ELECTROLYTIC CONDENSATION OF CARBOXYLIC ACIDS

G. E. Svadkovskaya and
S. A. Voitkevich

CONTENTS

Introduction 161

Effect of experimental conditions on the course of the Kolbe synthesis 162

1) Effect of anode material 162
2) Effect of current density 162
3) Effect of temperature 162
4) Effect of foreign anions 162
5) Effect of cations 162
6) Effect of the pH of the medium 163
7) Effect of concentration 163

Electrolytic condensation in non-aqueous solvents 163

Effect of the structure of acids on the course of the Kolbe synthesis 163

1) Saturated straight-chain acids 163
2) Half-esters of dibasic acids 164
3) Branched-chain acids and half-esters 164
4) Unsaturated acids 164
5) Aliphatic hydroxy- and alkoxyacids 166
6) Aldo-acids 166
7) Keto-acids 166
8) Halogeno-substituted acids 167
9) Amino-acids 168
10) Sulpho-acids 168
11) Alicyclic acids 168
12) Aromatic and aliphatic-aromatic acids 169
13) Dicarboxylic acids 170
14) Substituted dibasic acids 170
15) Unsaturated dibasic acids 170

"Crossed" electrolytic condensation 171

Mechanism of the Kolbe reaction 174

The peroxide theory 174
The free-radical theory 175
The Glasstone — Hickling theory 175

INTRODUCTION

Investigations on electrolytic condensation processes and, in general, on organic electrosynthesis, were first carried out in 1849 by Kolbe who obtained ethane and carbon dioxide at the anode during the electrolysis of an aqueous solution of potassium acetate (in the hope of separating the methyl radical)[1]. Later it was found that the electrolysis products also contained ethylene and methyl acetate[2].

Kolbe believed that the substances formed at the anode were products of the partial oxidation of acetic acid with oxygen which was liberated at the anode, and therefore found it impossible to evaluate the reaction that he had discovered. Electrolytic condensation methods were used extensively in preparative organic chemistry as early as the second half of the 19th century. The fundamental nature of the Kolbe reaction became clear: a discharge of the carboxylic acid anions with subsequent decarboxylation and "fusion" of the radicals:

$$\left.\begin{matrix}RCOO^-\\RCOO^-\end{matrix}\right\} \xrightarrow{-2e} R{-}R + 2CO_2.$$

In 1855 Würtz[3,4] first extended the use of the Kolbe synthesis by proving that it was possible to condense acids with varying numbers of carbon-atoms (the so-called "crossed" synthesis):

$$\left.\begin{matrix}R_1COO^-\\R_2COO^-\end{matrix}\right\} \xrightarrow{-2e} R_1{-}R_2 + 2CO_2.$$

Brown and Walker[5] found in 1891 that diesters of dicarboxylic acids could be synthesised by the electrolysis of salts of half-esters of aliphatic dicarboxylic acids:

$$2ROOC(CH_2)_nCOO^- \xrightarrow{-2e} ROOC(CH_2)_{2n}COOR + 2CO_2.$$

Subsequent detailed investigations on the electrolytic synthesis of diethyl succinate from ethyl malonate[6-8] confirmed that the Brown–Walker reaction was analogous to the electrolysis of salts of acetic acid and of other acids of the aliphatic series.

At present the term "Kolbe synthesis" is understood to imply electrocondensation at the anode not only of fatty acids but also of their various derivatives, such as the half-esters of dibasic acids. In this reaction water is usually used as solvent, but a series of publications quoted below describe the Kolbe synthesis in solvents such as alcohols, acetic acids, etc.

Side reactions usually occur during the formation of the desired compound, especially when the synthesis is carried out in an aqueous medium. This applies especially to the electrolysis of solutions of salts of carboxylic acids, as first shown by Hofer and Moest[9,10], when an alcohol containing one carbon-atom less than the original acid is also formed:

$$\left.\begin{matrix}RCH_2COO^-\\OH^-\end{matrix}\right\} \xrightarrow{-2e} RCH_2OH + CO_2.$$

The formation of alcohol, according to the Hofer–Moest reaction, can become predominant in an alkaline medium and in the presence of certain anions; in this case the hydroxyl group can occupy not only the α-position in relation to the carboxyl group of the initial compound, but also the β- or even the γ-position[11-15]. Frequently, especially at low current densities, saturated[16-18] and unsaturated[11,14,16,19-22] hydrocarbons* have been detected in the reaction products; these contain 2 carbon atoms less than the normal product:

$$2RCH_2CH_2COO^- \xrightarrow{-2e} RCH_2CH_3 + RCH{=}CH_2 + 2CO_2.$$

* The use of this side reaction for the synthesis of muscone from (3-oxocyclopentadecyl-1)-acetic acid[23] is interesting.

It has been shown that esters[2,16,24-26] and also aldehydes[11,24,27] and ketones[14,16] are formed as by-products during the Kolbe synthesis.

Despite these side reactions, the Kolbe condensation is a most convenient method for preparing various organic compounds. Recently numerous studies have been devoted to it and its practical applications. This review covers publications on anodic condensation reactions up to 1958*.

EFFECT OF EXPERIMENTAL CONDITIONS ON THE COURSE OF THE KOLBE SYNTHESIS

The yield of the principal electrocondensation product and the character of the side-reactions in the Kolbe synthesis are mainly determined by the reaction conditions (anodic current density, anode material, temperature, etc.). The effect of these conditions has been evaluated in detail for the electrolysis of aqueous solutions of alkali-metal acetates[8,35-38] and the synthesis of diethyl succinate from the monoester of malonic acid.

It may be assumed that basic principles, established for these cases, apply generally to electrolytic condensation in aqueous media. The following account of the dependence of the electrolytic condensation on the conditions of electrolysis applies only to aqueous solutions.

1) Effect of Anode Material

In the electrolysis of acetates, the highest yields of ethane are obtained by using a smooth platinum or iridium anode[39]; gold, nickel, and platinised platinum give negative results[37,40-42]. Graphite anodes give moderate yields of ethane, and the quantity of ethane formed depends on the fineness of division of the graphite surface[37]. Analogous effects were found on electrolysis of monoethyl malonate[6,43]. Table 1 shows how the yield of ethane (from potassium acetate – Glasstone and Hickling[37]) and of diethyl succinate (from the monoester of malonic acid – Hickling and Westwood[6]) depends on the anode material.

TABLE 1.

Anode	Smooth Pt	Platinised Pt	Au	Ni	Retort carbon	Graphite	PbO_2
Yield of ethane, %	89	3	0	0	21	4	0
Yield of diethyl succinate, %	74	0	12	0	26	35	0

TABLE 2.

Current density, A/dm^2	Yield of ethane, %	Current density, A/dm^2	Yield of diethyl succinate, %
0.5	52	1.0	40
2.5	71	5.0	48
5.0	77	10	68
25.0	89	20	76
50.0	89	50	74
		100	69
		200	66

** Some previously published reviews and monographs[28-34] were consulted when compiling the present survey.

2) Effect of Current Density

In the electrolysis of solutions of acetic acid and its salts, increase of current density usually favours the synthesis[44]. According to Glasstone and Hickling[45] the optimum current density for a smooth platinum anode in a solution containing equimolar quantities of acetic acid and potassium acetate is 25 A/dm^2. A further increase of current density does not increase the yield of ethane. A solution containing equimolar quantities of monoethyl malonate and of its potassium salt shows similar behaviour[6] (Table 2).

3) Effect of Temperature

As a rule the yield of ethane on electrolysing acetic acid–acetate solutions falls with increasing temperature[36,46,47]. Thus for a 20% solution of potassium acetate, the yield of ethane decreases from 83% at 0° to 12% at 95°;[36,46] for a 5% solution at 25 A/dm^2, the yield falls from 88.2% at 13° to 0.8% at 92°, and at 100° no ethane is formed[44]. In other words, the adverse effect of raising the temperature becomes more obvious the more dilute the solution.

The yield of diethyl succinate on electrolysis of aqueous potassium ethyl malonate[6] was 74% at 10° and only 22% at 90°; the current density was 50 A/dm^2 in both cases.

TABLE 3.

Added salt	Yield, %		Mobility of anions
	ethane	diethyl succinate	
Without additive	71	70	—
KF	30	47	47
$KClO_4$	20	20	64
KNO_3	19	23	62
KH_2PO_4	17	22	—
KCl	5	19	65
K_2SO_4	3	11	69
$K_3Fe(CN)_6$	0	8	97

4) Effect of Foreign Anions

Foreign anions inhibit the principal anodic reaction and their presence leads to the formation of by-products. In particular, methanol is formed instead of ethane (Hofer–Moest reaction[9,10,48]) when aqueous solutions of alkali-metal acetates are electrolysed in the presence of bicarbonates, sulphates, and perchlorates. The presence of foreign ions in the acetic acid solution may explain why some investigators did not succeed in preparing ethane by the Kolbe synthesis[49,50]. Glasstone, Hickling, and Westwood[6,37] have made a detailed study of the effect of such anions on the electrolysis of solutions of acetic acid and monoethyl malonate; the results are set out in Table 3.

The authors conclude that the inhibiting effect on the Kolbe synthesis increases with the mobility of the anion, and is considerably weaker in the electrolysis of solutions of salts of organic acids than in the electrolysis of aqueous solutions of the free acids.

5) Effect of Cations

The presence of certain metallic cations (Pb^{2+}, Mn^{2+}, Cu^{2+}, Fe^{2+}, and Co^{2+}) in relatively small amounts strongly affects the course of the Kolbe reaction in solutions of alkali-metal acetates, reducing the yield of ethane and in

several cases completely suppressing its formation[37,51]. For example, the addition of 0.001 M lead acetate to a solution containing acetic acid and potassium acetate in equimolar amounts reduces the yield of ethane from 70% to zero at current density 2.5 A/dm^2.[51] The effect of the cations follows the order $Pb^{"} > Mn^{"} > Cu^{"} > Co^{"} = Fe^{"}$ and is especially marked at low current densities. Analogous results were obtained when the same cations were added to potassium ethyl malonate[6].

However, the Kolbe synthesis is not inhibited by the presence of many other metal cations. Glasstone and Hickling[37] obtained ethane in satisfactory yields in the electrolysis of potassium, sodium, calcium, barium, and other acetate solutions (Table 4).

TABLE 4.

Cation	Na^+	K^+	NH_4^{+*}	Ca^{2+}	Sr^{2+}	Ba^{2+}	Mg^{2+}	Zn^{2+**}	Ni^{2+}	UO_2^{2+}
Yield of ethane, %	80	89	86	85	82	75	79	71	74	78

* Some acetamide, methylamine, and urea[154] were also found on electrolysis of ammonium acetate solution.

** In some cases, a theoretical yield of ethane was obtained on electrolysis of zinc acetate solution[53].

6) Effect of the pH of the Medium

The principal reaction product is usually formed when the pH of the electrolyte is low, its yield falling with increasing pH.[54,55] According to Glasstone, Hickling, and Westwood[6,45], the optimum pH values lie within the limits 3–5 (Table 5); the yield of the product decreases rapidly in an alkaline electrolyte (at pH > 10).

TABLE 5.

pH	Yield of ethane, %	pH	Yield of Diethyl succinate, %
2.3	67	1.4	70
4.3	70	2.9	75
4.7	77	3.5	74
5.2	74	4.8	74
9.5	71	7.0	70
11	50	8.3	64
	—	10	59

7) Effect of Concentration

Increased concentration of carboxylic-acid anions usually leads to higher yields of the principal condensation product[44,54,55], the extent of side reactions increasing as the concentration is lowered. For example the yield of ethane decreases during the electrolysis of dilute potassium acetate solutions, more ethylene and methane being formed[56,57]. Data[6,37] illustrating the effect of concentration are set out in Table 6.

TABLE 6.

Acetate ions, M	Yield of ethane %	Ethylmalonate ions, M	Yield of diethyl succinate, %
0.2	44	0.2	30
1.0	64	0.5	68
2.0	77	1.0	70
4.0	77	2.0	74
		4.0	78

ELECTROLYTIC CONDENSATION IN NON-AQUEOUS SOLVENTS

The first experiments on the use of ethanol, propanol, and butanol as solvents in the electrolysis of acetates were carried out in 1886[58]. The electrolysis of potassium acetate in glacial acetic acid was investigated in 1904.[59,60] Further experiments were carried out on the electrolysis of acetates, propionates, and formates in anhydrous acetic, propionic, and formic acids[19]. Detailed studies proved[40,44,56,61,62] that the anode material, current density, temperature, etc., have little effect on the yield of the product in the electrolysis of solutions of carboxylic-acid salts in non-aqueous solvents. Thus, the electrolysis of a potassium acetate solution in anhydrous acetic acid gives better yields of ethane when a gold or graphite anode is used instead of a platinum anode[44]; the ratio $C_2H_6 : H_2$ equals 0.96 for a platinum anode, 0.95 for a gold anode, and 0.89 for a graphite anode; the addition of even 1% of water to the electrolyte, when a gold anode is used decreases the yield of ethane to 65%; the yield falls to 1.6% in the presence of 10% of water. Similar results were obtained in the electrolytic condensation of potassium propionate dissolved in anhydrous methanol[40].

Detailed studies of the electrolysis of potassium acetate[63] and ethyl malonate[7] in an ethylene–glycol solution have also shown that only slight variations occurred in the yield of the principal product in the presence of foreign cations and anions, and when the anodic current densities, concentration, temperature, and anode material were varied.

In large-scale electrolysis these advantages are offset by difficulties due to the low electrical conductivity of the solutions and high voltage required when working in non-aqueous solvents.

EFFECT OF THE STRUCTURE OF ACIDS ON THE COURSE OF THE KOLBE SYNTHESIS

Numerous investigations have shown that the yield of the product in the Kolbe reaction is not only affected by the conditions of electrolysis mentioned above but also to a considerable degree by the structure of the acids condensed. Thus, α-substituted carboxylic acids, cannot, in general, be subjected to the Kolbe reaction or enter into the reaction only with great difficulty. The same applies to α,β- and β,γ-unsaturated acids. Consequently, the structure of the initial acids or carboxylic-acid esters has to be considered before using them in electrolytic-condensation reactions.

The behaviour of various acids, in relation to their structure, during electrosynthesis reactions is described below. The data (unless otherwise indicated) refer to the electrolysis of aqueous solutions of sodium or potassium salts of carboxylic acids, usually in the presence of free acids.

1) Saturated Straight-Chain Acids

Fatty acids with straight C-chains of varying lengths have been subjected to the Kolbe electrolytic-condensation reaction, and normal synthesis products in satisfactory yields have been obtained in all cases, with the exception of formic acid. Many investigators have failed in attempts to produce hydrogen as well as CO_2 at the anode, according to the Kolbe reaction, on electrolysing formic acid and its salts. CO_2 or CO_2 and oxygen usually appear at the anode and the hydrogen formed is oxidised[19,64-76] to water.

Some metals of the platinum group (rhodium[77-79], palladium[80-81] and especially osmium[82]) cause formic acid to decompose as follows:

$$HCOOH \rightarrow H_2 + CO_2.$$

Although this reaction suggests that electrodes made of these metals could be used in the electrolysis of formic acid, in actual experiments hydrogen did not appear at the anodes [83].

It has been mentioned above that yields of ethane (over 90%)* are obtained on electrolysing acetic acid or its salts under similar conditions. The values of the anode potentials have been measured in numerous investigations [37,41,85,86]. Experiments have been carried out on the electrolysis of acetates with alternating current [75,76,87-91], on the electrolysis of molten acetates [88,92-95], and on the acetates of various metals [53,96-102]. The electrolytic condensation of deuterated acetates and acetic acid, in ordinary and heavy water [103-105], has also been studied.

Many investigations have been devoted to the electrolysis of the following fatty acids: propionic [10,16,19,35,40,64,73,85,87,94,95,106-109], butyric [10,11,20,26,35,64,87,95,110], valeric [1,24], caproic [24,52,87,111-114], oenanthic [14,111,112], and caprylic [112,115]**.

On electrolysis of potassium laurate in aqueous alcohol [25]*** n-docosane $C_{22}H_{46}$ was obtained in 90% yield; under analogous conditions myristic and palmitic acids [25,117] gave the corresponding n-hexacosane (up to 89% yield) and n-triacontane (up to 88% yield). Pentadecanol and pentadecane are formed as by-products in the electrolysis of palmitic acid [21,22]. Stearic acid gives a 73.6% yield of n-tetratriacontane [25]; other workers [118,119] have also investigated this reaction.

2) Half-Esters of Dibasic Acids

Earlier it was shown that alkali-metal salts of dicarboxylic-acid monoesters react, on electrolysis, similarly to monobasic fatty acids and give diesters in high yields; an exception is the monoester of oxalic acid [120] which yields hydrogen, carbon dioxide, and ethylene on electrolysis.

The method proved to be very satisfactory for the production of up to C_{34} normal dicarboxylic acids. The optimum conditions are similar to those for the synthesis of ethane: high concentration of the electrolyte solution, low temperature, high anodic current density, etc. Table 7 shows the yields obtained.

3) Branched-Chain Acids and Half-Esters

The position of the substituent in alkyl-substituted acids affects the yield of the end product of the Kolbe reaction to a considerable extent. Branching of the chains in the α-position to the carboxylic group gives rise to the formation of olefins, alcohols, and other by-products; on electrolysis such acids or half-esters give a small yield or no yield of the required product. Thus, isobutyric acid gives only small quantities of 2,3-dimethylbutane, the predominant product being propylene; isopropyl alcohol and isopropyl butyrate are formed at the same time [26,35,64].

Electrolysis of α-methyl butyric acid gives negligible quantities of 3,4-dimethylhexane and leads to formation of but-2-ene, trimethyl carbinol, and its α-methylbutyric-acid ester [25]*.

Pivalic acid, in an analogous manner, yields predominantly isobutylene and but-2-ene and only insignificant quantities of hexamethylethane [24].

Swann [152] was unable to identify the desired reaction product on electrolysing α-methylvaleric acid and α-ethylbutyric acid. Later, more accurate investigations [153] on the electrolytic condensation of the latter acid made it possible to separate tetraethylethane together with other compounds (pent-2-ene, pentan-2-ol, pentan-3-one, etc.). It has also been shown that 17,18-dibutyltetratriacontane can be prepared by the electrolysis of α-butylstearic acid [154].

Monoesters of dicarboxylic acids, containing alkyl substituents in the α-position to the carboxyl group, behave similarly. Thus, the ethyl esters of methylmalonic, ethylmalonic, dimethylmalonic [120], diethylmalonic [120,155], and dipropylmalonic [156] acids give on electrolysis small yields of the products.

It is possible to prepare the diethyl ester of $\beta,\beta,\beta'\beta'$-tetramethyl adipic acid (5–8% yield) by electrolysing the monoethyl ester of α,α-dimethyl succinic acid in methanol [157]. More satisfactory results are obtained with β-, γ-, δ-, etc. mono- and dialkyl-substituted acids. Table 8 gives data on the Kolbe reaction with acids and esters containing a branched chain in positions other than the α-position.

The optical activity of the asymmetric carbon atom in the β-position to the carboxyl group is preserved during the Kolbe reaction. It is therefore possible to use the electrochemical method to prepare stereoisomers of the dimethyl ester of β,β'-dimethylsuberic acid, with an approximate yield of 70%, from the $L(+)$- and $D(-)$-methyl esters of β-methylglutaric acid [159].

4) Unsaturated Acids

Numerous investigations have proved that neither α,β- nor β,γ-unsaturated acids undergo electrolytic condensation. The former acids give small quantities of acetylenes on electrolysis; thus acetylene is formed from acrylic acid [164], and allylene and but-2-yne respectively from crotonic [165,166] and tiglic acids [167]. Negative results were obtained on electrolysis of fumarates [120,168], maleates [120,169], citraconates [120], esters of allylmalonic [120] and muconic acids [168].

Fichter and Holbro [170] carried out experiments on the electrolytic condensation of β,γ-hexenoic acid and obtained negative results; they ascertained at the same time that γ,δ-hexenoic acid gave the normal condensation product deca-2,8-diene, in addition to by-products (penta-1,3-diene, pent-2-ene-5-ol, and its hexenoic-acid ester).

The normal condensation product was obtained (55% yield) on electrolysis of 4-ethoxycarbonyl-3-methylbut-3-enecarboxylic acid [163] in methanol:

$$2C_2H_5OOCCH{=}C(CH_3)CH_2CH_2COOH \rightarrow [C_2H_5OOCCH{=}C(CH_3)CH_2CH_2]_2 .$$

Satisfactory results were also obtained with unsaturated acids in which the double bond is further removed from the

---

* In some cases [84] the electrolysis of an acetic acid solution differed from the usual course of the process.

** The yield of the principal condensation product has not been given.

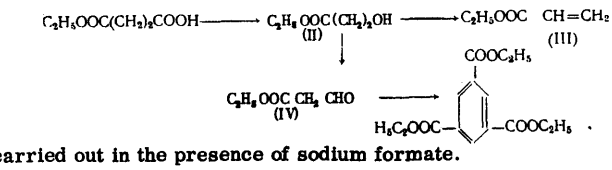
*** In one investigation methyl laurate was obtained on electrolysis of potassium laurate in boiling methanol, in the presence of potassium chloride (graphite anode, 3.5A, 90V) [116].

* The inactive 3,4-dimethylhexane formed on electrolysis of *d*- and *l*-α-methylbutyric acids [150], together with the inactive butan-2-ol and its α-methylbutyric acid ester [151].

TABLE 7. Kolbe reaction for half-esters of dicarboxylic acids with a straight $ROOC(CH_2)_nCOOH$ chain.

Initial half-ester			Solvent	Main product	By-products	Yield of main product, %	Reference
R	n						
C_2H_5	1	Ethyl malonate	H_2O	$H_5C_2OOC(CH_2)_2COOC_2H_5$	—	60	5
CH_3	2	Methyl succinate	CH_3OH	$H_3COOC(CH_2)_4COOCH_3$	ester $C_{12}H_{20}O_8$ probably $H_3COOC(CH_2)_2CH(CH_2COOCH_3)CH_2CH_2COOCH_3$	76	121
C_2H_5*	2	Ethyl succinate	H_2O	$H_5C_2OOC(CH_2)_4COO_2H_5$	—	35	5
					—	50	123
$C_6H_5CH_2$	2	Benzyl succinate	CH_3OH	$C_6H_5CH_2OOC(CH_2)_4COOCH_2C_6H_5$	—	50	124
CH_3	3	Methyl glutarate	CH_3OH	$H_3COOC(CH_2)_3COOCH_3$	—	62	125
C_2H_5	3	Ethyl glutarate	H_2O	$H_5C_2OOC(CH_2)_3COOC_2H_5$	—	28	5
$C_6H_5CH_2$	3	Benzyl glutarate	CH_3OH+ $+C_5H_5N$	$C_6H_5CH_2OOC(CH_2)_3COOCH_2C_6H_5$	—	24	126
CH_3	4	Methyl adipate	CH_3OH	$H_3COOC(CH_2)_4COOCH_3$	—	51—61	127
			CH_3OH	$H_3COOC(CH_2)_4COOCH_3$	—	74.3	129
			CH_3OH	$H_3COOC(CH_2)_4COOCH_3$		29	115**
C_2H_5	4	Ethyl adipate	H_2O	$H_5C_2OOC(CH_2)_4COO_2H_5$	$CH_2=CH(CH_2)_2COOC_2H_5$	—	129
CH_3	5	Methyl pimelate	CH_3OH	$H_3COOC(CH_2)_{10}COOCH_3$	—	47	127
							130
C_2H_5	5	Ethyl pimelate	H_2O	$H_5C_2OOC(CH_2)_{10}COOC_2H_5$	$H_5C_2OOC(CH_2)_3CH=CH_2$	—	131
						—	
CH_3	6	Methyl suberate	CH_3OH	$H_3COOC(CH_2)_{12}COOCH_3$	—	44	127
							132
C_2H_5	6	Ethyl suberate	C_2H_5OH + H_2O	$H_5C_2OOC(CH_2)_{12}COOC_2H_5$	$CH_2=CH(CH_2)_4COOC_2H_5$	— 25	5
CH_3	7	Methyl azelate	CH_3OH	$H_3COOC(CH_2)_{14}COOCH_3$		54	127
C_2H_5	7	Ethyl azelate	H_2O	$H_5C_2OOC(CH_2)_{14}COOC_2H_5$		21	133
			H_2O	$H_5C_2OOC(CH_2)_{14}COOC_2H_5$	$CH_2=CH(CH_2)_5COOC_2H_5$	—	134
C_2H_5	7	Ethyl azelate #II	H_2O	$H_5C_2OOC(CH_2)_{14}COOC_2H_5$	—	38—40	135
			CH_3OH	$H_5C_2OOC(CH_2)_{14}COOC_2H_5$	—	45	136
			C_2H_5OH+ $+H_2O$	$H_5C_2OOC(CH_2)_{14}COOC_2H_5$	$CH_2=CH(CH_2)_5COOC_2H_5$	—	132
CH_3	8	Methyl sebacate	CH_3OH	$H_3COOC(CH_2)_{16}COOCH_3$	—	42	127
			CH_3OH	$H_3COOC(CH_2)_{16}COOCH_3$	—	66	137,138
C_2H_5	8	Ethyl sebacate	H_2O	$H_5C_2OOC(CH_2)_{16}COOC_2H_5$	—	20	5
			H_2O	$H_5C_2OOC(CH_2)_{16}COOC_2H_5$	$CH_2=CH(CH_2)_6COOC_2H_5$	20—40	120
			H_2O	$H_5C_2OOC(CH_2)_{16}COOC_2H_5$	—	30—35	139
			H_2O	$H_5C_2OOC(CH_2)_{16}COOC_2H_5$	$CH_2=CH(CH_2)_6COOC_2H_5$ } $H_5C_2OOC(CH_2)_8COOC_2H_5$ }	18—25	140
			H_2O	$H_5C_2OOC(CH_2)_{16}COOC_2H_5$	—	—	141
			H_2O	$H_5C_2OOC(CH_2)_{16}COOC_2H_5$	—	44—48	142
			H_2O	$H_5C_2OOC(CH_2)_{16}COOC_2H_5$	—	16,5	143
			H_2O	$H_5C_2OOC(CH_2)_{16}COOC_2H_5$	—	—	144
			CH_3OH	$H_5C_2OOC(CH_2)_{16}COOC_2H_5$	—	32	145
			CH_3OH	$H_5C_2OOC(CH_2)_{16}COOC_2H_5$	—	—	136
			CH_3OH	$H_5C_2OOC(CH_2)_{16}COOC_2H_5$	—	65	137
C_2H_5	9	Ethyl nonane-1,9-dicarboxylate	CH_3OH	$H_5C_2OOC(CH_2)_{15}COOC_2H_5$	—	—	146
CH_3	10	Methyl decane-1,10-dicarboxylate	CH_3OH	$H_3COOC(CH_2)_{20}COOCH_3$	$CH_2=CH(CH_2)_8CCOCH_3$, probably $CH_3OOC(CH)_{30}COOCH_3$	43	147
			CH_3OH	$H_3COOC(CH_2)_{20}COOCH_3$	—	—	146
C_2H_5	10	Methyl decane-1,10-dicarboxylate	H_2O+ $+C_2H_5OH$	$H_5C_2OOC(CH_2)_{20}COOC_2H_5$	$CH_2=CH(CH_2)_8COOC_2H_5$	41	132
CH_3	11	Methyl brassylate	CH_3OH	$H_3COOC(CH_2)_{22}COOCH_3$	$CH_2=CH(CH_2)_9COOCH_3$		148
C_2H_5	12	Ethyl dodecane-1,12-dicarboxylate	H_2O+ $+C_2H_5OH$	$H_5C_2OOC(CH_2)_{24}COOC_2H_5$	—	5.1	132
CH_3	14	Methyl tetradecane-1,14-dicarboxylate	CH_3OH	$H_3COOC(CH_2)_{28}COOCH_3$	$H_3COOC(CH_2)_{14}COOCH_3$	6	146
C_2H_5	14	Ethyl tetradecane-1,14-dicarboxylate	CH_3OH	$H_5C_2OOC(CH_2)_{28}COOC_2H_5$	—	10	146
			C_2H_5OH+ $+H_2O$	$H_5C_2OOC(CH_2)_{28}COOC_2H_5$	—	4.7	132
C_2H_5	16	Ethyl hexadecane-1,16-dicarboxylate.	C_2H_5OH+ $+H_2O$	$H_2C_5OOC(CH_2)_{32}COOC_2H_5$	—	61	149

* The cyclic ester of trimesic acid is formed in the electrolysis of monoethyl succinate[122]. The authors assume that, the ester of β-hydroxypropionic (II) and acrylic (III) acids are formed according to the Hofer-Moest reaction; (II) is oxidised at the anode to the formalacetate (IV), which is then condensed to the trimesate (V):



** The electrolysis is carried out in the presence of sodium formate.

carboxyl group, such as undec-10-enoic [112,165,171,172], petroselinic [173], oleic [165,173-175], erucic [173], and ricinoleic [175,176].

The use of the Kolbe synthesis was further extended by Bounds et al. [171], who found that the geometrical configuration at the double bonds was preserved during the electrolysis of acids of the ethylene series; thus unsaturated compounds with known geometrical configuration can be synthesised by the electrochemical method. In the electrolytic condensation of oleic and elaidic acids in absolute methanol the authors obtained the corresponding *cis*–*cis*-tetratriaconta-9,25-diene (23% yield) and *trans*–*trans*-tetratriaconta-9,25-diene (44% yield).

In the electrolytic condensation of unsaturated acids the anode generally becomes coated with a layer of insoluble polymers which are formed during the reaction and inhibit it, especially when the acids contain several double bonds [177]. A large quantity of polymeric products separates during the electrolytic condensation of the monomethyl ester of dec-5-ene-1,10-dicarboxylic acid [178]; only small yields of the normal product (eicosa-5,15-diene-1,20-dicarboxylic acid) were obtained.

5) Aliphatic Hydroxy- and Alkoxyacids

Aliphatic hydroxyacids are not very suitable for the Kolbe reaction as the hydroxyl group is readily oxidised, especially when it is adjacent to the carboxyl group. Alkoxyacids are more stable.

On electrolysis, α-hydroxy- and α-alkoxyacids (e.g. glycolic [179], methoxy- and ethoxyacetic acids [180-182], α-hydroxyoenanthic acid [182], lactic [180,183,184], α-hydroxybutyric, and α-hydroxyisobutyric acids [180]) give an aldehyde or ketone as well as an acid containing one carbon atom less than the starting material. Lactic acid has thus been converted to pyruvic acid [185].

When the monoethyl esters of ethoxymalonic and symmetrical diethoxysuccinic acid were electrolysed [182], only small quantities of the condensation product (the diethyl ester of diethoxysuccinic acid) were separated in the first case, and none at all in the second case.

Negative results were obtained on electrolysing β-hydroxyacids; electrolytic condensation of hydracrylic acid [180,186], for example, only resulted in the formation of oxidation products (formic acid, CO_2, etc.). Formic acid, crotonaldehyde, and other oxidation products are obtained from β-hydroxybutyric acid [180].

β-Alkoxyacids undergo the Kolbe reaction; the diisopentyl ether of butane-1,4-diol (50% yield) was prepared by electrolysing β-isopentyloxypropionic acid [187,188]*.

In the electrolysis of γ-pentyloxybutyric acid [190] it was found that hydrolysis replaced the Kolbe reaction, leading to the formation of pentyl alcohol and γ-hydroxybutyric acid. In the electrolysis of γ-ethoxybutyric acid [191] it was possible to separate the diethyl ether of hexanediol (20% yield). Further electrolytic condensation experiments have been carried out with 4,8-dimethyl-9-ethoxynonanoic acid in anhydrous methanol [158] and 2,6,11,15-tetramethyl-1,16-diethoxyhexadecane was formed.

Satisfactory results were obtained by electrolysis of water-alcohol and alcoholic solutions of ricinoleic [175,176] and dihydroxystearic acids [176]. The electrolysis of (±)-*threo*-9,10-dihydroxystearic and (±)-*erythro*-9,10-dihydroxy stearic acid in absolute alcohol [171] gave the corresponding diastereoisomers of the tetrol in 50% and 20% yields respectively.

Attention should also be drawn to electrolytic condensation experiments with glyceric [180], β-methylglyceric, and β-methylglycidic acids [192], as well as with the *d*-tartaric-acid monoethyl ester [193]; they all gave negative results, as only oxidation products of the initial acids were formed.

In 1908 Neuberg [194] attempted to produce polyglycols by the electrolysis of aldonic acids (*d*-gluconic, *l*-arabonic, *i*-erythronic, and *i*-glyceric acid) and glycolic acid; however, aldehydes, apparently the decomposition products of the initial acids, were separated instead of the required condensation products:

$$CH_2OH(CHOH)_xCHO \mid HCOOH \rightarrow CH_2OH(CHOH)_xCHO + HCOOH.$$

By this method glucose can be converted stepwise to formaldehyde. It can be assumed that keto-acids of the type $CH_2OH(CHOH)_xCOCOOH$ are formed as by-products.

Electrolytic decomposition has also been used in conjunction with other carboxylic-acid derivatives of sugars, e.g. melibionic acid [195].

6) Aldo-Acids

Free aldo-acids are readily oxidised in the presence of oxygen and therefore, cannot be subjected to electrolytic condensation. However, their derivatives, the acetals, are stable under electrolysis conditions.

On electrolysing an aqueous solution of the potassium salt of β,β-diethoxypropionic acid (Pt anode, Ni cathode, 3A, 8–10 V) a 60% yield of bis-diethylacetal of succinaldehyde [196]* was obtained. Analogous experiments with the potassium salt of γ,γ-diethoxybutyric acid led to the formation of the bis-diethylacetal of adipaldehyde (35% yield); acrolein acetal was also formed in this reaction.

The bis-dimethylacetal of hexadecane-1,16-dial was obtained by electrolysing 9,9-dimethoxynonanoic acid in anhydrous methanol (3–4 A, 40–50 V, 50°–55°); under similar conditions 10,10-dimethoxydecanoic acid yielded the bis-dimethylacetal of octadecane-1,18-dial [198].

It is very difficult to prepare dialdehydes by purely chemical methods.

7) Keto-Acids

In the electrolytic condensation of keto-acids, the yield of the end product depends to a considerable degree on the position of the CO group in the molecule of the initial acid, Thus pyruvic acid, the simplest keto-acid, gives only small yields of butane-2,3-dione; the principal reaction consists in the oxidation of the keto-acid to acetic acid and carbon dioxide [199]. Electrolysis of a water–alcohol solution of pyruvic acid, in an electrolyser comprising a diaphragm,

* Experiments on a similar reaction via the thermal decomposition of di (β - isopentyloxypropionyl) peroxide were carried out by Fichter and Schnider [189].

* The electrolysis of β,β-diethoxypropionic acid was described by Japanese investigators [197].

TABLE 8. Kolbe reaction for acids and half-esters with branched chains.

Initial reactant	Solvent	Main product	By-products	Yield of main product	Reference
Isovaleric acid	H_2O	$H_3C\diagdown CH-CH_2-CH_2-CH_2\diagup CH_3$ (with H_3C and CH_3)	Isobutyl isovalerate, trimethylcarbinol, isobutyl alcohol, isobutyl aldehyde, 2-methylpropane, but-2-ene	—	24
Isocaproic acid	»	$H_3C\diagdown CH-(CH_2)_4-CH\diagup CH_3$ (with H_3C and CH_3)	—	20	152
4,8-Dimethyl-9-ethoxynonanoic acid	CH_3OH	$[C_2H_5OCH_2CH(CH_3)(CH_2)_3CH(CH_3)CH_2CH_2]_2$	—	—	158
10-Methyloctadecanoic acid	H_2O+ +C_2H_5OH	$CH_3(CH_2)_7CH(CH_3)(CH_2)_{16}CH(CH_3)(CH_2)_7CH_3$	—	8,3	119
Ethyl β,β-dimethyl succinate *	CH_3OH	$H_5C_2OOC-C(CH_3)_2CH_2CH_2C(CH_3)_2COOC_2H_5$	Ethyl β,β-dimethylacrylate, diethyl ester of asymmetric dimethylsuccinic acid, monoethyl ester of asymmetric dimethylsuccinic acid	32—35	157
Methyl β-methylglutarate	CH_3OH+ +H_2O	$CH_3OOCCH_2CH(CH_3)CH_2CH_2CH(CH_3)CH_2COOCH_3$	—	80	159
Ethyl β,β-dimethylglutarate	H_2O	$H_5C_2OOCCH_2C(CH_3)_2CH_2CH_2C(CH_3)_2CH_2COOC_2H_5$	—	42	160
Methyl β,β-dimethylglutarate	CH_3OH+ pet. ether	$H_3COOCCH_2C(CH_3)_2CH_2CH_2C(CH_3)_2CH_2COOCH_3$	—	75	161
Methyl methyladipate	CH_3OH	Dimethyl dimethylsebacate	—	78	162
Ethyl γ-methyladipate	CH_3OH	$H_5C_2OOCCH_2CH(CH_3)(CH_2)_4CH(CH_3)CH_2COOC_2H_5$	—	70	163
Methyl $\beta,\beta,\beta',\beta'$-tetramethylsuberate	CH_3OH+ pet. ether	$[H_3COOC\cdot CH_2\cdot C(CH_3)_2(CH_2)_2C(CH_3)_2CH_2]_2$	—	75	164
Ethyl 3,7-dimethylnonane-1,9-dicarboxylate	CH_3OH	$[H_5C_2OOCCH_2CH_2CH(CH_3)(CH_2)_3CH(CH_3)CH_2CH_2]_2$	Ethyl dimethyl-4,8-decanoate, ethyl 4,8-dimethyldec-9-enoate	48	164

* Here and subsequently the position of the substituent is given in relation to the free carboxyl group.

and graphite, platinum, or lead anodes, gave in all cases lactic[200] as well as acetic acid.

The monoethyl ester of acetone dicarboxylic acid[201] has been electrolysed yielding the diester of hexane-2,5-dione-1,6-dicarboxylic acid (12% yield).

Considerably better results were obtained in the electrolysis of aqueous solutions of levulinic acid[199] in which the normal product, octane-2,7-dione, was obtained in 50% yield. When this process is carried out in a 25% sulphuric-acid solution or in methanol, the yield increases to 66% and 70% respectively[202].

The electrosynthesis process is also favoured by increasing the distance between the keto- and the carboxyl group in the keto-acid molecule. Thus tetradecane-3,12-dione, the normal product, was obtained in 74.8% yield on electrolysis of δ-propionylvaleric acid[203].

8) Halogeno-Substituted Acids

Up to 1956 very little was published on the possibility of using the Kolbe reaction for the synthesis of halogeno-substituted compounds. Kaufler and Herzog[204] discovered in 1909 that electrolysis of chloro*-, bromo- and iodoacetic acids did not give products of the Kolbe reaction. Negative results were also obtained in the electrolysis of dichloro-[204,205], difluorochloro-[207], and trichloroacetic[208-211] acids. Only the electrolysis of trifluoroacetic acid gave traces of hexafluoroethane[207,212]. Unsatisfactory results were also obtained in attempts at synthesis from α,α-dichloropropionic[205], β-iodopropionic[205], 2,2,3-trichlorobutyric[213], and *d,l*-α-bromopropionic acids[214]. Japanese investigators[177] were also unsuccessful when they electrolysed tetrabromostearic acid in ethanol.

In 1953 Korsching[215] succeeded in isolating the normal product (1,20-dibromoeicosane, 20% yield) in the electrolysis of 11-bromoundecanoic acid; later[216] he succeeded in preparing 1,10-dibromodecane from ω-bromocaproic acid in a water-alcohol solution.

Detailed investigations on the electrolytic condensation of ω-halogenocarboxylic acids, carried out in 1956,[137] showed that normal products are obtained when β-chloropropionic, δ-chlorovaleric, 6-chlorohexanoic and 10-chlorodecanoic are electrolysed in absolute methanol (11–16 A/dm², 2 A, 110 V, 50°), in contrast to the reaction for chloroacetic and γ-chlorobutyric acid.

Halogen is split off during the electrolysis of lower ω-bromocarboxylic acids. Normal condensation reactions could only be observed with acids containing 11 or more carbon atoms in the chain. All ω-iodocarboxylic acids (containing 2–11 carbon atoms in the molecule) decompose on electrolysis. ω-Fluorocarboxylic acids give considerably better results. The lower members of this series (fluoroacetic, β-fluoropropionic, and γ-fluorobutyric acid) do not undergo the Kolbe reaction; the glass electrolyser is attacked – an indication that hydrogen fluoride is evolved in the process. However, δ-fluorovaleric, 6-fluorohexanoic, 7-fluoroheptanoic, 8-fluorooctanoic, 9-fluorononanoic 10-fluorodecanoic, and 11-fluoroundecanoic acids give satisfactory yields of ω,ω'-difluoroalkanes.

* See also refs. 92, 205, and 206 on the electrolysis of chloro-acetic acid.

Thus electrolytic condensation proves to be a convenient method for synthesising C_8 and higher dilfuorides and dichlorides as well as C_{20} and higher dibromides.

The yields of the products of electrolysis of ω-halogenocarboxylic acids are given in Table 9.

9) Amino-Acids

Lilienfeld[217] found in 1902 that ethylene diamine is formed on electrolysis of the copper salt of glycine, but later investigators[218-220] failed to confirm this.

The Kolbe reaction did not occur and complete destruction of the original molecule was observed in the electrolysis of other α- or β-amino-acids (α-alanine and leucine[220], aceturic acid, β-alanine, iminodiacetic acid, methylaminodiacetic acid, and α-aminoisobutyric acid[219]. Later it was proved[221] that the corresponding alkoxyalkylamides are formed when α-amino-acids are electrolysed in anhydrous alcohol in the presence of an alcoholate:

$$R_1CONH\cdot\underset{\displaystyle X}{\underset{|}{CH}}\cdot COOH + R_2OH \rightarrow R_1CO\cdot NH\cdot\underset{\displaystyle X}{\underset{|}{CHOR_2}} + CO_2,$$

where X = H or CH_3.

In 1947 Offe[222] established that aliphatic diamines or their derivatives can be synthesised by the Kolbe reaction under the following conditions: (1) the basic properties of the amino-group have to be weakened; (2) electrolysis of the amino-acid acid salt has to be carried out in a non-aqueous solvent; (3) the amino-group must not be in the α-position to the carboxyl group. He prepared *N*,*N*'-diacetyl decamethylene diamine* by electrolysing ε-acetylaminocaproic acid in methanol at a current density of 5–7 A/dm² at a platinum anode. Normal products were also obtained, under analogous conditions, from ε-benzoylaminocaproic, γ-phthalimidobutyric, ε-ethanesulphonylaminocaproic, ε-propanesulphonylaminocaproic acid and *N*-(5-methoxycarbonylpentanoyl)-ε-aminocaproic acid.

Unsatisfactory results were obtained with *N*-substituted benzenesulphonylamino-acids; e.g. during the electrolysis of *N*-(benzenesulphonyl)-ε-aminocaproic acid only benzene sulphonamide was separated. This confirmed the earlier observations that *N*-(*p*-toluenesulphonyl)-α-aminoisobutyric acid and *N*-(benzenesulphonyl)-*N*-methyl-α-aminoisobutyric acid do not give a Kolbe reaction[219].

Later the Kolbe synthesis was successfully carried out in methanol with many *N*-acyl-derivatives of amino-acids in which the amino-group was at a considerable distance from the carboxyl group[221]. The corresponding derivatives of polymethylene diamines were obtained in good yields (Table 10).

Satisfactory results were also obtained in the electrolysis of the half-amide of adipic acid in methanol, at a current density of 5–7 A/dm² at the anode[223,224].

Experiments were also carried out on the electrolytic condensation of cyanoacetic acid[225-226]. Only minute quantities of the normal reaction product (ethylene dicyanide) were isolated, most of the products resulting from decomposition: hydrocyanic acid, formaldehyde, carbon dioxide, etc.

* The same compound was also obtained on electrolysis of a mixture of ε-acetylaminocaproic and formic acids in methanol[115]

TABLE 9. Electrolysis of ω-halogencarboxylic acids $[X(CH_2)_nCOOH]$.

n	Yield, %			
	F	Cl	Br	I
1	0	0	0	0
2	0	39	0	0
3	0	0	0	0
4	45	51.5	0	0
5	45	55	0	0
6	57.5	—	—	—
7	64	—	0	—
8	65	—	—	—
9	69	82	0	0
10	61	—	54	0
15	—	—	31	—

10) Sulpho-Acids

The electrolysis of sulphoacetic acid should proceed according to the equation

$$2HO_3SCH_2COO^- \xrightarrow{-2e} \underset{\displaystyle HO_3SCH_2}{\underset{|}{HO_3SCH_2}} + 2CO_2,$$

in a manner analogous to the synthesis of ethane from acetic acid.

However, instead of ethane disulphonic acid the oxidation products of the initial compound were obtained (sulphuric acid, carbon dioxide, carbon monoxide, ethylene, formaldehyde, sulphur dioxide, and small quantities of methionic acid)[227,228].

On electrolysing β-sulphopropionic acid[228] only ethylene, sulphur dioxide, carbon dioxide, sulphuric, formic, and acetic acids were isolated*.

11) Alicyclic Acids

In their behaviour in the electrolytic condensation, cycloalkane acids resemble alkyl-substituted acids. Thus, cycloalkyl substituents in the α-position to the carboxyl group, inhibit the principal anodic reaction. An interesting example is the electrolysis of cyclopropanecarboxylic acid: the allyl ester of the initial acid is formed instead of the required bicyclopropyl[230,231].

TABLE 10.

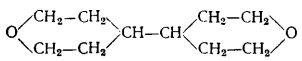
Initial reactant	Solvent	Product	Yield, %
$CH_3CONH(CH_2)_5COOH$	CH_3OH	$CH_3CONH(CH_2)_{10}NHCOCH_3$	31
$C_6H_5CONH(CH_2)_5COOH$	CH_3OH	$C_6H_5CONH(CH_2)_{10}NHCOC_6H_5$	23
$C_6H_5CH_2OCONH(CH_2)_5COOH$	CH_3OH	$C_6H_5CH_2OCONH(CH_2)_{10}NHOCOCH_2C_6H_5$	38
$C_6H_5CH_2OCONH(CH_2)_3COOH$	CH_3OH	$C_6H_5CH_2OCONH(CH_2)_6NHOCOCH_2C_6H_5$	35
$C_6H_5CONHCH_2CH_2COOH$	CH_3OH	$C_6H_5CONH(CH_2)_4NHCOC_6H_5$	20
$C_6H_5CH_2OCONHCH_2CH_2COOH$	CH_3OH	$C_6H_5CH_2OCONH(CH_2)_4NHOCOCH\ C_6H_5$	33

* Attempts[229] at the electrolytic condensation of a number of aromatic sulphonic acids (benzene-*p*-disulphonic acid, benzene-*m*-disulphonic acid, phenyl disulphide-4,4-disulphonic acid and phenol-2,5-disulphonic acid) were also unsuccessful.

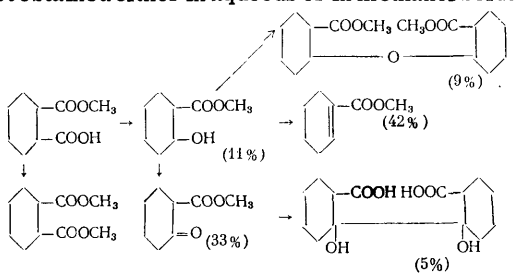
On electrolysis of the monomethyl ester of *cis*-cyclopropane-1,2-dicarboxylic-acid[232] ring cleavage occurs and the ester of hexa-2,4-diene-1,6-dicarboxylic acid* is formed. Negative results were obtained on electrolysis of cyclobutanecarboxylic acid[231,234], cyclohexanecarboxylic acid[231,235], and *p*-methylcyclohexanecarboxylic acid[236].

Later investigations of the electrolysis of cyclohexanecarboxylic acid showed that negligible quantities of the anodic-synthesis product, bi(cyclohexyl), are formed when the process is carried out in an acidic solution[237]; when a methanol-pyridine mixture is used as solvent, the yield of bi(cyclohexyl) is 14%.[238]

Satisfactory yields (20%) of 4,4-bis-tetrahydropyranyl were obtained by electrolysing an aqueous solution of the potassium salt of tetrahydropyran-4-carboxylic acid[239]; at the same time equal quantities of 4-hydroxytetrahydropyran, and its tetrahydropyran-4-carboxylic-acid ester were isolated.

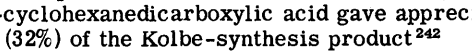


An aqueous solution of the monoethyl ester of cyclohexylmalonic acid gave, on electrolysis, α,α'-dicyclohexylsuccinic acid (a mixture of the two stereoisomers); the yield was 17%.[123] Detailed studies of the electrolysis of hexahydrophthalate showed that a number of by-products were formed (see below); the expected anodic-synthesis product was not obtained either in aqueous or in methanol solutions[240]



Later[241] it was proved that under the given conditions of electrolysis of monomethyl esters of *cis*- and *trans*-hexahydrophthalic acid in anhydrous methanol, normal condensation products, i.e. dimethyl *trans-anti-trans*- and *trans-syn-trans*-bi(cyclohexyl)-2,2'-dicarboxylate are formed, but only in small quantities; the principal reaction products are monomeric compounds – the methyl esters of cyclohex-1-ene-1-carboxylic, cyclohex-2-ene-1-carboxylic acid, and cyclohexanecarboxylic acids.

It should be pointed out that the isomeric methyl ester of *trans*-1,4-cyclohexanedicarboxylic acid gave appreciable quantities (32%) of the Kolbe-synthesis product[242]



Ester groups in the *p*-position obviously aid the electrolytic condensation.

Electrolytic condensation of several alicyclic dicarboxylic-acid esters was successfully carried out in a mixture of methanol and petroleum ether (Pt anode, 4–6 A/dm²). Thus, electrolysis of the monomethyl esters of cyclopentane-1,1-diacetic acid, 2,2,5,5-di(tetramethylene)hexane-1,6-dicarboxylic acid, cyclohexane-1,1-diacetic acid, and 2,2,5,5-di(pentamethylene)hexane-1,6-dicarboxylic acid[161] gave the dimethyl esters of the corresponding 2,2,5,5-di(tetramethylene)hexane-1,6-dicarboxylic acid, 2,2,5,5,8,8,11,11-tetra(tetramethylene)-dodecane-1,12-dicarboxylic acid, 2,2,5,5-di(pentamethylene)hexane-1,6-dicarboxylic acid (38% yield), and 2,2,5,5,8,8,11,11-tetra(pentamethylene)dodecane-1,12-dicarboxylic acid (14.5% yield).

Other investigations dealt with the electrolytic condensation of half-esters of camphoric acid[243-249].

12) Aromatic and Aliphatic-Aromatic Acids

For a long time it was assumed that salts of aromatic acids, unlike those of aliphatic acids, did not enter into the Kolbe reaction.

Experiments on the electrolytic condensation of solutions of salts of benzoic acid in water[92,250,251], sulphuric acid[252], and absolute methanol[253], and the electrolysis of fused benzoic acid[93,99] were indeed unsuccessful. The reaction products were, in general, benzene, free benzoic acid, oxygen, etc. The same was true of the electrolytic condensation of substituted benzoic acids such as *o*-nitrobenzoic[254], *p*-nitrobenzoic[217-255], *p*-toluic[236,256,257], opianic[258], salicylic, *m*-hydroxybenzoic, and *p*-hydroxybenzoic acids[92], 3,5-dimethyl- and 2,4-dimethylbenzoic acids[259], and ethyl phthalate[120].

On electrolysing 2,5-dimethyl-4-t-butylbenzoic acid in methanol[253] one of the methyl substituents in the aromatic nucleus was oxidised and, on subsequent esterification, the methyl ester of 6-methyl-4-t-butyl-1,2-phthalic acid was formed together with 1,3-dimethyl-5-t-butylbenzene.

Negative results were obtained on electrolysing some aromatic acids which contained the carboxyl group in the side chain, e.g. aqueous solutions of potassium salts of phenylacetic acid[260], diphenylacetic acid[261], and also of the ethyl ester of benzylmalonic acid[120]*.

In the 1930's Fichter et al. refuted the conclusion that aromatic acids do not undergo the Kolbe reaction. They proved that the characteristic electrosynthesis product (2,2'-diindanyl) is formed in the electrolysis of indane-2-carboxylic acid in methanol[263,264], although only in small quantities. Other aromatic acids can be electrolysed successfully by using a methanol-pyridine mixture as solvent. Thus, benzoic, phenylacetic, β-phenylpropionic, and phenoxyacetic acids[265] yielded the corresponding diphenyl, dibenzyl (50% yield), 1,4-diphenylbutane (37% yield), and the diphenyl ester of ethylene glycol (45% yield). Normal products (the respective yields being 27, 24, and 8%) were obtained on electrolysing *o*-, *m*-, and *p*-cresoxyacetic acids[267] under analogous conditions.

Under these conditions it was possible to prepare tetraphenylethane by electrolysing diphenylacetic acid[268,269], and also 1,4-diphenylbutane (34% yield), 1,6-diphenylhexane (37% yield), and 1,8-diphenyloctane (47% yield) from the corresponding β-phenylpropionic, γ-phenylbutyric, and δ-phenylvaleric acids[270].

Dibenzyl was produced in 1952 by electrolysing phenylacetic acid in anhydrous methanol and also by electrolysis of fused phenylacetic acid[266]. At the same time it was found that electrolysis of phenylacetic acid in acetic acid

* In the electrolysis of the monomethyl ester of cyclopropane-dicarboxylic acid in methanol the ester of the unsaturated dibasic acid, probably α,α'-dimethyleneadipic acid, was formed instead of the expected diester of dicyclopropanedicarboxylic acid[233].

* The diethyl ester of dibenzylsuccinic acid[262] is formed when the monoethyl ester of benzylmalonic acid is electrolysed in the presence of acetic acid.

and also of diphenyl- and triphenylacetic acids in acetic acid or anhydrous methanol caused the acetoxylation or methoxylation of the benzene nuclei respectively.

Results on the electrolysis of γ-phenylisovaleric, 3,3,3-triphenylpropionic, and 3,3,3-tri-*p*-t-butylphenylpropionic acid in methanol, using a platinum anode, were published recently[271]. Electrolysis of the first acid, in the presence of an excess of sodium acetate (15 A/dm^2, 60°) gave t-pentylbenzene (32%); 2,5-diphenyl-2,5-dimethylhexane and homologues of α-methylstyrene were separated as by-products. Electrolysis of the second acid led to the formation of the phenyl ester of 3,3-diphenyl-3-methoxypropionic acid, and the third acid gave the *p*-t-butylphenyl ester of 3,3-di-*p*-t-butylphenyl-3-methoxypropionic acid.

13) Dicarboxylic Acids

Alkali-metal salts of dicarboxylic acids do not undergo the Kolbe reaction at the anode.

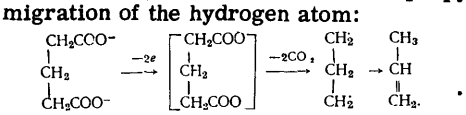
Only hydrogen, oxygen, carbon dioxide[70,73-76,272-276], and in some instances glycolic acid[277] could be detected in the electrolysis products of oxalic acid.

The higher dibasic acids (malonic to sebacic) form olefins and alcohols which contain two carbon atoms less than the original acid, and also saturated and unsaturated acids with one carbon atom less. Attempts to isolate cycloalkanes, the formation of which might be expected as 2 molecules of carbon dioxide are split off simultaneously from the dibasic-acid anion, were unsuccessful.

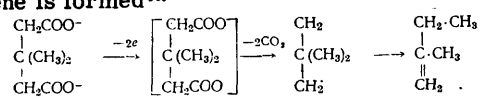
Ethylene, hydrogen, oxygen, carbon monoxide, and carbon dioxide are formed in the electrolysis of malonic acid[272,278]. Schall[279] found that in the electrolysis of the alkali-metal salts of malonic acid, hydrogen peroxide is formed on cooling, probably through the hydrolysis of the intermediate malonic-acid peroxide.

Electrolysis of succinic acid[272,280] leads to the formation of ethylene, oxygen, hydrogen, and carbon dioxide*; tartaric and oxalic acid were also isolated as oxidation products[282]. By electrolysing succinic acid in an alkaline solution in the presence of sodium perchlorate, Hofer and Moest[10] also prepared β-hydroxypropionic acid** together with acrylic acid, carbon monoxide, carbon dioxide, acetylene, acetaldehyde, methanol, and acetic and formic acids.

When an aqueous solution of the potassium salt of glutaric acid was electrolysed with the object of obtaining cyclopropane[284], the products were found instead to be propylene, carbon dioxide and oxygen. The formation of propylene is due to the migration of the hydrogen atom:



In the electrolysis of the salt of β,β-dimethylglutaric acid, where no hydrogen transfer can take place, the whole hydrocarbon group is shifted and the unsymmetrical methylethylethylene is formed[160]



* See Fichter and Fritsch's publications[281] on the decomposition of succinic-acid peroxide to carbon dioxide and ethylene.

** β-hydroxypropionic acid and the acrylic acid formed from it were also obtained by the thermal decomposition of monopersuccinic acid[283].

The cyclic product – dimethylcyclopropane – was not formed.

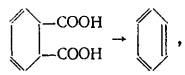
A number of higher dicarboxylic acids, such as adipic[285], pimelic[286-289], suberic[289-290], and sebacic[272] acids, have been electrolysed but in no case could the formation of cycloalkanes be detected.

14) Substituted Dibasic Acids

On electrolysis, methylmalonic acid yields ethylene, hydrogen, oxygen, and carbon monoxide and dioxide[92,272]; propylene, propanol, isopropyl alcohol, and other oxidation products[272] are formed from ethylmalonic acid and pyrotartaric acid.

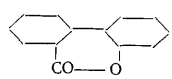
Salts of malic, tartaric, and pyrotartaric acids[291] have also been electrolysed; malic acid gave malonic acid, which was then readily oxidised to oxalic and formic acids and carbon dioxide. Formic acid was formed from the other two acids. Oxalic acid and carbon dioxide were obtained in the electrolysis of mesoxalic acid.

The preparation of benzene (70% yield) from *trans*-1,2-dihydrophthalic acid[292],



and propadiene[233] by opening the ring of 1,2-cyclopropanedicarboxylic acid on electrolysis of its salts, are isolated instances of the formation of unsaturated hydrocarbons in the electrolysis of substituted dibasic acids.

In 1957[293] *cis-syn-cis*-, *trans-anti-trans*-, and *trans-syn-trans*-perhydrodiphenic acids were electrolysed in anhydrous methanol. The principal reaction product (approx. 45%) was in all cases the corresponding isomeric γ-lactone; its structure was determined by synthesis:



15) Unsaturated Dibasic Acids

In the electrolysis of salts of fumaric[280] and maleic[169,280]* acids carbon dioxide and acetylene are formed at the anode, the maleic acid being partly converted to fumaric acid.

Acetylene, acrolein, carbon monoxide, and carbon dioxide are obtained when glutaconic acid is electrolysed[295].

Mesaconic acid[296] forms propyne, and acrylic and itaconic acids, whilst its isomers, itaconic[297-299] and citraconic[296] acids, yield propyne, and acrylic and mesaconic acids. The type of salt of the citraconic acid used in the electrolytic condensation determines the yield of propyne; thus the highest yield (52%) of propyne was obtained by electrolysing the rubidium salt of citraconic acid and the lowest yield (16%) when the lithium salt was used[300].

Fumaric acid and acetylene[301,302] have been prepared from acetylenedicarboxylic acid.

* Malic acid is formed in the electrolysis of hydroxymaleic acid[294].

"CROSSED" ELECTROLYTIC CONDENSATION

In this reaction acids or half-esters of dicarboxylic acids with different radicals are caused to react. Such reactions do not take place very readily and are seldom carried out. The main difficulty lies in the fact that the condensation process can proceed equally readily in three principal ways:

$$\left.\begin{matrix}RCOO^-\\ R_1COO^-\end{matrix}\right\} \xrightarrow{-2e} R{-}R_1 + 2CO_2 ,$$

$$2RCOO^- \xrightarrow{-2e} R{-}R + 2CO_2 ,$$

$$2R_1COO^- \xrightarrow{-2e} R_1{-}R_1 + 2CO_2 .$$

As in the simple Kolbe synthesis a series of side reactions accompany the electrolysis; this explains the comparatively small yield of the main reaction product ($R-R_1$).

The reaction was first carried out by Würtz in 1855[3,4], who succeeded in preparing a small quantity of heptane and decane by electrolysing a mixture of oenanthic and acetic acids and a mixture of oenanthic and valeric acids respectively* . It was later used by other investigators for synthesising a number of compounds. Mixtures of acids and half-esters of dicarboxylic acids with straight and branched chains were used and also carboxylic acids containing various substituents (keto- and amino-groups, halogens, etc.) and double and triple bonds in the chain.

Most publications on the "crossed" electrolytic condensation recommend that methanol solutions of potassium or sodium salts of the acids be used as electrolytes**. Electrolysis of a mixture of the methyl ester of adipic acid with acetic acid or hexanoic acid in anhydrous methanol (11–16 A/dm², 1–2 A, 110 V, 50°) yielded the corresponding methyl esters of hexanoic acid (42% yield)*** and decanoic acid (61% yield)[137].

The methyl ester of arachidic acid (41.5% yield) was obtained from the monomethyl ester of adipic and palmitic acids in boiling methanol (7 A/dm², 5.6 A, 12–38 V)[127,305] Under analogous conditions the methyl ester of adipic and stearic acids yielded the methyl ester of behenic acid (38% yield); electrolysis in methanol (4–12 A/dm², 40°–60°) of the methyl ester of adipic acid with butyric, capric, or lauric acids yielded the corresponding caprylic (30.6% yield), myristic (7% yield), and palmitic acids (23.4% yield)[304]****.

The use of benzyl esters as starting materials in place of the ethyl and methyl esters in syntheses of this kind makes it possible to avoid esterification with the methanol used as solvent, which very often accompanies "crossed" syntheses. Thus, palmitic (30% yield) and arachidic (25% yield) acids respectively[124] can be produced by condensing the benzyl ester of succinic and myristic or stearic acids in methanol (6–7 A/dm², 1–1.3 A, $t < 50°$) and hydrolysing the products.

According to other data[126] the use of monobenzyl esters as one component during the "crossed" electrolytic condensation of a mixture of half-esters of dicarboxylic acids, facilitates the isolation of the product. Thus the methyl ester of pimelic acid (24% yield) was obtained by electrolysing the benzyl ester of glutaric acid and the methyl ester of succinic acid in a methanol-pyridine mixture (Pt electrode, 0.2 A, 34 V, 35°) and subsequent hydrogenolysis of the reaction products. It has been shown[304] that addition of tetrahydrofuran is advisable in this synthesis. Electrolysis of the ethyl ester of adipic acid with myristic, pentadecanoic, and stearic acids in methanol in the presence of tetrahydrofuran (2.5–12.5 A/dm², 0.2–1 A, 40°–60°) gave the corresponding stearic (12.7% yield), nonadecanoic (6.7% yield), and behenic acids (4.7% yield).

The same rule as in simple Kolbe reactions applies here for substituted and unsaturated acids: the starting compound must not contain a branched chain, a functional group, or an unsaturated bond in the α-position to the carboxyl group. It should be pointed out, however, that Japanese chemists[307] succeeded in preparing 10-methyloctadecanoic acid by electrolysing a mixture of the ethyl ester of sebacic and methyloctalacetic acids (reaction conditions and yields are not given).

3-methylundecanoic acid (46% yield) was obtained in the electrolysis of monomethyl β-methylglutarate and octanoic acid in anhydrous methanol (10 A/dm², 2 A)[308]. The same authors synthesised the methyl ester of 10-methyloctadecanoic acid (38% yield) from the monomethyl ester of azelaic acid and 3-methylundecanoic acid (6.4–8.8 A/dm², 1.1–0.8 A); similarly, electrolysis of the monomethyl ester of γ-methyladipic acid with caproic acid gave 3-methyldecanoic acid (65% yield)[163]; electrolytic condensation of a mixture of ethyl β,β-methylethylglutarate and capric or lauric acids[309] yielded the corresponding β,β-methylethyltridecanoic and β,β-methylethylpentadecanoic acids.

Electrolysis in methanol at 10–20 A/dm² of monomethyl glutarate and 3-methylheptanoic acid, monomethyl succinate and 4-methyloctanoic acid, and the monomethyl ester of azelaic acid and 3,9-dimethyltridecanoic acid[310] yielded in the first two instances 6-methyldecanoic acid (35 and 32% yields), and in the last, 10,16-dimethyleicosanoic acid (54% yield). The same paper gives results on the "crossed" condensation when both initial acids contain branched carbon chains. Thus, 3,9-dimethyltridecanoic acid (51% yield) is formed in the electrolysis of monomethyl β-methylglutarate and 6-methyldecanoic acid. In an analogous manner 3,13,19-trimethyltrieicosanoic acid (18.5% yield) was prepared from monomethyl β-methylglutarate and 10,16-dimethyleicosanoic acid.

The electrolytic condensation of optically active substances has been very thoroughly investigated to find satisfactory methods for the synthesis of stereoisomers of compounds with branched chains of known structure. In this way it was possible to prepare D(+)-3-methylundecanoic acid (yield 35%)[311-313] by electrolysing an equimolar mixture of monomethyl L(+)-β-methylglutarate and caprylic acid in boiling methanol (Pt electrodes, 5 A, pH < 8)[311,313].

By an analogous method L(-)-3-methylundecanoic acid (35.5% yield) was synthesised from monomethyl D(-)-β-methylglutarate and caprylic acid. Electrolysis of a mixture of the monomethyl ester of sebacic acid and D(+)-3-methylundecanoic or L(-)-3-methylundecanoic acid led to the formation of the corresponding D(+)-11-methylnonadecanoic acid (24% yield) and L(-)-11-methylnonadecanoic acid (22.5% yield). Condensation of palmitic acid with the monomethyl esters of D(+)- and L(-)-β-methylsuccinic acid gave the corresponding D(-)- and L(+)-2-methyloctadecanoic acids[314].

* Schorlemmer[303] repeated Wurtz' experiment in 1865 and obtained similar results.

** Unless otherwise stated "crossed syntheses" discussed below refer to the electrolysis of sodium and potassium salts of carboxylic acids, carried out in the presence of free acids.

*** Hexanoic acid (40.8% yield) was also obtained in the electrolysis of the monoethyl ester of adipic acid and acetic acid[304] in ethanol (10 A/dm², 0.8 A, 40°–60°).

**** See also publications by Japanese authors[306] on the electrolysis of dibasic-acid esters with fatty acids.

Higher yields can be obtained by using, in similar syntheses, an excess of the optically inactive component. In the electrolysis of caprylic acid with the monomethyl esters of L(+)- and D(-)-β-methylglutaric acid, in anhydrous methanol (molar ratio of the optically inactive to the active component 2 : 1, 2 A, 10 A/dm^2), the corresponding D(+)- and L(-)-3-methylundecanoic acids (48% yield) were obtained. Under similar conditions, the monomethyl ester of azelaic acid and D(+)- and L(-)-3-methylundecanoic acid yielded the D(-)-10-methyloctadecanoic and L(+)-10-methyloctadecanoic acids (30–31% yield)[315].

Unsaturated acids, mixed with dicarboxylic-acid esters, also undergo "crossed" electrolytic condensation. Thus pentadecenoic acid was obtained by the electrolysis of a mixture of undecenoic acid and monomethyl adipate in anhydrous methanol (0.83 A/dm^2, 80–100 V); after purification (via the methyl ester) the yield was approximately 15%.[316] In later investigations it was possible to increase the yield to 30%.[171] A number of other unsaturated acids have also been synthesised by this reaction: 3,3-dimethyltetradec-13-enoic acid[317] by the electrolysis, in ethanol, of undecenoic acid and the ethyl ester of β,β-dimethylglutaric acid (10 A/dm^2, 100 V); docos-21-enoic acid from the ethyl ester of tetradecane-1,14-dicarboxylic acid and oct-1-enoic acid[318].

When double bonds are present in the α-position to the carboxyl group unsatisfactory results are obtained; electrolysis of a mixture of acetic acid and monoethyl fumarate or monomethyl muconate in absolute methanol did not lead to the formation of the expected unsymmetrical products:

$$CH_3CH{=}CHCOOC_2H_5 \text{ and } CH_3CH{=}CH{-}CH{=}CHCOOCH_3$$[168].

Bounds et al. showed that the geometrical configuration at the double bonds was maintained in the simple Kolbe reaction. They[125,171,319] proved that the configuration at the double bonds was also preserved during the "crossed" condensation.

In the electrolysis of oleic and elaidic acids with an excess of adipic acid monomethyl ester, in anhydrous methanol (Pt electrodes, 10 A/dm^2, 1.7 A, 50°) the "crossed" products were obtained in both cases; their hydrolysis gave the corresponding erucic and brassidic acids (approximate yield 30%)[171]. Similarly, electrolysis of the monomethyl ester of suberic acid with oleic or elaidic acids[125] gave, after hydrolysis, *cis*- and *trans*-tetracos-15-enoic acids respectively (respective yields 37% and 32%). The unsymmetric product *cis*-octadec-11-enoic acid (12% yield), was obtained in the electrolysis of a mixture of *cis*-hexadec-9-enoic and monomethyl succinate[319].

Studies by American chemists[320] on the preparation of esters of unsaturated α,ω-dicarboxylic acids by electrolysing a mixture of dicarboxylic-acid esters and conjugated dienes, are of great interest. They prepared the diethyl ester of deca-3,7-diene-1,10-dicarboxylic acid by the electrolysis, in methanol, of monoethyl malonate and butadiene (Pt electrodes, 1.1 A, -5°). The diethyl ester of dodeca-4,8-diene-1,12-dicarboxylic acid, the diethyl ester of hexadeca-6,10-diene-1,16-dicarboxylic acid, and other compounds were prepared by similar methods.

Satisfactory results have been obtained in the electrolytic condensation (in methanol) of acids of the acetylenic series[321]. Stearolic acid (octadec-9-ynoic acid) (6% yield) was obtained from pentadec-6-ynoic acid and monomethyl glutarate (6–7),A/dm^2). The same acid was obtained in the electrolytic condensation of tetradec-5-ynoic acid and monomethyl adipate at 15–16 A/dm^2 (24% yield). Electrolysis of a mixture of monomethyl adipate and stearolic acid (8–10 A/dm^2), pentanoic acid and the methyl ester of dodec-6-ynoic acid (6.8–8 A/dm^2), and hexanoic acid and the methyl ester of dec-5-ynoic acid led to the formation of the corresponding docos-13-ynoic (behenolic) acid (26% yield), pentadec-6-ynoic acid (25% yield), and tetradec-5-ynoic acid (27% yield). Octadec-6-ynoic acid (23% yield) was prepared from the monomethyl ester of dec-5-yne-1,10-dicarboxylic acid and caprylic acid[178].

TABLE 11.

Initial reactants		Molar ratio I:II	"Crossed" product	Yield, % (with respect to I)
I	II			
Levulinic acid	$CH_3(CH_2)_3COOH$	1 : 1	methyl hexyl ketone	35
ditto	CH_3COOH	1 : 3	methyl propyl ketone	20
»	$CH_3(CH_2)_2COOH$	1 : 6	methyl pentyl ketone	62
»	CH_3CH_2COOH	1 : 1	methyl n-butyl ketone	20
»	$(CH_3)_2CHCH_2COOH$	1 : 1	$CH_3CO(CH_2)_3CH(CH_3)_2$	—
»	$CH_3(CH_2)_4COOH$	1 : 2	methyl n-heptyl ketone	42
»	$CH_3(CH_2)_6COOH$	1 : 1	methyl n-nonyl ketone	31
»	$CH_3(CH_2)_8COOH$	2 : 1	methyl n-undecyl ketone	24
»	$CH_3(CH_2)_{10}COOH$	2 : 1	$CH_3CO(CH_2)_{12}CH_3$	20
»	$CH_3OOC(CH_2)_2COOH$	2 : 1	$CH_3CO(CH_2)_4COOCH_3$	25–30
»	$CH_3OOC(CH_2)_4COOH$	2 : 1	$CH_3CO(CH_2)_6COOCH_3$	20
»	$CH_3OOC(CH_2)_4COOH$	4 : 1	$CH_3CO(CH_2)_6COOCH_3$	38
»	$CH_3OOC(CH_2)_8COOH$	2 : 1	$CH_3CO(CH_2)_{10}COOCH_3$	12

Halogeno-substituted acids were also subjected to this type of electrolytic condensation. Electrolysis of 10-fluorodecanoic and 5-chloropentanoic acid (Pt anode, 16 A/dm^2, 50°) in methanol gave 13-fluorotridecyl chloride (24.4% yield)[137]. Under the same conditions 10-fluorodecanoic acid and the monomethyl ester of sebacic acid gave the methyl ester of 18-fluorostearic acid (4.8% yield).

The reactions of chloroacetic acid are of great interest; in the simple Kolbe reaction only oxidation products are obtained[204–206], but on electrolysis in a mixture with other acids its behaviour is similar to that of unsubstituted acetic acid. Cetyl chloride was obtained when chloroacetic and palmitic acids were electrolysed in a water-alcohol medium at 70°–75°.[322] Unsatisfactory results were obtained when trichloroacetic acid was used instead of chloroacetic acid.

Hunsdiecker[323] did much work on the electrolytic condensation of keto-acids with fatty acids. He prepared dodeca-2,5-dione (30–45% yield) by the electrolysis of a mixture of 4,7-diketooctanoic and caproic acids in anhydrous methanol (3–5 A, 50–90 V). 4,7-Diketooctanoic acid was also reacted, under analogous conditions, with propionic, butyric, valeric, isovaleric, caprylic, and lauric acids, and also with monomethyl succinate and adipate. Unsymmetrical products were obtained in each case (no yields are quoted). He prepared dodeca-3,6-dione by electrolysing a mixture of 4,7-diketononanoic and valeric acids. Japanese investigators[202,324,325] obtained very satisfactory results in the electrolytic condensation, in methanol, of keto-acids with saturated acids and half-esters of dicarboxylic acids (40 A/dm^2, 30°–35°) (Table 11).

Good results have been obtained with keto-acids and substituted aliphatic acids. Thus, 4,7-diketooctanoic acid was condensed with 5-methoxyvaleric and β-isopentyloxybutyric acid[326]; the yield of 9-isopentyloxydeca-2,5-dione was 30%.

The number of possible "crossed" electrolytic-condensation reactions of acids with various substituents is very large. The methyl ester of 14-methoxy-3-methyltetradecanoic acid (34.4% yield) has, for instance, been prepared by the electrolysis, in methanol, of monomethyl β-methylglutarate and 11-methoxyundecanoic acid (Ni anode, Pt cathode, 5–7 A, 80–100 V)[326].

Hexadeca-2,15-dione (31% yield)[327] was synthesised by electrolysis, in anhydrous methanol, of acetylvaleric and acetylpelargonic acids (12.5 A/dm², 5 A, 50 V, 40°–50°).

The methyl ester of 10-acetamidodecanoic acid was obtained by electrolysing 6-acetamidohexanoic acid and monomethyl adipate[223,328].

No "crossed" products were obtained in the electrolysis of monomethyl adipate with acetylglycine and cyanoacetic acid (both substituted in the α-position to the carboxyl group)[223]. However, contrary to the general rule, Japanese investigators obtained satisfactory results in the simultaneous electrolytic condensation of methyldodecylcyanoacetic acid and lauric acid, ethyldodecylcyanoacetic acid and undecanoic acid[329], ethyldodecylcyanoacetic and capric acid, and also in the electrolysis of a mixture of the methyl ester of diisopentylmalonic acid and isocaproic acid[330]. (No reaction conditions or yields are given in these papers).

Hydrolysis of the products obtained in the electrolysis of monomethyl adipate with *threo*- and *erythro*-9,10-dihydroxystearic acid[171] in anhydrous methanol, using Pt electrodes, yielded *threo*- and *erythro*-13,14-dihydroxybehenic acid (24% and 33% yields, respectively). *Threo*-11,12-dihydroxy arachidic acid was prepared by an analogous method[124] from monobenzyl succinate and *threo*-9,10-dihydroxystearic acid (13% yield).

Mixtures of aliphatic-aromatic and mixtures of aliphatic-aromatic and aliphatic acids have also been subjected to "crossed" electrolytic condensation. In one of the early investigations[210] the diethyl ester of α-methylhydrocinnamic acid was found in the electrolysis products of a mixture of acetic acid and monoethyl benzylmalonate. t-Pentylbenzene (32% yield) was obtained by electrolysing 3-phenylisopentanoic acid in methanol, in the presence of an excess of sodium acetate (Pt anode, 15 A/dm², 60°)[271]. Electrolysis of palmitic with phenylacetic and β-phenylpropionic acids led to the formation of the corresponding hexadecyl- and heptadecylbenzene[175]. Electrolytic condensation of a mixture of γ-phenylbutyric acid with β-phenylpropionic or δ-phenylvaleric acids (Pt anode, 30°–40°) in a methanol-pyridine mixture (2 : 1)* gives, in the first case, small quantities of 1,5-diphenylpentane, and in the second 36% of 1,7-diphenylheptane[270].

"Crossed" condensation as well as the simple Kolbe condensation can be carried out in alcoholic, water–alcohol, or aqueous media. Under these conditions (especially in the last case) side reactions occurring concurrently with the electrolytic condensation, decrease appreciably the yield of the desired product.

Japanese chemists investigated the electrolytic-condensation reaction in water–alcohol solutions. They electrolysed palmitic and acetic, propionic and butyric, and stearic and acetic acids[322] in dilute alcohol at 70°–75°, using a Pt anode, and obtained the expected products (no yields are given). Electrolysis of the methyl ester of 2,12-dimethyltridecane-1,13-dicarboxylic acid with 6-methyldecanoic acid (Pt anode, 8 A/dm², pH 6.8–7, 30°) in 50% ethanol gave 3,13,19-trimethyltrieicosanoic acid (11% yield)[331,332] Under the same conditions the monoethyl ester of sebacic acid and 3,7-dimethyloctanoic acid[333] gave the ethyl ester of 11,15-dimethylhexadecanoic acid. Stearic acid (21% yield)[138] was isolated from the electrolysis products of the monomethyl ester of sebacic acid and decanoic acid when the process was effected in a 35% aqueous-methanol solution at a molar ration 1 : 3 of the initial components.

Electrolytic condensation of monoethyl adipate with some fatty acids in a water–alcohol solution[304] gave good results (Table 12).

Greaves et al.[138] compared results obtained in the "crossed" electrolytic condensation in alcohol and water–alcohol solutions. Hexanoic acid (40% yield) was obtained by condensing monomethyl adipate with acetic acid in anhydrous methanol (1.5–2 A, 40°–50°) whilst in a water–alcohol solution (3 A, 30°) the yield was only 29% (the molar ratio of the ester to acetic acid was in both cases 1 : 6). Decanoic acid was prepared by the electrolysis of a mixture of monomethyl adipate and hexanoic acid (1 : 1); in anhydrous methanol the yield was 36%, in a water–alcohol medium 12%. The same acid was synthesised in 50% yield by electrolysis of the monomethyl ester of sebacic acid in aqueous methanol in the presence of a large excess of acetic acid (molar ratio of the starting materials 1 : 15).

The "crossed" synthesis in aqueous solutions has been investigated even less than in water–alcohol solutions; there are practically no published data.

In 1895[334] the electrolytic condensation of monoethyl succinate with propionic, butyric, and isobutyric acids and of monoethyl malonate with acetic acid was carried out in an aqueous medium. The expected "crossed" products were obtained in each case.

Acetone[199] was prepared in 1900 by the electrolysis of an aqueous solution of potassium pyruvate and acetate in an electrolyser with a diaphragm (1.5–2 A, 17–18 V). The same author electrolysed in an aqueous medium (2.5 A and up to 20 V) mixtures of pyruvic and butyric acids, and also of levulinic and acetic or pyruvic acids, and obtained in the first two cases methyl propyl ketone, and in the last acetonylacetone.

The electrolysis of an aqueous solution of a mixture of the potassium salts of the monoethyl esters of malonic and suberic acids (1.7 A, 7.5 V, 15°) was carried out in 1922[134]. After saponification of the electrolysis products, succinic and dodecane-1,2-dicarboxylic acids were obtained, as well

TABLE 12.

Initial reactants		Solvent	"Crossed" product (after hydrolysis)	Yield, %
I	II			
$H_5C_2OOC(CH_2)_4COOH$	$C_6H_{11}COOH$	aqueous CH_3OH	$CH_3(CH_2)_8COOH$	23.3
»	$C_7H_{15}COOH$	»	$CH_3(CH_2)_{10}COOH$	15
»	$C_{15}H_{31}COOH$	aqueous C_2H_5OH	$CH_3(CH_2)_{16}COOH$	11.4
»	$(CH_3)_2CHCH_2COOH$	»	$(CH_3)_2CH(CH_2)_6COOH$	8

* Pyridine is added to inhibit the formation of polymers which coat the anode during electrolysis.

as the "crossed" product – azelaic acid. The yields are not quoted, probably because they were small. Only Miller and Hofer[334] were able to record good results in similar electrolytic-condensation reactions. For example, using small quantities of reactants, they prepared ethyl butyrate (69.5% yield) by the electrolysis of the potassium salt of acetic acid and the ethyl ester of succinic acid.

Samokhvalov et al.[336] stated in 1952 that 3–5% yields of the "crossed" product can be obtained by electrolysis of 11-methoxyundecanoic acid and of monoethyl β-methylglutarate.

Recent investigations[336,337] have shown that under certain conditions "crossed" electrolytic condensation can be successfully carried out in an aqueous medium. The electrolytic condensation of monoethyl adipate and 11-acetoxyundecanoic acid in an aqueous solution (24 A/dm², 40°–65°) can, after hydrolysis, give a 25–27% yield (based on 11-acetoxyundecanoic acid) of 15-hydroxypentadecanoic acid. Electrolysis of 11-hydroxyundecanoic acid and monoethyl adipate (molar ratio 1 : 3) gives a 7% yield of 15-hydroxypentadecanoic acid[336].

MECHANISM OF THE KOLBE REACTION

The mechanism of the Kolbe reaction is not entirely clear despite the large number of publications on the electrolytic condensation of carboxylic acids. The principal product and by-products have been investigated fairly thoroughly and in a large number of cases; several versions of the mechanism of transformation of the organic acids have been put forward. The nature of the anodic process, however – its kinetics, the role of the electrode surface in the condensation reaction, and the effect of the magnitude of the anode potential on the course of the reaction – have hitherto not been elucidated. In this respect, the electrolytic-condensation reaction does not appear to be an exception amongst other anodic processes including such apparently simple ones as, for example, the anodic evolution of oxygen from aqueous solutions.

Theories of the mechanism of electrolytic condensation developed in parallel with the extension of our knowledge of anodic processes and, in particular, of the evolution of oxygen.

In Kolbe's time it was assumed that only oxygen could be evolved at the anode during electrolysis of aqueous solutions; Kolbe, therefore, endeavoured to show that the electrolytic condensation was due to the oxidation of acids by oxygen, formed at the anode during the decomposition of water. The mechanism proposed by Kolbe was supported by several other investigators[43,338]. These hypotheses, as well as Bourgoin's[339,340] statement that anhydrides of the original acids are formed as intermediates in the Kolbe reaction, are only of historic interest.

In 1896 Schall[341] suggested that carboxylic acids are oxidised by the active oxygen liberated at the anode, and that diacyl peroxides are formed; decomposition of the latter would give the product of the Kolbe synthesis:

$$2RCOOH + O \rightarrow (RCOO)_2 + H_2O \qquad (RCOO)_2 \rightarrow R{-}R + 2CO_2.$$

Schall's hypothesis constituted the basis of Fichter's[33,342-345] peroxide theory of electrolytic condensation which found many supporters[105,346-348].

According to Brown and Walker's theory[5] the discharge of the carboxylic-acid anions and formation of uncharged radicals constitutes the primary process. The radicals can be condensed with simultaneous splitting off of carbon dioxide:

$$2RCOO^- \xrightarrow{-2e} 2[RCOO], \quad 2[RCOO] \rightarrow R{-}R + 2CO_2.$$

This was later developed as the free-radical theory[15,16,91,103,104,108-110,349].

Glasstone and Hickling's views, published in the 1930's[8,37,45,51,350-353], postulated that hydrogen peroxide, formed by discharge of OH^- ions at the anode, is the basic intermediate product; this idea was closely associated with the mechanism of electrolytic condensation. The authors also used the results of their detailed investigations on the electrolytic condensation of acetic acid and malonic-acid half-ester[6,37,45] in support of their theory, which is not, however, accepted by the majority of electrochemists at the present time.

The basic assumptions of the three theories of the electrolytic-condensation reaction are briefly discussed below.

The Peroxide Theory

This theory, proposed by Fichter in 1934[344], starts from the following scheme of electrolytic condensation:

$$2RCOO^- \xrightarrow{-2e} 2[RCOO] \rightarrow RCO{-}O{-}O{-}OCR \rightarrow 2[R] + 2CO_2\,; \quad 2[R] \rightarrow R{-}R$$

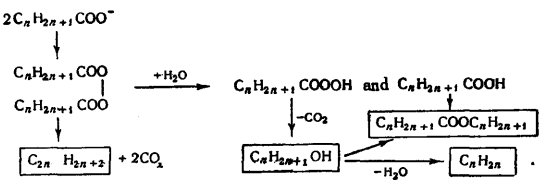
Unlike Schall, Fichter assumes that electrolytic condensation commences with the discharge of the carboxylic-acid anion, that diacyl peroxide is formed due to a further discharge of anions, and that the main product of the Kolbe synthesis is formed by the decomposition of the diacyl peroxide.

The formation of by-products is explained by the hydrolysis of the intermediate diacyl peroxide and the formation of the peracid which is converted to the alcohol by decarboxylation:

$$RCOO{-}OOCR + H_2O \rightarrow RCOOH + RCOOOH\,; \quad RCOOOH \rightarrow CO_2 + ROH.$$

In an alkaline medium and at low concentration of the initial anions, this decomposition of the peroxide is the principal reaction and alcohol is the principal product (Hofer–Moest reaction).

The alcohols can then be dehydrated to olefins (with the same number of carbon atoms), or react with the free acid, or the discharged anion, to form esters. Electrolytic condensation of saturated fatty acids can be represented as follows (according to the peroxide theory):



This scheme does not take into account the formation of saturated hydrocarbons C_nH_{2n+2}, which are usually obtained in significant quantities.

Many attempts have been made to prove the formation of the diacyl peroxide at the anode. Positive results were obtained only when electrolysis was carried out under special conditions, and the yields of peroxides were very small. Fichter et al.[129,354] succeeded in detecting diacyl peroxides and peracids during the electrolysis of caproate and the

half-ester of adipic acid, on strongly cooling the anode surface. Hallie[114], who carried out electrolysis experiments at low temperatures, using a circulating electrolyte, proved that small quantities of diacyl peroxides are formed during the electrolysis of acetates and caproates.

Many papers mention that the composition of the products of electrolytic condensation and of the chemical decomposition of diacyl peroxides is similar, which is regarded as a proof of the peroxide theory by its supporters. Diacetyl peroxide, for instance, decomposes on heating to form ethane, methane, and carbon dioxide[355-357].

A mixture of ethane and methane is formed when ultraviolet light acts on diacyl peroxides[357]. During the electrolysis of acetates, on the other hand, especially at low anodic current density, the formation of a mixture of ethane, methane, and carbon dioxide can also be observed[18,86,89,358].

Fichter suggests that the peroxide theory is also confirmed by the formation of glycolaldehyde during the electrolysis of acetate[33] and monoethyl malonate[7] in an ethylene-glycol solution. He regards the occurrence of the glycolaldehyde in both cases, as being due to the oxidation of ethylene glycol by the intermediate peroxides.

The Free-Radical Theory

This theory is the one most thoroughly developed at the present time and has many supporters.

During investigations on side reactions in the electrolytic condensation Hölemann and Clusius[103,104] carried out experiments on the electrolysis of deuterated acids dissolved in ordinary and in heavy water. They confirmed that a high current density is required in the electrolysis of acetates to produce ethane, and that a low current density (1 A/dm² and less) leads to the formation of methane. The deuterium content in the reaction products was proved to be determined solely by the composition of the acetate ion, not by the deuterium content of the water.

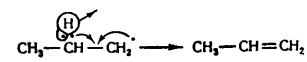
These results led the authors to the conclusion that the Kolbe reaction takes place via the formation of intermediate alkyl radicals – thus, in the electrolysis of acetates

$$CH_3COO^- \xrightarrow{-e} {}^{\cdot}CH_3COO\,,$$
$${}^{\cdot}CH_3COO \rightarrow {}^{\cdot}CH_3 + CO_2\,.$$

Dimerisation takes place readily at high current density because the concentration of the methyl radicals at the anode is high; at low current density the methyl radicals can react with the acetate ions or with the molecules of the organic solvent (e.g. with alcohol if this is added to the electrolyte) and form methane.

$${}^{\cdot}CH_3 + {}^{\cdot}CH_3 \rightarrow C_2H_6\,,$$
$${}^{\cdot}CH_3 + CH_3COO^- \rightarrow CH_4 + {}^{\cdot}CH_2COO^-\,,$$
$${}^{\cdot}CH_3 + C_2H_5OH \rightarrow CH_4 + {}^{\cdot}C_2H_4OH\,.$$

By following the isotope composition of the products in the electrolysis of deuteropropionic[15,109] and deuterobutyric[110] acids, the authors concluded that unsaturated hydrocarbons (with half the number of carbon atoms of the main Kolbe-reaction products) are formed from the alkyl radicals, by the splitting off of the hydrogen atom originally in the β-position to the carboxyl group. The hydrogen atoms of the molecule itself do not migrate.



The formation of propane as well as propylene in the electrolysis of butyric acid is explained by the disproportionation of hydrogen in the alkyl radicals:

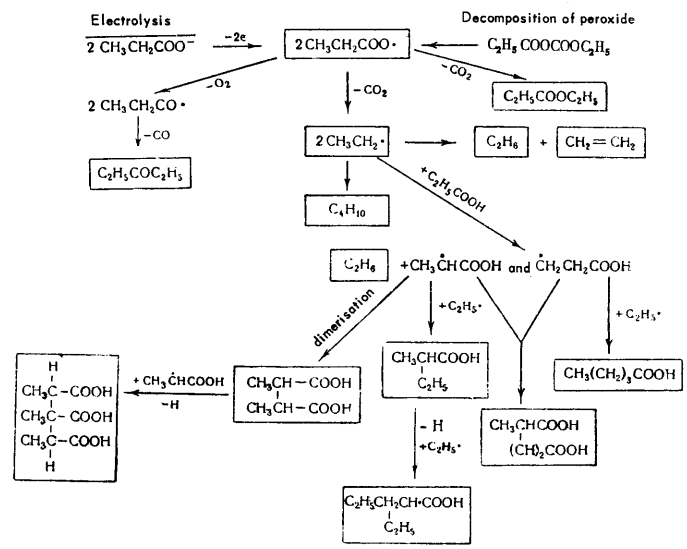
$$2CH_3{-}CH_2{-}CH_3 \rightarrow CH_3{-}CH_2{-}CH_3 + CH_3{-}CH{=}CH_2\,.$$

On electrolysis of an acid solution of α,α-dideuteropropionic acid (CH_3CD_2COOH), Kruis and Schanzer[15] obtained, among other products, a mixture of alcohols, containing 35% CH_3CD_2OH and 65% CD_2HCH_2OH, thus confirming that the oxidation of alkyl radicals to alcohols proceeds mainly at the β-position.

Goldschmidt and Stöckl[108] demonstrated the presence of free radicals during the electrolysis of fatty-acid salts by an indirect method, using the capacity of these radicals to initiate polymerisation of unsaturated compounds[359,360] (styrene, acrylonitrile). The formation of alkylpyridines when pyridine is present in the electrolyte is also regarded as an indirect proof of the presence of radicals[265,361].

Goldschmidt et al. made a detailed study of the composition of the electrolysis products of propionates in anhydrous propionic acid and compared them with the decomposition products of dipropionyl peroxide[16]. Later investigations dealt with the decomposition of symmetrical and unsymmetrical peroxides of dicarboxylic acids[362]. Goldschmidt stated that both the electrolysis of carboxylic acids and the decomposition of diacyl peroxides proceed via the formation of free radicals, but that the diacyl peroxides were not intermediate products in electrolysis.

The electrolysis of propionates and decomposition of dipropionyl peroxides, according to Goldschmidt, is shown in the following scheme:



The Glasstone–Hickling Theory

The theory[8,37,38,45,51,353] is based on the assumption that OH^- ions are discharged at the anode during the electrolysis

of aqueous solutions of fatty acids and form hydrogen peroxide; this reacts with the acid ions:

$$2RCOO^- + H_2O_2 \rightarrow R{-}R + 2CO_2 + 2OH^- .$$

The formation of radicals represents an intermediate stage:

$$2RCOO^- + H_2O_2 \rightarrow 2RCOO^{\cdot} + 2OH^-.$$

The latter may possibly combine and form diacyl peroxides – the intermediate products according to Fichter's theory:

$$2RCOO^{\cdot} \rightarrow [RCOO]_2.$$

When the concentration of hydrogen peroxide is not sufficiently high to effect the above reactions, or if the concentration of the anions is insufficient, hydrogen peroxide, or the active oxygen formed by its decomposition, will react with the acid and form the peracids:

$$RCOOH + H_2O_2 \rightarrow H_2O + RCOOOH \quad \text{or} \quad RCOOH + [O] \rightarrow RCOOOH.$$

The latter are decomposed to the alcohol and carbon dioxide:

$$RCOOOH \rightarrow ROH + CO_2.$$

Glasstone, Hickling, and Westwood carried out very detailed investigations on the electrolytic condensation of acetates [37,45] and monoethyl malonate [6] and endeavoured to correlate their results with the proposed mechanism, assuming the intermediate formation of hydrogen peroxide. The negative effect of the anode material (Ni, Fe, Au, etc.) and of foreign cations on the electrolytic condensation is related to their capacity to decompose hydrogen peroxide. The magnitude of the current density is related to the concentration of hydrogen peroxide set up in the layer close to the electrode. The effect of the pH of the medium on the yield of the main product is explained by the increased stability of hydrogen peroxide in acid solutions and by the decrease in the concentration of OH^- ions at lower pH.

Great importance is attached to the fact that the anode potential at which electrolytic condensation takes place is considerably higher than the potential at which oxygen is evolved from aqueous solutions. Hickling and Westwood [6] state that during the electrolysis of a 2 M solution of monoethyl malonate: (a) the potential is about 2.8 V on smooth platinum (when good yields of the diethyl succinate are obtained), and (b) on platinised platinum, gold, and lead dioxide the potential is approximately 2.0 V, in consequence of which no electrolytic condensation takes place. The polarisation curve for the evolution of oxygen in a phthalate buffer with identical pH was obtained for comparison. Oxygen was evolved when the anode potential was approximately 2.0 V.

Commenting on Hickling and Glasstone's work [45], Nekrasov pointed out that their assumption that "hydrogen peroxide, formed at the anode, gives rise to the formation of radicals which are capable of establishing a much higher potential than the potential of oxygen evolution" cannot be upheld, since changes in the anode surface and increases in oxygen overvoltage can occur, without any participation of hydrogen peroxide. Indeed, many publications [91,363] deny that the formation of hydrogen peroxide plays an indispensible part in anodic processes.

Glasstone and Hickling's proposed mechanism for the evolution of oxygen and other anodic processes is rejected by most electrochemists. All attempts to effect the Kolbe synthesis by the action of hydrogen peroxide on acetate solutions have proved unsuccessful [6,8,37]. The action of persulphates [6,37,343,364,365] and of fluorine [366,367], however, gives the same products as the electrolytic condensation.

Obviously, the electrochemical aspects of the Kolbe reaction can be elucidated completely only when much more is known about anodic processes, especially about the mechanism of oxygen overvoltage at the anode.

At present it can only be stated that the evolution of oxygen at a platinum anode proceeds in two stages: (a) interaction of an OH^- ion with the metal electrode, forming a higher platinum oxide; (b) decomposition of the higher oxide with formation of oxygen.

Some authors [368,369] assume that the discharge of OH^- ions is the slowest stage, determining the magnitude of the overvoltage. Others [370-373] attach great importance to the decomposition of the higher platinum oxides, the formation of which has been demonstrated in a number of investigations [371-373].

It can be assumed that the discharge of the carboxylic-acid ion and its simultaneous interaction with the higher platinum oxides (formed at the electrode) is a necessary condition for the electrolytic condensation.

The anomalously large anode potentials during the reaction, recorded by Glasstone and Hickling, are not surprising as the presence of carboxylic-acid ions, especially at high current densities, can increase the oxygen overvoltage to a considerable degree; this also occurs during the anodic evolution of oxygen from solutions containing SO_3^{2-} ions [372]. Apparently, under these conditions the discharge of $R\text{-}COO^-$ ions is energetically more probable than the discharge of hydroxyl ions, especially as the concentration of the latter is insignificant under conditions which are optimal for the electrolytic condensation.

1. H. Kolbe, Annalen, 69, 257 (1849).
2. T. Kempf and H. Kolbe, J. prakt. Chem., 4, 46 (1871).
3. A. Würtz, Jahresber., 1855, p. 572.
4. A. Würtz, Annalen, 96, 364 (1855).
5. A. C. Brown and J. Walker, ibid., 261, 107 (1891).
6. A. Hickling and J. V. Westwood, J. Chem. Soc., 1039 (1938).
7. A. Hickling and J. V. Westwood, ibid., 1109 (1939).
8. S. Glasstone and A. Hickling, Trans. Electrochem. Soc., 75, 333 (1939).
9. M. Moest, German Pat. 138442 (1901); Friedl, 7, 15 (1905).
10. H. Hofer and M. Moest, Annalen, 323, 284 (1902).
11. F. Fichter and A. Bürgin, Helv. Chim. Acta., 14, 90 (1931).
12. F. Fichter and F. Metz, ibid., 19, 880 (1936).
13. F. Fichter and R. Ruegg, ibid., 20, 1578 (1937).
14. F. Fichter and O. Leupin, ibid., 21, 616 (1938).
15. A. Kruis and W. Schanzer, Z. phys. Chem., 191A, 301 (1942).
16. S. Goldschmidt, W. Leicher, and H. Haas, Annalen, 577, 153 (1952).
17. R. Matsuda, J. Chem. Soc. Japan, 52, 249 (1931); Chem. Abs., 26, 5017 (1932).
18. S. N. Shukla and O. J. Walker, Trans. Faraday Soc., 27, 35 (1931).
19. K. Hopfgartner, Monatsch., 32, 523 (1911).
20. E. Denina, G. Ferrero, and F. Saverio de Paolini, Gazzetta, 68, 443 (1938); Chem. Abs., 32, 9041 (1938).
21. S. Landa and M. Landova, Chem. Listy, 24, 221 (1930); Chem. Zentr., II, 543 (1930).
22. S. Landa and M. Landova, Coll. Czech. Chem. Comm., 2, 31 (1930); Chem. Zentr., I, 1763 (1930).

23. L. Ružicka and M. Stoll, Helv. chim. acta, 17, 1308 (1934).
24. J. Petersen, Z. phys. Chem., 33, 295 (1900).
25. J. Petersen, Z. Elektrochem., 12, 141 (1906).
26. J. Hamonet, Compt. rend., 123, 252 (1896).
27. E. Baur, Helv. Chim. Acta, 22, 1120 (1939).
28. C. J. Brockman, "Electro-Organic Chemistry" (Translated into Russian), Izd. ONTI, 1937
29. N. M. Mel'nikov, Uspekhi Khim., 6, 4 (1937).
30. S. Swann, Trans. Electrochem. Soc., 69, 287 (1936).
31. S. Swann, ibid., 77, 459 (1940).
32. S. Swann, ibid., 88, 103 (1945).
33. F. Fichter, Organische Elektrochemie, Dresden und Leipzig, 1942.
34. B. C. L. Weedon, Quart. Rev., 6, 380 (1952).
35. N. A. Bunge, Zhur. Russ. Khim. Obshch., 21, 525 (1889).
36. T. S. Murray, J. Chem. Soc., 61, 10 (1892).
37. S. Glasstone and A. Hickling, ibid., 1878 (1934).
38. A. Hickling, Quart. Rev., 3, 121 (1949).
39. F. Foerster and A. Piguet, Z. Elektrochem., 10, 729 (1904).
40. D. A. Fairweather and O. J. Walker, J. Chem. Soc., 3111 (1926).
41. G. Preuner, Z. phys. Chem., 59, 670 (1907).
42. F. Foerster and A. Piguet, Z. Elektrochem., 10, 924 (1904).
43. J. B. Robertson, J. Chem. Soc., 127, 2057 (1925).
44. J. Robertson, Trans. Faraday Soc., 30, 1007 (1934).
45. S. Glasstone and A. Hickling, Chem. Rev., 25, 407 (1939); Uspekhi Khim., 10, 308 (1941).
46. T. S. Murray, Proc. Chem. Soc., 134, (1891).
47. M. Matsui, Ken-ichi-Kizaki, Mem. Coll. Sci. Kyoto Univ., 16A, 297 (1933); Chem. Abs., 29, 1018 (1935).
48. Kunugi Taiseki, J. Amer. Chem. Soc., 75, 1597 (1953).
49. R. Schreiner, Z. Elektrochem., 36, 953 (1930).
50. E. Baur, ibid., 37, 254 (1931).
51. S. Glasstone and A. Hickling, Nature, 133, 177 (1934).
52. F. Fichter and W. Lindenmaier, Helv. Chim. Acta, 12, 559 (1929).
53. L. Mermejo and L. Blas, Anales real Soc. espan. Fís. Quím. 27, 228 (1929); Chem. Zentr., II, 712 (1929).
54. R. Matsuda, J. Chem. Soc. Japan, 51, 632 (1930); Chem. Abs., 26, 382 (1932).
55. R. Matsuda and S. Morita, ibid., 51, 126 (1930); Chem. Abs., 24, 3698 (1930).
56. F. Fichter and R. E. Meyer, Helv. Chim. Acta, 16, 1408 (1933).
57. R. Matsuda, J. Chem. Soc. Japan, 52, 756 (1931); Chem. Abs., 26, 5017 (1932).
58. J. Haberman, Monatsch., 7, 529 (1886).
59. G. N. Antonov, Zhur. Russ. Khim. Obshch., 36, 5 (1904).
60. G. N. Antonoff, Z. angew. Chem., 17, 423 (1904).
61. J. Salause, Bull. Soc. chim. France, 37, 522 (1925).
62. J. Salause, Compt. rend., 180, 662 (1925).
63. S. Glasstone and A. Hickling, J. Chem. Soc., 820 (1936).
64. J. Petersen, Z. phys. Chem., 33, 99 (1900).
65. A. Renard, Jahresber., 1879, 481.
66. E. Müller and S. Tanaka, Z. Elektrochem., 34, 256 (1928)
67. E. Müller, ibid., 33, 561 (1927).
68. E. Baur, Helv. Chim. Acta, 11, 372 (1928).
69. A. Brester, Z. Chem., 9, 680 (1866).
70. A. Brester, Jahresber., 86 (1866).
71. N. A. Bunge, Ber., 9, 1598 (1876).
72. N. A. Bunge, Zhur. Russ. Khim. Obshch., 12, 415 (1880).
73. H. Jahn, Ann. Phys. und Chem., 37, 408 (1889).
74. F. Salzer, Z. Elektrochem., 8, 893 (1902).
75. A. Brochet and J. Petit, Compt. rend., 140, 442 (1905).
76. A. Brochet and J. Petit, Z. Elektrochem., 2, 441 (1905).
77. H. S. C. Deville and H. Debrau, Compt. rend., 78, 1782 (1874).
78. H. Schade, Z. phys. Chem., 57, 1 (1907).
79. T. Blackadder, ibid., 81, 385 (1913).
80. N. Zelinsky and N. Glinka, Ber., 44, 2305 (1911).
81. H. Wieland, Ber., 46, 3327 (1913).
82. E. Müller, Z. Elektrochem., 28, 307 (1922).
83. E. Müller, ibid., 29, 264 (1923).
84. L. Merle, Bull. Union Physiciens, 49, 360 (1955); Chem. Zentr., 3488 (1957).
85. G. Preuner and E. B. Ludlam, Z. phys. Chem., 59, 682 (1907).
86. S. N. Shukla and O. J. Walker, Trans. Faraday Soc., 27, 722 (1931).
87. J. W. Shipley and M. T. Rogers, Canad. J. Research [B], 17, 147, 167 (1939).
88. R. Lautie, Bull. Soc. Chim. France, Nos. 1–2, 63 (1948).
89. E. Baur, Z. Elektrochem., 29, 105 (1923).
90. C. L. Wilson and W. T. Lippincott, J. Electrochem. Soc., 103, 672 (1956).
91. C. L. Wilson and W. T. Lippincott, J. Amer. Chem. Soc., 78, 4290 (1956).
92. Lassar-Cohn, Annalen, 251, 335 (1889).
93. E. Berl, Ber., 37, 325 (1904).
94. G. B. Moorhouse, Trans. Faraday Soc., 28, 766 (1932).
95. J. Petersen, Z. Elektrochem., 20, 328 (1914).
96. M. E. Mulder, Rec. Trav. chim., 19, 146 (1900).
97. H. T. S. Britton and O. B. Westcott, Trans. Faraday Soc., 28, 627 (1932).
98. S. Schall and W. Melzer, Z. Elektrochem., 28, 474 (1922).
99. S. Schall, ibid., 28, 506 (1922).
100. S. Schall and H. Markgraf, Trans. Amer. Electrochem. Soc. 45, 161 (1924).
101. S. Schall and C. Thieme-Wiedtmarckter, Z. Elektrochem., 35, 337 (1929).
102. S. Schall and B. M. Schall, ibid., 40, 5 (1934).
103. P. Hölemann and K. Clusius, Z. phys. Chem., 35B, 261 (1937).
104. K. Clusius and W. Schanzer, ibid., 192A, 273 (1943).
105. H. Erlenmeyer and W. Schoenauer, Helv. Chim. Acta, 20, 222 (1937).
106. F. Muller, Z. Elektrochem., 33, 568 (1927).
107. H. R. Matsuda, Bull. Chem. Soc. Japan, 7, 297 (1932); Chem. Abs., 27, 269 (1933).
108. S. Goldschmidt and E. Stöckl, Ber., 85, 630 (1952).
109. P. Hölemann and K. Clusius, Ber., 70, 819 (1937).
110. W. Schanzer and K. Clusius, Z. phys. Chem., 190A, 241 (1942).
111. J. C. Brazier and G. Gofsleth, Annalen, 75, 249 (1850).
112. P. Rohland, Z. Elektrochem., 4, 120 (1897).
113. J. V. Karabinos, J. Sci. Counselor, 17, 3 (1954); Chem. Abs., 49, 4508 (1955).
114. G. Hallie, Rec. Trav. chim., 57, 152 (1938).
115. H. A. Offe, German Patent, 855 403 (1952); Chem. Abs., 49, 12163 (1955).
116. R. L. Kronenthal, U. S. Patent, 2 760 926 (1956); Chem. Abs., 51, 3329 (1957).
117. A. W. Schmidt, V. Schoeller, and K. Eberlein, Ber., 74B, 1313 (1941).
118. U. S. Patent, 2 022 894 (1932).
119. L. G. Ginger and R. J. Anderson, J. Biol. Chem., 157, 213 (1945).
120. A. C. Brown and J. Walker, Annalen, 274, 41 (1893).
121. L. Bouveault, Bull. Soc. chim. France, [3], 29, 1042, 1046 (1903).
122. F. Fichter and A. Maritz, Helv. Chim. Acta, 22, 265 (1939).
123. A. R. Murray and T. W. J. Taylor, J. Chem. Soc., 1450 (1937).
124. R. P. Linstead, B. C. L. Weedon, and B. Wladislaw, ibid., 1097 (1955).
125. D. G. Bounds, R. P. Linstead, and B. C. L. Weedon, ibid., 448 (1954).
126. L. Dolejs and L. Novotny, Chem. Listy, 48, 401 (1954); Chem. Abs., 49, 3881 (1955).
127. W. Fuchs and E. Dickersbach-Baronetzky, Fette. u. Seifen, 57, 675 (1955).
128. German Patent, 854 508 (1952); Chem. Abs., 52, 7914 (1958).
129. F. Fichter and H. Buess, Helv. Chim. Acta, 18, 445 (1935).
130. J. Walker and J. S. Lumsden, J. Chem. Soc., 79, 1197 (1901).

131. G. Kompa, Ber., 34, 895 (1901).
132. D. A. Fairweather, Proc. Roy. Soc. Edinburgh, 46, 71 (1926).
133. K. Stosius and K. Wiesler, Biochem. Z., 108, 75 (1920).
134. M. Carmichael, J. Chem. Soc., 2545 (1922).
135. E. K. Smol'yaninova, N. P. Solov'eva, G. E. Svadkovskaya and V. N. Belov, "Trudy Vsesoyuznogo Nauchno Issledovatel'skogo Instituta Sinteticheskikh i Natural'nykh Sinteticheskikh Veshchestv" (Transactions of the All-Union Research Institute for Synthetic and Natural Scents), 2nd Edition, Pishchepromizdat, 1954, p. 34.
136. G. M. Bennett and H. Gudgeon, J. Chem. Soc., 1679 (1938).
137. F. L. M. Pattison, J. B. Stothers, and R. G. Woolford, J. Amer. Chem. Soc., 78, 2255 (1956).
138. W. S. Greaves, R. P. Linstead, B. R. Shephard, S. L. S. Thomas, and B. C. L. Weedon, J. Chem. Soc., 3326 (1950).
139. V. M. Rodinov and E. K. Smol'yaninova, "Trudy Vsesoyuznogo Nauchno Issledovatel'skogo Instituta Sinteticheskikh i Natural'nykh Sinteticheskikh Veshchestv" (Transactions of the All-Union Research Institute for Synthetic and Natural Scents), 1st Edition, Pishchepromizdat, 1952, p. 63.
140. A. Franke and O. Liebermann, Monatsch., 43, 589 (1922).
141. "Organic Syntheses" (Translated into Russian), Vol. 3, Inostr. Lit., Moscow, 1952, p. 508.
142. E. A. Ogorodnikova, N. N. Shevyakova, E. K. Smol'yaninova, V. M. Rodionov, and V. N. Belov, Dokl. Akad. Nauk SSSR, 90, 553 (1953).
143. N. L. Drake, H. W. Carhart, and R. Mozingo, J. Amer. Chem. Soc., 63, 617 (1941).
144. Shichiro Shiina, J. Soc. Chem. Ind. Japan, 40, 324 (1937); Chem. Abs., 32, 499 (1938).
145. P. Pfeiffer and E. Lübbe, J. prakt. Chem., 136, 321 (1933).
146. L. Ružicka, M. Stoll, and H. Schinz, Helv. Chim. Acta, 11, 1174 (1928).
147. R. Signer and P. Sprecher, ibid., 30, 1001 (1947).
148. L. Ružicka and M. Stoll, ibid., 16, 493 (1933).
149. D. A. Fairweather, Proc. Roy. Soc. Edinburgh, 45, 283 (1925).
150. E. S. Wallis and F. H. Adams, J. Amer. Chem. Soc., 55, 3838 (1933).
151. J. Brenner and K. Mislow, J. Org. Chem., 21, 1312 (1956).
152. S. Swann, Trans. Electrochem Soc., 56, 457 (1929).
153. F. Fichter and M. Rudin, Helv. Chim. Acta, 24, 398E (1941).
154. S. Ishikawa and M. Tutui, Bull. Inst. Phys. Chem. Research (Tokio), Chem. Ed., 23, 47 (1944); Chem. Abs., 43, 7897 (1949).
155. J. Walker and A. P. Walker, J. Chem. Soc., 87, 961 (1905).
156. D. C. Chrichton, ibid., 89, 929 (1906).
157. E. H. Farmer and J. Krakovski, ibid., 2318 (1926).
158. P. Karrer, F. Benz, and M. Stoll, Helv. Chim. Acta, 16, 297 (1933).
159. R. P. Linstead, J. C. Lunt, and B. C. L. Weedon, J. Chem. Soc., 3333 (1950).
160. J. Walker and J. K. Wood, ibid., 89, 598 (1906).
161. S. F. Birch, V. E. Gripp, D. T. McAllan, and W. S. Nathan, ibid., 1363 (1952).
162. H. A. Offe, German Patent, 880 289 (1953); Chem. Abs., 52, 7914 (1958).
163. R. P. Linstead, J. C. Lunt, B. C. L. Weedon, and B. R. Shephard, J. Chem. Soc., 3621 (1952).
164. P. Karrer, F. Benz, R. Morf, H. Raudnitz, M. Stoll, and T. Takahashi, Helv. Chim. Acta, 15, 1399 (1932).
165. J. Petersen, Z. Elektrochem., 18, 710 (1912).
166. F. Fichter and J. Rosenzweig, Helv. Chim. Acta., 18, 238 (1935).
167. A. D. Petrov and D. A. Vyakhirev, Zhur. Obshch. Khim., 9, 513 (1939).
168. P. Karrer and M. Stoll, Helv. Chim. Acta, 14, 1189 (1931).
169. F. Fichter and A. Petrovitch, ibid., 24, 549 (1941).
170. F. Fichter and T. Holbro, ibid., 20, 333 (1937).
171. D. G. Bounds, R. P. Linstead, and B. C. L. Weedon, J. Chem. Soc., 2393 (1953).
172. L. Canonica, M. Martinolli, and T. Baccheti, Atti. Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat., 13, 61 (1952); Chem. Abs., 47, 11131 (1953).
173. S. Ueno and T. Tamura, J. Soc. Chem. Ind. Japan, 46, 1213 (1943); Chem. Abs., 42, 6735 (1948).
174. M. V. Dover and C. J. Helmers, Ind. Eng. Chem., 27, 455 (1935).
175. S. Kitaura, Bull. Inst. Phys. Chem. Res. Tokyo, 16, 765 (1937); Chem. Abs., 32, 4523 (1938).
176. German Patent 624 331 (1936); Chem. Abs., 30, 2504 (1936).
177. T. Teri, F. Ono, J. Toyama, and H. Marumo, J. Chem. Soc. Japan, Ind. Chem. Sect., 54, 47 (1951); Chem. Zentr., 5236
178. B. W. Baker, R. W. Kierstead, R. P. Linstead, and B. C. L. Weedon, J. Chem. Soc., 1804 (1954).
179. E. Tommila, Suomen Kem., 6, Nos. 9–10, 70 (1933); Chem. Zentr., I, 830 (1934).
180. W. von Miller and J. Hofer, Ber., 27, 461 (1894).
181. J. W. Walker, J. Chem. Soc., 69, 1278 (1896).
182. D. A. Fairweather, Proc. Roy. Soc. Edinburgh, 45, 23 (1925).
183. H. Kolbe, Annalen, 113, 244 (1860).
184. E. Tommila, Suomen Kem., 8B, 25 (1935); Chem. Abs., 29, 5752 (1935).
185. I. G. Smull and P. Subkov, Chem. and Met., 28, 357 (1923).
186. E. Tommila, Acta Chem. Fennicae, 7B, 87 (1934); Chem. Abs., 29, 2094 (1935).
187. J. Hamonet, Compt. rend., 132, 259 (1901).
188. J. Hamonet, Bull. Soc. Chim. France, [3], 33, 513 (1905).
189. F. Fichter and A. Schnider, Helv. Chim. Acta, 14, 857 (1931).
190. J. Hamonet, Compt. rend., 136, 96 (1903).
191. A. A. Noyes, Amer. Chem. J., 19, 766 (1897).
192. L. V. Pisarzhevskii, Zhur. Russ. Khim. Obshch., 29, 289, 338 (1897).
193. B. L. Vanzetti and E. Manca, Gazzetta, 56, 112 (1926); Chem. Zentr., I, 3138 (1926).
194. C. Neuberg, Biochem. Z., 7, 527 (1908).
195. C. Neuberg, L. Scott, and S. Lachmann, Biochem. Z., 24, 152 (1910).
196. A. Wohl and H. Schweitzer, Ber., 39, 890 (1906).
197. S. Sugasawa, J. Pharm. Soc. Japan, 1927, No. 545; Chem. Zentr., II, 1814 (1927).
198. N. Stoll and A. Rouve, Helv. Chim. Acta, 20, 525 (1937).
199. H. Hofer, Ber., 33, 650 (1900).
200. G. W. Rockwell, J. Chem. Soc., 24, 719 (1902).
201. R. Willstätter and A. Pfannenstiel, Annalen, 422, I (1921).
202. Motoki, Odaka, Nikhon Kagaku Dzassi, J. Chem. Soc. Japan, Pure Chem. Sec., 76, No. 8, 930 (1955); Ref. Zhur. Khim., No. 5, 15244 (1957).
203. F. Fichter and S. Lurie, Helv. Chim. Acta, 16, 885 (1933).
204. F. Kaufler and C. Herzog, Ber., 42, 3858 (1909).
205. J. Troeger and E. Ewers, J. prakt. Chem., [2], 58, 121 (1898)
206. N. A. Bunge, Zhur. Russ. - Khim. Obshch., 24, 690 (1892).
207. F. Swarts, Bull. Soc. chim. belges., 42, 102 (1933); Chem. Abs., 27, 4741 (1933).
208. K. Elbs, J. prakt. Chem., [2], 47, 104 (1893).
209. K. Elbs and K. Kratz, ibid., [2], 55, 502 (1897).
Bull. Classe Sci., Acad. roy. Belg., [5], 17 27 (1931);
210. K. Elbs, Z. Elektrochem., 18, 662 (1912).
211. F. Fichter, A. Fritsch, and P. Müller, Helv. Chim. Acta, 6, 502 (1923).
212. F. Swarts, Bull. Sci. Acad. Roy. Belg., [5], 17, 27 (1931); Chem. Abs., 25, 3252 (1931).
213. J. Troeger and E. Ewers, J. prakt. Chem., 59, 464 (1899).
214. G. W. Thiessen and R. Miller, J. Amer. Chem. Soc., 77, 770 (1955).

215. H. Korsching, Ber., 86, 943 (1953).
216. H. Korsching, Naturwiss, 44, 89 (1957).
217. M. Lilienfeld, German Patent 147 943 (1902); Friedl., 7, 83 (1905).
218. O. Kühling, Ber., 38, 1638 (1905).
219. F. Fichter and M. Schmidt, Helv. Chim. Acta, 3, 704 (1920).
220. F. Fichter and F. Kühn, ibid., 7, 167 (1924).
221. R. P. Linstead, B. R. Shephard, and B. C. L. Weedon, J. Chem. Soc., 2854 (1951).
222. H. A. Offe, Z. Naturforsch., 2b, 182 (1947).
223. H. A. Offe, ibid., 2b, 185 (1947).
224. German Pat., DBP 900 813 (1954); Chem. Zentr., 125, 4037 (1954).
225. G. E. Mooro, Ber., 4, 519 (1871).
226. F. Fichter and A. Schnider, Helv. Chim. Acta, 13, 103 (1930).
227. F. Fichter, Z. Elektrochem., 20, 471 (1914).
228. F. Fichter and T. Lichtenhahn, Ber., 48, 1949 (1915).
229. F. Fichter, R. Brändlin, and E. R. Hallauer, Helv. Chim. Acta, 3, 410 (1920).
230. F. Fichter and H. Reeb, ibid., 6, 450 (1923).
231. N. Ya. Tem'yanov, Zhur. Obshch. Khim., 61, 1861 (1929).
232. F. Fichter and H. Spiegelberg, Helv. Chim. Acta, 12, 1152 (1929).
233. F. Fichter, Z. Elektrochem., 35, 710 (1929).
234. N. Ya. Demyanow and M. Doyarenko, Ber., 40, 2594 (1907).
235. N. Ya. Dem'yanov, Zhur. Russ. Khim. Obshch., 35, 314 (1904).
236. F. Fichter and C. Simon, Helv. Chim. Acta, 17, 717 (1934).
237. F. Fichter and W. Siegrist, ibid., 15, 698 (1932).
238. F. Fichter and A. Petrovitch, ibid., 23, 806 (1940).
239. C. T. Blood, N. J. Gartwright, and R. P. Linstead, J. Chem. Soc., 2268 (1952).
240. F. Fichter and C. Simon, Helv. Chim. Acta, 17, 1218 (1934).
241. C. G. Overberger and P. Kabasakalian, J. Org. Chem., 21, 1124 (1956).
242. F. Fichter and T. Holbro, Helv. Chim. Acta, 21, 141 (1938).
243. J. Walker, J. Chem. Soc., 63, 495 (1893).
244. J. Walker and J. Henderson, ibid., 67, 337 (1895).
245. J. Walker and J. Henderson, ibid., 69, 748 (1896).
246. J. Walker and J. Henderson, Chem. News, 73, 254 (1896).
247. J. Walker and J. K. Wood J. Chem. Soc., 77, 383 (1900).
248. J. Walker and W. Cormack, ibid., 77, 374 (1900).
249. J. Walker and W. Cormack, Proc. Chem. Soc., 16, 58 (1901).
250. W. Löb, Z. Elektrochem., 2, 663 (1896).
251. C. Schall, ibid., 6, 102 (1899).
252. F. Fichter and E. Uhl, Helv. Chim. Acta, 3, 22 (1920).
253. F. Fichter and R. E. Meyer, ibid., 17, 535 (1934).
254. C. Schall, Z. Elektrochem., 24, 154 (1918).
255. C. Schall, ibid., 21, 69 (1915).
256. H. Labhardt and R. Zschoche, ibid., 8, 93 (1902).
257. A. J. Allmand and A. Puttik, Trans. Faraday Soc., 23, 641 (1927).
258. V. M. Rodionov, V. N. Belov, and V. V. Levchenko, Zhur. Obshch. Khim., 5, 1817 (1935).
259. F. Fichter, H. Stenzl, and E. Beglinger, Helv. Chim. Acta, 21, 375 (1938).
260. T. Slawik, Ber., 7, 1051 (1874).
261. H. Katagishi, J. Ginbayashi, and M. Matsui, Mem. Coll. Sci. Kyoto Univ., 12A, 57 (1929); Chem. Zentr., I, 2980, 1929.
262. W. Von Miller, Z. Elektrochem., 4, 55 (1897).
263. F. Fichter and H. Stenzl, Roczniki Chem., 18, 510 (1938); Chem. Abs., 33, 4136 (1939).
264. F. Fichter and H. Stenzl, Helv. Chim. Acta, 22, 425 (1939).
265. F. Fichter and H. Stenzl, ibid., 22, 970 (1939).
266. R. P. Linstead, B. R. Shephard, and B. C. L. Weedon, J. Chem. Soc., 3624 (1952).
267. F. Fichter and K. Kestenholz, Helv. Chim. Acta, 25, 785 (1942).
268. A. J. von der Hock and W. T. Nauta, Rec. Trav. chim., 61, 845 (1942).
269. L. Riccoboni, Gazzetta, 70, 748 (1940); Chem. Abs., 35, 6252 (1941).
270. E. A. Evans and M. Whalley, J. Chem. Soc., 3642 (1954).
271. H. Breederveld and E. C. Koyman, Rec. Trav. chim., 76, 297 (1957).
272. J. Petersen, Z. phys. Chem., 33, 698 (1900).
273. N. Bunge, Ber., 9, 78 (1876).
274. F. Oettel, Z. Elektrochem., 1, 90 (1894).
275. O. Mumm, Z. phys. Chem., 59, 497 (1907).
276. F. Ageno and G. Donini, Gazzetta, 40, I, 21 (1910); Chem. Zentr., I, 1426 (1910).
277. L. Balbiano and A. Alessi, Ber., 15, 2236 (1882).
278. H. von Miller, J. prakt. Chem., [2], 19, 326 (1879).
279. C. Schall, Z. Elektrochem., 22, 422 (1916).
280. A. Kekulé, Annalen, 131, 79 (1864).
281. F. Fichter and A. Fritsch, Helv. Chim. Acta, 6, 329 (1923).
282. C. H. Clarke and E. F. Smith, J. Amer. Chem. Soc., 21, 967 (1899).
283. A. M. Clover and A. C. Houghton, Amer. Chem. J., 32, 43 (1904).
284. B. L. Vanzetti, Gazzetta, 34, II, 511 (1904).
285. B. L. Vanzetti, ibid., 37, II, 338 (1907); Chem. Abs., 2, 3341 (1908).
286. B. L. Vanzetti, Atti Accad. naz. Lincei, Rend. Classe. Sci. fis. mat. nat., [5], 17, II, 331 (1908); Chem. Zentr., II, 1774 (1908).
287. B. L. Vanzetti, Gazzetta, 38, I, 47 (1908); Chem. Zentr., I, 643 (1909).
288. B. L. Vanzetti, Gazzetta, 39, I, 46 (1909); Chem. Abs., 3, 1004 (1909).
289. B. L. Vanzetti, Atti. Accad. naz. Lincei, Rend. Classe. Sci. fis. mat. nat., [5], 16, II, 79, 139 (1907); Chem. Zentr., II, 1061 (1907).
290. B. L. Vanzetti, Gazzetta, 37, II, 386 (1907); Chem. Zentr., II, 2038 (1907).
291. E. Tommila, Ann. Acad. Sci. Fennicae, Ser. 36A, No. 1, 7 (1932); Chem. Zentr., II, 2310 (1932).
292. E. A. Pasquinelli, Anal. Asoc. quim. argentina, 31, 181 (1943); Chem. Abs., 38, 5734 (1944).
293. C. G. Overberger and P. Kabasakalian, J. Amer. Chem. Soc., 79, 3182 (1957).
294. M. E. Bourgoin, Ber., 7, 1039 (1874).
295. F. Henrich and A. Herzog, Ber., 52, 2126 (1919).
296. G. Aarland, J. prakt. Chem., [2], 7, 142 (1873).
297. G. Aarland and E. Garstanjen, ibid., [2], 4, 376 (1871).
298. G. Aarland, ibid., [2], 6, 256 (1873).
299. W. Lossen, Annalen, 342, 157 (1905).
300. F. Henrich and W. Schenk, Ber., 52, 2120 (1919).
301. B. L. Vanzetti, Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat., [5], 24, I, 611 (1915); Chem. Zentr., II, 178 (1915).
302. B. L. Vanzetti, Gazzetta, 46, I, 49 (1916); Chem. Zentr., I, 881 (1916).
303. C. Schorlemmer, Annalen, 136, 257 (1865).
304. H. Ageta and A. Tanaka, J. Pharm. Soc. Japan, 76, 960 (1956); Ref. Zhur. Khim., 1957, 30, 500, No. 9.
305. German Pat., DBP 960 188 (1957);
306. Koichi Kimura, Mitsuo Takahashi, Akira Tanaka, and Jakugaky Zasshi, J. Pharm. Soc. Japan, 78, 802 (1958); Chem. Abs., 52, 16085 (1958).
307. M. Asano and J. Ohta, J. Pharm. Soc. Japan, 65, 10 (1945); Chem. Abs., 45, 4302 (1951).
308. R. P. Linstead, J. C. Lunt, and B. C. L. Weedon, J. Chem. Soc., 3331 (1950).
309. M. Asano, J. Kamdta, and T. Wada, J. Pharm. Soc. Japan, 65, 5 (1945); Chem. Abs., 45, 5617 (1951).

310. R. P. Linstead, B. R. Shephard, B. C. L. Weedon, and J. C. Lunt, J. Chem. Soc., 1538 (1953).
311. R. Cavanna and S. Ställberg-Stenhagen, Ricerca sci., 20, 1709 (1950); Chem. Abs., 45, 6573 (1951).
312. S. Ställberg-Stenhagen, Arkiv Kemi., 2, 95 (1950); Chem. Abs., 44, 7761 (1950).
313. R. Cavanna and S. Ställberg-Stenhagen, Atti. Acad. naz. Lincei, Rend. Classe Sci. fis. mat. nat., 3, 31 (1950); Chem. Abs., 45, 9470 (1951).
314. G. Ställberg, Arkiv Kemi., 12, 153 (1958); Chem. Abs., 52, 13 635 (1958).
315. R. P. Linstead, J. C. Lunt, and B. C. L. Weedon, J. Chem. Soc., 1130 (1951).
316. L. Ružicka, M. Stoll, W. Scherrer, H. Schinz, and C. F. Seidel, Helv. Chim. Acta, 15, 1459 (1932).
317. G. Gustbee and E. Stenhagen, Svensk. kem. Tidskr., 54, 243 (1942); Chem. Abs., 38, 3611 (1944).
318. L. Ružicka, M. Stoll, and H. Schinz, Helv. Chim. Acta, 11, 670 (1928).
319. D. G. Bounds, R. P. Linstead, and B. C. L. Weedon, J. Chem. Soc., 4219 (1954).
320. U. S. Patent, 2 680 713 (1954); Chem. Abs., 48, 9847 (1954).
321. B. W. Baker, R. P. Linstead, and B. C. L. Weedon, J. Chem. Soc., 2218 (1955).
322. Motooki Matsui and Shingo Arakawa, Mem. Coll. Sci. Kyoto, Univ., 15A, 189 (1932); Chem. Abs., 26, 5264 (1932).
323. H. Hunsdiecker, Ber., 75, 447 (1942).
324. Motoki and Odaka, J. Chem Soc. Japan, Pure Chem. Sec., 77, No. 1, 163 (1956).
325. Jap. Patent, 6628 (1957); Chem. Abs., 52, 9821 (1958).
326. H. Hunsdiecker, Ber., 75, 460, 1197 (1942).
327. M. Stoll, Helv. Chim. Acta, 34, 1817 (1951).
328. German Patent, 857 496 (1952); Chem. Abs., 52, 10 158 (1958).
329. M. Asano, J. Kameda, and T. Wada, J. Pharm. Soc. Japan, 64, 25 (1944); Chem. Abs., 45, 4302 (1951).
330. M. Asano, J. Kameda, and T. Wada, ibid., 65, 15 (1945); Chem. Abs., 45, 4303 (1951).
331. T. Moroe, ibid., 70, 416 (1950); Chem. Abs., 45, 2396 (1951).
332. T. Moroe, ibid., 71, 123 (1951); Chem. Abs., 45, 8456 (1951).
333. T. Moroe, ibid., 71, 121 (1951); Chem. Abs., 45, 8456 (1951).
334. W. von Miller and H. Hofer, Ber., 28, 2427 (1895).
335. G. I. Samokhvalov, V. E. Sibirtseva, E. I. Genkin, and N. A. Preobrazhenskii, Dokl. Akad. Nauk SSSR, 84, 729 (1952).
336. G. E. Svadkovskaya, S. A. Voĭtkevich, E. K. Smol'yaninova, and V. N. Belov, Zhur. Obshch. Khim., 27, 2146 (1957).
337. G. E. Svadkovskaya, E. K. Smol'yaninova, and V. N. Belov, Zhur. Obshch. Khim., 28, 2268 (1958).
338. R. E. Gibson, J. Chem. Soc., 127, 475 (1925).
339. M. E. Bourgoin, Compt. rend., 65, 892, 998 (1867).
340. M. E. Bourgoin, Ann. Chim. Phys., [4], 14, 151 (1868).
341. C. Schall, Z. Elektrochem., 3, 83 (1896).
342. F. Fichter and E. Krummenacher, Helv. Chim. Acta, 1, 146 (1918).
343. F. Fichter, Trans Electrochem. Soc., 56, 8 (1929); Chem. Zentr., I, 501 (1930).
344. F. Fichter, Bull. Soc. chim. France, [5], 1, 1585 (1934).
345. F. Fichter, Trans Electrochem. Soc., 75, 309 (1939).
346. H. R. Matsuda, Bull. Chem. Soc. Japan, 7, 18 (1932); Chem. Zentr., I, 2703 (1932).
347. R. Matuda and S. Ikuta, Bull. Chem. Soc. Japan, 15, 322 (1940); Chem. Abs., 45, 985 (1941).
348. E. Brenner, Helv. Chim. Acta, 8, 651 (1925).
349. S. Goldschmidt, Angew. Chem., 69, 132 (1957).
350. S. Glasstone and A. Hickling, J. Chem. Soc., 2345, 2800 (1932).
351. S. Glasstone and A. Hickling, ibid., 829 (1933).
352. S. Glasstone and A. Hicking, ibid., 10, 1772 (1934).
353. S. Glasstone and A. Hickling, Trans. Electrochem. Soc., 75, 18 (1939); Chem. Abs., 33, 2815 (1939).
354. F. Fichter and R. Zumbrunn, Helv. Chim. Acta, 10, 869 (1927).
355. O. J. Walker, J. Chem. Soc., 2040 (1928).
356. O. J. Walker and G. L. E. Wild, ibid., 207 (1935).
357. O. J. Walker and G. L. E. Wild, ibid., 1132 (1937).
358. S. N. Shukla and O. J. Walker, Trans. Faraday Soc., 28, 457 (1932).
359. G. V. Shulz, Z. phys. Chem., [B], 30, 379 (1935).
360. K. Ziegler, W. Deparade, and H. Kühlhorn, Annalen, 567, 151 (1950).
361. S. Goldschmidt and M. Minsinger, Ber., 87, 956 (1954).
362. S. Goldschmidt and K. Dachs, Ber., 88, 583 (1955).
363. M. Haissinsky and M. Cotton, Compt. rend., 224, 392, 467 (1947).
364. F. Fichter and J. Heer, Helv. Chim. Acta, 18, 704 (1935).
365. F. Fichter and J. Heer, ibid., 19, 149 (1936).
366. F. Fichter and K. Humpert, ibid., 9, 692 (1926).
367. F. Fichter and E. Brunner, ibid., 12, 573 (1929).
368. L. M. Volchnova and A. I. Krasil'shchikov, Zhur. Fiz. Khim., 23, 441 (1949).
369. Ts. I. Zalkind and B. V. Ershler, Zhur. Fiz. Khim., 25, 565 (1951).
370. F. Förster, Z. Elektrochem., 13, 414 (1907).
371. K. I. Rozental' and V. I. Veselovskii, Zhur. Fiz. Khim., 27, 1163 (1953).
372. T. I. Borisova and V. I. Veselovskii, ibid., 27, 1195 (1953).
373. K. I. Rozental' and V. I. Veselovskii, Dokl. Akad. Nauk SSSR, 111, 637 (1956).

Research Institute for Synthetic and Natural Scents

THE MECHANISM OF TRANSPORT OF MATTER IN POROUS SORBENTS

D. P. Timofeev

CONTENTS

Introduction 181

I. Transport of non-adsorbed gases 181

Viscous flow 181

Molecular diffusion 182

Gas flow in the transition region 183

Model of a porous body. Mixed transport 184

II. Transport of adsorbed gases 185

Diffusion along the sorbent surface 185

Activation energy of the diffusion process in porous bodies 187

Other methods for appraising the role of the migration effect 189

Flow of liquid adsorbates 189

Capillary flow 189