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Free Radical Reactions in Organic Electrode Processes. VII.[*1] Anodic Reaction of Benzoic Acid with Aromatic Hydrocarbons[*2]

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The anodic reaction of benzoic acid in acetonitrile containing tiethylamine was carried out in the presence of toluene, ethylbenzene, cumene, and tetralin. The amounts of carbon dioxide evolved during the electrolyses were smaller than those expected to be produced through the spontaneous decomposition of the benzoyloxy radical. An examination of nongaseous products indicated that the anodic reaction proceeds by means of the formation of the benzoyloxylates and phenylates of the aromatic hydrocarbons present. The occurrence of the nuclear benzoyloxylation, to a relatively great extent, suggested that the aromatic hydrocarbons were oxidized at the anode.

In a previous paper from this laboratory, it has been shown that the anodic reaction of some aromatic carboxylic acids in the presence of anisole resulted in the formation of *o*- and *p*-methoxyphenyl esters of the corresponding acids in fairly good yields, together with traces of the Kolbe dimer and of carbon dioxide.[1] The results were interpreted as being due to a simultaneous oxidation of anisole at the anode, leading to the formation of its cation radical.

As has been pointed out by Zweig *et al.*,[2] the aromatic compounds with electron-rich molecular π-orbitals, such as methoxybenzenes, easily lose an electron and so form their cation radicals.

$$\mathrm{ArH} \xrightarrow{-e^-} \mathrm{ArH}\cdot^+$$

$$\mathrm{ArH} \xrightarrow{-2e^-} \mathrm{ArH}^{2+} \xrightarrow{+\mathrm{ArH}} 2\mathrm{ArH}\cdot^+$$

In fact, recent studies of the polarographic oxidation of aromatic compounds have indicated that the half-wave polarographic oxidation potential of aromatic hydrocarbons decreases with an increase in the number of electron-releasing substituents on the benzene ring, or with an increase in the number of fused rings in a series of polynuclear aromatic hydrocarbons.[3,4]

On the other hand, recent studies concerning the

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anodic substitution reactions[1,5–10] have indicated that the organic substrates participate in the electrochemical process, generating the cationic intermediates (either the cation radical or the dication), which then react with anions to give the substitution products.

$$\mathrm{ArH} \xrightarrow{-e^-} \mathrm{ArH}\cdot^{+} \xrightarrow{+Y^-} \mathrm{ArHY}\cdot$$

$$\longrightarrow \mathrm{ArY} + \mathrm{H}^+ + e^-$$

or

$$\mathrm{ArH} \xrightarrow{-2e^-} \mathrm{ArH}^{2+} \xrightarrow{+Y^-} \mathrm{ArY} + \mathrm{H}^+$$

The present investigation was undertaken to see if such a mechanism could also be operative in the anodic reaction of benzoic acid with aromatic hydrocarbons with relatively high polarographic oxidation potentials.

Results and Discussion

The electrolyses were carried out in acetonitrile containing triethylamine in the presence of toluene, ethylbenzene, cumene, and tetralin at a temperature of 18—25°C, at a current of 0.08—0.11 A, and with a relatively high applied potential (40—65 V), until a calculated amount of current (2.6—3.0 A-hr) had been passed through the solution.

The gaseous products were then collected, and analyzed by means of a column packed with silica gel. The non-gaseous products, after having been worked up in the usual ways, were separated into unchanged benzoic acid and benzene-soluble and benzene-insoluble materials. The chromatographic separation of the benzene-soluble products yielded a mixture of phenylated and benzoyloxylated aromatic compounds; the mixture was then saponified with alcoholic potassium hydroxide. The products obtained after the saponification were analyzed by vapor-phase chromatography. On the basis of the structure of those characterized phenols and hydrocarbons, the products formed during the electrolysis were determined. In all cases, considerable amounts of benzene-insoluble polymeric residues were produced. Their IR spectra suggested that they had an ester function, but they could not be completely hydrolysed. The results are summarized in Table 1.

The percentage yields given for the non-gaseous products are based on the amounts of benzoic acid not recovered at the end of the electrolysis; the Coulombic yields were calculated for the hydrogen and carbon dioxide evolved.

If the over-all electrode reaction of the carboxylic acids proceeds in exactly the following manner:

$$2\mathrm{RCOO}^- \rightarrow 2\mathrm{CO}_2 + \mathrm{R\text{-}R} + 2e^- \quad (1)$$

$$2\mathrm{H}^+ + 2e^- \rightarrow \mathrm{H}_2 \quad (2)$$

the quantity should approach two moles of unrecovered carboxylic acid, two moles of carbon dioxide, and one mole of hydrogen per two faradays. However the results, apparently indicate that the addition of aromatic hydrocarbons alters the course of the reaction; the evolved hydrogen reaches 86—100% of the theoretical amount, while the amounts of carbon dioxide are very small. This diminished evolution of carbon dioxide may be

TABLE 1. ELECTROLYSIS OF BENZOIC ACID IN THE PRESENCE OF AROMATIC COMPOUNDS

Acid: Benzoic acid (0.05 mol)
Aromatic compound: 0.4 mol
Solvent: MeCN (50 m*l*) containing Et_3N (2.8 m*l*)
Electrode: 2Pt-Foils (15×20 mm; space, 10 mm apart)
Temperature: 18—28°C
Current: 0.08—0.12 A

Aromatic compound	Acid not recovered (%)	Product					
		Gaseous (%)[a]		Nongaseous			
		H_2	CO_2	Benzene-soluble (g)	Benzene-insoluble (g)	Phenylate (%)[b]	Benzoyloxylate (%)[b]
Toluene	57	100	3.4	2.8	0.9	1	1.2
Toluene[c]	82	79	4.6	4.3	—	0.1	0.2
Ethylbenzene	75	86	7.5	3.2	0.7	4.0	0.8
Cumene	72	98	4.8	3.1	1.2	1.3	1.6
Tetralin[d]	57	90	1.8	5.2	0.6	neutral: 0.5 g phenolic: 0.3 g	

a) Coulombic yield
b) Based on the acid not recovered
c) Solvent: MeOH (50 m*l*) containing MeONa (0.02 mol)
d) 0.35 mol

interpreted as being due to the suppressed decarboxylation of an anodically-adsorbed benzoyloxy radical or as being due to the participation of other electrode reactions in which the discharge of the benzoate anion is not significantly operative. From a consideration of the quantitative relationship between hydrogen and the unrecovered acid, it may be suggested that a considerable portion of the hydrogen is not supplied from the electrolysis of benzoic acid, but is, rather supplied from the aromatic substrate present.

Two primary electrode reactions (Eqs. (3) and (4)) are possible in the Kolbe electrolysis:

$$\mathrm{RCOO^- \rightarrow R\cdot + CO_2 + e^-} \qquad (3)$$

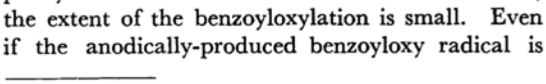
(simultaneous bond-breaking)

$$\mathrm{RCOO^- \rightarrow RCOO\cdot + e^-} \qquad (4)$$

On the basis of the calculations of the standard potentials and rate constants for the two reactions, Eberson has suggested that, in the anodic reaction of benzoic acid, the latter reaction (Eq. (4)) is probable, and that it is followed by radical decomposition to the phenyl radical and carbon dioxide.[11] A sequent electrode reaction (Eq. (5)) can be ruled out since the ionization potential (9.2 eV)[12] of the phenyl radical is above the critical potential of 8 eV.

$$\mathrm{Ph\cdot \rightarrow Ph^+ + e^-} \qquad (5)$$

At least three active species, *i.e.*, $\mathrm{PhCOO^-}$, PhCOO·, and Ph·, which can participate in the anodic substitution may be generated from benzoic acid in these systems. Of these however, only the phenyl radical can take part in the phenylation. Thus, the observed phenylation appears to proceed in a free radical manner, while the formation of biphenyl suggests the generation of phenyl radicals:



$$\mathrm{ArH + Ph\cdot \rightarrow Ar\cdot(H)(Ph) \rightarrow Ar\text{-}Ph + H^+ + e^-}$$

The other two species, $\mathrm{PhCOO^-}$ and PhCOO·, can participate in the anodic benzoyloxylation. Homolytic benzoyloxylation has been observed when benzoyl peroxide decomposes in benzene,[13] chlorobenzene,[14,15] nitrobenzene,[14,16] and biphenyl.[13,16] With the mono-substituted benzenes, the extent of the benzoyloxylation is small. Even if the anodically-produced benzoyloxy radical is stabilized by adsorption of the electrode surface, it can undergo spontaneous decomposition; thus, the homolytic phenylation should still proceed as the main reaction. The yields of benzoyloxylates in this anode reaction are, however, rather larger than those expected to be produced by the homolytic processes.

Therefore, it is reasonable to assume that the majority of the benzoyloxylates arise from the reaction of the benzoate anion with a cationic intermediate generated from the aromatic substrate at the anode.

$$\mathrm{ArH \xrightarrow{-e^-} ArH\cdot^+ \xrightarrow{+PhCOO^-} ArOCOPh + H^+ + e^-}$$

or

$$\mathrm{ArH \xrightarrow{-2e^-} ArH^{2+} \xrightarrow{+PhCOO^-} ArOCOPh + H^+}$$

Experimental

All the melting and boiling points are uncorrected. The IR spectra were obtained with a Shimadzu IR spectrophotometer IR-27C. A Toyo GC-S-7 (gas chromatograph) apparatus was employed in the analysis of the products. The electrolyses were carried out in an undivided cylindrical cell (*ca.* 100 m*l*) fitted with a reflux condenser and a thermometer. Two platinum electrodes (15×20 mm; space, 10 mm apart) were inserted into the center of the cell through a ground-glass joint at the top. The cell was connected through the condenser to a gas-collection apparatus.

Materials. Commercially-availlable benzoic acid (mp 121°C), toluene (bp 110—111°C), ethylbenzene (bp 136°C), cumene (bp 152°C), tetralin (bp 77°C/10 mmHg), acetonitrile (bp 82°C), triethylamine (bp 90°C), and methanol were purified by the usual ways.

Electrolysis of Benzoic Acid in the Presence of Toluene. A solution of benzoic acid (6.1 g, 0.05 mol) and toluene (36.8 g, 0.4 mol) in acetonitrile (50 m*l*) containing triethylamine (2.8 m*l*) was electrolyzed at 18—24°C (current: 0.08—0.11 A, voltage: 40—65 V, total current passed: 2.73 A-hr).

The gas evolved during the electrolysis was then analyzed by using a silica gel column at 20—40°C; it was found to consist of hydrogen (1140 m*l*) and carbon dioxide (80 m*l*). The non-gaseous product was distilled under reduced pressure to recover the solvent and the bulk of the uncharged toluene (22.6 g, 0.25 mol). The residue (9.1 g) was separated into unchanged benzoic acid (2.6 g, mp and mixed mp 120—121°C) and benzene-soluble (2.8 g) and benzene-insoluble (0.9 g) portions. The benzene-insoluble solid (mp over 250°C) displayed IR bands assignable to the ester function at 1240—1280 and 1740 $\mathrm{cm^{-1}}$; it was treated with alcoholic potassium hydroxide under reflux for 15 hr. However, it could not saponified completely. The saponification gave an acid (0.23 g), phenolic compounds (0.1 g) and other materials (0.44 g). These substances were not investigated further.

The benzene-soluble portion gave at least three major spots on TLC and was subjected to chromatographic separation (adsorbent: silica gel; eluent:

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benzene). On the basis of the IR spectra and the results of TLC analysis, the collected fractions were combined after the evaporation of the eluent. The main combined residue (0.5 g) was saponified with alcoholic potassium hydroxide under reflux for 15 hr to give an acid (0.1 g) phenolic compounds (0.09 g) and a neutral portion (0.2 g). The latter two portions were analyzed by vapor-phase chromatography (column: 3-m Cu-column packed with 25% Silicone HV on a fire brick; carrier gas: He, 70 and 37 m*l*/min respectively; column temperature: 180 and 210°C respectively). The phenolic portion consisted of *m*- and/or *p*-cresol (30.4%), *o*-cresol (9.7%), and other materials. The neutral fraction consisted of *m*- and/or *p*-methylbiphenyl (16.5%), *o*-methylbiphenyl (2.1%), biphenyl, and at least two other unidentified substances.

Additionally, the electrolysis of benzoic acid (6.1 g, 0.05 mol) in methanol (50 m*l*) containing sodium methoxide (1.1 g) was examined in the presence of toluene (36.8 g, 0.4 mol) under similar conditions (19—24°C; 0.12 A, 15—16 V, 4 A-hr). The gaseous product consisted of hydrogen (1320 m*l*) and carbon dioxide (110 m*l*). The benzene-soluble residue (4.3 g) was separated after saponification into acid (1.1 g), a phenolic (0.1 g), and a neutral (0.9 g) portions. The phenolic portion consisted of *m*- and/or *p*-cresol (17.3%), *o*-cresol (8.8%), and other, unidentified substances. The neutral portion consisted of *m*- and/or *p*-methylbiphenyl (1.4%), *o*-methylbiphenyl (0.5%), biphenyl, and other materials.

Electrolysis of Benzoic Acid in the Presence of Ethylbenzene. A solution of benzoic acid (6.1 g, 0.05 mol) ethylbenzene (42.4 g, 0.4 mol) in acetonitrile (50 m*l*) containing triethylamine (2.8 m*l*) was electrolyzed at 16—28°C, at a current of 0.07—0.11 A and with an applied potential of 48—69 V, for 25 hr.

The gaseous product consisted of hydrogen (980 m*l*) and carbon dioxide (170 m*l*). The non-gaseous product was worked up in manners similar to those employed for toluene, and gave unchanged ethylbenzene (30 g, 0.23 mol), benzoic acid (1.5 g), a benzene-soluble portion (3.2 g), and a benzene-insoluble polymeric solid (0.7 g). The chromatographic separation of the benzene-soluble portion gave a hydrocarbon - benzoate mixture (0.7 g) and a dark-brownish residue. The mixture was treated with alcoholic potassium hydroxide to give benzoic acid (0.17 g), phenolic (0.19 g), and neutral (0.37 g) portions. The phenol portion was found to consist of *o*-ethylphenol (6.6%), *p*-ethylphenol (16.2%), and other materials. The vapor-phase chromatographic analysis of the neutral substances showed it to contain *o*-ethylbiphenyl (21.5%), *p*-ethylbiphenyl (49.8%), biphenyl (traces), α-phenylethanol, and at least two other substances.

Electrolysis of Benzoic Acid in the Presence of Cumene. A solution of benzoic acid (6.1 g) and cumene (48 g, 0.4 mol) in acetonitrile containing triethylamine was electrolyzed under similar conditions (17—25°C, 0.04—0.11 A, 54—60 V, 2.97 A-hr). A mixture of hydrogen (1100 m*l*) and carbon dioxide (120 m*l*) was obtained as the gaseous product. From the electrolyzed mixture, unchanged cumene (33.5 g, 0.28 mol) and residual tar (8.8 g) were obtained. The residue was spearated into benzoic acid (1.7 g), benzene-soluble (3.1 g), and insoluble (1.2 g) portions. A hydrocarbon - benzoate mixture (0.57 g) was obtained from the benzene-soluble portion. The mixture gave, after saponification, benzoic acid (0.2 g), phenol (0.1 g) and neutral (0.32 g) portions. The characterized components of the phenol portion were *o*-isopropylphenol (8.7%) and *p*-isopropylphenol (37.6%). *o*-Isopropylbiphenyl (7%), *p*-isopropylibiphenyl (19.7%), biphenyl (traces), and α-cumenol (traces) could be identified as the components of the neutral fraction.

Electrolysis of Benzoic Acid in the Presence of Tetralin. The electrolysis was carried out by using tetralin (47.8 g, 0.35 mol) under similar conditions (18—28°C, 0.08—0.11 A, 56—68 V, and 2.63 A-hr).

The gaseous product consisted of hydrogen (990 m*l*) and carbon dioxide (40 m*l*). Tetralin (14 g, 0.31 mol) and a residual oil (13.7 g) were obtained from the crude product. The residual oil gave benzoic acid (2.6 g), benzene-soluble (5.2 g), and insoluble (0.6 g) fractions. Portions (2 g) of the benzene-soluble fraction were chromatographed on silica gel and eluted with a benzene - methanol mixture to give a hydrocarbon - benzoate mixture (1.06 g) The saponification of the mixture yielded benzoic acid (0.2 g), phenolic (0.15 g) and neutral (0.3 g) parts. The VPC analysis of the neutral part failed to show the presence of 1-hydroxy-1,2,3,4-tetrahydronaphthalene.