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Kinetics of Ozone–Olefin Reactions in Aqueous Solutions

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Abstract—The kinetics of the reactions of ozone with 12 substituted olefins in aqueous solutions at 293 K are studied by the stopped-flow method. Second-order rate constants are determined for these reactions. The dependence of the reactivity of olefins in H_2O on their structure can be described by the Taft equation.

The kinetics of ozone–olefin reactions in CCl_4 have been studied in detail [1–8]. These reactions are described by second-order rate equations. At the same time, quantitative data for the interaction between ozone and olefins in aqueous solutions are scarce [9–12].

In this work, the reactivity of several substituted olefins with the general formula $X^1X^2C{=}CX^3X^4$ toward ozone in aqueous solutions was studied by measuring O_3 consumption using the stopped-flow method [13]. The following olefins were studied: acrylonitrile (**1**), 1,2-*cis*-dichloroethene (**2**), 1,2-*trans*-dichloroethene (**3**), trichloroethene (**4**), 1,3-dichlorobutene-2 (**5**), vinylsulfone (**6**), allyl alcohol (**7**), 3-bromopropene (**8**), methacrylic acid (**9**), methyl methacrylate (**10**), 3,4-dichlorobutene-1 (**11**), and 1-hexen-4-ol (**12**).

EXPERIMENTAL

Olefins were purified using a standard procedure [14, 15]. *tert*-Butanol (analytical grade) was boiled over calcined calcium oxide, twice distilled, and multiply recrystallized. Fresh twice-distilled water was used as the solvent.

Reaction kinetics were studied using a setup with a total dead time (interval between the instant the reactants are mixed and the beginning of measurements) not exceeding 5–7 ms. The absorbance of the solution of O_3 was measured at 270 nm for the reason that the absorbances of the olefins and their oxidation products at this wavelength could be neglected [16, 17]. The concentration of O_3 was calculated using a molar absorption coefficient of $\varepsilon = 2700$ l mol^{-1} cm^{-1} [18]. Experimental data were mathematically processed for a 95% confidence interval.

Experiments were carried out at 293 ± 1 K. The initial concentration of an olefin in the reaction mixture ($[Ol]_0$) was chosen from the range of 2×10^{-5} to 1×10^{-2} mol/l with consideration for the olefin's solubility and reactivity. The initial concentration of ozone ($[O_3]_0$) was varied between 0.1×10^{-4} and 7.0×10^{-4} mol/l. It was established by special experiments that the rate at which ozone decomposes in the solvent is negligible as compared to the rates at which it reacts with olefins under the same conditions.

The solubility limits of olefins in water were determined as the onset points of absorption at $\lambda = 450$ nm, which indicated that the system had become heterogeneous and the olefin had stopped dissolving. The solubility of **1**–**12** in H_2O was increased by adding *tert*-butanol. Olefins are soluble in lower alcohols, including *tert*-butanol [19]. The addition of *tert*-butanol was, therefore, expected to increase the solubility of **1**–**12** in water, and this was actually observed: the solubility of olefins in H_2O increased by a factor of 1.5–2 upon addition of 1 wt % (~0.1 mol/l) *tert*-butanol (TB). The rate of ozone consumption in the oxidation of *tert*-butanol (w_{TB}) is at least two orders of magnitude lower than the rate of reaction between O_3 and any olefin examined (w). Indeed, under our experimental conditions (293 K, [TB] = 0.1 mol/l, [Ol] = 1×10^{-3} mol/l, $[O_3] = 1 \times 10^{-4}$ mol/l), the ratio of the rate of the ozone–*tert*-butanol reaction ($k_{TB} = 2 \times 10^{-3}$ l mol^{-1} s^{-1} [20]) to the rate of the ozone–trichloroethene reaction, which is characterized by the lowest rate constant of $k = 24$ l mol^{-1} s^{-1} (Table 1), is

$$\frac{w_{TB}}{w} = \frac{k_{TB}[TB][O_3]}{k[Ol][O_3]} = 0.0083.$$

For the other olefins, which have larger k values (Table 1), this ratio is lower. Thus, the addition of 1 wt % TB to aqueous solutions of **1**–**12** exerts no substantial effect on the overall rate of ozone decomposition but increases the solubility of the olefins in water.

It was, therefore, possible to attain an excess of **1**–**6** over the ozone in the solution ($[Ol]_0 \gg [O_3]_0$), so the reaction could be studied under pseudo-first-order conditions. An excess of **7**–**12** could not be achieved because of the limited solubility of the olefins. In this case, comparable concentrations of the reactants ($[Ol]_0 \cong [O_3]_0$) were reacted.

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† Deceased.

Table 1. Rate constants of ozone–olefin reactions in H_2O at 293 K

No.	Olefin		$k \times 10^{-3}$, l mol^{-1} s^{-1}
	name	formula	
1	Trichloroethene	$Cl_2C{=}CHCl$	0.024 ± 0.004
2	1,2-*cis*-Dichloroethene	*cis*-$ClCH{=}CHCl$	0.234 ± 0.020
3	Vinylsulfone	$CH_2{=}CHSO_2CH{=}CH_2$	0.584 ± 0.042
4	Acrylonitrile	$CH_2{=}CHCN$	0.933 ± 0.075
5	1,2-*trans*-Dichloroethene	*trans*-$ClCH{=}CHCl$	2.87 ± 0.42
6	Methacrylic acid	$CH_2{=}C(CH_3)COOH$	3.47 ± 0.28
7	1,3-Dichlorobutene-2	$ClCH_2CH{=}C(Cl)CH_3$	5.24 ± 0.45
8	3,4-Dichlorobutene-1	$CH_2{=}CHCH(Cl)CH_2Cl$	26.2 ± 3.2
9	Methyl methacrylate	$CH_2{=}C(CH_3)C(O)OCH_3$	33.0 ± 2.8
10	3-Bromopropene	$CH_2{=}CHCH_2Br$	70.0 ± 8.4
11	1-Hexen-4-ol	$CH_2{=}CHCH_2CH(OH)C_2H_5$	200 ± 35
12	Allyl alcohol	$CH_2{=}CHCH_2OH$	210 ± 40

RESULTS AND DISCUSSION

For the oxidation of **1–6** (when $[Ol]_0 \gg [O_3]_0$), the ozone consumption curves can be linearized on first-order reaction coordinates with a correlation coefficient of $r = 0.993$–0.999:

$$\ln([O_3]_0/[O_3]) = k't, \tag{1}$$

where k' is the effective rate constant (s^{-1}). k' increases linearly ($r = 0.995$–0.999) with increasing $[Ol]_0$:

$$k' = k[Ol]_0, \tag{2}$$

which indicates that the reaction is first-order with respect to olefin. Relationships (1) and (2) for acrylonitrile are plotted in Fig. 1.

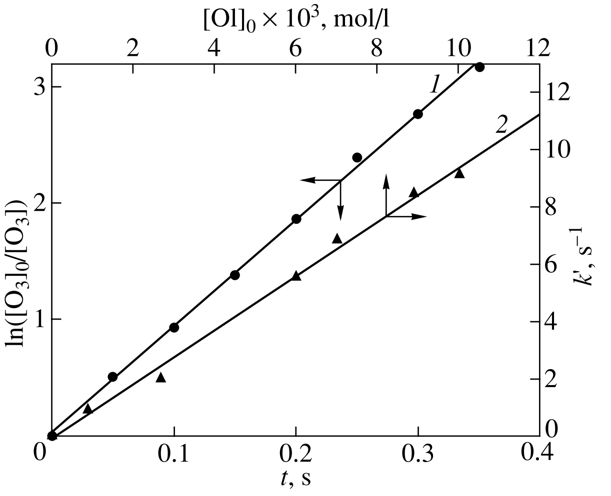

Fig. 1. (*1*) Semilogarithmic anamorphosis of the O_3 consumption curve ($[Ol]_0 = 1 \times 10^{-2}$ mol/l) and (*2*) k' versus $[Ol]_0$ for the reaction of ozone with acrylonitrile at 293 K.

For the oxidation of **7–12** (at $[Ol]_0 \cong [O_3]_0$), the ozone consumption curves fit, with $r = 0.995$–0.999, a rate equation of overall order 2:

$$Y = \ln([Ol]_0/[O_3]_0) + ([Ol]_0 - [O_3]_0)kt, \tag{3}$$

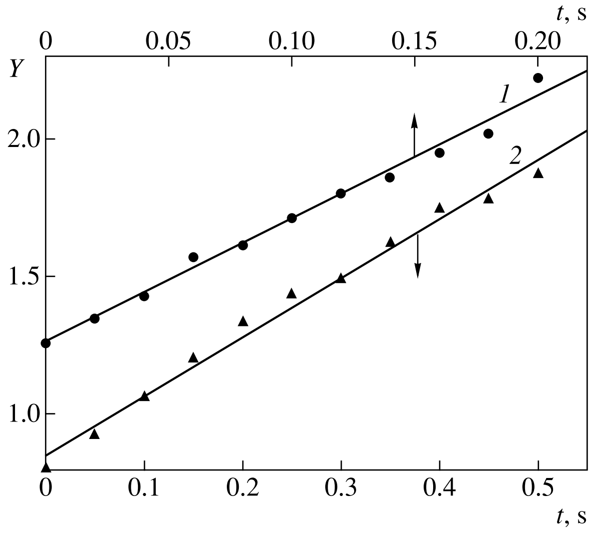

Fig. 2. Y versus t for the reactions of ozone with (*1*) allyl alcohol and (*2*) 3-bromopropene at 293 K: (*1*) $[CH_2{=}CH{-}CH_2OH]_0 = 3 \times 10^{-5}$ mol/l and $[O_3] = 1 \times 10^{-5}$ mol/l; (*2*) $[CH_2{=}CH{-}CH_2Br]_0 = 6 \times 10^{-5}$ mol/l and $[O_3]_0 = 2.7 \times 10^{-5}$ mol/l.

Table 2. Comparison of the rate constants of ozone–olefin reactions in water and CCl_4 at 293 K

No.	Olefin	$\Sigma\sigma^{*(1)}$	$\log k_{H_2O}$	$\log k^{(2)}_{CCl_4}$
1	$Cl_2C{=}CHCl$	8.89	1.380; 1.230 [11]	0.455 [2]; 0.261 [6]; 0.204 [8]
2	$Cl_2C{=}CH_2$	6.74	2.041 [11]	1.266 [2]; 1.377 [6]
3	*cis*-ClCH=CHCl	6.74	2.369	1.465 [2]; 1.281 [6]
4	$CH_2{=}CHSO_2CH{=}CH_2$	5.03	2.766	–
5	$CH_2{=}CHCN$	5.10	2.970	2.076 [6]; 2.362 [8]
6	*trans*-ClCH=CHCl	6.74	3.458	2.709 [2]; 2.672 [6]
7	$CH_2{=}C(CH_3)COOH$	3.92	3.540	–
8	$ClCH_2CH{=}C(Cl)CH_3$	4.30	3.719	–
9	$CH_2{=}CHCHClCH_2Cl$	2.55	4.418	–
10	$CH_2{=}C(CH_3)C(O)OCH_3$	2.98	4.518	4.362 [8]
11	$CH_2{=}CHCH_2Br$	2.47	4.845	4.140 [6]; 4.013 [8]
12	$CH_2{=}CHCH_2CH(OH)C_2H_5$	1.62	5.301	–
13	$CH_2{=}CHCH_2OH$	1.97	5.322	–

(1) The $\Sigma\sigma^*$ values were found using an additive scheme.

(2) The k values determined at 298 K [2] were recalculated to 293 K according to a published procedure [8].

where $Y = \ln\{([Ol]_0 - [O_3]_0 + [O_3])/[O_3]\}$. The plots of Y versus t for allyl alcohol and 3-bromopropene are presented in Fig. 2.

Thus, the rate of ozone consumption in the oxidation of substrates of both groups (**1**–**6** and **7**–**12**) obeys the second-order equation

$$w = -d[O_3]/dt = k[Ol][O_3],$$

where k is the rate constant of the reaction of O_3 with Ol (l mol^{-1} s^{-1}).

In this work, the rate constants k for all of olefins **1**–**12** were determined using Eqs. (1) and (2) or (3) (Table 1). In Table 2, we list the logarithms of k (both as determined in this work and found in the literature) for the reactions of ozone with the olefins in H_2O and CCl_4 and the sums of Taft's inductive constants for substituents X^1, X^2, X^3, and X^4 (the σ^* values were taken from [21–23]). It follows from the data presented in Table 2 that the $\log k$ values for the reactions of O_3 with the olefins in aqueous solutions correlate with the sum of Taft's constants σ^*:

$$\log k_{H_2O} = (6.06 \pm 0.37) - (0.56 \pm 0.07)\Sigma\sigma^*$$

($r = 0.983$, the number of points is $n = 13$, and the rate constant of the reaction between O_3 and 1,2-*trans*-dichloroethene is excluded from the correlation). The negative value of the reaction series constant, $\rho = -0.56 \pm 0.07$, indicates the electrophilic character of ozone in the reaction. This inference is consistent with the negative ρ value for the reaction of O_3 with Ol in the organic solvent CCl_4 [3–5, 7, 8].

Comparison of the rate constants of the reactions of ozone with olefins in H_2O and CCl_4 (Table 2) shows that the reactivity of O_3 toward Ol in an aqueous medium is always higher. Note that a similar situation is observed for ozone–alcohol reactions [24]: the second-order rate constants are larger for water than for CCl_4. This is probably due to the fact that the polar solvent (H_2O) increases the reactivity of polar reactants over their reactivity in the nonpolar solvent (CCl_4).

A linear relationship is observed between the logarithms of the rate constants of the ozone–olefin reactions in water and CCl_4:

$$\log k_{H_2O} = (1.04 \pm 0.14) + (0.883 \pm 0.065)\log k_{CCl_4},$$

where $r = 0.991$ and $n = 17$. This relationship makes it possible to predict the reactivity of O_3 toward Ol in a solvent from the reaction rate constant for another solvent.

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