Influence of Acetone and Acetonitrile Content on the Epoxidation of Allyl Alcohol with Hydrogen Peroxide over TS-1 Catalyst

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The influence of content of the aprotic solvents (acetone and acetonitrile) on the yield and selectivity of glycidol, allyl glycidyl ether, and glycerol synthesis has been investigated. The changes of conversion of allyl alcohol and hydrogen peroxide were presented. In the epoxidation process of allyl alcohol with hydrogen peroxide glycidol and allyl glycidyl ether can be obtained with a high selectivity using the acetone content of 80 mass % in the reaction mixture. The decrease of acetone content results in the increase of selectivity of glycerol synthesis and the decrease of selectivity of glycidol and allyl glycidyl ether. Higher selectivities of glycidol and allyl glycidyl ether synthesis are achieved when the process is run in the presence of acetone as a solvent.

The TS-1 catalyst developed in the 80s has found a number of important applications in the oxidation process with 30 % hydrogen peroxide. The most significant ones include: the oxidation of alkanes [1—3], the epoxidation of unsaturated compounds of the type of ethylene [4—8], the hydroxylation of aromatic compounds (phenol, benzene) [4, 6, 9—12], the ammoxidation of cyclohexanone to oxime [13, 14], the oxidation of alcohols to aldehydes and ketones [6], the oxidation of N-methylmorpholine [6], the oxidation of aniline to azoxybenzene [15], the epoxidation of styrene [16].

There are several reports concerning the epoxidation of allyl alcohol with hydrogen peroxide over the titanium-silicalite catalysts [17—21].

The procedure of this process carried out at ambient temperature for 12 h, at n(allyl alcohol)/n(H$_2$O$_2$) = 1:1, in the presence of 18 mass % t-butyl alcohol as solvent and 2.3 mass % titanium silicalite TS-1 catalyst was described in the U.S. patent [17]. As a result of such performed reaction glycerol was obtained as the major product with 86 mole % yield.

Hutchings et al. [18, 19] have achieved high selectivity of glycidol synthesis (98.1 mole %) at a low conversion of alcohol (maximum 20.5 mole %) in the environment of methanol, ethanol, and t-butanol. A higher conversion led to the formation of the products of epoxy ring opening by water and alcohol. The epoxidation results are also affected by the method of the catalyst synthesis, its acidity, the temperature of the process, and the type of alcohol (solvent).

In the studies [22—24] we have found that under the conditions: the reaction time 24 h, temperature 20 °C, n(allyl alcohol)/n(H$_2$O$_2$) = 1:1, the catalyst content 0.1 mass %, the acetone content 80 mass %, glycidol and allyl glycidyl ether was formed with

the yield of 9.7 mole % and 19.3 mole %, respectively. Under these conditions, the selectivity of glycidol synthesis related to the consumed allyl alcohol amounts to 33.3 mole %, and for allyl glycidyl ether 66.7 mole %, whereas the conversion of allyl alcohol and hydrogen peroxide amounts to 29.0 mole % and 92.2 mole %, respectively. The following reaction products were also found: glycerol, diallyl ether, acrolein, acrylic acid, acetol, 3-hydroxypropionaldehyde, and 3-allyloxypropane-1,2-diol.

Since the work with such a large amount of solvent (80 mass %) is inconvenient (significant losses of solvent as a result of its volatility), it seems purposeful to examine how the decrease of the acetone content affects the proceeding of the epoxidation process, in particular the yield of glycidol and allyl glycidyl ether. It is also important to examine the course of the epoxidation process of allyl alcohol over TS-1 catalyst in the presence of other aprotic solvents (acetonitrile) and in relation to various contents of this solvent in the reaction mixture.

Glycidol and allyl glycidyl ether are valuable raw materials for many branches of industry [25]. Glycidol finds the application in the cosmetic industry (for the synthesis of N,N-dimethyl-N-(dihydroxypropyl)amine, which is used as a cleaning and moistening agent for skin), varnish industry (the manufacture of rust-proof varnish), and food industry (the production of margarine, ice-cream, and vegetable butter). It is also used for the preparation of the block copolymer of cellulose, in the manufacture of rubber as plasticizer, and in the production of the fire-resistant thermoplastic resins.

Allyl glycidyl ether is utilized in the production of varnish, dyestuff compositions, and foam hardeners [22].

EXPERIMENTAL

Allyl alcohol (Fluka), acetone, and 30 % hydrogen peroxide (both P.O.Ch. Gliwice, Poland) were used.

The samples of the TS-1 catalyst were prepared by the method described by *Thangaraj et al.* [26]. As the raw materials tetraethyl orthosilicate, tetrabutyl orthotitanate, and tetrapropyl ammonium hydroxide – TPAOH (all Fluka) were used. The obtained hydrogels were crystallized at 175 °C for 8 d under static conditions. The crystals were separated from the parent liquid, dried in a dryer at 120 °C for 12 h and were then calcined in the oven at 550 °C for 24 h. The calcined catalyst was activated by washing with 10 % aqueous solution of ammonium acetate at 80 °C and was then recalcined at 550 °C for 24 h.

The catalyst characterization was performed with the aid of the conventional techniques. The composition of the samples was determined by X-ray fluorescence spectroscopy (XRF) using a VRA 30 spectrometer. The obtained results are presented in Table 1 (the completion to 100 mass % comprises water).

Table 1. The Compositions of Prepared Titanium Silicalite TS-1 Catalysts

Sample number	w_i(Catalyst)/%	
	TiO$_2$	SiO$_2$
1	**4.09**	78.60
2	2.05	82.70
3	3.79	79.00
4	1.03	78.01
5	2.23	74.88
6	2.77	74.37
7	1.54	77.43
8	2.22	64.56

The crystalline structure of the samples was confirmed by the X-ray diffraction (XRD) analysis method using a DRON 3 diffractometer with cobalt lamp with iron filter. The obtained diffraction patterns exhibit the reflections in the same range of 2Θ angle as in the case of the TS-1 catalysts described in the literature [27—29].

The IR spectra were recorded on a Specord 75 IR (Zeiss, Jena) by the method of the solid state in the solid state (KBr). The catalyst concentration in KBr amounted to $\approx$ 1.4 mass %. The infrared spectra of all samples exhibit an absorption band at $\bar{\nu} \approx 960$ cm^{-1}. Its existence was assigned to the presence of $\equiv$Ti—O—Si$\equiv$ bonds in the silicalite structure [28].

The morphology of crystals was determined on the basis of SEM micrographs performed by scanning electron microscopy, Jeol type JSM-6100.

At the epoxidation allyl alcohol, acetone, 30 % hydrogen peroxide, and TS-1 catalyst were placed in a teflon-lined stainless steel autoclave with the capacity of 10 cm^3. The amounts of the substrates were selected in such a manner that the filling ratio did not exceed 80 % of the autoclave capacity. The autoclave was fixed in a shaker holder and immersed in the oil bath the temperature of which was controlled by a thermostat. The shaker was set in motion (stirring) and the reaction was performed. A post-reaction mixture was weighed, analyzed and balanced. The conversion of allyl alcohol does not take place in the process carried out without the catalyst TS-1 (blank test).

The reaction products were analyzed by gas chromatography. The determinations were performed on a Fisons GC 8000 apparatus with a flame ionization detector (FID). The two capillary columns were combined with each other: DB-5 (30 m × 0.25 mm, 0.25 μm film thickness) and FFAP (15 m × 0.54 mm, 1 μm film thickness).

Glycerol was determined by the method of periodate [29], the consumption of hydrogen peroxide was measured by iodometric titration [30]. The epoxidation results were described with the aid of the following magnitudes
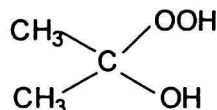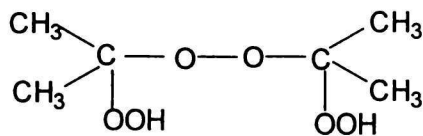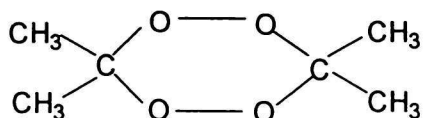
$$\begin{array}{l}\text{Conversion of substrates (allyl alcohol, H}_2\text{O}_2\text{) } K_{AA} \text{ or } K_{H_2O_2} \end{array} = \frac{\text{Amount of substance of substrate consumed}}{\text{Initial amount of substrate substance}} \cdot 100\%$$

$$S_{\text{org.}/H_2O_2} = \frac{\text{Amount of substance of product}}{\text{Amount of substance of H}_2\text{O}_2 \text{ consumed}} \cdot 100\%$$

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

$$Y_{\text{product}/AA} = \frac{\text{Amount of substance of product}}{\text{Amount of substance of allyl alcohol introduced into reactor}} \cdot 100\%$$

Note: Through the use of GC and HPLC method it was ascertained that the organic compounds with the explosive properties given below were not present under reaction conditions studied [31]

CH$_3$—C(OOH)(OH)—CH$_3$

acetone α-hydroxyhydroperoxide

(CH$_3$)$_2$C(OOH)—O—O—C(OOH)(CH$_3$)$_2$

diacetone α,α'-dihydroperoxyperoxide

diacetone cyclic gem-diperoxide

Hydrogen peroxide probably exhibits a greater ability for the reaction with the active site of the catalyst (Ti atom) than for that with acetone.

Similarly in the environment of acetonitrile the occurrence of the product of its reaction with H$_2$O$_2$ – acetamide was not confirmed. This type of the reaction requires the alkaline media of reaction [32, 33].
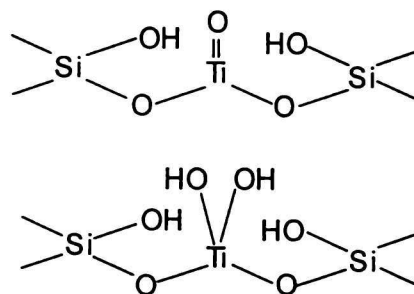
RESULTS AND DISCUSSION

Based on our earlier studies [22—24] of the epoxidation of allyl alcohol with hydrogen peroxide over TS-1 catalyst in acetone (aprotic solvent) the following reaction conditions were used as the most appropriate: temperature 20°C, the reaction time 24 h, catalyst content 0.1 mass %, n(allyl alcohol)/n(H$_2$O$_2$) = 1:1, and acetone content 80 mass %. They permitted the synthesis of glycidol with a relatively high yield (9.7 mole %). Under these conditions also allyl glycidyl ether is formed with the yield of 19.3 mole %. Both compounds are the most desirable on account of numerous applications. The above-mentioned conditions permit almost complete inhibition of the hydrolysis of glycidol to glycerol.
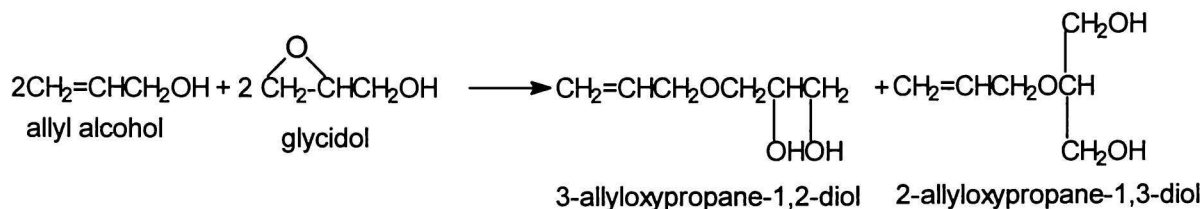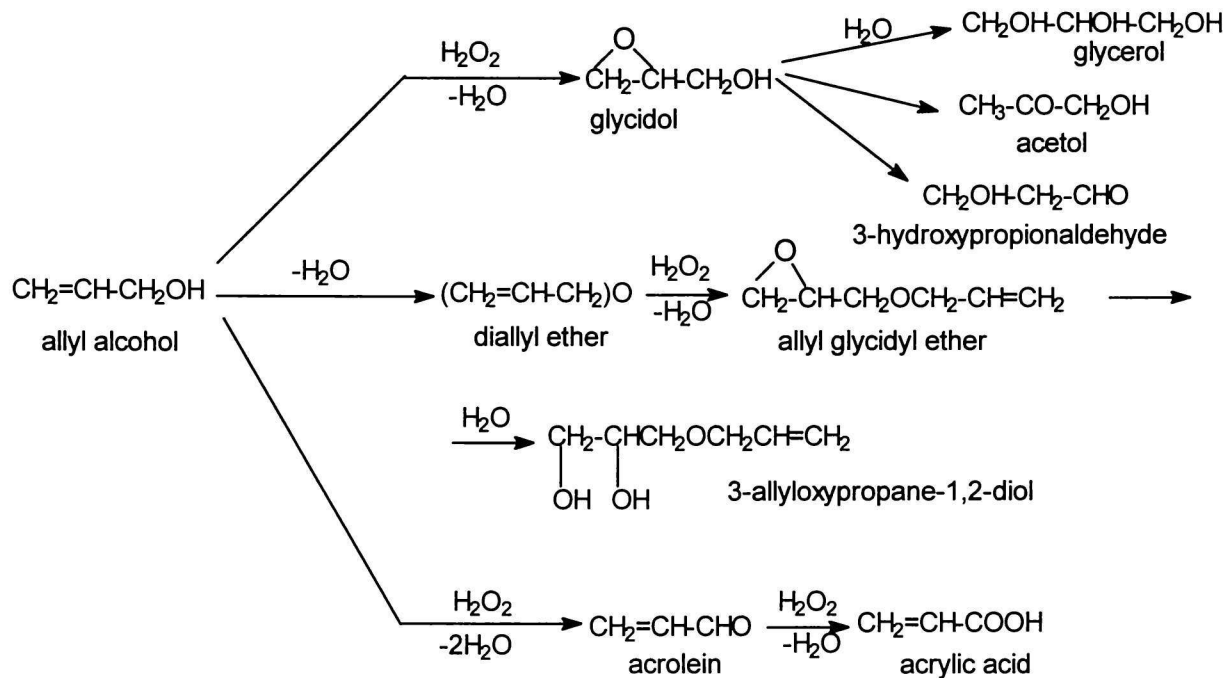
In the presence of the protic solvents such as water, methanol, the prevalent reaction product is glycerol as a result of a high rate of the hydration of initially formed glycidol [24]. The epoxidation carried out with diluted hydrogen peroxide (30 % aqueous solution) under the same conditions as previously leads to the formation of the major products with the following yields: glycidol 1.0 mole %, allyl glycidyl ether 5.0 mole %, glycerol 29.0 mole %, and acrolein 2.0 mole %. Acrylic acid, 3-hydroxypropionaldehyde, and diallyl ether were also formed in the process. The conversion of allyl alcohol amounted to 44.0 mole %, whereas the H$_2$O$_2$ conversion was 99.0 mole %. Similar results

were obtained when the epoxidation was performed in the presence of methanol as a solvent. In the aqueous environment or in the presence of methanol the process is less selective from the point of view of the synthesis of glycidol and allyl glycidyl ether. However, this process is posing convenient conditions for glycerol synthesis.
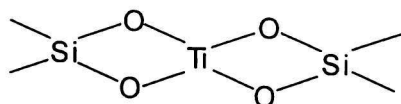
It results from our studies that the reaction of allyl alcohol with 30 % hydrogen peroxide in the presence of the TS-1 catalyst can be described by the equations presented in Scheme 1. Glycidol is formed as a result of the epoxidation of allyl alcohol, which readily undergoes hydration to glycerol or slightly isomerizes to acetol and 3-hydroxypropionaldehyde under the reaction conditions. The hydrolysis of glycidol is caused by water which is introduced with 30 % hydrogen peroxide as well as water formed as a result of the conversion of hydrogen peroxide. According to the reaction presented in Scheme 1, the formation of allyl glycidyl ether proceeds by the formation of diallyl ether. Both compounds occur in the products. Heating at 30°C (24 h, the TS-1 catalyst – 0.1 mass %, acetone as solvent) of an equimolar mixture of allyl alcohol and glycidol leads to the mixture of 3-allyloxypropane-1,2-diol and 2-allyloxypropane-1,3-diol (Scheme 1). However, allyl glycidyl ether was not formed in this reaction under these conditions. In the epoxidation products of allyl alcohol with hydrogen peroxide under certain process conditions (aqueous environment) acrolein and acrylic acid were found. Moreover, 3-allyloxypropane-1,2-diol was identified. This compound may be formed via both the hydration of allyl glycidyl ether and as a result of the etherification of glycidol and allyl alcohol.

The epoxidation of allyl alcohol over the TS-1 catalyst probably proceeds according to the nonradical mechanism (electrophilic oxidation) [34, 35]. The active site of the catalyst is constituted by the Ti^{4+} ion which is incorporated into the crystalline structure of silica. This is a structure of the MFI type. The channels are a combination of linear and zig-zag ones [36] (Fig. 1). The pores of the TS-1 catalyst have the dimensions 0.56 nm × 0.54 nm [37]. The connection of Ti^{4+} in the zeolite structure has not been explained completely so far, hence the following proposals of the structures are encountered [38]

Scheme 1. The reaction proceeding during the epoxidation of allyl alcohol with hydrogen peroxide over TS-1 catalyst.

The Ti^{4+} ion may also coordinate the neutral ligand (e.g. H_2O) [34] and change the coordination number from IV to VI

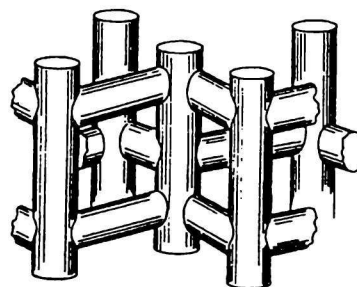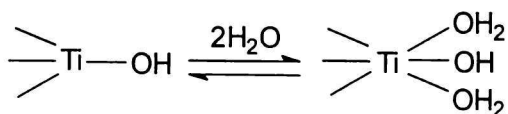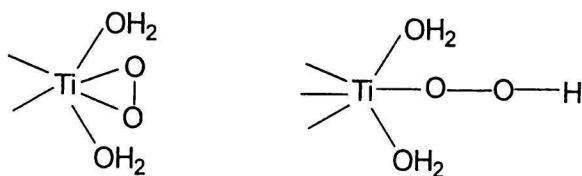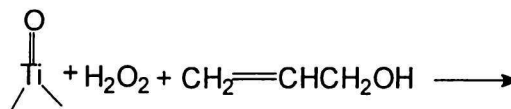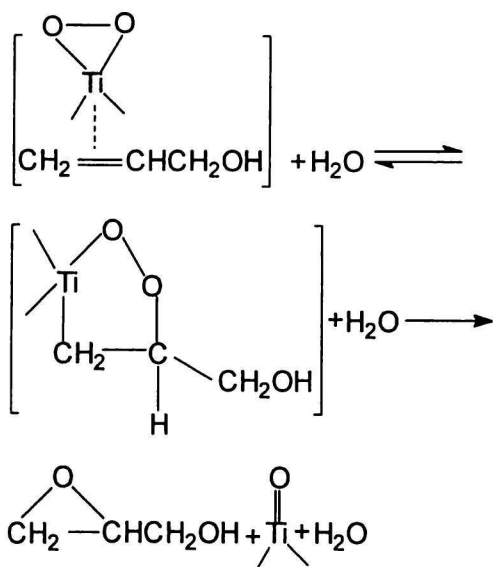Fig. 1. System of channels of the TS-1 catalyst.

The H_2O_2 molecules also undergo the coordination with the titanium with the formation of peroxide or hydroperoxide bonds [34, 35].

The mechanism of nonradical oxidation of allyl alcohol can be also presented in the following form [34, 35]

The effect of the aprotic solvents with various polarity on the epoxidation of allyl alcohol was examined with the use of acetone and acetonitrile as an example (relative dielectric constant of acetone, acetonitrile, and of water amount $\varepsilon = 20.7$, $\varepsilon = 37.5$, and $\varepsilon = 80.4$, respectively). The syntheses with the participation of solvents were carried out under conditions presented previously. The contents of solvents in the subsequent syntheses amounted to 5, 10, 20, 50, and 80 mass %. Sample *1* with the highest content of TiO_2 was used as a catalyst (Table 1).

The results of the epoxidation of allyl alcohol with hydrogen peroxide over TS-1 catalyst at acetone concentrations mentioned above are presented in Table 2. It results from these data that in the range of acetone content 0—80 mass % together with the decrease of the acetone content the decrease of glycidol yield from 9.7 mole % to 1.0 mole % is observed ($Y_{GLYC/AA}$) in relation to allyl alcohol introduced into the reactor.

The selectivity of glycidol synthesis in relation to consumed allyl alcohol ($S_{GLYC/AA}$) decreases in the same manner. Allyl glycidyl ether was obtained with the yield $Y_{AGE/AA} = 19.3$ mole % at acetone content of 80 mass %. In the region of low acetone contents (from 30 mass %) there is a decrease of the yield of this compound to the constant value $Y_{AGE/AA} = 5.0$ mole %. At the acetone content of 80 mass % the glycerol is not formed, $S_{GL/AA} = 0.0$ mole %. As the acetone content is decreased the yield of glycerol increases and amounts to $Y_{GL/AA} = 29.0$ mole % in the solvent-free environment, with the selectivity of glycerol synthesis in relation to consumed allyl alcohol $S_{GL/AA} = 65.9$ mole %.

The results of allyl alcohol epoxidation at various contents of acetonitrile and for the remaining invariable parameters are shown in Table 3. The highest yield of glycidol in relation to allyl alcohol introduced to the reactor $Y_{GLYC/AA} = 8.3$ mole % was achieved at acetonitrile content of 80 mass %. The decrease of the solvent content results in the reduction of the glycidol yield. Over a wide range of the acetonitrile contents (10—50 mass %) the yield of glycidol amounts to $Y_{GLYC/AA} = 2.0$—3.0 mole %. This tendency of changes is preserved in the case of the selectivity of glycidol synthesis in relation to consumed allyl alcohol $S_{GLYC/AA}$. The yield of allyl glycidyl ether $Y_{AGE/AA}$ and the selectivity of allyl glycidyl ether $S_{AGE/AA}$ decrease during decreasing the acetonitrile content in the reaction mixture. The glycerol yield $Y_{GL/AA}$ increases with the decrease of acetonitrile content from 8.3 mole % at 80 mass % to 29.0 mole % in the absence of solvent. This tendency of changes is maintained in the case of the selectivity of glycerol synthesis with respect to consumed allyl alcohol $S_{GL/AA}$. In the presence of acetonitrile, at relatively significant amounts acrolein is additionally formed. The maximum yield of acrolein $Y_{ACR/AA} = 17.6$ mole % was achieved at 20 mass % acetonitrile content.

Table 2. Results of Allyl Alcohol Epoxidation with Hydrogen Peroxide in Acetone over TS-1 Catalyst (24 h, 20 °C, 0.1 mass % of TS-1, $n(AA)/n(H_2O_2) = 1:1$)

$S_i(Y_i)$/mole %	w(Acetone in the reaction mixture)/%						
	80	50	30	20	10	5	0^a
$S_{GLYC/AA}$/mole %	33.3	34.2	34.2	30.0	23.2	18.3	2.3
$Y_{GLYC/AA}$/mole %	**9.7**	**9.6**	**9.0**	**7.5**	**6.5**	**5.5**	**1.0**
$S_{GL/AA}$/mole %	0.0	30.2	46.0	50.0	59.0	65.0	65.9
$Y_{GL/AA}$/mole %	**0.0**	**8.5**	**12.1**	**12.5**	**16.5**	**19.5**	**29.0**
$S_{AGE/AA}$/mole %	66.7	35.6	19.8	20.0	17.8	16.7	11.4
$Y_{AGE/AA}$/mole %	**19.3**	**10.0**	**5.2**	**5.0**	**5.0**	**5.0**	**5.0**
C_{AA}/mole %	29.0	28.1	26.3	25.0	28.0	30.0	44.0
$C_{H_2O_2}$/mole %	92.2	92.8	98.9	98.2	98.3	98.5	99.0
$S_{org./H_2O_2}$/mole %	18.7	23.4	20.7	17.0	16.1	33.3	40.1

GLYC – glycidol, GL – glycerol, AGE – allyl glycidyl ether, AA – allyl alcohol. *a*) In this synthesis there were also formed: acrylic acid, 3-hydroxypropionaldehyde, acrolein, diallyl ether.

Table 3. Results of Allyl Alcohol Epoxidation with Hydrogen Peroxide in Acetonitrile over TS-1 Catalyst (24 h, 20 °C, 0.1 mass % of TS-1, $n(AA)/n(H_2O_2) = 1:1$)

$S_i(Y_i)$/mole %[a]	w(Acetonitrile in the reaction mixture)/%						
	80	50	30	20	10	5	0[b]
$S_{GLYC/AA}$/mole %	33.2	11.6	6.1	4.9	5.1	4.2	2.3
$Y_{GLYC/AA}$/mole %	8.3	2.8	2.3	2.2	2.2	1.5	1.0
$S_{GL/AA}$/mole %	33.2	44.4	43.9	44.7	50.0	60.6	65.9
$Y_{GL/AA}$/mole %	8.3	10.7	16.7	20.2	21.6	21.8	29.0
$S_{AGE/AA}$/mole %	33.6	33.2	14.7	11.5	12.0	13.9	11.4
$Y_{AGE/AA}$/mole %	8.4	8.0	5.6	5.2	5.2	5.0	5.0
$S_{ACR/AA}$/mole %	0.0	10.8	35.3	38.9	32.9	21.3	4.5
$Y_{ACR/AA}$/mole %	0.0	2.6	13.4	17.6	14.2	7.7	2.0
C_{AA}/mole %	25.0	24.1	38.0	45.2	43.2	36.0	44.0
$C_{H_2O_2}$/mole %	74.2	94.2	96.0	94.7	96.0	96.7	99.0
$S_{org./H_2O_2}$/mole %	24.2	20.1	24.7	45.6	39.1	31.0	40.1

a) Denotations are the same as in Table 2, moreover ACR – acrolein. b) In this synthesis there were also formed: acrylic acid, 3-hydroxypropionaldehyde, diallyl ether.

The conversion of allyl alcohol C_{AA} amounts to 28—30 mole % in the presence of acetone over the content range investigated 5—80 mass %, whereas it is 24—45 mole % in acetonitrile. The conversion of hydrogen peroxide $C_{H_2O_2}$ rises from 92.2 mole % to 98.5 mole % with the decrease of the acetone content. A similar tendency occurs in the case of acetonitrile ($C_{H_2O_2}$ = 74.2—96.7 mole %). In the case of both acetone and acetonitrile the selectivity of sum of organic compounds synthesis in relation to consumed H_2O_2 $S_{org./H_2O_2}$ is slightly different from the conversion of allyl alcohol. It results from the performance of the process at n(allyl alcohol)$/n(H_2O_2) = 1:1$, and almost a complete conversion of H_2O_2 takes place in the process.

From the point of view of the needs of industry the most desirable products of allyl alcohol conversion in the presence of hydrogen peroxide are: glycidol and allyl glycidyl ether. In comparison with the experiments performed without a solvent at acetone content of 80 mass % the yield of glycidol is about 10 times higher, whereas of allyl glycidyl ether about 4 times. The synthesis selectivities of glycidol and allyl glycidyl ether are then 14 and 6 times higher.

CONCLUSION

The epoxidation of allyl alcohol with hydrogen peroxide over the TS-1 catalyst under the conditions: temperature 20 °C, the reaction time 24 h, content of the TS-1 catalyst 0.1 mass %, n(allyl alcohol)$/n(H_2O_2) = 1$ leads to the formation of glycerol with the yield of 29.0 mole % at the selectivity of glycerol synthesis in relation to consumed allyl alcohol amounting to 65.9 mole %. The other products of the synthesis comprise glycidol, allyl glycidyl ether and in a significantly smaller amount acrolein, acrylic acid, 3-hydroxypropionaldehyde diallyl ether. The incorpo-

ration of acetone (80 mass %) to the reaction system results in the inhibition of the glycerol formation. The major products of the reaction in that case are glycidol ($S_{GLYC/AA}$ = 33.3 mole %) and allyl glycidyl ether ($S_{AGE/AA}$ = 66.7 mole %). The decrease of the content of this solvent results in the decrease of selectivity of the conversion of these compounds and the increase of the fraction of glycerol and acrolein. For comparable contents of the solvents, both the yield and selectivity of glycidol and allyl glycidyl ether synthesis in relation to allyl alcohol are higher in the case of acetone in comparison with that for acetonitrile.

REFERENCES

1. Huybrechts, D. R. C., De Breuycker, L., and Jacobs, P. A., *Nature 345*, 240 (1990).
2. Hulea, V., Dumitriu, E., Patcas, F., Ropot, R., Graffin, P., and Moreau, P., *Appl. Catal. 170*, 169 (1998).
3. Tatsumi, T., Nakamura, M., Negishi, S., and Tominga, H., *J. Chem. Soc., Chem. Commun. 1990*, 476.
4. Milchert, E. and Tarachowicz, L., *Chemik 1*, 19 (1996).
5. Clerici, M. G., Bellussi, G., and Romano, U., *J. Catal. 129*, 159 (1991).
6. Pielichowski, J. and Gurtat, P., in *Proceedings of the International Symposium and Exhibition*; Warsaw, *S-2 L-6*, 79 (1996).
7. Muller, C. A., Maciejewski, M., Mallat, T., and Baiker, A., *J. Catal. 184*, 280 (1999).
8. Yoo, Jeong-Woo, Mouloungui, Z., and Gasset, A., WO 40371 (1998).
9. Vetter, S., Schulz-Ekloff, G., Kulawik, K., and Jaeger, N. I., *Chem. Eng. Technol. 17*, 348 (1994).
10. Martens, J. A., Buskkens, P., and Jacobs, P. A., *Appl. Catal. 99*, 71 (1993).
11. Thangaraj, A., Kumar, R., and Ratnasamy, P., *J. Catal. 131*, 294 (1991).
12. Tuel, A. and Ben Taarit, Y., *Appl. Catal. 102*, 69 (1993).

13. Thangaraj, A., Sivasanker, S., and Ratnasamy, P., *J. Catal. 137*, 252 (1992).
14. Thangaraj, A., Sivasanker, S., and Ratnasamy, P., *J. Catal. 131*, 394 (1991).
15. Selvam, T. and Ramaswamy, A. V., *Catal. Lett. 31*, 103 (1995).
16. Kumar, S. B., Mirajkar, S. P., Pais, P. C. G., Kumar, P., and Kumar, R., *J. Catal. 156*, 163 (1995).
17. Taramasso, M., Pergo, G., and Notari, B., *U.S.* 4410501 (1983).
18. Hutchings, G. J., Lee, D. F., and Minihan, A. R., *Catal. Lett. 33*, 369 (1995).
19. Hutchings, G. J., Lee, D. F., and Minihan, A. R., *Catal. Lett. 39*, 83 (1996).
20. Hutchings, G. J. and Lee, D. F., *J. Chem. Soc., Chem. Commun. 1994*, 1095.
21. Hutchings, G. J., Lee, D. F., and Williams, C. D., *Stud. Surf. Sci. Catal. 69*, 389 (1991).
22. Milchert, E. and Wróblewska, A., *Przem. Chem. 77*, 92 (1998).
23. Milchert, E. and Wróblewska, A., in *Proceedings of the 8th International Summer School of Chemical Engineering*; Sozopol, *C10*, 283 (1998).
24. Wróblewska, A. and Milchert, E., in *Proceedings of the IIIrd International Symposium FORUM CHEMICZ-NE*; Warsaw, 75 (1997).
25. Milchert, E. and Wróblewska, A., *Przem. Chem. 75*, 367 (1996).
26. Thangaraj, A., Kumar, R., and Ratnasamy, P., *Appl. Catal. 57*, L1-L3 (1990).
27. Perego, G., Bellussi, G., Corno, C., Taramasso, M., Buonomo, F., and Esposito, A., *Stud. Surf. Sci. Catal. 28*, 129 (1986).
28. Thangaraj, A., Kumar, R., Mirajkar, S. P., and Ratnasamy, P., *J. Catal. 130*, 1 (1991).
29. Golora, B. M., Motovilyak, L. V., Politovskii, S. F., Stiepanov, M. V., and Czelyadin, V. T., *Zavod. Lab. 40*, 1192 (1974).
30. Brill, W. F., *J. Am. Chem. Soc. 85*, 141 (1963).
31. Hiatt, R., *Organic Peroxides.* Wiley, New York, 1970.
32. Payne, G. B., Deming, P. H., and Williams, P. H., *J. Org. Chem. 26*, 659 (1961).
33. Payne, G. B., *Tetrahedron 18*, 763 (1962).
34. Notari, B., *Catal. Today 18*, 163 (1993).
35. Huybrechts, D. R. C., Buskens, P. L., and Jacobs, P. A., *J. Mol. Catal. 71*, 129 (1992).
36. Kokotailo, G. T., Lawton, S. L., and Olson, D. H., *Nature 272*, 437 (1978).
37. Tuel, A. and Ben Taarit, Y., *Appl. Catal. 102*, 69 (1993).
38. Notari, B., *Stud. Surf. Sci. Catal. 60*, 243 (1990).