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Kinetics of Allyl Chloride Epoxidation with Hydrogen Peroxide

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Abstract—The kinetics of allyl chloride oxidation to epichlorohydrin in the presence of titanium-containing zeolite was studied. The influence of the concentrations of the initial substances, reaction products, and temperature on the rate of the process was considered. The mathematical model of the process was constructed on the basis of the experimental data obtained. The rate constants, adsorption equilibrium constants, and activation energies of the reactions were calculated.

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Epichlorohydrin is an important product of the bulk chemicals industry. Epichlorohydrin contains a reactive epoxy group and a mobile chlorine atom and readily reacts with organic compounds of various classes, due to which it is used in the production of a wide variety of products applied in many areas of industry. Among the products produced from epichlorohydrin, there are various varnishes, paints, glues, synthetic fibers, ion-exchange resins, and rubbers characterized by high oil resistance, thermal stability, gas impermeability, and other useful properties [1–3]. At the same time, in spite of the variability of the products obtained from epichlorohydrin, most of them (about 68%) are used in the production of epoxy resins.

Epoxy resins, which have high adhesion, elasticity, hardness, strength, and photoresistance and good dielectric properties and are odorless, have become widely popular within the short time. Resins produced from epichlorohydrin are used in various applications, such as production of vanishes, paints, glues for diverse materials, cast and molded pieces, layered materials, stabilizers, and synthetic fibers. Epoxy resins are becoming especially significant in chemical industry due to their high corrosion resistance. Articles produced from fiberglass reinforced plastics by the impregnation of glass fiber with epoxy resin (apparatuses, vessels, pipelines) are very strong, light, and resistant to many corrosive media. Use of epoxy resins in building, where they are applied as components of castable and impregnating glues, sealants, binders for reinforced plastics, etc., is very promising.

The world output of epichlorohydrin is over 1.3 million tons per year [4]. Two industrial epichlorohydrin production plants are working in Russia, whose total annual production capacity does not exceed 55000 t, which is only about 4.2% of the world output. Experts assert that even now the existing plants cannot satisfy the growing market demand for the main products based on epichlorohydrin, first of all, epoxy resins and synthetic glycerol. According to estimates, already in 2010 the increase in the consumption of epoxy resins would have been 7–8%. In fact, the average annual growth rate of their production is only 4% and is primarily held back by difficulties in increasing the epichlorohydrin production capacity.

Thus, the problem of improving the existing epichlorohydrin production technologies, developing more promising ones, and raising the epichlorohydrin output is becoming increasingly challenging.

Our analysis of the methods for the preparation of epichlorohydrin showed [5] that the liquid-phase oxidation of allyl chloride with hydrogen peroxide in an organic solvent over a heterogeneous catalyst (titanium-containing zeolite) is the most promising [6]. However, physicochemical data for this process are lacking in the literature. The purpose of this work was to study the kinetics and to develop a mathematical model for the liquid-phase epoxidation of allyl chloride with aqueous hydrogen peroxide in an organic solvent in the presence of the titanium-containing zeolite.

EXPERIMENTAL

The following reagents were used: methanol (analytical grade, Russian State Standard GOST 2222-95), epichlorohydrin (high-purity grade, USSR State Standard GOST 12844-74), 33–34% hydrogen peroxide (special purity grade, Russian Specifications TU 2611-069-05807977-2006), and allyl chloride (USSR Specifications TU 6-01-753-77).

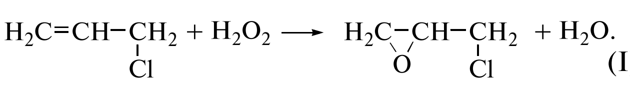
Allyl chloride was oxidized in a temperature-controlled metallic batch reactor at 30–60°C under vigorous stirring (200–600 rpm). The reaction was assumed to begin at the instant hydrogen peroxide (0.02–0.12 mol) was added to the reaction mixture containing allyl chloride (0.02–0.24 mol) and methanol (0.49–1.22 mol). The catalyst content ranged from 6.81 to 33.0 g/l. The catalyst was a powdered titanium-containing zeolite prepared by a standard procedure [7] with a Ti content of 3.16% (in terms of TiO_2), Si/Ti = 25, and pore sizes of 5.1 × 5.5 and 5.3 × 5.6 nm.

The oxidation products were identified by mass spectrometry. A GC-MS analysis was carried out using a Kristall MS instrument equipped with a DSQ II mass spectrometric detector (Thermo Electron). The epichlorohydrin, 1-chloro-3-methoxypropan-2-ol, and 1-chloropropane-2,3-diol contents were determined by GLC on a Tsvet-500 chromatograph equipped with a flame-ionization detector and a stainless steel column with a diameter of 3 mm and a length of 2 m filled with Chromaton-N-AW-DMCS (0.2–2.25 mm) with supported adsorbent Reoplex-400 (15% of the support weight). The hydrogen peroxide content of the reaction mixture was monitored by iodometric titration.

Estimation based on the results of 5–7 replica experiments showed that the root-mean-square measurement error did not exceed 5%.

RESULTS AND DISCUSSION

Allyl chloride is epoxidation with an aqueous solution of hydrogen peroxide on the titanium-containing zeolite is conducted in the presence of a solvent, which may be alcohol, ketone, or ether. Our studies showed that the highest epoxidation rate and a satisfactory yield of epichlorohydrin are achieved with methanol, so the kinetics of the reaction was studied in a methanol medium. The target product forms via the reaction

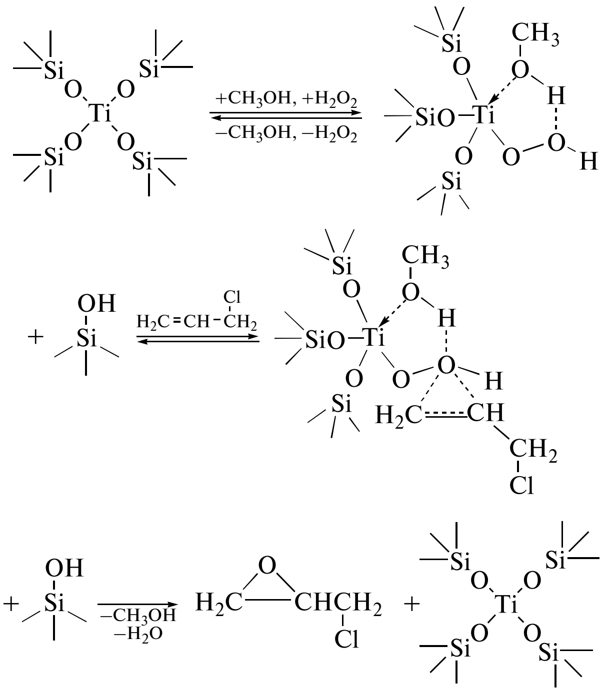


$$\underset{\text{AC}}{H_2C{=}CH{-}CH_2Cl} + \underset{\text{HP}}{H_2O_2} \longrightarrow \underset{\text{ECH}}{H_2C\overset{O}{-}CH{-}CH_2Cl} + \underset{\text{W}}{H_2O}. \quad \text{(I)}$$

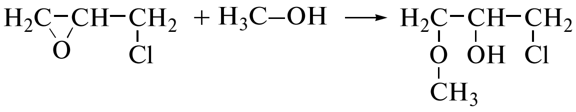
AC **HP** **ECH** **W**

where AC is allyl chloride, HP is hydrogen peroxide, ECH is epichlorohydrin, and W is water.

Hydrogen peroxide interacts with the Ti-containing sites of the catalyst to produce the active form of the catalyst, namely, a titanium hydroperoxo complex stabilized by a solvent molecule [8]. Next, the resulting five-membered complex participates in the epoxidation of allyl chloride to give epichlorohydrin as the target product.



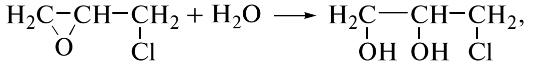
A number of side reactions occur in the system along with the desired formation of epichlorohydrin. The product of the reaction between epichlorohydrin and methanol (1-chloro-3-methoxypropan-2-ol), the product of the reaction between epichlorohydrin and water (1-chloropropane-2,3-diol), and traces of other substances were identified by the GLC and GC-MS methods among the oxidation products of allyl chloride. The formation of the observed by-products is satisfactorily explained in terms of the following reactions occurring in the system:



$$H_2C\overset{O}{-}CH{-}CH_2Cl + H_3C{-}OH \longrightarrow H_2C(OCH_3){-}CH(OH){-}CH_2Cl, \quad \text{(II)}$$

ECH **M** **CMP**

where M is methanol and CMP is 1-chloro-3-methoxypropan-2-ol,



$$H_2C\overset{O}{-}CH{-}CH_2Cl + H_2O \longrightarrow H_2C(OH){-}CH(OH){-}CH_2Cl, \quad \text{(III)}$$

ECH **W** **D**

where D is 1-chloropropane-2,3-diol,

$$2H_2O_2 \longrightarrow 2H_2O + O_2, \quad \text{(IV)}$$

HP **W** **O**

where O is oxygen.

The typical kinetic curves are presented in Fig. 1.

It was experimentally found that the resulting epichlorohydrin retards epoxidation. This is likely due to the fact that epichlorohydrin is adsorbed on the active sites of the catalyst, thus decreasing the fraction of the free surface and the probability of formation of the five-membered complex.

Thus, the following steps of the epoxidation process can be distinguished: adsorption of hydrogen peroxide by the active sites of the catalyst, surface reaction, and epichlorohydrin desorption. Each step can be rate-determining. The following mechanism of allyl chloride oxidation with aqueous hydrogen peroxide in the presence of the titanium-containing catalyst (Cat) can be proposed on the basis of all the data obtained:

$$\mathrm{Cat} + \mathrm{MeOH} \xrightleftharpoons[\text{rapidly}]{K_M} \mathrm{Cat} \cdot \mathrm{MeOH},$$

$$\mathrm{Cat} \cdot \mathrm{MeOH} + \mathrm{HP} \xrightleftharpoons{K_{HP}} \mathrm{Cat} \cdot \mathrm{MeOH} \cdot \mathrm{HP},$$

$$\mathrm{Cat} \cdot \mathrm{MeOH} \cdot \mathrm{HP} + \mathrm{AX} \xrightarrow{k_1} \mathrm{Cat} \cdot \mathrm{MeOH} \cdot \mathrm{ECH} + \mathrm{H_2O},$$

$$\mathrm{Cat} \cdot \mathrm{MeOH} \cdot \mathrm{ECH} \xrightleftharpoons{K_{ECH}} \mathrm{Cat} \cdot \mathrm{MeOH} + \mathrm{ECH}.$$

The following assumptions were made in order to mathematically describe the epoxidation process and to calculate the apparent rate constants of the reactions and activation energies:

(1) the surface reaction is the rate-determining step of the process, and all adsorbed components are in equilibrium;

(2) the reaction occurs between hydrogen peroxide adsorbed on the catalyst surface and dissolved allyl chloride;

(3) the side reactions occur on the catalyst surface.

Under these assumptions, the kinetic model will appear as follows:

$$r_1 = \frac{k_1 K_{HP} C_{HP} C_{AC}}{1 + K_{HP} C_{HP} + K_{ECH} C_{ECH}} \frac{m}{V}, \quad (1)$$

$$r_2 = k_2 C_{ECH} C_M \frac{m}{V}, \quad (2)$$

$$r_3 = k_3 C_{ECH} C_W \frac{m}{V}, \quad (3)$$

$$r_4 = k_4 C_{HP} \frac{m}{V}, \quad (4)$$

where r_1 is the rate of target reaction (I) in mol s^{-1} l^{-1}; r_2, r_3, and r_4 are the rates of side reactions (II), (III), and (IV), respectively, in mol s^{-1} l^{-1}; k_1 is the rate constant of the target reaction in l s^{-1} g^{-1}; k_2 and k_3 are the rate constants of side reactions in l^2 mol^{-1} s^{-1} g^{-1}; k_4 is the rate constant for hydrogen peroxide decomposition in l s^{-1} g^{-1}; K_{HP} and K_{ECH} are the adsorption equilibrium constants of hydrogen peroxide and epichlorohydrin, respectively, in l/mol; C_{HP}, C_{AC}, C_{ECH}, C_M, and C_W are the hydrogen peroxide, allyl chloride, epichlorohydrin, methanol, and water concentrations, respectively, in mol/l; m is the catalyst weight in g; and V is the volume of the reaction mixture in l.

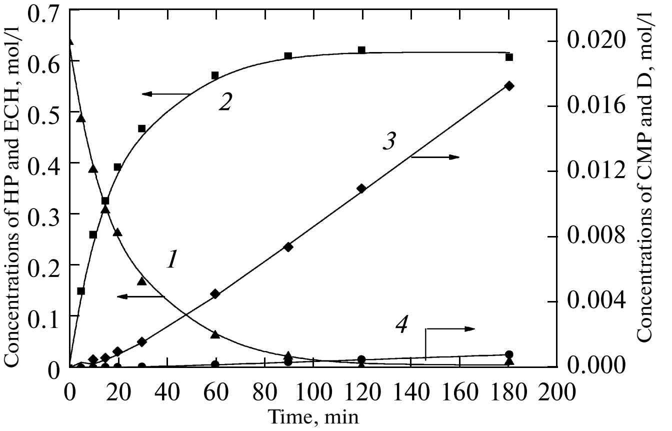


Fig. 1. Kinetics of allyl chloride epoxidation with a 30% hydrogen peroxide solution: (*1*) HP, (*2*), ECH; (*3*) CMP; and (*4*) D. Points are experimental values, and lines are calculated data. $C_{0,AC}$ = 1.93 mol/l, $C_{0,HP}$ = 0.64 mol/l, $C_{0,M}$ = 19.3 mol/l, 40°C, and the catalyst content is 7.9 g/l.

The temperature dependences of the rate constants of reactions (I)–(IV) and those of the adsorption equilibrium constants of hydrogen peroxide (K_{HP}) and epichlorohydrin (K_{ECH}) were described by the Arrhenius and van't Hoff equations, respectively:

$$k_i = k_{0,i} \exp\left(-\frac{E_i}{RT}\right), \quad (i = \mathrm{I, II, III} \text{ or } \mathrm{IV}), \quad (5)$$

$$K_{HP} = K_{0,HP} \exp\left(\frac{Q_{HP}}{RT}\right), \quad (6)$$

$$K_{ECH} = K_{0,ECH} \exp\left(\frac{Q_{ECH}}{RT}\right). \quad (7)$$

The material balance in the isothermal batch reactor used in the synthesis of epichlorohydrin was described by the following system of differential equations:

$$\frac{dC_{AC}}{dt} = -r_1, \quad (8)$$

$$\frac{dC_{HP}}{dt} = -r_1 - 2r_4, \quad (9)$$

$$\frac{dC_W}{dt} = r_1 - r_3 + 2r_4, \quad (10)$$

$$\frac{dC_M}{dt} = -r_2, \quad (11)$$

$$\frac{dC_{ECH}}{dt} = r_1 - r_2 - r_3, \quad (12)$$

$$\frac{dC_{CMP}}{dt} = r_2, \quad (13)$$

$$\frac{dC_D}{dt} = r_3, \quad (14)$$

$$\frac{dC_O}{dt} = r_4. \quad (15)$$

Equations (8)–(11) express the rates of consumption of allyl chloride, hydrogen peroxide, water, and methanol, respectively, in the formation of the reac-

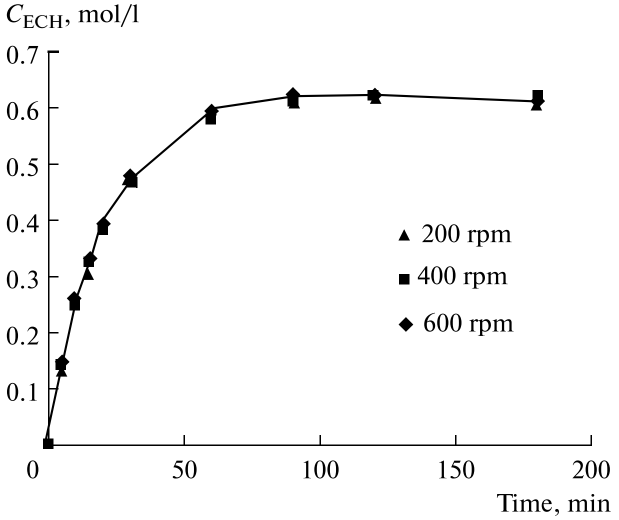


Fig. 2. Variation of the epichlorohydrin concentration during the reaction at various stirring rates. $C_{0,AC} = 1.93$ mol/l, $C_{0,HP} = 0.64$ mol/l, $C_{0,M} = 19.3$ mol/l, 40°C, and the catalyst content is 7.9 g/l.

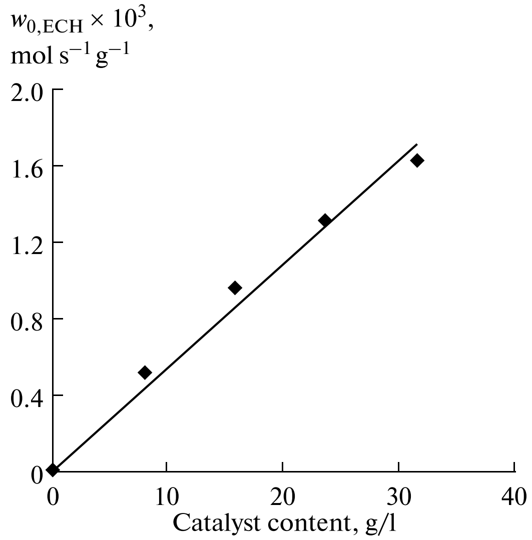


Fig. 3. Initial rate of epichlorohydrin formation versus catalyst content in the reaction mixture. $C_{0,AC} = 1.93$ mol/l, $C_{0,HP} = 0.64$ mol/l, $C_{0,M} = 19.3$ mol/l, 40°C.

tion products, and Eqs. (12)–(15) describe the rates of formation of the products (epichlorohydrin, 1-chloro-3-methoxypropan-2-ol, 1-chloropropane-2,3-diol, and oxygen, respectively). The accepted model ignores the side reactions yielding epichlorohydrin oligomers, because the consumption of hydrogen peroxide in these reactions does not exceed 1–2% and they can be neglected in engineering calculations.

Several series of experiments under various initial conditions were carried out to determine the unknown parameters of the equations. The temperature (30–60°C), initial hydrogen peroxide concentration (0.46–1.67 mol/l), initial allyl chloride concentration (1.73–3.64 mol/l), epichlorohydrin concentration at the initial moment (0–0.94 mol/l), methanol concentration (14.55–19.64 mol/l), and catalyst content (6.81–33.0 g/l) were varied in these experiments. The reaction without a catalyst was carried out at 60°C. The hydrogen peroxide conversion in this case did not exceed 0.5% in 30 min, suggesting the absence of a noncatalytic reaction.

A series of experiments in which the rotational speed of the stirrer was changed at fixed initial reactant and catalyst contents was carried out to determine the rate-limiting factor for allyl chloride epoxidation with aqueous hydrogen peroxide over the titanium-containing zeolite as the catalyst in the batch reactor (Fig. 2).

Figure 2 shows that, at the rotational speeds of the stirrer from 200 to 600 rpm, the concentration of epichlorohydrin in the reaction mixture is independent of the stirring rate, other conditions being equal; i.e., the reaction is kinetically controlled. A rotation rate of 200 rpm was chosen for subsequent experiments. In addition, the dependence of the initial epoxidation rate on the catalyst content is linear (Fig. 3), which also confirms that the reaction occurs under kinetic control. Therefore, the epoxidation of allyl chloride is not subject to diffusion limitations.

The numerical values of the rate constants and adsorption coefficients of the components were determined by minimizing the function F:

$$F = \frac{1}{n}\sum_j\sum_i\left(\frac{C_{ij}^{\exp} - C_{ij}^{\text{calc}}}{C_{ij}^{\exp}}\right)^2 \nu_{ij}, \qquad (16)$$

where n is the number of experimental data points; $C_{ij}^{\exp}$ and C_{ij}^{calc} are the experimental and calculated values of molar concentrations of the components, respectively; and ν_{ij} is the weighting factor. The summation was performed over all components (index i) and over all experimental points in each experiment (index j).

At the first step of determination of the unknown parameters of the model, we found the values of $k_{0,1}$, $K_{0,\text{HP}}$, E_1, and Q_{HP}. The calculation was performed for the initial portions of the hydrogen peroxide consumption curves in experiments carried out at various initial concentrations of hydrogen peroxide and at various temperatures. This approach makes it possible to level the influence of the resulting epichlorohydrin and side reactions. In the further processing of the kinetic data, these values were fixed and were used to determine the other unknown parameters. We calculated the preexponential factors $k_{0,2}$, $k_{0,3}$, and $k_{0,4}$; the

Table 1. Parameters of the Arrhenius equation

Reaction	$k_{0,i}$	E_i, J/mol
(I)	$(6.06 \pm 0.3) \times 10^6$ l s^{-1} g^{-1}	$(64.62 \pm 3.2) \times 10^3$
(II)	$(1.01 \pm 0.05) \times 10^4$ l^2 mol^{-1} s^{-1} g^{-1}	$(73.49 \pm 3.7) \times 10^3$
(III)	$(1.55 \pm 0.08) \times 10^4$ l^2 mol^{-1} s^{-1} g^{-1}	$(71.31 \pm 3.6) \times 10^3$
(IV)	$(2.93 \pm 0.15) \times 10$ l s^{-1} g^{-1}	$(50.92 \pm 2.5) \times 10^3$

Table 2. Parameters of the van't Hoff equation

Equation	$K_{0,HP} \times 10^3$	$K_{0,ECH} \times 10^2$	Q_{HP}	Q_{ECH}
	l/mol		kJ/mol	
(6)	2.25 ± 0.11	–	15.63 ± 0.78	–
(7)	–	1.26 ± 0.06	–	11.32 ± 0.57

values of $K_{0,ECH}$; the apparent activation energies E_2, E_3, and E_4; and the heat of adsorption of epichlorohydrin, Q_{ECH}.

The results of the calculations are presented in Tables 1 and 2.

The proposed kinetic model makes it possible to predict the composition of the reaction mixture at various temperatures, initial concentrations of the reactants, and hydrogen peroxide conversions. The calculated and experimental data on the current concentrations of the initial reactants and reaction products are shown in Fig. 1. As can be seen, they are in good agreement. Therefore, the system of differential equations (8)–(15) rather exactly describes the real process of liquid-phase allyl chloride epoxidation with an aqueous solution of hydrogen peroxide in the presence of the titanium-containing heterogeneous catalyst and can be used in engineering calculations for designing epoxidation reactors.

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