Kolbe's Reaction of Higher Fatty Acids. III. Anode Potential in the Electrolysis of Lauric Acid with Platinum Anode

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Several investigators who have dealt with the anodic potentials of Kolbe's reaction and of those closely related to it in the electrolysis of acetic acid[1-5] have found that there are two stages of the anodic potential with a smooth platinum anode. They are 1.8~2.0 and 2.2~2.8 V. vs. hydrogen electrode, which are regarded as the potentials of oxygen evolution and the discharge of acetate ion respectively. In the electrolysis of the aqueous solution of acetic acid, Kolbe's reaction normally occurs. In other words, the discharge of acetate ions, which have a higher discharge potential than hydroxyl ions, predominates over that of the latter under ordinary conditions. This fact will be, according to Hickling[1], a formidable problem for any theory of anodic reactions. Adam and others[6] have stated that the formation of a surface film of acetate ions would disturb the discharge of hydroxyl ions and give rise to a higher potential. However, Hickling emphasized that the anode showed the higher potential from the very beginning of the electrolysis; therefore, it was not a question of the replacement of a lower potential process by one of a higher potential after the electrolysis had been run for some time. Aoyagi and Sugino[4] have mentioned that the realization of the higher potential stage was caused by the adsorption by the anode of such ions as were not oxidized or discharged at the potential of oxygen evolution.

The present authors have not come across any work on the characteristic nature of the anodic potential in the Kolbe reaction of higher fatty acids, which might behave somewhat unlike the lower members, and so have undertaken the study of the anodic potential with a smooth platinum anode in the electrolysis of lauric acid.

Experimental

Electrolyte Solution.—Either ethanol or methanol is often employed, together with water, to increase the poor solubility of lauric acid in water. In order to avoid the effect of such an alcohol as that mentioned above on the anodic potential, however, electrolyte solutions were made by adding an aqueous solution of potassium hydroxide of a proper concentration to a solution of lauric acid and potassium carbonate which had been prepared by treating a mixture of these two solutes with warm water. The composition of the electrolyte solutions employed is shown in Table I, in which [La], [K_1] and [K_2] denote the concentrations in mol./l. of lauric acid, potassium hydroxide and potassium carbonate respectively. The lauric acid was obtained by recrystallizing two times a raw lauric acid which was 99.9% pure with a mixture of ethanol and water. The other chemicals were of the special grade for analysis.

Apparatus and Electrodes.—The electrolytic cell employed in the current-potential and time-potential measurements was a glass cylinder, and 100 ml. of the electrolyte solution were used for each run. The anode was a smooth platinum plate with a total surface area of 0.5 cm^2. To keep the current distribution as uniform as possible, the anode was surrounded by a platinum plate cathode which had an area of about 5 cm^2 on each side, almost large enough to avoid the effect of cathodic polarization. Before electrolysis, both electrodes were thoroughly cleaned with ethanol, with concentrated nitric acid and finally with pure water. The reproducibility of the equilibrium potential of the anode in the electrolyte solution was about ±0.02 V. The Luggin capillary, which was 1 mm. in outside diamete at its tip, was filled with the electrolyte solution and then connected to a saturated calomel electrode through a potassium chloride solution. At the middle of the capillary tube a glass stop cock was fitted; this was kept closed during the experiment to prevent the contamination of the electrolyte solution with potassium chloride. The potential was measured by an electronic valve potentiometer, the imput impedance of which was 10 MΩ.

Since Kolbe's reaction of lauric acid produces docosane[7], which is solid and oily at room

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[1] A. Hickling, *Discussions Faraday Soc.*, 1, 227 (1947).

[2] B. G. Preuner and E. B. Ludlam, *Z. physik. Chem.*, 59, 682 (1907).

[3] S. N. Shukla and O. J. Walker, *Trans. Faraday Soc.*, 27, 722 (1931).

[4] S. Aoyagi and K. Sugino, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 79, 1202 (1958).

[5] S. Aoyagi and K. Sugino, *J. Electrochem. Soc.*, 103, 166 (1956).

[6] N. K. Adam et al., *Discussions Faraday Soc.*, 1, 248 (1947).

[7] T. Mizuta, T. Hisano and R. Matsuda, This Bulletin, 33, 700 (1960).

TABLE I. COMPOSITION OF ELECTROLYTE SOLUTIONS

Solute	Soln. 1	2	3	4	5	6	7	8
[La]	0.012	0.012	0.100	0.057	0.114	0.171	0.229	0.057
[K_1]	1.776	0.306	0.100	0.857	0.714	0.571	0.429	0
[K_2]	0.017	0.017	0.145	0.031	1.062	0.093	0.124	0.031
[K_1]/[La]	150	25	1.0	15	6.3	3.3	1.9	0
[K_2]/[La]	1.4	1.4	1.4	0.54	0.54	0.54	0.54	0.54

temperature and 40°C respectively, the electrolysis was conducted at 40±0.5°C without any mechanical agitating device.

Determination of the Current Efficiency of Oxygen Evolution.—Both the anode and cathode employed in this case had a larger surface area (7 and 100 cm^2 respectively) than those mentioned above. The electrolytic cell was fitted with a side tube in order to adjust the level of the electrolyte solution, and the cell was completely filled with the solution before electrolysis. During electrolysis the constant anodic potential was maintained by manual adjustment of the current. The evolved gas, which was collected into a syringe of a 20 ml. capacity, was treated with potassium hydroxide and alkaline pyrogallol solutions succesively. Special attention was paid to prevent the entrance of air into the gas samples. The efficiency of the oxygen evolution at the anode was calculated, assuming that the efficiency of hydrogen evolution was 100% at the cathode and that the residual gas after absorption contained hydrogen only. According to these assumptions, the current efficiency of oxygen evolution will be lower than it should be if the electrolytic gas contained any unabsorbable gas other than hydrogen.

Results and Discussion

From Fig. 1, showing the relation between the current and anodic potential in the electrolysis of solutions 1, 2 and 3, in which the value of [K_2]/[La] was always equal to 1.4, the following two facts may be observed. First, when [K_1] is not very high compared with [La], as in the cases of curves 2 and 3, two stages of anodic potential are clearly marked. The first stage lies at 1.5~1.6 V., and the second at a potential a little higher than about 2.3 V. Secondy, when [K_1] is very large compared with [La], the current increases so much that it reaches beyond the estimation range, and the second stage of potential disappears. In the potential range between 1.5 and 2.4 V., both curves 2 and 3 have a plateau which looks as if it were a saturation or limiting current. However, strictly speaking, this is not the case, since it is impossible to maintain a constant current at a constant potential, particularly in a part of the potential range below 2.4 V. The current decreases if the potential is kept constant. Moreover, as the current approaches a certain high value, the potential increases more rapidly than with the former. For these reasons curves 2 and 3 were obtained by reading the potential immediately after adjusting the current to as constant a level as possible. The values of the height of the plateau in curves 2 and 3 are, consequently, not very precise. Yet it is clear that the height

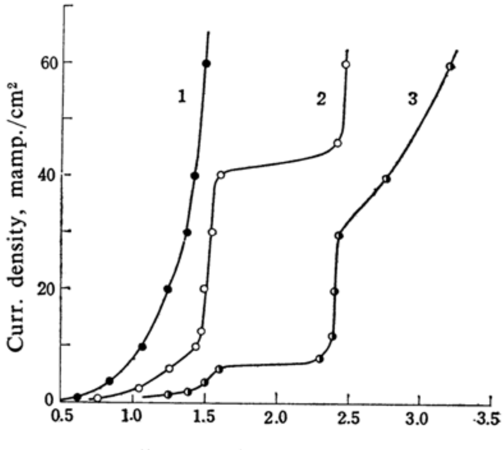

Fig. 1. Relation between anodic current and potential. Curves 1, 2 and 3 are related to solutions 1, 2 and 3 respectively.

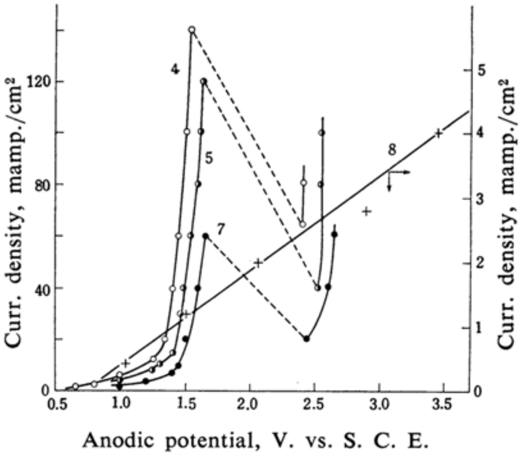

Fig. 2. Relation between anodic current and potential. Curves 4, 5, 7 and 8 are related to solutions 4, 5, 7 and 8 respectively.

of the plateau has a close connection with the value of $[K_1]$.

The relation between the current and potential was also observed for solutions 4, 5, 6, 7 and 8. In this case the current was left without adjustment during the rapid potential transition. Some of the results are represented in Fig. 2. According to these curves, there occurs a phenomenon something like the passivity of a soluble anode. The first and second potential stages are situated like that case, at 1.5～1.6 V. and 2.4～2.6 V. vs. S. C. E. respectively. Curve 8 represents the case of a solution which contains lauric acid and potassium carbonate but no potassium hydroxide. This curve is nearly linear and shows that a higher anodicpot ential is attained by a lower current density than with the other curves. It can well be considered that this is due to the resistance overpotential caused by some filmy substance on, in the vicinity of, the anode. As a matter of fact, a transparent viscous substance was observed on the anode during electrolysis, although it disappeared after opening the circuit. This is probably potassium laurate liberated.

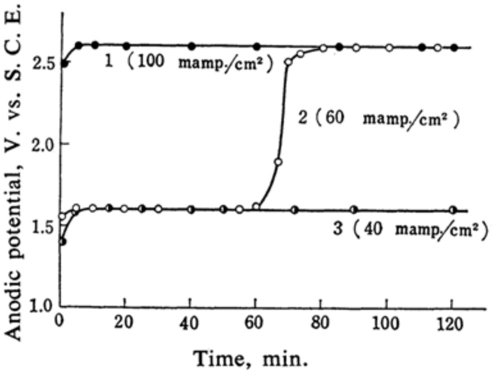

Fig. 3. Variation of anodic potential during electrolysis of solution 7 at constant current.

Figure 3 shows typical curves observed as to the variation in anodic potential during the electrolysis of solution 7 under a constant current. Whereas curves 1 and 3 reach 2.6 and 1.6 V. respectively soon after the commencement of electrolysis, and both remain constant as time goes on, curve 2 proceeds along with curve 3 for the first period and then ascends quickly to 2.6 V. and remains constant thereafter. With an ordinary electronic valve potentiometer, the potential under high current densities is observed to be 2.4～2.6 V. from the beginning of electrolysis, as illustrated by curve 1. A cathode ray oscillograph, however, shows distinctly that, under the same conditions as mentioned above, the rapid displacement of the potential stage from the first to the second still occurs at the moment of closing the circuit. At any rate, it is evident from these observations that the displacement of the potential stage takes place at a certain time after the beginning of the electrolysis of alkali laurate.

The relation between current density and the time of potential displacement will be reported on later.

From the result mentioned above, the transition of the potential and the realization of the higher potential stage in preference to the lower one may by supposed to be caused by the formation of some sort of film on the anode surface. Three possible types of film which can bring about an abnormally high overpotential are as follows;

(1) a highly resistant film of the oxide of the anode material;

(2) a film of a resistant substance formed of discharged anion, and

(3) a film of adsorbed anion⁽⁴⁾.

In the present study, (2) or (3) is likely to occur, but (1) is unlikely since it is already known⁽⁸⁾ that the steady evolution of oxygen on a platinum anode occurs on its oxide layer, which has an unusual capacity for electron conduction.

TABLE II. ELECTROLYSES AT TWO CONSTANT POTENTIALS

Anode area, 7.0 cm²; Solution, 6.

Anode potential, V.	1.5～1.6	2.5～2.6
Mean curr. density, mamp/cm²	11	57
Quantity of electricity, coulombs	ca. 300	120～345
Curr. efficiency of O_2 evolution, %	99.2±0.1	25.0±2.4
Docosane formation	None	Confirmed

Table II represents the current efficiency of oxygen evolution at two constant anode potentials. The value at the lower potential stage amounts to 99% and differs decidedly from that at the higher stage. That is, the anode reaction occuring at the lower potential was almost entirely the evolution of oxygen. In the electrolysis at the higher stage of anode potential, the solution became utterly opaque soon after the commencement of electrolysis, and a floating substance, which was identified by its melting point as docosane, rose to the surface of the solution. During electrolysis at the lower potential, the solution was clear or only slightly opaque. If docosane be formed at the lower potential stage, its appearance on the surface of the solution would be perceptible

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8) H. A. Laitinen and C. G. Enke, *J. Electrochem. Soc.*, 107, 773 (1960).

after the electrolysis had been conducted with a sufficiently large quantity of electricity, since it is sparingly soluble in the solution employed. However, no floating substance was found after electrolysing 250 ml. of solution 6 with 8000 coulombs of electricity at the constant potential of 1.5~1.6 V. Although the above-mentioned method is not complete for the detection of docosane, it seems not to be right, by reason of the following observation, to suppose that the displacement of the anode potential is due to the formation of a resistant film of docosane which is produced out of the discharged laurate ions. The displacement of the lower potential by the higher one was observed not immediately but some time after the start of a second run of electrolysis at the lower potential of a certain solution which, for the first time, had been electrolyzed for a long time at the higher potential and, therefore, should have been saturated with docosane and other products.

In conclusion, it seems, to the authors, as far as the present study is concerned, that the most probable mechanism of the displacement of the anode potential stages in the electrolysis of the alkali laurate solution is related to the formation of an adsorbed film of laurate ions, and that at the lower potential stage of 1.5~1.6 V. vs. S. C. E. the main reaction is the evolution of oxygen. As laurate ions are adsorbed on the anode surface, the effective surface area of the latter for the discharge of hydroxyl ions decreases; therefore, the potential rises to 2.4~2.6 V., at which point laurate ions begin to discharge.

As has previously been reported[9] docosane is formed on a graphite anode with a pulsating direct current, whereas with ordinary direct current there occurs a rapid diminution of current; thus it will be interesting to investigate the behavior of graphite and platinized platinum anodes in the light of the anodic potential, since these have atomically irregular surfaces, on which large laurate ions may be expected to be adsorbed in a manner somewhat dissimilar to that which is the case with a smooth platinum surface.

Summary

An aqueous solution of lauric acid, containing potassium hydroxide and potassium carbonate, was electrolysed at 40±0.5°C with smooth platinum electrodes. Not only were two constant anodic potential stages, 1.5~1.6 and 2.4~2.6 V. vs. S. C. E., clearly found, but also an abrupt shift from the lower stage to the higher one was distinctly observed. The main reaction at the lower stage is the evolution of oxygen. In addition, at the higher stage the discharge of laurate ions is accompanied by an oxygen evolution that is markedly retarded compared with that at the lower stage. It may therefore, be inferred that the transition of potential from the lower stage to the higher is caused by the formation of a film of adsorbed laurate ions.

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[9] R. Matsuda, T. Hisano and D. Kubota, This Bulletin, 34, 649 (1961).