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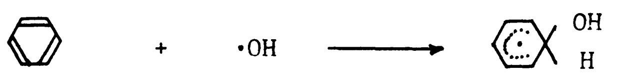
ELECTROLYTIC PRODUCTION OF PHENOLS FROM BENZENE USING Cu(I)/Cu(II) COUPLE

Kazuo SASAKI*, Sotaro ITO, Tatsuyuki KINOSHITA, and Junji HARADA
Department of Applied Chemistry, Faculty of Engineering,
Hiroshima University, Higashi-Hiroshima-shi 724

Phenol can be produced continuously from benzene by aerial oxidation in an aqueous sulfuric acid when Cu(I)/Cu(II) couple is used as a current mediator. Experimental conditions to optimize the phenol production are discussed.

Recently, one-step oxidation of benzene to phenol with H_2O_2 in the presence of Fe(II) salts (Fenton reagent) has been extensively studied.[1-7] The mechanistic study by Walling[1,2] revealed that the oxidation of benzene by Fenton reagent proceeds via hydroxycyclohexadienyl radical [I], which is formed by addition of hydroxyl radical to benzene:



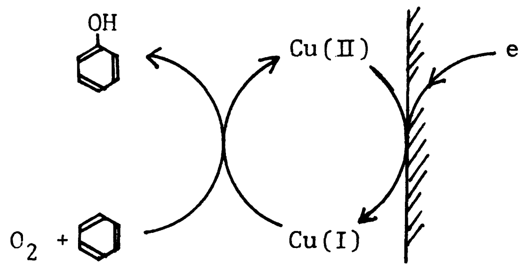
------------- (1)

[I]

Hydroxyl radical is generated from H_2O_2 according to Eq.(2),

$$H_2O_2 + Fe(II) \longrightarrow \cdot OH + OH^- + Fe(III) \quad \text{------------} \quad (2)$$

and thus H_2O_2 cannot be replaced by molecular oxygen. In the previous communication,[8] we have shown that *aerial* oxidation of benzene to phenol does occur under ambient conditions (25°C and atmospheric pressure) when cuprous chloride is present in the solution. The oxidation of benzene by $CuCl-O_2$ system is, however, non-catalytic process, i.e., cuprous chloride is gradually oxidized to inactive Cu(II) ion as the reaction proceeds.



Scheme 1

In the present study, we wish to demonstrate that continuous production of phenol from benzene can be done by a combination of electroreduction of Cu(II) ion to Cu(I) species and aerial oxidation of Cu(I) species as shown in Scheme 1.

A small H-type glass cell having a sintered glass frit to divide cathodic to anodic compartments was used as the reaction vessel. The cathode electrode was a graphite rod of 13 mm in diameter and 20 mm in length. The counter electrode was a platinum plate. The cathode potential was controlled with a potentiostat to keep the potential in the range of 0 to 0.1 volt sce. A mixed solvent composed of 0.1 N H_2SO_4 and acetonitrile in the volume ratio of 9 to 1 was used because cuprous ion is unstable in an aqueous sulfuric acid solution. Cupric sulfate (0.8-8 mmol) and one ml of benzene (11.2 mmol) was added to the catholyte (16 ml) and the mixture was agitated by a magnetic stirrer. Air was fed through a capillary glass tube at a rate of 7 ml/min. All the reactions were carried out in a themostated bath at 25°C. The reaction products were analyzed with a high pressure liquid chromatograph installing a ZORBAX ODS column (Du Pont, 4.6 mm x 150 mm).

The main product was phenol in all experiments. Hydroquinone, catechol and a few other unidentified products were found as by-products. Biphenyl and resorcin (m-dihydroxybenzene) were not detected. Among these products, the molar ratio of hydroquinone to phenol was 1 to 3 at the highest, while the amount of catechol was less than one-tenth of that of hydroquinone.

Fig. 1(a) indicates the accumulation of phenol in the catholyte with the increasing duration of reaction time. The curve is the steepest at the initial stage and becomes dull progressively. This is the reflection of the pH increase in the catholyte. In fact, in this particular example, the pH value was ca. 5 at the end of the electrolysis. The effect of pH is pronounced and the optimum is around pH = 1.[8] The scale of abscissa attached to the upper marginal of Fig. 1 stands for the number of recycle of generating cuprous ion.[9] Fig. 2(a) indicates the coulomic efficiency[10] for the phenol production against the concentration of cupric sulfate added initially. For each run of this figure, the total quantity of electricity was fixed at 20 mAH. It is clearly indicated that the coulomic efficiency goes down gradually with increasing copper ion concentration after passing a maximum (CE = 10 %) appearing at about 200 mM. It is somewhat a difficult task to compare the efficiency of the present process with other methods hitherto reported. Osa et al[5] reported that toluene was hydroxylated by the reaction of Fe(II) ion with H_2O_2 electrogenerated

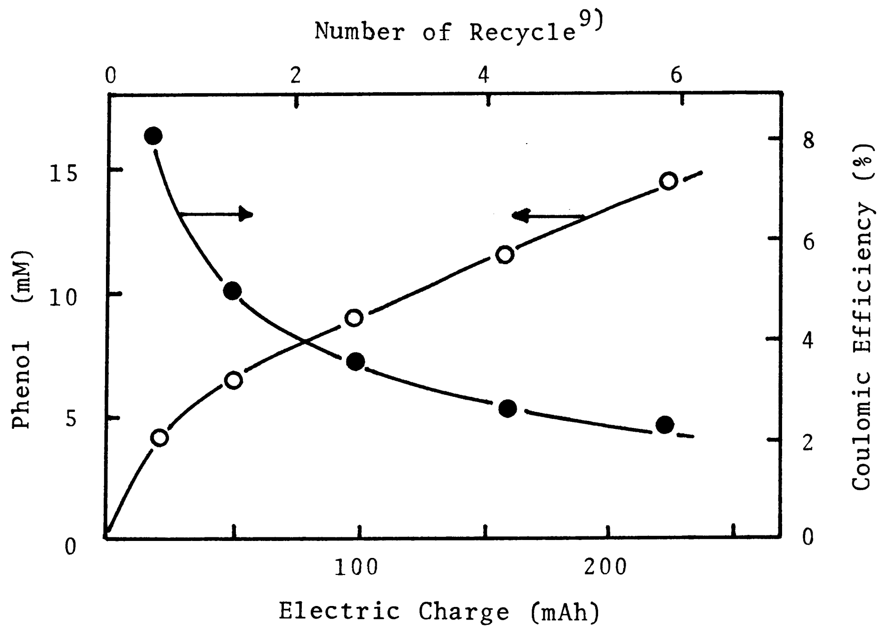


Figure 1 Accumulation Curve of Phenol in Aerial Oxidation of Benzene Catalyzed by Electrogenerated Cuprous Ion at 25°C.

○ : Amount of phenol produced, ●: coulomic efficiency.[10)]

Benzene: 1 ml, total copper ion: 100 mM, solvent 16 ml (acetonitrile/0.1N-H_2SO_4=1/9, flow rate of air: 7 ml/min, cathode potential: +0.1 V vs SCE.

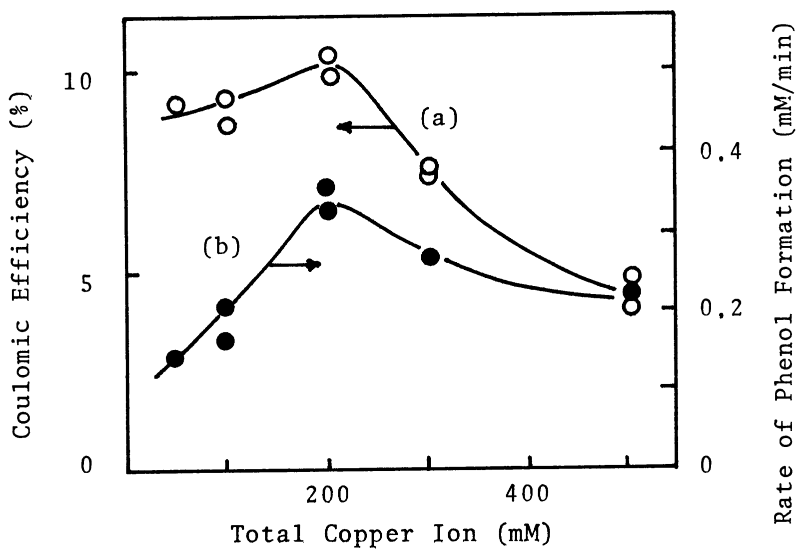


Figure 2 Effects of Concentration of Copper Ion on (a) Coulomic Efficiency and (b) Rate of Phenol Formation.

The reaction conditions are the same as in Figure 1.

from O_2. The coulomic efficiency[10] for the formation of isomeric mixture of cresols was 2.4 %, which is equivalent to the current efficiency of 4.8 % for n = 2.[5] The current corresponding to the generation of cuprous ion increases with increasing concentration of copper salt. Accordingly, the rate of phenol production (mM/min.) has more practical significance than the coulomic efficiency. This is shown in Fig. 2(b). An optimum concentration appears again at about 200 mM of copper ion concentration. It is interesting that the relative yield of hydroquinone to phenol decreased drastically with increasing concentration of copper salt. The values were 0.39, 0.26, 0.14, 0.13 and almost null for the concentration of copper salt 20, 50, 100, 200, and 500 mM, respectively.

It should be emphasized that our process does not use hydrogen peroxide. In addition, in order to maintain the solution pH at a suitable value, a hydrogen electrode can be utilized as the counter electrode. In this case, at least in principle, no external power source is necessary.

References

1) C. Walling and R. A. Johnson, Acc. Chem. Res., 8, 125 (1975).
2) C. Walling and R. A. Johnson, J. Am. Chem. Soc., 97, 363 (1975).
3) E. Steckhan and J. Wellmann, Angew. Chem. Int. Ed. Engl., 15, 294 (1976).
4) J. Wellmann and E. Steckhan, Chem. Ber., 110, 3561 (1977).
5) T. Matsue, M. Fujihira, and T. Osa, J. Electrochem. Soc., 128, 2565 (1981).
6) M. Fujihira, Y. Sato, and T. Osa, Bull. Chem. Soc. Jpn., 55, 666 (1982).
7) M. A. Brook, L. Castle, and J. R. Lindsay Smith, J. Chem. Soc., Perkin Trans. 2, 1982, 687.
8) K. Sasaki, S. Ito, Y. Saheki, T. Kinoshita, T. Yamasaki, and J. Harada, Chem. Lett., 1983, 37.
9) The number of recycle can be calculated by dividing the quantity of electricity by the amount of copper salt added.
10) The coulomic efficiency (CE) was defined here as the number of moles of phenol produced per one Faraday (1F = 26.8 Ah) of electricity.

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