Russian Journal of General Chemistry, Vol. 73, No. 2, 2003, pp. 204–212. Translated from Zhurnal Obshchei Khimii, Vol. 73, No. 2, 2003, pp. 224–232. Original Russian Text Copyright © 2003 by Dvorko, Koshchii, Ponomareva.

Kinetics and Mechanism of Monomolecular Heterolysis of Commercial Organohalogen Compounds: XXXIV.¹ Solvent Effect on the Heterolysis Rate of 1-Chloro-1-methylcyclohexane. Correlation Analysis of Solvation Effects in Heterolysis of 1-Chloro-1-methylcyclohexane and 1-Chloro-1-methylcyclopentane

G. F. Dvorko, I. V. Koshchii, and E. A. Ponomareva

Kievskii Polytekhnicheskii Institut National Technical University of Ukraine, Kiev, Ukraine

Received December 29, 2000

Abstract—The kinetics of heterolysis of 1-chloro-1-methylcyclohexane in 9 protic and 25 aprotic solvents at 25°C were studied by the verdazyl method. The kinetic equation is v = k[RCl] (*E*1 mechanism). The heterolysis rate of 1-chloro-1-methylcyclohexane in protic solvents is two orders of magnitude lower than that of 1-chloro-1-methylcyclopentane, whereas in low-polarity and nonpolar aprotic solvents the rates are close. A correlation analysis was made to reveal the solvation effects in heterolysis of both chlorides in a set of 9 protic and 25 aprotic solvents, and separately in protic and aprotic solvents.

The solvolysis kinetics of 1-chloro-1-methylcyclohexane I in 80% aqueous ethanol was studied in [2, 3]; $k_{25} = 2.94 \times 10^{-6} \text{ s}^{-1}$. This reaction is three times slower than solvolysis of t-BuCl and 125 times slower than solvolysis of 1-chloro-1-methylcyclopentane II. Similar rate ratios were found for ethanolysis of these compounds [4]. The rate of monomolecular heterolysis of a six-membered substrate is always lower than that of its five-membered analog. For example, in solvolysis of 1-methylcycloalkyl p-nitrobenzoates in 80% aqueous acetone, the rate ratio is 39 [5], in solvolysis of 1-chloro-1-phenylcycloalkanes in the same solvent it is 369 [6], and in ethanolysis of 1-bromo-1-methylcycloalkanes it is 104 [1]. The difference in the solvolysis rates of the cyclopentyl and cyclohexyl derivatives is usually accounted for by variation of the internal strain at the sp^3-sp^2 rehybridization of the ring carbon atom [2, 4, 5]. The low solvolysis rate of the six-membered compound is attributed to formation of a carbocationic intermediate in the form of twist conformer A [3].

However, data on solvolysis of allyl dinitrobenzoates of structure **B** in 80% aqueous acetone [7] and on electrophilic addition to methylenecycloalkanes in



 CH_2Cl_2 [8, 9] (in these reactions, formation of the carbocationic intermediate involves no rehybridization) show that variation of the internal strain at rehybridization is not a decisive factor. In the first case, the six-membered substrate is less active than its five-membered analog by a factor of 5; in the second case, it is less active by a factor of 50 in addition of the ditolylcarbenium ion [9] and by a factor of 37 [8] in addition of the phenylanisylcarbenium ion. The high activity of cyclopentyl substrates in these cases is accounted for by a higher stability of the carbocationic intermediate.

In [1, 10, 11], we studied in detail the solvent effect on the heterolysis rates of 1-bromo-1-methylcyclopentane and 1-bromo-1-methylcyclohexane. We found that, in protic solvents, the ratio of the rate constants of solvolysis of the five- and six-membered substrates only weakly depends on the ionizing power

¹ For communication XXXIII, see [1].

of the solvent, being about 10^2 , whereas in aprotic solvents this ratio decreases from 10^2 to about 10^1 in going to γ -butyrolactone (a solvent with a high ionizing power) to chlorobenzene [1]. Correlation analysis of the solvation effects showed that this is due to a higher sensitivity of the five-membered compound to electrostatic and electrophilic solvation.

The solvent effect on the heterolysis rate of chloride II is studied more extensively as compared to I [12, 13]; the rate constants at 25° C have been determined in 12 protic and 26 aprotic solvents.

Monomolecular heterolysis of tertiary derivatives of cycloalkanes occurs as a E1 reaction in aprotic solvents and as E1 + SN1 reaction in protic solvents [1-6, 10-13]. The rate of this reaction is controlled by ionization of the covalent bond, which occus via successive formation of contact, loose, and solvent-separated ion pairs [14].

$$RX \iff R^+X^- \iff R^+ \cdots X^- \iff R^+ |Solv|X^-$$
$$\longrightarrow Reaction products.$$

In the limiting stage, the contact ion pair interacts with the solvent cavity [14, 15]. A loose ion pair is formed, which rapidly transforms into a solventseparated ion pair, which, in turn, rapidly transforms into the reaction products.

The rate of SN1 and E1 reactions is described by a first-order kinetic equation

$$v = k[\mathbf{RX}]. \tag{1}$$

In this work, we studied the solvent effect on the heterolysis rate of chloride I and performed a correlation analysis of solvation effects for chlorides I and II in the same set of solvents.

The reaction kinetics was monitored by the verdazyl method [16], with 1,3,5-triphenylverdazyl **III** as indicator. The reaction occurs as follows:



The verdazyl indicator rapidly and quantitatively

reacts with the solvent-separated ion pair of the substrate, which allows spectrophotometric monitoring of the reaction rate by a decrease in the verdazyl concentration (λ_{max} 720 nm). The reaction yields verdazylium salt **IV** and the verdazyl alkylation product, which rapidly decomposes into 1-methylcyclohexene and leucoverdazyl **V**. Equation (1) satisfactorily describes the reaction rate in all the solvents.

The rate constants of heterolysis of chlorides **I** and **II** (for **II**, data are taken from [13]) in 34 solvents and of *t*-BuCl in 22 solvents [17] are listed in the table together with solvent parameters [15, 18, 19].

The correlation analysis of solvation effects was performed with the Koppel–Palm equation [18] (with the additionally included cohesion energy density δ^2 [19]) [Eq. (2)] and Eq. (3).

$$\log k = a_0 + a_1 \frac{\varepsilon - 1}{2\varepsilon + 1} + a_2 \frac{n^2 - 1}{n^2 + 2} + a_3 E + a_4 B + a_5 \delta^2,$$
(2)

$$\log k = a_0 + a_1 E_T(Z) + a_2 B + a_3 \delta^2.$$
 (3)

Here, ε is the dielectric permittivity of the solvent; *n*, refractive index; *E* and *B*, empirical electrophilicity and nucleophilicity parameters; E_T and *Z*, solvatochromic parameters of the ionizing power of a solvent [15], reflecting its polarity, polarizability, and electrophilicity [20]; $\delta^2 = (\Delta H_m - RT)/V_m$, parameter characterizing the energy of the solvent self-association; ΔH_m , molar heat of vaporization; V_m , molar volume; and a_0-a_5 , empirical coefficients.

The figure illustrating the dependences of $\log k_{\rm I}$, $\log k_{II}$, and $\log k_{t-BuCl}$ on Z and the table show that the heterolysis rates of II and *t*-BuCl similarly vary depending on the ionizing power of the solvent; in all the solvents, the heterolysis rate of **II** is approximately 1.5 orders of magnitude higher than that of *t*-BuCl. The heterolysis rate of \mathbf{I} depends on Z considerably less significantly. The heterolysis of *t*-BuCl is faster than that of **I** only in the most polar solvent, MeOH; in the other alcohols, the rates are similar, and in dipolar aprotic solvents, the heterolysis of t-BuCl is slower than that of **I**; the difference in the heterolysis rates grows with decreasing Z. In polar solvents, heterolysis of **II** is faster than that of **I** by approximately two orders of magnitude, in dipolar aprotic solvents, by one order of magnitude, and in aprotic low-polarity (halobenzenes) and nonpolar (alkylbenzenes, cyclohexane) solvents the rates are similar.

Comparison of the solvent effects on the heterolysis of I, II, and *t*-BuCl shows that the effect of solvation on the heterolysis rate of I is less pronounced as compared to II and *t*-BuCl.

Heterolysis rates of 1-chloro-1-methylcyclohexane I, 1-chloro-1-methylcyclopentane II, and t-BuCl at 25°C in various solvents, in relation to solvent parameters

									E _T ,	Ε,	В,	δ²,
No.	Solvent	$k_{\mathbf{I}} \times \frac{10^{10}}{\mathrm{s}^{-1}}, \mathbf{a}$	–log k _I	–log k _{II}	–log k _{t-BuCl}	ε(20)	n ²⁰ _D	kJ/mol _N	kJ/mol	kJ/mol	kJ/mol	kJ l ⁻¹ mol ⁻¹
1	МеОН	2110 ± 10	6.68	4.74	6.07	32.7	1.3286	350	232	62.3	2.61	941
2	EtOH	533 ± 8	7.27	5.34	7.06	24.3	1.3614	333	217	48.5	2.81	703
3	BuOH	261 ± 4	7.58	5.89	7.28	17.1	1.3992	325	210	43.1	2.76	552
4	HexOH	253 ± 2	7.60	5.80	7.45	12.5	1.4182	320	204	39.7	2.84	485
5	PrOH	223 ± 10	7.65	5.91	7.33	20.3	1.3854	328	212	44.4	2.67	607
6	Cyclo-	181 ± 1	7.74	6.32	8.07	15.0	1.4674	314	196	28.9	2.89	515
	hexanol											
7	<i>i</i> -PrOH	161 ± 1	7.79	5.84	7.83	18.3	1.3773	319	203	33.6	2.82	565
8	t-BuOH	97.8 ± 0.2	8.01	6.38	8.39	10.9	1.3848	298	184	21.8	2.95	460
9	t-AmOH	28.8 ± 0.2	8.54	6.82	8.77	5.80	1.3859	296	175	22.6	2.95	460
10	1,1,2,2-Tetra-	296 ± 1	7.57	6.77	_	8.20	1.4944	269	162	8.8	0.35	418
	chloroethane											
11	DMSO	244 ± 1	7.61	6.13	7.88	48.9	1.4783	294	188	13.4	4.33	636
12	Propylene	202 ± 2	7.69	6.57	8.31	70.0	1.4189	303	195	20.5	2.18	736
	carbonate											
13	CHCl ₃	150 ± 1	7.82	7.37	9.72	4.81	1.4459	264	164	13.8	0.17	341
14	CH ₂ Cl ₂	117 ± 6	7.93	7.49	9.54	9.08	1.4246	269	172	11.3	0.28	408
15	MeCN	105 ± 1	7.98	6.70	8.64	37.5	1.3416	298	193	21.8	1.91	594
16	γ-Butyro-	59.7 ± 0.3	8.22	6.61	8.58	39.0	1.4360	290	185	12.1	2.48	695
	lactone											
17	PhNO ₂	25.0 ± 1	8.60	7.74	9.86	34.8	1.5546	278	176	0.80	0.80	477
18	MeCOEt	23.6 ± 0.4	8.63	8.07	_	18.5	1.3785	268	173	5.4	2.50	362
19	1,2-Dichloro-	18.0 ± 0.1	8.74	7.97	10.64	10.4	1.4451	265	175	12.6	0.48	411
	ethane											
20	Cyclo-	10.0 ± 0.2	9.00	8.35	9.61	18.3	1.4510	271	171	2.1	2.89	431
21	hexanone	7.82 ± 0.01	0.11	8 20	0.61	20.7	1 2599	275	177	00	268	202
$\frac{21}{22}$	PhCN	7.82 ± 0.01 7.26 ± 0.16	9.11	8.20 7.73	10.00	20.7	1.5388	273	176	33	2.08	515
23	PhCl	7.20 ± 0.10 7 30 + 0 03	9 14	9.12	-	23.2 5.62	1.5202	253	157	2.1	0.45	386
24	PhI	6.52 ± 0.27	9.19	8.51	_	4.62	1.6212	255	159	5.4	0.45	418
25	PhCOMe	5.95 ± 0.02	9.23	8.34	10.13	17.4	1.5350	274	173	2.9	2.42	464
26	o-Dichloro-	$5.36\!\pm\!0.2$	9.27	8.84	_	9.80	1.5510	251	159	0.0	0.33	444
	benzene											
27	PhBr	$4.51\!\pm\!0.07$	9.35	9.09	_	5.40	1.5560	253	157	2.1	0.48	423
28	C ₆ H ₆	2.66 ± 0.07	9.58	9.60	—	2.28	1.5011	226	144	8.8	0.57	350
29	PhMe	2.50 ± 0.30	9.60	9.58	—	2.34	1.4969	233	142	5.9	0.69	333
30 21	PhCO ₂ Et	2.00 ± 0.07	9.70	9.26	_	6.02 2.27	1.5052	256	159	5.8 5.0	1./0	392
31 32	p-Aylene	1.92 ± 0.24 1.87 ± 0.02	9.12	9.19	12 70	2.27 1 31	1.4908	230 226	140 145	5.0 0.0	0.81	525 241
32	<i>a</i> -Xylene	1.67 ± 0.02 1.53 ± 0.07	9.75	9.25	12.70	+.34 2 57	1.5527	230 235	145	5.0	0.81	2+1 327
34	Cyclohexane	1.34 ± 0.02	9.88	9.87	_	2.02	1.4262	218	131	0.0	0.01	281
	, source and the second s			,			02			0.0		-01

^a Average of 2-3 determinations. ^b Data of [17].



Effect of the solvent ionizing power Z on (a) $\log k_{II}$, (b) $\log k_{III}$, and (c) $\log k_{t-BuCI}$. The solvent numbering is the same as in the table.

The correlation analysis of solvation effects in heterolysis of **II** using Eqs. (2) and (3) showed [13] that, in protic solvents (n = 12), the effects of the solvent polarity and ionizing power on the reaction rate are positive, and the effect of the nucleophilicity is negative. In aprotic solvents (n = 26), the effects of the solvent polarity, electrophilicity, and ionizing power are positive, and the effect of nucleophilicity is insignificant. However, within a narrower range of fairly nucleophilic aprotic solvents (ketones, nitriles, etc.), the negative effect of nucleophilic solvation can be revealed [21]. A similar pattern of solvation effects is observed in heterolysis of *t*-BuCl [17].

The goal of this study was to elucidate the differences between the solvation effects in heterolysis of **I** and **II**; to this end, we performed a correlation analysis for both chlorides in the same set of solvents.

The values of $\log k_{I}$ and $\log k_{II}$ in 34 solvents show a satisfactory mutual correlation:

 $\log k_{\mathbf{I}} = -(4.13 \pm 0.23) + (0.580 \pm 0.030)\log k_{\mathbf{II}}; R 0.960,$ S 0.253, F 378 (250), n 34.

Here, F is the actual and critical (in parentheses) Fisher test for the confidence level of 95%; since the actual Fisher test exceeds the critical value, the correlation is reliable.

After excluding four polychlorinated organic solvents (nos. 10, 13, 14, 19; here and hereinafter, the solvent numbering is the same as in the table), which are not commonly used in correlation analysis of solvation effects [22], the correlation becomes noticeably better:

$$\log k_{\mathbf{I}} = -(4.26 \pm 0.18) + (0.570 \pm 0.023)\log k_{\mathbf{II}}; R \ 0.978,$$

S 0.195, F 602 (249), n 30.

It is seen that, in this set of solvents, the logarithm of the heterolysis rate constant of the five-membered

substrate is by a factor of 1.8 more sensitive to the solvent effect as compared to the six-membered sub-strate.

The correlation between $\log k_{II}$ and $\log k_{t-BuCl}$ in 22 solvents (see table) is also satisfactory, but the Fisher test shows that the dependence is not sufficiently reliable.

$$\log k_{\mathbf{II}} = -(0.590 \pm 0.461) + (0.720 \pm 0.052) \log k_{t-\text{BuCl}};$$

$$R \ 0.952, \ S \ 0.359, \ F \ 192 \ (240), \ n \ 22.$$

The correlation between $\log k_{\rm I}$ and $\log k_{t-{\rm BuCl}}$ is bad (*R* 0.889). A satisfactory correlation is obtained only after exclusion of the five most outlying points (nos. 13, 14, 20, 21, 25).

$$\log k_{\mathbf{I}} = -(4.36 \pm 0.307) + (0.435 \pm 0.036) \log k_{t-\text{BuCl}};$$

R 0.953, S 0.230, F 148 (246), n 17.

Thus, the logarithm of the heterolysis rate constant of *t*-BuCl is more sensitive to the solvent effects by a factor of 1.4 as compared to **II** and by a factor of 2.3 as compared to **I**.

Application of Eqs. (2) and (3) to 34 solvents gives similar dependences. After exclusion of four polychlorinated organic solvents, Eq. (3) gives the following correlations:

$$\log k_{\mathbf{I}} = -(14.6 \pm 0.6) + (0.0191 \pm 0.0030)Z + (0.0242 \pm 0.0580)B + (0.00134 \pm 0.00100)\delta^{2};$$

R 0.966, S 0.250, F 120 (8.64), n 30.

$$\log k_{\mathbf{II}} = -(18.2 \pm 0.7) + (0.0343 \pm 0.0040)Z + (0.148 \pm 0.072)B + (0.00143 \pm 0.00100)\delta^{2};$$

R 0.982, S 0.312, F 234 (8.64), n 30.

The errors for the coefficients at the solvent nucleophilicity and cohesion parameters show that the effect of these parameters is insignificant. Indeed, exclusion of these parameters makes the correlations only slightly worse:

$$\log k_{\mathbf{I}} = -(15.4 \pm 0.4) + (0.0243 \pm 0.0010)Z; R 0.958,$$

S 0.265, F 315 (249), n 30.

$$\log k_{\mathbf{II}} = -(19.5 \pm 0.5) + (0.0426 \pm 0.0020)Z;$$

R 0.978, S 0.335, F 602 (249), n 30.

The logarithm of the heterolysis rate constant of II in a set of 9 protic and 21 aprotic solvents is by a factor of 1.8 more sensitive to the solvent ionizing power as compared to heterolysis of I.

Application of Eq. (2) to 30 solvents gives satisfactory five-parameter correlations:

$$\begin{split} \log k_{\mathbf{I}} &= -(11.2\pm0.6) + (2.71\pm0.98)f(\varepsilon) + (0.468\pm1.88)f(n) \\ &+ (0.0285\pm0.0050)E + (0.0772\pm0.0730)B \\ &+ (0.00149\pm0.00100)\delta^2; \ R \ 0.963, \ S \ 0.269, \\ & F \ 61.8 \ (4.53), \ n \ 30. \\ \\ \log k_{\mathbf{II}} &= -(12.5\pm0.9) + (5.25\pm1.43)f(\varepsilon) + (1.98\pm2.76)f(n) \\ &+ (0.0491\pm0.0080)E + (0.262\pm0.107)B \\ &+ (0.00177\pm0.00100)\delta^2; \ R \ 0.973, \ S \ 0.394, \\ & F \ 86.2 \ (4.53), \ n \ 30. \end{split}$$

Here, $f(\varepsilon) = (\varepsilon - 1)/(2\varepsilon + 1)$ and $f(n) = (n^2 - 1) \times (n^2 + 2)^{-1}$.

The effects of the polarizability, nucleophilicity, and cohesion parameters are insignificant; their exclusion only slightly affects the regression coefficients.

$$\log k_{\mathbf{I}} = -(11.0 \pm 0.2) + (4.36 \pm 0.64)f(\varepsilon) + (0.0364 \pm 0.0030)E; R 0.954, S 0.282, F 138 (19.5), n 30.$$
$$\log k_{\mathbf{II}} = -(12.0 \pm 0.4) + (8.30 \pm 1.00)f(\varepsilon)$$

+ $(0.0597 \pm 0.0050)E$; R 0.964, S 0.429, F 179 (19.5), n 30.

Thus, the heterolysis rate of \mathbf{I} and \mathbf{II} in a set of 9 protic and 21 aprotic solvents depends on the solvent ionizing power or (which actually is the same [20]) on the solvent polarity and electrophilicity; the logarithm of the heterolysis rate constant of \mathbf{II} , as compared to \mathbf{I} , is more sensitive to the polarity parameter by a factor of 1.9 and to the electrophilicity parameter by a factor of 1.6.

In 25 aprotic solvents, the correlation between $\log k_{II}$ and $\log k_{III}$ is approximate. After exclusion of polychlorinated organic solvents, the following correlation is obtained:

 $\log k_{\mathbf{I}} = -(4.250 \pm 0.327) + (0.570 \pm 0.038) \log k_{\mathbf{II}}; R \ 0.959,$

S 0.200, F 220 (249), n 21.

Aprotic solvents affect the logarithm of the heterolysis rate constant of **II** by a factor of 1.75 more strongly as compared to **I**.

Application of Eqs. (2) and (3) to correlation analysis of solvation effects in 25 aprotic solvents leads to unsatisfactory results. After exclusion of polychlorinated organic solvents, Eq. (3) gives the following correlations:

+

$$\log k_{\mathbf{I}} = -(13.5 \pm 1.2) + (0.0128 \pm 0.0070)Z$$

$$+ (0.0475 \pm 0.0710)B + (0.00235 \pm 0.00100)\delta^{2};$$

$$R \ 0.928, \ S \ 0.279, \ F \ 35.4 \ (8.64), \ n \ 21.$$

$$\log k_{\mathbf{II}} = -(16.0 \pm 1.4) + (0.0215 \pm 0.0070)Z$$

$$+ (0.173 \pm 0.077)B + (0.00384 \pm 0.00100)\delta^{2};$$

$$R \ 0.971, \ S \ 0.302, \ F \ 93.1 \ (8.64), \ n \ 21.$$

Similar correlations were obtained with another parameter of the ionizing power:

$$\log k_{\mathbf{I}} = -(13.0 \pm 0.9) + (0.0169 \pm 0.0080)E_T$$

+ (0.0479 \pm 0.0690)B + (0.00241 \pm 0.00100)\delta^2;
R 0.930, S 0.276, F 36.0 (8.64), n 21.
$$\log k_{\mathbf{II}} = -(15.2 \pm 1.0) + (0.0293 \pm 0.0090)E_T$$

+ (0.169 \pm 0.073)B + (0.00382 \pm 0.00100)\delta^2;
R 0.973, S 0.290, F 101 (8.64), n 21.

In these cases, the effect of the solvent nucleophilicity is insignificant; exclusion of this parameter only slightly affects the correlation quality.

$$\begin{split} \log k_{\mathbf{I}} &= -(14.0 \pm 1.0) + (0.0154 \pm 0.0050)Z \\ &+ (0.00209 \pm 0.00100)\delta^2; \ R \ 0.926, \ S \ 0.274, \\ F \ 54.5 \ (19.4), \ n \ 21. \\ \log k_{\mathbf{II}} &= -(17.8 \pm 1.2) + (0.0309 \pm 0.0060)Z \\ &+ (0.00289 \pm 0.00100)\delta^2; \ R \ 0.962, \ S \ 0.335, \\ F \ 112 \ (19.4), \ n \ 21. \\ \log k_{\mathbf{I}} &= -(13.3 \pm 0.8) + (0.0201 \pm 0.0070)E_T \\ &+ (0.00217 \pm 0.00100)\delta^2; \ R \ 0.927, \ S \ 0.272, \\ F \ 55.4 \ (19.4), \ n \ 21. \\ \log k_{\mathbf{II}} &= -(16.4 \pm 0.9) + (0.0408 \pm 0.0080)E_T \\ &+ (0.00299 \pm 0.00100)\delta^2; \ R \ 0.965, \ S \ 0.324, \\ F \ 120 \ (19.4), \ n \ 21. \end{split}$$

The effect of the ionizing power and cohesion of aprotic solvents on the logarithm of the heterolysis rate constant of **II**, compared to **I**, is stronger by factors of 2 and 1.4, respectively.

The effect of the cohesion of aprotic solvents is relatively weak; exclusion of this parameter only slightly affects the correlation quality, but the resulting one-parameter correlations are insufficiently reliable according to the Fisher test.
$$\begin{split} \log k_{\mathbf{I}} &= -(15.6 \pm 0.7) + (0.0252 \pm 0.0030) Z; \\ R & 0.907, S & 0.298, F & 88.3 & (246), n & 21. \\ \log k_{\mathbf{II}} &= -(20.0 \pm 0.9) + (0.0444 \pm 0.0030) Z; \\ R & 0.950, S & 0.374, F & 175 & (246), n & 21. \\ \log k_{\mathbf{I}} &= -(14.6 \pm 0.6) + (0.0335 \pm 0.0040) E_T; \\ R & 0.905, S & 0.301, F & 86.2 & (246), n & 21. \\ \log k_{\mathbf{II}} &= -(18.1 \pm 0.7) + (0.0592 \pm 0.0040) E_T; \\ R & 0.950, S & 0.372, F & 177 & (246), n & 21. \end{split}$$

In these cases, the ionizing power of aprotic solvents affects the logarithm of the heterolysis rate constant of II by a factor of 1.8 more strongly as compared to I.

Application of Eq. (2) to 21 aprotic solvents gives five-parameter correlations:

$$\log k_{\mathbf{I}} = -(10.9 \pm 0.7) + (2.16 \pm 1.25)f(\varepsilon) - (0.644 \pm 2.60)f(n) + (0.0321 \pm 0.0220)E + (0.0304 \pm 0.080)B + (0.00226 \pm 0.00100)\delta^{2}; R 0.936, S 0.280, F 21.4 (4.60), n 21.
$$\log k_{\mathbf{II}} = -(11.9 \pm 0.8) + (3.66 \pm 1.43)f(\varepsilon) - (1.20 \pm 2.99)f(n) + (0.0246 \pm 0.0250)E (0.155 \pm 0.092)B + (0.00461 \pm 0.00100)\delta^{2}; R 0.971, S 0.322, F 49.1 (4.60), n 21.$$$$

The effects of the nucleophilicity and polarizability parameters are insignificant; exclusion of these parameters only slightly affects the correlation quality.

$$\begin{split} \log k_{\mathbf{I}} &= -(11.1\pm0.3) + (2.64\pm0.92)f(\varepsilon) \\ &+ (0.0391\pm0.0150)E + (0.00188\pm0.00100)\delta^2; \\ R & 0.935, \ S & 0.266, \ F & 39.3 & (8.69), \ n & 21. \\ \log k_{\mathbf{II}} &= -(12.4\pm0.3) + (5.50\pm1.18)f(\varepsilon) \\ &+ (0.0457\pm0.019)E + (0.00345\pm0.00100)\delta^2; \\ R & 0.962, \ S & 0.344, \ F & 70.4 & (8.69), \ n & 21. \end{split}$$

In aprotic solvents, polarity, electrophilicity, and cohesion affect the logarithm of the heterolysis rate constant of **II** more strongly as compared to **I** by factors of 2.1, 1.2, and 1.8, respectively.

In nine protic solvents, the correlation of $\log k_{\rm II}$ with $\log k_{\rm II}$ is satisfactory.

$$\log k_{\mathbf{I}} = -(2.89 \pm 0.47) + (0.808 \pm 0.080) \log k_{\mathbf{II}};$$

R 0.967, *S* 0.137, *F* 102 (237), *n* 9.

The effect of protic solvents on the heterolysis rate constant of II as compared to I is stronger by a factor of 1.25.

Application of Eq. (3) to nine protic solvents gives satisfactory three-parameter correlations:

$$\begin{split} \log k_{\mathbf{I}} &= -(23.3\pm6.5) + (0.0340\pm0.0110)Z + (1.60\pm1.28)B \\ &+ (0.000578\pm0.00100)\delta^2; \ R \ 0.964, \\ S \ 0.171, \ F \ 21.7 \ (9.01), \ n \ 9. \\ \\ \log k_{\mathbf{II}} &= -(23.3\pm7.4) \ + \ (0.0368\pm0.0130)Z \\ &+ \ (1.78\pm1.43)B \ + \ (0.00107\pm0.00100)\delta^2; \\ R \ 0.968, \ S \ 0.192, \ F \ 24.8 \ (9.01), \ n \ 9. \end{split}$$

In protic solvents, the effects of cohesion and nucleophilicity are insignificant. Their exclusion only slightly affects the correlation coefficients, but the correlations become insufficiently reliable.

$$\begin{split} \log k_{\mathbf{I}} &= -(16.8 \pm 1.2) + (0.0286 \pm 0.0040)Z; \\ R & 0.949, S & 0.171, F & 62.8 & (237), n & 9. \\ \log k_{\mathbf{II}} &= -(16.9 \pm 1.4) + (0.0342 \pm 0.0040)Z; \\ R & 0.950, S & 0.202, F & 64.5 & (237), n & 9. \\ \log k_{\mathbf{I}} &= -(13.4 \pm 0.7) + (0.0282 \pm 0.0030)E_T; \\ R & 0.957, S & 0.157, F & 75.6 & (237), n & 9. \\ \log k_{\mathbf{II}} &= -(12.7 \pm 0.8) + (0.0337 \pm 0.0040)E_T; \\ R & 0.955, S & 0.191, F & 72.9 & (237), n & 9. \end{split}$$

The ionizing power of protic solvents affects the heterolysis rate constant of II by a factor of 1.2 more strongly compared to I.

Application of Eq. (2) to nine protic solvents gives satisfactory two-parameter correlations:

 $\log k_{\mathbf{I}} = -(11.6 \pm 1.2) + (6.78 \pm 3.07) f(\varepsilon)$

+ $(0.0246 \pm 0.0070)E$; R 0.960, S 0.164, F 35.0 (19.3), n 9.

$$\log k_{\rm II} = -(9.60 \pm 1.48) + (5.29 \pm 3.79)f(\varepsilon)$$

+ $(0.0349 \pm 0.0080)E$; R 0.957, S 0.203, F 32.6 (19.3), n 9.

The polarity of protic solvents affects the heterolysis rate constant of \mathbf{I} by a factor of 1.3 more strongly compared to \mathbf{II} , whereas the effect of electrophilicity is stronger (by a factor of 1.4) in the case of \mathbf{II} . Hence, the stronger effect of the ionizing power of a protic solvent on the heterolysis rate of \mathbf{II} is due to the electrophilic assistance effect exerted by the solvent.

The higher sensitivity of **II** to the electrophilicity

of protic solvents and polarity of aprotic solvents may be due to weaker conformational effects in formation of the transition state from **II**. Indeed, the initial envelope conformer of **II** only slightly differs in the geometry from the nearly planar carbocationic transition state, whereas the initial *chair* conformer of **I** strongly differs from the carbocationic twist conformer [23]. As for the stronger effect of the polarity of protic solvents on the heterolysis rate of **I** compared to **II**, this is difficult to explain. Presumably, the electrostatic solvation in these solvents strongly shifts the conformational equilibrium toward the *twist* conformer.

In protic solvents, the heterolysis rate of both substrates is independent of the solvent nucleophilicity. This is due to the fact that as protic solvents we used aliphatic alcohols only; their nucleophilicity (parameter *B*) varies in a narrow range, 2.61-2.95 kJ mol⁻¹. In [13], along with aliphatic alcohols, we also considered AcOH (*B* 1.66 kJ mol⁻¹) and CF₃CH₂OH (*B* 1.3 kJ mol⁻¹) and revealed a decrease in the reaction rate with increasing nucleophilicity of the solvent:

$$\log k_{II} = -(7.25 \pm 1.68) + (16.4 \pm 3.6)f(\varepsilon)$$

- (2.14 ±0.21)B; R 0.964, S 0.375, F 58.9 (19.3), n 12.
$$\log k_{II} = -(15.4 \pm 3.1) + (0.0381 \pm 0.0080)Z$$

- (0.948 ±0.300)B; R 0.969, S 0.347, F 69.4 (19.3), n 12.

In the set of protic solvents considered here, *B* approximately correlates with both the electrophilicity parameter and the parameter of the solvent ionizing power:

$$B = (3.12 \pm 0.055) - (0.00814 \pm 0.001)E;$$

$$R \ 0.914, \ S \ 0.0506, \ F \ 35.5 \ (237), \ n \ 9.$$

$$B = (4.84 \pm 0.342) - (0.00635 \pm 0.001)Z;$$

$$R \ 0.914, \ S \ 0.0506, \ F \ 35.4 \ (237), \ n \ 9.$$

This correlation explains why the heterolysis rate of both substrates in our set of protic solvents depends only on Z (or E_T) or on $f(\varepsilon)$ and E.

The negative effect of nucleophilic solvation is more clearly revealed in a set consisting of equal numbers of protic and aprotic solvents [1, 13, 17]. In a set of seven protic (nos. 1–3, 5–7, 9) and seven aprotic solvents (nos. 12, 15–17, 20–22), we obtain the following correlation:

 $\log k_{\rm I} = -(3.75 \pm 0.38) + (0.653 \pm 0.057) \log k_{\rm II};$ R 0.957, S 0.220, F 132 (244), n 14.

Application of Eq. (3) to these 14 solvents gives

good three-parameter correlations [in this set of solvents, there is no correlation between B and the other solvent parameters appearing in Eqs. (2) and (3)].

$$\log k_{\mathbf{I}} = -(15.8 \pm 0.6) + (0.0240 \pm 0.0030)Z$$

- (0.108 ± 0.090)B + (0.00120 ± 0.00010)δ²;
R 0.981, S 0.163, F 84.1 (8.81), n 14.
$$\log k_{\mathbf{II}} = -(18.3 \pm 1.0) + (0.0360 \pm 0.0050)Z$$

- (0.0135 ± 0.137)B + (0.00133 ± 0.00100)δ²;
R 0.979, S 0.248, F 77.6 (8.81) n 14.

The negative sign of the coefficient at the nucleophilicity parameter in these equation and the positive sign of the coefficient at the cohesion parameter are indicative of the negative effect of nucleophilic solvation [14]. However, the nucleophilicity parameter is of low significance (see above); its exclusion has no noticeable effect on the correlation quality.

$$\log k_{\mathbf{I}} = -(15.6 \pm 0.6) + (0.0221 \pm 0.0030)Z + (0.00141 \pm 0.00010)\delta^2; R 0.978, S 0.166, F 120 (19.4), n 14.$$
$$\log k_{\mathbf{II}} = -(18.3 \pm 0.9) + (0.0358 \pm 0.0040)Z + (0.00136 \pm 0.00100)\delta^2; R 0.979, S 0.237, F 128 (19.4), n 14.$$

Cohesion affects the logarithms of the heterolysis rate constants of both substrates to approximately equal extent, whereas the effect of the solvent ionizing power is stronger by a factor of 1.6 in the case of **II**.

Exclusion of the cohesion parameter makes the correlations appreciably worse; they remain satisfactory but become insufficiently reliable.

$$\log k_{\mathbf{I}} = -(16.5 \pm 0.7) + (0.0278 \pm 0.0020)Z;$$

R 0.957, S 0.220, F 132 (244), n 14.

$$\log k_{\mathbf{II}} = -(19.2 \pm 0.9) + (0.0414 \pm 0.0030)Z;$$

R 0.970, S 0.269, F 193 (244), n 14.

In this case, the solvent ionizing power affects the heterolysis rate constant of **II** by a factor of 1.5 more strongly compared to **I**.

Application of Eq. (2) to 14 solvents gives satisfactory five-parameter correlations:

$$\log k_{\mathbf{I}} = -(10.9 \pm 2.0) + (2.05 \pm 3.69)f(\varepsilon) + (1.75 \pm 2.99)f(n) + (0.0309 \pm 0.0070)E - (0.0644 \pm 0.173)B + (0.00140 \pm 0.00100)\delta^2; R 0.961, S 0.257, F 19.5 (4.82), n 14.$$

$$\log k_{II} = -(8.31 \pm 2.73) - (3.34 \pm 4.92)f(\varepsilon) + (3.45 \pm 3.98)f(n) + (0.0458 \pm 0.0090)E - (0.0470 \pm 0.231)B + (0.00228 \pm 0.00100)\delta^{2}; R 0.968, S 0.342, F 23.9 (4.82), n 14.$$

The effects of polarity, polarizability, and nucleophilicity are insignificant; exclusion of these parameters only slightly affects the correlation quality:

$$\log k_{I} = -(9.79 \pm 0.30) + (0.00254 \pm 0.0050)E$$

+ (0.00185 \pm 0.00100)\delta^2; R 0.954, S 0.238,
F 56.0 (19.4), n 14.
$$\log k_{II} = -(8.83 \pm 0.40) + (0.0428 \pm 0.0060)E$$

+ (0.00193 \pm 0.00100)\delta^2; R 0.962, S 0.317,
F 69.1 (19.4), n 14.

Here, cohesion affects the logarithms of the heterolysis rate constants of both substrates to approximately equal extent, whereas the effect of electrophilicity is by a factor of 1.7 stronger in the case of **II**.

Thus, variation of the ratio of the heterolysis rates of **II** and **I** in the range from ~100 in polar solvents to 1 in nonpolar solvents is due to specific features of solvation effects in heterolysis of **I**, namely, to lower sensitivity of the heterolysis rate of **I** to electrostatic and especially electrophilic solvation, which, in turn, is associated with conformational features. For example, the ionizing power of aprotic and protic solvents affects the logarithm of the heterolysis rate constant of **II**, compared to **I**, more strongly by factors of 1.8 and 1.2, respectively; both the polarity and electrophilicity of aprotic solvents exert a stronger effect on **II** also. At the same time, in protic solvents, polarity affects more strongly the heterolysis of **I**, and electrophilicity, the heterolysis of **II**.

1-Chloro-1-methylcyclohexane was prepared and purified according to [2]; bp 42°C (15 mm), n_D^{20} 1.4578; published data [2]: bp 83–84°C (100 mm). The other chemicals and solvents were prepared and purified as described in [1, 13]. The kinetic experiments were performed in a temperature-controlled cell of an SF-26 spectrophotometer. The concentration of **I** in kinetic runs was 0.01–0.8 M, and that of the verdazyl indicator, $(1-2) \times 10^{-4}$ M. The degree of substrate conversion in kinetic runs was 0.01–0.0005%. Calculation with Eqs. (2) and (3) were performed by the least-squares method using Spss program package; confidence range 95%.

212

REFERENCES

- 1. Dvorko, G.F., Koshchii, I.V., and Ponomareva, E.A., *Zh. Obshch. Khim.*, 2003, vol. 73, no. 1, p. 110.
- Brown, H.C. and Borkowski, M., J. Am. Chem. Soc., 1952, vol. 74, no. 8, p. 1894.
- Ranganayakulu, K., Vasamathi Devi, M., Balaji Rao, R., and Rajeswari, K., *Can. J. Chem.*, 1980, vol. 58, no. 6, p. 1484.
- Le, N.G. and Felkin, M.H., C. R. Acad. Sci., 1959, vol. 248, no. 13, p. 2021.
- 5. Peters, E.N. and Brown, H.C., J. Am. Chem. Soc., 1975, vol. 97, no. 10, p. 2892.
- 6. Tahida, H. and Tsuchima, T., J. Am. Chem. Soc., 1970, vol. 92, no. 11, p. 3397.
- 7. Richey, H.G., Fletcher, R., and Overmoyer, R.G., *Tetrahedron Lett.*, 1970, vol. 11, no. 20, p. 3703.
- Roth, M., Shade, Ch., and Mayr, H., J. Org. Chem., 1994, vol. 59, no. 1, p. 169.
- Mayr, H. and Pock, R., *Chem. Ber.*, 1986, vol. 119, no. 10, p. 2473.
- Dvorko, G.F., Vasil'kevich, A.I., Ponomareva, E.A., and Koshchii, I.V., *Zh. Obshch. Khim.*, 2000, vol. 70, no. 5, p. 776.
- Ponomareva, E.A., Koshchii, I.V., Pervishko, T.L., and Dvorko, G.F., *Zh. Obshch. Khim.*, 2000, vol. 70, no. 6, p. 973.
- 12. Takeuchi, K., Ohga, Y., Ushino, T., and Takasuka, M., *J. Phys. Org. Chem.*, 1997, vol. 10, no. 4, p. 717.

- Dvorko, G.F., Koshchii, I.V., Prokopets, A.M., and Ponomareva, E.A., *Zh. Obshch. Khim.*, 2002, vol. 72, no. 11, p. 1902.
- Dvorko, G.F., Ponomarev, N.E., and Ponomareva, E.A., *Zh. Obshch. Khim.*, 1999, vol. 69, no. 11, p. 1835.
- 15. Reichardt, Ch., Solvents and Solvent Effects in Organic Chemistry, Weinheim: VCH, 1988.
- 16. Dvorko, G.F. and Ponomareva, E.A., Usp. Khim., 1991, vol. 60, no. 10, p. 2089.
- 17. Dvorko, G.F., Zaliznyi, V.V., and Ponomarev, N.E., *Zh. Obshch. Khim.*, 2002, vol. 72, no. 10, p. 1644.
- Palm, V.A., Osnovy kolichestvennoi teorii organicheskikh reaktsii (Principles of the Quantitative Theory of Organic Reactions), Moscow: Khimiya, 1977.
- 19. Makitra, R.G. and Pirig, Ya.N., Zh. Obshch. Khim., 1986, vol. 56, no. 3, p. 657.
- Marcus, Y., J. Solution Chem., 1991, vol. 20, no. 2, p. 929.
- Dvorko, G.F., Koshchii, I.V., Prokopets, A.M., and Ponomareva, E.A., *Zh. Obshch. Khim.*, 2002, vol. 72, no. 12, p. 1989.
- Abraham, M.H., Doherty, M.R., Kamlet, M.J., Harris, J.M., and Taft, R.W., *J. Chem. Soc.*, *Perkin Trans.* 2, 1987, no. 3, p. 913.
- 23. Isaacs, N.S., *Physical Organic Chemistry*, New York: Wiley, 1992.