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ONE-STEP OXIDATION OF BENZENE TO PHENOL UNDER AMBIENT CONDITIONS

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Aerial oxidation of benzene suspended in aqueous sulfuric acid produces an appreciable amount of phenol. The reaction proceeds under ambient conditions only when cuprous ions are present in the solution.

Benzene is believed to be resistant to either oxidation or reduction under ambient conditions. Thus it has been one of the industrial demands to obtain phenol by one-step oxidation of benzene.1) A Polish group reported2) that, in a system of corroding copper immersed in aqueous sulfuric acid containing benzene, an appreciable amount of phenol was produced with a little amount of dihydroxybenzenes. The reaction proceeded at room temperature under the atmospheric pressure. The attacking species on benzene was assumed to be hydroxyl radical generated according to Eq.(1),2) though the formation of neither cuprous ion nor hydrogen peroxide has been confirmed experimentally. Furthermore, it was not specified by them whether the metal surface of corroding copper was indispensable to the reaction.

$$Cu^{+} + H_2O_2 \longrightarrow Cu^{++} + OH + OH^{-} \qquad \text{-----} \ (1)$$

We thus studied the reaction in more detail. The results revealed that the presence of metallic copper is unnecessary. The indispensable conditions for this reaction were found to be the presence of only monovalent copper ion incorporated with certain oxygen source. Aerial oxygen is sufficient for this purpose although hydrogen peroxide seems to be effective to some extent. The process will reply to the demand of "one-step oxidation" of benzene to phenol. We have already confirmed that the aerial oxidation of benzene to phenol can be brought into practice, at least in principle, by utilizing electrochemical regeneration of catalyst copper.

All the measurements were carried out in a 100 ml glass flask which contained 25 ml of aq. H_2SO_4 (0.05 M in most cases) and 0.75 ml of benzene (8.45 mmol). The reaction was started by adding a known amount of copper salt to the solution. Cuprous salt dissolved gradually as the reaction proceeded. During the reaction, the flask was shaken at a given rate in a thermostated bath (25°C) either under aerial or N_2 atmosphere. The determination of phenol was carried out by use of HPLC (column: Permaphase ETH (2.1 mm x 1 m), solvent: 0.1 M phosphoric acid (pH 2.5)).3)

A part of results obtained are listed in Table 1. It is clearly indicated that cupric salts are ineffective on the production of phenol even in the presence of O_2 or H_2O_2. On the contrary, addition of cuprous chloride does lead to the

Table 1 Oxidation of Benzene to Phenol in the Presence of Copper Salts[a)]

Copper salt	H_2O_2 (mmol)	Atmosphere	Phenol (mmol)	Phenol/Cu salt added
$CuCl_2$	0	Air	0	0
$CuSO_4$	0.5	Air	0	0
CuCl	0	N_2	0	0
CuCl	0	Air	0.083	0.083
CuCl	0.5	Air	0.110	0.110

a) Temp.:25°C, copper salt:40 mM (1.0 mmol), solvent:25 ml of 0.05 M H_2SO_4, benzene:0.75 ml (8.45 mmol), agitation:shaking at 175 oscillations/min, reaction time:2 hours.

formation of phenol. When H_2O_2 was added extraneously (the bottom in Table 1), the yield of phenol increased certainly. However the increment due to H_2O_2 was only 33%, suggesting that H_2O_2 is not essential for the formation of phenol. A further study is required on the role of H_2O_2. The yield of phenol was sensitive to the concentration of both chloride ion and H_2SO_4. The addition of KCl (0.01-1.0 M) gradually lowered the yield of phenol, while an optimum concentration of H_2SO_4 appeared at 0.05 M. A linear relationship between the amounts of CuCl added and phenol produced was observed in the range of 5-40 mM of CuCl, while benzene (0.75-5.0 ml/25 ml of aq-H_2SO_4) and O_2 (0.24-1.1 mM) had minor effects on the yield of phenol. Under the optimum condition, the yield of phenol was 8.3% based on the cuprous salt added.

Fenton's reagent (20 mM of $FeSO_4$ plus 10 mM of H_2O_2 in 0.05 M of H_2SO_4) also oxidized benzene to phenol but the yield of phenol was about one-third of that observed in the CuCl-O_2 system. In contrast to the CuCl-O_2 system, Fenton's reagent always produced an appreciable amount of biphenyl. The molar ratio of biphenyl to phenol was 0.6-1.7 depending on the initial concentration of H_2O_2 (10-40 mM). This result as well as the data in Table 1 indicates that the attacking species on benzene nucleus is not hydroxyl radical. At the present stage, it seems quite reasonable to assume that the percupryl ion (CuO_2^+)[4)] is incorporated in the key step of reaction sequence. The inhibition effect of chloride ion on the formation of phenol may be explained by the decrease in the equilibrium concentration of CuO_2^+ due to the complex formation between Cu^+ and Cl^-.

Referenes

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