

Epoxidation of 1-buten-3-ol under atmospheric pressure over the Ti-Beta catalyst

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The results of 1-buten-3-ol (1B3O) epoxidation with 30% hydrogen peroxide over the Ti-Beta catalyst were presented. The studies were performed under the atmospheric pressure and at the presence of methanol as a solvent. There was examined the influence of the following parameters: the temperature (0 – 60°C), the molar ratio of 1B3O/H₂O₂ (1:1 – 5:1), methanol concentration (5 – 90 wt%), the Ti-Beta catalyst concentration (0.1 – 5.0 wt%) and the reaction time (0.5 – 5.0 h). The optimal parameters were determined by using the following functions: the selectivity of the transformation to 1,2-epoxy-3-butanol (1,2E3B) in relation to 1B3O consumed, the selectivity of the transformation to organic compounds in relation to hydrogen peroxide consumed, the conversions of 1B3O and hydrogen peroxide. The main product of epoxidation was 1,2-epoxy-3-butanol, epoxide having several applications.

Keywords: liquid phase epoxidation, 1,2-epoxy-3-butanol, Ti-Beta catalyst.

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INTRODUCTION

Hydrogen peroxide is a very interesting oxidizing agent in an organic synthesis¹. Mainly, because it is cheap and easily received. The product of its decomposition is water, so all the processes using hydrogen peroxide are more ecologically safe (they generate less amount of waste). One of the processes, where the hydrogen peroxide found an application, is epoxidation of olefins to olefin oxides (epoxides). It can be performed by using titanium-silicalite zeolites as catalysts. An important advantage of this catalysts is the ease of their regeneration and quite big stability when the proper conditions of reaction are followed². The Ti-Beta catalyst is a member of the titanium silicalite catalysts family. Apart from silicon atoms, oxygen and titanium, it contains in its structure aluminium atoms². It causes a formation of additional negative charges in the zeolite structure. Titanium and aluminium take the main part in the stabilization of the zeolite Ti-Beta structure. The presence of aluminium makes Brønsted acidity and decides about the hydrophilic chemical character of the catalyst³. The Ti-Beta zeolite crystallizes in the tetragonal system, the size of the channels is 0,74nm, and the entrance holes into the channels are limited by twelve edges. It is synthesized during hydrothermal crystallization in the presence of tetraethyloammonium hydroxide as a clatrating compound³.

The epoxidation of 1-butene-3-ol with 30% hydrogen peroxide over the Ti-Beta catalyst leads to the formation of 1,2-epoxy-3-butanol (1,2E3B). This compound has various applications. It belongs to the optically active compounds. (2S,3R)-1,2-Epoxy-3-butanol is used in the synthesis of drugs: Epothilone B⁴ and A⁵. Epothilone B is macrolide which was isolated from bacterial culture *Sorangium Cellulosum* and is currently in clinical studies. It blocks the division of cancer cells and is more efficient in this action than taxol⁶. 1,2-Epoxy-3-butanol was also applied in the synthesis of (-)-rhodinoside, a sugar component of such antibiotics as rhodomycin and

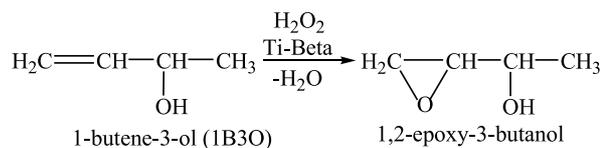
streptolydigin⁷. Streptolydigin is an antibiotic that impedes RNA polymerase (enzyme forming the RNA molecule on the matrix of one DNA chain). The studies of 1B3O epoxidation was undertaken to find such technological conditions of the process performing, in which 1,2E3B is formed: with the highest selectivity and at the same time a high conversion of 1B3O and the selectivity of transformation to organic compounds in relation to 1B3O reacted.

EXPERIMENTAL

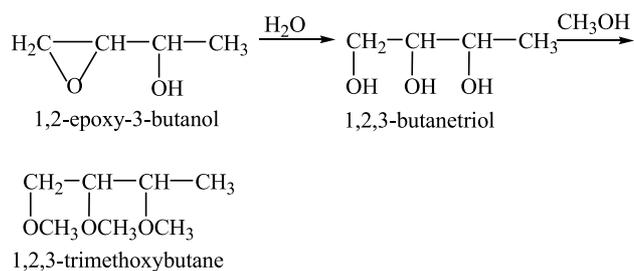
In the process of 1-buten-3-ol epoxidation there were used: 1-buten-3-ol (1B3O) (97%, Fluka), hydrogen peroxide (30-proc. water solution, POCh Gliwice), methanol (POCh Gliwice), the Ti-Beta catalyst (prepared in the Institute of Organic Chemical Technology). The Ti-Beta catalyst was prepared using the method described by Cambor et al.⁸ The epoxidation was performed under the atmospheric pressure in the three-necked flask fitted with a reflux condenser, thermometer and the dropping funnel. The reactants were introduced in the following order: catalyst, 1B3O and methanol (solvent). Hydrogen peroxide was dropped at the reaction temperature while mixing intensively. Mixing was performed with a magnetic stirrer. The Products were examined quantitatively using a gas chromatography. The chromatographic analysis was performed on the Focus apparatus with the flame ionization detector (FID), fitted with the Quadrex capillary column (30m x 250µm x 0,25µm). The parameters of the chromatographic separation were as follows: the pressure of helium 35kPa, the detector temperature 250°C, the temperature of the samples' chamber 150°C. The temperature of the thermostat increased as follows: isothermally at 40°C for 3 minutes, followed by an increase of the temperature at the rate of 10°C/minute, isothermally at 250°C for 5 minutes and cooling to 40°C. Hydrogen peroxide consumption was determined iodometrically⁹.

RESULTS

Epoxidation of 1B3O with 30% hydrogen peroxide over Ti-Beta catalyst leads to 1,2-epoxy-3-butanol as a main product:



1,2E3B is sensitive to an attack of a nucleophilic compound (especially water and methanol), which are present in the reaction medium. As a result of it a break of an epoxide ring takes place and 1,2,3-butanetriol and 1,2,3-trimethoxybutane are formed.



Scheme 1. The products of 2-butene-1-ol epoxidation

Depending on the process parameters there can be received some etheric products such as: 3-(3-methyl-1-propene)-3-methyl-1,2-epoxypropane ether, bis(3-methyl-1-propene) ether, 4-(1-methyl-2-propene)-butane-2,3-diol ether, bis(3-methyl-1,2-epoxypropane) ether, bis(2,3-dihydroxybutane) ether, 3-(2,3-dihydroxybutane)-3-methyl-1,2-epoxypropane ether. Using the proper parameters of the process their formation can be eliminated.

In the studies of the influence of temperature on the course of epoxidation process there were taken the following starting conditions: the molar ratio of 1B3O/H₂O₂=1:1, solvent concentration (methanol) 40 wt%, catalyst concentration 3 wt% and the time reaction time 3h. Taking an analysis the influence of temperature on the selectivity of transformation to 1,2-epoxy-3-butanol in relation to 1B3O consumed (Figure 1a) it was found that an increase in temperature from 0 to 20°C leads to a rise in the value of the function from 0.0 mol% to 34.1 mol%. The further increase in temperature to 60°C causes only a slight decrease in the value of the function to 22.1 mol%. It is caused by the increase in the speed of hydration of 1,2-epoxy-3-butanol to 1,2,3-butanetriol as well as the formation of 1,2-epoxy-3-methoxybutane. The conversion of 1B3O increases with the increases of the temperature from 0.0 mol% (0°C) to 83.9 mol% (20°C). The further increase in temperature does not make the other important changes of the value of the function. The selectivity of the transformation to organic compounds in relation to H₂O₂ consumed changes in the similar way. The conversion of H₂O₂ is constant in the range of the investigated temperatures and is about 97.0 mol%. On the basis of the studies the optimum temperature was taken as 20°C.

The influence of the molar ratio of 1B3O/H₂O₂ was examined in the range of 0.5:1 – 5:1. The syntheses were performed at the temperature of 20°C, the other param-

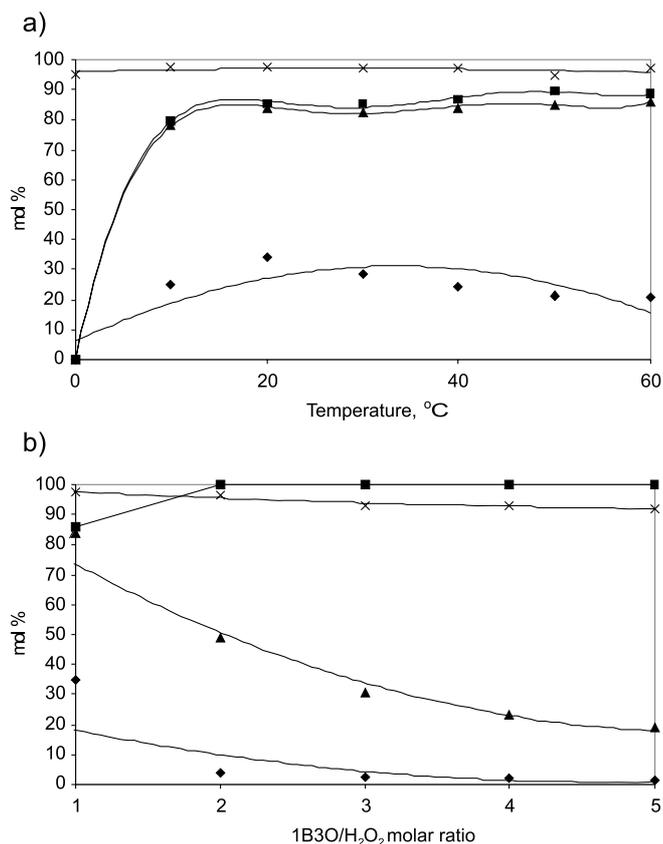


Figure 1. The effect of: a) the temperature on the selectivity of the transformation to 1,2-epoxy-3-butanol in relation to 1B3O consumed (♦), the selectivity of the transformation to the organic compounds in relation to the consumed H₂O₂ (■), the conversion of 1B3O (▲) and the conversion of H₂O₂ (x); b) the molar ratio 1B3O/H₂O₂ on the selectivity of the transformation to 1,2-epoxy-3-butanol in relation to 1B3O consumed (♦), the selectivity of the transformation to the organic compounds in relation to the consumed H₂O₂ (■), the conversion of 1B3O (▲) and the conversion of H₂O₂ (x)

eters were identical as in the previous series of examinations. From Figure 2b it results that the molar ratio of the reagents considerably affects the selectivity of the transformation of 1B3O to 1,2E3B. The highest selectivity of the transformation to 1,2E3B was achieved at the molar ratio 1B3O/H₂O₂=1:1. With the increase in the molar ratio over 1, the main product is formed with less and less selectivity, which is a result of an excess of 1B3O in relation to H₂O₂. The conversion of 1B3O also decreases because of the same reason. The selectivity of the transformation to organic compounds in relation to H₂O₂ consumed increases with the increase in the molar ratio of 1B3O/H₂O₂ from 0.5:1 – 1:1 (amounts 85.7 mol% for the equimolar ratio of the reagents), and for the molar ratio over 1:1 the whole hydroxide peroxide will react effectively. The conversion of H₂O₂ is practically constant in the examined range of the parameters and amounts 92.0 – 98.0 mol%. On the basis of the studies the molar ratio of 1B3O/H₂O₂=1:1 was considered as the most useful because of the high selectivity of the transformation of 1B3O do 1,2E3B (34.8 mol%), and also the highest conversion of 1B3O (84.0 mol%).

The influence of the solvent concentration (methanol) was examined in the range of 5 – 90 wt% and at the

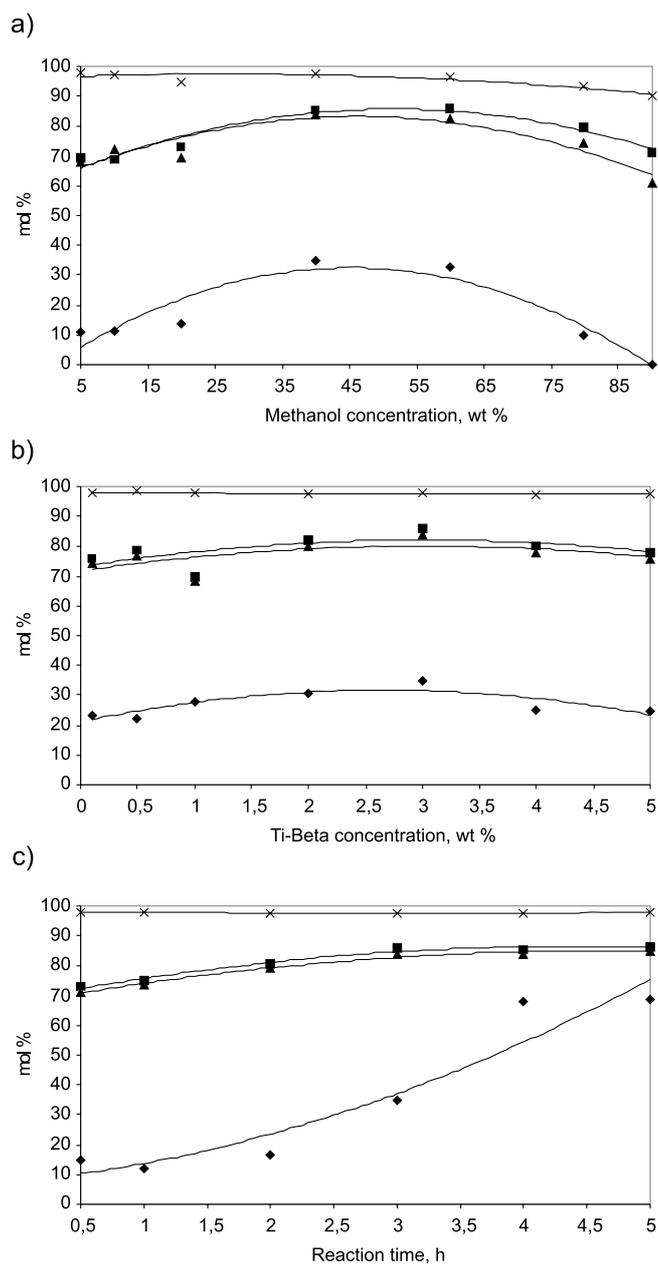


Figure 2. The effect of: a) methanol concentration on the selectivity of the transformation to 1,2-epoxy-3-butanol in relation to 1B3O consumed (◆), the selectivity of the transformation to the organic compounds in relation to the consumed H₂O₂ (■), the conversion of 1B3O (▲) and the conversion of H₂O₂ (x); b) the Ti-Beta catalyst concentration on the selectivity of the transformation to 1,2-epoxy-3-butanol in relation to 1B3O consumed (◆), the selectivity of the transformation to the organic compounds in relation to consumed H₂O₂ (■), the conversion of 1B3O (▲) and the conversion of H₂O₂ (x); c) the reaction time on the selectivity of the transformation to 1,2-epoxy-3-butanol in relation to 1B3O consumed (◆), the selectivity of the transformation to the organic compounds in relation to the consumed H₂O₂ (■), the conversion of 1B3O (▲) and the conversion of H₂O₂ (x)

temperature of 20°C and at the molar ratio of 1B3O/H₂O₂=1:1. The rest parameters were identical as the starting ones. From Figure 2a it results that with the increase in methanol concentration from 5 to 40 wt% the selectivity of the transformation of 1B3O to 1,2E3B increases

from 10.8 to 34.8 mol%. For the concentrations of methanol over 40 wt% there is a decrease in the value of the function as far as 0 mol% at the concentration of methanol 90 wt%. The conversion of 1B3O takes the maximum values at the concentrations of methanol 40 and 60 wt%. The selectivity of the transformation to organic compounds in relation to H₂O₂ consumed is at these two concentrations about 86.0 mol%, which means that almost the whole H₂O₂ reacted effectively in the process of 1B3O epoxidation. The conversion of H₂O₂ is constant in the whole range of the concentrations of methanol and amounts 90.0 – 98.0 mol%. According to the received results the concentration of methanol 40 wt % was considered as the most useful in the epoxidation of 1-buten-3-ol.

The studies of the influence of the Ti-Beta catalyst concentration were performed in the range 0.1 – 5.0 wt%. The highest selectivity of the transformation of 1-buten-3-ol to 1,2-epoxy-3-butanol was received at the concentration of Ti-Beta 3.0 wt% (34.8 mol%) – Figure 2b. At the higher concentrations of the catalyst the value of the function slightly decreases to 24.5 mol%. It probably occurs because the Ti-Beta catalyst at the higher concentrations in the reaction mixture catalyses, also not effective decomposition of H₂O₂, in relation with it the epoxidation of 1B3O cannot be performed in the same degree as at the lower concentrations of the catalyst. The selectivity of the transformation to the organic compounds in relation to H₂O₂ consumed changes slightly in the examined range of the concentrations of the catalyst and amounts about 78.0 mol%. Almost identically the conversion of 1B3O changes and amounts about 76.0 mol%. The lack of the increase in the values of these two mentioned above functions is probably caused by the decrease in the activity of the catalyst, it can be done by leaching the titanium from the active centers of the catalyst by H₂O₂. The conversion of H₂O₂ equals about 97.0 mol%. On the basis of the studies the optimum Ti-Beta catalyst concentration was taken as 3.0 wt%.

The influence of the reaction time on the course of the epoxidation was examined in the range of 0.5 – 5 h. The other parameters were the same as established as optimal in the previous stages of examinations. The analysis of the changes of the selectivity of the transformation of 1B3O to 1,2E3B showed that the prolongation of the reaction time from 0.5 h to 5.0 h causes the increase in the value of the function from 14.6 to 69.0 mol% (Figure 2c). Functions: the conversion of 1B3O and the selectivity of the transformation to the organic compounds in relation to H₂O₂ consumed take maximum values after 3.0h (the conversion of 1B3O 84.0 mol% and the selectivity of the transformation to organic compounds in relation to H₂O₂ consumed 85.9 mol%) and then are not practically changed. The conversion of H₂O₂ is 98.0 mol% in the whole range of the investigated reaction time. After the analyses of the results the time 5 h was taken as optimum.

CONCLUSIONS

The optimal parameters of 1-buten-3-ol epoxidation are: temperature 20°C, the molar ratio of 1B3O/H₂O₂=1:1, methanol concentration 40 wt%, the Ti-Beta catalyst concentration 3 wt%, and the reaction time of 5h. Under

these conditions the selectivity of the transformation to 1,2-epoxy-3-butanol in relation to 1-buten-3-ol consumed equals 69.0 mol%, the selectivity of the transformation to organic compounds in relation to 1-buten-3-ol consumed 86.4 mol%, and the conversion of a 1-buten-3-ol 85.1 mol%. The fact that the great amount of hydrogen peroxide, which reacts in the process, is effectively transformed into the organic compounds should be considered. From the point of view of the separation of products by distillation after the process, the high conversion of the hydrogen peroxide (98,0% mol) is useful because we do not need to decompose hydrogen peroxide before distillation.

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LITERATURE CITED

(1) Pielichowski J., Łukasiewicz M.: Nadtlenek wodoru w nowoczesnych procesach technologii organicznej, *Przem. Chem.*, **2002**, 81(8), 509.

(2) Milchert E., Tarachowicz L.: Synteza i zastosowania katalizatora tytanowo-silikalitowego, *Chemik*, **1995**, 9, 251.

(3) van der Waal J. C., Rigutto M. S., Van Bekkum H.: Zeolite titanium beta catalyst as a selective catalyst in the epoxidation of bulky alkenes, *Appl. Catal. A: General*, **1998**, 167, 331.

(4) Valluri M., Hindupur R. M., Bijoy P., Labadie G., Avery M. A.: Total synthesis of epothilone B, *Org. Lett.* **2001**, 23, 3607.

(5) Hindupur R. M., Panicker B., Valluri M., Avery M. A.: Total synthesis of epothilone A, *Tetrahed. Lett.*, **2001**, 42, 7341.

(6) Kąkol B., Jegierska-Zięba M., Kamiński J., Beldowicz M., Szpakiewicz M., Soliński J.: Chlorowodorek (2R, 3S)-fenyloizoseryny jako półprodukt do otrzymywania Paclitaxelu, *Przem. Chem.*, **2002**, 81, 780.

(7) Hatakeyama S., Samurai K., Takano S.: Preparation of o-protected (2S,3S)-1,2-epoxy-3-butanols. Enantioselective syntheses of (-)-rhodinose and (+)-epimuscarine iodide, *Heterocycles*, **1986**, 24, 633.

(8) Cambor M. A., Corma A., Martinez A., Perez-Pariente J.: Synthesis of a titaniumsilicoaluminate isomorphous to zeolite beta and its application as a catalyst for the selective oxidation of large organic molecules, *J. Chem. Soc.*, **1992**, 8, 589.

(9) Brill W. F.: The origin of epoxides in the liquid phase oxidation of olefins with molecular oxygen, *J. Am. Chem. Soc.*, **1963**, 85, 141.