

# Electrolysis of a Mixture of Two Fatty Acids

By

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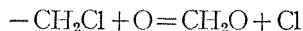
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Kolbe's reaction, which various fatty acids undergo on electrolysis, is not always the same, even when the electrolysis is conducted under exactly the same conditions; some produce a saturated hydrocarbon such as methane or ethane, and others an unsaturated one like ethylene, and not seldom alcohols and esters are formed instead of hydrocarbons. Whether the anodic reactions which give rise to these different products fundamentally differ from each other, or whether the reaction which primarily takes place at the anode is always the same but the products of the primary reaction undergo secondary reactions in many different ways is still an unsettled problem.

In the hope of contributing to the solution of this problem, authors took up the study of the electrolysis of two fatty acids mixed together. The idea was as follows: If propylene, which is the main product of electrolysis of propionic acid, is the substance primarily formed anodically, the existence of the ethyl radical in considerable concentration at the anode cannot be imagined, and as a consequence, the reaction in which the ethyl radical may be regarded to have taken part will never be expected to occur in that electrolysis. Nevertheless, as is described in the experimental part of this report, when propionic acid was electrolysed together with a higher fatty acid such as palmitic or stearic acid, a new hydrocarbon consisting of the alkyl radicals of both fatty acids is produced, besides the hydrocarbons formed in the electrolysis of each individual acid. Moreover, the molecular proportion of two hydrocarbons  $C_{17}H_{36}$  and  $C_{30}H_{62}$  formed from a mixture of propionic acid and palmitic acid was nearly the same as that of two hydrocarbons  $C_{16}H_{34}$  and  $C_{30}H_{62}$  produced from a mixture of acetic acid and palmitic acid, as is seen in the following table:—

Acid	Molecular proportion, taken	Hydrocarbon
CH <sub>3</sub> CO <sub>2</sub> H C <sub>15</sub> H <sub>31</sub> CO <sub>2</sub> H	1.5 : 1	C <sub>16</sub> H <sub>34</sub> C <sub>30</sub> H <sub>62</sub> (1.3 : 1)
CH <sub>3</sub> CO <sub>2</sub> H C <sub>17</sub> H <sub>35</sub> CO <sub>2</sub> H	1.5 : 1	C <sub>18</sub> H <sub>38</sub> C <sub>34</sub> H <sub>70</sub> (1.5 : 1)
C <sub>2</sub> H <sub>5</sub> CO <sub>2</sub> H C <sub>15</sub> H <sub>31</sub> CO <sub>2</sub> H	1.5 : 1	C <sub>17</sub> H <sub>30</sub> C <sub>30</sub> H <sub>62</sub> (1.4 : 1)
C <sub>3</sub> H <sub>7</sub> CO <sub>2</sub> H C <sub>15</sub> H <sub>31</sub> CO <sub>2</sub> H	1.5 : 1	C <sub>18</sub> H <sub>38</sub> C <sub>30</sub> H <sub>62</sub> (1.4 : 1)
ClCH <sub>2</sub> CO <sub>2</sub> H C <sub>15</sub> H <sub>31</sub> CO <sub>2</sub> H	1 : 1	C <sub>16</sub> H <sub>33</sub> Cl C <sub>30</sub> H <sub>62</sub> (1.1 : 1)

It is very remarkable that monochloracetate ion, which has hitherto<sup>1</sup> been considered never to give off  $-\text{CH}_2\text{Cl}$  radical even for a moment, but immediately to decompose into  $\text{CH}_2\text{O} + \text{CO} + \text{Cl}$  at the instant of its discharge, behaves in a manner exactly analogous to acetate and other fatty acid ions, when electrolysed in the presence of higher fatty acids. There remains, therefore, no room to doubt the primary formation of the chloracetyl radical in the electrolysis of chloracetic acid. The reason why ethylene chloride is not formed electrolytically can be explained by assuming that the radical is more liable to undergo oxidation than polymerisation, and therefore changes into formaldehyde and chlorine without giving rise to ethylene chloride.



The apparently different anodic reactions of various fatty acids may perhaps be attributed to the different stability and other chemical properties of the products formed by the primary anodic reaction, which must be regarded as being always the same throughout all fatty acids. What kind of substance that primary product is cannot be decided at present. Still, the authors are much inclined to believe it

1. F. Kaufler and C. Herzog, Ber. **42**, 3858 (1909); **43**, 266 (1910); C. J. Brockman, *Electro-organic Chemistry*, 1 Ed., p. 46.

to be the peroxide. Recently R. Matsuda<sup>1</sup>, studying the relation between Kolbe's reaction and hydrogen ion concentration, observed the very interesting fact that Kolbe's reaction is always accompanied by the formation of a substance having a peroxide nature, and that these two actions never take place independently of each other. Evidence recently obtained by Shukla and Walker<sup>2</sup>, showing the presence of long overlooked methane amongst the anode gases, provides another strong argument for the peroxide theory.

## Experimental

### 1. Acetic acid and Palmitic acid

To prepare the electrolytic solution, 15 grams of palmitic acid and 5 grams of potassium carbonate were warmed with 50 c.c. of water, and to the solution thus formed 17 grams of potassium acetate dissolved in 25 c.c. of water and 5 grams of palmitic acid dissolved in 50 c.c. of 95% alcohol were added. After the bath had been cooled internally and externally the electrolytic solution was electrolysed by passing a current of 12–13 amperes to electrodes consisting of platinum plates 15 sq. cms. in area. The temperature was always maintained at 70°–75°. In the course of the electrolysis the solution was charged twice with 5 grams of palmitic acid at intervals of 4 hours, and also with some sodium carbonate to regulate the current strength. Thus the total quantity of palmitic acid taken for electrolysis was 30 grams, and that of acetic acid 10.5 grams. After the electrolysis began, the solution became gradually coloured and finally separated into three layers. The middle (alcoholic) and the undermost (aqueous) layers contained no particular substance deemed to be the synthetic product; so, only the uppermost layer consisting chiefly of hydrocarbons was taken for examination.

The uppermost layer, which solidified on cooling, was warmed in a water-bath, after sufficient potassium carbonate solution had been added in order to remove free palmitic acid and ester. This treatment was repeated several times, and the residue was well washed with hot water and dried. The dry hydrocarbon mixture was then treated repeatedly with ether, in which a lower hydrocarbon, C<sub>16</sub>H<sub>34</sub>, dissolved,

1. Bull. Chem. Soc., Japan, **7**, 18 (1932).
2. Trans. Faraday Soc. **27**, 35 (1931).

together with a small quantity of a higher homologue,  $C_{30}H_{62}$ . The main part of the latter remained undissolved. The part soluble in ether was fractionated twice by distilling it under 5 mm. pressure, and nearly pure hexadecane having the following physical constants was obtained:

M. P.,  $170^{\circ}$ ; B. P.  $138^{\circ}-140^{\circ}$  (5 mm.),  $280^{\circ}-285^{\circ}$  (760 mm.)

The results of analysis and molecular weight determination were as follows:

0.1347 gm. of the substance gave 0.4163 gm.  $CO_2 + 0.1842$  gm.  $H_2O$

	Found	Calc. for $C_{16}H_{34}$
C (%)	84.29	84.96
H (%)	15.19	15.04

0.2230 gm. of the substance in 20.3056 gms. of benzene lowered the freezing point of the solvent by  $0.232^{\circ}$ .

Mol. Wt., 230 (calc., 226)

Triacotane  $C_{30}H_{62}$  was identified without much trouble, as it was easily isolated in a far purer state than hexadecane, though its melting point was found to be a little lower than that given by Petersen<sup>1</sup>.

## 2. Acetic acid and Stearic acid

A mixture of acetic acid and stearic acid was electrolysed under conditions similar to those given in 1, and the solution after electrolysis was also treated just in the same manner as in 1. Octadecane which was isolated, melted at  $27^{\circ}$  and boiled at  $155^{\circ}-160^{\circ}$  under 5 mm. pressure and at  $308^{\circ}$  under ordinary pressure. The results of analysis and molecular weight determination were as follows:

- 0.1241 gm. of the substance gave 0.3846 gm.  $CO_2 + 0.1679$  gm.  $H_2O$
- 0.1169 gm. " " " 0.3619 gm. " + 0.1585 gm. "

	Found		Calc. for $C_{18}H_{38}$
	1	2	
C (%)	84.54	84.43	85.04
H (%)	15.03	15.06	14.96

Benzene, 24.8436 gms.; the hydrocarbon, 0.2378 gm.; Depression of F. P.,  $0.184^{\circ}$ . Mol. Wt., 255 (Calc., 254)

Another hydrocarbon produced was identified as tetratriacontane,  $C_{34}H_{70}$ .

1. Zeit. Elektrochem., **12**, 143 (1906).

### 3. Propionic acid and Palmitic acid

Of two hydrocarbons obtained by electrolysing a mixture of propionic acid and palmitic acid in an analogous way, heptadecane,  $C_{17}H_{36}$ , was identified as follows:

M. P.,  $22^\circ$ ; B. P.,  $148^\circ - 150^\circ$  (5 mm.),  $290^\circ$  (760 mm.)

Mol. WT., 238 (Calc., 240)

Benzene, 25.7705 gms.; the substance, 0.1624 gm.; Depression of F. P.,  $0.130^\circ$ .

The results of analysis were:

1. 0.1148 gm. of the substance gave 0.3545 gm.  $CO_2$  + 0.1570 gm.  $H_2O$ .
2. 0.1182 gm. " " 0.3658 gm. " + 0.1607 gm. "

	Found		Calc. for $C_{17}H_{36}$
	1	2	
C (%)	84.22	84.40	84.94
H (%)	15.19	15.11	15.06

Another hydrocarbon was identified as triacontane.

### 4. Monochloroacetic acid and Palmitic acid

On electrolysing a mixture of monochloroacetic acid and palmitic acid under conditions similar to those employed in 1, cetyl chloride  $C_{16}H_{33}Cl$  was obtained as an oil boiling at  $150^\circ$  under 5 mm. pressure. It decomposed when boiled under ordinary pressure. Its specific gravity at  $12^\circ$  was found to be 0.842. The molecular weight determined by the cryoscopic method was as follows:

0.1270 gm. of the substance dissolved in 23.0007 gms. of benzene lowered the freezing point of the solvent by  $0.113^\circ$ . Mol. Wt., 250 (Calc. 261).

The chlorine content was determined by reducing the chloride with sodium amalgam and titrating the sodium chloride thus formed with a silver nitrate solution.

0.2362 gm. of the substance gave 0.03078 gm. Cl.

	Found	Calc. for $C_{16}H_{33}Cl$
Cl (%)	13.03	13.63

It is perhaps superfluous to say that triacontane was also obtained besides cetyl chloride.

### 5. Monophenylacetic acid and Palmitic acid

Thirty grams of palmitic acid mixed with an equivalent quantity of monophenylacetic acid was electrolysed under conditions similar to those used in 1. Soon after the electrolysis was commenced, the odour of benzaldehyde became recognizable. The main product was benzaldehyde; triacontane was also produced, along with a small quantity (about 3 grams) of another hydrocarbon, which was possibly cetylbenzene,  $C_{22}H_{38}$ . As the quantity of it was not sufficient to allow of its purification, its identification could be performed only very roughly, thus—

M. P.,  $27^{\circ}$ ; B. P.,  $163^{\circ}-165^{\circ}$ <sub>(5 mm.)</sub>

0.2280 gm. of the substance in 23.7920 gms. benzene lowered the freezing point of the solvent by  $0.18^{\circ}$ . Mol. Wt., 270 (Calc., 302). The presence of the phenyl radical in this hydrocarbon was confirmed qualitatively.

From a mixture of trichloroacetic acid and palmitic acid no synthetic product could be obtained, as the high temperature necessary for electrolysis of palmitic acid acted destructively upon trichloroacetic acid.

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