Kinetics and Catalysis, Vol. 45, No. 6, 2004, pp. 781–787. Translated from Kinetika i Kataliz, Vol. 45, No. 6, 2004, pp. 829–835.
Original Russian Text Copyright © 2004 by Zimin, Gusmanov, Khursan.

PEROXIDES-XI

Chemiluminescence in the Course of Methyl Ethyl Ketone Oxidation by Ozone in Acidic Aqueous Solutions

Yu. S. Zimin, A. A. Gusmanov, and S. L. Khursan

Bashkortostan State University, Ufa, 450074 Bashkortostan, Russia

Received July 10, 2003

Abstract—Chemiluminescence in the visible spectral region is observed in the course methyl ethyl ketone oxidation by ozone in neutral and acidic aqueous solutions. The spectral composition of the chemiluminescence is studied. On going from neutral to acidic aqueous solutions of methyl ethyl ketone, the initial intensity of the signal increases and the kinetics of a decrease in the chemiluminescence intensity changes. A radical scheme of the process is proposed to explain the results obtained.

INTRODUCTION

It has been shown earlier [1–3] that the oxidation of methyl ethyl ketone by atmospheric oxygen in neutral organic and aqueous solutions is accompanied by chemiluminescence in the visible spectral region. The triplet-excited diketone (diacetyl) formed in an elementary act of disproportionation of peroxy radicals was established [1, 4, 5] to be the chemiluminescence emitter. In this work, chemiluminescence was observed during the oxidation of methyl ethyl ketone by ozone not only in neutral but also in acidic aqueous solutions. According to [6, 7], the reaction of O_3 with the keto form of methyl ethyl ketone occurs in neutral aqueous solutions via a radical-chain mechanism, whereas in acidic solutions ozone reacts with the enol form of methyl ethyl ketone via a molecular mechanism. Based on these data, one could expect a decrease in the chemiluminescence intensity on going from neutral to acidic aqueous solutions. On the contrary, the addition of an acid to the reaction mixture increased the intensity of a chemiluminescence signal. To understand the nature of this phenomenon, we studied the kinetics of methyl ethyl ketone oxidation by ozone in neutral and acidic aqueous solutions.

EXPERIMENTAL

An ozone–oxygen mixture was prepared by a ozonator described earlier [8]. Methyl ethyl ketone (reagent grade) was purified by multiple vacuum distillations. Fresh water distilled twice was used as a solvent. The acidity of the reaction mixture was changed by adding HNO_3 or $HClO_4$ (reagent grade).

A chemiluminescence setup consisted of a light-proof chamber in which a glass constant-temperature reactor was placed. The reactor was equipped with a reflux condenser and a bubbler for supply of an ozone–oxygen mixture (the O_3 concentration in the mixture was 1–2 vol %).

Experiments were carried out as follows. An aqueous solution of methyl ethyl ketone (14 ml) with a certain concentration was placed in the reactor, and the temperature of the solution was maintained at a specified level for 15 min. Then, the ozone–oxygen mixture was supplied at a rate of 6–7 l/h. When the intensity of a chemiluminescence signal reached a certain value, the mixture supply was interrupted and a change in the chemiluminescence in the visible spectral region was observed.

Experiments in an acidic medium were carried out in a different manner. An aqueous solution (13.4 ml) of an acid (HNO_3 or $HClO_4$) with a certain concentration (0.005–0.05 mol/l) was placed in the reactor, and the temperature of the solution was maintained constant for 15 min. Then, the solution was saturated with an ozone–oxygen mixture for 5 min, after which an aqueous solution (0.6 ml) of methyl ethyl ketone (2.33 mol/l) was rapidly injected via a syringe with stirring. A change in the chemiluminescence intensity in the visible spectral region was recorded on an S8-13 storage oscilloscope.

In all experiments, the inequality $[RH]_0 \geqslant [O_3]_0$ was fulfilled, where $[RH]_0$ and $[O_3]_0$ are the initial concentrations of methyl ethyl ketone and ozone in the solution, respectively.

The overall concentration of acidic reaction products was determined by alkalimetry (NaOH). The concentration of peroxide products was determined by the spectrophotometric method using a procedure described in [9].

Quantum-chemical calculations were performed using the Gaussian98 program package [10]. All calculations were carried out in the framework of the density functional theory using the B3LYP hybrid functional and a split-valence basis set including polarization functions of the *d*-type for non-hydrogen atoms and of the *p*-type for hydrogen atoms (6-31G(*d*,*p*)). The energy characteristics and structures of some com-

0023-1584/04/4506-0781 © 2004 MAIK "Nauka/Interperiodica"

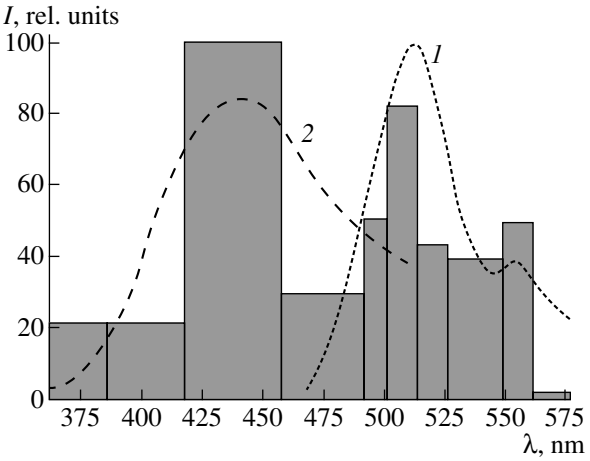


Fig. 1. Spectral composition of luminescence upon the oxidation of methyl ethyl ketone by ozone (338 K, $[RH]_0$ = 0.1 mol/l); phosphorescence spectra of (*1*) diacetyl ketone [5] and (*2*) butyraldehyde.

pounds with at most eight nonhydrogen atoms were also calculated by the G2MP2 composite method.

RESULTS AND DISCUSSION

In this work, chemiluminescence spectra that appeared upon the oxidation of methyl ethyl ketone by ozone in neutral and acidic aqueous solutions were studied using boundary light filters. The spectral composition of the emission (Fig. 1) turned out to remain unchanged with a change in the acidity of the medium. Analysis of the chemiluminescence spectrum, taking into account the phosphorescence spectra of diacetyl [5] and a model compound (butyraldehyde) and the fluorescence spectrum of the oxidate, suggests the presence of two emitters in the reaction of O_3 with methyl ethyl ketone: triplet-excited diacetyl and β-oxobutyraldehyde.

In neutral aqueous solutions, the kinetics of methyl ethyl ketone ozonation were studied as a decrease in chemiluminescence intensity. The studies were carried out at 330–350 K, and the initial concentration of methyl ethyl ketone in the reaction mixture was varied in the range 0.01–0.1 mol/l. The variation of the chemiluminescence intensity I in the reaction of ozone with methyl ethyl ketone and its semilogarithmic linearization is shown in Fig. 2. These data show that in the neutral medium the luminescence intensity obeys the first order law. The rate constant k' found from the semilogarithmic plot increases linearly with an increase in the initial concentration of methyl ethyl ketone (Fig. 3):

$$k' = k[RH]_0,$$

where k is the second-order rate constant.

Thus, the oxidation of methyl ethyl ketone by ozone in neutral aqueous solutions is limited by a second-order reaction (it has the first order with respect to particular components). This step is the initiation of the radical-chain oxidation of methyl ethyl ketone [11]:

$$RH + O_3 \longrightarrow R^{\cdot} + HO^{\cdot} + O_2,$$

$$R^{\cdot} + O_2 \longrightarrow RO_2^{\cdot},$$

$$RO_2^{\cdot} + RO_2^{\cdot} \longrightarrow (\eta_1)\,{}^3(>C{=}O) + (1 - \eta_1)\,>C{=}O + \text{products},$$

$${}^3(>C{=}O) \xrightarrow{(\eta_2)} >C{=}O + h\nu.$$

Electron-excited compounds (chemiluminescence emitters) are formed in the act of $RO_2^{\cdot}$ radical dispro-

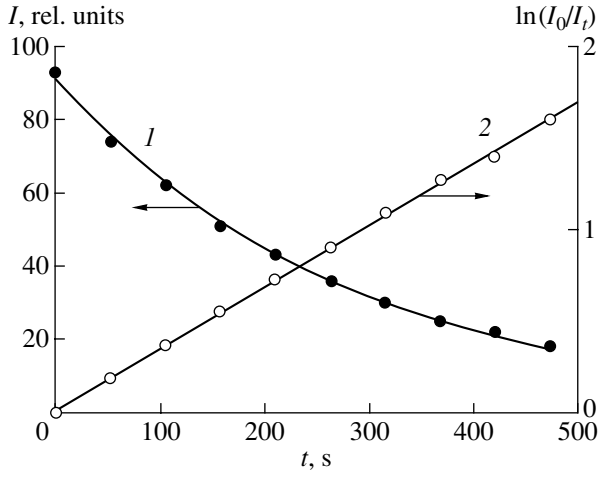


Fig. 2. (*1*) Chemiluminescence intensity curve for the reaction of ozone with methyl ethyl ketone and (*2*) its semilogarithmic linearization (333 K, $[RH]_0$ = 0.07 mol/l).

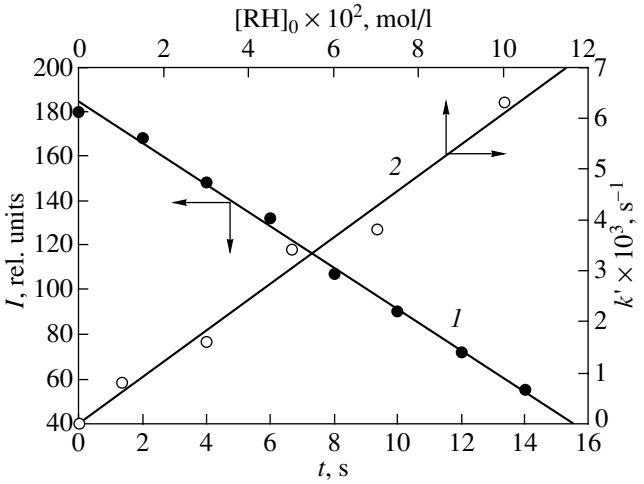


Fig. 3. (*1*) Chemiluminescence intensity curve for the reaction of O_3 with methyl ethyl ketone and (*2*) the plot of k' vs. methyl ethyl ketone concentration: (*1*) 338 K, $[RH]_0$ = 0.1 mol/l, $[H^+]_0$ = 0.05 mol/l; and (*2*) 333 K, $[H^+]_0$ = 0.0 mol/l.

portionation (η_1 and η_2 are the $^3(>C=O)$ excitation and emission yields, respectively).

For the reaction of ozone with methyl ethyl ketone in a neutral medium, we studied the Arrhenius dependence of the rate constant k (Table 1) and determined the activation parameters of the process

$$\log k = (11.9 \pm 1.1) - (20.1 \pm 0.4)/\Theta, \text{ [l mol}^{-1}\text{ s}^{-1}\text{]},$$

where $\Theta = 2.303RT$ kcal/mol.

In acidic aqueous solutions, experiments were carried out at a constant concentration of methyl ethyl ketone ($[RH]_0 = 0.1$ mol/l) in the temperature interval from 330 to 350 K. The concentrations of HNO_3 and $HClO_4$ were varied from 0.005 to 0.05 mol/l. In the presence of strong inorganic acids, the initial chemiluminescence intensity in methyl ethyl ketone oxidation by ozone noticeably increases (Table 2). Then, the chemiluminescence intensity decreases with time at a constant rate w (Fig. 3). The w value increases linearly with an increase in the initial methyl ethyl ketone concentration (Fig. 4). The reaction rate also increases linearly with an increase in the initial acid concentration (Fig. 4)

$$w = k_{eff}[H^+]_0,$$

where k_{eff} is the effective constant of chemiluminescence-intensity decrease. These results indicate the first-order reaction with respect to methyl ethyl ketone and acid. Thus, in acidic aqueous solutions, the oxidation of methyl ethyl ketone by ozone is controlled by the enolization step, which is confirmed by the published data [6, 7, 12, 13] on the oxidation of ketones by ozone in an aqueous medium. In these papers, the zero order of the reaction with respect to ozone and the first order with respect to the substrate and acid were observed by the spectrophotometric method by monitoring O_3 consumption in the liquid phase.

The temperature dependence of the rate constant k_{eff} of the reaction of ozone with methyl ethyl ketone in an acidic aqueous medium (Table 1) was studied, and the apparent activation energy was determined (36.3 ± 2.7 kcal/mol).

We studied the kinetics of accumulation of the acid and hydroperoxide products under conditions of continuous bubbling of the ozone–oxygen mixture through acidic solutions of methyl ethyl ketone (Fig. 5). As can be seen from data in Fig. 5, peroxides are rapidly accumulated in the initial period of the reaction. Their concentration achieves a maximum for ~30 min and then decreases. The curve of acid accumulation is S-shaped. The consumption of peroxide products is accompanied by a sharp enhancement of the chemiluminescence signal, whose intensity passes through a maximum.

Comparison of the resulting plots suggests that the formation of chemiluminescence emitters is related to peroxide decomposition. Ozone is known [14] to lead to efficient radical decomposition of hydroperoxides. Therefore, an increase in the chemiluminescence intensity can be related to an increase in the initiation rate due to the ROOH + O_3 reaction. A decrease in the chemiluminescence intensity is probably caused by several factors: a decrease in the methyl ethyl ketone concentration, a decrease in the concentration of peroxides decreasing the initiation rate in the reaction with ozone, an increase in the rate of nonradical acid-catalyzed decomposition of peroxides related to acid accumulation in the system, and quenching of emitters by oxidation products.

Table 1. Temperature dependences of k and k_{eff}

T, K	k, l mol^{-1} s^{-1}	k_{eff}, rel. u. l mol^{-1} s^{-1}
330	0.041 ± 0.008	5.0 ± 0.9
333	0.058 ± 0.013	9.8 ± 1.5
336	0.066 ± 0.007	13.6 ± 1.7
338	0.082 ± 0.016	20.1 ± 3.7
341	0.13 ± 0.02	28.9 ± 4.2
344	0.15 ± 0.01	52.7 ± 7.3
347	0.18 ± 0.03	109 ± 15
350	0.24 ± 0.05	126 ± 14

Table 2. Initial luminescence intensity in the reaction of ozone with methyl ethyl ketone at different acid concentrations; 338 K, and $[RH]_0 = 0.1$ mol/l

$[H^+]_0$, mol/l	I_0, rel. units
0.001	65
0.005	97
0.01	108
0.03	111
0.05	180

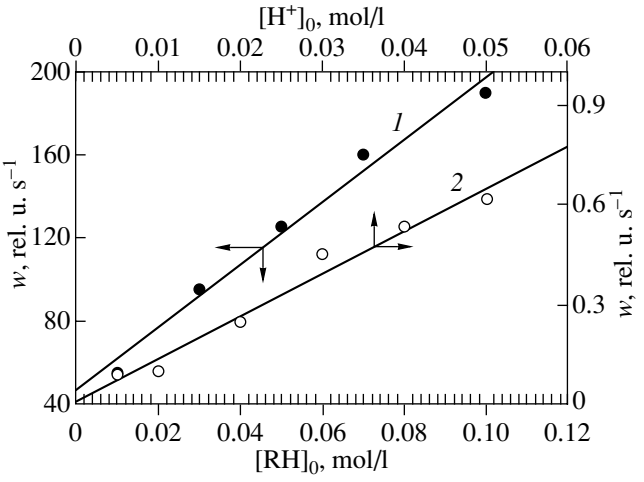


Fig. 4. Plots of the reaction rate w vs. concentrations of (*1*) methyl ethyl ketone and (*2*) acid: (*1*) 338 K, $[H^+]_0$ = 0.05 mol/l; and (*2*) 336 K, $[RH]_0 = 0.1$ mol/l.

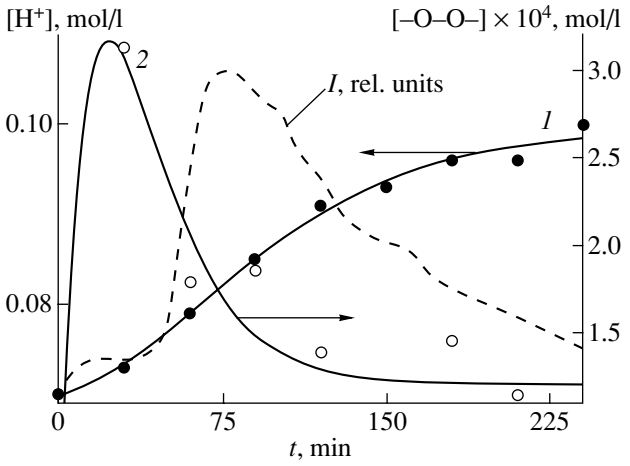


Fig. 5. Kinetics of accumulation of (*1*) total acid and (*2*) total peroxides and *I* the change in the chemiluminescence intensity (323 K, $[RH]_0$ = 1.0 mol/l, $[H^+]_0$ = 0.07 mol/l).

To verify the hypothesis on the role of hydroperoxides in the formation of chemiluminescence emitters, we studied changes in the emission intensity in the reaction of ozone with methyl ethyl ketone (at 333 K) in the presence of various amounts of hydrogen peroxide, which is known to be a source of free radicals in the presence of O_3. The $O_3 + H_2O_2$ (1 mol/l) system produces no emission, while the addition of ketone (0.1 mol/l) to hydrogen peroxide containing no ozone produces luminescence of comparatively low intensity.

When ozone is supplied to the H_2O_2 + methyl ethyl ketone system, the intensity of the chemiluminescence signal sharply increased, and the intensities were equal in acidic ($[H^+]_0$ = 0.1 mol/l) and neutral solutions. An increase in the chemiluminescence intensity is related, most likely, to an increase in the radical initiation rate due to hydrogen peroxide. Indeed, under our conditions (333 K, $[H_2O_2]_0$ = 1 mol/l), $[RH]_0$ = 0.1 mol/l), ozone is largely consumed in the reaction with hydrogen peroxide ($k_{HOOH + O_3}$ = 0.828 l mol^{-1} s^{-1} [15]) and virtually does not react with ketone ($k_{RH + O_3}$ = 0.058 l mol^{-1} s^{-1}, Table 1):

$$\frac{w_{HOOH + O_3}}{w_{RH + O_3}} = \frac{k_{HOOH + O_3}[HOOH][O_3]}{k_{RH + O_3}[RH][O_3]} = \frac{0.828 \times 1.0}{0.058 \times 0.1} \approx 143.$$

Hydroxy radicals formed react with both methyl ethyl ketone ($k_{RH + OH} = 9.1 \times 10^8$ l mol^{-1} s^{-1} [16]) and hydrogen peroxide ($k_{HOOH + OH} = 4.5 \times 10^7$ l mol^{-1} s^{-1} [16]),

$$\frac{w_{RH + OH}}{w_{HOOH + OH}} = \frac{k_{RH + OH}[RH][OH^\cdot]}{k_{HOOH + OH}[HOOH][OH^\cdot]} = \frac{9.1 \times 10^8 \times 0.1}{4.5 \times 10^7 \times 1.0} \approx 2,$$

resulting in methyl ethyl ketone peroxy radicals and chemiluminescence. This is confirmed by the fact that the chemiluminescence increased sharply when ozone was supplied again to the reaction system.

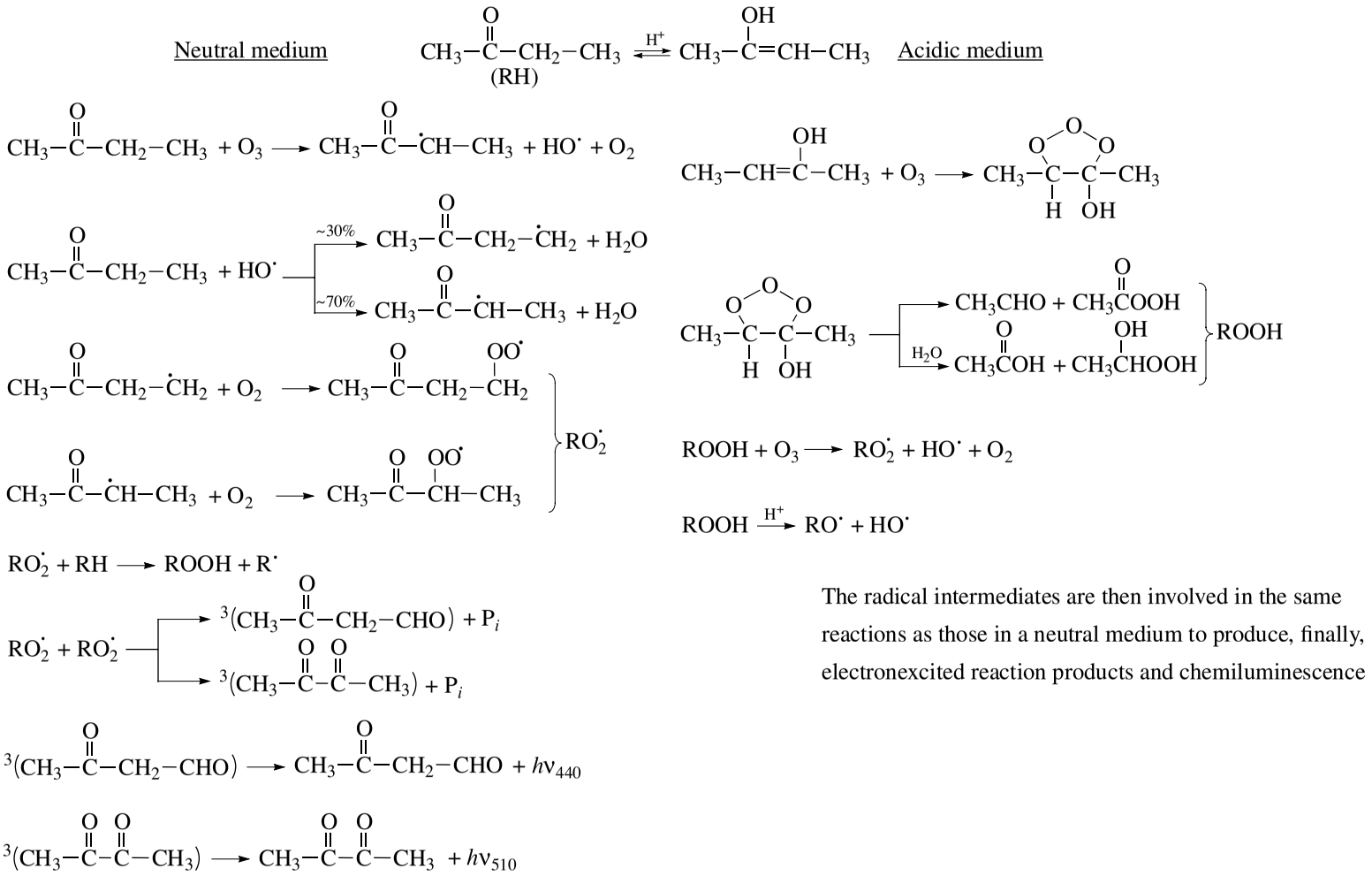
In this work, quantum-chemical calculation of the steps of the process was performed using the enol form of methyl ethyl ketone as an example to additionally check the above hypotheses. Calculations were performed by the G2MP2 method and DFT in the B3LYP/6-31G(*d*,*p*) approximation. The reaction of ozone with the enol form of methyl ethyl ketone was considered in the framework of the classical model of ozone interaction with unsaturated compounds via the Criegee mechanism. The results obtained are collected in Table 3.

According to the Criegee mechanism, the primary molecular product of ozone addition to enol is a cyclic ozonide (Table 3, reaction (I)), which undergoes decomposition via two pathways to form: (1) aldehyde and hydroxycarbonyl oxide, which is subsequently rearranged spontaneously to form peracid due to the very high instability (reaction (II)) and (2) carbonyl oxide and acid (reaction (III)). The calculated activation energies of ozonide decomposition via the first (13.8 kcal/mol) and second (12/6 kcal/mol) pathways are commensurable, hence, the decompositions of ozonide via both routes are equally probable.

The decomposition products of ozonide lead to peroxide products (reactions (IV) and (V)), which agrees with data in Fig. 5 concerning the accumulation of peroxides. When interacting with ozone, hydroperoxides and hydrogen peroxide produce free radicals $RO_2^\cdot$ and $HO^\cdot$ (reactions (VI)–(VIII)). Peroxy radical disproportionation produces chemiluminescence emitters. Hydroxy radicals initiate new oxidation routes leading to the additional formation of $RO_2^\cdot$ radicals.

Thus, in acidic aqueous solutions (as well as in neutral media), chemiluminescence appears when peroxy radicals undergo disproportionation. An increase in the chemiluminescence intensity is related to the appearance of an additional initiation channel due to the interaction of ozone with organic hydroperoxides, which are the ozonolysis products of the enol form of methyl ethyl ketone.

Based on the above experimental and calculated results and taking into account published data [4–7, 11–14, 17, 18], we propose the following scheme for methyl ethyl ketone oxidation by ozone in acidic aqueous solutions:

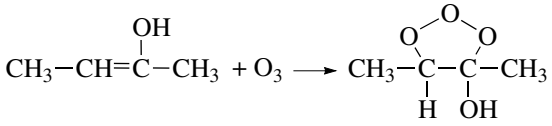
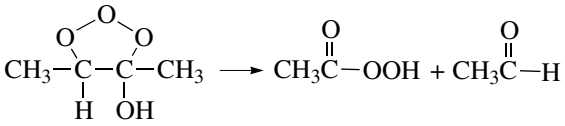
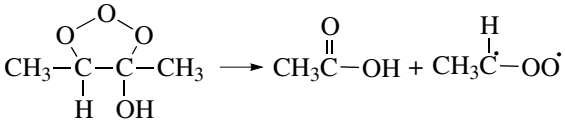
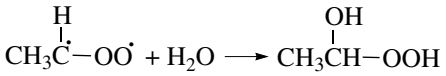
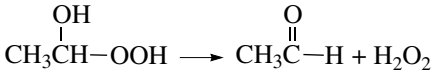
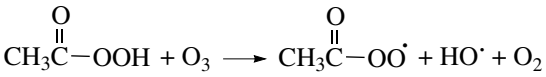
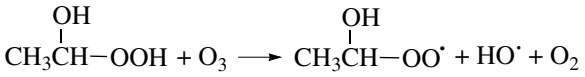
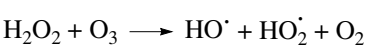


P_i are other reaction products of the decay of methyl ethyl ketone peroxy radicals

Scheme.

The radical intermediates are then involved in the same reactions as those in a neutral medium to produce, finally, electronexcited reaction products and chemiluminescence

Table 3. Enthalpies of the model reactions of methyl ethyl ketone oxidation by ozone in an acidic medium

Reaction		ΔH^0, kcal/mol
	(I)	–40.0
	(II)	–73.1
	(III)	–88.0
	(IV)	–42.2
	(V)	17.2
	(VI)	23.1
	(VII)	12.4
	(VIII)	11.5

To estimate the fraction of primary peroxy radicals in the total amount of $RO_2^{\bullet}$ radicals of methyl ethyl ketone, we calculated the partial rate constants of the reaction of the $^{\bullet}OH$ radicals with the C–H bonds of methyl ethyl ketone, using published data [16] on the reactivity of the hydroxy radicals in hydrogen atom abstraction from organic compounds of different classes. Using the rate constant of the reaction of the $^{\bullet}OH$ radical with acetone (8.8×10^7 l mol^{-1} s^{-1}), we found $k_{\alpha CH_3} = 4.4 \times 10^7$ l mol^{-1} s^{-1} (the subscript indicates an attacked group). The partial rate constant of hydrogen atom abstraction from the β-CH_3 bond was calculated from the rate constants of the reactions of the hydroxy radical with *n*-alkanes (i.e., the carbonyl group is assumed to have no effect on the reactivity of the β-CH_3 bond). It was found that $k_{\beta CH_3} = 2.81 \times 10^8$ l mol^{-1} s^{-1}. Then, using the rate constant of the reaction of the $^{\bullet}OH$ radical with methyl ethyl ketone (9.0×10^8 l mol^{-1} s^{-1}), one can easily calculate $k_{\alpha CH_2} = 5.75 \times 10^8$ l mol^{-1} s^{-1}. The data obtained show that the probability of $CH_3C(O)CH_2CH_2OO^{\bullet}$ radical formation in the reaction of $^{\bullet}OH$ with methyl ethyl ketone is 31%, which, taking into account the cross-recombination $CH_3C(O)CH_2CH_2OO^{\bullet} + CH_3C(O)CH(OO^{\bullet})CH_3$, provides ~40% probability of chain termination and, hence, generation of the chemiluminescence emitter at the primary peroxy radicals.

Let us use data presented in Table 1 and Fig. 3 to estimate the ratios of rates for the reactions of ozone with the keto and enol forms of methyl ethyl ketone. Under comparable conditions (333 K, $[RH]_0 = 0.1$ mol/l, $[O_3]_0 = 2 \times 10^{-4}$ mol/l), the initial rate of the reaction of O_3 with the keto form of methyl ethyl ketone is $w_{RH} = k_{RH}[RH][O_3]_0 = 1.2 \times 10^{-6}$ mol l^{-1} s^{-1}. As can be seen from Fig. 3, the time of complete ozone consumption (t) in acidic aqueous solutions ($[H^+]_0 = 0.05$ mol/l) is ~20 s. Therefore, $w_{En} = [O_3]_0/t = 1 \times 10^{-5}$ mol l^{-1} s^{-1}. These quantitative estimates agree with the experimentally determined half-lives for ozone conversion, which are 30–300 s in the neutral medium and 3–10 s in the acidic medium. It follows from the ratio of reaction rates that even at the initial moment ~90% of ozone reacts with the enol form of methyl ethyl ketone. In an acidic medium, the reaction rate is independent of ozone concentration (Fig. 3) and, therefore, the propor-

tion of the reaction En + O_2, which raises ozone conversion, will be even greater.

The enhancement of chemiluminescence upon acid addition is related to the appearance of an additional initiation channel via the reaction of hydroperoxides with ozone. The estimate of this reaction rate ($(1.2–1.4) \times 10^{-6}$ mol l^{-1} s^{-1} at 333 K [19]) indicates that the reaction of ROOH with O_3 has almost no effect on the rate of ozone decomposition in the reaction with the enol form of methyl ethyl ketone ($w_{En} \geq 1 \times 10^{-5}$ mol l^{-1} s^{-1}). This fact explains the zeroth order with respect to the O_3 concentration (Fig. 3).

At the same time, the rate of the reaction ROOH + O_3 is comparable with the rate of the reaction of the methyl ethyl ketone keto form with ozone ($w_{RH} = 1.2 \times 10^{-6}$ mol l^{-1} s^{-1}). Therefore, the decomposition of hydroperoxides under the action of ozone provides a substantial increase in the initiation rate and an increase in the chemiluminescence signal intensity.

CONCLUSIONS

Methyl ethyl ketone oxidation in an acidic medium by an ozone–oxygen mixture is an interesting example of a chemiluminescence process where the photoreaction is a side reaction which nevertheless allows one to study the kinetics of the main reaction (the reaction of ozone with the enol form of methyl ethyl ketone, which exhibits no emission) by the chemiluminescence method.

REFERENCES

1. Vasil'ev, R.F. and Rusina, I.F., *Dokl. Akad. Nauk SSSR*, 1964, vol. 156, no. 6, p. 1402.
2. Zaikov, G.E., Maizus, Z.K., and Emanuel', N.M., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1968, no. 1, p. 53.
3. Zaikov, G.E., Maizus, Z.K., and Emanuel', N.M., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1968, no. 2, p. 256.
4. Belyakov, V.A., Vasil'ev, R.F., and Fedorova, G.F., *Izv. Akad. Nauk SSSR, Ser. Fiz.*, 1968, vol. 32, no. 8, p. 1325.
5. Vasil'ev, R.F. and Fedorova, G.F., *Opt. Spektrosk.*, 1968, vol. 24, no. 3, p. 419.
6. Gerchikov, A.Ya., Kuramshin, E.M., Komissarov, V.D., and Denisov, E.T., *Kinet. Katal.*, 1974, vol. 15, no. 1, p. 230.
7. Komissarov, V.D., Gerchikov, A.Ya., and Denisov, E.T., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1974, no. 11, p. 2616.
8. Vendillo, V.P., Emel'yanov, Yu.M., and Filippov, Yu.V., *Zavod. Lab.*, 1959, vol. 25, p. 1401.
9. Antonovskii, V.L. and Buzlanova, M.M., *Analiticheskaya khimiya organicheskikh peroksidnykh soedinenii* (Analytical Chemistry of Organic Peroxide Compounds), Moscow: Khimiya, 1978.
10. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Zakrzewski, V.G., Montgomery, J.A., Stratmann, R.E., Burant, J.C., Dapprich, S., Millam, J., Daniels, M.A.D., Kudin, K.N., Strain, M.C., Farkas, O., Tomasi, J., Barone, V., Cossi, M., Cammi, R., Mennucci, B., Pomelli, C., Adamo, C., Clifford, S., Ochterski, J., Petersson, G.A., Ayala, P.Y., Cui, Q., Morokuma, K., Malick, D.K., Rabuck, A.D., Raghavachari, K., Foresman, J.B., Cioslowski, J., Ortiz, J.V., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Gomperts, R., Martin, R.L. Fox, D.J., Keith, T., Al-Laham, M.A., Peng, C.Y., Nanayakkara, A., Gonzalez, C., Challacombe, M., Gill, P.M.W., Johnson, B.G., Chem, W., Wong, M.W., Andres, J.L., Head-Gordon, M., Replogle, E.S., and Pople, J.A., *Gaussian 98* (Revision A.7). Pittsburgh: Gaussian, 1998.
11. Zimin, Yu.S., Gusmanov, A.A., and Gainullina, A.M., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 2002, vol. 45, no. 4, p. 134.
12. Zimin, Yu.S., Trukhanova, N.V., Rafikova, G.M., and Komissarov, V.D., *Kinet. Katal.*, 1998, vol. 39, no. 4, p. 503.
13. Zimin, Yu.S., Trukhanova, N.V., Gerchikov, A.Ya., Butasova, E.M., and Zubairova, E.A., *Kinet. Katal.*, 2000, vol. 41, no. 6, p. 823.
14. Antonovskii, V.L. and Khursan, S.L., *Fizicheskaya khimiya organicheskikh peroksidov* (Physical Chemistry of Organic Peroxides), Moscow: Akademkniga, 2003.
15. Sehested, K., Corfitzer, H., Holcman, J., and Hart, E.J., *J. Phys. Chem.*, 1992, vol. 96, p. 1005.
16. Pikaev, A.K. and Kabakchi, S.A., *Reaktsionnaya sposobnost' pervichnykh produktov radioliza vody. Spravochnik* (Reactivity of Primary Products of Water Radiolysis: A Handbook), Moscow: Energoizdat, 1982.
17. Emanuel', N.M., Zaikov, G.E., and Maizus, Z.K., *Rol' sredy v radikal'no-tsepnykh reaktsiyakh okisleniya organicheskikh soedinenii* (Role of a Medium in the Chain-Radical Oxidation Reactions of Organic Compounds), Moscow: Nauka, 1973.
18. Denisov, E.T., Mitskevich, N.I., and Agabekov, V.E., *Mekhanizm zhidkofaznogo okisleniya kislorodsoderzhashchikh soedinenii* (The Mechanism of Oxidation of Oxygen-Containing Compounds), Minsk: Nauka Tekhnika, 1975.
19. Kurz, M.E. and Pryor, A., *J. Am. Chem. Soc.*, 1978, vol. 100, no. 25, p. 7953.