Kinetics and Catalysis, Vol. 41, No. 6, 2000, pp. 749–752. Translated from Kinetika i Kataliz, Vol. 41, No. 6, 2000, pp. 827–830.
Original Russian Text Copyright © 2000 by Zimin, Trukhanova, Strel'tsova, Komissarov.

Kinetics of Polyol Oxidation by Ozone in Aqueous Solutions

Yu. S. Zimin, N. V. Trukhanova, I. V. Strel'tsova, and V. D. Komissarov
Bashkortostan State University, Ufa, 450007 Bashkortostan, Russia

Received March 14, 2000

Abstract—Spectrophotometry is applied to study the oxidation of ethylene glycol, triethylene glycol, glycerol, etriol, pentaerithritol and mannitol by ozone in aqueous solutions at 277–304 K. Rate constants and activation parameters of the reaction are measured. It is proposed that the oxidation of these alcohols by ozone occurs via the same mechanism. The formation of an intermediate complex is a rate-limiting step in the case of diols; the decomposition of the complex is a rate-limiting step for tri- to hexatomic alcohols.

INTRODUCTION

The kinetics of the oxidation of monatomic alcohols with ozone in CCl_4 and H_2O solutions was studied for many substrates (**S**) [1–6]. The second-order rate law describes ozone consumption:

$$w = -d[O_3]/dt = k[S][O_3], \qquad (1)$$

where k is the rate constant for the reaction.

Kinetic data on the oxidation of polyols by ozone are very scarce [7–9]. The reaction of ozone with diatomic alcohols (trimethylene, tetramethylene, pentamethylene, diethylene and neopentyl glycols) was studied in aqueous solutions [9]. The rate constants, but not the activation parameters, were determined for alcohols with a greater number of hydroxy groups (glycerol and pentaerithritol) [7]. However, the structure of an alcohol can substantially affect the kinetics of its reaction with ozone.

In connection with this, the goal of this work was to study the kinetics of the oxidation of 2–6-atomic alcohols using ethylene glycol (**I**), triethylene glycol (**II**), glycerol (**III**), trimethylol propane (**IV**), pentaerithritol (**V**), and mannitol (**VI**) in aqueous solutions at 277–301 K. **I** and **II** are diatomic alcohols, and **III**, **IV**, **V** and **VI** are tri-, tetra-, penta- and hexatomic alcohols, respectively.

EXPERIMENTAL

To study the reaction kinetics, ozone consumption in a liquid medium [9] was monitored by spectrophotometry. Experiments were performed in a constant temperature cell of an SF-16 UV spectrophotometer. Optical density was measured at $\lambda = 270$ nm.

Ethylene glycol (chemically pure) was dried with anhydrous Na_2SO_4 and distilled under vacuum. Triethylene glycol (chemically pure) and glycerol (chemically pure) were distilled under vacuum. Pentaerithritol (chemically pure) and trimethylol propane (chemically pure) were recrystallized two times from doubly distilled water and acetone (extra-pure), respectively. Mannitol (extra-pure) was used without purification. Doubly distilled water was used as a solvent.

RESULTS AND DISCUSSION

Experiments were performed at $[S]_0 \gg [O_3]_0$, where $[S]_0$ and $[O_3]_0$ are the initial concentrations of the substrate and ozone, respectively. In special experiments, we found that the rate of ozone decomposition was negligible compared with the rate of ozone reaction with S under similar conditions.

Figure 1 shows typical semilogarithmic anamorphoses of ozone consumption for alcohol oxidation. It follows from Fig. 1 that the reaction is a first-order process with respect to ozone:

$$-d[O_3]/dt = k_{app}[O_3],$$

where k_{app} is the apparent rate constant of the reaction.

We observed the first order of the reaction with respect to ozone for every alcohol over the whole range of experimental conditions.

In the case of diatomic alcohols **I** and **II**, the rate constant k_{app} linearly increases with an increase in the initial concentration of the substrate (Fig. 2):

$$k_{app} = k[S]_0,$$

and, in agreement with [9],

$$w = -d[O_3]/dt = k_{app}[O_3] = k[S][O_3]. \qquad (2)$$

We found from the dependence of the second-order rate constant k ($l\ mol^{-1}\ s^{-1}$) on temperature (Table 1) that

$$\log k = (14.6 \pm 1.9) - (20.2 \pm 2.6)/\Theta,$$

for **I**, and

$$\log k = (12.7 \pm 1.9) - (17.6 \pm 2.5)/\Theta,$$

for **II**; $\Theta = 2.303RT$ kcal/mol.

In the case of alcohols **III**–**VI**, the apparent second-order rate constant $k_{app} = k_{exp}/[S]_0$ decreases with an increase in the substrate concentration: Table 2 illus-

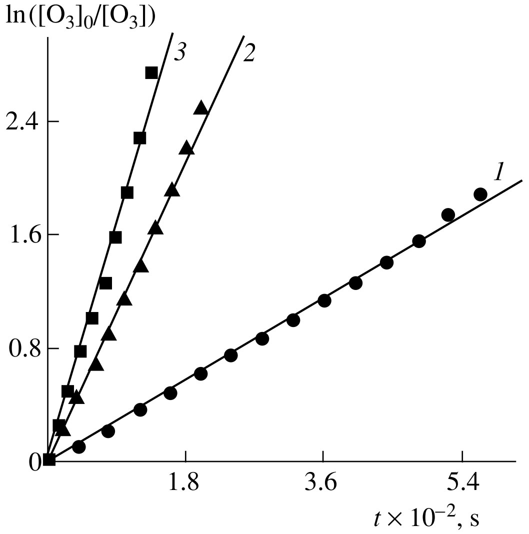

Fig. 1. Semilogarithmic anamorphoses of ozone consumption in the reaction with (*1*) ethylene glycol, (*2*) trimethylol propane, and (*3*) pentaerithritol at 277 K; $[S]_0 = 8 \times 10^{-2}$ mol/l.

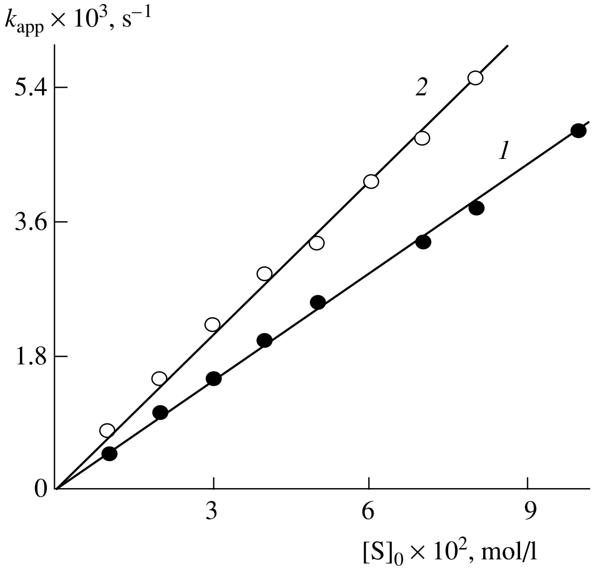

Fig. 2. The apparent rate constant k_{app} versus the concentration of (*1*) ethylene glycol and (*2*) triethylene glycol at 277 K.

trates this with the data obtained at 277 K. The analysis of the data shows that $1/k_{app}$ increases linearly with an increase in $[S]_0$ (Fig. 3).

It is possible to explain the results of this work assuming that the hydrated molecules of reactants form a complex of alcohol with ozone X before the formation of oxidation products; besides, we can neglect the association of alcohol over the studied range of the substrate concentration [10]:

$$S + O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} X,$$

$$X \xrightarrow{k_2} \text{Products.}$$

The formation of a substrate complex with ozone is typical of the ozonation reactions. Thus, the formation

Table 1. Rate constants for the reactions of ozone with ethylene glycol and triethylene glycol at different temperatures

$HOCH_2CH_2OH$ (**I**)		$H(OCH_2CH_2)_3OH$ (**II**)	
T, K	*k*, l mol^{-1} s^{-1}	*T*, K	*k*, l mol^{-1} s^{-1}
277	0.043 ± 0.005	277	0.067 ± 0.008
283	0.087 ± 0.009	281	0.116 ± 0.017
290	0.151 ± 0.027	285	0.140 ± 0.008
297	0.427 ± 0.054	289	0.223 ± 0.018
304	1.200 ± 0.140	293	0.310 ± 0.035
		297	0.532 ± 0.065
		301	0.920 ± 0.140

Table 2. Apparent rate constant k_{app} at different concentrations of alcohols **III–VI** at 277 K*

$[S] \times 10^2$, mol/l	k_{app}, l mol^{-1} s^{-1}			
	III	**IV**	**V**	**VI**
1.0	0.497	0.263	0.755	1.426
2.0	0.353	0.223	0.466	0.901
3.0	0.260	0.195	0.364	0.727
4.0	0.190	0.190	0.298	0.509
5.0	0.169	0.166	0.256	0.454
6.0	0.154	0.152	0.247	0.412
7.0	0.125	0.141	0.228	0.379
8.0	0.135	0.154	0.244	0.343

* **III**—glycerol, **IV**—trimethylol propane, **V**—pentaerithritol, **VI**—mannitol.

of ozone complexes with a number of saturated hydrocarbons was justified in [11, 12]. Ozone also forms labile intermediate complexes with aliphatic alcohols, unsaturated and aromatic hydrocarbons, phenols, and other compounds [1, 13, 14].

If all X molecules transform into reaction products ($k_{-1} \ll k_2$, $[X] \ll [O_3]$), the formation of an intermediate complex determines the overall process rate:

$$w = k_1[S][O_3]. \quad (3)$$

This is the case of ozone reaction with mono- and diatomic alcohols, and in this case, $k = k_1$ in Eqs. (1) and (2).

Decomposition of the intermediate complex is the rate-limiting step in the oxidation of alcohols **III**–**VI**. Under quasiequilibrium conditions ($k_{-1} \gg k_2$), the rate of ozone consumption is described by the equation

$$w = \frac{K_1 k_2 [S]_0 [O_3]_\Sigma}{1 + K_1 [S]_0}, \quad (4)$$

where $K_1 = k_1/k_{-1}$; $[O_3]_\Sigma = [O_3] + [X]$ is the total concentration of unbound ozone and ozone bound in the complex.

It follows from Eq. (4) that

$$k_{app} = \frac{K_1 k_2}{1 + K_1 [S]_0} \quad (5)$$

and

$$\frac{1}{k_{app}} = \frac{1}{K_1 k_2} + \frac{1}{k_2}[S]_0. \quad (6)$$

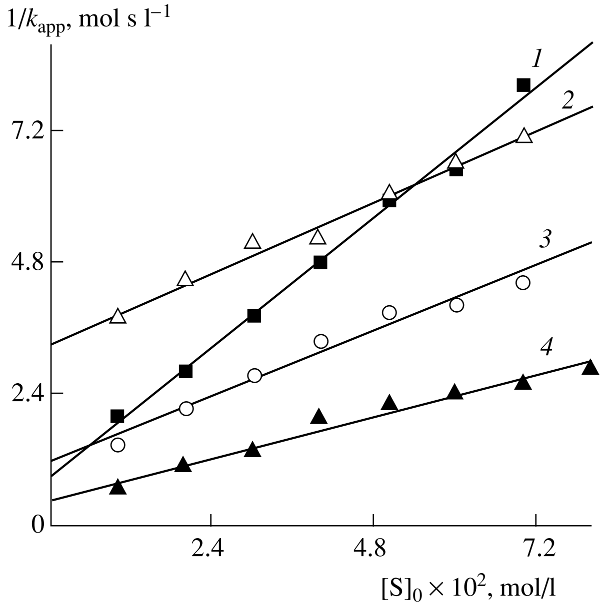

Fig. 3. $1/k_{app}$ versus the concentration of (*1*) glycerol, (*2*) trimethylol propane, (*3*) pentaerithritol, and (*4*) mannitol at 277 K.

The latter equation agrees well with the experimental results (Fig. 3); this confirms the suggested scheme of the process and enables us to find the rate constants k_2 and the equilibrium constants K_1. Table 3 contains the values of constants for the studied temperature range. Table 4 shows the activation parameters of the decomposition of the intermediate complex calculated from the data of Table 3. The error of the equilibrium

Table 3. k_2 an $K_1$for the reaction of ozone with alcohols **III**–**VI** as a function of temperature

T, K	$k_2 \times 10^2$, s^{-1}				$K_1 \times 10^2$, l/mol			
	III	**IV**	**V**	**VI**	**III**	**IV**	**V**	**VI**
277	1.0	1.9	1.8	3.2	1.0	0.2	0.6	0.6
281	1.2	2.3	2.4	3.6	1.0	0.4	0.7	0.5
285	2.2	3.6*	3.4	7.7	1.6	0.2*	2.0	0.2
289	3.9	6.1**	4.5	11.2	1.3	0.2**	2.5	0.9
293	4.7	9.2***	4.5	15.1	0.3	0.2***	1.6	0.6
297	7.0	7.9	4.8	33.8	0.4	0.2	3.0	0.3
301	–	16.2	7.9	–	–	0.2	4.9	–

* 286 K.
** 290 K.
*** 294 K.
III—glycerol, **IV**—trimethylol propane, **V**—pentaerithritol, **VI**—mannitol. The measuring error was ~15% (k_2) and ~30–35% (K_1).

Table 4. Activation parameters for the decomposition of the intermediate complex in the oxidation of alcohols **III**–**VI** with ozone

Alcohol	$\log A_2$ [s^{-1}]	E_2, kcal/mol
$HOCH_2CH(OH)CH_2OH$ (**III**)	10.5 ± 1.6	15.8 ± 2.1
$C_2H_5C(CH_2OH)_3$ (**IV**)	10.5 ± 1.5	15.6 ± 1.9
$C(CH_2OH)_4$ (**V**)	6.1 ± 1.5	10.0 ± 1.9
$HOCH_2(CHOH)_4CH_2OH$ (**VI**)	13.7 ± 3.9	19.3 ± 5.0

constant K_1 determination was rather high; we only can consider the values K_1 as rough estimates.

Note, that E_2 linearly depends on $\log A_2$ for alcohols **III**–**VI** (compensation effect):

$$E_2 = (2.6 \pm 0.7) + (1.23 \pm 0.13)\log A_2\,.$$

This may indicate the existence of a unified mechanism of the rate-limiting step in the oxidation of alcohols **III**–**VI** with ozone.

REFERENCES

1. Shafikov, N.Ya., *Cand. Sci. (Chem.) Dissertation*, Ufa: Bashkortostan State University, 1985.
2. Williamson, D.G. and Cvetanovic, R.J., *J. Am. Chem. Soc.*, 1970, vol. 92, no. 10, p. 2949.
3. Gerchikov, A.Ya., Kuznetsova, E.P., and Denisov, E.T., *Kinet. Katal.*, 1974, vol. 15, no. 2, p. 509.
4. Shereshovets, V.V., Galieva, F.A., Akhunov, I.R., *et al.*, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, no. 5, p. 1011.
5. Rakovski, S. and Cherneva, D., *Int. J. Chem. Kinet.*, 1990, vol. 22, no. 4, p. 321.
6. Gerchikov, A.Ya., Zimin, Yu.S., Trukhanova, N.V., and Evgrafov, V.N., *React. Kinet. Catal. Lett.*, 1999, vol. 68, no. 2, p. 257.
7. Shereshovets, V.V., Galieva, F.A., Tsarkov, A.V., and Bikbulatov, I.K., *Reakt. Kinet. Catal. Lett.*, 1982, vol. 21, no. 3, p. 413.
8. Takahashi, N. and Katsuki, O., *J. Chem. Soc.*, 1987, vol. 5, no. 2, p. 862.
9. Zimin, Yu.S., Trukhanova, N.V., Shamsutdinov, R.R., and Komissarov, V.D., *React. Kinet. Catal. Lett.*, 1999, vol. 68, no. 2, p. 237.
10. Graja, A., *Acta Phys. Pol.*, 1976, vol. 50, no. 2, p. 197.
11. Varkony, H., Pass, S., and Mazur, Y., *J. Chem. Soc., Chem. Commun.*, 1974, no. 11, p. 437.
12. Varkony, H., Pass, S., and Mazur, Y., *J. Chem. Soc., Chem. Commun.*, 1975, no. 17, p. 709.
13. Hoigne, J. and Bader, H., *Water Res.*, 1983, vol. 17, no. 1, p. 173.
14. Razumovskii, S.D., *Zh. Vses. Khim. o-va im. D.I. Mendeleeva*, 1990, vol. 35, no. 1, p. 77.