*Kolbe's Reaction of Higher Fatty Acids. II. Electrolysis of Lauric Acid by a Pulsating Current with an Artificial Graphite Anode**

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(Received August 27, 1960)

In the previous paper1) a study of electrolysis of lauric acid was reported with respect to the relation between the current efficiency of Kolbe's reaction and the anodic current density as well as the alkalinity of the electrolyte, and it was thereby conculded that nickel anode behaved almost similarly to platinum one towards Kolbe's reaction of lauric acid. In connection with the above mentioned result it was undertaken to study behaviors of other anode materials concerning the electrolysis of lauric acid in the present paper.

In Exp. 1 artificial graphite, lead, tantalum, molybdenum, tungsten and iron anodes were employed for electrolysis by direct current, but none of these anodes gave rise to Kolbe's reaction of lauric acid. Accordingly a pulsating current was applied instead of a direct current with the same anodes as those mentioned above, and it was found that only the artificial graphite anode was suitable for Kolbe's reaction. The other anodes were not desirable, being either unable to get the current flow or dissolved partly or entirely in the electrolyte solution. In Exp. 2 the effect of the anodic current density of the pulsating current upon the current efficiency of Kolbe's reaction in the electrolysis with an artificial graphite anode was studied, and comparison was made with the corresponding case employing direct current reported in the previous paper. Exp. 3 dealt with the effect of alkalinity of the electrolyte on the current efficiency of Kolbe's reaction and the result was compared with the corresponding case of the previous paper to discuss the mechanism of Kolbe's reaction.

Experimental

The electrolytic vessel was the same as described in the previous paper. Four electrolytic solutions were prepared, each of them containing 1 mol. lauric acid and different portion of potassium hydroxide in a mixture of 800 cc. ethanol and 550 cc. water: thus solutions A, B, C and D contained 0.25, 0.5, 0.75 and 1.00 mol. potassium hydroxide respectively and 1 mol. lauric acid. Each electrolysis was conducted with 40 cc. electrolyte at 40°C. In each case 2200 coulombs of either direct or pulsating current were supplied, this quantity of electricity being nearly 90% of that electrochemically equivalent to the lauric acid present in the solution. The pulsating current was generated by a mercury filled Tunger rectifier, and consisted of half-waves of an approximately perfect sinnusoidal curve. The frequency was 60 cycles per second.

Results and Discussion

Experiment 1.—Artificial graphite, lead, tantalum, molybdenum, tungsten and iron were used as anode to investigate the influence of anode material on Kolbe's reaction. The anode was a square plate 1×1 cm. except that of tungsten having a spiral form made of a wire 0.5 mm. of diameter and 15 cm. long. The cathode in each case was a square plate with the effective surface area ten times as large as the anode, and stood face to face with the latter. The anodic current density was 0.4~1.0 amp./cm^2. The result is summarised in Tables I and II.

TABLE I. BEHAVIORS OF VARIOUS ANODES IN THE ELECTROLYSIS WITH DIRECT CURRENT

Anode	C	Pb	Ta	Mo	W	Fe
Cathode	C	Pb	Ni	Ni	Ni	Fe
Current	none	none	none	flow	flow	flow
Kolbe's reaction	none	none	none	none	none	none

TABLE II. BEHAVIORS OF VARIOUS ANODES IN THE ELECTROLYSIS WITH PULSATING CURRENT

Anode	C	Pb	Ta	Mo	W	Fe
Cathode	C	Pb	Ni	Ni	Ni	Fe
Current	flow	flow	none	—	flow	flow
Kolbe's reaction	partly occurred	none	none	—	none	none

Graphite Anode.—The artificial graphite anode was coupled with a cathode of the same material. When direct current was applied through the circuit, its intensity decreased with unexpected rapidity, e. g., the initial amperage of 80 m amp. decaying to 5 m amp. in ten minutes. No appreciable change of the anode surface was observed during this period. When pulsating current was applied in place of direct current through the electrolyte which had just been treated with the latter, a stationary current was observed at 3 V. A fresh solution was then electrolyzed with pulsating current, and 0.87 g. docosane was obtained with a small amount of alcohol. The content of the vessel after electrolysis was heated with potassium carbonate and filtered. The precipitate was made alkaline with potassium carbonate solution and extracted with ether. The ethereal extract was concentrated and distilled under

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* D. Kubota's graduation thesis at Tokushima University.

1) T. Mizuta, T. Hisano and R. Matsuda, This Bulletin, 33, 700 (1960).

reduced pressure, and the resulted 0.75 g. of the fraction with $K_7=110\sim130°C$ was tested by diazo and Bittre color reactions. By both reactions the alcohol was detected. The anode surface was not changed in its appearance by either current. According to Kunugi[2] the use of the artificial graphite anode brought about $11\sim12\%$ current efficiency of Kolbe's reaction when acetic acid was electrolyzed with direct current.

Lead Anode.—Direct current did not flow through the lead anode coupled with a lead cathode, neither changed the surface of the former electrode. However, by applying the pulsating current at $20\sim23$ V., the current of 0.6 amp. was observed to pass, and the anode was entirely dissolved in the electrolyte solution after some thirty minutes.

Tantalum Anode.—The tantalum anode was coupled with a nickel cathode. Neither direct nor pulsating current flowed and no apparent change of the anode occurred.

Molybdenum Anode.—The molybdenum anode was entirely dissolved in the solution by direct current at $12\sim13.5$ V.

Tungsten Anode.—The tungsten anode was coupled with a nickel cathode, and direct current flowed through it, but neither Kolbe's reaction nor any change of the anode occurred. Pulsating current flowed too, but it did not give rise to Kolbe's reaction.

Iron Anode.—Both direct and pulsating currents flowed through the iron anode which was coupled with an iron cathode. The anode was partly dissolved in the solution, but no Kolbe's reaction occurred. The reaction is, however, reported[2] to take place to a small extent when acetic acid is electrolyzed with the same anode as above mentioned by direct current.

Experiment 2. As the electrolysis by pulsating current with the artificial graphite anode was the only case which was found to be suitable for Kolbe's reaction in Exp. 1, the influence of current density upon the current efficiency was investigated under such condition as mentioned above. As shown in Fig. 1 the increase of current density of the pulsating current favored the current efficiency of Kolbe's reaction. Exp. 2 of the previous paper which dealt with the influenceof current density of direct current upon the current efficiency of Kolbe's reaction showed that there was a similar tendency. In comparing these two cases of electrolysis, however, it is to be born in mind that the solution of the present experiment is more concentrated with respect to potassium hydroxide than the other, and also that higher concentration with respect to the alkali is disadvantageous to the current efficiency of Kolbe's reaction irrespective of the nature of the current. In dealing with the current density of the artificial graphite anode itsporosity has to be taken into consideration.

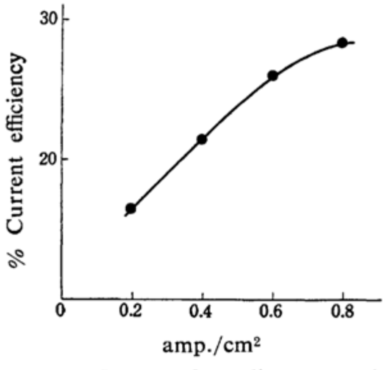

Fig. 1. Influence of anodic current density of pulsating current on docosane production.

Experiment 3. The influence of alkalinity of the electrolyte solutions upon Kolbe's reaction with the artificial graphite anode by pulsating current was studied and the result is shown in Fig. 2.

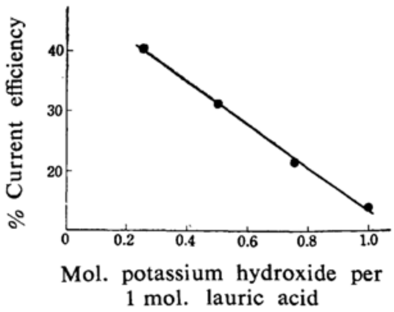

Fig. 2. Influence of alkalinity of solution on docosane production.

Corresponding cases with platinum and nickel anodes by direct current were described in the previous paper. When these two electrolyses are compared with the present case, it is seen that there is a common tendency between them that the current efficiency of Kolbe's reaction decreases linearly with increasing alkalinity. When the alkalinity is the highest one, the current efficiencies of the three cases are close to each other. With the decrease of alkalinity the current efficiency with the artificial graphite anode increases more slowly than the other two. At any rate it is evident that Kolbe's reaction of lauric acid has a close relationship with the alkalinity or the hydrogen ion concentration of the electrolyte solution. Matsuda[3] pointed out that there is an important relationship between Kolbe's reaction and hydrogen ion concentration when the aqueous solution of acetic acid is electrolyzed.

The authors wish to express their thanks to Nippon Oils and Fats Co., Ltd. who kindly offered them the lauric acid.

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[2] T. Kunugi, *J. Electrochem. Soc. Japan (Denkikagaku)*, **20**, 208 (1952).

[3] B. Matsuda, This Bulletin, 7, 18, 297 (1932).