Two Pathways of Arenesulfonyl Chlorides Hydrolysis. Anionic Intermediates in S_AN-Hydrolysis of 4-Nitrobenzenesulfonyl Chloride

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Abstract—Arenesulfonyl chlorides undergo the hydrolysis in water and binary aqueous solvents along two pathways of S_AN mechanism involving cyclic intermediate with pentacoordinate sulfur atom $(H_2O)_nSO_2(Cl)Ar$ and through anionic intermediate $HO^-SO_2(Cl)Ar(H_2O)_n$. The contribution of the process involving anionic intermediates grows with increasing σ_p constant and attained maximum value for 4-nitrobenzenesulfonyl chloride. In water and 17 water–dioxane mixtures the relation of apparent first-order rate constants and activation parameters to the molar fraction of dioxane in the mixture (0–0.25) are not monotonic, and the hydrolysis process is catalyzed by dioxane.

The reaction series for hydrolysis of substituted arenesulfonyl chlorides in water and its mixtures with nonelectrolytes suffers significant deviations from the linear Hammett's plot for lg$k$ of compounds containing substituents 4-NO$_2$, 4-CN, 4-F, and 4-CH$_3$O [1–4]. The hydrolysis rates for sulfonyl chlorides containing 4-NO$_2$-, 4-CN-, and 4-CH$_3$O-substituents considerably exceed the values appropriate for the σ-constants. The largest deviation in the lg$k$ value observed in the case of 4-nitrobenzenesulfonyl chloride (**I**) attracts great interest of researchers to investigation of its hydrolysis [3–5].

The reason of deviations resulting in the U-like form of the log k–σ plot was formerly attributed [1] to a concept that with growing Hammett's σ-constants occurred a transition from S_N1 mechanism (C < 0) to S_N2 one with a "compressed" transition state (C > 0). Haughton et al. [3] presumed that hydrolysis of sulfonyl chlorides passed through a stage of fast formation of intermediate with a pentacoordinate sulfur followed by the cleavage of the S–Cl bond in the course of a slow stage. The formation of a pentacoordinate intermediate in keeping with addition-elimination mechanism S_AN was assumed for reactions of arenesulfonyl fluorides [6], thiophenesulfonyl halides [7] with anionic and neutral nucleophiles, for hydrolysis of 2,4,6-trimethylbenzenesulfonyl chloride [8]. However this mechanism was rejected [9–13] due to the lack of experimental proofs that this intermediate actually formed. At the same time the existence of this mechanism suggests the presence of a linear correlation between Hammett's σ-constants and logarithms of apparent constants of hydrolysis in water for *meta*-and *para*-substituted benzenesulfonyl chlorides. According to Haughton *et al.* [3] this relation may be regarded as linear (C = –0.421± 0.014, *r* 0.965, *n* 13) on excuding from the reaction series the rate constants of the above mentioned substituted sulfonyl chlorides.

Haughton et al. [3] regarded as the cause of deviations of the log k–σ plot from linear dependence a direct polar conjugation of substituents 4-NO$_2$ and 4-CN with the sulfonyl chloride moiety; these substituents thus were electron-donors with respect to strongly electron-deficient sulfonyl atom. On the contrary, under the effect of 4-F substituent that was considered to be incapable to enter into a direct polar conjugation [3] the sulfonyl chloride group hydrolyzed slower than would be predicted from the σ-constant of this substituent.

Nowadays the arenesulfonyl chlorides hydrolysis is regarded as synchronous S_N2 process where the order of S…OH$_2$ bond formation and S…Cl bond cleavage within the transition state depends on the nature of the substituent and on its position in the benzene ring [9, 10]. As the electron-withdrawing quality of the substituent grows, increases the order of the S…OH$_2$ bond in the compressed transition state. This conception rationalizes the absence of linear dependence and U-like form of the plot ln k–σ.

Beside the positive deviation of log k_I value from the linear plot ln$k$–σ the hydrolysis of compound **I** is distinguished by some other specific features: at growing content in binary mixture with water of dioxane (up to ~30 vol% [1, 10, 11]), acetone, and acetonitrile (to 20 and 10 vol% respectively[5]) the apparent rate constants of compound **I** hydrolysis do not first decrease as with the differently substituted compounds but grow forming a flat maximum; the hydrolysis of compound **I** is suppressed on cationic micelles 4–5 times weaker, and its reaction with carboxylate anions incorporated into the zwitter-ionic micelles on the contrary is accelerated considerably stronger than the corresponding reactions of, for example, 4-bromobenzenesulfonyl chloride [13]. The sum of these features of compound **I** hydrolysis did not find any compelling explanations for none among them took into account the decisive factor of the medium

In this connection the goal of this study was investigation of solvation effects in the hydrolysis of sulfonyl chloride **I** in water–dioxane mixtures. We presumed that the results of the study would elucidate the specific features of compound **I** hydrolysis and provide additional information on the laws of arenesulfonyl halides hydrolysis.

Apparent hydrolysis rates k_T (s^{-1}) of compound **I** were determined by conductometric method at 6–7 various temperatures within the range 284–322 K in water and 17 water–dioxane mixture with molar fraction of dioxane X_2 0–0.25. The solutions with a low dioxane content (X_2 0–0.05) were subjected to the most thorough investigations. Experimental values of k_T for one of the 17 solutions are compiled in Table 1, and interpolated values of k_{298} calculated with the use of quasithermodynamic activation parameters are given in Table 2. The plot of k_{298} as a function of X_2 for hydrolysis of compound **I** is presented on Fig.1 (curve k_I). For comparison analogous curve (k_{II}) is plotted for 2-methylbenzenesulfonyl chloride [14]. Different trends in variations of the apparent rate constants with decreasing water content are very prominent: the k_I values go through a flat maximum at X_2 ~ 0.05 (20 vol%) and afterwards weakly diminish, whereas the k_{II} values sharply decrease with growing X_2 within the total concentration range.

Table 1. Apparent rate constants of hydrolysis of sulfonyl chloride **I** in water–dioxane mixture with X_2 0.0806 at various temperatures

T, °C	$(k_T \pm \Delta k)\cdot 10^3$, s^{-1}	$\tau_{\exp(1/2)}$ [a]
11.79	0.812+0.007	1.90
15.11	1.118+0.004	2.21
20.00	1.505+0.005	2.19
24.80	2.219+0.009	1.36
30.25	3.641+0.026	2.31
35.10	5.441+0.021	3.38
40.70	8.029+0.032	4.05

[a] $\tau_{\exp(1/2)}$ is half-conversion time.

The different effect of solvent composition on the reactivity of compounds **I** and **II** can be understood taking into account the results of quantum-chemical calculations [15, 16], and also the concept [5] of general basic catalysis of the hydrolysis of sulfonyl chloride group by a molecule of the nonaqueous component.

Quantum-chemical simulation of benzenesulfonyl chloride hydrolysis in a gas phase [15] and water clusters [16] (PM3 method, supermolecular approximation) revealed that the hydrolysis of benzenesulfonyl chloride in the form of hydrate (A) proceeded as a two-stage process through a pentacoordinate intermediate PhSO$_2$(H$_2$O)Cl (B) of low stability (Scheme 1).

The rate constants of intermediate (B) formation and transformation into reaction products proved to be of comparable value. This means that the apparent hydrolysis constant of PhSO$_2$Cl is affected by both stages. The sharp dependence of hydrolysis rate constants of compound **II** on water concentration originates from the fact that the partial reaction order with respect to water m in the water–dioxane solution is close to three [14]. Therewith the process is char-acterized by low values of activation entropy [−70... −120 J mol^{-1} K^{-1}], and the activation barrier to the stage of intermediate (B) decomposition through transition state (C) is the most decreased in cyclic clasters [16] where water (H$_2$O)$_{n+1}$ close a ring to the structural fragment S–Cl (n is a number of H$_2$O molecules taking part in catalysis of the hydrolysis, $n = m -$

Scheme 1.

A   B   C
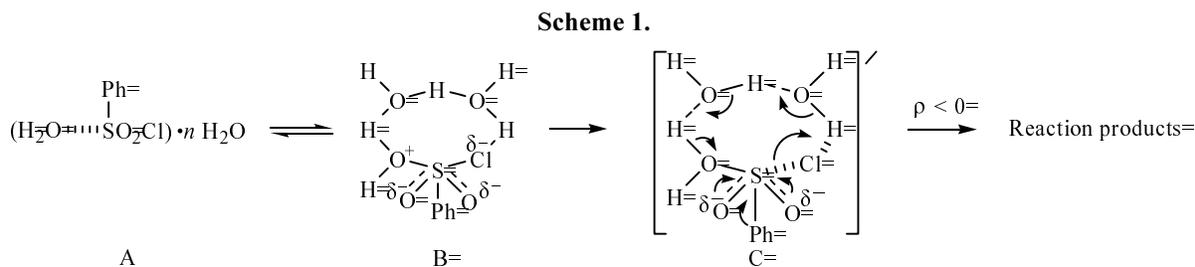
Table 2. Activation parameters and interpolated rate constants (k_{298}) for hydrolysisa of sulfonyl chloride **I** in water–dioxane mixture

x_2	$\Delta H^{\#} \pm SE(\Delta H^{\#})$, kJ mol^{-1}	$-\Delta S^{\#} \pm SE(\Delta S^{\#})$, J mol^{-1} K^{-1}	$(k_{298} \pm \Delta k) \times 10^3$, s^{-1}	r[a]	n[b]	ΔT, K[c]
0.0	74.1±1.4	46.1 ± 4.6	2.54 ± 0.13 [d]	0.9992	7	28.5
0.0025	67.9 ± 0.9	68.7 ± 3.1	2.04 ± 0.08	0.9997	6	27.7
0.0075	68.0 ± 1.2	67.4 ± 3.8	2.28 ± 0.14	0.9979	6	27.7
0.0107	70.8 ± 1.0	56.6 ± 3.3	2.69 ± 0.09	0.9996	6	25.0
0.0175	76.2 ± 2.0	40.7 ± 6.6	2.04 ± 0.13	0.9970	6	25.4
0.0199	77.9 ± 1.1	37.2 ± 3.7	1.59 ± 0.06	0.9988	7	31.4
0.0225	68.3 ± 0.8	65.9 ± 2.5	2.47 ± 0.07	0.9989	7	28.5
0.0247	69.1 ± 0.8	61.9 ± 2.7	2.90 ± 0.09	0.9991	7	29.8
0.0531	61.0 ± 0.6	88.2 ± 2.0	3.15 ± 0.07	0.9997	7	29.7
0.0806	56.7 ± 1.4	105 ± 5	2.40 ± 0.12	0.9991	7	28.9
0.0902	59.5 ± 1.3	94.8 ± 4.4	2.59 ± 0.14	0.9996	6	28.1
0.1014	60.3 ± 1.0	93.4 ± 3.4	2.22 ± 0.07	0.9995	7	23.4
0.1202	57.7 ± 1.3	103 ± 4	2.11 ± 0.10	0.9976	7	30.2
0.1308	50.6 ± 0.9	125 ± 3	2.55 ± 0.09	0.9995	7	28.1
0.1507	50.4 ± 0.8	127 ± 3	2.15 ± 0.07	0.9992	7	28.1
0.2002	42.4 ± 0.9	155 ± 3	1.86 ± 0.06	0.9986	7	28.0
0.2502	37.2 ± 0.4	174 ± 2	1.59 ± 0.03	0.9997	7	27.6

[a] r is correlation factor for Arrhenius plot.

[b] n is the number of rate constants used in the temperature relation.

[c] ΔT is the temperature range where the kinetic measurements were done.

[d] $(2.48 \pm 0.02) \times 10^{-3}$ [4], 2.62×10^{-3} [5], 2.45×10^{-3} s^{-1} [13].

1 = 1 – 3). These facts correspond to a catalytic nucleophilic substitution mechanism at the sulfonyl reaction center [15, 16] with cooperative participation of $n + 1$ water molecules in a cyclic transition states.

The n values for various sulfonyl halides in water–dioxane solutions were found experimentally to be from 1 to 2 [1, 9–11, 14]. The partial orders with respect to "free" water for hydrolysis of sulfonyl chloride **II** in systems water–i-PrOH and water–t-BuOH were determined experimentally [18], and with accounting for the limiting hydrate numbers of 2-propanol and *tert*-butanol (N_γ^0 7 and 13.5 respectively) [19] these values were found at about 2 (consequently, $n = 1$).

We believe that the hydrolysis mechanism presented on Scheme 1 is valid also for the other arenesulfonyl halides with electron-donor substituents at the aromatic ring, among them for methyl-substituted derivatives of benzenesulfonyl chloride and benzenesulfonyl bromide [14, 17, 20]. For instance, at growing dioxane concentration the fourth-order rate constants $k_{\rm II}/[{\rm H_2O}]^3$ remain actually constant [14]. In keeping with Scheme 1 this fact evidences that bimolecular hydrolysis of compound **II** is catalyzed with two additional water molecules.

It is appropriate to consider now the special features of catalysis of sulfonyl chloride group hydrolysis. The

hydrolysis of benzenesulfonyl chloride is characteristically subject to the general basic catalysis with triethylamine [21]. Bentley et al [5] believe that for the sulfonyl chlorides with electron-withdrawing substituents the general basic catalysis occurs also involving molecules of nonaqueous component of the solvent (acetone, acetonitrile, 1,4-dioxane). In an earlier publication [22] Bentey successfully described the hydrolysis of 4-nitrobenzoyl chloride (**III**) with equation (1), where account is taken of the effect of one reactive water molecule and one molecule of nonaqueous component serving as catalyst:
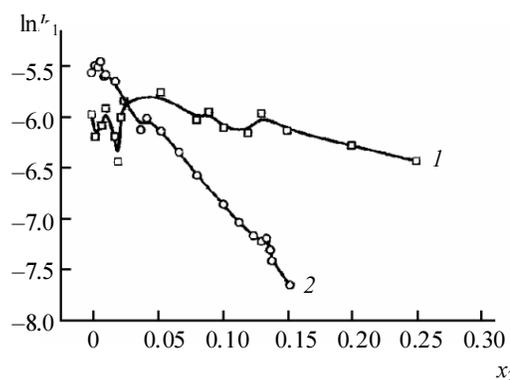
Fig. 1. Plots of ln k_i vs molar dioxane fraction (x_2) at 298 K for hydrolysis of sulfonyl chlorides **I** (*1*) and **II** (*2*).

$$k_{III}/c_1{}^2 = k_{III\,(1)} + k_{III\,(2)}{\cdot}c_2/c \qquad (1)$$

Here k_{III} is apparent rate constant of compound **III** hydrolysis; $k_{III\,(1)}$ and $k_{III\,(2)}$ are catalytic third-order rate constants accounting for catalysis of compound **III** hydrolysis with molecules of water and nonaqueous component respectively; c_1, c_2 are consentrations of water and nonaqueous component respectively (mol l^{-1}).

However for hydrolysis of compound **I** in mixtures of water with aprotic solvents (acetone, acetonitrile, and 1,4-dioxane) Bentley *et al.* [5] considered the correlation according to equation (1) not sufficiently good, especially at the use of water–dioxane solution.* The main reason of the insufficiently good correlation is apparently the neglecting in [5] of the involvement of an additional water molecule in the activated complexesof the sulfonyl chlorides hydrolysis.

For the assumed in [5] overall third order of the reaction [substrate + H$_2$O + dioxane (C$_4$H$_8$O$_2$)] the solvation complex (E) should include a four-membered ring that according to calculations [16, 23, 24] is energetically unfavorable. To form more stable six-membered ring as in complex (D) an additional water molecule is necessary.

The formation of solvation complexes of (D) type with a cycle having water bridges of two H$_2$O molecules is as feasible from the thermodynamical viewpoint as formation of solvation complexes of (A) type with bridges of three water molecules. This conclusion is consistent with that of [25] where the clasters of phenol with two molecules of water having cyclic structure like water trimer were stated to be the most stable.

In keeping with the above reasoning the following equation can be written for the hydrolysis rate of sulfonyl chlorides:
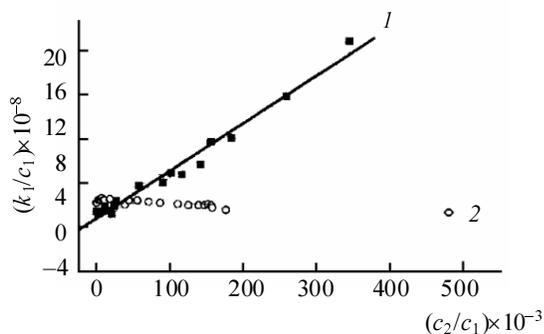
Fig. 2. Dependence of k_i/c_1^3 on the ratio c_2/c_1 for hydrolysis of compounds **I** (*1*) and **II** (*2*) in aqueous dioxane.

* In [5] were used the data on water–dioxane mixed solvents of early publications [1] (up to 30% of dioxane) and [3] (50–90% of dioxane).

$$v = k_{i\,(1)}c_i{\cdot}c_1{}^3 + k_{i\,(2)}c_i{\cdot}c_2{\cdot}c_1{}^2 \qquad (2)$$

Here c_i is concentration of sulfonyl chloride (i) (mol l^{-1}); $k_{i\,(1)}$ and $k_{i\,(2)}$ are catalytic fourth-order rate constants accounting for catalysis of compound **I** hydrolysis (i) with molecules of water and dioxane respectively in cyclic activated complexes forming from solvation complexes (A) and (D). Taking into account expression (2) equation (3) can be written that is more convenient to be presented in form (4):

$$k_i = k_{i\,(1)}{\cdot}c_1^3 + k_{i\,(2)}{\cdot}c_1^2{\cdot}c_2 \qquad (3)$$

$$k_i/c_1{}^3 = k_{i\,(1)} + k_{i\,(2)}{\cdot}c_2/c_1 \qquad (4)$$

According to equation (4) the k_i/c_1^3 should be in linear dependence on the molar ratio of the components of the binary solvent $c_2/c_1 = $ [dioxane]/[H$_2$O]. The treatment of linear relations $k_i/c_1^3 = f(c_2/c_1)$ presented on Fig. 2 provided rate constants $k_{(I)1}$ and $k_{(I)2}$ for hydrolysis of compound **I**.

$$k_{(I)}/c_1^3 = (0.83 \pm 0.22) \times 10^{-8} + (43.8 \pm 1.7) \times 10^{-8}\, c_2/c_1$$

$$r\,0.989, N\,17, SD\,0.662$$

The sharp difference in relations (4) for compounds I and II (a strong acceleration of compound **I** hydrolysis and virtually unchanging hydrolysis rate constant of compound **II**) at increse in dioxane concentration obviously indicates dissimilar mechanisms of hydrolysis process for these sulfonyl chlorides.

It should be noted that the reaction mechanism shown on Scheme 1 does not rationalize the positive sign of the resonance sensitivity constant ρ_R 3.01 that we have found by statistical processing of kinetical data on hydrolysis in water medium of *meta*- and *para*-substituted benzenesulfonyl chlorides [12]. Large positive ρ_R value as distinct from the "normal" negative constants $\rho_I = -0.78$ and $\rho_R^+ = -4.44$ indicates that in the hydrolysis of sulfonyl chlorides alongside the processes occurring in compliance to Scheme 1 the hydrate complexes ArSO$_2$Cl$\cdot n$H$_2$O may be converted into the reaction products via a stage of formation of intermediate anions HO$^-$–SO$_2$(Cl)Ar$\cdot n$H$_2$O [12] (Scheme 2).

Thus the arenesulfonyl halides can undergo hydrolysis in water along two parallel pathways where the solvation complexes (A) transform either into intermediates (B) (Scheme 1), or into intermediates (F) (Scheme 2). The rates ratio of these two processes depends on the character of substituent attached to benzene ring. In the hydrolysiɛ of benzenesulfonyl halides containing electron-donating substituents at the ring dominates

Scheme 2.

$$(H_2O\text{''''}\overset{\displaystyle Ar|}{SO_2Cl})\cdot n\,H_2O \underset{\rho>0}{\overset{1–2}{\rightleftharpoons}} (HO^-\text{—}\overset{\displaystyle Ar|}{SO_2Cl})\cdot n\,H_2O + H^+ \overset{2–2}{\longrightarrow} ArSO_2OH + Cl + H^+ + nH_2O$$

A   F

pathway *1*, and the part of pathway *2* in the overall process grows with increasing electron-attracting character of the substituent attached to the benzene ring. The electron-withdrawing substituents are capable of delocalizing the negative charge OH$^-$ and thus of stabilizing the intermediate anion (F). As a result the equilibrium of anion (F) formation shifts to the right [14]. The most spectacular example of a process taking pathway *2* is the hydrolysis of compound **I**. The electron-donating substituents destabilize anion (F). The acceleration of compound **I** hydrolysis by dioxane (and the other nonaqueous components: acetone, acetonitrile, methanol, ethanol [5]) evidences that the molecules of nonaqueous components playing the role of general bases shift the equilibrium 1–3 (Scheme 3) even more to the right.

In the water–acid medium the ratio of pathways *1* and *2* strongly changes in favor of the first one. It is seen from the ratio of values k_I/k_{II} that in water is 0.66, in 12% H_2SO_4 0.43, and in 50% H_2SO_4 0.10 [26].

The above rationalization of results is consistent with conclusions of [13] where has been carried out an attempt to elucidate the sign of charges on transition states in hydrolysis of *para*-substituted benzenesulfonyl chlorides by comparison of process inhibition on micelles of cationic and anionic type. The hydrolysis of arenesulfonyl chlorides is decelerated less on cationic than anionic micelles, and also at growing electron-attracting properties of substituent. These facts [13] testify to anion-like character of the transition states in the synchronous mechanism S_N2 where the processes of bonds O…S formation dominate over processes of bond S…Cl rupture. The value of the negative charge on the transition state grows with the electron-withdrawing character of substituent and is maximum in hydrolysis of compound **I**.

According to [11] replacement of H_2O by D_2O in hydrolysis of $ArSO_2Cl$ with the following R substituents at the benzene ring: 2,4,6-*i*-Pr$_3$, 4-*t*-Bu, H, 4-Br, 4-NO$_2$ in 70% and 40% aqueous dioxane (X_2 in these mixtures was 0.32 and 0.12 respectively) the reaction constant ρ diminished and not increased as it was expected in keeping with the concept of more "compressed" transition state in the case of D_2O. This observation may be understood as resulting from reduction of the contribution from the pathway through intermediates (G) in the hydrolysis of sulfonyl chlorides at replacement of H_2O by D_2O.

Scheme 3.

$$(H_2O\text{''''}\overset{\displaystyle Ar|}{SO_2Cl})\cdot(n-1)\,H_2O\cdot HK$$

D

$$\underset{\rho>0}{\overset{1–3}{\rightleftharpoons}} (HO\text{—}\overset{\displaystyle Ar|}{SO_2Cl})\cdot(n-1)\,H_2O\cdot HK + H^+$$

G

$$G \overset{2–3}{\longrightarrow} ArSO_2OH^+Cl^- + (n-1)\,H_2O + HK + H^+$$

Interestingly, in the hydrolysis of sulfonyl chloride **I** in the range of water–dioxane mixtures (X_2 0–0.025) although the k_I does not strongly decrease with the growing dioxane concentration, the nonmonotonic character of $k_I–X_2$ relation is quite clear (the changes in k_I largely exceed the possible measurement errors). In the hydrolysis in the same medium of chloride **II** and

Fig. 3. Dependence of activation enthalpy (*a*) and contribution C (*b*) on the molar fraction of dioxane for hydrolysisa of compounds **I** (*1*) and **II** (*2*).

other methyl-substituted benzenesulfonyl halides similar dependences are more smooth (Fig. 1). The main cause of weak alteration of k_I values and of decreasing activation parameters in the all range of concentrations studied is the catalysis of the process along pathway *2* effected by dioxane molecules (Scheme 3).

The dependences of activation parameters on the medium composition for hydrolysis of sulfonyl chlorides **I** and **II** are nonmonotonic (Fig. 3) with extrema at virtually the same values of X_2 (in the region of small X_2 values 0–0.05 they go nearly parallel). In the range X_2 0–0.13 the relations $\Delta H^{\neq}_I > \Delta H^{\neq}_{II}$ and $\vartheta_I < \vartheta_{II}$ (meaning $\Delta S^{\neq}_I > \Delta S^{\neq}_{II}$, for ϑ are fractions expressed in percents of values $|-T\Delta S^{\neq}|$ in $\Delta G^{\neq}$ [18]) are observed, whereas at $X_2 > 0.13$ these relations acquire a reverse sense. The frontier concentration X_2 dividing the regions $\Delta H^{\neq}_I \gg \Delta H^{\neq}_{II}$ and $\Delta H^{\neq}_I < \Delta H^{\neq}_{II}$ coincides virtually with the value of the critical concentration of hydrophobic interaction for water–dioxane solutions (X_2 0.12–0.13) [27]. The observed general trend in diminishing of the activation parameters with increasing dioxane concentration in the binary solvent is caused by the structural stabilization of the solvent [14]. More steep decrease in $\Delta H^{\neq}$ and $\Delta S^{\neq}$ with growing X_2 for pathway *2* compared to pathway *1* is due to increase in activity of anion HO⁻SO₂(Cl)–Ar.

The probable causes of extrema on the concentration dependences of activation parameters and rate constants of arenesulfonyl halides hydrolysis in the water-rich mixtures H₂O–dioxane (Figs. 1 and 3) are the same for sulfonyl chlorides **I** and **II**, and they have been thoroughly discussed before [14, 17, 18, 20].

EXPERIMENTAL

A commercial sample of 4-nitrobenzenesulfonyl chloride **I** was purified by recrystallization till its melting point was 79–80°C (publ.: mp 80.5°C [28]). Water solutions of dioxane were prepared as described in [14, 20]. The rate constants were determined by conductometric method [17, 20]. The measurements were carried out in a cell of volume ~5 cm³ with platinum electrodes using an a.c.impedance bridge P-5030. The reagent was charged into the cell with a micropipet as a drop of a concentrated solution in dioxane preliminary kept at the temperature required for the experiment. The first-order rate constants were calculated by Guggenheim procedure. The initial concentration of sulfonyl chloride in the water–dioxane solvent was of the order of magnitude 10^{-4}–10^{-5} mol l⁻¹.

pH of the mixtures insignificantly changed in the course of experiments. We did not use buffer mixtures for the dependence of apparent rate constants of arenesulfonyl chlorides hydrolysis on pH in acid media [2, 9, 29].

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