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# Paired Electrooxygenation of Benzene in Undivided Cell

Sotaro ITO,* Noriya FUKUMOTO, Atsutaka KUNAI, and Kazuo SASAKI
Department of Applied Chemistry, Faculty of Engineering,
Hiroshima University, Saijo, Higashi Hiroshima 724

The combination of anodic dissolution of copper electrode with cathodic reduction of copper(II) ions in an undivided cell brought about efficient electrooxygenation of benzene to give hydroquinone and p-benzoquinone.

One of the strategies in electroorganic synthesis is effective utilization of the reaction(s) at the counter electrode. Several patents on the so-called paired electrosynthesis have appeared,$^{1-3)}$ in which two different organic compounds are separately reduced on the cathode and oxidized on the anode to give two different products.

In the previous papers,$^{4-8)}$ we have demonstrated that copper(I) species such as copper(I) chloride and electrogenerated copper(I) ions activate molecular oxygen to give hydroxyl radicals,$^{4)}$

$$2\,Cu^{+} + O_2 + 2\,H^{+} = 2\,Cu^{++} + H_2O_2 \tag{1}$$

$$Cu^{+} + H_2O_2 + H^{+} = Cu^{++} + \cdot OH + H_2O \tag{2}$$

which readily attack benzene nucleus to produce phenol,$^{4,5)}$ hydroquinone,$^{6,7)}$ and p-benzoquinone.$^{8)}$ Since copper(I) species can be generated by anodic dissolution of metallic copper as well as by cathodic reduction of copper(II) ions, the combination of these redox reactions in a single electrolytic cell effectively (presumably by two times) produces copper(I) species as illustrated in Scheme 1, and is expected to double the current efficiency of phenols.

$$\begin{tikzcd}
\mathrm{Cu(0)} \arrow[r, "-e", "\text{anode}"'] & \mathrm{Cu(I)} \arrow[d, "+\,O_2"] & \mathrm{Cu(II)} \arrow[l, "+e"', "\text{cathode}"] \\
 & \cdot\mathrm{OH} &
\end{tikzcd}$$

Scheme 1. Simultaneous production of copper(I) species.

Into a 180 ml-tall beaker (5 cm in diameter and 9 cm in height), 120 ml of a 0.1 M acetate buffer of pH 4.6 containing 5 mM of copper(II) sulfate, 50 mM of sodium acetate, 5 ml of acetonitrile, and 3 ml of benzene was added. By use of a carbon rod (13 mm in diameter and 15 cm$^2$ in surface area) as cathode and a copper plate (15 cm$^2$ in surface area) as anode, copper(II) sulfate was electrolyzed at cathode under the controlled potential (-0.5 V vs. Hg/$Hg_2SO_4$ electrode) at 25 °C.$^{8)}$ During the electrolysis, the solution was stirred vigorously to suspend benzene and oxygen gas was bubbled into the solution at 10 ml min$^{-1}$. The amount of copper ion electrolytically dissolved was determined colorimetrically by bathocuproine disulfate method.$^{9)}$ The oxidation products were analyzed with HPLC.$^{4)}$

Table 1. Paired Electrooxygenation of Benzene at 25 °C and pH 4.6[a)]

| Run | Cell | | Products / μmol | | | |
|---|---|---|---|---|---|---|
| | | | Hydroquinone | Benzoquinone | Phenol | HQ+BQ |
| 1 | H-type | anode | 39 | 71 | 21 | 110 |
| | (divided) | cathode | 22 | 33 | 9 | 55 |
| | | total | 61 | 104 | 30 | 165 |
| 2 | H-type<br>(undivided) | | 63 | 100 | 30 | 163 |
| 3 | Beaker-type<br>(undivided) | | 50 | 102 | 23 | 152 |

a) Electric charge passed was 0.5 mF (0.83 F mol-$CuSO_4^{-1}$).

Several experiments using a conventional H-type cell with a cation-exchange membrane (Tokuyama Soda CM-1) were done initially in order to see the relative contribution of the anodic and cathodic reactions. After passing 0.5 mF of electric charge, the amount of copper ion in the anolyte increased by 0.59 ± 0.06 mmol (1.18 mol $F^{-1}$), indicating that the copper anode is electrolytically dissolved according to the reaction in Scheme 1. In agreement with this observation, hydroquinone (HQ) and p-benzoquinone (BQ) were formed in the anode as well as in the cathode, as shown in Table 1 (Run 1). The electolysis in the H-type cell without the separator (Run 2) did not decrease the yield of HQ and BQ, showing that the anodic oxidation of copper(I) species is negligible. The electrolysis in the beaker-type cell (Run 3) gave, as expected from the result of Runs 1 and 2, essentially the same amount of HQ and BQ. The total yield of HQ plus BQ was 304-330 mmol $F^{-1}$, which corresponds to 160-175% of total apparent current efficiency (40-50% for HQ (n = 4) and 120-125% for BQ (n = 6)).

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