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Anodic Oxidation of Benzoic Acid in Nitriles

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The anodic oxidation of benzoic acid in acetonitrile and propionitrile was studied. Electrolysis was employed under a controlled potential or current. Benzoic acid was changed into an intermediate benzoyloxy radical through de-electronation in acetonitrile, and the resulting radical was reacted with acetonitrile to give *N*-acetylanthranilic acid in a 38% yield under constant potential electrolysis. In propionitrile, the anodic oxidation gave *N*-propionylanthranilic acid, *N*-propionylbenzamide, and dipropionylamine. No Kolbe-type reaction was observed.

Many works[1-3] have been reported on the anodic oxidation of aliphatic carboxylic acids, which is connected with the Kolbe reaction. On the other hand, the anodic oxidation of aromatic carboxylic acids has been investigated by only a few workers[4-8], and the mechanism has not yet been discussed. Therefore, it is of interest to investigate the anodic oxidation of aromatic carboxylic acids and discuss its mechanism. Fichter and Uhl[8] have reported that the anodic oxidation of benzoic acid in an aqueous solution gave hydroxybenzoic acid, hydroquinone, and catechol.

In an attempt at testing the solvent effect on the anodic oxidation of benzoic acid, we used acetonitrile and propionitrile instead of water. The electrolysis was employed under a controlled potential or current. Benzoic acid was changed into a benzoyloxy radical, the intermediate, through de-electronation in acetonitrile, and the resulting radical was reacted with the nitrile to give *N*-acetylanthranilic acid in a 38% yield under a constant potential electrolysis. In pro-

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[1] S. Glasstone and A. Hickling, *Trans. Electrochem. Soc.*, **75**, 333 (1939).

[2] C. L. Wilson and W. J. Lippincott, *J. Amer. Chem. Soc.*, **78**, 4290 (1956).

[3] K. Sugino, T. Sekine and N. Sato, *Electrochem. Technol.*, **1**, 112 (1963).

[4] M. J. Allen, "Organic Electrode Process", Reinhold Publishing Corporation, New York, N. Y. (1958), p. 107.

[5] S. Arita, N. Hirai, K. Yamamoto and K. Takeshita, *Kogyo Kagaku Zasshi*, **71**, 2018 (1968).

[6] K. Koyama, K. Yoshida and S. Tsutsumi, Thi sBulletin, **39**, 516 (1966).

[7] K. Sasaki and W. J. Newdy, *J. Electroanal. Chem.*, **20**, 162 (1969).

[8] F. Fichter and E. Uhl, *Helv. Chim. Acta*, **3**, 22 (1920).

pionitrile, the anodic oxidation afforded *N*-propionylanthranilic acid, *N*-propionylbenzamide, and dipropionylamine. No Kolbe-type reaction was observed.

Experimental

Reagents. The benzoic acid, lithium perchlorate, acetonitrile, and propionitrile used were reagents guaranteed by JIS and the Wako Pure Chemical Ind. Co., Ltd. The nitriles were refluxed over phosphorus pentoxide and distilled.

Electrodes and Electrolytic Cells. A platinum wire sealed into a glass tube with the surface area of 0.289 cm^2 was used as the anode for the study of the mechanism. The volume of the H cell with a sintered glass disk diaphragm was 50 ml. In the electrolysis at a constant current or potential, a platinum plate with the effective surface area of 2×2 cm^2 was used as the anode, and the volume of the cell was 200 ml. The electrodes were polished with emery paper and then immersed in acetone for 10 min. Iron, nickel, lead, lead oxide, titanium, tantalum, and gold were also tested as anode materials. The base electrolyte solutions were nitriles containing lithium perchlorate, and benzoic acid was added to the anode compartment. The reference electrode was a saturated calomel electrode or a silver nitrate electrode (Ag/0.1 M $AgNO_3$ in CH_3CN), and a Luggin capillary and a salt bridge were used for the junction between a test electrode and a reference electrode. The cathode was a mercury-pool electrode. Triangular potential waves were generated by using a potentiostats and a function generator. The electrolysis was generally operated at a constant current or at a constant potential.

Measurement of Current-potential Curves. Argon gas was bubbled into the electrolyte for 10 min before the electrolysis. In the measurement by the stationary method, the anode potential was kept at each initial voltage in the range from 1.6 to 1.9 V (*vs.* SCE) for 5 min, and then the potential was anodically moved. In the case of single-sweep voltammetry, the anode potential was initially kept at 1.7 V (*vs.* Ag/0.1 N Ag^+) for 5 min, and then the potential was anodically swept at the rate of 16.2 mV/sec.

Anodic Oxidation of Benzoic Acid in Acetonitrile at a Constant Current. During the electrolysis, lithium perchlorate was sometimes added to the electrolyte to suppress the rise in the electric resistance of the electrolyte by the consumption of benzoic acid and lithium perchlorate. After the electrolysis, the solvent acetonitrile was removed from the anolyte by distillation and 100 ml of water was added to the residue. The aqueous solution was extracted with 100 ml of ether. After washing with 50 ml of water, the ether solution was dried over anhydrous sodium sulfate and concentrated. The residue (1.78 g) was chromatographed on Wakogel ($SiO_2 \cdot xH_2O$). Upon chromatography, the first fraction (eluent: n-hexane) gave 0.23 g of a yellow liquid (unidentified). The second fraction (eluent : benzene) afforded 0.37 g of benzoic acid. The third fraction gave 0.76 g of *N*-acetylanthranilic acid (mp 180—181°C (lit,[9] 186°C)); a mixed-mp determination with an authentic sample showed no depression. The structure was also identified by IR and mass spectra. The fourth fraction gave 0.40 g of a brown viscous liquid (unidentified). When the catholyte was treated by the same procedure, *N*-acetylanthranilic acid (0.13 g), benzoic acid (0.67 g), and an unidentified substance (0.95 g) were obtained.

Anodic Oxidation of Benzoic Acid in Propionitrile at a Constant Current. After electrolysis, the anolyte and the catholyte were basified with aqueous sodium hydroxide and organic materials were extracted with 100 ml of ether, respectively. The organic layer was concentrated, and the residue (1.65 g) from the anolyte was chromatographed on Wakogel. The first fraction (eluent : hexane) gave 0.11 g of an unidentified liquid. The second fraction (eluent : benzene) afforded 0.48 g of *N*-propionylbenzamide (mp 97.0°C (lit,[10] 98°C)); the structure was identified as above. The third fraction (eluent : ether) afforded 0.39 g of dipropionylamine (mp 153—154°C (lit,[11] 153—154°C)); a mixed-mp determination with an authentic sample showed no depression; the structure was identified as above. The fourth fraction (eluent : ether and methanol) gave 0.63 g of a dark brown viscous liquid (unidentified). The aqueous layer was acidified with aqueous sulphuric acid, and then extracted with ether. After the removal of the ether, the residue (1.50 g) was similarly chlomatographed on Wakogel. The first fraction (eluent : hexane) gave 0.09 g of a brown viscous liquid (unidentified). The second fraction (eluent : benzene) gave 0.17 g of recovered benzoic acid, while the third fraction (eluent : benzene) gave 0.13 g of an unidentified yellow viscous liquid. The fourth fraction (eluent : ether) afforded 0.88 g of *N*-propionylanthranilic acid (mp 116—117°C (lit,[12] 117°C)); a mixed-mp determination with an authentic sample showed no depression; the structure was identified by means of the IR, mass, and NMR spectra. The fifth fraction (eluent : methanol) gave 0.21 g of a dark brown viscous liquid (unidentified). The catholyte was treated in the same way as above, giving *N*-propionylanthranilic acid (0.18 g), recovered benzoic acid (0.11 g), dipropionylamine (trace), and an unidentified substance (1.58 g).

Anodic Oxidation of Benzoic Acid in Acetonitrile at a Constant Potential. The anode potential was kept at 2.20 V against a silver nitrate electrode. The reaction products were treated in the same way as in the anodic oxidation of benzoic acid in acetonitrile at a constant current.

Results and Discussion

A typical potential-current curve of benzoic acid in acetonitrile obtained by the stationary method using a platinum-wire electrode is shown in Fig. 1. The anodic oxidation current was observed beyond 2.0 V against SCE. Similar potential-current curves were obtained in the anodic oxidation of benzoic acid in propionitrile. The single-sweep voltammetry was also applied. The shapes of the potential-current curves were similar to that obtained by the stationary method, and the oxidation current of benzoic acid was observed over 1.9 V against a Ag/0.1 N Ag^+ electrode.

By using single-sweep voltammetry, some materials were tested for the anode in acetonitrile containing lithium perchlorate in order to observe the effect of the base electrolyte. In the cases of platinum and gold electrodes, the current resulting from the anodic oxidation of the electrolyte was observed over approxi-

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[9] A. Kaufmann, *Ber.*, **42**, 3480 (1909).

[10] B. Prager, P. Jacobson, P. Schmidt and D. Stern, Beilsteins Handbuch der Organischen Chemie, Vierte Auflage, **9**, 213 (1926).

[11] R. Otto and J. Tröger, *Ber.*, **23**, 759 (1890).

[12] B. Prager, P. Jacobson, P. Schmidt and D. Stern, Beilsteins Handbuch der Organischen Chemie, Vierte Auflage, **14**, 340 (1931).

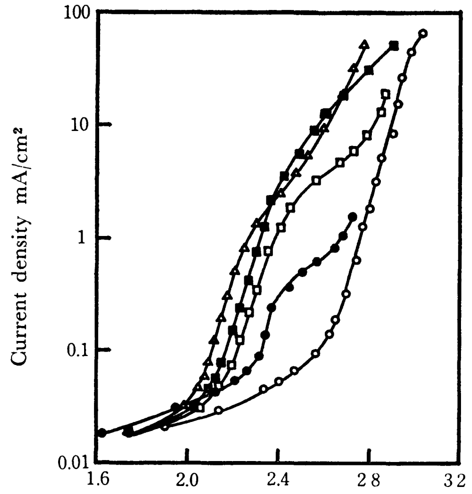

Fig. 1. Relation between anode potential and logarithm of current density on the anodic oxidation of benzoic acid in acetonitrile by stationary method. 30°C, Pt electrode.
—○—: acetonitrile+0.5 M $LiClO_4$
—●—: acetonitrile+5×10^{-4} M benzoic acid+0.5 M $LiClO_4$
—□—: acetonitrile+5×10^{-3} M benzoic acid+0.5 M $LiClO_4$
—■—: acetonitrile+5×10^{-2} M benzoic acid+0.5 M $LiClO_4$
—△—: acetonitrile+5×10^{-1} M benzoic acid+0.5 M $LiClO_4$

Table 1. Results of anodic oxidation of benzoic acid in acetonitrile at a constant current

Anode: Pt, Cathode: Hg, Supporting electrolyte: 1.0 M $LiClO_4$, 30—36°C, 6 hr, Current: 0.4 A, Cell voltage: 18—45 V, Anode potential: 2.45—2.75 V *vs.* SCE, Initial content of benzoic acid: 4.00 g (32.8 mmol)

Product	*N*-Acetylanthranilic acid	Unidentified substance	Recovered benzoic acid
Anolyte	0.76 g (4.2 mmol)	0.63 g	0.37 g (3.0 mmol)
Catholyte	0.13 g (0.72 mmol)	0.95 g	0.67 g (5.5 mmol)

Evolved gas in anode compartment: $CO_2 > H_2 > CH_4$.

mately 2.3 V. Therefore, these electrodes were suitable for use as anodes in this study. In contrast, on the iron, nickel, lead, lead oxide, titanium, and tantalum anodes, the oxidation current of the electrolyte not containing benzoic acid appeared below 1.9 V. This result shows that these materials are not suitable as anodes.

The anodic oxidation of benzoic acid at a constant current gave mainly *N*-acetylanthranilic acid in a 20% yield,[13] together with unreacted benzoic acid and a small amount of unidentified products. The overall results of the electrolysis are shown in Table 1. The *N*-acetylanthranilic acid obtained in the catholyte must have migrated from the anolyte through the diaphragm.

During the electrolysis, a gas, which was confirmed by gas chromatography to be composed of nitrogen, oxygen, carbon dioxide, hydrogen, and methane, was evolved on both the anode and the cathode. The imbalance in the material balance in Table 1 must be due to the gas evolution.

The anodic oxidation of benzoic acid in propionitrile at a constant current was done under conditions corresponding to those in acetonitrile. The overall experimental results are shown in Table 2. *N*-Propionylanthranilic acid, *N*-propionylbenzamide, and dipropionylamine were produced. During the electrolysis, the evolution of a gas composed of hydrogen, carbon dioxide, ethane, and ethylene was similarly observed.

The results of the anodic oxidation of benzoic acid at a constant potential are shown in Table 3. In this electrolysis, no gas evolution was observed, since the polarization on the anode was suppressed.

The comparison of the current efficiencies of the anodic oxidation of benzoic acid in acetonitrile between that at a constant current and that at a constant potential are shown in Table 4; we assumed that two electrons are consumed in the reaction process to produce *N*-acetylanthranilic acid. In the anodic oxidation at a constant potential, gas was not evolved and the side reactions was probably suppressed. Therefore, the material balance in Table 3 is explicable.

For the purpose of clearing the reaction mechanism, some electrochemical measurements were applied; the single-sweep voltammetry was introduced initially. A remarkable anodic oxidation current was measured over 2.0 V against the reference electrode. The Tafel relation was obtained in the potential range from 2.05 to 2.20 V, when the base current due to the anodic

Table 2 Results of anodic oxidation of benzoic acid in propionitrile at a constant current

Anode: Pt, Cathode: Hg, Supporting Electrolyte: 0.1 M $LiClO_4$, 30—37°C, 15 hr, Current: 0.2A, Cell voltage: 50—80 V, Anode potential: 2.20—2.24 V *vs.* SCE, Initial content of benzoic acid: 5.00 g (40.9 mmol).

Product	*N*-Propionyl-anthranilic acid	*N*-Propionyl-benzamide	Dipropionylamine	Unidentified substance	Recovered benzoic acid
Anolyte	0.88 g (4.6 mmol)	0.48 g (2.7 mmol)	0.39 g (3.0 mmol)	1.17 g	0.17 g (1.4 mmol)
Catholyte	0.18 g (0.93 mmol)	— —	trace trace	1.58 g	0.11 g (0.90 mmol)

Evolved gas in anode compartment: $H_2 > CO_2 \gg C_2H_6$, C_2H_4.

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[13] The yield was calculated as the ratio of the numbers of moles of the *N*-acetylanthranilic acid produced and the benzoic acid reacted.

Table 3. RESULTS OF ANODIC OXIDATION OF BENZOIC ACID IN ACETONITRILE AT A CONSTANT POTENTIAL

Anode: Pt, Cathode: Hg, Supporting electrolyte: 0.5 M $LiClO_4$, 30°C, Anode potential: 2.20 V *vs.* Ag/Ag^+, 1690 coul., Initial content of benzoic acid: 2.00 g (16.4 mmol)

Product	*N*-Acetylanthranilic acid	Unidentified substance	Recoverd benzoic acid
Anolyte	0.25 g (1.4 mmol)	0.11 g	0.70 g (5.7 mmol)
Catholyte	0.18 g (1.0 mmol)	0.08 g	0.54 g (4.4 mmol)

Table 4. CURRENT EFFICIENCIES OF THE ELECTROLYSIS OF BENZOIC ACID AT A CONSTANT CURRENT AND A CONSTANT POTENTIAL

	Yield of *N*-acetyl-anthranilic acid[a]	Current efficiencies of the electrolysis based on the yield of *N*-acetylanthranilic acid
At a constant potential	38%	28%
At a constant current	20%	16%

a) The yield was calculated as the ratio of the numbers of the *N*-anthranilic acid produced and the benzoic acid reacted.

oxidation of the electrolyte not containing benzoic acid was deduced from each current value in order to estimate the net oxidation current of benzoic acid. These results are shown in Fig. 2. The linear relation between the logarithm of the concentration of benzoic acid and the current was obtained from the data shown in Fig. 3. Since the slope of the lines in Fig. 3 was 1, the reaction order for benzoic acid in the first electrochemical process should be first-order.

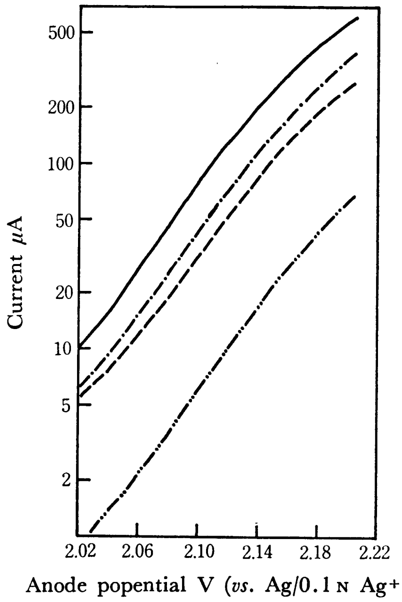


Fig. 2. Relation between anode potential and logarithm of current (deducted residual current) by single-sweep method. 0°C, sweep rate 16.2 mV/sec, Pt electrode (0.289 cm^2)
———: acetonitrile + 10^{-3} M benzoic acid + sat. $LiClO_4$
———: acetonitrile + 4×10^{-3} M benzoic acid + sat. $LiClO_4$
———: acetonitrile + 6×10^{-3} M benzoic acid + sat. $LiClO_4$
———: acetonitrile + 10^{-2} M benzoic acid + sat. $LiClO_4$

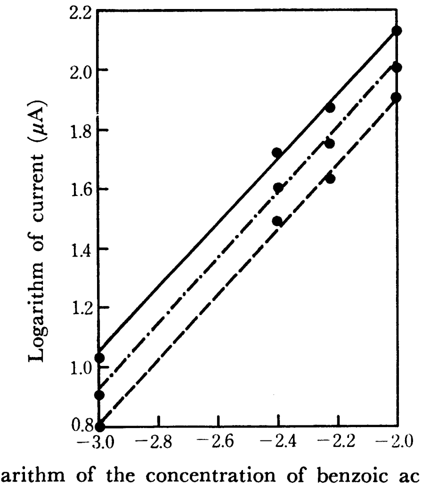
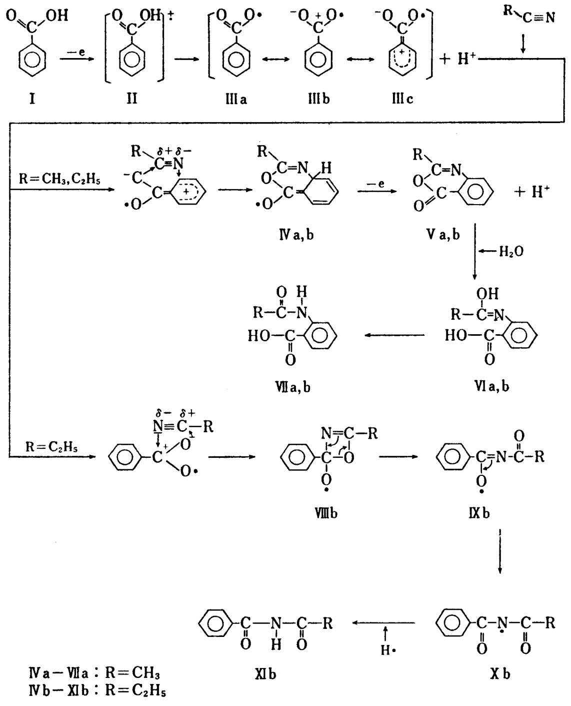


Fig. 3. Relation between logarithm of the concentration of benzoic acid and logarithm of the current by single-sweep method. 0°C, sweep rate 16.2 mV/sec, Pt electrode (0.289 cm^2)
Anode potential
———: 2.10 V (*vs.* Ag/0.1 N Ag^+)
———: 2.11 V (*vs.* Ag/0.1 N Ag^+)
———: 2.12 V (*vs.* Ag/0.1 N Ag^+)

On the basis of the results mentioned above, the rate determining process for the anodic oxidation of benzoic acid could be suggested to be a charge-transfer reaction and its reaction would be first-order for benzoic acid.

At the initial stage, the de-electronation of benzoic acid would produce the radical cation, $[PhCOOH]^{+\cdot}$, on the anode. This radical cation would easily release a proton to yield a benzoylxy radical, as is shown in Scheme 1.



Scheme 1.

In general, the benzoyloxy radical generated by the pyrolysis of benzoyl peroxide in acetonitrile dose not react with acetonitrile to give *N*-acetylanthranilic acid. As acetonitrile is presumed to be inactive in this system, a considerable part of the benzoyloxy radical is expected to be decarbonated. In addition, some part of the benzoyloxy radical abstracts hydrogen from acetonitrile to form benzoic acid and the cyanomethyl radical, which then dimerizes to yield 1,2-dicyanoethane.

However, in this study, the benzoyloxy radical (III in Scheme 1) on the anode does not abstract hydrogen but reacts with acetonitrile, which would be rather active on the anode, to give a new radical (IVa). This radical (IVa) would be immediately oxidized and deprotonated on the anode to give an unstable product, 2-methyl-6*H*-1,3-benzoxazin-6-one (Va). During working-up, this unstable product (Va) would then be hydrolyzed to give *N*-acetylanthranilic acid (VIIa). The reaction mechanism of the anodic oxidation of benzoic acid in acetonitrile is outlined in Scheme 1. A similar reaction is considered for the formation of *N*-propionylanthranilic acid (VIIb) by the anodic oxidation of benzoic acid in propionitrile. Accordingly, on the anodic oxidation of benzoic acid in acetonitrile or propionitrile, the hydrogen at the ortho-position of benzoic acid is displaced by the acetamide or propionamide group in the main process.

On the anodic oxidation of benzoic acid in propionitrile, *N*-propionylbenzamide (XIb) and dipropionylamine were obtained, besides *N*-propionylanthranilic acid (VIIb), though the origin of these different reactivities between the solvent acetonitrile and the propionitrile has not yet been clarified. *N*-Propionylbenzamide (XIb) would be formed according to Scheme 1. Dipropionylamine might be obtained through the coupling of propionitrile and the following hydrolysis, or through the coupling of the propionyl and the *N*-propionyl radicals which arise from the successive electrolysis of the compound (XIb).

In conclusion, the anodic oxidation of benzoic acid in acetonitrile gave *N*-acetylanthranilic acid through the formation of a benzoyloxy radical, its reaction with acetonitrile to form 2-methyl-6*H*-1,3-benzoxazin-6-one, and the following hydrolysis. The anodic oxidation of benzoic acid in propionitrile gave *N*-propionylanthranilic acid, *N*-propionylbenzamide, and dipropionylamine.

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