Electrolytic Synthesis of Benzoic Anhydride
from Benzoic Acid

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Electrolysis of benzoic acid was investigated by means of controlled current operation in acetonitrile with platinum disk electrodes. Benzoic anhydride was obtained from an anolyte at 20–30% of current efficiency as one electron reaction. At the same time, acetamide and hydrogen perchlorate were obtained from the anolyte, and triethylamine was obtained from the catholyte. The yield of acetamide was nearly equal to benzoic anhydride. On the other hand, the yield of triethylamine approximately agreed with the sum of benzoic anhydride and hydrogen perchlorate. Addition of cyclohexene to the system caused to decrease the current efficiency of benzoic anhydride.

From these results, reaction mechanism that is shown in equation (4) to (6) was considered the most reasonable to the formation of benzoic anhydride. The same electrolysis was applied to toluic acids and corresponding anhydrides were obtained at reasonable current efficiency.

Introduction

Electrolytic oxidation of carboxylic acids especially fatty acids had been mainly investigated on Kolbe reaction[1], and it was well known that Kolbe reaction of aromatic carboxylic acids had hardly taken place[2].
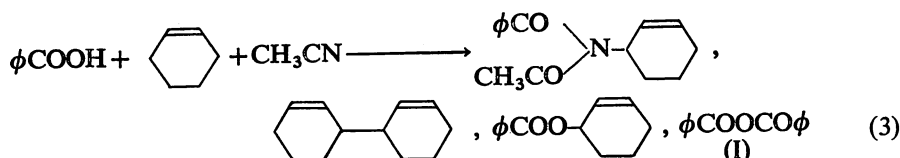
It has been reported that the electrolysis of benzoic acid in DMF, using platinum disk electrodes, gave N-benzoxymethyl-N-methylformamide according to equation (1), at fairly good current efficiency[3].

$$\phi COOH + CH_3 \overset{CH_3}{\underset{|}{N}} CHO \xrightarrow{2F} \phi COOCH_2 \overset{CH_3}{\underset{|}{N}} CHO + H_2 \tag{1}$$
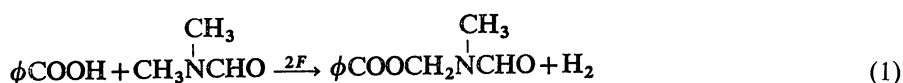
When furan was added to the above reaction system, cis-and trans-2, 5-dibenzoxy-2, 5-dihydrofuran were obtained according to equation (2)[4].

$$2\phi COOH + \underset{O}{\boxed{}} \xrightarrow{2F} \phi COO \frown O \frown OCO\phi \tag{2}$$
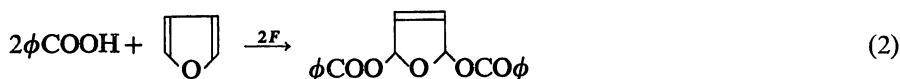
On the other hand, when the solvent was changed from DMF to acetonitrile, and cyclohexene was added to reactant solution, N-3-cyclohexenyl-N-acetylbenzamide, 3-cyclohexenyl benzoate, bicyclohexenyl and benzoic anhydride (I) were produced according to equation (3)[5,6].

$$\phi COOH + \hexagon + CH_3CN \longrightarrow \underset{CH_3CO}{\overset{\phi CO}{N}}-\hexagon ,$$

$$\hexagon-\hexagon , \phi COO-\hexagon , \phi COOCO\phi \tag{3}$$
$$\qquad\qquad\qquad\qquad\qquad (I)$$

From the over-all stoichiometry of the formation of (I), this reaction was regarded as electrolytic dehydration.   The purpose of this investigation is to determine the reaction mechanism of such a electrolytic dehydration and the effects of the reaction condition that affected the yield of (I).

1. Experimental

1. 1 Materials

Tetraethylammonium chloride (Et_4NCl) and tetraethylammonium bromide (Et_4NBr) used as supporting electrolyte were obtained commercially.   Tetraethylammonium iodide(Et_4NI) was prepared from triethylamine and ethyl iodide, and recrystallized from absolute ethanol several times.   Tetraethylammonium perchlorate (Et_4NClO_4) was prepared from Et_4NI and sodium perchlorate, and recrystallized from water until halide ion could not be detected in the mother liquor.   Benzoic acid and toluic acids obtained commercially were purified by recrystallization from water.   These supporting electrolytes and acids were dehydrated under reduced pressure and stored in a sealed tube.   Acetonitrile used as solvent was dehydrated by distillation and stored in a desiccator.

1. 2 Experimental equipment

Details of the electrolysis cell is shown in Fig. 1.   This cell consisted of two compartments which
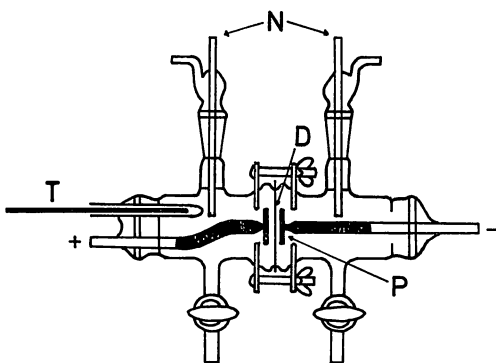

Fig. 1 Electrolysis cell with diaphragm.
N: N_2 inlet,   P: platinum disk electrode,   T: thermometer,   D: paraffine paper

were divided with parafine paper diaphragm.   The volume of each compartment was 55 ml and the diameter of the platinum disk was 2 cm.   The platinum disks were placed face to face and spacing of electrodes was adjusted to about 4 mm.   For the purpose of agitation, dry N_2 was continuously blown into the electrolyte of both compartments.   Each run was carried out at constant current density controlled with a Yanagimoto controlled potential electrolyzer VE–10.   The electrolytes were taken out at constant time intervals from both compartments and the concentration of benzoic acid, the yield of hydrogen perchlorate, (I) and triethylamine were measured by the following methods.

1. 3 Analysis

Concentration of benzoic acid was measured by means of potentiometric titration using benzene-

methanol solution of sodium methoxide.   Yield of hydrogen perchlorate was measured with the titration using ethylene glycol-isopropyl alcohol solution of sodium hydroxide.   Yield of (I) was measured by modified Siggia-Hanna's method[7].   Triethylamine produced in cationic compartment was determined by means of titration using ethylene glycol-isopropyl alcohol solution of hydrochloric acid.   After the time required since the electrolysis started, the electrolyte taken out separately from each compartment was evaporated under reduced pressure to remove the solvent.   The residue was dissolved in 150 ml of benzene and supporting electrolyte which could not dissolve in benzene was separated by filtration.   The filtrate was washed with 100 ml of 1 M sodium bicarbonate and 1 N hydrochloric acid several times and neutral product (water insoluble) was obtained by evaporation of benzene but water soluble products could not be obtained in this treatment.   To obtain the products, residue was extracted by water and after water was evaporated under reduced pressure, the residue was re-extracted by benzene.   Some products contained benzoic acid was obtained by the removal of benzene and they were analyzed by gas chromatography.

2. Results and Discussion

2. 1 Identification of products

Water insoluble neutral products from both compartments were collected by means of preceding procedure.   From the anolyte solution, 1.0–1.5 g of neutral products were obtained but trace amount from catholyte.   Neutral products from the anolyte were separated by means of column chromatography ($CHCl_3$, silica-gel).   It was found that almost all products were (I) and other products that shows in equation (3) could not be observed.

Since the catholyte became basic at end of the electrolysis, the solution was carefully distilled and picric acid (in methanol) was added to the distillate.   Yellow crystal was obtained (mp. 172–173°C), and from the melting point and IR spectrum, it was found that the crystal was picrate of triethylamine (pure compound: mp. 173–174°C).

On the other hand, since the anolyte became acidic, it was titrated by sodium methoxide.   As a result, its titration curve and end point were perfectly coincided with that of pure hydrogen perchlorate solution.   But, in this electrolysis, chloride ion could not be detected from both electrolyte solution, that is, further decomposition of perchlorate ion did not occur.

0.3–0.4 g of water soluble products were obtained from anolyte but no product could be obtained from catholyte similarly to that of water insoluble neutral products.   The water soluble products were separated by means of gas chromatography (Thermol-3, 1.5 m, 200°C).   Acetamide as main product was identified by the retention time of gas chromatograph, IR and NMR spectra.   The yield of acetamide

Table 1.   Yield of acetamide and (I)

run	electrolysis time (hr)	acetamide (m mol)	(I) (m mol)	theoritical (m mol)
101	3	3.4	3.6	11.19
102	3	3.3	3.8	11.19
103	3	3.1	3.6	11.19
104	2	2.1	2.4	7.45
105	2	2.0	2.1	7.45

analyzed by gas chromatography is shown Table 1 with the yield of (I).

In consequence, it was considered that acetamide was quantitatively produced by the addition of H_2O formed with (I) to acetonitrile used as solvent.

In general, at an electrolysis in non-aqueous solvents, contamination or formation of water would trend to decrease a current efficiency of desired products. But, in this investigation, acetamide produced instead of water was contributed to increase the yield of (I) as shown Fig. 2.
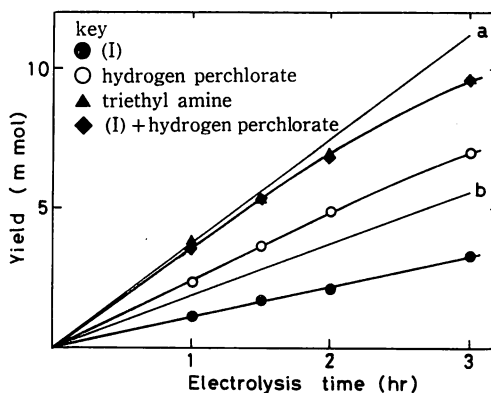

Fig. 2   Relationship between yield of products and electrolysis time.

2. 2   Relationships between electrolysis time and yield of (I), hydrogen perchlorate and triethylamine

Fig. 2 shows the relationships between electrolysis time and yields of (I), hydrogen perchlorate and triethylamine under the condition shown in Table 2. Straight line a and b in Fig. 2 shows the theoritical yield of one-electron and two-electron reaction respectively. In this electrolysis, it was concluded that each mole of products except (I), was produced from 1 F. However, the total amounts of (I) and hydrogen perchlorate were almost agreed with that of triethylamine. These results suggested that (I) and hydrogen perchlorate were produced competitively in the anodic compartment by one-electron reaction.

Table 2.   Experimental conditions

supporting electrolyte;	0.3 mol/l
benzoic acid;	0.5 mol/l
current density;	0.318 A/cm²
electrolysis time;	3 hrs
cell voltage;	9–27 V

The yield of (I) using Kolbe type electrolysis cell was one-fifth of that with diaphragm[5]. It seemed that when anolyte was mixed with catholyte, the reaction according to equation (3) proceeded preferentially. To examine the effect of mixing, triethylamine which would be produced under the condition shown in Table 2 was added to the electrolysis solution and electrolysis was carried out under the same condition. The yield of (I) was decreased to one-tenth of normal yield and when equimolar triethylamine was added to benzoic acid, (I) could not be observed.

In consequence, it was concluded that to increase the current efficiency of this electrolytic dehydration, anolyte should be acidic, that is, existence of free acid was indispensable.

2. 3   The effect of addition of cyclohexene on the yield of (I)

When benzoic acid was electrolyzed with a olefin like cyclohexene in Kolbe-type electrolysis cell, unsymmetrical carboxyimides were mainly produced[6]. To examine the effect of olefin in the electrolysis cell shows in Fig. 1, cyclohexene was added to the electrolysis solution. Fig. 3 shows the relationship
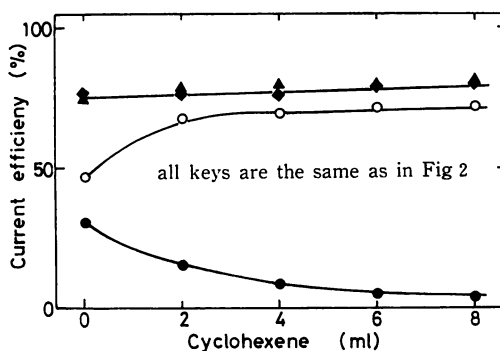

Fig. 3   Relationship between current efficiency and amount of cyclohexene.

between current efficiencies of (I), hydrogen perchlorate and triethylamine, and the amounts of cyclohexene. Although the current efficiency of (I) rapidly decreased with the amounts of cyclohexene, that of (I) + hydrogen perchlorate and triethylamine was nearly constant. When cyclohexene was added to both electrolysis solution, blue material was produced from anode and diffused over anolyte. After one hour since electrolysis started, the anolyte became blue. However, when the anolyte was mixed with anilline, methanol or water, this color disappeared immediately. Thus, it was suggested that this material was a radical which participated in perchlorate radical and cyclohexene. But, authors are leaving for further discussion about this material for another opportunity.

2. 4   The effect of supporting electrolytes

Et_4NClO_4 was only used as supporting electrolyte in preceding experiments, but supporting electrolyte was seemed to play an important role in this electrolysis. Now, other tetraethylammonium salts i.e. Et_4NCl, Et_4NBr and Et_4NI were used as supporting electrolytes. Table 3 shows the effect of supporting electrolytes on current efficiencies of (I) and triethylamine.

When Et_4NCl was used as supporting electrolyte, Cl_2 evolved from anodic compartment. On the other hand, in case of Et_4NBr and Et_4NI, neither Br_2 nor I_2 was deposited and current efficiency of (I) was nearly the same as Et_4NClO_4. However, using these tetraethylammonium halides as supporting electrolyte, addition of cyclohexene to the electrolysis solution resulted in decrease of current efficiency of (I). And 1, 2-dihalogenocyclohexane was isolated from the water insoluble neutral products. Especially, using Et_4NBr, 1, 2-dibromocyclohexane was the only product. Thus it was suggested that halogen radicals produced with anode favorably attacked on double bond of cyclohexene to produce 1, 2-dihalogeno-cyclohexane. On account of this formation, current efficiency of (I) was decreased. The first step of (I) formation was considered to form the halogen or perchlorate radicals by discharge

Table 3.　Effect of supporting electrolyte on current efficiency of (I) and triethylamine

cyclohexene (ml)	supporting electrolyte	(I) (%)	triethylamine (%)
0	Et_4NClO_4	30.6	71.9
0	Et_4NCl	16.6	72.6
0	Et_4NBr	25.5	90.4
0	Et_4NI	28.6	78.1
1	Et_4NClO_4	19.8	74.9
1	Et_4NCl	7.7	92.1
1	Et_4NBr	0.99	82.7
1	Et_4NI	3.9	88.7

of the supporting electrolytes.

2. 5　Reaction mechanism

From above results, we submit to the reaction as follows;

$$X\cdot + \phi COOH \longrightarrow H^+ + \phi COO\cdot + X^- \tag{4}$$
$$(X = ClO_4, Cl, Br, I)$$

$$(4')$$

$$(5)$$

$$(6)$$
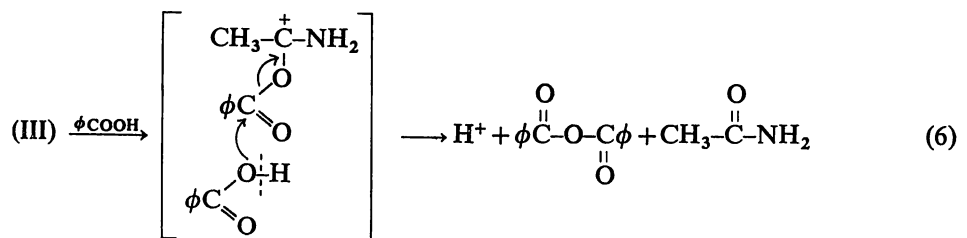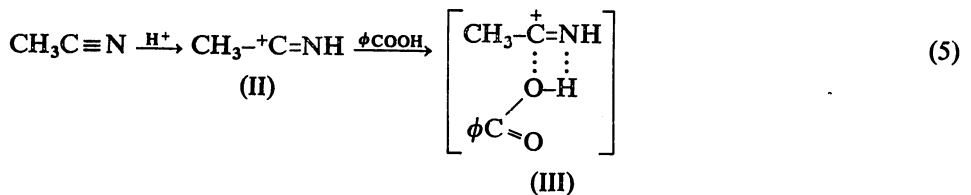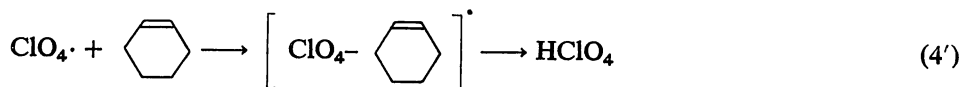
At first, halogen or perchlorate radical produced on discharge of supporting electrolytes reacted with benzoic acid to form a hydrogen ion according to equation (4).　Acetonitrile used as solvent was attacked with hydrogen ion to produce intermediate (II) according to equation (5), and (II) reacted with benzoic acid to form a intermediate (III), finally, (III) further reacted with one more benzoic acid to produce (I) and acetamide according to equation (6).　When cyclohexene was added to the electrolysis solution, halogen radicals reacted with cyclohexene.　On the other hand, perchlorate radical could not be added to the double bond of cyclohexene, and produced a new radical containing cyclohexene

Table 4. Result of electrolysis of toluic acids

acid	electrolysis time (hr)	current efficiency of anhydride (%)	current efficiency of triethylamine (%)
o-toluic acid	2	15.1	61.5
m-toluic acid	2	28.4	83.8
p-toluic acid	2	28.3	74.4
benzoic acid	2	30.6	78.6

according to equation (4'). The formation of this radical prevented formation (I) shown in equation (4) to (6).

The electrolysis of toluic acids was carried out under the same condition as benzoic acid. Table 4 shows the results of electrolysis of toluic acids. Corresponding pure anhydrides were synthesized by methods given in literature[8] and identified by melting point, IR and NMR spectra. It was found that the current efficiencies of meta- and para-toluic anhydrides were nearly coincided with that of benzoic anhydride, but current efficiency of ortho-toluic anhydride decreased owing to the steric hindrance of the ortho position. Authors attempted to electrolyze the other acids having a substituent group on ortho position (chloro, methoxy, and tertbutyl) but failed to electrolyze because all acids could not be dissolve in acetonitrile.

References

1) B. C. L. Weeden, "Advance in Organic Chemistry", vol. 1, Interscience Pub. Inc., New York (1960), p. 1.
2) B. C. L. Weeden, Quart. Rev., 6, 380 (1952).
3) S. Arita, K. Tasaki, S. Uchida, and K. Takeshita, The Reports of Research Institute of Industrial Science, Kyushu University, No. 46, 39 (1967).
4) S. Arita, Y. Nagahiro, and K. Takeshita, Kogyo-Kagaku-Zasshi, 72, 282 (1969).
5) S. Arita, Y. Takahashi and K. Takeshita, The 23th Annual Meeting of Chemical Sociaty of Japan, vol. 3, p. 1640 (1970).
6) S. Arita, Y. Takahashi and K. Takeshita, The 24th Annual Meeting of Chemical Sociaty of Japan, vol. 3, p. 1712 (1971).
7) S. Siggia and J. G. Hanna, Anal. Chem., 23, 1717 (1951).
8) S. Iwanami, S. Arita, and K. Takeshita, Yuki-Goseikagaku-Kaishi, 26, 375 (1968).