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Kinetics of the Reaction of Ozone with *tert*-Butanol

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Abstract—The kinetics of *tert*-butanol (ROH) oxidation by ozone in CCl_4 and H_2O solutions at 295 K is studied by spectrophotometry under batch conditions. The rate-limiting step of the process in both solvents is the reaction of ozone with the monomeric form of ROH. In H_2O, the hydrated molecules of ROH and ozone react with each other. In CCl_4, the association of ROH molecules, which changes the kinetics and mechanism of the process, should be taken into account. The reaction kinetic parameters and the dimerization constant of ROH in CCl_4 are determined.

INTRODUCTION

The kinetics and mechanism of the liquid-phase oxidation of alcohols with ozone have been extensively studied [1–19]. In primary and secondary alcohols, ozone mainly reacts with the α-CH bond of the substrate [9, 17, 18], and the oxidation of these alcohols in various solvents (H_2O, CCl_4, etc.) occurs as an overall second-order reaction [2–4, 5, 6, 8–10, 12–18]. In *tert*-butanol, ozone reacts with the OH bond rather than with the CH bond of the alcohol [3, 9]; this can change the kinetics of the process. Indeed, we found that the experimental second-order rate constant of *tert*-butanol oxidation in CCl_4 is not constant, as was stated earlier [2, 3, 5], but depends on the alcohol concentration. A kinetic scheme is proposed to explain this effect.

EXPERIMENTAL

The reaction kinetics was studied at 295 K under batch conditions using the spectrophotometric determination of O_3 consumption in the liquid phase [3, 14]. The initial concentrations of *tert*-butanol $[ROH]_0$ and ozone $[O_3]_0$ were varied within the ranges 0.02–2.0 and $(0.3–3.0) \times 10^{-4}$ mol/l, respectively.

After boiling over calcined calcium oxide, *tert*-butanol (analytical grade) was subjected to double distillation and multiple recrystallization. The purification of CCl_4 (analytical grade) was performed in accordance with a published procedure [20]; twice-distilled water was used.

RESULTS AND DISCUSSION

Figure 1 demonstrates a typical kinetic curve of ozone consumption in the reaction with ROH in a CCl_4 solution and its semilogarithmic anamorphosis. We can conclude that

$$-d[O_3]/dt = k'[O_3],$$

where k' is the effective rate constant of the reaction. The first order of reaction with respect to ozone was observed within the whole range of $[ROH]_0$.

The dependence of k' on the alcohol concentration in a CCl_4 solution is given in the table, which suggests that the effective second-order rate constant k, formally determined as $k = k'/[ROH]_0$, decreases with an increase in $[ROH]_0$.

The kinetic data can be explained using the following scheme that includes the reaction of ozone with the monomeric form of the alcohol as a rate-limiting step (assuming that the associated substrate forms $(ROH)_n$ and $(ROH)_{n+1}$ are almost inactive toward ozone):

$$ROH + (ROH)_n \xrightleftharpoons{K} (ROH)_{n+1},$$

$$ROH + O_3 \xrightarrow{k_m} \text{Products}.$$

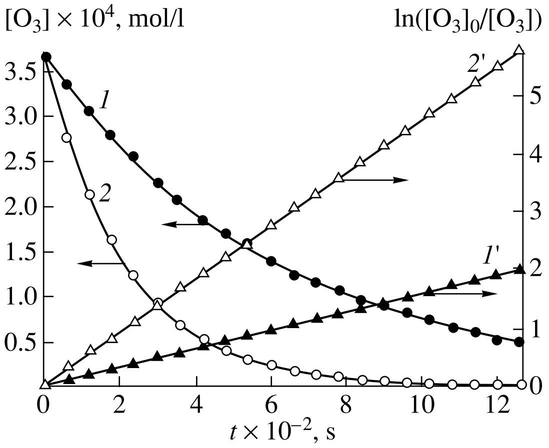

Fig. 1. Kinetic curves of O_3 consumption in the reaction with *tert*-butanol and their semilogarithmic anamorphoses in (*1*, *1*') CCl_4 and (*2*, *2*') H_2O solutions at 295 K; $[ROH]_0 = 2.0$ mol/l.

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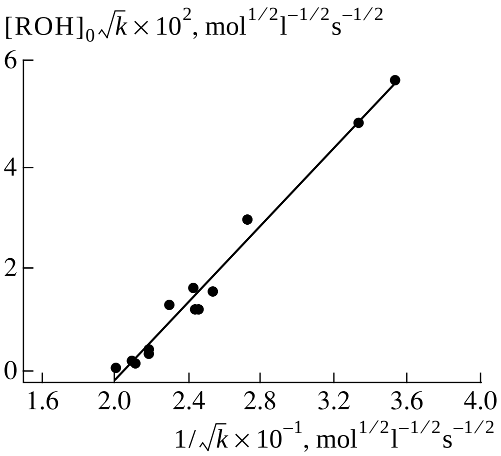

Fig. 2. $[ROH]_0\sqrt{k}$ vs. $1/\sqrt{k}$.

Here, $n = 1, 2, 3, \ldots$; $K = [(ROH)_{n+1}]/([ROH][(ROH)_n])$; and k_m is the reaction rate constant of ozone with the monomer.

An expression for the equilibrium constant K (assuming that K is independent of n) has the form [21]

$$K = \frac{1 - \sqrt{\alpha_1}}{\alpha_1 [ROH]_0}, \tag{1}$$

where

$$\alpha_1 = [ROH]/[ROH]_0.$$

Effective rate constants k' and k at different initial concentrations of *tert*-butanol

$[ROH]_0$, mol/l	$k' \times 10^4$, s^{-1}		$k \times 10^3$, $l\,mol^{-1}\,s^{-1}$
	CCl_4	H_2O	CCl_4
0.02	0.5	6.06	2.50
0.02	–	5.84	–
0.04	0.9	7.1	2.25
0.05	1.15	5.81	2.30
0.05	–	5.96	–
0.08	1.7	6.57	2.10
0.10	–	6.99	–
0.10	2.10	6.7	2.10
0.30	4.95	12.94	1.65
0.30	5.55	12.49	1.85
0.30	5.7	–	1.90
0.40	6.2	–	1.55
0.40	6.8	16.37	1.70
0.80	10.8	22.45	1.35
1.60	14.4	35.73	0.90
2.00	16.0	45.87	0.80

Note: The determination error in k' is ~10%; solvents, CCl_4 and H_2O.

The initial concentration of the alcohol is determined by the sum of the concentrations of its monomeric ROH and n-meric $(ROH)_n$ forms:

$$[ROH]_0 = [ROH] + [(ROH)_2] + [(ROH)_3] + \ldots .$$

Taking into account that, in accordance with the proposed mechanism,

$$-d[O_3]/dt = k[ROH]_0[O_3] = k_m[ROH][O_3],$$

we have $\alpha_1 = k/k_m$. Substituting this α_1 value into Eq. (1) and rearranging gives

$$[ROH]_0\sqrt{k} = -\frac{\sqrt{k_m}}{K} + \frac{k_m}{K}\frac{1}{\sqrt{k}}.$$

This equation satisfactorily (with the correlation coefficient $r = 0.991$) describes the experimental results (see Fig. 2):

$$[ROH]_0\sqrt{k} = -(7.54 \pm 0.84) \times 10^{-2}$$
$$+ (3.72 \pm 0.33) \times 10^{-3}(1/\sqrt{k}).$$

Thus, we can determine the values of k_m and K:

$$k_m = (2.43 \pm 0.07) \times 10^{-3}\ l\ mol^{-1}\ s^{-1},$$
$$K = 0.65 \pm 0.11\ l/mol.$$

This K value (to within the experimental error) is identical to the known dimerization constant of *tert*-butanol $K = 0.58$ l/mol (298 K; solvent, CCl_4) [22].

To obtain further evidence for the suggested kinetic scheme, we studied ROH oxidation in an aqueous solution under the same conditions. In this case, we expected that the effect of alcohol dimerization would be completely suppressed by hydration [23], and this effect would not be observed because of the very low molar fraction of the alcohol in the reaction mixture (3×10^{-4}–4×10^{-3}).

As in a CCl_4 solution, the reaction in an aqueous solution is of first order with respect to ozone (Fig. 1) over the whole $[ROH]_0$ range. The relevant effective rate constants k' are given in the table; from these data we found that k' linearly increases with the initial concentration of the alcohol ($r = 0.996$): $k' = k_0 + k_1[ROH]_0$, $k_0 = (5.8 \pm 0.4) \times 10^{-4}\ s^{-1}$, and $k_1 = (2.00 \pm 0.05) \times 10^{-3}\ l\ mol^{-1}\ s^{-1}$.

Therefore, we have

$$-d[O_3]/dt = k'[O_3] = k_0[O_3] + k_1[ROH]_0[O_3].$$

The rate constant k_0, which characterizes ozone decomposition in water, was also determined in independent experiments without ROH to be $k_0 = (5.0 \pm 0.4) \times 10^{-4}\ s^{-1}$, which coincides with the above value to within the experimental error.

Thus, the reaction of O_3 with the monomeric form of ROH is the rate-limiting step of the process in both of the solvents. In this case, the hydrated molecules of ROH and ozone react with each other in H_2O and alcohol dimerization can be neglected. At the same time, in a CCl_4 solution, the dimerization of ROH is significant and affects the kinetics and mechanism of the process.

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