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Kinetics and Mechanism of Monomolecular Heterolysis of Commercial Organohalogen Compounds: XXXV.[1] Solvation Effects on the Activation Parameters of Heterolysis of 1-Bromo-1-methylcyclopentane and 1-Bromo-1-methylcyclohexane. Correlation Analysis of Solvation Effects

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Abstract — Kinetics of heterolysis of 1-bromo-1-methylcyclopentane and -cyclohexane in protic and aprotic solvents were studied. Correlation analysis of the effect of solvent parameters on $\Delta G^{\neq}$, $\Delta H^{\neq}$, and $\Delta S^{\neq}$ was performed.

Some data are available in current literature regarding the effect of solvents on the rate of heterolysis of 1-bromo-1-methylcyclopentane (**I**) and 1-bromo-1-methylcyclohexane (**II**) at 25°C. Heterolysis of bromide **I** have been studied in 11 protic and 31 aprotic solvents [2, 3], and heterolysis of bromide **II**, in 10 protic and 29 aprotic solvents [3, 4]. In aprotic solvents these reaction occur by the E1 mechanism and in protic, by the SN1 + E1 mechanism, and their rate is described by the first-order kinetic equation (1).

$$v = k[\mathrm{RBr}]. \qquad (1)$$

The rate of SN1 and E1 reactions is determined by ionization of the covalent bond, which involves consecutive formation of three ion pairs: contact, loose, and solvent-separated [5].

$$\mathrm{RX} \rightleftharpoons \mathrm{R^+X^-} \rightleftharpoons \mathrm{R^+\cdots X^-} \rightleftharpoons \mathrm{R^+ \,|\, \mathit{Solv} \,|\, X^-}$$

$$\longrightarrow \text{Reaction products}$$

In the limiting stage, the contact ion pair of the substrate interacts with the solvent void [5, 6] to form the loose ion pair which fast converts into the solvent-separated ion pair; finally, the latter fast converts into reaction products.

Correlation analysis of solvation effects in heterolysis of bromides **I** and **II** in terms of linear free energy equations showed that the reaction rate in aprotic solvents is fairly described by the ionizing ability or polarity and electrophilicity solvent parameters; therewith, these parameters exert a stronger rate effect with the five-membered substrate compared with six-membered [2, 3]. The reaction rate in protic solvents is described by the polarity, electrophilicity, and polarizability parameters, and, therewith, polarizability adversely affects the reaction rate, providing evidence for a negative nucleophilic solvation effect [5]. The polarity of a protic solvent exerts a stronger effect on the rate of heterolysis of bromide **II**, while electrophilicity, of bromide **I**. In aprotic solvents, the effect of solvent polarity is stronger in aprotic solvents and of solvent electrophilicity, in protic. The ionizing ability of a protic solvent only slightly affects the ratio of the rate constants of the five- and six-membered substrates, $k_{\mathbf{I}} : k_{\mathbf{II}} \approx 1 : 100$. In going from dipolar to low-polarity aprotic solvents, this ratio decreases to one order [3].

The same pattern of solvation effects in characteristic of the activation Gibbs energy which, like the reaction rate, is strongly temperature-dependent. The published data on heterolysis of *t*-BuCl [7, 8] and 1-chloro-1-methylcyclopentane [9] show that such solvation parameters as the activation enthalpy and entropy, which are temperature-independent in the temperature range studied, exhibit different patterns of solvation effects. Studying solvent effects on $\Delta G^{\neq}$, $\Delta H^{\neq}$, and $\Delta S^{\neq}$ gives one a deeper insight into the nature of solvation effects.

Here we present data on the effect of temperature

[1] For communication XXXIV, see [1].

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Table 1. Solvent and temperature effects on the rate of heterolysis of 1-bromo-1-methylcyclopentane (**I**)[a]

Solvent	*t*, °C	$k \times 10^5$, s^{-1} [b]	Solvent	*t*, °C	$k \times 10^5$, s^{-1} [b]
Methanol	25.0	100 ± 3	Benzonitrile	25.0	0.435 ± 0.013
	26.0	114 ± 10		30.5	0.814 ± 0.004
	30.0	154 ± 1		34.5	1.10 ± 0.05
	33.0	216 ± 3		39.0	1.56 ± 0.02
	37.5	319 ± 2		42.0	2.03 ± 0.03
	40.0	360 ± 5		44.0	2.41 ± 0.01
1-Butanol	14.0	1.85 ± 0.1	Nitrobenzene	25.0	0.895 ± 0.027
	19.0	3.55 ± 0.1		30.0	1.44 ± 0.01
	25.0	6.85 ± 0.2		35.0	2.20 ± 0.01
	30.0	14.3 ± 0.5		40.0	3.85 ± 0.15
	35.0	23.8 ± 1.0		45.0	6.26 ± 0.01
	40.0	38.5 ± 0.8			
Cyclohexanol	25.0	1.59 ± 0.04	Acetone	14.0	0.151 ± 0.005
	31.0	2.94 ± 0.01		20.0	0.340 ± 0.003
	36.0	5.47 ± 0.10		25.0	0.634 ± 0.020
	40.5	8.12 ± 0.01		30.0	1.10 ± 0.03
	49.5	18.7 ± 0.8		35.0	2.00 ± 0.1
2-Propanol	25.0	5.60 ± 0.02	Cyclohexanone	25.0	0.202 ± 0.001
	30.0	8.55 ± 0.1		30.0	0.356 ± 0.004
	41.0	24.7 ± 0.1		35.0	0.631 ± 0.003
	45.0	35.8 ± 0.2		40.0	1.17 ± 0.02
	51.0	59.6 ± 0.4		45.0	1.88 ± 0.12
2-Methyl-2-propanol	25.0	2.72 ± 0.01	Acetophenone	25.0	0.440 ± 0.003
	27.5	3.21 ± 0.03		29.5	0.672 ± 0.001
	30.0	3.96 ± 0.01		35.5	1.23 ± 0.06

Table 1. (Contd.)

Solvent	t, °C	$k \times 10^5$, s^{-1} [b]	Solvent	t, °C	$k \times 10^5$, s^{-1} [b]
2-Methyl-2-propanol	32.5	5.24 ± 0.04		39.5	1.74 ± 0.02
	37.5	6.97 ± 0.03		43.0	2.36 ± 0.01
	45.0	12.8 ± 0.1			
	49.0	17.2 ± 0.1			
1,1-Dimethyl-1-propanol	25.0	1.01 ± 0.01	1,2-Dichloroethane	25.0	0.340 ± 0.004
	30.0	1.58 ± 0.01		26.5	0.443 ± 0.02
	35.5	2.27 ± 0.01		30.0	0.615 ± 0.003
	46.0	4.75 ± 0.02		34.5	1.02 ± 0.01
	50.0	6.21 ± 0.04		40.5	1.74 ± 0.04
				43.5	2.18 ± 0.05
γ-Butyrolactone	14.0	5.34 ± 0.01	Toluone	25.0	0.748 ± 0.004
	20.0	10.0 ± 0.2		30.0	1.23 ± 0.02
	25.0	17.3 ± 0.2		35.0	2.16 ± 0.02
	30.0	26.6 ± 0.2		40.0	3.77 ± 0.05
	35.0	43.9 ± 0.5		45.0	6.18 ± 0.01
Acetonitirile	13.0	3.00 ± 0.03	Cyclohexane	25.0	0.252 ± 0.025
	20.0	6.44 ± 0.03		29.5	0.418 ± 0.008
	25.0	9.20 ± 0.1		34.5	0.728 ± 0.006
	30.0	14.6 ± 0.2		41.0	1.46 ± 0.07
	35.0	22.6 ± 0.3		44.5	2.05 ± 0.02

[a] Averaged over 2–3 runs. [b] For toluene and cyclohexane, $k \times 10^8$.

on the rate of heterolysis of bromides **I** and **II** in 6 protic and 10 aprotic solvents. The kinetic experiments were performed by the verdazyl method [10]. The reaction rate is always fairly described by Eq. (1). Tables 1 and 2 list the rate constants of heterolysis of bromides **I** and **II** at various temperatures in 17 solvents, and Table 3 lists the logarithms of rate constants at 25°C, as well as activation parameters,

Table 2. Solvent and temperature effects on the rate of heterolysis of 1-bromo-1-methylcyclohexane (**II**)[a]

Solvent	*t*, °C	$k \times 10^6$, s^{-1} [b]	Solvent	*t*, °C	$k \times 10^6$, s^{-1} [b]
Methanol	25.0	8.51 ± 0.04	Benzonitrile	25.0	0.218 ± 0.004
	30.0	16.6 ± 0.09		30.5	0.387 ± 0.001
	33.0	31.1 ± 0.1		34.5	0.521 ± 0.004
	40.0	71.0 ± 0.9		39.0	0.807 ± 0.003
	44.0	103 ± 3		44.0	1.24 ± 0.01
1-Butanol	25.0	0.716 ± 0.001	Nitrobenzene	25.0	0.0759 ± 0.0002
	31.0	1.59 ± 0.03		30.0	0.159 ± 0.001
	35.0	2.78 ± 0.01		35.0	0.294 ± 0.002
	39.5	5.04 ± 0.02		40.0	0.541 ± 0.001
	45.0	9.52 ± 0.02		45.0	0.996 ± 0.002
				50.0	1.57 ± 0.01
Cyclohexanol	25.0	0.333 ± 0.002	Acetone	25.0	0.162 ± 0.004
	32.5	0.924 ± 0.004		25.5	0.169 ± 0.005
	34.0	1.07 ± 0.03		30.0	0.259 ± 0.001
	36.5	1.34 ± 0.01		35.0	0.426 ± 0.002
	40.0	1.95 ± 0.05		39.0	0.601 ± 0.008
	45.0	3.66 ± 0.01		44.0	0.899 ± 0.003
	48.0	4.78 ± 0.02			
2-Propanol	25.0	0.652 ± 0.002	Cyclohexanone	25.0	4.26 ± 0.03
	30.0	1.16 ± 0.02		32.0	9.62 ± 0.01
	35.0	2.15 ± 0.01		36.0	13.3 ± 0.1
	41.5	4.13 ± 0.11		40.0	20.5 ± 0.2
	45.0	6.20 ± 0.01		45.0	33.1 ± 0.1
2-Methyl-2-propanol	25.0	0.300 ± 0.001	Acetophenone	25.0	10.9 ± 0.2
	30.0	0.535 ± 0.003		30.0	17.3 ± 0.1
	35.5	0.904 ± 0.002		35.0	27.1 ± 0.1
	39.5	1.45 ± 0.01		39.5	41.5 ± 0.1
	45.5	2.55 ± 0.02		44.0	58.6 ± 0.1
1,1-Dimethyl-1-propanol	25.0	0.0568 ± 0.001	1,2-Dichloroethane	25.0	22.6 ± 0.4
	33.5	0.204 ± 0.005		30.0	32.5 ± 0.1
	39.5	0.396 ± 0.001		34.5	44.1 ± 0.1
	46.0	0.846 ± 0.001		39.5	63.1 ± 0.3
	50.0	1.29 ± 0.02		44.0	84.9 ± 0.2
Acetonitrile	25.0	0.973 ± 0.003	Diphenyl ether	25.0	0.200 ± 0.004
	30.0	1.70 ± 0.1		32.5	0.604 ± 0.001
	34.5	3.10 ± 0.2		36.0	0.923 ± 0.005
	40.0	5.03 ± 0.02		40.0	1.45 ± 0.02
	44.5	7.87 ± 0.02		45.0	2.68 ± 0.01
	45.0	8.60 ± 0.01			

[a] Averaged over 2–3 runs. [b] For cyclohexanone, acetophenone, 1,2-dichloroethane, and diphenyl ether, $k \times 10^8$.

log (k/T)–$1/T$ correlation coefficients, and solvent parameters [6, 12, 13].

The correlation analysis of solvation effects was performed in terms of the Koppel–Palm equation [12] augmented by the cohesive energy density parameter δ^2 [14] [Eqs. (2) and (3)].

$$\varphi = a_0 + a_1\frac{\varepsilon - 1}{2\varepsilon + 1} + a_2\frac{n^2 - 1}{n^2 + 2} + a_3E + a_4B + a_5\delta^2, \quad (2)$$

$$\varphi = a_0 + a_1E_T(Z) + a_2B + a_3\delta^2. \quad (3)$$

Here φ is a parameter to be correlated ($\Delta G^{\neq}$, $\Delta H^{\neq}$, and $\Delta S^{\neq}$), ε is the dielectric constant of the solvent, n is

the refractive index, E and B are the empirical electrophilicity and nucleophilicity parameters, E_T and Z are the solvatochromic solvent ionizing ability parameters which are fairly described by the first three parameters of Eq. (2)[15], $\delta^2 = (\Delta H_m - RT)/V_m$ is the solvent self-association parameter, ΔH_m is the molecular vaporization heat, and V_m is the molar volume.

As seen from Table 3, the two-orders-of-magnitude rate decrease in going from the five-membered bromide to six-membered is associated with increasing $\Delta H^{\neq}$. The similtaneous increase of $\Delta S^{\neq}$ compensates in part for the rate decrease produced by increasing activation enthalpy.

The $\Delta H^{\neq}$ value, or, more exactly, reaction potential energy $\Delta E_r = \Delta H^{\neq} = \Delta G^{\neq}$ at $\Delta S^{\neq} = 0$ [16, 17], relates to stability of the cationoid intermediate in monomolecular heterolysis reactions. It will be shown below that this value for bromide **II** is 11 kJ/mol larger than for bromide **I**. The $\Delta S^{\neq}$ value in SN1(E1) reactions is a measure of solvation effects in the course of formation of the transition state [6, 18]. The fact that the activation entropy increases in going from bromide **I** to bromide **II** suggests stronger solvation of bromide **I**. Changes in the activation entropy in protic solvents hardly reveal the nature of solvation effects, since ion pair origination, on the one hand, results in solvent structuring around the cationic intermediate (electrostriction effect), which decreases $\Delta S^{\neq}$, and on the other, destroys the structure of the protic solvent, which increases $\Delta S^{\neq}$ [18, 19].

A different pattern is observed in aprotic solvents. In γ-butyrolactone, PhCN, PhCOMe, acetone, cyclohexane, and 1,2-dichloroethane, the decrease of the reaction rate of 1–2 orders of magnitude in going to the five- to six-membered ring is associated with a decrease of $\Delta S^{\neq}$, which is compensated for in part by decreasing $\Delta H^{\neq}$. However, the ΔE_r value for the six-membered substrate is still higher by 3 kJ/mol than for five-membered (see below). Consequently, the rate decrease in going from the five- to six-membered ring in the mentioned aprotic solvents may be partially contributed by decreased stability of the six-mem-

Table 3. Solvent effect on the rate and activation parameters of heterolysis of 1-bromo-1-methylcyclopentane (**I**) and 1-bromo-1-methylcyclohexane (**II**)

No.	Solvent	I					II				
		$-\log k_{25}$	$\Delta G^{\neq}$, kJ/mol	$\Delta H^{\neq}$, kJ/mol	$\Delta S^{\neq}$, J mol^{-1} K^{-1}	R	$-\log k_{25}$	$\Delta G^{\neq}$, kJ/mol	$\Delta H^{\neq}$, kJ/mol	$\Delta S^{\neq}$, J mol^{-1} K^{-1}	R
1	MeOH	3.00	90 ± 3	65.1 ± 1.7	84 ± 5	0.9971	5.07	102 ± 9	102 ± 4.5	–2 ± 14	0.9951
2	BuOH	4.16	96 ± 4	85.9 ± 2.3	36 ± 7	0.9989	6.15	108 ± 2	100 ± 0.9	26 ± 3	0.9998
3	*i*-PrOH	4.25	97 ± 2	71.3 ± 1.1	87 ± 3	0.9996	6.19	108 ± 2	85.8 ± 1.1	75 ± 3	0.9997
4	Cyclohexanol	4.80	100 ± 3	78.4 ± 1.8	74 ± 5	0.9990	6.48	110 ± 4	88.9 ± 1.9	71 ± 6	0.9986
5	*t*-BuOH	4.56	99 ± 3	59.0 ± 1.4	134 ± 4	0.9987	6.52	110 ± 2	79.8 ± 1.1	102 ± 3	0.9995
6	*t*-PentOH	5.00	102 ± 2	55.0 ± 1.1	156 ± 3	0.9994	7.25	114 ± 6	96.6 ± 3.0	60 ± 9	0.9985
7	γ-Butyrolactone	3.76	94 ± 2	71.0 ± 1.0	79 ± 3	0.9996	6.00[a]	107 ± 5	68.6 ± 2.4[b]	130 ± 7[b]	0.9967
8	MeCN	4.04	95 ± 4	63.6 ± 1.9	109 ± 6	0.9985	6.01[c]	107 ± 3	82.3 ± 1.8[c]	84 ± 5[c]	0.9987
9	$PhNO_2$	5.05	102 ± 4	74.2 ± 2.0	93 ± 6	0.9984	7.12	114 ± 4	94.8 ± 2.1	63 ± 6	0.9990
10	PhCN	5.36	104 ± 3	66.3 ± 1.8	125 ± 5	0.9977	6.66	111 ± 2	68.8 ± 1.2	142 ± 4	0.9992
11	Acetone	5.20	102 ± 2	87.4 ± 1.0	52 ± 3	0.9997	6.79	112 ± 2	69.1 ± 0.9	143 ± 3	0.9996
12	PhCOMe	5.36	104 ± 1	71.0 ± 0.6	109 ± 2	0.9998	6.96	113 ± 1	67.6 ± 0.7	151 ± 2	0.9997
13	Cyclohexanone	5.69	105 ± 2	86.6 ± 1.3	63 ± 4	0.9991	7.37[d]	115 ± 3	77.6 ± 1.5[d]	126 ± 4[d]	0.9991
14	1,2-Dichloroethane	5.47	104 ± 4	75.3 ± 2.1	97 ± 6	0.9977	6.65	111 ± 0.5	52.2 ± 0.3	197 ± 1	0.9999
15	Sulfolane	–	–	–	–	–	5.52[e]	105 ± 5	68.9 ± 2.8[e]	119 ± 8[e]	0.9957
16	Ph_2O	–	–	–	–	–	8.70	122 ± 4	100 ± 2.0	74 ± 6	0.9989
17	Toluene	8.13	119 ± 2	81.6 ± 1.2	127 ± 4	0.9995	–	–	–	–	–
18	Cyclohexane	8.60	122 ± 0.6	82.3 ± 0.3	133 ± 1	0.9999	–	–	–	–	–

Table 3. (Contd.)

No.	Solvent	ε(20)	n_D^{20}	*Z*, kJ/mol	E_T, kJ/mol	*E*, kJ/mol	*B*, kJ/mol	δ^2, kJ mol^{-1} l^{-1}
1	MeOH	32.7	1.3286	350	232	62.3	2.61	941
2	BuOH	17.1	1.3992	325	210	43.1	2.76	552
3	*i*-PrOH	18.3	1.3773	319	203	33.6	2.82	565
4	Cyclohexanol	15.0	1.4674	314	196	28.9	2.89	515
5	*t*-BuOH	10.9	1.3848	298	184	21.8	2.95	460
6	*t*-PentOH	5.8	1.3859	296	175	22.6	2.95	460
7	γ-Butyrolactone	39.0	1.4360	290	185	12.1	2.48	695
8	MeCN	37.5	1.3416	298	193	21.8	1.91	594
9	$PhNO_2$	34.8	1.5546	278	176	0.8	0.8	477
10	PhCN	25.2	1.5282	272	176	3.3	1.85	515
11	Acetone	20.7	1.3588	275	177	8.8	2.68	393
12	PhCOMe	17.4	1.5350	274	173	2.9	2.42	464
13	Cyclohexanone	18.3	1.4510	271	171	2.1	2.89	431
14	1,2-Dichloroethane	10.4	1.4451	265	175	12.6	0.48	411
15	Sulfolane	44	1.4830	295	184	9.6	1.88	690
16	Ph_2O	3.68	1.5826	240	148	0.0	1.06	427
17	Toluene	2.34	1.4969	233	142	5.9	0.69	333
18	Cyclohexane	2.02	1.4262	218	131	0.0	0.0	281

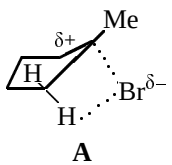
[a] Taken from [4]. [b] Taken from [11]. [c] In [11], $-\log k_{25}$ 6.00, $\Delta H^{\neq}$ 71 kJ/mol, $-\Delta S^{\neq}$ 122 J mol^{-1} K^{-1}. [d] In [11], $-\log k_{25}$ 7.10, $\Delta H^{\neq}$ 77 kJ/mol, $-\Delta S^{\neq}$ 122 J mol^{-1} K^{-1}. [e] Taken from [11].

bered intermediate. However, the major contribution comes from enhancing steric hindrances to solvation of the transition state.

In MeCN and $PhNO_2$, like in protic solvents, the rate decrease in going from bromide **I** to bromide **II** is associated with increasing $\Delta H^{\neq}$, which is compensated for in part by increasing $\Delta S^{\neq}$. Solvation of the transition state in heterolysis in MeCN and alcohols is probably explained by H-complex formation of the substrate nucleofuge, while the rate variation in $PhNO_2$, by specific dipolar solvation.

Nitrobenzene, unlike the other solvents, is available neither for nucleophilic nor electrophilic solvation (Table 3).

Noteworthy are very low $S^{\neq}$ values for heterolysis of bromide **I** in such nonpolar solvents as cyclohexane and toluene. This fact might be explained in term of formation of a four-membered transition state **A**.



A

The formation of state **A** should sharply decrease the activation entropy [20]. However, in heterolysis of *t*-BuCl in hexane and in the gas phase, where such complexes are more probable to form because of the higher electronegativity of the halogen, $\Delta S^{\neq}$ ~0 [18]. The same is true of heterolysis of *t*-BuBr and *t*-BuI in the gas phase [18]. The low $\Delta S^{\neq}$ value in heterolysis of bromide **I** in nonpolar solvents appears to be due to the formation in the transition state of complex associates with several solvent molecules: Coordination of one monodentate ligand is accompanied by an entropy loss of about 45 J mol^{-1} K^{-1} [21]. This assumption is consistent with the fact that in heterolysis of *p*-$MeC_6H_4CCl_3$ in cyclohexane, where such a four-membered transition state cannot form, $\Delta S^{\neq}$ –234 J mol^{-1} K^{-1} [22], whereas in heterolysis of 7α-bromochlesterol benzoate, where formation of a four-membered transition state with a hydrogen atom at the β-tertiary carbon atom is more probable, $\Delta S^{\neq}$ 24 J mol^{-1} K^{-1} [23].

The $\Delta G^{\neq}$, as well as log *k* values for heterolysis of bromides **I** and **II** in the same solvent set (nos. 1–14; here and hereinafter, the solvent numbers are the same as in Table 3) only approximately correlate with each other, implying an appreciable difference in solvation effects for these two substrates.

$$\log k_{\mathbf{I}} = 2.81 + 1.15 \log k_{\mathbf{II}};$$

$$R\ 0.912,\ S\ 0.327,\ n\ 14.$$

$$\Delta G^{\neq}_{\mathbf{I}} = -28300 + 1.16\ \Delta G^{\neq}_{\mathbf{II}};$$

$$R\ 0.9\ 20,\ S\ 1850,\ n\ 14.$$

Here and hereinafter, the activation parameters are measured in J/mol. As seen from the above equations, solvent effects are pronounced in heterolysis of bromide **I**.

In protic solvents we have fair correlations.

$$\log k_{\mathbf{I}} = 1.76 + 0.964 \log k_{\mathbf{II}};$$

$$R\ 0.966,\ S\ 0.206,\ n\ 6.$$

$$\Delta G^{\neq}_{\mathbf{I}} = -8070 + 0.970\ \Delta G^{\neq}_{\mathbf{II}};$$

$$R\ 0.9\ 64,\ S\ 1210,\ n\ 6.$$

In this case, there are roughly the same solvent effects with both bromides.

In aprotic solvents, the $\log k_{\mathbf{I}}$–$\log k_{\mathbf{II}}$ and $\Delta G^{\neq}_{\mathbf{I}}$–$\Delta G^{\neq}_{\mathbf{II}}$ correlations are poor (R ~0.7). Consequently, the strongest differences in solvation effects in heterolysis of bromides **I** and **II** are observed in aprotic solvents. Therewith, stronger rate effects should be expected with bromide **I**.

The figure depicts the $\Delta H^{\neq}$–$\Delta S^{\neq}$ correlations for both substrates. Exclusion of the point in Ph_2O renders this dependence for bromide **II** fair, while with bromide **I** it gets only approximate even after exclusion of three points (nos. 13, 17, and 18).

$$\Delta H^{\neq}_{\mathbf{II}} = 107000 + 272\Delta S^{\neq}_{\mathbf{II}};$$

$$R\ 0.97\ 0,\ S\ 3650,\ n\ 15.$$

$$\Delta H^{\neq}_{\mathbf{I}} = 96100 + 264\Delta S^{\neq}_{\mathbf{I}};$$

$$R\ 0.904,\ S\ 4250,\ n\ 13.$$

In 6 protic solvents, there is a fair correlation for bromide **I** and an approximate correlation for bromide **II**.

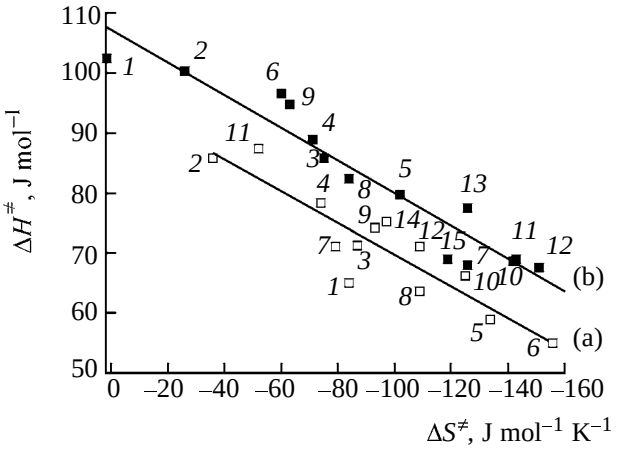
$$\Delta H^{\neq}_{\mathbf{I}} = 93700 + 258\Delta S^{\neq}_{\mathbf{I}};$$

$$R\ 0.950,\ S\ 4090,\ n\ 6.$$

$$\Delta H^{\neq}_{\mathbf{II}} = 105000 + 224\Delta S^{\neq}_{\mathbf{II}};$$

$$R\ 0.94\ 0,\ S\ 3390,\ n\ 6.$$

In the first case, ΔE_r 93.7 and in the second, 105 kJ/mol. The difference (~11 kJ/mol) reflects the relative stability of the carbocationic intermediates. Excluding the point in MeOH in the first case and in t-$C_5H_{11}OH$ in the second we obtain an excellent and a good correlations, respectively.



$\Delta H^{\neq}$–$\Delta S^{\neq}$ correlations for (a) 1-bromo-1-methylcyclopentane (**I**) and (b) 1-bromo-1-methylcyclohexane (**II**). For solvent numbers, see Table 3.

$$\Delta H^{\neq}_{\mathbf{I}} = 96000 + 268\Delta S^{\neq}_{\mathbf{I}};$$

$$R\ 0.993,\ S\ 1720,\ n\ 5. \qquad (4)$$

$$\Delta H^{\neq}_{\mathbf{II}} = 104000 + 229\Delta S^{\neq}_{\mathbf{II}};$$

$$R\ 0.98\ 4,\ S\ 1980,\ n\ 5. \qquad (5)$$

In aprotic solvents, the $\Delta H^{\neq}$–$\Delta S^{\neq}$ correlations are poor or approximate. Exclusion of three points (nos. 7, 17, and 18) for compound I and the point in Ph_2O for compound **II** renders these correlations fair.

$$\Delta H^{\neq}_{\mathbf{I}} = 106000 + 333\Delta S^{\neq}_{\mathbf{I}};$$

$$R\ 0.950,\ S\ 3130,\ n\ 7.$$

$$\Delta H^{\neq}_{\mathbf{II}} = 109000 + 290\Delta S^{\neq}_{\mathbf{II}};$$

$$R\ 0.951,\ S\ 3910,\ n\ 9.$$

Here ΔE_r for the six-membered substrate is 3 kJ/mol higher than for five-membered.

The $\Delta G^{\neq}$–$\Delta S^{\neq}$ correlations are always poor.

The $\Delta H^{\neq}$–$\Delta S^{\neq}$ compensation effect is commonly associated with the manifestation of the isokinetic relationship [16,17,20]. If so, the log k–1/T straight lines for different solvent should meet at one point corresponding to the isokinetic temperature. To check this assumption, we chose the best correlations for protic solvents: Eqs. (4) and (5). Computer analysis showed that in the first case the log k–1/T plots intersect in the range 10–248°C, where log k varies from –4.97 to +1.27, while in the second, in the range from –6 to +117°C, where log k varies from –7.08 to –3.11. Consequently, the isokinetic relationship in heterolysis of bromides **I** and **II** is not fulfilled. The same is

true of heterolysis of 1-chloro-1-methylcyclopentane in protic and aprotic solvents [24].

Correlation of solvent parameters with Gibbs activation energies for bromides **I** and **II** in the same solvents (nos. 1–14) by Eq. (2) leads to fair five-parameter correlations.

$$\Delta G_{\mathbf{I}}^{\neq} = (11200 \pm 13000) - (24600 \pm 28300)f(\varepsilon) + (36500 \pm 21600)f(n) - (0.0380 \pm 0.0650)E + (0.0264 \pm 0.825)B - (0.0189 \pm 0.0080)\delta^2;$$

$$R\ 0.933,\ S\ 2080,\ F\ 10.8\ (3.28),\ n\ 14.$$

$$\Delta G_{\mathbf{II}}^{\neq} = (127000 \pm 10000) - (33700 \pm 21800)f(\varepsilon) + (21400 \pm 10600)f(n) - (0.0566 \pm 0.0500)E + (0.533 \pm 0.636)B - (0.0129 \pm 0.0060)\delta^2;$$

$$R\ 0.937,\ S\ 1600,\ F\ 11.5\ (3.28),\ n\ 14.$$

Here F is the observed and critical (in parentheses) Fisher criteria at a 95% confidence level; excess of the observed value over critical gives evidence for the reliability of the model [25]. The activation and solvent parameters are measured in J/mol. As follows from the uncertainties in the coefficients of solvent parameters, polarity, electrophilicity, and nucleophilicity in the first case and electrophilicity and nucleophilicity in the second case are of no significance. Actually, the quality of the correlation is not deteriorated by exclusion of the corresponding parameters.

$$\Delta G_{\mathbf{I}}^{\neq} = (10300 \pm 5070) + (38500 \pm 14900)f(n) - (0.0241 \pm 0.040)\delta^2;\ R\ 0.926,\ S\ 1870,\ F\ 33.1\ (2.91),\ n\ 14.$$

$$\Delta G_{\mathbf{II}}^{\neq} = (125000 \pm 7860) - (26300 \pm 19600)f(\varepsilon) + (27000 \pm 13500)f(n) - (0.0175 \pm 0.0040)\delta^2;$$

$$R\ 0.922,\ S\ 1590,\ F\ 19.0\ (2.91),\ n\ 14.$$

In this case, solvent polarizability increases the activation Gibbs energy, thereby decreasing the reaction rate; at the same time, polarity and cohesion exert a positive rate effect, and, therewith, the rate effect of the first parameter is observed only with the six-membered substrate.

Exclusion of two the most deviating points (nos. 7 and 14) of a total of 14 gave fair five-parameter correlations.

$$\Delta G_{\mathbf{I}}^{\neq} = (95000 \pm 9260) - (14100 \pm 16900)f(\varepsilon) + (38700 \pm 12300)f(n) - (0.171 \pm 0.047)E + (2.46 \pm 0.82)B - (0.00238 \pm 0.0060)\delta^2;$$

$$R\ 0.981,\ S\ 1150,\ F\ 30.8\ (4.06),\ n\ 12. \qquad (6)$$

$$\Delta G_{\mathbf{II}}^{\neq} = (133000 \pm 10400) - (46200 \pm 19000)f(\varepsilon) + (14500 \pm 13800)f(n) - (0.106 \pm 0.053)E + (0.119 \pm 0.925)B - (0.00672 \pm 0.0060)\delta^2;$$

$$R\ 0.965,\ S\ 1300,\ F\ 16.3\ (4.06),\ n\ 12. \qquad (7)$$

Polarizability and cohesion in the first case and nucleophilicity and cohesion in the second are insignificant and their exclusion has no effect on the correlation quality.

$$\Delta G_{\mathbf{I}}^{\neq} = (86300 \pm 4060) + (39000 \pm 11800)f(n) - (0.193 \pm 0.024)E + (3.04 \pm 0.61)B;$$

$$R\ 0.977,\ S\ 1105,\ F\ 55.5\ (3.34),\ n\ 12. \qquad (8)$$

$$\Delta G_{\mathbf{II}}^{\neq} = (140000 \pm 6320) - (57500 \pm 13800)f(\varepsilon) - (0.166 \pm 0.020)E;$$

$$R\ 0.952,\ S\ 1230,\ F\ 43.7\ (3.13),\ n\ 12. \qquad (9)$$

The above regressions point to different solvation effects in heterolysis of bromides **I** and **II** in a set of 6 protic and 6 aprotic solvents. In the case of bromide **I**, electrophilicity increases the reaction rate and polarizability and nucleophilicity decrease it. A negative effect of nucleophilic solvation is observed, which results from nucleophilic solvation of the contact ion pair formed before the limiting stage [5]. This stabilizes the intermediate and hinders S$_N$1 nucleofuge cleavage. The negative effect of polarizability appears to be explained by facilitated formation of the above solvation complex. The dependence of the reaction rate on solvent nucleophilicy is not an artifact, since in this solvent set the parameter B does not correlate with the other four parameters of Eq. (2), R 0.756. In heterolysis of bromide **II** in the set of 6 protic and 6 aprotic, the reaction rate is independent of solvent nucleophilicity, and it increases with increasing solvent polarity and electrophilicity. These parameters only approximately describe the rate of heterolysis of bromide **I**, whereas the two-parameter correlation (10) is sufficiently reliable.

$$\Delta G_{\mathbf{I}}^{\neq} = (123000 \pm 9290) - (41500 \pm 20300)f(\varepsilon) - (0.208 \pm 0.029)E;$$

$$R\ 0.928,\ S\ 1820,\ F\ 27.9\ (3.13),\ n\ 12. \qquad (10)$$

Since correlations (9) and (10) were obtained for the same solvent set, then from the ratio of the coefficients at a parameter one can judged about the relative effect of the parameter [3]. Thus, the polarity effect on the rate of heterolysis of bromide **II** is stronger by a factor of 1.4 compared with bromide **I**,

whereas the electrophilicity effect is stronger by a factor of 1.3 in the case of bromide **I**; therewith, the effect of solvent polarizability suggests a negative effect of nucleophilic solvation on heterolysis of bromide **I** [Eq. (8)].

It is hard to explain why the rate of heterolysis of bromide **I** depends on solvent nucleophilicity, whereas that of bromide **II** no. A probable reason may lie in a higher stability of the cationic intermediate formed from the five-membered substrate, which allows nucleophilic solvation.

The activation Gibbs energy can be described by a different three-parameter equation (not including the nucleophilicity parameter), but the correlation quality here is worse than with Eq. (8).

$$\Delta G_{\mathbf{I}}^{\neq} = (118000 \pm 9440) - (46300 \pm 19500) f(\varepsilon) + (24700 \pm 17300) f(n) - (0.172 \pm 0.037) E;$$

$$R\ 0.943,\ S\ 1720,\ F\ 21.4\ (3.34),\ n\ 12.$$

Comparison of correlations (6)–(9) shows that even slight changes in the solvent set strongly affect the character of correlations.

Treatment by Eq. (2) of 16 data points (nos. 1–14, 17, and 18 for bromide **I** and nos. 1–16 for bromide **II**) results in fair five-parameter correlations.

$$\Delta G_{\mathbf{I}}^{\neq} = (129000 \pm 6030) - (63200 \pm 10100) f(\varepsilon) + (34400 \pm 20600) f(n) - (0.0693 \pm 0.061) E + (0.385 \pm 0.776) B - (0.0137 \pm 0.0070)\delta^2;$$

$$R\ 0.979,\ S\ 2100,\ F\ 45.9\ (2.82),\ n\ 16.$$

$$G_{\mathbf{II}}^{\neq} = (137000 \pm 8750) - (56500 \pm 13600) f(\varepsilon) + (25000 \pm 19000) f(n) - (0.0417 \pm 0.0530) E + (0.355 \pm 0.729) B - (0.0139 \pm 0.0050)\delta^2;$$

$$R\ 0.949,\ S\ 1880,\ F\ 18.0\ (2.82),\ n\ 16.$$

The electrophilicity and nucleophilicity parameters are insignificant in both cases, and their exclusion only slightly affects the correlation quality [Eqs. (11) and (12)].

$$\Delta G_{\mathbf{I}}^{\neq} = (126000 \pm 15480) - (64100 \pm 8060) f(\varepsilon) + (51700 \pm 16500) f(n) - (0.0188 \pm 0.050)\delta^2;$$

$$R\ 0.975,\ S\ 2100,\ F\ 75.8\ (2.60),\ n\ 16. \qquad (11)$$

$$\Delta G_{\mathbf{II}}^{\neq} = (135000 \pm 6650) - (52600 \pm 12000) f(\varepsilon) + (31400 \pm 12200) f(n) - (0.0168 \pm 0.0040)\delta^2;$$

$$R\ 0.945,\ S\ 1770,\ F\ 33.2\ (2.60),\ n\ 16. \qquad (12)$$

In these sets of 16 solvents, 14 of which are common for both substrates, polarity and cohesion increase the reaction rate, while polarizability decreases it, i.e. a negative effect of nucleophilic solvation takes place in both cases. Comparing correlations (8) and (9) (heterolysis in 12 solvents) with correlations (11) and (12) (heterolysis in 16 solvents) we can see that in going from the former to latter the nucleophilicity effect on the heterolysis rate attenuates in the case of the five-membered substrate and enhances in the case of six-membered. This result can be explained by that different solvents are added. In the first case, the additional solvents are non-nucleophilic toluene and cyclohexane, while in the second, fairly nucleophilic sulfolane and Ph_2O.

Treatment by Eq. (3) of 14 data points gave approximate three-parameter correlations.

$$\Delta G_{\mathbf{I}}^{\neq} = (127000 \pm 8520) - (0.0870 \pm 0.0630) E_T - (0.330 \pm 0.817) B - (0.0190 \pm 0.0080)\delta^2;$$

$$R\ 0.904,\ S\ 2210,\ F\ 15.0\ (2.91),\ n\ 14.$$

$$\Delta G_{\mathbf{II}}^{\neq} = (132000 \pm 6430) - (0.0829 \pm 0.0480) E_T + (0.406 \pm 0.617) B - (0.0145 \pm 0.0060)\delta^2;$$

$$R\ 0.913,\ S\ 1670,\ F\ 16.8\ (2.91),\ n\ 14.$$

Solvent nucleophilicity is insignificant, and its exclusion has almost no effect on the correlation quality.

$$\Delta G_{\mathbf{I}}^{\neq} = (127000 \pm 8140) - (0.0942 \pm 0.059) E_T - (0.0186 \pm 0.0070)\delta^2;$$

$$R\ 0.903,\ S\ 2130,\ F\ 24.2\ (2.91),\ n\ 14.$$

$$\Delta G_{\mathbf{II}}^{\neq} = (132000 \pm 6220) - (0.0739 \pm 0.0450) E_T - (0.0150 \pm 0.0060)\delta^2;$$

$$R\ 0.910,\ S\ 1630,\ F\ 26.3\ (2.91),\ n\ 14.$$

Here the rate effects of solvent ionizing ability and cohesion are stronger by factors of 1.3 and 1.2 in the case of the five-membered substrate compared with six-membered.

The increase in reaction rate with enhancing solvent cohesion in E1 (S_N1) reactions are commonly associated with a negative effect of nucleophilic solvation [5]: the stronger cohesion, the more difficult the solvent molecule to liberate for nucleophilic solvation of the contact ion pair. The above correlations show that these effects are stronger in the case of the five-membered substrate.

Thus, the rate of heterolysis of bromides **I** and **II** in a set of protic and aprotic solvents increases with

increasing solvent ionizing ability, electrophilicity, and cohesion and decreases with increasing nucleophilicity and polarizability, and, therewith, these effects are stronger in the case of the five-membered compound. Solvent polarity in some cases stronger increases the reaction rate of the five-membered substrate, and in some others, of six-membered.

The solvent parameters in Eqs. (2) and (3) for 12-, 14-, and 16-solvent data sets are independent variables. The strongest collinearity [26] between the parameters is observed for the 12-solvent data set: δ^2–E_T (R 0.876), δ^2–E (R 0.802), $f(n)$–E (R 0.673), and $f(\varepsilon)$–B (R 0.526). For the 14- and and 16-solvent data sets these values are lower.

Teatment by Eq. (6) of data for 6 protic solvents gives rise to fair two-parameter correlations (13) and (14) (no more than two parameters can be used with 6 points).

$$\Delta G_{\mathbf{I}}^{\neq} = (19600 \pm 33500) - (6490 \pm 30400)f(\varepsilon) + (28.53 \pm 7.82)B;$$
$$R\ 0.959,\ S\ 1490,\ F\ 17.1\ (9.01),\ n\ 6. \qquad (13)$$

$$\Delta G_{\mathbf{II}}^{\neq} = (76500 \pm 28600) - (49500 \pm 25900)f(\varepsilon) + (19.17 \pm 6.67)B;$$
$$R\ 0.970,\ S\ 1270,\ F\ 23.8\ (9.01),\ n\ 6. \qquad (14)$$

Solvent polarity increases the rate of both reactions and nucleophilicity decreases it, and, therewith, the nucleophilicity effect is 1.5 times stronger with the five-membered substrate. Exclusion of the polarity parameter has almost no effect on the quality of the first correlation and much deteriorates the second [see Eqs. (15) and (16)].

$$\Delta G_{\mathbf{I}}^{\neq} = (13100 \pm 12600) + (29.80 \pm 4.45)B;$$
$$R\ 0.958,\ S\ 1300,\ F\ 44.8\ (6.26),\ n\ 6. \qquad (15)$$

$$\Delta G_{\mathbf{II}}^{\neq} = (27200 \pm 15900) + (28.82 \pm 5.61)B;$$
$$R\ 0.932,\ S\ 1640,\ F\ 26.4\ (6.26),\ n\ 6. \qquad (16)$$

In our set of protic solvents, there is a good correlation between the nucleophilicity and electrophilicity parameters.

$$B = 3130 - 0.00849E;\ R\ 0.995,\ S\ 15.0,\ n\ 6.$$

Therefore, with the electrophilicity parameter we obtain one-parameter correlations analogous to correlations (15) and (16).

$$\Delta G_{\mathbf{I}}^{\neq} = (106000 \pm 1460) - (0.254 \pm 0.038)E;$$
$$R\ 0.957,\ S\ 1320,\ F\ 43.8\ (6.26),\ n\ 6. \qquad (17)$$

$$\Delta G_{\mathbf{II}}^{\neq} = (117000 \pm 1920) + (0.244 \pm 0.050)E;$$
$$R\ 0.924,\ S\ 1730,\ F\ 23.5\ (6.26),\ n\ 6. \qquad (18)$$

With both substrates, electrophilicity decreases $\Delta G^{\neq}$, thereby accelerating the reaction. Poor two-parameter correlations were obtained with the E and B parameters.

$$\Delta G_{\mathbf{I}}^{\neq} = (51800 \pm 155300) - (0.106 \pm 0.423)E + (17.45 \pm 49.60)B;$$
$$R\ 0.959,\ S\ 1490,\ F\ 17.2\ (9.01),\ n\ 6.$$

$$\Delta G_{\mathbf{II}}^{\neq} = (3910 \pm 197000) - (0.0639 \pm 0.538)E + (36.26 \pm 63.00)B;$$
$$R\ 0.932,\ S\ 1890,\ F\ 9.36\ (9.01),\ n\ 6.$$

Consequently, the use in the correlation equation of mutually strongly correlating parameters results in negation of the effect of both parameters.

With bromide **II**, a reliable two-parameter correlation (19) was obtained with the polarity and electrophilicity parameters.

$$\Delta G_{\mathbf{II}}^{\neq} = (138000 \pm 8670) - (53800 \pm 22120)f(\varepsilon) - (0.159 \pm 0.049)E;$$
$$R\ 0.975,\ S\ 1160,\ F\ 29.2\ (9.01),\ n\ 6. \qquad (19)$$

Thus, the $\Delta G_{\mathbf{I}}^{\neq}$ value in protic solvents is fairly described in terms of a single solvent parameter, electrophilicity or nucleophilicity [Eqs. (13) and (17)]. Both solvation effects are important. It is known that electrophilic solvent assistance is a driving force of monomolecular heterolysis reactions [5, 27], and the negative effect of nucleophilic solvation has revealed itself in a set of protic and aprotic solvents [Eq. (8)].

The rate of heterolysis of bromide **II** in protic solvents increases with increasing solvent polarity and electrophilicity and decreases with increasing nucleophilicity; therewith, in this solvent set, nucleophicility exerts a weaker rate effect with the six-membered substrate compared with five-membered.

Treatment by Eq. (3) of data for heterolysis of bromides **I** and **II** in protic solvents leads to fair two-parameter correlations.

$$\Delta G_{\mathbf{I}}^{\neq} = (124000 \pm 9800) - (0.0993 \pm 0.068)E_T - (0.0113 \pm 0.0080)\delta^2;$$
$$R\ 0.967,\ S\ 1340,\ F\ 21.6\ (9.01),\ n\ 6.$$

$$\Delta G_{\mathbf{II}}^{\neq} = (142000 \pm 8880) - (0.150 \pm 0.061)E_T - (0.00546 \pm 0.00700)\delta^2;$$
$$R\ 0.973,\ S\ 1210,\ F\ 26.4\ (9.01),\ n\ 6.$$

The cohesion parameter is significant with bromide **I** and insignificant with bromide **II**, and its exclusion much deteriorates the correlation in the first case.

$$\Delta G_{\mathbf{I}}^{\neq} = (136000 \pm 6840) - (0.190 \pm 0.034)E_T;$$

$$R\ 0.942,\ S\ 1530,\ F\ 31.3\ (6.26),\ n\ 6.$$

$$\Delta G_{\mathbf{II}}^{\neq} = (148000 \pm 5160) - (0.194 \pm 0.026)E_T;$$

$$R\ 0.973,\ S\ 1210,\ F\ 26.4\ (6.26),\ n\ 6.$$

The fact that $\Delta G_{\mathbf{I}}^{\neq}$ and $\Delta G_{\mathbf{II}}^{\neq}$ correlate with E_T suggests roughly similar effects of the ionizing ability of a protic solvent on the rate of heterolysis of both the five-membered and six-membered substrates.

In our set of protic solvents, there is a strong correlation between certain parameters of Eqs. (2) and (3). In addition to the above data for B and E we have: B–E_T (R 0.980), δ^2–E (R 0.943), δ^2–B (R 0.927), δ^2–E_T (R 0.898), $f(\varepsilon)$–E (R 0.770), and $f(\varepsilon)$–B (R 0.758). This fact prevents reliable conclusions as to the nature of solvation effects in protic solvents.

Treatment by Eq. (2) of data for heterolysis of both substrates in 8 aprotic solvents (nos. 7–14) results in fair two-parameter correlations.

$$\Delta G_{\mathbf{I}}^{\neq} = (119000 \pm 3150) - (0.241 \pm 0.096)E - (0.0310 \pm 0.0070)\delta^2;$$

$$R\ 0.951,\ S\ 1630,\ F\ 23.4\ (4.88),\ n\ 8.$$

$$\Delta G_{\mathbf{II}}^{\neq} = (122000 \pm 2220) - (0.224 \pm 0.067)E - (0.0189 \pm 0.0050)\delta^2;$$

$$R\ 0.952,\ S\ 1150,\ F\ 24.0\ (4.88),\ n\ 8.$$

In aprotic solvents, electrophilicity and cohesion stronger affect the rate of heterolysis of the five-membered substrate (by factors of 1.1 and 1.6, respectively).

In 10 aprotic solvents (nos. 7–14, 17, and 18 for bromide **I** and nos. 7–16 for bromide **II**), the rate of heterolysis of bromides **I** and **II** depends, apart from electrophilicity and cohesion, on solvent polarity.

$$\Delta G_{\mathbf{I}}^{\neq} = (141000 \pm 1870) - (55600 \pm 5970)f(\varepsilon) - (0.263 \pm 0.074)E - - (0.0236 \pm 0.0060)\delta^2;$$

$$R\ 0.993,\ S\ 1280,\ F\ 150\ (4.10),\ n\ 10.$$

$$\Delta G_{\mathbf{II}}^{\neq} = (147000 \pm 5560) - (53800 \pm 13460)f(\varepsilon) - (0.246 \pm 0.096)E - (0.0236 \pm 0.0060)\delta^2;$$

$$R\ 0.963,\ S\ 1710,\ F\ 25.6\ (4.10),\ n\ 10.$$

Treatment by Eq. (3) of data for 10 aprotic solvents gives two-parameter correlations.

$$\Delta G_{\mathbf{I}}^{\neq} = (178000 \pm 4670) - (0.377 \pm 0.039)E_T - (0.0188 \pm 0.0060)\delta^2;$$

$$R\ 0.992,\ S\ 1280,\ F\ 226\ (3.68),\ n\ 10.$$

$$\Delta G_{\mathbf{II}}^{\neq} = (175000 \pm 9170) - (0.321 \pm 0.062)E_T - (0.0145 \pm 0.0060)\delta^2;$$

$$R\ 0.957,\ S\ 1710,\ F\ 37.8\ (3.68),\ n\ 10.$$

Thus, in aprotic solvents, solvent ionizing ability, electrophilicity, polarity, and cohesion accelerate both reactions, and the effect is always stronger with bromide **I**.

The parameters of Eqs. (2) and (3) in sets of 8 and 10 aprotic solvents are independent variables. The strongest collinearity in the 8-solvent set is observed for the following pairs: δ^2–E_T (R 0.743), $f(n)$–E (R 0.802), $f(\varepsilon)$–δ^2 (R 0.674). For one 10-solvent set (nos. 7–14, 17, and 18) we have: δ^2–E_T (R 0.817), $f(n)$–E (R 0.689), $f(\varepsilon)$–δ^2 (R 0.732), $f(\varepsilon)$–B (R 0.684), B–E_T (R 0.626). For the other 10-solvent set (nos. 7–16), the highest R values were found for the following pairs: E–$f(\varepsilon)$ (R 0.818), δ^2–E_T (R 0.619). In all the other cases, $R < 0.5$.

Correlation analysis of the effect of solvent parameters on the activation enthalpy and entropy of heterolysis of bromides **I** and **II** gives worse results than with the Gibbs activation energy. In many cases, unsatisfactory results were obtained.

Treatment by Eq. (3) of the activation enthalpies of bromide **I** in 6 protic solvents gives a good and an approximate teo-parameter correlations.

$$\Delta H_{\mathbf{I}}^{\neq} = (329000 \pm 45110) - (1.540 \pm 0.174)Z - (0.154 \pm 0.019)\delta^2;$$

$$R\ 0.981,\ S\ 2920,\ F\ 39.1\ (9.01),\ n\ 6.$$

$$\Delta H_{\mathbf{I}}^{\neq} = (109000 \pm 37800) - (1.250 \pm 0.261)E_T - (0.122 \pm 0.029)\delta^2;$$

$$R\ 0.940,\ S\ 5170,\ F\ 11.4\ (9.01),\ n\ 6.$$

The correlations with $\Delta H_{\mathbf{II}}^{\neq}$ are poor.

The ionizing ability of a protic solvent increases the activation enthalpy, and cohesion decreases it. Considering these data one should bear in mind that in our set of protic solvents there is a strong correlation between $Z(E_T)$ and the nucleophilicity and electrophilicity parameters (see above). The ionizing ability is fairly described by the polarity, polarizability, and electrophilicity parameters which can differently affect $\Delta H^{\neq}$ [8]. The increase in $\Delta H^{\neq}$ with

increasing solvent ionizing ability we observed earlier in heterolysis of 1-chloro-1- methylcyclopentane and *t*-BuCl [8, 9].

The effect of cohesion is probably associated with electrostatic solvation of the transition state, as judged from the fact that δ^2 fairly correlates with solvent dipole moments [18].

Treatment by Eq. (2) of data for 6 protic solvents gave an approximate correlation for bromide **II**.

$$\Delta H^{\neq}_{\mathbf{II}} = (163000 \pm 35100) - (219000 \pm 89650)f(\varepsilon) + (0.756 \pm 0.197)E;$$

$$R\ 0.913,\ S\ 4690,\ F\ 7.49\ (9.01),\ n\ 6.$$

As seen, nonspecific solvation decreases $\Delta H^{\neq}$, whereas specific solvation increases it. Similar effects were earlier observed in heterolysis of 1-chloro-1-methylcyclopentane and *t*-BuCl [8, 9]. The effect of the $Z(E_T)$ and E parameters is presumably explained by solvation of the initial state.

With 6 aprotic solvents (nos. 7, 8, 10–13), only approximate correlations were obtained by Eq. (2).

$$\Delta H^{\neq}_{\mathbf{I}} = (117000 \pm 14700) - (4.54 \pm 2.49)B - (0.110 \pm 0.029)\delta^2;$$

$$R\ 0.929,\ S\ 4820,\ F\ 9.39\ (9.01),\ n\ 6.$$

$$\Delta H^{\neq}_{\mathbf{II}} = (11400 \pm 13600) - (8.70 \pm 2.29)B (0.0865 \pm 0.0260)\delta^2;$$

$$R\ 0.942,\ S\ 4450,\ F\ 11.9\ (9.01),\ n\ 6.$$

The nucleophilicity of an aprotic solvent in both cases increases the activation enthalpy, which points to a negative effect of nucleophilic solvation. With the five-membered bromide, this is evidenced by decrease in $\Delta H^{\neq}$ with enhancing solvent cohesion. With bromide **II** whose heterolysis rate weaker depends on solvent nucleophilicity, cohesion increases the activation enthalpy, probably, on account of dipolar solvation of the contact ion pair of the substrate.

Thus, the negative effect of nucleophilic solvation in heterolysis of bromide **I** [Eq. (8)] is explained by the solvent effect on the activation enthalpy.

The solvent parameters in Eq. (3) for a set of 6 aprotic solvents are independent variables. The strogest collinearity is observed for the E_T–δ^2 (R 0.798) and B–E_T (R 0.157) pairs.

Treatment by Eq. (2) of data for a set of 6 protic and 8 aprotic solvents (nos. 1–8, 10–13, 15, 16) results in a fair two-parameter correlation.

$$\Delta H^{\neq}_{\mathbf{II}} = (166000 \pm 12600) - (211000 \pm 28500)F(\varepsilon) + (0.605 \pm 0.072)E;$$

$$R\ 0.950,\ S\ 4500,\ F\ 51.3\ (2.91),\ n\ 14.$$

In this case, like in protic solvents, polarity decreases $\Delta H^{\neq}$, whereas electrophilicity increases it.

Treatment by Eq. (3) of the $\Delta S^{\neq}$ values in protic solvents results in the following two-parameter correlations.

$$\Delta S^{\neq}_{\mathbf{I}} = -(774 \pm 98) + (0.00446 \pm 0.00100)E_T - (0.000367 \pm 0.000050)\delta^2;$$

$$R\ 0.971,\ S\ 13.3,\ F\ 24.8\ (9.01),\ n\ 6.$$

$$\Delta S^{\neq}_{\mathbf{II}} = (2620 \pm 1110) - (0.00313 \pm 0.00200)E_T - (0.722 \pm 0.271)B;$$

$$R\ 0.944,\ S\ 15.9,\ F\ 12.3\ (9.01),\ n\ 6.$$

The E_T parameter increases the activation entropy for the five-membered substrate and decreases it for six-membered. In the first case, the fact that $\Delta S^{\neq}$ increases with increasing solvent ionizing ability may be associated with enhanced solvation of the transition state. This process should be hindered by increasing solvent association energy, and, therefore, cohesion decreases the activation entropy of heterolysis of the five-membered substrate. The formation of the intermediate *twist* conformer from the six-membered substrate is probably accompanied by resolvation [4], and therefore, the E_T and $B(E)$ parameters which favor solvation of the intermediate in the first case hinder this process in the second.

The results of correlation by Eq. (2) of data for 6 protic solvents are consistent with this conclusion: Polarity and nucleophilicity decrease $\Delta S^{\neq}$.

$$\Delta S^{\neq}_{\mathbf{II}} = (1300 \pm 296) - (653 \pm 269)f(\varepsilon) - (0.378 \pm 0.069)B;$$

$$R\ 0.961,\ S\ 13.2,\ F\ 18.3\ (9.01),\ n\ 6.$$

Treatment by Eq. (2) of data for 6 aprotic solvents (nos. 8, 10–14) gives the following correlations.

$$\Delta S^{\neq}_{\mathbf{I}} = (203 \pm 67) - (969 \pm 222)f(n) + (0.00463 \pm 0.00050)E;$$

$$R\ 0.931,\ S\ 13.5,\ F\ 9.76\ (9.01),\ n\ 6.$$

$$\Delta S^{\neq}_{\mathbf{II}} = -(954 \pm 237) - (191 \pm 185)f(n) + (1870 \pm 474)f(\varepsilon);$$

$$R\ 0.934,\ S\ 16.9,\ F\ 10.2\ (9.01),\ n\ 6.$$

These results show that the decrease in the reaction rate with increasing solvent polarizability is associated with the solvent effect on the activation entropy.

Treatment by Eq. (2) of data for 4 protic and 6 aprotic solvents (nos. 1, 3, 4, 6, 8, 10–14) results in fair correlations.

$$\Delta S_{\mathbf{I}}^{\neq} = -(803 \pm 95) + (1160 \pm 164)f(\varepsilon) - (0.000375 \pm 0.000050)E + (0.0725 \pm 0.0120)B;$$

$$R\ 0.950,\ S\ 18.6,\ F\ 18.6\ (4.10),\ n\ 10.$$

$$\Delta S_{\mathbf{II}}^{\neq} = (15.3 \pm 64.7) - (354 \pm 141)f(\varepsilon) - (0.00248 \pm 0.00050)E;$$

$$R\ 0.975,\ S\ 12.3,\ F\ 66.8\ (3.68),\ n\ 10.$$

With bromide **I**, polarity and nucleophilicity increase $\Delta S^{\neq}$, which is accounted for by enhanced solvation of the transition state. With bromide **II**, polarity and electrophilicity decrease $\Delta S^{\neq}$, which provides evidence for the proposed resolvation during formation of the transition state.

Thus, the ionizing ability, polarity, electrophilicity, and cohesion of the solvent accelerate heterolysis of bromides **I** and **II**, whereas polarizability and nucleophilicity exert the opposite rate effect. These effects all are stronger in the case of the five-membered substrate. The specific solvation effects in heterolysis of the six-membered substrate is explained by profound conformational changes in the course of formation of the ion-pair intermediate accompanied by resolvation. Solvation pattern is much dependent on the solvent set used.

The results of correlation analysis of the effects of solvent parameters on the activation entropy and enthalpy give a deeper insight into the nature of solvation effects. In protic solvents, the increase in the rate of heterolysis of bromide **I** with increasing solvent ionizing ability or electrophilicity is explained by the effect on the activation entropy, whereas the increase in the rate of heterolysis of bromide **I** with increasing solvent polarity is explained by the effect on the activation enthalpy. In aprotic solvents, the increase in the reaction rate with increasing solvent cohesion is associated with $\Delta H^{\neq}$, whereas the rate increase with increasing solvent ionizing ability, with $\Delta S^{\neq}$.

In a set of protic and aprotic solvents, electrophilicity and polarity increase the reaction rate by increasing $\Delta S^{\neq}$, whereas nucleophilicity, by decreasing $\Delta H^{\neq}$. The negative polarizability effect is explained by the solvent effect on $\Delta S^{\neq}$. For more general conclusions, more solvents should be examined.

EXPERIMENTAL

Synthesis of bromides **I** and **II** and purification of solvents were performed as described in [2, 4, 28]. Kinetic experiments were performed in a temperature-controlled cell of an SF-26 spectrophotometer. The concentrations of bromides **I** and **II** in the kinetic experiments were 0.01–0.5 M, and the concentration of the verdazyl indicator was $(1–3) \times 10^{-4}$ M. The substrate conversions in the kinetic experiments were 0.01–0.0005 wt%. Calculations by Eqs. (2) and (4) were performed by the least-squares method using the Spss program; confidence level 95%.

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