

Technological Parameters of the Epoxidation of Allyl Alcohol with Hydrogen Peroxide over TS-1 and TS-2 Catalysts

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The course of epoxidation of allyl alcohol with a 30 % hydrogen peroxide over the TS-1 and TS-2 catalysts has been investigated. Two types of solvents, aprotic (acetone) and protic (methanol), were used in the studies. The optimum conditions were established for the epoxidation of allyl alcohol in the presence of acetone and methanol using the TS-1 catalyst. The studies with TS-2 catalyst were performed under the same reaction conditions. The effect of the following process parameters was studied: temperature (20–120 °C), the mole ratio AA—H₂O₂ ((1–10):1), solvent content (10–80 mass %), catalyst content (0.1–2.0 mass %), and reaction time (1–8 h). It was found that the highest yield of glycidol (64.4 mole % over TS-1, 88.3 mole % over TS-2) was achieved in the presence of methanol independently of the catalyst type. The optimum parameters were the same: temperature 20 °C, the mole ratio of AA—H₂O₂ = 5, methanol content 80 mass %, reaction time 1 h, but the catalyst content in the reaction mixture was different and amounted to 1 mass % for TS-1 and 0.1 mass % for TS-2.

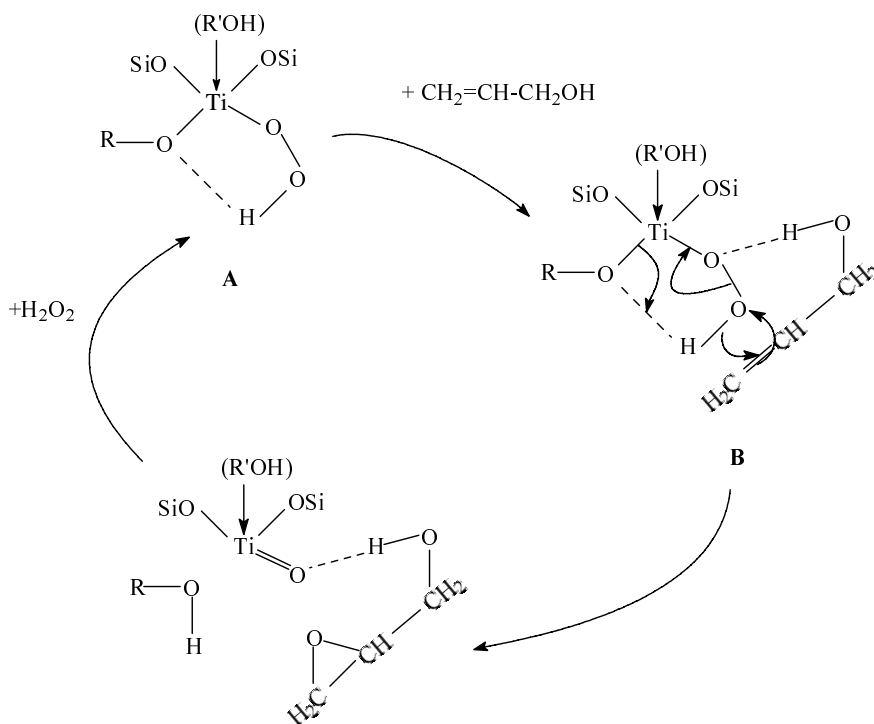
Glycidol is a bifunctional compound with many interesting and important applications. It belongs to a group of the major semiproducts mostly used in the synthesis of the surface-active agents. These agents are the components of the cosmetic formulations for moistening and cleaning of skin (cosmetics neutral for skin), shampoo, bath fluids, toothpaste, mouthwash, detergents for washing (including the detergents for washing in cold water), and disinfectants [1]. The surface-active agents are also used as food emulgators in the production of margarine, ice-creams, and vegetable butters [1, 2]. Other groups of the applications of glycidol derivatives include dispersing agents, plasticizers for resins and rubber [3], and the detergents in petroleum industry [4, 5].

Glycidol is most frequently obtained from the following compounds: epichlorohydrin, 1-chloropropan-2,3-diol, allyl alcohol or acrolein [1]. Allyl alcohol can be epoxidized to glycidol by percarboxylic acids, organic hydroperoxides, and hydrogen peroxide. Several papers reporting on the epoxidation of allyl alcohol with a 30 % hydrogen peroxide over the titanium silicalite catalysts (TS-1, TS-2) and aluminosilicate Ti-BETA have been recently published [6–11]. Glycidol can be prepared by this method under the mild conditions (low temperature and pressure) with a high selectivity \approx 90 %. According to the U.S. patent specification glycerol is produced with a high yield in the reaction of allyl alcohol and 30 % H₂O₂ [6]. The process was carried out at ambient temperature for 12 h at the mole ratio of allyl alcohol to H₂O₂ equal to 1

in the presence of an 18 mass % *t*-butyl alcohol as the solvent and with 2.3 mass % of the TS-1 catalyst.

Hutchings et al. [7, 8] have obtained a maximum (100 mole %) selectivity of transformation to glycidol in relation to consumed allyl alcohol, however, the conversion of allyl alcohol was low (maximum 5 mole %). The reaction was carried out in the medium of methyl and *t*-butyl alcohol. In the case of higher conversion of allyl alcohol the products of the reaction of glycidol with alcohol (solvent) and water were formed. The product composition was also affected by the method of catalyst synthesis, its acidity, the nature of the solvent, and temperature.

Clerici and Ingallina [9] reported allyl alcohol as one of the reagents among several unsaturated compounds used for the epoxidation. These studies demonstrated the differences in the rate of epoxidation of unsaturated compounds with various structures and enabled to establish the mechanism of olefins epoxidation over the titanium silicalite catalyst. Allyl alcohol undergoes relatively hardly the epoxidation because it contains the —OH group in the position α to the double bond. The —OH group as an electrophilic substituent in this position causes a decrease of the electron density of this bond. This, in turn, decreases the reactivity of allyl alcohol in the reaction with an electrophilic reagent (*e.g.* H₂O₂). The recent views [9, 10] concerning the mechanism of allyl alcohol epoxidation with hydrogen peroxide over the titanium silicalite catalysts (TS-1, TS-2) have assumed the formation of the active adduct A (Scheme 1).



Scheme 1. Mechanism of allyl alcohol epoxidation over the titanium silicate catalyst.

This is a five-membered hydroperoxide adduct, in which both the H₂O₂ molecule and alcohol molecule (protic solvent) are associated with the active centre (the Ti⁴⁺ ion). In this adduct there is also the hydrogen bond between oxygen of the alcohol molecule and hydrogen of the hydroperoxide group. ROH is an additional solvent molecule or the water molecule, which is coordinatively bonded to the active centre. Adam *et al.* [10] have proposed the mechanism of allyl alcohol epoxidation over the titanium silicalite catalysts (electrophilic oxidation) (Scheme 1).

In the structure B the allyl alcohol molecule is associated with the active adduct A through the hydrogen bond formed between the —OH group of allyl alcohol and the oxygen atom located close to the Ti atom in the active adduct A. This hydrogen bond stabilized the entire system. The presented mechanism reveals that the nature of the solvent plays a very important role in the course of epoxidation. Hence it would be interesting to compare the course of epoxidation in the protic and aprotic solvent and to establish the optimum parameters for the synthesis. In this work acetone and methanol were used. The determination of the optimum parameters for the synthesis also enables the investigation of the influence of operating conditions such as: temperature, mole ratio of allyl alcohol to hydrogen peroxide ($n(\text{AA})/n(\text{H}_2\text{O}_2)$), catalyst content, and process running time on the synthesis run. This concerns each of the catalyst (TS-1 and TS-2) and the solvent (methanol and acetone).

EXPERIMENTAL

The TS-1 catalyst was prepared by the method described by Thangaraj *et al.* [12], whereas TS-2 was obtained according to the method described by Reddy *et al.* [13]. Characterization of the catalysts was performed by different conventional techniques (XRF, XRD, IR, UV VIS, and SEM). The catalyst composition (mainly the content of Ti) was determined by X-ray fluorescence (XRF). The TS-1 catalyst contained 2.1 mass % of TiO₂, whereas TS-2 1.8 mass % of TiO₂. The crystalline structure of TS-1 and TS-2 was confirmed by the XRD method. The IR and UV VIS spectra presented the absorption bands ($\tilde{\nu} = 960 \text{ cm}^{-1}$ and $\lambda = 220 \text{ nm}$) confirming the incorporation of titanium into the crystal structure of silica. The size of crystallites for both catalysts amounted to 0.3 μm (hexagonal lumps).

Method of Epoxidation

The epoxidation was carried out in a stainless steel autoclave equipped with PTFE insert of 7 cm³ capacity, which was charged with allyl alcohol (AA), solvent (methanol or acetone), catalyst (TS-1 or TS-2), and 30 % hydrogen peroxide. The autoclave was fixed in a shaker holder and immersed in the oil bath the temperature of which was controlled by a thermostat. After the reaction was completed, a post-reaction mixture was weighed, analyzed, and balanced. The concentration of glycidol and diallyl ether was determined

by means of gas chromatography. Glycerol was determined by means of periodate titration [14], whereas the consumption of hydrogen peroxide was measured by iodometric titration [15]. The epoxidation results were described with the aid of the following magnitudes

$$\text{Conversion of substrates (allyl alcohol, H}_2\text{O}_2) = \frac{\text{Amount of substance of substrate consumed}}{\text{Initial amount of substrate substance}} \cdot 100 \% \\ C_{AA} \text{ or } C_{\text{H}_2\text{O}_2}$$

$$\text{Selectivity to organic compounds in relation to consumed H}_2\text{O}_2 = \frac{\text{Amount of substance of product}}{\text{Amount of substance of H}_2\text{O}_2 \text{ consumed}} \cdot 100 \% \\ S_{\text{org}/\text{H}_2\text{O}_2}$$

$$\text{Selectivity to given product in relation to consumed allyl alcohol} = \frac{\text{Amount of substance of product}}{\text{Amount of substance of allyl alcohol consumed}} \cdot 100 \% \\ S_{\text{product}/AA}$$

$$\text{Product yield in relation to allyl alcohol} = \frac{\text{Amount of substance of product}}{\text{Amount of substance of allyl alcohol induced into reactor}} \cdot 100 \% \\ Y_{\text{product}/AA}$$

The basic conditions of the studies (for both TS-1 and TS-2) were as follows: the mole ratio AA—H₂O₂ = 3, solvent content 40 mass %, the catalyst content 1 mass %, reaction time 2 h.

RESULTS AND DISCUSSION

The effect of temperature, the AA—H₂O₂ mole ratio, catalyst content, reaction time, content and the nature of the solvent (aprotic – acetone and protic – methanol) on the epoxidation of allyl alcohol with 30% H₂O₂ over the TS-1 and TS-2 catalysts was investigated. The process was evaluated in terms of the yield of glycidol and glycerol in relation to allyl alcohol introduced into the reactor ($Y_{\text{gl}/AA}$ and $Y_{\text{glyc}/AA}$), the selectivities of transformation to glycidol in relation to consumed allyl alcohol and H₂O₂ ($S_{\text{gl}/AA}$, $S_{\text{gl}/\text{H}_2\text{O}_2}$), allyl alcohol conversion (C_{AA}), hydrogen peroxide conversion ($C_{\text{H}_2\text{O}_2}$). The selectivity of transformation to the sum of organic compounds (glycidol, glycerol, diallyl ether) in relation to consumed hydrogen peroxide ($S_{\text{org}/\text{H}_2\text{O}_2}$) was also investigated. The yield of glycidol, the selectivity of transformation to glycidol, the conversion of allyl alcohol and H₂O₂ were taken into account to assess the value of examined parameter as optimum.

The studies of the influence of temperature on the course of allyl alcohol epoxidation in acetone over TS-1 catalyst were carried out in the range from 20—120 °C. The AA—H₂O₂ mole ratio amounted to 3, the content of acetone was 40 mass %, the content of TS-1 1 mass %, the reaction time 2 h. The highest yield $Y_{\text{gl}/AA} = 14.9$ mole % and the selectivity of transformation to glycidol in relation to allyl alcohol $S_{\text{gl}/AA} = 79.5$ mole % was achieved at 20 °C. As temperature was increased, the glycidol yield decreased to $Y_{\text{gl}/AA} = 10.1$ mole % at 120 °C. The yield of glycerol also decreases with increasing temperature from $Y_{\text{glyc}/AA} = 5.4$ mole % (at 20 °C) to $Y_{\text{glyc}/AA} = 1.5$ mole % (at 120 °C). The highest conversion of allyl alcohol $C_{AA} = 21.7$ mole % was also achieved at 20 °C. The hydrogen peroxide conversion amounted to $C_{\text{H}_2\text{O}_2} = 100$ mole % over the considered range of temperatures as well as within the studied areas of variations of the remaining process parameters. This is associated with the fact that H₂O₂ undergoes readily the decomposition into H₂O and O₂ under the conditions studied. The selectivity of transformation to diallyl ether increases from 6.6 to 11.1 mole % during the increase of temperature over the area studied. The highest selectivity of transformation to the sum of organic compounds in relation to consumed H₂O₂ $S_{\text{org}/\text{H}_2\text{O}_2} = 56.9$ mole % was also achieved at 20 °C. The yield and the selectivities of transformation to glycidol in relation to allyl alcohol and H₂O₂ are also the highest at a temperature of 20 °C.

The yield of glycidol decreases with increasing the mole ratio AA—H₂O₂ from $Y_{\text{gl}/AA} = 23.6$ mole % ($n(\text{AA})/n(\text{H}_2\text{O}_2) = 1:1$) to $Y_{\text{gl}/AA} = 7.1$ mole % ($n(\text{AA})/n(\text{H}_2\text{O}_2) = 10:1$). The selectivity of transformation to glycidol within the range considered increases from $S_{\text{gl}/AA} = 59.5$ mole % to $S_{\text{gl}/AA} = 71.1$ mole %. The allyl alcohol conversion is the highest at the mole ratio AA—H₂O₂ = 1:1 ($C_{AA} = 39.6$ mole %). The high selectivity of transformation to the sum of organic compounds and glycidol in relation to consumed H₂O₂ was achieved above the mole ratio AA—H₂O₂ = 4:1. Hence, an excess of allyl alcohol enables a more effective utilization of H₂O₂ decreasing the rate of its decomposition. Taking into consideration the discussed parameters describing the process the mole ratio AA—H₂O₂ = 5:1 was assessed as optimum at temperature of 20 °C. The remaining parameters of the synthesis were the same as the basic parameters: the content of TS-1 1 mass %, time 2 h.

An increase of acetone content enhances the glycidol yield ($Y_{\text{gl}/AA}$) and the selectivity of transformation to glycidol ($S_{\text{gl}/AA}$). A dilution with acetone impedes the interaction of the molecules of formed glycidol with water. As a consequence of this, the hydrolysis of glycidol to glycerol proceeds less intensively. The course of variation of the selectivity of transformation to the particular products as a function of the acetone content is shown in Fig. 1. The selectivity of trans-

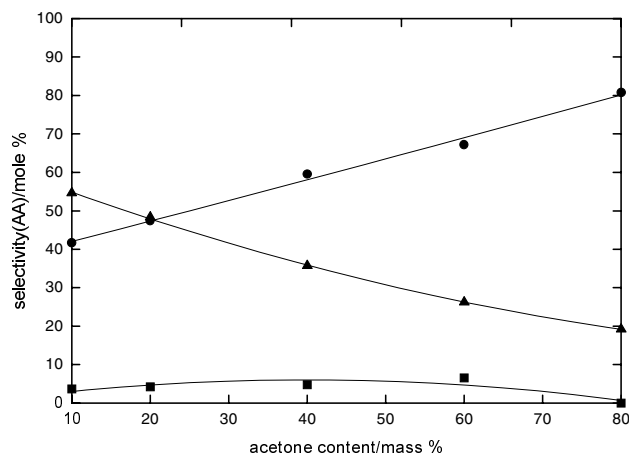


Fig. 1. Variation of selectivity of transformation to epoxidation products in relation to consumed AA as a function of acetone content over TS-1 catalyst in the acetone medium (temperature 20 °C, the mole ratio AA—H₂O₂ = 5, TS-1 content 1 mass %, reaction time 2 h). ● Glycidol, ▲ glycerol, ■ diallyl ether.

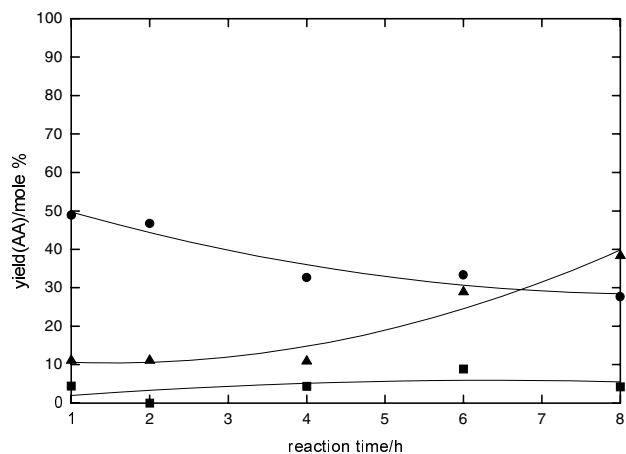


Fig. 2. Yields of products in relation to introduced AA as a function of reaction time using TS-1 catalyst in the acetone medium (temperature 20 °C, the mole ratio AA—H₂O₂ = 5, acetone content 80 mass %, TS-1 content 1 mass %). ● Glycidol, ▲ glycerol, ■ diallyl ether.

formation to the sum of organic compounds over the area examined is constant $S_{\text{org}/\text{H}_2\text{O}_2} = 55$ mole %. The highest content of acetone equal to 80 mass % influences most advantageously the transformation in the direction of glycidol.

The effect of the TS-1 content in the reaction mixture, at the acetone content of 80 mass %, the mole ratio AA—H₂O₂ = 5:1, the reaction time of 2 h, at 20 °C was investigated. The maximum glycidol yield over the examined range of catalyst content (0.1—2.0 mass %) was reached for the content of 1.0 mass % ($Y_{\text{gl}/\text{AA}} = 46.7$ mole %). For this catalyst content the allyl alcohol conversion amounted to $C_{\text{AA}} = 57.8$ mole %, and the selectivity of transformation to the sum of organic compounds $S_{\text{org}/\text{H}_2\text{O}_2} = 55.3$ mole %.

The effect of reaction time over a period of 1—8 h on the yield of glycidol was studied at temperature of 20 °C, the mole ratio AA—H₂O₂ = 5, acetone content 80 mass %, and the TS-1 catalyst content of 1 mass %. The highest glycidol yield was obtained after 1—2 h of the process running $Y_{\text{gl}/\text{AA}} = 48.9$ mole %. As the reaction time was prolonged, the rate of hydrolysis of glycidol to glycerol increased. A decrease of the glycidol yield $Y_{\text{gl}/\text{AA}}$ and the selectivity of transformation to glycidol $S_{\text{gl}/\text{AA}}$ is accompanied by the increase of the glycerol yield $Y_{\text{glyc}/\text{AA}}$ and the selectivity of transformation to glycerol $S_{\text{glyc}/\text{AA}}$ (Fig. 2). The longer reaction time also decreases the yield of glycidol $Y_{\text{gl}/\text{H}_2\text{O}_2}$ and the selectivity of the transformation to glycidol $S_{\text{gl}/\text{H}_2\text{O}_2}$ in relation to introduced and consumed H₂O₂. As the optimum time for the glycidol synthesis in this process should be 1 h.

From the studies of the influence of temperature, the AA—H₂O₂ mole ratio, the content of acetone and TS-1 catalyst, and time on the epoxidation of allyl alcohol with 30 % H₂O₂ it results that the optimum

parameters of the glycidol synthesis are as follows: temperature 20 °C, the mole ratio AA—H₂O₂ = 5, the content of acetone 80 mass % and of TS-1 1 mass %, and the reaction time 1 h. The yields of glycidol in relation to allyl alcohol $Y_{\text{gl}/\text{AA}} = 48.9$ mole % and in relation to H₂O₂ $Y_{\text{gl}/\text{H}_2\text{O}_2} = 46.8$ mole % are the highest under these conditions. The selectivities corresponding to them $S_{\text{gl}/\text{AA}} = 75.8$ mole %, $S_{\text{gl}/\text{H}_2\text{O}_2} = 48.8$ mole % are also the highest. The yield of diallyl ether in relation to allyl alcohol amounts 4.5 mole %. The allyl alcohol conversion is $C_{\text{AA}} = 64.4$ mole %, and the selectivity of transformation to the sum of organic compounds $S_{\text{org}/\text{H}_2\text{O}_2} = 57.8$ mole %. The process proceeds with the complete conversion of H₂O₂, $C_{\text{H}_2\text{O}_2} = 100$ mole %.

The epoxidation of allyl alcohol in methanol over the TS-1 catalyst was carried out under the same conditions as in the experiments with acetone. The course of variations of the selectivities of transformation to glycidol and glycerol in relation to consumed allyl alcohol as a function of temperature is shown in Fig. 3. The highest yield of glycidol and the highest selectivities of transformation to glycidol in relation to both allyl alcohol and H₂O₂ were achieved at temperature of 20 °C. At this temperature the allyl alcohol conversion $C_{\text{AA}} = 21.7$ mole % and the selectivity of transformation to the sum of organic compounds $S_{\text{org}/\text{H}_2\text{O}_2} = 63.8$ mole % were also the highest.

The studies concerning the influence of the AA—H₂O₂ mole ratio (temperature 20 °C, methanol content 40 mass %, the TS-1 catalyst content 1 mass %, reaction time 2 h) on the selectivity demonstrated that as the mole ratio is enhanced the selectivity of transformation to glycidol $S_{\text{gl}/\text{AA}}$ increases. A significant decrease of the allyl alcohol conversion C_{AA} results in a simultaneous decrease of the yield of glycidol from

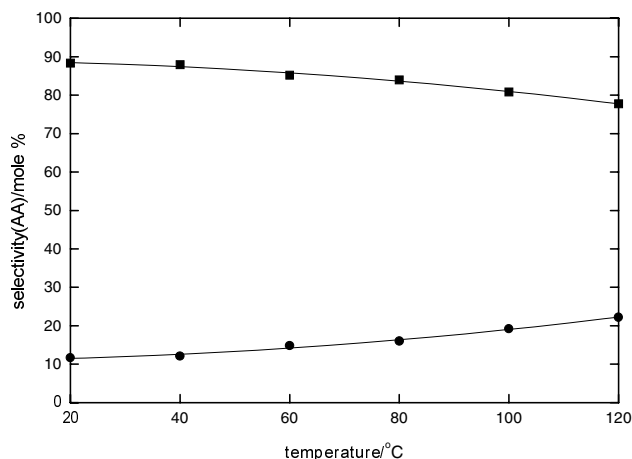


Fig. 3. Selectivity of transformation to glycidol (■) and to glycerol (●) in relation to consumed AA as a function of temperature. TS-1 catalyst, methanol as solvent (the mole ratio AA—H₂O₂ = 3, methanol content 40 mass %, TS-1 content 1 mass %, reaction time 2 h).

$Y_{\text{gl/AA}} = 22.6$ mole % ($n(\text{AA})/n(\text{H}_2\text{O}_2) = 1:1$) to $Y_{\text{gl/AA}} = 5.4$ mole % ($n(\text{AA})/n(\text{H}_2\text{O}_2) = 10:1$). The highest allyl alcohol conversion $C_{\text{AA}} = 31.1$ mole % is achieved at the mole ratio AA—H₂O₂ = 1. On the contrary, the selectivity of transformation to glycidol and to the sum of organic compounds (glycidol + glycerol) in relation to consumed H₂O₂ increases during the increase of the AA—H₂O₂ mole ratio. However, the advantages for the glycidol synthesis arising from this fact do not justify the enhancement of the AA—H₂O₂ mole ratio above 5:1. The influence of the methanol content on the course of allyl alcohol epoxidation was investigated at the mole ratio AA—H₂O₂ = 5, temperature 20 °C, since these parameters are the most advantageous from the point of view of the synthesis of glycidol. The catalyst content amounted to 1 mass %, the reaction time was 2 h. An increase of methanol content increases the glycidol yield and this yield amounts to $Y_{\text{gl/AA}} = 58.7$ mole % at the content of 80 mass %, whereas the yield of glycerol decreases to $Y_{\text{glyc/AA}} = 6.3$ mole %. A similar trend was presented in the case of the selectivities $S_{\text{gl/AA}}$ and $S_{\text{glyc/AA}}$. The allyl alcohol conversion ($C_{\text{AA}} = 65.2$ mole %) and the selectivity of transformation to the sum of organic compounds $S_{\text{org/H}_2\text{O}_2} = 66.7$ mole % are also the highest for the methanol content of 80 mass %.

The effect of the TS-1 catalyst content on the allyl alcohol epoxidation was investigated at temperature 20 °C, the mole ratio AA—H₂O₂ = 5:1, the methanol content of 80 mass %, for the reaction time of 2 h. The maximum yield of glycidol was reached at the TS-1 content of 1 mass % ($Y_{\text{gl/AA}} = 58.7$ mole %). The conversion of allyl alcohol and the selectivity of transformation to the sum of organic compounds were also the highest ($C_{\text{AA}} = 65.2$ mole % and $S_{\text{org/H}_2\text{O}_2}$

= 66.7 mole %) under these conditions.

The influence of the reaction time on the epoxidation of allyl alcohol was studied under the previously mentioned parameters and the catalyst content of 1 mass %. The highest yield of glycidol ($Y_{\text{gl/AA}} = 64.4$ mole %) and the highest selectivity of transformation to glycidol ($S_{\text{gl/AA}} = 93.5$ mole %) were achieved after 1 h. Under these conditions the conversion of allyl alcohol amounts to $C_{\text{AA}} = 68.9$ mole %. The selectivity of transformation to the sum: glycerol + glycidol in relation to consumed H₂O₂ ($S_{\text{org/H}_2\text{O}_2}$) is the same.

The studies of epoxidation on TS-1 catalyst in the methanol medium demonstrated that the most advantageous parameters of the glycidol synthesis are the same as in the case of acetone. The maximum yield of glycidol amounts to $Y_{\text{gl/AA}} = 64.4$ mole %, simultaneously with a high conversion of allyl alcohol and the selectivity of transformation to the sum of organic compounds $C_{\text{AA}} = S_{\text{org/H}_2\text{O}_2} = 68.9$ mole %. However, the yield of glycidol is higher in the presence of methanol than that in the presence of acetone. Diallyl ether is not formed in the medium of methanol.

At the epoxidation of allyl alcohol over TS-2 catalyst in the acetone medium the increase of the temperature in the range 20—120 °C results in a small decrease of the glycidol yield from $Y_{\text{gl/AA}} = 15.5$ mole % to $Y_{\text{gl/AA}} = 12.7$ mole % and of the yield of glycerol from 4.0 to 2.9 mole %. The selectivity of transformation to glycidol is high at 20 °C and amounts $S_{\text{gl/AA}} = 80.8$ mole %. It decreases to $S_{\text{gl/AA}} = 74.5$ mole % with increasing temperature to 120 °C. The temperature of 20 °C is the most advantageous from the point of view of the glycidol synthesis. At this temperature the highest values of the allyl alcohol conversion can be achieved, $C_{\text{AA}} = 20.5$ mole %, the selectivities of transformation to glycidol in relation to H₂O₂ and to the sum of organic compounds (glycidol, glycerol, diallyl ether) amounted to $S_{\text{gl/H}_2\text{O}_2} = 46.7$ mole % and $S_{\text{org/H}_2\text{O}_2} = 56.4$ mole %, respectively.

The effect of the AA—H₂O₂ mole ratio was studied at 20 °C under the initial parameters used previously (acetone content 40 mass %, the TS-2 content 1 mass %, reaction time 2 h). Based on these studies it was found that the optimum mole ratio of reagents amounts to 5:1. At this ratio the glycidol yield $Y_{\text{gl/AA}} = 10.1$ mole % and the allyl alcohol conversion $C_{\text{AA}} = 19.2$ mole % are slightly lower than those at lower mole ratios. This results from the use of excess of AA in relation to H₂O₂ and the accepted method of calculations. The selectivity of transformation to diallyl ether over the studied range ($n(\text{AA})/n(\text{H}_2\text{O}_2) = 1—10$) remains constant $S_{\text{DAE/AA}} = 5.6$ mole % (Fig. 4). However, the selectivity of transformation to glycidol and to the sum of organic compounds $S_{\text{gl/H}_2\text{O}_2}$ and $S_{\text{org/H}_2\text{O}_2}$ in relation to consumed H₂O₂ increases with the increase of the AA—H₂O₂ mole ratio.

The studies of the effect of acetone content were carried out at 20 °C, the mole ratio AA—H₂O₂ = 5:1,

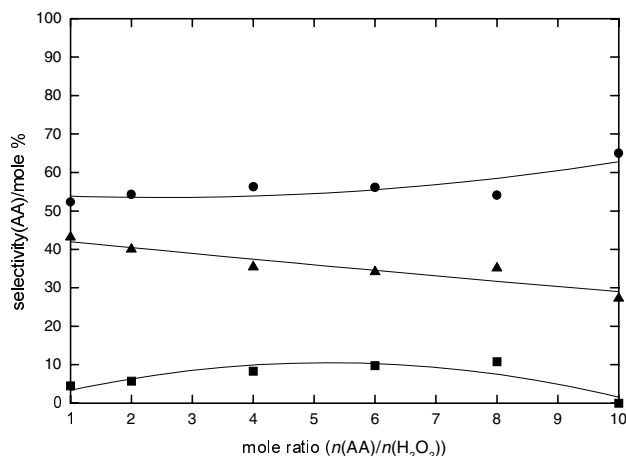


Fig. 4. Selectivity of transformation to glycidol (●), glycerol (▲), and diallyl ether (■) in relation to consumed AA as a function of the AA—H₂O₂ mole ratio. TS-2 catalyst, acetone as solvent (temperature 20 °C, acetone content 40 mass %, TS-2 content 1 mass %, reaction time 2 h).

the TS-1 catalyst content 1 mass %, for 2 h. The yields of glycidol $Y_{gl/AA} = 18.0$ mole % and the selectivities of transformation to glycidol $S_{gl/AA} = 49.0$ mole % were obtained over the range of acetone content of 10–60 mass %. At the acetone content of 10–20 mass % the highest selectivities and yields of glycidol in relation to H₂O₂ were obtained. The highest conversion of allyl alcohol $C_{AA} = 54.9$ mole % was achieved at the acetone content of 10 mass %. This concentration should be accepted as the most advantageous in the glycidol synthesis. An increase of this content up to 80 mass % causes that glycerol becomes the major reaction product.

The effect of the TS-2 catalyst content in the 0.1–2.0 mass % range on the allyl alcohol epoxidation in acetone was studied at 20 °C, the mole ratio AA—H₂O₂ = 5, acetone content of 10 mass % after 2 h. A high yield and the selectivity of transformation to glycidol were obtained in relation both to H₂O₂ and allyl alcohol over the entire range of concentrations considered. High selectivities and yields of glycidol can be achieved at the catalyst content equal to 0.1 mass %.

The effect of epoxidation time of allyl alcohol on the synthesis of glycidol was studied under the most advantageous parameters previously determined. The maximum selectivity of transformation to glycidol $S_{gl/AA} = 63.2$ mole % and the maximum yield of glycidol $Y_{gl/AA} = 47.1$ mole % were achieved after 1 h. The allyl alcohol conversion $C_{AA} = 74.4$ mole %, the selectivities of transformation to glycidol $S_{gl/H_2O_2} = 50.1$ mole %, and the sum of organic compounds $S_{org/H_2O_2} = 76.8$ mole % are the highest under these conditions.

The epoxidation of allyl alcohol to glycidol using a 30 % hydrogen peroxide over the TS-2 catalyst in acetone proceeds most advantageously under the following conditions: temperature 20 °C, the mole ratio

AA—H₂O₂ = 5, acetone content of 10 mass %, the TS-2 catalyst content of 0.1 mass %, and the reaction time of 1 h.

The starting conditions of the epoxidation of allyl alcohol over TS-2 catalyst in the methanol medium were the same as previously. The highest yields and the selectivities were achieved at temperature of 20 °C in this version of the process. The maximum selectivities of transformation to glycidol amount to $S_{gl/AA} = 71.2$ mole %, $S_{gl/H_2O_2} = 46.7$ mole %, the glycidol yield $Y_{gl/AA} = 15.1$ mole %, $Y_{gl/H_2O_2} = 45.7$ mole %. An increase of the temperature decreases these values.

The effect of the AA—H₂O₂ mole ratio was investigated at 20 °C, whereas the remaining parameters were the same as in the previous experiments. Enhancement of the AA—H₂O₂ mole ratio causes the increase of the selectivities of transformation to glycidol in relation to both allyl alcohol and H₂O₂. The yield of glycidol in relation to allyl alcohol decreases from $Y_{gl/AA} = 23.4$ mole % at AA—H₂O₂ = 1:1 to $Y_{gl/AA} = 0.3$ mole % at $n(AA)/n(H_2O_2) = 10:1$. This is a consequence of increased excess of allyl alcohol. However, this excess results in a two-fold increase of the selectivity and yield of glycidol in relation to H₂O₂ over the variation range of $n(AA)/n(H_2O_2) = (1–10):1$. The consequence of this excess is also a decrease of allyl alcohol conversion. Relatively high selectivities of transformations were achieved in the range of $n(AA)/n(H_2O_2) = (4–7):1$. The mole ratio of substrates for the glycidol synthesis amounting to AA—H₂O₂ = 5:1 should be considered as an optimum.

In spite of the variations of the concentration of protic solvent the conversion of H₂O₂ amounts to 100 mole %. An increase of methanol concentration causes the increase of the magnitudes describing the glycidol synthesis: $S_{gl/AA}$, S_{gl/H_2O_2} , $Y_{gl/AA}$, and Y_{gl/H_2O_2} . The content of methanol amounting 80 mass % should be accepted as optimum. The course of variation of the selectivities of transformation to glycidol and glycerol in relation to AA and H₂O₂ as a function of methanol content is shown in Fig. 5.

An increase of the TS-2 catalyst content in the 1.0–2.0 mass % range causes a decrease of the selectivity of transformation to glycidol ($S_{gl/AA}$) by about 8 mole %. This decline is lower in the content range of 0.1–1.0 mass %. The selectivity of transformation to glycerol simultaneously increases almost symmetrically. This can be attributed to the fact that the process catalyst accelerates both the epoxidation of allyl alcohol and the hydration of glycidol. The most appropriate content of the catalyst in this process amounts to 0.1 mass %.

The highest selectivities of transformation to glycidol were obtained after the reaction time of 1–2 h: $S_{gl/AA} = 90.4$ mole %, $S_{gl/H_2O_2} = 76.2$ mole %. The allyl alcohol conversion amounts to $C_{AA} = 97.7$ mole %. Prolongation of the reaction time decreases all the results of the glycidol synthesis due to its transforma-

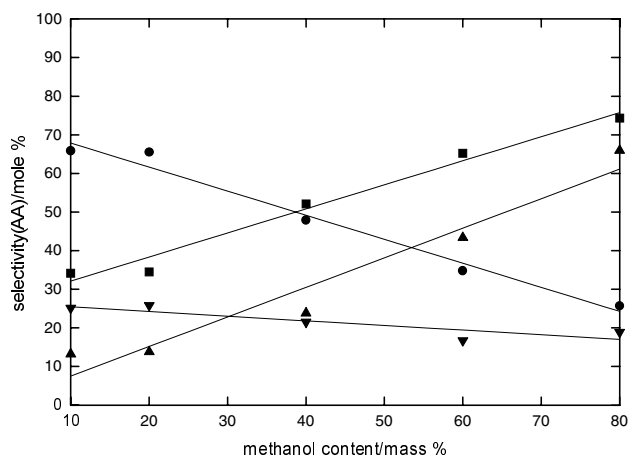


Fig. 5. Selectivity of transformation to glycidol and glycerol in relation to consumed AA and H_2O_2 as a function of methanol content over the TS-2 catalyst (temperature 20°C , the mole ratio AA— $\text{H}_2\text{O}_2 = 5$, TS-2 content 1 mass %, reaction time 2 h). ■ Glycidol/AA, ● glycerol/AA, ▲ glycidol/ H_2O_2 , ▼ glycerol/ H_2O_2 .

tion into glycerol. The following technological parameters: temperature 20°C , the mole ratio AA— $\text{H}_2\text{O}_2 = 5:1$, methanol content 80 mass %, the TS-2 catalyst content of 0.1 mass %, reaction time 1 h were found to be the most advantageous from the point of view of the glycidol synthesis in the methanol medium.

CONCLUSION

The optimum parameters of epoxidation of allyl alcohol with 30 % hydrogen peroxide in the direction of glycidol over the TS-1 and TS-2 catalysts in the presence of an aprotic solvent – acetone and protic solvent – methanol with corresponding to them selectivities, yields, and conversions were compiled in Table 1. The highest values of mentioned quantities were achieved over the TS-2 catalyst in the methanol medium. A change of the catalyst for TS-1 decreases these quan-

ties. This particularly concerns the C_{AA} and $Y_{gl/AA}$. An important role in the glycidol synthesis is played by the nature and concentration of the solvent. This particularly concerns methanol and confirms the epoxidation mechanism discussed in the introduction section [10]. The presence of methanol in the reaction medium causes that methanol participates in the formation of active adduct. This role is performed by water in the presence of the aprotic solvent. However, the electrophilic properties of the active adduct with the participation of water are weaker than those with the participation of methanol. For this reason the epoxidation in the aprotic solvent – acetone proceeds slowly. The acidic properties of titanium silicalite catalysts TS-1 and TS-2 in combination with aqueous medium facilitate the opening of oxirane ring. This in turn causes that in the presence of protic solvent glycerol is the only by-product. Moreover, the acidic properties of the catalyst in the presence of the aprotic solvent – acetone cause a slight etherification of allyl alcohol. The selectivity of transformation to diallyl ether in relation to consumed allyl alcohol is of the order 2–7 mole %. Methanol is a more suitable solvent in the process of the epoxidation of allyl alcohol to glycidol, mainly due to a higher selectivity of transformation to glycidol. The TS-2 catalyst is more active, because a higher conversion of allyl alcohol both in acetone and methanol can be achieved. However, the selectivity of transformation during the epoxidation of allyl alcohol to glycidol is lower due to a simultaneous acceleration of the hydration of glycidol to glycerol. The most advantageous conditions for the glycidol synthesis are as follows: temperature 20°C , the mole ratio AA— $\text{H}_2\text{O}_2 = 5:1$, methanol content of 80 mass %, the TS-2 catalyst content of 0.1 mass %, reaction time 1 h. Under these conditions the conversion of H_2O_2 amounts to 100 mole %, of allyl alcohol to 97.7 mole %, the selectivities of transformation to glycidol in relation to allyl alcohol and to H_2O_2 amounted to 90.4 mole % and 76.2 mole %, respectively.

Table 1. The Optimum Parameters of Glycidol Synthesis over TS-1 and TS-2 Catalysts in Acetone and Methanol with Corresponding to them Selectivities, Yields, and Conversions

	TS-1		TS-2	
	Acetone	Methanol	Acetone	Methanol
Temperature/ $^\circ\text{C}$	20	20	20	20
Mole ratio $n(\text{AA})/n(\text{H}_2\text{O}_2)$	5	5	5	5
Solvent content/mole %	80	80	10	80
Catalyst content/mole %	1.0	1.0	0.1	0.1
Reaction time/h	1	1	1	1
Yield ($Y_{gl/AA}$)/mole %	48.9	64.4	47.1	88.3
Selectivity ($S_{gl/AA}$)/mole %	75.9	93.6	63.2	90.4
Selectivity (S_{gl/H_2O_2})/mole %	48.8	67.5	50.1	76.2
Conversion (C_{AA})/mole %	64.4	68.9	74.4	97.7
Selectivity (S_{org/H_2O_2})/mole %	57.8	68.9	76.8	93.5

H_2O_2 conversion ($C_{\text{H}_2\text{O}_2}$) = 100 mole % for each set of the optimum parameters.

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