

Isolation of 1,2-epoxybutane-3-ol and 2,3-epoxybutane-1-ol from post-reaction mixtures

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Attempts were made to isolate 1,2-epoxybutane-3-ol and 2,3-epoxybutane-1-ol from post-reaction mixtures left after the epoxidation of 1-butene-3-ol and 2-butene-1-ol with hydrogen peroxide by thin film distillation. From the raw mixture containing about 8.3 wt% of the epoxide at the first stage the concentration of epoxide is increased to 32 wt%. At the second stage of distillation the epoxide fraction is concentrated to about 76 wt%. After the third stage of thin film distillation the epoxide fraction of 99.6% purity can be obtained. The concentration of this fraction by azeotropic distillation with n-propanol as an azeotropic agent permits obtaining epoxide of 99.6 wt% purity.

Keywords: thin film distillation, isolation of epoxides.

INTRODUCTION

Epoxidation of 1-butene-3-ol (1B3O) and 2-butene-1-ol (crotyl alcohol – AKR) with hydrogen peroxide over titanium-silicalite catalysts leads to epoxides (1,2-epoxybutane-3-ol and 2,3-epoxybutane-1-ol). Because of a wide range of applications of these epoxides, this method has become of great interest. It has some attractive advantages such as mild conditions of the process, the use of cheap oxidizing agent (H_2O_2) and production of small amounts of by-products. The success of the technology of obtaining 1,2-epoxybutane-3-ol and 2,3-epoxybutane-1-ol by the epoxidation over titanium-silicalite catalyst depends on the effectiveness of the isolation of the epoxides from the post-reaction mixture. When rectification is applied, the epoxy ring undergoes hydration and solvolysis. Moreover, the concentration of the epoxides in the post-reaction mixture is relatively low (up to 10 wt%). For this reason, the method applied to isolate epoxides was thin film distillation¹⁻². The method permits fast concentration of the post-reaction mixture in mild conditions, with no risk of hydrolysis and solvolysis of the epoxy ring. The contact of the raw mixture with the heater is relatively short and the short distance between the evaporating surface and the liquefying surface ensures fast mass exchange³⁻⁸.

EXPERIMENTAL

The isolation of 1,2-epoxybutane-3-ol and 2,3-epoxybutane-1-ol was performed on the Rotafilm LG 50 type apparatus – its scheme is given in Figure 1. The raw mixture flows at a constant rate over the heating surface (11) forming a thin film on it. On the surface cooled with water (12) the evaporated particles get condensed and the distillate formed is collected in the receiver (5) making the so-called water fraction. The distillation tails in the form of the so-called epoxide fraction is collected in a box receiver (6). The vapours of the components that were liquefied are passed to a cold-finger condenser (8) and after the condensation are collected in receiver (7) as the so-called methanol fraction.

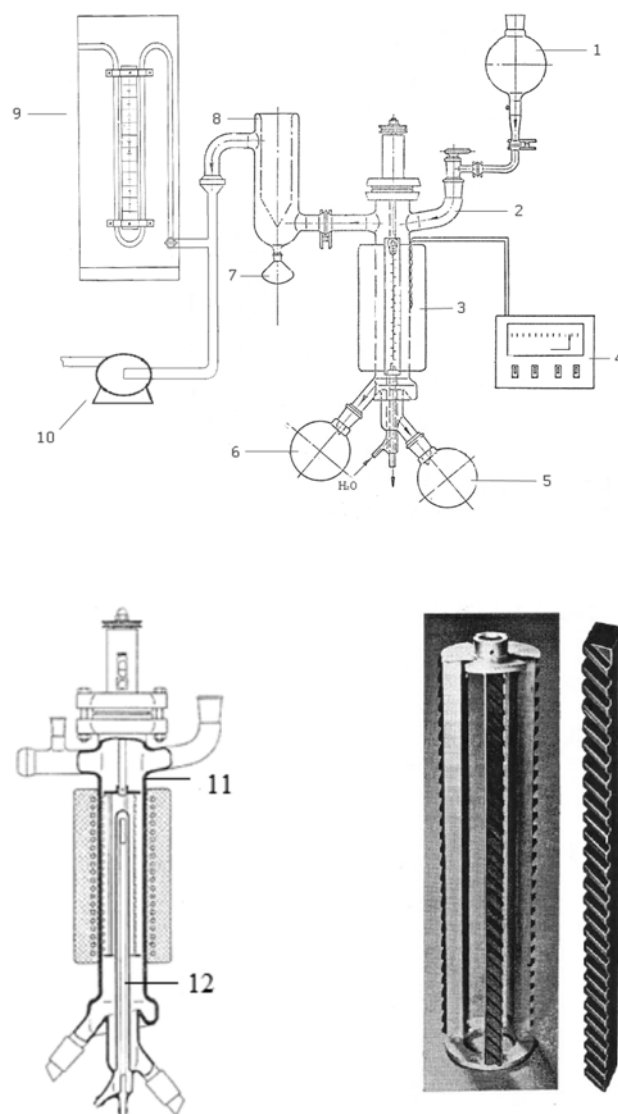


Figure 1. Apparatus for thin film distillation (film distillation) – Rotafilm LG 50 type and the cross section showing the rotor and the spreader liner: 1 – container with the raw material for distillation, 2 – elbow connecting container and evaporator, 3 – heating mantle, 4 – panel controlling temperature, vacuum, turnovers of rotor, 5 – distillate receiver, 6 – tail box receiver, 7 – light ends receiver, 8 – cold-finger condenser, 9 – manometer, 10 – vacuum pump, 11 – heating surface, 12 – cooling surface

RESULTS AND DISCUSSION

At the first stage of the experiment, isolation of 1,2-epoxybutane-3-ol from the post-reaction mixture was studied. To establish the optimum conditions of isolation, the standard mixture of the following composition was used [in wt%]: 8.3 glycidol, 1.1 1B3O, 80.0 CH₃OH and 10.6 H₂O. The composition of the mixture corresponded to that of the post-reaction mixture obtained after the epoxidation of 1B3O in the optimum conditions. Glycidol was used instead of 1,2-epoxybutane-3-ol because of its similarity in physico-chemical properties and commercial availability. Both compounds glycidol and 1,2-epoxybutane-3-ol are oxides of similar structure. The boiling point of glycidol (165°C) is only by a few degrees lower than that of 1,2-epoxybutane-3-ol. In view of the above it was assumed that the parameters of distillation of glycidol are close to those that could be used for the isolation of 1,2-epoxybutane-3-ol and 2,3-epoxybutane-1-ol.

At the first stage of concentration, the influence of temperature, the rate of raw mixture supply and the pressure on the efficiency of glycidol isolation from the standard mixture was checked. The distillation was performed at 100°C, 130°C and 150°C, under the pressure of 220 mmHg and at the rate flow of the raw mixture of 7 cm³ min⁻¹. The influence of temperature on the concentrations of glycidol in individual fractions is illustrated by the data given in Table 1. According to the results, the effect of temperature on the efficiency of glycidol isolation is significant. With increasing the temperature the rate of evaporation increases, leading to a reduction of the epoxide fraction received (tail), so increasing the temperature brought the consequences contrary to the desired effect, lower amount of glycidol and its lower concentration in the epoxide fraction. The raw mixture supply at the rate

of about 7 cm³ min⁻¹ also proved inadequate as the mixture was kept for too long time at elevated temperature. The maximum concentration of glycidol of 30 wt% was obtained at 100°C.

The influence of pressure changed in the range 220 – 340 mmHg was studied at 100°C and at the rate of flow of the raw mixture of about 7 cm³ min⁻¹. The results are presented in Table 2. Pressure changes in the range 220 – 340 mmHg at 100°C and raw mixture flow rate of 7 cm³ min⁻¹ had little influence on the efficiency of glycidol isolation. The maximum of its concentration about 30 wt% was obtained at 250 mmHg.

The influence of the rate of supply of the raw mixture was studied for three rates of 7, 13 and 17 cm³ min⁻¹ at three temperatures 100°C, 130°C, 150°C under the pressure of 220 mmHg. The results are presented in Tables 3, 4 and 5. The increase in the rate of the supply of the raw mixture to 13 cm³ min⁻¹ at 100°C leads to a decrease in the glycidol concentration in the epoxide fraction (to 19.7 wt%) and in the water fraction (to 2 wt%). This result could be a consequence of slower water and methanol evaporation. At the supply rate of 7 cm³ min⁻¹ water and methanol evaporated faster and were collected in the water fraction. The maximum concentration of glycidol of about 30 wt% was obtained in the epoxide fraction for the process performed at 100°C and at the raw mixture supply rate of 7 cm³ min⁻¹.

At 130°C and under the pressure of 220 mmHg the most effective isolation of glycidol was obtained at the rate of supply of the raw mixture of 13 cm³ min⁻¹. The composition of the epoxide fraction was [in wt%]: 32.2 glycidol, 46.2 methanol, 1.8 1B3O and 19.8 H₂O.

When the process was performed at 150°C under 220 mmHg and at the rate of supply of 13 cm³ min⁻¹, the

Table 1. The influence of temperature on the amount of individual fractions, content and concentration of glycidol in the fractions (pressure 220 mmHg, rate of raw mixture supply 7 cm³ min⁻¹)

Temp	Fraction		
°C	Epoxide 1) Amount of fraction/ amount of glycidol, g 2) Concentration of glycidol, wt%	Water 1) Amount of fraction/ amount of glycidol, g 2) Concentration of glycidol, wt%	Methanol 1) Amount of fraction/ amount of glycidol, g 2) Concentration of glycidol, wt%
100	88.0/ 26.4 30.0	187.5/ 6.4 3.4	119.8/ 0.2 0.2
130	13.5/ 2.6 19.1	196.1/ 29.8 15.2	181.7/ 0.7 0.4
150	2.3/ 0.5 23.2	213.5/ 32.0 15.0	175.5/ 0.5 0.3

Table 2. The influence of pressure on the amount of individual fractions, amount of glycidol and its concentration in the fractions (100°C, rate of raw mixture supply 7 cm³ min⁻¹)

Pressure	Fractions		
mmHg	Epoxide Amount of fraction/ amount of glycidol, g Concentration of glycidol, wt%	Water Amount of fraction/ amount of glycidol, g Concentration of glycidol, wt%	Methanol Amount of fraction/ amount of glycidol, g Concentration of glycidol, wt%
220	88.0/ 26.4 30.0	187.5/ 6.4 3.4	119.8/ 0.2 0.2
250	92.4/ 27.4 29.7	185.5/ 5.6 3.0	98.0/ 0.1 0.1
280	105.2/ 29.0 27.6	177.4/ 3.9 2.2	113.8/ 0.1 0.1
310	91.4/ 27.6 30.2	215.6/ 5.4 2.5	90.35/ 0.1 0.1
340	93.8/ 27.5 29.3	290.1/ 5.8 2.0	14.3/ 0.04 0.3

Table 3. The influence of the rate of supply of the raw mixture on the amounts of fractions, amount and concentration of glycidol in the fractions (100°C, 220 mmHg)

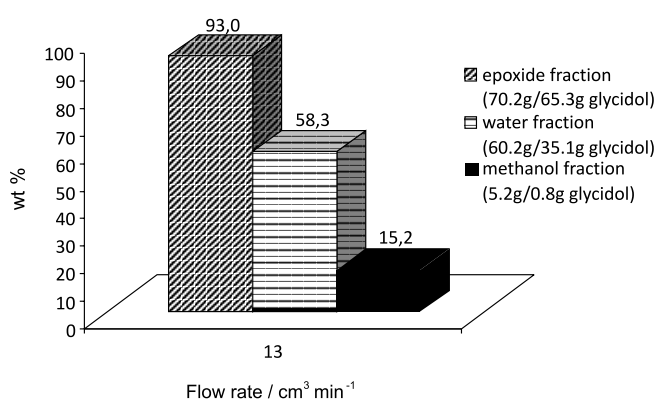
Rate of supply	Fraction		
cm ³ min ⁻¹	Epoxide Amount of fraction/ amount of glycidol, g Concentration of glycidol, wt%	Water Amount of fraction/ amount of glycidol, g Concentration of glycidol, wt%	Methanol Amount of fraction/ amount of glycidol, g Concentration of glycidol, wt%
13	158.7/ 31.3 19.7	103.3/ 2.1 2.0	132.6/ 0.0 0.0
7	88.0/26.4 30.0	187.5/6.4 3.4	119.8/0.2 0.2

composition of the epoxy fraction was [in wt%]: 33.1 glycidol, 45.3 methanol, 1.8 1B3O and 19.8 H₂O. The results were similar to those obtained under the same pressure at the same rate of supply but at 130°C.

At the second stage of the experiment we used the raw mixture for the distillation of the following composition [in wt%]: 32.7 glycidol, 45.7 CH₃OH, 1.9 1B3O and 19.7 H₂O. Measurements were made in the conditions established as optimum in the first stage, i.e. at 130°C or 150°C, under the pressure of 220 mmHg and at the rate of raw mixture supply of about 13 cm³ min⁻¹. The results are presented in Table 6. The influence of temperature on the efficiency of glycidol isolation from the raw mixture of the concentration of 32.7 wt% is significant. With the increased temperature the concentration of glycidol in the epoxy fraction increased as it did in the water fraction. Further investigation was carried out at 150°C, despite a greater loss of glycidol as a result of its collection in the water fraction. At this temperature a lower concentration of water was obtained in the epoxy fraction.

At the third stage of distillation, the raw mixture for distillation was composed of [in wt%]: 75.8 glycidol, 7.7 CH₃OH, 0.3 1B3O and 16.2 H₂O. The process of distillation was performed at 150°C, under 220 mmHg and at the rate of raw mixture supply of 13 cm³ min⁻¹. The results are presented in Figure 2. As a result of the distillation of the raw mixture of the above composition and in the above conditions, the concentration of glycidol in the epoxide fraction reached 93 wt%, although the concentration of glycidol in the water fraction was also considerable and amounted to 58.3 wt%.

The 93 wt% solution of glycidol was concentrated by column rectification under atmospheric pressure and later under reduced pressure. Prior to the distillation, n-propanol as an azeotropic agent was added and the mixture had the following composition [in wt%]: 93 glycidol, 4.8 CH₃OH, 0.2 1B3O and 2.0 H₂O. The azeotrope of n-propanol with water has a boiling point of 87°C under

**Figure 2.** Concentration of glycidol after the third stage of concentration, conditions: 150°C, 220 mmHg and rate of supply 13 cm³ min⁻¹

atmospheric pressure and it contains 28.3 wt% of water. As a result of rectification glycidol concentration was increased to 99.6 wt% (boiling point 76°C at 14 mmHg).

For the isolation of 1,2-epoxybutane-3-ol we used 800g of the mixture composed of [in wt%]: 8.3 1,2EB3, 1.1 1B3O, 80.0 CH₃OH and 10.6 H₂O, obtained as a result of epoxidation of 1B3O at 20°C, at the 1: 1 molar ratio of 1B3O/H₂O₂, 80 wt% methanol concentration, 3 wt% concentration of TS-1 catalyst, after 3 hours. The compound 1,2-epoxybutane-3-ol was produced at the selectivity of 100% mol, at 1B3O conversion of 84 mol% and H₂O₂ conversion of 98 mol%. The distillation was performed in the optimum conditions of the separation of the glycidol mixture, i.e. 130°C at the first stage, 150°C at subsequent stages, 220 mmHg and rate of supply of 13 cm³ min⁻¹. At the first stage from the raw mixture containing 8.3 wt% of 1,2-epoxybutane-3-ol the obtained epoxide fraction (not undergoing evaporation) contained about 33.0 wt% of 1,2-epoxybutane-3-ol. At the second stage the concentration of this compound was increased to 76.1 wt% and at the third to 93.4 wt%. Finally as a result of

Table 4. The influence of rate of supply of the raw mixture on the amounts of fractions and concentration of glycidol in the fractions (130°C, 220 mmHg)

Rate of supply	Fraction		
cm ³ min ⁻¹	Epoxide Amount of fraction/ amount of glycidol, g Concentration of glycidol, wt%	Water Amount of fraction/ amount of glycidol, g Concentration of glycidol, wt%	Methanol Amount of fraction/ amount of glycidol, g Concentration of glycidol, wt%
17	164.9/ 31.7 19.2	109.2/ 1.5 1.4	110.0/ 0.1 0.1
13	90.3/ 29.1 32.2	121.1/ 3.0 2.5	166.2/ 0.8 0.5
7	13.5/ 2.6 19.1	196.1/ 29.4 15.0	181.7/ 0.7 0.4

Table 5. The influence of the rate of supply of the raw mixture on the amounts of fractions and concentration of glycidol in the fractions (150°C, 220 mmHg)

Rate of supply	Fraction		
cm ³ min ⁻¹	Epoxide Amount of fraction/ amount of glycidol, g Concentration of glycidol, wt%	Water Amount of fraction/ amount of glycidol, g Concentration of glycidol, wt%	Methanol Amount of fraction/ amount of glycidol, g Concentration of glycidol, wt%
13	84.7/ 28.0 33.1	101.2/ 4.1 4.1	155.5/ 1.1 0.7
7	2.3/ 0.5 23.2	213.5/ 32.0 15.0	175.5/ 0.5 0.3

Table 6. The influence of temperature on the amounts of fractions, amount and concentration of glycidol in the fractions after the second separation (220 mmHg, rate of supply of 13 cm³ min⁻¹)

Temperature	Fraction		
°C	Epoxide Amount of fraction/ amount of glycidol, g Concentration of glycidol, wt%	Water Amount of fraction/ amount of glycidol, g Concentration of glycidol, wt%	Methanol Amount of fraction/ amount of glycidol, g Concentration of glycidol, wt%
130	192.5/ 120.1 62.4	117.0/ 10.2 8.7	88.4/ 1.7 1.9
150	146.8/ 111.3 75.8	125.5/ 18.0 14.3	122.9/ 3.1 2.5

the column rectification in the presence of n-propanol the concentration of 1,2-epoxybutane-3-ol was 99.6 wt% (boiling point $t_w=70^\circ\text{C}$ at 28 mmHg). Similar results were obtained for the distillation of the post-reaction mixture with 2,3-epoxybutane-1-ol.

CONCLUSIONS

Isolation of 1,2-epoxybutane-3-ol and 2,3-epoxybutane-1-ol from the post-reaction mixtures after the epoxidation of 1B3O and AKR has been found similarly effective as that of glycidol from its model solution. From the raw mixture containing about 8.3 wt% of the epoxide at the first stage the concentration of this compound is increased to 32 wt%. The optimum conditions of this stage are: temperature of 130°C, pressure of 220mmHg and the raw mixture supply rate of 13cm³min⁻¹. At the second stage of distillation the epoxide fraction is concentrated to about 76 wt%. The optimum conditions of this stage are: temperature of 150°C, pressure of 220 mmHg and raw mixture supply rate of 13cm³min⁻¹. At the third stage in the same conditions the epoxide fraction is concentrated to 93 wt%. Finally, the concentration of this fraction by azeotropic distillation permits obtaining each of the epoxides studied in the concentration of 99.6 wt%.

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