Russian Journal of General Chemistry, Vol. 71, No. 4, 2001, pp. 591–598. Translated from Zhurnal Obshchei Khimii, Vol. 71, No. 4, 2001, pp. 635–643.

Specific Features of Solvation Effects in Monomolecular and Bimolecular Solvolysis

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Received November 9, 1999

Abstract—A method was suggested for distinguishing monomolecular and bimolecular solvolysis on the basis of reaction kinetics in water, MeOH, EtOH, *i*-PrOH, cyclohexanol, and *t*-BuOH. In solvolysis of *n*-PrBr, CH_2=$CHCH_2Br$, PhCOCl, and $MeOClO_3$ (SN2 reactions), a linear correlation is observed between $\log k$ and the solvent ionizing power Z, whereas in solvolysis of *t*-BuBr, *t*-BuCl, and 1-AdI (SN1, *E*1 reactions) this correlation is nonlinear. Deviations from linearity are due to steric hindrance decreasing the negative effect of nucleophilic solvation.

Solvolysis (1) can occur by monomolecular (SN1, *E*1) or bimolecular (SN2) mechanism [1].

$$\mathrm{RX + R'OH \longrightarrow ROR' + HX}. \qquad (1)$$

In the first case, the limiting stage is formation of an active intermediate (ion pair), whereas in the second case the reaction is controlled by interaction of the solvent with a covalent substrate (SN2 reaction) or with an intermediate (SN2-ion pair reaction [2]). Under conditions of solvolysis (excess of nucleophilic agent), these reactions are kinetically indiscernible; in both cases the reaction rate is described by a first-order kinetic equation (2):

$$v = k[\mathrm{RX}]. \qquad (2)$$

In some cases, comparison of the solvent effects on rate of solvolysis of various substrates allows conclusions about the reaction mechanism [3]. As a rule, various binary mixtures of protic solvent with protic or aprotic solvents are used. Under such conditions, it is often impossible to distinguish the effects of the polarity and nucleophilicity of the solvents [4, 5]. This problem can be overcome by using fluorinated alcohols whose nucleophilicity is low but the ionizing power and electrophilicity are high [3, 6]. However, in this case, another problem arises: distinguishing the effects of electrophilic and nucleophilic solvation [6, 7].

To determine the solvation mechanism and reveal the role of solvation effects, most authors use a one- (3) or two-parameter (4) Grunwald–Winstein equation [2, 3]. In the first case, the parameter is the ionizing power of the solvent *Y* calculated from data on solvolysis of *t*-BuX or AdX, and the second equation includes, along with *Y*, the nucleophilicity parameter *N*. These equations often lead to ambiguous and sometimes erroneous conclusions [8–10].

$$\log k/k_0 = mY, \qquad (3)$$

$$\log k/k_0 = mY + lN. \qquad (4)$$

Here k_0 and k are the rate constants of solvolysis in 80% aqueous ethanol and in the solvent being studied; m and l are the parameters of sensitivity of the solvolysis reaction to the ionizing power and nucleophilicity of the solvent. For *t*-BuX (AdX) and MeCl (MeOTs) m and l are taken as unity.

In correlation analysis of solvation effects with Eqs. (3) and (4), as a rule, data for binary solvent mixtures are used. The use of a mixed solvent severely complicates interpretation of the solvation effects. In this case, major deviations are possible, because the structures of the solvation shells of the initial reactants and transition state can vary differently with changing solvent composition. This fact is probably one of the causes of large dispersion of the $\log k$–Y correlations. The deviation should be the larger, the stronger the difference between the mixed solvent components in properties. Indeed, the largest deviations are observed with mixtures of prot3ic and aprotic solvents [11, 12]. For example, the dependence of $\log k$ for solvolysis of 2-$AdOClO_3$ on Y_{OTs} in methanol–acetone mixtures passes through a maximum at a 50% content of MeOH [13]. Kinetic study of the solvolysis of $PhCCl_3$ in water–acetonitrile mixtures showed that with increasing water content the reaction mechanism abruptly switches from SN2 to SN1 [14]; this fact

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was explained by changes in the structure of the solvation shell of the substrate.

Equations (3) and (4) are hardly suitable for elucidating the solvolysis mechanism and revealing the nature of solvation effects also because of the fact that parameters *Y* and *N* are not independent [2] and cannot be related to a single specific property of a solvent [15]. However, these equations are used for this purpose for already 50 years [3, 16, 17], especially actively in recent studies [3, 18–20].

The role of the nucleophilic effect of a solvent in monomolecular solvolysis is the subject of especial controversy [3, 7, 10]. Some authors believe that these reactions occur without nucleophilic assistance of the solvent [7, 10, 21, 22]; others have the opposite opinion [3, 23, 24], including the case of solvolysis of *tert*-butyl halides.

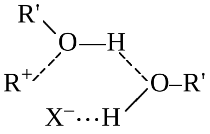
Study by the verdazyl procedure [25] of solvation effects in monomolecular heterolysis (SN1, *E*1, solvolysis) of various substrates in a wide range of individual protic and aprotic solvents revealed no nucleophilic assistance of the solvent [7, 10, 21, 25–29]. This conclusion was based on correlation analysis of solvation effects for 15 substrates (*t*-BuX, 1-AdX, 2-bromo-2-methyladamantane, Ph_2CHBr, *p*-$MeO \cdot C_6H_4CCl_3$, PhCHClMe, Ph_2CCl_2, $PhCMe_2Cl$, 7α-bromocholesterol benzoate, *p*-methoxyneophyl tosylate) using Koppel–Palm [28] and Kamlet–Taft [29] multiparameter equations including the parameters of polarity, polarizability, nucleophilicity, electrophilicity, and cohesion density of the solvents. The heterolysis rate is mainly governed by the polarity and electrophilicity parameters. In the case of Ph_2CHBr, PhCHClMe, and 7α-bromocholesterol benzoate, the rate is independent of the solvent nucleophilicity [30, 31], and in the other cases it decreases with increasing solvent nucleophilicity [7, 10, 21]. The negative effect of the nucleophilic solvation is also revealed by other methods of analysis of solvation effects. This was demonstrated for solvolysis of *p*-methoxyneophyl tosylate [32] and 2-phenyl-2-adamantyl *p*-nitrobenzoate [33] and for heterolysis of 2-bromo-2-methylpentane in DMF [34].

According to modern views [10, 21, 25], heterolysis of a covalent bond occurs via successive formation of three ion pairs: contact, loose, and solvent-separated:

$$\mathrm{RX} \rightleftarrows \mathrm{R^+X^-} \rightleftarrows \mathrm{R^+\ldots 3X^-} \rightleftarrows \mathrm{R^+}\,|\,\mathrm{Solv}\,|\,\mathrm{X^-} \longrightarrow \text{Reaction products.} \qquad (5)$$

In the limiting stage, a contact ion pair transforms into a loose ion pair through interaction with solvent cavities formed by fluctuations of the liquid density [35] and occupying about 10% of the liquid volume [36]. The resulting loose ion pair rapidly transforms into a solvent-separated ion pair, which (also rapidly) transforms into reaction products.

It is believed [10, 21, 25] that the negative effect of nucleophilic solvation in monomolecular solvolysis is due to formation of a cyclic solvation complex of a contact ion pair **A**:



A

This process stabilizes the ion pair and hinders separation of ions. At high temperatures, complex **A** is unstable, and the reaction rate becomes independent of the solvent nucleophilicity [10]; this was demonstrated for *t*-BuCl at 120°C [27]. The negative effect of nucleophilic solvation should decrease as the steric hindrance to nucleophilic solvation increases [10]. Such hindrance increases in going from water to primary, secondary, and then tertiary alcohols [37]. Indeed, the greatest steric hindrance arises in nucleophilic solvation in *t*-BuOH [10].

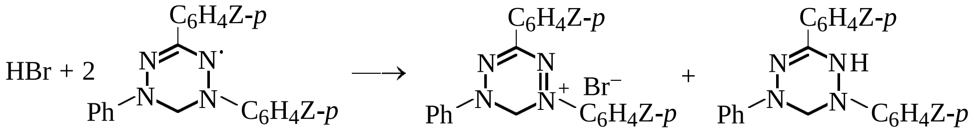
Thus, the rate of monomolecular solvolysis should either be independent of the solvent nucleophilicity or decrease with increasing nucleophilicity, whereas the rate of bimolecular solvolysis should increase with increasing nucleophilicity, with the steric effect taking place in both cases.

We decided to use this difference between the solvation effects in monomolecular and bimolecular solvolysis for distinguishing these reactions. It was necessary to compare the rates of SN2 and SN1 (*E*1) reactions in water, methanol, ethanol, 2-propanol, cyclohexanol, and *tert*-butanol, i.e., in a series of solvents with increasing steric parameter of substituent $-E_S$ [37].

Data on solvolysis in these solvents at 25°C are available for *t*-BuBr [38] and 1-AdI [7]; also, there are incomplete data for *t*-BuCl [38] and PhCHClMe [31] (SN1, *E*1 reactions), and also for PhCOCl [39] and $MeOClO_3$ [40]. The solvation mechanism for the latter two substrates is insufficiently clear. Solvolysis of PhCOCl is believed to occur by the SN2-ion pair or SN2-intermediate mechanism [2, 10, 41]. In the first case, the limiting stage involves the nucleophilic attack of the solvent at the contact ion pair, and in the second case the contact ion pair is formed in the limiting stage by the nucleophilic attack of the solvent at the covalent substrate. Also, solvolysis of PhCOCl can start with addition of the solvent to the C=O group [42]. The C–O bond in $MeOClO_3$ is very polar; in this case the SN2-intermediate reaction is also possible [43].

In this connection, we studied the kinetics of alcoholysis of allyl bromide (**I**) (SN2-ion pair reaction [41]) and *n*-PrBr (SN2 reaction). The kinetics of hydrolysis of these substrates were studied previously [44, 45].

The kinetic experiments were performed by the verdazyl method [25] using as internal references 1,3,5-triphenylverdazyl (**II**) and 1-phenyl-3,5-di(4-methoxyphenyl)verdazyl (**III**). The reactions follow stoichiometric equations (1) and (6).


(6)

Z = H (**II**), OMe (**III**).

The hydrogen bromide released in solvolysis rapidly and quantitatively reacts with verdazyl [25]. The reaction rate was monitored by spectrophotometric by the decrease in the indicator concentration (λ_{max} 720 nm). The reaction rate is independent of the concentration and nature of the indicator and is satisfactorily described by Eq. (2). The conversion of the substrate in the kinetic experiments was 0.01–0.002%. The conditions and results of the kinetic experiments are listed in Tables 1 and 2.

The verdazyl method is usually used for studying the SN1 and *E*1 reaction kinetics [25]. In this case, verdazyl rapidly and quantitatively reacts after the limiting stage with the intermediate solvent-separated ion pair of the substrate. In solvolysis by the SN2 mechanism, verdazyl should react with the released acid. To check our method for monitoring the reaction rate, we determined the rate of hydrolysis of bromide **I** in 40% aqueous dioxane at 30°C. The rate constant determined by this method, (3.94 ± 0.54) ×

Table 1. Kinetics of solvolysis of allyl bromide in alcohols

Solvent	Temperature, °C	$[\mathbf{II}]\times 10^4$, M	$[\mathbf{I}]\times 10^2$, M	$k\times 10^7$, s^{-1}	$k_{av}\times 10^7$, s^{-1}
40% aqueous dioxane	30.0	3.25	3.07	4.75	3.94 ± 0.54
	30.0	2.23	7.81	3.48	
	30.0	1.26	5.22	3.59	
t-BuOH	25.0	2.38	31.5	0.143	0.148 ± 0.005
	25.0	2.03	22.9	0.152	
Cyclohexanol	25.0	1.48	20.7	0.256	0.245 ± 0.011
	25.0	1.57	33.5	0.234	
2-PrOH	25.0	1.44	24.5	0.360	0.386 ± 0.026
	25.0	3.72	24.4	0.411	
EtOH	25.0	1.57	8.14	1.15	1.15 ± 0.01
	25.0	1.79	8.60	1.14	
MeOH	25.0	2.24[a]	6.13	5.10	5.13 ± 0.19
	25.0	1.63[a]	7.86	5.83	
	25.0	1.87[a]	2.11	4.44	
$PhCH_2OH$	25.0	1.03	4.51	1.80	1.82 ± 0.01
	25.0	1.19	6.42	1.82	
	25.0	1.02	6.67	1.84	
	31.0	0.968	6.83	4.65	
	35.6	1.34	5.65	5.80	
	40.0	1.07	5.43	7.10	
	44.2	1.18	4.90	10.8	

[a] Experiments were performed with indicator **III**.

Table 2. Kinetics of solvolysis of *n*-propyl bromide in alcohols

Solvent	Temperature, °C	[**II**] $\times 10^4$, M	[*n*-PrBr] $\times 10^2$, M	$k \times 10^9$, s^{-1}	$k_{av} \times 10^9$, s^{-1}
t-BuOH	25.0	1.91	8.63	0.302	
	28.6	2.35	11.2	0.372	
	32.5	2.43	11.5	0.623	
	35.0	1.38	11.2	0.867	
	38.0	1.92	6.40	1.40	1.38 ± 0.02
	38.0	1.56	11.5	1.36	
	42.5	1.13	11.3	1.71	1.89 ± 0.18
	42.5	2.44	11.4	2.07	
	45.5	1.77	11.3	2.58	2.49 ± 0.09
	45.5	1.69	11.3	2.40	
Cyclohexanol	25.0	0.957	10.7	0.619	0.615 ± 0.059
	25.0	1.24	10.9	0.521	
	25.0^a	1.45	10.7	0.705	
2-PrOH	25.0	–	–	0.752^b	
	24.5	0.648	11.3	0.672	
	28.0	1.79	11.5	1.41	
	30.0	1.69	11.4	1.66	
	33.5	1.28	11.5	2.21	
	35.5	1.61	10.7	3.03	
	38.0	1.42	11.4	4.45	
	41.5	1.50	10.6	5.34	6.30 ± 0.67
	41.5	1.57	10.6	7.31	
	41.5	1.51	10.4	6.25	
	43.0	1.30	11.2	7.83	
EtOH	25.0	1.01	9.29	1.46	1.82 ± 0.22
	25.0^a	0.962	9.26	2.05	
	25.0^a	1.57	9.31	1.96	
MeOH	25.0^a	1.98	9.15	2.43	2.08 ± 0.24
	25.0	1.68	12.4	1.84	
	25.0	0.992	11.6	1.96	

[a] Experiments were performed with indicator **III**. [b] Calculated from the temperature dependence.

10^{-7} s^{-1}, reasonably agrees with the value obtained titrimetrically, 4.32×10^{-7} s^{-1} [46].

In Table 3 are given the $\log k_{25}$ values for the selected substrates in water and alcohols, analogous published data for PhCOCl, *t*-BuBr, 1-AdI, and $MeOClO_3$ [6, 38, 39, 40], and some solvent parameters [28, 36, 47].

The rate of solvolysis of all the substrates increases with increasing ionizing power of the solvent:

$$t\text{-BuOH} < \text{cyclohexanol} < \text{2-PrOH} < \text{EtOH} < \text{MeOH} < H_2O. \qquad (7)$$

In this order both solvent polarity (ε) and electrophilicity (*E*), determining its ionizing power *Z*, increase. The steric parameter of substituents ($-E_S$) also increases in order (7), but the nucleophilicity (*B*) decreases.

Figure 1 shows the correlations between $\log k_{25}$ of solvolysis of **I** in water and alcohols and the similar quantities for PhCOCl, $MeOClO_3$, *n*-PrBr, 1-AdI, and *t*-BuBr. For the substrates reacting by the S_N2 mechanism, these correlations are linear (r ~0.995); in the case of 1-AdI and *t*-BuBr, which react by the S_N1 (*E*1) mechanism, the correlations are nonlinear.

Thus, comparison of the solvolysis rates in H_2O and primary, secondary, and tertiary alcohols allows us to distinguish monomolecular and bimolecular solvolysis.

In all solvolysis reactions, the transition state is more polar than the initial state [1, 10, 41], as indicated by the growth of the reaction rate with increas-

Table 3. Solvent effect on solvolysis of *n*-PrBr, $CH_2=CHCH_2Br$ (**I**), *t*-BuBr, 1-AdI, PhCOCl, and $MeOClO_3$; solvent parameters

Run no.	Solvent	$-\log k_{25}$						Z, kJ mol^{-1}	$\varepsilon(20)$	E, kJ mol^{-1}	B, kJ mol^{-1}	$-E_S$
		n-PrBr	**I**	*t*-BuBr	1-AdI	PhCOCl	$MeOClO_3$					
1	H_2O	6.57	4.80	0.119	2.00	–0.15	2.75	400	80.4	91.2	1.87	–1.24
2	MeOH	8.62	6.32	3.90	7.08	2.4	3.20	350	32.7	62.3	2.61	0.00
3	EtOH	8.74	6.94	5.36	8.43	3.1	3.50	333	24.3	48.5	2.81	0.07
4	2-PrOH	9.12	7.41	6.06	9.16	4.3	3.70	319	18.3	33.6	2.82	0.47
5	Cyclohexanol	9.21	7.61	6.11	9.59	–	–	314	16.0	28.9	2.89	0.71
6	*t*-BuOH	9.41	7.83	6.28	9.86	4.9	3.90	298	10.9	21.8	2.95	1.54

ing solvent polarity. The sensitivity of the reaction to solvent polarity should strongly depend on the solvolysis mechanism. The more polar the transition state, the stronger should be the effect of the solvent ionizing power on the reaction rate. Below are given the differences between the logarithms of the solvolysis rates in water and *t*-BuOH at 25°C for the chosen substrates:

$$\begin{array}{ccccccc} \text{1-AdI} & > & \text{PhCHClMe} & > & t\text{-BuCl} & > & t\text{-BuBr} \\ 7.9 & & 7.1 & & 6.8 & & 6.2 \end{array}$$

$$\begin{array}{ccccccc} > \text{PhCOCl} & > & \mathbf{I} & > & n\text{-PrBr} & > & \text{MeOClO}_3. \\ 5.0 & & 3.0 & & 2.8 & & 1.1 \end{array} \qquad (8)$$

In monomolecular solvolysis (the first four substrates), the most polar transition state is formed, involving separation of ions in the contact ion pair. Indeed, in this case the dependence of the reaction rate on the solvent polarity is the strongest. The reaction rate also significantly depends of the natures of the substrate and leaving group. In solvolysis by the S_N2-ion pair mechanism, at the nucleophilic attack of the solvent molecule at the contact ion pair, a less polar transition state is formed. A typical example of such reactions is solvolysis of bromide **I**, whose rate changes by only three orders of magnitude in going from H_2O to *t*-BuOH [for $S_N1(E1)$ reactions, the effect is by 3–5 orders of magnitude more pronounced]. It is believed that solvolysis of PhCOCl also follows this mechanism [41, 48]. A strong effect of the solvent on the rate of this reaction, on the one hand, suggests that reaction follows a pathway other than addition of the solvent across the C=O bond and, on the other hand, shows that the polarity of the transition state in this case is close to that in S_N1 reactions. However, it is known that the rate of solvolysis of PhCOCl increases with increasing nucleophilicity of the solvent [48, 49], i.e., an S_N2 reaction takes place. Probably, solvolysis of PhCOCl follows the $S_N2(C^+)$ mechanism, in which the reaction rate is limited by nucleophilic attack of the solvent at the solvent-separated ion pair.

Of particular interest is the fact that the rates of solvolysis of bromide **I** and *n*-PrBr depend on the solvent polarity to a similar extent. This fact suggests that solvolysis of *n*-PrBr occurs by the S_N2-intermediate mechanism (the limiting stage involves formation of a contact ion pair by nucleophilic attack of the solvent at the covalent substrate [41, 50], rather than by the classical single-stage S_N2 mechanism (continuous displacement of the leaving group by the nucleophile [41]). In this case, the polarity of the transition state should be close to that observed in S_N2-ion pair reactions, which is the case.

The activation parameters of solvolysis of *n*-PrBr and **I** are listed in Table 4. The increase in the reaction rate by approximately two orders of magnitude in going from *n*-PrBr to **I** is due to the lower activation enthalpy, with the $\Delta S^{\neq}$ values being similar. This fact is consistent with the assumptions that the transition

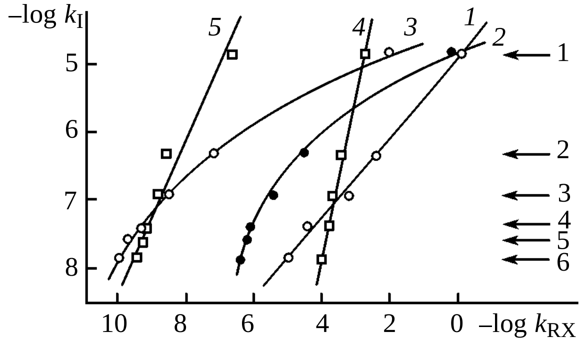


Fig. 1. Correlations between $\log k$ of solvolysis of allyl bromide **I** and $\log k$ of solvolysis of (*1*) PhCOCl, (*2*) *t*-BuBr, (*3*) 1-AdI, (*4*) $MeOClO_3$, and (*5*) *n*-PrBr. The solvent numbering is the same as in Table 3.

Table 4. Activation parameters of solvolysis of *n*-PrBr and allyl bromide **I**

Solvent	*n*-PrBr		**I**	
	$\Delta H^{\neq}$, kJ mol^{-1}	$-\Delta S^{\neq}$, J mol^{-1} K^{-1}	$\Delta H^{\neq}$, kJ mol^{-1}	$-\Delta S^{\neq}$, J mol^{-1} K^{-1}
H_2O	102	28	93	25
2-PrOH	95.9±0.5	98±2	–	–
t-BuOH	83.5±0.5	147±2	69.4±0.5[a]	141±2[a]

[a] In $PhCH_2OH$.

states in solvolysis of these substrates are structurally similar.

It is interesting that the rate of solvolysis of $MeOClO_3$, which occurs by the classical SN2 mechanism according to [40] and by the SN2-ion pair mechanism according to [43], depends on the solvent polarity to the least extent. This is probably due to the high polarity of the initial state [40].

Figure 2 shows the dependence of log *k* of solvolysis of the substrates in water and alcohols on the parameter *Z*. The substrates reacting by the SN2 mechanism give excellent linear correlations ($r \geq 0.99$, s ~0.1). In the case of substrates reacting by the SN1 (*E*1) mechanism, the dependences are nonlinear, and the correlation log *k*–*Z* is only satisfactory (r ~0.97, s ~0.6).

In solvolysis of the second group of substrates, the deviation from the linearity in going from water to *t*-BuOH is toward larger log *k*; it increases with increasing nucleophilicity of the solvent. This trend might be due to nucleophilic assistance of the solvent to heterolysis [3]. However, such effect could be expected for bimolecular solvolysis, rather than for monomolecular solvolysis realized in this case. The nucleophilic solvation of 1-AdI from the rear side is impossible, and in the case of *t*-BuBr it is severely hindered sterically. The nonlinearity of the log *k*–*Z* correlations for monomolecular solvolysis is due to the negative effect of nucleophilic solvation, decreasing in going from H_2O to *t*-BuOH owing to growing steric hindrance [7, 10, 21]. This conclusion is confirmed by the fact that additional inclusion into the log *k*–*Z* correlation of the nucleophilicity parameter (*B*) or steric parameter ($-E_S$) leads to excellent or good two-parameter correlations:

$$\log k_{t\text{-BuBr}} = 4.18 + 0.0259Z - 3.50B;\ r\ 0.987,\ s\ 0.286,$$

$$\log k_{1\text{-AdI}} = -0.279 + 0.0213Z - 5.47B;\ r\ 0.997,\ s\ 0.178,$$

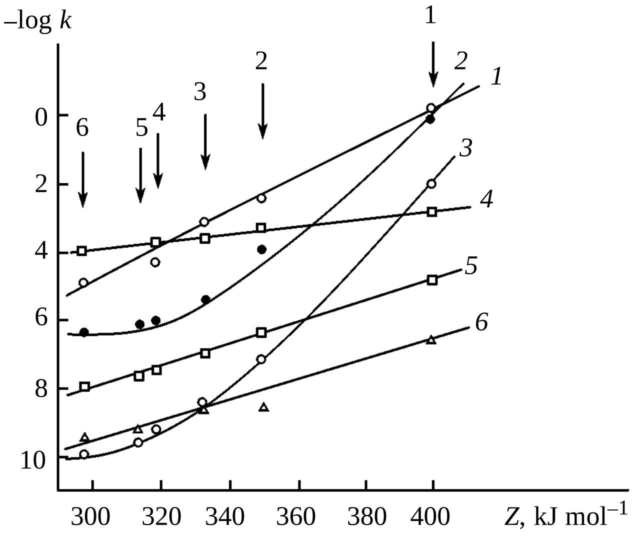


Fig. 2. Correlation between log *k* of solvolysis of (*1*) PhCOCl, (*2*) *t*-BuBr, (*3*) 1-AdI, (*4*) $MeOClO_3$, (*5*) bromide **I**, and (*6*) *n*-PrBr at 25°C and the ionizing power *Z* of the solvent (water, alcohols). The solvent numbering is the same as in Table 3.

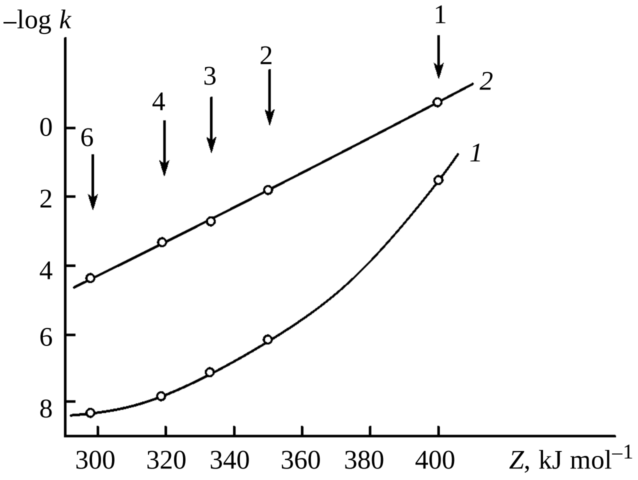


Fig. 3. Correlation between the rate (–log *k*) of solvolysis of *t*-BuCl at (*1*) 25 and (*2*) 120°C and the ionizing power *Z* of the solvent (water, alcohols). The solvent numbering is the same as in Table 3.

$$\log k_{t\text{-BuBr}} = -4.02 + 0.105Z + 1.84E_S;\ r\ 0.979,\ s\ 0.434,$$

$$\log k_{1\text{-AdI}} = -52.2 + 0.131Z + 2.21E_S;\ r\ 0.987,\ s\ 0.364.$$

The fact that the parameter B appears in the correlation equation with the minus sign is consistent with the decelerating effect of nucleophilic solvation on solvolysis of *t*-BuBr and 1-AdI, and the influence of E_S reflects the fact that the negative effect of nucleophilic solvation decreases in going from water to *t*-BuOH.

A similar pattern of the solvent effect is observed with monomolecular solvolysis of *t*-BuCl in water and alcohols at 25°C [38]. However, at 120°C the log *k*–Z correlation for *t*-BuCl becomes linear (Fig. 3; data of [51]). This is due to instability of solvation complex **A** at high temperature, so that the negative effect of nucleophilic solvation does not take place.

Thus, a question arises: Why is the log *k*–Z correlation for SN2 reactions linear if the reaction rate also depends on the solvent nucleophilicity and the Z–*B* correlation is nonlinear (*r* 0.969, *s* 8.9)? However, if we additionally take into account the steric constant, we obtain an excellent two-parameter correlation (9):

$$Z = 468 - 47.7B + 20.1E_S;\ r\ 0.990,\ s\ 3.8. \quad (9)$$

The effects of the parameters B and E_S are mutually compensating. This fact explains why the log *k*–*Z* correlation is linear and shows that in SN2 reactions the steric hindrance to nucleophilic attack at the covalent substrate is also significant.

Thus, the log *k*–*Z* correlations for solvolysis reactions in water and primary, secondary, and tertiary alcohols give insight into the reaction mechanism and into the nature of solvation effects.

EXPERIMENTAL

Allyl bromide and *n*-PrBr were dried over K_2CO_3 and purified by fractional distillation in a 45-cm packed column (8 TP). Solvents of chemically pure (methanol, 2-propanol) or analytically pure (cyclohexanol, *tert*-butanol) grade were refluxed for 8–10 h over CaO, fractionated, and rectified. Rectified alcohol was dried over anhydrous $CuSO_4$, refluxed over CaO for 10 h, fractionated, and rectified. Kinetic experiments were performed in a temperature-controlled cell of an SF-26 spectrophotometer.

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