basis of an electrolytic synthesis, but it too failed to yield synthetic products.

The present author conducted a series of experiments in order to discover the limits of electrolytic synthesis: results showed these to be comparitively restricted and firmly fixed, oxidation occurring with remarkable facility and vigour, in many cases the intensity being so great that the molecule was completely smashed up into carbon dioxide and water. For example although synthesis occurred during the electrolysis of the fatty acids and their salts it failed when one of the hydrogen atoms in the α alkyl group was replaced by chlorine, sodium chloracetate being completely oxidised even in the presence of an equal quantity of a strong reducing agent like a formic acid.

Previous investigators had discovered that aromatic acids behaved like unsaturated acids in undergoing practically complete oxidation at the anode and the following fresh investigations yielded /

yielded no more satisfactory results although they show the remarkable oxidising effect the electric current has upon aromatic compounds under the most diverse circurmstances.

A concentrated aqueous solution of sodium benzoate yielded no synthetic product; on electrolysis a precipitate of benzoic acid and caustic soda separated while rapid charring occurred which continued even in the presence of sodium formate and sodium acetate. Of the many acid and alkaline reducing agents used in order to control the oxidation sodium sulphite was found to be the most successful, but success was only relative for no synthetic product was isolated. Electrolysis of the benzoate in strongly alkaline and strongly acid solutions yielded only benzoic acid; still, one notable results was the fact that practically no charring was observed when 10% sulphuric acid was used as solvent.

When the current was passed through a mixture containing 8 cubic centimetres of sodium ethyl malonate and 2 cubic centimetres of sodium benzoate an interesting result was observed - charring was modified, a precipitate of benzoic acid was obtained, but contrary to expectation no oily layer of diethyl succinate separated:/

separated: this seems to indicate a close connection between electrosynthesis and discharge potential, the benzoate ion being discharged at a much lower potential than the malonate one.

The same results were obtained when a 50% solution of sodium salicylate was subjected to the action of the electric current; under none of the aforementioned conditions was it possible to obtain a synthetic product.

Burnishing of the platinum anode to diminish the surface area had no appreciable effect on the electrolytic phenomena; change of solvent was likewide useless, charring taking place with great rapidity with methyl alcohol; even the substitution of the mobile solvent by a viscous one like glycerine did not check the oxidation.

To ascertain the effect of the electric current upon an organic compound containing, in addition to the dibasic fatty acid structure an aromatic grouping in the β position, the diethyl ester of Benzyl malonic acid was prepared by reacting upon sodium ethylate in alcoholic solution with malonic ester and then with benzyl chloride.
The desired product, which ~~is~~ distilled at 200°C at 14 millemetres of mercury was half saponified in one stage.

On/

On subjecting a 59% aqueous solution to electrolysis, charring occurred showing, that even if the aromatic radicle is situated on the β carbon from the ordinary point of attack for the Kolbe synthesis, it is not protected from electrolytic decomposition and oxidation.

Investigators have concentrated upon the electrolysis of the fatty acids and their ethereal derivatives and, as before stated Murray discovered that during the electrolysis of potassium acetate the presence either of acid or alkali, even in comparatively small quantities, reduces the yield of ethane. During the present research it was found that when glycerine was used as a solvent in place of water in potassium ethyl malonate electrolysis, electrosynthesis occurred exactly as in the case of the aqueous solution but the oily layer was slightly diminished in volume; hence both in the case of monobasic and dibasic acids the solvent affects, though slightly, the ultimate products of electrolysis.

A remarkable result was obtained when a gold spiral was used as anode and subsequently replaced by a platinum one after the current had passed for two hours. No oily layer appeared during the electrolysis/

electrolysis of a 50% aqueous solution of potassium ethyl malonate when the gold anode was employed. When however, it was removed and the platinum one substituted, on passing the current for another hour a well defined layer of yellow oil separated on the surface of the electrolyte, the volume of this oil being 18% of the volume of the original solution. This indicates the vital part played by the electrode material in electrolytic synthesis and it is not without the bounds of possibility that a suitable material remains yet to be discovered whereby universal application of the Kolbe synthesis may be achieved.