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REACTIONS OF OZONE WITH ALCOHOLS, KETONES, ETHERS AND HYDROXYBENZENES (PART 2)

Keywords: ozonation, alcohols, ketones, ethers, hydroxybenzenes, kinetics, mechanisms.

The paper 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 ozone reactions with these compounds in organic solvents are discussed in details, the reaction schemes and the corresponding kinetic and some thermodynamic parameters are given. 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. The various possible applications of ozonolysis are specified and discussed. All these reactions have practical importance for the protection of the environment.

Ключевые слова: озонирование, спирты, кетоны, эфиры, гидроксибензены, кинетика, механизмы.

В статье рассматривается разложение органических веществ путем озонирования различных классов кислородсодержащих органических соединений – спиртов, кетонов, эфиров и гидроксибензенов. Обсуждены механизмы реакций озона с этими соединениями в органических растворителях, представлены соответствующие схемы реакций и приведены соответствующие кинетические и некоторые термодинамические параметры. Выявлены зависимости кинетики и механизма реакций озонирования от структуры соединений, среды и условий проведения реакций. Указаны и обсуждены различные возможности применения озонолиза. Все эти реакции имеют практическое значение для защиты окружающей среды.

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 57% up to 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 the precise determination of the rate constants of ozonolysis of some more widely occurring representatives of the studied classes of organic compounds. 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.

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 a 5 cm quartz gas cell.

Methods

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

Kinetic Measurements

Static Method

Pure reagent or reagent solution was injected into thermostatic 1 cm quartz cuvette, containing a solution of ozone in CCl_4, the time of mixing being less than 0.2 second. Ozone concentration was monitored spectro-photometrically in the region of 270-290 nm. At $[RH]_o/[O_3]_{lo}>100$, the ozone pseudomonomolecular constant $k`=k[RH]_o$ was determined on the basis of the equation $lg([O_3]_{lo}/[O_3]_{lt})=k`t$ where $[O_3]_{lo}$ and $[O_3]_{lt}$ are the initial and current concentrations of ozone in solution, respectively (27).

Dynamic Method

The ozone was bubbled through a cylindrical glass reactor with inner diameter ∅=1.7-3.7 cm and height 7-15 cm, supplied with porous glass grit-G2 at its bottom. The accuracy of maintaining constant temperature was ±0.1°C. Conventionally, gas flow rate was v=0.1 L/min; the solutions volume was V=10 ml; the ozone concentrations at the reactor inlet ($[O_3]_o$) varied from 10^{-6} to 10^{-3} M; the solvent was CCl_4; $[RH]_o=10^{-4}$-10^{1} M. The inlet and outlet ozone concentrations were measured in the gas phase in the 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):

$$\omega([O_3]_o-[O_3]_g) = k[O_3]_l[RH] \qquad (1)$$

where ω is the relative flow rate of ozone–oxygen gas mixture (in litres per L of solution per sec); $[O_3]_o$ and $[O_3]_g$ are the ozone concentrations at the reactor inlet and outlet, respectively, $[O_3]_l$ is ozone concentration in the solution; [RH] is 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 Henry's Law, $[O_3]_l$ is substituted with $\alpha[O_3]_g$, where α is Henry's coefficient, Eq. (1) can be transformed into Eq. (2) (1):

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

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

$$D_{O3}.k_1'/k_L^2 << 1$$

where D_{O3} is the diffusion coefficient of ozone in the solution; $k_L=D_{O3}/\delta$ is the coefficient of mass transfer in the liquid phase, and δ is thickness of the boundary layer in the hydrodynamic model of renovation surface; or $k_L=(D_{O3}.s)^{1/2}$, 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) then $k_L=0.31x(g\nu)^{1/3}x(D_{O3}/\nu)^{2/3}$, where $\nu=\eta/\rho$, is the kinematic viscosity of the solvent, η is the viscosity of the solvent, ρ 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 $k_1`=k[RH]_o$ in most of the cases it is possible to select such values for $[RH]_o$, at which the criterion for applicability of Henry's Law is fulfilled (34).

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 of the kinetic curves are selected, which appear to be practically parallel or only slightly inclined with respect to the abscissa: $k_1`\alpha[O_3]_g >> d[O_3]_g/d\tau$. The advantages and limitations of this method have been discussed in detail in (37, 38). Despite some contradictory observations, the significant part of rate constants of ozone with organic compounds and polymers are obtained on the basis of Eq. (2) (1, 34).

Results and their discussion

Ketones

Reactions of ozone with alcohols were considered in the first part of the review (39). The investigation of the reactions of ozone with ketones is of interest from the viewpoint of the theory of reactivity, the ozone chemistry, preparation of oxygen-containing compounds, and the degradation and stabilization of organic materials. In particular, the ozonation of methylethylketone (MEK) (40-42) yielded acetic acid (AcAc), diacetyl and hydroperoxide as the main reaction products in CCl_4. It has been assumed that the process is not an 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 (40). The addition of nitric acid accelerates enolization, which is evidenced by the increase of the oxidation rate (42). 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 $RO_2^•$ to $RO^•$. 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 α-ketohydroperoxides, monocarboxylic acids, keto alcohols and alkylbutyric lactones. However, it should be noted that the conclusions in these studies were based on 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 1.6×10^{-2} $M^{-1}.s^{-1}$ and 11.2 kcal/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 (43-45): 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 1.

Table 1 - Kinetic parameters of the reaction of ozone with some aliphatic ketones at 21 °C

Ketone	$k_0\times10^3$, $M^{-1}.s^{-1}$	$k_{st}\times10^3$, $M^{-1}.s^{-1}$	k_{rel}	lg A	E_a, kcal/mol
CH_3COCH_3	3.5	7.7	0.2	10.823	18
$CH_3COC_2H_5$	12	24	0.7	10.63	17
$CH_3COC_5H_{11}$	23	67	1	10.54	16.5
$CH_3COC_6H_{13}$	45	58	2.4	10.46	16
$CH_3COC_7H_{15}$	448	54	2.3	10.31	15.8
$CH_3COC_{10}H_{21}$	42	113	2.2	10.58	16.2
$C_2H_5COC_5H_{11}$	20	74	1	11.48	15.5
CH_3COCH_2CO-CH_3	29000	-	-	-	-
c-$C_7H_{12}O$	87	80	4.1	9.00	17
CH_3CO-2-Naph	22000	-	-	5.77	6
4-CH_3-*c*-C_6H_9O	117	101	6.2	8.97	12
4-*t*-Bu-*c*-C_6H_9O	166	123	8.1	7.93	11.8

Note: k_o is calculated according to Equation 2; k_{rel} is the relative rate constant determined by gas chromatography relative to ethylpentylketone.

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

(1) Acetone containing only α-C-H bonds,

(2) Ketones with the general formula $CH_3CO(CH_2)_nCH_3$, where n = 1, 4, 5, 6 and 9, which contain secondary α, β, γ C-H bonds,

(3) Ketones with the general formula $CH_3(CH_2)_m CO(CH_2)_nCH_3$, where m = 1, n = 4, which contain α, α'-secondary C-H bonds and cycloheptanone, which contains α, β and γ secondary C-H bonds, 4-4-methyl or 4-*tert*-butyl cyclohexanone with γ-*tert*-C-H bond,

(4) 2-Naphthylmethylketone with various substituents, and

(5) Acetylacetone containing α-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 appearance of the C+C-double bonds.

$CH_3\text{-}CO\text{-}CH_2\text{-}CO\text{-}CH_3 \Leftrightarrow CH_3\text{-}CO\text{-}\mathbf{CH{=}C}(OH)\text{-}CH_3$

The values of k vary, depending on the ketone structure, particularly on the content of primary, secondary or tertiary α-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 to the activation of α-C-H-bonds by the keto group. Ozone is sensitive not only to the activation of the α-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 α-C-H bond in the methyl group.

Another interesting observation is the higher values of E_a compared with those of paraffins (with some 2-3 kcal/mol). As ozone is an electrophilic reagent and the activation of the α-C-H bonds from the keto group favours the nucleophilic attack, it is reasonable to expect an increase in E_a.

Figure 1 shows a typical kinetic curve illustrating the change of ozone concentration at the reactor outlet during ozonolysis of ketones in solution.

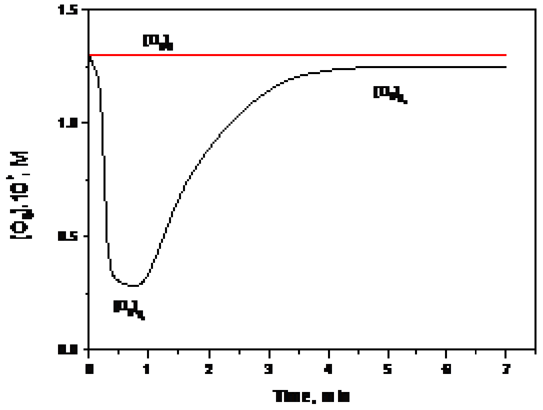


Fig. 1 - Ozonolysis of 0.712 mmol cycloheptylketone in 10 ml CCl_4, 21°C, v - 0.1 L/min

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 (Figure 1) is complicated and this implies that ozone reacts with more than one compound (46-48). 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 (46).

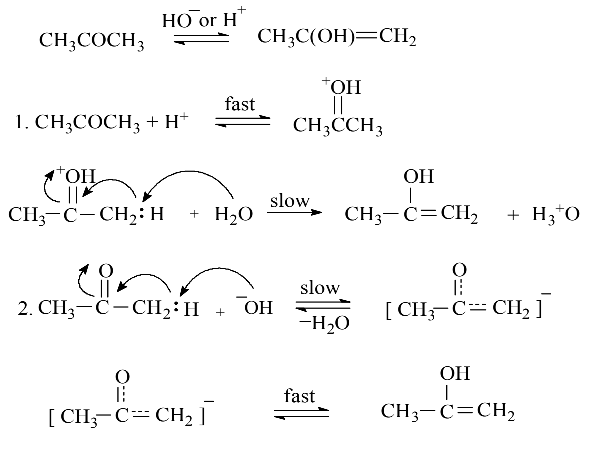
The processes corresponding to the ozone-gas curve (Figure 1) are the following:

(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.



$$CH_3COCH_3 \xrightleftharpoons{HO^- \text{ or } H^+} CH_3C(OH){=}CH_2$$

$$1.\ CH_3COCH_3 + H^+ \xrightleftharpoons{\text{fast}} CH_3\overset{\overset{+}{O}H}{\overset{||}{C}}CH_3$$

$$CH_3{-}\overset{\overset{+}{O}H}{\overset{||}{C}}{-}CH_2{:}H + H_2O \xrightarrow{\text{slow}} CH_3{-}\overset{OH}{\overset{|}{C}}{=}CH_2 + H_3^+O$$

$$2.\ CH_3{-}\overset{O}{\overset{||}{C}}{-}CH_2{:}H + {}^-OH \xrightleftharpoons[-H_2O]{\text{slow}} [\,CH_3{-}\overset{O}{\overset{\vdots}{C}}{=\!=}CH_2\,]^-$$

$$[\,CH_3{-}\overset{O}{\overset{\vdots}{C}}{=\!=}CH_2\,]^- \xrightleftharpoons{\text{fast}} CH_3{-}\overset{OH}{\overset{|}{C}}{=}CH_2$$

The concentration of the enolic form can be estimated from the area enclosed below the kinetic curve in Figure 1 and then the equilibrium constant of enolization could be measured:

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:

$$K_e=[Enol]_e/[Keton]_e,$$

and it amounts to 1.9×10^{-2}.

Based on the curve in Figure 1 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 curve ($[O_3]_{g1}$) and by using Equation 2, the value of the rate constant with the enolic form is found to be $k_E = 2.9\times10^2$ $M^{-1}.s^{-1}$ and therefore the second rate constant with the keto form is $k_K = 0.048$ $M^{-1}.s^{-1}$. In this way the possibility of application of the method of ozone titration to the measurement of the equilibrium constant and the rate constants of ozone interaction with the two tautomeric forms in one kinetic experiment has been demonstrated.

With a view 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 the conditions of mass transfer on these values

It is evident that the rate constants of ozone interaction with ketone, measured by the static method (Figure 2) through mixing of ozone and ketone solutions at $[K]_o>>[O_3]_o$ are higher than those found by the bubbling method (Table 1). 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.

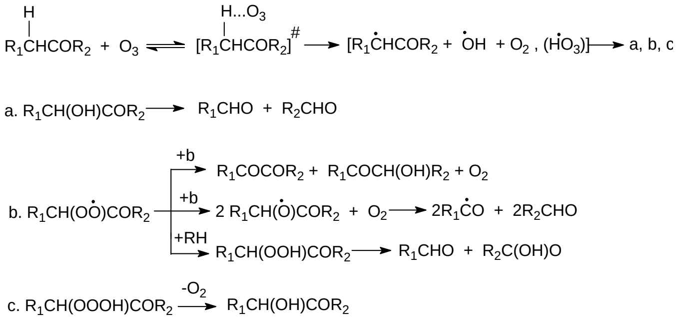
The results from the calculation of the equilibrium constants of keto-enol tautomerism for some aliphatic ketones in CCl_4 are given in Table 2. The data for acetylacetone and 2-naphthylmethylketone are not presented in the table because in the former case the rate of reaching the equilibrium is commensurable 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 21 °C to 3 °C and agree with data from the literature (49-52).

The kinetics of ozone reactions with ketones is also determined using gas chromatographic analyses. The relative rate constants shown in Table 1, column 4 demonstrate that only acetone and methylketone possess 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 methylethylketone are 2-hydroxymethylethylketone, diacetyl, peroxides - alkyl and hydro, acetaldehyde and AcAc.

Table 2 - Equilibrium constants of keto-enol tautomerism of some ketones in CCl_4 solution at 21°C determined by titration with ozone

Ketone	$K_e \times 10^4$
CH_3COCH_3	1.2
$CH_3COC_2H_5$	1.2
$CH_3COC_5H_{11}$	46
$CH_3COC_6H_{13}$	29
$CH_3COC_7H_{15}$	96
$CH_3COC_{10}H_{21}$	130
c-$C_7H_{12}O$	190

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



Scheme 3

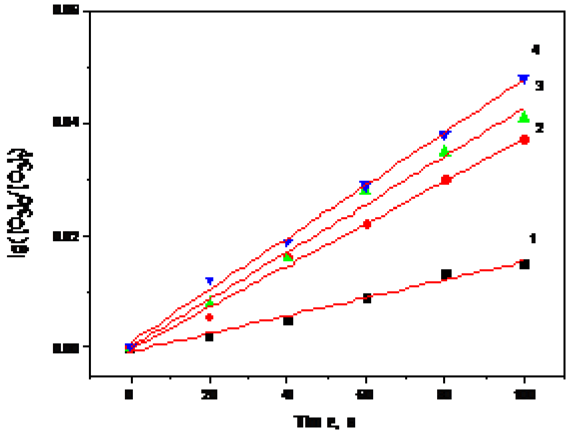


Fig. 2 - Semilogarithmic anamorphosis of the kinetic curve of ozonolysis of: 1 - methylethylketone; 2 - methylpentylketone; 3 – ethylpentylketone; and 4 – cycloheptylketone; 21°C, ketone concentration 28 mM at $[O_3]_{lo} = 1.10^{-3}$ M

Ozone attacks the α-H atom forming a 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 α-C-H bond leading to the formation of a radical (or ion) pair. Then α-hydroxyketone, α-peroxyketone radicals and α-hydroxytrioxyketone appear as a result of C-C bond breaking can decompose into two aldehydes.

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

References

1. Razumovskii, S.D.; Rakovsky, S.K.; Shopov, D.M.; Zaikov, G.E. Publishing House of the Bulgarian Academy of Sciences: Sofia, Bulgaria, 1983.
2. Bailey, P.S., In *Ozonation in Organic Chemistry, Volume 2 - Nonolefinic Compounds*; Academic Press: New York, NY, USA, 1982, p 255.
3. Waters, W.L.; Rollin, A.J.; Bardwell, C.M.; Schneider, J.A.; Aanerud, T.W. *J. Org. Chem.* 1976, *41*, 889.
4. Otal, E.; Mantzavinos, D.; Delga, M.V.; Hellenbrand, R.; Lebrato, J.; Metcalfe, I.S.; Livingston, A.G. *Journal of Chemical Technology and Biotechnology* 1997, *70*(2), 147.
5. Benitez, F.J.; Beltran-Heredia, J.; Acero, J.L.; Pinilla, A. *Journal of Chemical Technology and Biotechnology* 1997, *70*(3)*,* 253.
6. Amalric, L.; Guillard, C.; Pichat, P. *Research on Chemical Intermediates* 1995, *21*(1)*,* 33.
7. Heinzle, E.; Stockinger, H.; Stern, M.; Fahmy, M.; Kut, O.M. *Journal of Chemical Technology and Biotechnology* 1995, *62*(3)*,* 241.
8. Beltran, F.J.; Alvarez, P.M.; Legube, B.; Allemane, H. *Journal of Chemical Technology and Biotechnology* 1995, *62*(3), 272.
9. Lee, M.J.; Arai, H.; Miyata, T. *Chemistry Letters*, 1994, *6*, 1069.
10. Benko, E.M. ; Kovaleva, V.V.; Mamleeva, N.A.; Mitrofanova, A.N.; Voblikova, V.A.; Pryakhin, A.N.; Lunin, V.V. *Zhurnal Fisicheskoi Khimii* 1994, *68*(11), 1964.
11. Artemev, Y.M.; Artemeva, M.A.; Vinogradov, M.G.; Ilika, T.I. *Russian Journal of Applied Chemistry* 1994, *67*(9) (Part 2), 1354.
12. Scheuer, C.; Wimmer, B.; Bischof, H.; Nguyen, L.; Maguhn, J.; Spitzauer, P.; Kettrup, A.; Wabner, D. *Journal of Chromatography A*, 1995, *706*(1-2), 253.
13. Hoger, B.; Gilbert, E.; Eberle, S.H. *Vom Wasser*, 1993, *80*, 187.
14. Ruck, W.; *Vom Wasser* 1993, *80*, 253.
15. Gab, S.; Turner, W.V.; Wolff, S.; Becker, K.H.; Ruppert, L.; Brockmann, K.J. *Atmospheric Environment* 1995, *29*(18), 2401.
16. Takeuchi, K.; Fushimi, C.; Nakamura, K.; Ibusuki, T. *Bunseki Kagaku* 1993, *42*(10), 625.
17. Pan, G.Y.; Chen, C.L.; Gratzl, J.S.; Chang, H.M. *Research on Chemical Intermediates* 1995, *21*(3-5), 205.
18. Wada, H.; Naoi, T.; Kuroda, Y. *Nippon Kagaku Kaishi* 1995, *4*, 306.
19. Marco, A.; Chamarro, E.; Esplugas, S. *Afinidad* 1994, *51*(452), 265.
20. Starek, J.; Zukal, A.; Rathousky*,* J. *Carbon* 1994, *32*(2), 207.
21. Mvula, E.; von Sonntag, C. *Organic & Biomolecular Chemistry* 2003, *1*(10), 1749.
22. Ben'ko, E.M.; Bokova, M.N.; Pryakhin, A.N.; Lunin, V.V. *Russian Journal of Physical Chemistry* 2003, *77*(5), 739.
23. Ramseier, M.K.; von Gunten, U. *Ozone-Science & Engineering* 2009, *31*(3), 201.
24. Valsania, M.C.; Fasano, F.; Richardson, S.D.; Vincenti, M. *Water research* 2012, *46*, 2795.
25. Rakovsky, S.K.; Cherneva, D.R. *International Journal of Chemical Kinetics* 1990, *22*(4), 321.
26. Rakovsky, S.K.; Cherneva, D.R.; Shopov, D.M.; Razumovskiy, S.D. *Communications of the Department of Chemistry, Bulgarian Academy of Sciences* 1976, *9*(4), 711.
27. Rakovsky, S.K.; Cherneva, D.R. *Oxidation Communications* 1989, *12*(3), 108.
28. Rakovsky, S.K.; Kulak, L.G.; Kuramshin, E.M.; Zlotsky, S.S.; Rakhmankulov, D.L. *Communications of the Department of Chemistry, Bulgarian Academy of Sciences* 1989, *22*(3), 722.
29. Rakhmankulov, D.L.; Zlotsky, S.S.; Rudnik, L.Z.; Teregulova, G.T.; Rakovsky, S.K. *Communications of the Department of Chemistry, Bulgarian Academy of Sciences* 1989, *22*(3), 652.
30. Anachkov, M.P.; Rakovsky, S.K.; Stoyanov, A.K.; Fotty, R.K., *Thermochemica Acta* 1994, *237*, 213.
31. Rakovsky, S.K.; Cherneva, D.R.; Deneva, M., *International Journal of Chemical Kinetics* 1995, *27*(2), 153.
32. Rakovsky, S.K.; Cherneva, D.R.; Deneva, M.; Ershov, V.V. *Oxidation Communications* 1997, *20*(2), 169.
33. Rakovsky, S.K.; Sheldon, R.A.; Rantwijk, F.V. *Oxidation Communications* 1996, *19*(4), 482.
34. Zaikov, G.E.; Rakovsky, S.K., *Ozonation of Organic & Polymer Compounds*, *i*Smithers, Smithers Rapra, Shawbury, Shreswsbury, Shropshire, SY4 4NR, UK, 2009.
35. Popova, D.; Rakovsky, S.; Anachkov, M. *Oxidation Communications* 2007, *30*(3), 529.
36. Eyring, H.; Lin S.H.; Lin S.M. *BASIC Chemical Kinetics*, Moskow, Mir, 1983 (In Russian).
37. Rozovskii, A.Ja. *Heterogeneous Chemical Reactions (Kinetics and Macrokinetics)*, Nauka: Moscow, 1980, (In Russian).
38. Rozenberg, M.M.; Brun, E.B. *Teor. Osn. Khim. Teknol.* (In Russian), 1990, *24*(2), 198.
39. Slavcho Kirillov Rakovsky, Metody Anachkov, G.E. Zaikov, O.V.Stoyanov, S.Yu.Sofina. Reactions of ozone with alcohols, ketones, ethers and hydroxybenzenes (part 1). Vestnik Kazanskogo tekhnologicheskogo universiteta. – 2013. – T.16. – №4. – P.11-17.
40. Gerchikov, A.Ya.; Komissarov, V.D.; Denisov, E.T.; Kochemassov, G.B., *Kinetika i Kataliz* **1972**, *13*(1126); *Kinetika Kataliz* **1974**, *15*, 509.
41. Gerchikov, A.Ya.; Komissarov, V.D.; Denisov, E.T.; *Kinetika i Kataliz* **1974**, *15*, 230.
42. Gerchikov, A.Ya.; Komissarov, V.D.; Galimova, L.G.; Denisov, E.T. *Doklady Akademii Nauk SSSR*, **1973**, *213*, 881.
43. Korotkova, N.P.; Syroezhko, A.M.; Proskuryakov, V.A. *Zhurnal Prikladnoi Khimii* **1981**, *54*, 885.
44. Komissarov, V.D.; Galimova, L.G.; Denisov, E.T. *Kinetika i Kataliz* **1974**, *15*, 1063.
45. Syroezhko, A.M.; Korotkova, N.P.; Vihorev, A.A.; Proskuryakov, V.A. *Zhurnal Prikladnoi Khimii* **1978**, *15*, 2562.
46. Razumovskii, S.D.; Rakovsky, S.K.; Shopov, D.M.; Zaikov, G.E. Publishing House of the Bulgarian Academy of Sciences: Sofia, Bulgaria, 1983.
47. Rakovsky, S.K.; Cherneva, D.R.; Shopov, D.M.; Razumovskiy, S.D. *Communications of the Department of Chemistry, Bulgarian Academy of Sciences* **1976**, *9*(4), 711.

48. Rakovsky, S.K.; Cherneva, D.R. *Oxidation Communications* **1989**, *12*(3), 108.

49. Barton, D.; Li, V.D., Eds., *General Organic Chemistry*, Volume 2, p 577, Khimiya Publishers: Moscow, 1982.

50. House, H.O.; Benjamin, W.A., Eds., *Modern Synthetic Reactions*; 2nd Edition, Menlo Park, CA, USA, 1972.

51. Zabicky, J., Ed., *The Chemistry of the Carbonyl Group*, (2 Volumes) Interscience Publishers, London, UK, 1970.

52. Alcais, P.; Brouillard, R. *Journal of the Chemical Society - Perkin II* **1972**, *1214*.

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