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AGNIESZKA WRÓBLEWSKA, EWELINA ŁAWRO, EUGENIUSZ MILCHERT*

EPOXIDATION OF CROTYL ALCOHOL OVER TITANIUM SILICATE TS-2 CATALYST

EPOKSYDACJA ALKOHOLU KROTYLOWEGO NA KATALIZATORZE TS-2

Abstract

The results of epoxidation of 2-butene-1-ol with 30 wt.% hydrogen peroxide have been presented. Methanol was used as a solvent. The process was carried out over titanium silicalite catalyst TS-2. The influence of temperature (20–120ºC), molar ratio of crotyl alcohol/H_2O_2 (5:1–5:1), methanol concentration (5–90 wt.%), catalyst concentration (0.1–5.0 wt.%) and reaction time (30–300 min.) were investigated. The obtained results were utilized for determination of optimum conditions of running 2-butene-1-ol epoxidation process.

Keywords: epoxidation, 2,3-epoxybutane-1-ol, TS-2

Streszczenie

W artykule przedstawiono wyniki badań epoksydacji 2-buten-1-olu 30% nadtlenkiem wodoru. Jako rozpuszczalnik zastosowano metanol. Proces prowadzono na katalizatorze tytanowo-silikalitowych TS-2. Zbadano wpływ: temperatury (20–120ºC), stosunku molowego alkohol krotylowy/H_2O_2 (5:1–5:1), stężenia metanolu (5–90% wag.), stężenia katalizatora (0,1–5,0% wag.) i czasu reakcji (30–300 min). Otrzymane wyniki posłużyły do określenia optymalnych parametrów prowadzenia procesu epoksydacji 2-buten-1-olu.

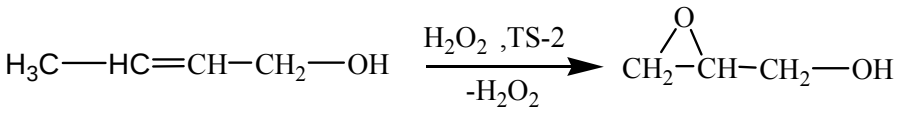
Słowa kluczowe: epoksydacja, 2,3-epoksybutanol, TS-2

* Dr inż. Agnieszka Wróblewska, mgr inż. Ewelina Ławro, prof. dr hab. inż. Eugeniusz Milchert, Instytut Technologii Chemicznej Organicznej, Wydział Technologii i Inżynierii Chemicznej, Politechnika Szczecińska.

1. Introduction

One of the major challenges of contemporary chemical industry is the need to implement the principles of green chemistry. The new processes should be more efficient, consume less energy and new materials, and they should affect the environment to minimum degree possible. Such processes include epoxidation of crotyl alcohol (CRA, 2-butene-1-ol) with 30 wt% hydrogen peroxide over titanium silicate TS-2 catalyst in methanol as a solvent. The 30 wt% hydrogen peroxide solution is characterized by a large redox potential and a high content of active oxygen. Its advantage is that in oxidation reactions it decomposes into water and oxygen, therefore hydrogen peroxide is ranked to so-called clean oxidants. Moreover, hydrogen peroxide is produced nowadays on a large scale, is easily available and it has a relatively low price which makes it applicable in more and more novel branches of economy. Titanium silicate TS-2 catalyst applied in epoxidation process allows carrying out epoxidation with high selectivity and good yield; moreover, this catalyst can be separated from the post-reactive mixture and can be used repeatedly for syntheses.

As a result of the epoxidation of 2-butene-1-ol (CRA) over TS-2 catalyst 2,3--epoxybutane-1-ol (EB) is obtained as the major product:



The development of preparation technology of this compound is important with regard to its numerous applications. EB is an important intermediate in the synthesis of acetoxyazetidinone, which is applied for the preparation of bicyclic ring in the molecule of 1β-methylkarbapene and other carbapenemic antibiotics [1]. 2,3-Epoxybutane-1-ol is used for the synthesis of C1-C12 segment of leptomycine B [2]. Leptomycine B is an unsaturated, branched chain of fatty acid with lactose ring. The compound finds applications in medicine as an anti-fungal pharmaceutical with anti-swelling action. It is also used as an inhibitor of protein translocation of HIV virus type 1. The synthesis of (2RS,3S)-[4,4,4-$^2H_3$] valine responsible for the biosynthesis of B5 vitamin (pantothenic acid) needed for proper metabolism of proteins sugar and fats as well as for the synthesis of some hormones starts from (2R,3S)-trans-epoxybutane-1-ol. Pantothenic acid is essential for a regular course of energy release process, prevents exhaustion and rationalizes cardiac--vascular, nervous and food systems; moreover, it participates in tissue regeneration and improves skin and hair pigmentation [3]. (2R, 3S)-Epoxybutane-1-ol is also used as a substrate for preparation of female pheromone of tobacco beetle Lasioderma serricon [4]. This beetle is the largest pest of healthy tobacco leaves, as well as a frequent pest in flour mills, bakeries, chocolate factories and retail shops. This compound is also utilized for the formation of pheromone traps to catch adult males of tobacco beetles in order to reduce the population of these insects. Aplysiatoxin and debromoaplysiatoxin are natural substances isolated from gastric juice of marine mollusks – Stylochelius longicauda. These compounds are neurotoxines and they stimulate the formation of cancer cells. With regard to their unique chemical constitution, they comprise attractive compounds for many syntheses [5, 6].

The by-products of epoxidation process of CRA over TS-2 catalyst are: crotyl aldehyde, crotonic acid, dimethoxybutane-1-ol, 1,2,3-butanetriol, 4-(2,3-epoxybutenoxy)-2-butene and bis(2-butene) ether.

2. Experimental

The following raw materials were used in the syntheses: 2-butene-1-ol (97% Fluka), hydrogen peroxide (30 wt.% aqueous solution, POCh Gliwice) and methanol (analytical grade, POCh Gliwice). TS-2 catalyst was prepared according to the procedure reported by Reddy et al [7].

The epoxidation was carried out in an autoclave under autogenic pressure. The autoclave was equipped with a PTFE insert of 7cm^3 capacity. The substrates were introduced in the following order: catalyst, CRA, methanol (solvent) and hydrogen peroxide. The autoclave was placed in a shaker holder and when the temperature of epoxidation process was higher than 20ºC, it was immersed in an oil bath the temperature of which was controlled by a thermostate. After completing the reaction, the autoclave was cooled and the post-reactive mixture was weighed.

The products were analyzed by means of gas chromatography. Unreacted hydrogen peroxide was determined by iodometric method [8]. During epoxidation of CRA the influence of the following parameters was investigated: temperature (20–120ºC), molar ratio of CRA/H_2O_2 (5:1–5:1), methanol concentration (5–90 wt.%), catalyst concentration (0.1–5.0 wt.%) and reaction time (30–300 min). The initial parameters of the process were as follows: molar ratio CRA/H_2O_2 = 1:1, solvent (methanol) concentration 40 wt.%, catalyst concentration 0.1 wt.% and reaction time 180 min. After performing mass balance for each of the syntheses the main functions characterizing the process were calculated: selectivity of transformation to EB in reaction to CRA consumed, CRA conversion and selectivity of transformation to organic compounds in relation to H_2O_2 consumed. These values were calculated according to the following equations:

$$S_{\mathrm{EB/CRA}} = \frac{\text{Amount of 2,3-epoxybutane-1-ol}}{\text{Amount of crotyl alcohol consumed}} \cdot 100\,[\mathrm{mol\,\%}]$$

$$S_{\mathrm{org/H_2O_2}} = \frac{\text{Amount of obtained organic compounds}}{\text{Amount of } \mathrm{H_2O_2} \text{ consumed}} \cdot 100\,[\mathrm{mol\,\%}]$$

$$C_{\mathrm{CRA\ or\ H_2O_2}} = \frac{\text{Amount of substrate consumed (CRA or } \mathrm{H_2O_2})}{\text{Initial amount of substrate (CRA or } \mathrm{H_2O_2})} \cdot 100\,[\mathrm{mol\,\%}]$$

3. Results and discussion

The influence of temperature on the course of CRA epoxidation in the autoclave was studied in the range of 20–120°C and the remaining above-mentioned initial parameters. Analyzing the influence of temperature on selectivity of transformation to EB in relation to CRA consumed (Fig. 1) it was found that the increase of temperature from 20 to 120°C

causes a decrease of the value of this function from 82 mol % (20°C) to 1 mol % (120°C). This was caused by the formation of by-products such as: crotyl aldehyde, crotonic acid, dimethoxybutane-1-ol, 1,2,3-butanetriol and ethers. In the case of CRA conversion and selectivity of transformation to organic compounds in relation to H_2O_2 consumed, an increase of the values of these functions was observed during process temperature elevation. The conversion of CRA increases from 35 mol % (20°C) to 79 mol % (120°C), whereas the selectivity of transformation to organic compounds in relation to H_2O_2 consumed increases from 36 mol % (20°C) to 64 mol % (120°C). On the basis of these relationships, the most advantageous temperature was assumed to be 20°C.

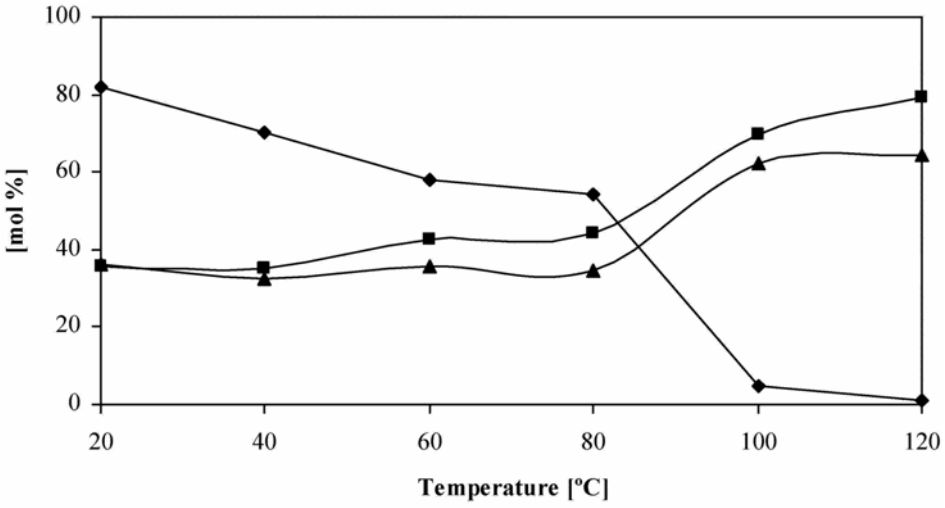


Fig. 1. Influence of temperature on epoxidation of crotyl alcohol: ♦ - selectivity of transformation to 2,3-epoxybutane-1-ol in relation to CRA consumed ($S_{EB/CRA}$), ■ – conversion of crotyl alcohol (C_{CRA}), ▲ – selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed ($S_{org/H2O2}$)

Rys. 1. Wpływ temperatury na epoksydację CRA: ♦ – selektywność przemiany do EB w odniesieniu do przereagowanego CRA, ■ – konwersja CRA, ▲ – selektywność przemiany do związków organicznych w odniesieniu do przereagowanego H_2O_2

The influence of molar ratio of CRA/H_2O_2 was investigated in the range 0.5:1–5:1. The synthesis were carried out at the temperature of 20°C, while maintaining all remaining parameters constant (Fig. 2). These studies demonstrated that along with the increase of reagents molar ratio, the selectivity of transformation to EB in relation to CRA consumed also decreases from 97 mol % (0.5:1) to 83% mol (5:1). The CRA conversion decreases along with an increase in molar ratio from 47 mol % (CRA/H_2O_2 = 0.5:1) do 21 mol % (CRA/H_2O_2 = 5:1). On the other hand, the selectivity of transformation to organic compounds in relation to H_2O_2 consumed increased from 24 mol % (CRA/H_2O_2 = 0.5:1) to 100 mol % (CRA/H_2O_2 = 5:1). This means that the entire hydrogen peroxide underwent a reaction to organic compounds. Analyzing the obtained results, equimolar ratio of CRA/H_2O_2 was found to be the most advantageous.

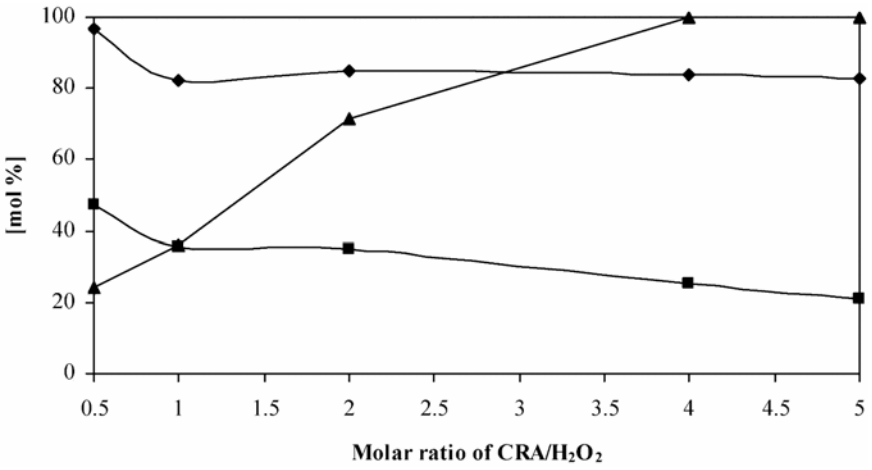


Fig. 2. Influence of CRA/H_2O_2 molar ratio on epoxidation of crotyl alcohol: ♦ – selectivity of transformation to 2,3-epoxybutane-1-ol in relation to CRA consumed ($S_{EB/CRA}$), ■ – conversion of crotyl alcohol (C_{CRA}), ▲ – selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed (S_{org/H_2O_2})

Rys. 2. Wpływ stosunku molowego CRA/H_2O_2 na epoksydację CRA: ♦ – selektywność przemiany do EB w odniesieniu do przereagowanego CRA, ■ – konwersja CRA, ▲ – selektywność przemiany do związków organicznych w odniesieniu do przereagowanego H_2O_2

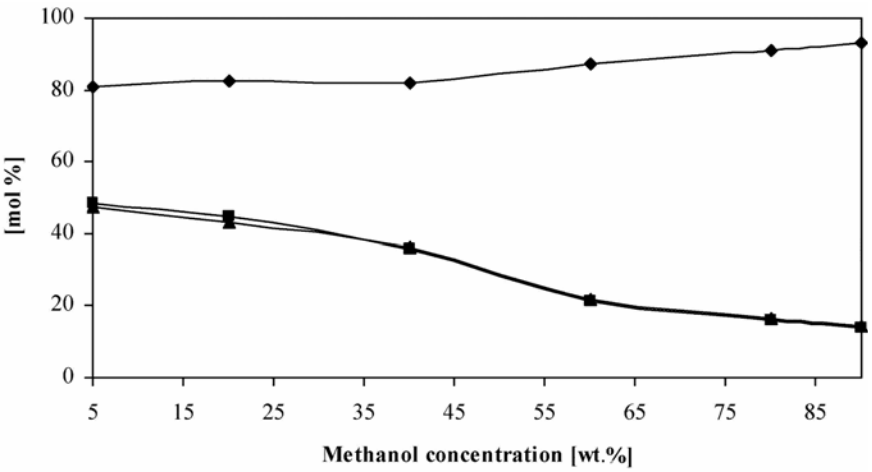


Fig. 3. Influence of solvent concentration on epoxidation of crotyl alcohol: ♦ – selectivity of transformation to 2,3-epoxybutane-1-ol in relation to CRA consumed ($S_{EB/CRA}$), ■ – conversion of crotyl alcohol (C_{CRA}), ▲– selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed (S_{org/H_2O_2})

Rys. 3. Wpływ stężenia metanolu na epoksydację CRA: ♦ – selektywność przemiany do EB w odniesieniu do przereagowanego CRA, ■ – konwersja CRA, ▲ – selektywność przemiany do związków organicznych w odniesieniu do przereagowanego H_2O_2

The influence of solvent (methanol) concentration was studied in the range 5–90 wt.%, at the temperature of 20°C and molar ratio of CRA/H_2O_2 = 1:1. All remaining parameters were the same as initial ones. It results from Fig. 3 that the increases in the solvent concentration causes an increase in the value of the selectivity of transformation to EB in relation to CRA consumed from 81 mol % (5 wt.%) to 93 mol % (90 wt.%). CRA conversion amounts 48 mol % (5 wt.%), and subsequently decreases to 14 mol % (90 wt.%). The selectivity of transformation to organic compounds in relation to H_2O_2 consumed changes in a similar way. At this stage of the investigations, methanol concentration equal 90 wt.% was found to be the most advantageous.

The effect of TS-2 catalyst concentration in the range 0.1–5 wt.% was studied at the temperature of 20°C, the molar ratio of CRA/H_2O_2 = 1:1, methanol concentration 90 wt.%, and for reaction time of 180 min. The selectivity of transformation to EB in relation to CRA consumed (Fig. 4) is constant and amounts to nearly 90 mol %. CRA conversion increases from 1 mol % (0.1 wt.%) to 26 mol % (5 wt.%). Elevation of catalyst concentration causes a decreases of the value of the selectivity of transformation to organic compounds in relation to H_2O_2 consumed from 1.5 mol % (1 wt.%) to 31 mol % (5 wt.%). Hence, the most advantageous concentration of the catalyst is 1 wt.%.

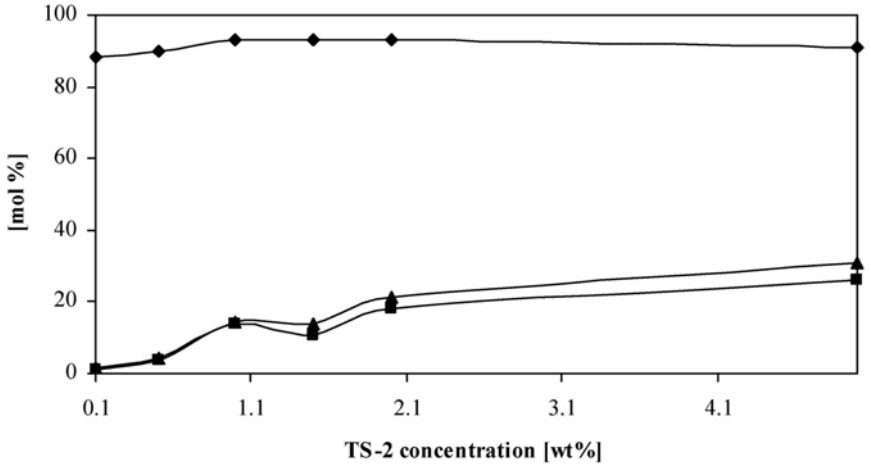


Fig. 4. Influence of TS-2 concentration on epoxidation of crotyl alcohol: ♦ – selectivity of transformation to 2,3-epoxybutane-1-ol in relation to CRA consumed ($S_{EB/CRA}$), ■ – conversion of crotyl alcohol (C_{CRA}), ▲ – selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed (S_{org/H_2O_2})

Rys. 4. Wpływ stężenia katalizatora TS-2 na epoksydację CRA: ♦ – selektywność przemiany do EB w odniesieniu do przereagowanego CRA, ■ – konwersja CRA, ▲ – selektywność przemiany do związków organicznych w odniesieniu do przereagowanego H_2O_2

The influence of the reaction time was investigated in the range 30 to 300 min. The remaining parameters corresponded to the values recognized as the most advantageous during the previous stages of studies. It results from analysis of Fig. 5 that prolongation of the reaction time from 30 to 300 min does not cause significant changes of the values of the

main function describing the process – selectivity of transformation to EB in relation to CRA consumed amounts to nearly 94 mol %, CRA conversion assumes a value of 13 mol %, and selectivity of transformation to organic compounds in relation to H_2O_2 consumed amounts to nearly 14 mol %. The by-product which was formed under these conditions is crotonic acid. Analysis of the results indicates that the most advantageous reaction time is 30 min.

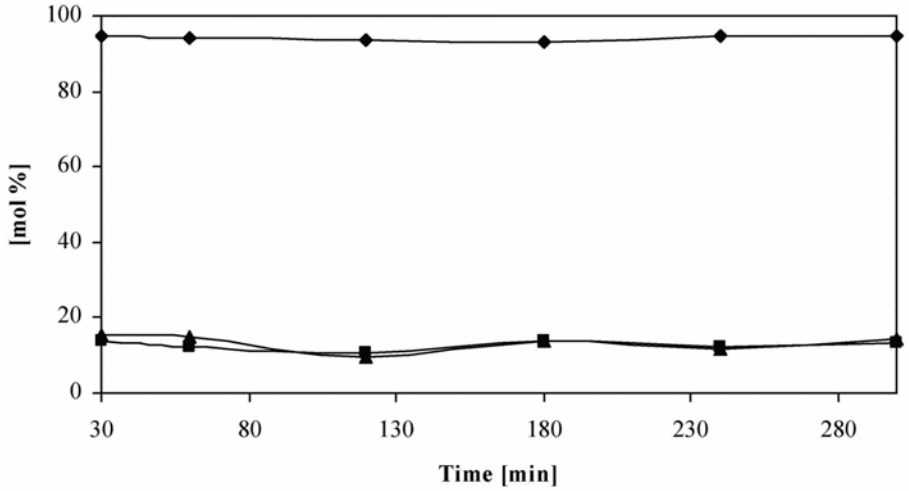


Fig. 5. Influence of reaction time on epoxidation of crotyl alcohol: ♦ – selectivity of transformation to 2,3-epoxybutane-1-ol in relation to CRA consumed ($S_{EB/CRA}$), ■ – conversion of crotyl alcohol (C_{CRA}), ▲ – selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed (S_{org/H_2O_2})

Rys. 5. Wpływ czasu reakcji na epoksydację CRA: ♦ – selektywność przemiany do EB w odniesieniu do przereagowanego CRA, ■ – konwersja CRA, ▲ – selektywność przemiany do związków organicznych w odniesieniu do przereagowanego H_2O_2

4. Conclusions

The studies presented in the paper allowed establishing the influence of the following technological parameters: temperature, molar ratio of CRA/H_2O_2, methanol concentration, catalyst concentration and the time of process duration on the course of CRA epoxidation over TS-2 catalyst. The obtained results demonstrate that epoxidation of CRA with a 30 wt.% hydrogen peroxide in the presence of methanol as a solvent over TS-2 catalyst proceed the most advantageous at a temperature of 20°C, molar ratio of CRA/H_2O_2 = 1:1, methanol concentration 90 wt.%, catalyst concentration 1 wt.% and reaction time 30 min. These are relatively mild reaction conditions and they do not require high energy expenditure. The amount of the by-products is very small – the epoxide is obtained with selectivity of 94 mol %, and these by-products can by separated and recycled. Hence, the described process is practically a waste-free technology and fulfills the requirements of modern organic chemical technology.

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