Kolbe's Reaction of Higher Fatty Acids. I. Electrolysis of Lauric Acid[*]

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Kolbe's reaction of fatty acids in general has been studied by many investigators but that of lauric acid[1] in particular not in detail. In the previous paper[2], one of the present authors, R. Matsuda, studied electrolysis of acetic and propionic acids for the purpose of clarifying the mechanism of the reaction. The present study was undertaken to find a clue to approach its true aspect, dealing with higher members of fatty acid.

Four electrolytes were employed which consisted of an ethanolic solution of lauric acid and potassium hydroxide. These were different from each other with respect to the alkali content. In Experiment 1 the effect of changing anodic current density 0.08~1.20 amp./cm^2 upon the current efficiency of docosane production which is due to Kolbe's reaction was examined with one of the electrolytes. The increase of current efficiency with that of the anodic current density was observed with nickel anode as well as platinum anode. The former anode resulted in current efficiency which was close, but a little inferior, to that by means of the latter.

In Experiment 2 the effect of the alkalinity of the electrolyte upon the current efficiency was examined with the four solutions, and it was found that the less alkaline the electrolyte, the greater was the current efficiency. Nickel and platinum anodes behaved as in Experiment 1. In the case of lower members of fatty acid, nickel anode is known not to give rise to Kolbe's reaction.

Experimental

An anode of platinum plate was coupled with a cathode of the same material, and so was an anode of nickel plate with a cathode of the same. The cathode in each case was in the shape of a square box without top or bottom, the horizontal section being 10×20 mm., and the height 20 mm. The anode which was rectangular 5×10 mm. was placed at the center of the cathode in each case. The upper part of the electrlytic cell was cylindrical 100 mm. long and 30 mm. in diameter, and its lower part was 50 mm. long, being flattened so as to have the two faces 25 mm. apart. The vessel was inclined by some 30° when in operation. Such a cell together with the electrodes helped not only to lessen the volume of the electrolyte and the voltage required, but also to ease the agitation of the solution without mechanical device. This sort of agitation might have the disadvantage of not always being uniform, because of the varied amount of evolving gas. It was, however, sufficiently useful for the present purpose. The lauric was 99.9 % pure, the neutralization value being 279.5 against the theoretical value of 280.23 and the m. p. 44.1°C. Four solutions were prepared for electrolysis, each of which contained 1 mol. lauric acid and a different portion of potassium hydroxide in a mixture of 800 cc. ethanol and 533 cc. water: Solutions A, B, C and D contained 0.14, 0.34, 0.68 and 1.02 mol. potassium hydroxide respectively.

Each electrolysis was conducted with 40 cc. of the solution at 40°C. An oily mass floated, consisting mainly of docosane, as it was produced by

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1) J. Petersen, *Z. Electochem.*, 12, 143 (1906); Y. Minami, F. Ono and Y. Toyama, *J. Chem. Soc. Japan, Ind. Chem. Sec.*, (*Kogyo Kagaku Zasshi*), 53, 393 (1950).

2) R. Matsuda, This Bulletin, 7, 18, 297 (1932).

electrolysis. The content of the vessel was cooled after electrolysis, and the coagulated crude docosane was taken out, melted in 70~80°C water, and cooled again. This product was purified by extracting with benzene four to five times, and then by recrystallizing with ethanol three to four times. It was subsequently identified as docosane by the melting point, the elementary analysis and the molecular weight determination. M. p. 44.0~44.5°C (the reported m. p. 44.4°C)[3].

Found: C, 85.30; H, 14.81. Calcd. for $C_{22}H_{46}$: C, 85.39; H, 14.61%. Mol. wt. (Rast's method). Found: 292. Calcd.: 310.31.

Experiment 1. Solution C was electrolyzed with the nickel as well as the platinum electrodes. The anodic current density was varied 0.08~1.20 amp./cm² in order to see the influence of anodic current density on Kolbe's reaction, 2200 coulombs were supplied for each electrolysis. This quantity was nearly 90% of that necessary to electrolyze lauric acid in the solution. The docosane production is shown in Table I and Fig. 1.

TABLE I. INFLUENCE OF ANODIC CURRENT DENSITY UPON DOCOSANE PRODUCTION

Anodic current density amp./cm²	Pt-electrodes docosane current efficiency		Ni-electrodes docosane current efficiency	
	g.	%	g.	%
0.08	1.20	34.0	1.12	31.8
0.20	1.23	34.8	1.21	34.3
0.40	1.31	37.1	1.27	36.0
0.80	1.39	39.4	1.30	36.8
1.20	1.42	40.2	1.35	38.2

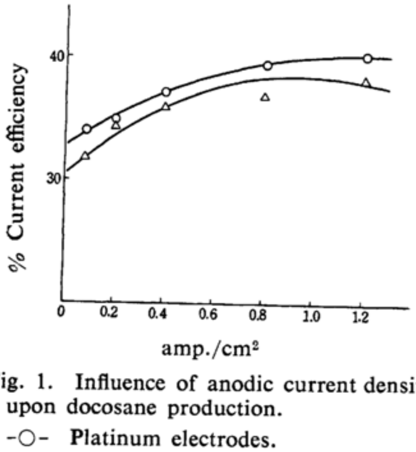

Fig. 1. Influence of anodic current density upon docosane production.

-○- Platinum electrodes.
-△- Nickel electrodes.

Experiment 2. In order to see the influence of alkalinity, solutions A, B, C and D were electrolyzed with 2200 coulombs at a constant anodic current density of 0.4 amp./cm², employing the platinum as well as the nickel electrodes. The current efficiency of docosane production in these cases is shown in Table II and Fig. 2.

TABLE II. INFLUENCE OF ALKALINITY OF SOLUTION UPON DOCOSANE PRODUCTION

Solution	Mol. KOH per 1 mol. lauric acid	Pt-electrodes Docosane	C. E.	Ni-electrodes Docosane	C. E.
A	0.14	2.29g.	64.9%	2.23g.	63.2%
B	0.34	1.88	53.3	1.88	53.3
C	0.68	1.31	37.1	1.27	36.0
D	1.02	0.67	19.0	0.54	15.3

C. E. denotes current efficiency.

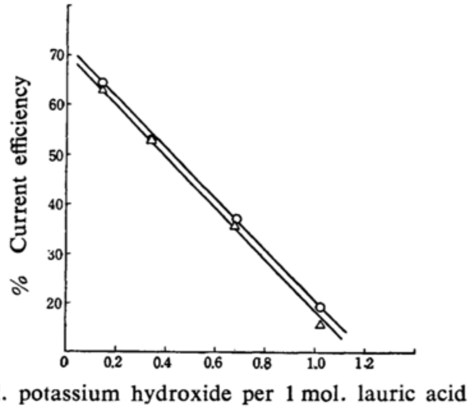

Fig. 2. Influence of alkalinity of solution upon docosane production.

-○- Platinum electrodes.
-△- Nickel electrodes.

Discussion

According to Experiment I the increase of anodic current density favored Kolbe's reaction, the influence being more noticeable when the current density was smaller. This tendency was also observed with acetic acid, in which case it was mentioned that proper regions of concentration and pH should be maintained[4]. Larger current density means a larger number of anions discharged per unit surface area of the anode. The result of Ex-periment I will be understood if it is assumed that the discharge of lauric acid anions which is responsible for Kolbe's reaction occurs dominantly under the favored condition. When the current density was larger than 1.2 amp./cm², the gas evolution made it impossible to keep the current uniform and to obtain a reliable result. It is presumed that docosane production decreases for the following two reasons: first that with current density above 1.2 amp./cm² the discharge of more easily movable hydroxyl ions might dominate, and second that the migration velocity of lauric acid ions reaches the maximum. Docosane production consequently decreased.

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[3] The reported value: 44.0~44.5°C, F. Kraft, *Ber.*, **40**, 4783 (1907).

[4] R. Matsuda, *J. Chem. Soc. Japan* (*Nippon Kwagaku Kwaishi*), **51**, 662 (1930).

Platinum and nickel were compared as anode material. The latter was found as good for Kolbe's reaction of lauric acid as the former, which had been regarded practically as the superlative material for Kolbe's reaction of fatty acid in general.

It was shown by Experiment 2 that docosane production quickly dropped off with the increase of potassium hydroxide, and there was no maximum point in the curves of Fig. 2 as was expected. It seems that the discharge of lauric acid ions steadily gave place to that of hydroxyl ions as potassium hydroxide increased, and docosane production decreased. Platinum and nickel were compared again as anode material and found close to each other with respect to the current efficiency of docosane production, although the former was superior to the latter as in Experiment 1. Fichter(5) considered that oxidation of fatty acid by means of anodic atomic oxygen resulted in Kolbe's reaction. There is, however, a great difference between the oxygen overvoltages of platinum and nickel. If the overvoltage should have anything to do with anodic atomic oxygen, hence with Kolbe's reaction, these two metals would behave differently as anode material, platinum with its high over-voltage being favorable to the reaction. Besides, Kameyama(6) describes that when acetate is electrolyzed with nickel, iron or gold as an anode no Kolbe's reaction takes place, oxygen being the dominant product of the anodic reaction.

In addition to the fact that nickel was available as an good anode for Kolbe's reaction in the present case, dimethlyglyoxime failed to detect nickel ions in the electrolyzed solution, and the nickel anode showed no apparent change after electrolysis. It is likely that the nickel anode assumed the passive state during electrolysis.

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5) Fr. Fichter, *Trans. Am. Electrochem. Soc.*, **45**, 131 (1924).

6) N. Kameyama, "Theory and Application of Electrochemistry (Denki-Kagaku no Riron oyobi Oyo)" Vol. II. Maruzen, Tokyo (1953), p. 225.