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Solvent Effect on the Kinetics of Arylsulfonation of Benzhydrazide with 3-Nitrobenzenesulfonyl Chloride in Aqueous-Organic Solutions

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Abstract — A comparative study is made of the solvent effect on the kinetics of arylsulfonation of benzhydrazide with 3-nitrobenzenesulfonyl chloride in aqueous-organic solutions (water–2-propanol, water–dioxane, water–tetrahydrofuran, and water–acetonitrile) at 298 K. The arylsulfonation product can be obtained in nearly theoretical yield at the initial reactant concentrations of 0.1 M in the water–dioxane, water–MeCN, and water–THF mixtures containing above 30 wt % water.

The capability of influencing the reaction rate through association with reactants makes water promising as a component of solvents used in arylsulfonation of arenecarboxylic acid hydrazides with arenesulfonyl chlorides. Therefore, in this work we studied the kinetics of this reaction in aqueous-organic binary solvents.

Previously we reported on the reactivity of arenecarboxylic acid hydrazides toward arenesulfonyl chlorides in several aqueous-organic solvents [1, 2]. The goal of this work was to study the kinetics of arylsulfonation of benzhydrazide **I** with 3-nitrobenzenesulfonyl chloride **II** in water–acetonitrile (MeCN) and water–tetrahydrofuran (THF) binary solvents and also the effect of the water content in H_2O–*i*-PrOH, H_2O–dioxane, H_2O–THF, and H_2O–MeCN on the kinetics of this reaction at 298 K. Arylsulfonation of arenecarboxylic acid hydrazides proceeds in two stages: formation of arylsulfonation product [reaction (1)] and binding of the liberated HCl [reaction (2)]. However, since the latter reaction proceeds practically instantly [its rate is higher by four orders of magnitude than that of (1)], arylsulfonation of arenecarboxylic acid hydrazides should be considered as a single-stage reaction.

$$\underset{\mathbf{I}}{C_6H_5CONHNH_2} + \underset{\mathbf{II}}{3\text{-}NO_2C_6H_4SO_2Cl}$$

$$\xrightarrow{k_a} C_6H_5CONHNHSO_2C_6H_4NO_2\text{-}3 + HCl, \tag{1}$$

$$\mathbf{I} + HCl \xrightarrow{\text{fast}} C_6H_5CONHNH_2 \cdot HCl. \tag{2}$$

In aqueous-organic solvents, hydrolysis of sulfonyl chloride **II** [reaction (3)] occurs as a side reaction.

$$\mathbf{II} + H_2O \xrightarrow{k_h} \underset{\mathbf{III}}{3\text{-}NO_2C_6H_4SO_3H} + HCl. \tag{3}$$

Therefore, the rate constant k_h of hydrolysis of sulfonyl chloride **II** should be taken into account in estimating the arysulfonation rate constant k_a. Assuming $c^0_{\mathbf{I}} = 2c^0_{\mathbf{II}}$, the kinetic equation takes the form of Eq. (4).

$$k_a = k_h[e^{-k_h\tau}(c^0_{\mathbf{II}} - x) - c^0_{\mathbf{II}}]/[2c^0_{\mathbf{II}}(c^0_{\mathbf{II}} - x)(1 - e^{-k_h\tau})]. \tag{4}$$

Here x is the change in the sulfonyl chloride **II** concentration by time τ; $c^0_{\mathbf{II}}$, its initial concentration; and $c^0_{\mathbf{I}}$, initial concentration of benzhydrazide **I**.

The rate constants of the reaction under consideration in H_2O–THF and H_2O–MeCN and also the rate constants of hydrolysis of sulfonyl chloride **II** are given in Table 1.

Table 1 shows that, as expected, in H_2O–THF, k_a increases with increasing water content w in the binary solvent. At water contents of 60 and 70% (here and hereinafter, wt %), hydrolysis prevailed, and k_a could not be estimated. In the case of H_2O–MeCN, k_a changes irregularly with increasing water content, slightly varying over the experimental w range. With increasing w from 10 to 50%, k_a increases by a factor of about 1.5, while in H_2O–THF, the corresponding factor is 3.

For the reaction in aqueous THF, we studied the temperature dependence of k_a over the range 298–318 K. The activation characteristics of the reaction were determined with a computer using an original

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Table 1. k_a and k_h in H_2O–THF and H_2O–MeCN (298 K)

$w(H_2O)$, %	H_2O–THF		H_2O–MeCN	
	$k_a \times 10^2$, $l\ mol^{-1}\ s^{-1}$	$k_h \times 10^4$, s^{-1}	$k_a \times 10^2$, $l\ mol^{-1}\ s^{-1}$	$k_a \times 10^4$, s^{-1}
10	3.47 ± 0.07	2.11 ± 0.04	19.7 ± 0.20	0.57 ± 0.01
20	5.29 ± 0.34	2.53 ± 0.04	–	–
30	7.18 ± 0.71	2.62 ± 0.02	23.3 ± 0.20	1.51 ± 0.01
40	8.29 ± 0.95	3.58 ± 0.01	22.3 ± 0.20	2.13 ± 0.03
50	10.40 ± 0.57	4.79 ± 0.01	32.6 ± 0.40	2.84 ± 0.06
60	–	4.73 ± 0.01	21.1 ± 0.40	3.89 ± 0.03
70	–	7.14 ± 0.10	–	–

code. The results are given in Table 2 along with data on k_a.

As seen, k_a grows insignificantly with increasing temperature (as the temperature increases by 10°C, k_a grows by a factor of about 1.5 for all the compositions of the H_2O–THF binary solvent). The reaction under consideration is characterized by relatively low activation energy and entropy. With increasing water content in H_2O–THF, the activation characteristics change only slightly (to within the experimental error).

Previously [1] we studied the kinetics of the reactions of benzhydrazide **I** with 4-nitrobenzenesulfonyl chloride and sulfonyl chloride **II** in H_2O–*i*-PrOH and H_2O–dioxane, respectively.

The kinetic parameters of reaction (1) in H_2O–MeCN, H_2O–*i*-PrOH, H_2O–dioxane, and H_2O–THF are given in Table 3 for various water contents. As seen, k_a increases with increasing water content in aqueous-organic solvents. The highest k_a was obtained in the H_2O–MeCN system. The lack of a linear correlation between k_a and the Kirkwood function for the reaction of benzhydrazide **I** with sulfonyl chloride **II** in the aqueous-organic solvents studied (see figure) suggests that specific solvation plays a dominant role in this process, while nonspecific interactions contribute only insignificantly.

The observed noticeable differences in the kinetics

Table 2. Kinetic and activation parameters of arylsulfonation of benzhydrazide **I** with sulfonyl chloride **II** in H_2O–THF (298–318 K)

$w(H_2O)$, %	T, K	$k_a \times 10^2$, $l\ mol^{-1}\ s^{-1}$	$k_h \times 10^4$, s^{-1}	E_a, kJ mol^{-1}	$-\Delta S^{\neq}$, J mol^{-1} K^{-1}	$-\Delta H^{\neq}$, kJ mol^{-1}
10	298	3.47 ± 0.07	2.11 ± 0.04	21.0 ± 3.0	211 ± 9	18.5 ± 2.9
	303	3.57 ± 0.28	2.15 ± 0.04			
	308	4.20 ± 0.65	3.00 ± 0.10			
	313	4.76 ± 1.08	3.22 ± 0.10			
	318	5.87 ± 0.90	3.48 ± 0.10			
20	298	5.29 ± 0.34	2.53 ± 0.04	23.2 ± 1.0	200 ± 3	20.6 ± 1.0
	303	6.11 ± 0.27	2.79 ± 0.03			
	308	6.95 ± 0.86	4.03 ± 0.10			
	313	8.43 ± 0.01	4.74 ± 0.10			
	318	9.39 ± 0.56	6.34 ± 0.04			
30	298	7.18 ± 0.71	2.62 ± 0.02	21.4 ± 1.0	204 ± 3	18.9 ± 1.0
	303	8.17 ± 0.31	3.55 ± 0.02			
	308	9.59 ± 0.65	4.87 ± 0.03			
	313	11.13 ± 0.50	6.44 ± 0.03			
	318	12.13 ± 1.12	8.45 ± 0.03			
40	298	8.29 ± 0.95	3.58 ± 0.01	21.7 ± 2.9	201 ± 9	19.1 ± 2.9
	303	9.83 ± 0.15	4.78 ± 0.01			
	308	12.20 ± 0.54	6.59 ± 0.01			
	313	13.47 ± 0.58	8.79 ± 0.02			
	318	14.03 ± 0.17	11.70 ± 0.01			
50	298	10.40 ± 0.57	4.79 ± 0.01	19.7 ± 1.6	206 ± 5	17.2 ± 1.6
	303	12.27 ± 0.48	6.13 ± 0.01			
	308	13.88 ± 0.60	9.08 ± 0.02			
	313	15.23 ± 0.50	11.90 ± 0.02			
	318	–	16.00 ± 0.01			

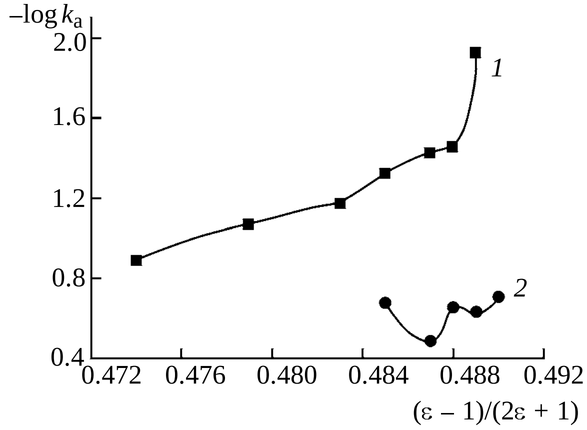
Table 3. $k_a \times 10^2$ ($l\ mol^{-1}\ s^{-1}$) in aqueous-organic solvents (298 K)[a]

$w(H_2O)$, %	H_2O–THF	H_2O–dioxane	H_2O–MeCN	H_2O–*i*-PrOH
10	3.47 ± 0.07	–	19.7 ± 0.20	1.19 ± 0.16
20	5.29 ± 0.34	–	–	3.50 ± 0.06
30	7.18 ± 0.71	6.05 ± 0.03	23.3 ± 0.20	3.61 ± 0.17
40	8.29 ± 0.95	9.39 ± 0.03	23.3 ± 0.20	4.79 ± 0.40
50	10.40 ± 0.57	11.29 ± 0.06	32.6 ± 0.40	6.72 ± 0.19
60	–	25.10 ± 0.12	21.1 ± 0.40	8.49 ± 0.30
70	–	–	–	12.86 ± 0.17

[a] Constant k_a was estimated using the correlation equation from [1].

of arylsulfonation of benzhydrazide **I** with sulfonyl chloride **II** in various solvents can be attributed, in our opinion, to the formation of heteromolecular associates (clusters) between the components of the aqueous-organic solvents [3]. Increase in the content of the organic component can distort the water structure, which, evidently, is responsible for the observed differences in the rate constants of reaction (1).

Molecules of many solvents are involved in solvation through hydrogen bonding and donor–acceptor interaction. In aqueous-alcohol solvents, both solvent components and solutes can be involved in hydrogen bonding. It is known [4] that H complexes of alcohols with amines are mostly more reactive as compared to the initial reactants. In contrast to alcohols, MeCN contains no hydrogen atom capable of forming hydrogen bonds with water molecules and reactants. Therefore, MeCN can participate in solvation only via donor–acceptor interaction. Evidently, the reactivity of the resulting molecular complexes is higher than that of the complexes reactant–solven formed in H_2O–alcohol systems. As a result, the highest k_a was obtained just in the H_2O–MeCN system. Taking the resultant effect of the solvent polarity and factors controlling the specific solvation into consideration, we can conclude that the interaction between the components of a binary solvent is the weakest in aqueous acetonitrile.



Logarithm of the rate constant k_a of arylsulfonation of benzhydrazide **I** with sulfonyl chloride **II** in (*1*) H_2O–*i*-PrOH and (*2*) H_2O–MeCN vs. the Kirkwood function.

The H_2O–THF and H_2O–dioxane binary solvents are similar in the nature of an organic component: both THF and dioxane are cyclic ethers. Therefore, it should be expected that the kinetic parameters of reaction (1) in these solvents will be similar. This assumption was well supported by the experiment (Table 3). The rate constants of arylsulfonation in H_2O–THF and H_2O–dioxane were found to be nearly equal at the same water contents.

Since hydrolysis (3) is the side reaction in arylsulfonation of benzhydrazide **I** in aqueous-organic solvents, acid **III** will always be contained in the system in addition to the main product. The yields of the main and side products α_a and α_h were estimated by analysis of the experimental kinetic data (Table 3). A system of differential equations (5) and (6) was solved by the fourth-order Runge–Kutta method. The results for the case of full completion of the reaction are given in Table 4.

$$\begin{cases} d\alpha_a/d\tau = 2k_a c^0_{\mathbf{II}}(1 - \alpha_a - \alpha_h)^2, & (5) \\ d\alpha_h/d\tau = k_h(1 - \alpha_a - \alpha_h)\,. & (6) \end{cases}$$

The results suggest that the solvents H_2O–THF, H_2O–MeCN, and H_2O–dioxane with the water content above 30% are more favorable for reaction (1), since in these binary mixtures the yield of the main product was obtained to be above 91% at the initial reactant concentrations of 0.1 M. The solvent H_2O–*i*-PrOH (50–70% H_2O) can also be used, but in this case the yield of the arylsulfonation product is lower (83–87%).

Table 4. Yield α_a of arylsulfonation of benzhydrazide **I** with sulfonyl chloride **II** in aqueous-organic solvents at 298 K

$w(H_2O)$, %	$c^0_{\mathbf{II}}$, M	α_a, %			
		H_2O–THF	H_2O–dioxane	H_2O–MeCN	H_2O–*i*-PrOH
10	0.01	55.73	–	93.85	26.68
	0.1	55.73	–	99.05	72.67
20	0.01	60.66	–	–	40.70
	0.1	91.02	–	–	82.52
30	0.01	65.90	90.80	88.67	36.24
	0.1	92.66	98.51	98.14	79.90
40	0.01	62.68	89.40	85.43	38.77
	0.1	91.67	98.26	97.44	81.43
50	0.01	61.41	87.49	86.15	41.40
	0.1	91.26	97.89	97.63	82.90
60	0.01	–	89.89	77.21	43.93
	0.1	–	98.35	95.67	84.22
70	0.01	–	–	–	50.33
	0.1	–	–	–	87.15

EXPERIMENTAL

Benzhydrazide **I** (chemically pure grade) was purified by triple recrystallization from water. Sulfonyl chloride **II** was synthesized by the procedure described in [5] and recrystallized from benzene. THF (chemically pure grade) was distilled on a column at the ambient pressure. MeCN (chemically pure grade) was dried over P_2O_5 and distilled on a column. The kinetics of arylsulfonation of benzhydrazide **I** and hydrolysis of sulfonyl chloride **II** was studied by the conductivity method using an E7-14 immittance meter. The errors of determination of the constant k_a were estimated by the standard statistical procedure at a 0.95 confidence level [6].

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