

Epoxidation of 1,5,9-cyclododecatriene with H_2O_2 in the presence of tungstophosphoric acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$)

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The influence of the technological parameters on the epoxidation of 1,5,9-cyclododecatriene (CDT) to 1,2-epoxy-5,9-cyclododecadiene (ECDD) by the phase-transfer catalysis method (PTC) in the presence of tungstophosphoric heteropolyacid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) and hydrogen peroxide as the oxidizing agent has been presented. The phase-transfer catalyst was Aliquat® 336 (methyltriocetylammmonium chloride). The epoxidation of CDT to ECDD in the PTC system proceed under the relatively mild condition: low temperature, lack of solvent, short reaction time.

The effect of: the mixing velocity, the molar ratio of $\text{CDT}:\text{H}_2\text{O}_2$ and $\text{H}_2\text{O}_2:\text{H}_3\text{PW}_{12}\text{O}_{40}$, the nature of the solvent and its concentration, was studied. The most advantageous technological parameters were: the mixing rate 400 – 600 rpm, the molar ratio of $\text{CDT}:\text{H}_2\text{O}_2 = 3:1 - 1.5:1$, the molar ratio of $\text{H}_2\text{O}_2:\text{H}_3\text{PW}_{12}\text{O}_{40} = 200:1 - 400:1$, the temperature 40 – 50°C, solvent: dichloromethane or lack of the solvent, dichloromethane concentration: 10 – 50 vol%, reaction time 35 – 50 min. The application of the above-mentioned parameters allows to achieve the yield of 44 – 47% ECDD in relation to introduced CDT.

Keywords: phase-transfer catalysis, epoxidation, hydrogen peroxide, heteropolyacids, 1,5,9-cyclododecatriene.

INTRODUCTION

1,2-epoxy-5,9-cyclododecatriene (ECDD) is a valuable intermediate with regard to the presence of two double bonds and the oxirane ring. This compound is used in the production of polymer components of paints and adhesives¹. As a result of catalytic hydrogenation of the double bonds epoxycyclododecene and epoxycyclododecane are obtained. Epoxycyclododecane is utilized in the vulcanization process of special rubber and is oxidized to cyclododecanone. Cyclododecanone is converted to lactame, lactone and dicarboxylic acids.

New epoxidation methods rely on the application of the phase-transfer catalysis (PTC).

In the process of this type a heterogeneous system of two liquid phases occurs. One phase constitutes an aqueous solution of an inorganic reagent and a parent phase-transfer catalyst, the other constitutes an organic reactant, often in a solvent². The PTC is mostly utilized in the production of pharmaceutical agents e.g. penicillin, alkoxyipyridazine, and pesticides such as: pyrethroids (fenvalerate, cypermethrin and their different analogies)³.

A significant advantage resulting from the application of the PTC in the epoxidation processes is a high yield and the selectivity of transformation to epoxide and product stability resulting from the lack of contact with acid aqueous phase. Owing to a high activity of PTC system the epoxidation processes can be carried out under mild conditions with the application of diluted solutions of hydrogen peroxide. The epoxidation of olefins with hydrogen peroxide is commonly known. Several processes of epoxidation of CDT to ECDD have been described, however, the majority of them are characterized by a low yield of the desired product or hazardous and toxic reagents are used in these processes. A process of monoepoxidation CDT with hydrogen peroxide in the presence of formic acid was developed⁴. A fundamental drawback of this process is a low yield of ECDD in relation to the introduced hydrogen peroxide as well as to

CDT. The monoepoxidation of CDT with hydrogen peroxide in the presence of selenium dioxide, selenium acid or alkyltrioxoselenium ether as the catalysts and a 90% solution of hydrogen peroxide in the presence of tungstic acid as a catalyst⁵. In the case of toxic compounds of selenium, a long reaction time is required. The low yields of ECDD were obtained in the presence of tungstic acid, moreover the application of the concentrated solution of hydrogen peroxide created a problem with assurance of the safety condition of the reaction.

An interesting method of the ECDD synthesis relies on the epoxidation of CDT with hydrogen peroxide in the presence of sodium tungstate, quaternary onium salt and mineral acid (H_3PO_4)⁶⁻⁸. However, the process proceeds with too low selectivity. Moreover the second and third double bond in CDT also undergoes the epoxidation.

The most advantageous seems to be the epoxidation of CDT with hydrogen peroxide in the presence of tungstophosphoric acid – $\text{H}_3\text{PW}_{12}\text{O}_{40}$ as the catalyst and methyltriocetylammmonium chloride as the phase-transfer catalyst⁹. In the described multi-stage continuous oxidation apparatus at the temperature of 75°C and after the reaction time of 6.5 h, the ECDD was obtained with the selectivity of 91.2% in relation to the consumed CDT. However, the ECDD yield in relation to the introduced CDT was too low – 19.6 mol%.

In this paper the results of the studies on the influence of the technological parameters on the epoxidation of CDT to ECDD with 30% H_2O_2 in the PTC system, with the application of a significantly less complex reaction system were presented.

EXPERIMENTAL

Reagents

(*Z,E,E*)-1,5,9-cyclododecatriene, 98%, from Aldrich, hydrogen peroxide, 30%, reagent grade, produced by POCh, Gliwice, tungstophosphoric acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$),

from Fluka and methyltrioctylammonium chloride (Aliquat® 336) and dodecane (internal standard), $\geq 99\%$, both from Aldrich were used in the experiments. As the solvents: chloroform, dichloromethane, 1,2-dichloroethane, toluene, cyclohexane, heptane, and pentane – all reagent grade, produced by POCh, Gliwice, were used.

Epoxidation procedure

The epoxidation was carried out periodically, in a three-necked flask (capacity of 25 cm³), immersed in an oil bath with controlled temperature. A proper amount of heteropolyacid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) and 30% H_2O_2 was introduced into the reactor. The content was heated to reach the reaction temperature and was mixed at this temperature for 30 min. After the introduction of Aliquat® 336, the mixing was continued for 30 min, and a mixture of CDT and the internal standard (dodecane) was then added. From this moment, the samples of the reaction mixture were taken every 15 min. The analysis of the process was performed based on the ECDD yield, calculated as the amount obtained ECDD in relation to CDT introduced into the reactor.

Analytical methods

The samples of the reaction mixture were analysed by means of a gas chromatograph (TRACE 2000 GC, Thermo Finigan) with a flame-ionization detector (FID). The following conditions of determinations were used: a DB-5 capillary column of J&W Scientific, 30 m \times 0,25 mm \times 0,25 μm ; a detector temperature of 250°C, a sample chamber temperature of 200°C. The analysis were performed using a programmed temperature gradient: 2.5 min isothermally at the temperature of 50°C, the temperature increase to 250°C at the rate of 20°C/min; 2.5 min isothermally at temperature of 250°C. The most favourable conditions of the separation of the determined compounds were achieved with a simultaneous application of a programmed increase of carrier gas (helium) pressure: 75 kPa (start); increase of pressure to 140 kPa at the rate of 5 kPa/min, 140 kPa isobaric for 2 min. The quantitative determinations of the components in the post-reaction mixtures were performed by an internal standard method using dodecane. The concentration of hydrogen peroxide was determined by an iodometric method.

RESULTS AND DISCUSSION

The epoxidation of CDT with hydrogen peroxide was carried out by the PTC method in the liquid-liquid system. The mechanism of CDT epoxidation is in agreement with the general mechanism of olefine epoxidation in the PTC system described, among others, by Kozhevnikov¹⁰ (Fig. 1). The aqueous phase contains an oxidizing agent – H_2O_2 , the oxidation catalyst – $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and phase transfer catalyst – Aliquat® 336. The organic phase constitutes CDT. In the first stage of the reaction, the heteropolyacid – $\text{H}_3\text{PW}_{12}\text{O}_{40}$ is activated by hydrogen peroxide with the formation of peroxo-polyoxotungstates. Peroxo-polyoxotungstates subsequently undergo the reaction with lipophilic methyltrioctylammonium cation of phase transfer catalyst, owing to this, they are transferred to the organic phase.

In this phase the reaction of electrophilic addition proceeds – the oxygen atom originating from methyltrioctylammonium peroxopolyoxotungstate (electrophilic reagent) becomes connected with the double bond of nucleophilic CDT with formation of ECDD. A reduced form of the catalyst (methyltrioctylammonium polyoxotungstate) passes on the phase boundary, where it is activated by hydrogen peroxide with the formation of the active form of the catalyst.

In the case of a synthesis without the addition of Aliquat® 336 the epoxidation reaction does not proceed. The lipophilic cation of phase transfer catalyst is a factor causing the transport of peroxopolyoxotungstate formed in the aqueous phase by the reaction of the heteropolyacid – $\text{H}_3\text{PW}_{12}\text{O}_{40}$ with hydrogen peroxide to the organic phase.

An agreement of the general mechanism of olefine epoxidation in the PTC system with the epoxidation mechanism of CDT was also confirmed by the data of the synthesis, in which all the reactants were placed simultaneously in the reactor. By a comparison of the results obtained in this syntheses with those obtained in the reactions, in which the reagents were introduced in the half-hour intervals, according to a specified order, it was noticed that the ECDD yield and the selectivity of the transformation to ECDD was higher, when the reactants were introduced into the reactor every 30 min. The addition of the reactants in the half-hour intervals in the sequence $\text{H}_3\text{PW}_{12}\text{O}_{40}$ together with H_2O_2 , Aliquat® 336, and a mixture of CDT and dodecane influences advanta-

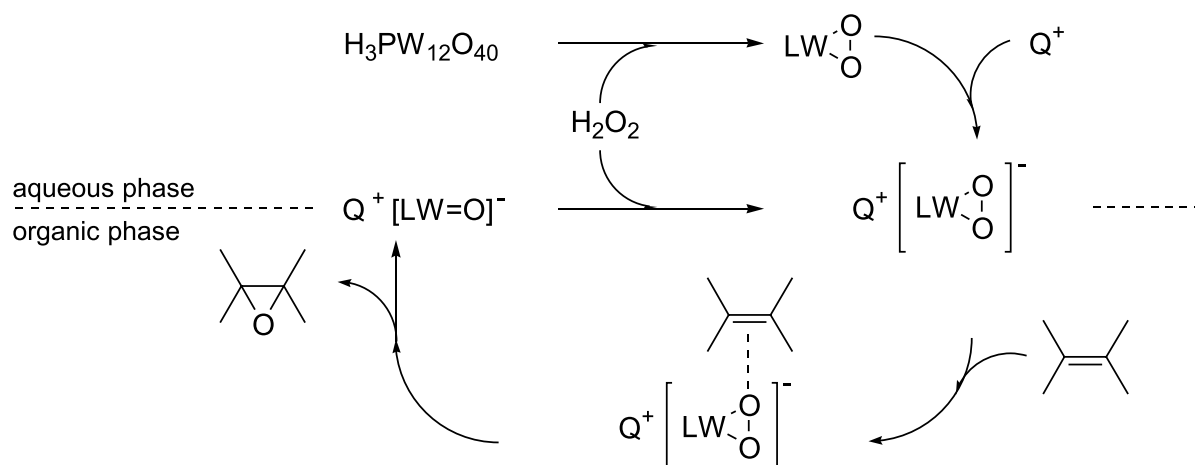


Figure 1. Mechanism of olefine epoxidation in the PTC system according to Kozhevnikov¹⁰

geously the formation of the catalytic system before the epoxidation reaction of CDT, owing to this peroxopolyoxotungstate are faster transferred by the phase-transfer catalyst into the organic phase. Almost identical conversion of CDT and H_2O_2 were achieved in both reactions after 60 min of the reaction, however the ECDD yield was significantly higher in the experiments with a consecutive addition of the components. A gradual addition of the reactants increases the rate of epoxidation.

When the mixing rate increases in the range of 300 – 800 rpm the higher yields ECDD were obtained (Fig. 2). A higher mixing rate increases the interfacial surface, which causes an increase of the rate of mass transfer, hence, an increase of the reaction rate. Simultaneously, the amount of the evolved heat increases due to an increase of reaction rate. This facilitates the formation of the side products. At the mixing rate of 600 and 800 rpm, the diepoxides were found in the products. In the case of the lowest mixing rate – 300 rpm, the ECDD yield was increasing with the prolongation of the synthesis time (15 – 60 min). At high mixing rate (400 – 800 rpm), a decrease of the ECDD yields was observed along with the elapsed time. The maximum yield of ECDD (23.5%) was obtained after 30 min at the mixing rate of 800 rpm. Taking into account the obtained yields of ECDD as well as the fact of the formation of the side products in the reactions carried out at higher mixing rate, the mixing rate in the range 400 – 600 rpm was found as the most effective.

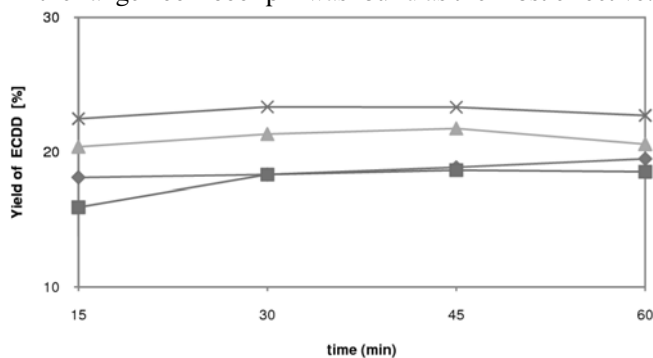


Figure 2. The changes in ECDD yield over time as a function of mixing rate (◆ – 300 rpm, ■ – 400 rpm, ▲ – 600 rpm, × – 800 rpm)

In many works discussing the epoxidation of olefines in the PTC system^{2, 9, 11, 12} it has been demonstrated that an excess of olefine in relation to hydrogen peroxide is recommended to obtain the high selectivity. In our studies it was found that a decrease of the molar ratio of CDT: H_2O_2 , in the range of 3:1 – 1:1 caused the achievement of higher yields of ECDD. After the reaction time of 60 min, the yield was increased from 18.0% for CDT: H_2O_2 = 3:1 to 47.5% for CDT: H_2O_2 = 1:1 (Fig. 3). A decrease of the molar ratio of CDT: H_2O_2 to 0.5:1 caused a decrease of ECDD yield to 34.2%. At the molar ratio of CDT: H_2O_2 = 0.5:1, the intensity of heat evolution (thermal effect, heat effect) was so large that the temperature of the reaction system increased to 84°C (a desired temperature was 50°C) in spite of intensive cooling by water-ice mixture. Based on the obtained results and the safety of the process operation it was found that it is most advantageous to carry out the CDT epoxidation process at the molar ratio of CDT: H_2O_2 = 2:1 – 1.5:1.

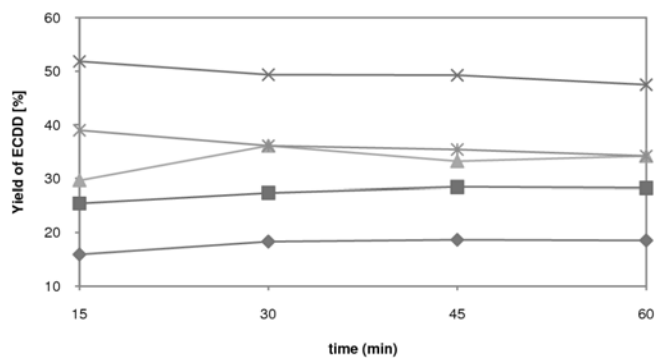


Figure 3. The influence of molar ratio of CDT/ H_2O_2 and time on the ECDD yield (◆ – 3:1, ■ – 2:1, ▲ – 1.5:1, × – 1:1, * – 0.5:1)

The studies of the influence of the molar ratio of H_2O_2 : $\text{H}_3\text{PW}_{12}\text{O}_{40}$ demonstrated that the molar ratio of H_2O_2 : $\text{H}_3\text{PW}_{12}\text{O}_{40}$ in the range of 200:1 – 500:1 lead to the highest yields of ECDD (Fig. 4). An increase of the molar ratio of H_2O_2 : $\text{H}_3\text{PW}_{12}\text{O}_{40}$ to 500:1 causes an increase of the ECDD yield only by 6.2% in comparison with a process carried out at the molar ratio of 300:1. Hence, the CDT epoxidation in the studied system proceeds with a high yield of ECDD at the molar ratio of H_2O_2 : $\text{H}_3\text{PW}_{12}\text{O}_{40}$ = 300:1 – 500:1.

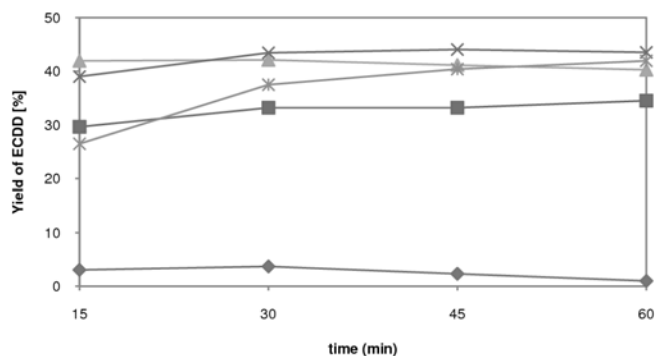


Figure 4. The influence of molar ratio of H_2O_2 / $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and time on the ECDD yield (◆ – 100, ■ – 200, ▲ – 300, × – 400, * – 500)

The studies of the effect of the temperature demonstrated that the process proceeds the most effectively at temperatures of 30 – 50°C (Fig. 5). The maximum yield – 44.7% was achieved after 30 min at 40°C. This yield is only by 0.5% higher than that obtained at the temperature of 30°C. The ECDD yield, in the temperature range of 30 – 60°C, increases along with the time of the reaction duration. At the temperature of 30°C, a rapid increase

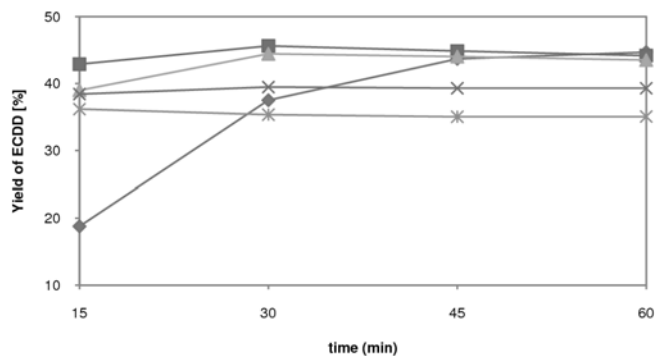


Figure 5. The changes in ECDD yield over time and as a function of temperature (◆ – 30°C, ■ – 40°C, ▲ – 50°C, × – 60°C, * – 70°C)

of ECDD yield takes place over the period of time from 15 to 30 min. After 15 min at the temperature of 30°C the yield of only 18.8% was obtained, whereas the yield amounted to 36.2 – 42.9% at higher temperatures.

The lowest yield of ECDD after the reaction time 60 min (35.1%) was obtained at 70°C. A decrease of the yield along with the elapsed reaction time takes place only at this temperature.

The influence of the nature of the solvent on the epoxidation of CDT was investigated in the presence of aprotic solvents immiscible with water such as: chloroform, 1,2-dichloroethane, dichloromethane, toluene, cyclohexane, pentane, and heptane. Here the solvent assists the extraction of the catalyst active form the water phase to the organic phase¹². The highest yields were achieved in the presence of the chloric solvents (Fig. 6). The lowest values of the ECDD yield were obtained in the presence of alkanes and cyclohexane. In the case of toluene, the ECDD yield was the highest after 15 min of reaction and was decreasing along with the prolongation of the reaction time to 60 min.

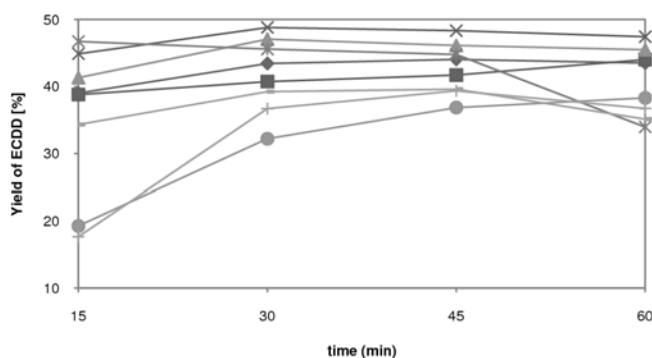


Figure 6. The effect of the nature of solvent and time on the ECDD yield (◆ – without solvent, ■ – CHCl_3 , ▲ – $\text{C}_2\text{H}_4\text{Cl}_2$, × – CH_2Cl_2 , * – $\text{C}_6\text{H}_5\text{CH}_3$, ● – C_3H_{12} , + – C_7H_{16} , — – C_5H_{12})

The ability to separate the water phase from the organic phase after completing the reaction also decided about the suitability of the solvent. The difficulties in the separation of the phases occurred in the presence of 1,2-dichloroethane.

An analysis of the ECDD yield in the presence of different solvents indicates that the reaction proceeds with a high yield in the presence of dichloromethane. The relatively good results were achieved without the application of the solvent. A significant advantage of the CDT epoxidation in the presence of dichloromethane was the facilitation of keeping the constant reaction temperature. A substantial fraction of the reaction heat was removed as a result of evaporation of dichloromethane, which was recycled to the reactor after the condensation.

Dichloromethane was utilized in the studies of the effect of solvent concentration (Fig. 7). The ECDD yield after 60 min of reaction in the processes with the use of 10 – 70 vol% of dichloromethane were located in the range of 13.5 – 47.4%. After the application of 90 vol% of dichloromethane, the yield was decreased to 35.7%. After exceeding 70 vol% of dichloromethane, foaming occurred and it was difficult to maintain the reaction temperature at 50°C. An intensive evaporation of the solvent lowered the reaction temperature. This explains

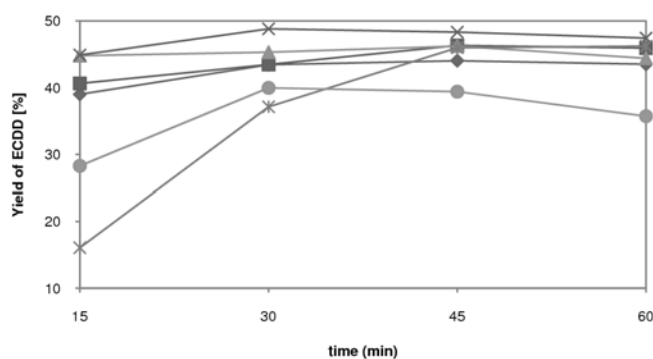


Figure 7. The influence of dichloromethane concentration and time on the ECDD yield (◆ – without solvent, ■ – 10% obj., ▲ – 30% obj., × – 50% obj., * – 70% obj., ● – 90% obj.)

the lower yields obtained at a higher concentration of dichloromethane.

The presence of the solvent – dichloromethane in the amount of 10 – 50 vol% is purposeful in the case of short reaction times (10 – 30 min). After the time of 60 min and the above range of dichloromethane concentration the yields were similar as in the case without the solvent.

CONCLUSIONS

A significant advantage of the discussed system is the application of hydrogen peroxide as the oxidizing agent. The epoxidation of CDT to ECDD in the PTC system proceeds under relatively mild conditions: low temperature, lack of the solvent, short reaction time. The studies of the influence of the technological parameters on the epoxidation of CDT to ECDD enable to determine the range of their changes, allowing to achieve the high values of ECDD yield: the mixing rate 400 – 600 rpm, the molar ratio of $\text{CDT}:\text{H}_2\text{O}_2 = 3:1 - 1.5:1$, the molar ratio of $\text{H}_2\text{O}_2:\text{H}_3\text{PW}_{12}\text{O}_{40} = 200:1 - 400:1$, the temperature 40 – 50°C, solvent: dichloromethane or lack of solvent, dichloromethane concentration: the 10 – 50 vol%, reaction time 35 – 50 min.

The application of the above-mentioned parameters allows to achieve the yield of 44 – 47% ECDD in relation to the introduced CDT. The side products of the process are diepoxides.

They are formed as a result of the successive reaction of ECDD with hydrogen peroxide.

The amount of the side products, practically independently of the reaction conditions, was very low. The yield of diepoxides in relation to introduced CDT amounted to about 0 – 3.6%.

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