Kinetics and Products Distribution of Selective Catalytic Hydration of Ethylene- and Propylene Oxides in Concentrated Aqueous Solutions

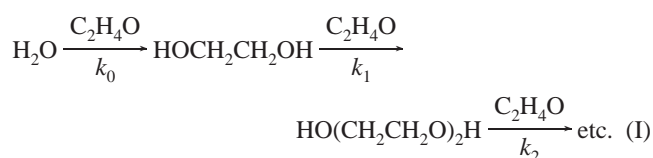I. A. Kozlovsky, R. A. Kozlovsky,* A. V. Koustov, M. G. Makarov, J. P. Suchkov, and V. F. Shvets

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Abstract:

The kinetics of selective hydration of ethylene- and propylene oxides in concentrated aqueous solutions is studied during homogeneous catalysis by sodium bicarbonate. The mathematical model of the process with determined parameters adequately describing the rate of the reaction and products distribution is developed.

Introduction

The reaction of ethylene- and propylene oxides hydration is an industrial way of obtaining of glycols, in particular ethylene glycol—one of the most-produced large-scale products of industrial organic synthesis, with the world annual production in 2000 of about 15.3 million t/year.[1] The oxide hydration reaction proceeds on a serial-to-parallel route with a formation of homologues of glycol:

$$H_2O \xrightarrow[k_0]{C_2H_4O} HOCH_2CH_2OH \xrightarrow[k_1]{C_2H_4O}$$
$$HO(CH_2CH_2O)_2H \xrightarrow[k_2]{C_2H_4O} \text{etc.} \quad (I)$$

where k_0, k_1, k_2 are the rate constants of the series stages.

Presently, all ethylene- and propylene glycol is produced in industry by a noncatalyzed reaction. Product distribution in the reaction I is regulated by the oxide-to-water ratio in the initial reaction mixture. The ratio of rate constants for the stages of reaction I is unfavorable for monoglycol formation (the distribution factor $b = k_1/k_0$ for a noncatalyzed reaction of ethylene oxide with water according to different data sources gives value 1.9–2.8[2]). For this reason considerable excess of water (molarity up to 20×) is applied to increase the monoglycol yield in industry. This results in a considerable power cost at the final stage of product isolation from dilute aqueous solutions.

One of the ways of increasing the monoglycol selectivity and, therefore, of decreasing water excess is the application of catalysts to accelerate only the first stage of the reaction I. Such catalysts are the anions of salts of some acids[3–6]

and metalate anions.[7–8] The kinetics and reaction mechanism of the hydration of α-oxides using homogeneous catalysis by salts have been explicitly studied.[3,10,11] The kinetic data obtained have shown that at a concentration of some salts of about 0.5 mol/L the distribution factor $b = k_1/k_0$ is reduced 10-fold more (to 0.1–0.2). This enables the production of monoglycol with high selectivity at water/oxide molar ratios close to 1. We have used hereinafter homogeneous nucleophilic catalysts with the above-mentioned properties for the creation of industrial heterogeneous catalysts of a selective hydration of ethylene- and propylene oxides by means of an immobilization of anions of salts on heterogeneous carriers.[12–17] The largest ethylene glycol producers Shell,[18–24]

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Dow,[25,26] BASF,[27] Union Carbide,[28–30] and Mitsubishi[31] conduct researches on the elaboration of selective catalysts of ethylene oxide hydration in the same direction.

The Kinetic Model. The mechanism of the catalysis of α-oxides hydration by anions consists of the nucleophilic addition of anion (A$^-$) of the catalyst to a solvated molecule of α-oxide:[8–10]

$$\text{(II)}$$

$$\text{(III)}$$
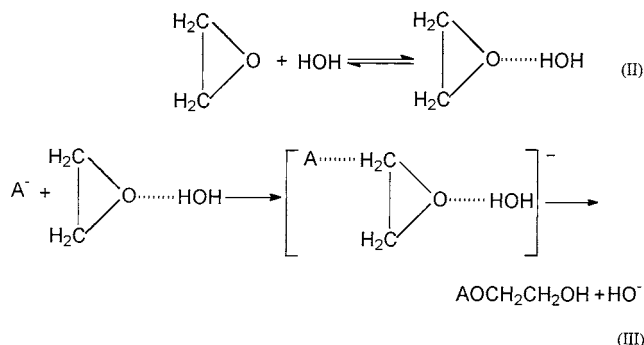
and subsequent hydrolysis of an intermediate ester with the formation of glycol and regeneration of the catalyst:

$$AOCHCHOH + HO^- \rightarrow A^- + HOCH_2CH_2OH \quad \text{(IV)}$$

The rate-determining stage in most cases is the formation of an intermediate ester by reaction III, and in dilute aqueous solutions the rate of the reaction is described by the following kinetic equation:[4]

$$r = k[C_2H_4O][A^-] \quad \text{(1)}$$

The kinetic model of reaction III, suitable for the quantitative description of the heterogeneous catalytic process in a wide range of concentrations of water and glycol is indispensable for the implementation of the industrial catalytic process of the hydration of concentrated water solutions of α-oxide. The kinetic experiments conducted by us have shown that the immobilization of anions on ion-exchange resin does not change selectivity, the kinetic equation, or its parameters. It gives the basis to use the results of experiments on a homogeneous catalytic hydration for obtaining the demanded model. Let's deduce such a model on the basis of a trimolecular mechanism of an oxide ring-opening (II, III), which is also valid for a noncatalyzed reaction of an α-oxide hydration:

$$\text{(V)}$$
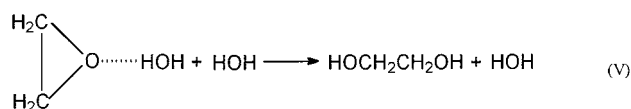
and reaction of polyglycols formation:[32]

$$\text{(VI)}$$
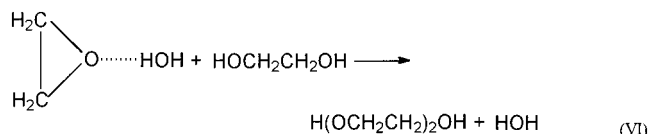
In concentrated aqueous solutions of glycols it is necessary to take into account that the oxide is solvated in equilibrium II not only by water, but also by glycols.[33] Having designated the effective concentration of proton donor materials activating an oxide cycle through a hydrogen bond formation by [SH], we obtain:

$$[SH] = [H_2O] + p\sum[Gly_i] \quad \text{(2)}$$

where $\Sigma[Gly_i]$ is the sum of the concentrations of monoglycol and all polyglycols obtained by reaction I; p is the parameter describing the efficiency of α-oxide solvation by glycols relative to water.

Supposing, that the equilibrium II is established quickly and is shifted to the left, eq 1 for concentrated glycol solutions can be presented by the equation:

$$r = k_{ct}[A^-][C_2H_4O][SH] \quad \text{(3)}$$

Taking into account the parallel noncatalyzed reactions of α-oxide (reaction I) proceeding according to the mechanism (V, VI), we obtain a general kinetic equation of α-oxide consumption in concentrated solutions at a nucleophilic catalysis:

$$-d[C_2H_4O]/dt = (k_0([H_2O] + b\Sigma[Gly_i]) + k_{ct}[A^-])([H_2O] + p\Sigma[Gly_i])[C_2H_4O] \quad \text{(4)}$$

In the derivation of eq 4 it was also assumed[2] that the rate constants of series stages of the reaction I after the first (k_0) are equal, that is

$$b = k_1/k_0 = k_2/k_0 = k_3/k_0 = ...$$

The determination of the parameters of the eq 4 was conducted for a homogeneous catalysis using a bicarbonate ion, one of the most active and accessible nucleophilic catalysts of α-oxide hydration.

Experimental Section

Materials. NaHCO$_3$, ethylene glycol, diethylene glycol, triethylene glycol, and propylene glycol were purchased from commercial suppliers and used without further purification. Ethylene oxide and propylene oxide were purified by distillation under solid NaOH. Water was purified by distillation.

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Table 1. Products distribution and monoglycol yields of a noncatalyzed reaction of ethylene- and propylene oxide hydration calculated according to the eqs 6 and 7 and experimental values

β	monoglycol, % mass		diglycol, % mass		triglycol, % mass		monoglycol yields, %	
	calc	exp	calc	exp	calc	exp	calc	exp
	Ethylene Oxide, First Six Points at 94 °C, the Rest at 90 °C, $b = 2.6 \pm 0.1$							
0.0454	12.57	12.27	1.21	−	0.065	−	89.3	87.2
0.0722	17.74	17.0	2.65	−	0.22	−	83.9	80.4
0.102	22.11	21.4	4.56	−	0.52	−	78.6	76.1
0.136	25.74	24.2	6.88	−	1.03	−	73.1	68.8
0.174	28.49	26.6	9.44	−	1.76	−	67.8	63.3
0.22	30.58	28.1	12.4	−	2.85	−	62.1	57.0
0.1	21.84	21.74	4.41	3.38	0.49	0.292	78.9	78.5
0.2	29.82	32.63	11.2	10.87	2.35	2.04	64.4	70.5
0.3	32.09	35.20	16.83	16.09	5.04	4.16	53.8	59.0
0.4	31.86	35.02	20.98	21.91	7.97	7.83	45.7	50.2
	Propylene Oxide, 94 °C, $b = 2.85 \pm 0.13$							
0.0253	9.03	8.95	−	−	−	−	91.3	90.5
0.0601	18.06	17.61	−	−	−	−	84.8	82.7
0.0848	22.13	21.98	−	−	−	−	78.8	78.2
0.103	24.20	24.42	−	−	−	−	74.0	74.7
0.13	26.64	27.23	−	−	−	−	68.8	70.4
0.197	31.38	31.08	−	−	−	−	61.7	61.1
0.217	30.8	31.7	−	−	−	−	57.1	58.8
0.311	32.56	32.34	−	−	−	−	49.6	49.3

Apparatus. The rate of the reaction was measured by the pressure drop of ethylene or propylene oxide vapors over the reaction mixture using a manometer.[34] The other experiments were carried out in the isothermal batch autoclave, equipped with an automatic temperature controller.

Analysis. The contents of mono-, di-, and triethylene glycols and propylene glycol in the reaction products was determined by GLC, using a 1 m × 3 mm × 10^{-3} m glass column packed with 15% FFAP on INERTON AW-DMCS (0.2−2.25 mm). 2-Ethoxyethanol was used as an internal standard.

Results and Discussion

During the first stage of the determination of the parameters a series of experiments on the analysis of products distribution in a noncatalyzed hydration of ethylene- and propylene oxides was conducted to obtain a more precise definition of the distribution factor b. The experiments were conducted at an oxide/water molar ratio of $\beta = 0.045-0.4$ in an autoclave at 90−94 °C up to full transformation of oxide. The obtained yields are listed in the Table 1.

According to the eq 4 the rate of glycol and polyglycol formation is described in the absence of the catalyst by the equations:

$$-d[Gly_1]/dt = k_0([H_2O] - b[Gly_1])([H_2O] + p\sum[Gly_i])[C_2H_4O] \quad (5)$$

$$-d[Gly_i]/dt = k_0 b([Gly_{i-1}] - [Gly_i])([H_2O] + p\sum[Gly_i])[C_2H_4O]$$

Having divided eq 5 by eq 4 at $k_{ct}[A^-] = 0$, we obtain equations for the calculation of products distribution, presented in the Table 1:

(34) Lebedev, N. N.; Shvets, V. F. *Kinetics Catal.* (Russ.) **1968**, *9*, 504.

$$d[Gly_1]/d[C_2H_4O] = ([H_2O] - b[Gly_1])/([H_2O] + b([H_2O]_0 - [H_2O])) \quad (6)$$

$$d[Gly_i]/d[C_2H_4O] = b([Gly_{i-1}] - [Gly_i])/([H_2O] + b([H_2O]_0 - [H_2O])) \quad (7)$$

where $[H_2O]_0 =$ initial concentration of water, mol/L;

$$\sum[Gly_i] = [H_2O]_0 - [H_2O]$$

The best correspondence of computed and experimental values of product concentrations listed in the Table 1 is obtained with b values of 2.6 ± 0.2 for the hydration of ethylene oxide and 2.85 ± 0.13 for hydration of propylene oxide.

For the determination of the other unknown parameters of eq 4 a series of kinetic experiments with variation of the concentrations of sodium bicarbonate, water, glycol, and temperature was carried out. The initial concentrations of ethylene or propylene oxides were within the limits 0.5−1.0 mol/L, water concentrations in the glycol−water mixtures were changed from 20 up to 80% of mass. Under these conditions the first-order kinetics of ethylene or propylene oxide consumption were observed:

$$r = k_{exp}[oxide]$$

The experimental values of the first-order rate constants were calculated as tangents of straight-line angles in coordinates $\ln P -$ time, where P is partial pressure of ethylene or propylene oxide. These experimental rate constants are listed in Table 2. According to the eq 4 they can be represented by:

$$k_{exp} = (k_0([H_2O] + b\sum[Gly_i]) + k_{ct}[HCO_3^-])([H_2O] + p\sum[Gly_i]) \quad (8)$$

Table 2. Experimental (k_{exp}) and calculated (k_{calc}) rate constants ($\times 10^5$ s^{-1}) of ethylene oxide hydration

	70 °C		80 °C		90 °C	
[HCO$_3^-$], mol/l	k_{exp}	k_{calc}	k_{exp}	k_{calc}	k_{exp}	k_{calc}
Ethylene Glycol:Water Mass Ratio = 0:1						
0	3.63	3.65	8.07	8.14	16.76	17.39
0.1	5.41	5.46	13.04	12.49	27.81	27.30
0.3	8.46	9.08	21.41	21.15	47.98	47.07
0.5	12.0	12.7	30.65	29.79	64.08	66.78
Ethylene Glycol:Water Mass Ratio = 1:4						
0	3.17	3.34	7.66	7.46	15.62	15.94
0.1	6.03	5.02	11.71	11.47	25.74	25.09
0.3	8.19	8.36	19.84	19.48	45.67	43.35
0.5	10.20	11.70	25.54	27.46	60.60	61.55
Ethylene Glycol:Water Mass Ratio = 2:3						
0	2.84	3.03	6.62	6.77	13.43	14.45
0.1	4.38	4.56	10.75	10.44	22.50	22.82
0.3	7.13	7.62	19.41	17.75	49.93	39.52
0.5	9.59	10.67	25.99	25.05	55.71	56.16
Ethylene Glycol:Water Mass Ratio = 3:2						
0	2.47	2.71	5.54	6.06	10.79	12.93
0.1	4.29	4.10	9.31	9.37	19.66	20.49
0.3	6.60	6.86	16.17	15.97	33.32	35.56
0.5	8.91	9.61	23.41	22.56	45.23	50.58
Ethylene Glycol:Water Mass Ratio = 4:1						
0	1.92	2.39	4.33	5.33	8.16	11.38
0.1	3.59	3.62	8.86	8.27	19.02	18.09
0.3	6.26	6.07	15.02	14.13	33.16	31.47
0.5	7.98	8.51	21.85	20.00	45.19	44.80

Table 3. Experimental (k_{exp}) and calculated (k_{calc}) rate constants ($\times 10^5$ s^{-1}) of propylene oxide hydration (in the brackets there are catalyst concentrations which differ from standard values)

	[HCO$_3^-$], mol/L							
	0.0		0.1		0.3		0.5	
T, °C	k_{exp}	k_{calc}	k_{exp}	k_{calc}	k_{exp}	k_{calc}	k_{exp}	k_{calc}
Propylene Glycol:Water Mass Ratio = 0:1								
70	3.15	6.96	—		—	—	—	—
80	7.56	10.62	11.0	12.98	12.1 (0.15)	14.16	15.4 (0.26)	16.76
84.5	—	—	15.4	16.12	24.4	22.88	20 (0.2)	19.5
90	15.9	15.82	22.5	20.99	35.0	31.32	30.3 (0.2)	26.16
Propylene Glycol:Water Mass Ratio = 1:4								
90	12.67	12.92	18.33	17.41	27.83	26.39	38.17	35.36
100	20	18.85	29.5	28.26	52.17	47.07	70.5	65.89
110	30	26.96	42.5	45.93	—	—	—	—
Propylene Glycol:Water Mass Ratio = 2:3								
90	9.5	10.18	14.17	13.96	20.83	21.53	28.0	29.1
100	14.42	14.85	21.67	22.78	36.5 (0.31)	39.43	52.0	54.5
110	21.7	21.2	35.83	37.23	60.5	69.21	-	-
Propylene Glycol:Water Mass Ratio = 3:2								
90	6.17	7.61	9.33	10.66	17.5	16.77	22.83	22.87
100	9.17	11.11	15.07	17.5	29.0	30.29	43.0	43.09
110	13.67	15.87	29.5	28.77	52.67	54.58	80.0	80.38
Ethylene Glycol:Water Mass Ratio = 4:1								
90	3.33	5.25	5.83	7.54	9.0	12.12	12.5	16.71
100	7.833	7.65	11.02 (0.08)	11.49	18.33	22.07	25.0	31.68
110	11.67	10.94	23.67	20.63	43.0	40.0	69.83	59.39

The best values of parameters of eq 8 which gives an adequate description of the experimental data are listed below:

ethylene oxide

$$k_0 = \exp(9.077 - 9355/T) \; \text{L}^2/(\text{mol}^2\,\text{s})$$

$$k_{ct} = \exp(18.24 - 10574/T) \; \text{L}^2/(\text{mol}^2\,\text{s}); \quad p = 1.88$$

Propylene oxide

$$k_0 = \exp(-2.71 - 5111/T) \; \text{L}^2/(\text{mol}^2\,\text{s})$$

$$k_{ct} = \exp(16.02 - 10020/T) \; \text{L}^2/(\text{mol}^2\,\text{s}); \quad p = 1.1$$

According to experimental data the kinetic equation of α-oxide hydration can be presented as:

$$-d[\text{oxide}]/d\tau = (k_0([\text{H}_2\text{O}] + b\sum[\text{Gly}_i]) + k_{ct}[\text{HCO}_3^-])([\text{H}_2\text{O}] + p\sum[\text{Gly}_i])[\text{oxide}] \quad (9)$$

The adequacy of the obtained kinetic equation is confirmed by good agreement of experimental and calculated values of the first-order rate constants in a broad band of experimental conditions (Tables 2 and 3).

The additional checking of the eqs 4 and 8 with determined parameters was made in three series of experiments on the analysis of monoglycol formed after full conversion of oxide in the catalyzed hydration of the oxide−water mixture in a wide range of oxide/water ratios (Table 4). As it is clear from the Table 4 and Figures 1 and 2 the

Table 4. Values of experimental and computed concentrations and yields of ethylene- and propylene oxide at different initial molar ratios of oxide/water (β)

	[Gly], mol/L		monoglycol yield, %	
β	exp	calc	exp	calc
Ethylene Oxide				
$T = 90$ °C, [NaHCO$_3$] = 0.25 mol/L, $k_{ct}/k_0 = 306$				
0.062	2.81	2.79	94.1	93.3
0.082	3.51	3.47	92.5	91.6
0.101	4.10	4.04	91.1	89.8
0.124	4.73	4.66	89.6	88.3
$t = 94$ °C, [NaHCO$_3$] = 0.2 mol/L, $k_{ct}/k_0 = 314$				
0.039	1.94	1.90	97.9	96.0
0.072	3.15	3.11	92.6	91.5
0.098	3.98	3.92	90.7	89.3
0.131	4.8	4.75	87.1	86.2
0.178	5.72	5.72	83.0	83.0
0.220	6.32	6.38	79.6	80.3
Propylene Oxide				
$T = 94$ °C, [NaHCO$_3$] = 0.25 mol/L, $k_{ct}/k_0 = 211$				
0.0297	1.45	1.44	96.0	95.3
0.0664	2.8	2.77	92.1	91.1
0.068	2.82	2.82	91.0	91.0
0.088	3.405	3.39	89.9	89.0
0.103	3.78	3.76	87.9	87.4
0.106	3.872	3.83	88.2	88.4
0.134	4.4	4.4	84.6	84.6
0.186	5.33	5.23	82.5	81.0
0.202	5.2	5.43	76.6	79.9
0.254	5.58	5.97	71.9	76.9

yields of monoglycol are much higher in the presence of NaHCO$_3$. The reason is a quantitative monoglycol formation
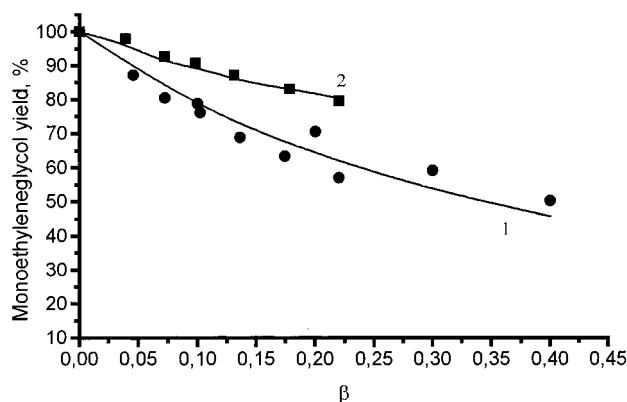
Figure 1. Calculated curves of monoethylene glycol yields vs molar ratio (β) ethylene oxide/water and experimental points: (1) noncatalytic reaction at 90 and 94 °C; (2) reaction catalyzed by NaHCO$_3$ (0.2 mol/L) at 94 °C.
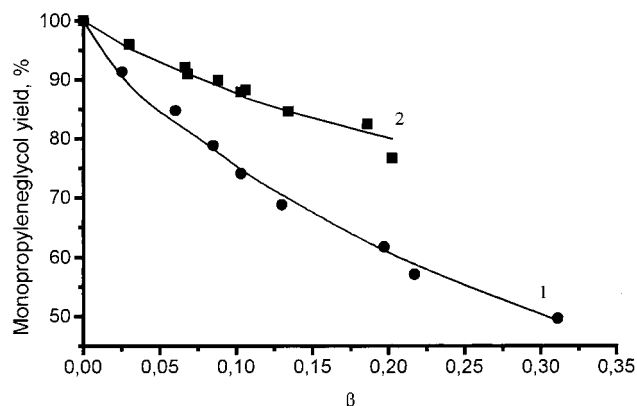

Figure 2. Calculated curves of monopropylene glycol yields vs molar ratio (β) propylene oxide/water and experimental points: (1) noncatalytic reaction at 94 °C; (2) reaction catalyzed by NaHCO$_3$ (0.25 mol/L) at 94 °C.

according to the reactions II−IV. The obtained kinetic model makes it possible to calculate yields of monoglycol formed in the presence of NaHCO$_3$. By division of eq 5 for catalytic reaction by eq 4 we shall receive an equation for the calculation of the yield of monoglycol with different concentrations of NaHCO$_3$ and different oxide/water ratios:

$$\frac{d[Gly_1]}{d[C_2H_4O]} = \frac{k_0([H_2O] - b[Gly_1]) + k_{ct}[HCO_3^-]}{k_0([H_2O] + b\sum[Gly_i]) + k_{ct}[HCO_3^-]} \quad (10)$$

Such calculations with the parameters obtained from kinetic data give a good correlation of computed and experimental values of monoglycol yields (Table 4, Figures 1 and 2). That is the most convincing confirmation of the kinetic model obtained and the mechanism of catalytic reaction proposed with quantitative formation of monoglycol.

Conclusions

On the basis of the mechanism of the catalysis of selective hydration of α-oxides proposed (reactions II−VI) the kinetic model describing the rates of the main (eq 9) and side (eq 5) reactions and products distribution (eq 10) is obtained.

The parameters of the model were found from experimental data that were obtained in a broad range of concentrations of reactants. The model can be utilized for design and optimization of the working conditions of the industrial catalytic reactor of a selective hydration of α-oxides in concentrated aqueous solutions.