—Note—

Aerial Oxidation of Benzene Mediated with $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$ Couple in Aqueous Chloride Solutions

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1 INTRODUCTION

The electrochemical oxidation of benzene to phenol is the subject of current interest¹⁾. We have reported that the electrolytic reduction of copper (II) ion in the presence of O_2 and benzene, which is suspended in aqueous acetonitrile solutions, gives phenol, hydroquinone and *p*-benzoquinone²⁻⁴⁾. The active species, hydroxyl radical, are generated according to reactions (1) and (2)⁵⁾.

The products distribution depends on pH of the catholyte and *p*-benzoquinone is formed selectively at pH 4-5 by the catalytic cycle shown in Scheme 1^{3, 6)}.

Scheme 1

The electrolytic system shown in Scheme 1 requires acetonitrile (AN) for the oxidation of benzene^{2,3)}. Since AN is toxic and relatively expensive chemicals, we have studied on the substitute of AN in the electrolytic oxidation.

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2 EXPERIMENTAL

Into an H-shaped glass cell (5 cm diam and 9 cm high) divided by a cation membrane (Tokuyama Soda C-655T or CM-1), 100 ml of anolyte (0.05M H_2SO_4) and 100 ml of catholyte (0.1 M acetate buffer of pH 4.6 containing 5 mM of copper (II) sulfate, 50 mM of sodium sulfate, 20-100 mM of potassium chloride and 1 ml of benzene) were added. The cell was placed in a thermostated bath at 25°C and the catholyte was stirred vigorously with a magnetic stirrer. Using a carbon rod of 13 mm diam (15 cm²) as cathode and a platinum plate as counter electrode, copper(II) sulfate was electrolyzed with bubbling of O_2 (10 ml/min) under controlled potential conditions (-0.5 V vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$ electrode). The current density was about 1 mA/cm². After the electrolysis was stopped, an aliquot of the reaction mixture was subjected to HPLC analysis (separation column : Cica-Merck Hibar Lichrosorb RP-18 (5 μm)). Non-electrochemical oxidation of benzene with copper (I) chloride and O_2 was also done. In an Erlenmeyer flask (100 ml) with a glass stopper were placed 0.05 M H_2SO_4 (25 ml) and benzene (0.75 ml, 8.4 mmol). After addition of 99 mg (1.0 mmol) of copper (I) chloride to the solution, the flask was shaken for 2 h at 25°C under the aerial atmosphere. The determination of the oxidation products was performed with HPLC.

3 RESULTS AND DISCUSSION

It is well known that electrochemical reduction of copper (II) ion produces metallic copper in a two-electron step, while the addition of chloride ion to the electrolyte favors the formation of copper (I) species. In accordance with these observations, the controlled-potential reduction of copper (II) sulfate dissolved in 20-100 mM of KCl solutions gave phenol, hydroquinone (HQ) and *p*-benzoqui-

Table 1 Aerial oxidation of benzene mediated by electrogenerated Cu^I ion.

Additive (mM)	Faradaic yield/mmol F ⁻¹				a)
	HQ	BQ	HQ+BQ	PhOH	
None	trace	trace	trace	trace	-
KCl (20)	52	25	77	6	0.93
" (30)	53	29	82	5	0.94
" (30) b)	56	43	99	26	0.79
" (40)	44	36	80	12	0.87
" (60)	48	39	87	8	0.91
" (80)	43	45	88	11	0.89
" (100)	46	46	92	3	0.97
KBr (40)	4	6	10	5	0.67
AN (1650)	47	54	101	26	0.80

a) Molar ratio.

b) AN (1650mM) was added.

none (BQ) when both benzene and O₂ are also present, while only a trace amount of these products were obtained in the absence of chloride ion (Table 1). The total Faradaic yield (ca. 88 mmol/F) of the oxidation products in the chloride solutions were slightly less than that (100 mmol/F) in the aqueous acetonitrile solution. In the presence of both AN and KCl, the effect of AN (giving higher Faradaic yield and lower selectivity of HQ plus BQ) predominates, as seen in Table 1. Addition of 40 mM of KBr produced these products but the total Faradaic yield was less than one-sixth that in the chloride system.

In the range from 20 to 100 mM, the concentration of chloride ion scarcely affects the Faradaic yield of the products and the products distribution. In separate experiments using copper (I) chloride instead of electrogenerated copper (I) species, the effect of added chloride ion is marked as shown in Table 2, which is apparently in conflict with the result in Table 1. The copper (I) species

generated from the reduction of copper (II) sulfate in the chloride solution, therefore, should be different from that in the CuCl/KCl system. In the CuCl system, the presence of chloride ion favors the formation of dimeric copper (I) species such as Cu₂Cl₃⁻ and Cu₂Cl₄²⁻, which will accelerate the decomposition of hydrogen peroxide without generating •OH according to reaction (3).

In the electrolytic system, the starting species is copper (II) sulfate and the dimeric copper (I) species hardly formed even in the presence of 20–100 mM of chloride ion.

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Table 2 Effect of chloride ion on aerial oxidation of benzene promoted by copper (I) chloride^{a)}.

KCl (mM)	PhOH (μmol)
0	60
10	53
50	21
100	15
500	6

a) CuCl=1 mmol, pH =1.3.