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A NOVEL PAIRED ELECTROSYNTHESIS OF p-BENZOQUINONE AND HYDROQUINONE FROM BENZENE

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ABSTRACT: The combination of anodic oxidation of benzene on PbO_2 electrode with "cathodic oxidation of benzene" using Cu(I)/Cu(II)[2] mediator in a single H-type electrolytic cell gives p-benzoquinone and hydroquinone in the total current efficiency of 94%.

Benzene is anodically oxidized to give p-benzoquinone (BQ) by use of either PbO_2 electrode[1-3] or Ag^+/Ag^{2+} mediator.[4,5]

$$\text{Benzene} + 2\,H_2O = \text{p-Benzoquinone} + 6\,H^+ + 6\,e^- \qquad (1)$$

In these anodic oxidations of benzene, cathodic current is wastefully consumed to reduce hydrogen ions to hydrogen gas. In the previous papers, we have shown that benzene is "cathodically" oxidized to give BQ and hydroquinone (HQ) using Cu^+/Cu^{2+} redox couple as a current mediator,[6,7] and the reaction mechanism of the formation of HQ was proposed.[8-10] The cathodic reaction in the Cu^+/Cu^{2+} system is reduction of copper(II) to copper(I) ions, which activate molecular oxygen to generate hydroxyl radicals according to the following reactions.

$$Cu^{2+} + e^- = Cu^+ \qquad (2)$$

$$2\,Cu^+ + O_2 + 2\,H^+ = 2\,Cu^{2+} + H_2O_2 \qquad (3)$$

$$Cu^+ + H_2O_2 + H^+ = Cu^{2+} + {\cdot}OH + H_2O \qquad (4)$$

The combination of these anodic (1) and cathodic reactions (2) in a single H-type electrolytic cell, therefore, should constitute a novel paired electrolytic system to oxidize benzene in both anode and cathode chambers simultaneously to give BQ and HQ.

Into a conventional H-shaped glass cell (5 cm in diameter and 9 cm in height) divided by a cation-exchange membrane (Tokuyama Soda CM-1), 120 ml of anolyte (1 M H_2SO_4 containing 10 ml of benzene) and 100 ml of catholyte (0.1 M acetate buffer of pH 4.6 containing 50 mM of copper(II) sulfate, 50 mM of sodium sulfate, 10 ml of benzene, and 5 ml of acetonitrile) were added. Benzene and copper(II) sulfate were electrolyzed on a PbO_2 anode (15 cm^2)[3] and a carbon-rod cathode (15 cm^2)[7], respectively, at 25±2°C under controlled cathode-potential conditions (−0.5 V vs Hg/Hg_2SO_4 electrode) with aid of a potentiostat (Nikko Keisoku NPOT-2501) and a digital coulometer (Nikko Keisoku NDCM-4). During the electrolysis, both the anolyte and catholyte were

Table 1. Paired Electrosynthesis of Benzoquinone and Hydroquinone[a]

Run	Electrolysis	Current density	Electric charge	Product/μmol				
				Anode	Cathode			Total
		mA cm^{-2}	mF	BQ	BQ	HQ	PhOH	BQ+HQ
1	Controlled cathode-potential at -0.5 V[b]	0.91	1.00	66	45	125	30	236
2		1.02	1.00	60	50	125	24	235
3		1.07	1.00	67	44	102	23	213
4		1.13	1.00	68	41	112	30	221
			mean	65 (39%)	45 (9%)	116 (46%)	27 (5%)	226 (94%)
5	Controlled current	1.07	1.50	(5%)	(11%)	(48%)	(2%)	(64%)
6	Controlled anode-potential at +1.15 V[b]	25	3.58	(42%)	(0.4%)	(7%)	(0%)	(49%)

[a] The values in parentheses are the current efficiencies calculated as n=6 for BQ (anode), n=2 for BQ (cathode), n=4 for HQ, and n=2 for PhOH, respectively. [b] vs Hg/Hg_2SO_4 electrode.

stirred vigorously with magnetic stirrers, and oxygen gas was bubbled into the catholyte at 10 ml min^{-1}. The oxidation products were analyzed with HPLC.[8]

As summarized in Table 1, an efficient system for the simultaneous oxidation of benzene was realized: an appreciable amounts of dioxygenated products were obtained in the anode as well as in the cathode chambers under the controlled cathode-potential conditions (Run 1-4). The total yield of BQ plus HQ were 226 μmol, which is ca. 1.4 times the theoretical yield (167 μmol per 1 mF) for the anodic oxidation of benzene on PbO_2 electrode.[1-3] The total current efficiency for BQ plus HQ amounts to 94%. In the field of electroorganic synthesis, this is the first example of the production of the same compound from the same starting material both in the anode and cathode chambers. The electrolyses under the controlled current (Run 5) and anode-potential (Run 6) conditions gave lower CE as shown in Table 1.

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