

*Slavcho Rakovsky<sup>1</sup>, Metody Anachkov<sup>1</sup>, Mikhail Belitskii<sup>2</sup>  
and Gennady Zaikov*

## KINETICS AND MECHANISM OF THE OZONE REACTION WITH ALCOHOLS, KETONES, ETHERS AND HYDROXYBENZENES

<sup>1</sup> *Institute of Catalysis, Bulgarian Academy of Sciences,*

*11, Acad. G. Bonchev str., 1113 Sofia, Bulgaria; rakovsky@ic.bas.bg*

<sup>2</sup> *N.M. Emanuel Institute of Biochemical Physics, Russian Academy of Sciences,*

*4, Kosygin str., 119334 Moscow, , Russia*

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**Abstract.** The review, based on 92 references, is focused on degradation of organics by ozonation and it comprises various classes of oxygen-containing organic compounds – alcohols, ketones, ethers and hydroxybenzenes. The mechanisms of a multitude of ozone reactions with these compounds in organic solvents are discussed in details, presenting the respective reaction schemes. The corresponding kinetic parameters are given and some thermodynamic parameters are also listed. The dependences of the kinetics and the mechanism of the ozonation reactions on the structure of the compounds, on the medium and on the reaction conditions are revealed. Various possible applications of ozonolysis are specified and discussed. All these reactions have practical importance for the protection of the environment.

**Keywords:** ozonation, alcohol, ketone, ether, hydroxybenzene, kinetics, mechanism.

### 1. Introduction

The ozonolysis of oxygen-containing compounds is a promising process that takes place under mild conditions and yields compounds of a higher oxidation state than that of the starting compounds. It may find various applications in chemical and pharmaceuticals industries, fine organic synthesis, *etc.* [1-2]. The widest application, in this respect, has been found for the oxidation of primary and secondary alcohols respectively into their corresponding aldehydes and ketones. For example in the cases of the oxidation of open-chain (simple) and cyclic secondary alcohols the yield of ketones is within the range of 57–83 % [3]. Moreover, the considered interactions are extremely important from an ecological point of view for the utilization and purification

of industrial wastewaters, originating from hydroxybenzene production, through their partial or complete oxidation [4-24]. The importance of this process for theory and practice gave us an impetus to carry out systematic investigations [25-35]. The aim of the present paper is to determine the ozonolysis rate with the above cited oxygen-containing organic compounds and to clarify the role of oxygen in mechanism and reaction ability. Applying the activated complex method (ACT) [36] and collision theory (CT) [36] some theoretical investigations have also been carried out elucidating the structure of the transition state formed in the course of the reaction. On the basis of the correlation between the results from the experimental and theoretical studies some peculiarities in the mechanism of ozone reactions with the considered classes of oxygen containing compounds have been established.

### 2. Experimental

*Ozone* has been obtained from dry oxygen by means of a silent discharge of 5–8 kV at an oxygen flow rate of 0.1 l/min. The ozone concentration,  $10^{-5}$ – $10^{-3}$  M, has been measured spectrophotometrically in the wavelength region of 254–300 nm in 5 cm quartz gas cell.

The UV, IR, ESR spectra were registered on standard equipments, as well as HPLC, and GC analyses.

#### 2.1. Kinetic Measurements

##### 2.1.1. Static method

Pure reagent or reagent solution was injected into thermostatic 1 cm quartz cuvette, containing a solution of ozone in  $\text{CCl}_4$ , the time of mixing being less than 0.2 s. Ozone concentration was monitored spectro-photo-

metrically in the region of 270–290 nm. At  $[\text{RH}]_o/[\text{O}_3]_{lo} > 100$ , the ozone pseudomonomolecular constant  $k' = k[\text{RH}]_o$  was determined on the basis of the equation  $\lg([\text{O}_3]_{lo}/[\text{O}_3]_{li}) = k't$  where  $[\text{O}_3]_{lo}$  and  $[\text{O}_3]_{li}$  are the initial and current concentrations of ozone in the solution, respectively [27].

### 2.1.2. Dynamic method

The ozone was bubbled through a cylindrical glass reactor with the inner diameter  $f = 1.7\text{--}3.7$  cm and height 7–15 cm, supplied with porous glass grit-G2 at its bottom. The accuracy of maintaining constant temperature was  $\pm 0.1$  K. Conventionally, a gas flow rate was  $v = 0.1$  l/min; the solutions volume was  $V = 10$  ml; the ozone concentrations at the reactor inlet ( $[\text{O}_3]_o$ ) varied from  $10^{-6}$  to  $10^{-3}$  M; the solvent was  $\text{CCl}_4$ ;  $[\text{RH}]_o = 10^{-4}\text{--}10^1$  M. The inlet and outlet ozone concentrations were measured in the gas phase in 254–300 nm wavelength range. The determination of rate constants is based on the approach, which connects the balance of consumed ozone with the rate of the chemical reaction – Eq. (1):

$$w([\text{O}_3]_o - [\text{O}_3]_g) = k[\text{O}_3]_l[\text{RH}] \quad (1)$$

where  $w$  is the relative flow rate of ozone-oxygen gas mixture (in litres per litre of solution per sec);  $[\text{O}_3]_o$  and  $[\text{O}_3]_g$  are the ozone concentrations at the reactor inlet and outlet, respectively,  $[\text{O}_3]_l$  is ozone concentration in the solution;  $[\text{RH}]$  is the concentration of the reagent.

This model is valid in 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 the Henry's law,  $[\text{O}_3]_l$  is substituted with  $\alpha[\text{O}_3]_g$ , where  $\alpha$  is the Henry's coefficient, Eq. (1) can be transformed into Eq. (2):

$$k = w\Delta[\text{O}_3]/([\text{RH}] \cdot \alpha[\text{O}_3]_g) \quad (2)$$

One of the widely applied criteria with respect to the conditions of validity (applicability) of the Henry's law is the expression:

$$D_{\text{O}_3} \cdot k_1' / k_L^2 \ll 1$$

where  $D_{\text{O}_3}$  is the diffusion coefficient of ozone in the solution;  $k_L = D_{\text{O}_3}/d$  is the coefficient of mass transfer in the liquid phase, and  $d$  is thickness of the boundary layer in the hydrodynamic model of renovation surface; or  $k_L = (D_{\text{O}_3} \cdot s)^{1/2}$ , where  $s$  is the time interval of renovation.

In the case of applying the bubbling method with small bubbles (diameters up to 2.5–3 mm)

$$k_L = 0.31 \cdot (gn)^{1/3} \cdot (D_{\text{O}_3}/n)^{2/3}$$

where  $n = h/r$ , is the kinematic viscosity of the solvent,  $h$  is the viscosity of the solvent,  $r$  is the solvent density,  $g$  is the earth acceleration.

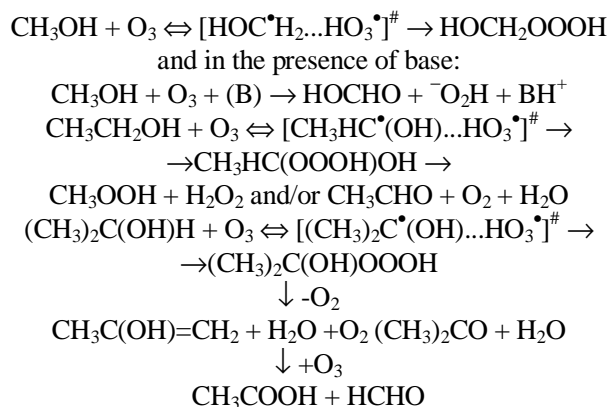
Usually the  $k_L$  values are of the order of 0.1–0.05 cm/s. As  $k_1' = k[\text{RH}]_o$  in the most cases it is possible to select such values for  $[\text{RH}]_o$ , under which the criterion for applicability of the Henry's law is fulfilled (34).

In order to minimize the influence of the so-called “effect of delay in the response function” –  $[\text{O}_3]_g = f(t)$  upon calculating the values of  $k$  such sections of the kinetic curves are selected, which appear to be practically parallel or only slightly inclined with respect to the abscissa:  $k_1' \alpha [\text{O}_3]_g \gg d[\text{O}_3]_g/dt$ . The advantages and limitations of this method have been discussed in detail in [37, 38]. Despite some contradictory observations, the significant part of ozone rate constants with organic compounds and polymers are obtained on the basis of Eq. (2) [1, 34].

## 3. Results and Discussion

### 3.1. Alcohols

A number of authors have tried to elucidate the kinetics and mechanism of the ozonolysis of alcohols and their application to the selective preparation of ketones and aldehydes in high yields under mild conditions [3, 39–46]. The basic concepts of such reactions are discussed in several references [1, 2, 25, 34, 35, 39]. It has been established that the rate of ethanol ozonolysis does not change when the hydroxyl group is deuterated [43] and its value is 4.17 times higher than in case the methylene group is deuterated. On the basis of this fact, together with the data from the analysis of the product composition and the kinetics of their formation the authors have suggested that the H-atom abstraction by the ozone molecule is the rate-determining step of the reaction. This conclusion is confirmed by the data in Table 1 as reported by various authors [41–43]. The ratio between the relative reactivities of tertiary: secondary: primary alcohols is 1:12:241 according to Ref. [41], or 1:156:817 according to Ref. [7]. On the basis of the studies of the reaction of ozone with methyl, ethyl and 2-propyl alcohol, the following reaction mechanism is proposed (Scheme 1) [40]:



Scheme 1

It is supposed that an intermediate ion or pair of radicals are formed, which recombination in the kinetic cage yields  $\alpha$ -hydroxy-hydrotrioxide. The latter leaves the cage and passes into the volume of solution.

Table 1

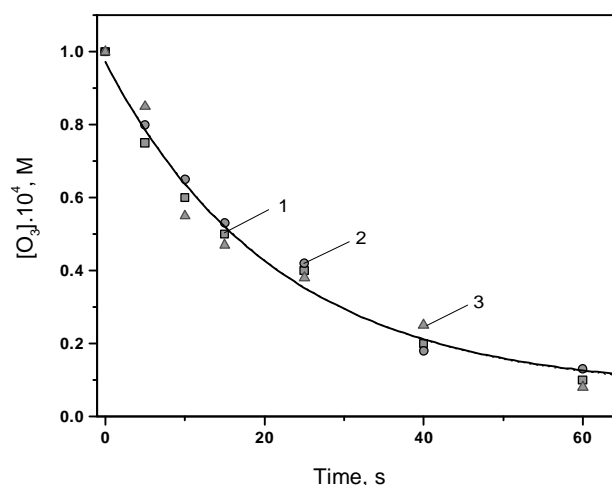
**Kinetic parameters of the ozone reaction with aliphatic alcohols at 298 K**

Alcohols	k, $M^{-1}\cdot s^{-1}$	lg A	E, kJ/mol	Ref.
<i>tert</i> -Butanol	0.01	4.6	37.6	[32]
<i>tert</i> -Butanol	0.05	–	–	[31]
Ethanol	0.35	6.7	41.0	[32]
Ethanol	0.25 (295 K)	6.7	41.0	[33]
<i>n</i> -Butanol	0.54	7.3	43.1	[32]
<i>n</i> -Butanol	0.39			[31]
<i>iso</i> -Propanol	0.89	7.3	41.80	[32]
Cyclopentanol	1.35			[31]

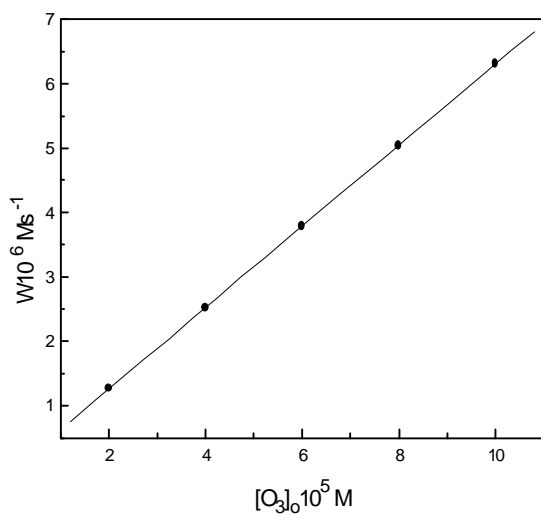
The authors [40] found that the product composition of 2-propanol ozonolysis depends on the method of propanol purification. Taking into account the above given consideration about the reaction pathway, in our opinion, the mechanism still remains unclear and new data should be provided for its elucidation. In this connection we have carried out intensive experimental studies on the kinetics of ozonolysis of MeOH, *t*-BuOH, EtOH, *n*-PrOH, *n*-BuOH, *i*-PrOH, *s*-BuOH, *c*-HexOH both by the static and barbotage methods, the results of which are summarized in Figs. 1-3 and Tables 2-4.

Fig. 1 demonstrates the kinetic data of ozone consumption in solutions of methanol, ethanol and *iso*-

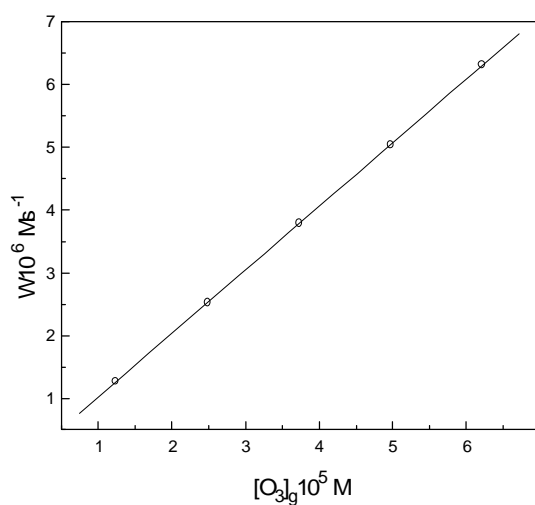
propanol by means of the static method with time interval of mixing less than 0.2 s. It is seen that regardless of the type of alcohol being ozonized, the kinetic curves coincide with the first-order rate law. From the point of view of more precise evaluation and comparison of the respective rate constants such concentrations of the respective alcohols have been selected, at which the rates of ozone consumption have close values. The kinetic curves of ozone reactions with MeOH, EtOH and *i*-PrOH gave the following values of the rate constants: 0.057, 0.17 and 1.13  $M^{-1}\cdot s^{-1}$ , respectively.



**Fig. 1.** Kinetics of ozone consumption in the reaction of ozone with: methanol, 295 K, 0.74 M (1); ethanol, 276 K, 0.24 M (2) and isopropanol, 276.5 K, 0.037 M (3)



a)



b)

**Fig. 2.** Dependence of the ozone consumption rate on the ozone concentrations: inlet  $[O_3]_0$  (a) and outlet  $[O_3]_g$  (b) at methanol concentration of 0.74 M

Table 2

Kinetic parameters of ozone reaction with MeOH in carbon tetrachloride (CCl<sub>4</sub>) and pure MeOH solutions: 295 K,  $w = 0.167 \text{ s}^{-1}$ ;  $v = 1.67 \times 10^{-3} \text{ l/s}$ , maximum rate of ozone inlet is  $1.67 \times 10^5 \text{ M}\cdot\text{s}^{-1}$

[MeOH], M	[O <sub>3</sub> ] <sub>0</sub> ·10 <sup>5</sup> , M	[O <sub>3</sub> ] <sub>g</sub> ·10 <sup>5</sup> , M	Δ[O <sub>3</sub> ] <sub>g</sub> ·10 <sup>5</sup> , M	W·10 <sup>6</sup> , M·s <sup>-1</sup>	k, M <sup>-1</sup> ·s <sup>-1</sup>
0	10	0	10	0	-
0.247	10	8.32	1.68	2.80	0.057
0.439	10	7.35	2.65	4.43	0.056
0.618	10	6.64	3.36	5.61	0.058
0.740	10	6.22	3.78	6.31	0.055
0.987	10	5.53	4.47	7.46	0.057
1.0	10	5.49	4.51	7.53	0.056
2.0	10	3.79	6.21	10.37	0.055
3.0	10	2.89	7.11	11.87	0.057
4.0	10	2.34	7.66	12.79	0.058
5.0	10	1.96	8.04	13.42	0.054
10.0	10	1.09	8.91	14.88	0.056
24.7	10	0.47	9.53	15.91	0.058
0.740	8	4.98	3.02	5.04	0.057
0.740	6	3.73	2.27	3.79	0.055
0.740	4	2.49	1.51	2.52	0.056
0.740	2	1.24	0.76	1.27	0.058

Table 3

Dependence of  $k$  on the temperature in K for ozone reaction with three types of alcohols

$k, \text{M}^{-1}\cdot\text{s}^{-1}$	273	283	293	298	303
MeOH	0.008	0.021	0.049	0.072	0.108
<i>t</i> -BuOH	0.005	0.013	0.029	0.045	0.064
EtOH	0.14	0.28	0.54	0.74	1.10
<i>n</i> -PrOH	0.19	0.36	0.67	0.89	1.18
<i>n</i> -BuOH	0.15	0.30	0.56	0.76	1.10
<i>i</i> -PrOH	0.93	1.61	2.71	3.46	4.39
<i>s</i> -BuOH	0.88	1.54	2.58	3.29	4.18
<i>c</i> -HexOH	0.92	1.59	2.65	3.37	4.27

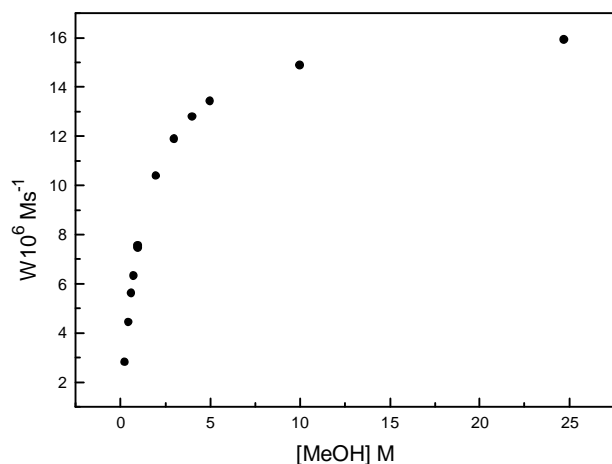
The same values were also obtained by carrying out the reactions in a bubble reactor. The values of  $k$  are calculated on the basis of Eq. (2) – the data are given in Table 2 and they are represented graphically in Figs. 2 and 3.

Processing the data from Table 2, columns 2, 3, and 5, based on Eq. (2), yield the linear dependencies shown in Fig. 2. The dependence of the rate  $W$  on  $\Delta\text{O}_3$  has also been found out to be a linear one. The dependence of the rate  $W$  on the concentration of alcohol [ROH] (column 1) is a curve, which approaches a limit value at  $W = 1.67 \cdot 10^{-5} \text{ M}\cdot\text{s}^{-1}$ . The nonlinear character of this relationship is in accordance with the complexity of Eq. (2) (see also Fig. 3). In the case when  $[\text{ROH}] \rightarrow \infty$ , then we have  $[\text{O}_3]_{\text{g}} \rightarrow 0$  and  $\Delta\text{O}_3 \rightarrow [\text{O}_3]_0$ . The values of  $k$ , calculated based on Eq. (2) at each one of the points on the curve (Fig. 3), are equal to 0.057.

Therefore the experimentally obtained linear dependences of  $W$  on  $[\text{O}_3]_0$ ,  $[\text{O}_3]_{\text{g}}$  and on  $\Delta[\text{O}_3]$  as well as

the profile of the curve in Fig. 3 correspond to the mathematical description of ozonolysis in a barbotage reactor – Eq. (2).

Judging from the analysis of the data obtained (Tables 3 and 4) it follows that the rate constant and the activation energies are strongly dependent on the alcohol structure. The interaction of ozone with MeOH possessing primary  $\alpha$ -H atoms and with *tert*-BuOH having only primary C–H bonds has been found to be the slowest, and the value of  $k$  at 293 K per one  $\alpha$ -H atom in the first case is  $1.62 \cdot 10^{-2} \text{ M}^{-1}\cdot\text{s}^{-1}$ , and in the second case, related to one primary H atom, is  $3.22 \cdot 10^{-3} \text{ M}^{-1}\cdot\text{s}^{-1}$ . The difference in the values of these constants is due to the fact that while the OH group in MeOH directly affects the  $\alpha$ -H atom, in the case of the *tert*-BuOH, which does not possess any  $\alpha$ -H atoms, the effect of the OH groups is transferred through one  $\sigma$ -bond and so it is considerably weaker.



**Fig. 3.** Dependence of the ozone consumption rate on methanol concentration at  $[O_3]_0 = 1 \cdot 10^{-4} M$  ( according to Eq. (1))

As a result of this, the reactivity of *tert*-BuOH becomes similar to that of methane and neopentane. The interactions of ozone with EtOH, *n*-PrOH, *n*-Bu OH take place at higher rates and the values of  $k$  per one  $\alpha$ -H atom amount to: 0.27, 0.34 and 0.28, respectively. The higher rates of the ozone reactions with these alcohols are associated with the presence of secondary  $\alpha$ -H atoms in their molecules, which have lower bond energies than the primary ones. The enhanced reactivity of *n*-PrOH compared with that of EtOH could be assigned to the donor effect of the second  $CH_3$  group while the donor effect of the  $C_2H_5$  group in *n*-BuOH is weaker than that of

the methyl group and therefore  $k$  is lower. It has been found that the reactions of ozone with *i*-PrOH, *s*-BuOH and *s*-HexOH alcohols possessing *tert*-H atoms with the lowest bond energies is the fastest with  $k$  equal to 2.71, 2.58 and 2.65, respectively, *i.e.*, in fact they are almost the same. The ratio between the reduced values of  $k$  at 298 K for methanol:ethanol:*sec*.butanol are 1:15:137. Simultaneously, the value of  $E_a$  decreases with the decrease of the  $\alpha$ -H atoms bond energy ( $D$ ) and their ratio is 1:0.78:0.61 [12, 15]. This fact can be regarded as an important evidence for the mechanism of  $\alpha$ -C-H-atom abstraction by ozone.

The theoretical estimates of  $A$  were performed considering two possible structures of the activated complex (AC): linear (LC) and cyclic (CC) (Fig. 4). The good agreement between the experimental data and theoretical estimates for  $A$  allows the determination of the AC structure and on this basis enables the selection of the most probable mechanism. Simultaneously the value of the pre-exponential factor was calculated by the collision method and by comparing its value with the one calculated based on the AC theory the steric factor  $-p$  was determined (Eq. (3)) [48-52]:

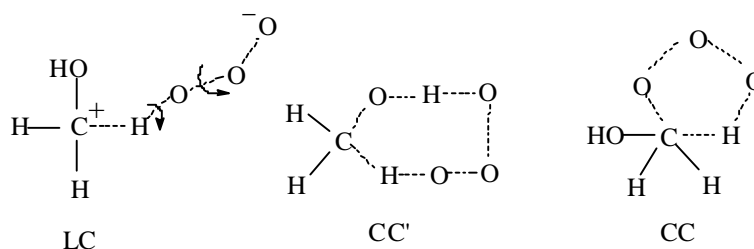
$$k = p \cdot Z_0 \cdot \exp(-E_a/RT) \quad (3)$$

where:  $Z_0 = p \cdot (r_A + r_B)^2 \cdot (k_B T / pm^*)^{1/2}$ ;  $Z_0$  is the collision factor;  $r_A$  and  $r_B$  are the Van der Waals radii of the reagents;  $k_B$  is the Boltzmann's constant;  $T$  is the absolute temperature; and  $m^*$  is the reduced mass.

Table 4

**Kinetic parameters of ozone reaction with some alcohols at 298 K**

Parameters	MeOH	<i>t</i> -BuOH	EtOH	<i>n</i> -PrOH	<i>n</i> -BuOH	<i>i</i> -PrOH	<i>s</i> -BuOH	<i>c</i> -HexOH
$k \cdot 10^2, M^{-1} \cdot s^{-1}$	7.2	4.5	74	89	76	346	329	337
$n, \alpha$ -C-H	3	9 ( $\beta$ -C-H)	2	2	2	1	1	1
$k \cdot 10^2/n, M^{-1} \cdot s^{-1}$	2.4	0.5	37	44	38	346	329	337
$E_a, kJ/mol$	58.1	57.3	45.6	42.2	43.5	35.5	35.5	35.1
$A \cdot 10^{-7}, M^{-1} \cdot s^{-1}$	41	5.8	3.9	2.4	1.7	0.62	0.59	0.51



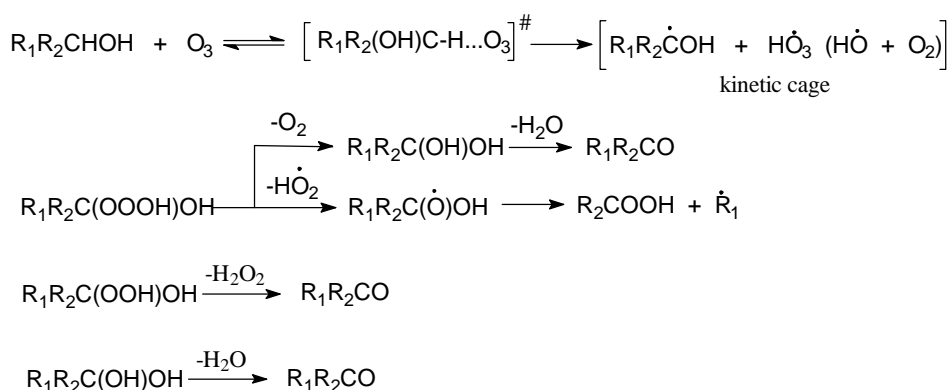
**Fig. 4.** Structure of the probable activated complexes in the reaction of ozone with aliphatic alcohols: LC – linear with free fragment rotation; CC' and CC – cyclic complexes without free rotation

Table 5

The values of  $A$  calculated by ACT with LC and CC and by CT, the sums ( $R_{fr}$ ) and energy ( $E_{fr}$ ) of inner rotation, steric factors ( $p$ ), VDW radii of the molecules ( $r$ ) and the ratio between the calculated and experimental values of pre-exponentials  $A^{LC}_{cal}/A_{obs}$

Parameters	MeOH	EtOH	<i>n</i> -PrOH	<i>i</i> -PrOH	<i>n</i> -BuOH	<i>s</i> -BuOH	<i>t</i> -BuOH	<i>c</i> -HexOH
$A^{CC} \cdot 10^{-4}, M^{-1} \cdot s^{-1}$	52	8.3	3.7	3.5	2.4	2.2	6.3	1.6
$A^{LC} \cdot 10^{-4}, M^{-1} \cdot s^{-1}$	56	15	6.7	6.3	4.4	4.0	4.9	2.9
$F_{fr} \cdot 10^{-2}$	7.1	9.8	12	11	13.8	12.6	12.9	12.6
$A^{LC}_{cal} \cdot 10^{-7}, M^{-1} \cdot s^{-1}$	40	15	8.1	6.8	6.1	5.0	6.3	3.6
$r, \text{\AA}$	2.24	2.57	2.91	2.88	3.13	3.23	3.13	3.23
$A^{CT} \cdot 10^{-11}, M^{-1} \cdot s^{-1}$	2.6	2.6	2.7	2.7	2.8	2.8	2.8	2.7
$p \cdot 10^5$	22	5.8	2.5	2.3	1.6	1.4	1.8	4.1
$A^{LC}_{cal}/A_{obs}$	1.0	3.8	3.4	11	3.1	8.3	1.1	7.2
$E_{fr}, \text{kJ/mol}$	0	3.05	2.80	5.71	2.92	4.89	0.22	4.51

Note:  $A^{LC}$  is the pre-exponential factor calculated with LC without free fragment rotation (it is absent at  $E_{fr} \geq 16.6$  kJ);  $A^{CC}$  – calculated with CC;  $A^{LC}_{calc}$  – at free fragment rotation, i.e., when  $\exp(-E_{fr}/RT) = 1$  or  $E_{fr} = 0$  kJ;  $A^{CT}$  – calculated according to the collision theory at 300 K and  $r$  – calculated by the Alinger method (PCMOD4 program) at the radius of the ozone molecule of 2 Å;  $E_{fr}$  – the calculated values of the rotation energy at ratio of  $A^{LC}_{cal}/A_{obs} = 1$ .



Scheme 2

The pre-exponential factors for the reactions of ozone with alcohols, calculated according to the activated complex method (ACT) and collision theory (CT) are represented in Table 5.

An interesting fact is the good agreement between the values of  $A^{LC}$  and  $A^{CC}$ . The values of  $A^{CC}$  with five- and seven-member cyclic form of AC are practically similar as they differ by not more than 1 %. However the free rotation produces an increase in  $A^{LC}_{cal}$  by three orders of magnitude compared with that of  $A^{CC}$ . The steric factor has a value, which is in agreement with a liquid phase reaction. The ratio between the calculated and experimental values of  $A^{LC}$  is increasing in the sequence primary:secondary:tertiary alcohols as follows: 1:3.4:8.8. This is connected with the fact that  $E_{fr}$  is not zero and it is increasing with the changes in the alcohol structure in the same sequence. It has been found that the values of  $A^{LC}_{calc}$  and  $A_{obs}$  coincide when the values of rotation energy are

those given in line 10 in Table 5. We have obtained the same values by means of the *MOPAC 6* software package and therefore the data on the free rotation energy ( $E_{fr}$ ) in line 10 can also be considered as theoretically evaluated.

The good agreement between  $A^{LC}_{calc}$  and  $A_{obs}$  suggests that the rate-determining step of the ozone reaction with alcohols involves the formation of linear AC and abstraction of the  $\alpha$ -H atom from the alcohol molecule.

The experimental and theoretical results are in good agreement with Scheme 2.

Ozone attacks the  $\alpha$ -H atom, forming LC, which further undergoes decomposition into a radical (or ion) pair in one kinetic cage. The  $\alpha$ -hydroxy alcohol,  $\alpha$ -hydroxyperoxy alcohol and  $\alpha$ -hydroxytrioxy alcohol being unstable leave the cage and decompose rapidly to the corresponding aldehyde or ketone liberating water, hydroperoxide and oxygen or lead to the formation of

hydroperoxy and alkoxy radicals. The latter species can further undergo monomolecular decomposition.

### 3.2. Ketones

The investigation of the reactions of ozone with ketones is of interest from the viewpoint of the reactivity theory, the ozone chemistry, preparation of oxygen-containing compounds, and the degradation and stabilization of organic materials. In particular, the ozonation of methylethylketone (MEK) [53-55] yielded acetic acid (AcAc), diacetyl and hydroperoxide as the main reaction products in  $\text{CCl}_4$ . It has been assumed that the process is not the oxidation chain-radical reaction. Similar products are also formed when the reaction takes place in water. However, in this case ozone interacts with the enol form of MEK [53]. The addition of nitric acid accelerates enolization, which is evidenced by the increase of the oxidation rate [55]. The decrease of the oxygen content in the ozone-oxygen mixture results in an increase of the oxidation rate, which is due to a change of the radical leading to oxidation, from  $\text{RO}_2^\bullet$  to  $\text{RO}^\bullet$ . The ozonation of isomeric decanones indicates that the reactivity of ketones depends on the length and structure of the alkyl chain. In this case the main products are  $\alpha$ -keto-hydroperoxides, monocarboxylic acids, keto-alcohols and alkylbutyric lactones. However, it should be noted that the conclusions in these studies were based on the product analysis at very high degrees of conversion whereby the secondary reactions play an important role in the product formation. This gives us reasons to doubt whether the proposed mechanism describes adequately the initial steps of the reaction. The rate constant and the activation energy of interaction between cyclohexanone and ozone are  $1.6 \cdot 10^{-2} \text{ M}^{-1} \cdot \text{s}^{-1}$  and 46.7 kJ/mol, respectively.

The reactivity of ozonized methyl derivatives of cyclohexanone is considerably higher than that of the H form. An increase in the rate of interaction between the above derivatives and ozone is also observed depending on the location of substitution and it follows the sequence [56-58]: 3-methylcyclohexanone < 4-methylcyclohexanone < 2-methylcyclohexanone.

It is evident from the foregoing that so far no systematic investigations on the ozonolysis of ketones have been carried out. In our studies on the ozonolysis of ketones we combined the kinetic approach and product analysis with theoretical methods. The results from the ozonolysis of some aliphatic ketones are shown in Table 6.

The following six types of ketones have been the subject of our investigations:

- (1) Acetone containing only  $\alpha$ -C-H bonds,
- (2) Ketones with the general formula  $\text{CH}_3\text{CO}(\text{CH}_2)_n\text{CH}_3$ , where  $n = 1, 4, 5, 6$  and  $9$ , which contain secondary  $\alpha, \beta, \gamma$  C-H bonds,
- (3) Ketones with the general formula  $\text{CH}_3(\text{CH}_2)_m\text{CO}(\text{CH}_2)_n\text{CH}_3$ , where  $m = 1, n = 4$ , which contain  $\alpha, \alpha'$ -secondary C-H bonds and cycloheptanone, which contains  $\alpha, b$  and  $g$  secondary C-H bonds, 4-4-methyl or 4-*tert*-butyl cyclohexanone with  $\gamma$ -*tert*-C-H bond,
- (4) 2-Naphthylmethylketone with various substituents, and
- (5) Acetylacetone containing  $\alpha$ -C-H bond activated by two keto-groups.

The rate constant of keto-enol tautomerism for the latter compound is considerably higher than those of the other ketones studied, because of the C=C-double bonds appearance.

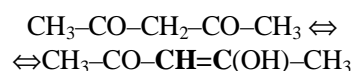


Table 6

Kinetic parameters of the ozone reaction with some aliphatic ketones at 294 K

Ketone	$k_0 \cdot 10^3, \text{M}^{-1} \cdot \text{s}^{-1}$	$k_{sr} \cdot 10^3, \text{M}^{-1} \cdot \text{s}^{-1}$	$k_{rel}$	lg A	$E_a, \text{kJ/mol}$
$\text{CH}_3\text{COCH}_3$	3.5	7.7	0.2	10.823	75.1
$\text{CH}_3\text{COC}_2\text{H}_5$	12	24	0.7	10.63	71.0
$\text{CH}_3\text{COC}_5\text{H}_{11}$	23	67	1	10.54	68.8
$\text{CH}_3\text{COC}_6\text{H}_{13}$	45	58	2.4	10.46	66.7
$\text{CH}_3\text{COC}_7\text{H}_{15}$	448	54	2.3	10.31	65.0
$\text{CH}_3\text{COC}_{10}\text{H}_{21}$	42	113	2.2	10.58	67.6
$\text{C}_2\text{H}_5\text{COC}_5\text{H}_{11}$	20	74	1	11.48	64.6
$\text{CH}_3\text{COCH}_2\text{COCH}_3$	29000	—	—	—	—
<i>c</i> - $\text{C}_7\text{H}_{12}\text{O}$	87	80	4.1	9.00	71.0
$\text{CH}_3\text{CO-2-Naph}$	22000	—	—	5.77	25.0
4- $\text{CH}_3$ - <i>c</i> - $\text{C}_6\text{H}_9\text{O}$	117	101	6.2	8.97	50.0
4- <i>t</i> -Bu- <i>c</i> - $\text{C}_6\text{H}_9\text{O}$	166	123	8.1	7.93	49.2

Note:  $k_0$  is calculated according to Eq. (2);  $k_{rel}$  is the relative rate constant determined by gas chromatography relative to ethylpentylketone.

The values of  $k$  vary, depending on the ketone structure, particularly on the content of primary, secondary or tertiary  $\alpha$ -C-H bonds, in a wide range. The ratio of their reactivities is 1:(3.4–24.8):(33.4–47.4). In contrast to paraffins these values are more similar, which are associated with the activation of  $\alpha$ -C-H bonds by the keto-group. Ozone is sensitive not only to the activation of the  $\alpha$ -C-H bonds but also to the keto-enol equilibrium. The rate of its reaction with acetylacetone is by three orders of magnitude higher than that with monoketones. Ketones with different substituents, for example, 2-naphthylmethylketones also show higher reactivity than the aliphatic ketones. It is concluded that the reaction centre in this case is the naphthyl ring and not the  $\alpha$ -C-H bond in the methyl group.

Another interesting observation is the higher values of  $E_a$  compared with those of paraffins (with some 8–12 kJ/mol). As ozone is an electrophilic reagent and the activation of the  $\alpha$ -C-H bonds from the keto-group favours the nucleophilic attack, it is reasonable to expect an increase in  $E_a$ .

Fig. 5 shows a typical kinetic curve illustrating the change of ozone concentration at the reactor outlet during ozonolysis of ketones in the solution.

The horizontal line describes the inlet ozone concentration and the curve corresponds to the change in its concentration at the reactor outlet. It is seen that the addition of ketone results in a sharp decrease in the ozone concentration, followed by a section with only slight changes of  $[O_3]_{g1}$ . After some time the ozone concentration rises up again to reach a region, where the respective curve is practically parallel to the abscissa ( $[O_3]_{g2}$ ).

The shape of the kinetic curve of ozone consumption (Fig. 5) is complicated and this implies that ozone reacts with more than one compound [1, 26, 27]. The two horizontal sections of the curve are the result of the interaction of ozone with two compounds, the rate constants of which differ considerably. The areas over the curve correspond to the amount of absorbed ozone. Knowing the concentrations of the reacted compounds the stoichiometry coefficients and other kinetic parameters can be calculated.

This type of kinetic curve for the ketones is associated with the keto-enol equilibrium and with the ability of ozone to react with the C=C bonds 106 times faster than with the C-H bonds with almost zero activation energy [1].

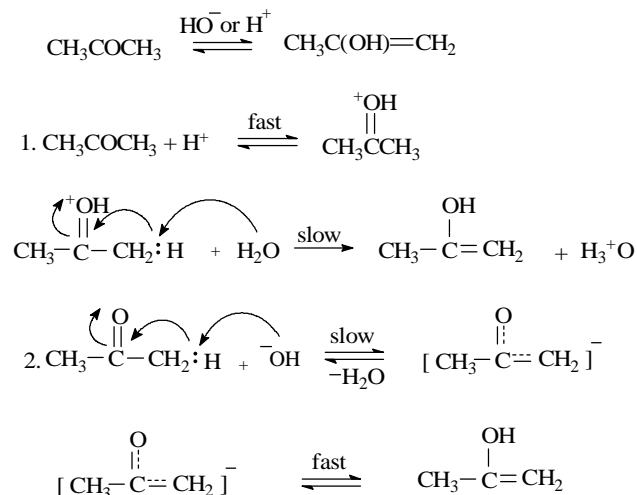
The processes corresponding to the ozone-gas curve (Fig. 5) are the following:

(1) the ozone starts its reaction with ketone (probably with the enolic form) and an abrupt fall of its concentration is registered;

(2) when the rate of ozone supply becomes equal to the rate of the chemical reaction, the first step is formed;

(3) the end of the step is connected with the consumption of the enolic form and the ozone concentration begins to rise up;

(4) at this moment the ozone begins to react with the keto-form and the second step is formed, whereby the rate of ozone supply becomes equal to the rate of the second reaction. The sharp transition between the two steady-state regions gives evidence that the rate of restoration of the keto-enolic equilibrium is considerably lower than the rate of ozone interaction with the keto-form.



The concentration of the enolic form can be estimated from the area enclosed below the kinetic curve in Fig. 5 and then the equilibrium constant of enolization could be measured.

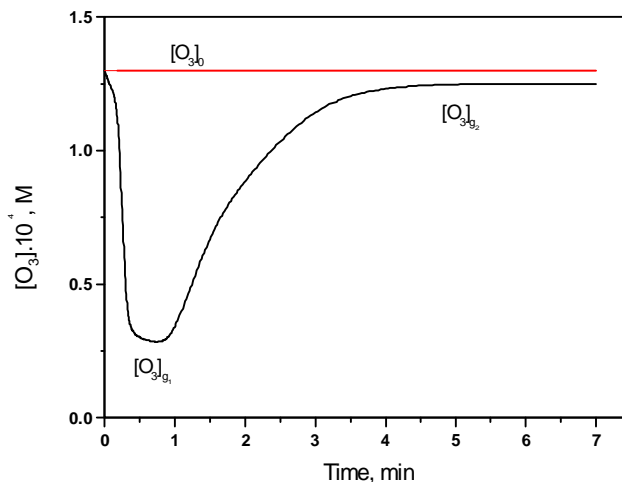


Fig. 5. Ozonolysis of 0.712 mmol cycloheptylketone in 10 ml  $CCl_4$ , 294 K,  $v = 0.1$  l/min

It is known that the stoichiometry of the reaction of ozone with C=C is 1:1 and thus the amount of the enolic



form can be judged based on the amount of absorbed ozone, *i.e.*, in this particular case the concentration of the enolic form is 0.134 mM. As the initial concentration of ketone is known, the equilibrium quantity will be the difference between the initial concentration and that of the enolic form. Then the equilibrium constant can be easily calculated using the formula:  $K_e = [\text{Enol}]_e / [\text{Keton}]_e$  and it amounts to  $1.9 \cdot 10^{-2}$ .

Based on the curve in Fig. 5 one can also determine the rate constants of the ozone interaction with the two tautomeric forms. Taking into account the parameters of the first section of the curve ( $[\text{O}_3]_{\text{gl}}$ ) and by using Eq. (2), the value of the rate constant with the enolic form is found to be  $k_E = 2.9 \cdot 10^2 \text{ M}^{-1} \cdot \text{s}^{-1}$  and therefore the second rate constant with the keto-form is  $k_K = 0.048 \text{ M}^{-1} \cdot \text{s}^{-1}$ . In this way the possibility of application of the ozone titration method to the measurement of the equilibrium constant and the rate constants of ozone interaction with two tautomeric forms in one kinetic experiment has been demonstrated.

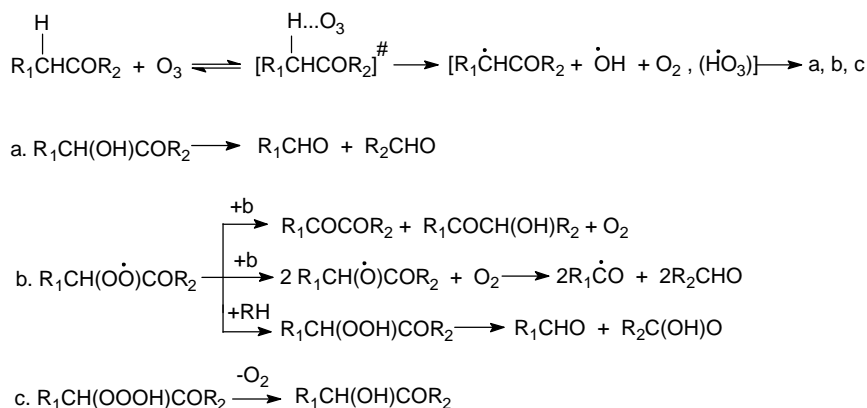
In order to evaluate the possible influence of the processes of mass transfer on the values of the rate constants, determined by the barbotage method, beside the observation of the criteria, described in the experimental section, some additional experimentation has been carried out, connected with the changes in the size of the reactor, in the volume of the solution, and in the concentration of the ozone at the reactor inlet. The results, obtained upon varying the above-listed parameters within the range up to about 30–50 %, did not show any significant deviations in the respective values of  $k$ , and therefore there is noticeable effect of mass transfer conditions on these values.

It is evident that the rate constants of ozone interaction with ketone, measured by the static method (Fig. 6) through mixing of ozone and ketone solutions at  $[\text{K}]_0 \gg [\text{O}_3]_0$  are higher than those found by the bubbling method (Table 6). This is not difficult to explain because in the former case the obtained values represent the total effective constant of interaction of both the enol- and the keto-form.

The results from the calculation of the equilibrium constants of keto-enol tautomerism for some aliphatic ketones in  $\text{CCl}_4$  are given in Table 7. The data for acetylacetone and 2-naphthylmethylketone are not presented in the table because in the former case the rate of reaching the equilibrium is commensurable with the rate of ozone consumption and in the latter case the ozone reacts with the double bonds in the naphthyl ring. The equilibrium constants do not differ from those found within the temperature range of 294 to 276 K and agree with data from the literature [59–62].

The kinetics of ozone reactions with ketones is also determined using the gas chromatographic analyses. The relative rate constants shown in Table 6, column 4 demonstrate that only acetone and methylketone possess the lower reactivity than the standard. It is seen that the rate constants, calculated from the relative values and the value of the standard constant correspond to those found by the bubbling method. The main products of ozone interaction with methyl-ethylketone are 2-hydroxy-methylethylketone, diacetyl, peroxides – alkyl and hydro, acetaldehyde and AcAc.

On the basis of the kinetic results obtained and the product analyses we suggest Scheme 3 for the proceeding of ketone ozonolysis:

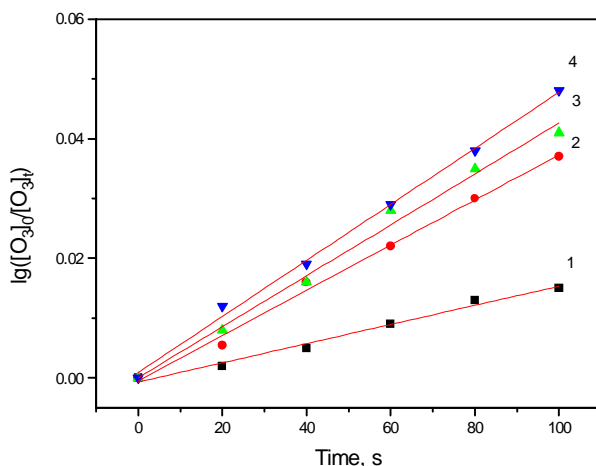


Scheme 3

Table 7

Equilibrium constants of keto-enol tautomerism of some ketones in  $\text{CCl}_4$  solution at 294 K determined by titration with ozone

Ketone	$\text{CH}_3\text{COCH}_3$	$\text{CH}_3\text{COC}_2\text{H}_5$	$\text{CH}_3\text{COC}_5\text{H}_{11}$	$\text{CH}_3\text{COC}_6\text{H}_{13}$	$\text{CH}_3\text{COC}_7\text{H}_{15}$	$\text{CH}_3\text{COC}_{10}\text{H}_{21}$	<i>c</i> - $\text{C}_7\text{H}_{12}\text{O}$
$K_e \cdot 10^4$	1.2	1.2	46	29	96	130	190



**Fig. 6.** Semilogarithmic anamorphosis of the kinetic curve of ozonolysis of methylethylketone (1); methylpentylketone (2); ethylpentylketone (3) and cycloheptylketone (4).  $T = 294$  K, ketone concentration 28 mM at  $[O_3]_0 = 1 \cdot 10^{-3}$  M

Ozone attacks the  $\alpha$ -H atom forming LC, which further undergoes decomposition into a radical (or ion) pair in one kinetic cage, or leads to the formation of hydroperoxy and alkoxy radicals. The latter can further undergo monomolecular decomposition.

The intermediate formation of LC is assumed in the first stage, followed by breaking of  $\alpha$ -C-H bond leading to the formation of a radical (or ion) pair. Then  $\alpha$ -hydroxyketone,  $\alpha$ -peroxyketone radicals and  $\alpha$ -hydroxytrioxyketone which appear as a result of C-C bond breaking can decompose into two aldehydes.

The  $\alpha$ -peroxyketone radical, reacting with the initial ketone, can be transformed into  $\alpha$ -hydroxyperoxyketone, which is decomposed through breaking of the C-C bond to aldehyde and acid or two radicals recombine giving rise to diketone and  $\alpha$ -hydroxyketone or two  $\alpha$ -oxyketone radicals. The latter react with the initial ketone and are transformed into  $\alpha$ -hydroxyketone or through a monomolecular decomposition and breaking of the C-C bond to an alkoxy radical and aldehyde.  $\alpha$ -Hydroxytrioxyketone is converted into  $\alpha$ -hydroxyketone and it is transferred in its turn into two aldehydes.

### 3.3. Ethers

Investigations of ozone reactions with ethers began as early as the last century [63-67]. Results of these studies are summarized and reported by Bailley in his review [67]. The main products formed during ozonolysis of aliphatic ethers are alcohols, aldehydes, esters, acids, hydrotrioxides (HTO), hydrogen and organic peroxides, singlet oxygen and water. Price and co-workers [68]

proposed the so-called "insertion" mechanism, according to which ozone is inserted into the  $\alpha$ -C-H bonds at the first step through 1,3-dipolar addition, thus forming unstable HTO. This mechanism was also supported by the data of Erickson and Bailey [2, 67, 69], Murray and co-workers [70], who measured the activation parameters of the decomposition of a series of HTO, obtained by the ozonolysis of some ethers. Giamalva and co-workers [71] summarized the possible mechanisms known today, *i.e.* interaction with the ether oxygen atom, 1,3-dipolar insertion of ozone into the  $\alpha$ -C-H bonds, homolytic abstraction of the  $\alpha$ -H atom and heterolytic abstraction with carboanion and carbocation formation. These authors clearly indicate the predominance of the one-step mechanisms with transfer of a hydrogen atom, hydride anion or cation.

As it was mentioned above, the low-temperature ozonolysis of ethers yields HTO, which however are stable at very low temperatures. At normal temperatures the composition of the products is found to be different from that after the decomposition of HTO. These two reasons gave us impetus to carry out extended studies of the ozone reaction with ethers in order to establish the real mechanism of these reactions at normal temperatures.

It was estimated, based on kinetic curve of ozone consumption (Fig. 7 and Eq. (2)), that the kinetic constant of the ozonation of diethyl ether (DEE) at  $T = 268$  K is  $0.9 \text{ M}^{-1}\text{s}^{-1}$ . Taking into account the area, comprised between the straight line  $y = [O_3]_0$  and the kinetic curves of DEE, similar to that in Fig. 5, which have been obtained at the lower concentrations of the reactant, the amount of ozone, consumed in the reaction has been determined. Juxtaposing this amount with the initial quantity of DEE in the reactor the stoichiometric coefficient of DEE ozonolysis has been estimated to be 1.

The calculated stoichiometric coefficient of the ozonation reaction with other ethers was also unity. The kinetics of ozonolysis was studied with the example of *n*-dibutylether (DBE). The kinetic curves of the reaction product formation and the initial ether consumption are shown in Fig. 8.

The following products were identified by the gas chromatography-mass spectrometry in the reaction mixture after 10 min (mass spectra of the obtained compounds are given below):

130 \* 57 41 87 56 55 101 39 130 43 45 \* *n*-Dibutylether,  
 74 \* 56 41 43 42 55 39 57 45 40 41 \* *n*-Butanol,  
 72 \* 44 43 41 72 57 42 38 37 40 71 \* Butanal,  
 88 \* 60 73 41 42 43 45 39 55 61 88 \* Butyric acid;  
 144 \* 71 89 56 43 41 57 60 73 55 42 \* Butyl butyrate and  
 164 \* & 247 \* - Chloro-containing compounds like:  
 $\text{CH}_3(\text{CH}_2)_2\text{CH}(\text{Cl})\text{O}(\text{CH}_2)_3\text{CH}_3$  ( $M_w$  164.4) and  
 $\text{CH}_3(\text{CH}_2)_2\text{CH}(\text{CCl}_3)\text{O}(\text{CH}_2)_3\text{CH}_3$  ( $M_w$  247)

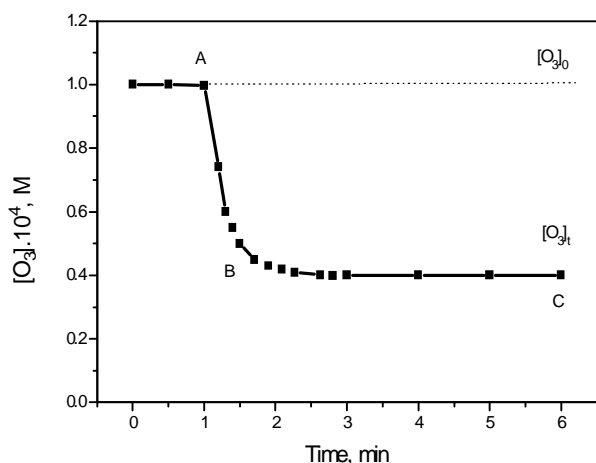


Fig. 7. Kinetic curve of ozone concentration at the reactor outlet: 10 ml, 92 mM DEE, at 268 K

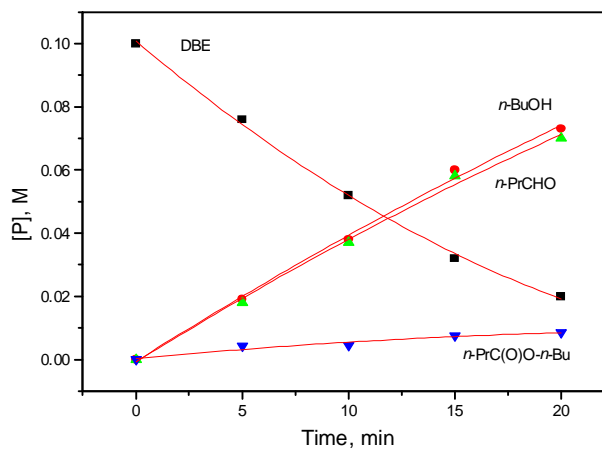
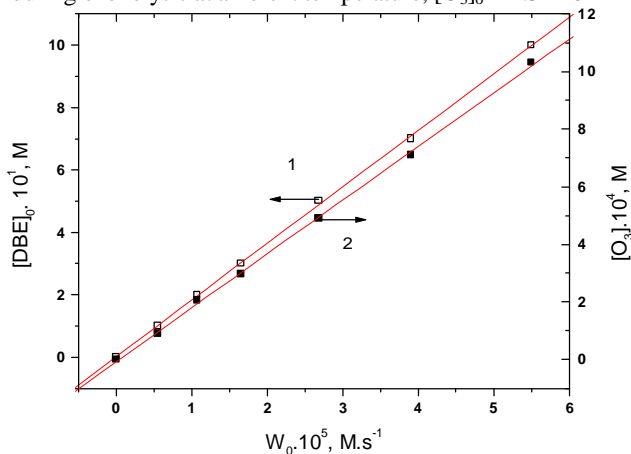


Fig. 8. Kinetics of product formation and consumption of DBE during ozonolysis at ambient temperature,  $[O_3]_0 = 2.34 \cdot 10^{-4} \text{ M}$

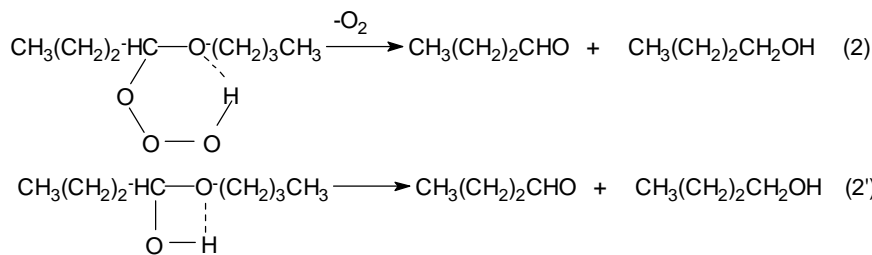
Fig. 9. Dependence of the reaction rate of DBE ozonation (294 K) on the concentration of ozone (1) at  $[DBE] = 10 \text{ mM}$  and DBE (2) at  $[O_3] = 0.1 \text{ mM}$



The rate of DBE decomposition ( $7.4 \cdot 10^{-5} \text{ M} \cdot \text{s}^{-1}$  determined on the basis of Fig. 8) is almost equal to the sum of butanal ( $6.5 \cdot 10^{-5} \text{ M} \cdot \text{s}^{-1}$ ), butanol ( $6.71 \cdot 10^{-5} \text{ M} \cdot \text{s}^{-1}$ ) and butyl butyrate ( $1.0 \cdot 10^{-5} \text{ M} \cdot \text{s}^{-1}$ ) formation rates. The kinetic curves of butanol and butanal formation have almost the same slope and they start without any induction period. This could mean that they are formed in parallel reactions from a common precursor. The rate of butylbutyrate accumulation, as it is demonstrated by its kinetic curve, is approximately 7 times lower. The latter indicates that their formation is occurring in a parallel reaction to butanol (butanal) formation, most probably from the same

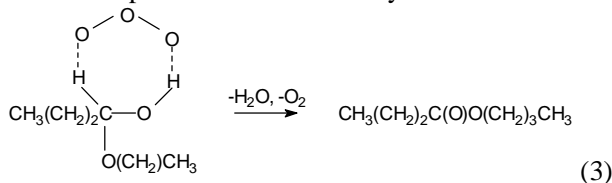
precursor. The ratio of the product amount to the initial DBE amount after 10 min was found to be 1:1. This means that the share of the auto-oxidation process is negligibly small, although we have identified some butyric acid by its IR spectrum ( $1765 \text{ cm}^{-1}$  (monomer) and  $\epsilon = 1470 \text{ M}^{-1} \cdot \text{cm}^{-1}$ ) resulting from the butanal oxidation.

The possible existence of a common precursor raises the question about its nature. Such a precursor could be either  $\alpha$ -hydroxyether (EOH) or  $\alpha$ -hydrotrioxyether (E00OH), which can produce further through the intermolecular disproportionation simultaneously aldehyde and alcohol:



Probably, the intermolecular reaction of EOOH disproportionation is preferable, because of the six-member-ring transition state, while EOH disproportionation occurs via a strained four-member-ring transition state, which is energetically unfavorable.

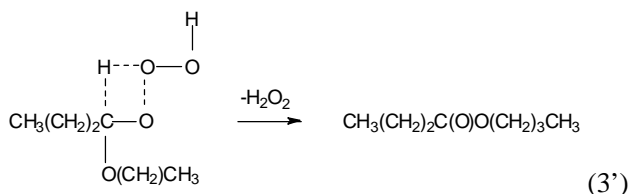
If EOH is assumed to be the precursor, then the butylbutyrate should be a major reaction product as a result of the rapid oxidation of EOH by ozone:



which has not been observed experimentally.

When EOH is assumed to be the precursor, it is difficult to imagine its one-step transformation into an ester without any additional assumptions. Also the solvent,  $\text{CCl}_4$ , could not affect this transformation at all, bearing in mind its weak oxidizing properties and its non-specificity.

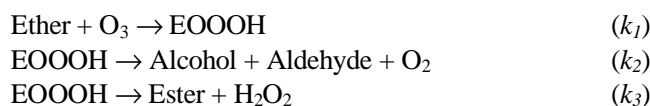
The formation of the ester from EOOH in a single step can be easily presented through a four-member-ring transition state:



The formation of four-member transition state will be more unfavourable than the six-member transition state. This conclusion is in agreement with the kinetic data, namely, the rate of ester formation is approximately 7 times lower than that of alcohol and aldehyde formation. Direct evidence for EOOH formation was found only after prolonged ozonation for 24 h at 195 K [72-75]. The NMR spectrum of the oxidate has a signal at  $d = 13.52$  ppm, which is attributed to OOOH.

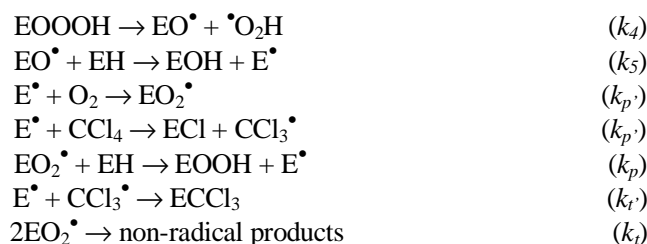
Fig. 9 represents the dependences of DBE ozonation rate on ozone and DBE concentrations. Judging from the linear character of the dependences, in conformity with Eq. (2), it follows that the order of the reaction is unity with respect to each one of the two reactants and therefore the rate law can be written in the form  $W = k \cdot [\text{DBE}][\text{O}_3]$ .

Based on the results discussed above, a scheme of the ozone reaction with aliphatic ethers is proposed (Scheme 5).



#### Scheme 5

The formation of chlorine-containing compounds (1–2 %) can be explained by the presence of radical intermediates in the reaction mixture. This means that EOOH will be also decomposed *via* the radical route:



The validity of the mechanism, indicated above, was confirmed by the good agreement between the experimental points on the DBE decomposition curve and the product accumulation and by the theoretical curves, calculated according to the scheme and given in Fig. 8. For example, the curve describing the DBE consumption is obtained from Eq. (4):

$$[\text{DBE}]_t = [\text{DBE}]_0 \cdot \exp(-k't) \quad (4)$$

where  $k'$  is the constant, measured by the stop-flow method equal to  $1.26 \cdot 10^{-3} \text{ s}^{-1}$ , while the corresponding bimolecular constant is  $6.3 \text{ M}^{-1} \cdot \text{s}^{-1}$ .

Table 8

**Rate constants of ethers ozonations at various temperatures (K)**

Ether	258	267	268	276.5	277	283	286	294	297
EtE	0.5	0.9	1.0	1.2	1.6	2.2	2.4	3.1/3.0*	3.6
DCIEtE	–	–	0.009	0.016	–	–	0.028	0.035/0.04*	–
<i>i</i> -PrE	–	–	1.6	1.9	–	–	3.4	5.4/5.1*	–
<i>n</i> -ButE	–	–	1.9	2.1	–	–	4.3	6.3/6.3*	–
<i>i</i> -AmE	–	–	1.9	2.5	–	–	4.1	7.8/7.0*	–
<i>n</i> -AmE	–	–	2.2	2.8	–	–	4.2	7.8/7.5*	–

Note: \* after the slash the values of the constants determined by a stop-flow method are given.

A comparison of the experimental values and calculated estimates of  $A$ , assuming linear (LC) and cyclic (CC) forms of the activated complex (AC) has been made. The kinetic constants of ozone reaction with diethylether (EtE), dichlorodiethylether (DCIEtE), di-*iso*-propylether (*i*-PrE), di-*n*-butylether (*n*-ButE), di-*iso*-amylether (*i*-AmE) and di-*n*-amylether (*n*-AmE) in  $\text{CCl}_4$  are given in Table 8.

The rate constants for EtE, *n*-ButE, *i*-AmE and *n*-AmE have similar values. All these ethers have close  $\alpha$ -C-H bond energies and similar electronic environment. The value of the rate constant for *i*-PrE ozonation is also close to those mentioned above, while the constant for DCIEtE has 100 times lower value. In DIPE the presence of *tert*-C-H bonds, should contribute to their higher reactivity because of the lower energy of these bonds [34]. The presence of oxygen, however, and the more difficult

stabilization of the transition state due to steric factors, makes this interaction slower. The very low rate constant of DCIEtE ozonation can be attributed to the strong electron-accepting properties of the chlorine atom.

Arrhenius parameters, calculated on the basis of the data in Table 8, are summarized in Table 9.

The comparison of the results, obtained with the reference data, shows a good coincidence in regard to the values of the rate constants at 294 K. Only a slight difference in the activation energies was observed. Perhaps, it is the heat of ozone dissolution in  $\text{CCl}_4$  that needs to be taken into account as the reason for these differences.

All reaction schemes, found in the current literature, describe the ozonation of ethers proceeding through two geometric forms of the activated complex – LC and CC:

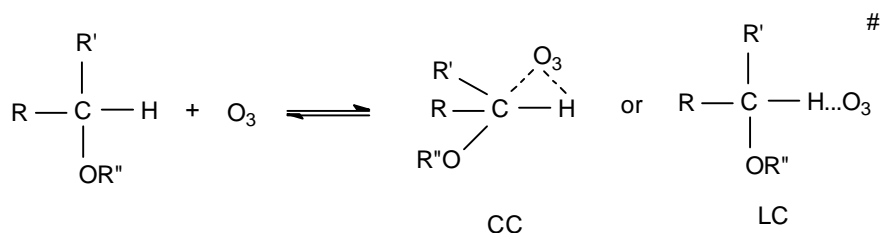


Table 9

Arrhenius parameters of ozone reaction with some aliphatic ethers

Ether	$k, \text{M}^{-1}\cdot\text{s}^{-1}$	$\lg A$	$E_a, \text{kJ/mol}$
EtE	3.1	6.4 (7.3)	32.9 (41.3)
DCIEtE	0.035	4.9 (5.5)	34.6 (42.1)
<i>i</i> -PrE	5.4	6.3 (7.9)	31.7 (41.7)
<i>n</i> -ButE	6.3 (6.0)	6.6 (7.4)	32.5 (40.4)
<i>i</i> -AmE	6.8	6.6	32.5
<i>n</i> -AmE	7.8	6.5	31.7
THydP	(1.3)	(6.8)	(40.4)
THydF	(12.3)	(6.6)	(34.2)

Note: The values in brackets are taken from Ref. [43]; THydP and THydF are tetrahydropyrane and tetrahydrofuran, respectively.

Table 10

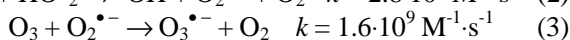
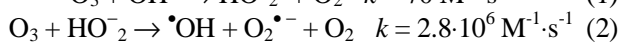
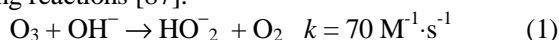
Heats of formation ( $\Delta H$ ) in kJ of initial, intermediate and final products, Van der Waals radii of the ethers and free rotation energy ( $E_{fr}$ ) around H-O bond

Ether	$r, \text{\AA}$	$\Delta H, \text{EH}$	$\Delta H, \text{EOOOH}$	$\Delta H, \text{E}^*$	$\Delta H, \text{E}^+$	$E_a, \text{kJ/mol}$
EtE	3.18	-68	-66	-32	135	5.4
dClEtE	3.51	-74	-73	-41	132	9.2
<i>i</i> -PrE	3.48	-76	-74	-42	125	5.8
<i>n</i> -ButE	4.03	-81	-79	-47	120	5.4
<i>i</i> -AmE	4.31	-87	-86	-53	115	5.4
<i>n</i> -AmE	4.45	-86	-85	-51	116	5.4



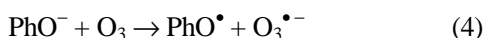
ozonation in water medium are 220 and 70, respectively. Provided that the rate constant of phenol ozonation is known [75], the calculated values of the rate constants of pyrocatechol and resorcinol ozonation are  $2.86 \cdot 10^5 \text{ M}^{-1} \cdot \text{s}^{-1}$  and  $9.1 \cdot 10^4 \text{ M}^{-1} \cdot \text{s}^{-1}$ , respectively. However, in the case when the reaction is carried out in organic solvents the values are quite different. For example, in  $\text{CCl}_4$  and at room temperature the following values have been obtained for: benzene – 0.06, ethylbenzene – 0.2, anisole – 1.1, phenol – 230 and pyrocatechol –  $3.2 \cdot 10^3 \text{ M}^{-1} \cdot \text{s}^{-1}$  [70-73]. One of the possible explanations for different values of the rate constants of hydroxyphenols ozonation obtained by various researchers could be the great influence of water on this reaction, for example for phenol they vary within the range of  $100\text{--}180 \text{ M}^{-1} \cdot \text{s}^{-1}$ ,  $500 \text{ M}^{-1} \cdot \text{s}^{-1}$  for pyrocatechol and  $300 \text{ M}^{-1} \cdot \text{s}^{-1}$  for 3,6-di-*tert*-butyl-pyrocatechol. Pryor and co-workers [72] have reported that the rate constants of ozone reaction with  $\alpha$ -tocopherol in  $\text{CCl}_4$  and water are  $5.5 \cdot 10^3 \text{ M}^{-1} \cdot \text{s}^{-1}$  and  $1 \cdot 10^6 \text{ M}^{-1} \cdot \text{s}^{-1}$ , with  $\alpha$ -tocopherol acetate –  $1.45 \cdot 10^2 \text{ M}^{-1} \cdot \text{s}^{-1}$  and for the reaction with  $\alpha$ -tocopherolquinone it is  $1.15 \cdot 10^4 \text{ M}^{-1} \cdot \text{s}^{-1}$ .

Ozone is unstable when dissolved in water. The mechanism and the kinetics of the elementary reactions, involved in the ozone decomposition, have been investigated in numerous studies [87, 88, and references therein]. The stability of the ozone depends to a great extent on the water matrix, especially on its pH value. The pH value of water is important because the hydroxide ions initiate the ozone decomposition, which involves the following reactions [87]:



In aqueous solution the ozonide radical decomposes quickly into OH radical,  $\text{O}_2$  and OH anion [87, 88].

Additionally in the case of ozone reaction with electron-rich compounds, such as phenols (phenolates) and alkoxyated aromatics in aqueous phase OH radicals are formed again, most probably *via* the mechanism of formation of the respective ozone adduct [88, 89]. For example it has been established that as a result of the electron transfer from phenol to ozone (reaction 4) at neutral pH the radical anion  $\text{O}_3^{\bullet -}$  is obtained with 22 % yield [90].



As a result the rate constant of one and the same compound (of phenols or alkoxyated aromatics type) in water, determined on the basis of its ozone consumption, varies within a wide range of values depending on the pH values, and on the presence of hydroxyl radical scavengers minimizing the interfering radical chain reactions. This rate constant differs from that one, determined on the basis of

the compound consumption [91]. However, this aspect requires special studies and discussion, which are beyond the scope of the present investigation.

While pyrocatechol ozonation in the aqueous medium 3 moles of ozone are absorbed and  $\text{CO}_2$  (24.8 %), CO (6 %), formic acid (32.5 %) and glyoxal (4.2 %) are formed. As  $\text{CO}_2$  and formic acid are the main reaction products, it seems very likely that most of the pyrocatechol undergoes anomalous ozonolysis [82]. Radical formation has been observed during 2,6-di-*tert*-butylphenol ozonolysis. When 0.8 mol of ozone are absorbed by phenol, 50 % viscous yellow oil is formed and 3,5, 2,6-di-*tert*-butyl-*o*-quinone have been identified in the products [85]. In 3,6-di-*tert*-butyl-pyrocatechol ozonation the corresponding quinone was found to be the main product after complete consumption of the initial substrate [86]. Side products such as 2, 5-di-*tert*-butyl-, 3-hydroxy-*p*-quinone and 3,6-di-*tert*-butyl-1,2-phenylacetal-5-hydroxy-3,6-di-*tert*-butyl-*p*-benzophenone have also been found. The rate constant of this reaction amounts to  $3 \cdot 10^2 \text{ M}^{-1} \cdot \text{s}^{-1}$ . The same constant with the corresponding pyrocatechol with *O*-hydroxy-acetylated groups has been estimated to have the magnitude value two orders lower. A mechanism has been supposed to involve the formation of either 1,3-cyclic activated complex between two hydrogen atoms from two OH groups and one ozone molecule or *p*- or *s*-complexes, formed with the benzene ring.

Different values of the literature constants and various mechanisms proposed for this reaction impose the necessity of further research of its kinetics and reaction pathway. In this connection we have studied the ozonolysis of the following hydroxybenzenes (Scheme 6).

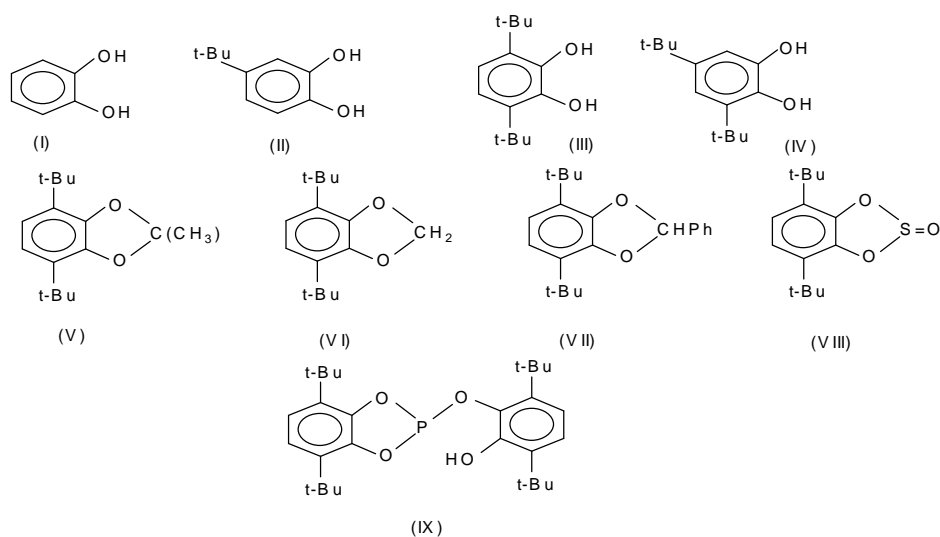
The probable mechanisms of ozone interaction with dihydroxybenzenes are represented in Scheme 7.

The mechanism A with a cyclic complex (CC) formation in the transition state was supposed by Razumovskii and co-workers [86]. The mechanism B with linear complex LC-II in the transition state was put forward and discussed by Bailey [2]. The interaction of ozone with C–H bonds with the formation of trioxide [71, 73] as a possible parallel reaction is indicated in mechanism C. The acetylated forms of dihydroxybenzenes can react only *via* attack on the benzene ring according to the mechanism D or C. Formally, the mechanism D can be regarded as an extended version of mechanism B, involving the formation of TS similar to  $\pi$ - or  $\sigma$ -complexes. We propose a new mechanism, an extended version of the Razumovskii mechanism, whereby the transition state is linear with LC-I structure.

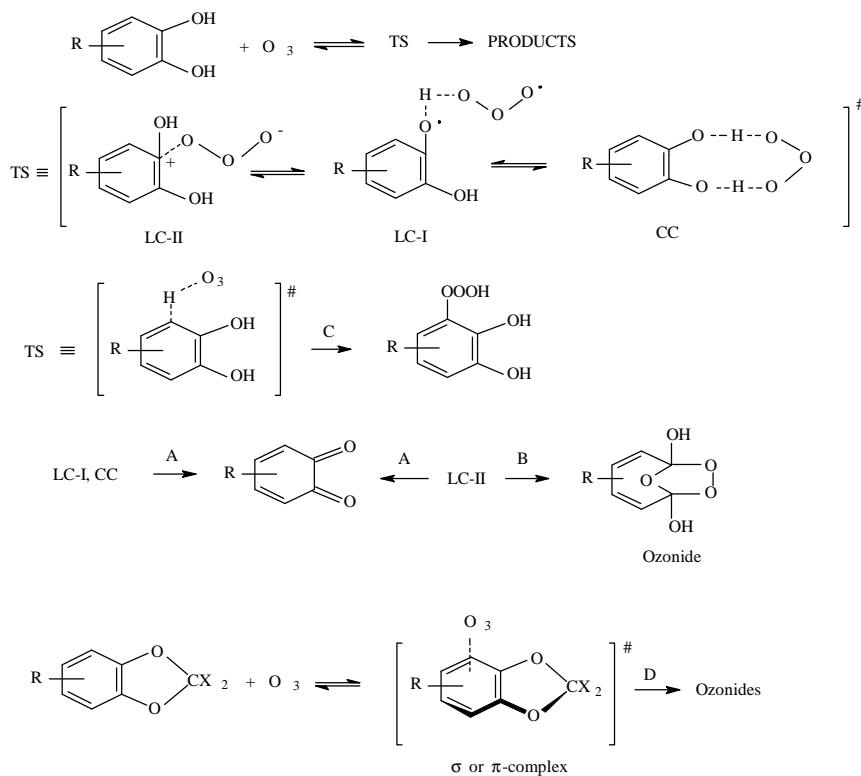
Upon ozonation of any of the investigated catechols directly inside the electron spin resonance cell or after freezing the reaction products in liquid nitrogen no signals have been detected.

The kinetic curve of the changes in the ozone concentration at the bubbling reactor outlet (Figs. 10, 1) is characterized by three different regions: AB – fast ozone consumption after the addition of pyrocatechol, BC – steady-state part, when the rate of the chemical reaction becomes equal to the rate of ozone supply, and CD – the ozone concentration begins to rise up due to the pyrocatechol consumption. The BC part of

the curve allows calculation of the rate constant, and based on the area below the curve ABCD – evaluation of the stoichiometry of the reaction. The straight line designated  $[O_3]_0$  is the ozone concentration at the reactor inlet. Curve 2 presents the *o*-quinone formation in the course of the reaction time. Its profile suggests the intermediate formation of *o*-quinone.

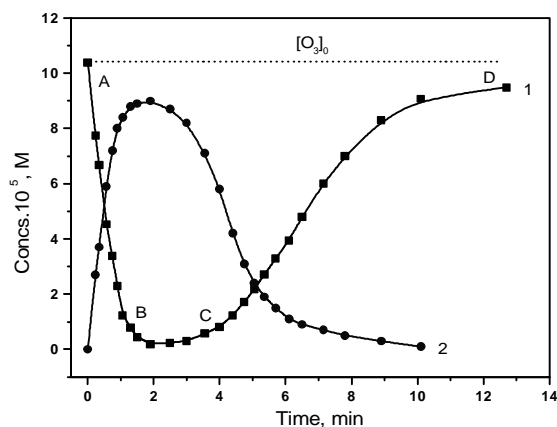


Scheme 6

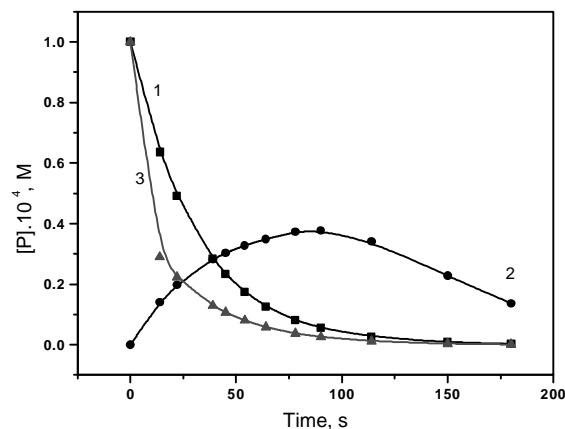


Scheme 7

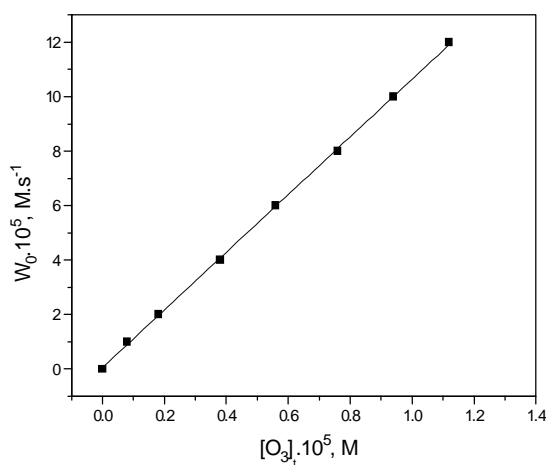




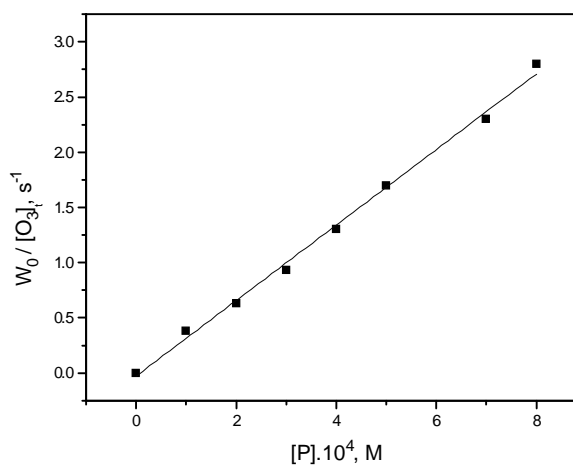
**Fig. 10.** Kinetic curves of ozone absorption at reactor outlet (1) and *o*-quinone accumulation (2) in the course of pyrocatechol ozonation at ambient temperature,  $[PC] = 0.227 \text{ mM}$  in  $\text{CCl}_4$  (10 ml) during bubbling of ozone with 0.1 l/min flow rate



**Fig. 11.** Kinetics of pyrocatechol consumption (1), *o*-quinone accumulation (2) and *o*-quinone consumption (3) at ambient temperature;  $[\text{O}_3] = 1 \cdot 10^{-5} \text{ M}$



a)



b)

**Fig. 12.** Dependence of the pyrocatechol ozonation rate on the concentration of ozone (a) and pyrocatechol (b)

The kinetic curves of the product formation in the pyrocatechol ozonolysis, its consumption and *o*-quinone consumption during its ozonation in a separate experiment are given in Fig. 11. The rate constants of pyrocatechol and *o*-quinone consumption, calculated based on the kinetic curves are shown in Fig. 11, and equal to  $3.2 \cdot 10^4 \text{ M}^{-1} \cdot \text{s}^{-1}$  and  $7.1 \cdot 10^4 \text{ M}^{-1} \cdot \text{s}^{-1}$ , respectively. The initial rate of the *o*-quinone formation had almost the same value as that of pyrocatechol consumption. The small variation of the constants is due to the participation of pyrocatechol in parallel reactions. Actually, during the reaction small amounts of open-chain products have been identified.

Pyrocatechol ozonation at 15 % conversion degree gave the following yields: *o*-quinone – 85 %, pyrogallol – 3 %, ozonide – 10 %, muconic acid – 2 %, maleic acid and fumaric acids and the polymeric products – 1 %. The ratio between the amount of absorbed ozone and the

consumed pyrocatechol was calculated to be 6. Similar ratio values have also been obtained for other hydroxybenzenes with free hydroxy groups.

It was found that with the increase of the conversion degree from 0 to 100 %, the amount of open-chain products is continuously increasing, while that of the remaining products passes through a maximum. The individual compounds identified by  $^{13}\text{C}$ -NMR are: muconic semialdehyde and acid – 20 %, maleic and fumaric semialdehyde and acid – 40 %, glyoxal, formic acid, oxalic acid, carbon dioxide and polymeric products – 40 %. The reaction rate of dihydroxybenzene ozonation follows the first-order kinetics in relation to each reagent (Fig. 12).

Table 13 represents the obtained experimental kinetic data on the ozonation of the investigated dihydroxybenzenes at various temperatures.

A drastic difference between the values of the kinetic parameters of catechols I-IV and V-IX, in which the OH groups are acetylated, has been observed. The rate constants of catechols I-IV manifested 4–28 times higher values than those of catechols of V-IX types. On the other hand the pre-exponential factors demonstrated with about two orders of magnitude lower values with the former compounds. The activation energies are  $8.3 \pm 2$  and  $5.9 \pm 2$  kJ/mol, respectively, or the acetylation of the HO groups leads to an increase in  $E_a$  by about 72.5 kJ/mol. The ozone probably reacts predominantly with the hydrogen atoms of the HO groups and, only to a very small extent, with the benzene ring. The ratio of these ozone interactions varies from 94:4 to 80:20 depending on the hydroxybenzene nature. The lower activation energies of catechols I-IV with respect to those of V-IX are more consistent with the formation of an activated complex of contact type in the transition state, *i.e.*, with structure LC-I (Scheme 7). This assumption could also be confirmed by the analysis of the kinetic parameters of the ozonation of anizol, benzenes, phenol and toluene. The reaction of ozone with benzene proceeds at a low specific rate of  $0.06 \text{ M}^{-1}\cdot\text{s}^{-1}$  and a relatively high activation energy equal to 53.4 kJ/mol. The methyl derivatives of benzene, *i.e.*, toluene, reacts 6.7 times faster and  $E_a$  is decreased by 10.4 kJ/mol, and the rate of anizol ozonation is even higher –  $10 \text{ M}^{-1}\cdot\text{s}^{-1}$ . The substitution of ketyl group by a hydroxyl one leads to a significant acceleration of the ozonation reaction rate and it approaches the value of  $160 \text{ M}^{-1}\cdot\text{s}^{-1}$ , and the activation energy is reduced by 24.2 kJ/mol. Probably in this case the mechanism of the reaction is changed and ozone interacts predominantly with the hydrogen atoms of the OH groups. The decrease in the reactivity of anizol compared with that of phenol (~16 times) supports this assumption.

The analysis of the kinetic parameters of catechols in the acetylated form and those of benzene, toluene, anizol and phenol shows that the rate constants increase and the activation energies go down upon increasing the number of the electron-donating substituents (Table 13). The high values of the pre-exponential factors could be associated with the high values of the energy of free rotation in the activated complex as a result of the steric hindrances caused by the presence of the bulky *tert*-butyl groups. This means that in the case when the hydroxyl groups are acetylated, the activated complex should have LC-II like structure and the ozonation would lead only to the formation of ozonides and open ring products.

The kinetic parameters of some dihydroxybenzenes have been determined in the case of ozonation in aqueous medium (for those ones, which are water soluble – I-IV, VIII and IX). However, we have found that because of the diffusion limitations in the bubbling reactor we have not been able to measure constants higher than  $1\cdot 10^4 \text{ M}^{-1}\cdot\text{s}^{-1}$ .

In fact, the literature values for some of these constants are of this order, but they have been measured by a modified stop-flow technique [32].

The analyses made so far show that the reaction path of the ozone reactions with dihydroxybenzenes depends strongly on their nature and they precede via transition states with activated complex – LC-I or LC-II. The parameters needed for the calculations are represented in Table 14.

In addition, we have calculated the heats of formation: pyrogallol –490.4 kJ/mol (–537.9 kJ/mol [92]), 3-trihydroxy pyrocatechol –246.59 kJ/mol,  $\text{H}_2\text{O}_3$  –88.4 kJ/mol (–73.8 kJ/mol [92]).

Thus, the heats of the ozonation reaction according to different mechanisms have been calculated and they amount to the following values: A – 138.0; B and D – 192.2 and C – 133.8 kJ/mol. All the mechanisms are exothermic and, therefore thermodynamically favorable. In this case only the magnitude of the activation energy and the entropy benefits will determine the reactivities of these compounds and the reaction pathway.

Calculated pre-exponential factors (Table 15) were compared with those obtained experimentally (Table 13) and it is seen that A values have lower ones (~10 times) for the cyclic form of the activated complex, if compared with the experimental values. At the same time the values of A for LC are about 200 times higher. The values of A for CC are the highest as predicted by the theory and they are lower than the experimental values. This supposes that the reaction takes place *via* a cyclic complex. The values of A calculated for LC in Table 15 have been obtained without taking into account the energy of free rotation. The latter was calculated as a sum of the rotation around H–O and O–O axes (by *Mopac6*) and it amounts to 12.9 kJ. This means that the real values in column 4 are about 200 times smaller. The comparison between the A values corrected in this way and the experimental data for the compounds I-IV reveals the complete agreement.

The reaction pathway of the ozonation reactions of compounds V-IX is quite different as the transition state includes the formation of *s*- or *p*-complex. For these compounds the formation of AC in the transition state is impeded due to the breaking of their aromatic character but simultaneously the free rotation is facilitated, which energy may be even zero, due to the action of the principle of the lowest energy. If the energy of free rotation is assumed to be very low then the values of A calculated for LC-II would coincide with the experimentally found ones. Such a coincidence is observed for compound V in column 5 (Table 15).

The basic conclusion from the analysis of the results obtained for this reaction is that the kinetics and mechanism of the ozonation reaction of dihydroxybenzenes depend strongly on their structure and the type of the reaction medium.

Table 13

Kinetic data of dihydroxybenzene ozonolysis in CCl<sub>4</sub>, 293 K

Substrate	$k, M^{-1}\cdot s^{-1}$	lgA	$E_a, kJ/mol$
I	3230	5.35	10.4
II	3100	4.91	7.9
III	3100	5.07	8.8
IV	3200	4.80	7.1
V	500	7.14	25.2
VI	749	7.17	24.2
VII	828	7.06	23.3
VIII	598	6.84	23.0
IX	111	6.81	26.7
Benzene	0.06	8.32	53.4
Toluene	0.40	7.05	43.0
Anisole	10	-	-
Phenol	160	7.31	29.1

Table 14

Symmetry numbers ( $s$ ), VdW radii ( $r$ ), heats of formation ( $DH$ ) of dihydroxybenzenes and the corresponding quinones and ozonides

Substrate	$s$	$r, \text{\AA}$	$\Delta H, kJ/mol$	$\Delta H^{quinone}, kJ/mol$	$\Delta H^{ozonide}, kJ/mol$
I	2	3.02	-258.5(-354.4)	-162.3 (-179.3)	-304.4
II	1	3.82	-366.9	-275.2	-412.8
III	2	4.46	-454.5	-358.6	-521.3
IV	1	4.39	-458.7	-375.3	-512.9
V	2	5.07	-483.7	-	-531.3
VI	2	4.56	-375.3	-	-521.3
VII	1	5.37	-262.7	-	-358.6
VIII	1	4.77	-394.4	-	-321.1
IX	1	5.30	-562.9	-	-583.8
Benzene	6	2.86	79.2 (54.2)	-	87.6
Toluene	1	3.37	50.9 (12.5)	-	45.9
Anisole	1	3.45	-66.7 (-108.4)	-	-83.4
Phenol	1	2.96	-87.6 (-158.5)	-	-100.1

Note: The experimental values are in parentheses [92].

Table 15

## Calculated pre-exponential values for ozone reaction with dihydroxybenzenes

Substrate	lgA, TC	lgA, CC	lgA, LC	lgA, calc.	$A_{calc}/A_{obs}$	lgp
I	2	3	4	5	6	7
I	11.318	4.346	7.69	5.39	1.10	5.928
II	11.422	3.905	7.25	4.95	1.10	6.472
III	11.500	4.070	7.42	5.12	1.12	6.380
IV	11.490	3.780	7.12	4.82	1.05	6.670
V	11.572	4.017	7.36	7.36	1.66	4.212
VI	11.511	4.056	7.40	7.40	1.70	4.102
VII	11.801	3.934	7.28	7.28	1.66	4.521
VIII	11.533	3.717	7.06	7.06	1.66	4.473
IX	11.575	3.689	6.88	6.88	1.10	4.695
Benzene	11.319	5.124	8.47	8.47-	1.41	2.849
Phenol	11.322	4.196	7.54	7.54	1.70	3.782

Note:  $p$  is the collision factor.

## 4. Conclusions

The ozone does not react directly with oxygen atoms in the organic molecules.

The ozone attacks the  $\alpha$ -C-H-bonds adjacent to the same carbon atom as oxygen. If there are no adjacent C-H-bonds, ozone interacted with  $\beta$ -C-H-bonds attached to the nearest to oxygen one containing carbon atoms, like it is in ethers and ketones.

Tautomerism plays an important role in the reaction ability of ozone.

The kinetics and mechanism of ozone reactions with oxygen-containing organic compounds strongly depend on the C-H bond energy. The reaction ability of organics is increased in the presence of oxygen due to the donating functions of OH-groups. The mechanism of ozone reactions with oxygen-containing organic compounds depends on their structure *via* the mechanism of hydrogen abstraction and 1,3-ozone insertion.

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### КІНЕТИКА І МЕХАНІЗМ РЕАКЦІЇ ОЗОНУ З СПИРТАМИ, КЕТОНАМИ, ЕТЕРАМИ І ГІДРОКСИБЕНЗЕНАМИ

**Анотація.** В огляді, що базується на 92 посиланнях, розглянуто руйнування органічних речовин внаслідок озонування та стосується різних класів кисневмісних органічних сполук – спиртів, кетонів, етерів та гідроксibenzenів. Обговорено механізми реакції цих сполук з озоном в органічних розчинниках і представлені відповідні схеми реакції. Приведені кінетичні і деякі термодинамічні параметри. Показано залежність кінетики та механізму реакції озонування від структури сполук, середовища і умов реакції. Зазначено і обговорено різні можливості застосування озонолізу. Наведені реакції мають практичне значення для захисту навколишнього середовища.

**Ключові слова:** озонування, спирт, кетон, етер, гідроксibenzen, кінетика, механізм.