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Liquid-phase oxidation of thiols with chlorine dioxide

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The products and kinetics of the liquid-phase oxidation of 11 aliphatic and aromatic thiols with chlorine dioxide were studied at −10—+70 °C in organic media. The rate constants and activation parameters of the reaction were determined. The influence of the thiol structure on its reactivity was studied. A strong solvent effect on the reaction rate constant was found, and the reaction mechanism was proposed.

Key words: thiols, chlorine dioxide, oxidation, kinetics, solvent effect.

Chlorine dioxide is an efficient oxidant and accessible product widely used for cellulose bleaching and water decontimination.[1] However, the chemistry of chlorine dioxide is poorly studied. The most part of works are devoted to reactions of chlorine dioxide in an aqueous medium.[1] Detailed data on reactions of ClO_2 with organosulfur compounds, in particular, thiols (RSH), are lacking.

In this work, we studied the chemistry and kinetics of liquid-phase oxidation of thiols with chlorine dioxide, measured the activation parameters of the reaction, and considered the influence of the structure of thiols and solvents on the rate constants of their reactions with ClO_2.

Experimental

Solvents were purified by standard procedures.[2] Chlorine dioxide was prepared as described previously[1] and purified from a Cl_2 admixture by adsorption on silica gel. Ethanethiol (**1**), propanethiol-1 (**2**), 2-methylpropanethiol-1 (**3**), hexadecanethiol-1 (**4**), decanethiol-1 (**5**), hexadecanethiol-1 (**6**), cyclohexanethiol (**7**), thiophenol (**8**), 2-methylthiophenol (**9**), phenylmethanethiol (**10**), and 2-mercaptoethanol (**11**) were purified by distillation. Purity of thiols was monitored by GLC.

The reaction kinetics was studied spectrophotometrically by ClO_2 consumption at λ = 354—362 nm on an SF-26 spectrophotometer in thermostatted quartz cells with an optical path length of 1 cm at temperatures from −10 °C to +70 °C. *n*-Heptane, 1,4-dioxane, CCl_4, benzene, diethyl ether, ethyl acetate, acetone, and acetonitrile were used as solvents.

A solution of thiol (0.1—0.9 mL) was added to a solvent (2.0—2.5 mL) in the cell, which was thermostatted at −10—+70 °C, and a solution of ClO_2 (0.1—0.2 mL) was added. The initial concentrations of ClO_2 and thiols in the cell were $(1{-}4) \cdot 10^{-4}$ and $2 \cdot 10^{-3}{-}1 \cdot 10^{-1}$ mol L^{-1}, respectively.

The reaction products were analyzed by ^1H NMR spectroscopy using a Bruker AM-300 spectrometer. A solution containing ClO_2 ($(1{-}1.5) \cdot 10^{-4}$ mol) was added to a solution of thiol ($1.5 \cdot 10^{-3}$ mol) in CCl_4. After ClO_2 was completely consumed, $CDCl_3$ was added to the solution, and the ^1H NMR spectrum of the reaction products was detected (Me_4Si as standard).

Results and Discussion

Reaction products. At the ratio of initial concentrations $[RSH]_0 : [ClO_2]_0 \geq 10$, the corresponding disulfides are the main products of the oxidation of thiols.

$$\mathrm{RSH} \xrightarrow{\mathrm{ClO_2}} \mathrm{RSSR}$$

$$\mathrm{R = Et, Pr^n, HOCH_2CH_2}$$

The oxidation products of thiols **1**, **2**, and **11** in CCl_4 were identified by a previously described procedure.[3]

Kinetic regularities. At $[RSH]_0 \gg [ClO_2]_0$ in all solvents in wide ranges of concentrations of the reactants and temperatures with the high correlation coefficient $r > 0.98$, the kinetics of ClO_2 consumption obeys the first order equation.

The apparent rate constants k' (s^{-1}) were calculated from the semilogarithmic anamorphoses of the kinetic curves of ClO_2 consumption. The apparent constants $k' = k[RSH]_0{}^n$ (k is the reaction rate constant) linearly depend on $[RSH]_0$, which indicates the first order with respect to RSH. A typical anamorphosis of the kinetic curve of ClO_2 consumption in the reaction with thiol **2** and the plot of k' *vs.* $[Pr^nSH]_0$ in 1,4-dioxane are presented in Fig. 1.

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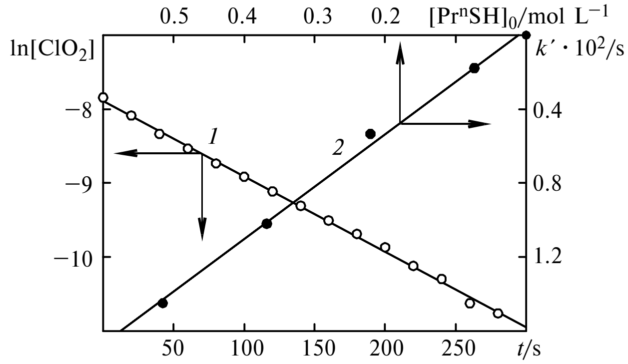


Fig. 1. Semilogarithmic anamorphosis of ClO_2 consumption in the reaction with Pr^nSH in 1,4-dioxane (*1*) at $[ClO_2]_0 = 7.8 \cdot 10^{-4}$ mol L^{-1}, $[Pr^nSH]_0 = 3.68 \cdot 10^{-1}$ mol L^{-1}, 22 °C and the plot of the apparent rate constant k' *vs.* $[Pr^nSH]_0$ (*2*), solvent 1,4-dioxane, 22 °C.

The kinetic equation for the reaction of thiols with ClO_2 has the following form:

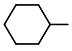
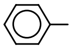
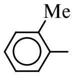
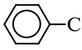
$$-d[ClO_2]/dt = k[ClO_2][RSH].$$

The activation parameters for the reaction in CCl_4 were calculated from the temperature plots of *k* for the compounds studied using the Arrhenius equation (Tables 1 and 2).

Influence of the thiol structure on the reaction kinetics. It is seen in Table 1 that the thiols can be arranged by reactivity in the following order: **8** > **9** > **11** > **2** > **3** > **1** > **4** > **6** > **7** > **5** > **10**.

The *k* value weakly changes with an increase in the chain length of the hydrocarbon radical R for thiols **1**—**7**. However, the replacement of the alkyl substituent by phenyl or 2-methylphenyl increases the rate constant by more than an order of magnitude.

Table 1. Kinetic parameters for oxidation of thiols **1**—**11** (RSH) by chlorine dioxide in CCl_4 at 40 °C

Thiol	R	k_{exp}*	logA	E_a	ΔH	ΔG	−ΔS /cal mol^{-1} K^{-1}
				kcal mol^{-1}			
1	Et	$1.0 \cdot 10^{-1}$	—	—	—	—	—
2	Pr^n	$2.1 \cdot 10^{-1}$	6.8±1.8	10.7±2.5	10.07	19.33	29.52
3	Bu^i	$2.0 \cdot 10^{-1}$	8.8±1.6	13.7±2.32	13.09	19.45	20.37
4	C_6H_{13}	$1.0 \cdot 10^{-1}$	11.9±1.7	18.3±2.6	16.58	19.67	9.83
5	$C_{10}H_{21}$	$4.1 \cdot 10^{-2}$	8.71±0.9	14.5±1.3	13.88	20.41	20.81
6	$C_{16}H_{33}$	$7.4 \cdot 10^{-2}$	7.8±3.0	12.7±4.5	12.08	19.88	24.95
7		$7.3 \cdot 10^{-2}$	11.9±1.7	18.3±2.6	17.68	19.62	6.17
8		4.2	12.4±0.2	16.8±0.3	16.17	17.39	3.88
9		3.1	9.2±1.6	12.6±2.2	11.99	17.78	18.54
10	 $-CH_2-$	$1.5 \cdot 10^{-2}$	8.3±2.1	15.7±3.2	15.07	22.18	22.66
11	$HOCH_2CH_2$—	$3.2 \cdot 10^{-1}$	6.9±1.0	10.6±1.4	9.98	19.09	29.07

* Error in determination of the constant ≤15%.

Table 2. Kinetic parameters for oxidation of propanethiol-1 (**2**) and 2-mercaptoethanol (**11**) by chlorine dioxide in various solvents at 25 °C

Solvent	ε*	k**/L mol^{-1} s^{-1}		logA		$E_a^{\neq}$/kcal mol^{-1}	
		2	**11**	**2**	**11**	**2**	**11**
n-Heptane	1.92	$1.7 \cdot 10^{-3}$	—	5.5±1.4	—	11.3±2.3	—
1,4-Dioxane	2.21	$7.2 \cdot 10^{-2}$	$1.1 \cdot 10^{-1}$	14.2±3.0	7.4±1.4	21.0±4.5	11.4±4.4
CCl_4	2.23	$3.9 \cdot 10^{-2}$	$1.4 \cdot 10^{-1}$	6.8±1.8	6.9±4.2	10.7±2.5	10.6±5.8
Benzene	2.28	$2.6 \cdot 10^{-3}$	$8.3 \cdot 10^{-1}$	3.1±0.8	8.3±4.0	7.7±1.2	11.4±5.6
Diethyl ether	4.34	0.8	2.8	8.4±3.0	4.4±0.8	11.5±3.8	5.4±0.8
Ethyl acetate	6.02	0.1	$1.1 \cdot 10^{-1}$	8.6±2.5	4.34±2.1	13.0±3.6	7.25±3.0
Acetone	20.7	3.8	5.5	12.4±1.3	7.7±0.2	16.1±1.9	9.48±5.17
Acetonitrile	36.2	52.7	11.4	12.5±3.5	8.9±4.1	14.7±4.4	10.7±5.0

* Dielectric constant according to published data.[2]

** Error in determination of the constant ≤15%.

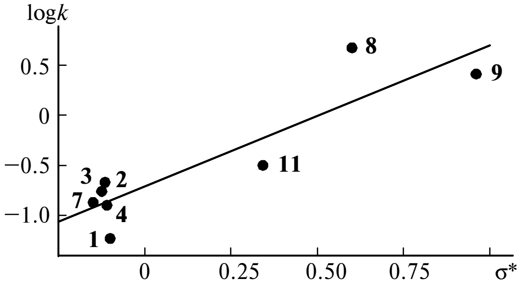


Fig. 2. Rate constants for oxidation of thiols **1**, **2**, and **8—11** with ClO_2 (log*k*) as functions of the thiol structure in the Taft coordinates; solvent CCl_4, 40 °C, $r = 0.90$.

We studied (Fig. 2) the influence of the substituents on the reaction rate constant in the coordinates of the Taft equation $\log k = \log k_0 + \rho^*\sigma^*$ (the σ^* values are taken from Refs. 4 and 5). Found: $\rho^* = 1.41\pm0.29$, $\log k_0 = -0.71\pm0.12$, $r = 0.94$. The positive sign of the ρ^* coefficient indicates that electron-withdrawing substituents accelerate the reaction.

The plot of the *k* constant *vs.* p*K* of thiols (the p*K* values are taken from Refs. 6 and 7) shows (Fig. 3) that *k* increases with a decrease in p*K*. On going from phenylmethanethiol (p$K = 11.8$) to thiophenol (p$K = 7.75$), the *k* value increases from $1.5 \cdot 10^{-2}$ to 4.2 L mol^{-1} s^{-1}. A similar dependence of the oxidation rate constant on the dissociation constant of thiol was found for the oxidation of thiols with molecular oxygen.[6] This is related to the fact that in this case the key stage is thiol dissociation to form the thiolate anion, which is further oxidized to the thiyl radical, and the limiting step is electron transfer from RS^- to O_2.[6]

Solvent effect on the reaction rate of thiols with ClO_2. The solvent effect on the reaction rate was studied for the oxidation of thiols **2** and **11**. The latter was chosen because the molecule of **11** contains the OH group, which is prone, as the SH group, to specific solvation.[8] Analysis of the reaction products showed that the oxidation of thiol **11** occurs only at the SH group. *n*-Heptane, 1,4-dioxane, CCl_4, benzene, diethyl ether, ethyl acetate, acetone, and acetonitrile were used as solvents.

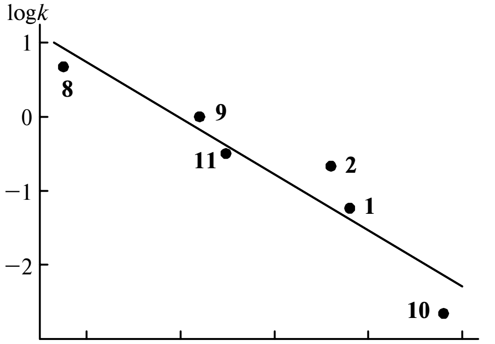


Fig. 3. Rate constants for oxidation of thiols with ClO_2 (log*k*) as functions of the dissociation constant of thiols; solvent CCl_4, 40 °C, $r = 0.94$.

Note that both thiols **2** and **11** exhibit a strong dependence of *k* on the solvent polarity (see Table 2). For example, for thiol **2**, on going from a poorly polar *n*-heptane ($\varepsilon = 1.92$) to more polar acetonitrile ($\varepsilon = 36.2$), the reaction rate constant increases by more than four orders. This indicates the formation of highly polar intermediates in the studied reaction. In the case of thiol **11**, the rate constant increases by two orders on going from 1,4-dioxane ($\varepsilon = 2.21$) to acetonitrile. The high negative activation entropy of the reaction of thiols with ClO_2 (see Table 1) also confirms the polar character of the activated complex, which is stabilized due to solvation. According to the Leydler—Eyring equation, the dependence of the reaction rate constant on the dielectric constant of the solvent

$$\log k = \log k_0 + y(\varepsilon - 1)/(2\varepsilon + 1)$$

gives for thiols **2** and **11**, respectively,

$$\log k = (-4.59\pm0.79) + (11.82\pm2.4)(\varepsilon - 1)/(2\varepsilon + 1) \quad (r = 0.90)$$

and

$$\log k = (-2.18\pm0.39) + (6.73\pm1.13)(\varepsilon - 1)/(2\varepsilon + 1) \quad (r = 0.95).$$

The kinetic data were processed with the Koppel—Palm equation that takes into account both specific and non-specific solvations,[9]

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

where $\log k_0^0$ is the reaction rate constant in the gas phase at $Y = P = E = B = 0$, $Y = (\varepsilon - 1)/(2\varepsilon + 1)$, $P = (n^2 - 1)/(n^2 + 2)$; *E* and *B* are the electrophilicity and nucleophilicity parameters of the solvent; *y*, *p*, *e*, and *b* are the coefficients characterizing the sensitivity of the reaction to the influence of non-specific (polarity, polarizability) and specific (electrophilicity, nucleophilicity) solvations. The parameters obtained are presented below.

Parameter	**2**	**11**
$\log k_0^0$	-2.36 ± 1.42	-0.06 ± 0.04
y	8.81 ± 5.60	5.85 ± 3.75
p	-5.03 ± 3.59	-5.76 ± 3.24
e	$(1.24\pm1.16) \cdot 10^{-1}$	$(-3.23\pm3.28) \cdot 10^{-2}$
b	$(1.11\pm1.16) \cdot 10^{-3}$	$(-1.51\pm2.75) \cdot 10^{-3}$
r	0.89	0.95

The oxidation of thiol **2** illustrates (see Table 3) the contribution of each component to the reaction kinetics. It is seen that in almost all solvents the polarity and polarizability mainly affect the reaction rate and the influence of specific electrophilic and nucleophilic solvation is comparatively low.

Based on the data obtained for the composition of the oxidation products, reaction kinetics, and solvent

Table 3. Contributions of different types of solvation to the oxidation rate constant of propanethiol-1 (**2**) with ClO_2 at 25 °C*

Solvent	yY	$-pP$	eE	bB	log*k*	
					Calculation	Experiment
n-Heptane	1.68	1.59	0	0	−2.28	−2.78
1,4-Dioxane	1.97	1.70	$5.21\cdot10^{-1}$	$2.62\cdot10^{-1}$	−1.32	−1.15
CCl_4	1.99	1.82	0.00	0.00	−2.19	−1.04
Benzene	2.03	1.94	$2.60\cdot10^{-1}$	$5.30\cdot10^{-2}$	−1.96	−2.60
Diethyl ether	3.04	1.48	0.00	$3.09\cdot10^{-1}$	−0.49	−0.09
Ethyl acetate	3.39	1.54	$1.98\cdot10^{-1}$	$2.00\cdot10^{-1}$	−0.12	−0.98
Acetone	4.10	1.50	$2.60\cdot10^{-1}$	$2.48\cdot10^{-1}$	0.74	0.57
Acetonitrile	4.23	1.44	$6.45\cdot10^{-1}$	$1.77\cdot10^{-1}$	1.25	1.71

* For parameters *Y*, *P*, *E*, and *B*, see Ref. 9.

effect, we can propose the reaction mechanism for the case of excess RSH (Scheme 1).

Scheme 1

$$RSH \rightleftharpoons RS^- + H^+ \qquad (1)$$

$$ClO_2 + H^+ \rightleftharpoons HClO_2{}^{\cdot+} \qquad (2)$$

$$RS^- + ClO_2 \longrightarrow RS^\cdot + ClO_2{}^- \qquad (3)$$

$$RSH + ClO_2 \longrightarrow RS^\cdot + HOClO \qquad (4)$$

$$HClO_2{}^{\cdot+} + ClO_2{}^- \longrightarrow HClO_2 + ClO_2 \qquad (5)$$

$$RS^\cdot + RS^\cdot \longrightarrow RSSR \qquad (6)$$

In Scheme 1 stage (3) seems to be rate-determining. Stage (4) is of low significance because one-electron oxidation rather than H atom abstraction is more characteristic of ClO_2.[1] The increase in the rate of reaction (3) when electron-withdrawing substituents are introduced into the thiol molecule is related to a decrease in *K* and facilitation of acidic dissociation.

Since the polar thiolate ion is formed during the reaction, the increase in the consumption rate of ClO_2 with an increase in the solvent polarity is explained by the solvation of the RS^- ion by the solvent and the subsequent reaction of the formed solvate with ClO_2.

The high reactivity of ClO_2 with respect to thiols allows its use for demercaptanation processes.

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