

Kinetics and mechanism of the ozone reaction with cyclohexane in liquid phase

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The peculiarities of the ozone reaction with cyclohexane in liquid phase have been studied under conditions of degree of conversion of the cycloalkane lower than 1 %. The ozone solubility in cyclohexane at various temperatures has been characterized by determination of the respective values of the Henry's coefficient. It was found out that the values of the rate constant (at 20 °C) and the activation energy of the reaction were $0.009 \text{ l}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ and 57.6 kJ/mol respectively. Dicyclohexyl was identified among the reaction products. The kinetics of formation of the cyclohexanol, cyclohexanone and dicyclohexyl were investigated in details by GC/MSD. A revised scheme of cyclohexane ozonolysis has been proposed.

Keywords: ozone, ozonolysis, cyclohexane, liquid phase, oxidation

INTRODUCTION

An important feature of the ozone reaction with cyclohexane in liquid phase, unlike its oxidation with molecular oxygen, is proceeding of the ozonolysis at ambient temperatures. This reaction is considered in the literature to be a model for the investigation of oxidation processes of alkanes and for polyolefines ageing, and on the other side as a reaction of selective oxidation of cyclohexane to cyclohexanone [1-3]. There are some works, in which kinetics of the reaction and the reaction products are studied depending on the oxidation conditions such as ozone/oxygen ratio, reaction temperature and degree of conversion. Different reaction schemes have been proposed [2, 4], and even a mathematical model of the cyclohexane ozonolysis has been published [3, 5]. The analysis of the literature data shows considerable discrepancies in relation to the kinetic schemes and also in view of the composition of reaction products and the respective proportions within them [1-3]. Probably part of these differences are due to the reactions of ozone with some of the primary products, whose rate constants are considerably higher in comparison with the corresponding value of the ozone-cyclohexane interaction [3, 6].

In the present work, we report a study on the reaction kinetics and the formation of some reaction products during liquid phase ozonolysis of cyclohexane, under conditions of low degrees of conversion.

EXPERIMENTAL

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

Ozonation

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

Determination of the amount of consumed ozone and the degree of conversion of cyclohexane

The ozone absorption process has been studied by continuous monitoring of the ozone concentrations at the reactor outlet, under conditions of constant values of initial ozone concentration at the reactor inlet. The $[\text{O}_3]_g = f(\tau)$ dependence was recorded on a computer, connected to the ozone analyzer (Fig. 1). The area of the surface enclosed between the curves $[\text{O}_3]_g = f(\tau)$ and the line $y = [\text{O}_3]_0$ is proportional to the amount of ozone consumed in the reaction. This amount has been calculated by using the coefficient of ozone extinction at UV wavelength 254 nm – $3000 \text{ l cm}^{-1} \text{ mol}^{-1}$ [7] and the respective inlet flow rate of the ozone–oxygen mixture.

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The real determination of the decrease in cyclohexane concentrations under conditions of extremely low depths of the reaction (< 1%) is inaccurate and practically impossible. In order to realize some kind of objective characteristic of the ozonolysis we will use a special value of "ozone conversion of cyclohexane" (in %), defined as the ratio of consumed ozone (mols) to initial amount of cyclohexane in the bubbling reactor (mols).

GC-MS analyses were performed on Agilent Technologies model 7890A instrument, equipped with mass-selective detector model 5975C. The capillary column DB-WAXETR of 30 m length and 0.25mm i.d., coated with polyethylene glycol (0.25 μm), was used in the experiments.

RESULTS AND DISCUSSIONS

Monitoring of the ozone absorption

The kinetic curve of the ozone absorption in cyclohexane is represented in Fig.1. It is seen that the respective curve could be divided into two sections: first one where saturation of cycloalkane with ozone is proceeding and a second one where the curve is parallel to the abscissa as a result of equilibrium between the feeding rate of ozone-oxygen mixture and the rate of the chemical reaction.

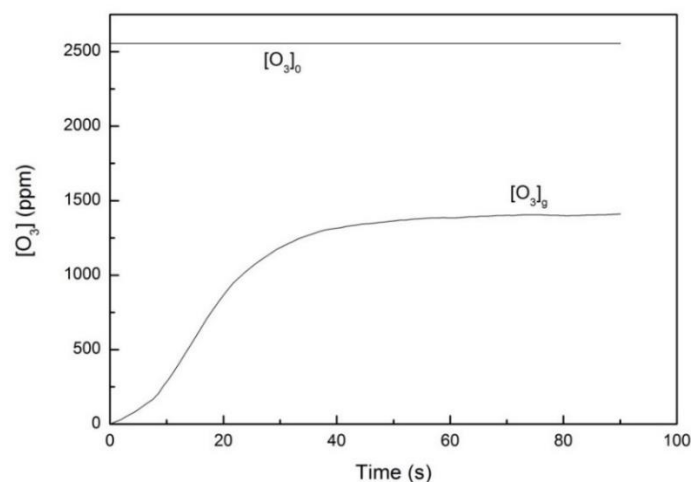


Fig.1 Dependence of the ozone concentration in gas phase ($[O_3]$) on the bubbling time of the ozone-oxygen gas mixture. Cyclohexane volume-15 ml, gas feeding rate - $1.18 \cdot 10^{-3}$ l/s, temperature-24 °C. $[O_3]_0$ -ozone concentration at the reactor inlet, $[O_3]_g$ -ozone concentration at the reactor outlet.

S.D. Razumovskii et al. [8], which expresses the 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 ozone-oxygen gas mixture (in litres per l of solution per sec); $[O_3]_0$ and $[O_3]_g$ are the ozone concentrations at the reactor inlet and outlet, respectively, $[O_3]_l$ is the dissolved ozone concentration in the liquid phase; $[RH]$ is the concentration of the reagent. This model is valid in

The reliability of the kinetic results derived from the data about the ozone concentrations in gas phase at the reactor outlet requires validity of Henry's law, which determines quantitatively the ratio between the equilibrium concentrations of ozone in liquid and in gas phase respectively. One of the widely applied criteria with respect to the conditions of validity of Henry's Law is the expression [8]:

$$D_{O_3} \cdot k_1' / k_L^2 \ll 1$$

where D_{O_3} is the diffusion coefficient of ozone in the solution; $k_L = D_{O_3} / \delta$ is the coefficient of mass transfer in the liquid phase, and δ is the thickness of the boundary layer in the hydrodynamic model of renovation surface; or $k_L = (D_{O_3} \cdot s)^{1/2}$, where s is the time interval of renovation; $k_1' = k[RH]_0$ where k and $[RH]_0$ are the rate constant of ozonolysis of the investigated compound and its initial concentration, respectively. The presented in [6, 8] detailed analysis of the mass transfer of the reagents, under conditions which are practically identical with those in our experiments, shows unconditional applicability of Henry's law to all of those cases ($\approx 0.01 \ll 1$). The determination of rate constants is based on the approach, proposed by

all cases, when the rate of ozone absorption is considerably greater than the rate of the chemical reactions. If in the case of a bimolecular reaction, in accordance with Henry's Law, $[O_3]_l$ is substituted by $\alpha[O_3]_g$, where α is Henry's coefficient (in mol.l⁻¹ in liquid/mol.l⁻¹ in gas phase), then Eq. (1) can be transformed into Eq. (2).

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

In order to minimize the influence of the so-called "effect of delay in the response function"- $[O_3]_g = f(\tau)$,

upon calculating the values of k such sections on the kinetic curves are selected, which appear to be practically parallel or only slightly inclined with respect to the abscissa: $k_1 \cdot \alpha \cdot [O_3]_g \gg d[O_3]_g/d(\tau)$. The advantages and limitations of this method have been discussed in detail in [8-10]. Despite some contradictory observations, significant number of the rate constants of ozone reactions with organic compounds and polymers are obtained on the basis of Eq. (2) [8].

It follows from equation (2) that for computation of the rate constant, the respective value of Henry's coefficient for cyclohexane should be known. However so far there are no literature data available concerning the solubility of ozone in cyclohexane at all. The most studied cases are the solubility of ozone in water and in chlorinated and fluorinated hydrocarbons [8, 11]. Usually the evaluation of solubility of ozone in liquids is based on the different forms of the Henry's coefficient or some other values, connected with them [11]. There are a little data in the literature about values of Henry's coefficients for hexane, octane and decane with insufficient correlation between them [8, 11].

Our attempt for the determination of α was based on the proposed by SD Razumovskii equation [8], which describes the balance of consumed ozone for the nonstationary part of the curve in Fig.1 (Eq. (3)).

$$\omega([O_3]_g - [O_3]_g)\tau' = \alpha[O_3]_g + \alpha k[RH] \int_0^{\tau'} [O_3]_g d\tau \quad (3)$$

It follows from Eq. (3) that the α value is equal to the expression (4):

$$\alpha = \frac{\omega([O_3]_g - [O_3]_g)\tau' - \alpha k[RH] \int_0^{\tau'} [O_3]_g d\tau}{[O_3]_g} \quad (4)$$

where τ' is the time interval, necessary of $[O_3]_g$ to reach its equilibrium value. At this moment

$$d[O_3]_g/d\tau = \omega([O_3]_o - [O_3]_g) - k[O_3]_g[RH] = 0.$$

Therefore $\alpha \cdot k[RH]$ is equal to $\omega([O_3]_o - [O_3]_g)$, and the expression $\int_0^{\tau'} [O_3]_g \cdot d\tau$ is computed by graphical integration of the respective section of $[O_3]_g$ curve in Fig.1. The determined, in this way, value of the Henry's coefficient of the ozone solubility in cyclohexane is equal to 1.21 (24 °C). The dependence of α on the temperature was also investigated in the interval 10-41 °C. Fig. 2 (curve 1) shows that the dependence $\ln \alpha = f(1/T)$ is linear and the respective values of α increase with lowering of the temperature.

As it will be shown hereinafter the cyclohexane ozonolysis is a complicated multi stages process. Some of the data concerning values of the rate constant are obtained under different conditions and the attempts to systematize them do not lead to good results [1, 3, 12]. Furthermore the cyclohexane solutions in CCl_4 are usually applied for determination of k , although it is known that the identified chlorinated derivatives during cyclohexane ozonolysis in CCl_4 show partially participation of the solvent in the reaction [4].

The already determined value of the Henry's coefficient of ozone allows application of eq. (2) for calculation of the respective k value under conditions of extremely low values of ozone conversion degree of cyclohexane ($\ll 0.03\%$), when involvement of secondary reactions are practically excluded. The value of $1.25 \cdot 10^{-2} \text{ l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ (24 °C) was obtained. In Fig. 2, curve 2 represents the k dependence on the temperature in Arrhenius coordinates. The derived from Fig. 2 k value (at 20 °C) and activation energy (E_a) are $0.009 \text{ l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ and 13.78 kcal/mol respectively. These values are in good correlation with some of the literature data for cyclohexane solutions in CCl_4 [1, 12].

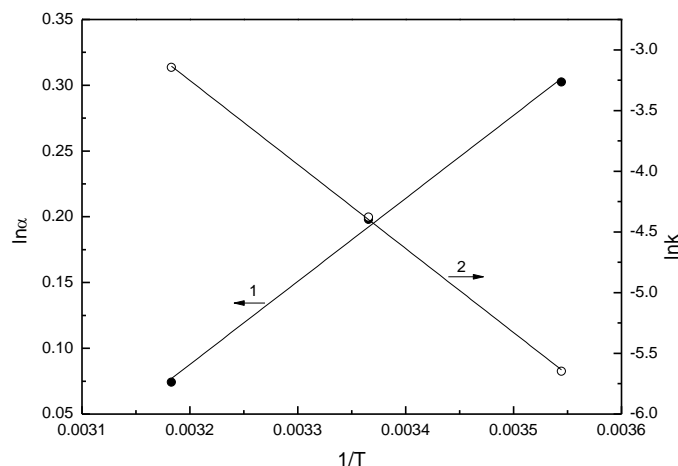


Fig. 2. Dependences of $\ln \alpha$ (1) and $\ln k$ (2) on $1/T$, where α is Henry's coefficient (in mol/l in solution / mol/l in gas phase); k is the rate constant of cyclohexane ozonolysis (in $\text{l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$).

Analysis of the products and the reaction scheme

It was found out that during cyclohexane ozonolysis a number of organic compounds such as cyclohexanol, cyclohexanone, different kinds of peroxides and hydroperoxides, acids and some others were identified as reaction products; formation of water was also observed [2-4]. However the data concerning the individual yields usually differ from each other and in many cases are contradictory [1-3]. The dependence of the product composition on the reaction conditions such as ozone/oxygen ratio, temperature of the reaction, depth of conversion of cycloalkane has been reported in the literature [3, 5]. At higher degrees of cyclohexane conversion additional compounds are identified, that could be considered as products of ozonolysis of the already mentioned primary reaction products [1, 3].

It has been accepted that cyclohexanol and cyclohexanone are the basic primary products of the ozonolysis and their additive yield, at low degree of conversion, varies within the range of 50-70% [3]. Fig. 3 shows the kinetics of formation of

cyclohexanol; cyclohexanone and dicyclohexil. It is seen that the alcohol concentrations are higher than the respective one of the cyclohexanone.

It is logical that the formation of every reaction product is explained by one or more elementary steps. Also attempts for modeling of the cyclohexane ozonolysis were made [3, 5]. On the basis of the model 28 reactions have been set, but they do not cover all of the identified products, especially at higher degree of conversion. It should be noted that there are serious contradictions with respect to some of the elementary steps, concerning their real existence as well as the values of their rate constants [1-3, 5]. The latest ones determine the contributions of the respective reactions in the formation of considered compounds. Since our aim was to investigate kinetics and mechanism of the formation of primary products at extremely low degrees of conversion, without proposing complete description of the scheme of ozonolysis, we have selected only those elementary steps, for which we suppose that they exert significant influence on the formation of the reaction products under our experimental conditions. They are represented in Scheme 1.

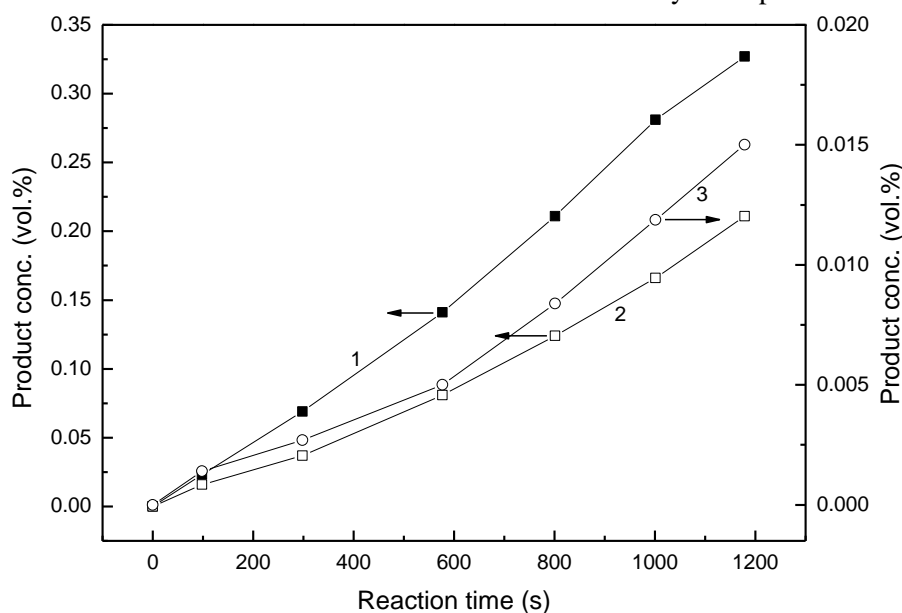
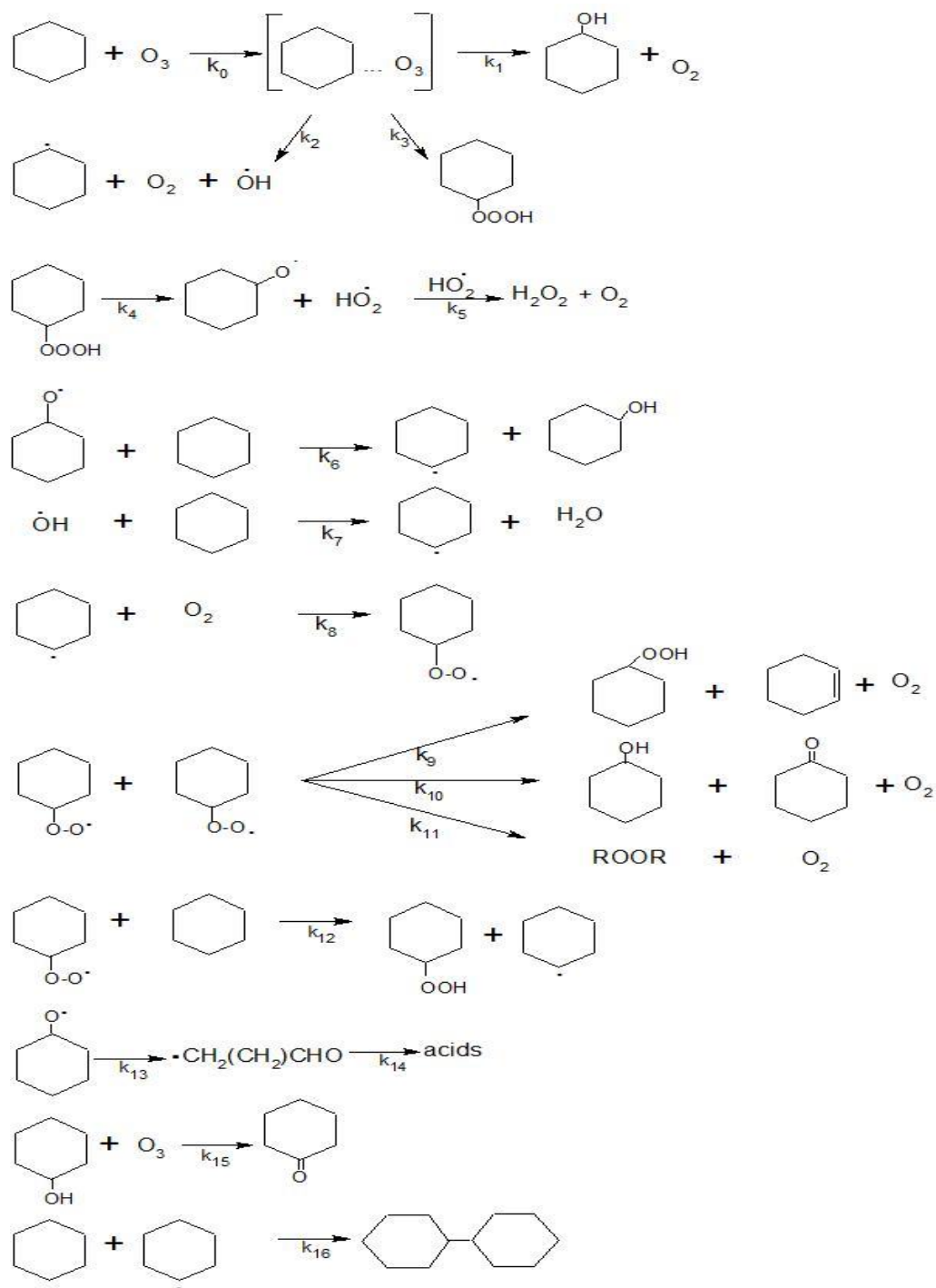


Fig. 3. Dependence of the product concentrations on the reaction time for 1- cyclohexanol; 2-cyclohexanon; 3- dicyclohexil. Cyclohexane volume-10 ml, $[O_3]_0$ -17600 ppm, gas feeding rate - $1.30 \cdot 10^{-3}$ l/s, temperature-24 °C.

It is seen from Scheme 1 that the products of the disproportionation of two peroxy radicals are cyclohexanol and cyclohexanone (Scheme 1, reaction 10). Additional quantities of cyclohexanol can be formed during the reactions 1 and 6 and in this way the higher yield of the alcohol, compared with the respective ketone (Fig 3), could be

explained. When the ratio cyclohexanol/ cyclohexanone is considered, especially at higher degrees of conversion, the values of the rate constants of the reactions of ozone with alcohol and ketone, which are at 20 °C 2.65 (reaction 15) and $1.6 \cdot 10^{-2} \text{ l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ respectively [1], should also be taken into account.



Scheme 1. Cyclohexane ozonolysis.

Particular attention is paid to the third component in the Figure 3- dicyclohexil. Although most of the proposed schemes suggest the formation of alkyl radicals (Scheme 1, reactions 2, 6, 7, 12), there are no reports about possible interaction between them. Till now the presence of dicyclohexil among the identified reaction products is not mentioned in the

literature (reaction 16). In the cases of ozonolysis in CCl_4 it is known only that there occurs the formation of small amounts of chloroderivates of the cyclohexane [1, 4]. As it is seen in Fig.3 the shape of the respective curve is similar to that of cyclohexanone, but the dicyclohexil concentrations are approximately 20 times of magnitude lower.

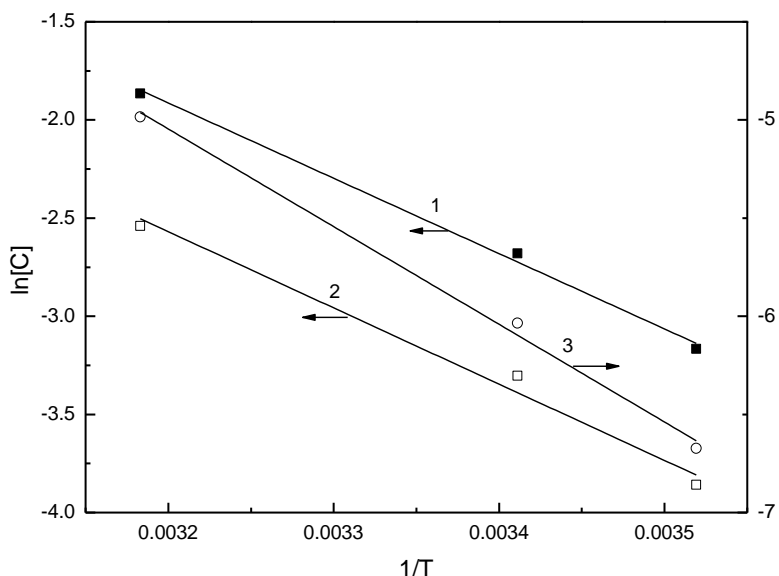


Fig. 4. Dependence of $\ln[C]$ on $1/T$ for 1- cyclohexanol; 2-cyclohexanon; 3-dicyclohexil. Cyclohexane volume-10 ml, gas feeding rate - $1.30 \cdot 10^{-3}$ l/s, reaction time-300 s, $[O_3]_0$ -17600 ppm.

The dependences of cyclohexanol, cyclohexanone and dicyclohexil concentrations on the temperature and ozone concentrations were also investigated. Fig. 4 represents the concentrations of respective reaction products in Arrhenius coordinates. It is found out that all three dependences are linear, as the concentrations of the cyclohexanol, cyclohexanone within the interval 10-41 °C, increase 367 and 374 % respectively, and that of dicyclohexil 540 %. The dependences of the concentrations of reaction products on the ozone concentration, under ozone

conversion of 0.1 %, are represented on Fig. 5. It is characteristic for the three curves that in the 0 -7500 ppm intervals a significant increase in the respective concentrations is observed, whereas from 7500 to 25 000 ppm there are no noticeable changes. This feature most probable is due to the requirement of achievement of "critical values" of the steady state concentrations of the peroxy and alkyl radicals or other precursors of the investigated reaction products.

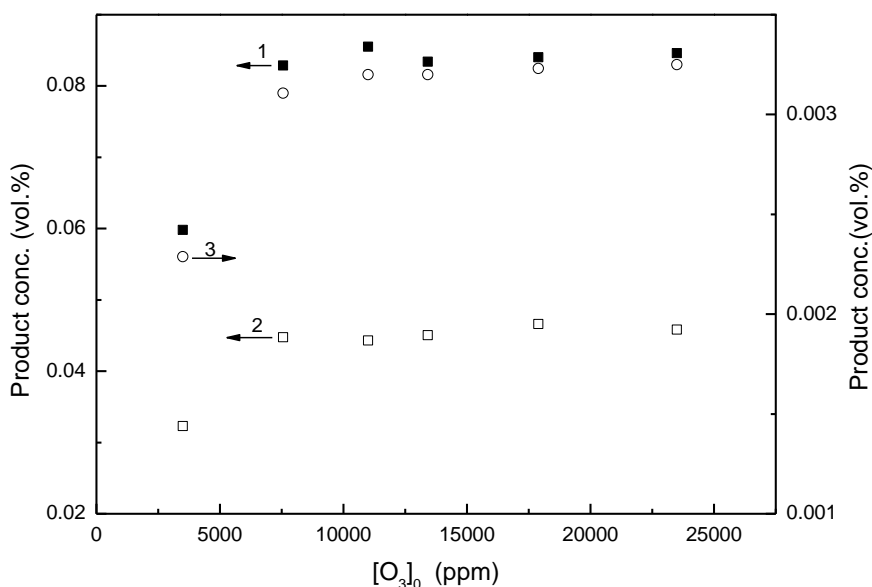


Fig. 5. Dependence of the product concentrations on the ozone concentration at the reactor inlet ($[O_3]_0$) for 1- cyclohexanol; 2-cyclohexanon; 3-dicyclohexil. Cyclohexane volume-10 ml, gas feeding rate - $1.30 \cdot 10^{-3}$ l/s, ozone conversion of cyclohexane-0.1%

CONCLUSIONS

The peculiarities of the ozone reaction with cyclohexane in liquid phase have been studied under conditions of degrees of low ozone conversion degrees of the cycloalkane between 0.03 and 0.43%.

The ozone solubility at various temperatures has been characterized by determination of the respective values of Henry's coefficient (1.25 at 20 °C). It was found out that the values of the rate constant (at 20°C) and the activation energy of the reaction were 0.009 l.mol⁻¹.s⁻¹ and 57.6 kJ/mol respectively.

Dicyclohexyl was identified among the reaction products. The kinetics of formation of the cyclohexanol, cyclohexanone and dicyclohexyl were investigated in details by GC/MSD. A revised scheme of the cyclohexane ozonolysis has been proposed.

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КИНЕТИКА И МЕХАНИЗЪМ НА РЕАКЦИЯТА НА ОЗОНА С ЦИКЛОХЕКСАН В ТЕЧНА ФАЗА

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(Резюме)

Изследвани са особеностите на реакцията на озона с циклохексан в течна фаза при степени на конверсия на въглеродорода по-ниски от 1 %. Разтворимостта на озона в циклохексан при различни температури е охарактеризирана посредством определянето на съответните стойности на коефициента на Хенри. Установено е, че стойностите на скоростната константа при 20 °C и на енергията на активация на реакцията са съответно 0.009 l.mol⁻¹.s⁻¹ and 57.6 kJ/mol. Дициклохексил е идентифициран сред продуктите на озонизирания. Кинетиката на образуване на циклохексанол, циклохексанон и дициклохексил е изследвана посредством GC/MSD хроматография. Предложена е ревизирана схема на озонизацията на циклохексан.