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Kinetics of Arylsulfonation of Aminobenzoic Acids with *m*-and *p*-Nitrobenzenesulfonyl Chlorides in the System Water–2-Propanol

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Abstract—The concentrations of the uncharged and anionic forms of *m*- and *p*-aminobenzoic acids participating in arylsulfonation of the acids with *m*- and *p*-nitrobenzenesulfonyl chlorides in the system water–2-propanol at 298 K at various water contents and pHs were estimated. The resulting data were used to estimate the rate constants for the reactions of the above forms with nitrobenzenesulfonyl chlorides, based on experimental kinetic data.

Kalinina and Kuritsyn [1, 2] previously studied the kinetics of acylation of isomeric benzoyl chloride in the system water–dioxane and determined the rate constants of reactions of the anionic and uncharged forms of *m*- and *p*-aminobenzoic acids with benzoyl chlorides. The kinetics of reaction of aminobenzoic acids with arenesulfonyl chlorides have not yet been studied. This is associated with some objective difficulties, including, first, moderate reactivity of arenesulfonyl chlorides toward arylamines [3–5] and, second, the necessity of carefully controlling pH which affects not only the ratio of ionic forms of the amino acids, but also the rate of hydrolysis of the arenesulfonyl chlorides [6].

At the same time, to know the kinetics of this reaction is important for polymer chemistry [7] and for fundamental kinetic studies on amino acid reactions.

In the present work we set ourselves the task to study the kinetics of arylsulfonation *o*-, *m*-, and *p*-aminobenzoic acids (**Ia**–**Ic**) with *m*- and *p*-nitrobenzenesulfonyl chlorides (**IIa, IIb**) in water–2-propanol mixtures at 298 K.

In water and aqueous organic solvents, amino acids **Ia**–**Ic** can be present in the nonionized and various ionized forms [scheme (1)]:.

$$\begin{tikzcd}
 & {}^+NH_3C_6H_4COO^- \arrow[d, shift left, "K"] \arrow[dr, leftrightarrow, "K_3"] & \\
{}^+NH_3C_6H_4COOH \arrow[ur, leftrightarrow, "K_1"] \arrow[dr, leftrightarrow, "K_2"'] & & NH_2C_6H_4COO^-. \\
 & NH_2C_6H_4COOH \arrow[u, shift left] \arrow[ur, leftrightarrow, "K_4"'] &
\end{tikzcd} \quad (1)$$

Here K, K_1, K_2, K_3, and K_4 are the equilibrium constants.

It is known [8] that arenesulfonyl chlorides can react only with nonprotonated amino group. Therefore, the reaction of amino acids **Ia**–**Ic** with sulfonyl chlorides **IIa, IIb** in the system water–2-propanol occurs by two concurrent directions [schemes (2) and (3)]:

$$\begin{gathered} NH_2C_6H_4COOH + NO_2C_6H_4SO_2Cl \\ \longrightarrow COOHC_6H_4NHSO_2C_6H_4NO_2 + HCl, \end{gathered} \quad (2)$$

$$\begin{gathered} NH_2C_6H_4COO^- + NO_2C_6H_4SO_2Cl \\ \longrightarrow O\text{–}COC_6H_4NHSO_2C_6H_4NO_2 + HCl. \end{gathered} \quad (3)$$

Moreover, in aqueous 2-propanol, along with arenesulfonation of amino acids **Ia**–**Ic**, hydrolysis of sulfonyl chlorides **IIa, IIb** takes place [scheme (4)]:

$$NO_2C_6H_4SO_2Cl + H_2O \longrightarrow NO_2C_6H_4SO_3H + HCl. \quad (4)$$

The variation in the concentration of sulfonyl chlorides **IIa, IIb** (c_s) in the course of reactions (2)–(4) is described by Eq. (5):

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Table 1. Rate constants k_{app}, k_h, and k

c_{H_2O}, wt%	$c_I^0 \times 10^2$, M	$k_{app} \times 10^3$, s^{-1}	$k_h \times 10^3$, s^{-1}	$k \times 10^2$, l mol^{-1} s^{-1}
Ia + IIb				
9.48	4.00	0.44±0.03	3.40±0.13	0.25
19.69	4.01	0.83±0.06	5.05±0.01	0.81
29.74	4.00	1.23±0.01	6.50±0.01	1.45
39.89	3.99	1.39±0.01	7.60±0.03	1.58
49.91	4.00	1.65±0.01	9.40±0.07	1.77
60.81	4.01	2.77±0.03	10.75±0.10	4.23
69.59	4.00	5.87±0.05	11.90±0.01	11.70
Ib + IIa				
19.63	4.99	5.59±0.12	3.33	10.52
29.90	5.00	8.96±0.21	4.25	17.07
40.16	4.99	12.51±0.50	5.00	24.03
51.02	4.99	17.10±0.80	6.20	33.35
60.38	5.00	20.23±0.81	6.96	39.07
69.45	5.00	41.61±0.90	7.84	81.65
Ic + IIb				
9.48	4.01	0.98±0.23	3.40±0.13	1.60
19.69	4.00	1.13±0.14	5.05±0.01	1.56
29.74	4.00	1.29±0.18	6.50±0.01	1.60
39.89	4.01	1.71±0.11	7.60±0.03	2.37
49.91	4.00	2.41±0.06	9.40±0.07	3.67
60.81	4.00	3.67±0.09	10.75±0.10	6.49
69.59	3.99	6.79±0.28	11.90±0.01	14.00

$$-dc_s/d\tau = k_0 c_0^I c_s + k_- c_-^I c_s + k_h c_s. \quad (5)$$

Here k_0, k_-, and k_h are the rate constans of reactions (2)–(4), respectively, and c_0^I and c_-^I are the current concentrations of the uncharged and anionic forms of amino acids **Ia**–**Ic**.

In view of the occurrence of the concurrent reactions (2) and (3), the overall rate constant of the reaction of amino acids **Ia**–**Ic** with sulfonyl chlorides **IIa, IIb** (k) can be represented by Eq. (6):

$$k = k_0\alpha_0 + k_-\alpha_-. \quad (6)$$

Here α_0 and α_- are the fractions of the uncharged and anionic forms of amino acids **Ia**–**Ic** in the solution. On condition that amino acids **Ia**–**Ic** are present in a considerable excess (10^2–10^3 times) compared with arenesulfonyl chlorides **IIa, IIb** and with account for Eq. (6), we can write Eq. (5) in form (7):

$$-dc_s/d\tau = (k_0 c_I^0 \alpha_0 + k_- c_I^0 \alpha_- + k_h)c_s = (k c_I^0 + k_h)c_s$$
$$= k_{app} c_s. \quad (7)$$

Here c_I^0 is the initial concentration of amino acid **Ia**–**Ic**, and k_{app} is the apparent rate constant of the reaction.

The kinetics of the reaction of amino acids **Ia**–**Ic** with sulfonyl chlorides **IIa, IIb** were studied following the concentration of arenesulfonyl chloride by the spectrophotometric indicator technique [9]. The indicator used was lithium 2,6-dinitrophenolate. The apparate rate constant k_{app} was calculated by the Guggenheim equation (8):

$$\ln\ln(T_1/T_2) = \ln[T_\infty/T_0(1 - e^{-\Delta k_{app}})] - k_{app}\tau_1. \quad (8)$$

Here T_1 and T_2 are transmission coefficients of the reaction mixture at times τ_1 and $\tau_2 = = \tau_1 + \Delta$, and T_0 and T_∞ are the transmission coefficients of the solution before and after the reaction. The errors in k_{app} were calculated at a confidence level of 0.95, the random error in k_{app} was no higher than 2–3%.

Table 1 lists the k_{app} and k_h values taken from [10, 11], as well as $k = (k_{app} - k_h)/c_I^0$.

As follows from Table 1, the reactivity of the amino acids increases in the order **Ia** < **Ic** < **Ib**. The same reactivity orders are characteristic of other monosubstituted anilines, such as toluidines and chloroanilines [12, 13]. Table 1 shows that as the fraction of water is increased from 20 to 70 wt%, the arylsulfonylation rate constants of amino acids **Ia**–**Ic** increase, on average, by an order of magnitude. The increase in the rate constants of the reaction of amino acids **Ia**–**Ic** with sulfonyl chlorides **IIa, IIb** with increasing fraction of water in the reaction medium can be explained by specific solvation of the reagents and transition state and also by a change in the structure of the system water–2-propanol.

We considered it interesting to compare experimental and calculated k values. In this connection, based of thermodynamic data for dissociation of amino acids **Ib, Ic** and using the scheme of ionic equilibria (1), we estimated the fractions of the anionic and neutral forms of amino acids **Ib, Ic** by Eqs. (9) and (10):

$$\alpha_- = K_3 c_{H^+}^{-1}/(1 + K_3 c_{H^+}^{-1} + K_3 K_4^{-1} + K_2^{-1} K_3 K_4^{-1} c_{H+}), \quad (9)$$

$$\alpha_0 = K_3 K_4^{-1}/(1 + K_3 c_{H^+}^{-1} + K_3 K_4^{-1} + K_2^{-1} K_3 K_4^{-1} c_{H^+}). \quad (10)$$

It should be noted that the equilibrium constants K_1, K_2, K_3, and K_4 are related to the dissociation constants $K_{(1)}$ and $K_{(2)}$, determined by acid and base titration [14], by Eqs. (11) and (12):

$$K_{(1)} = K_1 + K_2, \quad (11)$$

$$K_{(2)}^{-1} = K_3^{-1} + K_4^{-1}. \qquad (12)$$

From scheme (1) that includes equilibria between uncharged and charged forms of amino acids **Ia**–**Ic** we can obtain Eq. (13):

$$K_1K_3 = K_2K_4. \qquad (13)$$

However, three equations are insufficient for calculating four rate constants. The fourth equation can be obtained having determined K_2 by the Hammett equation, which is possible with acids **Ib** and **Ic** from data for the reaction series: $C_6H_5NH_3^+ \rightleftarrows C_6H_5NH_2 + H^+$ [14]. All thermodynamic equilibrium constants K_1–K_4 and dissociation constants $K_{(1)}$ and $K_{(2)}$ for compounds **Ib** and **Ic**, required for estimation of α_- and α_0, were taken from [14] for water.

To estimate α_- and α_0, we were also to measure pH in the working solution. To this end, we applied potentiometric titration. The measured pH values for working solutions of amino acids **Ib, Ic**, as well as the fractions of the anionic and uncharged forms of the acids, estimated by Eqs. (9) and (10), are listed in Table 2.

Rigorous pH control is needed for two reasons. First, at pH > 7 hydrolysis of arenesulfonyl chlorides **IIa, IIb** is strongly enhanced, and, second, the concentration of H^+ ions affects the fraction of the ionic form of the amino acids, involved in arylsulfonation. The dependence of the rate constants of the reaction of amino acids **Ib, Ic** with sulfonyl chlorides **IIa, IIb** on the pH of the medium is given in Fig. 1 for the system water (30 wt%)–ethanol. As seen from Fig. 1, the arylsulfonation rate constant is much pH-dependent, and in going from pH 1 to pH 6 it changes by two (**Ic**) or four (**Ib**) orders of magnitude.

The k_- and k_0 values for amino acids **Ib, Ic** can be determined by the correlation equation (14) taken from [5].

$$\log k = -1.16 - 2.15\sigma^- + 1.09\sigma + 1.00S - 0.89\sigma^-\sigma$$
$$+ 0.5\sigma^-S - 0.18\sigma S - 0.90\sigma^-\sigma S. \qquad (14)$$

Here σ^- and σ are the substituent constants for arylamine and arenesulfonyl chloride, respectively, S is the solvent parameter (for 2-propanol, $S = -0.17$). The k_- and k_0 values, $l\,mol^{-1}\,s^{-1}$, are 5.51×10^{-1} and 3.07×10^{-2} (**Ib**) and 3.48×10^{-1} and 3.15×10^{-3} (**Ic**), respectively.

Table 3 lists the rate constants for the reaction of amino acids **Ib, Ic** with sulfonyl chlorides **IIa**, **IIb** in the system water–2-propanol, calculated by Eq. (6) (k_c) and experimental (k_e).

Table 2. pH of working solutions and α_- and α_0 values for amino acids **Ib** and **Ic**

c_{H_2O}, wt%	pH	α_-	α_0
Ib			
40.16	4.6	0.429	0.350
51.02	5.0	0.658	0.214
60.38	5.2	0.754	0.155
69.45	5.85	0.932	0.049
Ic			
39.89	3.5	0.070	0.248
49.91	3.85	0.147	0.230
60.81	4.0	0.196	0.218
69.59	4.4	0.380	0.168

As seen from Table 3, the rate constants calculated by Eq. (6) fit closely the corresponding experimental values for arylsulfonation of amino acids **Ib, Ic** in aqueous 2-propanol containing 40–70 wt% of water.

The dependences of the rate constants for the arylsulfonation of **Ib, Ic** (calculated and experimental) on the composition of the system water–2-propanol are given in Fig. 2.

EXPERIMENTAL

Amino acids **Ia**–**Ic** (pure grade) were recrystallized from water. *m*-Nitrobenzenesulfonyl chloride (pure grade) was recrystallized from hexane. *p*-Nitrobenzenesulfonyl chloride was synthesized by the procedure [15] and recrystallized from benzene. Lithium 2,6-dinitrophenolate was synthesized from the corresponding dinitrophenol. Perchloric acid (analytical grade) was used as received. 2-Propanol (analytical grade)

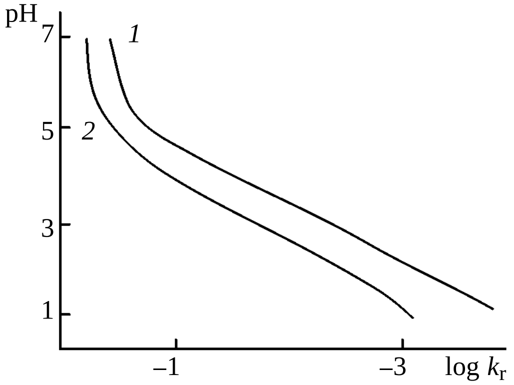

Fig. 1. Dependendence of the logarithm of the rate constant k_e of the reactions (*1*) **Ib** + **IIa** and (*2*) **Ic** + **IIb** on the pH of the medium in the solvent water (30 wt%)–ethanol.

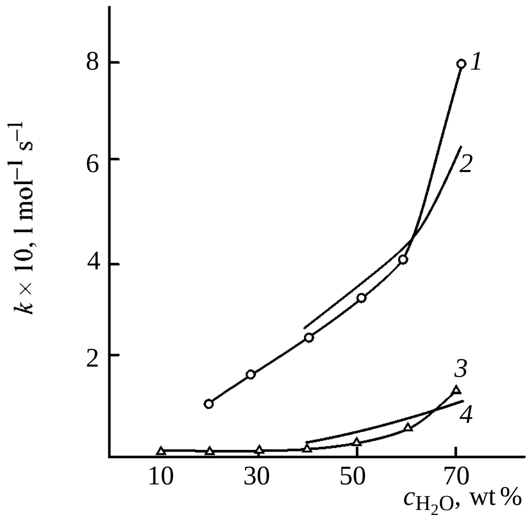

Fig. 2. Dependences of the rate constants of arylsulfonation of amino acids (*1, 2*) **Ib** and (*3, 4*) **Ic** on the composition of the system water–2-propanol (298 K). (*1, 3*) Experimental values and (*2, 4*) calculated by Eq. (6).

was dried over $CaCl_2$ and distilled. All aqueous working solutions were prepared using twice distilled water.

The reaction kinetics were followed by the absorbance of the indicator (400 nm) by means of a KFK-2 photoelectrocalorimeter with a temperature-controlled cell compartment. pH measurements were performed by potentiometry. The galvanic cell comprised a glass and a silver–silver chloride electrode (cell without transport), the EMF was measured by means of a pH meter operated in the millivoltmeter mode. The electrodes were calibrated against $HClO_4$.

Table 3. k_c and k_e values, l mol^{-1} s^{-1}

c_{H_2O}, wt%	**Ib** + **IIa**		**Ic** + **IIb**	
	k_c	k_e	k_c	k_e
40	0.247	0.240	0.025	0.024
50	0.369	0.334	0.052	0.037
60	0.420	0.391	0.069	0.065
70	0.637	0.817	0.133	0.140

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