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Kinetics and Mechanism of the Catalytic Hydration of Propylene Oxide

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Abstract—The kinetics of propylene oxide hydration in the presence of bis(ethane-1,2-diol)molybdate is reported. A mathematical description of PO disappearance and propylene glycol formation is suggested. The most probable scheme for the process is presented. The basic kinetic constants are calculated.

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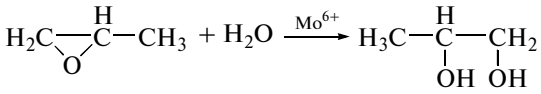
Propylene glycol is a product of large-scale organic synthesis. It is used in the production of the environmentally safest and least toxic industrial and domestic heat carriers, as well as polyester resins. The synthesis of propylene glycol by conventional noncatalytic and acid-catalyzed methods yields large amounts of di- and tripropylene glycols [1].

A high selectivity of the epoxide ring opening reactions catalyzed by the molybdenum-containing compounds has been reported recently [2]. Our preliminary study demonstrated that the monopropylene glycol (MPG) formation selectivity in the presence of molybdenum glycolates can be as high as 97–99 mol %. Therefore, investigation of the catalytic activity of the molybdenum-containing compounds in the hydration of olefin oxides is interesting from both theoretical and practical standpoints.

Here, we report the basic regularities of propylene oxide (PO) hydration in the presence of a molybdenum-containing catalyst:



The occurrence of a single reaction not complicated by other transformations considerably facilitates the study of hydration details.

EXPERIMENTAL

The starting chemicals were PO (USSR State Standard GOST 23001-88), distilled water, and bis(ethane-1,2-diol)molybdate synthesized from ammonium paramolybdate and ethylene glycol [3]. The hydration of PO was carried out in a batch, magnetically stirred reactor fitted with a thermometer and a reflux condenser. The volume of the reaction mixture was 200 ml. Reaction kinetics was studied under isothermal conditions at 50, 60, and 70°C. The initial PO concentration was varied between 0.42 and 1.45 mol/l; the catalyst concentration, between 0.001 and 0.007 (g-atom Mo)/l. The influence of the reaction product MPG, (which was introduced into the reactor at concentrations of 1.2 and 2.4 mol/l) on the PO hydration rate was studied under the same conditions.

Three parallel 1-ml samples were taken at certain time intervals during the reaction. The reaction products were analyzed with a chromatograph. In addition, the PO content of the reaction mixture was determined by a standard method. A sample was placed in a saturated magnesium chloride solution containing 0.02 N hydrochloric acid and was stored for 15 min at room temperature. The residual hydrochloric acid was titrated with a KOH solution. The PO conversion in all entries was 70–95%.

RESULTS AND DISCUSSION

The following investigation strategy was accepted.

(1) At the first stage, the initial PO hydration rates were measured and a reaction scheme was postulated based on the mathematical description of the initial stage of the reaction.

(2) At the second stage, we used nonlinear regression to obtain a mathematical description of the process in time (i.e., a so-called physical model reflecting the real course of the reaction) and calculated the rate constant of PO hydration and the constants of some equilibria observed in the reaction medium.

Study of the Reaction by Measuring the Initial Rates

Several series of single-factor experiments were carried out, in which only one process parameter

Table 1. Initial PO hydration rates* at a catalyst concentration of $[Mo]_0 = 0.0043$ g-at/l

$[PO]_0$, mol/l	w_0, mol l^{-1} min^{-1}								
	50°C			60°C			70°C		
	MPG added, mol/l			MPG added, mol/l			MPG added, mol/l		
	0.0	1.2	2.4	0.0	1.2	2.4	0.0	1.2	2.4
0.42	0.040	0.013	0.006	0.083	0.034	0.016	0.212	0.092	0.053
	(0.039)	(0.01)	(0.006)	(0.081)	(0.023)	(0.014)	(0.22)	(0.087)	(0.054)
	[0.040]	[0.011]	[0.006]	[0.083]	[0.024]	[0.015]	[0.209]	[0.087]	[0.054]
0.78	0.045	0.020	0.009	0.096	0.037	0.023	0.258	0.138	0.089
	(0.042)	(0.015)	(0.009)	(0.097)	(0.036)	(0.022)	(0.25)	(0.12)	(0.079)
	[0.044]	[0.016]	[0.009]	[0.104]	[0.039]	[0.024]	[0.265]	[0.12]	[0.077]
1.45	0.046	0.026	0.013	0.110	0.061	0.042	0.275	0.158	0.105
	(0.045)	(0.021)	(0.014)	(0.108)	(0.052)	(0.034)	(0.27)	(0.15)	(0.106)
	[0.047]	[0.023]	[0.014]	[0.12]	[0.055]	[0.036]	[0.283]	[0.15]	[0.097]

Note: Data calculated using formula (8) is given in parentheses, and data calculated using formula (15) are in brackets.

(temperature, catalyst concentration, or the initial PO or MPG concentration) was varied in each series and the other parameters remained unchanged. The parameter variation ranges are specified above.

Since the reaction was carried out in excess water, the water concentration exerted no effect on the hydration kinetics. Formally this means that the partial order of the reaction with respect to H_2O can be taken to be zero.

The partial order with respect to the catalyst was determined at 60°C and catalyst and PO concentrations of 0.001–0.007 g-at Mo/l and 1.24 mol/l, respectively. An analysis of PO disappearance curves showed that the initial reaction rates depended linearly on the catalyst concentration; i.e., the reaction order with respect to the catalyst (Cat) was unity.

Thus, the initial reaction rate can mathematically be described by the expression

$$w_0 = [\mathrm{Cat}] f_1 [\mathrm{PO}]_0. \quad (1)$$

The initial hydration rates at different initial PO and MPG concentrations in the temperature range from 50 to 70°C are listed in Table 1. The dependences of the initial reaction rates on the initial PO concentration $[PO]_0$ (Fig. 1a) are nonlinear and appear as curves with a plateau. Such curves are typical of almost all reactions catalyzed by metal complexes [4] and are described by a homographic function whose denominator is usually a polynomial in substrate concentra-

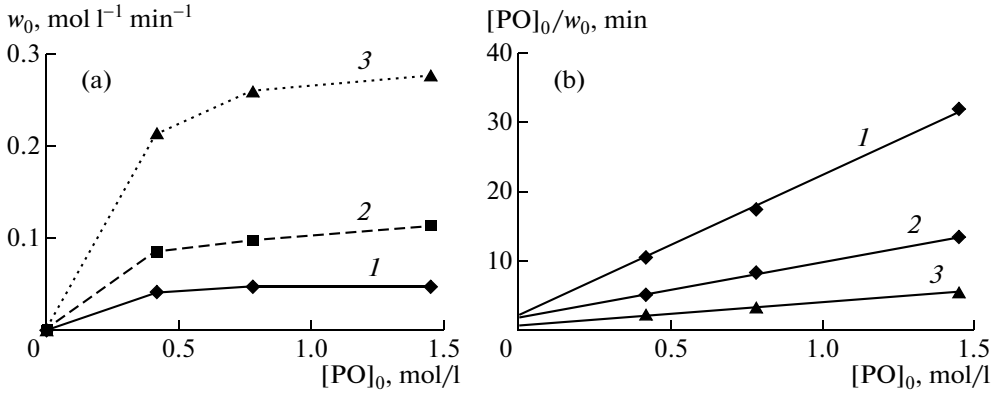


Fig. 1. (a) Dependences of the initial PO hydration rate on the initial PO concentration and (b) the anamorphoses of these dependences at (*1*) 50, (*2*) 60, and (*3*) 70°C.

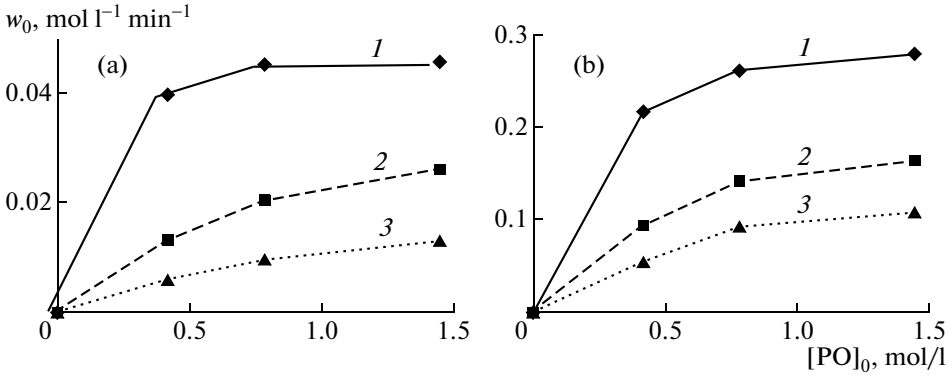


Fig. 2. Effect of MPG additions on the initial rate of PO hydration at (a) 50 and (b) 70 °C: (*1*) no MPG, (*2*) $[MPG]_0 = 1.2$ mol/l, and (*3*) $[MPG]_0 = 2.4$ mol/l.

tions. In the case considered, this function is $f_2[PO]_0$, where f_2 is the so-called catalyst "complexation" function. This kind of relationship is due to the equilibrium formation of complexes of the catalyst with reactants and reaction products [4]. Thus, Eq. (1) takes a more definite form:

$$w_0 = \frac{[Cat][PO]_0}{f_2[PO]_0}. \quad (2)$$

Indeed, the dependences of $[PO]_0/w_0$ on $[PO]_0$ at a constant catalyst concentration (Fig. 1) between 50 and 70°C are linear and are described by the equation

$$-\frac{[PO]_0}{w_0} = \alpha' + \beta'[PO]_0. \quad (3)$$

At [Cat] = const, Eq. (2) will appear as

$$w_0 = \frac{[PO]_0}{\alpha' + \beta'[PO]_0}. \quad (4)$$

The numerical values of the constants α' and β' are as follows: at 50°C α' = 2 and β' = 21; at 60°C α' = 1.8 and β' = 8; at 70°C α' = 0.5 and β' = 3.4.

Equation (4) describes the initial rates of the process and corresponds to the reaction scheme that assumes the rapid primary formation of a catalyst–PO complex followed by attack by water on this complex [4]:

$$[Cat] + [PO] \overset{K_p}{\rightleftharpoons} [Cat \cdot PO] \xrightarrow{k(+H_2O)} [Cat] + [MPG]. \quad (I)$$

It is likely that the high epoxide ring opening selectivity under the action of water is due to PO coordination in the ligand sphere of molybdenum, which is accessible to attack only by the small molecules of water.

We attempted to describe PO disappearance during the reaction in terms of the differential form of Eq. (4) obtained by replacing the initial PO concentration $[PO]_0$ by the current PO concentration [PO] using the above constants α' and β':

$$-\frac{d[PO]}{dt} = \frac{[PO]}{\alpha' + \beta'[PO]}. \quad (5)$$

However, this attempt was unsuccessful. The calculated curves coincided with experimental curves only in the initial region. Beyond this region, they ran far below the experimental curves. Therefore, substances inhibiting the hydration of PO appear during the reaction. It is reasonable to assume that MPG is one of these substances. The addition of MPG to the reaction medium indeed sharply decreases the initial PO disappearance rate at various $[PO]_0$ values (Table 1). The inhibiting effect of MPG is illustrated in Fig. 2.

This effect of MPG can be explained by the equilibrium formation of the catalyst complexes with MPG or mixed complexes including the catalyst, PO, and MPG. Similar complexes were described earlier [5–7].

The dependence of the initial PO hydration rate on $[PO]_0$ somewhat changes upon the addition of MPG. At comparable $[PO]_0$ and $[MPG]_0$ values, the "curvature" of the dependence decreases, indicating that the formation constants of the catalyst complexes with PO and MPG are approximately equal. Thus, the equation for the initial rate of PO hydration should have the following form:

$$w_0 = \frac{[Cat][PO]_0}{f_2([PO]_0,[MPG]_0)}. \quad (6)$$

In order to determine the type of the catalyst complexation function f_2, we constructed the plots shown in Fig. 3. These plots can be fitted to linear functions. This means that α' and β' in Eq. (3) depend on the initial MPG concentration; i.e., $\alpha' = f[MPG]_0$ and $\beta' = f[MPG]_0$:

$$\text{at } 50°C: \quad \alpha' = 2 + 25[MPG]_0,$$

$$\beta' = 21 + 3[MPG]_0;$$

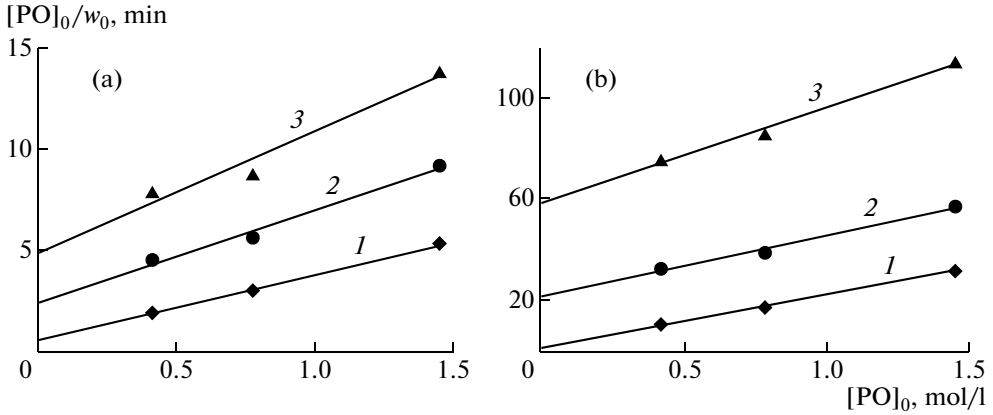


Fig. 3. Effect of MPG additions on the dependence of the $[PO]_0/w_0$ ratio on $[PO]_0$ at (a) 50 and (b) 70°C: (*1*) no MPG, (*2*) $[MPG]_0 = 1.2$ mol/l, and (*3*) $[MPG]_0 = 2.4$ mol/l.

$$\begin{gathered}\text{at } 60^\circ\text{C:}\quad \alpha' = 1.8 + 10[\text{MPG}]_0,\\ \beta' = 7 + 1.5[\text{MPG}]_0;\\ \text{at } 70^\circ\text{C:}\quad \alpha' = 0.5 + 2[\text{MPG}]_0,\\ \beta' = 3.4 + 1.0[\text{MPG}]_0.\end{gathered} \tag{7}$$

After the α' and β' values were substituted into Eq. (4), we obtained a mathematical model for the initial rates for PO hydration under the conditions examined:

$$\begin{gathered}\text{at } 50^\circ\text{C}\\ w_0 = \frac{[\text{PO}]_0}{2 + 25[\text{MPG}]_0 + (21 + 3[\text{MPG}]_0)[\text{PO}]_0},\\ \text{at } 60^\circ\text{C}\\ w_0 = \frac{[\text{PO}]_0}{1.8 + 10[\text{MPG}]_0 + (8 + 1.5[\text{MPG}]_0)[\text{PO}]_0},\\ \text{at } 70^\circ\text{C}\\ w_0 = \frac{[\text{PO}]_0}{0.5 + 2[\text{MPG}]_0 + (3.4 + 1.0[\text{MPG}]_0)[\text{PO}]_0}.\end{gathered} \tag{8}$$

The initial rates calculated using Eq. (8) coincide well with the observed values in all series of experiments (Table 1). The correlation coefficient is $R = 0.99$, which indicates that Eq. (8) provides a good fit to the initial rates of PO hydration on the molybdenum catalyst under various conditions.

However, the influence of the reaction products on the PO hydration rate still remains unclear. Evidently, MPG can exert an inhibiting effect due to the formation of an equilibrium complex with the catalyst:

$$[\text{Cat}] + [\text{MPG}] \overset{K_i}{\rightleftharpoons} [\text{Cat} \cdot \text{MPG}]. \qquad \text{(II)}$$

This is indicated by the appearance of a term containing $[MPG]_0$ in the denominator of Eqs. (8). The presence of the $[MPG]_0[PO]_0$ term indicates that a mixed complex can form:

$$[\text{Cat} \cdot \text{PO}] + [\text{MPG}] \overset{K_{pi}}{\rightleftharpoons} [\text{Cat} \cdot \text{PO} \cdot \text{MPG}]. \qquad \text{(III)}$$

The rate-determining step of the process is the reaction of the complex [Cat · PO] with water (reaction (I)). The formation of complexes via reactions (II) and (III) and the resulting inhibition of the main process was called inhibition by reaction products and "cross" inhibition [4].

In view of the catalyst balance equation

$$\begin{gathered}[\text{Cat}]_0 = [\text{Cat}] + K_p[\text{Cat}][\text{PO}]\\ + K_i[\text{Cat}][\text{MPG}] + K_pK_{pi}[\text{PO}][\text{MPG}],\end{gathered} \tag{9}$$

the initial rate of the reaction can be expressed as

$$w_0 = \frac{kK_p[\text{Cat}]_0[\text{PO}]_0}{1 + K_i[\text{MPG}]_0 + K_p[\text{PO}]_0 + K_iK_{pi}[\text{MPG}]_0[\text{PO}]_0}. \tag{10}$$

At the next stage of the study, we confirmed the formation of all of the above complexes in the reaction mixture and refined the numerical values of the parameters in Eqs. (8).

Study of the Reaction by Kinetic Curve Analysis

For this purpose, it was necessary to analyze all kinetic curves describing PO concentration variation during the reaction. We attempted to describe the PO disappearance kinetics by Eq. (8) in differential form. The replacement of w_0 by the corresponding derivative and the replacement of the initial concentrations $[PO]_0$ and $[MPG]_0$ by the current concentrations led to the following equations:

$$\text{at } 50^\circ\text{C}$$

$$-\frac{d[\text{PO}]}{dt} = \frac{[\text{PO}]}{2 + 25[\text{MPG}] + (21 + 3[\text{MPG}])[\text{PO}]},$$

at 60°C

$$-\frac{d[\mathrm{PO}]}{dt} = \frac{[\mathrm{PO}]}{1.8 + 10[\mathrm{MPG}] + (8 + 1.5[\mathrm{MPG}])[\mathrm{PO}]}, \quad (11)$$

at 70°C

$$-\frac{d[\mathrm{PO}]}{dt} = \frac{[\mathrm{PO}]}{0.5 + 2[\mathrm{MPG}] + (3.4 + 1.0[\mathrm{MPG}])[\mathrm{PO}]},$$

where [PO] and [MPG] are the current concentrations and $[\mathrm{MPG}] = [\mathrm{MPG}]_0 + [\mathrm{PO}]_0 - [\mathrm{PO}]$.

Use of standard integration programs resulted in small and nonsystematic deviations of the calculated PO concentrations from the experimental values. To refine the numerical values of the parameters in Eq. (11), we performed a statistical analysis of its integral form. Since the current MPG and PO concentrations are linearly interrelated (due to the high selectivity of the process), Eq. (11) can be transformed into

$$-\frac{d[\mathrm{PO}]}{dt} = \frac{[\mathrm{PO}]}{\alpha^* + \beta^*[\mathrm{PO}] + \gamma[\mathrm{PO}]^2}. \quad (12)$$

The parameters α*, β*, and γ are functions of the initial PO and MPG concentrations and take the following values:

$$\begin{aligned}
&\text{at } 50^\circ\mathrm{C} \quad \alpha^* = 2 + 25([\mathrm{MPG}]_0 + [\mathrm{PO}]_0),\\
&\beta^* = -4 + 3([\mathrm{MPG}]_0 + [\mathrm{PO}]_0), \quad \gamma = -3;\\
&\text{at } 60^\circ\mathrm{C} \quad \alpha^* = 1.8 + 10([\mathrm{MPG}]_0 + [\mathrm{PO}]_0),\\
&\beta^* = -2 + 1.5([\mathrm{MPG}]_0 + [\mathrm{PO}]_0), \quad \gamma = -1.5;\\
&\text{at } 70^\circ\mathrm{C} \quad \alpha^* = 0.5 + 2([\mathrm{MPG}]_0 + [\mathrm{PO}]_0),\\
&\beta^* = 1.4 + 1.0([\mathrm{MPG}]_0 + [\mathrm{PO}]_0), \quad \gamma = -1.0.
\end{aligned} \quad (13)$$

Integrating Eq. (12) yields

$$F(\alpha,\beta,\gamma) = \alpha^*\ln\left(\frac{[\mathrm{PO}]_0}{[\mathrm{PO}]}\right) + \beta^*([\mathrm{PO}]_0 - [\mathrm{PO}]) + \gamma([\mathrm{PO}]_0^2 - [\mathrm{PO}]^2) - t = 0, \quad (14)$$

where t is the reaction time.

The parameters α*, β*, and γ were determined by processing experimental data using the least-squares method for nonlinear functions. The values corresponding to the initial rates were chosen as the initial approximations. Next, the square deviations of the $[F(\alpha^*, \beta^*, \text{and } \gamma)]^2$ function were minimized and α*, β*, and γ values somewhat differing from those corresponding to the initial rates were obtained.

As a result of this optimization, we arrived at the following mathematical description of the kinetics of the process:

$$\begin{aligned}
&\text{at } 50^\circ\mathrm{C} \quad -\frac{d[\mathrm{PO}]}{dt} = \frac{[\mathrm{PO}]}{3.0 + 23[\mathrm{MPG}] + (20.9 + 2.3[\mathrm{MPG}])[\mathrm{PO}]},\\
&\text{at } 60^\circ\mathrm{C} \quad -\frac{d[\mathrm{PO}]}{dt} = \frac{[\mathrm{PO}]}{2.2 + 9.2[\mathrm{MPG}] + (6.8 + 1.6[\mathrm{MPG}])[\mathrm{PO}]},\\
&\text{at } 70^\circ\mathrm{C} \quad -\frac{d[\mathrm{PO}]}{dt} = \frac{[\mathrm{PO}]}{0.96 + 1.5[\mathrm{MPG}] + (2.5 + 2.0[\mathrm{MPG}])[\mathrm{PO}]}.
\end{aligned} \quad (15)$$

The initial rates calculated using Eq. (15) also coincide with the observed values (Table 1). By comparing Eq. (15) with Eq. (12), we calculated the rate constant and equilibrium constants for complex formation (Table 2). The dependences of these constants on the reaction temperature T are described by the expressions

$$k_{\mathrm{app}} = 1.6\times10^{14}e^{-\frac{11500}{T}}\ \mathrm{l^2\ mol^{-1}\ min^{-1}},$$

$$K_{\mathrm{p}} = 2.6\times10^{-7}e^{\frac{5500}{T}}\ \mathrm{l/mol},$$

$$K_{\mathrm{i}} = 1.1\times10^{-11}e^{\frac{8800}{T}}\ \mathrm{l/mol},$$

$$K_{\mathrm{pi}} = 1.1\times10^{18}e^{-\frac{14200}{T}}\ \mathrm{l/mol}.$$

Table 2. Constants in Eq. (10)

T, °C	k_{app}, $\mathrm{l^2\ mol^{-2}\ min^{-1}}$	K_{p}, l/mol	K_{i}, l/mol	K_{pi}, l/mol
50	0.05	6.97	7.70	0.10
60	0.15	3.09	4.18	0.18
70	0.40	2.60	1.56	1.33

The adequacy of the model was estimated in terms of the Fischer criterion F. The following results were obtained for a significance level of 0.05:

$$F_{\mathrm{calcd}} = 2.95 < F_{\mathrm{tabl}} = 19.3,$$

which proves that the model is adequate to the experimental results.

The analysis of the kinetics of PO hydration catalyzed by molybdenum glycolate indicates a rather complicated behavior of the process. The main reaction is complicated by the formation of a number of complexes of the catalyst with PO and MPG and the mixed complex. In the latter case, both PO and MPG are present in the ligand sphere of the central Mo atom. The catalyst–PO complex interacts with water to form the reaction products via reaction (I). The high epoxide ring opening selectivity is due to the coordination of PO in the ligand sphere of molybde-

num, which is accessible to attack only by the small molecules of water. The formation of complexes via reactions (II) and (III) withdraws part of the catalyst from the process (inhibition by the reaction products and "cross" inhibition [4]), thus inhibiting the entire hydration process.

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