Regularities of glycidol synthesis by the liquid-phase epoxidation of allyl alcohol with hydrogen peroxide

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The main features of the liquid-phase epoxidation of allyl alcohol by hydrogen peroxide in an organic solvent in the presence of the titanium-containing zeolite in the batch reactor were studied. The influence of the amount of the solvent, ratio of reactants, and temperature on the rate of glycidol synthesis was revealed.

Key words: glycidol, allyl alcohol, hydrogen peroxide, epoxidation, titanium-containing zeolite TS-1.

Glycidol is a valuable intermediate in the production of synthetic glycerol and its derivatives, as well as surfactants, plasticizers, textile dyes, photochemicals, drugs, pesticides, a series of rubbers, varnishes, and thermoreactive resins and plastics.¹

Several methods of glycidol synthesis are known, in particular, dehydrohalogenation of glycerol monochlorohydrin,^{2,3} hydrolysis of epichlorohydrin, and the reaction of allyl alcohol with perbenzoic acid.^{4,5} The primary disadvantages for these methods are many by-products, high expenses of energy sources, and hardly utilized effluents. Ecological and economical requirements dictate the necessity to develop a novel, environmentally friendly, and alternative technology of glycidol synthesis.

One of the most promising methods for glycidol synthesis is the liquid-phase epoxidation of allyl alcohol by an ecologically safe oxidant, hydrogen peroxide, in the presence of synthetic titanium-containing zeolites.⁶ The main objective of this work was to investigate the influence of the amount of solvent, reaction temperature, and reactant ratio on the liquid-phase oxidation of allyl alcohol by an aqueous solution of hydrogen peroxide on titanium-containing zeolite.

Experimental

Methanol and glycidol (TU 6-09-14-2635-79) (both highpurity grade), 33-34% hydrogen peroxide (special-purity grade, TU 2611-069-05807977-2006), and allyl alcohol (TU 6-01-753-77) were used. The catalyst (titanium-containing zeolite) was prepared using a known procedure.⁷

The catalyst was synthesized in an autoclave at 170 °C for 40 h with stirring. The solid precipitate formed after cooling of

the suspension was washed with water to pH 7–8, dried for 12 h at 120 °C *in vacuo* (20 Torr), and calcined in a muffle furnace at 550 °C for 6 h.

The specific surface, total pore volume, and pore-size distribution were measured on a TriStar 3020 automated gas adsorption analyzer (Micromeritics). Using the data obtained, the following parameters of the porous catalyst structure were calculated in the automatic mode: specific surface 316.66 m² g⁻¹, and pore volume 0.182 cm³ g⁻¹ with most of the pores being in the range from 32 to 45 Å. The Ti content based on TiO₂ is 3.16 wt.%, and the Si/Ti molar ratio is 25.

The epoxidation of allyl alcohol was studied in a laboratory batch reactor equipped with an electromagnetic stirrer and a system of constant temperature maintenance. The calculated amounts of allyl alcohol, solvent, and catalyst were loaded into the reactor. Then the magnetic stirrer drive was connected to the thermostat, and the temperature of the reactor was maintained at a specified temperature for 10-15 min. Then the reactor was loaded with hydrogen peroxide, and the time of experiment onset was detected. Sampling for analysis was performed with a capillary at certain time intervals.

The composition of the reaction mixture was determined by gas chromatography on a Khromos GKh-1000 instrument equipped with a flame-ionization detector with a metallic column (2 m \times 3 mm) packed with a Chromaton-N-AW support with the Carbowax 6000 chromatographic phase in an amount of 15% of the support weight. Nitrogen was used as a carrier gas at flow rate of 50 mL min⁻¹. The temperatures of the evaporator and the thermostat of the columns were maintained at 180 and 130 °C, respectively. The temperature of the detector was 200 °C. The composition of the reaction mixture was determined by the absolute calibration method, and the amount of hydrogen peroxide was determined by iodometric titration. The procedures used were evaluated averaging results of 5–7 parallel experiments, and their root-mean-square error did not exceed 5%. The initial reaction rate of the process was calcu-

Published in Russian in Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 12, pp. 2647–2651, December, 2014. 1066-5285/14/6312-2647 © 2014 Springer Science+Business Media, Inc. lated based on the kinetic curves of hydrogen peroxide consumption from the slope of the initial reaction period. The yield of glycidol was calculated based on loaded hydrogen peroxide.

Results and Discussion

Allyl alcohol was epoxidized with an aqueous solution of hydrogen peroxide on the titanium-containing zeolite in the presence of an organic solvent. Allyl alcohol sufficiently well dissolves aqueous hydrogen peroxide and, hence, no solvent is required. Nevertheless, as shown by our studies, for the selective preparation of glycidol, it is reasonable to conduct epoxidation of allyl alcohol in the presence of the solvent (Fig. 1). The use of the solvent in allyl alcohol oxidation in an amount of 40% increases the selectivity of glycidol formation from 78.6% to 94.7%.

Alcohols, ketones, ethers, and other compounds can be used as solvents in this process.⁸ However, the best results were obtained with methanol. The highest epoxidation rates are observed and a high yield of glycidol is achieved in the presence of methanol and, therefore, all studies in this work were carried out in methanol.

The target product is formed *via* the reaction shown in Scheme 1.

Scheme 1

$$H_2C=CH-CH_2OH + H_2O_2 \longrightarrow$$

 $H_2C-CH-CH_2OH + H_2C$

Along with the target reaction, side reactions occur: hydration of glycidol leading to the formation of glycerol (Scheme 2) and the reaction of glycidol with methanol to form 3-methoxy-1,2-propanediol (Scheme 3).



Fig. 1. Influence of the methanol concentration (*C*) on the yield of glycidol (*X*) at 90% conversion of hydrogen peroxide (T = 40 °C, $C_{AA}^0 = 1.79 - 10.26 \text{ mol } \text{L}^{-1}$, $C_{AA}^0/C_{HP}^0 = 3$, catalyst content 3.04–17.46 g L⁻¹).

Scheme 2

 $\begin{array}{cccc} \mathsf{H}_2\mathsf{C}-\mathsf{C}\mathsf{H}-\mathsf{C}\mathsf{H}_2\mathsf{O}\mathsf{H} &+& \mathsf{H}_2\mathsf{O} &\longrightarrow& \mathsf{H}_2\mathsf{C}-\mathsf{C}\mathsf{H}-\mathsf{C}\mathsf{H}_2\mathsf{O}\mathsf{H}\\ \mathsf{O} && \mathsf{O}\mathsf{H} &\mathsf{O}\mathsf{H} \end{array}$

Scheme 3

$$H_2C-CH-CH_2OH + MeOH \longrightarrow H_2C-CH-CH_2OH$$

O MeO OH

Influence of the solvent amount. According to the existing concepts, a solvent molecule delivers allyl alcohol and hydrogen peroxide to the solid catalyst surface, where they interact. Moreover, it can then directly participate in the oxygen atom transfer to the C=C bond of allyl alcohol. The organic substrate is epoxidized due to the formation of an intermediate Ti-containing peroxo complex formed by the hydrogen peroxide molecule on the titanium site of the catalyst and stabilized by the solvent molecule.⁹ In addition, due to high exothermicity of the process $(\Delta H = -271.8 \text{ kJ mol}^{-1})$, the presence of the solvent makes it possible to efficiently remove the heat evolved during the reaction. Therefore, the solvent concentration in the reaction mixture along with the solvent nature exerts a substantial effect on the liquid-phase epoxidation.⁸

A series of experiments at different solvent concentrations and constant amounts of allyl alcohol and catalysts was carried out to study the influence of the solvent amount on epoxidation and to determine the real concentration of hydrogen peroxide in the reaction mixture needed for the reaction to occur. When synthesizing glycidol, the solvent content was varied from 20 to 80 wt.%. The chosen range of solvent concentrations provides a sufficiently high selectivity in allyl alcohol epoxidation.

Our studies showed that a decrease in the solvent content in the reaction mixture increased the initial rate of glycidol formation (Fig. 2). Under other equivalent conditions, a decrease in the solvent content in the reaction mixture results in an increase in the concentration of the reactants (allyl alcohol and hydrogen peroxide), which causes an increase in the initial rate of the process.

The change in the methanol concentration in the range from 40 to 85 wt.% exerts almost no effect on the yield of glycidol, which remains nearly unchanged and equal to 83.0—84.8% at 90% conversion of hydrogen peroxide.

Thus, it is reasonable to use methanol in an amount of 40–60 wt.% (10.89–15.79 mol L^{-1}) for the epoxidation of allyl alcohol. Under these conditions, fairly high reaction rate and yield of the target product are attained.

For the formation of glycidol, a decrease in the solvent concentration significantly decreases the selectivity of the process. When the content of the solvent was above the range indicated above, a considerable increase in the se-



Fig. 2. Initial rate of glycidol formation $(r_0/\text{mol } L^{-1} \text{ (g of catalyst)}^{-1})$ vs solvent concentration $(T = 40 \text{ °C}, C_{AA}^0 = 1.79 - 10.26 \text{ mol } L^{-1}, C_{AA}^0/C_{HP}^0 = 3).$

lectivity was not observed. Instead, the decrease in the epoxidation rate and complications at this step of target product isolation due to the strong dilution of the reaction mixture were recorded.

Influence of the initial ratio of allyl alcohol to hydrogen peroxide (C_{AA}^0/C_{HP}^0). It is reasonable to perform epoxidation involving hydrogen peroxide in an excess of allyl alcohol. The use of excess H_2O_2 is undesirable, since an industrial 30% aqueous solution of hydrogen peroxide was used in the work as a source of H_2O_2 . It can be expected that excess H_2O_2 significantly increases the water concentration in the reaction mixture, which would exert a negative effect on the selectivity of the process. In addition, the subsequent isolation and recirculation of allyl alcohol are not so less difficult as the return of unreacted hydrogen peroxide to the reaction mixture. Thus, the application of an excess of allyl acohol with respect to H_2O_2 is most reasonable.

To evaluate the influence of the C_{AA}^0/C_{HP}^0 ratio on the main regularities of glycidol formation, we carried out a series of experiments at different initial ratios of the reactants. The C_{AA}^0/C_{HP}^0 molar ratio was varied in the range (1–6) : 1. The change in C_{AA}^0/C_{HP}^0 affects the initial rate of the process (Fig. 3).

When the excessive amounts of allyl alcohol over hydrogen peroxide were increased, the initial rate of glycidol formation decreased. At the same time, the change in C_{AA}^0/C_{HP}^0 significantly affects the yield of glycidol (Fig. 4). It is seen from Fig. 4 that the yield of glycidol increases considerably at the same 80% conversion of hydrogen peroxide and with an increase in C_{AA}^0/C_{HP}^0 from 1 to 3, whereas at higher ratios an increase in the yield of the target product is insignificant.

The established dependence is explained by the fact that a decrease in C_{AA}^0/C_{HP}^0 increases the concentration of hydrogen peroxide in the reaction mixture. As a result, a longer residence time of H_2O_2 in the reaction mixture needed to achieve the complete conversion promotes un-



Fig. 3. Initial rate of glycidol formation $(r_0/\text{mol } L^{-1} \text{ (g of catal-yst)}^{-1})$ vs C^0_{AA}/C^0_{HP} ratio $(T = 40 \text{ °C}, C^0_{AA} = 3.46 \text{ mol } L^{-1})$.



Fig. 4. Yield of glycidol (*X*) vs C_{AA}^0/C_{HP}^0 ratio at 80% conversion of hydrogen peroxide (T = 40 °C, $C_{AA}^0 = 3.46 \text{ mol } \text{L}^{-1}$, catalyst content 5.08 g L⁻¹).

desirable processes of consecutive transformations of the formed glycidol.

A large excess of allyl alcohol should be used to enhance selectivity. However, this results in a decrease in the epoxidation rate and, as a consequence, a decrease in productivity. Therefore, when determining the optimum C_{AA}^0/C_{HP}^0 ratio, both the selectivity and initial rate of the process should be taken into account. A high yield of glycidol and a sufficiently high rate are attained at the ratio $C_{AA}^0/C_{HP}^0 = 2-4$.

Temperature effect. A series of experiments was carried out in the temperature range 30-60 °C to evaluate the temperature effect on the epoxidation process. Figure 5 shows the temperature dependence of the initial epoxidation rate, which is described by a straight line in the coordinates of the Arrhenius equation (Fig. 6).

The activation energy of the target process is 63.1 kJ mol^{-1} .

An increase in the temperature of allyl alcohol epoxidation intensifies both the target reaction of glycidol for-



Fig. 5. Initial rate of glycidol formation $(r_0/\text{mol } L^{-1} \text{ (g of catalyst)}^{-1})$ vs temperature $(C_{AA}^0 = 5.73 \text{ mol } L^{-1}, C_{AA}^0/C_{HP}^0 = 3)$.



Fig. 6. Logarithm of the initial rate of glycidol formation vs reciprocal temperature ($C_{AA}^0 = 5.73 \text{ mol } \text{L}^{-1}$, $C_{AA}^0/C_{HP}^0 = 3$).

mation and also a series of side transformations, which is confirmed by a decrease in the yield of the target product (Fig. 7).

Thus, the final choice of the optimum temperature of glycidol synthesis is determined by the rate of glycidol formation and selectivity of the process and demand of the formed by-products. It is most reasonable to carry out epoxidation at 40-50 °C.

Influence of the catalyst amount. A series of experiments in which the catalyst content was varied from 0 to 30 g L^{-1} was carried out to evaluate the influence of the catalyst amount. The amount of the catalyst exerts a substantial effect on the initial rate of the process (Fig. 8).

The dependence of the initial epoxidation rate on the catalyst content is linear. This confirms the assumption that the reaction proceeds in the kinetic region. A change



Fig. 7. Yield of glycidol (*X*) vs temperature at 90% conversion of hydrogen peroxide ($C_{AA}^0 = 5.73 \text{ mol } \text{L}^{-1}$, $C_{AA}^0/C_{HP}^0 = 3$, catalyst content 5.01 g L⁻¹).



Fig. 8. Initial rate of glycidol formation $(r_0/\text{mol } L^{-1} s^{-1})$ vs catalyst content $(C/g L^{-1})$ in the reaction mixture $(C^0_{AA} = 5.08 \text{ mol } L^{-1}, C^0_{HP} = 1.69 \text{ mol } L^{-1}, T = 40 \text{ °C}).$

in the catalyst content exerts no effect on the yield of glycidol, which remains nearly unchanged. Thus, for epoxidation in the batch reactor, the catalyst amount primarily affects the rate of the process. Therefore, the catalyst content should mainly be determined by the possibility of removal of the evolved heat of the chemical reactions.

Thus, the epoxidation of allyl alcohol in a medium of the organic solvent (methanol) occurs especially efficiently at a solvent content of 40 wt.%, initial ratio $C_{AA}^0/C_{HP}^0 = 3$, and temperature 40 °C. The experiments under the conditions close to optimum make it possible to obtain glycidol in a yield of 91.5% at the 98.4% conversion of hydrogen peroxide. The content of glycidol, 3-methoxy-1,2-propanediol, and glycerol in the reaction mixture is 1.78, 0.041, and 0.016 mol L⁻¹, respectively.

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