

Oxidation of valeraldehyde by chlorine dioxide

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The product of the reaction of valeraldehyde with chlorine dioxide was determined, and the solvent effect on the reaction kinetics was studied. The major oxidation product is valeric acid. The reaction rate is described by the second-order equation $w = k[\text{RCHO}] \cdot [\text{ClO}_2]$. The rate constants were measured in the 297–328 K interval, and the activation parameters of the reaction were determined.

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

The oxidation of acetaldehyde and *n*-butyraldehyde by chlorine dioxide in an aqueous solution yields the corresponding carboxylic acids.^{1,2} Benzaldehyde dispersed in water interacts with chlorine dioxide with explosion. At the same time, it is reported that chlorine dioxide does not react with hexanal and 2-methylbutanal.³

We identified the products and studied the kinetic regularities of valeraldehyde oxidation by chlorine dioxide in organic solvents.

Experimental

Chlorine dioxide was obtained according to a known procedure.⁴ The solvents *n*-C₇H₁₆ (1), CCl₄ (2), benzene (3), 1,4-dioxane (4), ethyl acetate (5), acetone (6), *tert*-butanol (7), acetonitrile (8), and ethanol (9) were purified by known procedures.⁵ The kinetics of valeraldehyde oxidation by chlorine dioxide in various solvents was studied on a Specord M40 spectrophotometer (Carl Zeiss Jena) by a decrease in the absorbance at the absorption maxima of ClO₂ at 356, 359, 360, 354, 358, 361, 362, 363, and 360 nm in a medium of solvents 1–9 under the condition that $[\text{ClO}_2]_0 \ll [\text{RCHO}]_0$, where $[\text{ClO}_2]_0$ and $[\text{RCHO}]_0$ are the initial concentrations of chlorine dioxide and aldehyde. A solution of valeraldehyde was placed in the working quartz cell, and the reference cell was filled with a solvent. The temperature of the cells was maintained at 24–55 °C in the spectrophotometer chamber. Then the necessary amount of a solution of chlorine dioxide was added to the working cell, and the change in the absorbance was monitored. The initial concentrations of valeraldehyde and chlorine dioxide were varied within $(0.7\text{--}27.0) \cdot 10^{-2} \text{ mol L}^{-1}$ and $(0.5\text{--}1.2) \cdot 10^{-3} \text{ mol L}^{-1}$, respectively.

The oxidation products were analyzed by the ¹H and ¹³C NMR with a Bruker AM-300 spectrometer at a frequency of 300 MHz using CDCl₃ as the solvent and SiMe₄ as standard and by GLC on a Chrom-5 instrument (column *l* = 3.5 m, *d* = 3 mm, 5% SE-30 on Chromatone) after sample treatment

with CH₂N₂. Benzene was used as a reference in the quantitative determination of the products.

Results and Discussion

The oxidation of valeraldehyde by chlorine dioxide in the organic solvents listed above gives rise to valeric acid with a high yield (>94%), and the complete conversion of aldehyde is observed at the reactant mole ratio ClO₂/RCHO = 1.

The curve change of the chlorine dioxide concentration as a function of time in excess aldehyde fits a first-order equation with a correlation coefficient of 0.990–0.999. The kinetic curves of chlorine dioxide consumption in the reaction with valeraldehyde in 1,4-dioxane and their semilogarithmic transforms are presented in Fig. 1. The apparent first order rate constants

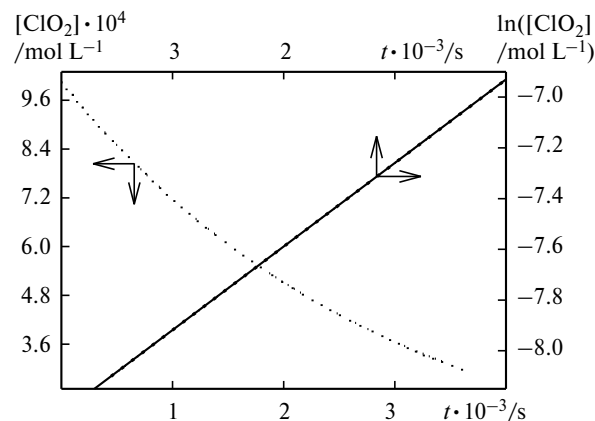


Fig. 1. Kinetic curve of chlorine dioxide consumption in the reaction of valeraldehyde in 1,4-dioxane at 317 K ($[\text{RCHO}]_0 = 0.27 \text{ mol L}^{-1}$).

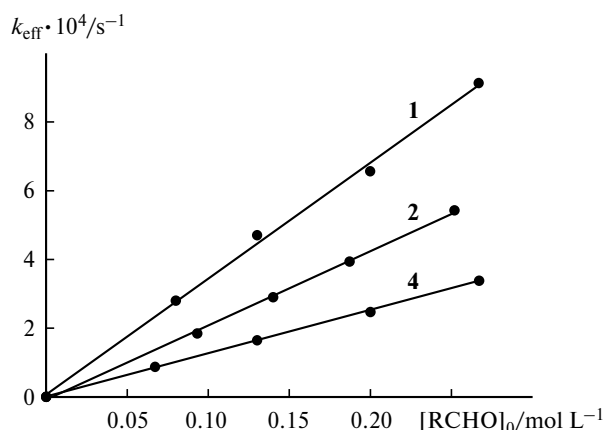


Fig. 2. Dependence of the apparent rate constant for the oxidation of valeraldehyde by chlorine dioxide on the aldehyde concentration in heptane (**1**), 1,4-dioxane (**4**) at 317 K and in CCl₄ (**2**) at 315 K.

$k_{app} = k \cdot [RCHO]^n$ (k is the second order rate constant) were calculated for all the solvents. The plot of k_{app} vs $[RCHO]_0$ is linear indicating the first order with respect to aldehyde. The linear dependences of the apparent rate constants for the oxidation of valeraldehyde by chlorine dioxide in 1,4-dioxane, tetrachloromethane, and heptane are shown in Fig. 2. The kinetic equation of the reaction takes the form

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

The temperature dependence of the oxidation rate constant was studied for all the solvents in the interval from 278 to 323 K, and the activation parameters were determined (Table 1).

The increase in the activation energy is accompanied by an increase in the pre-exponential factor: $E_a = (19.4 \pm 3.2) + (5.7 \pm 0.3) \cdot \log A$ ($r = 0.98$). Analogously, the activation enthalpy increases with an increase in the activation entropy: $\Delta H^\ddagger = (92.3 \pm 3.4) + (0.29 \pm 0.02) \cdot \Delta S^\ddagger$

Table 1. Activation parameters of the oxidation of valeraldehyde by chlorine dioxide in solvents **1–9** (the experimental error does not exceed 10%)

Solvent	k_{303}^a	$\log A$	kJ mol^{-1}			
			E_a	ΔH^\ddagger_{303}	ΔG^\ddagger_{303}	$\Delta S^\ddagger_{303}^b$
<i>n</i> -C ₇ H ₁₆ (1)	11.0	6.9	57.1	54.5	91.2	-121.1
CCl ₄ (2)	6.4	10.6	79.9	77.4	92.7	-50.3
Benzene (3)	10.0	7.5	60.8	58.3	91.4	-109.4
1,4-Dioxane (4)	4.6	7.3	61.6	59.0	93.3	-113.2
Ethyl acetate (5)	13.8	8.9	68.1	65.6	90.6	-82.7
Acetone (6)	6.5	9.4	72.9	70.3	92.7	-73.6
Bu ^t OH (7)	3.3	9.9	77.5	75.0	94.1	-63.2
MeCN (8)	13.3	16.5	112.2	109.7	90.8	-62.3
EtOH (9)	0.7	9.8	80.8	78.3	97.4	-63.2

^a $k_{303} \cdot 10^4 / \text{L mol}^{-1} \text{ s}^{-1}$. ^b $\Delta S^\ddagger_{303} / \text{J mol}^{-1} \text{ K}^{-1}$.

Table 2. Rate constants ($k / \text{L mol}^{-1} \text{ s}^{-1}$) for the oxidation of valeraldehyde by chlorine dioxide in various solvents at 243 and 333 K

Solvent	$k_{243} \cdot 10^6$	Y_{243}^*	$k_{333} \cdot 10^3$	Y_{333}^*	E_T^N
<i>n</i> -C ₇ H ₁₆ (1)	4.0	0.1998	8.5	0.1839	0.012
CCl ₄ (2)	0.3	0.2424	11.4	0.2186	0.052
Benzene (3)	2.7	0.2315	9.0	0.2226	0.111
1,4-Dioxane (4)	1.1	0.2190	4.3	0.2257	0.164
Ethyl acetate (5)	1.8	0.4032	16.0	0.3500	0.228
Acetone (6)	0.5	0.3166	9.0	0.4588	0.355
Bu ^t OH (7)	0.2	0.4422	5.4	0.4077	0.389
MeCN (8)	0.02	0.4835	76.7	0.4796	0.460
EtOH (9)	0.03	0.4774	1.3	0.4629	0.654

* $Y = (\epsilon - 1) / (2\epsilon + 1)$.

($r = 0.98$). The isokinetic temperature calculated from the dependence of the activation energy on the activation entropy is 299 ± 3 K.

To determine the effect of the dielectric constant of the solvent on the reaction kinetics, we calculated the bimolecular reaction rate constants by the Arrhenius equation at 243 and 333 K in all the solvents studied (Table 2) and analyzed them in the framework of the Kirkwood equation⁶

$$\log k = \log k^0 - \frac{1}{4\pi\epsilon_0} \frac{N_A}{RT} \frac{\epsilon - 1}{2\epsilon + 1} \left(\frac{\mu_A^2}{r_A^2} + \frac{\mu_B^2}{r_B^2} - \frac{\mu^{\ddagger 2}}{r^{\ddagger 2}} \right),$$

where k^0 is the reaction rate constant under the conditions accepted as standard ones; ϵ is the dielectric constant of the medium; r and r^\ddagger are the effective dipole radius in the ground and transition states, respectively; μ and μ^\ddagger are the dipole moments of the reactants and transition state, respectively.

The reaction rate constant at 243 K decreases insignificantly with an increase in the dielectric constant of the solvent (the exceptions are tetrachloromethane and ethyl acetate) indicating the lower dipole moment of the transition state compared to the initial reactants (Fig. 3).

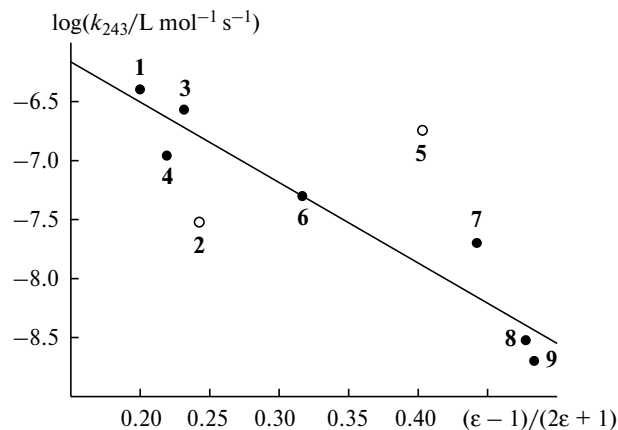


Fig. 3. Dependence of the logarithm of the reaction rate constant on the solvent parameter Y_{243} at 243 K.

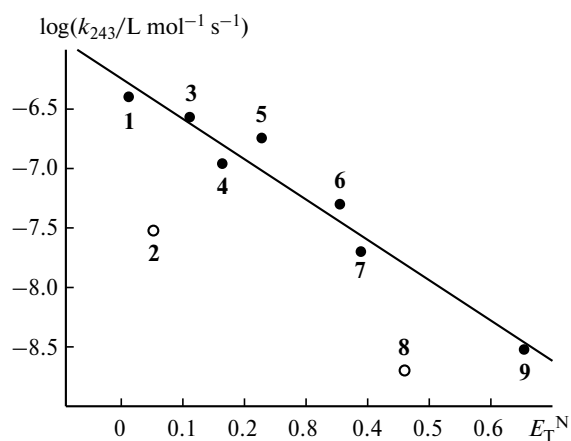


Fig. 4. Dependence of the logarithm of the reaction rate constant on the solvent parameter E_T^N at 243 K.

$$\log k_{243} = -(4.1 \pm 0.3) - (6.9 \pm 0.9) \cdot (\epsilon - 1)(2\epsilon + 1), r = 0.96,$$

$$\left(\frac{\mu_A^2}{r_A^3} + \frac{\mu_B^2}{r_B^3} - \frac{\mu_{\neq 2}^2}{r_{\neq 3}^3} \right) = (3.1 \pm 0.2) \cdot 10^{-31} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}.$$

At 333 K the reaction rate constant does not increase with increasing dielectric constant of the solvent (the exceptions are acetonitrile and ethanol). This also indicates a low-polarity transition state.

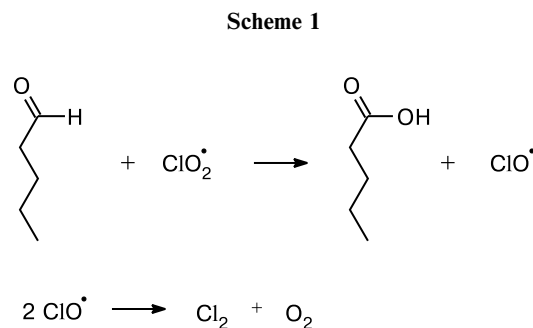
Similar results were obtained by using the empirical parameter of solvent polarity E_T^N that characterizes the electronic transition energy of the betaine dye in the solvent.^{6,7} For 243 K the dependence of $\log k$ on E_T^N turned out to be linear with the correlation coefficient 0.97 (the exceptions are tetrachloromethane and acetonitrile) (Fig. 4)

$$\log k = -(6.3 \pm 0.1) - (3.4 \pm 0.4)E_T^N.$$

The slope of the straight line characterizes the change in the polarity upon the transition from the reactants to the transition state. The negative value shows that the transition state is less polar than the reactants. At 333 K the solvent exerts no effect on the reaction kinetics suggesting a low-polarity of the transition state.

The mechanism of the process is not quite clear, because data on the chemistry of chlorine oxides are

lacking. However, the hypothetical oxidation scheme can be proposed (Scheme 1).



The oxygen atom of chlorine dioxide is inserted at the C—H bond to form acid thus explaining the low value of the activation entropy of the process. The ClO^\bullet radical formed recombines to form chlorine and oxygen.⁸ The formation of Cl_2 is confirmed by the formation of dichlorine derivatives upon the introduction of olefins into the system.

Thus, the possibility of the oxidation of valeraldehyde by chlorine dioxide to the corresponding acid with a high yield in organic solvents was shown for the first time.

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