

Kinetics and mechanism of the ozone reaction with cyclohexanol in solution

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Dedicated to the 80th anniversary of Professor Lachezar Petrov, DSc,
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Ozone absorption by cyclohexanol solution during ozonolysis in a bubbling reactor has been studied by continuous monitoring of the ozone concentration at the reactor outlet under conditions of constant values of the initial ozone concentration at the reactor inlet. It was found that the values of the rate constant (at 25 °C) and the activation energy of the reaction were $3.1 \text{ M}^{-1}\cdot\text{s}^{-1}$ and 10.2 kcal/mol, respectively. Infrared spectroscopy and GC/MSD were employed to determine the products obtained at 24% conversion degree of the substrate by oxidation of a 1% solution of cyclohexanol in CCl_4 at room temperature. Three bands at 1710, 1724, and 1776 cm^{-1} were observed in the IR spectra of the ozonized solutions, which are characteristic of acidic, ketone, and ester functional groups, respectively. Based on the obtained IR and GC data it was established that cyclohexanone is the main reaction product of the cyclohexanol ozonolysis. Cyclohexanone and 2-chlorocyclohexanone to ester quantitative ratio determined by GC/MSD analysis was found to be 53/47. The amount of the main ester product, hexanedioic acid, dicyclohexyl ester, was 37% of the total ester yield.

Keywords: ozone, ozonolysis, cyclohexanol, solution, oxidation

INTRODUCTION

It is well known that ozonolysis of alcohols could be used for selective preparation of ketones and aldehydes that have various applications in the chemical and pharmaceuticals industries, fine chemicals synthesis, etc. [1, 2]. These reactions proceed under mild conditions and are characterized by high yields of the respective carbonylic compounds [3]. In some cases of oxidation of open chain (simple) and cyclic secondary alcohols the yield of corresponding ketones lies in the range of 57–83% [4].

On the other hand, alcohols have been considered the first oxidation step during ozonolysis of alkanes and cycloalkanes [1, 5]. A characteristic feature of the alcohols is their significantly higher reactivity with respect to ozone in comparison with that of the corresponding alkanes [3, 6]. For this reason, it could be expected that some of the compounds identified in the model reaction of cyclohexane ozonolysis, are products of cyclohexanol ozonolysis [5]. In this connection, there are theoretical and experimental works dealing mainly with reaction kinetics studies [6, 7].

Except for cyclohexanone, there is a problem with the identification of other reaction products related to the reaction mechanism [8, 9].

The aim of the present paper is the precise determination of the kinetic parameters of the cyclohexanol ozonolysis, identification, and

quantitative characterization of the main reaction products.

EXPERIMENTAL

Ozone was obtained by passing a dried oxygen flow (99.99%) through a 4–9 kV discharge in a self-made design of tubular type of ozone generator.

The ozonation experimental runs were performed in a bubbling reactor containing 10–15 ml of 1% solution of p.a. grade cyclohexanol in CCl_4 . An ozone-oxygen mixture with ozone concentration within the range of 1000–25000 ppm (4.5×10^{-5} – $1.2 \times 10^{-3} \text{ mol}\cdot\text{l}^{-1}$) was passed through the reactor at a flow rate of about $(1.3 \pm 0.3) \times 10^{-3} \text{ l}\cdot\text{s}^{-1}$ at room temperature. Ozone concentrations in the gas phase at the reactor inlet ($[\text{O}_3]_0$) and outlet ($[\text{O}_3]_g$) were measured spectrophotometrically by a BMT model 964 ozone analyser.

IR spectra of the samples were recorded on a Nicolet 6700 FTIR spectrometer (Thermo Electron Corporation, USA). The spectra were collected in the middle IR region using 100 scans at a resolution of 4 (data spacing 1.928 cm^{-1}).

GC-MSD analyses were performed on an Agilent Technologies model 890A instrument equipped with mass-selective detector model 5975C. A DB-WAXETR capillary column of 30-m length and 0.25-mm i.d., coated with polyethylene glycol (0.25 μm), was used in the experiments. The temperature settings were as follows: injector temperature 200 °C; column temperature program from 40 to 260 °C;

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transfer line temperature 230 °C; detector temperature 150 °C; electronic source 230 °C, carrier gas He (5.0) at a rate of 0.7 ml/min, volume of the injected samples 0.2 µl; split 20:1. The quantitative ratios among reaction products were determined by the Internal Standard (ISTD) method.

Thermal treatment of the ozonized solutions was applied. Samples of ozonized solutions sealed in glass ampoules were heated for 2 hours at 100 °C. After the treatment, the samples were examined by IR spectroscopy and GC-MS analysis under the same conditions as those for the unheated samples.

RESULTS AND DISCUSSION

The ozone absorption process was studied by continuous monitoring of the ozone concentration at the reactor outlet under constant initial ozone concentration at the reactor inlet. The $[O_3]_g = f(\tau)$ dependence was recorded on a computer connected to the ozone analyser (Fig. 1).

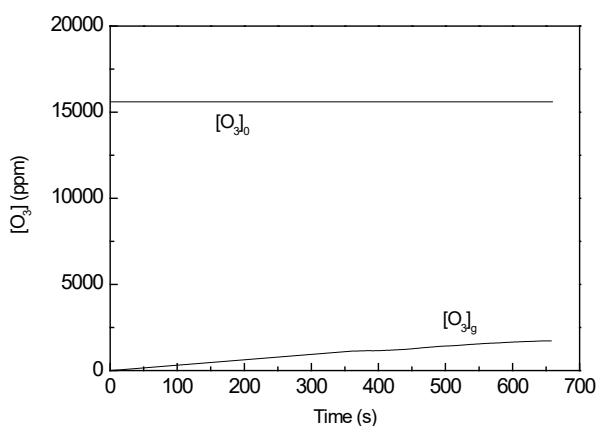


Fig. 1. Dependence of the ozone gas phase concentration ($[O_3]$) in the ozone-oxygen mixture on bubbling time: 1% solution of cyclohexanol in CCl_4 , gas feeding rate – $1.3 \times 10^{-3} \text{ l.s}^{-1}$, temperature – 24°C, $[O_3]_0$ – ozone concentration in the reactor inlet, $[O_3]_g$ – ozone concentration in the reactor outlet.

Considerable differences between $[O_3]_0$ and $[O_3]_g$ were observed, which indicate that a significant amount of bubbling ozone in the reactor is consumed during the reaction. The area enclosed between the $[O_3]_g = f(\tau)$ and $y = [O_3]_0$ curves is proportional to the amount of ozone consumed in the reaction. This amount was calculated by using the coefficient of ozone extinction at 254-nm UV-C wavelength, $3000 \text{ l.cm}^{-1} \cdot \text{mol}^{-1}$ [5], and the respective inlet flow rate of the ozone-oxygen mixture. In this way, it was determined that the amount of consumed ozone corresponds to 20% of the initial amount of cyclohexanol in the reactor.

As a rule, the low values of the $[O_3]_g/[O_3]_0$ ratio, which are characteristic of cyclohexanol ozonolysis (Fig. 1), if compared with those during ozone reaction with cyclohexane, could be explained by a significantly higher rate constant of the alcohol. One of the most often used methods for determination of the rate constants of ozonolysis of organic compounds is based on the approach proposed by Razumovskii *et al.* [3], which is a relationship between the balance of consumed ozone and the rate of the chemical reaction, Eq. (1):

$$\omega([O_3]_0 - [O_3]_g) = k[O_3]_l[RH], \quad (1)$$

where ω is the relative flow rate of the ozone-oxygen gas mixture (as litres per litre of solution per sec); $[O_3]_0$ and $[O_3]_g$ are ozone concentrations at the reactor inlet and outlet, respectively, $[O_3]_l$ is the concentration of ozone dissolved in the liquid phase; $[RH]$ is the concentration of the reagent. This model is valid in all cases when the rate of ozone absorption is considerably higher than the rate of the chemical reaction. In accordance with Henry's law for a bimolecular reaction, if $[O_3]_l$ is replaced by $[O_3]_g$, where α is Henry's coefficient (as mol.l^{-1} in liquid/ mol^{-1} in the gas phase), then Eq. (1) can be transformed into Eq. (2):

$$k = \omega \Delta[O_3] / ([RH] \cdot \alpha [O_3]_g) \quad (2)$$

Kinetic parameters of cyclohexanol ozonolysis were determined according to Eq. (2) in special experiments, which were carried out in accordance with the requirements for complete elimination of the diffusion limitation during the reaction [6]. It was found that the values of the rate constant (at 25 °C) and of the activation energy of the reaction were $3.1 \text{ M}^{-1} \cdot \text{s}^{-1}$ and 10.2 kcal/mol, respectively. These values are close to some other reported in the literature [6]. It is interesting to note that the k value of the cyclohexanol ozonolysis is more than two orders of magnitude higher than that of cyclohexane ozonolysis.

Infrared spectroscopy was employed to determine the different functional groups obtained at 24% ozone conversion of a 1% solution of cyclohexanol in CCl_4 at room temperature. The IR spectrum of the ozonized solution is presented in Fig. 2. The main peculiarity of the spectrum is the appearance of three bands at 1710, 1724, and 1776 cm^{-1} . According to literature data, these bands could be ascribed to acidic, ketone, and ester functional groups, respectively [10]. It is seen that the most intense band is observed at 1724 cm^{-1} , which is characteristic of cyclohexanone absorption.

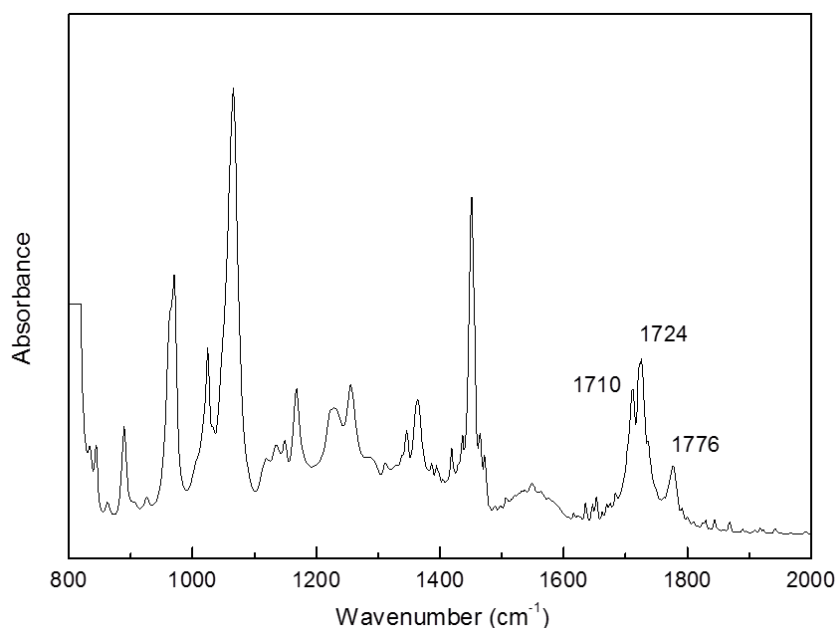


Fig. 2. IR spectrum of ozonized 1% solution of cyclohexanol in CCl_4 (24% conversion, NaCl cuvette 0.61 mm)

In contrast to infrared spectroscopy, the GC/MSD method provides a possibility of identification of individual reaction products. It should be noted that cyclohexanol conversion determined by chromatography was about 24%, while the amount of consumed ozone in the reactor reached 20% with respect to cyclohexanol initial content. Results of the identification and quantitative characterization of the organic compounds with a noticeable contribution among the mixture of reaction products are displayed in Table 1. It is seen that the basic products are ketones and esters. Also, small amounts of lactones, caprolactone and δ -valerolactone, and cyclohexane, 1,1'-[methylenebis(oxy)]bis- were detected.

Table 1. GC/MSD-determined content of the reaction products after ozonolysis of 1% solutions of cyclohexanol in CCl_4 under conditions of 24% conversion.

	Compound	Content, %
1	Cyclohexanone	39.68
2	Cyclohexyl formate	5.03
3	Cyclohexanone, 2-chloro	13.08
4	Pentanoic acid, cyclohexyl ester	3.50
5	5-Chloropentanoic acid, cyclohexyl ester	4.17
6	Hexanoic acid, 2-hexenyl ester, (E)-	2.37
7	Hexanoic acid, cyclohexyl ester	5.35
8	Cyclopentanecarboxylic acid, pentyl ester	9.42
9	Hexanedioic acid, dicyclohexyl ester	17.44

According to Table 1, the ketone/ester ratio is 53/47. The acidic components of the esters are pentanoic acid, 5-chloropentanoic acid, hexanoic acid, cyclopentanecarboxylic acid, and hexanedioic acid. The amount of the main ester product, hexanedioic acid dicyclohexyl ester, is about 37% of the total ester yield.

Significant amounts of identified cyclohexanone, 2-chloro- and 5-chloropentanoic acid, cyclohexyl ester could be regarded as a piece of evidence for ongoing radical processes with the participation of CCl_4 .

It is important to note that the results, discussed above, differ significantly from those published in Ref. [9]. Owing to ozonolysis of pure cyclohexanol, the cyclohexanone/ester ratio determined by Korotkova *et al.* under comparable conditions of reagent conversion (27.7%) and reaction temperature (40 °C) is 47.8/22.9. In this case, however, 'esters' refer to a mixture of cyclic esters (lactones) and classic esters. Furthermore, according to their analysis of the reaction products, the amount of caprolactone is about 70%, whereas the major acidic component of the classic esters is acetic acid. In our opinion, these differences can be explained by the formation of HCl due to solvent participation in the reaction. It is well known that mineral acids are capable of catalysing the interaction between organic acids and alcohols (cyclohexanol), which leads to the formation of the respective esters.

Although the IR spectra indicate presence of acidic groups among the reaction products, chromatographic identification of individual acids is

not possible within the limits of the available experimental equipment. Assuming that the main amounts of the esters having cyclohexanol as alcohol component are mostly obtained by the classical esterification reaction, it follows that formic, pentanoic, 5-chloropentanoic, hexanoic, and hexanedioic acids are present in the reaction mixture. Reported data in Table 1 show that the largest amount is concerned with hexanedioic (adipic) acid. According to literature data, cyclohexanone to acid ratio is 47.8/16.3, while that of monocarboxylic to dicarboxylic acids is about 0.20–0.22. Acetic, butyric, valeric, and caproic acids have been identified as monocarboxylic acids, whereas adipic acid is dominating among the dicarboxylic acids (77–94%) [9].

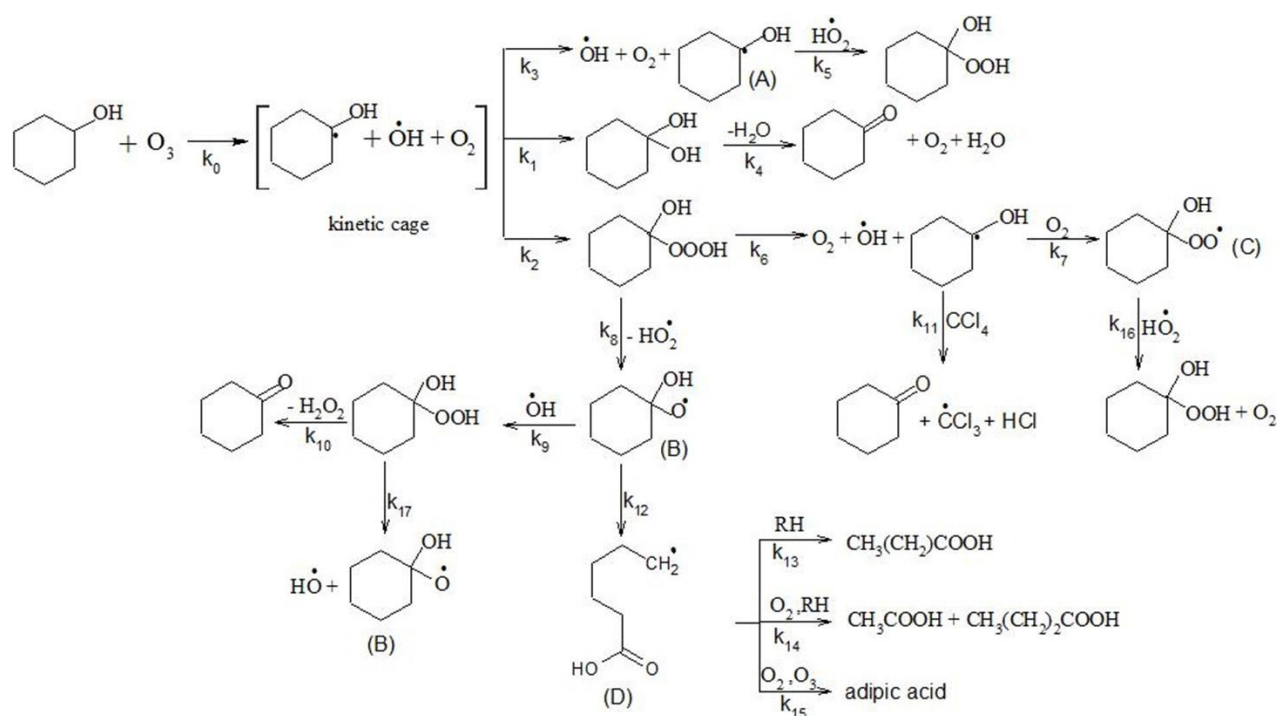
Different types of compounds containing peroxide-bonded oxygen are known to be among the major reaction products of cyclohexanol ozonolysis [6, 8, 9]. However, IR spectroscopy and gas chromatography are not suitable methods to identify and quantify individual hydroperoxide and peroxide compounds. Moreover, they are thermally unstable and practically inseparable from the reaction mixture. Bearing in mind reference data on iodometric titration, the ratio of cyclohexanone to the total amount of organic compounds containing O-O bonds is 47.8/9.7 [9]. Hydrogen peroxide formation has also been determined. The following products containing peroxide-bonded oxygen have been identified by thin layer chromatography: 1,1-

hydroxy-cyclohexyl hydroperoxide; 1-oxy-1'-hydroperoxi-dicyclohexyl peroxide; 1,1'-dioxy-dicyclohexyl peroxide [8, 9].

An attempt to incorporate different reaction routes, which lead to the formation of basic type of ozonolysis products, is presented in Scheme 1.

Ozone attacks the α -H atom to form a linear complex, which further undergoes decomposition into a radical pair in one kinetic cage. Being unstable, the α -hydroxy alcohol leaves the cage and rapidly decomposes to the corresponding ketone by liberating water and oxygen (reactions 1, 2). This scheme shows that the cyclohexanone is also formed as a result of decomposition of the 1,1-hydroxycyclohexyl hydroperoxide (reaction 10). Korotkova *et al.* proposed interaction between α -hydroxycyclohexyl radical and CCl_4 , which leads to the formation of respective ketone and hydrochloric acid (reaction 11) [9]. Significant amounts of cyclohexanone, 2-chloro- and 5-chloropentanoic acid, cyclohexyl ester among the reaction products are also indicative of solvent participation in various radical reactions.

It is accepted that the classical route to prepare various acids begins with the isomerization of α -hydroxyalkoxycyclohexyl radicals (Scheme 1, reaction 12) [9, 11]. The scheme displays the formation of caproic, butyric, acetic, and adipic acids (reactions 13, 14 and 15).



Scheme 1. Ozonolysis of cyclohexanol

Another route to prepare adipic acid could be the ozonation of cyclohexanone (cyclohexanone \rightarrow ϵ -caprolactone \rightarrow adipic acid).

One of the directions of hydroxytrioxy alcohol decomposition is the formation of hydroxyl radical, oxygen, and hydroxycyclohexyl radical (reaction 6). Interaction of the latter with oxygen from the air gives rise to α -hydroxyperoxidecyclohexyl radical (reaction 7). The 1,1-hydroxy-cyclohexyl hydroperoxide is obtained during a recombination process between the matching peroxide and hydroperoxide radicals (reaction 15). Reactions between the α -hydroxyalkoxycyclohexyl and hydroxyl radicals on the one hand (reaction 9), and between the hydroxycyclohexyl and hydroperoxyl radicals on the other hand (reaction 5), may also cause the formation of the discussed 1,1-hydroxy-cyclohexyl hydroperoxide. Contribution of reaction 5 is supposed to be small due to the high reactivity of the hydroxycyclohexyl radical with respect to oxygen [8, 9]. In the literature sources, the hydroxyl-cyclohexyl hydroperoxide is considered a main peroxide product, which is also the source for preparation of the other two peroxide compounds [8].

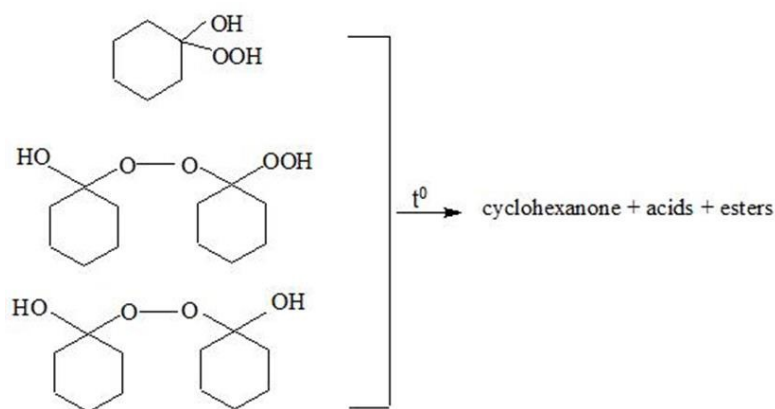
Reaction between organic acid and alcohol in the presence of Lewis or Brønsted acid sites is regarded as the most common route to prepare corresponding esters. The reaction mechanism of the so-called 'Fischer esterification' includes proton addition to the respective acidic groups to become electrophiles that are more reactive. A nucleophilic attack of the alcohol produces a tetrahedral intermediate with two equivalent hydroxyl groups. One of these groups is eliminated after a proton shift (tautomerism) to give water and ester [12]. In our case, it could be assumed that this reaction is the main source for the formation of hexanedioic acid dicyclohexyl ester, hexanoic acid cyclohexyl ester, pentanoic acid cyclohexyl ester, possibly 5-chloropentanoic acid cyclohexyl ester, and cyclohexyl formate. Most likely, this type

of esterification is catalysed by hydrochloric acid, which is the product of various radical reactions involving carbon tetrachloride participation [9].

The presence of hexanoic acid 2-hexenyl ester (E)-, and cyclopentanecarboxylic acid pentyl ester shows that there should be some alternative reaction pathways for the formation of the considered reaction products, because 2-hexen-1-ol and pentanol are not identified among the reaction products. It is seen in Table 1 that there are some esters, formed from acidic and alcoholic components, which have less than six carbon atoms. Changes in the carbon skeleton of cyclohexanol during ozonolysis are most likely related to transformation of various radical intermediates, such as hydroxycyclohexyl (A), α -hydroxy-alkoxy-cyclohexyl (B), α -hydroxyperoxidecyclohexyl (C), and isomerized α -hydroxyalkoxycyclohexyl (D) radicals. The degradation reactions of the mentioned radicals are known from literature sources [11, 13] and are not discussed in detail in the present work.

Since peroxide type products are thermally unstable, their decomposition could also be considered a source for ester formation [14]. It has been established that thermal treatment of various organic peroxides and hydroperoxides causes the formation of acids, carbonyl compounds, and esters (Scheme 2) [15–17]. Furthermore, it could be expected that heating of the reaction mixture during chromatographic analysis could lead to partial or complete decomposition of some of the products containing peroxide-bonded oxygen.

It is generally accepted that the first step on decomposing peroxide-type products is scission of the O-O bond that precedes formation of the corresponding radicals [14, 15]. Further, radical intermediates undergo various transformations and interactions, depending on chemical structure and reaction conditions (temperature and presence of oxygen), resulting in a wide range of ketones, acids, and esters [14, 18].



Scheme 2. Thermal decomposition of peroxide-type products.

In the process of thermal degradation, various gases such as CO₂, CO, and H₂ have also been detected [17, 18]. In this study, a mixture of three different peroxide-type compounds was thermally degraded in the presence of cyclohexanol, cyclohexanone, and a few acids. Under these conditions, differentiation of individual routes that are responsible for the preparation of specific compounds (ketones, acids, and esters) is practically impossible.

In order to study the chromatographically identified contents of the reaction products, samples from the reaction mixture after thermal degradation of peroxide-type compounds were further thermally treated under conditions that according to literature reports provide complete decomposition of all types of peroxides. [14, 18]. It was found that after thermal treatment of the ozonized samples the intensity of the bands at 1724 cm⁻¹ (cyclohexanone) and 1776 cm⁻¹ (esters) was increased by 29 and by about 53%, respectively. In addition, it is important to note that the band at 1710 cm⁻¹ was not changed while the intensity of the peak at 3344 cm⁻¹ due to the cyclohexanol hydroxyl group was reduced.

The chromatographic analysis did not indicate any formation of new products after thermal degradation of the peroxide-type compounds. A significant difference is an increase in share of hexanedioic acid dicyclohexyl ester with respect to the total ester amount from 37% in the initial sample to 66% after thermal treatment. In our opinion, thermal treatment of the ozonated samples creates favourable conditions for esterification between the cyclohexanol and the dominating adipic acid. The intensity of the peak at 1710 cm⁻¹ is not changed, since the amount of acidic groups consumed in the esterification reaction is compensated by that gained because of thermal degradation.

CONCLUSIONS

Upon cyclohexanol ozonolysis the values of the rate constant (at 25 °C) and of the activation energy of the reaction were found to be 3.1 M⁻¹.s⁻¹ and 10.2 kcal/mol, respectively.

Cyclohexanone and 2-chlorocyclohexanone to ester quantitative ratio determined by GC/MSD analysis was 53/47. The amount of the main ester product (hexanedioic acid, dicyclohexyl ester) was 37% of the total ester yield.

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