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Solvation Bifunctional Catalysis of the Hydrolysis of Sulfonyl Chlorides by Hydration Complexes of 2-Propanol: Influence of the Substrate Structure

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Abstract—The temperature dependence of rate constants for the pseudo-first-order hydrolysis of 2-methylbenzenesulfonyl chloride, 1,5-naphthalenedisulfonyl chloride, and 4-acetamidobenzenesulfonyl chloride in water–2-propanol mixtures is studied in the *i*-PrOH mole fraction range $x_2 = 0$–0.10. The concentration dependences of the enthalpy of activation and the entropy contribution ($\vartheta = 100(-T\Delta S^{\neq})/\Delta G^{\neq}$, %) for the hydrolyses of all sulfonyl chlorides are nonmonotonic, depending on the sulfonyl chloride structure and the degree of complementarity of the hydration complexes to the solvent structure. The sulfonyl chlorides are hydrolyzed via two pathways: one of them involves a water dimer as a bifunctional catalyst along with a water molecule as a nucleophile, and the other involves an alcohol hydrate.

INTRODUCTION

The kinetic parameters of many liquid-phase reactions are determined by structural properties of the medium. This is the reason why methods of chemical kinetics have recently become a convenient tool for studying the structure and molecular organization of associated solutions [1].

A nonaqueous component added to water, even if its mole fraction is as small as $x_2 < 0.01$, brings about structural and hydrophobic effects [2, 3]. These effects play an important role in biochemical reactions [4, 5] and bifunctional catalysis of acyl transfer involving water [6]. Under the action of a nonaqueous component, the structure of a binary solvent undergoes a local reorganization propagating throughout the network of hydrogen bonds [2, 3, 7]. The structural stabilization of the solvent induces solvation effects resulting in nonmonotonic concentration dependences of the physical and thermodynamic properties of the aqueous system [2, 7, 8]. The kinetic parameters of the hydrolysis of a third component in an aqueous–organic solvent show nonmonotonic concentration dependences, especially in water-rich regions [9]. Very nonmonotonic concentration dependences of activation parameters are observed for the hydrolysis of *t*-BuCl [10], esters [11, 12], and halides of aromatic carboxylic [9, 13] and sulfonic acids [14–16] in aqueous solutions of nonelectrolytes with $x_2 < 0.15$. For example, the activation parameters of the hydrolysis of 2-methyl-substituted benzenesulfonyl halides (bromide [15] and chloride [16]), which are most sensitive to variations in the composition of the water–dioxane solvent, each reaches a minimum at $x_2 = 0.005$–0.01 and 0.12–0.13.

Extremes in the activation parameters are due to the solvation interaction of the hydration complexes of sulfonyl halide with the *V*-structures of solvent [7]. The set of configurations of these structures is determined by the concentration of the nonaqueous component. During the structural stabilization of the solvent, which progresses as a hydrophobic component is added [17, 18], bulk water in certain narrow intervals of x_2 is complementary [19] to the hydration complexes[1] of sulfonyl halide. Strengthening of the bifunctional interaction in the chains of hydrogen bonds closed by the sulfonyl center leads to a decrease in the activation enthalpy of sulfonyl halide hydrolysis and to a corresponding decrease in the entropy factor. Satisfactory mutual compensation of the activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ is observed in binary aqueous systems [15, 16].

The conditions under which the bulky water and the hydration shells of the substrate are complementary are determined by the nature of the nonaqueous component and the structure and hydrophobic properties of the substrate itself [9, 11]. Previously, we studied the concentration dependence of the activation parameters only for aqueous dioxane, using aryl sulfonyl halides with a hydrophobic methyl group as substrates. To study the influence of the nature of the nonaqueous component, the molar volume of the hydrolyzed compound, and the hydrophobicity of the substituent in the aryl sulfonyl halide on the concentration dependence of the activation parameters, we carried out precision

[1] According to quantum-chemical calculations [20], hydration complexes of the $-SO_2Hal$ groups are water bridges $(H_2O)_m$ between the sulfonyl reaction center and the leaving group; that is, they link the $S^{\delta+}$ and $Hal^{\delta-}$ atoms; $m = 2$–4.

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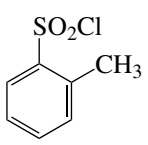
measurements of the rate constants of hydrolysis 2-methylbenzenesulfonyl chloride for (**1**), 1,5-naphthalenedisulfonyl chloride (**2**), and 4-acetamidobenzenesulfonyl chloride (**3**) in water-rich water–2-propanol mixtures as a function of temperature.



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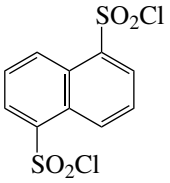

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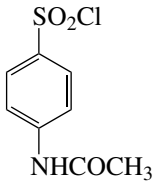

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EXPERIMENTAL

A commercial sample of compound **1** was purified by vacuum distillation until $n_D^{20} = 1.3382$ (according to the literature, $n_D^{20} = 1.3383$ [21]). Compound **2** was synthesized by reacting commercial 1,5-naphthalenedisulfonic acid with a threefold molar excess of PCl_5. The disulfonyl chloride was recrystallized from a hexane–2-propanol mixture until a sample with T_m = 183°C was obtained (according to the literature, T_m = 184°C [22]). Compound **3** was synthesized by treating acetanilide with chlorosulfonic acid according to a standard procedure [23]. Samples with T_m = 148°C (T_m = 149.5°C [23]) were used. 2-Propanol (analytical grade) was purified using a previously described procedure [24]. Binary mixtures based on fresh twice-distilled water with a conductivity of 1×10^{-5} S/cm and 2-propanol were prepared gravimetrically. A spectrophotometric method [14] was used to measure the hydrolysis rate of compound **1**, and a conductometric method was used for compounds **2** and **3** [15, 16]. Rate constants for the pseudo-first-order hydrolysis reaction of sulfonyl chlorides were determined by the Guggenheim method at five to seven temperature points, as a rule, in a temperature interval of at least 25°C. The quasi-thermodynamic activation parameters were determined by the least-squares fitting of rate constant data to the linearized Eyring equation [15, 16].

The hydrolysis of all of the sulfonyl chlorides in excess solvent obeys a pseudo-first order rate equation. The hydrolysis of compound **2** is irreversible and involves sulfonylchloride groups in succession, with $k'' > k'$, because the substituent constants of the SO_2Cl- and SO_2O^- groups are related as $\sigma_{SO_2Cl} > \sigma_{SO_2O^-}$ (σ_{SO_2Cl} = 0.86; $\sigma_{SO_2O^-}$ = 0.09 [25]) and the reaction constant is $\rho < 0$ [26]:

$$\underset{\mathbf{2}}{C_{10}H_6(SO_2Cl)_2} + H_2O \xrightarrow{k'} \underset{\mathbf{2a}}{ClO_2SC_{10}H_6SO_2O^-} + H^+ + Cl^-, \quad \text{(I)}$$

$$ClO_2SC_{10}H_6SO_2O^- + H_2O \xrightarrow{k''} C_{10}H_6(SO_2O^-)_2 + H^+ + Cl^-. \quad \text{(II)}$$

In a steady state, the rates of formation and consumption of 5-chlorosulfonyl-1-naphthalenesulfonic acid (**2a**), which forms as an intermediate, are equal: $k'C_2 = k''C_{2a}$ and $C_{2a} \ll C_2$. Therefore, the hydrolysis rate of compound **2** at one sulfonyl chloride group is half the rate of HCl formation (determined conductometrically):

$$dC_{HCl}/d\tau = k'C_2 + k''C_{2a} = 2k'C_2 = k_2C_2, \quad (1)$$

where C_2, C_{2a}, and C_{HCl} are the current concentrations of disulfonyl chloride, the intermediate product, and the HCl evolved, respectively. Thus, $k' = k_2/2$.

By way of example, we list in Table 1 the apparent hydrolysis rate constants k_1 and k_3 for compounds **1** and **3** in one solvent and the apparent HCl formation rate constant k_2 for the hydrolysis of compound **2** at different temperatures. Tables 2–4 present the quasi-thermodynamic activation parameters for hydrolyses of compounds **1**, **2**, and **3** in binary mixtures, the apparent pseudo-monomolecular rate constants of hydrolysis for each compound (k_i) interpolated to 298 K, and ϑ values equal to the entropy contributions $|-T\Delta S^{\neq}|$ to the Gibbs activation energy ($\vartheta = -T\Delta S^{\neq} \times 100/\Delta G^{\neq}$, %).

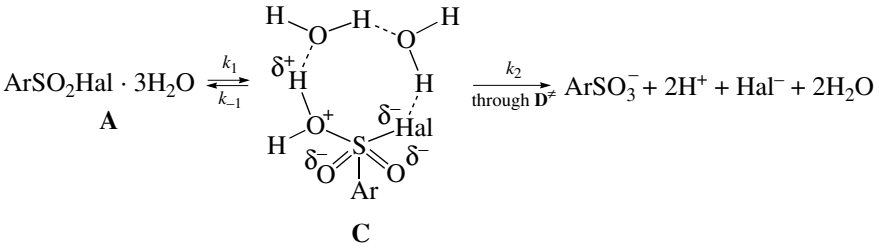
RESULTS AND DISCUSSION

The hydrolysis kinetics of compounds **1**, **2**, and **3** must be similar to those observed earlier for the hydrolysis of other sulfonyl halides. For instance, the formal reaction order of the hydrolysis of methyl-substituted benzenesulfonyl halides [15, 16], in particular, compound **1** [16] in aqueous dioxane mixtures was found to be 3. The quantum chemical simulation of the hydrolysis of benzenesulfonyl chloride in the gas phase [27] and water clusters [20] (PM3 method, supermolecular approximation) showed that the hydrolysis of this compound is a two-step exothermic process that includes the formation of the unstable pentacoordinated intermediate $PhSO_2(H_2O)Cl$ (designated as **C** in the scheme).

Table 1. Apparent hydrolysis rate constants for aryl sulfonyl chlorides in water–2-propanol solvents at different temperatures

Compound **1**, $x_2 = 0.0395$		Compound **2**, $x_2 = 2.170$		Compound **3**, $x_2 = 0.0425$	
T, °C	$(k_i \pm \Delta k_i) \times 10^3$, s^{-1}	T, °C	$(k_i \pm \Delta k_i) \times 10^3$, s^{-1}	T, °C	$(k_i \pm \Delta k_i) \times 10^3$, s^{-1}
22.75	2.58 ± 0.01	15.19	0.436 ± 0.012	20.30	1.81 ± 0.01
26.78	3.20 ± 0.01	20.15	0.786 ± 0.003	25.07	2.55 ± 0.02
32.24	5.25 ± 0.04	25.22	1.32 ± 0.005	30.05	3.62 ± 0.05
34.66	5.75 ± 0.02	30.03	1.93 ± 0.02	40.05	6.65 ± 0.06
39.17	8.10 ± 0.05	35.11	3.67 ± 0.01	44.97	10.1 ± 0.1
46.04	11.40 ± 0.05	39.98	4.85 ± 0.04	49.85	12.6 ± 0.1
52.60	17.7 ± 0.2	44.50	6.91 ± 0.02		

Note: x_2 is the mole fraction of the nonaqueous component (2-propanol).

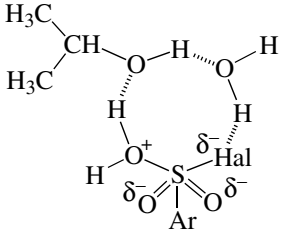


Scheme.

The activation barrier of the decomposition of the intermediate **C** is reduced to the greatest extent in cyclic clusters in which $(H_2O)_3$ bridges form a ring with a S–Cl fragment. Thus, the results of both kinetic studies [15, 16] and calculations [20] indicate that nucleophilic substitution at the sulfonyl reaction center occurs by a catalytic mechanism with the cooperative participation of three water molecules in cyclic transition states. The number of H_2O molecules catalyzing the hydrolysis of sulfonyl halides is equal to **2**, and the solvation complex **C** (scheme) is an eight-membered cycle optimal for bifunctional catalysis [6].[2]

The hydrolysis of compound **1** in aqueous dioxane slows down with decreasing water concentration, and the rate constant of the catalyzed reaction, which is equal to the ratio $k_1/[H_2O]^3 \times 10^8$ l^3 mol^{-3} s^{-1} (here, $[H_2O]$ is the water concentration, mol/l), is unchanged throughout the concentration range examined [16]. For the hydrolysis of all sulfonyl chlorides in aqueous solutions of 2-propanol, the $k_i/[H_2O]^3$ ratio increases with increase in the nonelectrolyte concentration, in contrast to the case of aqueous dioxane hydrolysis. This suggests that there is a pathway other than hydrolysis catalyzed by two water molecules. In the transition state of the second pathway, an alcohol molecule occupies the site of one water molecule. In this case, alcohol hydrate $ROH \cdot H_2O$ can act as a solvation bifunctional catalyst of the hydrolysis of aromatic sulfonyl chlorides [6]. This pathway of the reaction is not observed in the hydrolysis of methyl-substituted sulfonyl halides in aqueous dioxane [15, 16].

The cyclic bifunctional character of transition states inherent in the aqueous-catalyst pathway [16] must manifest itself in the solvation complex **E**, in which an alcohol molecule is included in the eight-membered cycle, as in **C** [6].



E

[2] It is indicated in [6] that bifunctional catalysis of nucleophilic substitution at the sulfonyl center is impossible because of steric hindrance to the formation of cyclic transition states, since, according to traditional views, during a *back* attack, the nucleophile and leaving group should be aligned. Quantum chemical simulation of benzenesulfonyl chloride hydrolysis in the gas phase [27] showed that the *axial* attack of a water molecule on the sulfonyl atom is energetically more favorable. This implies that cyclic transition states are possible for the hydrolysis of aromatic sulfonyl chlorides, and this is confirmed by the results of this work.

Table 2. Activation parameters and interpolated hydrolysis rate constants for compound **1** in H_2O–*i*-PrOH solvents at 298 K

x_2	$\Delta H^{\neq}$, kJ/mol	$-\Delta S^{\neq}$, J mol^{-1} K^{-1}	ϑ, %	$k_{\mathbf{1}} \times 10^3$, s^{-1}
0	64.7 ± 0.8	74.6 ± 2.7	25.5	3.59*
0.0025	60.4 ± 1.9	88.0 ± 6.2	30.3	4.07
0.0050	53.8 ± 1.9	109 ± 6	37.7	4.55
0.0068	51.6 ± 1.7	117 ± 6	40.4	4.23
0.0075	53.6 ± 1.4	110 ± 4	38.0	4.30
0.0078	52.8 ± 2.5	114 ± 8	39.1	4.14
0.0080	54.8 ± 2.1	107 ± 7	36.9	4.00
0.0101	60.7 ± 1.3	88.3 ± 4.3	30.2	3.59
0.0120	56.6 ± 0.4	99.6 ± 1.3	34.4	4.81
0.0149	54.8 ± 2.6	107 ± 8	36.8	4.03
0.0194	50.7 ± 1.5	120 ± 5	41.5	4.20
0.0250	48.1 ± 1.3	129 ± 4	44.5	4.12
0.0280	41.9 ± 1.4	151 ± 4	51.7	3.90
0.0299	41.9 ± 1.7	151 ± 5	51.8	3.67
0.0330	46.0 ± 2.0	137 ± 6	47.1	3.54
0.0347	48.7 ± 0.9	128 ± 3	44.0	3.64
0.0395	49.2 ± 1.5	128 ± 5	43.7	3.01
0.0504	49.1 ± 0.4	129 ± 1	43.9	2.84
0.0803	54.0 ± 1.4	120 ± 4	39.9	1.08
0.0892	52.5 ± 1.2	134 ± 3	42.3	0.92
0.0971	53.1 ± 1.4	128 ± 4	41.8	0.64
0.1002	56.7 ± 2.7	117 ± 8	38.1	0.56

* 3.82 ± 0.37 [16].

Table 3. Activation parameters and interpolated hydrolysis rate constants for compound **2** in H_2O–*i*-PrOH solvents at 298 K

x_2	$\Delta H^{\neq}$, kJ/mol	$-\Delta S^{\neq}$, J mol^{-1} K^{-1}	ϑ, %	$k_{\mathbf{2}} \times 10^3$, s^{-1}	$k' \times 10^3$, s^{-1}
0.0	79.0 ± 1.9	34.0 ± 6.5	11.4	1.52	0.760
0.0035	78.5 ± 1.3	36.5 ± 4.2	12.2	1.36	0.680
0.0069	76.9 ± 1.7	41.5 ± 5.7	13.8	1.34	0.670
0.0080	77.5 ± 1.4	40.2 ± 4.5	13.4	1.33	0.665
0.0103	77.2 ± 1.0	40.7 ± 3.4	13.6	1.33	0.665
0.0120	75.4 ± 2.8	46.0 ± 9.6	15.4	1.50	0.750
0.0130	69.3 ± 1.5	67.0 ± 5.0	22.4	1.43	0.710
0.0140	67.5 ± 1.3	72.4 ± 4.2	24.2	1.54	0.760
0.0147	68.0 ± 0.8	70.8 ± 2.7	23.7	1.54	0.760
0.0155	71.3 ± 0.9	60.8 ± 2.9	20.3	1.37	0.685
0.0160	74.6 ± 0.8	50.3 ± 2.7	16.7	1.26	0.630
0.0175	66.9 ± 0.8	74.9 ± 2.7	25.0	1.45	0.725
0.0180	64.4 ± 2.1	82.5 ± 7.0	27.6	1.45	0.725
0.0188	66.8 ± 0.9	75.0 ± 3.0	25.1	1.48	0.740
0.0200	70.7 ± 0.6	62.8 ± 1.9	20.9	1.32	0.660
0.0217	68.5 ± 1.2	70.8 ± 4.0	23.6	1.22	0.610
0.0250	65.2 ± 0.7	81.2 ± 2.4	27.1	1.34	0.670
0.0280	56.9 ± 2.1	109 ± 7	36.4	1.28	0.640
0.0350	58.3 ± 1.5	104 ± 5	34.8	1.36	0.680
0.0400	56.1 ± 1.5	112 ± 5	37.4	1.21	0.605
0.0500	57.1 ± 1.5	111 ± 5	36.8	1.36	0.680
0.0599	58.5 ± 0.4	107 ± 1.2	35.3	0.870	0.435
0.0700	64.7 ± 1.1	91.6 ± 3.4	29.7	0.467	0.234
0.0776	65.9 ± 2.4	88.3 ± 7	28.5	0.429	0.215

Taking into account both reaction pathways, we obtain the following equations:

$$k_i = k_{i,\mathbf{1}}[H_2O]^3 + k_{i,2}[H_2O]^2[PrOH], \quad (2)$$

$$k_i/[H_2O]^3 = k_{i,\mathbf{1}} + k_{i,\mathbf{2}}[PrOH]/[H_2O], \quad (3)$$

where $k_{i,\mathbf{1}}$ and $k_{i,\mathbf{2}}$ (l^3 mol^{-3} s^{-1}) are the hydrolysis rate constants at 298 K for the sulfonyl halide in the cyclic activated complexes with two water molecules and an *iso*-$C_3H_7OH \cdot H_2O$ hydrate and $[H_2O]$ and [PrOH] are the concentrations[3] of free water and propanol (mol/l).

[3] These relationships were obtained taking into account the concentration of "free" water: $[H_2O] = [H_2O]^* - N_\gamma^0[PrOH]^*$ (where $[H_2O]^*$ and $[PrOH]^*$ are the stoichiometric concentrations of water and alcohol, respectively; $N_\gamma^0 = 7$ is the limiting hydration number of 2-propanol [28]).

The $k_i/[H_2O]^3 = f([PrOH]/[H_2O])$ data for the hydrolyses of compounds **1**, **2**, and **3** (Fig. 1) are characterized by fairly high linear correlation coefficients, confirming the validity of Eq. (3). Processing these data allows one to determine the rate constants for hydrolysis of these compounds in water–2-propanol mixtures:

$$k_{\mathbf{1}}/[H_2O]^3 = (2.49 \pm 0.10) \times 10^{-8} + (0.886 \pm 0.042) \times 10^{-6}[PrOH]/[H_2O], \quad (4)$$
$$r = 0.9823, \quad N = 18;$$

$$k_{\mathbf{2}}/[H_2O]^3 = (0.411 \pm 0.018) \times 10^{-8} + (0.168 \pm 0.008) \times 10^{-6}[PrOH]/[H_2O], \quad (5)$$
$$r = 0.9790, \quad N = 21;$$

$$k_{\mathbf{3}}/[H_2O]^3 = (2.11 \pm 0.09) \times 10^{-8} + (0.679 \pm 0.024) \times 10^{-6}[PrOH]/[H_2O], \quad (6)$$
$$r = 0.9943, \quad N = 11.$$

Catalysis by both water molecules and alcohol hydrate is most pronounced in the hydrolysis of compound **1** and is least pronounced in the hydrolysis of **2**: $k_{1,1} > k_{1,3} > k_{1,2}$, $k_{2,1} > k_{2,3} > k_{2,2}$. The ratio of the rate constants for alcoholic and pure aqueous catalysis is almost the same for sulfonyl chlorides **1** and **3** ($k_{2,i}/k_{1,i}$ = 36 and 32, respectively) and is somewhat higher in the case of **2** ($k_{2,2}/k_{1,2} = 41$). This might indicate a stronger influence of the base function of the bifunctional catalyst, which is enhanced due to the replacement of a water molecule by alcohol, and, hence, a later transition state of the hydrolysis of **2** as compared to the transition state of the reactions involving **1** and **3**.

The plots of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ versus the concentration of 2-propanol are very nonmonotonic (Fig. 2). Since the minima of the activation parameters correspond to the maxima of ϑ, it seems reasonable to use ϑ in further discussions about the concentration dependences of $\Delta H^{\neq}$ and $\Delta S^{\neq}$. As can be seen from Fig. 2, ϑ increases with increasing proportions of alcohol in the mixture.

In an earlier study [20], we demonstrated by calculations that the stabilization of an aqueous solvent structure due to any factor (including the addition of a nonelectrolyte to water) strengthens the H bonds in the water bridges of intermediate **C** and, as a result, decreases the apparent activation parameters of hydrolysis (increases ϑ). This tendency (Fig. 2), which is well pronounced for the hydrolyses of compounds **1**–**3** in water-rich mixtures, coincides with the manner of stabilization of the water structure due to addition of *i*-PrOH up to $x_2 = 0.09$ (in the case of dioxane, up to x_2 = 0.12) [7–9, 13, 29–31]. Note that the x_2 = 0.08–0.09 concentration range in water–2-propanol mixtures is called the region of critical concentrations of hydrophobic interaction (CCHI) [13].

The maximum of the solvent stabilization effect usually corresponds to the composition at which the enthalpy of solution of the hydrolyzed substrate achieves an endothermicity maximum and the activation enthalpy of the process is minimum [31]. For example, for $PhOSO_2Me$, which is a structural analogue of the compounds examined, Arnett *et al.* [30] were able to detect an incipient peak in the enthalpy of solution near $x_2 = 0.10$. Our measurements of the heat of solution of benzenesulfonyl fluoride (which is stable to hydrolysis in aqueous alcohol) in mixtures of water and 2-propanol also revealed a narrow endothermic peak at $x_2 = 0.088$ (Fig. 2) [32].

The ϑ versus x_2 curves for the hydrolyses of sulfonyl chlorides **1** and **2** are similar. However, while the ϑ versus x_2 plot in the low-alcohol region for compound **1** has one well-defined maximum at $x_2 = 0.010$, the same plot for **2** exhibits two nearby sharp peaks at $x_2 = 0.014$ and 0.018. The doublet of ϑ peaks is due to the ability of molecule **2** to exist as two conformers **F** and **G** differing in the mutual arrangement of sulfonyl chloride groups (Fig. 3). The existence of the rather stable conformers **F** and **G** follows from the results of quantum chemical calculation of the structure of the benzenesulfonyl chloride molecule [33]. This calculation shows that a conformation in which the projection of the S–Cl bond is perpendicular to the benzene ring plane and the barrier to the rotation of the $–SO_2Cl$ group is 6.5 kJ/mol

Table 4. Activation parameters and interpolated hydrolysis rate constants of compound **3** in H_2O–*i*-PrOH solvents at 298 K

x_2	$\Delta H^{\neq}$, kJ/mol	$-\Delta S^{\neq}$, J mol^{-1} K^{-1}	ϑ, %	$k_3 \times 10^3$, s^{-1}
0	66.4 ± 0.8	68 ± 3	23.4	3.60
0.0050	66.5 ± 0.7	69 ± 2	23.6	3.29
0.0102	64.1 ± 1.3	77 ± 4	26.4	3.40
0.0200	61.8 ± 0.9	85 ± 3	29.1	3.36
0.0297	57.4 ± 1.1	100 ± 4	34.2	2.96
0.0350	56.6 ± 0.5	103 ± 2	35.2	2.97
0.0385	55.0 ± 1.3	109 ± 4	37.1	2.77
0.0398	48.8 ± 1.0	131 ± 3	44.4	2.55
0.0425	49.7 ± 1.5	128 ± 5	43.4	2.53
0.0451	56.2 ± 1.2	106 ± 4	36.0	2.44
0.0501	52.3 ± 1.5	120 ± 5	40.6	2.20
0.0600	51.0 ± 0.2	127 ± 1	42.6	1.60
0.0700	46.0 ± 2.0	132 ± 3	46.1	1.29
0.0776	48.9 ± 0.9	138 ± 3	45.7	0.972
0.0851	55.3 ± 0.9	119 ± 2	39.1	0.790
0.0999	63.1 ± 0.9	97 ± 3	31.4	0.466

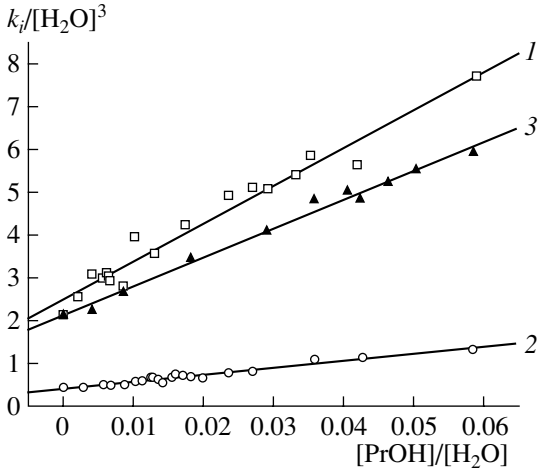


Fig. 1. Rate constant of the catalyzed reaction versus the *i*-PrOH/H_2O mole ratio for compounds (*1*) **1**, (*2*) **2**, and (*3*) **3**.

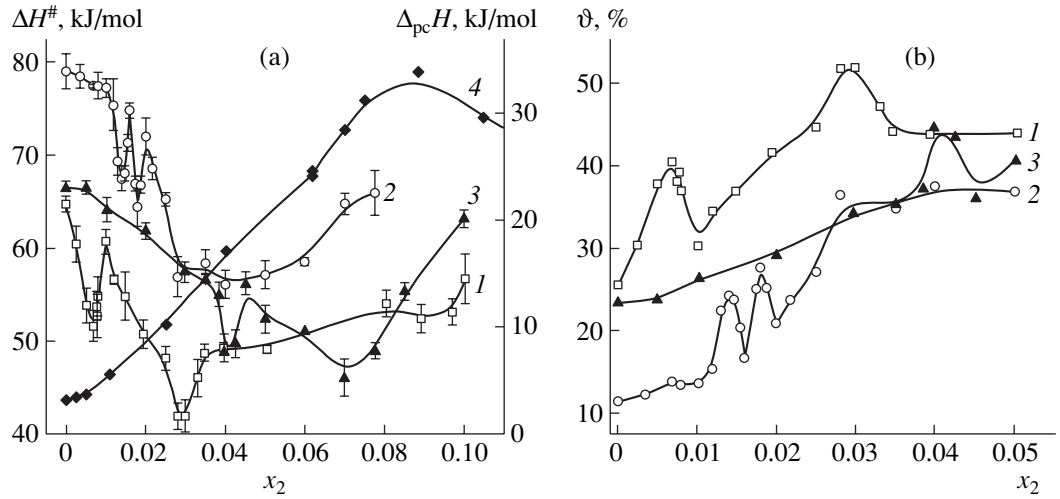


Fig. 2. (a) Activation enthalpy and (b) entropy contribution as functions of the solution composition for the hydrolyses of compounds (*1*) **1**, (*2*) **2**, and (*3*) **3** in aqueous *i*-PrOH; (*4*) heat of solution of benzenesulfonyl fluoride as a function of the system composition.

corresponds to the energy minimum.[4] Unlike **1**, molecule **2** has two possible conformations. The barriers to rotation of the methyl and sulfonyl chloride groups in molecule **1**, equal to 3.9 and 19.3 kJ/mol, respectively, and the nonvalent interactions Cl…H_{Me} and O…H_{Me} (Fig. 4) allow only one conformation [33].

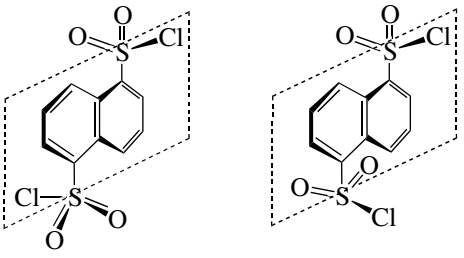
Thus, along with the alcohol-induced stabilization of the solvent structure, a set of *V* structures forms in bulk water at specific different compositions of the mixture. These structures show a maximum complementarity to the structure of hydration complexes **C** in the hydrolysis of chloride **1** and to the structures of conformers **F** and **G** in the hydrolysis of chloride **2**. Sharp, even if small, ϑ peaks for the hydrolysis of chloride **2** indicate that entropy decreases in the formation of these complexes at similar solvent compositions.

At x_2 = 0.01–0.03 in the hydrolyses of chlorides **1**–**3**, entropy contributions to the free activation energy increase distinctly. For the hydrolysis of chloride **1**, the increase in ϑ to a maximum at x_2 = 0.03 is due to the addition of two effects, namely, the continuing stabilization of the structure of bulk water by alcohol and the selective specific interaction of chloride with the intermolecular structure H_2O–*i*-PrOH, resulting in the formation of the catalytic solvation complex **E**. A similar endothermicity peak (at 7 mol % *i*-PrOH) upon the dissolution of an ester in aqueous 2-propanol was assigned [34] to the selective solvation of the ester by alcohol molecules. Therefore, the following experimental facts are noteworthy. At an *i*-PrOH concentration of about x_2 = 0.04, the isotherms of the adiabatic compressibility of mixtures reach a minimum, which is believed to indicate the appearance of a clathrate-like structure [35] that is not destroyed even in the presence of up to 2 mol/kg of sodium chloride. The existence of clathrate hydrates at an *i*-PrOH concentration of x_2 = 0.14–0.17 was proven by differential scanning calorimetry and dielectric relaxation measurements [36]. At x_2 = 0.04 and 0.13, the thermal expansion coefficient of the mixture is temperature-independent and has something like isosbestic points [37].

In the case of hydrolysis of chloride **2**, ϑ reaches a maximum at x_2 = 0.03 and then stops increasing sharply, and the $\vartheta = f(x_2)$ curve reaches a plateau at x_2 = 0.03–0.05, which may well result from the superimposition of two nonmonotonic $\vartheta = f(x_2)$ plots (for conformers **F** and **G**) having nearby ϑ maxima corresponding to the ϑ maximum at x_2 = 0.03 for the hydrolysis of sulfonyl chloride **1**.

An example of the strong influence of substituence in sulfonyl halide on the concentration dependence of the activation parameters is provided by the hydrolysis of 4-acetamidobenzenesulfonyl chloride (**3**). This compound and sulfonyl chloride **1** are similar in reactivity; however, the plots of ϑ versus solvent composition differ substantially for these compounds. The $\vartheta = f(x_2)$ function for the hydrolysis of **3** is more monotonic than corresponding functions for the other sulfonyl chlorides and is similar in the way ϑ varies to that observed for the esters [12]. The hydration complexes of the sulfonyl group are strongly affected by the hydration shell of the large hydrophilic substituent 4-$NHCOCH_3$– and, hence, cannot be complementary to the bulk water structure, in contrast to the case of sulfonyl chlorides with hydrophobic substituents. Therefore, the hydrolysis of compound **3** is characterized by neither a ϑ maximum at x_2 = 0.005–0.010 nor a steep $\vartheta = f(x_2)$ plot at x_2 = 0.02–0.03. In the case of sulfonyl chloride **3**, a

[4] For compound **1**, the quantum chemical calculation predicts a remarkable deviation of angle τ from 90° (τ = 68°). In **2**, this angle can differ from 90° as well. However, this does not rule out these conformations.



F **G**

Fig. 3. Possible stable conformers of compound **2**.

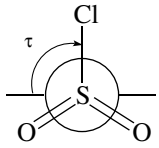


Fig. 4. Newman projection along the C–S bond of the most probable rotational form of the benzenesulfonyl chloride molecule.

monotonic increase in ϑ is interrupted by a rather sharp peak at $x_2 = 0.04$. In addition, the $\vartheta = f(x_2)$ curve has a flat maximum at $x_2 = 0.07$. The ϑ peak at $x_2 = 0.04$, like the peaks at $x_2 = 0.03$ for the hydrolyses of **1** and **2**, seems to be caused by the participation of an *i*-PrOH molecule in the formation of the solvation shell of the transition state for the reaction pathway catalyzed by the hydrate of this alcohol [6]. The ϑ peak at $x_2 = 0.07$ is close to the CCHI region [13].

Thus, the *V* structures complementary [20] to conformations of the solvation complexes of intermediate **C** (and transition state $\mathbf{D}^{\neq}$) are observed at definite concentrations of alcohol in the binary system. The formation of such complementary ensembles is accompanied by an almost complete mutual compensation of the enthalpy and entropy components of the Gibbs activation energy, which changes monotonically with solvent composition. Similar compensation is likely typical of reactions controlled by proton transfer [6, 7] and reactions in which hydrogen bonding changes due to the reorganization of the hydrate shell [38]. The following isokinetic dependences with large linear correlation coefficients are observed between the activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for sulfonyl chlorides **1**–**3** in the *i*-PrOH concentration range examined:

for compound **1**,

$$\Delta H^{\neq} = (86320 \pm 440) + (294.1 \pm 3.7)\Delta S^{\neq}, \quad r = 0.9987, \quad N = 18; \tag{7}$$

for compound **2**,

$$\Delta H^{\neq} = (88950 \pm 220) + (292.1 \pm 2.9)\Delta S^{\neq}, \quad r = 0.9992, \quad N = 18; \tag{8}$$

for compound **3**,

$$\Delta H^{\neq} = (85250 \pm 490) + (275.6 \pm 4.7)\Delta S^{\neq}, \quad r = 0.9986, \quad N = 14. \tag{9}$$

According to the concepts presented in [6], bifunctional catalysis[5] is effective in nonsolvating and weakly solvating media. In our case, such catalysis occurs in hydration shells, whose degree of complementarity to bulk water changes with solvent composition. An increase in ϑ indicates that complementarity improves, and vice versa. The nonmonotonic character of the concentration dependences of activation parameters may be due to successive strengthening and weakening of the bifunctional interaction in the chains of hydrogen bonds closed on the sulfonyl center. The first ϑ maximum, at $x_2 = 0$–0.02, appears when the hydration complexes of substrate **1** and the structure of bulk water achieve complementarity. The next maxima are caused by the direct inclusion of alcohol molecules in the solvation complexes. As a consequence, the number of ϑ maxima in a certain interval of nonelectrolyte concentrations is determined by the variety of transition-state solvation complexes.

Nonmonotonic compensating variation of entropy and enthalpy contributions to the free energy in a narrow concentration range is also observed for equilibria in aqueous–organic media [7, 38]. This phenomenon resembles, in some respects, the behavior of polymers solutions [1], in which an abrupt change in the structure of polymer balls (ball–globule phase transition) caused by variation of the temperature or composition of the solvent is accompanied by a abrupt change in some experimentally observable properties of the solution.

Molecules of the substrates studied in this work have functional groups similar to those in molecules of natural compounds. Therefore, knowledge of the dependence of solvation effects on the substituents at the sulfonyl reaction center of aryl sulfonyl halides makes it possible to predict the role of the medium in processes occurring near the reaction centers of molecules of proteins and biologically active compounds [4–6, 9, 12].

[5] Bifunctional catalysis by acetate anions was observed for the hydrolysis of sulfonyl fluorides [39] and the solvolysis of benzenesulfonyl halides in concentrated sulfuric acid and weak oleum [40].

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