

Optimization of the epoxidation process of (1Z,5E,9E)-1,5,9-cyclododecatriene to 1,2-epoxy-(5Z,9E)-5,9-cyclododecadiene with *tert*-butyl hydroperoxide – the influence of technological parameters on the hydroperoxide conversion

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The optimization studies of the epoxidation process of (1Z,5E,9E)-1,5,9-cyclododecatriene (CDT) with *tert*-butyl hydroperoxide (TBHP) over the molybdenum catalyst Mo(CO)₆ were performed. The reaction was examined in terms of a uniform-rotatable design. Three factors were analyzed: the reaction time, CDT:TBHP molar ratio, and the molar concentration of the catalyst (Mo(CO)₆). According to the design 20 experiments were performed at the constant temperature of 70°C.

Keywords: epoxidation, *tert*-butyl hydroperoxide, (1Z,5E,9E)-1,5,9-cyclododecatriene, 1,2-epoxy-(5Z,9E)-5,9-cyclododecadiene, design of experiments, optimization.

Presented at VII Conference Wasteless Technologies and Waste Management in Chemical Industry and Agriculture, Międzyzdroje, 12 – 15 June, 2007.

INTRODUCTION

Epoxides are a universal group of compounds used in laboratory and industrial syntheses of a wide range of chemical products such as: synthetic resins and fibers, surfactants, paints, adhesives, diluents of reactions, surface-active agents and many bioactive substances¹. Terminal epoxides (1-epoxides) are especially important for preparing bulk chemicals, while the more substituted epoxides are useful in the synthesis of structurally more complicated fine chemicals.

The most beneficial method of obtaining epoxides is direct epoxidation of olefins. Considering the necessity of effective atom technology, that is included in green chemistry rules², the procedure of epoxidation of olefins must be highly efficient and selective without any side products. In laboratory and industrial practice, various oxidants are used, but their applications are often limited because of the formation of a large amount of waste and their complicated and expensive syntheses. The type of the catalyst is also important. The commercial success of the catalytic epoxidation of propene with *tert*-butyl and ethyl-benzene hydroperoxides in the presence of the relatively cheap and readily available molybdenum catalysts, caused that the studies on the epoxidation of other olefins with hydroperoxides are still continued³.

From an economic perspective, it is very important to receive the high degree of conversion of substrates: (1Z,5E,9E)-1,5,9-cyclododecatriene and *tert*-butyl hydroperoxide. It is known that the mathematical design can help in establishing the best conditions of syntheses. The experimental design identifies the factors that may affect the result of an experiment and uses the statistical analysis to separate the effects of different factors⁴.

In this paper we report our results of the optimization studies of the epoxidation process of CDT with TBHP in 1,2-dichloroethane to 1,2-epoxy-(5Z,9E)-5,9-cyclododecadiene (ECDD). The studies were provided over the most common catalyst of the epoxidation – molybdenum hexacarbonyl Mo(CO)₆.

EXPERIMENTAL

Raw materials

Tert-butyl hydroperoxide in 1,2-dichloroethane was prepared in laboratory, (1Z,5E,9E)-1,5,9-cyclododecatriene 98% from Fluka, and molybdenum hexacarbonyl, Mo(CO)₆, pure from Merck-Schuchardt, were used in the experiments. Moreover, the analysis of the reaction mixture was performed using potassium iodide, sodium thiosulfate, isopropyl alcohol all analytically pure, produced by POCh Gliwice, Poland; glacial acetic acid-made by ZCh Oświęcim; dodecane 99% – Aldrich. All reagents were used without additional purification.

Method of measurement

Epoxidation of CDT with TBHP under the conditions without pressure was performed in the apparatus, the scheme of which is given in Fig. 1.

The proper amounts of CDT and the Mo(CO)₆ catalyst were introduced into the three-neck flask (1) (capacity 25cm³) equipped with a reflux condenser (2), dropping funnel (3), thermometer (4) and a mechanic stirrer (5). The proper amount of TBHP was placed in the dropping funnel. The flask was plunged in the open circulating bath (6) that maintained a constant temperature. After reaching the desired temperature in the flask, the TBHP was dozed dropwise. The rate of the addition drop by drop was controlled so as not to introduce too high changes of the temperature (max ±3°C). After ending the reaction, the product was quickly cooled to the ambient temperature in order to stop the reaction. The product was analyzed and for each experiment the mass balance and the conversion degree of TBHP were calculated.

Analytical method

The concentration of TBHP was determined by iodometric titration.

The concentrations of TBHP, CDT and ECDD were determined by the GC method. The chromatographic analyses were performed on the Trace GC 2000 Thermo-Finigan chromatograph, with the flame ionization detector, equipped with the computer system of collecting and

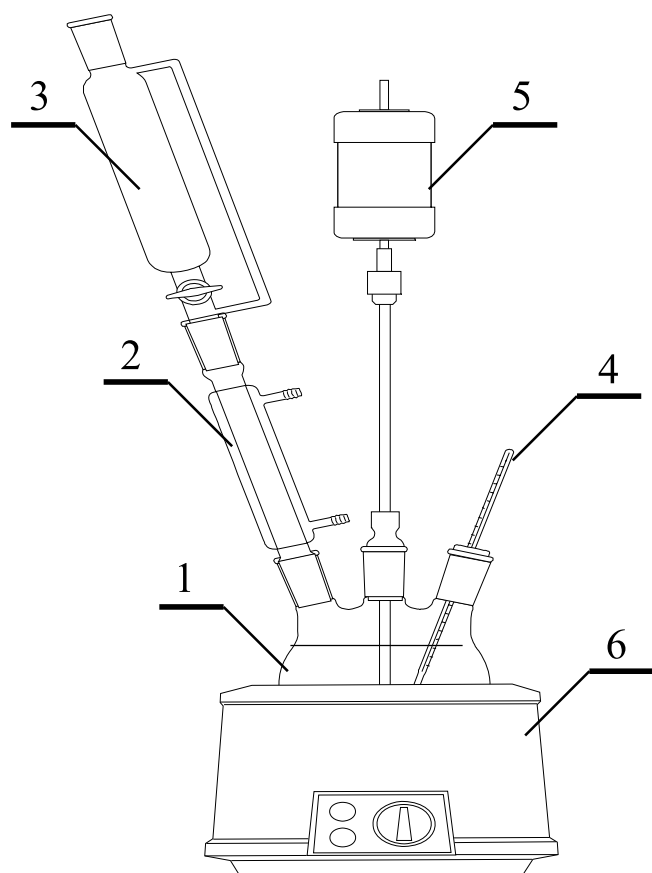


Figure 1. The scheme of the apparatus for epoxidation of CDT

interpreting the data. The following conditions were used: capillary column J&W Scientific 30mx0,25mm; the temperature of the detector – 250°C, the temperature of the injector was maintained at 200°C. The analysis was performed with the application of the programmed temperature: 2,5 min isothermally at 50°C, the increase of the temperature to 250°C with the rate of 20°C/min; 2.5 min isothermally at 250°C. The best conditions were achieved with the programmed pressure of the carrier gas (helium): 75kPa (start, time 0min); the increase of the pressure to 140kPa with the rate 5kPa/min; 140kPa isobarically for 2 min. The flows of the gases were as follows: air 350cm³/min, hydrogen 35cm³/min, the carrier gas (helium) 0.7cm³/min.

The identification of the peak on the chromatograms was performed on the bases of retention times of the standards. The additional confirmation of assigning the peak on the chromatograms was made by adding the standard method. The quantitative determination of the composition of the post-reaction mixture was made with the help of the internal standard method, with dodecane. The percentages of the determined components were calculated from the equation:

$$\%mas_i = f_i \frac{A_i}{A_w} \frac{m_w}{m_{pr}} \times 100$$

where:

f_i – the correction coefficient of the determined component; A_i – the surface of the peak of the determined component; A_w – the surface of the peak of the standard; m_w – the mass of the standard added to the sample; m_{pr} – the mass of the analyzed sample.

Table 1. The design matrix in the coded variables

Number of experiment	Molar ratio CDT/TBHP	Molar concentration of Mo(CO) ₆	Time
	X ₁	X ₂	X ₃
1	-1	-1	-1
2	1	-1	-1
3	-1	1	-1
4	1	1	-1
5	-1	-1	1
6	1	-1	1
7	-1	1	1
8	1	1	1
9	-2	0	0
10	2	0	0
11	0	-2	0
12	0	2	0
13	0	0	-2
14	0	0	2
15	0	0	0
16	0	0	0
17	0	0	0
18	0	0	0
19	0	0	0
20	0	0	0

The studies were performed according to the uniform-rotatable design. Three factors were analyzed: the reaction time, CDT:TBHP molar ratio, and the molar concentration of the catalyst (Mo(CO)₆). According to the design 20 experiments were performed (Table 1). The studies were performed at the temperature of 70°C.

In Table 2 the values of the natural and coded independent factors have been demonstrated.

Table 2. The natural and coded values of independent factors

Coded factor	Natural factor		
	X ₁ , CDT/TBHP [mol/mol]	X ₂ , Mo(CO) ₆ concentration [mol/dm ³]	X ₃ , time [min]
-1,6818	1	1·10 ⁻⁴	20
-1	1,81	2,82·10 ⁻⁴	40
0	3	5,5·10 ⁻⁴	70
1	4,19	8,18·10 ⁻⁴	100
1,6818	5	1·10 ⁻³	120

RESULT AND DISCUSSION

The studies demonstrate a considerable influence of all the analyzed factors on the conversion of TBHP. An increase of the molar ratio of CDT:TBHP, molar concentration of the catalyst in reaction and the time causes an increase in the conversion of TBHP.

At a fixed optimum the CDT:TBHP molar ratio a significant influence of the other parameters was seen. TBHP conversion was maximum at the molar concentration of the catalyst of 0.0004 ÷ 0.0010 mol/dm³, conducting the reaction for 55 ÷ 110min. The influence of the reaction time and the molar concentration of the catalyst at a fixed optimum molar ratio of CDT:TBHP was shown in Fig. 2.

At a fixed optimum of the molar concentration of the catalyst a similar influence of the other factors was observed (Fig 3.). The maximum conversion of TBHP is achieved at the wide range of the changes of the CDT:TBHP molar ratio (2:1 ÷ 5:1), conducting the reaction within the time not shorter than 55 min.

At the optimal reaction time, an increase of the molar ratio of CDT:TBHP above 2.2:1 does not cause a significant change of the TBHP conversion, because this conversion amounts to 100%. The optimal molar concentration

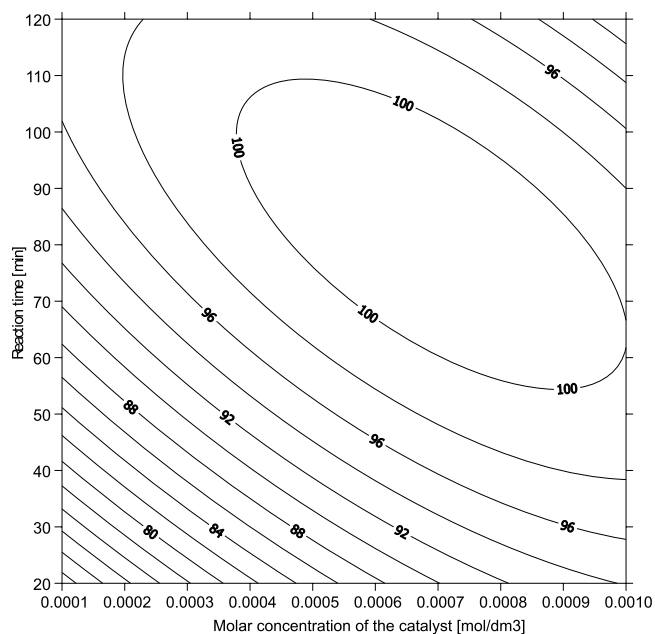


Figure 2. The degree of the TBHP conversion at the fixed optimum CDT:TBHP=4,2:1 molar ratio in relation to the molar concentration of the catalyst and the reaction time

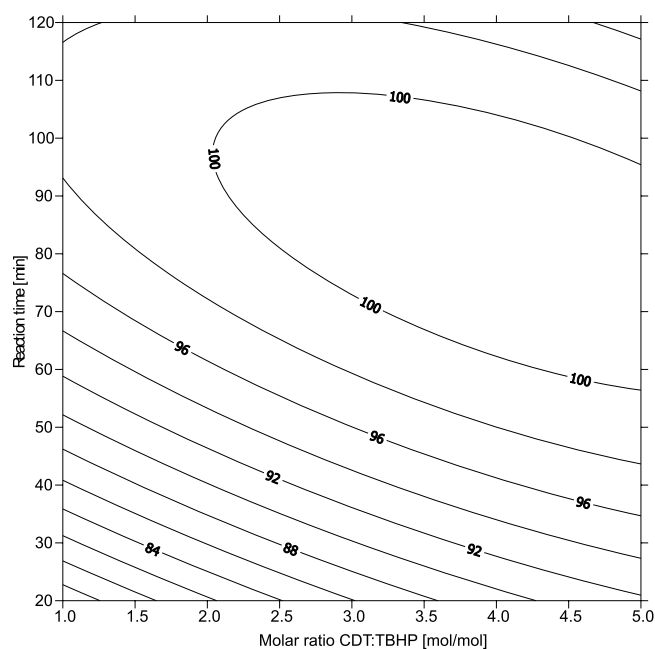


Figure 3. The degree of the TBHP conversion at the fixed optimum molar concentration of the $\text{Mo}(\text{CO})_6$ $0,0007 \text{ mol/dm}^3$ in relation to the CDT:TBHP molar ratio and the reaction time

of the catalyst reaches $0.00045 \div 0.00095 \text{ mol/dm}^3$. The influence of the molar ratio of CDT:TBHP and the molar concentration of the catalyst at the fixed reaction time was shown in Fig. 4.

CONCLUSIONS

The application of the mathematical methods of optimization allowed presenting in the form of a mathematical function the relation between the results of the reaction and the conditions of conducting the reaction. The maximum of the TBHP conversion was achieved at a molar ratio of CDT:TBHP above 2.2, at a molar concentration of the catalyst range of $0.00045 \div 0.00095 \text{ mol/dm}^3$, and at the reaction time not shorter than 55 min.

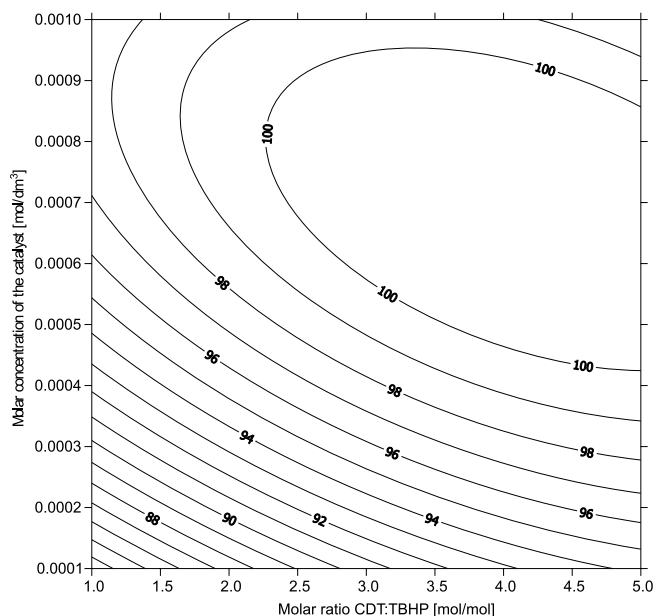


Figure 4. The degree of the TBHP conversion at the fixed optimum reaction time 82 min in relation to the molar concentration of the $\text{Mo}(\text{CO})_6$ and the CDT:TBHP molar ratio

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