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Kinetics and Mechanism of the Interaction of Phenol with Ethylene Oxide in the Presence of Ion-Exchange Resin Wofatit SBW as Catalyst

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The interaction of phenol and ethylene oxide to form phenoxyethanol has been studied in the presence of the basic ion-exchange resin Wofatit SBW as catalyst. The resin was used in its hydroxylated form and kinetic studies have been made using a batch reactor with mole ratios of ethylene oxide to phenol of 2.8 : 1 and 10 : 1 over the temperature range 50–90°C. The reaction is of zero order with respect to both reactants and the activation energy is 17.6 kcal/mole. The data show that the mechanism of the catalysis is the same as that found with basic nucleophilic catalysts in homogeneous media.

INTRODUCTION

The reaction of ethylene oxide with phenols is of great importance to industry. The obtained phenyl ethers of polyethylene glycols are valuable detergents (*1*). The latter are produced by condensation of alkylphenol with a large excess of ethylene oxide in the presence of sodium hydroxide, sodium, alkaline alcoholates, and other basic catalysts (*2*, *3*). However, in these cases the catalyst becomes included in the reaction products. This shortcoming of the homogeneously catalyzed reaction may be eliminated by applying ion-exchange resins as catalysts (*4*).

The aim of the present work was to study kinetically the catalytic monooxyethylation of phenol in the presence of the ion exchange resin Wofatit SBW.

EXPERIMENTAL

The catalyst, Wofatit SBW, is a basic ion-exchange resin with a gel particle (microreticular) structure, containing trimethylammonium active groups. Exchanged to the hydroxyl form, Wofatit SBW has an ion-exchange capacity of about 3 mequiv/g. The average diameter of the particles is 0.40 mm.

Investigations were carried out in a batch reactor. This was a thermostated tube with a volume of about 60 cm^3. After the mixture of phenol, ethylene oxide, and catalyst, dried to constant weight, had been stirred for a definite time, the reaction products were analyzed by a gas chromatograph (Chrom-3) equipped with a flame ionization detector.

RESULTS AND DISCUSSION

The initial concentration of ethylene oxide exerts some influence on the rate of phenol disappearance. From the data in Fig. 1 it can be seen that above a definite excess

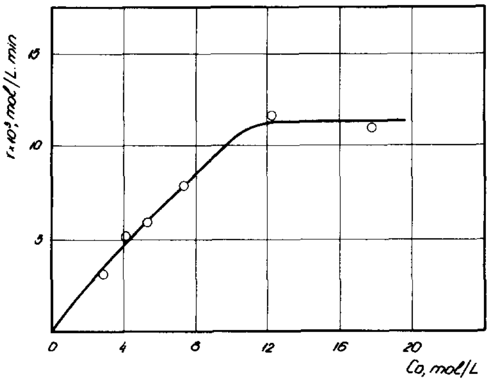

FIG. 1. Dependence of the rate of disappearance of phenol on the initial concentration of ethylene oxide. Temperature 70°C, c_{cat} = 0.131 g ion/liter.

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of ethylene oxide the rate of monooxyethylation no longer increases. The results obtained coincide with the data of other authors (*5*) who have studied the homogeneous catalytic process. Consequently, when the initial concentration of ethylene oxide is above 11–12 mole/liter (mole ratio ethylene oxide to phenol about 2.0–2.5) the reaction is of zero order with respect to oxide. Moreover, under the conditions of incomplete conversion of phenol, the only product of catalytic interaction is phenoxyethanol.

Further studies were carried out at a mole ratio of ethylene oxide to phenol of about 2.8 : 1 and at temperatures of 50–90°C. It was found that under these conditions transport phenomena do not influence the kinetics of the reaction.

Figures 2 and 3 show the data for consumption of phenol and accumulation of phenoxyethanol, respectively, at different temperatures. It was concluded that under the experimental conditions the dependence between the concentration of phenol and time is linear and the phenol disappearance rate does not change with time. The reaction is of zero order with respect to phenol and to ethylene oxide, because of the considerable surplus of the latter. Consequently, the observed rate (r) of the process coincides with the value of the effective rate constant k_{ef}, which depends only on the "concentration" of catalyst. k_{ef} is proportional to the quantity of catalyst in the range studied (Fig. 4). At the same time, zero order of reaction with respect to the reagents was retained.

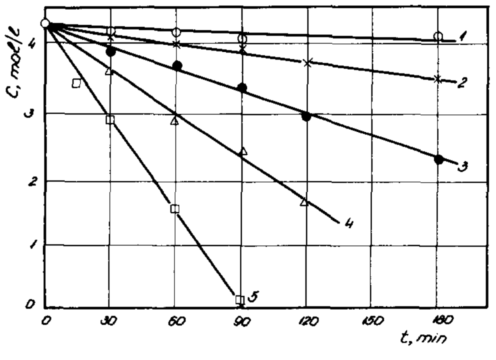

FIG. 2. Dependence of the concentration of phenol on time. c_{cat} = 0.131 g ion/liter. (1) T = 323 K; (2) T = 333 K; (3) T = 343 K; (4) T = 353 K; (5) T = 363 K.

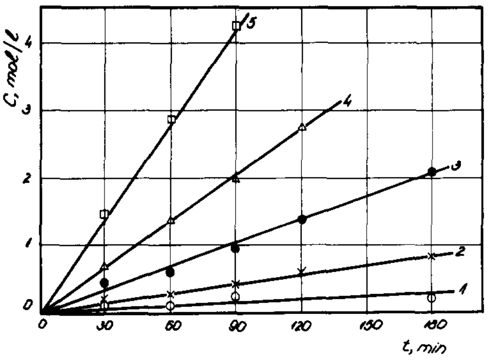

FIG. 3. Dependence of the concentration of phenoxyethanol on time. Mole ratio ethylene oxide to phenol 2.8 : 1, c_{cat} = 0.131 g ion/liter. (1) T = 323 K; (2) T = 333 K; (3) T = 343 K; (4) T = 353 K; (5) T = 363 K.

In Table 1 the values of the rate $r = k_{ef}$ at different temperatures and mole ratios are given. The increase of ethylene oxide surplus with respect to the amount of phenol does not essentially change the rate of reaction. The energy of activation E at both

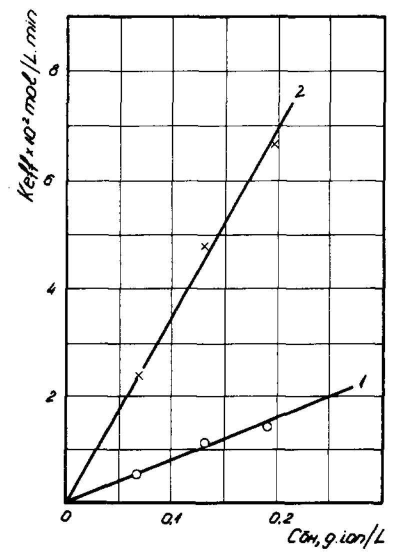

FIG. 4. Dependence of the effective rate constant on the "concentration" of catalyst. Mole ratio ethylene oxide to phenol 2.8 : 1. (1) T = 343 K; (2) T = 363 K.

TABLE 1

Rate of the Interaction of Phenol and Ethylene Oxide to Phenoxyethanol[a]

Temperature (K)	Rate of the reaction $r = k_{eff}$ (mole/liter · min)	
	Mole ratio ethylene oxide to phenol 2.8 : 1	Mole ratio ethylene oxide to phenol 10 : 1 ($\times 10^{-2}$)
323	2.00×10^{-3}	
333	4.50×10^{-3}	
343	1.15×10^{-2}	1.12
353	2.33×10^{-2}	2.13
363	4.75×10^{-2}	4.65

[a] Catalyst-Wofatit SBW in OH form, $C_{cat} = 0.131$ g ion/1

the investigated ratios (ethylene oxide to phenol = 2.8 : 1 and 10: 1) is approximately the same (Fig. 5).

It has been proved that at equal "concentration" of counterions ($\overline{OH}$ or $\overline{Cl}$) in the reaction system (equal amount of added anion exchanger Wofatit SBW, completely exchanged to the corresponding ionic form) the phenol disappearance rate in the two cases is equal. After being used in the reaction, Wofatit SBW was washed with benzene and ether to absence of phenol in the filtrate. Next by treatment of Wofatit SBW with diluted hydrochloric acid it was found (using gas chromatographic analysis) that phenol is present in the liquid. This means that the following ion-exchange process takes place:

$$\mathrm{R - N^+(CH_3)_3\overline{O}C_6H_5 + HCl \rightarrow R - N^+(CH_3)_3\overline{Cl} + C_6H_5OH}$$

Consequently, the strong basic anion exchanger Wofatit SBW contains the catalytically active phenolate counterion in the reaction medium. At the initial ion-exchange equilibrium the catalyst changes to phenolic form, according to the scheme:

$$R - \mathrm{N^+(CH_3)_3\overline{O}H + C_6H_5OH \rightleftarrows R - N^+(CH_3)_3\overline{O}C_6H_5 + H_2O}$$

In the reaction medium phenol is present in the form of association systems with ethylene oxide, because of the large excess of the latter. These systems react with the catalyst according to the scheme:

$$\mathrm{C_6H_5OH\ .\ .\ .\ .\ OC_2H_4 + R - N^+(CH_3)_3\overline{O}C_6H_5 \underset{k_1'}{\overset{k_1}{\rightleftarrows}} Complex \xrightarrow[\text{slow}]{k_2}}$$
$$\mathrm{\rightarrow C_6H_5OCH_2CH_2OH + R - N^+(CH_3)_3\overline{O}C_6H_5}$$

Using the kinetic equation from the work of Patat *et al.* (7):

$$r = k_2[\mathrm{Complex}] = \frac{k_2k_1[\mathrm{C_6H_5OH}] \cdot c_{\mathrm{cat}}}{k_1' + k_2 + k_1[\mathrm{C_6H_5OH}]}$$

it is obvious that in the present study we obtain:

$$k_1[\mathrm{C_6H_5OH}] \gg k_1' + k_2$$

i.e., the initial equilibrium of the complex formation is strongly withdrawn to the right. This conclusion is supported by the zero order of the reaction with respect to phenol. Therefore, the rate equation is:

$$r = k_{\mathrm{eff}} = k_2c_{\mathrm{cat}}.$$

The latter equation coincides well with the experimental results. The rate constant k_2 was calculated relating k_{eff} to the "concentration" of the catalytic hydroxyl ions of

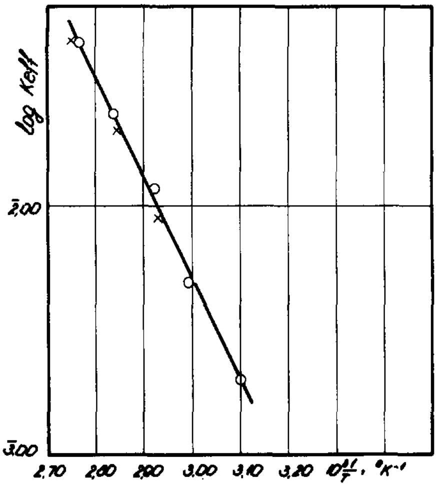

FIG. 5. Dependence of the effective rate constant on temperature. c_{cat} = 0.131 g ion/liter ○, Mole ratio ethylene oxide to phenol 2.8 : 1; ×, mole ratio ethylene oxide to phenol 10 : 1.

the resin in the solution. At T = 343 K (70°C) we obtain:

$$k_2 = \frac{k_{ef}}{c_{cat}} 8.8 \times 10^{-2} \text{ min}^{-1}.$$

From the value of k_2 and E the preexponential factor of the Arrhenius equation was determined:

$$Z = 1.35 \times 10^{10} \text{ min}^{-1} = 2.25 \times 10^{8} \text{ sec}^{-1}.$$

In Table 2 the values of the kinetic parameters are compared with those obtained by other authors (*6*, *8*) using homogeneous catalysts. The comparison leads to the conclusion that the mechanism of the catalytic action of Wofatit SBW in the hydroxyl form does not differ from that of homogeneous catalysts. The formation of the intermediate activated complex occurs in the sphere of influence of the catalytically active counterions within the particles of Wofatit SBW. This conclusion is supported by the high value of the activation energy, the zero order of the reaction with respect to reactants, as in the homogeneous medium (*6*), and the linear dependence of the rate on the amount of catalyst. On the basis of the data obtained it may be suggested that the mechanism of the studied process is analogous to that of homogeneous catalysis with C_6H_5ONa and $C_6H_5N(CH_3)_2$ (*7*, *8*).

TABLE 2

Values of Kinetic Parameters When Different Nucleophilic Catalysts Are Used in the Reaction

Catalyst	Rate constant k_2 at T = 343 K (min^{-1})	Energy of activation E (kcal/mole)	Preexponential factor Z sec^{-1} (×10^8)
C_6H_5ONa	0.35	16.0	0.88
$C_6H_5N(CH_3)_2$	0.49	16.4	2.22
Wofatit SBW	0.088	17.6	2.25

REFERENCES

1. Zimakov, P. B., Diment, O. N., and Bogoslovsky, N. A., "Ethylene Oxide," p. 97. Khimia, Moscow, 1967.
2. Nevolin, F. B., "Khimia i Tekhnologiya Moyustikh Sredstv," p. 184. Pistevaya promishlenost, Moscow, 1964.
3. Paushkin, I. M., "Neftekhimicheskii Syntez v Promishlenosty," p. 259. Nauka, Moscow, 1966.
4. Boeva, R., and Markov, K., Bulg. Pat. 24583 (1977).
5. Patat, F., Cremer, E., and Bobleter, O., *Monatsh. Chem.* **83**, 322 (1952).
6. Patat, F., and Woytech, B., *Markromol. Chem.* **37**, 1 (1960).
7. Patat, F., Cremer, E., and Bobleter, O., *J. Polym. Sci.* **12**, 489 (1954).
8. Patat, F., and Wittmann, E., *Z. Naturforsch.* **18a**, 169 (1963).