THE ELECTROSYNTHESIS OF
LONG CHAIN DICARBOXYLIC ACIDS

JEFFREY

THE ELECTROSYNTHESIS OF
LONG CHAIN DICARBOXYLIC ACIDS

A Thesis

by

Claire Osborne Jeffrey

Submitted to the Faculty of Graduate
Studies and Research in partial fulfilment of the requirements for the
degree of Master of Science

McGill University

September 1948

ACKNOWLEDGEMENTS

The writer wishes to acknowledge the advice and encouragement rendered by Dr. M. Morton, under whose direction this work was carried out.

Acknowledgement is also made to the National Research Council for the award of a Bursary held during the course of the investigation.

TABLE OF CONTENTS

GENERAL INTRODUCTION

The synthesis of long chain carbon compounds of known molecular weight is of interest in the field of high polymers, in connection with molecular weight determinations by comparative methods. Such compounds should prove useful as standards in calibrating this type of molecular weight determination apparatus.

The electrochemical oxidation of dicarboxylic acids is a possible method for the synthesis of straight chain compounds of high molecular weight. The purpose of the present investigation was to determine the limits to which this synthesis could be carried in order to yield pure high molecular weight compounds in reasonable quantities.

HISTORICAL INTRODUCTION

The Electrochemical Oxidation of Carboxylic Acids

The Kolbe Synthesis

Electrolysis of an aqueous solution of an acetate, alone or mixed with acetic acid, gives ethane and carbon dioxide, with a high efficiency, at the anode; the net reaction is

$$2\ CH_3COO^- \longrightarrow C_2H_6 + 2\ CO_2 + 2\mathcal{E}$$

The process was discovered by Kolbe in 1849 (1) and is known by his name. Although the simplest case, the electrolysis of acetates, has been investigated most extensively, the reaction has been applied to the salts of most aliphatic acids, and by its use paraffin hydrocarbons up to $C_{66}H_{134}$ have been obtained. The reaction also occurs with good efficiency in non-aqueous media.

By varying the conditions of the electrolysis, products due to competing reactions may be isolated. Although the Kolbe synthesis occurs readily at a smooth platinum anode in aqueous solution, the efficiency for the formation of ethane is very small at platinised platinum, palladium, gold and nickel anodes. If a platinised electrode is poisoned with mercury, however, the synthesis takes place to an appreciable extent. The presence of catalysts for the decomposition of hydrogen peroxide, or the addition of neutral salts to the electrolyte, inhibits the formation of ethane. In each case the current oxidizes the acetate to methyl alcohol by the so-called Hofer-Moest reaction (2).

$$CH_3COO^- + OH^- \longrightarrow CH_3OH + CO_2 + 2\mathcal{E}$$

With the higher acids a third reaction, leading to olefin formation, also occurs, thus

$$2\ CH_3CH_2COO^- \longrightarrow CH_2{=}CH_2 + CH_3CH_2COOH + CO_2 + 2\mathcal{E}$$

Several theories have been proposed to account for the Kolbe electrosynthesis; one, suggested by Brown and Walker (3) and widely accepted for a time, is that acetate ions are discharged directly at the anode and the resulting diradicals then react in pairs, thus

$$CH_3COO^- \longrightarrow CH_3COO + 1\mathcal{E}$$

and

$$2\ CH_3COO \longrightarrow C_2H_6 + 2\ CO_2$$

The main evidence for this view is that the evolution of ethane does not commence until a definite potential, regarded as the discharge potential of the acetate ions, is attained. It does not account, however, for the influence of electrode material or of added substances in aqueous solution, nor for the replacement of the Kolbe by the Hofer-Moest reaction. Also it is not easy to understand why oxygen evolution does not take place in preference, since the latter requires a lower potential. The hypothesis that the reaction is due to a chemical oxidation at the anode has been proposed by Fichter (4), (5), (6),

$$2\ OH^- \longrightarrow H_2O + O$$

followed by

$$2\ CH_3COO^- + O + H_2O \longrightarrow 2\ OH^- + (CH_3COO)_2$$

or

$$2\ CH_3COOH + O \longrightarrow H_2O + (CH_3COO)_2$$

and

$$(CH_3COO)_2 \longrightarrow C_2H_6 + 2\ CO_2$$

Active anodic oxygen oxidizes acetate ions, or acetic acid, to acetyl peroxide, which then decomposes spontaneously to yield ethane and carbon dioxide. The products of the thermal decomposition of acetyl and other peroxides, prepared chemically, have been shown to be similar to those obtained in the Kolbe electrosynthesis (4), (7), (8). The effect of anode material, of catalysts for hydrogen peroxide decomposition and of added salts cannot, however, be readily explained.

The hydrogen peroxide theory proposed by Glasstone and Hickling (9), (10) appears best able to account for the observed facts. The effective oxidizing agent is the hydroxyl radical, or hydrogen peroxide formed by combination of these radicals in pairs. This reacts with the acetate ions to form acetate radicals which then combine, possibly with the intermediate formation of acetyl peroxide, to yield ethane and carbon dioxide; thus

$$2\ OH^- \longrightarrow H_2O_2 + 2\varepsilon$$

$$2\ CH_3COO^- + H_2O_2 \longrightarrow 2\ CH_3COO + 2\ OH^-$$

$$2\ CH_3COO \longrightarrow (CH_3COO)_2$$

$$(CH_3COO)_2 \longrightarrow C_2H_6 + 2\ CO_2$$

A small proportion of the current is also devoted to the direct discharge of acetate ions, which then yield ethane and carbon dioxide as above. Catalysts for hydrogen peroxide decomposition, or electrode materials having the same effect, divert the hydroxyl radicals into an alternative path, that is, oxygen evolution, and the efficiency of ethane formation is decreased. The presence of added anions provides another means for the transport of current, and so the concentration of acetate ions near the anode is kept low and the Kolbe reaction is suppressed. Under these conditions peracetic acid is formed, thus

$$CH_3COO^- + 2\ OH \longrightarrow CH_3COOOH + OH^-$$

or

$$CH_3COO^- + H_2O_2 \longrightarrow CH_3COOOH + OH^-$$

or

$$CH_3COOH + O \longrightarrow CH_3COOOH$$

followed by its decomposition to give methyl alcohol, thus

$$CH_3COOOH \longrightarrow CH_3OH + CO_2$$

In support of this view it has been shown that the thermal decomposition of peracetic acid gives methyl alcohol and carbon dioxide (4), (11), and analogous compounds are obtained from other peracids.

In non-aqueous solutions the mechanism for the reaction is evidently different from that in water; the nature of the electrode now has little influence and hydrogen peroxide catalysts do not affect the oxidation efficiency. Here hydrogen peroxide or hydroxyl radicals cannot be formed, and hence direct discharge of acetate ions is the only possible process; the radicals probably combine to give acetyl peroxide which subsequently decomposes to ethane and carbon dioxide.

The Brown-Walker Reaction

On electrolysis of an alkali salt of a half-esterified dicarboxylic acid a reaction of the Kolbe type takes place; this synthesis is known by the names of its discoverers, Brown and Walker (3). The primary product of the reaction is the ester of a higher dicarboxylic acid.

$$2\ ROOC(CH_2)_nCOO^- \longrightarrow ROOC(CH_2)_{2n}COOR + 2\ CO_2 + 2\varepsilon$$

The salt of the half-saponified product may be again electrolysed, so that this reaction provides a useful method for the synthesis of long chain carboxylic acids.

In general the best conditions for the electrolysis are high current density, low temperature and high concentration of electrolyte. Any further oxidation of the synthetic esters is prevented since the esters are insoluble in water and separate out from the aqueous electrolyte. However, the solution must be prevented from becoming alkaline, thus causing hydrolysis of the esters formed. This may be done either by bubbling carbon dioxide around the cathode, or by adding free acid-ester to the electrolyte, and interrupting the electrolysis when the solution becomes alkaline. In the latter case the amount of salt undergoing electrolysis is equal to the amount of acid-ester added. Smooth platinum electrodes must be used; ester formation does not take place at either platinised platinum or gold anodes (12).

The Brown-Walker synthesis has been carried out on most of the available n-dicarboxylic acids. Potassium ethyl malonate yields diethyl succinate as the primary product (3).

$$2\ C_2H_5COCCH_2COO^- \longrightarrow C_2H_5OOC(CH_2)_2COOC_2H_5 + 2\ CO_2 + 2\mathcal{E}$$

Similarly the acid-ester salts of succinic acid (3), (13), (14), glutaric acid (3), adipic acid (3), pimelic acid (15), (16), suberic acid (3), azelaic acid (17), sebacic acid (3), (18), (19), (20), decanedicarboxylic acid (21), dodecanedicarboxylic acid (21), tetradecanedicarboxylic acid (21) and hexadecanedicarboxylic acid (18) have been electrolysed with the formation of the corresponding diesters. The acid-ester salts of the following substituted dicarboxylic acids also undergo the electrosynthetic reaction yielding the normal diester product: methyl and dimethylmalonic acids (13), ethyl and diethylmalonic acids (13), (22), dipropylmalonic acid (23) and β,β-dimethylglutaric acid (24). Mixtures of two different acid ester salts yield mixed synthetic esters on electrolysis; thus from potassium ethyl malonate and potassium ethyl succinate, diethyl glutarate can be obtained,

$$\begin{array}{c} C_2H_5OOCCH_2COO^- + C_2H_5OOC(CH_2)_2COO^- \\ \downarrow \\ C_2H_5OOC(CH_2)_3COOC_2H_5 + 2\ CO_2 + 2\varepsilon \end{array}$$

in addition to the products from each acid separately (25).

If a mixture of an acid-ester salt and an alkali salt of a monobasic acid is electrolysed, an ester of a higher monobasic acid results, in addition to other products (26); for example, a potassium acetate and potassium ethyl succinate mixture gives ethyl butyrate, thus

$$CH_3COO^- + C_2H_5OOC(CH_2)_2COO^- \longrightarrow CH_3(CH_2)_2COOC_2H_5 + 2CO_2 + 2\varepsilon$$

The formation of the diester of the dicarboxylic acid is always accompanied by the formation of an ester of an unsaturated monobasic acid. For example, the electrolysis of sodium ethyl succinate yields the ethyl ester of acrylic acid (13), (14).

$$\begin{array}{ll} 2\ C_2H_5OOC(CH_2)_2COO^- \longrightarrow & C_2H_5OOCCH{=}CH_2 \\ & \quad + \\ & C_2H_5OOC(CH_2)_2COOH + CO_2 + 2\varepsilon \end{array}$$

If conditions are unfavourable for the Brown-Walker synthesis, esters of monobasic hydroxy acids are formed at the anode, accompanied by oxygen evolution to a varying extent. For example, the ethyl ester of hydroxyacrylic acid has been isolated from the electrolysis of sodium ethyl succinate (14).

$$C_2H_5OOC(CH_2)_2COO^- + OH^- \longrightarrow C_2H_5OOC(CH_2)_2OH + CO_2 + 2\varepsilon$$

This is analogous to the formation of alcohols by the Hofer-Moest reaction.

Although the Brown-Walker reaction has frequently been used in the synthesis of long chain dicarboxylic acids, only recently has any work been done with a view to proposing a mechanism for the reaction. There is little experimental evidence for the view that the synthesis is due to the direct anodic discharge of acid-ester ions. The alternative hypothesis, that the reaction is due to a chemical oxidation at the anode, has received support from the work of Fichter and Lurie (27) and Fichter and Heer (28), who imitated the electrolysis by using potassium persulphate as chemical oxidizing agent. Electrode potential measurements by Robertson (12) using platinum, platinised platinum and gold anodes also appear to favour a chemical mechanism of the oxidation process.

More recently Hickling and Westwood (29) have carried out a qualitative and quantitative study of the electrolytic oxidation of potassium ethyl malonate both in aqueous and in non-aqueous solutions; and on the basis of their work have presented a comprehensive mechanism to account for the reaction.

The influence of the general factors of current density, concentration of electrolyte and temperature were found to be as follows. In the electrolysis of a solution molar with respect to both potassium ethyl malonate and ethyl hydrogen malonate, an optimum current density of about 0.12 amp. per sq. cm. was found; the current efficiency of diester production at this current density was about 76 percent. The efficiency was slightly less above 0.12 amp., and fell rapidly when the current density was reduced below this value.

The results produced by a change of concentration of the electrolyte are shown below.

K ethyl malonate M	2	1	0.5	0.25	0.1
Ethyl H malonate M	2	1	0.5	0.25	0.1
Efficiency %	78	74	70	68	30

Hence ester formation is seen to fall off rapidly at low concentration.

The current efficiency did not vary much with acidity, but tended to fall off in alkaline solutions. An efficiency of 70 percent at pH 7, decreasing to 59 percent at pH 10, was found.

An increase of temperature decreased the efficiency of ester formation, which fell from 74 percent at 10° C. to 22 percent at 90° C.

The influence of foreign anions was found to be similar to that observed in the electrolysis of acetates (Kolbe reaction). The addition of various potassium salts to a 2 M ethyl hydrogen malonate solution decreased the ester efficiency from 70 percent to 8-23 percent, depending on the mobility of the added anion. A weak electrolyte such as boric acid did not decrease the efficiency. In the cases where ester formation was inhibited, the chief oxidation product was ethyl glyoxylate.

Although the Brown-Walker synthesis takes place with good efficiency at a smooth platinum anode, it was found that at anodes which are good catalysts for the decomposition of hydrogen peroxide (platinised platinum, gold, lead dioxide and carbon) the efficiency of ester formation was small. The current here was mainly used in oxygen production.

The addition of salts which catalyse the decomposition of hydrogen peroxide had a marked influence on the reaction. The effect of the ions in decreasing the Brown-Walker synthesis was found to be proportional to their catalytic activity; the presence of Pb^{++} ion, which is a good catalyst, caused a 51 percent reduction in ester efficiency, while Ni^{++} ion, which is only feebly active, caused merely a 6 percent reduction. Here the current not used in the Brown-Walker synthesis was divided between oxygen evolution and ethyl glyoxylate formation.

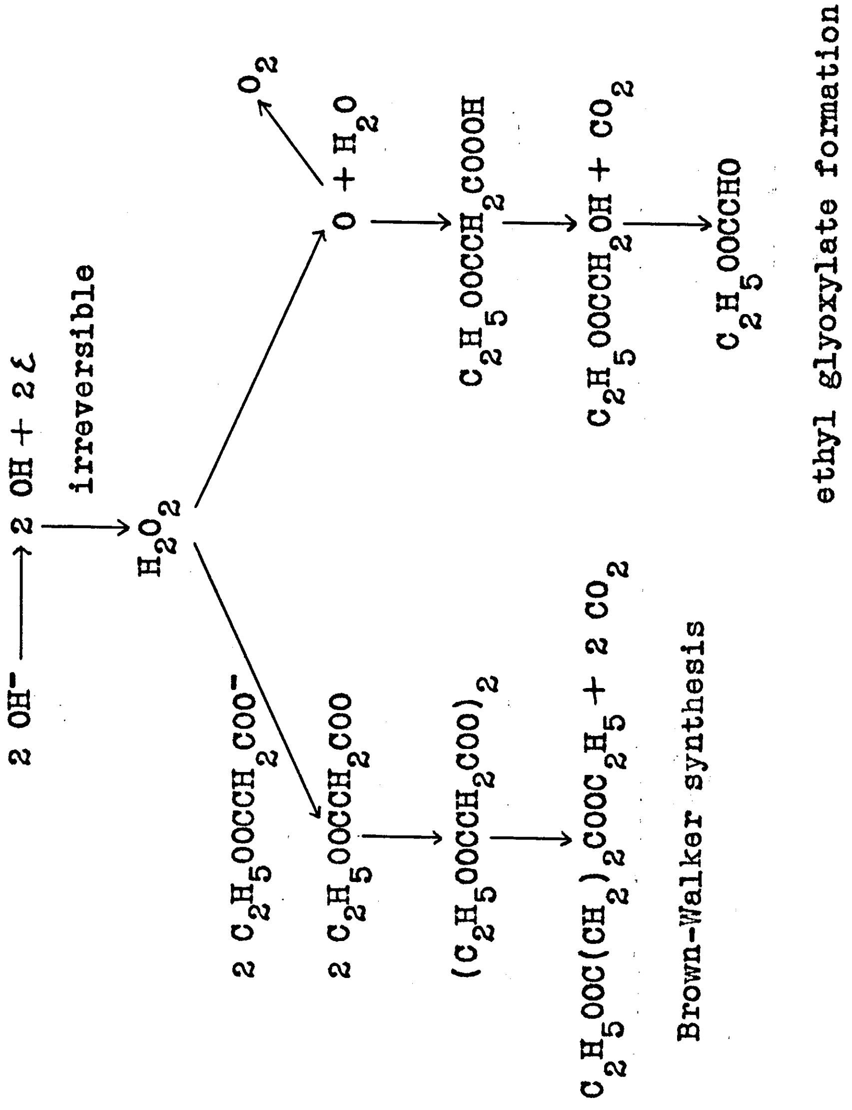
Measurements of anode potentials under various conditions showed some interesting results. When the Brown-Walker synthesis occurred with high efficiency, as at a smooth platinum anode, the potential, about 2.8 volts, was considerably higher than the oxygen evolution potential for the same solution, which is about 2.0 volts. When the synthesis was inhibited by using anodes which are good catalysts for hydrogen peroxide decomposition, the potential dropped to the region of oxygen evolution. In the ethyl hydrogen malonate solution the synthesis took place at approximately the same potential as in the salt solution. In the presence of foreign anions the initial potential was higher than for the acid alone, but as the current density rose the potential decreased.

The chemical oxidation of potassium and of hydrogen ethyl malonate was investigated by the same workers. By the action of concentrated hydrogen peroxide on the acid-ester and its potassium salt under various conditions, small amounts of ethyl glyoxylate were formed, but no synthesis of diethyl succinate could be definitely established. By using sodium persulphate, which is hydrolised steadily in solution to give hydrogen peroxide and therefore simulates more nearly conditions at an anode, the synthesis of diethyl succinate in small yield was accomplished. Usually ethyl glyoxylate was also formed in the oxidation.

From the above experimental results it is seen that during the electrolysis two main anodic reactions took place:

1. the Brown-Walker synthesis
2. the formation of ethyl glyoxylate, probably with ethyl glycollate as an intermediate stage, accompanied by oxygen evolution to a varying extent. Hickling and Westwood (29) have suggested that the hydrogen peroxide theory, which was proposed by Glasstone and Hickling (9) as a mechanism for the Kolbe reaction and which reconciles to some extent the older chemical and discharged ion theories, also accounts satisfactorily for the above process. It is postulated that hydrogen peroxide is formed as the primary product at the anode by the irreversible combination of discharged hydroxyl radicals. When sufficiently concentrated and in the presence of an adequate supply of ethyl malonate ions, the peroxide reacts to give diethyl succinate and carbon dioxide. It is probable that the formation of ethyl malonate radicals

is an intermediate stage, and under certain conditions the corresponding acid peroxide may also be formed. If conditions are not favourable to the stability of hydrogen peroxide, no high concentration of this substance can be formed at the anode, and the Brown-Walker synthesis is inhibited. In this case the hydrogen peroxide of low concentration and the oxygen arising from its decomposition may oxidize the ethyl hydrogen malonate to the corresponding per-acid, which decomposes to give ethyl glycollate, this being further oxidized to the fairly stable ethyl glyoxylate. The complete scheme is as represented below:


2 OH⁻
2 OH + 2 ε
irreversible
H2O2
O + H2O
O2
C2H5OOCCH2COOOH
C2H5OOCCH2OH + CO2
C2H5OOCCHO
ethyl glyoxylate formation
2 C2H5OOCCH2COO⁻
2 C2H5OOCCH2COO
(C2H5OOCCH2COO)2
C2H5OOC(CH2)2COOC2H5 + 2 CO2
Brown-Walker synthesis

This theory accounts for most of the phenomena observed in the electrolysis of potassium and hydrogen ethyl malonate solutions in water. At low current densities the concentration of hydrogen peroxide at the anode is low, and hence the rate of diester formation is slow and much of the hydrogen peroxide decomposes leading to the alternative oxidation products; this accounts for the falling off in efficiency at low current densities. A high concentration of ethyl malonate ions accelerates the diester synthesis and leads to a high efficiency, thus explaining the effect of concentration. Hydrogen peroxide is much less stable in alkaline than in acid solutions, and hence the efficiency should decrease as the pH of the electrolyte is raised, as is found to be the case. Rise of temperature increases the rate of hydrogen peroxide decomposition and thus decreases the efficiency.

The effect of foreign anions in inhibiting the synthesis at a platinum electrode in the acid-ester solution is explained as follows. For diester formation to occur a fairly high concentration of ethyl malonate ions is necessary at the anode to react with the hydrogen peroxide produced there. Most of these ions are brought to the anode by ionic transport; the number brought by diffusion is low since the acid is only weakly dissociated and the bulk concentration of ions is low. In the presence of an added strong electrolyte, the foreign anions compete with the ethyl malonate ions, and almost completely eliminate the transport of the current by them; the concentration of ethyl malonate ions near the anode, and hence the efficiency of the synthesis, decreases. In this case the high concentration of hydrogen peroxide reacts with the undissociated ethyl hydrogen malonate to yield ethyl glycollate. In potassium ethyl malonate solutions the effect of added salts is less. Here the concentration of ethyl malonate ions is much greater than in the acid and the ions can compete effectively in carrying the current; in addition ordinary diffusion is appreciable.

In the presence of metallic salts which are catalysts for the decomposition of hydrogen peroxide, the concentration of the latter would be insufficient for the formation of diethyl succinate. The failure of the Brown-Walker reaction to occur at platinised platinum, gold, lead dioxide and carbon anodes can be attributed to their catalytic activity in the decomposition of hydrogen peroxide. If the activity of a platinised platinum anode is reduced, either by poisoning or by anodic polarization, the efficiency is increased.

Since the evolution of oxygen and the formation of ethyl glyoxylate occur at lower potentials than the Brown-Walker synthesis, and yet the latter process generally occurs in preference to the others, the anode potential can only be indicative of secondary phenomena, and is not the factor which determines the reaction occurring. In the reaction of hydrogen peroxide with ethyl malonate ions, discharged ethyl malonate radicals are ostensibly liberated, and set up a characteristic static potential against the ethyl malonate ions in solution. Since the anodic formation of hydrogen peroxide involves an irreversible stage, this potential can be higher than that of the alternative electrode processes. If conditions are such that the hydrogen peroxide decomposes rapidly to give oxygen and the alternative oxidation products, the concentration of discharged ethyl malonate radicals is much lower. In this case the potential set up may fall below that corresponding to oxygen evolution, and the latter process then determines the observed potential. This explains the high potential of 2.8 volts at which the Brown-Walker synthesis occurs, and the fall in potential to 2.0 volts when there are catalysts for the decomposition of hydrogen peroxide present. In ethyl hydrogen malonate solutions the synthesis takes place at approximately the same potential as in the salt solution at low current densities, but at higher current densities the potential decreases. Here the ethane efficiency also falls off at high current densities, and this should lead to a decrease in the concentration of discharged ethyl malonate radicals at the anode surface; hence we should expect the potential also to fall. When foreign anions are added to the acid-ester solution, their first effect is to lower the concentration of ethyl malonate ions in the vicinity of the anode, but at low current densities the efficiency is not greatly affected, and so the concentration of discharged ethyl malonate radicals is probably not greatly diminished. Thus at low current densities foreign anions should raise the potential. At higher current densities, however, when the efficiency of diester formation is lowered markedly, we should expect the rapid falling off of potential that is found experimentally.

In non-aqueous solutions, where there are no hydroxyl ions available for the production of hydrogen peroxide, the course of the electrolytic reaction must be different. Hickling and Westwood (30) investigated the electrolysis of potassium and hydrogen ethyl malonate in ethylene glycol as solvent, and found that, in analogy to the Kolbe reaction, the nature of the anode material and the addition of catalysts for the decomposition of hydrogen peroxide had little influence on the reaction. They therefore postulate that ethyl malonate ions are discharged directly at the anode, and combine in pairs to form the acid peroxide, which then decomposes to diethyl succinate and carbon dioxide.

The Synthesis of Long Chain Compounds

The Brown-Walker synthesis has been carried out on most of the available n-dicarboxylic acids. Sebacic acid, $HOOC(CH_2)_8COOH$, is the highest dicarboxylic acid readily available commercially, and can be used as the starting point of the synthesis. Brown and Walker (3), Fairweather (18), Shiina (19) and Swann et al (20) have obtained diethyl hexadecanedicarboxylic acid by the electrolysis of potassium ethyl sebacate.

$$2C_2H_5OOC(CH_2)_8COO^- \longrightarrow C_2H_5OOC(CH_2)_{16}COOC_2H_5 + 2CO_2 + 2\mathcal{E}$$

Swann et al (20) electrolysed a 1.5 M solution of potassium ethyl sebacate, containing 50 g. of ethyl hydrogen sebacate. A current density of 0.2 amp. per sq. cm. was used, and the temperature was kept below 50° C. Yields of 40-55 percent were obtained.

In the electrolysis of dicarboxylic acids of higher molecular weight by Fairweather (18), (21) the following problems were encountered:

1. The temperature of the electrolyte solution had to be kept above the melting point of the synthetic diester so that the latter did not solidify on the anode and prevent passage of the current.

2. The sodium-ester salts of the higher dicarboxylic acids are of a soapy nature and could not be readily dealt with in a concentrated solution. The soapy nature begins with dodecanedicarboxylic acid, $HOOC(CH_2)_{12}COOH$. Thus two of the conditions favourable to electrosynthesis, high concentration of electrolyte and low temperature, were difficult to attain.

Petersen (31) synthesized paraffin hydrocarbons of high molecular weight by electrolysis of salts of the fatty acids (Kolbe synthesis).

$$2\ CH_3(CH_2)_{16}COO^- \longrightarrow CH_3(CH_2)_{32}CH_3 + 2\ CO_2 + 2\mathcal{E}$$

The electrosynthesis of n-hexahexacontane, $CH_3(CH_2)_{64}CH_3$ has been carried out by Francis (37). In these cases the difficulty of electrolysing a soapy solution was met by using aqueous alcohol as the solvent.

Fairweather (18) found that when a solution of sodium ethyl hexadecanedicarboxylate was electrolysed under the above conditions no synthesis took place. However by reducing the quantity of alcohol to a minimum necessary to avoid foaming, Fairweather succeeded in synthesizing diethyl duotriacontanedicarboxylate.

$$2C_2H_5OOC(CH_2)_{16}COO^- \longrightarrow C_2H_5OOC(CH_2)_{32}COOC_2H_5 + 2CO_2 + 2\mathcal{E}$$

Fairweather electrolysed a 0.6 M aqueous solution of the sodium salt containing 11 percent alcohol by volume at a temperature of 70-75° C. The product was separated and purified by fractional crystallization from ether. A yield of 12 percent was obtained. From the formula the molecular weight of diethyl duotriacontanedicarboxylate is 594. This is the highest dicarboxylic acid whose electrosynthesis has been described in the literature.

Esters and Half-Esters of Dicarboxylic Acids

An important step in the Brown-Walker synthesis is the preparation of the acid-ester of the dicarboxylic acid. The usual method of esterification, using excess alcohol as the solvent, leads of course to the diester. There are three general methods for the preparation of the acid-esters of dibasic acids, namely

1. The half-esterification of the dibasic acid
2. The half-saponification of the diester of the acid
3. The heating together of equimolar quantities of the acid and the diester.

The acid-esters of most of the n-dicarboxylic acids have been prepared by the method of half-saponification. Walker (33) half-saponified diethyl succinate by reacting the diester with an equivalent amount of potassium hydroxide in alcohol solution. The resulting mixture of unreacted diester, potassium-ester salt and dipotassium salt was separated by the following procedure. The water insoluble diester was removed by distilling off the alcohol, dissolving the residue in water and extracting the diester with ether. The aqueous solution was then evaporated to dryness, and the salts separated by taking advantage of the greater solubility of the potassium-ester salt in boiling absolute alcohol.

Walker and others (16), (22), (13) used this procedure in the preparation of the acid-esters of other dicarboxylic acids. It was found that for the higher acids it was necessary to carry out the saponification in stages and in the cold. The diester was dissolved in twenty times its weight of ethanol, the solution was cooled to 5° C. and to it was added a dilute alcoholic solution of potassium hydroxide; the amount of potassium hydroxide was one quarter or one half the amount necessary for half-saponification. The temperature was kept below 15° C. until neutrality was reached (about ten days). The acid-ester was isolated as above. Fairweather (18) prepared ethyl hydrogen hexadecanedicarboxylate by this method. Owing to the low solubility of the diester in cold alcohol, the reaction was carried out in very dilute (2 percent) alcohol solution. Under these conditions the sodium-ester salt remained in solution while the disodium salt (formed to the extent of 20 percent) precipitated.

More recently attention has been directed toward the method of half-esterification for the preparation of acid-esters. However, Drake and Melamed (34) reported 30 percent yields of acid-ester in the half-saponification of diethyl hexadecanedicarboxylate. Equivalent quantities of sodium ethoxide, water and diester in alcohol solution were used. The resulting mixture of unreacted diester, sodium-ester salt and disodium salt was separated as follows. The diester was removed by extraction from the dry sodium salts by petroleum ether (B.P.= 90-110° C.). After acidification of the salts, the separation of the half-ester from the diacid was accomplished by extracting the mixed free acids with petroleum ether (B.P.= 30-60° C.), which selectively dissolved the half-ester.

The acid-esters of the lower dicarboxylic acids have been prepared in good yield by the method of half-esterification. Swann, Oehler and Buswell (35) have prepared ethyl hydrogen sebacate by the half-esterification of sebacic acid.

$$\begin{tikzcd} HOOC(CH_2)_8COOH + C_2H_5OH \arrow[r, shift left] & C_2H_5OOC(CH_2)_8COOH + H_2O \arrow[l, shift left] \arrow[d, shift left, "C_2H_5OH"] \\ & C_2H_5OOC(CH_2)_8COOC_2H_5 + H_2O \arrow[u, shift left] \end{tikzcd}$$

This is an equilibrium reaction and addition of diester at the beginning of the reaction decreases its formation from the reactants so that the monoester becomes the main product. The reaction was carried out by refluxing together equivalent quantities of sebacic acid and ethanol in the presence of added diethyl sebacate. The product was separated by distillation under reduced pressure, yields of about 65 percent being obtained.

This method of preparation of acid-esters has been used successfully for acids up to and including brassylic acid. In the case of the higher acids distillation is not a practicable method of separation. Jones (35) used the following procedure in the preparation of ethyl hydrogen brassylate. After esterification the dibutyl ether and water were distilled under vacuum. The residue was poured into petroleum ether and the precipitated brassylic acid removed by filtration. The acid-ester was then separated from the diester by extraction with aqueous potassium carbonate solution. However, this method could not be applied to acids containing more than fourteen carbon atoms because of the stable emulsions which were formed during the last stage of the separation.

EXPERIMENTAL PROCEDURES

Succinic Acid

Esters and Half-Esters of Succinic Acid

Preliminary work was done using succinic acid to check the preparation and purification of the acid-ester.

Diethyl succinate was prepared by the direct esterification of succinic acid.

$$HOOC(CH_2)_2COOH + 2C_2H_5OH \longrightarrow C_2H_5OOC(CH_2)_2COOC_2H_5 + 2H_2O$$

118 g. (1 mole) of succinic acid (analytical reagent grade), 185 cc. of ethanol (95%), 320 cc. of benzene, (reagent grade) and 36 cc. of concentrated sulphuric acid (C.P.) were refluxed together for five hours on the steam bath. The benzene layer was separated from the aqueous layer and neutralized with potassium carbonate to remove unreacted acid. The benzene was distilled off and the diethyl succinate remaining was distilled under reduced pressure, B.P.= 95-97° C. at 8 mm. 157 g. of product was obtained, the yield being about 90% of the theoretical.

Ethyl hydrogen succinate was prepared by the half-saponification of diethyl succinate according to the procedure of Walker (32).

$$C_2H_5OOC(CH_2)_2COOC_2H_5 + KOH \longrightarrow C_2H_5OOC(CH_2)_2COOK + H_2O$$

174 g. (1 mole) of diethyl succinate was dissolved in 500 cc. of ethanol. A solution of 28 g. (0.5 mole) of potassium hydroxide (reagent grade) in 100 cc. of ethanol was added; the mixture was allowed to stand over night, then refluxed for five hours (solution neutral to phenolphthalein). The ethanol was removed by distillation, water being added towards the end of the distillation to dissolve the salts. The solution was cooled and the unreacted diethyl succinate removed by extraction with ether. Walker's method of separation of the potassium ethyl and the dipotassium salts was discarded in favour of the following procedure. The aqueous solution of the potassium salts was acidified in the cold with hydrochloric acid, liberating succinic acid and ethyl hydrogen succinate which floated as an oil on the surface. The oil was separated by extraction with ether, the ether was distilled off and the residue distilled under reduced pressure. Ethyl hydrogen succinate was collected at 124-126° C. at 7 mm. pressure. The yield was 27-31 g. which is 15-17% of the theoretical.

It was thought that the poor yield of ethyl hydrogen succinate might be due to the large excess of potassium hydroxide present at the beginning of the reaction, causing the potassium ethyl succinate formed to react immediately to form dipotassium succinate. To test this a saponification was carried out by adding the potassium hydroxide solution dropwise to the diester. Two moles of diethyl succinate was dissolved in 1000 cc. of ethanol in a three-neck flask fitted with a stirrer and a dropping-funnel. One mole of potassium hydroxide in solution in ethanol was added slowly through the dropping-funnel at room temperature, with stirring. Phenolphthalein was used as an indicator in the diester solution, and the rate of addition of the potassium hydroxide was regulated so that the solution remained colourless. The reaction took about twelve hours. The ethyl hydrogen succinate was separated as above. 42 g. of product was obtained, the yield being 23% of the theoretical amount.

Electrolysis of Potassium Ethyl Succinate

A preliminary electrolysis was carried out using potassium ethyl succinate.

$$2C_2H_5OOC(CH_2)_2COO^- \longrightarrow C_2H_5OOC(CH_2)_4COOC_2H_5 + 2CO_2 + 2\varepsilon$$

A 500 cc. tall-type beaker provided with a glass cooling coil, a thermometer, and a stirrer was used as the electrolysis cell. The electrodes were 8 inch lengths of platinum wire (20 gauge) wound into spirals.

To 30 g. of ethyl hydrogen succinate was added slowly, with cooling, a solution of 12 g. of potassium hydroxide in 275 cc. of water, yielding an approximately 0.75 N solution of potassium ethyl succinate. The solution was poured into the beaker, 25 g. of ethyl hydrogen succinate was added and a current of 5 amp. was passed through the cell. The temperature was kept below 35° C. The electrolysis was stopped when a few drops of the electrolyte gave an alkaline reaction when tested with phenolphthalein ($1\frac{3}{4}$ hours). The oily product floating on the surface was separated in a separatory funnel, washed with an equal volume of 10% potassium carbonate solution to remove any unchanged acid-ester, then with an equal volume of 3.5% hydrochloric acid, and finally twice with half its volume of water. A little ether was used to break up the emulsion which formed during the carbonate washing. The ether was distilled off and the oil distilled under reduced pressure. The first fraction was chiefly water. The lower esters (by-products of the electrolysis) came over below 110° C. at 7 mm. pressure. The diethyl adipate was collected at 110-112° C. at 7 mm. pressure. The product weighed 9.5 g., the yield being 55% of the theoretical amount.

Sebacic Acid

Esters and Half-Esters of Sebacic Acid

Owing to the poor yields of acid-ester obtained in the half-saponification of diethyl succinate, it was decided to use the method of half-esterification of Swann et al (39) in the preparation of ethyl hydrogen sebacate.

$$\begin{tikzcd} \mathrm{HOOC(CH_2)_8COOH + C_2H_5OH} \arrow[r, shift left] & \mathrm{C_2H_5OOC(CH_2)_8COOH + H_2O} \arrow[l, shift left] \arrow[d, shift left] \\ & \mathrm{C_2H_5OOC(CH_2)_8COOC_2H_5 + H_2O} \arrow[u, shift left] \end{tikzcd}$$

This is an equilibrium reaction and the addition of diester at the beginning of the reaction decreases its formation from the reactants so that the monoester becomes the main product.

Diethyl sebacate was prepared by the direct esterification of sebacic acid.

$$\mathrm{HOOC(CH_2)_8COOH + 2C_2H_5OH \longrightarrow C_2H_5OOC(CH_2)_8COOC_2H_5 + 2H_2O}$$

202 g. (1 mole) of sebacic acid (C.P.), 500 cc. of ethanol and 50 cc. of sulphuric acid were refluxed together for five hours. The ethanol was distilled off and the residue shaken up with water and ether to remove the sulphuric acid and extract the diester. The ethereal layer was separated, washed once with water

to remove any sulphuric acid and ethanol remaining, then with 10% potassium carbonate solution to remove unreacted sebacic acid. On acidification of the carbonate washings with hydrochloric acid the free sebacic acid was precipitated. The washing was continued until the acidified carbonate washings remained clear (three carbonate washings). The ethereal solution was dried over sodium sulphate, the ether distilled off and the residue distilled under reduced pressure. The diethyl sebacate was collected at 155-158° C. at 6 mm. pressure. 190 g. of product was obtained, the yield being about 75% of the theoretical amount.

Ethyl hydrogen sebacate was prepared by the half-esterification of sebacic acid according to the procedure of Swann et al (34).

$$HOOC(CH_2)_8COOH + C_2H_5OH \xrightarrow{\text{diester}} C_2H_5OOC(CH_2)_8COOH + H_2O$$

In a 500 cc. flask fitted with a reflux condenser was placed a mixture of 101 g. (0.5 mole) of sebacic acid, 75 g. (0.29 mole) of diethyl sebacate, 25 cc. of di-n-butyl ether (practical grade) and 12.5 cc. of concentrated hydrochloric acid (C.P.). The flask was heated in a bath of high-melting wax at 160-170° C. until the mixture was completely homogeneous (about 15 minutes). The temperature of the bath was then lowered to 120-130° C. and 30 cc. (0.5 mole) of ethanol was added to the solution through the condenser. The mixture was refluxed for two hours. At the end of this period an additional 10 cc. portion of ethanol was added to the solution and refluxing was continued for two hours longer. The reaction mixture was then distilled under reduced pressure in a 500 cc. modified Claisen flask having a column 30 cm. in length. The first fractions consisted of a little alcohol, water and di-n-butyl ether. The next fraction was diethyl sebacate, B.P. = 134-138° C. at 2 mm. pressure. The ethyl hydrogen sebacate was collected at 153-156° C. at 2 mm. The product melted at 35-38° C. and weighed 45-50 g. Refractionation of the fore-run (B.P. = 138-153° C. at 2 mm.) and the after-run (B.P. = 156-163° C. at 2 mm.) gave 12 g. more of pure monoester. The total yield was 45-50% of the theoretical based on the amount of sebacic acid used. The di-n-butyl ether was recovered in pure condition by a simple distillation after separating it from the water. The recovered diethyl sebacate (60-80 g.) was used directly in the subsequent preparation. Following this procedure, from 1600 g. of sebacic acid a total of 1000g. of ethyl hydrogen sebacate was prepared.

Electrolysis of Potassium Ethyl Sebacate

Potassium ethyl sebacate was electrolysed to form diethyl hexadecanedicarboxylate according to the procedure of Swann et al (20).

$$2C_2H_5OOC(CH_2)_8COO^- \longrightarrow C_2H_5OOC(CH_2)_{16}COOC_2H_5 + 2CO_2 + 2\varepsilon$$

The electrolysis was done in a 500 cc. tall-type beaker provided with a glass cooling coil, a thermometer, and a high speed stirrer. During the winter the circulation of tap water through the cooling coil was sufficient to keep the temperature of the cell below 50° C. However during the summer, when the tap water was about 15° warmer, it was found necessary to provide the cell with a water-jacket as well as the cooling coil.

The anode was a platinum sheet 6.0 x 3.8 cm. Two 12 inch lengths of platinum wire (20 gauge), wound into spirals, were used as cathodes, being placed equidistant from the anode to ensure uniform current density on both sides of the anode. The use of smaller cathodes proved impossible, since, with a current of 10 amp. passing through the cell, the current density at the cathodes was too high. Thus the cathodes became insulated by a layer of evolved hydrogen, and the current fell to zero. Unexplained blue flashes were also noted along the length of the cathodes.

The current source was an 110 volt D.C. line. Four 34 ohm 3.2 amp. rheostats connected in parallel reduced the voltage sufficiently and allowed the passage of 10 amp. without overloading the rheostats.

To 86.5 g. of ethyl hydrogen sebacate was added slowly with stirring 125-130 cc. of approximately 3 N potassium hydroxide. The mixture was diluted to 250 cc. and warmed slightly on the steam-cone to yield a homogeneous solution of 1.5 N potassium ethyl sebacate. The solution was poured into the electrolysis cell, 10 g. of ethyl hydrogen sebacate (liquid) was added and a current of 10 amp. was passed through the cell. To the solution was now added 40 g. more of ethyl hydrogen sebacate (liquid) in portions of 10 g. each over a period of ten minutes. If the 50 g. of acid-ester was added all at once excessive foaming occurred. The temperature of the cell was held between 40° and 45° C. The electrolysis was continued until a few drops of the electrolyte solution showed an alkaline reaction to phenolphthalein (60-90 minutes). The alkalinity was tested every 10 minutes after the first 50 minutes. When the solution had become alkaline the current was cut and the oily product floating on the surface was pipetted off. The oil was washed with an equal volume of 10% potassium carbonate solution to remove any unchanged acid-ester, then with an equal volume of 3.5% hydrochloric acid, and finally twice with half its volume of water. A little ether was used to break up the emulsion which formed during the carbonate washing. The ether was evaporated off, and the oil was crystallized from methanol, filtered by suction, and washed twice while in the funnel with ice-cold methanol. The product, white and waxy in appearance, was dried in a dessicator over sulphuric acid. The yield was 14-17 g. (35-42% of the theoretical amount) of material melting at 40-41° C. This figure for the % yield is based only on the 50 g. of ethyl hydrogen sebacate used in the second part and no account is taken of the 86.5 g. used in preparing the electrolyte solution. This preparation becomes practicable only if several consecutive runs are made, as was done in this case. After the oily product had been drawn off with a pipette more free acid-ester was added and the electrolysis continued. In this way fifteen 50 g. batches of ethyl hydrogen sebacate were converted. After about ten runs the yield gradually decreased to 10-12 g. A total of 210 grams of diethyl hexadecanedicarboxylate was prepared.

Hexadecanedicarboxylic Acid

Esters and Half-Esters of Hexadecanedicarboxylic Acid

The method of preparing the acid-ester of hexadecanedicarboxylic acid by half-saponification as reported by Drake and Melamed (33) looked promising. Accordingly the diester, available directly from the previous electrolysis, was half-saponified following this procedure.

Half Saponification

The reaction was carried out by treating a solution of the diester in ethanol with sodium ethoxide solution to which had been added an equivalent amount of water.

$$C_2H_5OOC(CH_2)_{16}COOC_2H_5 + C_2H_5ONa + H_2O \longrightarrow$$

$$C_2H_5OOC(CH_2)_{16}COONa + 2\ C_2H_5OH$$

In a 1-l. flask equipped with a reflux condenser was placed 100 cc. of absolute ethanol. 6.2 g. (0.27 mole) of freshly cut sodium was added slowly, the rate of addition being such that rapid refluxing was maintained. When the reaction was complete 4.9 cc. (0.27 mole) of water was added to the solution. To 135 cc. of absolute ethanol in a three-neck flask provided with a thermometer, a stirrer and a dropping-funnel was added 100 g. (0.27 mole) of diethyl hexadecanedicarboxylate. The mixture was warmed and stirred to dissolve the diester, then cooled until the diester started to precipitate (about 30° C.). The sodium ethoxide solution was then added dropwise with stirring. The sodium salts which formed, being almost insoluble in ethanol, precipitated. The mixture partially solidified almost immediately, so that stirring with the ordinary propeller-type stirrer was ineffective. A twisted wire stirrer substituted for the glass stirrer proved more effective, and the addition of the sodium ethoxide solution was continued to completion. The mixture was then allowed to stand overnight. The ethanol was removed by distillation and replaced by one litre of petroleum ether (B.P.= 90-120° C.). The mixture was heated and stirred to break up the solid and extract the diester, and finally cooled and filtered. The sodium salts were extracted twice with hot petroleum ether, then dried at 90° C. to yield 72 g. of brownish granular product; 10 g. of diester resulted from evaporation of the petroleum ether filtrates and crystallization of the residue from methanol. The dried sodium salts were suspended in one litre of hot water (80-90° C.) and were converted to the free acids by slow addition of excess hydrochloric acid to the well-stirred suspension. The acids were filtered from the cooled solution, dried, and extracted in a Soxhlet extractor using petroleum ether (B.P.= 30-60° C.) as the solvent. On evaporation to a small volume the petroleum ether solution deposited 9 g. of ethyl hydrogen hexadecanedicarboxylate. The product melted at 66-68° C. The yield was 10% of the theoretical.

The material insoluble in petroleum ether amounted to 62 g.; it melted at 112-116° C. and was largely the diacid. The total of products accounted for 90% of the starting material.

Half-Esterification

Owing to the poor yield of acid-ester obtained in the half-saponification above, it was decided to attempt the preparation of ethyl hydrogen hexadecanedicarboxylate by the method of half-esterification, employing a procedure similar to that used in the preparation of ethyl hydrogen sebacate (34).

<u>Hexadecanedicarboxylic acid</u> was prepared by the complete saponification of the diester.

$$C_2H_5OOC(CH_2)_{16}COOC_2H_5 + 2KOH \longrightarrow KOOC(CH_2)_{16}COOK + 2C_2H_5OH$$

80 g. (0.22 mole) of diethyl hexadecanedicarboxylate was dissolved in 800 cc. of ethanol in a three-neck flask provided with a mercury seal stirrer, a condenser and a dropping-funnel. A solution of 40 g. of potassium hydroxide in 400 cc. of ethanol was added, and the mixture was stirred and refluxed for one hour. About one half the solvent was then removed by distillation, the mixture was cooled and the potassium salt filtered off and dried by suction on the funnel. The salt was dissolved in 2 l. of hot water (90° C.), acidified

with excess hydrochloric acid, cooled, filtered and dried at 90° C. 62 g. of hexadecanedicarboxylic acid was obtained, M.P. = 123-125° C. This is a yield of 92 percent of the theoretical amount.

Ethyl hydrogen hexadecanedicarboxylate was prepared by the half-esterification of the diacid.

$$HOOC(CH_2)_{16}COOH + C_2H_5OH \xrightarrow{\text{diester}} C_2H_5OOC(CH_2)_{16}COOH + H_2O$$

In a 500 cc. flask equipped with a reflux condenser was placed a mixture of 124 g. (0.4 mole) of hexadecanedicarboxylic acid, 37 g. (0.1 mole) of diethyl hexadecanedicarboxylate, 50 cc. of di-n-butyl ether and 10 cc. of concentrated hydrochloric acid. The mixture was refluxed for one half hour, then 24 cc. of 95% ethanol was added and the heating continued for two hours. At the end of this period an additional 9 cc. of ethanol was added and the mixture refluxed for two hours longer. The water and dibutyl ether were then distilled under vacuum. To the residue was added 500 cc. of ethanol; the mixture was heated and stirred to dissolve the solid, then cooled to about 30° C. Alcoholic potassium hydroxide solution was added dropwise with stirring until the solution was just alkaline to phenolphthalein. The ethanol was removed by distillation and replaced by petroleum ether (B.P. = 90-120° C.). The mixture was heated and stirred to break up the solid and extract the diester, and finally cooled and filtered. The salts were extracted twice with hot petroleum ether; about 2.5 l. of petroleum ether was used altogether. 85 g. of dried mixed salts was obtained. From the evaporation of the petroleum ether filtrate, and recrystallization of the residue from methanol, 84 g. of diester was recovered. The salts were suspended in about 2 l. of hot water (80-90° C.) and acidified with hydrochloric acid to liberate the free acids. The acids, which were liquid under these conditions, rose to the surface and solidified to a solid cake on cooling the solution. The cake was separated from the water; further separation of solution was effected by remelting and cooling. 73 g. of mixed acids was obtained. The product was powdered and extracted in a Soxhlet extractor using petroleum ether (B.P. 30-60° C.) as solvent. On evaporating to a small volume the petroleum ether solution deposited 48 g. of ethyl hydrogen hexadecanedicarboxylate, the yield being 35% of the theoretical based on the amount of acid used. The product melted at 68-69° C. The material insoluble in petroleum ether amounted to 21 g.; it melted at 115-120° C. and was largely the diacid. The total of products accounted for 87% of the starting material.

An experiment was done using a smaller proportion of diester to acid than in the previous case. The half-esterification of 25 g. (0.08 mole) of hexadecanedicarboxylic acid in the presence of 5 g. (0.01 mole) of diester gave a 20% yield of acid-ester based on the amount of acid used.

Electrolysis of Potassium Ethyl Hexadecanedicarboxylate

Potassium ethyl hexadecanedicarboxylate was electrolysed to form diethyl duotriacontanedicarboxylate.

$$2C_2H_5OOC(CH_2)_{16}COO^- \longrightarrow C_2H_5OOC(CH_2)_{32}COOC_2H_5 + 2CO_2 + 2\varepsilon$$

A jacketed electrolysis cell 25 cm. high was made from 30 mm. glass tubing; it was arranged so that either cold water or steam could be passed through the jacket. The cell was provided with a high speed stirrer, a thermometer, a platinum sheet cathode and a platinum sheet anode 6 sq. cm. in area (one side).

Aqueous Solutions

To 8.2 g. of ethyl hydrogen hexadecanedicarboxylate was added 50 cc. of approximately 0.5 M potassium hydroxide (1.7 g. of potassium hydroxide in 50 cc. of water). The mixture was heated and stirred to form a homogeneous solution. The hot solution was poured into the electrolysis cell and diluted to 60 cc., yielding a 0.5 M solution of potassium ethyl hexadecanedicarboxylate. To this was added 4 g. of the finely powdered acid-ester. This mixture, which did not form a clear solution even at 90° C., could not be electrolysed on account of the foaming which took place. Accordingly

Dow Corning Anti-Foam, a silicone jelly which is inert to electrolysis, was used to control the foaming. A little D.C. Anti-Foam dissolved in 5 cc. of benzene was added to the solution. The soapy nature of the solution caused an emulsion to form, and the benzene evaporated. This solution was electrolysed with very little foaming. A current of 2-2.5 amp. was passed for two hours at a temperature of 80-85° C. At the end of this time the electrolyte solution was non-alkaline when tested with phenolphthalein. The electrolysis was continued for two hours longer, the current gradually rising to 5.5 amp. with the rheostat settings unchanged. The electrolysis was then stopped although the electrolyte was still non-alkaline. The oil which collected on the surface set to a brown wax-like solid on cooling. This was separated from the solution, remelted in hot water to remove any remaining salt, and crystallized from diethyl ether. A very small amount of white precipitate was obtained, M.P. = 67-68° C. This was unreacted ethyl hydrogen hexadecanedicarboxylate. No diester product was isolated. The ether filtrate was evaporated to dryness and the residue crystallized from petroleum ether (B.P. = 30-60° C.), 3 g. of unreacted acid-ester being recovered. The electrolyte solution no longer set to a soapy jelly on cooling, but remained liquid even at room temperature. Evidently during this electrolysis no Brown-Walker synthesis took place.

To test the effect of Anti-Foam on the reaction a control experiment using sebacic acid was made. The electrolysis of 50 g. of ethyl hydrogen sebacate in the presence of D.C. Anti-Foam gave 13 g. of diester product. This was a 34% yield, 6% lower than for the previous run, when no Anti-Foam was used.

Fairweather reported small yields of synthetic product from the electrolysis of aqueous-alcoholic solutions of potassium ethyl hexadecanedicarboxylate, reporting that the alcohol, although it cut down the yield, was necessary to control foaming. Although foaming could be controlled by the use of D.C. Anti-Foam, as shown above, no synthesis took place in this case. In view of these facts, it was decided to test the effect the addition of alcohol would have to the electrolyte solution.

Aqueous-Alcoholic Solutions

The electrolyte solution was 60 cc. of 0.5 M potassium ethyl hexadecanedicarboxylate (prepared as previously described), to which was added 8-9 cc. of ethanol and 2 g. of the finely powdered acid-ester. On heating and stirring a homogeneous, clear solution was obtained. A current of 2-3 amp. was passed through the cell, the temperature being kept between 70 and 75° C.

After 30-45 minutes the solution was alkaline to phenolphthalein. Without turning off the current 2 g. more of acid-ester was added, and the electrolysis continued as described. In this way a total of 8 g. of ethyl hydrogen hexadecanedicarboxylate was converted, the time required being about two and one half hours. Since some alcohol evaporated during the electrolysis it was necessary to add alcohol in 2 cc. portions as the solution tended to become viscous (every 60-90 minutes). When the electrolysis was stopped an oil rose to the surface, which solidified to a light brown wax on cooling. This was separated from the salt solution, melted twice in hot water to remove any remaining salt, and finally remelted and cooled to remove all possible water. The 7.5-8 g. of mixed esters thus obtained, (M.P.$=$60-65° C.), was crystallized from diethyl ether. The product, a white, wax-like solid, melted at 74-78° C. and weighed about 1.7 g. This was recrystallized from ether yielding 1.3-1.5 g. of diethyl duotriacontanedicarboxylate, M.P.$=$ 77-79° C. The yield was 20-22% of the theoretical, based on the amount of acid-ester used. The ether filtrates were evaporated to dryness and the residue crystallized from petroleum ether, yielding 1.0-1.5 g. of impure diester. On recrystallization from petroleum ether about 0.8 g. of diester was obtained, M.P. = 65-68° C. Evaporation of the petroleum ether filtrates gave a soft yellow wax which melted over the range from room temperature to 45° C. This was a mixture of esters -- by-products of the electrolysis.

The presence of free ethyl hydrogen hexadecanedicarboxylate at the end of the electrolysis was probably due to its solubility in the oily product. Owing to the fact that alcohol acts as a mutual solvent for the acid-ester and the aqueous salt solution, it was thought that the use of a larger proportion of alcohol in the electrolyte might reduce the amount of unreacted acid-ester. Accordingly the electrolyte from the previous electrolyses was evaporated to about one half its volume and 30 cc. of ethanol was added, the total volume being about 70 cc. Using this solution as electrolyte, 12 g. of acid-ester was converted as described previously. From the 9 g. of wax separated from the solution, 1.1 g. of diethyl duotriacontanedicarboxylate was obtained, M.P. = 76-79.5° C. This represents a yield of 11% of the theoretical amount. 1.3 g. of unreacted acid-ester was recovered. Thus, although in this case the proportion of acid-ester recovered was less, the yield of synthetic product was also smaller than previously.

Other Solvents

The electrolysis was carried out in the presence of methyl ethyl ketone to determine whether the ethanol played any other role besides that of solvent in the process. The solution from the previous electrolysis was evaporated to one half its volume to remove the alcohol. Then 8-10 cc. of methyl ethyl ketone, water to make up a volume of 60 cc. and 2 g. of acid-ester were added and the solution electrolysed as before. From a total of 8 g. of acid-ester, 1.1 g. of diester was obtained, M.P.$=$77-79.5° C. This represents a yield of 17% of the theoretical. 2.2 g. of acid-ester was recovered.

A larger proportion of methyl ethyl ketone had no appreciable effect on the reaction. 8 g. of acid-ester was electrolysed in the presence of 20 cc. of methyl ethyl ketone, the total volume of solution being 60 cc. 1.2 g. of diester product, melting at 76.5-79° C., was obtained, the yield being 18% of the theoretical. 2.4 g. of diester was recovered.

DISCUSSION OF RESULTS

Esters and Half-Esters of Dicarboxylic Acids

Two methods for the preparation of acid-esters of dicarboxylic acids were studied, as follows:

1. Half-esterification of the dicarboxylic acid.
2. Half-saponification of the diester of the acid.

Half-Saponification of Diesters

From the work done it appears that the yields of acid-ester obtainable by the process of half-saponification are not high, despite the fact that good yields were reported by some the the earlier investigators.

The half-saponification of diethyl succinate according to the procedure of Walker gave 15-17% yields of acid-ester. A modification of this procedure, whereby the large excess of alkali, present at the beginning of the previous reaction, was avoided, led to slightly greater yields of acid-ester. In this case the amount of acid-ester obtained was about 23% of the theoretical.

Fairweather noted that in the half-saponification of the diesters of the higher molecular weight acids only small quantities could be handled owing to the low solubility of the diester in cold ethanol. In view of this fact, and of the poor yields obtained above, no attempt was made to prepare ethyl hydrogen sebacate by the method of half-saponification.

However, the half-saponification of diethyl hexadecanedicarboxylate as reported by Drake and Melamed looked promising, and accordingly was attempted. A difficulty was encountered in that the sodium salts, which are almost insoluble in ethanol, precipitated immediately forming a semi-solid mass which could not be stirred effectively. This may account for the low yield (9%) of acid-ester which was obtained. It seems that, although it may be advantageous to have the sodium ester salt precipitate, thus protecting it from further reaction, the mechanical difficulty of handling a semi-solid mass outweighs this consideration. Owing to lack of time this was not further investigated, but attention was turned to the half-esterification process.

Half-Esterification of Diacids

Since esterification is an equilibrium reaction, leading to a mixture of diacid, acid-ester and diester, the addition of diester at the beginning of the reaction decreases its formation from the reactants, so that the acid-ester becomes the main product. Half-esterification of sebacic acid following the procedure of Swann et al gave 50% yields of ethyl hydrogen sebacate. This figure for the percentage yield is based on the amount of acid used in the process, no account being taken of the added diester, which was recovered at the end of the reaction. The percentage yield based on the total amount of acid plus diester used was 32%. Hence this method is more practicable in preparing a large quantity of acid-ester, so that several runs are made, the diester recovered in each run being used in the subsequent one. However even for one run the yield was considerably higher than any obtained by the half-saponification process.

The procedure of Swann et al. was applied to the preparation of ethyl hydrogen hexadecanedicarboxylate from the corresponding acid. Here the amount of reactant available was limited, and it was desired to prepare the largest possible amount of acid-ester in one operation. Accordingly the amount of diester added at the beginning of the reaction was decreased from 0.58 to 0.25 mole per mole of acid used. The yield of acid-ester was 35% of the theoretical based on the amount of acid used. This corresponds to a yield of 28% based on total acid plus diester used, which compares favourably with the yield of ethyl hydrogen sebacate calculated on the same basis. In one experiment 0.13 mole of diester per mole of acid was used. The yield of ethyl hydrogen hexadecanedicarboxylate, based on acid alone, was 20%, which corresponds to 18% based on total acid plus diester used.

In the half-esterification of this high molecular weight acid, the isolation of the acid-ester from the acid and the diester presented some difficulty. Purification by distillation under reduced pressure is not practicable in this case. Neither can the method of separation used by Jones in the preparation of ethyl hydrogen brassylate be followed, since with acids containing more than fourteen carbon atoms stable emulsions are formed during the process. However, the potassium ester and dipotassium salts can be separated from the diester by the procedure of Drake and Melamed. Accordingly the solvent was distilled from the esterification mixture, replaced by ethanol, and alcoholic potassium hydroxide added to form the mixed salts. A separation was then effected following the procedure of Drake and Melamed. The addition of alkali to the cold alcoholic solution of the acid, acid-ester and diacid does not appear to cause any saponification since good yields of acid-ester were obtained.

The Brown-Walker Synthesis

The electrolysis of the acid-ester salts of the lower dicarboxylic acids appears to yield a higher percentage of the synthetic diester product than in the case of the higher molecular weight acids. For example, yields of 60% of diethyl succinate are reported from the electrolysis of potassium ethyl malonate (3). High yields would be expected here since there are only two alternative reactions possible, i.e. the Brown-Walker synthesis and ethyl glycollate formation; the third reaction, leading to the formation of unsaturated esters of monobasic acids, is not possible.

However, as shown here, the electrolysis of potassium ethyl succinate gave diethyl adipate in 55% yield with no difficulty, although here the formation of unsaturated esters is expected.

$$2\ C_2H_5OOC(CH_2)_2COO^- \longrightarrow C_2H_5OOCCH{=}CH_2 + C_2H_5OOC(CH_2)_2COOH + CO_2 + 2\varepsilon$$

The electrolysis of potassium ethyl sebacate according to the procedure of Swann et al. gave diethyl hexadecanedicarboxylate in 35-42% yield. In this case the acid-ester, although insoluble in water, was soluble in the concentrated potassium ethyl salt solution. Hence the electrolyte, consisting of the aqueous salt solution containing added free acid-ester, was a homogeneous solution and could be electrolysed without difficulty.

The main points noted in the electrolysis of potassium ethyl hexadecanedicarboxylate were the following:

1. The electrolysis of the potassium ethyl salt solution, either alone or containing added free acid-ester, proved a physical impossibility owing to the foaming which occurred.
2. The addition of a small amount of D.C. Anti-Foam to the electrolyte controlled the foaming and allowed the passage of the current, but no synthetic diester was formed during the electrolysis.
3. When alcohol or methyl ethyl ketone was added to the solution (about 13% by volume), the Brown-Walker synthesis took place. The yields of diester were 18-20% of the theoretical.
4. The Anti-Foam in itself had no adverse effect, as was shown by a control experiment using sebacic acid, where the yield of diester was comparable with that obtained in the usual way.

The successful use of alcohol in the Brown-Walker synthesis appears to be due chiefly to its action as a solublizer for the potassium ester salt; it also acts as a mutual solvent for the free acid-ester and the aqueous solution. It may be supposed that the aqueous "solution" is a heterogeneous system, and the probability for the existence of molecularly dispersed acid-ester ions in the mixture is small. This is not unexpected in view of the soapy nature of the potassium ester salt and of the high concentration (16%) of the solution. The passage of a current through this system causes a change in the type of dispersion, as shown by the fact that before electrolysis the mixture sets to a semi-solid soap at about 55° C., while after electrolysis the solution remains liquid even at room temperature. The Brown-Walker synthesis does not take place because no acid-ester ions are discharged during the process. By the addition of alcohol the potassium ester salt is brought into true solution, and electrolysis then results in the discharge of acid-ester ions and the formation of the synthetic diester. This view is upheld by the experiments using methyl ethyl ketone, where yields only slightly less than with ethanol were obtained. Hence it appears that alcohol or some similar solvent does not decrease the yield, as suggested by Fairweather, but, on the contrary, is actually necessary for the formation of the diester product.

The efficiency of diester formation may depend on the proportion of solvent in the electrolyte solution. It was found that a high concentration of ethanol (43% by volume) lowered the yield of diester from 22% to 11%. A high concentration of methyl ethyl ketone, however, had no appreciable effect on the reaction.

In the present investigation 20-22% yields of diethyl duotriacontanedicarboxylate were obtained by the Brown-Walker synthesis, as compared with 12% yields reported previously. Further work on the optimum solvent concentration might prove useful in increasing the yield obtainable in this synthesis.

SUMMARY

1. The process of half-esterification was found to be superior to that of half-saponification in the preparation of the acid-esters of dicarboxylic acids. Yields of 35-50% were obtained in the former case as compared with 9-23% obtained by the half-saponification process. In the saponification procedure of Drake and Melamed the difficulty of dealing with a semi-solid mass of precipitated salts was encountered.

2. The electrolysis of aqueous potassium ethyl hexadecanedicarboxylate in the presence of ethanol or methyl ethyl ketone gave 18-22% yields of the normal synthetic diester, as compared to 12% yields previously reported.

3. The difficulties arising in the electrolysis of the higher molecular weight acid-esters seem to be due not only to foaming, but also to solubility limitations.

BIBLIOGRAPHY

1. Kolbe, H., Annalen, 69, 279 (1849).
2. Hofer, H. and Moest, M., Annalen, 323, 284 (1902).
3. Brown, C. and Walker, J., Annalen, 261, 107 (1891); Trans. Roy. Soc. Ed., 36, 211 (1891).
4. Fichter, F. and Krummenacher, E., Helv. Chim. Acta, 1, 146 (1918).
5. Fichter, F., Trans. Amer. Electrochem. Soc., 45, 131(1924).
6. Fichter, F., ibid., 56, 647 (1929).
7. Walker, O.J., J. Chem. Soc., 2040 (1928).
8. Fichter, F. and Fritsch, Helv. Chim. Acta, 6, 329 (1923).
9. Glasstone, S. and Hickling, A., J. Chem. Soc., 1878 (1934).
10. Glasstone, S. and Hickling, A., Chem. Rev., 25, 407 (1939).
11. Fichter, F. and Lindenmaier, Helv. Chim. Acta, 12, 567 (1929).
12. Robertson, J.B., J. Chem. Soc., 127, 2057 (1925).
13. Brown, C. and Walker J., Annalen, 274, 41 (1893); Trans. Roy. Soc. Ed., 37, 361 (1893).
14. Bouveault, Bull. Soc. Chim.,[3] , 29, 1038 (1903).
15. Komppa, Ber., 34, 900 (1901).
16. Walker, J. and Lumsden, J.S., J. Chem. Soc., 79, 1197 (1901).
17. Stosius, K. and Wiesler, K., Biochem. Zeit., 108, 75 (1920).

18. Fairweather, D.A., Proc. Roy. Soc. Ed., 45, 23 and 283 (1925).

19. Shiina, J. Soc. Chem. Ind. Japan, 40, Suppl. binding, 324 (1937).

20. Swann, S., Oehler, R. and Pinkney, Organic Synthesis, Vol. 21, 48 (1941).

21. Fairweather, D.A., Proc. Roy. Soc. Ed., 46, 71 (1926).

22. Walker, J. and Walker, A., J. Chem. Soc., 88, 961 (1905).

23. Crichton, D.C., J. Chem. Soc., 89, 929 (1906).

24. Walker, J. and Wood, J.K., J. Chem. Soc., 89, 598 (1906).

25. Vanzetti and Coppadoro, Atti R. Accad. Lincei, 12, ii, 209 (1903).

26. von Miller and Hofer, H., Ber., 28, 2427 (1895).

27. Fichter, F. and Lurie, Helv. Chim. Acta, 16, 885 (1933).

28. Fichter, F. and Heer, ibid., 18, 704, 1276 (1935); 19, 149 (1936).

29. Hickling, A. and Westwood, J.V., J. Chem. Soc., 1039 (1938).

30. Hickling, A. and Westwood, J.V., ibid., 1109 (1939).

31. Petersen, Z. Elektrochem., 12, 143 (1906).

32. Francis, F., King, A.M. and Willis, J., J. Chem. Soc., 999 (1937).

33. Walker, J., Trans. Chem. Soc., 51, 710 (1892); J. Chem. Soc., 61, 713 (1892).

34. Drake, N.L. and Melamed, S., J. Am. Chem. Soc., 70, 364 (1948).

35. Swann, S., Oehler, R. and Buswell, R.J., Organic Synthesis, Vol. 19, 45 (1939).

36. Jones, J. Am. Chem. Soc., 69, 2350 (1947).