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Kinetics of the Reactions of Ozone with Substituted Ethylenes

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Abstract—The rate constants of second-order reactions of ozone with 22 substituted ethylenes in CCl_4 solutions at 293 K were determined using the stopped-flow method. An analysis of the experimental results and published data demonstrated that the structure dependence of olefin reactivity can be described in terms of either the Taft equation or the Swain equation.

INTRODUCTION

Previously [1–6], it was found that the interaction of ozone with olefins is a second-order reaction; in this case, the logarithm of the rate constant correlates with the Taft induction constant σ^* [1, 2, 6].

In this work, we studied the kinetics of ozone reactions with 22 substituted ethylenes of the general formula $X^1X^2C{=}CX^3X^4$ using the stopped-flow method [7] based on O_3 consumption. The results were considered in the context of published data [3–6].

EXPERIMENTAL

The reaction kinetics were studied using a setup with the total dead time (from the instant of mixing the reactants to the onset of measurements) no longer than 5–7 ms. The concentration of ozone was determined by photometry on an SF-4A spectrophotometer from the absorbance of the solution at 270–290 nm. At this wavelengths range contributions from the absorption of olefins and their oxidation products can be ignored. Molar absorption coefficients published by Nakagawa *et al.* [8] were used for calculating the concentration of O_3.

The initial concentrations of olefins $[Ol]_0$ in reaction mixtures were chosen (depending on the reactivity) within a range from 1×10^{-4} to 0.25 mol/l; the initial ozone concentration $[O_3]_0$ was varied within the range $(0.5–7.0) \times 10^{-4}$ mol/l. The reaction was performed at 293 ± 1 K; CCl_4 was used as a solvent.

The purification of olefins was performed in accordance with published procedures [9, 10]; CCl_4 was purified as described by Nakagawa *et al.* [8].

RESULTS AND DISCUSSION

All the test olefins react with ozone in accordance with the following second-order rate equation:

$$-d[O_3]/dt = k[Ol][O_3].$$

In particular, this was supported by the results considered below.

At $[Ol]_0 \gg [O_3]_0$, the kinetic curves of ozone consumption are linearized on the coordinates of the first-order equation

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

where $[O_3]$ is the current ozone concentration. As an example, Fig. 1 demonstrates a semilogarithmic anamorphosis of the kinetic curve of ozone consumption in the reaction with 2-chloropropene.

The effective rate constant k' linearly increases with $[Ol]_0$:

$$k' = k[Ol]_0. \qquad (2)$$

This is indicative of a first order reaction with respect to the olefin. Thus, in particular, the values of k' (s^{-1}) for

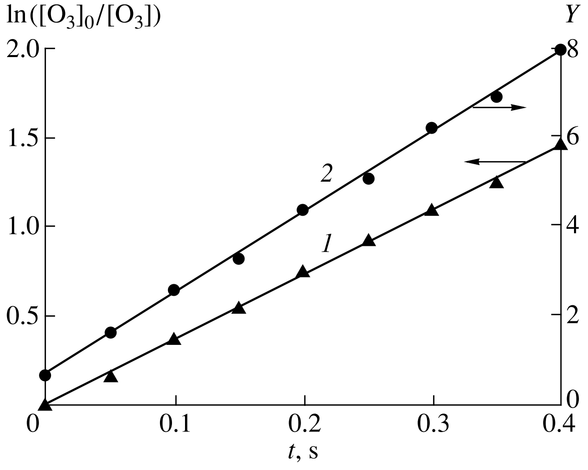

Fig. 1. (*1*) Semilogarithmic anamorphosis of the kinetic curves of ozone consumption in the reaction with 2-chloropropene and (*2*) *Y* as a function of *t* (see Eq. (3)) for the reaction of ozone with 1-decene: (*1*)$[CH_2{=}CClCH_3]_0 = 5 \times 10^{-3}$ mol/l; $[O_3]_0 = 5.2 \times 10^{-4}$ mol/l; (*2*) $[CH_2{=}CHC_8H_{17}]_0 = 3 \times 10^{-4}$ mol/l; $[O_3]_0 = 1.5 \times 10^{-4}$ mol/l.

[†] Deceased.

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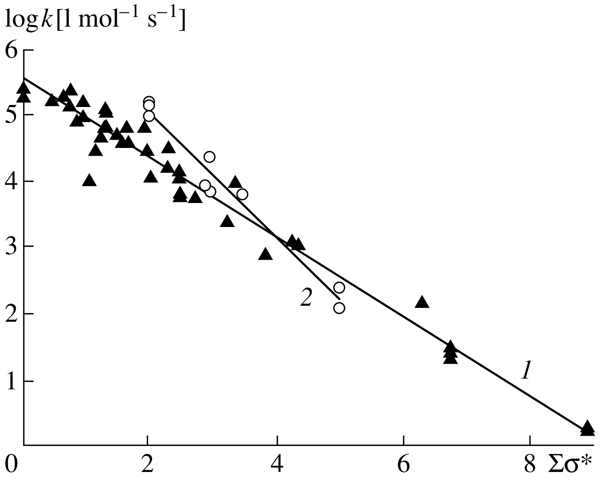

Fig. 2. $\log k$ as a function of the sum of Taft induction constants for the reaction of ozone with olefins from group (*1*) 1 or (*2*) 2.

2-chloropropene are 3.6, 10.8, and 36.4 at the initial concentrations $[\mathrm{Ol}]_0 \times 10^3$ (mol/l) equal to 5.0, 15.0, and 50.0, respectively; that is, the second-order rate constant is $k = (7.2 \pm 0.1) \times 10^2$ l mol^{-1} s^{-1}.

At comparable reactant concentrations, the kinetic curves of ozone consumption are described by the overall second-order equation (curve *2* in Fig. 1)

$$Y = \ln([\mathrm{Ol}]_0/[\mathrm{O}_3]_0) + ([\mathrm{Ol}]_0 - [\mathrm{O}_3]_0)kt, \quad (3)$$

where $Y = \ln\{([\mathrm{Ol}]_0 - [\mathrm{O}_3]_0 + [\mathrm{O}_3])/[\mathrm{O}_3]\}$.

The table summarizes the rate constants k, which were determined with the use of Eqs. (1)–(3), and published data [3–6]. The rate constants are presented in logarithmic form in ascending order (46 olefins and 62 rate constants). The values of k measured by Pryor *et al.* [5, 6] were adjusted to a temperature of 293 K based on the Arrhenius functions found. Williamson and Cvetanovic [3, 4] determined the rate constants at 298 K. To adjust them to a temperature of 293 K, the activation energies E for olefin nos. 1a, 2a, 3a, 4a, 7a, 13a, 36a, and 39a were taken from [5, 6]; E = 2.4 kcal/mol was taken for nos. 34, 35, 40–42, and 45a in accordance with [5, 6]. We also assumed that the activation energies of ozone reactions with olefin nos. 9 and 10 are equal.

An analysis of the results given in the table demonstrated that the kinetic data can be described not only by the Taft equation [11]

$$\log k = \log k_0 + \rho\Sigma\sigma^*, \quad (4)$$

but also by the following equation proposed by Swain *et al.* [12]:

$$\log k = h + f\Sigma F + r\Sigma R, \quad (5)$$

where $\log k_0$, ρ, h, f, and r are constants; $\Sigma\sigma^*$, ΣF, and ΣR are the sums of the induction, nonresonance, and resonance constants of the substituents X^1, X^2, X^3, and X^4, respectively. The values of σ^* were taken from [11, 13, 14], and F and R were taken from [12].

The test olefins can be subdivided into three groups in accordance with the character of correlation in Eqs. (4) and (5).

(1) Olefin nos. 1–5, 8–13, 17–19, 21, 23, 25–38, and 40–45, which contain substituents incapable of conjugation with the reaction center $>$C=C$<$.

For these olefins, we obtained (see Fig. 2)

$$\log k = (5.58 \pm 0.10) - (0.61 \pm 0.03)\Sigma\sigma^* \quad (6)$$

(the coefficient of correlation $r = 0.988$; the number of olefins $n_{\mathrm{Ol}} = 35$; the number of constants $n_k = 44$; constant nos. 1a, 1b, and 2a were excluded from the correlation).

A negative ρ is indicative of the electrophilic character of ozone in this reaction; this fact provides support to the conclusions drawn in previous publications [1, 2, 6].

According to Pryor *et al.* [6], $\rho = -0.83$ (298 K), which is somewhat different from the result obtained in this work. However, Pryor *et al.* [6] used only seven constants for constructing function (6) and the maximum difference between their logarithms was 1.2, whereas this difference was approximately equal to 5 in our case (see, for example, nos. 2b, 2c and 45a, 45b).

The effect of a steric factor on the kinetics of reaction can be illustrated by the example of olefin nos. 1–5, 8–10, 12, 13, 17–19, 23, 25, 28, 29, 31–38, and 40–45:

$$\log k = (5.51 \pm 0.22) - (0.61 \pm 0.03)\Sigma\sigma^* + (2.6 \pm 8.5) \times 10^{-2}\Sigma E_{S'} \quad (7)$$

($r = 0.989$; $n_{\mathrm{Ol}} = 30$; $n_k = 39$; constant nos. 1a, 1b, and 2a were excluded; the values of the steric constant $E_{S'}$ were taken from [15]).

From a comparison of Eqs. (6) and (7), we can conclude that the last term in Eq. (7) acts as a small correction; consequently, steric interactions between the substituents and the reaction center can be ignored in this case.

Equation (5) for the given group of olefins (nos. 1–5, 8, 9, 17, 25, 35, 41, 42, and 45) has the form

$$\log k = (4.20 \pm 0.54) - (2.10 \pm 0.21)\Sigma F - (0.74 \pm 0.51)\Sigma R \quad (8)$$

($r = 0.992$; $n_{\mathrm{Ol}} = 12$; $n_k = 17$; constant nos. 1a, 1b, and 2a were excluded).

(2) Olefin nos. 6, 14–16, 22, 24, and 39, which bear substituents capable of conjugation with the reaction center.

For these olefins, we obtained

$$\log k = (6.98 \pm 0.50) - (0.96 \pm 0.15)\Sigma\sigma^*$$

Rate constants of the reactions of ozone with substituted olefins in CCl_4 solutions at 293 K

No.	Olefin	$\Sigma\sigma^*$	$\Sigma E_{s'}$	ΣF	ΣR	$\log k^*$ [l mol^{-1} s^{-1}]	Reference
1a	$Cl_2C=CCl_2$	11.52	−0.08	2.88	−0.96	−0.138 (0)	[4]
1b	$Cl_2C=CCl_2$	11.5	−0.08	2.88	−0.96	−2.202	[5]
2a	$Cl_2C=CHCl$	8.9	1.06	2.16	−0.72	0.455 (0.556)	[4]
2b	$Cl_2C=CHCl$	8.9	1.06	2.16	−0.72	0.261	[5]
2c	$Cl_2C=CHCl$	8.9	1.06	2.16	−0.72	0.204	**
3a	$Cl_2C=CH_2$	6.74	2.20	1.44	−0.48	1.266 (1.344)	[4]
3b	$Cl_2C=CH_2$	6.74	2.20	1.44	−0.48	1.377	[5]
4a	*cis*-$ClCH=CHCl$	6.74	2.20	1.44	−0.48	1.465 (1.553)	[4]
4b	*cis*-$ClCH=CHCl$	6.74	2.20	1.44	−0.48	1.281	[5]
5	$Cl_2C=CHCH_3$	6.29	1.08	1.43	−0.89	2.126	[5]
6a	$CH_2=CHCN$	5.0	–	0.90	0.71	2.076	[5]
6b	$CH_2=CHCN$	5.0	–	0.90	0.71	2.362	**
7a	*trans*-$ClCH=CHCl$	6.74	–	1.44	−0.48	2.709 (2.772)	[4]
7b	*trans*-$ClCH=CHCl$	6.74	–	1.44	−0.48	2.672	[5]
8	$CH_2=CClCH_3$	3.86	2.22	0.71	−0.65	2.857	**
9	$CH_2=CHBr$	4.27	3.14	0.72	−0.18	3.047	[5]
10	$CH_2=CHCl$	4.35	3.34	0.72	−0.24	3.011 (3.072)	[4]
11	$CH_2=CHSiCl_3$	3.24	–	–	–	3.362	**
12	$CH_2=CHCH_2CN$	2.73	2.47	–	–	3.743	[6]
13a	$CH_2=CHCH_2Cl$	2.50	3.18	–	–	3.998 (4.041)	[4]
13b	$CH_2=CHCH_2Cl$	2.50	3.18	–	–	3.741	[5]
13c	$CH_2=CHCH_2Cl$	2.50	3.18	–	–	3.785	**
14	$CH_2=CHC(O)OCH_3$	3.47	–	–	–	3.792	[5]
15	$CH_2=CCH_3C(O)OCH_2C_6H_5$	2.98	–	–	–	3.845	**
16	$CH_3CH=CHCHO$	2.90	–	–	–	3.934	**
17	$ClCH=C(CH_3)_2$	3.37	1.1	0.70	−1.06	3.941	[5]
18a	$CH_2=CHCH_2Br$	2.47	3.12	–	–	4.140	[5]
18b	$CH_2=CHCH_2Br$	2.47	3.12	–	–	4.013	**
19	$CH_2=C(CH_3)CH_2Cl$	2.03	2.06	–	–	4.041	**
20	*trans*-$(CH_3)_3CHC=CHC(CH_3)_3$	0.38	−0.64	−0.22	−0.58	4.089	[6]
21	$CH_2=CHCH_2OC(O)CH_3$	2.3	–	–	–	4.190	[6]
22	$CH_2=C(CH_3)C(O)OCH_3$	2.98	–	–	–	4.362	**
23	$CH_2=CHCH_2OC_2H_5$	1.99	3.17	–	–	4.417	[6]
24a	$CH_2=CHOC(O)CH_3$	3.47	–	0.70	−0.04	4.460	[6]
24b	$CH_2=CHOC(O)CH_3$	3.47	–	0.70	−0.04	4.398	**
25	$CH_2=CHC(CH_3)_3$	1.17	1.93	−0.11	−0.29	4.461	[6]
26	$CH_2=CHCH_2OC_6H_5$	2.31	–	–	–	4.491	**
27	$CH_2=CHSi(OC_2H_5)_3$	1.59	–	–	–	4.556	**
28	*ortho*-$(HO)C_6H_4CH_2CH=CH_2$	1.67	2.97	–	–	4.580	**
29	$CH_2=CHCH(CH_3)C_2H_5$	1.26	2.36	–	–	4.636	[6]
30	$CH_2=CHCH_2Si(OC_2H_5)_3$	1.51	–	–	–	4.672	**
31	$CH_2=CHCH_2C(CH_3)_3$	1.3	1.73	–	–	4.785	[6]
32	$CH_2=CHCH_2C_6H_5$	1.67	2.97	–	–	4.785	[6]
33	$CH_3CH=CHCH_2Br$	1.95	2.0	–	–	4.799	**

Table. (Contd.)

No.	Olefin	$\Sigma\sigma^*$	$\Sigma E_{s'}$	ΣF	ΣR	$\log k^*$ [l mol^{-1} s^{-1}]	Reference
34	n-$C_3H_7CH{=}CH_2$	0.88	2.16	–	–	4.878 (4.908)	[4]
35	$CH_2{=}C(CH_3)_2$	0.98	2.24	–0.02	–0.82	4.957 (4.987)	[3]
36a	n-$C_4H_9CH{=}CH_2$	1.34	2.97	–	–	4.851 (4.881)	[3]
36b	n-$C_4H_9CH{=}CH_2$	1.34	2.97	–	–	5.011	[5]
36c	n-$C_4H_9CH{=}CH_2$	1.34	2.97	–	–	5.041	**
37	n-$C_8H_{17}CH{=}CH_2$	1.32	3.03	–	–	5.079	**
38	$CH_2{=}CHSi(CH_3)_3$	0.75	1.57	–	–	5.114	**
39a	$CH_2{=}CHC_6H_5$	2.02	–	0.25	–0.37	4.974 (5.013)	[4]
39b	$CH_2{=}CHC_6H_5$	2.02	–	0.25	–0.37	5.189	[5]
39c	$CH_2{=}CHC_6H_5$	2.02	–	0.25	–0.37	5.146	**
40	n-$C_3H_7CH{=}CHCH_3$	0.78	1.93	–	–	5.140 (5.170)	[3]
41	*cis*-$CH_3CH{=}CHCH_3$	0.98	2.24	–0.02	–0.82	5.182 (5.212)	[3]
42	$(CH_3)_2C{=}CHCH_3$	0.49	1.12	–0.03	–1.23	5.193 (5.223)	[3]
43	n-$C_8H_{17}CH{=}CH(CH_2)_7COOH$	0.68	1.6	–	–	5.255	**
44	*cis*-$CH_3CH{=}CHCH(CH_3)_2$	0.79	2.72	–	–	5.361	[6]
45a	$(CH_3)_2C{=}C(CH_3)_2$	0	0	–0.04	–1.64	5.271 (5.301)	[3]
45b	$(CH_3)_2C{=}C(CH_3)_2$	0	0	–0.04	–1.64	5.380	**
46	*trans*-$CH_3CH{=}CHCH(CH_3)_2$	0.79	–	–	–	5.387	[6]

* Original values of $\log k$ (298 K) are given in parentheses.

** This work.

($r = 0.985$; $n_{\mathrm{Ol}} = 6$; $n_k = 9$; constant nos. 24a and 24b were excluded, see Fig. 2) and

$$\log k = (3.73 \pm 0.68) + (8.24 \pm 1.20)\Sigma F - (3.17 \pm 0.76)\Sigma R$$

($r = 0.997$; nos. 6, 24, and 39; $n_k = 7$).

(3) *trans*-Olefins.

The scanty data given in the table did not allow us to perform a correct quantitative analysis of the reaction of ozone with *trans*-olefins. For example, note that the value of $\log k$ for olefin no. 46 lies in the straight line plotted using Eq. (6). At the same time, the rate constants of O_3 reactions with olefin nos. 7 and 20 do not obey Eqs. (6)–(8). In particular, it can be seen in the table that the activity of *trans*-olefin no. 7 is higher than that of its *cis* analog no. 4 by more than one order of magnitude.

The kinetics of ozone reactions with *trans*-olefins was studied in considerable detail by Carles and Fliszar [16], who found that the structure dependence of their reactivity obeys the Taft equation. However, quantitative data obtained in the cited work were questioned more recently by Pryor *et al.* [6].

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