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The Effect of Acids on the Kinetics of Cyclopentanone Oxidation by Decanesulfonic Peracid in an Acetonitrile Solution

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Abstract—The kinetics of cyclopentanone oxidation by *sec*-decanesulfonic peracid is studied. The reaction rate in an acetonitrile (MeCN) solution was lower than in CCl_4. Acid additives are shown to accelerate the reaction in a MeCN medium as distinct from the reaction in a CCl_4 solution. In the framework of the known mechanism of the Bayer–Williger reaction, an equation describing the observed relationships is proposed and parameters that characterize the process kinetics are determined.

INTRODUCTION

Alkanesulfonic peracids (RSO_2OOH) are primary molecular products of alkane sulfoxidation [1]. As was shown previously, RSO_2OOH oxidizes cyclic and aliphatic ketones to give corresponding lactones and esters with high yields [2]. In this work, the kinetics of cyclopentanone oxidation by *sec*-decanesulfonic peracid ($R = C_{10}H_{21}$) in an acetonitrile (MeCN) solution was studied.

EXPERIMENTAL

sec-Decanesulfonic peracid was synthesized by photochemical sulfoxidation of decane [3]. The peracid obtained was extracted from a reaction mixture with acetonitrile and carried to a CCl_4 solution, washed from admixtures (decanesulfonic acid and H_2SO_4) by water, dried over P_2O_5, and dissolved in MeCN. The content of sulfonic and sulfuric acids in obtained acetonitrile solutions did not exceed 1–2% with respect to the amount of RSO_2OOH. Cyclohexanesulfonic acid ($C_6H_{11}SO_2OH$) was prepared by sulfoxidation of cyclohexane and isolated as a crystalline hydrate insoluble in hydrocarbons. Trifluoroacetic acid (chemical grade) was used without additional purification. Cyclopentanone (C_5H_8O) was purified by vacuum distillation. Acetonitrile was previously ozonized for 0.5–1 h, boiled over P_2O_5, and distilled in an argon atmosphere. The RSO_2OOH concentration was determined by iodometric titration; $C_6H_{11}SO_2OH$ and H_2SO_4 were analyzed by potentiometric titration using tetrabutylammonium hydroxide as a titrant. The kinetics of oxidation was monitored by sampling and determining the concentration of peroxides. The ^{1}H NMR spectra were registered on a BS-497 Tesla spectrometer with an operating frequency of 100 MHz; tetramethylsilan (TMS) was used as an internal standard. The UV spectra were recorded using an SF-26 spectrophotometer and a Specord UV VIS spectrometer.

RESULTS AND DISCUSSION

The main products of the reaction between RSO_2OOH and C_5H_8O are valerolactone and RSO_2OH. Their yields are 95 and ~100%, respectively. If the reaction was carried out in a MeCN solution at $[RSO_2OH]_0 \ll [RSO_2OOH]_0$, the process was autocatalytic owing to RSO_2OH accumulation. This is confirmed by the acceleration of the reaction upon the addition of acids (HX) to the initial system ($C_6H_{11}SO_2OH$ or CF_3COOH were used as HX). Under condition of excess HX in initial reaction mixture, i.e., at $[HX]_0 > [RSO_2OOH]_0 \gg [RSO_2OH]_0$, the reaction is pseudounimolecular. The kinetic curves of the RSO_2OOH consumption are linearized well in the semilogarithmic coordinates: $\ln([RSO_2OOH]_0/[RSO_2OOH])$ versus $k't$ (henceforth, k' is the experimental rate constant of the reaction of RSO_2OH with C_5H_8O). If the experiments were carried out in the absence of acid additives, the k' values were determined from the initial portions of the kinetic curves at a RSO_2OOH conversion of 1–2 mol %. Under these conditions, the $[RSO_2OH]$ value does not exceed 3–4% of $[RSO_2OOH]$, and autocatalysis is virtually unnoticeable.

Both in the presence and in the absence of acid additives, the k' values linearly depend on $[C_5H_8O]_0$ (Fig. 1). The intercepts on the ordinate axis account for the contribution of the RSO_2OOH decomposition to the overall process of the peracid consumption [4]:

$$RSO_2OOH \longrightarrow RSO_2OH + 1/2O_2,$$

$$RSO_2OOH + HX \longrightarrow RSO_2OH + 1/2O_2 + HX.$$

The following intercepts on the ordinate axis are obtained from data presented in Fig. 1 (s^{-1}): $(5 \pm 12) \times 10^{-5}$, $(2 \pm 2.5) \times 10^{-4}$, and $(3 \pm 1.8) \times 10^{-4}$ at 40, 50, and 60°C, respectively ($[C_6H_{11}SO_2OH] = 0.1$ mol/l) and

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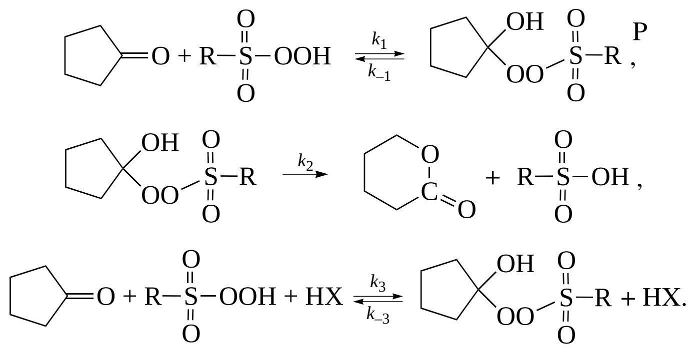
† Deceased.

$(3.8 \pm 0.8) \times 10^{-5}$ at 50°C ($[CF_3COOOH] = 0.2$ mol/l). The rate constants of sulfonic peracid decomposition (s^{-1}) in a MeCN solution at $[RSO_2OOH]_0 \approx (1–2) \times 10^{-2}$ mol/l in the absence of C_5H_8O and HX are equal to 1.1×10^{-5}, 3×10^{-5}, and 7.8×10^{-5} at 40, 50, and 60°C, respectively. Comparison of the obtained data shows that the values determined in the latter case are only a small fraction of the k' values obtained in the presence of C_5H_8O and HX (Fig. 1). Therefore, the RSO_2OOH decomposition can further be neglected.

The dependences of k' on $[HX]_0$ present the curves with a plateau (Fig. 2). A distinct feature of the system under study is that acid additives influence the reaction rate in some solvents but have no effect in others. Thus, in the $C_5H_8O–CF_3COOOH–CH_2Cl_2$ system, the rate of ketone oxidation increases upon the addition of CF_3COOH [5]. However, catalysis by acids was not observed for the reaction of RSO_2OOH with C_5H_8O in a CCl_4 solution [6]. Note that a substantial decrease in the rate of the reaction was found upon the addition of small amounts of MeCN to the $RSO_2OOH–C_5H_8O–CCl_4$ system, and in a MeCN solution, the k' value is about three order of magnitude lower than that in CCl_4 (Table 1).

Consider the results obtained in terms of the known scheme of the Bayer–Williger reaction [5, 7, 8]:


(I)

(II)

(III)

In the absence of acids, ketone is oxidized in two steps: the nucleophilic attack of RSO_2OOH at the carbon atom of a carbonyl group (forward reaction (I)), producing intermediate peroxide P and the rearrangement of P in reaction (II) to yield the products. In the ^1H NMR spectra of decanesulfonic peracid, a singlet is observed at $\delta = 11.24$ ppm, which may be assigned to the proton of the $HOOSO_2$ group. When small amounts of MeCN are introduced into the $RSO_2OOH–CCl_4$ system, the signal of this proton is shifted toward the high-field region (Table 1) owing to the formation of solvate $RSO_2OOH \cdot MeCN$. By analogy with data reported in [9], we may assume that the formation of the above solvate leads to the generation of the negative spin density at the acidic proton resulting in a decrease in the nucleophilic properties of the oxygen of the hydroxy group. Therefore, equilibrium (I) is shifted toward the initial products, and the rate of uncatalyzed oxidation drops, when MeCN is introduced into CCl_4 solutions. Upon the addition of acids to an initial reaction mixture or at high conversions of C_5H_8O in the absence of HX, equilibrium processes involving acids (reaction (III)) should be taken into account [7]. Reaction (III) appears to occur in two stages: the formation of the $C_5H_8O \cdot HX$ complex [5]

$$C_5H_8O + HX \rightleftharpoons C_5H_8O \cdot HX \qquad \text{(IIIa)}$$

and the following replacement of HX by RSO_2OOH

$$C_5H_8O \cdot HX + RSO_2OOH \rightleftharpoons \mathbf{P} + HX. \qquad \text{(IIIb)}$$

The existence of the $C_5H_8O \cdot HX$ complex is confirmed by the spectrophotometric method. The position of a maximum in the UV spectrum of a cyclopentanone solution in CCl_4 is shifted toward the short-wave region

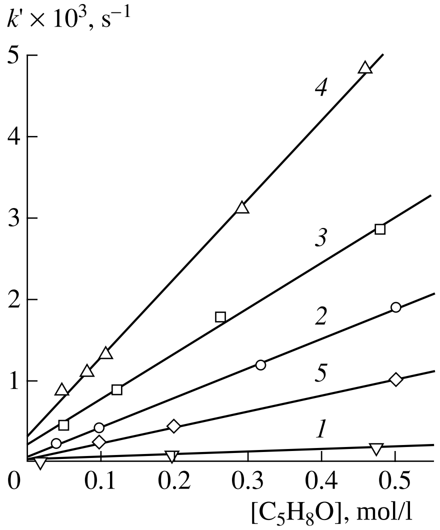


Fig. 1. Dependences of the experimental rate constant of the reaction between RSO_2OOH and C_5H_8O on the cyclopentanone concentration in a MeCN solution: (*1*) in the absence of acids ($[RSO_2OOH]_0 = 5 \times 10^{-3}$ mol/l, 50°C); (*2–4*) in the presence of 0.1 mol/l $C_6H_{11}SO_3H$ ($[RSO_2OOH]_0 = 5 \times 10^{-3}$ mol/l, at (*2*) 40, (*3*) 50, and (*4*) 60°C); and (*5*) in the presence of 0.2 mol/l CF_3COOH ($[RSO_2OOH]_0 = 2 \times 10^{-3}$ mol/l, 50°C).

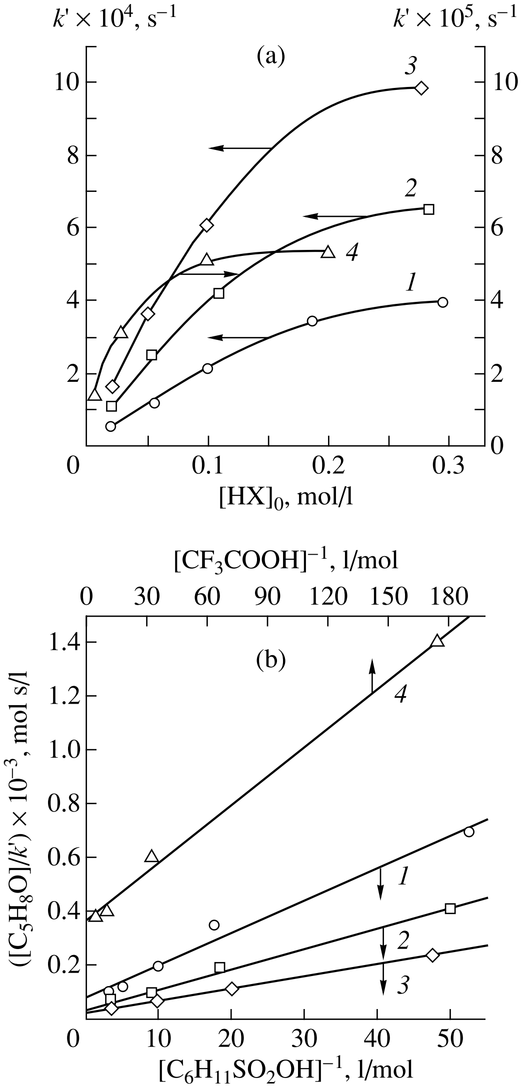


Fig. 2. (a) Dependences of the experimental rate constant of the reaction between RSO_2OOH and C_5H_8O in a MeCN solution on the content of (*1–3*) $C_6H_{11}SO_3H$ at: (*1*) 40°C, $[C_5H_8O]_0 = 4.1 \times 10^{-2}$, $[RSO_2OOH]_0 = 5 \times 10^{-3}$ mol/l; (*2*) 50°C, $[C_5H_8O]_0 = 4.5 \times 10^{-2}$, $[RSO_2OOH]_0 = 5 \times 10^{-3}$ mol/l; (*3*) 60°C, $[C_5H_8O]_0 = 4.0 \times 10^{-2}$, $[RSO_2OOH]_0 = 5 \times 10^{-3}$ mol/l; (*4*) of CF_3COOH at 50°C, $[C_5H_8O]_0 = 2.0 \times 10^{-2}$, $[RSO_2OOH]_0 = 3 \times 10^{-3}$ mol/l; (b) the dependences in the coordinates of Eq. (3) (reaction conditions and designations see Fig. 2a).

upon the addition of CF_3COOH to this system CCl_4–C_5H_8O (Table 1). The addition of MeCN to a solution containing C_5H_8O and CF_3COOH leads to the reverse effect (Table 1). A probable reason is the destruction of the $C_5H_8O \cdot HX$ complex due to the replacement of HX by the solvent. Thus, the steady-state concentration of the $C_5H_8O \cdot HX$ complex decreases in a MeCN medium, resulting in a decrease in the reaction rate. If the $[HX]_0$ values are low enough in MeCN solutions, forward reaction (IIIa) is the rate-limiting step in the sequence of reactions (IIIa)–(IIIb). The tendency for the attainment of a limiting value observed for the $[HX]_0$-dependence of *k*' is explained by a change of the rate-limiting step with an increase in the $[HX]_0$ value.

Under experimental conditions, iodometric analysis does not allow us to distinguish between RSO_2OOH and the intermediate peroxide P. Therefore, we measure the overall consumption of the –OO–groups in the course of the reaction.

Analysis of the above scheme in a steady-state approximation with respect to the intermediates, provided that RSO_2OOH is in the solvated state and a change in the ketone and acid concentrations is negligible ($[HX]_0 \gg [RSO_2OOH]_0$, $[C_5H_8O]_0 \gg [RSO_2OOH]_0$), results in the following expression for the rate of the peroxide group consumption

$$-\frac{d[-OO-]}{dt} = \left\{ k_2 \frac{k_1 + k_3[HX]_0}{k_{-1} + k_2 + k_{-3}[HX]_0}[C_5H_8O] \right\} \times [RSO_2OOH].$$

The experimentally determined rate constant *k*' is described by the equation

$$k' = k_2 \frac{k_1 + k_3[HX]_0}{k_{-1} + k_2 + k_{-3}[HX]_0}[C_5H_8O]. \qquad (1)$$

At the initial stage of the reaction ($[RSO_2OH] \ll [RSO_2OOH]_0$) in the absence of acid additives ($[HX]_0 = 0$), acid-catalyzed pathway (III) can be neglected. Then, Eq. (1) transforms to the formula

$$k' = \frac{k_1 k_2}{k_{-1} + k_2}[C_5H_8O].$$

The value of parameter $k_1k_2/(k_{-1} + k_2)$ equal to $(3.5 \pm 2.8) \times 10^{-4}$ l mol^{-1} s^{-1} at 50°C was calculated from the dependence of *k*' on $[C_5H_8O]_0$ obtained in the absence of acids (Fig. 1, line *1*). Comparison of the *k*' values measured in the presence and absence of HX (straight lines *3* and *1* in Fig. 1) shows that the contribution of reaction (I) to the overall acid-catalyzed process is unimportant. Therefore, in the case under consideration (at $[HX] \gg [RSO_2OOH]$), this reaction can be neglected. Then, Eq. (1) takes the form

$$k' = k_2 \frac{k_3[HX]_0}{k_{-3}[HX]_0 + k_2}[C_5H_8O]. \qquad (2)$$

Equation (2) shows that the *k*' values should be linearly proportional to $[C_5H_8O]_0$ in accordance with experimental data (Fig. 1). Table 2 presents the values of parameter $k_2k_3[HX]/(k_{-3}[HX] + k_2)$ determined from the above relationships.

Table 1. Dependences of the experimental rate constant (k'), the chemical shift of the NMR signal of the proton of the $-SO_2OOH$ group (δ), and the position of a maximum of the C_5H_8O absorption band (λ_{max}) on [MeCN]; dependence of λ_{max} on $[CF_3COOH]$ in CCl_4 solutions

16°C, $[RSO_2OOH]_0 = 1.4 \times 10^{-3}$, $[C_5H_8O]_0 = 1 \times 10^{-2}$, $[HX]_0 = 0$

[MeCN], mol/l	0	0.048	0.48	2.39	in MeCN solution
$k' \times 10^3$ s^{-1}	9.01	1.48	0.36	0.20	0.01

20°C, $[RSO_2OOH] = 0.15$, $[HX] = 0$

[MeCN], mol/l	0	0.0057	0.17	0.27	0.38	0.6	1.1	6.0
δ, ppm	11.24	11.18	11.15	11.05	10.95	10.82	10.43	8.26

20°C, $[C_5H_8O] = 2.25 \times 10^{-2}$, $[CF_3COOH] = 4.2 \times 10^{-2}$

[MeCN], mol/l	0	0.0057	0.0096	0.13	0.25	in MeCN solution
λ_{max}, nm	281	282.5	284	285.7	289	297

20°C, $[C_5H_8O] = 2.25 \times 10^{-2}$

$[CF_3COOH]$, mol/l	0	0.0038	0.0076	0.0115	0.0153	0.0191	0.0306	0.042
λ_{max}, nm	290	289	288	287	286	284	282	281

All concentrations are in mol/l.

However, Eq. (2) does not explain a nonlinear relationship between k' and $[HX]_0$ (Fig. 2a). The rearrangement of Eq. (2) gives the following equation

$$\frac{[C_5H_8O]}{k'} = \frac{k_{-3}}{k_2k_3} + \frac{1}{k_3[HX]_0}. \qquad (3)$$

According to Eq. (3), parameter $[C_5H_8O]\,(k')^{-1}$ linearly depends on $[HX]_0^{-1}$. Such relationships were experimentally obtained (see the corresponding linearization in Fig. 2b). Table 2 shows the k_{-3}/k_2k_3 and k_3 parameters determined from the intercepts on the ordinate axis and from the tangent of the slope of the straight lines, respectively. The following equations describe the temperature dependences of these parameters: $\log k_3 = (6.1 \pm 0.3) - (42.8 \pm 1.6)/\theta$ and $\log(k_{-3}/k_2k_3) = (7.0 \pm 0.5) - (53.0 \pm 3.4)/\theta$ (where $\theta = 2.3RT$ kJ/mol).

Table 2. Dependence of the kinetic parameters of Eq. (2) on the experimental conditions of cyclopentanone oxidation by RSO_2OOH

t, °C	$\frac{k_2k_3[HX]_0}{k_{-3}[HX]_0 + k_2} \times 10^3$, l mol^{-1} s^{-1}	$\frac{k_{-3}}{k_2k_3}$, mol l^{-1} s	k_3, l^2 mol^{-2} s^{-1}
40*	3.7 ± 0.4	75.3 ± 24.4	0.083 ± 0.008
50*	5.6 ± 0.9	37.5 ± 8.5	0.13 ± 0.01
50**	1.96 ± 0.03	372.0 ± 4.0	0.17 ± 0.01
60*	9.7 ± 0.7	22.2 ± 1.0	0.22 ± 0.01

* $[C_6H_{11}SO_3H] = 0.1$ mol l^{-1}.

** $[CF_3COOH] = 0.2$ mol l^{-1}.

Thus, we conclude that cyclopentanone oxidation by decanesulfonic peracid is a particular case of the Bayer–Williger reaction, and the experimental results are adequately described by the proposed mechanism.

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