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KINETIC STUDY OF ALKALINE HYDROLYSIS OF SUBSTITUTED PHENYL TOSYLATES.

XVIII. RESULTS OF KINETIC MEASUREMENTS OF o-SUBSTITUTED TOSYLATES IN 80 % AQUEOUS DIMETHYLSULFOXIDE

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Rate constants of alkaline hydrolysis of six ortho-substituted and three para-substituted phenyl tosylates $CH_3C_6H_4SO_2OC_6H_4$-X (X = 2-NO_2, 2-Cl, 2-F, 2-OCH_3, 2-CH_3, 2-$N(CH_3)_2$, 4-Cl, 4-OCH_3, 4-CH_3) were measured in 80 % (50.3 M %) aqueous dimethylsulfoxide at various temperatures.

Earlier[1,2] we have studied the kinetics of the alkaline hydrolysis of metha- and para-substituted phenyl tosylates in 80 % aqueous dimethylsulfoxide and its dependence on temperature (at 25°, 50°, and 75°C).

The present paper presents analogous data for six ortho-substituted and three para-substituted phenyl tosylates. We have previously reported[3,4] on the results of the treatment of the log k values for the alkaline hydrolysis of substituted phenyl tosylates in 2.25 molar tetrabutylammonium bromide aqueous solution, performed simultaneously for ortho-metha- and para-substituted derivatives according to equation:

$$\log k^{X}_{m,p(ortho)} = \log k^{H}_{o} + \rho^{o}_{m,p(ortho)}\sigma^{o} + \rho_{I(ortho)}\sigma_{I} \qquad (1)$$

In order to evaluate the ortho effect, the inductive σ_I scale was used.

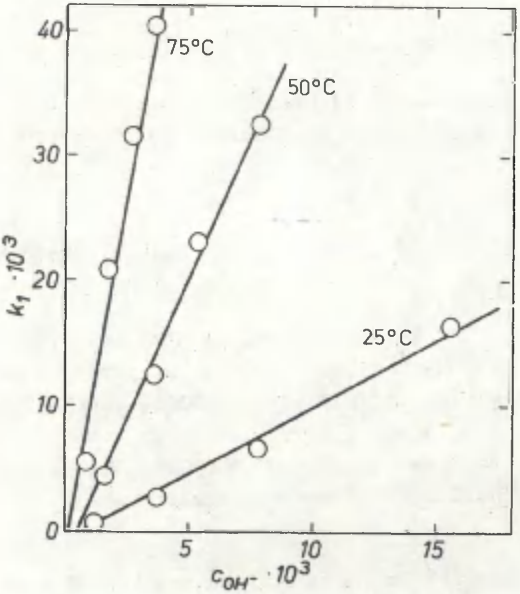

Fig. 1. Dependence of the k_1 values on C_{OH^-} for 2-NO_2-phenyltosylate at 75°, 50°, and 25°C.

The purpose of the present study was to find out the applicability of a similar data treatment method to the alkaline hydrolysis of substituted phenyl tosylates in 80 % aqueous dimethylsulfoxide solution.

It has been found[4,7] that in the case of the alkaline hydrolysis of substituted phenyl tosylates and phenyl benzoates the sensitivity towards metha- and para-substitutents increases similarly, when proceeding from water to 80 % aqueous dimethylsulfoxide and to 2.25 molar tetrabutylammonium bromide solution (approximately 0.8 units of ρ^{o}).

It is interesting to check if there are any analogous solvent effects with ortho-substituted derivatives.

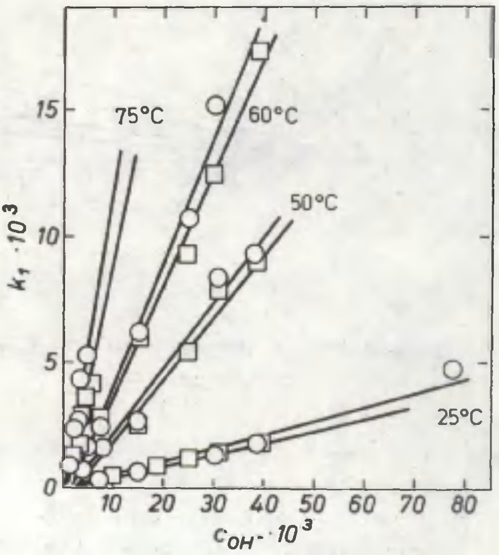

Fig. 2. Dependence of the k_1 values on C_{OH^-} for 2-Cl- and 2-F-phenyltosylate at 75°, 50°, and 25°C.

○ - X = 2-Cl , □- X = 2-F

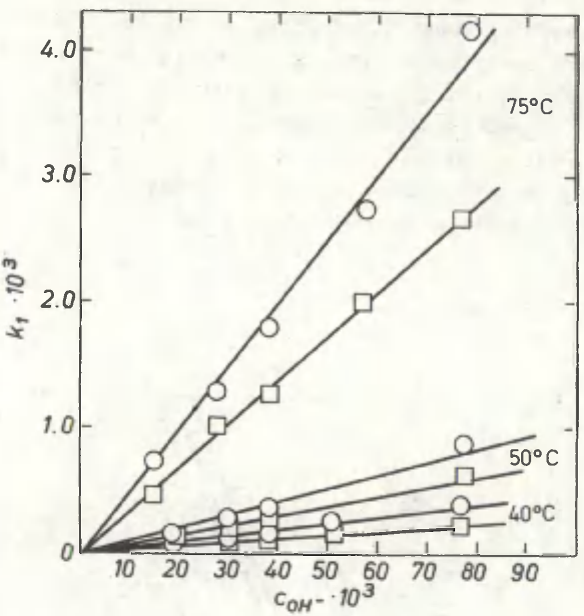

Fig. 3. Dependence of the k_1 values on C_{OH^-} for 2-CH_3 - and 2-OCH_3-phenyltosylate at 75°, 50°, and 40°C.
○ - X = 2-CH_3 , □ - X = 2-OCH_3

The present paper concentrates on the kinetics of the alkaline hydrolysis of substituted phenyl tosylates $CH_3C_6H_4SO_2OC_6H_4$-X for X = 2-NO_2, 2-F, 2-Cl, 2-CH_3, 2-OCH_3, 2-$N(CH_3)_2$, 4-Cl, 4-OCH_3, 4-CH_3 in 80 % (volume) aqueous (50.3 M%) dimethylsulfoxide solution at 25°, 40°, 50°, 60°, 75° C.

As alkali, tetra-n-butylammonium hydroxide was used.

The preparation and characteristics of phenyl tosylates, the purification of alkali and dimethylsulfoxide can be found in previous publications[1,6,8,9]. For kinetic measurements the spectrophotometric method was applied[8]. The wave lengths used are given in Table 1.

The kinetic measurements were carried out under pseudomonomolecular conditions. The rate constants for each phenyl tosylate were measured at various alkali concentrations. Normally, 2-10 parallel measurements were performed at each different alkali concentration. According to those measurements, the corresponding arithmetic means of the pseudofirst order rate constants k_1 were calculated.

When calculating the k_2 values according to the following equation:

$$k_1 = k_2 \cdot C_{OH^-} + \text{const} \qquad (2)$$

both the k_1 values for all parallel measurements at each hydroxide concentration and the corresponding arithmetic means at each hydroxide concentration were applied.

Table 1 contains the results of the data treatment of the preliminary kinetic measurements: the arithmetic means of the pseudofirst order rate constants for each alkali concentration k_1; number of measurements at the hydroxide concentration considered (n_1); the values of the second order rate constants calculated according to Eq. (1) when both k_1 values for all parallel measurements at any concentration of hydroxide ($k_2(1)$) and the values of the second order rate constants $k_2(2)$ calculated according to Eq. (1) are embraced. In the latter case, the calculations were based on the arithmetic means of the k_1 values at each hydroxide concentration included.

Figures 1-6 illustrate the plots of the arithmetic means of the pseudofirst order rate constants k_1 vs, hydroxide concentration in the case of substituted phenyl tosylates $CH_3C_6H_4SO_2OC_6H_4$-X studied (X = 2-NO_2, 2-Cl, 2-F, 2-OCH_3, 2-CH_3, 2-$N(CH_3)_2$, 4-Cl, 4-OCH_3, 4-CH_3) at various temperatures.

When investigating the kinetics of the alkaline hydrolysis of metha- and para-substituted phenyl tosylates in 80 % aqueous dimethylsulfoxide[1] and phenyl benzoate in 70 %

aqueous dimethylsulfoxide[10], it was noticed that the value of k_1/C_{OH^-} increased when using more concentrated alkali solutions.

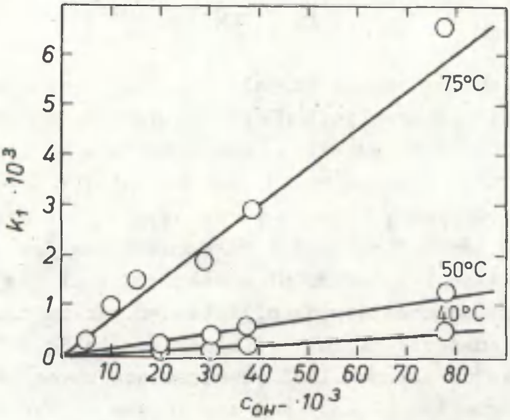

Fig. 4. Dependence of the k_1 values on C_{OH^-} for 2-$N(CH_3)_2$-phenyltosylate at 75°, 50°, and 40°C.

In order to obtain the "true" rate constants k_2^o, extrapolated to the infinite dilution of hydroxide solution, i.e. free from the influence of alkali concentration, we proceeded from the following equation:

$$k = k_1 + k_2 \cdot 10^{b[B]}B, \qquad (3)$$

Table 1

The Primary Experimental Values of Pseudofirst Order Rate Constants k_1 and the Results of the Kinetic Data Treatment According to Eq. (1) $k_1 = k_2 \cdot C_{OH^-} + const$ for the Alkaline Hydrolysis of Substituted Phenyl Tosylates $CH_3C_6H_4SO_2OC_6H_4$-X in 80 % (V/V) DMSO-Water Mixture

C_{OH^-} - concentration of n-Bu_4NOH hydroxide

k_1 - arithmetic means of the pseudofirst order rate constants

n_1 - number of measurements at the hydroxide concentration considered

$k_2(1)$ - the values of the second order rate constants calculated according to Eq. (1), the k_1 values for all parallel measurements at each hydroxide concentration are included

$k_2(2)$ - the values of the second order rate constants calculated according to Eq. (1), the arithmetic means of the k_1 values at each hydroxide concentration are included

n/n_0 - the denominator reflects the total number of the data involved in regression data processing and the numerator equals the number of the remaining points after excluding significantly deviating points

λ - wave lengths used in measurements

Table 1 continued

X and λ	Temperature °C	$10^3 \cdot C_{OH^-}$ (M)	$10^3 \cdot k_1$ (s^{-1})	n_1	$k_2(1)$ and* $k_2(2)$ ($M^{-1} \cdot s^{-1}$)	n/n_0	Eq.(1) $10^3 \cdot$const	Notes**
1	2	3	4	5	6	7	8	9
2-NO_2	25.0	1.54	0.684±0.062	3	1.12±0.04	13/13	-1.5±0.4	
410		3.85	2.84 ±0.08	3	1.16±0.05	4/4	-1.5±0.4	
		7.70	6.98 ±0.57	4				
		15.4	16.6 ±0.1	3				
	50.0	1.54	4.55 ±0.65	5	4.90±0.27	14/14	-3.5±1.3	
		3.85	12.7 ±1.3	3	4.76±0.52	4/4	-3.3±2.6	
		5.13	23.3 ±1.9	3				
		7.70	32.9 ±1.0	3				
	75.0	0.939	5.68 ±1.04	4	13.5 ±0.9	15/16	-6.5±0.2	
		1.88	21.0 ±2.3	4	13.3 ±0.8	4/4	-5.7±2.0	
		2.78	31.9 ±5.2	4				
		3.67	42.4 ±4.0	4				
2-Cl	25.0	7.7	0.253±0.034	2	0.0557±0.0028	11/11	-0.21±0.08	C_{OH^-} = 0.0770
308		15.4	0.609±0.006	3	0.0554±0.0019	4/4	-0.21±0.05	C_{OH^-} = 0.0770
		30.8	1.47 ±0.02	2	0.0682±0.0039	5/5	-0.0048±0.0016	
		38.5	1.96 ±0.19	4				
		77.0	4.92 ±0.22	4				
	50.0	3.85	0.747±0.048	3	0.279 ±0.009	17/19	-0.42±0.21	

Table 1 continued

1	2	3	4	5	6	7	8	9
		7.70	1.66 ±0.01	3	0.268 ±0.027	5/5	-0.56±0.63	
		15.4	2.65 ±0.54	3				
		30.8	8.59 ±0.25	6				
		38.5	9.34 ±1.22	4				
	60.0	5.13	1.74 ±0.28	2	0.515 ±0.017	14/14	-1.4 ±0.4	
		7.70	2.37 ±0.04	3	0.529 ±0.023	5/5	-1.5 ±0.5	
		15.4	6.35 ±0.17	3				
		25.6	11.65 ±0.21	3				
		30.8	15.30 ±0.28	3				
	75.0	1.88	0.909±0.115	3	0.812 ±0.113	16/16	-0.26±0.45	
		2.78	2.45 ±0.01	3	0.820 ±0.176	5/5	-0.37±0.68	
		3.68	2.59 ±0.06	3				
		4.65	2.92 ±0.14	3				
		5.37	4.34 ±0.59	4				
2-F	25.0	10.3	0.305±0.007	2	0.0544±0.0012	12/13	-0.28±0.03	
300		15.4	0.549±0.006	2	0.0539±0.0018	5/6	-0.25±0.04	
		19.3	0.852±0.157	2				
		25.6	1.085±0.064	2				
		30.8	1.410±0.014	3				
		38.5	1.830±0.071	2				
	50.0	15.4	3.59 ±0.41	2	0.262 ±0.031	11/11	-0.87±0.92	

Table 1 continued

1	2	3	4	5	6	7	8	9
		25.6	5.52 ±0.61	3	0.248 ±0.038	4/4	-0.30 ±1.09	
		30.8	8.03 ±0.39	3				
		38.5	9.04 ±0.02	3				
	60.0	7.70	2.66 ±0.16	3	0.458 ±0.021	13/14	-1.4 ±0.5	
		15.4	6.05 ±0.43	3	0.460 ±0.041	5/5	-1.3 ±1.1	
		25.6	9.07 ±0.95	2				
		30.8	12.65 ±0.07	3				
		38.5	17.30 ±0.28	3				
	75.0	1.88	0.945 ±0.047	2	0.892 ±0.081	16/18	-0.72 ±0.33	
		2.78	1.75 ±0.15	4	0.828 ±0.010	5/5	-0.58 ±0.04	
		3.67	2.47 ±0.07	3				
		4.65	3.27 ±0.22	4				
		5.37	3.85 ±0.92	5				
2-N$(CH_3)_2$	25.0	38.5	0.0525±0.0015	1	0.00168			
280		77.0	0.153 ±0.001	3				
	40.0	19.3	0.109 ±0.008	2	0.00548±0.00080	6/6	-0.063 ±0.0245	c_{OH^-}=0.0770
		30.8	0.160 ±0.004	2	0.00548±0.00078	3/3	-0.0003±0.0237	c_{OH^-}=0.0770
		38.5	0.216 ±0.025	2	0.00769±0.00055	4/4	-0.062 ±0.025	
		77.0	0.538 ±0.074	2				
	50.0	19.3	0.252 ±0.010	2	0.0137 ±0.0013	7/7	0.007 ±0.039	c_{OH^-}=0.0770

Table 1 continued

1	2	3	4	5	6	7	8	9
		30.8	0.443 ±0.038	2	0.0146 ±0.0015	3/3	-0.023±0.046	$C_{OH^-}=0.0770$
		38.5	0.529 ±0.023	2	0.0186 ±0.0010	4/4	-0.135±0.046	
		77.0	1.31 ±0.14	2				
	75.0	5.13	0.280 ±0.002	3	0.0724 ±0.0055	17/17	0.083±0.14	$C_{OH^-}=0.0770$
		10.3	1.03 ±0.05	3	0.0710 ±0.0010	5/5	0.16 ±0.23	$C_{OH^-}=0.0770$
		15.4	1.56 ±0.09	3	0.0847 ±0.0054	6/6	-0.067±0.21	
		28.9	1.97 ±0.22	4				
		38.5	2.96 ±0.37	4				
		77.0	6.64 ±0.92	5				
2-CH_3	25.0	77.0	0.107 ±0.005	3	0.00139			
300	40.0	19.3	0.0678±0.0006	1	0.00461±0.00059	6/6	-0.027±0.019	$C_{OH^-}=0.0770$
		30.8	0.109 ±0.005	2	0.00446±0.00068	4/4	-0.021±0.021	$C_{OH^-}=0.0770$
		38.5	0.155 ±0.008	2	0.00586±0.00031	5/5	-0.062±0.015	
		51.3	0.213 ±0.004	1				
		77.0	0.398 ±0.001	2				
	50.0	19.3	0.153 ±0.004	2	0.00970±0.00058	6/6	-0.033±0.018	$C_{OH^-}=0.0770$
		30.8	0.270 ±0.019	2	0.00970±0.00032	3/3	-0.033±0.010	$C_{OH^-}=0.0770$
		38.5	0.339 ±0.009	2	0.0130 ±0.0008	4/4	-0.127±0.035	
		77.0	0.890 ±0.028	2				
	75.0	15.4	0.728 ±0.059	2	0.0482 ±0.0026	14/14	-0.051±0.115	$C_{OH^-}=0.0770$

Table 1 continued

1	2	3	4	5	6	7	8	9
		28.9	1.30 ±0.02	3	0.0481 ±0.0014	4/4	-0.047±0.053	C_{OH^-}=0.0770
		38.5	1.80 ±0.04	3	0.0559 ±0.0038	5/5	-0.279±0.187	
		57.8	2.75 ±0.22	6				
		77.0	4.21 ±0.21	5				
2-OCH$_3$	25.0	77.0	0.0676±0.0053	2	0.000857			
300	40.0	30.8	0.0759±0.0074	2	0.00351 ±0.00024	6/6	-0.032±0.010	C_{OH^-}=0.0770
		38.5	0.104 ±0.006	2	0.00351 ±0.00005	3/3	-0.032±0.002	C_{OH^-}=0.0770
		51.3	0.148 ±0.003	2	0.00431 ±0.00026	4/4	-0.062±0.014	
		77.0	0.274 ±0.018	2				
	50.0	19.3	0.0992±0.0103	2	0.00771 ±0.00046	6/6	-0.046±0.014	C_{OH^-}=0.0770
		30.8	0.199 ±0.005	2	0.00772 ±0.00068	3/3	-0.047±0.021	C_{OH^-}=0.0770
		38.5	0.246 ±0.004	2	0.00848 ±0.00024	4/4	-0.068±0.011	
		77.0	0.599 ±0.012	2				
	75.0	15.4	0.496 ±0.001	2	0.0358 ±0.0022	11/12	-0.031±0.093	C_{OH^-}=0.0770
		28.9	1.00 ±0.01	2	0.0357 ±0.0012	4/4	-0.055±0.045	C_{OH^-}=0.0770
		38.5	1.28 ±0.10	3	0.0354 ±0.0058	5/5	-0.045±0.028	
		57.8	2.02 ±0.11	5				
		77.0	2.67 ±0.66	6				
4-OCH$_3$	40.0	30.8	0.0944±0.0016	2	0.00371 ±0.0031	6/6	-0.020±0.013	
262		38.5	0.123 ±0.010	2	0.00371 ±0.00001	3/3	-0.0200±0.00004	

Table 1 continued

1	2	3	4	5	6	7	8	9
		51.3	0.171 ±0.008	2				
	50.0	15.4	0.100 ±0.001	2	0.0106±0.0009	8/8	-0.067±0.029	
		30.8	0.250 ±0.001	2	0.0106±0.0004	4/4	-0.066±0.020	
		38.5	0.350 ±0.040	2				
		51.3	0.477 ±0.018	2				
	60.0	15.4	0.236 ±0.005	3	0.0192±0.0018	7/7	-0.061±0.050	
		30.8	0.583 ±0.026	2	0.0184±0.0036	3/3	-0.031±0.108	
		38.5	0.644 ±0.032	2				
	75.0	15.4	0.909 ±0.019	4	0.0670±0.0029	12/13	-0.31 ±0.17	$c_{OH^-}=0.0770$
		19.3	1.06 ±0.04	2	0.0669±0.0040	4/4	-0.27 ±0.17	$c_{OH^-}=0.0770$
		30.8	1.96 ±0.04	2				
		38.5	2.39 ±0.14	5				
		77.0	5.74 ±0.93	2				
4-Cl	25.0	10.3	0.0804±0.0012	2	0.0186±0.0008	13/13	-0.13 ±0.02	
324		15.4	0.159 ±0.001	3	0.0187±0.0010	6/6	-0.13 ±0.03	
		19.3	0.191 ±0.001	2	0.0137±0.0009	6/6	0	
	25.0	25.6	0.344 ±0.031	2				
		30.8	0.426 ±0.030	2				
		38.5	0.606 ±0.028	2				
	50.0	15.4	1.38 ±0.21	2	0.0911±0.0073	12/13	-0.18 ±0.22	

Table 1 continued

1	2	3	4	5	6	7	8	9
		25.6	2.08 ±0.01	3	0.0844 ±0.0054	4/4	-0.02 ±0.15	
		30.8	2.59 ±0.12	5				
		38.5	3.32 ±0.04	3				
	60.0	15.4	2.49 ±0.36	2	0.172 ±0.020	24/25	-0.78 ±0.38	
		25.6	3.43 ±0.62	8	0.153 ±0.019	4/4	-0.151±0.75	
		30.8	4.30 ±0.24	8				
		38.5	6.08 ±1.16	6				
	75.0	5.13	1.67 ±0.66	2	0.436 ±0.026	30/30	0.21 ±0.07	
		7.70	2.85 ±0.08	3	0.433 ±0.027	7/7	1.18 ±0.64	
		15.4	5.39 ±0.26	3				
		19.3	5.76 ±1.40	3				
		25.6	9.58 ±1.77	6				
		30.8	12.96 ±1.79	8				
		38.5	15.63 ±2.76	5				
4-CH_3 312	40.0	25.6	0.0766±0.0018	2	0.00285±0.00073	8/8	-0.006±0.032	
		38.5	0.1189±0.0003	2	0.00289±0.00023	3/3	-0.004±0.009	
		51.3	0.1507±0.0311	4				
	50.0	19.3	0.114 ±0.003	2	0.00850±0.00008	8/8	-0.05 ±0.003	
		25.6	0.168 ±0.001	2	0.00850±0.00006	4/4	-0.05 ±0.002	
		38.5	0.280 ±0.005	2				
		51.3	0.386 ±0.002	2				

Table 1 continued

1	2	3	4	5	6	7	8	9
	60.0	19.3	0.244±0.011	2	0.0149±0.0009	8/8	-0.03±0.03	
		25.6	0.350±0.001	2	0.0149±0.0015	4/4	-0.03±0.05	
		38.5	0.587±0.004	2				
		51.3	0.713±0.021	2				
	75.0	10.3	0.383±0.011	3	0.0470±0.0014	11/11	-0.12±1.29	
		19.3	0.741±0.065	4	0.0472±0.0024	3/3	-0.13±1.30	
		38.5	1.700±0.010	4				

x The third constant denotes the $k_2(2)$ values found in the course of the data treatment without exclusion of points before data processing.

xx The alkali concentration for which the k_1 value is excluded before data treatment.

Table 2

Results of Kinetic Data Treatment According to Equation

$$k = k_1 + k_2 \cdot 10^{b[B]} \cdot B$$

where $k_1 = X_1 \cdot 10^{(X_2/T)}$, $k_2 = X_3 \cdot 10^{(X_4/T)}$, $b = X_5$, k is the observed first order rate constant at the alkali concentration considered.

Substituent X	X_1	X_2	X_3	X_4	X_5	s_o	s	n/n_o
$2\text{-}NO_2$	0	0	$(1.51\pm1.76)\cdot10^{8}$	-2.516 ± 0.169	23.85 ± 8.59	0.191	0.101	12/12
2-Cl	0	0	$(5.73\pm4.13)\cdot10^{7}$	-2.754 ± 0.105	4.54 ± 1.02	0.148	0.067	20/20
2-F	$(1.33\pm0.60)\cdot10^{-4}$	0	$(1.43\pm0.83)\cdot10^{7}$	-2.553 ± 0.091	3.47 ± 1.12	0.090	0.043	20/20
$2\text{-}N(CH_3)_2$	0	0	$(1.11\pm1.14)\cdot10^{9}$	-3.544 ± 0.149	1.36 ± 0.88	0.145	0.075	14/14
$2\text{-}CH_3$	$(1.76\pm0.83)\cdot10^{-5}$	0	$(4.80\pm2.47)\cdot10^{7}$	-3.157 ± 0.080	1.68 ± 0.43	0.048	0.026	14/14
$2\text{-}OCH_3$	0	0	$(7.41\pm3.90)\cdot10^{7}$	-3.279 ± 0.075	1.80 ± 0.50	0.076	0.039	13/13
$4\text{-}OCH_3$	0	0	$(1.76\pm0.84)\cdot10^{10}$	-4.018 ± 0.069	2.48 ± 0.53	0.061	0.033	15/15
4-Cl	$(-2.49\pm1.71)\cdot10^{-5}$	0	$(1.31\pm0.71)\cdot10^{8}$	-3.007 ± 0.083	3.00 ± 0.11	0.084	0.054	21/21
$4\text{-}CH_3$	0	0	$(6.00\pm2.73)\cdot10^{8}$	-3.568 ± 0.067	1.83 ± 0.57	0.068	0.026	14/14

Table 3

Results of Kinetic Data Treatment According to Equations*

$$\log (k/OH^-) = X_0 + X_1[OH^-] + X_2(1000/T) + X_3[OH^-](1000/T) \quad (1)$$

$$\log (k/OH^-) = X_0 + X_1[OH^-] + X_2(1000/T) \quad (2),$$

where k - the arithmetic mean values of the observed first order rate constants in the case of the alkali concentration considered (see Table 1)**

Substituent X	Temperature Interval	X_0	X_1	X_2	X_3***	n/n_0	s_0	s
1	2	3	4	5	6	7	8	9
2-NO_2	25-75	8.744±0.380	24.22±5.98	-2.690±0.121	0	11/12	0.136	0.069
		8.379±0.568	22.80±9.20	-2.577±0.181	0	12/12	0.214	0.107
2-Cl	25-75	7.939±0.257	4.36±0.79	-2.808±0.083	0	19/20	0.112	0.052
		7.758±0.323	4.54±1.02	-2.754±0.105	0	20/20	0.147	0.067
2-F	25-75	7.758±0.175	5.02±0.175	-2.761±0.056	0	19/20	0.082	0.041
		7.664±0.209	5.60±1.00	-2.737±0.067	0	20/20	0.100	0.049
2-$N(CH_3)_2$	40-75	8.924±0.461	0	-3.488±0.152	0	13/13	0.056	0.080
2-CH_3	40-75	8.997±0.288	-18.30±6.04	-3.606±0.094	6.75±1.98	14/14	0.045	0.021
		8.153±0.167	1.93±0.40	-3.324±0.543	0(Eq.2)	13/14	0.056	0.028

Table 3 continued

1	2	3	4	5	6	7	8	9
2-OCH_3	40-75	9.282±0.392	-24.63 ±7.98	-3.749±0.129	8.74±2.62	13/13	0.055	0.026
		7.819±0.254	1.39 ±0.55	-3.253±0.083	0 (Eq.2)	13/13	0.088	0.044
4-OCH_3	40-75	10.24 ±0.210	2.48 ±0.53	-4.018±0.069	0	15/15	0.064	0.033
4-CH_3	40-75	8.778±0.204	1.83 ±0.57	-3.560±0.067	0	14/14	0.064	0.026
4-Cl	25-75	9.604±0.377	4.70 ±14.5	-3.509±0.122	16.93±4.69	20/20	0.066	0.041
		8.461±0.067	4.01 ±1.25	-3.125±0.067	0 (Eq.2)	21/21	0.095	0.059
H	25-75	9.516±0.114	0.721±0.136	-3.633±0.031	0	19/22	0.036	0.028
3-Cl	25-75	9.528±0.163	1.72 ±0.21	-3.289±0.051	0	28/28	0.067	0.040
3-NO_2	25-75	9.199±0.211	1.80 ±0.29	-2.924±0.066	0	17/18	0.074	0.040
4-NO_2	25-75	8.379±0.088	71.79 ±619.4	-2.615±0.273	-21.03±7.76	28/28	0.121	0.058
	25-75	9.315±0.140	1.16 ±0.24	-2.893±0.043	0 (Eq.2)	24/28	0.063	0.029

* Exclusion of significantly deviating points is oompleted before the exclusion of insignificant argument scales. The cross terms are formed as products of centrated basic argument scales.

** For data treatment in the case of H-, 3-Cl, 3-NO_2-, and 4-NO_2- derivatives the data given in publication[1] were used.

*** If $X_3 \neq 0$, the results of data treatment according to Eq. (2) are given as well.

Table 4

Results of Data Treatment for Alkaline Hydrolysis of Substituted Phenyl Tosylates $CH_3C_6H_4SO_2OC_6H_4$-X in 80 % (volume) Aqueous DMSO According to Equation

$$\log k_2' = \log k_2^0 + B\cdot C_{OH^-} , \quad \text{where } k' = k_1/OH^-$$

X	Temperature °C	log k_2^o	B	s_0	r	n/n_0	Notes*
1	2	3	4	5	6	7	8
2-NO_2	25.0	-0.124±0.167	0	0	-	4/4	
		-0.047±0.083	0	0	-	3/3	$C_{OH^-} = 1.54 \cdot 10^{-3}$
	50.0	0.569±0.089	0	0	-	4/4	
		0.424±0.066	26.5±2.3	0.12		3/3	$C_{OH^-} = 5.15 \cdot 10^{-3}$
	75.0	0.988±0.138	0	-	-	4/4	
		1.057±0.008	0	-	-	3/3	$C_{OH^-} = 9.39 \cdot 10^{-4}$
2-Cl	25.0	-1.471±0.028	3.89±0.67	0.33	0.943	5/5	
		-1.525±0.018	6.81±0.68	0.17	0.985	4/4	$O_{OH^-} = 0.0770$
	50.0	-0.689±0.064	0	0	-	4/4	
	60.0	-0.528±0.027	7.40±1.42	0.36	0.931	5/5	
	75.0	-0.163±0.102	0	0	-	5/5	
		-0.125±0.065	0	0	-	4/4	$C_{OH^-} = 0.00183$
2-F	25.0	-1.548±0.047	6.58±1.87	0.55	0.834	6/0	
	50.0	-0.628±0.034	0	0	-	4/4	

Table 4 continued

1;	2	3	4	5	6	7	8
	60.0	-0.410±0.047	0	0	-	5/5	
	75.0	-0.343±0.042	40.7 ±10.8	0.48	0.876	5/5	
		-0.256±0.033	21.9 ± 3.0	0.23	0.972	4/4	O_{OH^-} = 0.00188
2-N(CH$_3$)$_2$	40.0	-2.310±0.033	1.97± 0.7	0.56	0.828	4/4	
		-2.261±0.020	0	0	-	3/3	C_{OH^-} = 0.0770
	50.0	-1.919±0.019	1.93±0.41	0.14	0.937	4/4	
		-1.863±0.021	0	0	-	3/3	C_{OH^-} = 0.0770
	75.0	-1.100±0.103	0	0	-	6/6	
		-1.108±0.114	0	0	-	5/5	C_{OH^-} = 0.0770
2-CH$_3$	40.0	-2.524±0.020	3.08±0.43	0.24	0.967	5/5	
		-2.433±0.030	0	0	-	4/4	C_{OH^-} = 0.0770
	50.0	-2.153±0.011	2.78±0.23	0.14	0.990	4/4	
		-2.071±0.025	0	0	-	3/3	O_{OH^-} = 0.0770
	75.0	-1.317±0.032	0	0	-	5/5	
		-1.331±0.011	0	0	-	4/4	C_{OH^-} = 0.0770
2-OCH$_3$	40.0	-2.706±0.012	3.34±0.23	0.12	0.993	4/4	
		-2.572±0.035	0	0	-	3/3	O_{OH^-} = 0.0770
	50.0	-2.306±0.038	2.68±0.80	0.48	0.878	4/4	
		-2.223±0.055	0	0	-	3/3	C_{OH^-} = 0.0770
	75.0	-1.469±0.015	0	0	-	5/5	

Table 4 continued

1;	2	3	4	5	6	7	8
		-1.472 ± 0.016	0	0	-	4/4	$C_{OH^-} = 0.0770$
$4-OCH_3$	40.0	-2.566 ± 0.020	1.71 ± 0.01	0.004	0.999	3/3	
	50.0	-2.240 ± 0.038	4.48 ± 1.06	0.39	0.922	4/4	
	60.0	-1.772 ± 0.046	0	0	-	3/3	
	75.0	-1.275 ± 0.023	2.10 ± 0.55	0.48	0.876	5/5	
		-1.224 ± 0.029	0	0	-	4/4	$C_{OH^-} = 0.0770$
4-Cl	25.0	-2.107 ± 0.041	10.4 ± 1.87	0.32	0.946	6/6	
	50.0	-1.069 ± 0.018	0	0	-	4/4	
	60.0	-0.830 ± 0.040	0	0	-	4/4	
	75.0	-0.442 ± 0.052	0	0	-	7/7	
$4-CH_3$	40.0	-2.522 ± 0.011	0	0	-	3/3	
	50.0	-2.275 ± 0.026	3.17 ± 0.74	0.38	0.924	4/4	
	60.0	-1.859 ± 0.034	0	0	-	4/4	
	75.0	-1.461 ± 0.020	2.70 ± 0.38	0.20	0.966	3/3	

*The alkali concentration for which the log k'_2 value is excluded before the data treatment.

Table 5

Values of log k_2^o, Calculated According to Different Methods

Substituent X	Temperature ^oC	Eq. (4)		Eqs. (6) and (5)		Eq. (3)	
		log k_2^o (Table 4)	n/n_0	log k_2^o (Table 3)	n/n_0	log k_2^o (Table2)	n/n_0
1	2	3	4	5	6	7	8
2-NO_2	25.0	-0.124±0.167	4/4	-0.284±0.381	11/12	-0.265	12/12
		-0.047±0.083	3/3				
	50.0	0.569±0.089	4/4	0.416±0.533		0.399	
	75.0	0.988±0.138	4/4	1.013±0.513		0.948	
2-Cl	25.0	-1.471±0.028	5/5	-1.485±0.378	19/20	-1.484	20/20
		-1.525±0.018	4/4				
	50.0	-0.689±0.064	4/4	-0.755±0.362		-0.768	
	60.0	-0.528±0.027	5/5	-0.493±0.357		-0.512	
	75.0	-0.163±0.102	5/5	-0.131±0.350		-0.156	
2-F	25.0	-1.548±0.047	6/6	-1.505±0.256	20/20	-1.401	20/20
	50.0	-0.628±0.034	4/4	-0.787±0.246		-0.739	
	60.0	-0.410±0.047	5/5	-0.530±0.242		-0.511	
	75.0	-0.343±0.042	5/5	-0.174±0.238		-0.180	
		-0.256±0.033	4/4				
2-$N(CH_3)_2$	40.0	-2.316±0.035	4/4	-2.220±0.661	14/14	-2.276	14/14

Table 5 continued

1	2	3	4	5	6	7	8
		-2.261±0.020	3/3				
	50.0	-1.919±0.019	4/4	-1.875±0.652		-1.927	
		-1.863±0.021	3/3				
	75.0	-1.100±0.103	6/6	-1.101±0.635		-1.138	
		-1.108±0.114	5/5				
2-CH_3	40.0	-2.524±0.020	5/5	-2.524±0.416	13/14	-2.401	14/14
		-2.433±0.030	4/4	-2.467±0.240*	14/14		
	50.0	-2.153±0.011	4/4	-2.168±0.409		-2.092	
		-2.071±0.025	3/3	-2.148±0.236*			
	75.0	-1.317±0.032	5/5	-1.367±0.395		-1.290	
		-1.331±0.011	4/4	-1.400±0.228*			
2-OCH_3	40.0	-2.706±0.012	4/4	-2.696±0.568	13/13	-2.609	13/13
		-2.572±0.035	3/3	-2.698±0.295*	13/13		
	50.0	-2.306±0.038	4/4	-2.329±0.539*		-2.282	
		-2.223±0.055	3/3	-2.244±0.291*			
	75.0	-1.469±0.015	5/5	-1.489±0.540		-1.553	
		-1.472±0.016	4/4	-1.453±0.281*			
4-OCH_3	40.0	-2.566±0.002	3/3	-2.698±0.304	15/15	-2.594	15/15
	50.0	-2.240±0.038	4/4	-2.200±0.299		-2.196	
		-2.284±0.001	3/3				
	60.0	-1.772±0.046	3/3	-1.826±0.295		-1.823	

Table 5 continued

1	2	3	4	5	6	7	8
	75.0	-1.275±0.023	5/5	-1.308±0.289		-1.306	
4-Cl	25.0	-2.107±0.041	6/6	-2.179±0.557	20/21	-1.952	21/21
				-2.026±0.306[*]	21/21		
	50.0	-1.069±0.018	4/4	-1.259±0.533		-1.194	
				-1.214±0.293[*]			
	50.0	-0.830±0.040	4/4	-0.933±0.526		-0.914	
				-0.923±0.289[*]			
	75.0	-0.447±0.052	7/7	-0.481±0.515		-0.526	
				-0.520±0.283			
4-CH_3	40.0	-2.522±0.024	3/3	-2.596±0.295	14/14	-2.598	14/14
	50.0	-2.275±0.008	4/4	-2.244±0.291		-2.256	
	60.0	-1.859±0.034	4/4	-1.913±0.285		-1.925	
	75.0	-1.461±0.020	3/3	-1.453±0.280		-1.465	

[*] log k_2^o value, calculated according to Eq. (5), i.e., without cross term $X[OH^-](1000/T)$ (see Table 3)

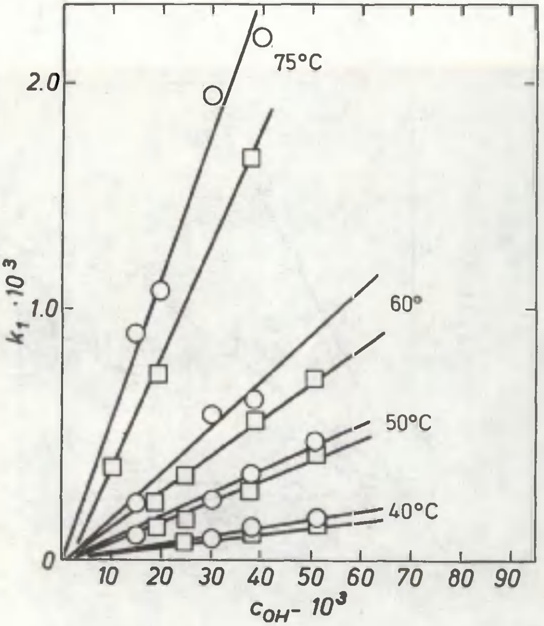

Fig. 5. Dependence of the k_1 values on C_{OH^-} for 4-OCH_3- and 4-CH_3-phenyltosylate at 75°, 60°, 50° and 40° C.

where k is the observed first order rate constant for the process

$$A + B \xrightarrow{k_2} \text{product},$$

$k_1 = X_1 \cdot 10^{(X_2/T)}$, $k_2 = X_3 \cdot 10^{(X_4/T)}$ and $b = X_5$.

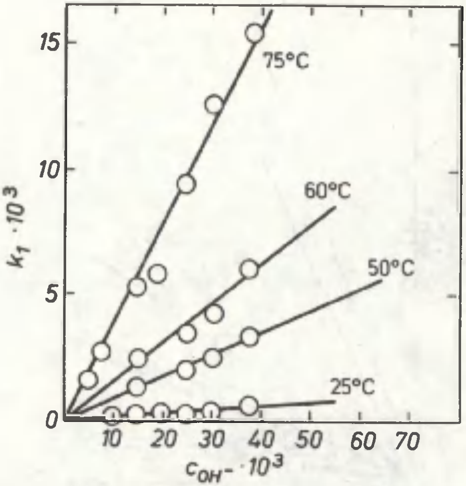

Fig. 6. Dependence of the k_1 values on C_{OH^-} for 4-Cl-phenyltosylate at 75°, 60°, 50° and 25° C.

The k_1 value could be interpreted as the rate constant for the spontaneous hydrolysis. But, if $X_2 = 0$, then $k_1 = X_1$ can be considered as product $k_2 \cdot BD$, where BD is the correction to the nominal concentration of B:

$$B + BD = B + X_1/k_2$$

$b = X_5$ is the coefficient in the equation of Setschenov (see ref.[11, 12])

$$\log k_2 = \log k_2^0 + b\,[B] \qquad (4)$$

It is assumed in Eq. (3) that the coefficient of the Setschenov equation b = X_5 does not depend on temperature, i.e., the concentration of reagent B does not affect the activation energy of the reaction.

As a result of the data treatment, according to Eq.(3) we calculated the values of the unknown parameters using the nonlinear least square methods. Thus, parameters X_1, X_2, X_3, and X_5 for all compounds studied in the present work were used (Table 2). For most cases, the values of X_1 and X_2 were found to be insignificant , while the X_5 value appeared significant. This confirms the applicability of the Setschenov equation.

It follows from the data of Table 2 that the term of spontaneous hydrolysis should be considered insignificant (k_1 = 0, as much as X_1=X_2=0). If k_1 = 0, Eq. (3) can be rewritten as follows:

$$\log (k/B) = \log X_3 + X_4(1/T) + X_5[B] \qquad (5)$$

Eq. (5) could be considered the isoenthalpic variant of the Setschenov equation. Eqs. (6) and (7) are the isokinetic and isoentropic variants, respectively:

$$\log (k/B) = \log X_3 + X_4(1/T) + X_5[B] + X_6[B](1/T) \qquad (6)$$

$$\log (k/B) = \log X_3 + X_4(1/T) + X_6[B](1/T) \qquad (7)$$

The results of the treatment of the log (k/OH^-) values for the alkaline hydrolysis of phenyl tosylates in 80 % aqueous DMSO according to Eqs. (5) and (6) are given in Table 3.

It follows from the data of Table 3 that in the relationships represented above, the terms $X_1[OH]$ and $X_2(1000/T)$ are also significant besides the intercept (log X_3 in Eqs. (5), (6) and (7)) X_0 = log A. In most cases the cross term $X_3[OH^-](1000/T)$ appeared to be insignificant. In such cases the results of data treatment by Eqs. (5) and (6) are identical. If the term $X_3[OH^-](1000/T)$ is significant, the results of the treatment of the log (k/OH^-) values according to Eq. (5) is also given.

Consequently, the data in the Table refer to the fact that a change in the alkali concentration mainly affects the entropic parameter of activation. It can be seen that in the case of ortho-substituted derivatives the influence of the alkali concentration on the entropic parameter is somewhat stronger than in the case of metha- and para-substituted derivatives. This conclusion could be considered with a precaution, as far as the observed effect tends to depend on the interval of the alkali concentration, used in the kinetic measurements.

If Eq. (7) was used, cross term $X[OH^-](1000/T)$ appeared to be insignificant for ten compounds (X = 2-NO_2, 2-$N(CH_3)_2$, 2-Cl, 2-CH_3, 2-OCH_3, 4-OCH_3, 4-Cl, 4-CH_3, H, 4-NO_2) out of thirteen. Consequently, the isoentropic variant of the Setschenov equation does not work.

For comparison, the log k_2^o values were calculated in three different ways. First, according to the Setschenov equation (4), using the log k values for each compound, separately at one and the same temperature. Then the arithmetic mean values of the measured constants divided by the alkali concentration were used. The results of the data processing are given in Table 4.

Secondly, when calculating log k_2, Eq. (6) was used and a simultaneous data treatment of the log k values for all temperatures was embraced (see Table 3).

For comparison, we calculated the log k_2^o values using Eq. (3). The log k_2^o values calculated by the above-mentioned methods are reported in Table (5). If the cross term $X_3[OH^-](1000/T)$ is significant for the data treatment according to Eq. (6) (see Table (3)), two values for log k_2^o will be given in Table (5). The first one considers the cross terms, the other one does not.

The log k_2^o values calculated by those three different methods are in good agreement with each other.

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KINETICS OF METHYL CHLOROFORMATE ETHANOLYSIS IN PRESENCE OF PYRIDINE-1-OXIDES

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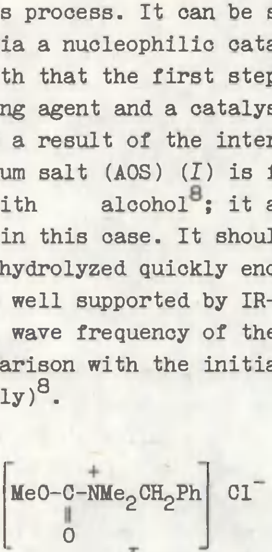
Kinetics of methyl chloroformate ethanolysis in presence of pyridine-1-oxide series has been investigated. The reaction proceeds according to the nucleophilic mechanism with general base comprehension. As the effectiveness of nucleophilic catalysis with the substituted pyridine-1-oxides increases, the contribution of general base participation decreases, except sterically hindered N-oxides. Kinetics of the first step of the catalytic process - interaction between methyl chloroformate and pyridine-1-oxides, has been studied and a quantitative account of the effect of the substituent in pyridine ring on the reaction rate was obtained within the framework of the Yukawa-Tsuno type equation.

Pyridine-1-oxides are known to be catalytically very active in the acyl transfer reactions[1,2]. However, up to now the process has been studied for benzoylchloride (see, for example, [3-6]), and there is only one work available dealing with the solvolytic reaction[5]. That is why it seems to be advisable to study the kinetics of alcoholysis of alkyl chloroformates in presence of pyridine-1-oxides. This reaction was investigated in detail under noncatalytic conditions[7].

The study was carried out with ethanolysis of methyl chloroformate (MCF) at 25°C. Pyridine-1-oxides turned out to accelerate the process substantially, whereas N,N-dimethylbenzylamine (DMBA) and 1,1,3,3-tetramethylurea (TMU) inhibited this process. It can be suggested that the reaction proceeds via a nucleophilic catalytic mechanism[2] and in accordance with that the first step is the interaction between an acylating agent and a catalyst.

As a result of the interaction of MCF with DMBA, the acylonium salt (AOS) (*I*) is formed which does not practically react with alcohol[8]; it arises from the process of inhibition in this case. It should be noted, however, that AOS (*I*) is hydrolyzed quickly enough and it acylates amines. This fact is well supported by IR-spectrum data of (*I*): the absorbing wave frequency of the carbonyl group is by far lower in comparison with the initial MCF (1715 and 1795 cm^{-1}, respectively)[8].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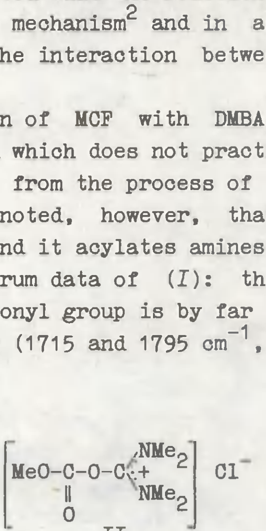
I


$\left[\mathrm{MeO{-}\underset{\underset{O}{\|}}{C}{-}O{-}\overset{+}{C}(NMe_2)_2}\right]\mathrm{Cl^-}$

II

The complex forming between MCF and TMU is followed by a similar (although somewhat smaller) decrease in $\nu_{C=O}$ (1765 cm^{-1}). Therefore, it is not surprising that AOS (*II*) is not a reactive acylating reagent either. The ionic structure of the product (*II*) has been confirmed by the conductivity of its solution in ethanol. The observed spectra, the results of coductometric studies and the data about the reactivity of the compound (*II*) agree well with the data about the structure and properties of the complexes including acyl chlorides and disubstitued amides[9–11].

The formation of complexes MCF with pyridine-1-oxides takes place easily under -15°C. Increasing temperature to the room condition results in rapid decarboxylation followed by heat release. But these adducts are rather stable in alcohol solutions and they tend to have high acylating reactivity as it results from the remarkable increase in the ethanolysis rate of MCF.

Taking into account the fact that the solutions of the complexes formed with MCF and N-oxides of pyridines in ethanol are electrically conductive and also comparing analogically AOS (*I* and *II*) and the adducts of pyridine-1-oxides and acyl chlorides[12] we can suggest that in this case the ionic structure (*III*) is also realized.

(*1*)

Thus, resulting from the interaction of all the investigated bases with MCF, the acylonium-type compounds are formed. In alcoholic solution they can dissociate into ions. The latter fact made it possible for us to measure independently the constants of reaction rate (*1*) and the formation of AOS (*I* and *II*) in ethanol by conductometric method.

Reaction (*1*) has general second order and the first one - on each of the reagents for all bases to be investigated. The results of the measurements are shown in Table 1.

The reactivity of the bases investigated changes in accordance with pK_a[1,12], but not with pK_{HB}[13]. Thus, DMBA has the maximal pK_a value in this series and its reaction rate with MCF is the fastest, as the pK_{HB} of DMBA is essentially lower than the pK_{HB} of pyridine-1-oxides.

For a quantitative estimation of the effects of structural factors on the reaction rate, Hammett's equation[14] was used applying different scales of σ-constants[15]. Experimental results for 3- and 4-substituents (*III*a-f) can be described best of all using the original σ-constants (*2*).

Table 1

The Rate Constants of Methyl Chloroformate Reaction With Substituted Pyridine-1-Oxides XPyO, DMBA and TMU in Ethanol, 25°C

Compound	X	k, $l \cdot mol^{-1} \cdot s^{-1}$	n^*
*III*a	4-MeO	14.4 ± 1.1	6
b	4-Me	5.10 ± 0.19	4
c	3-Me	2.53 ± 0.13	6
d	H	1.49 ± 0.09	6
e	3-Cl	0.122 ± 0.006	3
f	$4\text{-}NO_2$	$(9.8 \pm 0.5) \cdot 10^{-3}$	4
g	$3,5\text{-}Me_2$	0.397 ± 0.001	5
h	2-Me	1.17 ± 0.06	6
i	$2,3\text{-}Me_2$	0.869 ± 0.015	4
j	$2,6\text{-}Me_2$	0.168 ± 0.006	8
I		42.7 ± 0.1	5
II		$(1.01 \pm 0.02) \cdot 10^{-2}$	7

* Number of separate measurements of rate constants.

$$\log k = (0.24 \pm 0.10) - (2.96 \pm 0.27)\sigma \qquad (2)$$
$$n = 6, \quad r = 0.998, \quad s = 0.007$$

Principally, the effects of substituents in the ring of pyridine-1-oxides (including those in position 2) on their reactivity to MCF and phosgene[16] are similar, although the latter reaction series was investigated in methylene chloride. This fact along with a comparatively high absolute meaning of ρ can be considered an evidence for the closeness of transition states of these reactions. For 3,5-dimethylpyridine-1-oxide (*III*g) an unexpectedly low rate constant value was estimated and relationship (*2*) was obtained without taking into consideration the data for this compound. It is interesting to note that for the reaction between phosgene and pyridine-1-oxides[16] in methylene chloride, a similar effect was observed although it was not very obvious.

Both MCF, and pyridine-1-oxides are "rigid" reagents and their interaction must be controlled by the charge[17]. Then, as it was expected, the plot of rate constant logarithms against the dipole moment of pyridine-1-oxides[18] is in a *symbatic* relationship (Fig. 1).

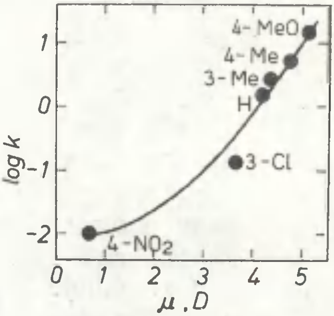


Fig. 1. The plot of rate constant logarithms of reaction between MCF and pyridine-1-oxides in ethanol (25°C) against the dipole moment of N-oxides.

The lack of linearity seems to depend on the essential influence of orbital interaction and on the difference in solvation of pyridine-1-oxides by ethanol. The maximal slope of the curve does not exceed the value of 2.2 D^{-1}, which is considerably lower than the corresponding value 3.61 D^{-1} for the reaction of pyridine-1-oxides with phosgene. It means that the charge in the reaction center decreases during the transition from phosgene to MCF. It results in decreasing of the coulomb part of interaction and increasing of the orbital one.

In order to compare the effects of electronic factors on the complex formation process between pyridine-1-oxides and MCF, phosgene[16] and 1-naphthol[13], it is necessary to estimate separately the inductive and resonance effects of a substituent using the Yukawa-Tsuno equation[14] as it was done in the case of the two last electrophiles[13,16]. Equation (3) was obtained:

$$\log k = (0.190 \pm 0.008) - (2.88 \pm 0.02)\sigma^{n} - (1.20 \pm 0.03)(\sigma^{+} - \sigma^{n}) \quad (3)$$

$$n = 6 \;;\; R = 0.999 \;;\; s = 0.0002$$

According to Hine's[19] principle, the reduction of the charge in the reaction center leads to a decrease in reaction sensitivity to the electron effects of the substituents especially concerning the resonance interaction. In illustration of it, we may take the plot which is close to square dependence, namely $|\rho^{R}|$, against $|\rho^{n}|$ for three reaction series - the interaction between pyridine-1-oxides and MCF, phosgene[16] and 1-naphthol[13] (Fig. 2).

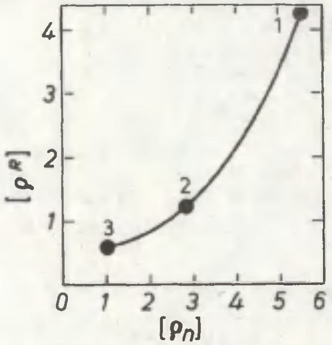


Fig. 2. The plot of $|\rho^{R}|$ against $|\rho^{n}|$ for the reaction between pyridine-1-oxides and phosgene (*1*), MCF (*2*) and 1-naphthol (*3*).

The values of logarithms of rate constants for the reaction between 3- and 4-substituted pyridine-1-oxides and MCF and phosgene correlate well with each other [Fig. 3, Eq. (*4*)]. Besides, a rather good linear dependence is observed also for the 2-substituents [Fig. 3, Eq. (*5*)], in spite of the minimal size of a sampling. The latter plot includes also the point for 3,5-dimethylpyridine-1-oxide (*IIIg*).

$$\log k_{MCF} = (0.223 \pm 0.049) + (0.413 \pm 0.002) \log k_{OOCl_2} \quad (4)$$

$$n = 5 \; ; \; r = 0.985 \; ; \; s = 0.03$$

$$\log k_{MCF} = -(0.295 \pm 0.028) + (0.511 \pm 0.025) \log k_{COCl_2} \quad (5)$$

$$n = 4 \; ; \; r = 0.975 \; ; \; s = 0.03$$

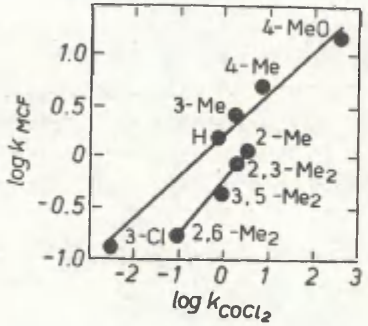


Fig. 3. Interdependence of rate constant logarithms of reaction of pyridine-1-oxides with MCF and phosgen.

Existence of individual correlations for *ortho*-substituents has been described and by and large, it is connected **with** the solvent effect[20]. As far as N-oxide(*IIIg*)is concerned it seems to have a particular effect.

For confirmation of the unusual properties of this compound, it seemed to be worth estimating its reactivity in another, related reaction series - the association with 1-naphthol in methylene chloride, that is, it was made using the ^{1}H NMR method[13]. At temperatures -30°, -10°, 10° and 28 °C the following association constants were gained (l/mol): 217±14, 100±3, 65±2 and 39±1. The value of chemical shift for the associate was 11.95±0.11 ppm, the enthalpy mean of its formation equals-18±1 kJ/mol. So, in accordance with the ability to the complex forming, N-oxide of 3,5-dimethylpyridine (*IIIg*) is compared with a similar ability for unsubstituted N-oxide (*III*d) and it is 2-3 times less effective for compound (*III*c)[13]. Consequently, we have to admit the steadily abnormal reactivity for the 3,5-disubstitution. Pyridine-1-oxides are known to be nucleophiles with particular α-effects[1,2]. Apparently, one of the factors concerning the display of "supernucleophility" of N-oxides is the opportunity to form quasiaromatic 10-electron transition states[21]. In this case, the atoms of pyridine ring in position 2 (or 6) are involved into the interaction, but the substituents in position 3 (or 5) seem to turn into *ortho*-substituents. Thus, the observed deviation for 3,5-dimethylpyridine-1-oxide may be caused by a kind of secondary *ortho*-effect. An indirect confirmation of it is the disappearance of abnormality in the transition to the real pyridines which do not have "supernucleophility" on the account of α-effect (see, for example, work[22]).

Therefore, proceeding to the analysis of the catalytic ethanolysis which runs in accordance with nucleophilic mechanism it can be concluded that the first step of this process is to a large extent defined with electron and steric effects of the substituents in pyridine-1-oxide ring.

Addition of small quantities of DMBA results in a decrease in the pseudo-first order rate constant value for MCF ethanolysis. After reaching the DMBA concentration about 15% of the initial MCF concentration undergoes a 20% decrease in the reaction rate and a simultaneous deviation of the process from the pseudo-first order kinetics. It is well explained by a rapid formation of stable nonreactive AOS (*I*). Probably, the lower thermodynamic stability of AOS (*II*) is the reason for the MCF ethanolysis rate decrease in a lower degree even in the presence of two-fold TMU redundant with respect to the initial MCF concentration. Contrary to this fact, even small quantities of pyridine-1-oxides are capable of accelerating the reaction under discussion by one order of magnitude (Table 2).

Table 2

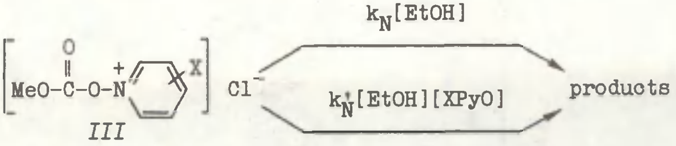
Observed Rate Constants for the MCF Ethanolysis in the Presence of Substituted Pyridine-1-Oxides XPyO, 25°C

X = H		X = 3-Me		X = 4-Me		X = 2,6-Me_2	
10^2[XPyO], mol/l	$k\cdot10^4$, s^{-1}	10^2[XPyO], mol/l	$k\cdot10^4$, s^{-1}	10^2[XPyO], mol/l	$k\cdot10^4$, s^{-1}	10^2[XPyO], mol/l	$k\cdot10^4$, s^{-1}
2.22	2.61±0.35	1.28	2.52±0.17	0.97	10 ± 1	0.56	0.51±0.05
3.17	3.84±0.39	2.64	4.76±0.48	2.48	26 ± 2	4.36	0.95±0.06
4.99	8.18±0.72	4.16	7.64±0.71	4.26	44 ± 8	6.73	1.35±0.08
6.64	12.2±0.8	5.59	11 ± 1	6.65	76 ± 10	7.54	1.62±0.06
7.23	15 ± 3	7.32	16 ± 1	7.89	94 ± 16	15.83	3.97±0.13
13.77	44 ± 7	11.43	28 ± 2	14.74	213±140	16.48	4.44±0.30
						16.64	4.54±0.21

The plots of the observed rate constants against concentration are nonlinear and they agree with Equation (6).

$$k = k_o + k_N[XPyO] + k'_N[XPyO]^2 \tag{6}$$

This fact shows that the reaction proceeds according to the nucleophilic catalytic mechanism connected with general base comprehension[2]. Here k_o - rate constant of noncatalytic ethanolysis, $(0.48\pm0.03)\cdot10^{-4}$ s^{-1}; k_N -rate constant of nucleophilic catalysis, determined by the reaction of AOS (*III*) and ethanol; k'_N - rate constant of nucleophilic catalysis connected with general base comprehension, characterizing the reaction of AOS (*III*) and the associate of ethanol with N-oxide. Thus, the MCF ethanolysis in the presence of pyridine-1-oxides may be shown as a combination of spontaneous (noncatalytic) reaction and reactions (*1*) and (*7*).



III

(7)

Constants k_N and k'_N were calculated using linearization in accordance with Equation (8) which was obtained by transformation of dependence (6).

$$\frac{k - k_o}{[XPyO]} = k_N + k'_N[XPyO] \qquad (8)$$

The calculated constants k_N and k'_N are shown in Table 3. Except sterically hindered 2,6-dimethylpyridine-1-oxide, there is a linear interdependence between the logarithms of rate constants of nucleophilic catalysis and formation AOS (*III*) (Fig. 4). It points out the determining role of the first step - AOS (*III*) formation - during the catalytic process of MCF ethanolysis.

Table 3

Values of k_N and k'_N MCF Ethanolysis in the Presence of Substituted Pyridine-1-Oxides XPyO at 25°

X	$k_N \cdot 10^3$, $l \cdot mol^{-1} \cdot s^{-1}$	k'_N, $l^2 \cdot mol^{-2} \cdot s^{-1}$	k'_N/k_N, $l \cdot mol^{-1}$
4-Me	90.7 ± 4.1	0.356 ± 0.047	3.93
3-Me	17.2 ± 1.1	0.088 ± 0.018	6.20
H	5.40 ± 0.66	0.190 ± 0.018	35.2
2,6-Me_2	0.589 ± 0.015	0.0108 ± 0.0011	18.3

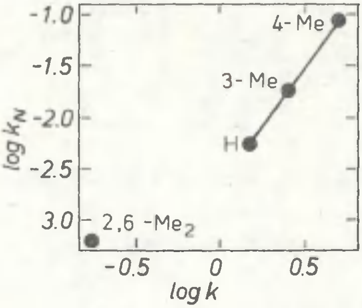


Fig. 4. Interdependence between logarithms of rate constants for nucleophilic catalysis and for AOS (*III*) formation; n=3, r=0.999, s=4·10^{-4}.

The rise of the efficiency of nucleophilic catalysis (k_N) in series X = H, 3-Me, 4-Me quite regularly decreases the share of general base cooperation (k_N/k'_N). The unproportional change of k'_N seems to be connected with the fact that this constant is characterized by several elemental interactions affected in different ways by the electron and steric effects of substituents in the N-oxide ring.

Experimental

The IR spectra were obtained in methylene chloride on *Specord IR-71*. The reagents and ethanol were purified as described in works[13,23].

O-Methyl-O-(α-dimethyliminio-α-dimethylaminomethyl)carbonate chloride (III). 1 g of TMU was added to the solution of 1 g of MCF in 5 ml dry heptane and it was allowed to stay at room temperature for some hours. The formed precipitate was filtered, washed with dry heptane and then dried in vacuum over P_2O_5. The yield of AOS (*II*) was practically quantitative. M.p. 56° (in closed capillary; decomp.). IR, sm^{-1}: 1765 (C=O), 1645 (C=N), 1150 (1150).

O-Methyl-O-(pyridinium-1-yl)carbonate chloride (IIId). The solution of 1 g of pyridine-1-oxide in minimal volume of dry CH_2Cl_2 was added to 1 g of MCF in 5 ml of the same solvent so that the temperature would not be above -15°C. The precipitate was filtered, washed with cold dry CH_2Cl_2 and dried in vacuum over P_2O_5. When during drying the temperature was raised to the room temperature, thermal decomposition of the product and the CO_2 release took place. The substituted pyridine-1-oxides had similar features.

All kinetic investigations were carried out in absolute ethanol. The reaction rates for the interaction of MCF with TMU, DMBA and substituted pyridine-1-oxides were measured by conductometric method observing the AOS concentration rise as it was described in ref.[24]. The ethanolysis kinetics of MCF in the presence of DMBA, TMU and pyridine-1-oxides were controlled titrimetrically[23].

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KINETICS OF THIOPHOSGENE SOLVOLYSIS IN ALIPHATIC ALCOHOLS

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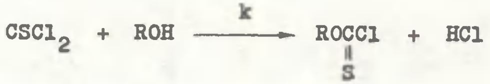
Kinetics of thiophosgene solvolysis in ROH alcohols (R = Me, Et, Pr, i-Pr, i-Bu, s-Bu, cyc-Hex) in the range of 4 - 62°C has been ivestigated. Thiophosgene reacts by a factor 10^3-10^4 slower than its oxygen analog. The effect of a substituent structure in alcohol is described by one parameter Taft's equation using the E_s constants for RCH_2-series, δ=2.67. In the correlation analysis, where E_s and temperature were used as parameters, a ratio was obtained in accordance with which the isokinetic temperature equals infinity.

In spite of the fact that thiophosgene is one of the oldest thiorganic compounds, its reactivity has been studied extremely poorly, especially the quantitative aspect[1]. The reaction of thiophosgene with alcohols is widely used at preparation of pharmaceutical compounds. at preparative synthesis[1], but there are no data available about the kinetics of this process. That is why the thiophosgene action during solvolysis in alcohol seemed worth investigating and these results and those for phosgene[2] were worth comparing.



$$\mathrm{CSCl_2} + \mathrm{ROH} \xrightarrow{k} \mathrm{RO\underset{\underset{S}{\|}}{C}Cl} + \mathrm{HCl}$$

The kinetic measurements were made by the conductometric and spectrophotometric methods, the results are presented in Table 1 and in Fig. 1 through the Arrhenius dependences.

Table 1

Rate Constants and Activation Parameters of Thiophosgene Solvolysis in ROH Alcohols

R	T, °C	Method	10^3k_1, s^{-1}	10^3k_2, $l \cdot mol^{-1} \cdot s^{-1}$	$\Delta H^{\neq}$, $\frac{kJ}{mol}$	$-\Delta S^{\neq}$, $\frac{J}{mol \cdot K}$
1	2	3	4	5	6	7
Me	6.5	C	13.12 ± 0.27	0.523 ± 0.011	47±3	140±9
	7.3	C	13.78 ± 0.29	0.550 ± 0.012		
	32.0	C	56.9 ± 2.4	2.34 ± 0.09		
	32.5	C	57.0 ± 2.3	2.34 ± 0.09		
	32.6	C	58.9 ± 0.7	2.42 ± 0.03		
	38.0	C	105.2 ± 1.8	4.35 ± 0.07		
	38.2	C	88.8 ± 2.7	3.67 ± 0.11		
	45.5	C	171 ± 11	7.15 ± 0.45		
	50.7	C	206 ± 2	8.67 ± 0.09		
	50.9	C	266 ± 12	11.2 ± 0.5		
Et	4.1	C	1.847 ± 0.005	0.1060 ± 0.0003	52±2	134±5
	4.1	C	2.15 ± 0.02	0.123 ± 0.001		
	9.2	S	2.48 ± 0.11	0.143 ± 0.007		
	9.2	S	2.19 ± 0.11	0.126 ± 0.006		
	9.5	S	2.29 ± 0.11	0.132 ± 0.006		
	11.75	C	3.62 ± 0.02	0.209 ± 0.001		
	17.5	C	6.69 ± 0.54	0.390 ± 0.031		

Table 1 continued

1	2	3	4	5	6	7
	20.05	C	5.36 ± 0.02	0.313 ± 0.001		
	20.05	C	6.77 ± 0.03	0.395 ± 0.002		
	27.5	S	13.08 ± 0.07	0.769 ± 0.004		
	27.5	S	9.42 ± 0.14	0.554 ± 0.008		
	27.8	C	10.91 ± 0.09	0.643 ± 0.005		
	27.8	C	10.15 ± 0.04	0.598 ± 0.002		
	34.4	S	19.8 ± 0.1	1.173 ± 0.004		
	34.9	C	17.8 ± 0.1	1.059 ± 0.008		
	35.0	C	14.9 ± 0.1	0.883 ± 0.003		
	40.2	S	25.3 ± 0.2	1.51 ± 0.01		
	41.5	S	26.6 ± 0.2	1.59 ± 0.01		
	41.5	S	28.5 ± 0.2	1.71 ± 0.01		
	42.5	S	32.9 ± 0.2	1.97 ± 0.01		
	43.0	C	26.5 ± 0.3	1.59 ± 0.02		
	46.1	S	42.0 ± 0.3	2.53 ± 0.02		
	48.0	S	43.4 ± 1.8	2.61 ± 0.11		
	51.0	S	50.2 ± 0.3	3.03 ± 0.02		
Pr	9.5	C	1.508 ± 0.006	0.1116 ± 0.0005	49±1	147±3
	15.2	S	1.97 ± 0.01	0.147 ± 0.001		
	16.5	S	1.94 ± 0.02	0.145 ± 0.001		
	19.0	S	2.48 ± 0.01	0.185 ± 0.001		
	22.2	S	3.54 ± 0.03	0.266 ± 0.002		
	22.2	S	3.27 ± 0.02	0.245 ± 0.002		
	22.2	S	3.18 ± 0.01	0.238 ± 0.001		
	22.4	S	3.10 ± 0.01	0.231 ± 0.001		
	25.6	S	3.93 ± 0.01	0.254 ± 0.001		
	25.8	S	4.25 ± 0.02	0.320 ± 0.001		
	32.0	S	6.04 ± 0.02	0.457 ± 0.002		
	32.0	S	6.08 ± 0.03	0.460 ± 0.002		
	32.0	S	5.95 ± 0.02	0.451 ± 0.002		
	34.0	S	7.15 ± 0.03	0.542 ± 0.002		
	34.0	S	7.19 ± 0.02	0.545 ± 0.002		
	38.9	S	10.3 ± 0.1	0.783 ± 0.010		
	39.0	S	10.1 ± 0.2	0.774 ± 0.014		

Table 1 continued

1	2	3	4	5	6	7
	44.2	S	13.9 ± 0.1	1.06 ± 0.01		
	44.9	S	14.3 ± 0.1	1.10 ± 0.01		
	45.0	S	14.2 ± 0.1	1.09 ± 0.01		
	52.9	S	24.4 ± 0.5	1.95 ± 0.04		
	53.5	S	23.4 ± 0.3	1.84 ± 0.02		
i-Pr	31.4	S	0.261 ± 0.002	0.0202 ± 0.0002	65±2	124±5
	32.6	S	0.271 ± 0.003	0.0210 ± 0.0002		
	36.2	S	0.358 ± 0.002	0.0279 ± 0.0002		
	37.0	S	0.393 ± 0.002	0.0306 ± 0.0001		
	38.7	S	0.389 ± 0.002	0.0304 ± 0.0001		
	39.5	S	0.447 ± 0.002	0.0349 ± 0.0002		
	41.5	S	0.523 ± 0.002	0.0410 ± 0.0001		
	41.5	S	0.570 ± 0.003	0.0477 ± 0.0002		
	42.6	S	0.566 ± 0.001	0.0444 ± 0.0001		
	58.5	S	2.09 ± 0.02	0.167 ± 0.001		
	59.5	S	2.16 ± 0.03	0.172 ± 0.002		
	59.7	S	2.24 ± 0.03	0.179 ± 0.002		
i-Bu	6.5	C	1.69 ± 0.01	0.154 ± 0.001	55±2	122±6
	8.9	C	1.57 ± 0.01	0.143 ± 0.001		
	10.1	C	1.65 ± 0.01	0.151 ± 0.001		
	17.6	C	3.33 ± 0.06	0.307 ± 0.005		
	17.7	C	3.33 ± 0.04	0.307 ± 0.003		
	25.6	C	7.59 ± 0.15	0.705 ± 0.014		
	33.3	C	14.7 ± 0.2	1.37 ± 0.02		
	33.5	C	13.2 ± 0.2	1.23 ± 0.02		
	40.2	C	18.5 ± 0.3	1.74 ± 0.03		
	46.5	C	27.5 ± 0.2	2.61 ± 0.02		
	47.5	C	30.4 ± 0.6	2.89 ± 0.06		
s-Bu	28.0	S	0.0780±0.0002	0.00723±0.00002	63±4	132±12
	32.0	S	0.203 ± 0.003	0.0189 ±0.0003		
	41.2	S	0.252 ± 0.001	0.0236 ± 0.0001		
	44.2	S	0.540 ± 0.002	0.0509 ± 0.0002		
	53.0	S	0.958 ± 0.005	0.0911 ± 0.0005		

Table 1 continued

1	2	3	4	5	6	7
	54.0	S	0.891 ± 0.007	0.0848 ± 0.0006		
	54.0	S	0.922 ± 0.007	0.0878 ± 0.0006		
	54.5	S	0.989 ± 0.009	0.0942 ± 0.0009		
	59.6	S	1.013 ± 0.007	0.0971 ± 0.0007		
	60.5	S	1.27 ± 0.03	0.122 ± 0.003		
	60.5	S	1.26 ± 0.02	0.121 ± 0.002		
	60.5	S	1.32 ± 0.02	0.126 ± 0.002		
	60.5	S	1.37 ± 0.02	0.132 ± 0.002		
	62.5	S	1.50 ± 0.04	0.144 ± 0.004		
	62.5	S	1.40 ± 0.01	0.134 ± 0.001		
cyc-Hex	32.0	S	0.206 ± 0.001	0.0219 ± 0.0001	68±2	112±5
	39.5	S	0.420 ± 0.002	0.0451 ± 0.0002		
	45.5	S	0.688 ± 0.010	0.0741 ± 0.0011		
	56.2	S	1.56 ± 0.05	0.169 ± 0.005		

[*] Measurement methods: C - conductometry,
S - spectrophotometry.

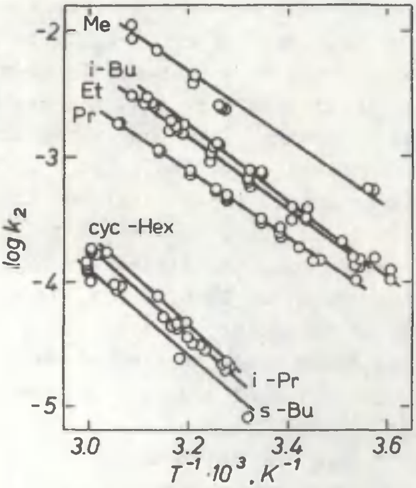


Fig. 1. Arrhenius plot for rate constants ($l \cdot mol^{-1} \cdot s^{-1}$) of thiophosgene solvolysis in ROH alcohols.

It follows from the comparison of these results and the data from work[2] that the rate of thiophosgene alcoholysis is by a factor 10^3-10^4 lower that that of phosgene. For hydrolysis[3] this ratio is about 100. During transition from phosgene to thiophosgene, the activation entropy changes slightly, while the enthalpy increases by 20 kJ/mole, on the average. The difference in reactivity accounts for the change in the electron structure of an acylating agent and it may be illustrated by the quantum chemical data.

For calculations, the CNDO/2 method in accordance with the latest experimental data for determining molecule geometry[4,5] was used. As it follows from the calculations, the charges on $CXCl_2$ atoms were distributed as follows:

	X	C	Cl
O	-0.1459	+0.3496	-0.1019
S	+0.0458	+0.0718	-0.0588

The substitution of sulfur for oxygen is shown to lead to a major charge decrease in the reaction center. This fact follows from the decrease in the effectiveness of orbitals' overlap during transition from 2p(O)-2p(C) to 3p(S)-2p(C), which is not compensated by a decrease in electronegativity. If we take into account the fact that the reaction is likely to be controlled by charge[6], its poorer reactivity can be explained by the aforesaid only. Really, the difference between the HOMO of methanol[6] (15.486 eV) and the LUMO of $CXCl_2$ molecules (Table 2) is quite essential, and so it changes very little if sulfur is substituted for oxygen.

Phosgene has two close LUMO, their energy difference being 0.0352 eV. In this case, in spite of a lower σ^*_{C-C}- orbital, the attack takes place on a more available $\pi^*_{C=O}$ -orbital[6], i.e., the mechanism of addition-elimination (AE) is realized but not S_N2. For thiophosgene where the sulfur atom has a positive charge, the antibonding orbital of the C-Cl bond is not screened by the negative potential site. It is well shown in the maps of molecular electrostatic potential (MESP) of phosgene((Fig.2a) and thiophosgene (Fig.3a) (data

Table 2

Properties of Two LUMO for $CXCl_2$ Molecules in Accordance with CNDO/2 Method

Type	Energy, eV	Contribution of atoms to MO		
		X	C	Cl
		X = O		
σ^*_{C-Cl}	0.0079	0.010	0.264	0.363
$\pi^*_{C=O}$	0.0431	0.325	0.327	0.174
		X = S		
$\pi^*_{C=S}$	-0.0355	0.651	0.211	0.069
σ^*_{C-Cl}, σ^*_{C-S}	0.0351	0.268	0.218	0.257

were calculated in approximation of point charges, the potentials are given in a.u.). But, in the case of thiophosgene, the $\pi^*_{C=S}$-orbital functions as LUMO and the difference between its energy and the energy of the next orbital which has σ^*_{C-Cl}, and where there is a significant contribution of the σ^*_{C-S}-orbital, exceeds the difference for phosgene, being, namely, 0,0706 eV. It can be concluded that the thiophosgene reaction with "rigid" nucleophiles according to the AE mechanism (attacks on the $\pi^*_{C=S}$-orbital perpendicularly to the molecule plane, Fig. 3b) is more probable than for phosgene. This conclusion is confirmed by the fact that during transition from carbonyl to thiocarbonyl compounds the stability of anionic form rises[7]. Consequently, the intermediate of type I (through its formation the reaction proceeds to the AE mechanism) must be more stable. Moreover, in the case of thiophosgene, unlike its O-analog, the participation of the intermediate with proton II transfer is quite possible.

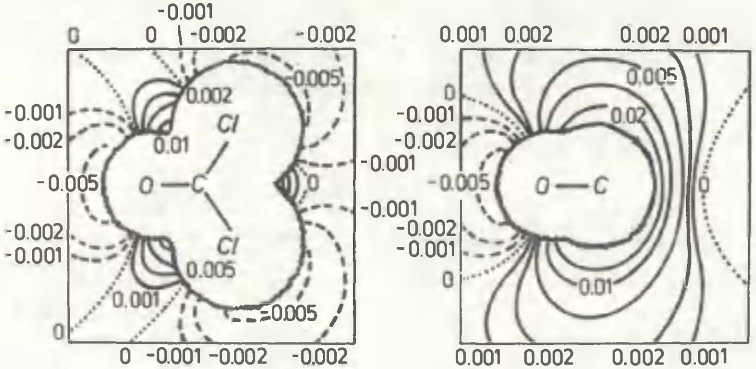


Fig. 2. The MESP map for phosgene[6]: a - in the molecule plane; b - in crossing perpendicular to molecule plane.

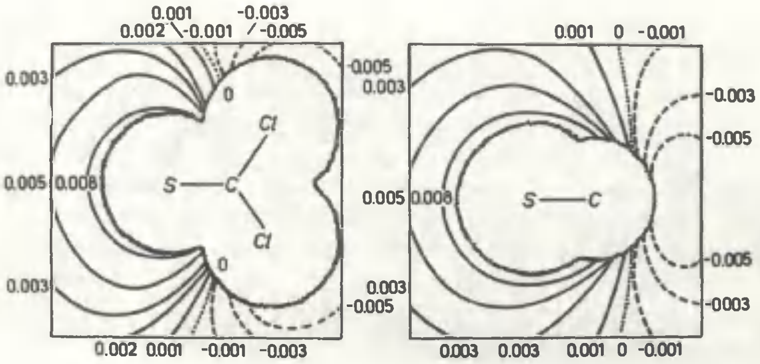
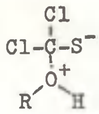


Fig. 3. The MESP map for thiophosgene: a - in the molecule plane; b - in crossing perpendicular to molecule plane.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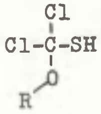
II

The effect of alcohol structure on the reaction rate was estimated using Taft's equation[8]. Steric constants in accordance with the principle of isosterism[9] were provided for the RCH_2 series. It was proved that for 25° C there is a good linear ratio between the logarithms of second order rate constants and the E_s value:

$$\log k_2 = -(2.433 \pm 0.096) + (2.67 \pm 0.14)E_s \qquad (1)$$

$$n = 7, \qquad r = 0.993, \qquad s = 0.017$$

As one can see from Eq. (1), the reaction series is rather susceptible to the steric factor. It means, the essential effect of the first step - the nucleophilic attack - on the general rate of the process. The δ value is in good agreement with similar values for phosgene[2,10,11].

Analogously with phosgene[2], we considered worth discussing the problem of the existence of isokinetic temperature β, using the basic equation (1). The analysis of the data of Table 1 by method[9] showed that the coefficients of term 1/T are always important, i.e., $\beta = \infty$, as it was observed in the case of phosgene[2]. As a result, Eq. (2) was obtained, which describes the effect of steric properties of the substituent on alcohol and temperature.

$$\log k_2 = (6.62 \pm 0.28) - (2730 \pm 80)1/T + (2.50 \pm 0.04)E_s \qquad (2)$$

$$n = 99, \qquad R = 0.985, \qquad s = 0.014$$

In this case, unlike a similar reaction series for phosgene[2], methanol does not fit the ratio. Besides, the introduction of an additional variable n_H (number α-hydrogen atoms in R) and the corresponding cross terms into the equation, as it was done in the case of phosgene[2], does not im-prove the correlation. It is likely that the difference in methanol behavior can be explained by an essential variety in the reactivity of these acyl chlorides and by various temperature intervals. The latter factor leads to changes in solvation equilibria, which have a remarkable effect on the process as it can be seen from works[10-12].

Experimental

Alcohols were purified by conventional techniques[13]. Thiophosgene ("Merck") was purified using multiple fraction distillation, and it was used as a fresh prepared solution in dry cyclohexane at concentration 0.01-0.1 mol/l.

Kinetic measurements were carried out in alcohol medium by conductometric[2] and spectrophotometric methods. In the latter case, the reaction was conducted in a temperature-controlled quartz cuvette, where the thickness of the absorbing layer was 10 mm. The recording was made on a spectrophotometer Hitachi 330, using the losses in optical density at 260 nm, which is close to the maximum of thiophosgene absorbance. The initial concentration of thiophosgene was 10^{-5} - 10^{-4} mol/l. The rate constants were calculated in papers[2,10].

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REACTIVITY OF DERIVATIVES OF PHENYLANTHRANILIC ACID. IX. ACID-BASE PROPERTIES OF SULFAMOYLIC DERIVATIVES OF PHENYLANTHRANILIC ACID IN MIXED SOLVENT DIOXAN-WATER

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Acid-base properties of sulfamoylic derivatives of phenylanthranilic acid in mixed solvent dioxan-water (60 volume % of dioxan) have been studied at 25° C. Effects of substituent's position and nature on pK_a value were analyzed in both phenyl fragments. Correlation equations corresponding to the pK_a relationships to the Hammett σ-constants and to σ_I and σ_C constants were calculated. A common general equation of pK_a correlation with the Hammett σ constants for substituents in anthranilic and non-anthranilic molecule fragments was found. The equation enables us to describe acid-base properties of 115 derivatives of phenylanthranilic acid.

To continue our research[1] into the acid-base properties of biologically active derivatives of phenylanthranilic acid, we have studied the dissociation of its 35 sulfamoylic substituents under standard conditions.

The ionization constants of the acid were determined using the method of potentiometric titration in a mixed dioxan-water solvent (60 vol % of dioxan).

Table 1 shows that the pK_a values are influenced both by the nature and position of substituents in a molecule. Consequently, after introducing an acceptor substituent, the acids will become stronger at the expence of its stabilizing effect onto the anion. The substitution of carbon radicals of various lengths for the hydrogen of sulfamide group brings about a slight decrease in the ionization level.

The Hammett equation was applied for quantitative estimation of the substituent effect in the nonanthranilic molecule fragment (Table 2). It is interesting to point out that the ρ values were very close for all series, coinciding with those for nitro- and chloroderivatives of phenylanthranilic acid studied previously[1].

An attempt to correlate the pK_as of sulfamoylic derivatives of phenylanthranilic acids with the induction constants of substituents failed, as statistical characteristics are unreliable (Table 3). Proceeding from that, we can presume that the acid-base properties of the studied compounds influence both the induction and conjugation effects.

For the purposes of quantitative estimation of the two effects, the pK_a was correlated with σ_I and σ_C:

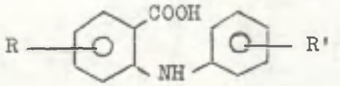
Series 1:
$$pK_a = (5.81 \pm 0.23) + (-0.71 \pm 0.10)\sigma_I + (-0.72 \pm 0.10)\sigma_C \qquad (1)$$
$$F = 235.4 \quad r = 0.935 \quad S = 0.002$$

Series 2:
$$pK_a = (5.88 \pm 0.05) + (-0.70 \pm 0.04)\sigma_I + (-0.71 \pm 0.03)\sigma_C \qquad (2)$$
$$F = 435.3 \quad r = 0.996 \quad S = 0.001$$

Series 3:
$$pK_a = (5.45 \pm 0.05) + (-0.72 \pm 0.04)\sigma_I + (-0.71 \pm 0.03)\sigma_C \qquad (3)$$
$$F = 440.6 \quad r = 0.996 \quad S = 0.001$$

Table 1

Ionization Constants pK_a of Sulfamoylio Derivatives of Phenylanthranilic Acid in Mixed Solvent of Dioxan-Water at 25° C



R' \ R	5-SO_2NH_2	5-$SO_2N(CH_3)_2$	5-$SO_2N(C_2H_5)_2$	5-$SO_2NHC_4H_9$	5-SO_2NHCH_3	4-Cl5-SO_2NH_2
H	5.76±0.05		5.88±0.03			5.46±0.04
2'-CH_3		5.88±0.03	5.98±0.02	5.92±0.04	5.85±0.02	5.56±0.01
4'-OH_3	5.86±0.05		6.00±0.04	5.94±0.03	5.86±0.01	5.58±0.03
2'.4'-$(CH_3)_2$			6.10±0.05			5.68±0.02
2'.5'-$(CH_3)_2$			6.03±0.03			
3'.4'-$(CH_3)_2$	5.93±0.02	5.96±0.02	6.05±0.05			5.63±0.04
3'.5'-$(CH_3)_2$			5.98±0.03			5.56±0.05
2'-OCH_3	5.95±0.02		6.08±0.07	6.02±0.02	5.97±0.01	5.65±0.04
4'-OCH_3	5.95±0.01	5.99±0.03	6.07±0.02	6.01±0.04	5.92±0.05	5.65±0.04
3'.4'-$(OCH_3)_2$	5.87±0.01				5.84±0.03	
2'-Cl						5.30±0.05
4-Cl						5.30±0.03
Series	1		2	3	4	5

Table 2

Parameters of Correlation Equations $pK_a = pK_a^o + \rho\sigma$ of Sulfamoylic Derivatives of Phenylanthranilic Acid

Series	pK_a^o	ρ	n	s	r
1	5.76±0.02	-0.71±0.11	6	0.0095	0.993
2	5.88±0.05	-0.72±0.03	9	0.0029	0.995
3	5.82±0.07	-0.72±0.07	4	0.0205	0.956
4	5.72±0.06	-0.72±0.05	5	0.0215	0.951
5	5.46±0.02	-0.72±0.03	10	0.0120	0.996

Table 3

Parameters of Correlation Equations $pK_a = pK_a^o + \rho_I\sigma_I$ of Sulfamoylic Derivatives of Phenylanthranilic Acid

Series	pK_a^o	ρ_I	n	s	r
1	5.87±0.11	-0.10±0.46	6	0.061	0.296
2	6.60±0.06	-0.25±0.46	9	0.065	0.426
5	5.60±0.10	-0.45±0.41	10	0.035	0.663

Table 4

Parameters of Correlation Equations $pK_a = pK_a^o + \rho\sigma$ of Phenylanthranilic Acid Derivatives

R'	pK_a^o	ρ	n	s	r
H	6.73±0.12	-1.85±0.13	9	0.067	0.997
2'-CH_3	6.79±0.09	-1.82±0.12	13	0.068	0.995
2'-OCH_3	6.89±0.10	-1.79±0.14	14	0.074	0.994
2'-Cl	6.57±0.17	-1.85±0.21	7	0.093	0.995
3'.4'-CH_3	6.88±0.20	-1.81±0.31	8	0.072	0.986
3'.5'-CH_3	6.97±0.24	-2.09±0.39	5	0.056	0.995
4'-CH_3	6.82±0.08	-1.82±0.12	12	0.064	0.995
4'-OCH_3	6.91±0.11	-1.88±0.15	14	0.082	0.992
4'-Cl	6.58±0.18	-1.86±0.23	7	0.102	0.994

It is interesting to mention that the values of of ρ_I practically coincide with those of ρ_C. It shows the equality of the influence of induction and conjugation effects onto the acid-base properties of the sulfomoylic derivatives of phenylanthranilic acid.

The data of the present paper as well as of those published earlier[1] have been applied for the estimation of substituent effect in the anthranilic molecule fragment according to the Hammett equation. The calculated parameters are given in Table 4.

The data in Table 4 evidence that the reaction constants ρ are almost identical in the case of all nine series. The absolute values of their reaction constants were usually higher for substituted benzoic acids and solvents[2].

Application of the induction constants of substituents (σ_I) in the correlation equations of pK_a-$f(\sigma_I)$ also makes statistical characteristics poorer (Table 5), though the deterioration is not as remarkable as in the case of substituents in a nonanthranilic fragment of the phenylanthranilic acid molecule (Table 3).

Table 5

Parameters of Correlation Equations $pK_a = pK_a^o + \rho_I \sigma_I$ of Derivatives of Phenylanthranilic Acid

R'	pK_a^o	ρ_I	n	s	r
H	6.70±0.54	-1.80±0.73	9	0.337	0.909
2'-CH_3	6.68±0.39	-1.65±0.56	13	0.299	0.890
2'-OCH_3	6.79±0.40	-1.69±0.58	14	0.296	0.898
2'-Cl	6.63±0.18	-1.86±0.34	7	0.305	0.903
3',4'-CH_3	6.56±0.63	-1.67±0.72	8	0.262	0.790
3',5'-CH_3	6.79±0.37	-1.88±0.59	5	0.277	0.903
4'-CH_3	6.73±0.40	-1.72±0.58	12	0.296	0.901
4'-OCH_3	5.78±0.39	-1.69±0.57	14	0.309	0.881
4'-Cl	6.63±0.24	-1.87±0.35	7	0.404	0.901

The pK_a values of 115 derivatives of phenylanthranilic acid (Table 1 and the data of ref.[1]) were used for calculation of the parameters of the general Hammett equation:

$$pK_a = \underbrace{(6.72\pm0.04)}_{pK_a{}^{o}}+\underbrace{(-1.87\pm0.05)}_{\rho_1}\sigma + \underbrace{(-0.73\pm0,07)}_{\rho_2}\sigma' \qquad (5)$$

$n = 115$; $F = 47.45$; $r = 0.993$; $s = 0.008$,

where σ, σ' are the Hammett constants for the substituents in the anthranilic and nonanthranilic molecule fragments.

Experimental

<u>Reagents</u>. The dioxan of "oscillation" type was not repurified.

For preparing the mixed solution, a freshly boiled bidistillate, liberated from CO_2 was used. The derivatives of phenylanthranilic acid were synthesized by a modified Ullman reaction[3,4]. The products were recrystallized from ethanol three times and dried at room temperature and at 105° C until achieving their constant weight. The purity of the compounds was checked by means of thin-layer chromatography. The physicochemical properties of the substances agreed with those given in[3,4].

<u>Measurement technique</u> was described in ref.[5]. The 0.05N aqueous solution of KOH, purified from CO_2 served as a titrating agent. The concentration of the titrated solutions at their polyneutralization point equalled 0,005 mol/l. Potentiometric titration was conducted on a pH-meter EV-74 with a glass electrode ESP-43-074 and silver chloride electrodes EVL-IM at 25° C. The pK_a of acidic acid was taken as a standard, its value also coinciding with literature data[6].

Three independent pK_a measurements were performed for each compound. The accuracy of the obtained results was estimated by means of the method of mathematical statistics (the reliability level was 0.95)[7]. The calculations were performed on a computer "Elektronika 85". The algorithms of the programs are given in ref. [8].

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ION-PAIR EQUILIBRIUM EFFECT ON SPECTRAL AND KINETIC CHARACTERISTICS OF THE YANOWSKI σ-COMPLEX

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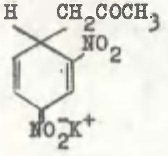
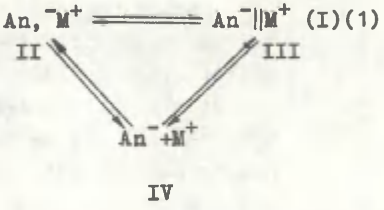
Medium polarity effect (in the case of binary tetrahydrofurane-acetone mixture) on spectral characteristics and kinetics of potassium 1-acetonide-2,4-dinitrocyclohexa-2,5-dienate decomposition by proton-donor agents has been studied. Changes in location and intensiveness of absorption maximums, as well as the variation of decomposition constant value depending on solvent content show that the Yanowski σ-complex exists as the equilibrium mixture of ions and various ion pairs having different activities. Ion pairs participate more actively in adduct decomposition than solvated anions.

Research has shown that in nonpolar media the reactivities of anionic σ-complexes are determined mainly by formation of ion pairs of cyclohexadienide anions with metal cations[1-2]. These effects have been thoroughly studied in connection with the Jackson-Meisenheimer complexes[3-6], but not with the Yanowski[7] complexes. To fill this gap, we have investigated the medium effect on the spectral and kinetic parameters of potassium 1-acetonyl-2,4-dinitrocyclohexa-2,5-dienate (I) in tetrahydrofurane (THF)-acetone system.

The absorption spectra show (Table 1, Figs. 1,2) that adding THF to acetone which is more polar brings about a remarkable bathochromic shift of the absortion band of the colored product and leads to the increase in its intensiveness. The value of the shift ($\Delta\lambda_{max}$) varies in accordance with the acetone content in the binary solvent. The value also depends on the nature of the σ-complex' cation. In the case of sodium cation it reaches 36 nm^2. Those regularities follow from the fact that there also exists the σ-complex in solutions alongside with the free ions of ion pairs the contributions of which grow if the medium polarity weakens. Consequently, transition from THF to acetone makes the ion-pair equilibrium (I) to undergo a shift from ion-pairs (II, III) to free ions (IV). In the case of the latter, the maximums have longer wave lengths and more intensive absorption.



I



where III - solvate-divided ion pairs
II - contact ion pairs

If THF contains about 60 vol. % of acetone, equilibrium (I) will almost fully be shifted towards free ions (IV); still higher acetone concentrations do not affect the spectra of the adduct.

Variations in the electron spectra of the σ-complex at adding macrocyclic ethers and salts to reaction solutions confirm the above statements. If dibenzo-18-crown-6-ether which destroys ion associates is conducted into the THF solution of complex (I), the bathochromic shift of the maximum and growth in the absorption intensiveness (Table 1) will follow.

On the other hand, if we add potassium perchlorate suppressing the dissociation of the complex at the expense of

Table 1

Spectral Characteristics of the Yancwski σ-Complex in THF-Acetone Mixture

	Para-meters*	THF % in acetone										
		100	90	80	70	60	50	40	30	20	10	0
$c_{comp.}$ $2.5\cdot10^{-4}$M	λ_1	353	353	354	355	356	357	357	358	358	358	358
	λ_2	553	554	556	558	561	567	572	572	572	572	572
	$\Delta\lambda_2$	0	1	3	5	8	14	19	19	19	19	19
	ε_1	8140	8560	8360	9520	9540	9880	10320	11080	10300	10360	-
	ε_2	15120	16200	16160	19480	20140	21240	22300	23248	22300	23020	21580
$c_{comp.}$ $2.5\cdot10^{-4}$M	λ_1	352	353	354	354	355	356	357	357	357	357	357
	λ_2	553	554	555	558	559	561	564	568	568	568	570
c_{KClO_4}	ε_1	8380	8400	8460	8360	9520	9860	9780	11380	10260	10480	9200
$2.5\cdot10^{-3}$M	ε_2	15600	15880	16380	16200	19580	20640	20900	24140	22060	22780	21460
$c_{comp.}$ $2.5\cdot10^{-4}$M	λ_1	348	349	349	349	349	350	351	356	354	354	355
	λ_2	534	541	541	544	546	549	552	554	555	558	560
c_{NaClO_4}	ε_1	7860	9260	8260	10540	10840	9540	9540	10820	9600	9320	9320
$2.5\cdot10^{-3}$M	ε_2	12700	13840	14380	16160	18200	18960	20200	22320	20320	19040	19500
$c_{comp.}$ $2.5\cdot10^{-4}$M	λ_1	353	355	356	357	358	358	358	358	358	-	-
	λ_2	555	559	563	568	569	569	569	569	569	-	-
$c_{crown\ ether}$	ε_1	8800	9380	9580	10240	10320	10540	10480	11240	11260	-	-
$4\cdot10^{-4}$M	ε_2	16840	18240	19140	22200	22360	23180	23180	23740	24260	-	-

* - values in nm, ε - l/mole·cm

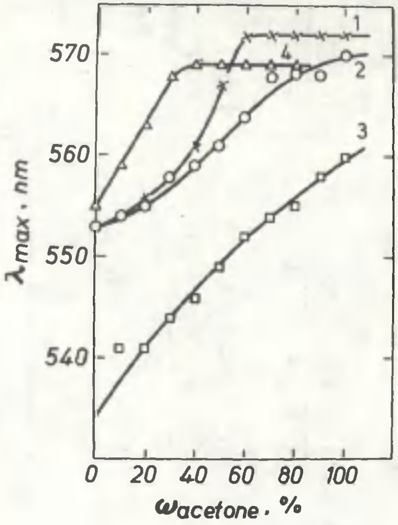


Fig. 1. Dependence of the location of long-wave length maximum of complex (1) on the content of the THF-acetone mixture ($c = 2.5 \cdot 10^{-4}$ M): 1 - original mixture; 2- solution of (I) + saturated solution of $KClO_4$; 3 - the same + $NaClO_4$; 4 - solution of (I) + saturated crown-ether solution.

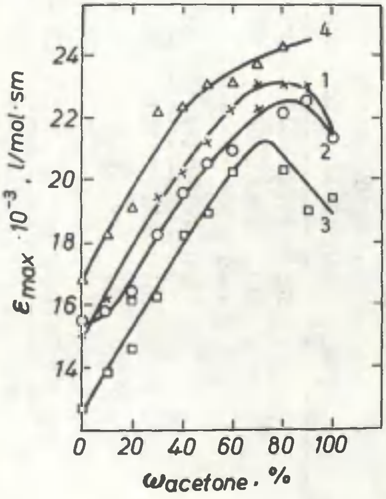


Fig. 2. Dependence of absorption intensity of complex (I) on the composition of THF-acetone mixture in long-wave length maximum ($c=2.5 \cdot 10^{-4}$M). For 1,2,3,4, see Fig. 1.

the total ion effect to acetone solution short-wave shifts of the absorption band will take place and the absorption intensity will weaken (Figs. 1,2). This tendency will be even more clearly expressed in case sodium perchlorate is used. We can explain it as follows. In the saturated $NaClO_4$ solution, the potassium cation of the σ-complex's ion pairs can be replaced by sodium ions which are smaller in their volumes and thus result in stabler ion pairs[8-12]. Introduction of THF into acetonic salt solutions and rising its concentration in mixed solvent leads to a further intensification of the ionic association of the complex, it is expressed by the hypochromic shift of the absorption maximum and by the decrease in its intensity (Figs. 1, 2; Table 1).

Previously[2] we have shown that in organic solvents, the dossociation constant of the σ-complex largely depends on the character of the alkaline metal cation. In acetone, its value is increasing as follows: $Na^+ < K^+ < Rb^+ < Cs^+$, while in THF, the components are in the opposite order. Consequently, in acetone containing $NaClO_4$, the absorption maximum of the σ-complex falls into the shorter wave-lengths' region than it has been observed at $KClO_4$ presence. A similar dependence of the λ_{max} of the σ-complex also holds for the solutions of those salts in THF. Yet, in the latter case, the adduct's dissociation level drops with the increase in the cation radius [2].

It is a well known fact[2] that as a result of a strong interaction between the solvent and the cation[13] the tetrahydrofurane solutions of σ-complexes contain both the contact and solvate-divided ion pairs. Adding alkaline metals to such solutions of perchlorates seems to result in the oversolvation of the cations participating in the formation of the solvate-divided ion pairs which lose their solvate shells, and finally bring about a concentration increase of the contact associates. In the saturated $NaClO_4$ solution sodium ions substitute for the potassium ions of the above particles and form stable ion pairs. Therefore, in tetrahydrofurane solution of $NaClO_4$ the absorption for the б-complex (I) takes place in the region of shorter wavelengths than that with $KClO_4$ participation.

The spectral analysis of the б-complex (I) gives evidence of certain differences in the ion association levels of aprotic solvents of different polarities. The ion-pair equilibrium state should essentially influence also the kinetics of the Yanowski б-complex's decomposition by proton-donor agents[14] in nonpolar media. In the binary THF-acetone system, the increase in acetone concentration really decelerates the reaction (Table 2). At the same time, the conductometric studies[2] have shown that adduct dissociation intensifies rather substantially. Thus, we can assume that the anions of the б-complex are less reactive than the corresponding ion pairs. It agrees with fact that in acetone, the rate of the complex decomposition does not depend on cation type. But in THF, the decomposition remarkably accelerates during transformation from sodium salt to rubidium salt[7].

Kinetic studies conducted in aprotic solvents at the presence of macrocyclic ethers and salts serve as additional evidence for the above statement. E.g., if we conduct crown ether into the б-complex (I) solution, thus destroying ion pairs, the studied process slows down both in the pure THF and its 50 % mixture with acetone (Table 2).

Acceleration of adduct decomposition in acetone and in its mixtures with 25 % THF in case of large enough amounts of salt additions (those of sodium and potassium perchlorates) is conditioned by the ion-pair equilibrium (I) shift towards ion pairs under the effect of a similar ion. Since in THF, complex (I) tends to exist mainly in the form of ion pairs, the deceleration of the process as a result of adding salt excess (Table 2) is connected with the increase in the ionic strength of the solvent. This reduces the activity of the components of the reaction.

The experimental data show that the ion pairs of types (II) and (III) have demonstrated better reactivities than free solvated ions (IV) during the decomposition of the Yanowski б-complexes of type (I). This at first sight abnor-

Table 2

Constants of Decomposition and Dissociation Rates of the Yanowski σ-complex in THF-Acetone Mixture

Cation	Addition	Constants	% of THF in acetone				
			100	75	50	25	0
K^+	-	$K_s \cdot 10^5, s^{-1}$	4.15	3.56	2.21	0.99	0.26
K^+	$KClO_4$	"	2.03	2.75	-	2.79	0.73
K^+	$NaClO_4$	"	2.72	-	3.03	2.01	-
K^+	crown-ether	"	1.77	-	1.39	-	-
Na^+	-	"	3.19	-	-	-	0.38
Rb^+	-	"	5.91	-	-	-	0.37
K^+	-	$K_d \cdot 10^4$, mole	2.65	-	3.68	12.6	28.5
K^+	-	α	0.32	-	0.45	0.66	0.77

mally sharp rise in the activity of the contact pairs of σ-complexes in their decomposition reactions springs from a partial cation compensation for the nitro group charge. It favors the attack of proton-donor agents on the reaction centers thus accelerating decomposition. The existence of a better reactivity of ion pairs in comparison with free ions was also established by Beletskaya et al.[15,16] for nucleophilic substitution of carboxylate salts of transition metals of VI, VII, VIII groups for fluorine atoms of perfluoroarene.

A more complicated ionic association effect on the σ-complex (I) decomposition kinetics appears if large quantities of salt are added to polar acetone-water (15 % vol. of water) system (Fig. 3). The effects found were caused by the sum of the effects of several factors. A growth in the ionic strength stabilizes the adduct at the beginning of the process. Continuing salt adding leads to a remarkable ion-pair shift (I) towards the more actively participating ion pairs. This acceleration overlaps the action of salt effect.

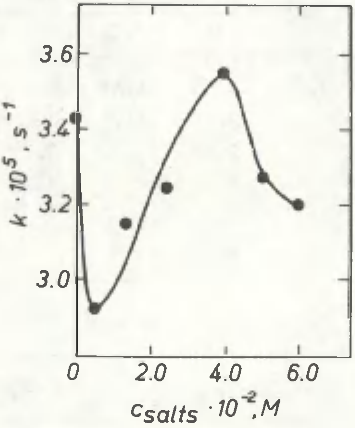


Fig. 3. Dependence of decomposition rate constant K_p of the σ-complex (I) in acetone-water mixture (15 vol. % of water) on concentration of salt added ($NaClO_4$).

After transforming the main body of the σ-complex (I) into ion pairs, at $NaClO_4$ concentration of 0.04 mole/l, the influence of the growth of the solvent strength again starts to dominate. The rate of decomposition is gradually reducing. The results of our studies show that in low-polarity media and in the polar systems, containing salts in high enough concentrations, the Yanowski σ-complex exists as the equilibrium mixture of free ions and various types of ion pairs. The ratio between the particles is determined by the nature and content of the solvent and it can significantly affect adduct's stability. In the reactions of σ-complex decomposition by polar-donor agents, ion pairs have appeared to be more active than free anions.

Experimental

The б-complex (I) was synthesized according to the methods described in[17]. Solvents were purified and dehydrated by using known methods[18,19]. Kinetic measurements were conducted in pseudomonomolecular conditions at large protonic component excess relative to the б-complex studied. Kinetic data were treated according to the first order equation

$$K = 2.303(\log D_1 - \log D_2).$$

The respective optical density changes in time were measured on a SF-14 spectrophotometer. Electronic spectra of the б-complex in mixed solvents were recorded on a spectrophotometer UV-VIS SPECORD M40.

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THE METHOD OF KINETIC CLEAVAGE IN NUCLEOPHILIC SUBSTITUTION REACTIONS

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Method for establishing rate constants of pure enantiomers based on kinetics of mixtures of nucleophile enantiomers and optically pure electrophilic reagent has been worked out. An equation showing the relationship between effective rate constant and total concentration of nucleophilic reagent and ratio of its enantiomers has been suggested.

Research into kinetic enantioselectivity as a parameter of non-bonding interactions in the diasteroisomeric transition state can only be successful after having accurately distinguished between the reagents. To solve this rather a complicated problem, we considered it reasonable to study the possibilities of kinetic enantioselectivity without previously separating the reaction components into pure enantiomers. The existing methods of kinetic cleavage (see[1], p. 44) enable us to find the correlation between the rate constants of pure enantiomers proceeding from the data on the optical yield of several transformation steps of non-symmetrical reactions. Yet, as the stereoselectivity and optical purity are not the same, those methods are not always suitable for determining the rate constants of pure enantiomers. The existing methods have shown good coincidence between the calculation and experimental results only in the case of single-route reactions. Nucleophilic substitution reactions are often hindered by catalytic flows and need therefore a more thorough approach.

The initial rate of asymmetrical nucleophilic substitution reactions with both bimolecular and termolecular processes can be expressed as follows:

$$\left(\frac{dx}{dt} \right)_o = k_2ab + k_3ab^2 \tag{1}$$

where $k_2(l \cdot mole^{-1} \cdot s^{-1})$ denote the bimolecular rate constant; $k_3(l^2 \cdot mole^{-2} \cdot s^{-1})$ - the rate constant of termolecular catalysis (the second amine-reagent molecule acts as the catalyst); a- the initial concentration of the optically pure chiralic electrophilic reagent; b - total initial concentration of the mixture of nucleophile enantiomers.

If we mark the concentrations of the S- and R-enantiomers with b^S and b^R, respectively, Eq. (2) expresses the initial rate of the reaction[*] discussed:

$$\left(\frac{dx}{dt}\right)_o = k_2^{SS}a^Sb^S + k_2^{SR}a^Sb^R + k_3^{SSS}a^Sb^Sb^S + k_3^{SSR}a^Sb^Sb^R + $$

$$+ k_3^{SRR}a^Sb^Rb^R + k_3^{SRS}a^Sb^Rb^S \tag{2}$$

The superscripts denote the configurations of the substrate, nucleophilic reagent, and nucleophilic catalyst, respectively.

The b^S and b^R values were found by means of polarimetry. Optical purity can be determined on the basis of polari-

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[*] The initial rate is chosen for the purposes of simplicity of expression. The only condition to be satisfied for studying kinetics is a<<b.

metric measurements, using Eq. (3):

$$\frac{[\alpha]}{[\alpha]_{max}} = \frac{b^S - b^R}{b^S + b^R} \qquad (3)$$

$[\alpha]$ and $[\alpha]_{max}$ denote the specific optical rotation of the mixture of enantiomers and of the pure enantiomer, respectively.

Relying on Eq.(3) and on the fact that $b = b^S + b^R$, we can show that the effective rate constant of the second order reactions is according to Eq. (2) in the case of each $[\alpha](k_{eff})$ value connected with the optical rotation of the mixture of the enantiomers, being expressed as follows:

$$k^{\alpha}_{eff} = \frac{k_2^{SS} + k_2^{SR}}{2} + \frac{k_2^{SS} - k_2^{SR}}{2[\alpha]_{max}} \cdot [\alpha] + \left[\frac{k_3^{SSS} + k_3^{SSR} + k_3^{SSR} + k_3^{SRS}}{4} - \right.$$

$$\left. - \frac{k_3^{SRR} - k_3^{SSS}}{2[\alpha]_{max}} \cdot [\alpha] + \frac{k_3^{SSS} - k_3^{SSR} + k_3^{SRR} - k_3^{SRS}}{4[\alpha]^2_{max}} \cdot [\alpha]^2 \right] b \qquad (4)$$

If the $[\alpha]_{max}$ is known, we can use Eq. (4) for calculating the k_2 and k_3 values for the reactions of pure nucleophile enantiomers, without resorting to the total cleavage of the mixture.

The kinetics of reactions of various mixtures of I-phenylethylamine enantiomers with 4-nitrophenyl ester of N-carbobenzoxy-S-phenylalanine (S-Z-Fal-ONP) in dioxan at 25° C was studied to prove the validity of Eq. (4). We have previously studied[4] the reactions of pure enantiomers of that amine with the above substrate under the same conditions. Their kinetic regularities also correspond to Eq.(1) (see also[4]). The table gives the values of $[\alpha]$, k_2 and k_3 for several enantiomeric mixtures of the amine, calculated from the set of k_{eff} for each mixture of enantiomers.

It follows from Eq. (4) that the rate constant of the bimolecular process (k_2) should have a linear relationship with the values of specific rotation of the mixture $[\alpha]$. But the rate constant of the termolecular process (k_3) must have a corresponding parabolic relationship. Equation (5) presents the above relationship for the studied bimolecular reactions. The experimental data of the present work only are used.

$$k_2 = (4.98 \pm 0.01)\cdot 10^{-3} - (1.91 \pm 0.02)\cdot 10^{-2}\cdot[\alpha] \qquad (5)$$

$$s = 3.73\cdot 10^{-4};\ r = 0.998;\ N = 5.$$

In Eq. (5), the second term equals the second term of Eq. (4). Using the experimentally found k_2^{SS} and k_2^{SR} values, we calculated the specific rotation for a pure S-enantiomer of the amine ($[\alpha]_D^{25} = -40.6^o$). According to ref.[5] $[\alpha]_D^{20} = -41.0^o$ (without solvent). A satisfactory coincidence of those values confirms linear dependence between the k_2 and specific rotation $[\alpha]$ values.

Table

Values of $k_2\cdot 10^3(l\cdot mole^{-1}\cdot s^{-1})$ and $k_3\cdot 10^3(l^2\cdot mole^{-2}\cdot s^{-1})$ for S·Z-Fal-ONP Reactions with 1-Phenylethylamine at Various Specific Rotations in Dioxan at 25° C

$[\alpha]_D^{25}$	k_2	k_3	$s\cdot 10^5$	r
-41.0*	5.77*±0.06	6.33*±0.81	4.06	0.995
-35.4	5.66 ±0.05	6.74 ±0.43	3.08	0.994
-30.8	5.55 ±0.06	6.48 ±0.96	6.81	0.979
-21.7	5.39 ±0.02	5.84 ±0.26	2.01	0.997
0*	4.99*±0.03	6.36*±0.21	3.21	0.996
+18.0	4.60 ±0.06	6.80 ±0.19	6.69	0.993
+31.9	4.37 ±0.04	6.08 ±0.63	4.59	0.992
+40.5*	4.22*±0.06	6.29*±0.83	3.18	0.994

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* values from ref.[4]

The analysis of the Table shows that the k_3 do not depend on $[\alpha]$. The reaction in dioxan depends very slightly on the nucleophilic catalyst's nature[4], which ensures the stability of the constants of the enantiomeric catalysis.

Eq. (4) can be modified, making it simpler. If the ratio of enantiomers in mixture $b^S/b^R = \beta$, then, applying value $b^S = \beta b/1+\beta$ and $b^R = b/1+\beta$, since $b = b^S + b^R$, we will get Eq.(6), relating the k^{α}_{eff} and β values.

$$k^{\alpha}_{eff} = \frac{1}{1+\beta}(k_2^{SR} + \beta k_2^{SS}) + \frac{1}{(1+\beta)^2}\left[k_3^{SRR} + \beta(k_3^{SSR} + k_3^{SRS}) + \right.$$
$$\left. + \beta^2 k_3^{SSS}\right]\cdot b \qquad (6)$$

Formulae (7) and (8), derived from (6) are more suitable for calculation of the k_2 and k_3.

$$k_2(1+\beta) = k_2^{SR} + k_2^{SS}\beta \qquad (7)$$

$$k_3(1+\beta)^2 = k_3^{SRR} + (k_3^{SSR} + k_3^{SRS})\beta + R_3^{SSS}\cdot\beta^2 \qquad (8)$$

Those values are equal for the reaction studied:

$$k_2(1+\beta) = (4.16 \pm 0.06)\cdot 10^{-3} + (5.77 \pm 0.01)\cdot 10^{-3}\cdot\beta \qquad (9)$$
$$s = 1.08\cdot 10^{-4};\quad r = 0.998;$$

$$k_3(1+\beta)^2 = (8.14 \pm 1.78)\cdot 10^{-3} + (7.67 \pm 0.88)\cdot 10^{-3}\cdot\beta +$$
$$+ (7.16 \pm 0.06)\cdot 10^{-3}\cdot\beta^2;$$
$$s = 2.72\cdot 10^{-3};\quad r = 0.999 \qquad (10)$$

The β values were calculated from the polymetrization data using the modified expression (11) of Eq. (3). This procedure enables us to remarkably reduce the errors of polarymetric measurements.

$$\beta = \frac{-[\alpha]_{max} - [\alpha]}{[\alpha] - [\alpha]_{max}} \qquad (11)$$

In a general case, β can be determined by means of any known methods[1].

Comparison of the coefficients of Eqs. (9) and (10) with the data of the Table demonstrates that the k_2 values of the previously studied pure enantiomers[4] agree with those obtained when using Eq. (7). As for termolecular process, the R values calculated according to Eq. (7) appeared to be a bit smaller than those found from the kinetic values of pure enantiomer reactions[4]. The coefficients of Eq. (10) are almost equal, which gives us evidence of the nonsensitivity of the catalytic flow towards the enantioselective effects in dioxan.

Thus, Eqs. (7) and (8) can be used for finding the enantioselectivity kinetics for the bi- and termolecular - processes. The calculations were based on the research into the kinetics of the reactions of partially separated enantiomeric mixtures of any of the reagents with a chiralic partner and on the correlation of enantiomers' concentrations. This method can be successfully used for studying the kinetic enantioselectivity of those chiralic compounds which have not been described in literature.

Experimental

4-Nitrophenyl ether of N-carbobenzoxy-S-phenylalanine[6] and 1-phenylethylamine[7] were obtained and identified according to the methods given in literature.

Samples of 1-phenylethylamine of different optical purity were prepared by means of separation of the racemic amine of the D-tartaric acid according to methods[8]. The optical rotations of those samples were recorded without a solvent on a circular SP-3 polarimeter.

The purification of dioxan proceeded in accordance with ref.[9].

Reaction rate was determined spectrophotometrically according to accumulation of 4-nitrophenol at 310 nm.

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ENE ADDUCTS OF N-SUBSTITUTED TRIAZOLINEDIONS

V. KINETICS OF REACTIONS OF N-ARYLIMIDES OF CIS-4-CYCLOHEXANE-1,2-DICARBOXYLIC ACID WITH 4-BENZYL-1,2,4-TRIAZOLINE-3,5-DION

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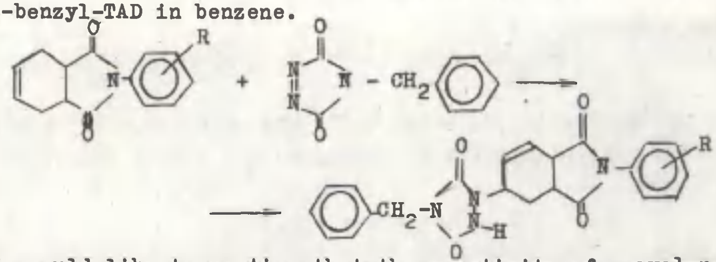
The present paper is aimed at studying the kinetics and determining the constants of ene reactions of N-arylimides of cis-4-cyclohexane-1,2-dicarboxylic acid with 4-benzyl-1,2,4-triazoline-3,5-dion in benzene at 10°, 20°, 30°, and 40° C. Applicability of the Arrhenius equation is demonstrated; activation parameters for the reactions are found. Quantitative regularities of substituent effects on reaction rate in substrate are established.

We have already worked out methods for synthesizing[1] and studied the stereochemistry of formation[2] of the ene-adducts of 4-benzyl-1,2,4-triazine-3,5-dion (4-benzyl-TAD) with N-substituted cis-4-cyclohexane-1,2-dicarbonylic acid (cis-4-CHDC) imides. Realization of the semichair conformation of cyclohexene ring which has pseudo-equatorially oriented urazolic groups in adduct is connected with the planar symmetry of the ene-component. To expand our research into the interaction between the structure and reactivity of cis-4-CHDC in the reactions of electrophilic addition[3-6], we studied the kinetics of ene reactions of those substrates with 4-benzyl-TAD in benzene.



We would like to mention that the reactivity of cycleneic compounds in enonic reactions with triazolinedions had not been studied before. With the exception of ref.[7] which presents the rate constants of cyclohexene and methylcyclohexene reactions with N-substituted triazolinedions.

Reaction rate constants were calculated according to the variation of the absorption of the 4-benzyl-TAD in time in the visible range of the spectrum found spectrophotometrically.

The reaction is first order concerning the substrate and reagent, and second order in its sum total. The stability of reaction rate constant values, calculated by means of [7] confirms the above statement:

$$k_2 = \frac{2\cdot 3}{(b-a)} \log \frac{1+\frac{K}{A}}{b/a} \quad , \qquad (1)$$

where k_2 - bimolecular rate constant, $l\cdot mol^{-1}\cdot s^{-1}$; a,b - initial concentrations of 4-benzyl-TAD and imide, respectively, $mol\cdot l^{-1}$; A - 4-benzyl-TAD in time τ; τ - time interval, s;

$K = \frac{A_o(b-a)}{a}$, where A_o = initial 4-benzyl-TAD concentration.

Table 1 contains the bimolecular rate constants of ene reactions of cis-4-CHDC N-arylimides with 4-benzyl-TAD in benzene at temperatures 10^o-40^oC. These data show that the reaction rate tends to depend rather definitely on the electronic properties of the substituent.

The values of log k obey the Arrhenius equation

$$\log k = \log A + E_a/RT \qquad (2)$$

which enabled us to calculate the activation energy (B_a) as well as the pre-exponential factor (log A) using this equation.

The activation enthalpy ($\Delta H^{\neq}$) and entropy ($\Delta S^{\neq}$) of the reaction were calculated according to the Eyring equation:

$$R \ln k/T = a \cdot \frac{1}{T} + b, \qquad (3)$$

where $a = \Delta H^{\neq}$; $b = R \ln K/h + \Delta S^{\neq}$, K - the Boltzmann constant; h = the Planck constant.

The free activation energy ($\Delta G^{\neq}$) was found according to the second Law of thermodynamics:

$$\Delta G^{\neq} = \Delta H^{\neq} - T \cdot \Delta S^{\neq} \qquad (4)$$

Table 2 presents the values of thermodynamic activation parameters.

As Tables 1 and 2 demonstrate, the rate constants and activation parameters of the studied reaction depends on substituents' properties and location in the aromatic nuclei of imides.

It follows from Table 1 that the introduction of electron-donor substituents ($-OCH_3$, $p-CH_3$) leads to the increase in the reaction rate constant value, but electron-acceptor substituents ($-Cl$, $-Br$, $-NO_2$) yield the opposite effect.

The E_a and log A values (Table 2) indicate that the introduction of electron-donor substituents into the imide molecule results in an activation energy decrease. The electron-acceptor substituents demonstrate the opposite effect. The log A values change similarly.

The effect of substituents' electronic nature on the $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values in the imide molecule is similar with their influence onto E_a and log A.

The free activation energy ($\Delta G^{\neq}$) will grow if the imides of electron acceptor substituents are conducted into

Table 1

Rate Constant Values of Ene Reactions of cis-4-CHDC N-arylimides with 4-benzyl-TAD in Benzene at Different Temperatures

R	$k_2 \cdot 10^4$, $l \cdot mole^{-1} \cdot s^{-1}$			
	283 K	293 K	303 K	313 K
4-OCH_3	7.28	13.30	26.51	51.77
2-OCH_3	7.07	13.73	26.13	51.47
4-CH_3	5.28	10.93	22.79	48.35
3-CH_3	5.00	10.45	21.74	46.28
2-CH_3	3.78	7.75	16.80	35.85
H	4.89	10.32	20.98	45.82
4-Cl	4.51	9.57	19.72	42.99
4-Br	4.33	9.23	18.90	41.57
3-Cl	3.92	8.51	18.43	40.31
3-NO_2	2.63	6.31	15.55	37.00

Note: The error of k_2 calculation does not exceed 3 %.

Table 2

Activation Parameter Values of Ene Reactions of cis-4-CHDC N-arylimides with 4-benzyl-TAD in Benzene

R	E_a, $kJ \cdot mole^{-1}$	log A	$\Delta H^{\neq}$ $kJ \cdot mole^{-1}$	$-\Delta S^{\neq}$ $J \cdot mole^{-1} \cdot K^{-1}$	$\Delta G^{\neq}$(298K) $kJ \cdot mole^{-1}$
4-OCH_3	48.00	5.71	45.52	143.90	85.39
2-OCH	48.50	5.79	46.03	142.33	88.44
4-CH_3	54.23	6.72	51.73	124.66	88.88
3-CH_3	54.46	6.74	51.98	124.23	89.00
2-CH_3	55.28	6.76	52.81	123.71	89.66
H	54.55	6.75	52.07	124.09	89.05
4-Cl	55.03	6.79	52.55	123.04	89.22
4-Br	55.13	6.80	52.66	123.01	89.32
3-Cl	57.07	7.12	54.55	116.98	89.45
3-NO_2	64.95	8.39	62.47	92.52	90.04

Note: Errors of calculating 1.2-1.6 $kJ \cdot mole^{-1}$, $\Delta S^{\neq}$ 4.5-6 $J \cdot mole^{-1} \cdot K^{-1}$

the aromatic nuclei of imides. Yet, the changes are small (85÷90 kJ/mol).

The substituent effect on the reactivity of N-arylimides of cis-4-CHDC was estimated according to the Hammett equation

$$\log k = \log k_o + \rho\sigma \,, \tag{5}$$

$$\log k = \log k_o + \rho_o\sigma^o , \tag{6}$$

where ρ, σ^o - sensitivity of the reaction series to the effect of R substituents, characterized by constants σ and σ^o for para- and meta-substituents, respectively.

The values of correlation parameters of Eqs. (5) and (6) are in Table 3.

Table 3

Correlation Parameters of the Hammett Equation for Ene Reactions of cis-4-CHDC N-arylimides with 4-benzyl-TAD in Benzene

T° K	Dependence type	$-\rho$	$-\log k_o$	r	S	n
283	σ	$0.37 \pm 4.6 \cdot 10^{-2}$	$3.29 \pm 1.5 \cdot 10^{-2}$	0.957	0.039	8[a]
	σ^o	$0.35 \pm 4.8 \cdot 10^{-2}$	$3.31 \pm 1.9 \cdot 10^{-2}$	0.982	0.029	4[b]
293	σ	$0.29 \pm 3.3 \cdot 10^{-2}$	$2.98 \pm 1.08 \cdot 10^{-2}$	0.964	0.028	8[a]
	σ^o	$0.28 \pm 3.2 \cdot 10^{-2}$	$2.99 \pm 1.3 \cdot 10^{-2}$	0.987	0.020	4[b]
303	σ	$0.21 \pm 2.03 \cdot 10^{-2}$	$2.66 \pm 6.3 \cdot 10^{-3}$	0.965	0.017	8[a]
	σ^o	$0.20 \pm 3.7 \cdot 10^{-2}$	$2.68 \pm 1.5 \cdot 10^{-2}$	0.973	0.023	4[b]
313	σ	$0.14 \pm 9.8 \cdot 10^{-3}$	$2.34 \pm 3.2 \cdot 10^{-3}$	0.986	0.008	8[a]
	σ^o	$0.13 \pm 6.9 \cdot 10^{-3}$	$2.34 \pm 2.8 \cdot 10^{-3}$	0.997	0.004	4[b]

[a] - X = 4-OCH_3, 4-CH_3, 3-CH_3, H, 4-Cl, 4-Br, 3-Cl, 3-NO_2.

[b] - X = 3-CH_3, H, 3-Cl, 3-NO_2.

The data of Table 3 give evidence of the applicability of the Hammett equation for the reaction series studied. Negative $\rho(\rho^o)$ value also serves to prove the validity of the electrophilic mechanism of the ene reactions of cis-4-CHDC N-arylimides with 4-benzyl-TAD. The small absolute value of $\rho(\rho^{o})$ refers to the relative nonsensitivity of the reaction center to structural changes, which seems to spring from strong electron-acceptor properties of the imide group. This is well illustrated by the comparison of the rate constant values of cis-4-CHDC N-phenylamide ($15.47 \cdot 10^{-4}$ l/mol·s) and cyclohexane ($112 \cdot 10^{-4}$ l/mol·s)[7] with 4-benzyl-TAD at 25°C (the former is approximately seven times smaller than the latter one). This is a result of the decrease in the electron density of the reaction center owing to the transfer of the electron-acceptor effect of the imide fragment through the molecular framework and through the space in the syn-boat conformation of cis-4-CHDC N-phenylimide[8,9].

If the temperature rises, the $\rho(\rho^{o})$ values will decrease. This agrees with the assumption that the sensitivity of the reaction center to the electron nature of substituents worsens in case of a temporary rise.

According to Table 3, the best correlation for ene reactions is observed with the σ^{o} substituent constants and it shows that the substituents' induction effect makes a substantial contribution into the stabilization of transition states of those reactions.

Experimental

The synthesis and properties of ene-adducts of cis-4-CHDC N-arylimides with 4-benzyl-TAD are described in[1].

We used well-known methods[10] for obtaining 4-benzyl-TAD and method[4] for getting the corresponding 4-benzyl-1,2,4-triazodine-3,5-dion. The inital N-arylimides of cis-4-CHDC were synthesized by condensating anilines with cis-4-CHDC anhydrides at temperatures 140°-150° C in dimethylformamide in accordance with methods[12].

Prior to kinetic experiments, N-arylimides of cis-4-CHDC were recrystallized from a suitable solvent; 4-benzyl-TAD was sublimed under reduced pressure. We used dehydrated benzene in kinetic experiments. The experiments were repeated three times, 6-7 measurements each. The accuracy of the obtained parameters was estimated by using the small sample statistics (confidence probability 0.95). The results were processed on a computer "Elektronika B3-34". We used standard programs[13].

Kinetic measurements were conducted as follows: we mixed standard solutions of imide and 4-benzyl-TAD in benzene (1.5 ml of each) and placed the mixture into the thermostated shells of a "Specord M-40" spectrometer. The changes in the 4-benzyl-TAD absorption (λ_{max} = 539) in the visible field were registered depending on time. The initial concentration of 4-benzyl-TAD was 10^{-2} mol/l. Kinetic experiments were conducted at 4-benzyl-TAD and cis-4-CHDC N-arylimides' 1:5 ratio.

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NUCLEOPHILIC SUBSTITUTION MECHANISM IN SERIES OF 1,3,5-TRIAZINE DERIVATIVES

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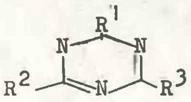
The review deals with the analysis of data on kinetics and reactivity of cyanuric halides and their mono- and disubstituted derivatives. Mechanisms of nucleophilic substitution reactions in 1,3,5-triazine cycle are alo discussed.

Researchers have become more and more interested in the practical application of the derivatives of 1,3,5-triazine[*] that have the general formula I:



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[*] As in the present paper we are concerned with the derivatives of unsymmetrical triazine, we will use the term triazine instead of 1,3,5-triazine.

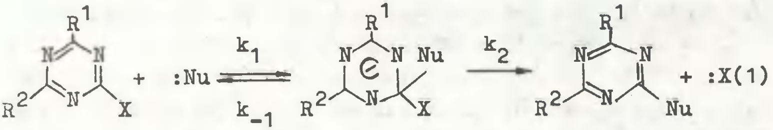
Those compounds are of special significance in the chemistry of high-molecular compounds where they are used as the initial monomers for obtaining polymers or as supplementary modifying additives for polymeric materials[1]. There are also several other fields of application (see[1], pp. 10-11,[2,3]) of triazine derivatives: agriculture (herbicides), rubber industry (antioxidants, stabilizers, vulcanizers), textile industry (dyes and bleaches), medicine (medicinal preparations), etc.

Usually, the derivatives of triazine I are obtained via a nucleophilic substitution reaction in 2,4,6-trichlorotriazine (cynuric chloride), which is one of the industrially most acceptable halogenated triazines.

The first attempts at generalizing the data on the reactivity of triazine derivatives in the nucleophilic substitution reactions were made in 1964-1965[3-5]. Those studies concentrated on the essential difference of the rate of a successive substitution of chlorine and cyanuric chloride atoms relying on the data about the properties of the forming products. The latter depend on such process conditions as time and temperature. The analysis of a limited number of kinetic data is rather superficial[3,4]. In 1971, R. Bakaloglu[6] made a more detailed survey of the research into the kinetics and reactivity of cyanuric chloride and its mono- and disubstituted derivatives. Nevertheless, owing to a very limited amount of experimental data, it was not possible to reach any general conclusion yet. Later on V.P. Mamaev et al[7-9] touched upon the problems of the reactivity of substituted triazine halides, being mainly interested in the electronic conductivity in azine systems. A recently published review[10] dealing with the problems of the regional selectivity of substitution in 6-member nitrogen heterocycles also contains a brief discussion of substitution in triazine systems.

Thus, we have been lacking a substantial analysis of the mechanism of nucleophilic substitution in the triazine cycle. This analysis would also be of essential importance in developing the theory of nucleophilic aromatic substitution mechanisms, which was basically created on the example of the reactions of benzene derivatives' series. Therefore, in the present paper we concentrate on the analysis of the existing quantitative data of the kinetics and reactivity of type I derivatives. Our aim is to give a complete explanation of the mechanisms of nucleophilic substitution in the vicinity of the carbon atom of the triazine ring.

The mechanisms of nucleophilic substitution in azine series have usually been interpreted quite the same way as those of aromatic nucleophilic substitution in benzene systems[7,11]. However, in azine systems, we can also come across such mechanisms (e.g., the ANRORC-mechanism) that cannot function in the case of arene derivatives. On the other hand, the recently discovered $S_{RN}1$-mechanism of substitution in benzene derivatives[12] does not have a similar counterpart in the series of azines yet. The two-stage S_N2Ar mechanism is most widely used now. When applied to the compounds of type I (R^3 - leaving group X), the mechanism's general scheme looks as follows:



I   II

The functioning of this mechanism can be proved by the existence of tetrahedral intermediates II, character of kinetic regularities, the effects of structure, medium, etc. Still, we cannot entirely exclude the possiblity of a single step reaction mechanism. Thus, the present report is first of all aimed at analyzing the kinetics and reactivities of triazine derivatives I in the framework of the mechanisms functioning in benzene series. We will also discuss how certain factors, including homogeneous catalysis, influence the steps of the process and changes in the rate determining step.

Kinetic Regularities

As a rule, in triazine derivatives the halide substitution (or the substitution of some other active groups) goes quantitatively and without any side processes[1-3]. If the entering nucleophile does not contain any mobile hydrogen electron, the products will take the form of I. In the opposite case (e.g., for substituents in I: OH, SH, NHR, CHR_2), the products can turn into their more stable tautomers as a result of proton transfer onto the nitrogen atom of the triazine ring. The hydrolysis of cyanuric chloride yields cyanuric acid as a keto-form[1] nonsoluble in water.

Up to now, kinetic experiments of various extent and quality have been conducted for reactions of neutral[13-16], acidic[14, 17-19], and alkaline hydrolysis[14,18,20-27] and alcoholysis[25-31] of mono-, di- and trichloroderivatives of triazine I both in aqueous and in aqueous-organic media. The experiments have also embraced hydrolysis and alcoholysis catalyzed by tertiary amines[32,33]. As for the formal kinetics, the aminolysis processes of the mentioned derivatives[34-54] have been studied quite thoroughly. Unfortunately there are almost no data available about the interaction of other nucleophiles[49,55]. The rates of the reactions, notwithstanding the nucleophile nature, substrate structure, solvent type and temperature level are described by kinetic equations, in which the concentration of each reagent is given in the first power. In the majority of cases, the reactions follow the second order. Thus, the above regularity controls alkaline hydrolysis[14,20,21,23-25,28], reactions with anionic nucleophiles[49,55], aminolysis processes in polar (methanol, acetonitrile, acetone, aqueous dioxan[44,46, 49,51-54]) or low-polarity, but specially solvating solvents (e.g., tetrahydrofuran)[36-38,45].

However, if either the system's reactivity (owing to a drop in amine basicity[38,39]) or the dissolving properties of the medium (benzene[41]) worsen, there will appear a termolecular pathway in the reaction equation which is connected with the autocatalysis of the reaction product, i.e., substituted arylaminotriazine. When studying the kinetics of the reactions of primary aliphatic amines with substituted chlorotriazines, Ostrogovich et al.[47] observed the autocatalysis of the primary amine with hydrochloride in 80 % aqueous acetone. It is interesting to mention that in the case of secondary amines, having approximately similar reactivities, there is no autocatalysis by amine hydrochloride[47]. The autocatalysis with the yield of hydrogen chloride takes also place during neutral hydrolysis of cyanuric chloride in water-acetone mixture[15].

The bimolecular rate law holds in the case of substitution in the series of fluorine derivatives of triazine: the aminolysis I ($R^1=R^2=R^3=F$; $R^1=R^2=F$; $R^3=NHAr$) in methanol[46,48], interaction of anions of transition metals of groups VI-VIII with I ($R^1=R^2=F$; $R^3=Mn(CO)_5$) in electron-donor media[56,57], and the alkaline hydrolysis of melamine ($R^1=R^2=R^3=NH_2$)[58,59]. There is only one example of the third kinetic order in literature[60] (the first order of the substrate and the second order of the amine) appearing during substitution in triazine cycle. It was the reaction of piperidine with 2-phenoxytriazine (I, $R^1=OPh$, $R^2=R^3=H$) in isooctane, where the phenolate anion was functioning as a leaving group.

The alcoholysis of cyanuric chloride and dichloroderivatives of I ($R^1=R^2=Cl$; $R^3=OCH_2H_5$, OC_2H_4Cl) at the presence of alkali in aqueous-organic media (see ref. [26,28]) obeys a kinetic equation where the concentrations of the substrate, alcohol and alkali are introduced in its first step. In fact, it corresponds to the bimolecular interaction of chlorine derivative and alcoholate anion. The latter is generated according to the acid-base equilibrium established between alcohol and alkali, while the equilibrium is strongly shifted towards non-ionized alcohol.

Another fact to be mentioned in connection with the analysis of kinetic regularities is that the aminolysis of halogen derivatives of triazine proceeded without the catalysis of the second amine molecule. At the same time, in in the case of nucleophilic aromatic substitution in activated chloro- and fluorobenzenes the second order of amine is quite common (see, e.g.[61-63]). In keeping with[63] the second amine molecule normally acts as a general-base catalyst in tetrahedral intermediates' decomposition. Therefore, in nonpolar media, the aminolysis of activated halobenzenes is efficiently catalyzed by organic compounds of different nature[61,63]. Consequently, the absence of the catalysis of the second molecule of amine at substitution in halogen derivatives I has two **explanations**: either it is the first step in Scheme (1) which determines the rate, or the structural peculiarities of the tertiary intermediate II are expressed so that its decomposition in the rate limiting step can proceed without a base-catalyst.

The authors of[60] connect the involvement of the catalysis of the second molecule of piperidine in its reaction with 2-phenoxytriazine in iso-octane with amine participation in the rate determining step of the intermediate II decomposition. Though, for this case, not the general base but the bifunctional catalysis mechanism is suggested. Hence, the other conditions being equal, the change in the rate determining step at substitution in I takes place within the groups which do not split off very easily, rather than during substitution in arene systems.

Effect of Leaving Group

The effect of leaving group's nature in a substrate ("element effect") is one of the main criteria in finding the rate determining state of the S_N2Ar substitution mechanism in the series of arenes and azines[7,57,64]. More often, the reactivities of various halogen derivatives have been compared (the relationship k_F/k_{Cl} being an especially conspicuous one). It has been established[7,64] that, depending on the substituent nature in the substrate, on the strength of the attacking nucleophile as well as on the medium properties, there are different reactivity series there. In a group of series, fluorine derivatives have better reactivities, in some other cases the reactivities are worse. The standard order of mobility of halides in protonic media and for strong nucleophiles $F \gg Br > Cl > I$ (sometimes $F \gg Cl = Br > I$) refers to the rate limiting nucleophilic attack upon the substrate (k_1 in Scheme (1)). Yet, the ratio k_F/k_{Cl} decreases and it can even become smaller than unity during transfer either to aprotic or low-polarity media. The above decrease is also observed when the attacking nucleophile's basicity becomes weaker or in case substituents are taken into a substrate with the lowest accelerating effect. That can be considered as a fact supporting the view that the intermediate decomposition (k_2 in Scheme (1)) functions as the rate limiting step.

Unfortunately, the data on the effect of the leaving group nature are too scarce, as concerns the nucleophilic substitution in triazine derivatives I. In[42] the kinetics of arylamines ($RC_6H_4NH_2$) substitution for a halide atom in cyanuric chloride and for cyanuric fluoride in diethyl ether (at -20°-0° C) have been studied. In the case of all amines used, the fluorine containing substrate demonstrated a considerably poorer reactivity, if compared with that of the chlorine derivative. Thus, owing to that and also because of the fact that in the former case the sensitivity to the structural effect of amine in the first case is higher ($\rho = -3.8$) than in the latter case ($\rho = -2.5$), the authors confirm the variation of the rate limiting step. In cyanuric fluoride reaction, it is the intermediate's decomposition that acts as a decelerator, while in cyanuric chloride reaction it is its formation.

Still, in our opinion, the "element effect" as a criterion of the rate limiting step is not quite correctly used in the present case, as far as the substrates compared differ both in their leaving group properties and in those of the two substituents which do not split off during aminolysis. According to[54], the Hammett ρ-value that characterizes the sensitivity of the substitution of amine for a chlorine atom ($R^3 = Cl$) to the effects of another two substituents R^1 and R^2 is extremely high in I (10.5). A rather close ρ value

(9.6) was obtained for the alkaline hydrolysis of the disubstituted triazine-4-N,N-dimethylaminopyridine salts (I. R^1 and R^2 denote variable substituents, $R^3 = \overset{+}{N}C_5H_4N(CH_3)_2$ is the leaving group) in water-dioxan mixture (1:1)[65]. The same concerns correlation in regard to heat effects of the reactions of monochlorine substituents of I with aniline in benzene ($\rho = 10.5$)[66]. Thus, substitution of two fluorine atoms ($\sum\sigma = 0.62$) for two benzene atoms ($\sum\sigma = 0.70$) favors a decrease in the reactivity. The latter may drop almost by an order. Therefore, ratio k_F/k_{Cl} calculated on the basis of[42], equalling 0.014÷0.03 (at different temperatures) is not too drastic, considering the "element effect". In the aminolysis of difluorine and dichlorine derivatives of I in methanol and acetone (Table 1) the former compound reacts faster than the latter one. In acetonitrile, the reactivity is three times poorer, which might result from a difference between the electronic effects of fluorine and chlorine as substituents but not as leaving groups.

Recently[67], a more correct comparison of the reactivities of halides in substrate I ($R^1 = R^2 = N(C_2H_5)_2$; R^2 = F, Cl, Br) reactions with 4-N,N-dimethylaminopyridine in acetonitrile has been carried out. The reaction rate variation depending on the leaving halide nature, is as follows: F > >Br>Cl. It agrees with the rate determining tertiary amine attack on the substrate.

Table 1

Rate Constants k of Reactions of Chlorine and Fluorine Derivatives I with Aniline in Different Solvents at 20° C[46]

R in I	k, $l \cdot mol^{-1} \cdot min^{-1}$		
	Methanol	Acetone	Acetonitrile
$R^1 = NH_6H_5$; $R^2=R^3=Cl$	2.0±0.2	0.08±0.01	0.086±0.01
$R^1 = NHC_6H_5$; $R^2=R^3=F$	6.5±0.5	1.05±0.2	0.031±0.005

Those, though rather limited data, permit us to presume that the regularities governing the leaving-group dependent variation in the rate determining step in case substitution has been carried out among the derivatives of I, are in general similar with the results for arene[64] and for other azine systems[7].

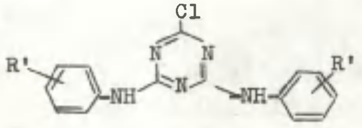
Effect of Substrate's Structure

Vast experimental material has been gathered about the effect of substrate's structure onto the rate of substitution in chlorotriazines. The influence of leaving group's nature has not been so thoroughly studied yet. Nevertheless, the former effect type can be further analyzed within the "ρ-σ" relationship in the common scale σ. Therefore we subjected all existing data to the correlation analysis. Those reaction series which had already been analyzed[20,32,35,36,38] were included as well.

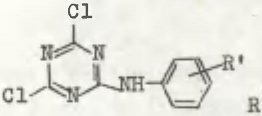
Table 2 contains the results of the treatment of the reaction rate constants of substrates 1a and 1b by the Hammett equation:

$$\log k = \log k_o + \rho(R')\sigma(R'), \qquad (2)$$

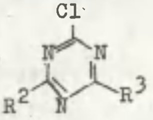
where $\sigma(R')$ - the Hammett constants σ for substituent R'



Ia



1b



Ic

Similar $\rho(R')$ values for reaction series of aminolysis of substrates 1,3,5 (25° C) or 2,4,6 (40° C) evidence the absence of the reciprocal influence of the R' substituents in the phenyl rings of two N-arylamino groups. Thus, a joint treatment of the data for series 1,3,5 (or 2,4,6) using a common correlation equation, yields us the average values

Table 2

Treatment of Data on Rate of Nucleophilic Substitution Reaction in Chlorotriazines Ia (R^1=Cl; R^2=R^3=$R'C_6H_4NH$) and Ib (R^1=R^2=Cl; R^3=$R'C_6H_4NH$) According to the Hammett Equation (2)

	R^2, R^3	Nucleophile	Reaction conditions	log k_o	$\rho_{R'}$	s	r	n	Ref.
1	2	3	4	5	6	7	8	9	10
1	R^2=R^3=$R'C_6H_4NH$ (R'=4-OCH_3, 4-CH_3, 3-CH_3, H, 4-Cl, 3-NO_2)	Benzylamine	Tetrahydrofurane 25° C	-3.89±0.03	0.93±0.04	0.070	0.995	6	36
2	"	"	" 40°C	-3.47±0.02	0.89±0.03	0.056	0.997	6	36
3	R^2=C_6H_5NH; R^3=$R'C_6H_4NH$ (R'=4-OCH_3, 4-CH_3, 3-CH_3, 4-Cl, 3-NO_2)	"	" 25°C	-3.87±0.01	0.93±0.02	0.018	0.999	5	36
4	"	"	" 40°C	-3.46±0.01	0.87±0.03	0.024	0.998	5	36
5	R^2=4-ClC_6H_4NH; R^3=$R'C_6H_4NH$ (R=4-CH_3, 3-NO_2)	"	" 25°C		0.91			2	36
6	"	"	" 40°C		0.90			2	36
7	Series 1,3,5	"	" 25°C	-3.88±0.01	0.93±0.02	0.047	0.996	13	36
8	Series 2,4,6	"	" 40°C	-3.46±0.01	0.89±0.02	0.040	0.997	13	36

Table 2 continued

1	2	3	4	5	6	7	8	9	10
9	R^2=Cl; R^3=R'C_6H_4NH (R'= =4-CH_3,3-CH_3,H)	4-toluidine	Tetrahydrofurane, 25°C	-1.90±0.01	0.89±0.06	0.010	0.997	3	38
10	R^2=Cl; R^3=R'C_6H_4NH (R'=4-CH_3O,4-CH_3,3-CH_3, H,4-Cl)	"	" 40°C	-1.58±0.01	1.15±0.08	0.031	0.992	5	38
11	R^2=Cl;R^3=R'C_6H_4NH (R'= =4-OCH_3,4-CH_3,3-CH_3,H, 3-OCH_3,4-Br,3-Cl,3-NO_2, 4-NO_2)	Pyridine	Aqueous acetone (11.3 mol/l 15°C	-2.26±0.04	0.74±0.09	0.094	0.954	9	32
12	"	"	" 25°C	-1.92±0.03	0.68±0.07	0.076	0.963	9	32
13	"	"	" 35°C	-1.60±0.02	0.60±0.06	0.064	0.965	9	32
14	R^2=Cl;R^3=R'C_6H_4NH (R'= =4-OC_2H_5,H,3-OCH_3,3-Cl, 4-Cl)	Aniline	Acetone 35°C	-2.60±0.02	1.28±0.07	0.032	0.996	5	35
15	R^2=Cl; R^3=R'C_6H_4NH (R'= H,3-SO_3^-,4-SO_3^-,4-Cl,4-NO_2)	OH^-	Water 25°C	-3.76±0.07	0.87±0.20	0.126	0.931	5	14

Note: Dimensions - k_o l/mol·s; for 1-8 in Eq. (2) $\sum \sigma_{R'}$ and for 9-15 - $\sigma_{R'}$ have been used.

of $\rho(R')$ for those series (7 and 8, Table 2). That refers to the additive influence of the two substituents in chlorotriazinee I onto the substitution of chlorine, the third substituent. Therefore, if all other conditions are equal, the comparison $\rho(R')$ appears to be correct for the mono-(Ia) and dichlorosubstituted (Ib) triazines. As the additivity law is observed, it will be possible to analyze the data for substitution of chlorine in chlorotriazine Ic according to the Hammett equation (3):

$$\log k = \log k_0 + \rho(R)\sum\sigma(R^2,R^3), \qquad (3)$$

where $\sigma(R^2)$ and $\sigma(R^3)$ denote the Hammett σ_m parameters which are commonly used for correlation of substitution rates in symmetrical triazines[19,20,54,66].

The results of the analyis are given in Table 3.

The $\rho(R)$ calculations for series 1-3,5,7,11,12,16 were made so that all data found in literature were embraced. Prior to that, we had to find the σ_m values for the $R'C_6H_4NH$, since they were unknown. We took reaction series 10 (Table 3) as a standard. Relying on the correlation parameter (3) of the mentioned series and on the log k for series 2,4,6 in Table 2, we calculated the σ_m values of the $R'C_6H_4NH$ groups. Their averaged values equal

R'	4-CH_3O	4-CH_3	3-CH_3	H	4-Cl	3-NO_2
σ_m	-0.158	-0.142	-0.136	-0.120	-0.082	-0.017

The σ_m value of the C_6H_5NH equals -0.120, which perfectly agrees with literature data[69]. There is an excellent correlation between the values of σ_m for the $R'C_6H_4NH$ groups and the Hammett parameters σ for the R' substituents:

$$\sigma(R'C_6H_4NH) = (-0.120\pm0.002) + (0.146\pm0.005)\sigma\,(R') \qquad (4)$$

$$s = 0.004, \qquad r = 0.988, \qquad N = 6.$$

Table 3

Results of Data Treatment According to the Hammett Equation (3) of the Rate of Nucleophilic Substitution in Clorotriazine Ic

	R^2, R^3	Nucleo-phile	Solvent	T° °C	log k_o	ρ_R	s	r	N	Ref.
1	2	3	4	5	6	7	8	9	10	11
1	R^2=Cl;R^3=$(CH_3)_2CHNH$, C_2H_5NH,R'C_6H_4NH (R'=H, 4-NO_2), C_6H_5O, Cl	Ethyl-amine	Acetone-water (4:1)	50	-0.97±0.17	3.5±0.4	0.23	0.976	6	47
2	"	Isopro-pyl amine	"	50	-1.11±0.13	3.3±0.2	0.10	0.983	6	47
3	R^2=Cl;R^3=$(CH_3)_2CHNH$, C_2H_5NH,R'C_6H_4NH (R'=H, 4-NO_2), C_6H_5O	Dietha-nol	"	50	-0.75±0.29	3.2±0.8	0.36	0.914	5	47
4	R^2=$(CH_3)_2CHNH$;R^3=$(CH_3)_2$-CHNH,C_2H_5NH,NH_2,CH_3O, CH_3S,Cl	Isopro-pyl amine	Water	25	1.08±0.14	3.7±0.3	0.21	0.983	6	42, 43
5	R^2=Cl;R^3=R'C_6H_4NH, (R'=4CH_3O,4-CH_3,3-CH_3, H,3-CH_3O,4-Br,3-Cl, 3-NO_2,4-NO_2)	Pyridine	Aqueous acetone (11.3 mol/l)	15	-3.44±0.08	4.8±0.3	0.04	0.990	9	32

Table 3 continued

;1	2	3	4	5	6	7	8	9	10	11
6	$R^2=Cl; R^3=R'C_6H_4NH$ ($R'=$ $4-CH_3O, 4-CH_3, 3-CH_3, H,$ $3-CH_3O, 4-Br, 3-Cl, 3-NO_2$)	Pyridine	Aqueous acetone (11.3 mol/l)	25	-3.10±0.15	4.7±0.5	0.08	0.959	9	32
7	"	"	"	35	-2.60±0.10	4.1±0.4	0.07	0.962	9	32
8	$R^2=R^3=Cl$; $R^2=Cl$, $R^3=$ $=C_6H_5NH$; $R^2=R^3=C_6H_5NH$	Aniline	Methanol	90	-0.16±0.25	5.8±0.5	0.36	0.996	3	44
9	$R^2=Cl$; $R^3=R'C_6H_4NH$ ($R'=$ $=4-C_2H_5O, H, 3-CH_3O, 3-Cl,$ $4-Cl$), $CH_3NH, C_2H_5NH,$ $H-C_4H_9NH$	"	Acetone	35	-4.16±0.16	6.2±0.7	0.20	0.960	8	35
10	$R^2=C_6H_5NH$; $R^3=n-C_4H_9NH,$ $CH_3NH, C_2H_5NH, (CH_3)_2N,$ $NH_2, C_6H_5NH, C_2H_5O, CH_3O, Cl$	Benzylamine	Tetrahydrofurane	40	-2.0 ±0.2	6.1±0.5	0.34	0.977	9	37
11	$R^2=Cl$; $R^3=R'C_6H_4NH$ ($R'=$ $4-Cl, H, 3-CH_3, 4-CH_3O$), NH_2 $(CH_3)_2N$, N⬡O, CH_3NH	4-toluene	"	40	-3.5 ±0.3	7.4±1.2	0.20	0.933	8	38
12	$R^2=Cl; R^3=R'C_6H_4NH$ ($R'=$ $4-CH_3, 3-CH_3, H$), $(CH_3)_2N,$ N⬡O, CH_3NH	"	"	35	-3.8 ±0.3	7.4±1.7	0.25	0.910	6	38

Table 3 continued

1	2	3	4	5	6	7	8	9	10	11
13	$R^2=R^3=Cl$; $R^2=Cl$; $R^3==C_6H_5O$; $R^2=Cl, R^3=CH_3O$, $R^2= R^3=C_6H_5O$; $R^2=Cl$, $R^3=(C_6H_5)_2N$	3-nitro-4-methyl-aniline	Aceto-nitrile	25	-8.5±1.0	10.5±1.8	0.53	0.950	5	54
14	$R^2=(C_2H_5)_2N$; $R^3=CH_3ONH$, $C_2H_5ONH, C_3H_7NH, C_6H_5$	CH_3O^-	Metha-nol	56	-1.2±0.5	4.0±1.3	0.35	0.907	4	55
15	"	$C_6H_5O^-$	"	56	-2.5±0.3	4.4±1.0	0.25	0.955	4	55
16	$R^2=Cl$; $R^3=R'C_6H_4NH$(R'= =H, $3-SO_3^-$, $4-SO_3^-$, 4-Cl, $4-NO_2$)	OH^-	Water	25	-5.2±0.4	5.8±1.5	0.14	0.914	5	14
17	$R^2=Cl$; $R^3=iso-C_4H_9NH$, $(CH_3)_2CHNH, C_2H_5NH, CH_3O$, CH_3S	OH^-	Acetone water (1:19)	25	-4.4±1.0	3.9±0.6	0.29	0.964	5	24
18	$R^2=(C_2H_5)_2N$ and $iso-C_3H_7NH$; $R^3=n-C_4H_9ONH, C_2H_5ONH, CH_3ONH$ $C_2H_5NH, CH_3O, CH_3S, Cl$	"	Ethy-lene-glycol water (3:1)	70	-3.7±1.9	5.6±0.7	0.36	0.954	9	20
19	$R^2=Cl$; $R^3=n-C_4H_9NH, (CH_3)_2CHO$, $n-C_4H_9S, iso-C_4H_9S, C_6H_5O$	H_2O	Acetone water (1:1)	40	-6.9±0.8	4.7±1.5	0.19	0.879	5	13

Table 3 continued

1	2	3	4	5	6	7	8	9	10	11
20	$R^1=R^2=OC_6H_5$, OCH_3, $N(C_2H_5)_2$; $R^1=OC_6H_5$, $R^2=OCH_3$, $N(C_2H_5)_2$; $R^1=OCH_3$, $R^2=N(C_2H_5)_2$	OH^-	Dioxan water (1:1)	25	-5.3	9.6				65

Note: Dimensions of k_o 1/mol·s; σ values for R^2 and R^3 substituents are given via the Hammett σ_m values taken from[68] or[20,69]; the values of σ_m not found in literature for $R'C_6H_4NH$ groups were calculated according to Eq. (4); instead of Cl, 4-N,N-dimethylamino pyridine acts as the leaving group for No 20.

The free member also coincides with the known values of σ_m for the C_6H_5NH groups[69]. Eq. (4) enables us to calculate σ_m for the $R'C_6H_4NH$ group. It may contain any R' substituent with the known σ value. Thus, it widens the scale of the Hammett σ_m parameters for the correlation effect of meta-substituents in arene and azine systems.

The analysis of Table 3 shows that depending on the nucleophile's nature and medium effects, the behavior of the $\rho(R)$ values is typical of the bimolecular nucleophilic substitution with the dominant formation of a new bond in the transition state at the break of the old one. The $\rho(R)$ values are increasing in proportion to the increase in nucleophile basicity and to the weakening of the solvating properties of the medium. The total effect of those properties ensures the $\rho(R)$ change from 3.2 to 10.5 in the aminolysis process studied. Relatively small $\rho(R)$ values are also characteristic of the reactions of anionic nucleophiles in protonic media (14-18, 20, Table 3).

For nucleophilic substitution in arene systems (4-, 2-nitro-4-, 2-nitro-3-, 2,6-dinitro-4- and 2,6-dinitro-3-halogenbenzenes) similar $\rho(R)$ values vary from 3 to 5[64], depending on conditions.

The analysis of the substituent effect onto the chemical shifts of aminogroups protons in the PMR spectra of the series of R^2R^3-disubstituted aminotriazines I $(R^1=NH_2)$[70-72], the ring protons in the PMR spectra of the R^3-monosubstituted triazines I $(R^1=R^2=H)$[73,74], as well as the shifts of F^{19} in the MNR spectra of the R^2,R^3-substituted fluorotriazines I $(R^1=F)$[75] shows that the conductivity of a symmetrical triazine system considerably exceeds that of the benzene one. The average difference is evaluated to be 2.2-2.5 times[8,70,72,75,76]. Table 3 contains the $\rho(R)$ values which were corrected taking into account the above-mentioned. The variation range is 1.8-4.7 (1.3-4.2). These values are rather close to the corresponding $\rho(R)$ ones for arene systems[64], which demonstrates that the charge distribution levels are quite the same in the transition state of the S_N2Ar substitution of activated benzene halides and substituted symm-triazine halides. Since in the first case, the formation of intermediate II acts as the rate determining step (Scheme (1)[64]). The same is valid for substitution in triazine halides I.

Effect of Nucleophilic Reagent Structure

Although the influence of nucleophile's nature on the substitution rate in triazine halides has been thoroughly studied[38,39,44-47,49,51-53,55,57], the data cannot be applied for a general quantitative analysis owing to a simultaneous variation of some parameters determining the sensitivity of the process to the nucleophile structure. The results concerning the sensitivities of the aminolysis of chlorine- and fluorine-substituted triazines (Table 4) are more or less suitable for comparison. As a rule, the literary sources lack the statistic values of correlation according to the Hammett equation. One cannot find free member values (log k_o), which are essential for conducting the analysis within the framework of the correlation "reactivity vs. selectivity". As for the nucleophilic substitution with the participation of aryl amines, the correlation by Eq. (5), where the induction and direct polar conjugation effects are considered separately seems to be more correct:

$$\log k_R/k_o = \rho^o\sigma^o + \rho_R^+\sigma_R^+ + \rho_R^-\sigma_R^- \qquad (5)$$

The results of the treatment of the data found in literature, using the above equation are given in Table 4 ($\rho_R^-\sigma_R^-$ is excluded because of the absence of the necessary number of points for electron-acceptor 4-substituents). The comparison of the absolute ρ^o and ρ_R^+ values and the analysis of the Fischer criterion of the significance of regression convince us that the role of the effect of a direct polar conjugation is rather insignificant in all reaction series. Thus, both the ρ^o and ρ Hammett values given in the Table can be used for the analysis of structure effects and reactivity.

Table 4

Substituent Effect on Aminolysis Rate of Chloro- and Fluorotriazines I in Arylamine (R^3 - leaving group)

	R^1	R^2	R^3	R in $RC_6H_4NH_2$	Temp- eratu- °C	Sol- vent	log k_o[a]	ρ^o [b]	ρ_R^+	s	R	Ref.
1	2	3	4	5	6	7	8	9	10	11	12	13
1	Cl	Cl	Cl	4-OCH_3,4-CH_3,3-CH_3, H,3-Cl,4-Cl,4-Br, 3-$COOCH_3$,3-$COCH_3$, 3-NO_2	0 "	CH_3OH	3.14± ±0.05	-2.48±0.15 -2.6	-0.28± ±0.18	0.10	0.992	44
2	C_6H_5NH	Cl	Cl	4-OCH_3,4-CH_3.H,4-Cl	20 "	"	-1.44± ±0.05	-2.29±0.21 -2.5	-0.22± ±0.14	0.06	0.997	46
	"	"	"	4-OCH_3,4-CH_3,H,4-Cl 3-Cl,4-Br,3-$COOCH_3$, 3-NO_2	30 "	"	-0.86± ±0.06	-2.61±0.16 -2.7	-0.62± ±0.20	0.11	0.993	44
	"	"	"		50 " 90	"	-0.25± ±0.05	-2.25±0.12 -2.4 -2.0	-0.73± ±0.14	0.07	0.998	44
3	C_6H_5NH	C_6H_5NH	Cl	4-OCH_3,4-CH_3H,4-Cl 3-Cl,4-Br,3-$COOCH_3$ 3-NO_2	90 "	"	-1.41± ±0.02	-0.65±0.06 -0.7	-0.12± ±0.07	0.03	0.990	44

Table 4 continued

1	2	3	4	5	6	7	8	9	10	11	12	13
4	C_6H_5NH	F	F	$4\text{-}OCH_3, 4\text{-}CH_3, H, 4\text{-}Cl$	20 "	CH_3OH	-1.01± ±0.05	-4.08±0.22 -4.2	-0.95± ±0.14	0.07	0.992	46
5	Cl	Cl	Cl	$H, 4\text{-}CH_3\text{-}3\text{-}NO_2, 3\text{-}NO_2$ $3\text{-}NO_2\text{-}5\text{-}COOCH_3,$ $3,5\text{-}(NO_2)_2$	25	CH_3CN	1.99± ±0.07	-3.43±0.07	-			53
6	"	"	"	$4\text{-}OCH_3, 3\text{-}CH_3, H, 4\text{-}Cl,$ $3\text{-}Cl$	-10 "	$(C_2H_5)_2O$	2.27± ±0.04	-3.18±0.16 -2.5	-0.18± ±0.12	0.06	0.998	45
7	F	F	F	"	" "	" "	0.76± ±0.08	-3.87±0.32 -3.8	-0.36± ±0.23	0.13	0.996	45

a - Scale of k in l/mol·s

b - The line below denotes the Hammett ρ value taken from the source in which it was used first.

It follows from Table 4 that temperature but slightly affects the sensitivity of the solution to the arylamine structure (see 1 and 2). Now we can compare the values ρ at various temperatures for the series having either substrate structure or a solvent as their varying parameters.

Comparison of ρ with series 1,2,3 shows that the sensitivity of the aminolysis of chlorotriazines decreases in proportion to the rate of conducting the electron-donor substituents into triazine cycle, i.e., proportionally to the decrease in the reactivity of the substrate. That can be explained with the anti-Hammond shift of the transition state along the reaction coordinate, which is fairly characteristic of the bimolecular processes with a prevailing bond formation on the break-off[77,78]. Yet, this change need not refer to the formation of the rate limiting step.

It is supposed[45] that a much smaller ρ value for cyanuric chloride (6) on the basis of its amine structure in comparison with cyanuric fluoride (7) in the first case confirms the formation of the rate determining step of the tetrahedral intermediate in the second and of the rate determining step of its decomposition in the second case. It seems to agree with a much better reactivity of chlorotriazine if compared with that of fluorine derivatives (see log k_0, Nos 6,7). The same is observed when comparing the ρ values of the aminolysis of dichloro- (No 2, 20°C) and difluoro-derivatives (4), although the reactivity relationship is converted (F > Cl), thus showing the rate determining step of the tetrahedral intermediate formation in the case of fluorotriazine only. The seeming contradiction probably springs from the incorrect comparison of the ρ values of the reaction series. Here both the leaving group and the substituents change simultaneously in the substrate (two in case of series 6,7 and one for series 2,4). Thus, at transition to another series, the variation of ρ concerning amine proceeds alongside with simultaneous changes in the two structure parameters in substrate molecule. Such a comparison is probably leading us to the erraneous conclusion that we have already discussed in the present report.

like transition state, which is also in good agreement with the bimolecular substitution mechanism. The absolute ρ values (Table 4) are close to the ones obtained in the case of the arylaminolysis of activated chloro- and fluoroarenes under similar conditions[64].

In report[47], there were studied the structure effects of the primary and secondary amines upon the rate of chlorine substitution in cyanuric chloride and of dichlorotriazine substituents in aqueous acetone. The authors have processed the values of the bimolecular rate constants by using the Taft equation. Various results were obtained for both the primary and secondary amines:

$$\text{Primary:} \quad \log k_R/k_{CH_3} = -3.60\sum\sigma^* + 0.95\sum E_s, \qquad (6)$$

$$\text{Secondary:} \quad \log k_R/k_{CH_3} = -0.40\sum\sigma^* - 0.18\sum E_s \qquad (7)$$

High sensitivity to substituents' induction effects in the case of primary amines, and the positive sign of δ (i.e. "steric acceleration") should also be considered as an evidence in favor of the rate limiting step of the decomposition. A small ρ^* value and the negative sign of δ refer to the rate limiting tetrahedral intermediate formation in the case of secondary amines. In our opinion, those conclusions are based on incorrect correlations. It is known[79] that the structural effects of aliphatic amines in nucleophilic substitution reactions do not obey the Taft equation. A modified Taft's equation has been suggested, where steric constants E_s are replaced by the E_N ones. Yet, the data treatment[47] conducted by the authors of the present paper using the equation given in[79] yielded poor correlation parameters. There is even more ground for doubts there. The kinetics[47] was complicated by the autocatalysis of the forming aliphatic amine hydrochloride. The authors have used a rather rude mathematical method for finding the rate constants of bimolecular and trimolecular routes. So, it makes the validity of rate constant values problematic.

The reactivity of amines (OH^-, CH_3O^-, $C_6H_5^-$, $RC_6H_4O^-$, where R = 3-CH_3, 4-CH_3, H, 4-Cl) relative to the substituents of chlorotriazines in methanol has been studied in[55]. The anion of triphenolate was found to react faster than that of a phenolate having a similar basicity, hydroxide and methoxide anions being slower. We can conclude on the basis of those limited data that the nucleophilic reactivities of the above-mentioned anions were also determined by the same factors as the other processes of nucleophilic substitution, i.e., by basicity, polarizability, and solvation.

Original data about the effect of nucleophile's nature upon the rate of halide (Cl, F) substitution in arene and azine (incl. triazine) systems are given in[57]. In that paper, the anions of transition metals of groups VI - VIII $M^+ \cdot M'(CO)_nL^-$ (III) act as nucleophiles, where $M^+ = Li^+, Na^+, K^+$ but $M'(CO)_nL' = C_5H_5Fe(CO)_2^-$, $C_5H_5W(CO_3)^-$, $C_5H_5Mo(CO)_3^-$, $Re(CO)_5^-$, $Mn(CO)_5^-$ are the trialkylstannites of $M^+\ {}^-SnR_3$(IV) and potassium salts of fluorine substituents - $K^+ \cdot {}^-R$ (V) . It was shown that the association of an organic anion and an alkali metal cation can in organic solvents (tetrahydrofurane, diethyl ether, hexamethanol, etc.) in several ways influence the reactivity of an anion towards the substrates mentioned. Thus, in the case of weak nucleophiles III and IV, the contact ion pairs (CIP) have better reactivities, while in the case of V, either the solvate-divided ion pair (SDIP) or the free anion tend to react faster.

The obtained data have been explained[57] in the framework of the S_N2Ar mechanism (1), the rate determining step change depending on the anionic particle's nature. When using comparatively weak nucleophiles III and IV, the C-N bond that forms in intermediate II is also rather unstable. Therefore, the contribution of the k_{-1} step into the rate is of essential importance, and the decomposition of the intermediate ($k_H = k_1k_2/k_{-1}$) and the electrophilic contribution of the cation determine the reaction rate. The aforesaid also explains the reactivity of CIP. In the case of strong nucleophiles (V), it is not necessary to return to stage k_{-1}, as the formation of intermediate II ($k_H=k_1$) acts as the rate determining step, as a result of which ceases the cation's electrophilic contribution into the leaving group separation. Either the SDIP or the free anion becomes the most reactive particle. To support this hypothesis[57] the following data can be given: the anions of carbonylic metals (III) in pentafluorochlorobenzene substitute for chlorine (k_2 - the rate determining step), while carbanions (V) substitute for fluor (k_1 - the rate limiting step).

Solvent Effects

Research into the arylaminolysis rates of 2,4-dichloro- (I, $R^1=R^2=Cl$, $R^3=NHC_6H_5$) and 2,4-difluoro-6-anilinotriazines (I, $R^1=R^2=F$, $R^3=NHC_6H_5$) in several media has shown[46] that in both cases the reactivity is increasing as follows: methanol > acetone > acetonitrile. For methanol the k_{Cl}/k_F relationship is smaller than one, for acetonitrile its value somewhat exceeds one, and for acetone it is more than ten (see Table 1). The authors connect these facts with different relationships of the rate limiting step depending on the properties of the medium. In protonic media it is the amine attack upon the substrate that acts as the slow step, while in aprotic media, the decomposition of the tetrahedral intermediate with the leaving group ejection (Cl^- or F^-) forms the slow step.

The aforesaid partially agrees with the conclusions drawn in ref.[47]. It was based on the analysis of the effect of the content of water-dioxan mixture (vol %) upon the rate of interaction of arylamines $YC_6H_4N = N-C_6H_4NH_2$ with chlorotriazines I. It was studied on the example of reaction series A and B:

A: $Y = 4\text{-}NO_2$, $R^1=R^2=R^3=Cl$

B: $Y = 4\text{-}NO_2$, $R^1=R^2=Cl$, $R^3=NHC_6H_4N=NC_6H_4\text{-}NO_2\text{-}4$

In order to characterize medium effects, the log k values were contrasted to the E_T parameters of Dimroth, Y-parameters of Grünwald-Winstein, and to concentrated water in a mixed solvent ($\log C_{H_2O}$). In other cases, the dependences exist in the form of broken lines, the bending points corresponding to the ≈40 % water content in dioxan. At the same time, sensitivity to the medium effect is weaker in the range of low water concentration than in the case of high ones. The authors of[47] relate the curvatures in correlation graphs to the changes in the rate determining step (the formation of a tetrahedral intermediate in mixtures with high water content and its decomposition) in mixtures with lower water content, which seems to be in keeping with the data of[46] for individual solvents. But it is not clear why a low sensitivity of the rate to the protonic solvent effect is claimed to be connected with the chloride ion detachment from a tetrahedral intermediate, and its high sensitivity with the amine attack onto the substrate. Actually according to rational logic, the situation is totally different. In the first case, we should expect the appearance of a more product-like, and in the second case a more reagent-like transition state.

Interestingly, for series

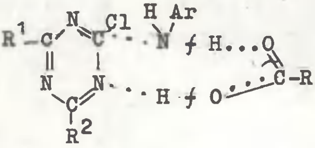
$$C: Y = H,\ R^1=R^2=Cl,\ R^3=NHC_6H_4N=NC_6H_5$$

the opposite situation can be noticed[47]. Rate's increased sensitivity to the water effect has been observed at its low concentrations, while the sensitivity is rather weak at high concentrations if the bending point of the corresponding relationships (≈40 % water in dioxan) is retained. The authors of[47] explain it with a converse correlation of rate limiting steps depending on series C, A, and B water contents, respectively. Still, it remains obscure why those drastic changes take place in the rate limiting step, while the reactivities vary but very slightly (e.g., the rates of reactions B and C in several mixtures differ only 2-5 times). Evidently, the conclusions reached in ref.[47] should be treated rather cautiously.

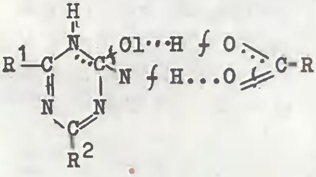
Catalysis of Nucleophilic Substitution Reactions in Triazine

In aqueous media, the substitution in chlorotriazines (hydrolysis, aminolysis) is catalyzed by acids[15,17]. In that aspect they differ from the substitution reactions of the same type taking place in benzene halides, which do not undergo acidic catalysis[80]. The difference springs from the azine cycle ability to protonate on the nitrogen atom. Consequently, the electrophilicity of the carbon center is increasing.

Kinetic studies of organic acidic and basic catalysis of the aminolysis, alcoholysis, phenolysis, and hydrolysis of triazine chlorides in organic media are presented in papers[31,32,39-41]. The best catalysts of arylaminolysis are carboxylic acids and 2-hydroxypyridine, the latter being more active: 2-hydroxypyridine > $CH_3COOH > CHCl_2COOH > C_6H_5COOH > CCl_3COOH$. Phenol and its substitution derivatives including the rather strong picric acid do not affect the aminolysis rate. Being supported by the above data, in[39-41] there has been suggested a bifunctional catalysis mechanism for carboxylic acids and 2-hydroxypyridine. According to that mechanism the catalysis is carried out during the formation of the tetrahedral intermediate via cyclic transition state VI.



VI



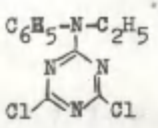
VII

The alternative of the bifunctional catalyst action during intermediate decomposition, which can be seen in VII is considered impossible under the following circumstances: first, in the case of the noncatalytic process, it is the amine attack onto the substrate that is prevailing as the rate determining step; second, bifunctional processes cannot be effective in similar processes involving activated benzene chlorides.

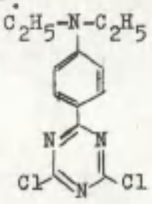
The bifunctional catalysis mechanism has also been stated to function for the second molecule of amine in the reaction of phenoxytriazine with piperidine in isooctane[60], referring to the facts that adding quinuclidine and diisopropylamine leads to the rate decrease, while 2-hydroxypyridine accelerates the process. The autocatalysis mechanism of aminolysis by the yields - aniline chlorotriazines[39] and amine hydrochloride[47] is also possible.

The catalysis by tertiary amines of the OH-[31,32] and NH-nucleophiles[41] reactions with triazine chlorides is usually considered to proceed according to the nucleophilic and general basic mechanisms. Both in the case of pyridine bases[32,81,82] and the tertiary aliphatic amines[31] the nucleophilic mechanism is preferable. Yet, there is no strict evidence in favor of that mechanism. Although the probability of the formation of N-triazinylpyridinic salts (nucleophilic catalysis intermediates) should not cause any objections (see[67,82]), their reactivities have not been studied yet. Thatswhy it is yet to be found if such intermediates can lie on the coordinate of substitution reaction in triazine chlorides.

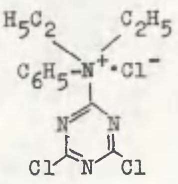
Studying synthetically the interaction of cyanuric chloride with tertiary amines (N,N-diethylamine, N,N-diethyl-1-napthylamine) has shown that there appears a mixture of products VIII and IX[83].



VIII



IX



X

It is assumed that N-triazinyl-ammonium salt X precedes at least the formation of product VIII. In such a salt, the tertiary amine is not usually substituted by another nucleophile. The salt is stabilized by alkyl chloride ejection. It makes us doubt in the validity of the nucleophilic catalysis mechanism for sterically hindered tertiary amines in the reactions in which participate such weak nucleophiles as phenols, alcohols and water[31]. Most probably, the catalysis of those reactions by sterically difficult tertiary amines proceeds according to the general basic mechanism.

Thus, the analysis of the data found in the literature concerning the nucleophilic substitution in the derivatives of triazine I within the relationship "reactivity-structure" and "reactivity-medium" shows that the mechanisms of the observed processes and of substitution reactions in arene systems are qualitatively similar. The only specific feature to be mentioned stands in different ways of expression of catalytic effects. When substitution is carried out in triazines, the catalysis by the basic compounds is but weakly expressed, bifunctional catalysts function more efficiently here. In the case of substitution in arenes, the situation is vice versa. One of the causes of the difference may be that in the case of "equal" structural characteristics and process conditions, it is the nucleophilic attack onto the substrate that is of major importance, while for substitution in arenes, decomposition in the first stage of the σ-complex plays the key role.

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KINETIC STUDY OF ALKALINE HYDROLYSIS OF SUBSTITUTED PHENYL TOSYLATES

XIX. DISCUSSION OF RESULTS OF KINETIC MEASUREMENTS FOR o-SUBSTITUTED TOSYLATES IN 80 % AQUEOUS DIMETHYLSULFOXIDE

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The results of kinetic measurements of the alkaline hydrolysis of ortho-substituted phenyl tosylates $CH_3C_6H_4SO_2OC_6H_4-X$ in 80 % (50.3 M %) aqueous DMSO published before are discussed.

The log k values for ortho-substituted derivatives were treated with simultaneous use of the data for metha- and para-substituted phenyl tosylates. When measuring the "ortho effect", an additional inductive σ_I scale was used.

The σ^o_{ortho} constants for ortho-substituted phenyls in 80 % aqueous DMSO as well as the parameters of the Arrhenius equation log A and E were determined.

It was found that the "ortho effect" - the difference log k^{o-x} - log k^{p-x} (k^{o-x} and k^{p-x} - rate constants for ortho- and para-substituted derivatives) - considerably decreased during transition from water to 80 % DMSO.

When passing from water to 80 % DMSO the influence of ortho-substituents increases to the same

extent as during transition from water to 2.25 M tetrabutylammonium bromide solution.

In the present paper the results of the kinetic measurements of the alkaline hydrolysis of ortho-substituted phenyl tosylates $CH_3C_6H_4SO_2OC_6H_4$-X (X = 2-NO_2, 2-Cl, 2-F, 2-OCH_3, 2-CH_3, 2-$N(CH_3)_2$) in 80 % (v/v, 50.3 M%) aqueous dimethylsulfoxide, published in our previous paper[1] are discussed.

Earlier[2] it has been found that the kinetic data for the alkaline hydrolysis of ortho-substituted phenyl tosylates in water and in 1 and 2.25 M tetrabutylammonium bromide could be treated together with the data for metha- and para-substituted derivatives while for measuring the ortho effect an additional term σ_I was included.

In the present paper we would like to check the applicability of an analogous data treatment method for the data in 80 % DMSO solution as well.

In the previous publications[2-4] it was found that the sensitivity towards metha- and para-substitutents during transition from water to 80 % DMSO solution increases to the same extent as when passing from water to 2.25 M tetrabutylammonium bromide solution (about 0.8 units of ρ^o). The purpose of the present work is to find out if the situation is similar also in the case of ortho-substituents((variation of solvents is the same).

Table 1 contains the logarithmic values of the second order rate constants $k_2(1)$, $k_2(2)$, k_2^o and $k_2^o(T)$ for the alkaline hydrolysis of ortho-substituted and some para-substituted phenyl tosylates, published in previous papers[1]. The analogous data for 3-Cl-, 3-NO_2-, 4-NO_2-substituted and unsubstituted phenyl tosylates published earlier[5], are also given in Table 1. The log $k_2^o(T)$ values for 3-Cl-, 3-NO_2-and 4-NO_2-substituted phenyl tosylates and for unsubstituted derivatives are calculated in the present work.

The values of $k_2(1)$ and $k_2(2)$ were calculated according to equation

$$k_1 = k_2 \cdot C_{OH^-} + \text{const}, \qquad (1)$$

without taking into consideration the influence of alkali concentration. When calculating the $k_2(1)$ constants, we included the results of all parallel measurements at each hydroxide concentration. The calculations of the $k_2(2)$ values embraced the corresponding arithmetic means as well.

As far as it was found[5,6] that k_1/OH^- value increased when passing to more concentrated alkali solutions, then for the purposes of comparison, we also determined the k_2^o constants, extrapolated to the infinitely diluted alkali solution.

The k_2^o values were calcultaed from the equation of Setschenov[7,8]:

$$\log k_2 = \log k_2^o + B \cdot C_{OH^-} \qquad (2)$$

using for each compound the $\log k_2$ values at one and the same temperature, where $\log k_2 = \log k_1/OH^-$, k_1 - pseudo-first order rate constants for the alkali concentration considered.

When estimating the $\log k_2^o(T)$ values, the isokinetic variant of the Setschenov equation was used:

$$\log (k_1/OH^-) = \log X_o + X_1(1/T) + X_2[OH^-] + X_3(1/T)[OH^-] \qquad (3)$$

The simultaneous data treatment according to Eq. (3) also embraced the k_1/OH^- values at all temperatures.

During transition from water to 80 % aqueous DMSO solution the rates of all ortho-substituted phenyl tosylates increase considerably, as it was found in the case of all metha- and para-substituted phenyl tosylates[3]. Nevertheless, the increase in the rate of ortho-substituted phenyl tosylates is somewhat lower than in the case of the corresponding metha- and para-substituted derivatives (NO_2, F and Cl substituents).

It should be reminded that the analogous situation was observed in the case of substituted phenyl tosylates in 1

Table 1

Values of log $k_2(1)$, log $k_2(2)$, log k_2^o and log $k_2^o(T)$

X	Temperature °C	log $k_2(1)$	log $k_2(2)$	log k_2^o	log $k_2^o(T)$
1	2	3	4	5	6
2-NO_2	25.0	0.049±0.015	0.064±0.018	-0.124±0.167	-0.284±0.401
				-0.047±0.083	
	50.0	0.690±0.22	0.669±0.043	0.569±0.089	0.416±0.533
	75.0	1.130±0.029	1.124±0.026	0.988±0.138	1.013±0.513
				1.057±0.008	
2-Cl	25.0	-1.254±0.022	-1.167±0.025	-1.471±0.028	-1.485±0.378
				-1.525±0.018	
	50.0	-0.554±0.026	-0.571±0.038	-0.689±0.064	-0.755±0.362
	60.0	-0.288±0.014	-0.276±0.019	-0.528±0.027	-0.493±0.357
	75.0	-0.090±0.060	-0.086±0.093	-0.163±0.102	-0.131±0.350
				-0.125±0.065	
2-F	25.0	-1.264±0.010	-1.268±0.014	-1.548±0.014	-1.505±0.256
	50.0	-0.582±0.051	-0.605±0.066	-0.628±0.034	-1.787±0.246
	60.0	-0.339±0.031	-0.337±0.061	-0.410±0.047	-0.530±0.242
	75.0	-0.050±0.039	-0.082±0.005	-0.343±0.042	-0.174±0.238
				-0.256±0.033	

Table 1 continued

1	2	3	4	5	6
2-N(CH$_3$)$_2$	25.0	-	-2.775		
	40.0	-2,261±0.063	-2.114±0.025	-2.316±0.033	-2.220±0.661
	50.0	-1,863±0,041	-1.731±0.031	-1.919±0.019	-1.875±0.652
	75.0	-1.140±0.033	-1.072±0.027	-1.100±0.103	-1.101±0.635
2-CH$_3$	25.0	-	-2,857	-3.118*	
	40.0	-2,336±0.056	-2.232±0.023	-2.524±0.020	-2.524±0.416** -2.467±0.240
	50.0	-2.013±0.026	-1.886±0.027	-2.153±0.011	-2.168±0.409** -2.148±0.236
	75.0	-1,317±0.013	-1.253±0.029	-1.317±0.032	-1.367±0.395** -1.400±0.228
2-OCH$_3$	25.0	-3,067	-	-3.313*	
	40.0	-2.455±0,030	-2.366±0.010	-2.706±0.012	-2.696±0.569** -2.698±0.295
	50.0	-2.113±0,026	-2,072±0.012	-2.306±0.038	-2.329±0.539** -2.244±0.291
	75.0	-1,446±0.027	-1.451±0.074	-1.469±0.015	-1.489±0.540** -1.453±0.281
4-OCH$_3$	25.0	-	-	-3.230*	
	40.0	-2.431±0.036	-2.430±0.001	-2.566±0.020	-2.698±0.304

Table 1 continued

1	2	3	4	5	6
	50.0	-1.974±0.020	-1.974±0.016	-2.240±0.038	-2.200±0.299
	60.0	-1.716±0.040	-1.735±0.085	-1.772±0.046	-1.826±0.295
	75.0	-1.173±0.019	-1.174±0.026	-1.275±0.023	-1.308±0.289
4-Cl	25.0	-1.723±0.021	-1.721±0.032	-2.107±0.041	-2.179±0.557**
					-2.026±0.306
	50.0	-1.040±0.035	-1.074±0.028	-1.069±0.018	-1.259±0.533**
					-1.214±0.293
	60.0	-0.764±0.050	-0.815±0.053	-0.830±0.018	-0.933±0.526**
					-0.923±0.289
	75.0	-0.361±0.026	-0.364±0.027	-0.497±0.052	-0.481±0.515
					-0.520±0.283
4-CH$_3$	25.0	-	-	-3.183*	
	40.0	-2.545±0.111	-2.539±0.035	-2.522±0.011	-2.596±0.295
	50.0	-2.070±0.004	-2.070±0.003	-2.275±0.026	-2.244±0.291
	60.0	-1.827±0.026	-1.827±0.044	-1.859±0.034	-1.913±0.285
	75.0	-1.328±0.013	-1.326±0.022	-1.461±0.020	-1.461±0.020
		-1.169±0.008***	-1.156±0.009***	-1.216±0.070***	
H^b	25.0	-2.592±0.014	-2.588±0.015	-2.686±0.019	-2.673±0.142
	50.0	-1.633±0.004	-1.620±0.013	-1.760±0.021	-1.732±0.137
	75.0	-0.880±0.002	-0.860±0.003	-0.925±0.008	-0.935±0.131

Table 1 continued

1	2	3	4	5	6
3-Cl[b]	25.0	-1.321±0.003	-1.318±0.013	-1.448±0.010	-1.485±0.169
	50.0	-0.561±0.002	-0.553±0.005	-0.714±0.017	-0.654±0.169
	75.0	0.126±0.006	0.150±0.006	-0.083±0.018	-0.075±0.169
$3-NO_2$[b]	25.0	-0.500±0.004	-0.503±0.009	-0.627±0.013	-0.614±0.200
	50.0	0.229±0.003	0.233±0.002	0.165±0.008	0.147±0.193
	75.0	0.798±0.017	0.825±0.035	0.770±0.047	0.795±0.186
$4-NO_2$[h]	25.0	-0.297±0.002	-0.303±0.002	-0.385±0.009	-0.273±0.305
	50.0	0.391±0.009	0.394±0.010	0.315±0.017	0.273±0.298
	75.0	1.030±0.003	1.056±0.007	0.776±0.042	0.864±0.284
				1.056±0.003	

---

a) when xcalculating, the log k value for the lowest alkali concentration was excluded

b) values of log $k_2(1)$, log $k_2(2)$ and log k_2^o were given in[5]

* values of log k calculated from those of log A and activation energies (used in some cases)

** At data processing, the value of log $k_2^o(T)$, found taking into account significant cross term $X_3[OH^-]1/T$ was used

*** in paper[5]

Table 2

Values of σ^{o}_{ortho} Calculated According to Eq. (4)

X	80 % DMSO,	from		Bu_4NBr		H_2O
	$k_2(2)$	k_2^o	$k_2^o(T)$	2.25 M	1 M	
			75°C			
NO_2	0.840	0.841	0,843	0.946	0.811	1.15
F	0.344	0.309	0.349	0.362	0.403	0.531
Cl	0.342	0.349	0.368	0.377	0.381	0.482
CH_3	-0.165	-0.139	-0.145	-0.176	-0.132	-0,188
OCH_3	-0,218	-0.252	-0.196	-0.211	-0,171	-0.078
NH_2	-	-	-	-0.014	-	0.066
$N(CH_3)_2$	-0.091	-0,085	-0,036	0.008	0.132	0.052
			50°C			
NO_2	0.897	0.871	0.835	0.835		1.15
F	0.403	0.434	0.385	0.351		0.543
Cl	0.416	0.412	0.396	0.429		0.492
CH_3	-0.143	-0.122	-0.133	-0.091		-0.193
OCH_3	-0.181	-0,214	-0.194	-0.191		-0.038
NH_2	-	-	-	-		0,102
$N(CH_3)_2$	-0.074	-0.037	-0.024	0,012		0.036
			25°C			water 15°C
NO_2	0.915	0.879	0.817	-	-	1.26
F	0.441	0.404	0.415	-	-	0.629
Cl	0.445	0.430	0.422	-	-	0.543
CH_3	-0,125	-0.119	-	-	-	-0.178
OCH_3	-0,156	-0.184	-	-	-	-0.094
NH_2	-	-	-	-	-	-0.136
$N(CH_3)_2$	-0.093	-	-	-	-	-0.144

and 2.25 molar tetrabutylammonium bromide solution and the pK_a values of benzoic acids in 7.75 molar solution of Bu_4NBr[2].

Using the data for the alkaline hydrolysis of phenyl tosylates in 80 % aqueous DMSO at 75°, 50° and 25° C, we calculated the values of σ^o_{ortho} for ortho-substituted phenyls according to the equation:

$$\sigma^o_{ortho} = \frac{\log k^X_{ortho} - \log k^H_o}{\rho^o_{m,p}} \qquad (4)$$

k^H_o is the rate constant for the unsubstituted derivative (X=H).

See Table 2 to compare the σ^o_{ortho} values for 80% DMSO calculated from constants $k_2(2)$, k^o_2 and $k^o_2(T)$ as well as for water and 1 and 2.25 M tetrabutylammonium bromide solution.

It follows from the σ^o_{ortho} values in Table 2 that the considerable positive ortho effect observed in the case of water solution when passing to 80 % DMSO solution as well as to 1 and 2.25 M tetrabutylammonium bromide solution undergoes a substantial decrease. At the same time the difference in the σ^o_{ortho} values calculated for different temperatures diminishes as well.

The data of Table 2 show that the σ^o_{ortho} value for 2-CH_3-substituent does not practically depend on the nature of solvent and on temperature.

In order to find out whether the σ_I scale could be used for taking into account the ortho effect in the case of the reaction series considered in 80 % DMSO solution we processed the $\log k_2(2)$, $\log k^o_2$ and $\log k^o_{2(T)}$ values for ortho-substituted derivatives simultaneously using the data for metha- and para-substituted derivatives according to the equation:

$$\log k^X_{m,p(ortho)} = \log k^H_o + \rho^o_{m,p(ortho)}\sigma^o + \rho_{I(ortho)}\sigma_I \qquad (5)$$

where $\sigma^o_{ortho} = \sigma^o_{para}$ were used.

The $\log k_2(1)$ values were not treated according to Eq. (5), since the $\log k_2(1)$ values but very slightly differ from the $\log k_2(2)$ values (see Table 1).

For comparison, the $\log k_2(2)$, $\log k_2^o$ and $\log k_2^o(T)$ values were treated according to the following equations as well:

$$\log k^X_{m,p} = \log k^H_o + \rho^o_{m,p}\sigma^o \qquad (6)$$

$$\log k^X_{ortho} = \log k^H_o + \rho_{I(ortho)}\sigma_I + \rho^o_{R(ortho)}\sigma^o_R \qquad (7)$$

The data treatment according to Eq. (7) also embraced the log k value for unsubstituted derivatives.

Table 3 presents the results of the statistical data treatment according to Eqs. (5)-(7).

Data treatment was carried out on a computer "PC/XT" using the program of multiple regression analysis compiled by V.A. Palm[9,10]. We assumed in data processing that in the case of 2-$N(CH_3)_2$-substituents there was no resonance term and in common data treatment we added the correction $\rho^o_{m,p}\sigma^o_R$ to the log k value of 2-$N(CH_3)_2$-derivative.

It follows from the results of the statistical data treatment that Eq. (5) statistically describes the whole data set of the alkaline hydrolysis of substituted phenyl tosylates in 80 % aqueous DMSO, as it was found previously in the case of 1 and 2.25 M tetrabutylammonium bromide solution and in the case of water[2].

Thus, in the case of the reaction studied in this work ortho-substitutents are affected by the additional inductive influence, represented by the $\rho_{I(ortho)}\sigma_I$ terms in Eq. (5). But, the value of the $\rho_{I(ortho)}\sigma_I$ term is considerably smaller than that of the water solution[2] (for water at 75°C $\rho_{I(ortho)} = 0.90$). At the same time the $\rho_{I(ortho)}$ values (see Table 3) for 80 % DMSO solution are comparable with the same values for 1 and 2.25 M tetrabutylammonium bromide solution[2].

The activation parameters $E(0)$, $E(0)_T$, $E(2)$ and $\log A(0)$, $\log A(0)_T$ and $\log A(2)$, calculated from the

Table 3

Results of Treatment of log k Values According to Equations:

$$\log k^{X}_{m,p} = \log k^{H}_{o} + \rho^{o}_{m,p}\sigma^{o} \qquad (1)$$

$$\log k^{X}_{m,p(ortho)} = \log k^{H}_{o} + \rho^{o}_{m,p(ortho)}\sigma^{o} + \rho_{I(ortho)}\sigma_{I} \qquad (2)$$

$$\log k^{X}_{(ortho)} = \log k^{H}_{o} + \rho_{I(ortho)}\sigma_{I} + \rho^{o}_{R(ortho)}\sigma^{o}_{R} \qquad (3)$$

Temperature °C	Eq.	Parameters	Calculated from		
			$\log k_2(2)$	$\log k^{o}_{2}$	$\log k^{o}_{2}(T)$
1	2	3	4	5	6
75,0	(1)	$\log k^{H}_{0}$	-0.917± ±0.054	-0.980± ±0.033	-1.017± ±0.043
		$\rho^{o}_{m,p}$	2.43± ±0.13	2.34± ±0.09	2.41± ±0.11
		r	0.991	0.993	0.993
		s	0.121	0.109	0.108
		s_o	0.137	0.118	0.114
		n/no	8/8	11/11	7/7
	(2)	$\log k^{H}_{0}$	-0.982± ±0.047	-1.024± ±0.031	-1.069± ±0.043
			-0.929± ±0.039 *	-0.987± ±0.025 *	-1.025± ±0.038 *
		$\rho^{o}_{m,p(ortho)}$	2.59± ±0.13	2.44± +0.08	2.52± ±0.11
			2.45± ±0.11 *	2.35± +0.07 *	2.41± ±0.11 *
		$\rho_{I(ortho)}$	0.22± ±0.21	0.24± ±0.13	0.30± ±0.19
			0.26± ±0.17 *	0.26± ±0.10 *	0.33± ±0.16 *
		r	0.986	0.991	0.989
			0.988*	0.993*	0.991*
		s	0.172	0.134	0.152
			0.137*	0.104*	0.126*

Table 3 continued

1	2	3	4	5	6
		s_o	0.169	0,135	0,144
			0.151*	0.115*	0.135*
		n/no	14/14	20/20	13/13
			13/13*	19/19*	12/12*
	(3)	log k_0^H	-0.952± ±0.116	-1.073± ±0.066	-1.042± ±0.106
			-0,929± ±0.104 *	-1.029± ±0,048 *	-1.022± ±0.096
		ρ_I(ortho)	2.85± ±0,41	2.82± ±0.25	2.85± ±0.37
			2.73± ±0,34 *	2.69± ±0.17 *	2.73± ±0.32 *
		ρ_R^o(ortho)	2,72± ±0,44	2.41± ±0.26	2.59± ±0,40
			2.29± ±0.43 *	2.13± ±0,19 *	2.20± ±0.40 *
		r	0.973	0.985	0.976
			0.974*	0,991*	0.977*
		s	0,266	0,183	0,242
			0.216*	0.122*	0.201*
		s_o	0.232	0.170	0.217
			0.226*	0,136*	0.213*
		n/no	7/7	10/10	7/7
			6/6*	9/9*	6/6*
50,0	(1)	log k_0^H	-1.645± ±0.049	-1.818± ±0.029	-1.812± ±0.052
		$\rho^o_{m,p}$	2.58± ±0.11	2.74± ±0,08	2.67± ±0.14
		r	0.995	0.998	0.992
		s	0.103	0.072	0.132
		s_o	0,103	0.068	0.126
		n/no	7/7	7/7	7/7
	(2)	log k_0^H	-1.625± ±0.054	-1.867± ±0,056	-1.769± ±0.073
			-1,625± ±0.042	-1.807± ±0.047	-1,699± ±0.059

Table 3 continued

1	2	3	4	5	6
		$\rho^o_{m,p}$(ortho)	2.70±0.14	2.85±0.14	2.53±0.18
			2.54±0.12 *	2.69±0.13 *	2.35±0.15 *
		ρ_I (orthc)	0.53±0.24	0.58±0.23	0.52±0.33
			0.57±0.18 *	0.62±0.20 *	0.59±0.26 *
		r	0.987	0.987	0.975
			0.991*	0.991*	0.981*
		s	0,188	0.195	0.257
			0.138*	0.157*	0.198*
		s_o	0.163	0.161	0.221
			0.137*	0.147*	0.192*
		n/no	13/13	13/13	13/13
			12/12*	12/12*	12/12
	(3)	log k_0^H	-1.643±0.132	-1.857±0.148	-1.822±0.164
			-1.616±0.107 *	-1.829±0.135 *	-1.790±0,029 *
		ρ_I (ortho)	3.24±0.47	3.47±0.53	3.13±0.58
			3.08±0.35 *	3.31±0.46 *	2.99±0.10 *
		ρ^o_R (ortho)	2.83±0.50	2.86±0.55	2.24±0.59
			2.31±0.45 *	2.33±0.56 *	1.61±0.11 *
		r	0.971	0.966	0.952
			0.977 *	0.966*	0.998*
		s	0.302	0.339	0.379
			0.224 *	0.282*	0.062*
		s_o	0.240	0.257	0.306
			0.215 *	0.254*	0.060*
		n/no	7/7	7/7	7/7
			6/6 *	6/6 *	6/6*

Table 3 continued

1	2	3	4	5	6
25,0	(1)	log k_0^H	-2.507± ±0.059	-2.717± ±0.091	-
				-2.762± ±0.040 **	-2.768± ±0.055
		$\rho^o_{m,p}$	2.81± ±0.16	2.92± ±0.23	
				3.00± ±0.11 **	3.04± ±0.15
		r	0,993	0.985	
				0.995**	0.993
		s	0.107	0.164	
				0.119**	0.140
		s_o	0.115	0.169	
				0.103**	0.117
		n/no	5/5	5/5	
				7/7**	7/7
	(2)	log k_0^H	-2.626± ±0.081	-2.605± ±0.054	-2.738± ±0.063
			-2.507± ±0.069 *	-2,739± ±0.047 ***	
		$\rho^o_{m,p(ortho)}$	3,05± ±0,20	2.69± ±0.16	
			2.80± ±0.19 *	2.93± ±0.13 ***	2.94± ±0.18
		$\rho_{I(ortho)}$	0,79± ±0.33	0.67± ±0.17	
			0.79± ±0.26 *	0.65± ±0.18 ***	0.56± ±0.26
		r	0.981	0.986	0.983
			0.982*	0.991***	
		s	0.258	0.144	0.209
			0.202*	0.165***	
		s_o	0.193	0.165	0.180
			0.186*	0.138***	
		n/no	11/11	10/10	12/12
			10/10*	14/14***	

x Values of log k for 2-$N(CH_3)_2$- derivative were excluded before data treatment.

xx Values of log k for 4-CH_3- and 4-OCH_3- derivative calculated from activation energies and log A are included.

xxx Values of log k for 4-CH_3-, 4-OCH_3-, 2-CH_3-, and 2-OCH_3- derivatives obtained from E(0) and log A(0) are included.

Table 4

Values of Activation Energies and log A

X	E $\frac{kcal}{mole}$	log A	s	s_o	r	n/n_o
1	2	3	4	5	6	7
using k_2^o						
2-NO_2	10.79±0.65	7.81±0.25	0.057	0.105	0,995	4/4
2-Cl	12,81±0.43	7,91±0.13	0.045	0.074	0.997	6/6
2-F	12.69±1.88	2.85±0.74	0,145	0.251	0.968	4/4[*]
	13.34±1.44	8.29±0.56	0,111	0.185	0.983	4/4[**]
2-CH_3	17.20±0,20	9.49±0.09	0,009	0,016	0.999	3/3
2-OCH_3	17.57±0.29	9.57±0.14	0.015	0.023	0.999	3/3
2-$N(CH_3)_2$	16.93±0.48	9.54±0,19	0.027	0.049	0.999	4/4
4-Cl	15.91±1.05	9,60±0.41	0.081	0.114	0,993	4/4
4-OCH_3	19,13±0.73	10.79±0.24	0.045	0.077	0.997	5/5
	18.62±1.13	10.41±0.53	0.067	0.085	0.996	3/3[***]
4-CH_3	17.45±1.80	9.61±0.62	0.115	0.210	0.978	5/5
	18.93±1,89	10.61±0.73	0.098	0.172	0.985	4/4
4-NO_2	12.92±1.46	8.58±0.57	0.127	0.205	0.978	4/4
using $k_2^o(T)$						
2-NO_2	11.79±0.83	8.38±0.57	0,107	0.214	0.977	12/12
	12.31±0.60	8.74±0.38	0,068	0.135	0.991	11/12
2-Cl	12.85±0.38	7.94±0.26	0.052	0.112	0.991	19/20
	12.60±0.48	7.16±0,32	0.067	0.147	0.989	20/20
2-F	12.63±0,26	7.76±0.18	0.041	0.082	0.997	19/20
	12.52±0.30	7.66±0.21	0.049	0.100	0.995	20/20
2-CH_3	16,50±0.43	9.00±0.29	0.021	0.045	0.999	14/14
	15.19±2.47	8.15±0.17	0.028	0.056	0.998	13/13
2-OCH_3	17,16±0.59	9.28±0.39	0.026	0.055	0.998	13/13
	14.89±1,16	7.82±0,25	0.044	0.088	0.996	13/13
2-$N(CH_3)_2$	15.96±0.70	8,92±0.46	0.080	0.156	0.988	14/14
4-Cl	16.06±0.56	9.60±0.38	0.041	0.066	0,998	20/20
	14.30±0.31	8.46±0.07	0.059	0.095	0,996	21/21

Table 4 continued

1	2	3	4	5	6	7
4-OCH$_3$	18.39±0.32	10.24±0.21	0.033	0.064	0.998	15/15
4-CH$_3$	16.29±0.31	8.78±0.20	0.026	0.064	0.998	14/14
H	16.62±0.44	9.52+0.10	0.028	0.036	0.999	19/22
3-Cl	15.05±0.23	9.53±0.16	0.040	0.067	0.998	28/28
3-NO$_2$	13.38±0.30	9.20±0.21	0.040	0.074	0.997	17/18
4-NO$_2$	12.72±0.20	8.99±0.19	0.048	0.106	0.994	26/28
	11.96±1.24	8.38±0.09	0.058	0.176	0.989	28/28
		using $k_2(2)$				
2-NO$_2$	10.08±0.36	7.46±0.10	0.027	0.051	0.999	3/3
2-Cl	10.54±0.73	6.58±0.29	0.057	0.120	0.997	4/4
2-F	11.43±0.45	7.13±0.18	0.035	0.068	0.998	4/4
2-OH$_3$	15.14±0.92	8.30±0.36	0.069	0.103	0.995	4/4
2-OCH$_3$	15.11±1.29	8.09±0.53	0.102	0.151	0.988	4/4
2-N(CH$_3$)$_2$	16.10±1.03	9.09±0.41	0.079	0.110	0.994	4/4
4-Cl	12.67±0.78	7.54±0.30	0.060	0.106	0.994	4/4
4-OOH$_3$	17.43±1.14	9.75±0.45	0.060	0.115	0.993	4/4
4-CH$_3$	16.83±1.14	9.25±0.44	0.059	0.117	0.993	4/4

* log k = -0.256 at 75° C was used

**- log k = -0.174 at 75° C was used

*** log k at 60°C was excluded before data treatment

$\log k_2^o$, $\log k_2^o(T)$ and $\log k_2(2)$ values, correspondingly, are given in Table 4. The values of E(0), E(2), log A(0) and log A(2) were calculated according to the Arrhenius equation (see Fig. 1), but the values $E(0)_T$ and $\log A(0)_T$ were found from Eq. (3).

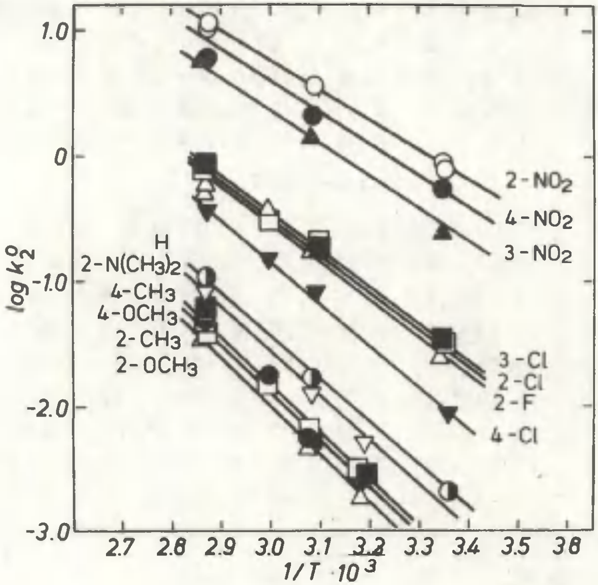

Fig. 1. Relationship between $\log k_2^o$ and 1/T.
(substituent X is given)

Fig. 2. illustrates the dependence of the E(0) values on the $\sigma^o_{m,p}$ constants. If in the case of ortho-substituted derivatives the values of $\sigma^o_{ortho} = \sigma^o_{para}$ were used, the pbints for ortho-substituted derivatives would deviate towards lower values and the deviations $E^X_{para} - E^X_{ortho}$ are proportional to the σ_I constants (Fig. 3).

An. analogous situation could be observed in the case of the log A values and of data treatment according to Eq. (5) .

We compared the substituents effects when passing from

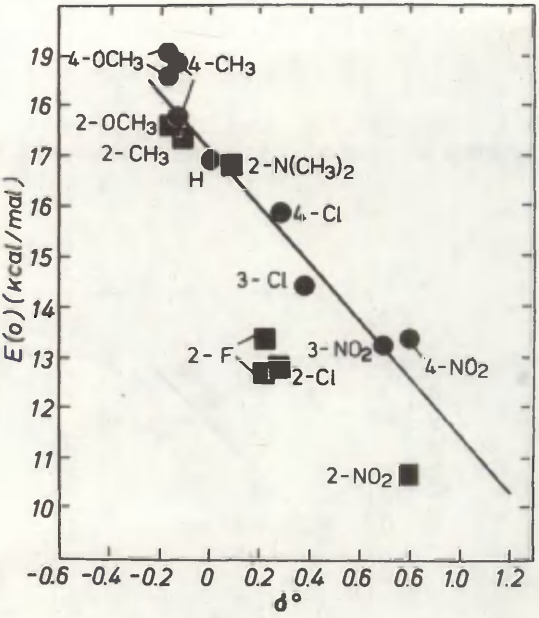

Fig. 2. Relationship between activation energies E(0) and σ^o. $\sigma^o_{ortho} = \sigma^o_{para}$ (substituent X is given).

water to 80 % DMSO solution and 1 and 2.25 M tetrabutylammonium bromide solutions in order to check the applicability of Eq. (8)

$$\log k^X_B = a + b \log k^X_D \qquad (8)$$

We derived Eq. (8) from the formula

$$(\log k^X - \log k^H)_B - (\log k^X - \log k^H)_0 = c + d\left[(\log k^X - \log k^H)_D - (\log k^X - \log k^H)_0\right] \qquad (9)$$

Indices B, D, and 0 denote the 2.25 M Bu_4NBr, 80 % DMSO and water solutions, respectively. If the substituent effects are similar during passing from water to 80 % DMSO and to 2.25 M Bu_4NBr solutions, then c=0 and d=1 and Eq. (9) is converted into Eq. (8), where

$$a = \log k_B^H - \log k_D^H \quad \text{and } b = 1.$$

Fig. 4 represents the relationship between $\log k^X$ (2.25 M Bu_4NBr) and $\log k^X$ (80 % DMSO) values at 75° and 50° C.

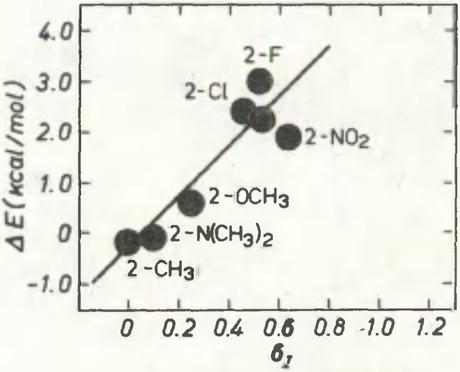

Fig. 3. Relationship between ΔE and σ_I for ortho-substituted derivatives. ΔE - deviations from relationship between E(0) and σ^0 (Fig. 2).

The results of the statistical treatment according to Eq. (8) are given in Table 5.

It follows from the data in Table 5 and Figure 4 that the slope of the dependence of $\log k_B$ values on $\log k_D$ values does not differ from unit in the case of ortho-substituted derivatives either. The value of intercept is the same at 75° C as at 50° C and it does not differ from the cor-

Table 5

Relationship between log k (2.25 M Bu_4NBr) and log k (80 % DMSO)

Substitution		log k	a	b	n/no	r	s
1	2	3	4	5	6	7	8
			75°C				
1.	meta and para	log k_2^o	-1.365±0.086	1,022±0.121	5/5	0.973	0.191
			-1.439±0.053	1,097±0.071	4/4	0.995	0.104
2.		log $k_2^o(T)$	-1,366±0.087	1.027±0.123	5/5	0.972	0,193
			-1.435±0.066	1.096±0.089	4/4	0.990	0.131
3.	ortho	log k_2^o	-1.252±0.033	1.146±0.037	6/6	0.997	0.081
4.		log $k_2^o(T)$	-1.256±0.034	1.138±0.037	6/6	0.990	0.081
5.	meta, para, ortho	log k_2^o	-1.323±0.043	1,083±0.050	11/11	0.989	0.142
6.		log $k_2^o(T)$	-1.323±0.043	1,083±0.050	11/11	0.989	0.141
			50°C				
1.	meta and para	log k_2^o	-1.380±0.028	1.160±0.032	4/4	0,999	0.053
2.		log $k_2^o(T)$	-1.368±0.071	1.201±0.083	4/4	0.999	0.013
3.	ortho	log k_2^o	-1.252±0.034	1.146±0.037	6/6	0.997	0.080
4.		log $k_2^o(T)$	-1,266±0.025	1.122±0.022	6/6	0,999	0.052

Table 5 continued

1	2	3	4	5	6	7	8
5.	meta, para, ortho	log k_2^o	-1.399±0.028	1.080±0.026	10/10	0.997	0.033
6.		log $k_2^\delta(T)$	-1.328±0.031	1.117±0,031	10/10	0.997	0.096
			75 and 50°C				
7.	meta and para	log k_2^o	-1.422±0.028	1.120±0.033	8/9	0.997	0.144
8.		log $k_2^\delta(T)$	-1.420±0.033	1.141±0.040	8/9	0.996	0.093
9.	ortho	log k_2^o	-1.267±0.028	1.118±0.027	11/12	0.997	0.095
10.		log $k_2^\delta(T)$	-1.241±0.022	1.135±0.022	12/12	0.998	0.077
11.	meta, para, ortho	log k_2^o	-1.352±0.026	1.094±0.026	21/21	0.994	0.118
12.		log $k_2^\delta(T)$	-1.340±0.025	1.104±0.024	20/20	0.996	0.107

responding values of log k_B^H - log k_D^H at 75° C and 50° C (see also ref.[5]).

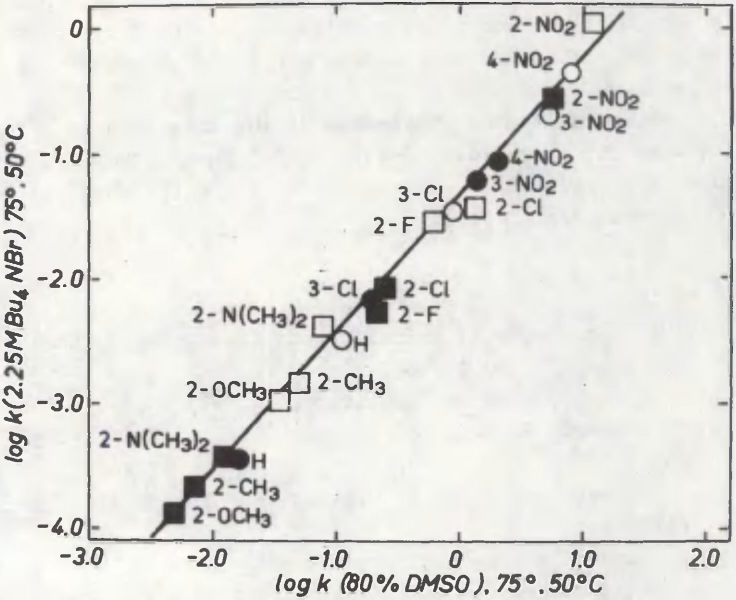

Fig. 4. Relationship between log k (2.25 M Bu_4NBr) and log k (80 % DMSO) at 75° and 50° C.

●■ - 50° C, ○□ - 75° C

It was found in[2-4] that during transition from water to

80 % DMSO solution the effect of metha- and para-substituents changed similarly to that when passing from water to 2.25 M Bu_4NBr solution.

The present paper demonstrated that an analogous conclusion is valid in the case of ortho-substituted derivatives as well. On the other hand, the fact that the points in Fig. 4. lie on one and the same line at both 75° C and 50° C, shows that in the case of the two solvents considered, the same isokinetic relationship holds for metha- and para-substituted derivatives and for ortho-substituted derivatives.

According to the discussion of the kinetic data for the alkaline hydrolysis of substituted phenyl tosylates in 80 % DMSO solution, constants k_2^o and $k_2^o(T)$ should be considered more probable.

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