Epoxidation of 1,5,9-cyclododecatriene with hydrogen peroxide under phase-transfer catalysis conditions: influence of selected parameters on the course of epoxidation

Grzegorz Lewandowski[1] · Marcin Kujbida[2] · Agnieszka Wróblewska[2]

Abstract

This work presents the studies on the epoxidation of 1,5,9-cyclododecatriene (CDT) with hydrogen peroxide as the oxidizing agent, under conditions of the phase transfer catalysis (PTC), and with the following catalytic system: $H_2WO_4/H_3PO_4/[CH_3(CH_2)_7]_3CH_3N^+HSO_4^-$ (compounds were mixed at the ratio of 2:1:1). The influence of the following parameters on the course of this process was investigated: catalyst content, molar ratio of H_2O_2:CDT, temperature and type of solvent. The highest yield of 1,2-epoxy-5,9-cyclododecadiene (ECDD) (54.9 mol%), at the conversion of CDT reached 72.3 mol%, was obtained at the temperature of 50 °C, for the catalyst content of 0.45 mol% (in relation to the introduced CDT), for the molar ratio of H_2O_2:CDT 1.5:1, with toluene as the solvent and after the reaction time of 30 min. Considering the he obtained results and numerous applications of ECDD, further research should be developed to provide a more efficient and environmentally friendly way of obtaining this compound.

✉ Grzegorz Lewandowski
   grzegorz.lewandowski@zut.edu.pl

✉ Agnieszka Wróblewska
   agnieszka.wroblewska@zut.edu.pl

1   Faculty of Chemical Technology and Engineering, Department of Chemical Organic Technology and Polymeric Materials, West Pomeranian University of Technology Szczecin, Pułaskiego 10, 70-322 Szczecin, Poland

2   Faculty of Chemical Technology and Engineering, Department of Catalytic and Sorbent Materials Engineering, West Pomeranian University of Technology Szczecin, Pułaskiego 10, 70-322 Szczecin, Poland

Graphic abstract
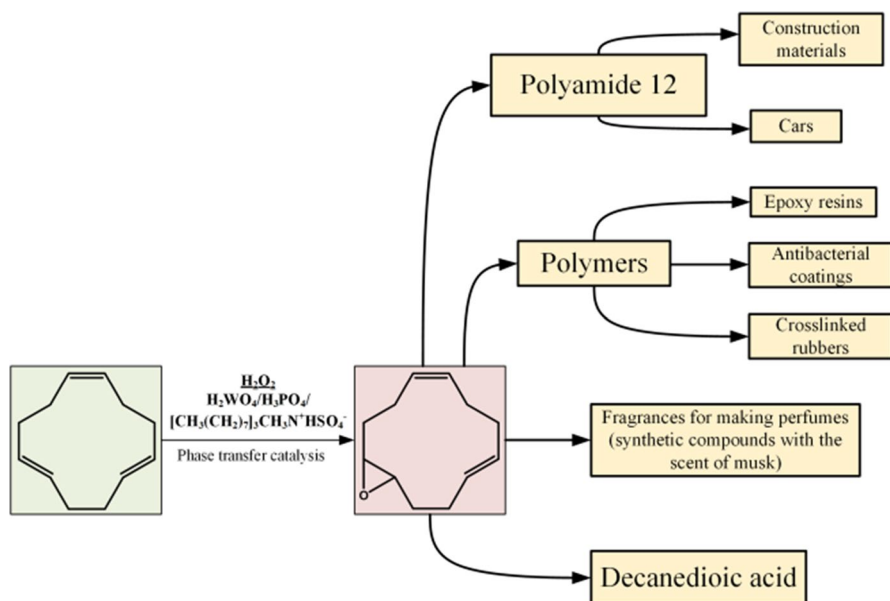
Introduction

1,2-Epoxy-5,9-cyclododecadiene (ECDD), due to the presence of two double bonds
in the molecule and an oxirane ring, is used as an additive increasing the degree
of crosslinking of polymers. Polymers with its addition can be used as elements of
lithium-ion batteries [1–4], as well as capacitors [5]. It can also be used in the pro-
duction of anti-static coatings [6, 7], cross-linked acrylic rubber resistant to oils at
high temperature [8] or antibacterial coatings [9]. Pure ECDD [10], as well as its
derivative, i.e. 4,8-cyclododecadien-1-one [11] can be used as ingredients for per-
fumes with musky and earthy scents. At present, studies are also conducted on the
use of this compound as an intermediate in the synthesis of cyclododecanol (CDOL)
and cyclododecanone (CDON), from which 1,10-decanedicarboxylic acid (DDDA)
and laurolactam can be obtained. Both of them are widely used as the raw materials
in the production of polyesters and polyamides (Fig. 1) [12].

Laurolactam is a raw material in the production of polyamide 12 (PA12),
which has the smallest share of amide groups in its molecule, which determines
its characteristic properties. Its high hydrophobicity causes significant dimen-
sional stability in conditions of changing humidity. PA12 is also known for its
exceptional impact strength even at low temperatures. It is also resistant to most
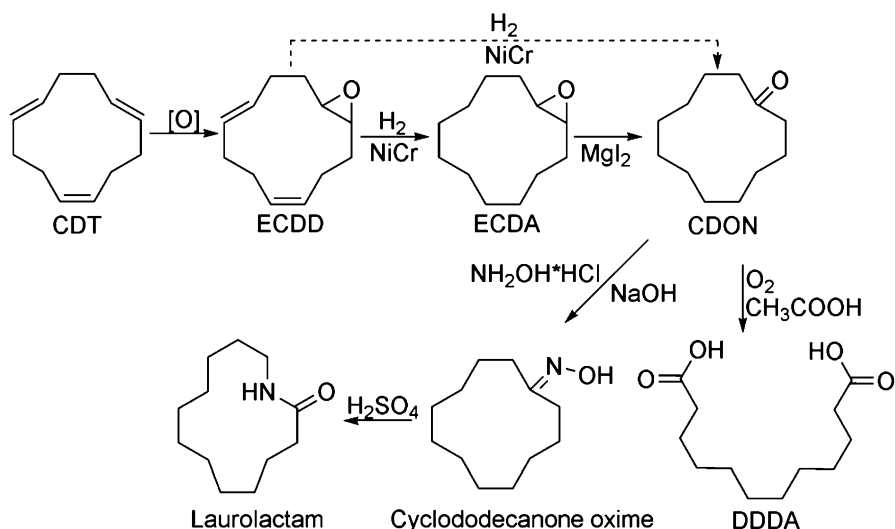
Fig. 1 Method of obtaining of laurolactam and decanedicarboxylic acid from CDT (*CDT* 1,5,9-cyclodo-decatriene, *ECDD* 1,2-epoxy-5,9-cyclododecadiene, *ECDA* epoxycyclododecane, *CDON* cyclododecan-one, *DDDA* 1,10-decanedicarboxylic acid)

chemicals: greases, fats, oils, fuels, solvents, salt solutions and others [13]. The above-mentioned properties make it an important construction material in the production of automotive fuel lines. Its key role in the automotive industry is demonstrated by the huge size of problems with the availability of raw materials for the production of car parts, caused by an accident at the Evonik factory in the city of Marl in Germany producing CDT, a raw material in the production of PA12 [14–16]. Fig. 2 shows the methods used to obtain ECDD.

Like most epoxides, ECDD can also be obtained in reacting of the appropriate olefin with an organic peracid, this reaction is sometimes named as the reaction of Prilezhaev [17]. During epoxidation of CDT using commercially available peracetic acid (PES-40), which is a mixture of: 40% peracetic acid, 40% acetic acid, 5% hydrogen peroxide, 14% water and 1% sulfuric acid (VI) (the molar ratio CDT:PES-40 was 1:1.1), the desired product (ECDD) was obtained with the yield of 84% (in relation to the introduced CDT) and within 4 h [18]. The reaction was carried out by dropping PES-40 into a solution of CDT in chloroform (the ratio 1:3 m/m), which contained anhydrous sodium carbonate (the molar ratio CDT: sodium carbonate 1:1) and at the temperature of 5 °C. A modification of this method is the application of hydrogen peroxide as an oxidant and as an organic catalyst of an aliphatic acid, with a dissociation constant ranging from 5.0×10^{-6} to 1.0×10^{-4} [19]. The advantage of this method is the reduction of the reaction time in comparison to the method presented above (from 4 to 1 h). By this method very high selectivity (in relation to reacted hydrogen peroxide) to monoepoxide (up to 98.8% at the conversion of H_2O_2 83.7% and at the conversion CDT 21%) is obtained. However, the increasing in the molar excess of CDT in relation to hydrogen peroxide (4:1 instead of 1:1.1) means that the maximum
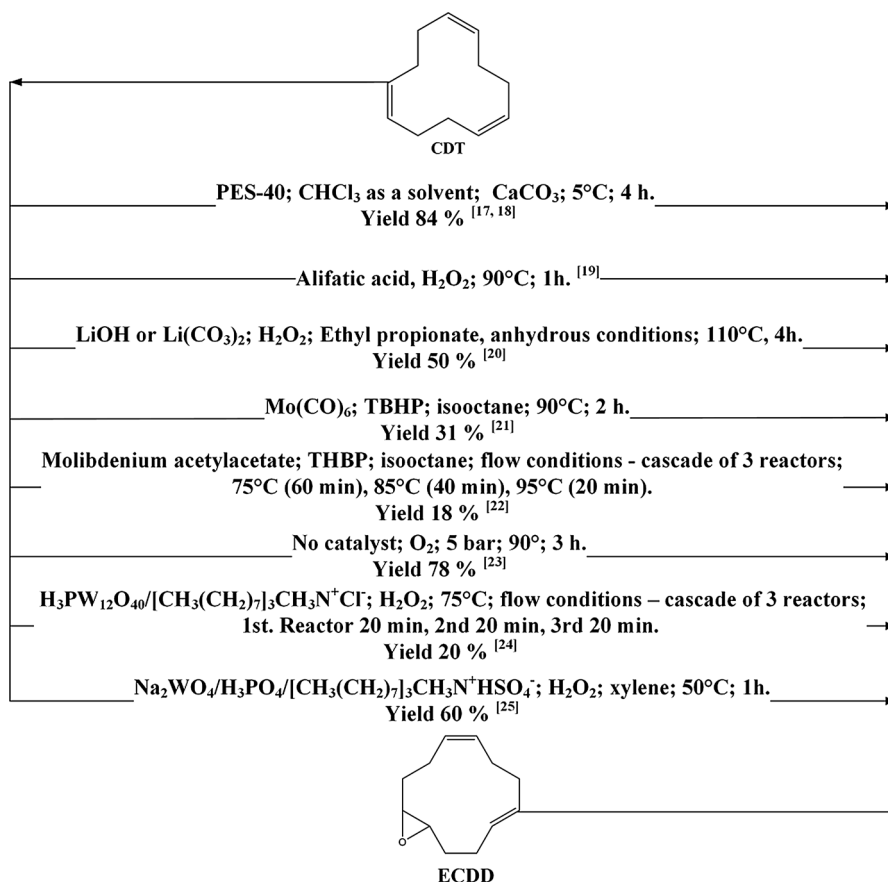
CDT

PES-40; CHCl₃ as a solvent; CaCO₃; 5°C; 4 h.
Yield 84 % [17, 18]

Alifatic acid, H₂O₂; 90°C; 1h. [19]

LiOH or Li(CO₃)₂; H₂O₂; Ethyl propionate, anhydrous conditions; 110°C, 4h.
Yield 50 % [20]

Mo(CO)₆; TBHP; isooctane; 90°C; 2 h.
Yield 31 % [21]

Molibdenium acetylacetate; THBP; isooctane; flow conditions - cascade of 3 reactors;
75°C (60 min), 85°C (40 min), 95°C (20 min).
Yield 18 % [22]

No catalyst; O₂; 5 bar; 90°; 3 h.
Yield 78 % [23]

H₃PW₁₂O₄₀/[CH₃(CH₂)₇]₃CH₃N⁺Cl⁻; H₂O₂; 75°C; flow conditions – cascade of 3 reactors;
1st. Reactor 20 min, 2nd 20 min, 3rd 20 min.
Yield 20 % [24]

Na₂WO₄/H₃PO₄/[CH₃(CH₂)₇]₃CH₃N⁺HSO₄⁻; H₂O₂; xylene; 50°C; 1h.
Yield 60 % [25]

ECDD

Fig. 2 Methods used for obtaining of ECDD

of CDT conversion can be only 25 mol%, which significantly reduces the yield of ECDD in relation to the introduced olefin.

Epoxidation of CDT with hydrogen peroxide using lithium as the catalyst is also possible. The highest ECDD yields (calculated on the introduced CDT) were obtained using lithium carbonate or hydroxide—50% and 51%, respectively. The reaction was carried out for 4 h at 110 °C. Anhydrous ethyl propionate was used as the solvent. In order to provide anhydrous reaction conditions, the introduced and formed water was discharged from the reaction medium in the form of a water: ethyl propionate azeotrope. Long reaction times and high reaction temperatures, as well as the need to provide an anhydrous environment, make this reaction inconvenient for industrial applications [20].

Lewandowski et al. [21] described the method of the obtaining of ECDD, consisting of epoxidation of CDT with *tert*-butyl hydroperoxide (TBHP) with the concentration of 20–80% and in the presence of a homogeneous molybdenum catalyst (molybdenum hexacarbonyl, molybdenyl acetylacetonate). The epoxidation of CDT

is carried out in the temperature range of 70–90 °C, at the atmospheric pressure, with the molar ratio of CDT to TBHP from 1:1 to 1:5, at the concentration of the appropriate solvent amounted to 13–70% (*iso*-octane, decane, nonane, di-*tert*-butyl peroxide, 1,2-dichloroethane) and for the reaction time from 1 to 5 h. The best results were obtained for the epoxidation performed at 90 °C for the reaction time 2 h and using isooctane as the solvent in the amount of about 22 wt% in relation to the mass of the reaction mixture. The catalyst was molybdenum hexacarbonyl and it was used in the molar ratio to TBHP of 5×10^{-4}. The molar ratio of CDT to TBHP was 2.94:1. In this way, the selectivity of transformation of CDT to ECDD was 99.6 mol%, at the conversion of CDT and TBHP amounted to 31.1 mol% and 99.8 mol%, respectively.

From the patent specification prepared by Lewandowski et al. [22] is also known the continuous way of conducting the epoxidation of CDT, using the same reagents, in a cascade of flow reactors with intensive mixing and dosing of CDT in the mixture with the catalyst to the first stage of the cascade and a gradual introduction of the TBHP solution in the solvent to the first and subsequent stages of the cascade, with which in the next stages of the cascade a gradient temperature rise is maintained. The best results were obtained when epoxidation was carried out in a three-stage reactor cascade. In subsequent stages of the cascade, higher and higher temperatures were maintained, while reducing the residence time of the reaction mixture in them. Temperatures and residence times in successive stages of the cascade were as follows: 75 °C and 60 min, 85 °C and 40 min, 95 °C and 20 min. TBHP was introduced into each cascade stage as a 6 M solution in isooctane also containing dissolved catalyst—0.007 M molybdenum acetoacetate. In this way, the selectivity of transformation of CDT to ECDD was 91 mol%, while the conversion of CDT and TBHP amounted to 19.8 mol% and 98 mol%, respectively.

Mahajan et al. [23] investigated the kinetics of non-catalysed oxidation of CDT with air oxygen. The reaction proceeded according to a radical mechanism, and its main by-product at lower temperatures and for shorter reaction times was cyclododecatryl hydroperoxide. When the temperature of epoxidation was increased, this hydroperoxide decomposed, increasing the selectivity of transformation to ECDD. The authors managed to obtain satisfactory CDT conversions and selectivity of transformation of CDT to ECDD, respectively: 84.5 and 92%, by conducting the reaction in a stainless-steel reactor for 3 h. The disadvantage of this method is the use of pure oxygen as an oxidizer, which creates a danger of an explosion.

Nobuyuki et al. patented the method of continuous obtaining of CDT under PTC conditions. The catalyst consisted of tungsten compounds (e.g. tungstic acid; sodium, potassium, lithium or ammonium tungstate; sodium, potassium, ammonium dodecatungstate; phosphotungstic acid, sodium phosphotungstate; silicotungstic acid; sodium silicotungstate) and ammonium or pyridinium salt, with possible addition of a mineral acid. Their method of carrying out this process consisted of conducting reactions in three subsequent reactors, with raw materials being fed only to the first of them. This process can be carried out at moderate temperatures (20–120 °C) and at the atmospheric, reduced or increased pressure. The best results were obtained when the process was carried out sequentially in three reactors for 20 min and at 75 °C. CDT, phosphotungstic acid, methyltrioctylammonium chloride

and 60% aqueous hydrogen peroxide were introduced into the first reactor (the molar ratio of CDT:H_2O_2 was about 4:1). After leaving the first reactor, the conversion of CDT and hydrogen peroxide was 15.3% and 68.8%, respectively. The oil phase after the reaction contained 76.4 wt% of CDT and 21.9 wt% of ECDD. This corresponded to the conversion of CDT reached 21.9 mol% and the selectivity of ECDD amounted to 93.2 mol%. The hydrogen peroxide conversion was 98.8%. After vacuum distilling the oil phase at 3.0 kPa and at 118 °C, CDT with the purity of 98.4% was recovered (it contained 1.4 wt% of ECDD). After distillation at 130 °C and 1.3 kPa pressure of the oil phase remaining after CDT recovery, ECDD was obtained with the purity of 99.6% [24].

Lewandowski et al. also described the method of the obtaining of ECDD [25], which involved epoxidation of CDT with hydrogen peroxide, in the presence of the organic solvent, in the presence of sodium tungstate and *ortho*-phosphoric acid as the epoxidation catalyst, and methyltrioctylammonium bisulfate as the phase transfer catalyst. The process was carried out at 30–70 °C, for 1–2 h and using intensive mixing. The molar ratio of sodium tungstate to *ortho*-phosphoric acid was 0.5–4.0:1. The molar ratio of hydrogen peroxide to sodium tungstate was 37–300:1, and the molar ratio of hydrogen peroxide to CDT was 0.75–1.5:1. As the organic solvent *m*-, *o*-, or *p*-xylene was used or a mixture of these solvents. The molar ratio of methyltrioctylammonium hydrogen sulfate to sodium tungstate was 0.3–0.5:1. In the process obtained relatively high ECDD yields in relation to the introduced CDT (18.3–59.7%), in comparison to classical CDT epoxidation methods, carried out with tert-butyl hydroperoxide and peracetic or perbenzoic acid. The disadvantage of this method of epoxidation of CDT is the relatively low activity of the sodium tungstate/*ortho*-phosphoric acid catalytic system, which requires a relatively high temperature, reaching even 70 °C and a long reaction time, even 2 h, to achieve full conversion of hydrogen peroxide.

The described methods for obtaining ECDD have disadvantages that limit their use in industrial conditions. Further research is needed to develop an environmentally friendly technology of obtaining this compound. Oxidation of CDT with hydrogen peroxide under the conditions of phase transfer catalysis (PTC) may be such a technology, however, the variants of this method described above have a number of drawbacks such as: long reaction time and low CDT conversion.

The purpose of the research presented in this work is to investigate the effect of changing the selected parameters (catalyst content, molar ratio CDT: H_2O_2, temperature and type of solvent) on the yield of ECDD and the conversion of CDT in the process of the epoxidation of CDT with hydrogen peroxide. The process will be carried out under PTC conditions, using the catalytic system consisting of tungsten (VI) acid, *ortho*-phosphoric acid (V) and methyltrioctylammonium hydrogen sulfate. No studies are available in the literature on the influence of the above-mentioned parameters on the course of the CDT epoxidation process using this complex catalytic system. We anticipate that there may be visible an increase in the reaction rate of ECDD formation, due to the higher acidity of the catalyst (replacement of the sodium salt of tungsten (VI) acid with tungsten (VI) acid), compared to the process carried out according to the patent [25]. Due to the numerous and new applications of ECDD (Nylon 12 and the component of musk fragrance compositions described

in this work), it is desirable to develop a new, efficient and environmentally friendly method of obtaining this compound.

Experimental section

Raw materials

Reactions and determinations were carried out using the following reagents (without further purification): *c,t,t*-1,5,9-cyclododecatriene (98%, Aldrich); hydrogen peroxide (30% aqueous solution, Chempur); methyltrioctylammonium hydrogen sulfate ($\geq$95%, Aldrich); *ortho*-phosphoric acid (85%, POCh Gliwice); dodecane ($\geq$99%, Aldrich); toluene (analytical grade, Chempur); sodium thiosulfate (analytical weight for preparation of 0.1 n solution, Chempur); potassium iodide (analytical grade, POCh), chloroform (analytical grade, Chempur); ethyl acetate (analytical grade, Chempur). The ECDD standard for GC was obtained and purified in our laboratory.

Method of CDT epoxidation

Into a glass reactor with a capacity of 25 cm^3 equipped with a thermometer, a mechanical stirrer and a reflux condenser, tungsten (VI) acid, methyltrioctylammonium hydrogen sulfate, *ortho*-phosphoric acid (V) in the form of a 10 wt% aqueous solution and hydrogen peroxide were added successively. The reactor contents were mixed at 1000 rpm for 15 min at a room temperature. After this time, a mixture consisting of CDT, solvent and dodecane as an internal standard was added to the reactor, its composition at the beginning was additionally determined by a gas chromatography method (GC). The reactor was then placed in a water bath having the appropriate temperature and its contents was mixed at a speed of 1000 rpm. Samples of the organic phase were taken after the reaction time: 5, 10, 15 and 30 min, and their composition was analyzed by the GC method. After the reaction time 60 min, the contents of the reactor were poured into a plastic tube, weighed and centrifuged at 4 °C for 15 min at 5000 rpm. The aqueous and organic phases were separated and weighed. In both phases, the content of unreacted hydrogen peroxide was determined using the iodometric method, and the composition of the organic phase was additionally determined by the GC method.

Parameters of chromatographic analyses

Quantitative analyses of the tested samples was carried out using the internal standard method (dodecane) using a Thermo-Finigan Trace GC 2000 chromatograph with a Chrom-Card for Trace GC data processing program. A DB-5 capillary column, J&W Scientific, 30 m×0.25 mm×0.25 μm was used for the analyses. The sample chamber temperature was 200 °C and the detector 250 °C. The oven's temperature program was as follows: isothermally 50 °C for 2.5 min, increase to 250 °C at the rate of 20 °C/min and isothermally 250 °C for 2.5 min. Carrier gas pressure (helium)

was changed as follows: initially 75 kPa, then an increase at a rate of 5 kPa/min to 150 kPa. Gas flows in the detector: air 350 cm^3/min, hydrogen 35 cm^3/min and helium (compensating gas) 10 cm^3/min. Internal calibration curve was made for ECDD using the following ECDD/dodecane weight ratios: 0.12; 0.25; 0.58; 1.00; 2.00 to get a directional coefficient of 0.9789 and a coefficient of R^2 equal to 0.9947. The curve for CDT was made for the weight ratio CDT/dodecane: 0.12; 0.25; 0.50; 1.00; 2.00 and its directional coefficient and R^2 were equal to 0.8431 and 0.9973, respectively. The content (in wt%) of the components of the reaction mixture was calculated from the following formula:

$$c_i = \alpha_i * \frac{A_i}{A_w} * \frac{m_w}{m_p} * 100\%$$

Here: α_i—directional factor of the calibration curve of the'i' component, A_i, A_w—peak areas of the established substance and standard, m_w, m_p—mass: standard and sample (g). The organic phase samples taken from the reactor were analyzed without additional dilution.

The method of calculating the results

The yield of ECDD (W_{ECDD}), and the conversions of CDT (K_{CDT}) and H_2O_2 ($K_{H_2O_2}$), were calculated using the following equations:

$$W_{ECDD} = \frac{n_{ECDD}}{n_{0,CDT}} * 100\%$$

$$K_{CDT} = \frac{n_{0,CDT} - n_{CDT}}{n_{0,CDT}} * 100\%$$

$$K_{H_2O_2} = \frac{n_{0,H_2O_2} - n_{H_2O_2}}{n_{0,H_2O_2}} * 100\%$$

n_{ECDD}, n_{CDT}—number of CDT moles: initial and at the time of measurement (mmol), n_{ECDD}—number of ECDD moles at the time of measurement (mmol), n_{0,H_2O_2}, $n_{H_2O_2}$—the number of moles H_2O_2: at the beginning of the reaction and at the time of measurement (mmol).

Results and discussion

Influence of the catalyst content

The first stage of the study was to examine the effect of the content of the catalyst in the form of the catalyst system: tungsten (VI) acid/*ortho*-phosphoric (V) acid/methyltrioctylammonium hydrogen sulfate on the course of the epoxidation of CDT.

Usually, the increase in the catalyst content increases the rate of reaction, but in case of the epoxidation of CDT, the desired product (ECDD) can be formed first in a series of follow-up reactions. There is also the possibility of simultaneous epoxidation of two or three double bonds and direct formation of diECDD and triECDD (Fig. 3) [26]. The formation of triECDD as a result of the simultaneous oxidation of two double bonds ECDD or direct oxidation of diECDD can not be excluded. There is no clear information on the mechanism of this process in the literature.

Thus, an increase in catalyst content may cause a reduction in the selectivity of the transformation CDT to ECDD due to the further epoxidation of ECDD and diECDD or the parallel epoxidation of two or three double CDT bonds. In this regard, it may be that there is an optimal catalyst content at which diECDD and triECDD are formed in a minimal amount.

In order to study the effect of this parameter on the kinetics of CDT epoxidation with hydrogen peroxide, a series of studies were performed with increasing content of the tungsten (VI) acid/*ortho*-phosphoric (V) acid/methyltrioctylammonium hydrogen sulfate (0.17; 0.30; 0.45; 0,55; 1.19 mol% CDT calculated per atom W) and with other parameters constant: the weight ratio CDT to toluene (solvent) 1:1, the molar ratio of H_2O_2:CDT 1.5:1, while the molar ratios of the catalyst components were as follows: H_2WO_4:H_3PO_4:$[CH_3(CH_2)_7]_3CH_3N^+HSO_4^-$ 2:1:1.

Table 1 presents the values of the conversion of CDT (the values of the yields of ECDD are also given in brackets) for reactions carried out with different catalyst contents.

Changes in conversion of CDT as a function of reaction time for increasing catalyst contents are shown in Fig. 4 and Table 1.

The results presented in Fig. 4 and Table 1 clearly show that the conversion of CDT is directly proportional to the catalyst content—the higher the content of the catalyst, the higher the conversion of CDT (after the given reaction time). It can be seen that the conversion of CDT in three syntheses with the highest catalyst content (1.19; 0.55; and 0.45 mol% CDT) tends to be similar after 60 min of reaction performing (about 93 mol%). In case of reactions carried out with
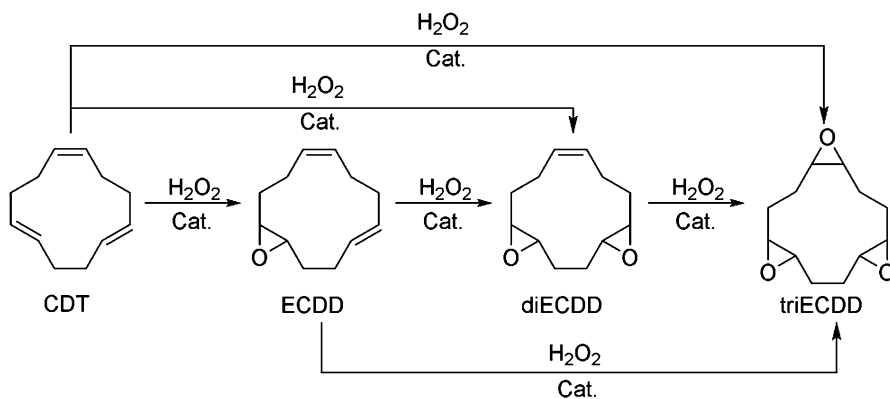

Fig. 3 Possible ways of ECDD, diECDD and triECDD obtaining

Table 1 The values of the conversion of CDT (the values of the yields of ECDD are also given in brackets) for reactions carried out with different catalyst contents[a]

Time (min)	Catalyst content (mol% CDT)				
	0.17	0.30	0.45	0.55	1.19
0	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)
5	14.5 (11.4)	22.6 (14.8)	25.5 (18.2)	35.6 (26.1)	41.0 (24.1)
10	17.4 (15.4)	30.7 (23.0)	36.6 (30.6)	48.6 (37.2)	61.2 (36.8)
15	24.9 (22.6)	40.5 (31.6)	48.1 (39.5)	59.5 (47.0)	76.8 (46.4)
30	40.7 (35.1)	58.7 (43.6)	72.3 (54.9)	83.3 (53.2)	91.7 (41.0)
60	66.0 (54.5)	86.2 (45.5)	91.7 (46.2)	93.3 (45.0)	92.9 (41.0)
60[b]	48.7	77.8	94.9	98.9	99.2

[a]The reaction conditions were the same as those given in the title in Fig. 4

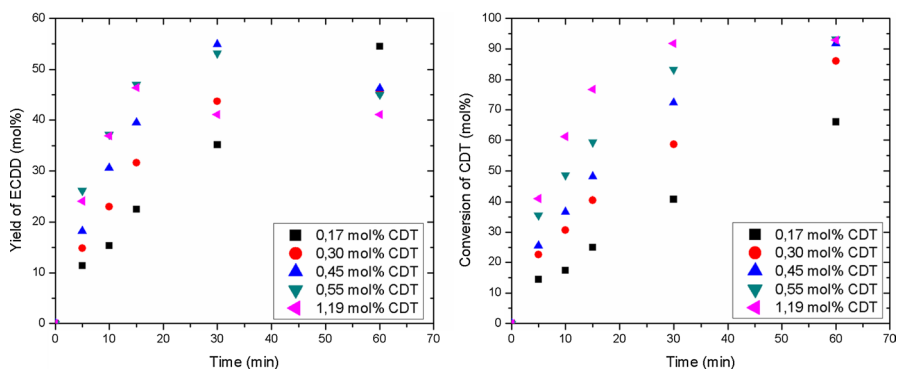[b]The values of conversion of H_2O_2

Fig. 4 Drawings showing the conversion of CDT and the yield of ECDD as a function of time for reactions with different catalyst contents. Reaction conditions: temperature 50 °C, stirring speed 1000 rpm, solvent content (toluene) 50 wt%, the molar ratios H_2WO_4:H_3PO_4:[$CH_3(CH_2)_7$]$_3CH_3N^+HSO_4^-$ 2:1:1

a smaller catalyst content (0.17 and 0.30 mol% CDT), the conversions of CDT after the reaction time of 60 min are lower and amount to 66.0 and 86.2 mol%, respectively. However, analyzing the course of changes in the conversion of CDT as a function of reaction time, it can be assumed that also in these cases, after appropriate extension of the reaction time, a similar conversion of CDT would be obtained as in other syntheses. Limitation of CDT conversion to approx. 93 mol% is caused by the depletion of H_2O_2, which is transformed not only in the reaction of ECDD formation, but also diECDD. A H_2O_2 decomposition reaction can not be excluded either.

Changes in the yield of ECDD yield as a function of reaction time shown in Fig. 4 also depend on the content of the catalyst, but they are not as easy to interpret as changes in the conversion of CDT. This is due to the aforementioned nature of CDT epoxidation—this is a reaction in which the by-products such as

diECDD and triECDD are formed as a result of subsequent epoxidation of ECDD and diECDD, respectively, or of parallel CDT epoxidation.

It should be emphasized that with the technological parameters used in this work, virtually no formation of triECDD was found. The only by-product was diECDD, whose amount in the post-reaction mixture increases as the conversion of CDT increases.

It is visible during the analysis the changes of yield of ECDD as a function of reaction time that when the conversion of CDT exceeds about 70 mol% (reactions with content of the catalyst 0.45, 0.55 and 1.19 mol CDT) yields of ECDD are decreasing. This may indicate a greater likelihood of diECDD formation due to a post-epoxidation of ECDD than parallel CDT epoxidation. Probably during the epoxidation of CDT, for the appropriate reaction time, there is already enough amount of ECDD in the reaction mixture that it becomes more readily available than CDT and may undergo further oxidation. The highest yield of ECDD was obtained by carrying out the epoxidation for 30 min with the catalyst content of 0.45 mol% CDT.

The conversion of hydrogen peroxide (Table 1) is also dependent on the catalyst content. For the smallest catalyst content (0.17 mol% CDT), the conversion of H_2O_2 after 60 min of reaction carrying out is only 48.7 mol%. Increasing in the catalyst content to 0.30 mol% CDT increases the conversion of H_2O_2 to 77.8 mol%. Further increasing in the catalyst content (to 0.45 mol% CDT) increases the conversion of H_2O_2 to 94.9 mol%.

For reactions carried out with the catalyst content of over 0.55 mol% CDT, the conversion of hydrogen peroxide is almost complete.

Influence of the molar ratio of H_2O_2:CDT

The next stage of our research was checking the influence of the molar ratio of H_2O_2:CDT on the results of the epoxidation. This parameter is important because the molar ratio of H_2O_2:CDT directly determines the side reactions of oxidation of the second and third double bonds in CDT molecule and the formation of larger amounts of diECDD and triECDD.

Five molar ratios of H_2O_2:CDT were checked: 0.75; 1; 1.25; 1.5 and 2:1. Other reaction parameters were as follows: temperature 50 °C, catalyst content 0.55 mol% CDT, and toluene as the solvent.

On the graph of changes in the conversion of CDT as a function of time (Fig. 5) it can be seen that for each reaction time studied, an increase in the H_2O_2:CDT molar ratio causes an increase in the conversion of CDT. In the range of reaction times from 5 to 30 min and for the molar ratios of H_2O_2:CDT 1–1.5:1, very similar values of conversions of CDT were obtained at individual reaction times. Extending the reaction time to 60 min, however, reveals significant differences in conversion of CDT as a function of the molar ratio of H_2O_2:CDT. The lowest conversion of CDT (64.1 mol%) was obtained for the molar ratio of H_2O_2:CDT 0.75, the highest (98.1 mol%) at the molar ratio of H_2O_2:CDT 2:1. At intermediate molar ratios of H_2O_2:CDT (in the range of 1–1.5:1) the conversions
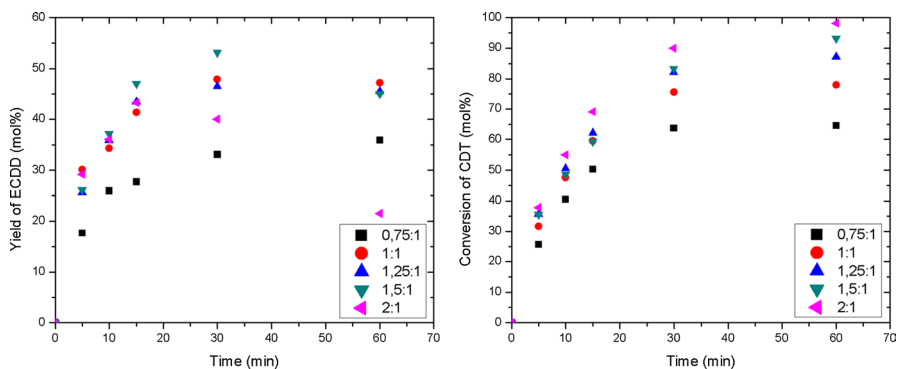
Fig. 5 Drawings showing the conversion of CDT and the yield of ECDD as a function of time for reactions with different molar ratios of H_2O_2:CDT. Reaction conditions were the same as those given in the title in Fig. 4

of CDT in the range of 78–93.3 mol% were obtained. Considering the conversion of H_2O_2 after 60 min of reaction carrying out (Table 2), which was close to the total for most reactions of this series of tests, it should be emphasized that as the molar ratio of H_2O_2:CDT increases from 0.75:1 to 2:1 the conversion of CDT also increases, however, the efficiency of H_2O_2 utilization is gradually decreasing. This is especially visible when comparing the syntheses carried out at the highest (2:1) and stoichiometric (1:1) molar ratio of H_2O_2:CDT. The conversions of H_2O_2 obtained for both syntheses are similar, but the yield of ECDD for the molar ratio of H_2O_2:CDT 2:1 is definitely lower. In this synthesis, the conversion of H_2O_2 was as much as 92.1 mol%, which indicates that more than 50% of H_2O_2 has undergone side reactions—formation of diECDD and unproductive degradation (decomposition of H_2O_2 into water and molecular oxygen).

Table 2 The values of the conversion of CDT (the values of the yields of ECDD are also given in brackets) for reactions carried out with a different molar ratios of H_2O_2:CDT[a]

Time (min)	Molar ratio of H_2O_2:CDT				
	0.75:1	1:1	1.25:1	1.5:1	2:1
0	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)
5	25.7 (17.7)	31.6 (30.1)	35.6 (25.6)	35.6 (26.1)	37.8 (29.2)
10	40.4 (25.9)	47.6 (34.3)	50.5 (35.9)	48.6 (37.2)	55.0 (36.0)
15	50.3 (27.7)	59.6 (41.3)	62.1 (43.4)	59.5 (47.0)	69.0 (43.3)
30	63.7 (33.1)	75.6 (47.9)	82.2 (46.5)	83.3 (53.2)	89.9 (40.0)
60	64.5 (35.9)	78.0 (47.2)	87.2 (45.5)	93.3 (45.0)	98.1 (21.5)
60[b]	99.4	99.7	99.0	98.9	92.1

[a]The reaction conditions were the same as those given in the title in Fig. 4

[b]The values of conversion of H_2O_2

In case of the yield of ECDD depicted as a function of reaction time in Fig. 5, it can be seen that up to 15 min for all tested molar ratios of H_2O_2:CDT, except 0.75:1, similar values of the yield of ECDD were obtained for all studied reaction time. In 30 min there is visible a division into reactions with still increasing (the molar ratio of H_2O_2:CDT 0.75:1), stabilized (the molar ratios of H_2O_2:CDT 1:1 and 1.25:1) and decreasing (the molar ratios of H_2O_2:CDT 1.5:1 and 2:1) values of the yield of ECDD. For the molar ratio of H_2O_2:CDT 2:1, a significant reduction in the yield of ECDD occurs after 15 min of reaction performing (from 43.3 to 21.5 mol%), and for the molar ratio of H_2O_2:CDT 1.5:1 after 30 min (from 53.2 to 45 mol%). This is most likely caused by subsequent reaction of oxidation of ECDD to diECDD. The decrease in the yield of ECDD is also noticeable for reactions in which the oxidant was used in a smaller excess or equimolar to olefin (1.25 and 1:1). However, in these cases the decrease in the yield of ECDD is very small, by 1.0 and 0.7 mol%, respectively. From a technological point of view, it does not seem beneficial to use a large excess of oxidant relative to the stoichiometric amount of CDT. At high molar ratios of H_2O_2:CDT relatively high yields of ECDD can be obtained. The highest yield of ECDD amounted to 53.2 mol% for the molar ratio of H_2O_2:CDT 1.5:1 and after 30 min of reaction carrying out, however, both the H_2O_2 utilization rate and the selectivity of transformation of CDT to ECDD are not optimal.

Influence of temperature

The kinetics of the CDT epoxidation with hydrogen peroxide was studied by carrying out the reaction at temperatures 40, 50, 60 and 70 °C and with constant values other parameters (catalyst content 0.55 mol% CDT, the molar ratio of H_2O_2:CDT 1.5:1; toluene as the solvent). The results of these studies are presented in Fig. 6 and Table 3.

On the graph showing the conversion of CDT as a function of reaction time (Fig. 6) it can be seen that it is highly dependent on the reaction temperature. It seems interesting to compare the values of conversion of CDT after 5 min of running
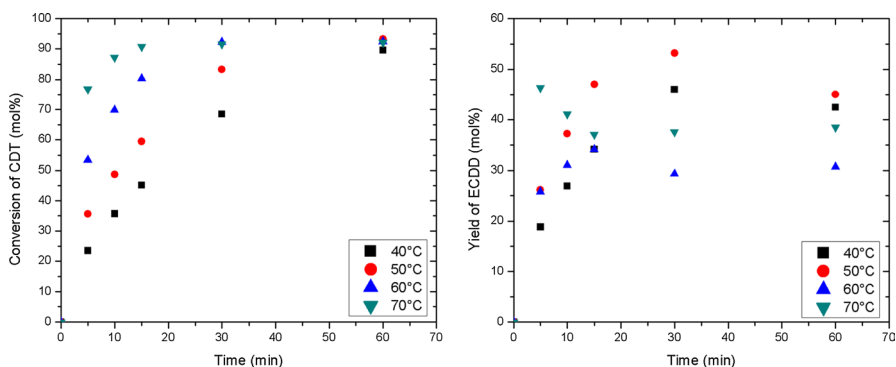

Fig. 6 Drawings showing the conversion of CDT and the yield of ECDD as a function of time for reactions carried out at different temperatures. Reaction conditions were the same as those given in the title in Fig. 4

Table 3 The values of the conversion of CDT (the values of the yields of ECDD are also given in brackets) for reactions carried out with a different temperatures[a]

Time (min)	Temperature			
	40 °C	50 °C	60 °C	70 °C
0	0 (0)	0 (0)	0 (0)	0 (0)
5	23.5 (18.8)	35.6 (26.1)	53.4 (25.8)	76.8 (46.3)
10	35.8 (26.8)	48.6 (37.2)	69.9 (31.0)	87.2 (41.1)
15	45.2 (34.1)	59.5 (47.0)	80.3 (34.1)	90.7 (37.1)
30	68.5 (46.0)	83.3 (53.2)	92.2 (29.3)	91.7 (37.6)
60	89.6 (42.4)	93.3 (45.0)	92.4 (30.6)	92.2 (38.5)
60b	86.7	98.9	99.1	99.6

[a]The reaction conditions were the same as those given in the title in Fig. 4

[b]The values of conversion of H_2O_2

the process at different temperatures. At the temperature of 40 °C, the conversion of CDT is only 23.5 mol%, while at the temperatures 50, 60 and 70 °C it increases successively to 35.6, 53.4 and 76.8 mol%. Such a large increase in the conversion of CDT indicates the dominant effect of temperature on the CDT epoxidation process. However, such large differences between the values of the conversion of CDT at individual temperatures occur at the initial stage of the reaction (5–15 min) and disappear in 60 min of the reaction carrying out. It should be emphasized that for all temperatures a very similar final maximum value of conversion of CDT of about 90–93 mol% is obtained, however, its achievement requires definitely different reaction times. For syntheses carried out at 40 and 50 °C, maximum of the conversion of CDT is obtained only after 60 min, at 60 °C after 30 min, and at 70 °C after 10–15 min of reaction performing.

The graph showing the yield of ECDD versus reaction time (Fig. 6) is more difficult to interpret because one dominant trend can not be seen. At the temperature of 40 °C, the yield of ECDD increases to 46 mol% for the reaction time to 30 min, then it decreases to 42.4 mol% (after the reaction time of 60 min). At the temperature of 50 °C the value of the yield of ECDD also increases to 30 min, but at this temperature it reaches the highest value of all—53.2 mol% and then decrease to 45 mol% while continuing the process. At 60 °C, the yield of ECDD increases to 34.1 mol% for the reaction time to 15 min, after which it decreases to about 30 mol% and remains constant until the end of the reaction. At the temperature 70 °C, the maximum of the yield of ECDD is probably reached for the reaction time shorter than 5 min. At this temperature, the yield of ECDD steadily decreases in the range of 5–15 min reaching the value of about 38 mol% and remains at this level until the end of the reaction. Among the tested temperatures, the best turned out to be 50 °C, at which the maximum of the yield of ECDD was 53.2 mol% after 30 min of reaction carrying out.

It is worth noting that in a two-phase PTC system, temperature affects the kinetics of the reaction in many different ways. It is possible to increase the reaction rate in the organic phase by increasing the energy of the reagents, as in single-phase

reactions [27]. However, one should not forget that the mutual solubility of the components of the reaction mixture depends on the temperature and the composition of the reaction mixture is complex and changes during the course of the reaction. Initially, the organic phase contains only CDT and solvent, and as the reaction progresses, ECDD as well as diECDD also appears in it. This obviously increases the polarity of the organic phase. It should also be remembered that the PTC mechanism is complex and there are still doubts as to the actual course of this reaction. The first hypothesis assumes the existence of an interfacial area into which the reagents are transported and in which the reaction takes place. The second is the extraction mechanism, which assumes that reagents in the form of lipophilic ionic pairs are transported from the inside of one phase to the other [28].

Indeed, independent of the real reaction mechanism, the increase in temperature should affect well on the accelerating of the reaction course. In case of the first mechanism, the increase in temperature is the key to accelerating the reaction by reducing the size of the micelles, resulting in increasing their number and, consequently, increasing in the total reaction surface. In case of the second mechanism, the increase in temperature may cause changes in the partition coefficient of the catalyst (its oxidized and reduced form) between the aqueous and organic phases, and smaller micelles additionally facilitate mass exchange between the phases.

The conversion of hydrogen peroxide was independent of the temperature of the process, the only exception was the reaction carried out at 40 °C, at which its value was much lower than the others. Conversions of hydrogen peroxide at 50, 60 and 70 °C were about 99 mol%. At the temperature of 40 °C, the conversion of hydrogen peroxide was 12 percentage points lower than at 50 °C, with the conversion of CDT differing by 3.7 percentage points, which may indicate that hydrogen peroxide decomposition reactions occur at higher temperatures.

Influence of solvent type

In order to study the effect of solvent type on the results of the CDT epoxidation, reactions were carried out using three different solvents: toluene, chloroform and ethyl acetate (EtOAc), as well as for the following process parameters: temperature 50 °C, solvent content 50 wt%, catalyst content 0.55 mol% CDT and the molar ratio H_2O_2:CDT 1.5:1. Chloroform and toluene were used because of their frequency of use in oxidation reactions under PTC conditions. Chloroform is used even in the Ishii catalytic system [29], and toluene in the Sato catalytic system [30]. Ethyl acetate was used because of its lower environmental impact in comparison to toluene and chloroform, and there are no reports about its use in oxidation reactions under PTC conditions. Table 4 and Fig. 7 show the results of studies involving selected solvents.

The conversions of CDT for ethyl acetate and chloroform were very similar throughout the duration of the reaction, slight differences only occurred at 30 min and disappeared at 60 min. For both of these solvents, the conversions of CDT were higher than those obtained with toluene throughout the entire duration of the reaction.

Table 4 The values of the conversion of the conversion of CDT (the values of the yields of ECDD are also given in brackets) for reactions carried out with different solvents[a]

Time (min)	Solvent		
	Toluene	CHCl$_3$	EtOAc
0	0 (0)	0 (0)	0 (0)
5	35.6 (26.1)	45.8 (31.1)	46.2 (33.8)
10	48.6 (37.2)	62.1 (39.5)	62.9 (42.3)
15	59.5 (47.0)	75.0 (44.2)	73.4 (44.1)
30	83.3 (53.2)	94.8 (36.9)	88.0 (41.9)
60	93.3 (45.0)	95.5 (34.4)	93.9 (34.7)
60[b]	98.9	99.4	99.6

[a]The reaction conditions were the same as those given in the title in Fig. 4

[b]The values of conversion of H$_2$O$_2$
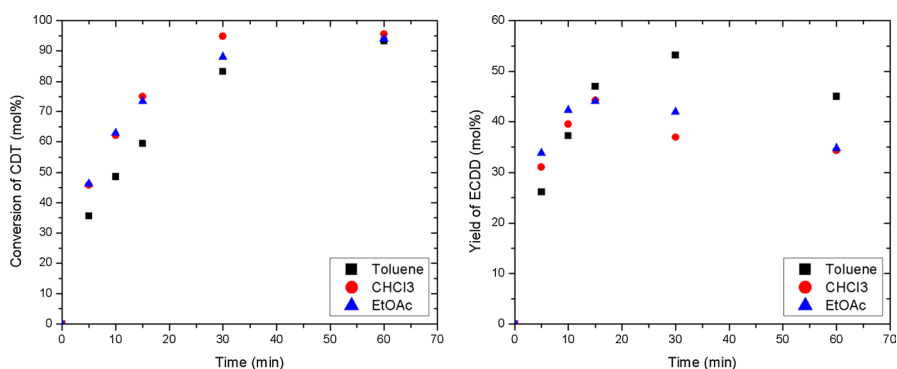
Fig. 7 Drawing showing the conversion of CDT and the yield of ECDD as a function of time for reactions with different solvents. Reaction conditions were the same as those given in the title in Fig. 4

The largest differences in the yield of ECDD between toluene and other solvents can be seen after 30 and 60 min. After this time, the yield of ECDD using it is more than 10 percentage points higher than using the other two solvents.

The higher yield of ECDD for the reaction carried out using toluene may result from its hydrophobicity, expressed by the polarity, whose value is lower than the values for chloroform and ethyl acetate (0.099; 0.259; 0.228 [31]). Lower polarity limits water availability and, consequently, inhibits the epoxy ring hydrolysis reaction. After the reaction was completed, almost complete conversion of hydrogen peroxide was obtained, regardless of the solvent used.

In this series of studies, the tendency to formation of emulsion was the feature that differentiated individual syntheses. In the case of toluene, the emulsion practically did not form, for ethyl acetate the formation of emulsion was noticeable, however, it disappeared after about 10–15 s after stopping of mixing, for chloroform the emulsion

formation intensified with the passage of time of reaction and after 30 min of reaction the emulsion did not separate even after waiting of 30 s after stopping of mixing.

The similarity of changes in the conversion of CDT for reactions carried out using $CHCl_3$ and EtOAc can be attempted to explain the similar polarity of these solvents (0.259 and 0.228, respectively), which is much higher than the polarity of toluene (0.099). The increased polarity of these solvents improves their solubility in water. Their increased content in the aqueous phase may in turn improve the solubility of the catalyst and facilitate the oxidation of its reduced form.

Conclusion

The possibility of epoxidation of CDT with H_2O_2 was investigated in the new catalytic system consisting of H_2WO_4, H_3PO_4 and $[CH_3(CH_2)_7]_3CH_3N^+HSO_4^-$, mixed together in the molar ratio 2:1:1 and under different reaction conditions. The influence of catalyst content, the molar ratio H_2O_2:CDT, temperature and type of solvent on the course of studied reaction was examined. The described catalyst system proved to be active in the epoxidation of CDT with hydrogen peroxide. The change of each of the examined process parameters affected the results of the conducted reaction, while each of the parameters affected the results of the reaction to a different degree. The highest yield of ECDD throughout the entire study was obtained for the reaction carried out using the catalyst content 0.45 mol% CDT, the molar ratio H_2O_2:CDT 1.5:1 and toluene as the solvent after 30 min of reaction carrying out. It was equal to 54.9 mol%.

For most reactions, there is a noticeable decrease in the value of the yield of ECDD after exceeding by the conversion of CDT value of 70 mol%. This is most likely associated with further oxidation of ECDD to diECDD.

In a series of studies to investigate the effect of the molar ratio of H_2O_2:CDT on the results of CDT epoxidation, it was found that the amount of hydrogen peroxide does not affect the initial reaction rate, however, the excess of oxidant adversely affects the yield of ECDD in the later stages of the reaction.

The similarity of the time course of CDT epoxidation reactions for the tested solvents indicates that the type of solvent only slightly affects the results of the reaction. Therefore, it is possible to replace chloroform with more environmentally friendly and safer ethyl acetate, without significantly reducing the efficiency of the process.

In the course of further research on the process of epoxidation of CDT with hydrogen peroxide using the catalytic system consisting of H_2WO_4, H_3PO_4 and methyltrioctylammonium hydrogen sulfate, further research should be carried out to determine the impact of other relevant process parameters, followed by their optimization. Considering the numerous applications of ECDD, further research on this process is desirable.

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