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THE EFFECTIVE HYDROXYLATION OF BENZENE BY HYDROGEN PEROXIDE IN A HETEROPHASE SYSTEM

E.A. KARAKHANOV, S.Yu. NARIN and A.G. DEDOV

Chemistry Department, Moscow State University, 119899 Moscow, U.S.S.R.

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We report upon the development of new catalytic systems for the selective hydroxylation of benzene under mild conditions. These involve the use of surfactant-transition metal salts and hydrogen peroxide.

The development of catalytic systems for the direct introduction of hydroxyl group into an aromatic ring has been attracting the attention of numerous researchers for a long time [1–7]. However, in the majority of cases, the selectivity of hydroxylation and the product yield were quite low due to the radical mechanism of the reaction.

Earlier, we reported the use of metal-polymer catalysts for the homogeneous oxidation of benzene by hydrogen peroxide [8]. The addition of polyethyleneglycol (PEG) to Fe(III)-H_2O_2 in aqueous acetonitrile solution enhanced the yield of phenol and the reaction selectivity. This was evidently due to the creation of the concentration gradient of the initial substances (benzene and hydrogen peroxide) and the catalyst in a polymer globule. The heterophase hydroxylation in the presence of surfactants is supposed to lead to a further increase in the phenol yield and in the selectivity of the process.

The hydroxylation of benzene by hydrogen peroxide in a two-phase system (water-substrate) has been studied. The catalysts were prepared using salts and complexes of Fe(II), Fe(III), Cu(II), Cu(I), Pd(II), Ni(II), Pt(II), Co(II) and Rh(III). As components of the catalytic systems, we used surfactants–quarternary ammonium salts (cetyltrimethylammonium bromide (CTMAB), tetrabutylammonium bromide (TBAB), tetrabutylammonium chloride (TBAC), tetrabutylammonium iodide (TBAI), benzyltriethylammonium chloride (BTEAC), N-cetylpyridinium bromide (N-CPB)), crown-ethers (dibenzo-18-crown-6 (DB-18-C-6), benzo-15-crown-5 (B-15-C-5), 15-crown-5 (15-C-5), dicyclohexano-18-crown-6 (DC-18-C-6)), a number of polymers (polyethyleneglycols of varying molecular weight, polypropyleneglycol (PPG), polyethyleneglycol ethers), potassium didodecylsebacinate sulphonium salts (DDS) and natrium cetylsulfonate salts (CS).

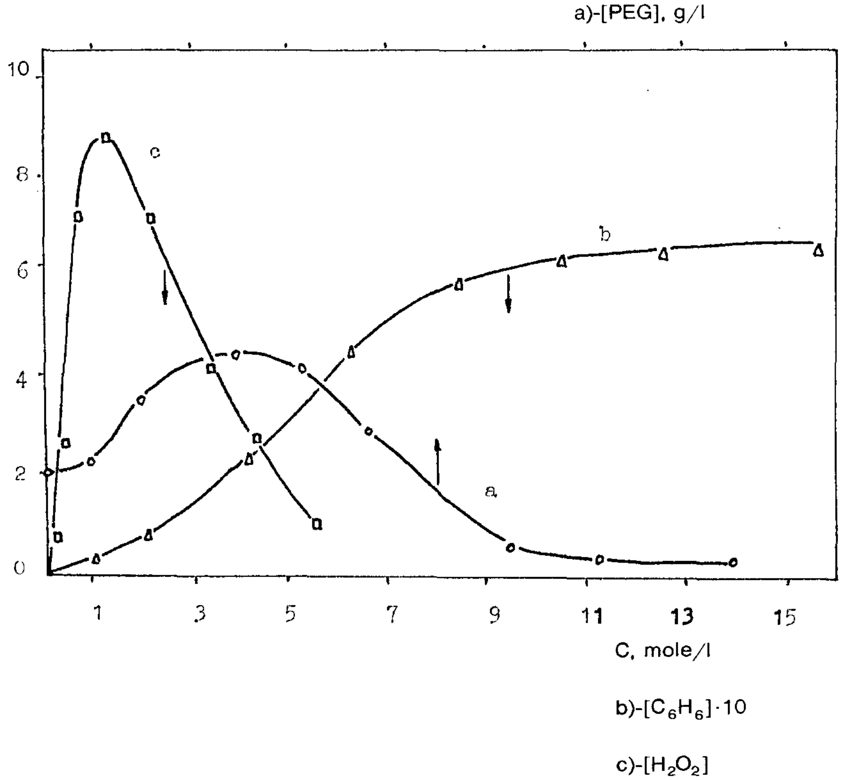

Fig. 1. The dependence of the initial rates of phenol accumulation in a heterophase system in the presence of Fe(III)-PEG on the concentration of: a – PEG-40000; b – C_6H_6; c – H_2O_2 (50 °C; pH 2.9).

The reaction was carried out at 20–60 °C, pH = 1.5–11.0 with intensive stirring. The molar ratios surfactant : transition metal ion : C_6H_6 : H_2O_2 varied sufficiently – (5.5–9.0) : (1.0–7.0) : 300 : (150–600) respectively.

We studied the influence of pH, temperature, reactants and surfactants concentration (fig. 1, 2) on the rate of hydroxylation of benzene. The phenol yield depended on the nature of surfactants and on the composition of transition metal salts and complexes (table 1, 2).

Fe(II)-, Fe(III)-based catalytic systems with CTMAB and BTEAC as surfactants proved to be the most efficient (table 1). They induce selective oxidation of benzene to phenol with rather high conversion – the yield of phenol reached up to 80% (based on benzene).

The use of PEG and crown-ethers in the catalytic systems instead of ammonium salts also gave the high yields of phenol. However, in these cases, along with the main product – phenol, dioxybenzenes (mostly, pyrocatechol) were detected with yields up to 10%.

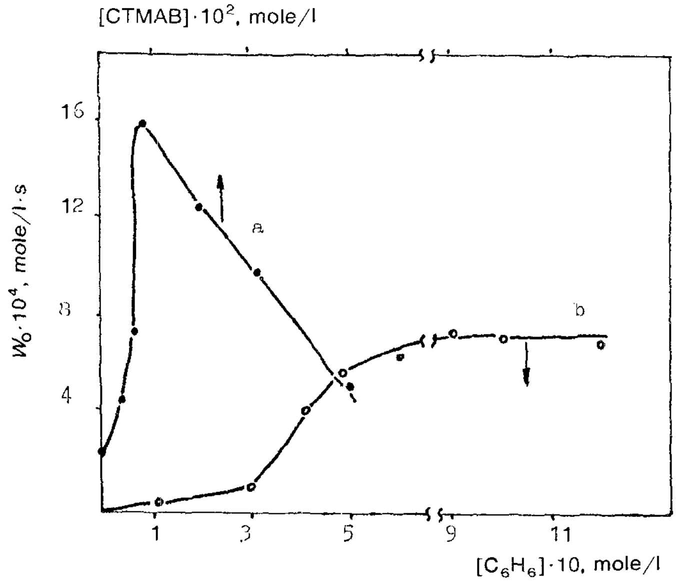

Fig. 2. The dependence of the initial rates of the hydroxylation of benzene to phenol in a heterophase system in the presence of Fe(III)-CTMAB on the concentration of: a – CTMAB; b – C_6H_6 (50 °C; pH 2.9; [Fe(III)] = $4.5 \cdot 10^{-3}$ mole/l).

The highest phenol yield in Fe(III)-PEG system was 50%, in Fe(III)-DB-18-C-6 system – 60%, selectivity – 90%. The rate of hydroxylation in a heterophase system when using surfactants was 10-fold more than in a homogeneous water-acetonitrile medium (fig. 1, 2). It should be also noted that the molar ratio benzene : Fe(III) reached up to 300 under optimal conditions.

Table 1
The hydroxylation of benzene by hydrogen peroxide in a heterophase water-benzene system in the presence of catalysts Fe(III)-surfactant (50 °C, $[H_2O_2]$ = 1.0 mole/l, $[C_6H_6]$ = 1.0 mole/l, [Fe(III)] = $3.35 \cdot 10^{-3}$ mole/l)

NN 1	Surfactant 2	Yield of phenol (wt.%) 3	NN 1	Surfactant 2	Yield of phenol (wt.%) 3
1.		8	10.	TBAB	30 *
2.	PEG-40000	50	11.	TBAC	35 *
3.	PEG-20000	42	12.	TBAI	38 *
4.	PEG-12000	30	13.	BTEAC	70 *
5.	PEG-6000	21	14.	DB-18-C-6	60
6.	PEG-sebacinate	40	15.	B-15-C-5	45
7.	PEG-monolaurilate	36	16.	15-C-5	39
8.	PPG	35	17.	DC-18-C-6	52
9.	CTMAB	80 *	18.	DDS	45

* Reaction proceeds selectively.

Table 2
The hydroxylation of benzene by hydrogen peroxide in a heterophase water-benzene system in the presence of transition metal ion: (50 ° C, $C_6H_6 : H_2O_2 = 1:1$; $[H_2O_2] = 1.0$ mole/l; [CTAMB] = 0.01 mole/l; $[M\,e^{n+}] = 3.35 \cdot 10^{-3}$ mole/l].

NN 1	Transition metal ion 2	Yield of phenol (wt.%) 3	NN 1	Transition metal ion 2	Yield of phenol (wt.%) 3
1.	–	0	6.	Pd(II)	10
2.	Fe(III)	80	7.	Pt(II)	15
3.	Fe(II)	65	8.	Co(II)	10
4.	Cu(II)	30	9.	Ni(II)	10
5.	Cu(I)	25	10.	Rh(III)	15

The rate of the benzene hydroxylation and the phenol yields increased with the lengthening of lipophilic chain in ammonium salts. The catalytic systems based on Fe(III) and PEG-ethers (adipinates, sebacinates, succinates, monolaurilates) exhibited similar activities as the Fe(III)-PEG-20000 system (table 1).

The comparative kinetic study of the catalytic decomposition of H_2O_2 and of the benzene hydroxylation has revealed that the use of the diluted solutions of H_2O_2 (less than 0.2 mole/l, fig. 1) has a low efficiency.

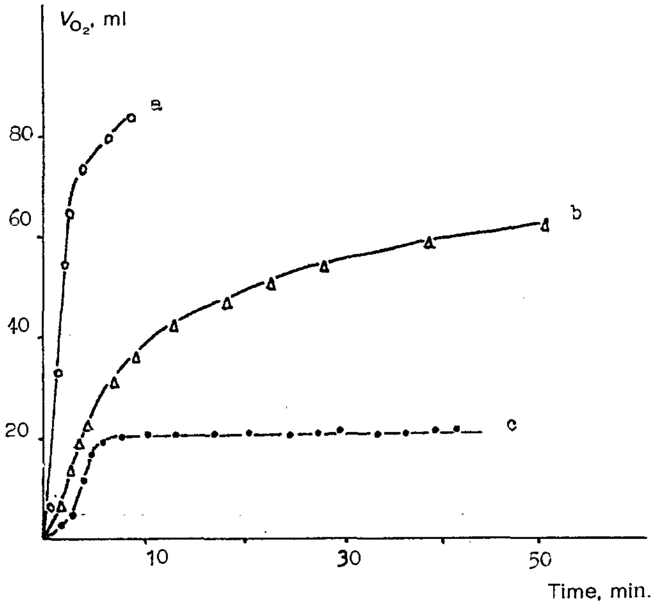

Fig. 3. The dependence of the volume of oxygen on the time of H_2O_2 decomposition at 40 ° C in the presence of different catalytic systems: a – Fe(III); b – Fe(II), CTMAB; c – Fe(III), CTMAB, C_6H_6 ($[C_6H_6] = 1.0$ mole/l; Fe(III) = $4.5 \cdot 10^{-3}$ mole/l; [CTMAB] = 0.09 mole/l).

The vigorous decomposition of concentrated hydrogen peroxide solutions (more than 2.5 mole/l) at the beginning of the reaction leads mainly to the release of oxygen (fig. 3) and to the decrease of the conversion of benzene due to the non-efficient expenditure of the oxidant. An obvious destruction of the surfactants has been observed.

The low value of the apparent activation energy, determined for the reaction in the presence of Fe(III)-CTMAB (21 kJ/mole) may be an indication of the radical initiation of the reaction.

The catalytic activity of transition metal ions is strongly dependent on pH. The highest phenol yields for Fe(III) and Fe(II) were achieved at pH = 2.5–3.5 for all surfactants independent of H_2O_2 concentration and reaction temperature. For Cu(I) and Cu(II), the optimal pH value shifted to 6.0–8.0. The optimal rate of H_2O_2 decomposition, catalysed by these metals, is observed at the same pH-values [8].

It has been shown that the highest catalytic activity is achieved when the molar ratio of Fe(III) : CTAMB is 1 : 3. The interaction of Fe(III) and ionic surfactants in aqueous and hydrochloric media was detected by the spectrophotometric method described in [9,10].

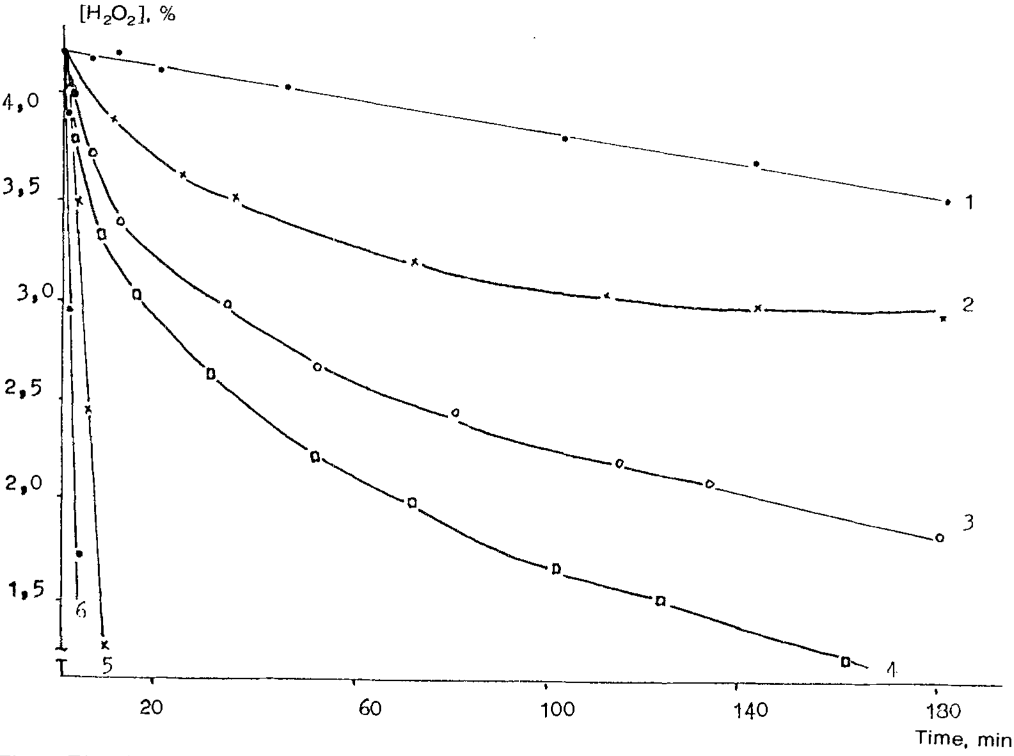

Fig. 4. The kinetic curves of the H_2O_2 decomposition at 50 ° C in the presence of different catalysts: 1 – thermal decomposition, 2 – Fe(III)-CS, 3 – Fe(III)-CTMAB; 4–Fe(II)-CTMAB; 5 – Fe(III); 6–Fe(II) ($[H_2O_2]_0 = 1.25$ mole/l; [Fe(II)] = [Fe(III)] = $2.25 \cdot 10^{-3}$ mole/l; [surfactants] = 0.01 mole/l).

The presented experimental data lead to the assumption that the hydroxylation of benzene by hydrogen peroxide in a heterophase system in the presence of surfactants and transition metal ions proceeds as a micellar catalysed process.

The role of metal ions; in the studied systems, is in the generation of active intermediates for subsequent hydroxylation of benzene.

Presumably, ionic surfactants form micelles at the concentration higher than the critical. The hydrophobic (hydrocarbon) nucleus of micelles in polar solvents (water, in particular) is capable of solubilizing benzene, which leads to the increase of the local benzene concentration in the solution.

The formation of micelles in CTMAB solutions by the conductivity method has been studied. Fe(III)-CTMAB exhibited the highest activity in the surfactants concentration area (more than 0.01 mole/l) which was close to the micelle existence area in solution.

The hydroxylation proceeds with an induction period. The addition of small amounts of phenol or pirocatechol ($1.1 \cdot 10^{-2}$ mole/l) leads to a considerable decrease of the induction period of the reaction and a noticeable increase in the initial rate of hydroxylation.

Besides, the addition of ethylene diaminotetraacetic acid to the catalytic system gives the destruction of Fe(II)-Fe(III) complex with phenol or pyrocatechol and the reaction rate as well as the phenol yield decrease.

Presumably, the most active forms of catalysts are the complexes of Fe(III) with pyrocatechol (or phenol) which are formed in the process of the reaction and are sorbed near the double electric layer of the micelle.

Thus, the developed catalytic system based on transition metal ions and surfactants has been proved to be efficient in the selective hydroxylation of benzene to phenol under mild conditions with rather high substrate conversions.

References

[1] R.A. Sheldon and J.K. Kochi, *Metal-Catalysed Oxidation of Organic Compounds* (Academic Press, New York, 1981).

[2] H.L.H. Fenton, J. Chem. Soc. 65 (1984) 899–910.

[3] G.A. Hamilton and L.P. Friedman, J. Amer. Chem. Soc. 85, 7 (1963) 1008–1009.

[4] M.A. Brook, L. Castle, J.R.L. Smith, R. Higgins and Morris, J. Chem. Soc. Perkin Trans. 11 (1982) 687–692.

[5] S. Udenfriend, C.T. Clark, L. Axelrod and B.B. Brodie, J. Biol. Chem. 208, 2 (1954) 731–739.

[6] C.R.E. Jefcoate, J.R.L. Smith and R.O.C. Norman, J. Chem. Soc. B 8 (1969) 1013–1018.

[7] A. Kunai, S. Hata, S. Yto and K. Sasaki, J. Amer. Chem. Soc. 108, 19 (1986) 6012–6016.

[8] E.A. Karakhanov, S.Yu. Narin, T.Yu. Philippova, Ye.A. Ivanova, S.M. Volkov and A.G. Dedov, Neftekhimiya 6 (1987) 791–795.

[9] K.B. Yatsimirsky, G.G. Talanova and E.V. Rybak-Akimova, Doklady AN SSSR, Khimiya. 288, 3 (1986) 646–649.

[10] H. Koshima and H. Onishi, Anal. Sci. 1, 4 (1985) 389–390.