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Oxidation of alcohols by chlorine dioxide in organic solvents

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The kinetics of oxidation of a series of alcohols (propan-2-ol, 2-methylpropan-1-ol, butan-1-ol, butan-2-ol, 3-methylpentan-1-ol, heptan-4-ol, decan-2-ol, cyclohexanol, borneol) by chlorine dioxide in organic solvents was studied using spectrophotometry. The reaction is described by the second-order rate equation $w = k[\mathrm{ROH}][\mathrm{ClO_2}]$. The rate constants were measured in the range of 10—60 °C, and the activation parameters of the processes were calculated. The products were identified, and the yields were determined.

Key words: oxidation, chlorine dioxide, alcohols, rate constants, activation parameters.

Chlorine dioxide finds wide use as a reagent for water preparation and, hence, the oxidation involving chlorine attracts attention of many researchers. The oxidation of alcohols in an aqueous solution was studied for methanol, propan-2-ol, and glucose, which reacts at the —CH_2OH group to form the aldehyde or carboxy group.[1—3] The reaction rate constants depend on the pH of the solution. They somewhat decrease in the interval pH 3.0—5.9 but increase considerably with the further increase in pH to 6.7 due to the interaction of the RO^- anion with chlorine dioxide.[1,2,4] The key step of the oxidation mechanism in an aqueous solution is the transfer of the hydride ion.[1,2,4] In the single work performed in the organic solvent, the oxidation of mytrenol and *trans*-verbenol was studied and a possibility of synthesis of mytrenal, mytrenic acid, and verbenone was shown.[5]

We studied the kinetic regularities for the reactions of alcohols with chlorine dioxide in a series of organic solvents. The following alcohols were chosen: propan-2-ol (**1**), 2-methylpropan-1-ol (**2**), butan-1-ol (**3**), butan-2-ol (**4**), 3-methylpentan-1-ol (**5**), heptan-4-ol (**6**), decan-2-ol (**7**), cyclohexanol (**8**), and borneol (**9**). The oxidation was carried out in n-C_7H_{16}, CCl_4, C_6H_6, 1,4-dioxane, C_6H_5Cl, AcOEt, 1,2-dichloroethane, and MeCN.

Experimental

Chlorine dioxide was obtained by the reaction of potassium chlorate with oxalic acid in the presence of sulfuric acid.[6] The argon—ClO_2 mixture was dehydrated by purging the flow through the trap with P_4O_{10} and then through the precooled to 0 °C column with silica gel, where ClO_2 was adsorbed. To prepare solutions of ClO_2, the column was heated in a thermostat to 30—35 °C and blown with argon into the trap with a solvent. The ClO_2 concentration in a solution was determined iodometrically using the Brey method[6] and spectrophotometrically.[7] Potassium chlorate and oxalic acid (reagent grade) were purified by recrystallization from water. Alcohols and solvents were purified using known procedures.[8,9]

The kinetics of alcohol oxidation was studied spectrophotometrically detecting the consumption of chlorine dioxide at λ_{max} = 356 nm on a Specord M40 instrument (Carl Zeiss Jena). A solution of the studied alcohol was placed in the working quartz cell, and a solvent was poured in the reference cell. The temperature of the cells were maintained at 10—60 °C in the spectrophotometer chamber. Then a necessary amount of a chlorine dioxide solution was added to the working cell, and the change in the absorbance was monitored. The initial concentrations of the oxidized substrates and chlorine dioxide were varied within $(0.1—10.0) \cdot 10^{-2}$ and $(0.5—1.2) \cdot 10^{-3}$ mol L^{-1}, respectively.

To study the oxygen effect on the kinetic regularities, the argon or solution was O_2 was purged through the solution, a necessary amount of chlorine dioxide was added, and the kinetics of its consumption was recorded.

The oxidation products were analyzed by GLC on a Chrom-5 instrument (column l = 3.5 m, d = 3 mm, 5% SE-30 on Chromatone) and by ^1H NMR on a Bruker AM-300 spectrometer with a frequency of 300 MHz using $CDCl_3$ as solvent and $SiMe_4$ as standard. Benzene was used as a label for the quantitative determination of products.

The direct and inverse kinetic problems were solved by numerical methods using the Kinetic System Solver (KSS) program, version 4.10 (see Refs 10 and 11).

Results and Discussion

Reaction products. The reactions of alcohols **1—9** with chlorine dioxide afford carbonyl compounds in good yields (Table 1). In the case of 2-methylpropan-1-ol (**2**) and 3-methylpentan-1-ol (**5**), chlorinated products are formed, which is due, most likely, to the formation of acids HClO and $HClO_2$ capable of chlorinating the oxidized substrates.

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Table 1. Oxidation products of alcohols by chlorine dioxide (CCl_4, 25 °C)

Alcohol	Product	Yield (%)
1	Propanone	96
2	2-Methylpropanal	77
	2-Chloro-2-methylpropan-1-ol	10
	2-Chloro-2-methylpropanal	5
3	Butanal	95
4	Butan-2-ol	94
5	3-Methylpentanal	55
	3-Chloro-3-methylpentan-1-ol	20
	3-Chloro-3-methylpentanal	7
6	Heptan-4-one	95
7	Decan-4-one	90
8	Cyclohexanone	95
9	Camphor	97

The complete consumption of alcohol is observed at the molar ratio ROH : ClO_2 = 1 : 2.

Reaction kinetics. The reaction kinetics was studied at $[ClO_2]_0 << [ROH]_0$, where $[ClO_2]_0$ and $[ROH]_0$ are the initial concentrations of chlorine dioxide and a substrate. For the compounds indicated, the kinetic curves with the high correlation coefficient (0.990—0.999) are described by the first-order rate equation. The semilogarithmic anamorphoses of the kinetic curves of chlorine dioxide consumption in the reaction with alcohol **8** are presented as an example in Fig. 1. The apparent rate constants of the first order reaction $k_{app} = k[ROH]^n$ (k is the second-order rate constant, and n is the reaction order with respect to alcohol) were calculated from the anamorphoses of the kinetic curves. The dependence of k_{app} on the substrate concentration is linear and has the form

$$k_{eff} = k[ROH] + k_d,$$

indicating two routes of ClO_2 consumption: the reaction with an alcohol (k) and decomposition (k_d) (Fig. 2). For instance, the dependences presented in Fig. 2 illustrate well that the k_d value calculated from the k_{app}—$[ROH]_0$ plot coincides with the k_d value obtained for the decomposition of ClO_2 in the corresponding solvent without a substrate.

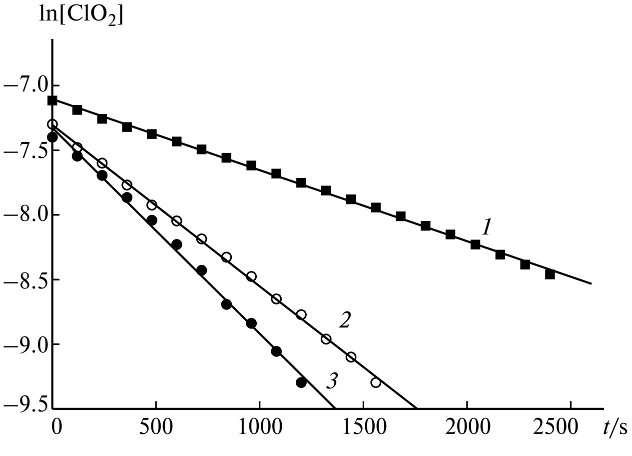


Fig. 1. Semilogarithmic anamorphoses of the kinetic curves of ClO_2 consumption in the reaction with cyclohexanol at 60 °C in heptane ($[ClO_2]_0 = 8 \cdot 10^{-4}$ mol L^{-1}; $[\mathbf{8}]_0$ = 0.19 (*1*), 0.39 (*2*) and 0.52 mol L^{-1} (*3*)).

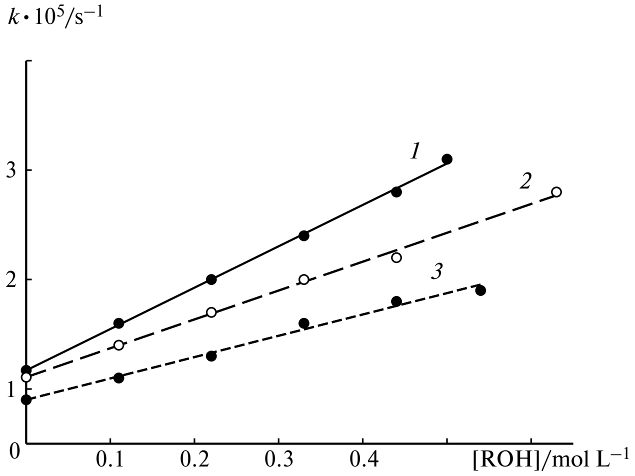


Fig. 2. Apparent rate constant for the oxidation of propan-2-ol by chlorine dioxide *vs* alcohol concentration at 30 °C in 1,4-dioxane (*1*), ethyl acetate (*2*), and acetonitrile (*3*).

Solvent	k_d/s^{-1} (30 °C)	Solvent	k_d/s^{-1} (30 °C)
n-C_7H_{16}	$5.3 \cdot 10^{-5}$	C_6H_5Cl	$1.1 \cdot 10^{-4}$
CCl_4	$4.1 \cdot 10^{-4}$	AcOEt	$9.2 \cdot 10^{-6}$
C_6H_6	$4.4 \cdot 10^{-5}$	1,2-Dichloroethane	$1.5 \cdot 10^{-5}$
1,4-Dioxane	$1.3 \cdot 10^{-5}$	MeCN	$1.1 \cdot 10^{-5}$

The dependence of k_{app} on $[ROH]_0$ is linear (see Fig. 2), indicating the first-order reaction with respect to alcohol and the absence of an effect of alcohol association on its reactivity in the studied concentration interval. The section cut in the ordinate is equal to the rate constant

Table 2. Activation parameters for the oxidation of alcohols **1—9** by chlorine dioxide (30 °C, heptane)

Alcohol	$k_{303} \cdot 10^5$ [a]	log$A$	E_a	$\Delta H^{\neq}_{298}$	$\Delta G^{\neq}_{298}$	$-\Delta S^{\neq}_{298}$ [b]
			kJ mol^{-1}			
1	6.4	4.9±0.3	53±2	50.5	97.8	158.7
2	6.1	5.5±0.3	56±2	53.7	98.0	148.7
3	3.4	6.0±0.4	60.8±2.2	58.3	99.5	138.4
4	13.7	2.2±0.1	35.2±2.8	32.7	95.7	211.1
5	6.0	3.0±0.2	41.9±3.1	39.4	97.8	195.8
6	4.9	8.4±0.5	73.7±3.3	71.3	98.8	92.4
7	15.6	3.7±0.2	43.6±2.4	41.1	95.5	182.4
8	25.7	7.2±0.5	62.6±3.4	60.2	94.6	115.4
9	64.3	4.1±0.2	42.3±2.7	39.8	91.9	174.8

[a] k_{303}/L mol^{-1} s^{-1}.
[b] $\Delta S^{\neq}$/J mol^{-1} K^{-1}.

Table 3. Activation parameters of propan-2-ol oxidation by chlorine dioxide in organic solvents (30 °C)

Solvent	$k_{303} \cdot 10^4$ /L mol^{-1} s^{-1}	lg$A$	E_a	$\Delta H^{\neq}_{298}$	$\Delta G^{\neq}_{298}$	$-\Delta S^{\neq}_{298}$ /J mol^{-1} K^{-1}
			kJ mol^{-1}			
n-C_7H_{16}	0.71	5.0±0.3	53±2	50.5	97.5	157.5
CCl_4	0.95	9.7±0.6	79.6±3.5	77.1	97.3	67.5
C_6H_6	0.76	6.5±0.4	61.6±3.4	59.1	97.5	129
1,4-Dioxane	0.29	3.8±0.2	48.5±2.5	46.0	99.8	181
C_6H_5Cl	0.43	11.3±0.7	90.5±3.5	88.0	99.0	36.9
AcOEt	0.20	4.1±0.2	51±2	48.5	100.7	175
1,2-Dichloroethane	0.38	7.8±0.5	71±3	68.5	99.5	104
MeCN	0.27	4.4±0.3	52±2	49.5	99.9	169

of thermal decomposition of chlorine dioxide, and the kinetic equation for the reaction has the form

$$-\mathrm{d}C/\mathrm{d}t = (k_d + k[\mathrm{ROH}]) \cdot C,$$

where $k_d + k[\mathrm{ROH}] = k_{app}$, k_d is the rate constant of thermal decomposition of chlorine dioxide, and C is the concentration.

The measured rate constants for oxidation of alcohols **2—9** by chlorine dioxide and the calculated activation parameters are given in Table 2. An increase in the activation energy is accompanied by an increase in the pre-exponential factor: $E_a = (21.7\pm3.3) + (6.0\pm0.5) \cdot \log A$ ($r = 0.98$). The activation enthalpy increases analogously with an increase in the activation entropy: $\Delta H^{\neq} = (99\pm4) + (0.32\pm0.08) \cdot \Delta S^{\neq}$ ($r = 0.98$), because $\Delta G^{\neq}$ remains nearly unchanged for the studied series of alcohols. The isokinetic temperature calculated from the slope of the plot of the activation enthalpy *vs* activation entropy is 37±4 °C and lies in the studied temperature interval from 30 to 60 °C. That is why, probably, we failed to detect any effect of the alcohol structure on the oxidation kinetics.

The solvent effect on the oxidation kinetics of alcohol **1** was studied. The kinetic regularities of chlorine dioxide consumption in organic solvents are analogous to those described above. The dependence of k_{app} *vs* $[\mathrm{ROH}]_0$ in all the solvents studied is linear, indicating the first-order reaction with respect to alcohol. The dependences of k_{app} on $[\mathrm{ROH}]_0$ for the oxidation of propan-2-ol by chlorine dioxide in ethyl acetate, acetonitrile, and 1,4-dioxane are presented in Fig. 2. The section cut in the ordinate (k_{app}) is equal to the rate constant of thermal decomposition of chlorine dioxide, and the kinetic equation of the reaction takes the form

$$-\mathrm{d}C_1/\mathrm{d}t = (k_d + k[\mathrm{ROH}]) \cdot C_1,$$

where $k_d + k[\mathrm{ROH}] = k_{app}$, and k_d is the thermal decomposition constant of chlorine dioxide.

The temperature dependence of the rate constant for propan-2-ol oxidation by chlorine dioxide was studied in all solvents, and the activation parameters of the reaction were determined (Table 3).

According to the data in Table 3, an increase in the activation energy is accompanied by an increase in the pre-exponential factor: $E_a = (27.1\pm1.7) + (5.5\pm0.2) \cdot \log A$ ($r = 0.99$). The activation enthalpy increases similarly with an increase in the activation entropy (see Fig. 2): $\Delta H^{\neq} = (97.6\pm1.1) + (0.29\pm0.02) \cdot \Delta S^{\neq}$ ($r = 0.99$). The isokinetic temperature is 15±2 °C.

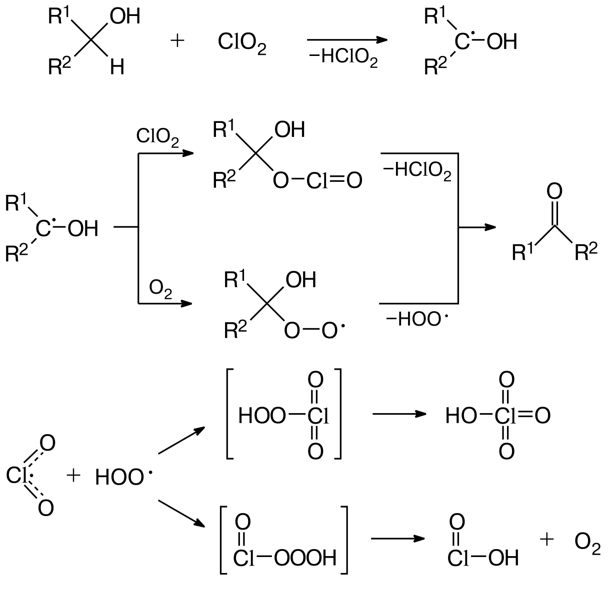
The reaction rate constants (k) and $\Delta G^{\neq}$ in various solvents differ slightly from each other (see Table 3), indicating a low polarity of the transition state.

The following experimental facts are necessary to discuss the mechanism of alcohol oxidation by chlorine dioxide: (1) the formal kinetic regularities (a first order with respect to the alcohol and oxidant) allow us to conclude that one chlorine dioxide molecule participates in the rate-determining step; 2) the low activation entropies suggest the highly ordered transition state (see Table 2); (3) no solvent effect on the reaction kinetics indicates a low polarity of the transition state; (4) alcohol is completely consumed at the reactant ratio alcohol : ClO_2 = 1 : 2. The reaction affords the corresponding carbonyl compounds as the major product, and the chlorine derivatives are observed in some cases (see Table 1).

The results obtained can be explained in the framework of Scheme 1.

In the first rate-determining step an electron is transferred from an alcohol molecule to a dioxide molecule, and the proton is abstracted. The radical formed interacts with the second chlorine dioxide molecule to give unstable chloric acid ester,[12,13] which then decomposes to a carbonyl compound and $HClO_2$. The second possible route for the consumption of the α-hydroxyalkyl radicals is the reaction with oxygen, and the peroxy radicals formed can decay in recombination reactions or decompose to give the carbonyl compound and $^{\bullet}OOH$. The solution of the direct kinetic problem by numerical methods[10,11] with allowance for *homo*-recombination reactions and using the experimental concentrations of the reactants and the known rate constants (recombination of $R_2C(OH)OO^{\bullet}$ $k_{298K} \approx 10^7$—10^6 L mol^{-1} s^{-1} (see Refs 14—16), decomposition of $R_2C(OH)OO^{\bullet}$ $k_{298K} \approx 1$—10^2 s^{-1} (see Refs 15 and 16)) gives the value 10^{-10} mol L^{-1} for the maximal

Scheme 1



concentration of the $R_2C(OH)OO^{\bullet}$ radicals. Therefore, the recombination of the peroxy radicals can be neglected. The $^{\bullet}OOH$ radical can abstract the proton from the substrate or recombine. The most probable route of its decay is the reaction with ClO_2, because the recombination of two radicals is much faster than proton abstraction at comparable concentrations of the substrate and chlorine dioxide. Then the main route of $^{\bullet}OOH$ consumption should be the interaction with ClO_2. This assumption explains the absence of an oxygen effect on the yield of the products, stoichiometry (ClO_2—substrate), and kinetic regularities of the process. The formation of the chlorinated products is due, most likely, to the reaction of alcohols with hypochlorous acid, which is formed by the disproportionation of the chlorite ions.[17]

$$2\ ClO_2^- + H^+ \longrightarrow HClO + ClO_3^-$$

The high yield of the reaction products in alcohol oxidation shows that the potential of chlorine dioxide as a reactant in organic synthesis is far from being exhausted.

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