Kinetics and Mechanism of Monomolecular Heterolysis of Commercial Organohalogen Compounds: XXXII.¹ Solvent Effects on Activation Parameters of Heterolysis of 1-Chloro-1-methylcyclopentane. Correlation Analysis of Solvation Effects

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Abstract—Kinetics of heterolysis of 1-chloro-1-methylcyclopentane in MeOH, BuOH, cyclohexane, *i*-PrOH, *t*-BuOH, *tert*-C₅H₁₁OH, γ -butyrolactone, MeCN, PhCN, PhNO₂, acetone, PhCOMe, cyclohexanone, and 1,2-dichloroethane at 25–50°C were studied by the verdazyl method. Correlation analysis of solvent effects on activation parameters of the reaction in 8 protic (additionally, AcOH and CF₃CH₂OH) and 8 aprotic solvents together and separately in either group of solvents was performed. In all the solvents studied, two $\Delta H^{\neq} - \Delta S^{\neq}$ compensation effects were revealed.

The effect of a solvent on the rate of a chemical process much depends on the mechanism of the reaction [2] and physicochemical properties of the solvent, such as polarity, polarizability, electrophilicity, nucleophilicity [3], and cohesion [4]. Solvent effects are most frequently discussed by comparing the logarithms of the rate constants and the free activation energies of the reaction. Correlation of these values with solvent parameters in terms of multiparameter linear free energy equations gives insight into the nature of the solvent effects [3, 5–9]. However, the diagnostic power of such correlations is limited by the ΔG^{\neq} fact that logk and are strongly temperature-dependent. At the same time, ΔG^{\neq} is a sum function of the activation enthalpy and entropy $(\Delta G^{\neq} = \Delta H^{\neq} - H \Delta S^{\neq})$, which are almost temperatureindependent in a given experimental range.

There has been little work on solvent effects on activation parameters, specifically on ΔH^{\neq} and ΔS^{\neq} . We can mention here the works on heterolysis of *t*-BuCl [10, 11], alcoholysis of α -ethylacryloyl chloride [12] and 3-phenylpropyl *p*-toluenesulfonate [13], acylation of aniline [14], and homolysis of polymeric peroxide of azelaic acid [15].

Of particular interest in terms of solvent effects are monomolecular heterolysis reactions (SN1, E1, solvolysis) [5, 10, 11, 16], since their rate is highly sensitive to solvent, and ΔS^{\neq} is mostly contributed by solvation effects.

The rate of these reactions is determined by ionization of the covalent bond [2, 3], which occurs via consecutive formation of three ion pairs: contact, loose, and solvent-separated [9, 16].

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

It is assumed that the limiting stage involves interaction of the contact ion pair with solvent void [16] (voids comprise $\sim 10\%$ of the volume of a liquid [17, 18]) to form the loose ion pair. The latter fast converts into the solvent-separated ion pair which then passes, also fast, into reaction products.

In [10], we found ΔG^{\neq} , ΔH^{\neq} , and ΔS^{\neq} values for heterolysis of *t*-BuCl (E1 + S_N1 reaction) in 8 protic and 15 aprotic solvents and revealed no $\Delta H^{\neq} -\Delta S^{\neq}$ (*R* 0.554) and $\Delta G^{\neq} -\Delta S^{\neq}$ (*R* 0.028) compensation effects. Correlation analysis of solvation effects on the transition state showed that ΔG_{Tr}^{\neq} decreases with increasing solvent dipolarity (polarity + polarizability), electrophilicity, and nucleophilicity and increases with solvent cohesion (*R* 0.91), while ΔH_{Tr}^{\neq} and ΔS_{Tr}^{\neq} increase with all the four parameters (*R* 0.81 and 0.89, respectively). The fact that ΔG_{Tr}^{\neq} correlates with the nucleophility parameter suggests nucleophilic solvent assistance. According to [10], all kinds of solvation,

¹ For communication XXXI, see [1].

both specific and nonspecific, increase ΔH^{\neq} , thus decreasing the reaction rate. The same factors increase ΔS^{\neq} and thus increase the reaction rate. Consequently, the reaction rate is increased exclusively by the increase in the activation entropy, and this effect is so strong that it fully compensates for the increase in the activation enthalpy.

In [11], no $\Delta H^{\neq} - \Delta S^{\neq}$ and $\Delta G^{\neq} - \Delta S^{\neq}$ compensation effects were revealed in heterolysis of t-BuCl in 15 protic and 16 aprotic solvents. However, in dipolar aprotic solvents, the $\Delta H^{\neq} - \Delta S^{\neq}$ compensation effect takes place, while in protic, two such effects. It was found that in all the solvents studied and in aprotic solvents, ΔG^{\neq} decreases with increasing solvent polarity, polarizability, and electrophilicity or ionizing ability (R > 0.95). In protic solvents, ΔG^{\neq} decreases with increasing ionizing ability (or electrophilicity) and cohesion and increases with increasing nucleophicility of the solvent (R > 0.95). The ΔH^{\neq} value decreases with increasing polarity and polarizability and increases with nucleophilicity $(R \ 0.90)$ of protic solvents and decreases with increasing polarity and increases with increasing polarizability and electrophilicity of aprotic solvents (R 0.92). The ΔS^{\neq} value in aprotic solvents increases with increasing nucleophilicty and electrophilicity and decreases with increasing polarizability of the solvent (R 0.92).

Consequently, according to [11], nucleophilic solvent assistance in heterolysis of *t*-BuCl is absent, and, moreover, a negative effect of nucleophilic solvation is observed in protic solvents, on account of the solvent effect on ΔH^{\neq} . Specific solvation effects that control orientation of solvent molecules with respect to substrate molecules increase ΔS^{\neq} and increase the reaction rate.

Thus, Abraham et al. [10] and Dvorko et al. [11] have come to different conclusions as to the solvent effect on the activation parameters of heterolysis of t-BuCl. The latter referees explain this controversy by the fact that Abraham et al. [10] used experimental activation parameters for only 14 of 23 solvents, and the ΔH^{\neq} and ΔS^{\neq} values for the other 9 solvents, as well as certain ΔG^{\neq} values were estimated by comparing with data for t-BuBr and t-BuI. Moreover, the analysis of solvent effects on ΔH^{\neq} and ΔS^{\neq} in that work included the whole set of solvents only. This is incorrect because of the different effects of protic and aprotic solvents on the activation entropy. Origination of an ion pair in a heterolysis reaction is accompanied by solvent structuring around the intermediate (electrostriction effect), which decreases ΔS^{\neq} . In the strongly structured protic solvents, breakdown of solvent structure occurs along with electrostriction,

thus increasing ΔS^{\neq} [17, 18]. Therefore, solvent effects on ΔH^{\neq} and ΔS^{\neq} should be considered separately for protic and aprotic solvents.

A different pattern of solvent effects on ΔH^{\neq} is observed in alcoholyses of α -ethylacryloyl chloride (14 alcohols) [12] and 3-phenylpropyl *p*-toluenesulfonate (17 alcohols) [13]; moreover, different patterns are characteristic of the two substrates. In the first case, polarity and nucleophilicity increase ΔH^{\neq} , whereas polarizabillity, electrophilicity, and cohesion exert the opposite effect. In the second case, ΔH^{\neq} decreases with increasing solvent nucleophilicity, electrophilicity, and polarizability.

In benzoylation of aniline (17 aprotic solvents), polarizability, electrophilicity, and nucleophilicity decrease ΔH^{\neq} . In acylation of aniline with carboranecarbonyl chloride (20 aprotic solvents), nucleophilicity and cohesion decrease ΔH^{\neq} , while polarizability increase it [14]. In the first case, polarizability, electrophilicity, and nucleophilicity decrease ΔS^{\neq} , whereas polarity and cohesion increase it. In the second case, polarity and electrophilicity increase ΔS^{\neq} , and nucleophilicity and cohesion decrease it.

The ΔH^{\neq} and ΔS^{\neq} values of each of the reactions in question differently vary with solvent parameters, both in protic and aprotic solvents. Thus, in solvolysis of α -ethylacryloyl chloride, electrophilicity decreases ΔH^{\neq} , while nucleophilicity increases it. In solvolysis of 3-phenylpropyl *p*-toluenesulfonate, both these parameters decrease ΔH^{\neq} , whereas in solvolysis of *t*-BuCl, electrophilicity has no effect on ΔH^{\neq} , and nucleophilicity decreases it. In the first case, solvent polarity increases ΔH^{\neq} , in the second, has no effect, and in the third, decreases it. The only solvent parameter that exerts the same effect in all the three reactions is polarizability: It operates to decrease ΔH^{\neq} . An even more intricate pattern is characteristic of aprotic solvents.

At present we still have insufficient experimental evidence for interpreting such a diversity of solvation effects. However, it is already obvious that the solvent effect on ΔH^{\neq} and ΔS^{\neq} is more specific than on ΔG^{\neq} .

Proceeding with research into solvent effects on the rate of heterolysis 1-halo-1-methylcycloalkanes, we dwelt on the temperature effect on the rate of heterolysis of 1-chloro-1-methylcyclopentane (I) in 6 protic (MeOH, BuOH, *i*-PrOH, *t*-BuOH, *tert*- C_5H_{11} OH, cyclohexanol) and 8 aprotic solvents (γ -butyrolactone, MeCN, PhCN, PhNO₂, acetone, PhCOMe, cyclohexanone, 1,2-dichloroethane). Correlation analysis of the effect of solvent parameters on the activation parameters of the reaction was



(a, b) $\Delta G^{\neq} - \Delta S^{\neq}$ and (c, d) $\Delta H^{\neq} - \Delta S^{\neq}$ dependences (for solvent numbering, see Table 2).

performed by the Koppel–Palm equation (1) [3, 5] augmented with the cohesion energy density parameter δ^2 [4], as well as by Eq. (2).

$$\begin{split} \phi &= a_0 + a_1 \, \frac{\varepsilon - 1}{2\varepsilon + 1} + a_2 \, \frac{n^2 - 1}{n^2 + 2} \\ &+ a_3 E \, + \, a_4 B \, + \, a_5 \delta^2, \end{split} \tag{1}$$

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

Here φ is a parameter to be correlated $(\Delta G^{\neq}, \Delta H^{\neq}, \Delta S^{\neq})$, χ is the dielectric constant of the solvent, *n* is the refractive index, *E* and *V* are the empirical electrophilicity and nucleophilicity parameters [3], E_T and *Z* are the solvatochromic ionizing ability parameters [17], $\delta^2 = (\Delta H_m - RT)/V_m$ is the self-association energy of the solvent, ΔH_m is the molar evaporation heat, and V_m is the molar volume.

Equations (1) and (2) are similar to each other, since the E_T and Z values are fairly accounted for by the polarity, polarizability, and electrophilicity solvent parameters [5]. Equation (2) has the advantage of the applicability to a smaller number of experimental points.

In [1] we studied the kinetics of heterolysis of chloride I at 25°C in 10 alcohols and 26 aprotic solvents, and Takuchi *et al.* [19] reported kinetic data for solvolysis of this substrate at various temperatures in MeOH, EtOH, and AcOH, as well as at 25°C in CF₃CH₂OH and various water–ethanol mixtures. In aprotic solvents, this reaction occurs by the E1 mechanism, while in protic, by the E1 + SN1 mechanism. The reaction rate is always described by a first-order equation (3).

$$v = k[\mathbf{I}]. \tag{3}$$

Kinetic experiments we performed by the verdazyl method [20] using 1,3,5-triphenylverdazyl (II) as internal indicator. The stoichiometric equation of the reaction is as follows:



It is assumed that verdazyl **II** rapidly and quantitatively reacts with the solvent-separated ion pair of the substrate, which allows one to follows the reaction rate to be followed spectrophotometrically by the decrease in the indicator concentration (λ_{max} 720 nm) [16, 20]. First verdazylium salt **III** and alkyl derivative of verdazyl **II** are formed, and the latter then rapidly decomposes into 1-methylcyclopentene and leucoverdazyl (**IV**). In protic solvents, chloride **I** undergoes partial solvolysys. Therewith, HCl evolves and rapidly and quantitatively reacts with verdazyl to form compounds **III** and **IV** [20]. Therewith, the stoichiometric relations in reaction (4) do not change.

The reaction rate is independent of the concentration of the indicator and on the nature of its substituents. The concentrations of the substrate and indicator in the kinetic experiments were 0.01-0.10 and $(1-3) \times 10^{-4}$ M, respectively, and the conversion of the substrate was 0.001-1%.

The rate constants in 14 solvents at various temperatures are given in Table 1. Table 2 lists our and published values of log k_{25} , ΔG^{\neq} , ΔH^{\neq} , and ΔS^{\neq} in 16 solvents and required solvent parameters.

The figure shows the $\Delta G^{\neq} - \Delta S^{\neq}$ and $\Delta H^{\neq} - \Delta S^{\neq}$ dependences. Two compensation effects are well defined: one for aprotic solvents (plots *a* and *c*) and the second, for protic (plots *b* and *d*). No $\Delta G^{\neq} - \Delta S^{\neq}$ and $\Delta H^{\neq} - \Delta S^{\neq}$ compensation effects are observed for all the 16 solvents. For 8 protic solvents, a good correlation was obtained [Eq. (5)].

$$\Delta H^{\neq} = (102000 \pm 1540) + (235 \pm 19) \Delta S^{\neq};$$

R 0.981, *S* 2700, *F* 156 (4.21), *n* 8. (5)

Solvent	t, °C	$k \times 10^7$, s ⁻¹	Solvent	t, °C	$k \times 10^7$, s ⁻¹
MeOH	25.0	184 ± 4^{b}	Benzonitrile	25.0	0.186 ± 0.004
	29.5	320 ± 3		30.0	0.386 ± 0.002
	35.0	646 ± 1		35.0	0.579 ± 0.015
	40.5	1150 ± 20		40.0	1.12 ± 0.01
	44.5	1770 ± 10		45.0	2.00 ± 0.02
BuOH	25.0	13.0 ± 0.1	Nitrobenzene	25.0	0.181 ± 0.008
	30.0	25.3 ± 0.7		30.0	0.311 ± 0.003
	35.0	45.2 ± 0.1		35.0	0.565 ± 0.001
	40.0	83.9 ± 0.4		41.0	1.14 ± 0.01
	44.5	140 ± 5		45.0	1.73 ± 0.02
Cyclohexanol	25.0	4.80 ± 0.01	Acetone	25.0	0.0625 ± 0.0003
	31.5	11.8 ± 0.4		25.5	0.0685 ± 0.0007
	35.0	17.1 ± 0.5		30.0	0.128 ± 0.001
	43.5	44.2 ± 0.2		35.0	0.248 ± 0.002
	49.5	95.5 ± 0.1		40.0	0.578 ± 0.001
				44.0	0.847 ± 0.001
<i>i</i> -PrOH	25.0	14.3 ± 0.2	Cyclohexanone	25.0	0.0442 ± 0.0002
	30.0	28.7 ± 0.2		30.5	0.0845 ± 0.0003
	35.0	49.7 ± 1.0		35.0	0.137 ± 0.004
	39.0	79.4 ± 0.1		45.0	0.345 ± 0.002
	44.0	126 ± 4		50.5	0.586 ± 0.002
t-BuOH	25.0	4.16 ± 0.05	Acetophenone	25.0	0.0453 ± 0.0001
	31.0	7.13 ± 0.03		29.5	0.0926 ± 0.0002
	35.0	10.6 ± 0.3		35.0	0.168 ± 0.003
	40.0	15.1 ± 0.1		39.5	0.319 ± 0.009
	46.0	23.3 ± 0.2		43.0	0.472 ± 0.007
	50.0	31.5 ± 0.1		48.5	0.808 ± 0.005
t-AmOH	25.0	1.50 ± 0.06	1,2-Dichloroethane	25.0	0.106 ± 0.002
	30.5	2.70 ± 0.02		30.5	0.227 ± 0.004
	35.5	4.58 ± 0.01		35.0	0.400 ± 0.010
	40.0	6.61 ± 0.01		39.5	0.705 ± 0.002
	41.0	7.35 ± 0.02		44.0	1.16 ± 0.03
	46.0	10.7 ± 0.5			
γ-Butyrolactone	25.0	2.47 ± 0.01			
	30.5	4.52 ± 0.01			
	34.5	7.13 ± 0.01			
	39.5	11.7 ± 0.2			
	45.5	21.3 ± 0.3			
	49.5	32.6 ± 0.1			
Acetonitrile	25.0	2.00 ± 0.02			
	29.5	3.84 ± 0.02			
	34.5	6.86 ± 0.01			
	40.0	12.1 ± 0.3			
	44.5	20.4 ± 0.5	ļ		
	L	L	I		1

Table 1. Solvent and temperature effects on the rate of heterolysis of 1-chloro-1-methylcyclopentane^a

^a Averages over 2–3 runs are given. ^b In [19], k_{25} 4.65×10⁻⁵ and k_{50} 86.1×10⁻⁵ s⁻¹.

Here and heteinafter, ΔH^{\neq} and ΔG^{\neq} are in J/mol, *F* are the apparent and critical (in parentheses) Fisher criteria at a 95% confidence level (the reliability of the model is confirmed by the excess of the apparent

value over critical).

The $\Delta G^{\neq} - \Delta S^{\neq}$ correlation for 8 protic solvents is absent (*R* 0.78). Upon exclusion of the points for

Solvent effects of	on the rate and	l activation par	rameters of het	erolysis of 1-cl	hloro
Solvent	$-\log k_{25}$ (k in s ⁻¹)	ΔG [≠] , kJ/mol	∆H [≠] , kJ/mol	$-\Delta S^{\neq},$ J mol ⁻¹ K ⁻¹	
MeOH ^a	4.74	100 ± 2	89±1.2	37±3	(
AcOH ^b	4.89	101	99	6	1
EtOH ^c	5.25	103	98	16	1
RuOH	5 89	107 ± 1	93 1 + 0 6	45 + 2	(

Table 2. -1-methylcyclopentane

No.	Solvent	$-\log k_{25}$ (k in s ⁻¹)	∆G [≠] , kJ/mol	∆H [≠] , kJ/mol	$-\Delta S^{\neq},$ J mol ⁻¹ K ⁻¹	r	E _T , kJ/mol
1	MeOH ^a	4.74	100 ± 2	89±1.2	37±3	0.9996	232
2	AcOH ^b	4.89	101	99	6	1.0	214
3	EtOH ^c	5.25	103	98	16	1.0	217
4	BuOH	5.89	107 ± 1	93.1 ± 0.6	45 ± 2	0.9999	210
5	<i>i</i> -PrOH	5.84	106 ± 4	87.4 ± 2.2	64 ± 7	0.9984	203
6	Cyclohexanol	6.32	109 ± 4	93.2 ± 2.1	53 ± 6	0.9992	196
7	t-BuOH	6.38	109 ± 2	62.1 ± 0.8	159 ± 2	0.9998	184
8	<i>tert</i> -C ₅ H ₁₁	6.82	112 ± 3	71.9 ± 1.4	134 ± 4	0.9984	175
9	γ-Butyrolactone	6.61	111 ± 1	81.1 ± 0.6	99 ± 2	0.9999	185
10	MeCN	6.70	111 ± 4	89.5 ± 1.9	73 ± 6	0.9989	193
11	PhNO ₂	7.74	117 ± 2	87.5 ± 1.1	99 ± 3	0.9997	176
12	PhCN	7.73	117 ± 6	89.1 ± 3.1	94 ± 9	0.9971	176
13	1,2-Dichlorethane	7.97	118 ± 2	96.6 ± 1.0	73 ± 3	0.9997	175
14	Acetone	8.20	120 ± 6	107.2 ± 3.0	42 ± 9	0.9980	177
15	PhCOMe	8.34	121 ± 5	94.7 ± 2.7	87 ± 8	0.9987	173
16	Cyclohexanone	8.35	121 ± 3	77.7 ± 1.5	144 ± 5	0.9995	171
No.	Solvent	Z, kJ/mol	ε(20)	$n_{\rm D}^{20}$	<i>E</i> , kJ/mol	<i>B</i> , kJ/mol	δ^2 , kJ l ⁻¹ mol ⁻¹
1	МеОН	350	32.7	1.3286	62.3	2.61	941
2	АсОН	331	6.15	1.3716	61.1	1.66	427
3	EtOH	333	24.3	1.3614	48.5	2.81	703
4	BuOH	325	17.1	1.3992	43.1	2.76	552
5	<i>i</i> -PrOH	319	18.3	1.3773	33.6	2.82	565
6	Cyclohexanol	314	15.0	1.4674	28.9	2.89	515
7	t-BuOH	298	10.9	1.3848	21.8	2.95	460
8	tert-C ₅ H ₁₁	296	5.8 ^d	1.3859	22.6	2.95	460
9	γ-Butyrolactone	290	39.0	1.4360	12.1	2.48	695
10	MeCN	298	37.5	1.3416	21.8	1.91	594
11	PhNO ₂	278	34.8	1.5546	0.8	0.8	477
12	PhCN	272	25.2	1.5282	3.3	1.85	515
13	1,2-Dichloroethane	265	10.4	1.4451	12.6	0.48	411
14	Acetone	275	20.7	1.3588	8.8	2.68	393
15	PhCOMe	274	17.4	1.5350	2.9	2.42	464
16	Cyclohexanone	271	18.3	1.4510	2.1	2.89	431

^a In [19], $\log k_{25}$ -4.33, $\log k_{50}$ -3.06, ΔH^{\neq} 91.1 kJ/mol, ΔS^{\neq} -23 J mol⁻¹ K⁻¹. ^b $\log k_{50}$ -3.51 [19]. ^c $\log k_{50}$ -3.88 [19], $\log k_{25}$ -5.34 [21]. ^d At 25°C.

MeOH and t-BuOH we obtained Eq. (6).

$$\Delta G^{\neq} = (102000 \pm 1220) - (79.8 \pm 18.1) \Delta S^{\neq};$$

R 0.910, *S* 1840, *F* 19.4 (6.26), *n* 6. (6)

Further exclusion of the point for cyclohexanol results in a fair correlation.

$$\Delta G^{\neq} = (102000 \pm 890) - (79.8 \pm 12.7) \Delta S^{\neq};$$

R 0.964, S 1300, F 39.2 (9.12), n 5.

The $\Delta H^{\neq} - \Delta S^{\neq}$ compensation effect is explained by the decrease both in ΔH^{\neq} and in ΔS^{\neq} .

The free terms in Eqs. (5) and (6) have the same value. This value, $\Delta G^{\neq} = \Delta H^{\neq}$ at $\Delta S^{\neq} = 0$, is equal to the potential energy of the reaction $\Delta E_r =$ 102 kJ/mol [22, 23].

The $\Delta H^{\neq} - \Delta S^{\neq}$ correlation for 8 aprotic solvents is poor, R 0.893. Exclusion of the point for MeCN results in an approximate correlation.

$$\Delta H^{\neq} = (118000 \pm 4980) + (300 \pm 52.1) \Delta S^{\neq};$$

R 0.932, S 3930, F 33.2 (4.95), n 7.

The same operation with γ -butyrolactone gives the following correlation.

$$\Delta H^{\neq} = (115000 \pm 4450) + (268 \pm 48) \Delta S^{\neq};$$

R 0.928, S 3700, F 30.8 (4.95), n 7.

A good correlation is obtained when both the solvents are excluded.

$$\Delta H^{\neq} = (118000 \pm 2310) + (288 \pm 24) \Delta S^{\neq};$$

R 0.986, S 1820, F 140 (6.26), n 6.

The $\Delta G^{\neq} - \Delta S^{\neq}$ correlation in aprotic solvents is absent.

It is assumed that the presence of a compensation effect points to the fulfillment of the isokinetic relationship which implies that there is some temperature point in a given reaction series, at which the reaction has the same rate in all the solvents [22–24]. This isokinetic temperature β is found by the following relationship:

$$\delta \Delta H^{\neq} = \beta \delta \Delta S^{\neq}.$$

The operator δ means the use of relative values of activation parameters. With EtOH as standart solvent, we have the following expression for protic solvents.

$$\delta \Delta H^{\neq} = 235 \delta \Delta S^{\neq}; R 0.981, S 2.7, n 8$$

Consequently, at -38° C, the rate of heterolysis of chloride I in all the protic solvents should be the same. However, the log k-1/T dependences for protic solvents reveal no isokinetic temperature. Thus, the same rates of solvolysis of chloride I in MeOH and BuOH are observed at -212° C (log k -67.1), in *tert*-C₅H₁₁OH and MeOH, at -97^{\circ}C (log k -15.9), in *tert*-C₅H₁₁ and *i*-PrOH, at -55^{\circ}C (log k -11.6), in *t*-BuOH and cyclohexanol, at 21^{\circ}C (log k -6.51), in *tert*-C₅H₁₁ and *t*-BuOH, at 125^{\circ}C (log k -3.52), and in cyclohexanol and *i*-PrOH, at 289^{\circ}C (log k 1.63). Thus, the presence of a compensation effect in a reaction series not necessarily implies the fulfillment of the isokinetic relationshiop.

The compensation effect points to a certain similarity of solvation effects [23]. In our case this seems obvious, as we observe two different compensation effects in protic and aprotic solvents, where the conditions of solvation of the transition state are much different. At the same time, it is solvation of the transition state in monomolecular heterolysis reactions which determines changes in ΔG^{\neq} , ΔH^{\neq} , and ΔS^{\neq} in going from one solvent to another, since the solvation energies of the ground state vary only slightly [10].

In protic solvents, the most important is electrophilic solvation of the substrate nucleofuge via formation of H complex **A**. This solvation is a driving force of the heterolysis reaction [16, 25]. Along with a linear quadrupole **A**, a cyclic quadrupole **B** may also form [1]. This assumption is supported by the strong decrease in ΔS^{\neq} is going from primary to secondary and further to tertiary alcohols (Table 2), which is accounted for by steric hindrances to formation of solvate **B**.



In dipolar aprotic solvents, too, cyclic **C** and linear **D** quadrupoles may form. In this case, ΔS^{\neq} should decrease by about 85 J mol⁻¹ K⁻¹ [26]. Such a decrease is indeed observed in γ -butyrolactone, MeCN, PhCN, PhNO₂, and 1,2-dichloroethane. In the series acetone–acetophenone–cyclohexane, ΔS^{\neq} decreases from -42 to -144 J mol⁻¹ K⁻¹. In acetone, a chargetransfer transition complex is likely to be formed. Actually, the coordination of one monodentate ligand decreases the activation entropy by ~45 J mol⁻¹ K⁻¹ [27]. The ΔS^{\neq} values in acetone and cyclohexanone suggest a quadrupole and a cyclic solvate **E** as transition states in the first and second cases, respectively. The formation of such cyclic complexes decreases ΔS^{\neq} by 150–200 J mol⁻¹ K⁻¹ [26, 28].

The presence of several compensation effects in one reaction series may imply different solvation

mechanisms. Different compensation effects in one and the same reaction series may be observed separately in protic and in aprotic solvents. For instance, two compensation effects have been reported for heterolysis of *t*-BuCl in protic solvents [11], as well as for heterolysis of 7 α -bromocholesterol benzoate in aprotic solvents [29]. The same conclusions follow from a comparison of ΔH^{\neq} and ΔS^{\neq} for heterolysis of Ph₂CHBr in aprotic solvents [30, 31].

Analysis of solvent effects on activation parameters for monomolecular heterolysis reactions shows that the reason for the observation of several compensation effects may lie in a narrow ΔS^{\neq} scale [6, 10, 11, 16, 32, 33].

The rate of heterolysis of chloride I is about two orders of magnitude higher that the rate of heterolysis of t-BuCl. The rate increase in AcOH and primary alcohols is mostly associated with a decrease in ΔH^{\neq} , since the ΔS^{\neq} values are roughly equal to each other. This result points to a greater stability of the 1-methylcyclopentyl cation compared with the tert-butyl cation and to similarity of solvation effects in heterolysis of both substrates. In *i*-PrOH, the ΔH^{\neq} values for both substrates (86 kJ/mol: here and hereinafter, values for t-BuCl are given) are almost equal to each other, and the rate decrease in going from chloride I to t-BuCl is explained by a decrease in ΔS^{\neq} [-106 J mol⁻¹ K⁻¹]. These data suggest that solvation of the transition state in heterolysis of t-BuCl involves stronger steric hindrances than in the case of chloride I. Therefore, the rate of heterolysis of t-BuCl in i-PrOH is two orders of magnitude lower compared with chloride I, whereas the respective difference in primary alcohols is only one and half orders of magnitude. In t-BuOH, the rate decrease of two orders of magnitude in going from chloride I to t-BuCl is explained by a sharp increase in ΔH^{\neq} (101 kJ/mol) with simultaneous increase in ΔS^{\neq} (-67 J mol⁻¹ K⁻¹). The steric hindrances to solvation of the transition state of chloride I in t-BuOH are so strong that here, compared with primary alcohols, quite a different solvate is formed, which shows up in a sharp decrease in ΔS^{\neq} . Of importance is also the fact that t-BuOH is (again for steric reasons) is a poorly structured solvent, and, therefore, breakdown of the solvent structure should only slightly affect ΔS^{\neq} .

In γ -butyrolactone, MeCN, PhCN, and PhNO₂, the rate decrease of two orders of magnitude in going from chloride **I** to *t*-BuCl is mostly contributed by an increase in ΔH^{\neq} , while the ΔS^{\neq} values are close to each other. In all the above solvents, apparently, solvates **C** and **D** are formed. However, in acetone, acetophenone, and cyclohexanone, the ΔS^{\neq} values for

t-BuCl (-148, -164, and -193 J mol⁻¹ K⁻¹, respectively) are much lower than for chloride **I**. This difference is presumably explained by hindrances to formation of solvates **C**, **D**, and **E**.

Analysis of solvation effects in heterolysis of chloride I in 8 protic and 8 aprotic solvents in terms of Eq. (1) gave a fair five-parameter correlation.

$$\Delta G^{\neq} = (121000 \pm 15700) + (10600 \pm 34600)f(\varepsilon)$$

- (7460 \pm 26600)f(n) - (0.288 \pm 0.062)E - (0.258 \pm 0.965)B
- (0.00959 \pm 0.0090)\delta^2;
R 0.952, S 2610, F 19.54 (2.91), n 16.

The errors in the polarity, polarizability, and nucleophilicity parameters show that these parameters has no rate effect. Actually, the quality of the correlation is practically almost unaffected on exclusion of these parameters.

$$\Delta G^{\neq} = (123000 \pm 2420) - (0.292 \pm 0.035)E$$
$$- (0.00779 \pm 0.0050)\delta^{2};$$
$$R \ 0.951, \ S \ 2310, \ F \ 62.03 \ (2.60), \ n \ 16.$$

In fact, ΔG^{\neq} depends only on the electrophilicity of the solvent.

$$\Delta G^{\neq} = (119000 \pm 955) - (0.321 \pm 0.031)E;$$

R 0.942, S 2430, F 110.4 (2.44), n 16.

Using Eq. (2) for 16 solvents leads to a fair and an approximate three-parameter correlations.

$$\begin{split} \Delta G^{\neq} &= (189000 \pm 6440) - (0.268 \pm 0.027)Z \\ &+ (1.10 \pm 0.731)B + (0.000477 \pm 0.0050)\delta^2; \\ R & 0.966, S & 2020, F & 56.27 & (2.60), n & 16. \\ \Delta G^{\neq} &= (179000 \pm 8570) - (0.356 \pm 0.057)E_T \\ &- (0.510 \pm 1.026)B + (0.00372 \pm 0.0080)\delta^2; \\ R & 0.926, S & 2950, F & 24.02 & (2.60), n & 16. \end{split}$$

In both cases, cohesion has no rate effect.

$$\Delta G^{\neq} = (189000 \pm 5730) - (0.266 \pm 0.020)Z + (1.10 + 0.703)B;$$

R 0.966, S 1940, F 91.36 (2.60), n 16.

 $\Delta G^{\neq} = (177000 \pm 7510) - (0.336 \pm 0.040) E_T - (0.455 \pm 0.989) B;$

The nucleophicity of the solvent has a negative, even if rather weak, rate effect, but the greatest contribution is from ionizing ability solvent parameters.

$$\Delta G^{\neq} = (187000 \pm 5970) - (0.254 \pm 0.020)Z;$$

R 0.960, S 2030, F 163.5 (2.44), n 16.

$$\Delta G^{\neq} = (177000 \pm 7280) - (0.341 \pm 0.038)E_T;$$

R 0.923, S 2780, F 80.64 (2.44), n 16.

Thus, in the set of 8 protic and 8 aprotic solvents, ΔG^{\neq} decreases with increasing solvent electrophilicity and ionizing ability. A weak negative effect of nucleophilic solvation is observed.

The solvent parameters in Eqs. (1) and (2) for the set of 8 protic and 8 aprotic solvents are independent variables. The strongest collinearity [8] is observed for the following pairs: $\delta^2 - E_T (R \ 0.707)$, $\delta_2 - Z (R \ 0.650)$, $\delta^2 - E (R \ 0.538)$, $f(n) - E (R \ 0.688)$, $f(\varepsilon) - \delta^2 (R \ 0.479)$. For the other pairs of parameters, R = 0.002 - 0.397.

Equation (2) for 8 aprotic solvents gives a good and a fair three-parameter correlations.

$$\begin{split} \Delta G^{\neq} &= (176000 \pm 9540) - (0.283 \pm 0.061) E_T \\ &+ (1.034 \pm 0.342) B - (0.0216 \pm 0.0040) \delta^2; \\ R & 0.989, S & 777, F & 61.63 & (6.09), n & 8. \\ \Delta G^{\neq} &= (172000 \pm 19100) - (0.167 \pm 0.081) Z \\ &+ (1.49 \pm 0.599) B - (0.0228 \pm 0.0090) \delta^2; \\ R & 0.967, S & 1360, F & 19.25 & (6.09), n & 8. \end{split}$$

Exclusion of the nucleophilicity parameter deteriorates the correlation considerable.

$$\Delta G^{\neq} = (182000 \pm 15100) - (0.313 \pm 0.098)E_T - (0.0187 \pm 0.0070)\delta^2;$$

R 0.965, S 1260, F 33.47 (4.88), n 8.

$$\Delta G^{\neq} = (166000 \pm 27000) - (0.134 \pm 0.114)Z - (0.0237 \pm 0.0120)\delta^2;$$

R 0.914, S 1940, F 12.7 (4.88), n 8.

Equation (1) for 8 aprotic solvents gives a good and an excellent three-parameter correlations.

 $\Delta G^{\neq} = (132000 \pm 2100) - (0.195 \pm 0.063)E$

+
$$(1.034 \pm 0.466)B$$
 - $(0.0304 \pm 0.0040)\delta^2$;

R 0.980, S 1060, F 32.7 (6.09), n 8. (7)

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$$\Delta G^{\neq} = (122000 \pm 2280) + (35700 + 6110)f(n) + (1.77 \pm 0.287)B - (0.0357 \pm 0.0020)\delta^{2}; R 0.993, S 632, F 93.72 (6.09), n 8. (8)$$

Exclusion of the nucleophilicity parameters much deteriorates correlation (7), making it fair.

$$\Delta G^{\neq} = (133000 \pm 2720) - (0.219 \pm 0.083)E$$
$$- (0.0283 \pm 0.0060)\delta^{2};$$
$$R \ 0.955, \ S \ 1410, \ F \ 26.14 \ (4.88), \ n \ 8.$$

Thus, in aprotic solvents, electrophilicity, ionizing ability, and cohesion decrease ΔG^{\neq} , whereas nucleophilicity and polarizability increase it. In this set of solvents, too, parameters of Eqs. (1) and (2) are independent variables. Collinearity between solvent parameters is slightly better in this case: $\delta^2 - Z$ (*R* 0.805), $\delta^2 - E_T$ (*R* 0.703), f(n) - E (*R* 0.802), $\delta^2 - f(\varepsilon)$ (*R* 0.674); for the other pairs of parameters, *R* = 0.009–0.452.

Equation (2) for 8 protic solvents gives two fair correlations.

$$\Delta G^{\neq} = (130000 \pm 31400) - (0.101 \pm 0.094)Z + (4.93 \pm 2.58)B - (0.0085 \pm 0.0090)\delta^{2}; R 0.967, S 1420, F 19.32 (6.09), n 8. \Delta G^{\neq} = (121000 \pm 14900) - (0.113 + 0.067)E_{T} + (4.64 \pm 1.95)B - (0.0075 \pm 0.0070)\delta^{2}; R 0.975, S 1230, F 26.06 (6.09), n 8.$$

Exclusion of the cohesion parameters deteriorates the correlation.

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$$\Delta G^{\neq} = (157000 \pm 12800) - (0.184 \pm 0.033)Z + (2.87 \pm 1.40)B;$$

$$R \ 0.960, \ S \ 1410, \ F \ 29.06 \ (4.88), \ n \ 8.$$

$$\Delta G^{\neq} = (135000 \pm 8070) - (0.182 + 0.029)E_T + (2.90 \pm 1.26)B;$$

(157000 + 10000) (0.104 + 0.000)

R 0.967, S 1270, F 36.10 (4.88), n 8. (9)

Exclusions of the nucleophilicity parameter renders the correlations approximate ($R \sim 0.93$).

Equation (1) for 8 protic solvents gives one good three-parameter and three fair two-parameter correlations.

$$\Delta G^{\neq} = (99900 \pm 6600) - (72200 \pm 11500) f(\varepsilon)$$

+
$$(69200 \pm 19000)f(n)$$
 + $(8.04 \pm 1.02)B$;

R 0.984, S 991, F 41.07 (6.09), n 8.

$$\Delta G^{\neq} = (109000 \pm 8520) + (26300 \pm 31700) f(n)$$

$$-(0.229\pm0.042)E;$$

$$\Delta G^{\neq} = (123000 \pm 6280) - (16100 + 14600) f(\varepsilon)$$

 $- (0.241 \pm 0.033)E;$ $R \ 0.961, \ S \ 1380, \ F \ 30.20 \ (4.88), \ n \ 8.$ $\Delta G^{\neq} = (121000 \pm 14900) - (0.113 + 0.067)E$ $+ (4.64 \pm 1.95)B - (0.0075 \pm 0.0070)\delta^{2};$

The greatest contribution is from the electrophilicity parameter.

$$\Delta G^{\neq} = (116000 \pm 1420) - (0.249 \pm 0.033)E;$$

R 0.951, S 1410, F 57.11 (4.21), n 8.

Thus, in protic solvents, ΔG^{\neq} decreases with increasing solvent electrophilicity or ionizing ability and increases with increasing solvent nucleophilicity. The strongest collinearity is characteristic of the following pairs of parameters of Eqs. (1) and (2): $\delta^2 - E_T (R 0.745)$, $\delta^2 - Z (R 0.764)$, $f(\varepsilon) - \delta^2 (R 0.719)$, B - E (R 0.716), $f(n) - \delta^2 (R 0.584)$, $\delta^2 - E (R 0.565)$; for the other pairs of parameters, R 0.118 - 0.453.

Correlation analysis of solvation effects in heterolysis of chloride **I** in 16 solvents showed that the reaction rate is most strongly contributed by the electrophilicity or ionizing ability of the solvent. Nucleophilic solvation exerts a negative rate effect, which is characteristic both of the entire set of solvents and for protic and aprotic solvents seprately. Earlier this effect was observed in protic solvents only, in heterolyses of *t*-BuX, 1-AdX, *p*-MeOC₆H₄CCl₃, 2-bromo-2methyladamantane, PhCMe₂Cl, Ph₂CCl₂, 1-bromo-1methylcyclohexane, and 1-bromo-1-methylcyclopentane [6, 9, 11, 16, 21, 32, 34]. The same effect we also found in heterolysis of chloride **I** in 12 protic solvents [1].

The negative effect of nucleophilic solvation is associated with the nucleophilic solvation of the contact ion pair of the substrate, which is formed before the limiting stage [16]. This stabilizes the intermediate and hinders nucleofuge elimination by the SN1 (E1) mechanism [35]. Nonequilibrium solvation of the transition state takes place only [36]. In protic solvents, solvates **A** and **B**, moving along the reaction coordinate, consecutively convert into contact, loose, and solvent-separated ion pairs and give reaction products. The decrease in the reaction rate is associated with the formation of a cyclic **F** [16] or a linear **G** products of nucleophilic solvation of the contact ion pair.

$$\begin{array}{ccc} O-H & R' \\ R^+ & O-R' & R' \\ Cl^- & H & H \end{array} O \cdots R^+ Cl^- \cdots HOR'$$

$$F & G$$

Formation of solvate G in monomolecular heterolysis reactions was discussed earlier [37–39]. The assumptions made in those works are also consistent with the fact that the polarizability of the solvent, which appears to favors formation of complexes \mathbf{F} and \mathbf{G} , too, exerts a negative rate effect.

The reason for the negative effect of nucleophilic solvation in our set of aprotic solvents is the high nucleophilicity of these solvents. Thus, γ -butyrolactone, acetone, acetophenone, and cyclohexanone are as nucleophilic as alcohols, and the nucleophilicity of PhCN and MeCN, too, is sufficiently high (Table 2). The negative effect of nucleophilic solvation may be associated with the formation of complexes **D** and **E**. Stoichiometric evidence for the formation of complexes **D** in SN1 (E1) reactions has been reported [40, 41].

Correlation analysis of the effect of solvent parameters on the ΔH^{\neq} of heterolysis of chloride **I** in the set of 8 protic and 8 aprotic solvents in terms of Eqs. (1) and (2) was unsuccessful (*R* 0.66). Exclusion of the most deviating poins (acetone and *t*-BuOH) did not improve the correlation.

The correlation by Eq. (1) for 8 aprotic solvents, too, was poor $(R \ 0.71)$. However, upon exclusion of the point for cyclohexanone, one excellent, on good, and two fair correlations were obtained.

$$\begin{split} \Delta H^{\neq} &= (126000 \pm 2860) + (0.384 \pm 0.085)E + (4.15 \pm 0.71)B \\ &- (0.0878 \pm 0.0060)\delta^2; \\ R \ 0.993, \ S \ 1410, \ F \ 68.18 \ (8.94), \ n \ 7. \ (10) \\ \Delta H^{\neq} &= (168000 \pm 13900) - (148000 \pm 47900)f(n) \\ &- (0.496 \pm 0.312)E - (0.0618 \pm 0.0110)\delta^2; \\ R \ 0.978, \ S \ 2430, \ F \ 22.35 \ (8.94), \ n \ 7. \ (11) \\ \Delta H^{\neq} &= (151000 \pm 9740) - (80900 \pm 26500)f(n) \\ &- (0.0715 \pm 0.0110)\delta^2; \\ R \ 0.960, \ S \ 2850, \ F \ 23.36 \ (6.16), \ n \ 7. \end{split}$$

$$\Delta H^{\neq} = (124000 \pm 6810) + (3.98 \pm 1.71)B$$
$$- (0.0769 \pm 0.014)\delta^{2};$$
$$R \ 0.942, \ S \ 3400, \ F \ 15.91 \ (6.16), \ n \ 7.$$

Thus, in aprotic solvents, ΔH^{\neq} is decreased by cohesion and polarizability and increased by nucleophilicity. The increase in the reaction rate with increasing δ^2 and f(n) is presumably explained by the formation of cyclic quadrupole C. Evidence for this assumption comes from the fact that δ^2 nicely correlates with the dipole moments of solvents [6], and increasing solvent polarizability should favor quadrupole formation. The effect of solvent nucleophilicity suggests that the negative effect of nucleophilic solvation is associated with solvent effect on the activation enthalpy of the reaction. Of interest is the effect of solvent electrophilicity on ΔH^{\neq} : on one hand, it favors quadrupole C formation and thus accelerates the reaction [Eq. (11)] and on the other, it favors solvate **F** formation and thus decelerates the reaction [Eq. (10)].

Equation (1) for 7 aprotic solvents (cyclohexanol excluded) gave an excellent three-parameter correlation.

$$\Delta S^{\neq} = (72.7 \pm 5.13) - (344 \pm 13.8)f(n)$$

+ (0.00540 ±0.0010)B - (0.000139 ±0.00001)\delta²;
R 0.999, S 1.42, F 410.7 (8.94), n 7.

Exclusion of the nucleophilicity parameter gives a good two-parameter correlation.

$$\Delta S^{\neq} = (84.7 \pm 18.0) - (374 \pm 48.8)f(n)$$

- (0.000127 \pm 0.00001)\delta^2;
R 0.978, S 5.27, F 43.1 (6.16), n 7.

The greatest contribution is from the polarizability parameter (R 0.727).

Thus, ΔS^{\neq} in aprotic solvents decreases with increasing polarizability and cohesion.

As shown above, the rate of heterolysis of chloride **I** in aprotic solvents is increased by the electrophilicity and cohesion of the solvent and decreased by polarizability and nucleophilicity [Eqs. (7) and (8)]. The revealed effects of solvent parameters on ΔH^{\neq} and ΔS^{\neq} suggests that positive solvation effects are associated with the effects of electrophilicity and cohesion on ΔH^{\neq} , whereas negative solvation effects, with the effects of polarizability on ΔS^{\neq} and of nucleophilicity on ΔH^{\neq} . These conclusions are consistent with the suggestion that the reaction is ac-

celerated by formation of solvates C and D and decelerated by formation of solvates E.

Equation (1) for 7 protic solvents (MeOH excluded) gave a fair three-parameter correlation.

$$\Delta H^{\neq} = -(61100 \pm 33500) + (365000 \pm 117000)f(n) + (0.90 \pm 0.15)E + (0.0514 \pm 0.022)\delta^{2}; R 0.969, S 4880, F 15.6 (8.94), n 7.$$

For 8 protic solvents, R 0.921. Equation (2) for 7 protic solvents gives the following correlation.

$$\Delta H^{\neq} = -(329000 \pm 211000) + (1.31 \pm 0.657)Z + (12.8 \pm 19.4)B - (0.067 \pm 0.094)\delta^{2}; R 0.937, S 6920, F 7.23 (8.94), n 7.$$

The greatest contribution is from the Z parameter $(R \ 0.926)$.

The effects of protic solvent parameters on the activation enthalpy, especially its increase with increasing solvent electrophilicity and ionizing ability seems paradoxical, since these parameters are considered to be primarily responsible for reaction acceleration. However, as seen from Table 2, such relations are the case. The same pattern has also been observed in solvolysis of *t*-BuCl [11], where ΔH^{\neq} and simultaneously E_T and E increased in the series *i*-PrOH-OctOH-HexOH-BuOH-EtOH. It should be noted that even though the activation enthalpy increases, the reaction rate increases rather than decreasing. This increase in the reaction rate is associated with the effect of the solvent on ΔS^{\neq} . Thus, for 7 protic solvents, after exclusion of the point for MeOH, we obtain one good and one fair three-parameter equations.

$$\Delta S^{\neq} = -(593 \pm 162) + (372 \pm 254)f(\varepsilon) + (908 \pm 534)f(n) + (0.00396 \pm 0.00100)E; R 0.963, S 22.1, F 12.64 (8.94), n 7. \Delta S^{\neq} = -(320 \pm 93.9) + (1300 \pm 364)f(n) - (0.129 \pm 0.015)E + (0.000551 \pm 0.00001)\delta^{2};$$

Equation (2) leads to a fair one-parameter correlation.

$$\Delta S^{\neq} = -(1250 \pm 148) + (0.00373 \pm 0.00001)Z;$$

R 0.963, S 17.0, F 64.2 (4.95), n 7.

Thus, in heterolysis of chloride I in protic solvents,

polarizability and cohesion (or ionizing ability) increase ΔS^{\neq} , whereas nucleophilicity decreases it.

According to Eq. (9), the ionizing ability solvent parameter increases the rate of heterolysis of chloride **I**, while the nucleophilicity parameter decreases it. It was found that a positive solvation effect is associated with the effect of electrophilic solvation on the acivation entropy and a negative solvation effect, by the effect of nucleophilic solvation on the activation enthalpy. The lack of rate effect of both the polarizability and cohesion parameters which increase both ΔH^{\neq} and ΔS^{\neq} is explained by compensation.

Similar solvation effects have been observed in heterolysis of *t*-BuCl in 15 protic solvents [11]. In this case, the reaction is decelerated by electrophilicity and cohesion and decelerated by nucleophilicity, and, therewith, positive solvation effects are explained by the solvent effects on ΔS^{\neq} , while negative, on ΔH^{\neq} .

The nature of solvation effects in monomolecular heterolysis reactions is controversial [9, 16, 42, 43]. This controversy not infrequently arises from the fact that some authors used individual solvents [1, 5, 6, 8-11, 16, 20, 21, 29, 32-34], and others, solvent mixtures [19, 25, 42–45], where the conclusions as to the nature of solvation effects may be incorrect [16]. One more reason for the controversy is that some authors used multiprameter equations [3, 5, 6, 11–16, 21, 32–34], and others, in one- and two-parameter Grunwald-Winstein equations [19, 42-45] which are of limited utility [16, 33]. However, even with individual solvents and multiparameter equations, different solvation effects are frequently observed with different substrates and solvent sets. The present work shows that the reason for this phenomenon may lie in different quantitative and qualitative effects of solvent parameters on activation enthalpies and entropies.

EXPERIMENTAL

Reagents and solvents were synthesized and purified as described in [1]. Kinetic measurements were performed in the temperature-controlled cell of an SF-26 spectrophtometer [11, 20]. Calculations by Eqs. (1) and (2) were performed by the least-squares procedure using the Spss package; confidence level 95%.

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