

# The pressure method of 1-butene-3-ol epoxidation over Ti-beta catalyst

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The investigations of 1-buten-3-ol (1B3O) epoxidation by 30% hydrogen peroxide over Ti-Beta catalyst were performed. The experiments were carried out under the autogenic pressure and at the presence of methanol as a solvent. The influence of the following technological parameters on the course of epoxidation: temperature (20 – 120°C), the molar ratio of 1B3O/H<sub>2</sub>O<sub>2</sub> (0.5:1 – 5:1), methanol concentration (5 – 90 wt%), Ti-Beta concentration (0.1 – 5.0 wt%) and the reaction time (0.5 – 5.0 h) was investigated. The main functions describing the process were: the selectivity of transformation to 1,2-epoxy-3-butanol in relation to 1B3O consumed, conversions of substrates as well as the selectivity of transformation to organic compounds in relation hydrogen peroxide consumed.

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

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## INTRODUCTION

Zeolites are heterogenic catalysts used in oxidations, hydroxylation and ammoxidation processes<sup>1</sup>. Zeolite Ti-Beta also is one of them. The structure of this highly porous material contains, apart from oxygen, silicon and titanium atoms, little amount of aluminium atoms<sup>2</sup>. Titanium is an active centre of the catalyst and it has an ability to activate H<sub>2</sub>O<sub>2</sub> in oxidation processes. The presence of aluminium gives the Ti-Beta catalyst the hydrophilic character<sup>2</sup>. The templating agent used in the synthesis of the catalyst is tetraethylammonium hydroxide (TEAOH). Ti-Beta crystallizes in the tetragonal system, and the size of its channels amounts 0.74 nm<sup>3</sup>.

Traditional methods of the epoxide synthesis rely on the intramolecular cyclization of chlorohydrins with the use of aqueous alkaline solutions or on the alkene epoxidation with per-acids. There have been developed new directions in the synthesis of this group of compounds in recent years. They rely on the elimination of organic wastes, by-products difficult to manage and on the limitation of the quantity of the generated sewage. These objectives were archived through the catalytic processes of the oxidation of olefinic compounds with organic hydroperoxides or hydrogen peroxide. Hydrogen peroxide is considered to be the most ecological oxidizing agent in the synthesis processes.

1,2-Epoxy-3-butanol is used in the synthesis of a drug called Epothilone B<sup>4</sup>, which can act against tumour. It is also an intermediate in the synthesis of treonine<sup>5</sup>, which has an important influence on the production in a human organism: collagen, elastin and tooth enamel.

## EXPERIMENTAL

There were used in the epoxidation of 1B3O the following raw materials: 1-buten-3-ol (1B3O) (97%, Fluka), hydrogen peroxide (30% water solution, POCh Gliwice), methanol (analytical grade, POCh Gliwice), Ti-Beta catalyst (prepared in Institute of Organic Chemical Technology, Szczecin University of Technology). Ti-Beta catalyst was synthesised by the method described by Cambor at

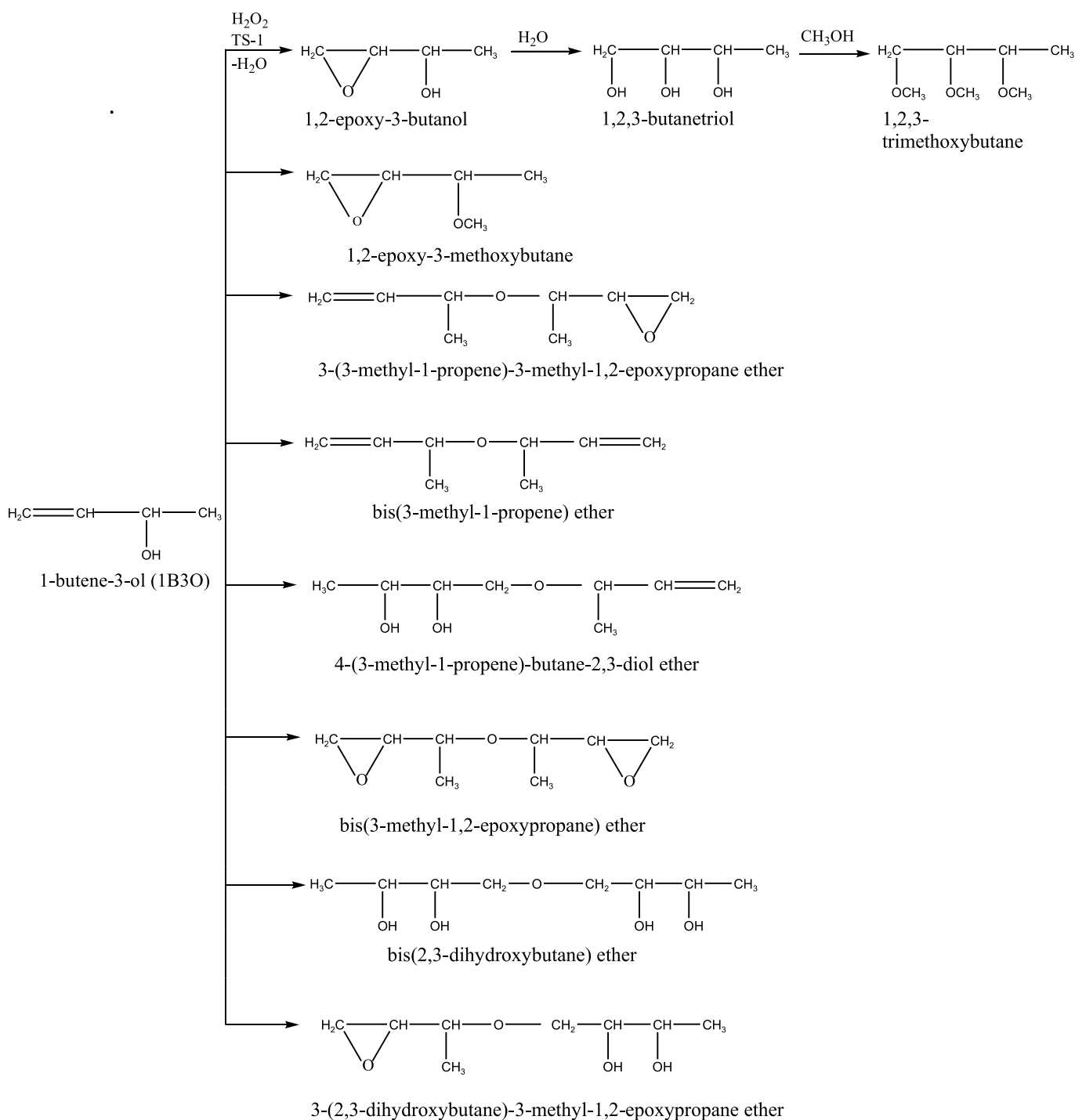
al.<sup>6</sup> The characterization of the catalyst was done using the following methods: XRD, XRF, IR, UV-VIS and SEM. The crystalline structure of Ti-Beta catalyst was confirmed using X-ray diffraction spectroscopy (XRD). The contents of titanium was established by the XRF method (0.40 wt% of TiO<sub>2</sub>). The examination was performed on the VRA 30 spectrometer. The IR spectrum of Ti-Beta catalyst was recorded on the JASCO FT/IR apparatus. There was an absorption band 960cm<sup>-1</sup> in the IR spectrum of the received catalyst. The UV-VIS spectrum was recorded on the SPECORD M40 apparatus. There was found in the spectrum an absorption band of 220 nm, which confirms the presence of Ti<sup>4+</sup> ions in the structure of the crystalline silica. The morphology of Ti-Beta crystallites was established basing on the SEM method (Figure 1) with the help of the Jeol JSM-6100 scanning microscope.

Epoxidation was performed in an autoclave under the autogenic pressure. The autoclave was fitted with a Teflon insert of the capacity of 7 cm<sup>3</sup>. The products were analyzed using a gas chromatography. The chromatographic analyses were done on the Focus apparatus equipped with the FID detector, on the Quadrex 30 m x 250μm x 0,25μm capillary column. Hydrogen peroxide which did not react was established iodometrically<sup>7</sup>.

After the mass balance of each synthesis was done, the main functions of the process were calculated: the selectivity of the transformation to 1,2E3B in relation to 1B3O consumed, conversions of 1B3O and hydrogen peroxide as well as the selectivity of the transformation to organic compounds in relation to hydrogen peroxide consumed.

## RESULTS

Epoxidation of 1B3O over the Ti-Beta catalyst using 30% hydrogen peroxide, in methanol as a solvent, leads to 1,2E3B as a main product. Depending on the conditions of the epoxidation there are formed and are established (with help of GC/MS method) different by-products in the process. The main and secondary reactions of the 1B3O epoxidation process are presented below:



The influence of temperature on the course of 1B3O epoxidation in the autoclave was investigated in the range of 20 – 120°C. The following beginning parameters were taken: the molar ratio of  $1\text{B3O}/\text{H}_2\text{O}_2=1:1$ , the concentration of the solvent 40 wt%, the concentration of Ti-Beta catalyst 3 wt% and the reaction time 3h. The analysis of the influence of temperature on the selectivity of the transformation to 1,2-epoxy-3-butanol in relation to 1B3O consumed showed (Figure 2a) that the increase of temperature from 20 – 120°C causes the decrease in the values of the function from 73 mol% to 25 mol%. It is caused by forming a higher amount of 1,2,3-butanetriol. At the temperatures of 100 and 120°C there was also established bis(3-methyl-1-propene)ether. The other products were formed in trace amount. The conversion of 1B3O is practically constant in the tested range of temperature and equals about 75 mol%. The selectivity of the transformation to organic compounds in relation to  $\text{H}_2\text{O}_2$

consumed decreases from 77 mol% (for temperatures 20 – 60°C) to 70 mol% (100°C) and 47 mol% (120°C). The conversion of  $\text{H}_2\text{O}_2$  is constant (96 mol%). At this stage of the experiment the temperature 20°C was considered as optimum. However, the fact that similar values of the functions can be taken in the range of temperatures from 20 to 55°C, must be taken into consideration.

The influence of the molar ratio of  $1\text{B3O}/\text{H}_2\text{O}_2$  was investigated in the range of 0.5:1 – 5:1 and at the temperature of 20°C. The other beginning parameters remained without any changes. The selectivity of the transformation to 1,2E3B in relation to 1B3O consumed (Figure 2b) decreases with an increase in the molar ratio of the reagents from 73 mol% to 18 mol%. It is caused by an excess of 1B3O comparing to  $\text{H}_2\text{O}_2$ . The conversion of 1B3O is the highest at the molar ratios of 0.5 – 1:1 and equals about 73 mol%. Over 1:1 there is its fall till 22 mol% (the molar ratio of  $1\text{B3O}/\text{H}_2\text{O}_2=5:1$ ). The selec-

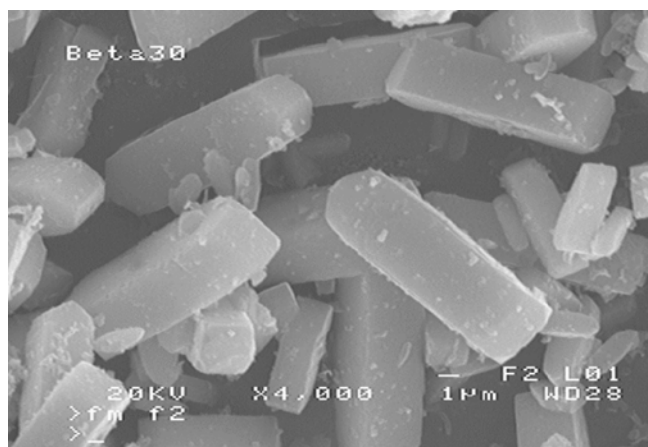


Figure 1. The SEM of the prepared Ti-Beta catalyst

tivity of the transformation to organic compounds in relation to  $\text{H}_2\text{O}_2$  consumed increases with an increase in the molar ratio from 37 mol% at molar ratio of the reagents 0.5:1 to 100 mol % at the molar ratio of the reagents 2:1 and than remains constant. It means, that the whole hydrogen peroxide reacted forming organic compounds.

The influence of the methanol concentration was examined in the range of 5 – 90 wt%, at the temperature of 20°C and at the molar ratio of  $1\text{B}3\text{O}/\text{H}_2\text{O}_2=1:1$ . The other parameters were identical to the first ones. It results from Figure 2c that an increase in methanol concentration from 5 to 40 wt% causes the situation that the selectivity of the transformation of 1B3O to 1,2E3B increases from 32 to 73 mol%. For methanol concentrations over 40 wt% there appears a sudden decrease in the function value up to 0 mol% at the methanol concentration of 90 wt%. This phenomenon is caused by forming 1,2,3-butanetriol. 1B3O conversion at concentrations from 5 to 40 wt% is practically constant and equals approximately 74 mol%. Beyond the concentration of 40 wt% its fall to 58 mol% was observed (methanol concentration 90 wt%). The selectivity of transformation to organic compounds in relation to  $\text{H}_2\text{O}_2$  consumed changes similarly. The conversion of  $\text{H}_2\text{O}_2$  is constant in the investigated range of methanol concentration and equals about 96 mol%. Methanol concentration of 40 wt% was considered as optimum at the stage of experiment.

The influence of the Ti-Beta catalyst concentration at the range of 0.1 – 5.0 wt% was investigated, at the temperature of 20°C, at the molar ratio  $1\text{B}3\text{O}/\text{H}_2\text{O}_2=1:1$ , methanol concentration 40 wt % and the reaction time 3h. The selectivity of the transformation to 1,2E3B in relation to 1B3O consumed (Figure 3a) increases with the rise in concentration of Ti-Beta from 30 mol% (0.1 wt%) to 73 mol % (3.0 wt %). At higher concentrations of Ti-Beta the value of the function slightly decreases to 67 mol% (5 wt% of the catalyst). The conversion of 1B3O increases from 50 mol % at the catalyst concentration 0.1 wt% to 76 mol% at the catalyst concentration 3 wt%. Rising the catalyst concentration to 5 wt% does not cause important changes in the value of the function. The selectivity of the transformation to organic compounds in relation to  $\text{H}_2\text{O}_2$  consumed has a similar course. The conversion of  $\text{H}_2\text{O}_2$  is constant at the range of the tested catalyst concentration and equals approximately 96 mol%. The most useful concentration of the catalyst equals 3 wt%. The highest selectivity of the transformation to

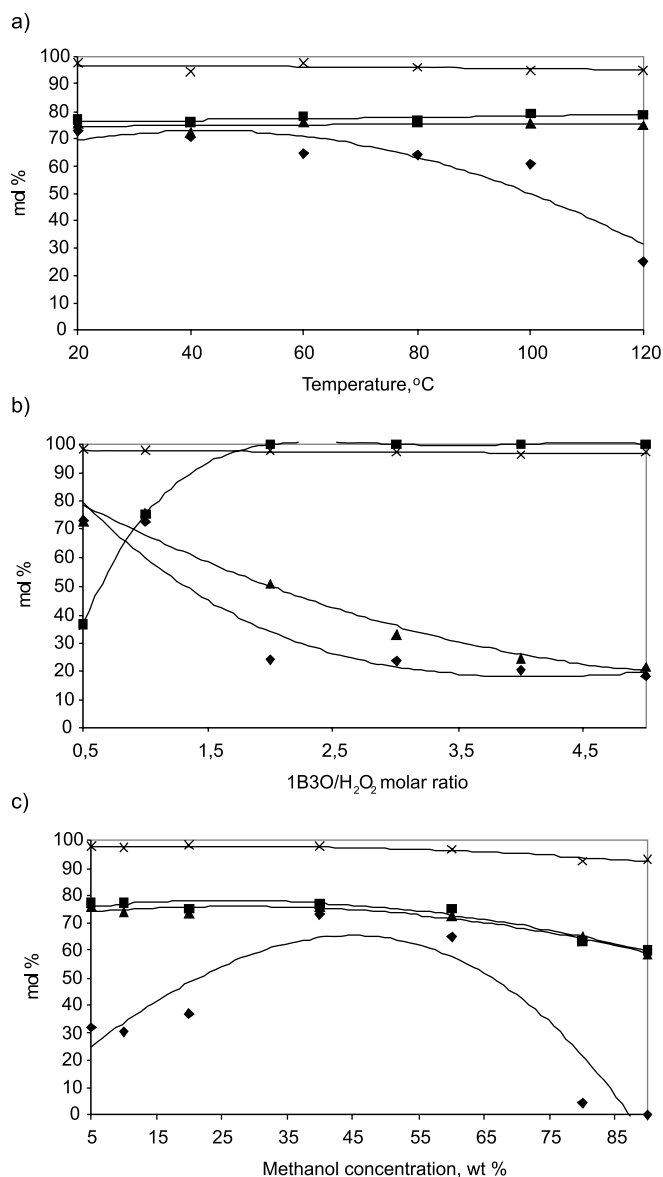
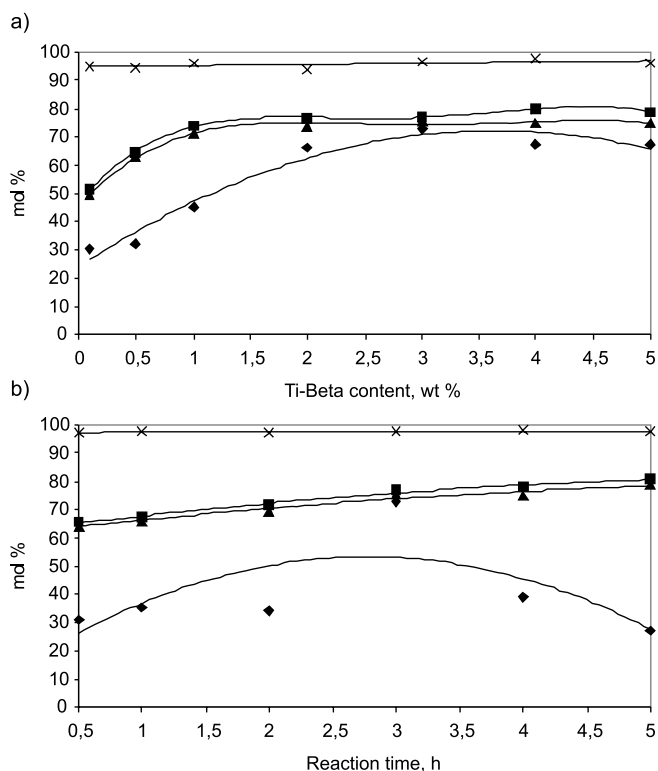


Figure 2. The effect of: a) the temperature on the selectivity of the transformation to 1,2-epoxy-3-butanol in relation to 1B3O consumed ( $\blacklozenge$ ), the selectivity of the transformation to the organic compounds in relation to the consumed  $\text{H}_2\text{O}_2$  ( $\blacksquare$ ), the conversion of 1B3O ( $\blacktriangle$ ) and the conversion of  $\text{H}_2\text{O}_2$  (x); b) the molar ratio MAC/ $\text{H}_2\text{O}_2$  on the selectivity of the transformation to 1,2-epoxy-3-butanol in relation to 1B3O consumed ( $\blacklozenge$ ), the selectivity of the transformation to the organic compounds in relation to the consumed  $\text{H}_2\text{O}_2$  ( $\blacksquare$ ), the conversion of 1B3O ( $\blacktriangle$ ) and the conversion of  $\text{H}_2\text{O}_2$  (x); c) methanol concentration on the selectivity of the transformation to 1,2-epoxy-3-butanol in relation to 1B3O consumed ( $\blacklozenge$ ), the selectivity of the transformation to the organic compounds in relation to the consumed  $\text{H}_2\text{O}_2$  ( $\blacksquare$ ), the conversion of 1B3O ( $\blacktriangle$ ) and the conversion of  $\text{H}_2\text{O}_2$  (x).

1,2E3B in relation to 1B3O consumed as well as high conversion decides about it.

The influence of the reaction time was investigated in the range from 0.5 h to 5.0 h. The other parameters corresponded to the values considered as the most useful at the previous stages of the experiment. From the analysis of the selectivity of the transformation to 1,2-epoxy-3-butanol in relation to 1B3O consumed (Figure 3b) it



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

results that extending the time reaction from 0.5 to 3h causes an increase in the value of the function from 31 mol% to 73 mol%. Further lengthening of the time causes fall in its value to 27 mol%. Lengthening the time reaction from 0.5h to 3h causes rise in the conversion of 1B3O from 63 to 76 mol%. Further lengthening of the reaction time to 5h does not have an important influence on the conversion. The selectivity of the transformation to organic compounds increases from 66 mol% to 81 mol% at the time range of 0.5 – 5.0h. The conversion of H<sub>2</sub>O<sub>2</sub> is constant at the investigated range of reaction times and equals approximately 98 mol %. The analysis of the results shows that the most useful time of the reaction equals 3h.

## CONCLUSIONS

The studies allowed to established the influence of technological parameters: the temperature, the molar ratio of 1B3O/H<sub>2</sub>O<sub>2</sub>, methanol concentration, Ti-Beta concentration and the reaction time on the course of 1B3O epoxidation. However, the received results also depend on the nature of Ti-Beta catalyst, its ability to ineffective decomposition of hydrogen peroxide, and also a loss in the activity of the catalyst due to leaching titanium from active centres. The formed complexes of titanium do not

have the same activity as the original catalyst. It results from the experiments that epoxidation of 1-buten-3-ol by 30% hydrogen peroxide at the presence of methanol as a solvent, over the Ti-Beta catalyst, performs the best at the temperature of 20°C, at the molar ratio of 1B3O/H<sub>2</sub>O<sub>2</sub> 1:1, the solvent concentration 40 wt%, the catalyst concentration 3 wt% and the reaction time 3h. Under such conditions the selectivity of the transformation to 1,2-epoxy-3-butanol in relation to 1B3O consumed, equals 73 mol%, the conversion of 1B3O 76 mol%, the selectivity of the transformation to organic compounds in relation to H<sub>2</sub>O<sub>2</sub> consumed 77mol%, and the conversion of H<sub>2</sub>O<sub>2</sub> 98 mol%.

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