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Kinetics of Ketone Oxidation by Ozone in Water Solutions

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Abstract—The spectrophotometric monitoring of ozone consumption in a liquid phase is used to study the kinetics of cyclopentanone and methyl butyl ketone oxidation. The rate of ozone reaction with ketones (RH) at 303–344 K in acidic ($HClO_4$) aqueous solutions is described by the equation $w = k_1[RH][O_3] + k_{En}[RH][HClO_4]$, where k_1 is the rate constant for the reaction of ozone with RH and k_{En} is the rate constant for the enolization of RH. The kinetic parameters of the process are found.

INTRODUCTION

Keto-enol equilibrium plays an important role in the oxidation of ketones with ozone [1–7]. Upon adding an acid, which is an enolization catalyst, the fraction of the reaction with the enol tautomer increases. In a neutral medium, ozone reacts predominantly with the ketone tautomer of the substrate [1, 7].

In this work, we continue to study the role of keto-enol equilibrium using of the oxidation of cyclopentanone and methyl butyl ketone with ozone in water solutions as an example.

EXPERIMENTAL

Methyl butyl ketone (chemically pure) was purified as described earlier [8]. Cyclopentanone (chemically pure) was doubly distilled in a vacuum twice. Fresh doubly distilled water was used as a solvent. Chemically pure $HClO_4$ was used to vary the acidity of the medium. An ozonizer with a known design [9] produced an O_3–O_2 mixture containing 1–2 vol % of ozone. The kinetics of ozone consumption in the liquid phase (303–344 K) was monitored by spectrophotometry at λ = 270 nm [8]. The initial concentrations of ketones (RH), ozone, and acid were as follows: $[RH]_0 = (0.5–5.0) \times 10^{-3}$, $[O_3]_0 = (0.2–2.0) \times 10^{-4}$, $[HClO_4]_0$ = 0.05–0.5 mol/l.

RESULTS AND DISCUSSION

The study of O_3 consumption in the reaction with cyclopentanone and methyl butyl ketone in neutral water solutions demonstrated that ozone consumption follows the second-order rate law

$$w = k_1[RH][O_3], \quad (1)$$

where k_1 is the rate constant for the reaction of ozone with RH. This follows from the satisfactory semilogarithmic anamorphoses of kinetic curves for ozone consumption under our experimental conditions ($[RH]_0 \gg [O_3]_0$), and from the linear dependence of pseudomonomolecular rate constants k' ($k' = k_1[RH]_0$) on $[RH]_0$ (Fig. 1). The apparent kinetics agrees with the data observed for the ozonation of methyl ethyl ketone [1] and cyclohexanone [7] in water solutions.

Unlike in neutral solutions, the rate of ozone consumption is constant in the acidic aqueous solutions; that is, the reaction rate w is independent of ozone concentration in the reaction mixture (Fig. 2).

The scheme that accounts for the reaction of ozone with both ketone (RH) and enol (EnH) tautomers [1, 7] can explain the results of this work:

$$RH + O_3 \xrightarrow{k_1} \text{Products},$$

$$RH + H^+ \underset{k_{-En}}{\overset{k_{En}}{\rightleftharpoons}} EnH + H^+,$$

$$EnH + O_3 \xrightarrow{k_2} \text{Products}.$$

According to this scheme, the rate of ozone consumption is described by

$$w = k_1[RH][O_3] + k_2[EnH][O_3] \quad (2)$$

or, assuming that the concentration of EnH is pseudostationary,

$$w = k_1[RH][O_3] + \frac{k_2 k_{En}[RH][HClO_4][O_3]}{k_{-En}[HClO_4] + k_2[O_3]}. \quad (3)$$

Because $k_2[O_3] \gg k_{-En}[HClO_4]$ [1], we can rearrange Eq. (3):

$$w = k_1[RH][O_3] + k_{En}[RH][HClO_4]. \quad (4)$$

This equation explains the above results. Indeed, in the absence of $HClO_4$, the first term of Eq. (4) deter-

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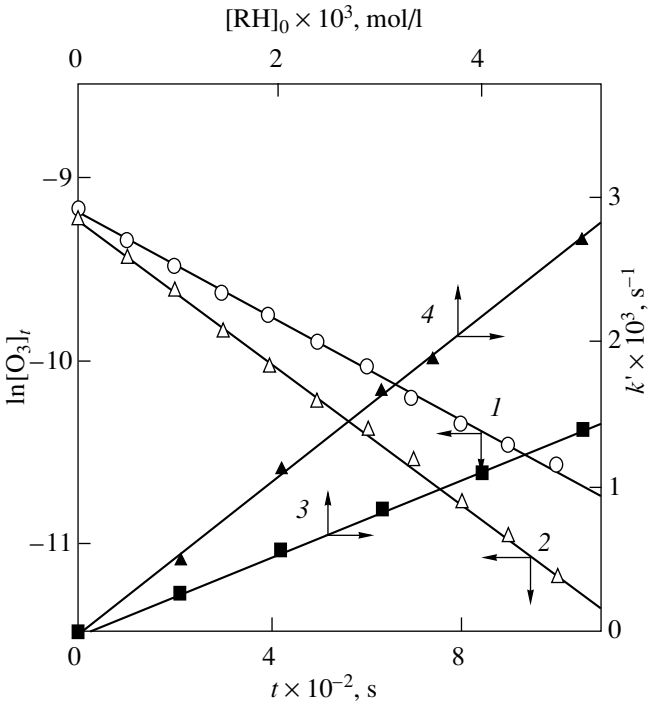

Fig. 1. Semilogarithmic plot (*1*, *2*) of ozone loss in the reaction ($[RH]_0$ = 0.005 mol/l) and (*3*, *4*) *k*' plotted versus $[RH]_0$ for (*2*, *4*) cyclopentanone and (*1*, *3*) methyl butyl ketone at 323 K.

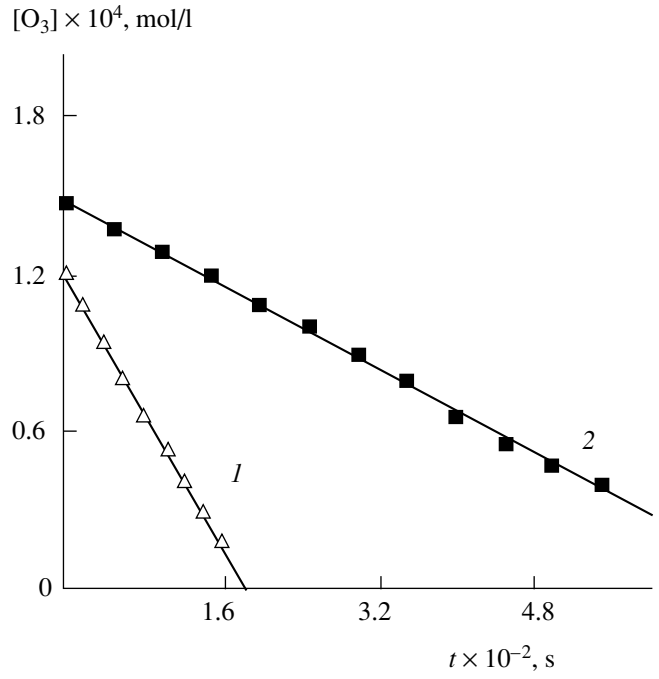

Fig. 2. Ozone loss in the reaction with (*1*) cyclopentanone and (*2*) methyl butyl ketone: $[RH]_0$ = 0.005 mol/l; $[HClO_4]_0$ = 0.05 mol/l; 323 K.

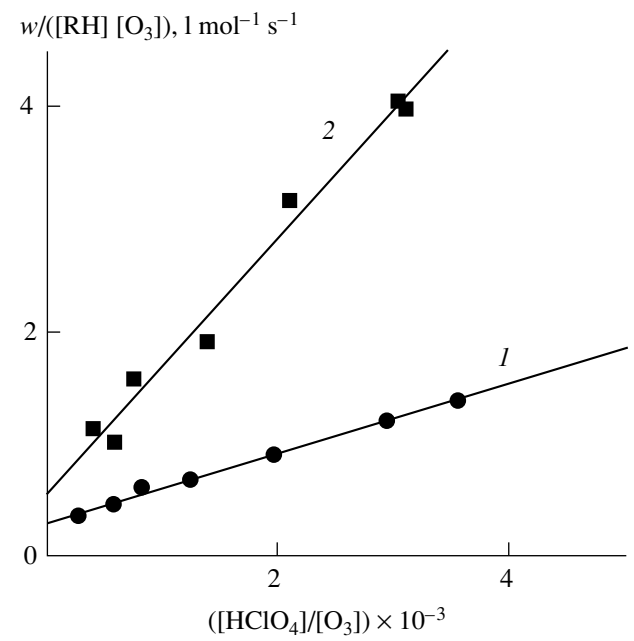

Fig. 3. $w/([RH][O_3])$ vs. $[HClO_4]/[O_3]$ for (*1*) methyl butyl ketone and (*2*) cyclopentanone oxidation at 323 K.

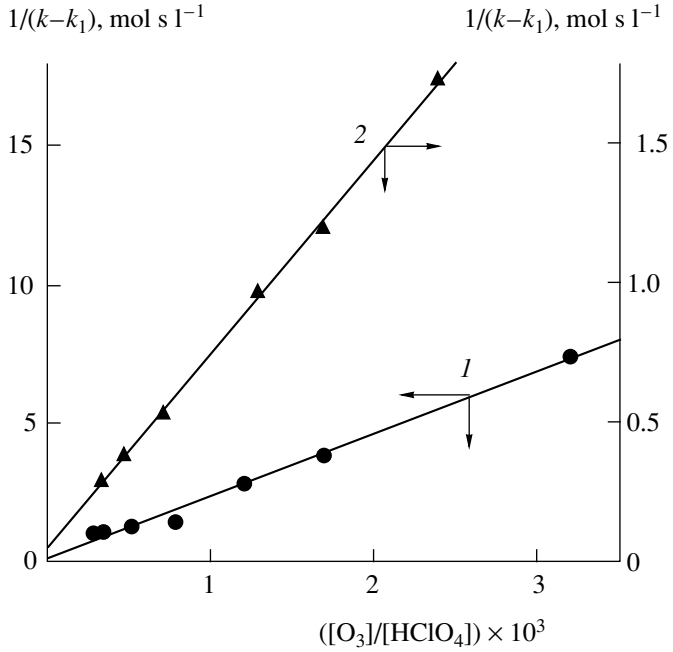

Fig. 4. $1/(k - k_1)$ vs. $[O_3]/[HClO_4]$ for (*1*) methyl butyl ketone and (*2*) cyclopentanone oxidation at 323 K.

mines the rate of ozone consumption (see Eq. (1)) in agreement with our experiment. Both ketone and enol tautomers of ketones react with ozone in the presence of the acid, and the fraction of the enol reaction increases with increasing $[HClO_4]$. Apparently, if the concentration of acid in the solution is high enough, the rate of enolization controls the process rate and results in the zero reaction order with respect to ozone.

Table 1. The rate constants k_1 and k_{En} at different temperatures

T, K	$k_1 \times 10$, l mol^{-1} s^{-1}		$k_{En} \times 10^4$, l mol^{-1} s^{-1}	
	Cyclopentanone	Methyl butyl ketone	Cyclopentanone	Methyl butyl ketone
303	0.96	0.99	1.67	0.67
309	0.85	2.28	3.75	1.08
316	2.23	2.86	7.87	1.72
323	5.35	2.91	11.5	2.82
330	8.75	10.3	21.0	3.74
337	37.9	13.7	23.7	7.55
344	31.6	23.6	63.0	8.74

Table 2. The activation parameters for the reaction of ozone with ketones

Rate constant	log$A$, [l mol^{-1} s^{-1}]		E, kcal/mol	
	Cyclopentanone	Methyl butyl ketone	Cyclopentanone	Methyl butyl ketone
k_1	11.9 ± 1.6	10.7 ± 1.2	18.0 ± 2.4	16.2 ± 1.7
k_{En}	9.2 ± 1.2	5.5 ± 0.9	17.9 ± 1.7	13.4 ± 1.1

Table 3. The constant of keto-enol equilibrium K as a function of temperature

T, K	$K \times 10^7$	
	Cyclopentanone	Methyl butyl ketone
303	0.38	0.12
309	0.74	0.16
316	1.26	0.15
323	2.43	0.36
330	4.34	0.77
337	4.36	1.02
344	13.02	1.99

Table 4. The thermodynamic parameters of keto-enol tautomerism

Thermodynamic parameter	Ketone	
	Cyclopentanone	Methyl butyl ketone
ΔH^0, kcal/mol	16.5 ± 3.1	14.1 ± 2.5
ΔS^0, cal mol^{-1} K^{-1}	20.7 ± 1.0	10.0 ± 0.8

If we rearrange Eq. (4),

$$w/([RH][O_3]) = k_1 + k_{En}([HClO_4]/[O_3]), \quad (5)$$

the linear plot of the experimental data in the coordinates of Eq. (5) gives us the rate constants k_1 and k_{En} (Fig. 3). Table 1 contains the values of the rate constant at different temperatures found by the described method. We calculated the activation parameters for the corresponding reactions using the data from Table 1. Table 2 presents the parameters.

The experimental data enabled us to estimate the constants of keto-enol equilibrium $K = k_{En}/k_{-En}$ for the studied ketones. For this purpose, we rearranged Eq. (3):

$$1/(k - k_1) = 1/k_2K + (1/k_{En})([O_3]/[HClO_4]), \quad (6)$$

where $k = w/([RH][O_3])$. To estimate the unknown constant k_2, we assumed that it is close to that typical of substituted olefins. The rate constants for the reaction of ozone with ethylene and vinyl chloride have values of $k_2 = 2.5 \times 10^4$ l mol^{-1} s^{-1} and 1.1×10^3 l mol^{-1} s^{-1}, respectively [10]. We assumed that the Taft relationship is applicable to the reaction under discussion and used the inductive Taft parameters $\sigma^* = 0$ and 2.78 for H and Cl substituents, respectively.[1] Thus, we estimated $k_2 \approx 6 \times 10^3$ l mol^{-1} s^{-1} for vinyl alcohol, which is the simplest enol ($\sigma^*_{OH} = 1.334$ [11]). Table 3 presents the values of K for cyclopentanone and methyl butyl ketone in water solution calculated using this value of k_2 according to Eq. (6) (Fig. 4). Table 4 contains the values of the entropy ΔS^0 and enthalpy ΔH^0 changes of the keto-enol equilibrium, calculated from the temperature dependence of K according to [12]

$$\log K = \Delta S^0/4.576 - \Delta H^0/(4.576T). \quad (7)$$

Note that the compensation effect is observed for these parameters; that is, ΔS^0 decreases with a decrease in the process enthalpy.

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REFERENCES

1. Gerchikov, A.Ya., Kuramshin, E.M., Komissarov, V.D., and Denisov, E.T., *Kinet. Katal.*, 1974, vol. 15, no. 1, p. 230.
2. Komissarov, V.D., Galimova, L.G., and Denisov, E.T., *Kinet. Katal.*, 1974, vol. 15, no. 4, p. 1063.
3. Gorbenko-Germanov, D.S., Baskova, N.K., and Vodop'yanova, N.M., *Khimicheskaya kinetika i kataliz*

[1] Average values of σ^* were borrowed from [11].

(Chemical Kinetics and Catalysis), Moscow: Nauka, 1979, p. 215.

4. Korotkova, N.P., Syroezhko, A.M., and Proskuryakov, V.A., *Zh. Prikl. Khim.*, 1981, vol. 54, no. 4, p. 885.
5. Niki, E., Yamamoto, Y., Saito, T., *et al.*, *Bull. Chem. Soc. Jpn.*, 1983, vol. 56, p. 223.
6. Rakovski, S. and Cherneva, D., *Oxid. Commun.*, 1989, vol. 12, no. 3–4, p. 108.
7. Zimin, Yu.S., Trukhanova, N.V., Rafikova, G.M., and Komissarov, V.D., *Kinet. Katal.*, 1998, vol. 39, no. 4, p. 503.
8. Gerchikov, A.Ya., Komissarov, V.D., Denisov, E.T., and Kochemasova, G.B., *Kinet. Katal.*, 1972, vol. 13, no. 5, p. 1126.
9. Vendillo, V.G., Emel'yanov, Yu.M., and Filippov, Yu.V., *Zavod. Lab.*, 1959, vol. 25, p. 1401.
10. Langlais, B., Reckhow, D.A., and Brink, D.R., *J. Am. Water Works Assoc.*, 1991, vol. 2, no. 1, p. 569.
11. Vereshchagin, A.N., *Konstanty zamestitelei dlya korrelyatsionnogo analiza* (Substituent Constants for Correlation Analysis), Moscow: Nauka, 1988, p. 102.
12. Poltorak, O.M., *Termodinamika v fizicheskoi khimii* (Thermodynamics in Physical Chemistry), Moscow: Vysshaya Shkola, 1991, p. 319.