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The Solvent Effect on the Rate of Reaction between Propanethiol and Chlorine Dioxide

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Abstract—The products and kinetics of the liquid-phase oxidation of propanethiol by chlorine dioxide in organic media (*n*-heptane, 1,4-dioxane, carbon tetrachloride, benzene, diethyl ether, ethyl acetate, acetone, and acetonitrile) at temperatures from –10 to 70°C were examined. The reaction rate constants and activation parameters were measured in the above solvents. A strong solvent effect on the reaction kinetics was found ($k = 1.67 \times 10^{-3}$ or 52.7 l mol^{-1} s^{-1} (25°C) in heptane or acetonitrile, respectively). The data were analyzed in terms of the Leydler–Eyring and Koppel–Palm equations. The formation of high-polarity intermediates in the test reaction was suggested.

INTRODUCTION

Thiols represent a class of sulfur-containing organic compounds, occurring in oil and petroleum products. These compounds present a number of technological and environmental problems associated with the corrosion of equipment and with the atmospheric emission of sulfur oxides. Along with hydrodesulfurization and extraction, oxidizing processes can be used for the removal of thiols. In this context, we call attention to chlorine dioxide, which is a promising oxidizing agent and a commercially available large-scale product. However, the reactions of chlorine dioxide with organic substances, in particular, sulfur-containing organic compounds, in organic media have almost not been studied at all.

In this work, we studied the kinetics of the liquid-phase oxidation of thiols with chlorine dioxide using propanethiol as an example and found a strong solvent effect on the reaction rate.

EXPERIMENTAL

The solvents were purified according to standard procedures [1]. Chlorine dioxide was prepared by the published procedure [2] and purified by adsorption on silica gel to remove chlorine. Chemically pure propanethiol was used without further purification.

The reaction kinetics was studied by spectrophotometry on an SF-26 spectrophotometer; the absorbance at 354–362 nm was measured using a chart recorder. Thermostatically controlled quartz cuvettes with an optical path length of 1 cm were used in the experiments. The measurements were performed at temperatures from –10 to 70°C. Heptane, 1,4-dioxane, carbon tetrachloride, benzene, diethyl ether, ethyl acetate, acetone, and acetonitrile served as solvents.

The experiments were performed according to the procedure described below. A required amount of a thiol solution (0.1–0.9 ml) was added to 2.0–2.5 ml of a solvent in the thermostated quartz cuvette, the contents were maintained at a specified temperature, and 0.1–0.2 ml of a chlorine dioxide solution was added. The initial concentrations of chlorine dioxide and propanethiol in the cuvette at the instant the reactants were mixed were $(1–4) \times 10^{-4}$ and 2×10^{-3}–1×10^{-1} mol/l, respectively.

The reaction products were analyzed by ^{1}H NMR spectroscopy on a Bruker AM 300 spectrometer.

RESULTS AND DISCUSSION

Reaction products. Under the experimental conditions ($[C_3H_7SH]_0/[ClO_2]_0 \geq 10$, where $[C_3H_7SH]_0$ and $[ClO_2]_0$ are the reactant concentrations (mol/l) at the instant of mixing), dipropyl disulfide $C_3H_7SSC_3H_7$ was the main product of propanethiol oxidation. The products of dipropyl disulfide oxidation—*S*-propanesulfonothioate $C_3HS_7S(O)SC_3H_7$ and *S*-propyl propanesulfonothioate $C_3H_7S(O_2)SC_3H_7$—were also detected in minor amounts.

Reaction kinetics. We found that the kinetics of chlorine dioxide consumption at $[C_3H_7SH]_0 \gg [ClO_2]_0$ in the test solvents obeys a first-order rate equation over wide ranges of reactant concentrations and temperatures with high coefficients of correlation $r > 0.98$. Apparent rate constants (s^{-1}) were calculated from the semilogarithmic anamorphoses of the kinetic curves of ClO_2 consumption. The apparent rate constants $k' = k[C_3H_7SH]_0^n$ (here, k is the reaction rate constant)

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† Deceased.

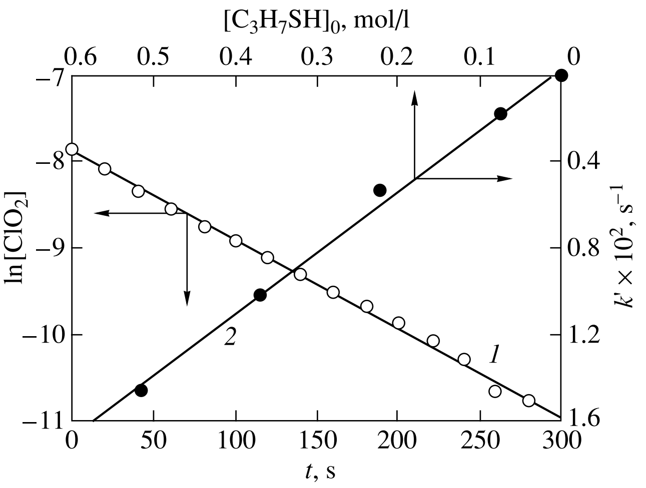


Fig. 1. (*1*) Semilogarithmic anamorphosis of ClO_2 consumption in the reaction with C_3H_7SH. Solvent, 1,4-dioxane; $[ClO_2]_0 = 7.8 \times 10^{-4}$ mol/l; $[C_3H_7SH]_0 = 3.68 \times 10^{-1}$ mol/l; 22°C; $r = 0.99$. (*2*) Apparent rate constant *k*' as a function of $[C_3H_7SH]_0$. Solvent, 1,4-dioxane; 22°C.

are linear functions of $[C_3H_7SH]_0$; this fact is indicative of a first order with respect to C_3H_7SH. As an illustration, Fig. 1 demonstrates a typical anamorphosis of the kinetic curve of chlorine dioxide consumption in the reaction with propanethiol and *k*' as a function of $[C_3H_7SH]_0$ in 1,4-dioxane.

Thus, the reaction rate equation has the form

$$-\frac{d[ClO_2]}{dt} = k[ClO_2][C_3H_7SH].$$

The activation parameters of the reaction were calculated from the temperature dependence of *k* using the Arrhenius equation. Table 1 summarizes these data.

It can be seen in Table 1 that *k* strongly depends on the polarity of the solvent. Thus, on going from nonpolar heptane (ε = 1.92) to polar acetonitrile (ε = 36.2), the reaction rate constant increased by more than four orders of magnitude. This fact is indicative of the formation of high-polarity intermediates in the test reaction. According to the Leydler–Eyring equation, the reaction rate constant as a function of solvent permittivity (ε) is expressed as follows (Fig. 2):

$$\log k = (-4.59 \pm 0.79) + (11.82 \pm 2.4)\frac{\varepsilon - 1}{2\varepsilon + 1}, \quad (r = 0.90). \tag{1}$$

According to Eq. (1), $\log k$ increases with $\frac{\varepsilon - 1}{2\varepsilon + 1}$. This fact indicates that the transition state of the test reaction is more polar than the starting reactants.

Table 1. Kinetic parameters of the reaction of propanethiol oxidation by chlorine dioxide in various solvents at 25°C

Solvent	ε*	k^{**}, l mol^{-1} s^{-1}	$\log A$	$E_a^{\neq}$, kcal/mol	$\Delta H^{\neq}$, kcal/mol	$\Delta G^{\neq}$, kcal/mol	$\Delta S^{\neq}$, cal mol^{-1} K^{-1}
Heptane	1.92	1.67×10^{-3}	5.48 ± 1.37	11.27 × 2.3	10.677	21.253	–35.466
1,4-Dioxane	2.21	7.18×10^{-2}	14.24 ± 3.03	21.00 × 4.5	20.407	19.025	4.634
Carbon tetrachloride	2.23	3.88×10^{-2}	3.38 ± 1.22	6.54 × 1.8	5.947	18.571	–42.330
Benzene	2.28	2.55×10^{-3}	3.07 ± 0.82	7.73 × 1.2	7.137	21.003	–46.498
Diethyl ether	4.34	0.82	8.37 ± 3.00	11.54 × 3.78	10.947	17.578	–22.236
Ethyl acetate	6.02	0.10	8.56 ± 2.51	13.02 × 3.57	12.427	18.799	–21.367
Acetone	20.7	3.83	12.37 ± 1.34	16.09 × 1.90	15.497	16.668	–3.926
Acetonitrile	36.2	52.70	12.52 ± 3.52	14.74 × 4.38	14.147	15.113	–3.239

Notes: * Permittivity [1].
** Determination error of the constant was no higher than 15%.

The dipole moment $\mu_{\neq} = 3.59$ D was estimated from the Leydler–Eyring equation

$$\ln k = \ln k_0 - \frac{1}{kT}\frac{\varepsilon - 1}{2\varepsilon + 1}\left(\frac{\mu^2_{\mathrm{ClO_2}}}{r^3_{\mathrm{ClO_2}}} + \frac{\mu^2_{\mathrm{C_3H_7SH}}}{r^3_{\mathrm{C_3H_7SH}}} - \frac{\mu^2_{\neq}}{r^3_{\neq}}\right)$$

where k is the reaction rate constant in solution; k_0 is the reaction rate constant in a gas phase; k_B is the Boltzmann constant; and μ and r are the dipole moments and effective radii, respectively, of the reactant molecules and the transition state.

The high negative entropy of activation (Table 1) also provides support to the polar character of the activated complex, which is stabilized by solvation.

The comparatively low coefficient of correlation results from the fact that, in addition to nonspecific electrostatic solvation, other types of solvation also affect the reaction. Therefore, we analyzed the results in terms of the Koppel–Palm equation, which takes into account both specific and nonspecific solvation [3]:

$$\log k_0 = \log k_0^0 + yY + pP + eE + bB,$$

where k_0^0 is the reaction rate constant in a gas phase at $Y = P = E = B = 0$; $Y = \frac{\varepsilon - 1}{2\varepsilon + 1}$; $P = \frac{n^2 - 1}{n^2 + 2}$; E and B are the solvent electrophilicity and nucleophilicity parameters, respectively; y, p, e, and b are coefficients that characterize the reaction sensitivity to nonspecific (polarity and polarizability) and specific (electrophilicity and nucleophilicity) solvation; and n is the refractive index of the solvent.

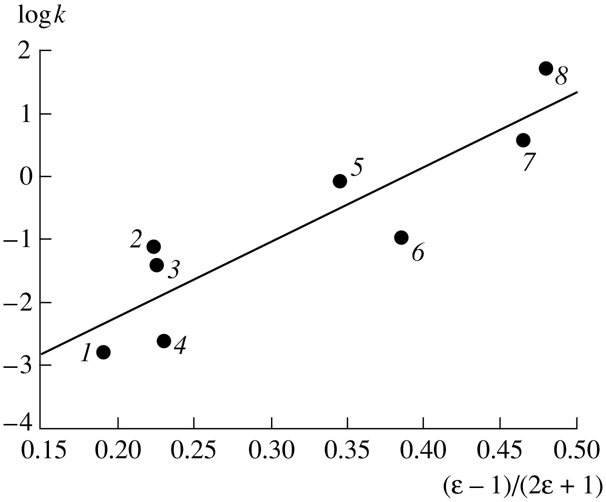


Fig. 2. Reaction rate constant of propanethiol oxidation by chlorine dioxide as a function of solvent permittivity (25°C; $r = 0.90$): (*1*) heptane, (*2*) 1,4-dioxane, (*3*) carbon tetrachloride, (*4*) benzene, (*5*) diethyl ether, (*6*) ethyl acetate, (*7*) acetone, and (*8*) acetonitrile.

We found by the computer treatment of kinetic data for the above solvents (Table 1) that log $\log k_0^0 = -2.27 \pm 0.59$, $y = 9.50 \pm 3.98$, $p = -5.92 \pm 1.89$, $e = (1.07 \pm 0.35) \times 10^{-1}$, $b = (1.74 \pm 1.04) \times 10^{-3}$, and $r = 0.96$ (data for ethyl acetate were ignored). The *Y*, *P*, *E*, and *B* parameters were taken from [3].

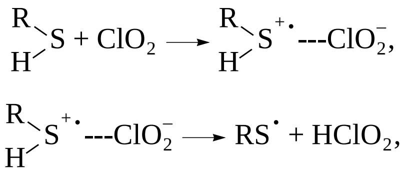
Table 2. Contributions from different types of solvation to the rate constant of the reaction of propanethiol with chlorine dioxide at 25°C

Solvent	*yY*	*pP*	*eE*	*bB*	log*k* (calculated)	log*k* (experimental)
Heptane	1.8126	–1.85727	0	0	–2.33239	–2.78
1,4-Dioxane	2.1217	–1.98670	0	0.49938	–1.29239	–1.14
Carbon tetrachloride	2.1502	–2.12212	0	0	–2.26225	–1.41
Benzene	2.1930	–2.26130	0.2247	0.08352	–2.05164	–2.59
Diethyl ether	3.2800	–1.72126	0	0.4872	–0.24217	–0.08
Acetone	4.4193	–1.74539	0.2247	0.38976	0.998857	0.58
Acetonitrile	4.5677	–1.67694	0.5564	0.27840	1.436424	1.7

Table 2 summarizes the contributions from particular components to the kinetics of propanethiol reaction with chlorine dioxide.

Solvent polarity and polarizability primarily affect the reaction rate in almost all of the solvents. The effects of specific electrophilic and nucleophilic solvation were comparatively weak. Positive values of the coefficients of $\frac{\varepsilon - 1}{2\varepsilon + 1}$, E, and B are indicative of the stabilization of the activated state due to electrostatic interactions and specific solvation.

Thus, the results suggest the following mechanism of the reactions of chlorine dioxide with thiols:



$$RHS + ClO_2 \longrightarrow RHS^{+\bullet}\text{---}ClO_2^-,$$

$$RHS^{+\bullet}\text{---}ClO_2^- \longrightarrow RS^\bullet + HClO_2,$$

$$RS^\bullet + RS^\bullet \longrightarrow RSSR.$$

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