NOTES Bull. Chem. Soc. Jpn., 60, 4166—4168 (1987) [Vol. 60, No. 11

The Magnetic Field Effects on Electrolysis. III.[1)] The Anodic Oxidation of Phenylacetate Ion

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(Received April 2, 1987)

Synopsis. In anodic oxidation of the phenylacetate ion, the formation yield of benzaldehyde increases by about 40% in the presence of a magnetic field (0.67 T), while 1,2-diphenylethane is insensitive to the field. The results are interpreted in terms of the magnetohydrodynamic mechanism.

In previous studies,[1,2)] we have investigated external magnetic field effects on inorganic electrochemical processes and demonstrated that the magnetohydrodynamic (MHD) effect plays an important role in redox reactions. In the MHD mechanism, a flow of electrons and ions is affected by an external magnetic field, resulting in the perturbation on the mass-transport process near the electrode. As an extention of the above-mentioned investigation, we have studied the magnetic field effects on organic electrochemical processes.

In the present paper, we report on the magnetic field effects on the electrolysis of the phenylacetate ion, as an example of the Kolbe reaction, which may be preparatively useful.

Experimental

Phenylacetic acid was prepared by the hydrolysis of ethyl phenylacetate,[3)] and was purified by recrystallization. Solvents for high-performance liquid chromatography (HPLC) grade, methanol, dioxane and water, were used as received.

The electrolysis was carried out using a potentio/galvano stat (Hokuto Denko, HA-102). An aerated methanol-dioxane solution (50 ml), containing phenylacetic acid (0.05 mol dm^{-3}) and its potassium salt (0.05 mol dm^{-3}), was electrolyzed between two platinum plate electrodes (5 mm×10 mm) at a constant density of 9 mA cm^{-2} for about 90 min (0.1 F mol^{-1}). Argon or oxygen gas was bubbled through the solution during the electrolysis, when necessary. A magnetic field was applied with an electromagnet (Tokin SEE-10).

The reaction products were analyzed on an HPLC apparatus (Waters model 590 liquid chromatograph) and a UV detector (Waters 481 LC-spectrophotometer). The products were identified from the agreement of their UV absorption spectra and retention times with those of authentic samples, by monitoring the absorbance at 260 nm.

Results and Discussion

Figure 1a shows a typical chromatogram of the reaction mixture obtained by electrolysis in the absence of a magnetic field. The five peaks in the chromatogram have been identified as benzaldehyde (PhCHO), benzyl methyl ether ($PhCH_2OCH_3$), toluene ($PhCH_3$), benzyl phenylacetate ($PhCH_2COOCH_2Ph$), and 1,2-diphenylethane ($PhCH_2CH_2Ph$), though the other two peaks with retention times of 10.2 and 16.8 min remain unidentified. Figure 1b shows the effects of a magnetic field (0.67 T) on the product yields. In the presence of a magnetic field, the yield of benzaldehyde increases by about 40%, while those of 1,2-diphenylethane and others are insensitive to the magnetic field (summarized in Table 1).

The electrolysis of substituted phenylacetate ions in methanol was studied in detail by Coleman et al.[4)] According to their proposed mechanism, the plausible

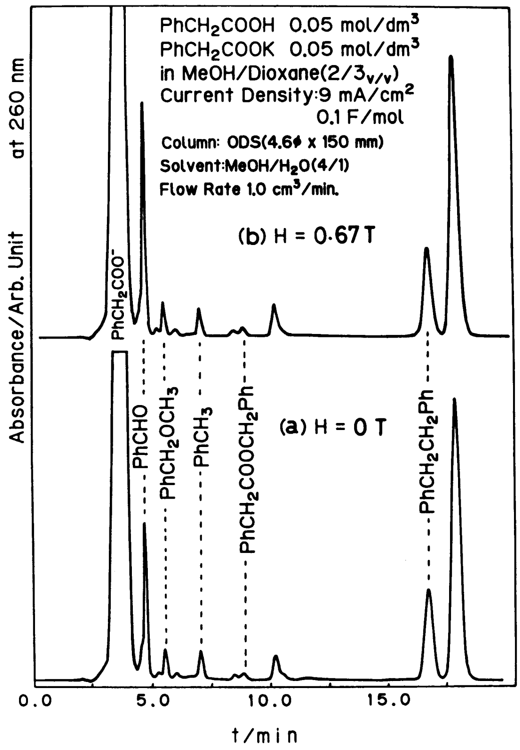

Fig. 1. Typical chromatograms of the reaction mixture after the electrolysis of an aerated solution of phenylacetic acid and its potassium salt in the absence (a) and in the presence (b) of a magnetic field (0.67 T).

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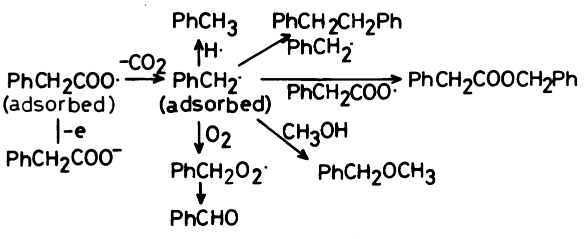
Table 1. The External Magnetic Field Effects on the Product Yields for the Electrolysis of an Aerated Phenylacetate Ion Solution$^{a)}$

	PhCHO	PhCH$_2$OCH$_3$	PhCH$_3$	PhCH$_2$COOCH$_2$Ph	PhCH$_2$CH$_2$Ph
$\phi(\mathrm{H})/\phi(\mathrm{O})^{b)}$	1.39	1.06	0.95	1.01	0.97
	(0.19)	(0.23)	(0.13)	(0.11)	(0.04)

a) Values in parentheses denote experimental errors. b) ϕ(H) and ϕ(O) are the relative yield in the presence and the absence of a magnetic field (0.67 T).

pathways of the present reaction could be summarized as follows:



The benzyl radical generated via the phenylacetoxy radical by the one-electron oxidation of phenylacetate ion, undergoes the following reactions: coupling of radicals and an addition of molecular oxygen. Benzaldehyde could result from the addition of oxygen to the benzyl radical.[5] The oxygen involved in the reaction could be either dissolved oxygen or oxygen produced electrochemically from the hydroxide ion.

In order to clarify the role of molecular oxygen in the benzaldehyde formation, electrolysis was carried out under two extreme conditions. In the electrolysis under the argon bubbling, the yield of benzaldehyde slightly decreased ($\approx$15%), while that of 1,2-diphenylethane remained unchanged on the removal of dissolved oxygen by argon. On the other hand, in a reaction under oxygen bubbling, a significant increase ($\approx$20 times) in the yield of benzaldehyde was observed in a concomitant decrease (70—80%) in that of 1,2-diphenylethane. These observations indicate that the dissolved molecular oxygen is responsible for the formation of benzaldehyde in aerated solutions. In argon-bubbled solutions, the molecular oxygen produced electrochemically from the hydroxide ion could be a major source of molecular oxygen in benzaldehyde formation.

In a previous study,[1] the external magnetic field effects on electrolytic currents in hexacyanoferrate(II) and hexacyanoferrate(III) solutions were investigated under various conditions by means of potentiometry. All the results were interpreted in terms of the MHD mechanism, in which a flow of electrolyte is affected by a MHD force $\boldsymbol{F}$ with the relation $\boldsymbol{F}=\boldsymbol{j}\times(\mu\boldsymbol{H})$, $\boldsymbol{j}$, μ, and $\boldsymbol{H}$ being the electrolytic current density, the magnetic permeability, and the magnetic field, respectively. Furthermore, it was demonstrated that, in electrochemical oxidation of gold, a MHD-induced flow even causes a visual change in the color of the electrode surface, in addition to that in the potential–current curve.[2] Taking the above-mentioned observations into account, the magnetic field effects on the present oxidation reaction can mostly be interpreted in terms of the MHD mechanism. The mass-transport from the bulk solution to the electrode surface occurs via diffusion, convection, and electrophoretic migration in the absence of a magnetic field. In the presence of a magnetic field, a MHD-induced flow of electrolyte opens a new and efficient process of mass-transport from the bulk solution to the electrode. In the present electrolysis of phenylacetate ion, the reaction between benzyl radical and dissolved molecular oxygen is responsible for the formation of benzaldehyde. Thus, in a presence of a magnetic field, the supply of molecular oxygen from the bulk solution to the electrode surface can be improved because of the MHD flow. This results in the acceleration on the reaction of benzyl radical and molecular oxygen to yield benzaldehyde on the electrode surface. An effort to measure the magnetic field effects on the potential–current curve of the present solution was failed because of its high impedance (typically $\approx$20 V cm^{-1}).

An external magnetic field is expected to decrease the yields of the coupling products, which are formed via the competing paths with the benzaldehyde formation. However, no effects were detected concerning the yield of 1,2-diphenylethane and other coupling products, as shown in Table 1. In the present current conditions (9 mA cm^{-2}), benzaldehyde could be a minor product, since the relative yields of 1,2-diphenylethane, benzyl methyl ether, and benzaldehyde were reported to be 1:0.48:0.12 at the current density of about 7 mA cm^{-2}.[4] Therefore, magnetic-field-induced change of benzaldehyde yield does not influence appreciably those of the coupling products because of the material balance.

The external magnetic field effects on photochemical and thermal reactions have been interpreted in terms of the radical pair model, in which triplet and singlet intersystem crossing of a radical pair, a short-lived intermediate, is affected by a magnetic field.[6] Magnetic field effects due to a radical pair mechanism might be effective in the present reaction, since the coupling reaction of radicals, such as benzyl radicals, on the electrode could proceed via the radical-pair intermediate. However, we could not observe any appreciable magnetic field effects on the yield of 1,2-diphenylethane. The rate-determining step for the present coupling of radicals adsorbed on the electrode might not be the intersystem crossing in the radical pair, since the diffusion of adsorbed radicals on the electrode could be quite slow. Otherwise, the intersystem crossing might be accelerated by a magnetic-field-independent path, i.e., the spin-orbit interaction,[7,8] since the radical pairs (radicals) are strongly adsorbed on the platinum electrode.

To our knowledge, this is the first report of the magnetic field effect in organic electrochemistry, though a large number of papars have been concerned with inorganic electrochemistry.[1,2,9–11] We believe that the present finding demonstrates the applicability of an external magnetic field effect to the mechanistic study of organic electrochemistry.

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