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The Anodic Oxidation of a Propionate-Propionic Acid Solution in the Presence of Several Organic Compounds

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The anodic oxidation of the propionate anion in aqueous solutions of propionic acid at a platinum electrode has been studied in the presence of several organic compounds in order to demonstrate the formation of both propionoxy and ethyl radicals as the reaction intermediates. One of the following organic compounds was added to each solution: two vinyl monomers (acrylic acid and acrylamide), two alkylbenzenes (toluene and cumene), and two aliphatic alcohols (methanol and isopropanol). The electrooxidation of sodium propionate in the presence of acrylamide resulted in polymerization, which was confirmed to be initiated by the ethyl radical. Acrylic acid, unlike acrylamide, gave no polymers. In this case, both the current efficiency for the formation of carbon dioxide and the yield ratio of ethylene to carbon dioxide were always less than those observed in the absence of acrylic acid. While the addition of alcohols gave no definite results, the addition of toluene or cumene resulted in an appreciable decrease in the yield ratio of ethylene to carbon dioxide, but affecting neither the ratio of ethane to carbon dioxide nor the current efficiency for the carbon-dioxide evolution. These results indicate that the anodic oxidation of the propionate anion proceeds through the consecutive formation of propionoxy and ethyl radicals as the reaction intermediates.

Although many studies have been made of the electrolytic Kolbe reaction, work has mainly been restricted to the acetic acid-acetate system. A few papers have been published on the propionate system.[1-4] The acetate system seems, however, somewhat exceptional in the series of straight-chain fatty acids, because, for instance, the yield efficiency of ethane is exceptionally high (90%) and no olefinic compound is found in the products. Putting aside the acetate system, the relative yield of alkenes increases and that of alkenes generally decreases with an increase in the carbon numbers in the series of straight-chain fatty acids.[5] Accordingly, it might be expected that the propionate system is more adequate for the Kolbe reaction than the acetate system.

The purpose of the present paper is to elucidate in detail the mechanism of the anodic oxidation of the propionate anion in aqueous solutions containing propionic acid. The effects of the presence of several organic compounds on the anodic oxidation of the propionate anion have been studied. Particular attention was paid to the current efficiency for the evolution of carbon dioxide and to the relative yield of ethane and ethylene to carbon dioxide.

Experimental

Reagents. Reagent-grade sodium propionate, methanol, toluene, and sodium hydroxide were used without further purification. Propionic acid, acrylic acid, cumene, and isopropanol were distilled under reduced pressure. The acrylic acid distilled was stocked in an ice box. Reagent-grade acrylamide was recrystallized from benzene and dride at about 60°C.

Solutions. An aqueous solution containing 2M propionic acid and 2M sodium propionate was used as the base solution (pH 4.8) for the experiments using acrylic compounds or alcohols. Each solution was made up to 1 or 0.5M. In the case of acrylic acid, sodium hydroxide was added to maintain the same pH as that of the base solution. Toluene and cumene were dissolved in 95% aqueous solutions of propionic acid containing 1M sodium propionate.

Apparatus. The electrolytic cell used in the present experiment was an H-shaped glass vessel having anode and cathode compartments separated by a sintered glass disk. The temperatures were 25±0.3°C for the voltammetric experiments and 5—10°C for the macroscale electrolysis. The electrode used for the voltammetric measurements was a smooth platinum wire, 1.1 cm in

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1) P. Holeman and K. Clusius, *Ber.*, **70**, 819 (1937).

2) C. L. Willson and W. Lippincott, *J. Amer. Chem. Soc.*, **73**, 4290 (1950).

3) G. S. Pande and S. N. Shukla, *Electrochim. Acta*, **4**, 215 (1961).

4) K. Sasaki, K. Uneyama and S. Nagaura, *ibid.*, **11**, 891 (1966).

5) M. J. Allen, "Organic Electrode Processes," Reinhold Publishing Corp., New York, N. Y. (1958), p. 103.

length and 0.03 cm in diameter, sealed at one end of a soft glass tube. The other end of the electrode was fused into a small glass bead to avoid any edge effect. The electrode was then subjected to repeated anodic and cathodic polarizations in a 10% sulfuric acid solution. The electrodes used for the macroscale electrolysis were cut from a sheet of platinum foil and spot-welded to a platinum wire.

Procedures. Cyclic voltammograms were obtained with a Nichia Keiki-type HE-Potentiostat in conjunction with a triangular sweep function generator and with an X–Y recorder, Model XYR–IA, of Toa Denpa, Ltd. Macroscale electrolysis were mainly using a Yanagimoto Model VE-3 controlled potential electrolyser. The current was recorded with a potentiometer-type recorder. The total quantity of electricity passed through was graphically determined.

In the polymerization experiment, the solution was agitated by bubbling in oxygen-free nitrogen gas before and during the electrolysis. The polymerization products were precipitated by adding a large amount of methanol. The precipitate was purified by repeated dissolution and precipitation, and was finally dried for weighing.

Gases evolved from the anodic chamber were collected in a gas buret. The first 60 cc portion of the gas was thrown away in order to avoid any error caused by air in the dead space. The composition of the sample gas was analysed by means of a Yanagimoto GCG-220 gas chromatograph equipped with an active charcoal column. The current efficiency for the formation of carbon dioxide was calculated by assuming that one mole of the gas corresponds to two faradays.

All the potential measurements are referred to the SCE with a salt bridge.

Results and Discussion

Cyclic Voltammetry. Shukla[3] reported that the current-potential curves for the propionate oxidation were monotonous and that the anode potential increased with an increase in the current density applied. This is in contrast with the curves observed with acetate, which exhibit a shoulder prior to the final rise of the current. The current-potential curve for the propionate oxidation has, therefore, been re-examined using the potential sweep method. When the anode potential was swept from 0.4 to 2.5 V (*vs.* SCE), the curve in the first sweep was monotonous, but a shoulder appeared at about 2.0 V in the succeeding sweeps. The critical potential*1 was dependent on both the sweep rate and propionate concentration, as in the case of the acetate oxidation.[6]

In Fig. 1, similar curves obtained with acrylic acid and acrylamide are shown by curves B and C respectively. It should be noted that the curve B, which was obtained in the presence of acrylic acid, exhibits a shoulder at a higher potential region than the curve A. Such a shoulder is not seen, however, in the curve C for the acrylamide solution. Similar behavior in acrylic compounds was observed in the acetic acid-acetate system,[7] although the reason why the critical potential shifted was uncertain.

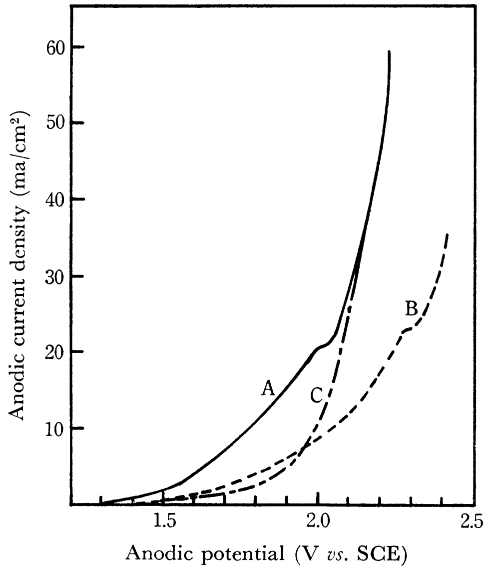

Fig. 1. Current-potential characteristics of aqueous propionate solutions with and without vinyl monomers.
A: 0.5M sodium propionate and 0.5M propionic acid with no additives
B: with 1.0M acrylic acid
C: with 1.0M acrylamide
pH of all solutions; 4.8, Potential sweep rate; 0.1 V/sec.

Electroinitiated Polymerization. In order to examine whether or not the anodic oxidation of propionate proceeds through the radical intermediate, a series of experiments on the electropolymerization of acrylic acid in aqueous propionate solutions has been carried out. The electrolysis of solutions containing 1M sodium propionate, 1M propionic acid, and 1.9M acrylic acid under constant-current conditions gave polymers in the cathodic chamber. No polymerization was observed in the anodic chamber, even when the anode potential was as high as 2.5 V (*vs.* SCE). When acetate was used in place of propionate, olygomers were obtained in the anodic chamber under similar conditions.[8] The reason why no polymer was obtained with propionate could be attributed to the fact that neither radical species was included in the anodic process of propionate, or to the fact

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*1 The potential corresponding to the shoulder is called the "critical potential."

[6] A. Kunugi, S. Iseki, K. Ohashi and S. Nagaura, *Denki Kagaku*, **36**, 237 (1968).

[7] I. Izumi, A. Kunugi and S. Nagaura, to be published.

[8] I. Izumi, A. Kunugi and S. Nagaura, *Mem. Fac. Eng. Osaka City Univ.*, **9**, 59 (1967).

TABLE 1. THE EFFECT OF VINYL MONOMERS ADDED ON THE COMPOSITION OF ANODIC GASES IN THE ELECTROLYSIS OF AN AQUEOUS SOLUTION OF 1.0M SODIUM PROPIONATE AND 1.0M PROPIONIC ACID AT 27 ma/cm^2

Monomer added	Composition of gases (volume %)						Current efficiency for CO_2 evolution (%)*	Volume ratio of C_2H_4/CO_2
	O_2	CO	CO_2	C_2H_2	C_2H_4	C_2H_6		
None	1.1	trace	52.1	—	46.3	0.3	73.0	0.89
Acrylic acid** (1.3M)	36.8	trace	43.2	1.5	18.2	0.2	42.8	0.42
Acrylamide (1.3M)	0.1	trace	57.6	—	40.6	0.9	74.0	0.71

* Calculated as required two faradays for 1 mol of CO_2 evolved.

** pH was adjusted to 4.8 by adding NaOH solution

that the products formed were of a very low molecular weight, such as the dimer or the trimer.[*2]

In order to make this point clear, gases evolved from the anodic chamber were analysed. Table 1 summarizes the experimental results on the propionate solution with and without acrylic acid. It is evident from the table that there is a marked decrease in the current efficiency for the formation of carbon dioxide when acrylic acid is present. The yield ratio of ethylene to carbon dioxide also decreases in the presence of acrylic acid. This probably indicates that both propionoxy and ethyl radicals attack the acrylic acid molecule to form its dimers or trimers. It seems, therefore, probable to assume that acrylic acid itself does not participate in the charge-transfer reaction and that the propionate ion is the only species which is electroactive. Exploratory experiments showed that the anodic oxidation of acrylic acid (1.0M) at 2.6 V in a 0.5M sodium hydroxide solution at 25±3°C resulted in a minor formation of carbonaceous compounds, while gases consisting mainly of oxygen (more than 95%), plus minor portions of carbon dioxide, ethylene, acetylene, and carbon monoxide, were detected.

A series of studies of the electroinitiated polymerization was undertaken, using acrylamide as a monomer. With this substance, polymers were obtained in both the anodic and the cathodic chambers. The polymer yields at the anode electrode were found to increase linearly with increases in the concentrations of both propionate and acrylamide. When sodium sulfate and sulfuric acid were used in place of sodium propionate and propionic acid as electrolytes, the polymerization of acrylamide did not occur, suggesting that the presence of the propionate anion is essential for the polymerization. In addition, the presence of *p*-benzoquinone was found to inhibit the polymerization totally. This indicates that the polymerization of acrylamide under the present conditions was initiated by radicals originating from the propionate oxidation, while, on the other hand, *p*-benzoquinone trapped radicals to inhibit the polymerization.

The analysis of gases evolved from the propionate-acrylamide system showed that the addition of acrylamide resulted in a decrease in the yield ratio of ethylene to carbon dioxide. No appreciable change was observed in the current efficiency for the formation of carbon dioxide (see Table 1). On the basis of these findings, it can be concluded that the polymerization of acrylamide is initiated by the ethyl, not by propionoxy, radicals.

Effect of Aromatic Hydrocarbons. The base solution used in the experiment described here was composed of propionic acid containing 1M sodium propionate and 5% water. A desired quantity of the aromatic compounds was dissolved in this solution. Upon the electrolysis of the base solution, the anodic gases produced were almost entirely carbon dioxide and ethylene in a mole ratio of approximately 1 to 0.35. The formation of carbon dioxide required 2 F per mole. Other gaseous products (oxygen, ethane, and carbon monoxide) were also found (see Table 2). The addition of two aromatic hydrocarbons, toluene and cumene, to

TABLE 2. THE EFFECT OF ALKYLBENZENES ADDED ON THE COMPOSITION OF ANODIC GASES IN THE ELECTROLYSIS OF A SOLUTION OF 1.0M SODIUM PROPIONATE IN PROPIONIC ACID CONTAINING 5% WATER AT 14ma/cm^2

Alkylbenzene added	Composition of gases (volume %)					Current efficiency for CO_2 evolution (%)	Volume ratio of C_2H_4/CO_2	Volume ratio of C_2H_6/CO_2
	O_2	CO	CO_2	C_2H_4	C_2H_6			
None	0.8	trace	70.2	24.2	4.7	85.0	0.35	0.07
Toluene (1.92M)	1.5	trace	77.5	14.9	6.0	86.0	0.19	0.08
Cumene (2.0M)	1.5	trace	71.5	20.6	6.4	82.6	0.29	0.09

[*2] Neither a dimer nor a trimer is precipitated by the method used here.

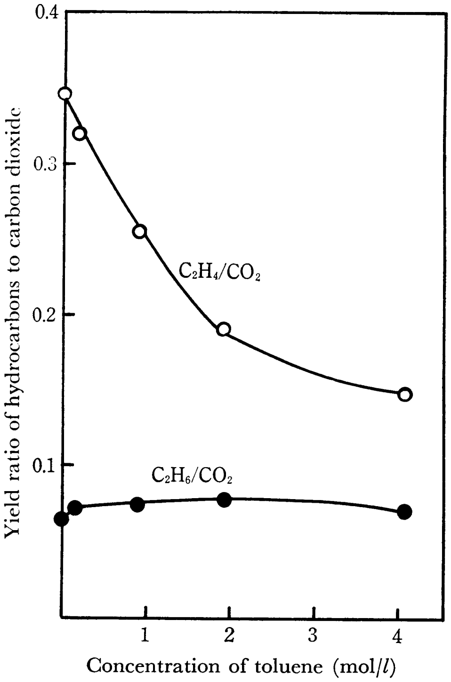

Fig. 2. The effect of the concentration of toluene added on the composition of gases evolved. Solution: 1.0M sodium propionate in propionic acid containing 5% water.

the solution resulted in profound changes in the composition of the gases produced during the electrolysis (see Table 2). The following discussion is based on the assumption that either the aromatic substrates examined in the present study are totally inactive to the electrooxidation or, even if they were oxidized, the oxidation is incomplete and no carbon dioxide is formed. If this assumption is acceptable, the determinations of the relative yields of the gases evolved, namely, ethane to carbon dioxide and ethylene to carbon dioxide, will serve as a sensitive means for the discussion of the mechanism of the reaction concerned. If the ethyl radical originating from propionate abstracts the hydrogen atom in the aromatic substrate, the ethane to carbon dioxide ratio will increase and the ethylene-to-carbon dioxide ratio will decrease. On the other hand, if the radical species effective in the hydrogen abstraction is propionoxy instead of the ethyl radical, the yield ratio of ethane to carbon dioxide will remain constant and the ratio of ethylene to carbon dioxide will vary with the type of termination reaction.

The experimental results are summarized in Table 2 and also in Fig. 2. It is evident from the table that the ethylene-to-carbon dioxide ratio is significantly decreased, while the ethane-to-carbon dioxide ratio was unchanged, when toluene or cumene was present. It should be noted that the ethan formation was not affected by changing the aromatic substrate from toluene to cumene, since it is accepted[9] that the rate of hydrogen abstraction is much greater in cumene than toluene. The current efficiency for the carbon dioxide evolution was found unaffected by the presence of the aromatic substrates. The results in Fig. 2 indicate that the ethylene-to-carbon dioxide ratio decreases and the ethane-to-carbon dioxide ratio increases, though slightly, with an increase in the concentration of toluene. Accordingly, two possibilities can be considered: (1) the hydrogen atom is abstracted from the side chain of aromatic substrates by the propionoxy radical, and the resultant benzyl radical combines with the ethyl radical, and (2) hydrogen abstraction occurs at the aromatic ring by means of the propionoxy radical and the aromatic radical so generated combines with the ethyl radical.

Ross and his co-workers[10] have reported that, when the acetic acid-acetate system was electrolyzed in the presence of ethylbenzene, the methylation occurred to both the side chain and the aromatic ring with greater ease than with the side-chain methylation. This indicates that the possibility (1) is the preferred reaction mode. The anodic oxidation of the propionate ion in the presence of an aromatic substrate, *e.g.*, toluene, can thus be considered to proceed in the following manner:

$$2C_2H_5CO_2^- \longrightarrow 2C_2H_5CO_2\cdot + 2e$$

$$C_2H_5CO_2\cdot \longrightarrow C_2H_5\cdot + CO_2$$

$$C_6H_5CH_3 + C_2H_5CO_2\cdot \longrightarrow C_6H_5CH_2\cdot + C_2H_5CO_2H$$

$$C_6H_5CH_2\cdot + C_2H_5\cdot \longrightarrow C_6H_5CH_2C_2H_5$$

Effect of Alcohols Added. Fioshin *et al.*,[11] have reported the effect of alcohol addititives on Kolbe's electrosynthesis. The addition of aliphatic alcohols up to hexanol to aqueous solutions of acetate or mono-methyl adipate increased the yields of ethane or di-methyl sebacate. In the present experiment, however, no such definite effects nor any others of alcohols were observed, as is shown in Table 3.

Mechanisms of the Anodic Oxidation of Propionate. The foregoing discussion revealed that both the propionoxy and ethyl radicals are involved in the anodic oxidation of the propionate anion. It was also confirmed that the yield ratio of ethylene to carbon dioxide was approximately unity, that the ratio of ethane to ethylene was very small (*ca.* 10^{-2}), and that a charge of 2 F was required for the formation of 1 mol of carbon

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[9] W. A. Pryor, "Free Radical," McGrow-Hill Book Co., New York (1966), p. 170.

[10] S. D. Ross, M. Finkelstein and R. C. Petersen, *J. Amer. Chem. Soc.*, **86**, 4139 (1964).

[11] M. Ya. Fioshin, G. P. Girina, Yu. B. Vasil'ev, M. V. Khrulev, M. K. Polievktov and A. G. Artem'ev, *Chem. Abstr.*, **56**, 12658 (1962).

TABLE 3. THE EFFECT OF ALCOHOLS ADDED ON THE COMPOSITION OF ANODIC GASES IN THE ELECTROLYSIS OF AN AQUEOUS SOLUTION OF 1.0M SODIUM PROPIONATE AND 1.0M PROPIONIC ACID AT 27 ma/cm^2

Alcohol added	Composition of gases (volume %)					Current efficiency for CO_2 evolution(%)	Volume ratio of C_2H_4/CO_2
	O_2	CO	CO_2	C_2H_4	C_2H_6		
None	1.1	trace	52.1	46.3	0.3	73.0	0.89
Methanol (1.0M)	4.3	trace	51.0	44.3	0.3	68.0	0.86
Isopropanol (1.0M)	6.6	trace	51.4	41.4	0.5	70.2	0.81

dioxide. Therefore, two mechanisms can be considered for the formation of ethylene, *i.e.*:

I) Disproportionation reaction;

a) $2C_2H_5CO_2^- \longrightarrow 2C_2H_5CO_2\cdot + 2e$

b) $C_2H_5CO_2\cdot \longrightarrow C_2H_5\cdot + CO_2$

b′) $C_2H_5CO_2\cdot + C_2H_5\cdot \longrightarrow C_2H_4 + C_2H_5CO_2H$

II) Decomposition reaction;

$C_2H_5CO_2^- \longrightarrow C_2H_5CO_2 + e$

$C_2H_5CO_2\cdot \longrightarrow C_2H_5\cdot + CO_2$

$C_2H_5\cdot \longrightarrow C_2H_4 + H$

$H \longrightarrow H^+ + e$

or

$C_2H_5\cdot \longrightarrow C_2H_4 + H^+ + e$

At the present stage, it is impossible to differentiate the two mechanisms without ambiguity. Wilson and Lippincott$^{2)}$ have suggested, though, that the anodic formation of ethylene proceeds through a second-order reaction with respect to the reaction intermediate. If this is the case, and if the intermediate with which they are concerned is the propionoxy radical, the mechanism I seems more likely.

On the other hand, the formation of ethane can be accounted for by the radical reactions shown below, where RH is the solvent or solute molecules:

III) $C_2H_5\cdot + C_2H_5\cdot \longrightarrow C_2H_6 + C_2H_4$

IV) $C_2H_5\cdot + RH \longrightarrow C_2H_6 + R\cdot$

Considering the fact that, in the electrolytic oxidation of anions of saturated aliphatic acids, the yield ratio of paraffins to olefines increases with an increase in the carbon numbers in the series of acids, the reaction III seems more favourable for the formation of ethane.

Although ethylene is formed in two ways, *i.e.*, disproportionation between two ethyl radicals (III) and disproportionation between propionoxy and ethyl radicals (I-b′), Reaction I-b′ might be concluded to be the dominant one because of the one-sided formation of ethylene *vs.* ethane.