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HYDROXYLATION OF BENZENE WITH HYDROGEN PEROXIDE BY THE USE OF HYDROPHOBIC CATECHOLS AND Fe^{3+} COMPLEXES AS THE CATALYST

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Hydroxylation of benzene with H_2O_2 was carried out in the presence of a variety of catechols and Fe^{3+} in a benzene-H_2O biphase system. The hydrophobic catechols were found far more effective as the catalyst than the hydrophilic ones.

Direct hydroxylation of aromatic hydrocarbons is one of fundamental enzymic reaction processes in a living cell. Thus far, various attempts have been made to explore the efficient catalyst systems[1] mimicking catalase and peroxidase[2]. In spite of considerable activity in this area, few successful catalytic system have been reported.

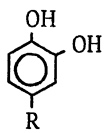
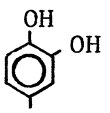
In this work, we have examined the utility of hydrophobic catechols instead of hydrophilic ones in the hydroxylation of benzene with an Fe^{3+}-catechol - H_2O_2 system of Hamilton[3] and have now found that the hydrophobic ones have unique advantages over water-soluble ones.

The general reaction procedure is as follows: A solution of catechol(0.1 mmol) in benzene (20 cm^3) was added to 3 cm^3 of acetate buffer (0.33 M) containing 0.1 mmol of Fe^{3+}. After vigorous shaking of the mixture for 1 min., 2 cm^3 of an 0.5 M H_2O_2 solution was added all at once and then shaken again at 25°C for 2.5 h. Phenol formed was extracted with ether and analyzed by an HPLC with anisole as the internal standard. Neither catechols nor Fe^{3+} alone was effective to catalyze the reaction. The result thus obtained are summarized in the Table.

With water-soluble catechols (Ia, Ib, IIa, and IIb) as the ligand, the yield of phenol is no more than 6% in any cases. The use of higher concentrations of catechol and H_2O_2 did not improve the yield of phenol due to the rapid oxidation of water-soluble catechols to by-products.

On the other hand, the hydrophobic catechols (I; R=Bu, hexyl, benzyl, and β-phenethyl) are more effective as the catalyst than are the hydrophilic ones under identical conditions. In every case, the reaction is almost complete in 60 min.. Maximum catalytic efficiency is attained when pH approaches 4.0 in acetate buffer at which the yield goes up to 60 %. The higher yield observed with hydrophobic catechols is accounted for by effective protection of catechol itself or catechol-Fe^{3+} complex in benzene phase from the attack of H_2O_2 in aqueous phase. The reaction mechanism has not yet been well understood. It is reasonably supposed, however, that the catalytic reaction takes place in a benzene-water interphase. This is the first example of successful applications of using hydrophobic ligands to the hydroxylation of aromatic compounds. Furthermore, this concept appears to have a great future possibility both for synthetic and biomimetic chemistry. Extention of the work on the utility of hydrophobic catalysts instead of hydrophilic ones is underway in this laboratories.

Table. Hydroxylation of benzene in acetate buffer at pH=3.0[a)]

R	Yield of Phenol (%)[b)]	R'	Yielf of Phenol (%)
 (I)	(a) CH_3 1.7	 (II)	(a) H 3.0
	(b) C_2H_5 6.0		(b) CH_3 6.0
	(c) n-C_4H_9 41.2		(c) n-C_7H_{15} 31.0
	(d) n-C_6H_{13} 47.8		(d) n-$C_{13}H_{27}$ 17.0
	(e) $PhCH_2$ 55.5		(e) n-$C_{19}H_{39}$ 27.8
	(f) $Ph(CH_2)_2$ 48.6 (57.8)[c)]		

a) Reaction conditions are shown in the text. b) Yields are based on H_2O_2 (1.0 mmol). They should be multiplied by ten if based on catechol (1.0 mmmol).
c) In formate buffer at pH=3.0.

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