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DETERMINATION OF THE KINETIC - EQUILIBRIUM PARAMETERS OF THE REACTION OF TRIPHENYLALUMINIUM WITH BENZOPHENONE

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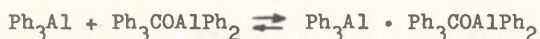
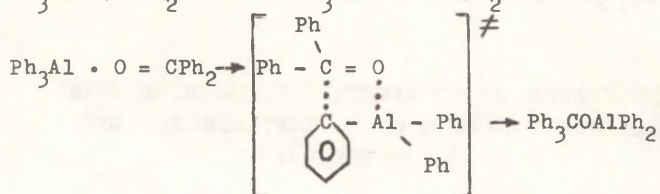
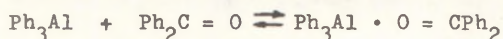
An inverse kinetic problem for the reaction of addition of triphenylaluminum to benzophenone in benzene at 25°C studied earlier has been solved, making use of the nonlinear least-squares method.

Twelve independent kinetic curves (85 lines of data) with different initial concentrations of reagents were treated simultaneously. The values of the rate and equilibrium constants characterizing the mechanistic scheme (3) of the reaction have been estimated.

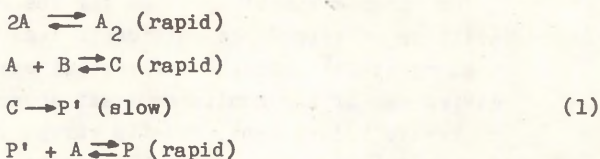
Introduction

Earlier the kinetics of the addition of triphenylaluminum to benzophenone in benzene in 1:1 ratio or at the excess of benzophenone (up to 1:3,6) at 25°C has been studied<sup>1</sup>. At the excess of triphenylaluminum a different reaction mechanism is expected to function<sup>1,2</sup>.

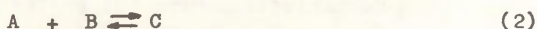
For these ratios of reagents the following mechanism has been suggested<sup>1,2</sup>:



If A-triphenylaluminium, B-benzophenone, C-donor-acceptor complex of triphenylaluminium with benzophenone, P'-product of the complex rearrangement and P is complex of product with triphenylaluminium, this scheme could be rewritten:

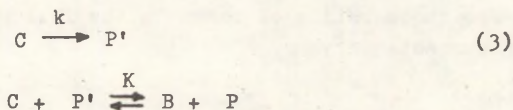


The dimer - monomer equilibrium is considered as very rapid,<sup>2</sup> as well as the equilibrium of complex formation:



The latter equilibrium is strongly shifted to the right<sup>3</sup>. Taking into account the equilibrium (2) and the excess of benzophenone in the reaction mixture one can conclude that triphenylaluminium is practically absent in the latter:

$[\text{A}]_0 \gg [\text{A}]$  ( $[\text{A}]_0$  is the initial concentration of triphenylaluminium), Hence, the scheme of the reaction is simplified:



The reaction kinetics was followed using two methods<sup>1</sup>: the direct spectrophotometric observation of the complex C concentration change and the method of samples where the total concentration of benzophenone  $[X]$  was determined spectrophotometrically, after quenching by ethanol. The total concentration of benzophenone  $[X]$  equals to the sum of concentrations in reaction mixture of benzophenone and of the complex resulting in benzophenone after quenching:

$$[X] = [B] + [C].$$

It was indicated<sup>1</sup> that equilibrium



is shifted to the right. This conclusion is based on the fact that at close initial concentrations of reagents the completely shifted equilibrium is a good approximation when the corresponding data are processed. At such conditions the reaction fits the first order equation and corresponding rate constant  $k_c = (1.23 \pm 0.14) \cdot 10^{-4} \text{ sec}^{-1}$  obtained as a result of direct observation of the complex C disappearance is approximately equal to the doubled rate constant  $k_x$  ( $2k_x = (0.74 \pm 0.06) \cdot 10^{-4} \text{ sec}^{-1}$ ) obtained when the change of  $[X]$  is observed. This result is compatible with such a simplified reaction scheme.

But, when the data obtained at the excess of benzophenone have been treated, the equilibrium (4) must be taken into account.

The simultaneous estimation of rate constant  $k$  and constant  $R = \frac{1}{K} = \frac{[C][P']}{[P][B]}$  was attempted<sup>1</sup>. In terms of the expression for  $[C]$  and differential equation  $\frac{d[X]}{dt} = -k[C]$ ,  $R$  and  $k$  were obtained by the use of the method <sup>dt</sup> of successive approximations.  $R$  values were varied to minimize the relative mean-square error of constant  $k$ , taking into account all experimental points for a single kinetic curve. However, these iterations did not converge. The  $k$  value varies insignificantly when  $R$  is varied in the range from .1 to 10. Therefore, value  $R = 1$  was fixed. The rate constant value of  $k = (0.34 \pm 0.04) \cdot 10^{-4} \text{ sec}^{-1}$  close to  $k_x$  value was obtained. But the equilibrium constant value remained uncertain.

### Procedure and Results of Data Processing.

The results of a more correct attempt to solve the problem described are represented in this paper. The nonlinear least-square approach (NLS) was applied. The universal version of the program of NLS<sup>\*\*\*</sup> was used. A special subprocedure for the calculation of the function  $F_1$  to be parametrized was prepared.

The algorithm of the nonlinear parametrization program used for the determination of standard deviation of calculated values of function  $F_1$  to be parametrized from corresponding experimental values  $Y_1$  includes the following procedures :

1. The linear least-square problem (multilinear regression) for the following system of equations is solved:

$$\sum_{L=1}^N \frac{\partial F_1}{\partial X_L} \Delta X_L = Y_1 - F_1; \quad i = 1, M \quad (5)$$

where  $F_1$  is the value of function to be parametrized for a given set (the temporal approximation) of parameters  $X_L$  to be estimated. The partial derivatives in the left side of the equation (5) are calculated by digital differentiation. Corrections  $\Delta X_L$  for parameters  $X_L$  are considered as components of the vector which determines the antigradient direction. Using the parabolic approximation, the minimum of the standard deviation is determined on the axis of that direction.

2. Points /1/<sup>\*\*\*</sup>, /2/ and /3/ corresponding to the three successive approximations of  $X_L$  (minimums on the given directions) are specified in the solution space (formed by coordinates  $X_L$  ). The next direction of minimization is de-

<sup>\*\*\*</sup> The program of NLS has been prepared by V. Palm in FORTRAN. Detailed description of this program algorithm will be published separately.

<sup>\*\*\*</sup> Point /1/ is identified with the initial approximation.

defined as a straight line joining points /1/ and /3/. Point /4/ is defined as a minimum in this direction and the re-definition of the points is performed as follows:

/1/ = /2/, /2/ = /3/ and /3/ = /4/.<sup>8</sup> This procedure is repeated until either the criterion of the end of the procedure or the change criterion for the "valley" procedure is satisfied for the two following iteration steps.

3. A special "valley" procedure of searching for a minimum on the smooth bottom of the deep "valley" in the solution space.

At the beginning of the next iteration cycle procedure 1 is executed twice, giving the three first points in the solution space. Then procedure 2 is executed. Depending on the value of corresponding criterion the passage from procedure 2 to the "valley" procedure may be either practically compulsory or excluded at all.

The algorithm used demands the elimination of both the significantly deviating (according to the Student's criterion) experimental points (lines) at the given progressively growing risk levels as well as the statistically insignificant parameters to be evaluated.

The standard deviations of the parameters to be evaluated are equalized to the values of standard deviations for the corresponding corrections  $\Delta X_L$  found as the result of the execution of procedure 1 at the solution point. Two sets of them,  $S_{X_L}$  (total) and  $S_{X_L}$  (single), were calculated. The former is  $S_{X_L}$  obtained when the corrections for all statistically significant parameters are evaluated simultaneously. Each of  $S_{X_L}$  (single) is obtained when only the correction for a single parameter  $X_L$  is evaluated, all other parameters being fixed at the solution point.

In terms of the material balance equations and expressions for rate and equilibrium constants the following differential equation was derived:

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<sup>8</sup> The procedure is described as "a method of parallel tangents" .<sup>4,5</sup>

$$\frac{d[Z]}{[C]_0 - [Z] - \frac{[D]_0 - K[C]_0}{2(1-K)} \left( \sqrt{1 + \frac{4K[Z](1-K)([C]_0 - [Z])}{[D]_0 - K[C]_0}} - 1 \right)} =$$

$$= \varphi([Z]) d[Z] = kdt \quad (6)$$

where  $[Z] = [P] + [P'] = [B]_0 - [X]$  denotes the sum of concentrations of reaction products,  $[C]_0 = [A]_0$  (see equilibrium (2)) corresponds to the concentration of the donor-acceptor complex and  $[D]_0 = [B]_0 - [A]_0$  corresponds to the concentration of free benzophenone at the initial moment of the reaction ( $t=0$ ).

Although this equation could be reduced to quadratures, the corresponding integral could not be expressed explicitly via elementary functions.

If  $K=1$  the equation (6) proceeds as follows:

$$\frac{d[Z]}{[A]_0 - [Z] - \frac{[Z]([A]_0 - [Z])}{[A]_0 - [D]_0}} = \varphi'([Z]) d[Z] = kdt$$

After integrating from zero to  $f_i$  where  $f_i$  is the quantity identified with the sum of reaction products' concentrations  $[Z]_i$  ( $i$  is the index of the data line) being also the function of time, the initial concentrations and the temporal approximations of parameters  $k$  and  $K$ , we get:

$$\int_0^{f_i} \varphi([Z]_i) d[Z] = kt_i \quad (7)$$

or

$$\int_0^{f_i} \varphi'([Z]_i) d[Z]_i = kt_i \quad (8)$$

Quantity  $f_i$  was used as an implicitly defined function  $F_i$  to be parametrized in the course of data processing. Values  $[Z]_i$  were used as  $Y_i$ , rate and equilibrium constants

k and K were considered as parameters  $X_L$  to be evaluated.

The values of function  $f_i$  to be parametrized were calculated using the iterative procedure. Approximating the dependence of  $f_i$  on  $t_i$  with the equation for a monomolecular curve we obtained:

$$f_i = [C]_{0_i} - ([C]_{0_i} - G_i) e^{-k\Delta t_i}$$

where  $G_i$  is the previous  $f_i$  approximation and  $\Delta t_i = t'_i - t_i$  where  $t'_i$  is the temporal approximation of the time moment and  $t_i$  is its experimental value. On the bases of the  $f_i$  approximation obtained the values of  $t'_i$  were found by equations (7) or (8). Then the new values of  $\Delta t_i$  and the additional approximation of  $f_i$  were obtained until the temporal value of  $\Delta t_i$  became smaller than the given precision criterion (6 sec). For the first iteration cycle  $G_i = 0$  and  $\Delta t_i = -t_i$  were assumed. If the iteration was not convergent the bisection of the segments was used. Equations (7) and (8) were solved using the Simpson method of digital integration (the criterion of relative precision was equalized to 0.01).

The initial data used were the experimental values of  $[Z]_1$  and corresponding values of  $t_i$  and values of initial concentrations  $[C]_{0_i}$  and  $[B]_{0_i}$  as well as the initial approximation of K. The initial approximation of rate constant k was calculated by equation:  $k = \frac{[Z]_n - [Z]_1}{(t_n - t_1)C}$ , where  $[Z]_1$

and  $t_1$  correspond to the initial period of reaction and C is the value of  $[C]_0$  for the given kinetic curve.

Twelve independent kinetic curves with different initial concentrations and ratios of reagents, altogether 85 lines of data, were treated simultaneously. (see Table 1).

The exclusion from the treatment of the significantly deviating points was executed on three risk levels: 0.01, 0.03, 0.05 (1, 3 and 5 per cent).

The results of calculations obtained proceeding from the different initial approximations of parameter K to be estimated are given in Table 2. It can be seen from the latter that the values of rate and equilibrium constants obtained,

in the limits of their uncertainty, do not depend on the initial approximation of K.

Since the dependence of k values on the variation of K in a rather wide range of its value is weak, the presence of the deep "valley" with a smooth bottom may be assumed in the solution space.

Table 1

Values of the Initial Concentration of Triphenylaluminium ( $[A]_0$ ) and Benzophenone ( $[B]_0$ ) in mole/l and the Total Number of Experimental Points (n) for Independent Kinetic Sets.

$A_0$	$B_0$	n
0.0515	0.0522	7
0.0256	0.0525	7
0.0289	0.0978	7
0.0274	0.0499	7
0.0264	0.0410	7
0.0272	0.0506	7
0.0228	0.0267	8
0.0294	0.1001	7
0.0475	0.0533	7
0.0256	0.0419	7
0.0224	0.0274	7
0.0219	0.0271	7

But application of the "valley" procedure for the detection of the standard deviation minimum leads to the values of parameters to be found which are indistinguishable, in the first approximation, from the values obtained without using this procedure. Apparently, the cause is that the bottom of the "valley" is rather slightly distorted. Nevertheless, it should be mentioned that the two values of K (12.0 and 13.9) obtained using the "valley" procedure are less deviating from the average value than the other results.

Table 2

Results of the Parametrization, Obtained Proceeding from Different  
Initial Approximations for K

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N	INITIAL APPROXIMATION FOR K	APPLICATION OF "VALLEY" PROCEDURE	RISK LEVEL PER CENT	A NUMBER OF POINTS INCLUDED	$S_0^a$	$S^b \cdot 10^4$ MOLE/L	$K \cdot 10^4$ SEC <sup>-1</sup>	$S_K^c$ (TOTAL) $\cdot 10^4$ SEC <sup>-1</sup>	$S_K^d$ (SINGLE) $\cdot 10^4$ SEC <sup>-1</sup>	K	$S_K^e$ (TOTAL)	$S_K^f$ (SINGLE)
1	2.0	NO	1	81	0.153	8.4	0.393	0.010	0.007	13.4	3.7	2.7
		NO	3	72	0.122	6.5	0.388	0.008	0.006	17.6	3.2	2.6
		NO	5	66	0.105	5.4	0.395	0.007	0.006	14.4	2.5	2.0
2	2.0	YES	1 <sup>c</sup>	83	0.164	8.9	0.402	0.009	0.008	12.0	1.7	1.5
		NO	3 <sup>c</sup>	66	0.104	5.4	0.402	0.007	0.006	16.2	2.3	1.8
3	0.1	NO	1 <sup>c</sup>	82	0.160	8.7	0.398	0.007	0.008	10.2	1.7	1.4
		NO	3 <sup>c</sup>	66	0.101	5.4	0.398	0.007	0.006	11.0	1.9	1.4
4	50.0	NO	1 <sup>c</sup>	82	0.161	8.8	0.412	0.010	0.008	15.2	2.9	2.4
		NO	3 <sup>c</sup>	66	0.104	5.4	0.402	0.007	0.006	17.9	1.8	1.6
5	0.1	YES	1	81	0.154	8.4	0.395	0.009	0.007	13.9	1.8	1.6
		NO	3	77	0.138	7.4	0.395	0.009	0.007	18.3	5.0	3.7
		NO	5	65	0.103	5.3	0.388	0.007	0.005	9.6	1.5	1.2
AVERAGE VALUES			1		0.158 <sup>d</sup>	8.7 <sup>d</sup>	0.400	0.009 <sup>d</sup>	0.007 <sup>d</sup>	12.9	2.5 <sup>d</sup>	2.3 <sup>d</sup>
			5		0.104 <sup>d</sup>	5.4 <sup>d</sup>	0.397 <sup>e</sup>	0.007 <sup>d</sup>	0.006 <sup>d</sup>	11.9 <sup>e</sup> 13.8 <sup>e</sup> 13.5 <sup>e</sup>	2.0 <sup>d</sup>	1.6 <sup>d</sup>

- a) Total standard deviation in normed scaling.
- b) Total standard deviation in natural scaling.
- c) At the 5% risk level the same results were obtained.
- d) Averaged values of standard deviations are calculated by equation:

$$S_{(\text{aver.})} = \sqrt{\sum_i S_i^2 / n}$$

- e) Standard deviation of arithmetical mean value is calculated by equation:  $S_{\bar{x}} = \sqrt{\sum_i (x_i - \bar{x})^2 / n-1}$
- f) Standard deviation of constants k or K obtained as a result of simultaneous evaluation of corrections for both parameters to be evaluated.
- g) Standard deviation of k or K obtained as a result of evaluation of corrections for the given parameter, only.

The average values of parameters obtained taking into account the experimental points from 81 up to 83 (risk level is 1%) and those from 65 up to 66 (risk level 5%) are indistinguishable from each other, too. Such stability of the solution indicates that the deviations of excluded points are rather accidental in their nature.

A slight difference between the values of  $S_{X_T}$  (total) and  $S_{X_I}$  (single) indicates a rather high degree of effective orthogonality (absence of a strong "overpumping" effect between parameters).

Thus, we can accept the following values of rate and equilibrium constants characterizing the mechanism (3) of the reaction between triphenylaluminium and benzophenone:

$k = (0.400 \pm 0.008) \cdot 10^{-4} \text{ sec}^{-1}$  and  $K = 12.9 \pm 1.9$   
 at risk level 1% and  $k = (0.397 \pm 0.06) \cdot 10^{-4} \text{ sec}^{-1}$  and  $K = 13.8 \pm 3.5$  at risk level 5%.

As it may be assumed, the k value detected is indistinguishable from the average value of  $k_x = (0.37 \pm 0.03) \cdot 10^{-4} \text{ sec}^{-1}$  obtained earlier without taking into account the equilibrium (4). It is actually caused by a rather high value of the equilibrium constant K.

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PROPORTIONAL SUSCEPTIBILITY OF SUBSTITUTED ANTHRA-  
QUINONE AND NITROBENZENE TO THE SOLVENTS OF LONG-  
-WAVELENGTH ABSORPTION PEAKS

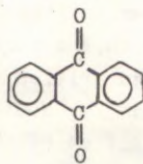
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Method of proportional susceptibility was applied in order to show that the physico-chemical properties of 9,10 - anthraquinones containing strong electron-donor substituents are analogous to the corresponding derivatives of p-substituted nitrobenzene. A number restrictions on the use of such analogues have been established. Empirical equations enabling to calculate the unknown values for the corresponding anthraquinone derivatives according to the  $\lambda_{\max}$  of longwave absorption bands of the nitrobenzene p - substituents were suggested.

9,10-anthraquinone derivatives have been intensively studied in several countries; they are widely used first of all as synthetic dyes, pigments, luminescent solids, biologically active substances and drugs.

According to the X-ray structural data and quantum-chemical calculations, the 9,10-anthraquinone (I) plain molecule consists of two aromatic rings connected with carbonylic groups. Such a structure of 9,10-anthraquinone might refer to the existence of similar features in the physico-chemical behavior of the corresponding anthraquinone substituents in



I

benzene. For instance, proportional shift of the  $pK_a$  values for 1-amino-2- and/or -4-(di)bromoanthraquinones as well as for bromine - substituted anilines<sup>2</sup>, and also for 1-phenyl-aminoanthraquinones and anilines<sup>3</sup> has been found. However, the substituent effect on the position of the longwave absorption peaks

is not sufficiently characterized by the  $\sigma$ -substituent constants, given for the benzene series<sup>4</sup>. This is valid even in case of the monosubstituted anthraquinones. Our attempts to describe this effect via the spectroscopic constants, suggested<sup>5</sup> for the substituents in benzene series also failed.

Evidently, the analogy between the physico-chemical properties of the anthraquinone and benzene derivatives is not firm enough. The derivatives of benzene, containing electron-acceptor substituents seem to be more close in this connection. There is also a number of facts speaking of certain similarities between the behavior of the anthraquinone and nitrobenzene substituents. Thus, it has been established that the reactivity of haloanthraquinones and halonitrobenzenes<sup>6</sup> in the reactions of nucleophilic substitution is quite similar. That concerns also alcoxyanthraquinones and nitroanilines<sup>7</sup> in the above-mentioned reactions. The  $\lambda_{max}$  values of the  $\pi^1$ ,  $\pi^*$  absorption bands of 2-substituted anthraquinone curvilinearly depend<sup>8</sup> on the  $\sigma_S^+$ -constants of Bloor found from the substituent effect on the position, of the longwave absorption bands of the nitrobenzene p-substituents. It has been shown<sup>9</sup> that the solvatochromic Kamlet - Taft<sup>10</sup> equation can be applied for the monosubstituted anthraquinone. The parameters were obtained by the shifts of absorption peaks of various indicators (p-substituents of nitrobenzene included) under the influence of solvents.

Certainly, the p-substituents of nitrobenzene do not constitute the best model for the monosubstituted anthraquinone. In the benzene series, aniline substituted in positions 3 and 4 by carbonyl containing substituents (eg. 3,4-diacetylaniline) can function as such a model for e.g. 2-aminanthraquinone.

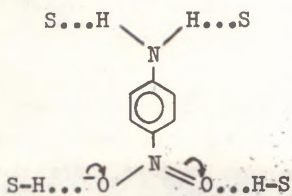
But such compounds, unlike the nitrobenzene p-substituents have not been studied sufficiently enough, though, the modeling is hardly of some practical value. The regularities of the proportional susceptibility type, proposed by Mostoslavskij, Izmailskij, and Shapkina<sup>11</sup> and exemplified by the ticiindigoide dyes, serve as a convenient means for establishing the analogy between the physico-chemical properties of the two compounds compared. It was proved that this method can also be used with the anthraquinone<sup>12</sup> and nitrobenzene<sup>10</sup> substituents. According to the method, the compounds having close structure are characterized by a proportional shift of the longwave absorption peaks if they are influenced by the same solvent. If the interaction mechanisms of the compared compounds differ from a certain number of solvents, the corresponding points deviate from the straight line<sup>10</sup>.

In the present work, the method of proportional susceptibility has been used for the first time for the purposes of the comparison of compounds which belong to different classes, in order to determine certain similarities in their physico-chemical behavior.

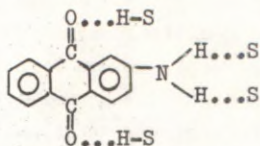
According to the contemporary view (see e.g.<sup>13-14</sup>), one can differentiate between the non-specific and specific solute-solvent interaction. The latter interaction type, characterized by the formation of intermolecular hydrogen bonds (IHB) can be divided into the following groups:

- 1) the interactions of the proton-donor solvent and proton-acceptor atom of the dissolved compound, on account of the hydrogen atom;
- 2) the interactions of the proton-releasing group of the dissolved compound's molecule and the proton-accepting atom of the solvent on account of the hydrogen atom. According to<sup>15</sup>, p-nitroaniline (II) can form the both types of the IHB. The aforesaid concerns also 2-aminoanthraquinone (III) where S denotes the solvent.

The major difference in the interaction of these compounds with solvents lies in the fact that the molecules of proton-donor solvents interact with two oxygen atoms of one and the same p-nitroaniline nitrogroup, and two oxygen atoms of



II.



III

two carbonylic groups of the anthraquinone derivative.

The comparison of the  $\nu_{\max}$  values proved (Fig.1, Table 1 eq.1) that these values excellently correlate with each other.

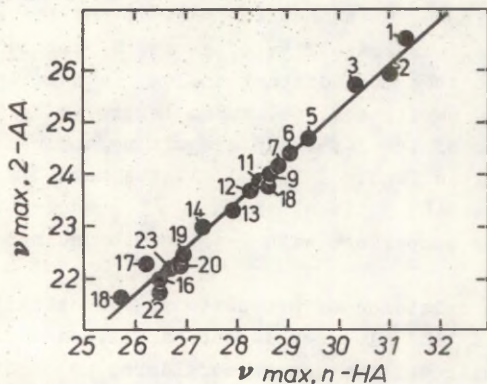


Fig. 1. 2-aminoanthraquinone and p-nitroaniline proportional susceptibility to the solvents. Solvent numbers correspond to those of Table 2.

The  $\nu_{\max}$  values, determined both in neutral (which cannot form the IHB) solvents as well as in those having proton - donor and proton - acceptor properties have been included into the correlation. The exclusion of the values taken in alcohols does not give a better correlation. Consequently, compounds II and III interact similarly with solvents and the above difference is not expressed spectrophotometrically. The

value of angle coefficient  $a$  given in equation (I) shows that the 2-aminoanthraquinone  $\nu_{\max}$  is not so susceptible to the solvents as that of p-nitroaniline.

1-aminoanthraquinone differs from its 2-isomer, since in the former case only one hydrogen atom of the aminogroup participates in the IHC, the another forming the intramolecular hydrogen bond<sup>16</sup>. However, in this case the proportional susceptibility to the solvents of two monoaminoanthraquinones can still be observed:

$$\nu_{\max} (I) = (0.29 \pm 0.03) \nu_{\max} (2) + (14.51 \pm 0.68) \text{ kK}$$

$$n = 21, r = 0.979, SD = 0.08 \text{ kK}$$

2-acetylaniline should be considered analogous to 1-aminoanthraquinone in the benzene series. But the existence of proportional susceptibility of 1- and 2- aminoanthraquinones refers also to a more distant analogy between 1-aminoanthraquinone and p-nitroaniline, which is proved by the excellent correlation of the 1-aminoanthraquinone and p-nitroaniline  $\nu_{\max}$  values (Table 1 Eq. 2). At the same time, a substantial decrease (3.5 times) in the  $\nu_{\max}$  susceptibility to the solvents in comparison with 2-aminoanthraquinone was observed.

As the existence of proportional susceptibility has been established<sup>12,17</sup> also for 1-mono- and 1,4-diaminoanthraquinones, p-nitroaniline can be considered as an analogue to 1,4-diaminoanthraquinone (Table 1, Eq. 3). The decrease of the proportional susceptibility coefficient value seems to be the result of the interaction of aminogroups in positions 1 and 4 of the anthraquinone nucleus<sup>17</sup>. The angle coefficient value in equation 3 refers to the even lower 1,4-diaminoanthraquinone  $\nu_{\max}$  susceptibility to the solvents.

An analogous result is obtained in case the  $\nu_{\max}$  values of 2-oxyanthraquinone and p-nitrophenole are compared (Eq.4). At the same time, the 1- and 2-methoxyanthraquinones' and p-nitroanizole proportional susceptibility was observed in aprotic solvents, only (Fig. 2., Table 1 Eqs. 5, 6). The

Table 1

## Proportional Susceptibility Parameters of Anthraquinone and Nitrobenzene

$$\sqrt{\frac{\Delta Q}{\max}} = a \sqrt{\frac{\Delta NB}{\max}} + B$$

Equation	Anthraquinone derivatives	Nitrobenzene derivatives	Solvent number	Correlation coefficient	Mean-square deviation, $\text{kK}^*$	a	b, $\text{kK}$
1	2-amino-	p-nitroaniline	19	0.989	0.20	$0.89 \pm 0.06$	$-(1.40 \pm 0.10)$
2	1-amino-	p-nitroaniline	21	0.982	0.08	$0.24 \pm 0.02$	$14.57 \pm 0.62$
3	1,4-diamino-	p-nitroaniline	14	0.957	0.06	$0.10 \pm 0.02$	$15.36 \pm 0.46$
4	2-oxy-	p-nitrophenol	9	0.976	0.12	$0.41 \pm 0.08$	$13.99 \pm 2.72$
5	1-methoxy-	p-nitroanisole	8	0.964	0.08	$0.38 \pm 0.08$	$14.21 \pm 2.77$
6	2-methoxy-	p-nitroanisole	8	0.985	0.06	$0.38 \pm 0.06$	$14.83 \pm 0.06$

\* I  $\text{kK} = 10^{-3} \text{cm}^{-1}$

points for alcohol deviate from the straight line towards lower values for the anthraquinone derivatives. The values of these deviations tend to increase after the elimination of the alkylic chain of alcohol. If the correlation embraces also the values registered in alcohols, a remarkable decrease in the correlation coefficient values takes place. Thus, it drops from 0.964 to 0.841 for 1-methoxyanthraquinone and from 0.985 to 0.946 for its 2-isomer.

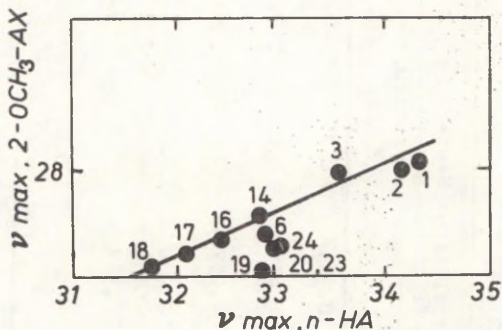


Fig. 2. 2-methoxyanthraquinone and p-nitroanizole proportional susceptibility to the solvents. Solvent numbers correspond to those of Table 2.

The obtained result correlates well with<sup>9</sup>, where it has been shown for the monosubstituted anthraquinone that the IHB solvents<sup>1</sup> (forming on account of the hydrogen atom of the proton - donor group of the solute) contribution into the total effect considerably exceeds that of IHB, in which the active hydrogen atom belongs to the proton - releasing solvent. In the case of amino- and oxyathraquinones IHB (forming on account of the amino- and oxygroup atoms) play the leading role in their specific interaction with solvents.

The difference in the proton - releasing solvent interaction with carbonylic groups of the anthraquinone derivative and the substituted nitrobenzene nitrogroup is not expressed since the contribution of this interaction type is insignificant. Methoxide derivatives do not contain an active hydro-

gen atom which could lead to the IHB formation, thus revealing the difference in the proton-donor solvents' action.

It should be borne in mind that such a comparison of the  $\nu_{\max}$  values holds only in case of the bands with a similar absorption nature. Consequently, the regularity found can be applied only with the anthraquinone derivatives which have longwave  $\pi\pi^*$  - absorption. This regularity is not valid for the non-substituted anthraquinone and its derivatives, containing the **electron-accepting** substituents, as the absorption spectra of these compounds lack the  $\pi\pi^*$  spectra.

Thus, the method of proportional susceptibility has enabled to prove the validity of the analogy between the 9,10-anthraquinones' physico-chemical behavior in the interaction with strong electron-releasing substituents and the corresponding benzene substituents, containing **electron-accepting** substituents, e.g. the nitrobenzene p-substituents. At the same time a number of restrictions for the application of such analogues have been established. These regularities enable to calculate the location of the  $\pi\pi^*$  band of anthraquinone derivatives, proceeding from the  $\nu_{\max}$  values of the long-wave absorption bands of nitrobenzene derivatives, measured in a large number of solvents. Since the solvent effect either on various physico-chemical parameters of the compounds or on their reactivity fall under the same type<sup>14</sup>, one can expect some proportional changes in other physico-chemical characteristics of the compounds discussed.

### Experimental

The  $\nu_{\max}$  values for the nitrobenzene p-substituents have been taken from<sup>10</sup> for 1-methoxy-, 2-oxy- and 1-aminoanthraquinones from<sup>9,17</sup> for 1,4-diaminoanthraquinone from<sup>17,18</sup>. The values for 2-amino- and 2-methoxyanthraquinones are given in Table 2. The compounds and solvents were purified according to the known methods. The absorption spectra were measured on a spectrophotometer Specord UV-Vis, the calculations were done with the assistance of T.P. Kosacheva on a computer Mir-1 at 0.95 risk level.

Table 2

$\nu_{\max}$  Values of  $\pi 1, \pi^{\#}$ - Bands in Various Solvents

No	Solvent	2-methoxyanthra-quinone		2-aminoanthraquinone	
		$\nu_{\max}$ , kK	Reference	$\nu_{\max}$ , kK	Reference
1	2	3	4	5	6
1	hexane	28.05	17	26.63	
2	cyclohexane	28.01		25.97	
3	carbon tetrachloride	27.62	17	25.71	
4	p-xylene	-	-	24.39	12
5	toluene	-	-	24.69	12
6	benzene	27.40	17	24.39	17
7	chlorobenzene	-	-	24.15	
8	chloroform	-	-	24.04	19
9	methylenechloride	27.22	17	24.04	
10	o-dichlorobenzene	-	-	24.21	17
11	dichloroethane	-	-	23.87	
12	diethyl ether	-	-	23.81	22
13	dioxane	27.47	-	23.70	17
14	ethylacetate	27.47	-	23.26	20
15	acetone	-	-	22.99	17
16	triethylphosphate	27.32		21.98	
17	dimethylphormamide	27.17		22.30	12
18	dimethylsulfoxide	27.03		21.74	
19	methanol	27.03		22.47	17
20	ethanol	27.25		22.27	17
21	propanol	27.20		23.26	21
22	2-propanol	27.20		21.74	17
23	butanol	27.28		22.22	12
24	tert-butyl alcohol	27.32		-	-
25	benzyl alcohol	26.80		-	-

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FACTORS EFFECTING THE RATE OF MENSHUTKIN  
REACTION 2. INTERDEPENDENCE OF REAGENTS' STRUCTURE  
EFFECTS

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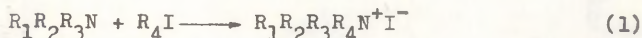
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Substituent effect in the substrate and the interdependence of the structure of substrate and nucleophile on the Menshutkin reaction have been estimated by means of multilinear regression analysis. A conclusion has been drawn that the transition state becomes more product-like and "loose" in case of the increase of the reaction center steric screening in the substrate .

It has been shown in our previous contribution<sup>1</sup> that the nucleophilicity of amines in reaction (1) depends basically on their steric and inductive substituent effect at the nitrogen atom:



where  $R_1, R_2, R_3$  denote H or Alk;  $R_4 -$  Alk;  $X - I$ .  
Our studies concentrated on the influence of radical's structure in the substrate upon the rate of these processes. With this aim rate constants of *i*-AmI, *i*-BuI and *i*-PrI interaction with various aliphatic amines in acetonitrile were determined

Table 1

Rate Constants ( $k \cdot 10^5$ ,  $M^{-1} \cdot \text{sec}^{-1}$ ) of Amine Reactions with Alkyl iodide  
in Acetonitrile at 25°C

No	Nucleophile	Substrate, reaction series number <sup>a</sup>		
		i-AmI, 4	i-BuI, 5	i - PrI, 6
1.	MeNH <sub>2</sub>	24.6 ± 1	4.31 ± 0.16	6.01 ± 0.24
2.	i-BuNH <sub>2</sub>	11.8 ± 0.3	-	-
3.	i-PrNH <sub>2</sub>	6.07 ± 0.12	0.931 ± 0.040	0.887 ± 0.045
4.	t-BuNH <sub>2</sub>	2.74 ± 0.05	0.401 ± 0.020	0.295 ± 0.015
5.	Me <sub>2</sub> NH	128 ± 8	-	-
6.	Et <sub>2</sub> NH	9.34 ± 0.31	1.63 ± 0.08	0.914 ± 0.045
7.	i-Bu <sub>2</sub> NH	1.56 ± 0.06	0.462 ± 0.030	0.231 ± 0.009
8.	i-Pr <sub>2</sub> NH	-	0.0240 ± 0.0010	0.0020 ± 0.0008 <sup>b</sup>
9.	Piperidine	148 ± 5	21.0 ± 0.8	23.3 ± 1.0
10.	Me <sub>3</sub> N	61.3 ± 1.7	21.0 ± 2.0	10.9 ± 0.6
11.	Me <sub>2</sub> BuN	12.1 ± 0.4	4.68 ± 0.23	1.50 ± 0.08
12.	Me <sub>2</sub> BzN	-	0.990 ± 0.050	0.395 ± 0.019
13.	MeEt <sub>2</sub> N	-	1.65 ± 0.06	0.270 ± 0.015
14.	Et <sub>3</sub> N	-	0.319 ± 0.017	0.0262 ± 0.0027

<sup>a</sup> - Reaction series of all substances have the same numbers. Constants for series 1 (MeI), 2(EtI) and 3(n-PrI) are given in ref.<sup>1</sup>

<sup>b</sup> - The great error is conditioned by an insignificant contribution of the substitution route into the total rate of the process (see the text).

(Table 1). The data about the MeI, EtI and n-PrI reactivity with amines<sup>1</sup> in the same solvent and the obtained data together provide a sufficient set for the estimation of the substituent effect in substrate as well as the effect of the substance and nucleophile structures on the process rate and character.

Alkyl iodides, containing branched alkyl substituents react with amines either by means of nucleophilic substitution (eq. (1)) or via the elimination, when alongside with the amine iodide hydrate or the tetra-ammonium salt the formation of the corresponding ethylene derivatives can be observed. In this case the values of the substituent rate constants (Table 1) have been obtained by means of subtracting the elimination rate constants which are determined independently<sup>2</sup> from the gross rate constants of the two reaction channels.

The Charton<sup>2</sup> constants  $\nu'$  proposed for the reactions of bimolecular nucleophilic substitution (eq. 2) were used while estimating the influence of alkyl radicals in the substance, since the steric constants of Taft  $E'_s$  give<sup>3</sup> the worst correlation (eq. 3)).

$$\log k = (-0.33 \pm 0.11) - (5.31 \pm 0.23)\nu' \quad (2)$$

$s = 0.13$ ;  $r = 0.995$ ;  $N = 6$  (all substrates are presented as  $RCH_2I$ , in case of i-PrI as  $R_2CHI$  and then  $\nu' = 2\nu'_{CH_3}$ ).

$$\log k = (-2.24 \pm 0.19) + (1.50 \pm 0.27)E'_s \quad (3)$$

$s = 0.46$ ;  $r = 0.938$ ;  $N = 5$  (no point for i-PrI).

The data on the reactivity of 6 alkyl iodides with all amines (97 constants) were treated according to eq. (4) by means of the multilinear regression analysis program (MLRA)<sup>4</sup>.

$$\log k = \log k_0 + \rho^{\Sigma} \Sigma \delta^{\Sigma} + \delta E_N + \psi' \nu' + \alpha E_N \nu' \quad (4)$$

where  $\Sigma \delta^{\Sigma}$  is the sum of the inductive substituent constants

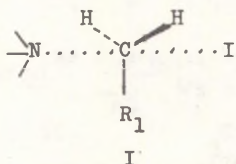
<sup>2</sup> The effect of reagents' structure on the rate of elimination reactions will be dealt with later.

<sup>3</sup> The correlation parameters of the reactivity of alkyl iodides with trimethylamine have been presented.

at the nitrogen atom in amine.  $E_N$  - steric effect of the amine as a whole;  $\nu'$  - the Charton steric constants for the alkyl substituents in substrate  $\rho^\pi, \delta, \psi', \alpha$  denote the susceptibility to the corresponding factor.

The results of data treatment are presented in Table 2. In order to check their confidence, the calculations were conducted at two risk levels - 0.01 and 0.05. Omission of the preticably deviating points does not lead to a significant change of the coefficients found. It seems to prove that the points are scattered quite at random.

The analysis of susceptibility parameters  $\rho^\pi, \delta, \psi'$  and  $\alpha$  calculated in the normalized scale permits to define contribution of each separate effect into the total process rate. Thus, the reaction is more susceptible to the steric screening of the reaction center in the substrate -  $|\psi'_{\text{norm}}| = 0.91$  (risk level 0.05). The vicinity of the nitrogen atom in nucleophile has a somewhat weaker effect -  $|\delta'_{\text{norm}}| = 0.74$ . It can evidently be explained with the fact that in transition state 1 the C-N bond is shorter than that of C-R<sub>1</sub>.



The substituent inductive effect at the nitrogen atom has still weaker influence:  $|\rho^\pi_{\text{norm}}| = 0.62$

In eq. (4) cross term  $\alpha_{E_N} \nu'$  whose presence is due to the amine-alkyl iodide interaction, is of decisive meaning.

The existence of cross terms in correlation equations refers to the possible existence of isoparametric points, i.e. such values of substituent constants in case of which there is no susceptibility to the corresponding effect<sup>5</sup>. We calculated the values of the  $\nu'$  and  $E_N$  parameters in case of which the reaction rate would not be susceptible to the steric proximity of the corresponding nitrogen atom in nucleophile or that of carbon atom in substrate. The phenomenon of isoparametricity should be observed if value  $\nu' = -0.99$  or  $E_N = 5.5$ , but unfortunately, this is experimentally unrealizable, as values  $\nu' > 0$ , and  $E_N < 0$ .

The existence of the cross term leads to certain conclusions about the transition state changes at the reaction co-

Correlation Parameters<sup>a</sup> of Rate Constants of Aliphatic Amines' Reactions with Alkyl iodides According to Eq. (4).

Table 2

N (number of points Risk level <sup>b</sup> )	log k <sub>o</sub>		ρ <sup>≠</sup>		δ		ψ'		α		s		R
	norm.	nat.	norm.	nat.	norm.	nat.	norm.	nat.	norm.	nat.	norm.	nat.	
96 <sup>c</sup> 0.01	0.87 (0.06)	1.30 (0.10)	-0.60 (0.03)	-2.24 (0.10)	0.76 (0.03)	0.74 (0.04)	-0.85 (0.01)	-4.02 (0.09)	0.14 (0.01)	0.80 (0.08)	0.14	0.21	0.989
81 <sup>d</sup> 0.05	0.85 (0.05)	1.24 (0.07)	-0.62 (0.02)	-2.24 (0.07)	0.74 (0.02)	0.73 (0.03)	-0.91 (0.01)	-4.10 (0.07)	0.13 (0.01)	0.74 (0.07)	0.11	0.16	0.994

<sup>a</sup> Standard deviations for regression coefficients are given in parenthesis.

<sup>b</sup> Risk level of the exclusion of deviating points according to the t - criterion.

<sup>c</sup> Point 12 from series 3<sup>1</sup> is excluded

<sup>d</sup> Points 8, 9, 14 series 2; points 4, 11, 12, 16, 17, 18, 19, 21 - series 3, points 4, 6 series 4, points 3 series 5, points 8 and 14 series 6 are excluded.

ordinate. The Thornton - O'Ferral model was applied (see, e.g.<sup>6</sup>). The  $\rho^{\ddagger}$  value does not practically depend on the substance type and solvent character<sup>1</sup>. It evidently shows the steady charge development at the nitrogen atom in transition state and, consequently, at the same time the ratio of  $k_I/k_{Br}$  increases during the transition from Me Hal to i-Bu Hal (Table 3), referring to the shift of the transition stage on axis 1-4 (fig. 1).

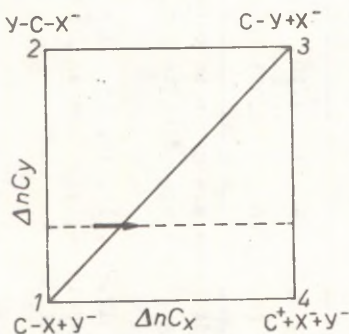


Fig.1. Arrow marks the expected shift of the transition state.

According to various data<sup>7,8</sup> the level of bond formation between the nitrogen atom and the reaction center in the transition state of Menshutkin reaction is approximately 30% (the dotted line in fig. 1). In order to more accurately establish the location of the transition state on the reaction co-ordinate, the second order kinetic isotopic effect was found in reaction (1). Thus for the interaction of the corresponding alkyl iodides with piperidine (acetonitrile, at 25°C)  $k_{CH_3I}/k_{CD_3I} = 0.905 \pm 0.025$  and  $k_{C_2H_5I}/k_{C_2D_5I} = 1.024 \pm 0.011$

Table 3  
Rate Constants ( $k \cdot 10^3, M^{-1}c^{-1}$ ) of Reactions of Methyl-  
and Isobutylhalides with Certain Amines in Acetonitrile  
at 25°C

Amine	Alkylhalides					
	MeI	MeBr	$\frac{k_I}{k_{Br}}$	i-BuI	i-BuBr	$\frac{k_I}{k_{Br}}$
Me <sub>3</sub> N	490 <sup>±</sup> ±12	279 <sup>±</sup> ±3	1.76	0.210 <sup>±</sup> ±0.020	0.0380 <sup>±</sup> ±0.0002	5.52
MeEt <sub>2</sub> N	102 <sup>±</sup> ±3	46.8 <sup>±</sup> ±1.2	2.18	0.0165 <sup>±</sup> ±0.0006	0.00252 <sup>±</sup> ±0.00008	6.55

There is a slight difference between the  $k_H/k_D$  ratio and 1.00, consequently, the transition state of the studied reaction is close to the symmetrical one. This transition state for MeI is situated above diagonal and for EtI below diagonal 1-3 (fig.1), corresponding to the synchronous disruption and the formation of the C-I and C-N bonds, as for the "pure" S<sub>N</sub>2 processes  $k_H/k_D < 1$  but for the reactions of S<sub>N</sub>1 type  $k_H/k_D > 1.2$ <sup>9</sup>. The change of the secondary kinetic isotope effect reflects the transition state shift perpendicularly with the reaction coordinate (directions 2-4) (see e.g.<sup>10</sup>), thus, in case of the  $k_H/k_D$  increase the transition state becomes more "loose".

This also explains the comparatively low reaction susceptibility towards the inductive effect of the substituents in the substrate which is likely to depend nonlinearly on their type.

Consequently, the increase in the volume of the substituents leads to a more productlike and loose transition state.

#### Experimental

Acetonitrile, amines and alkyl iodides were purified according to the known methods. Owing to the low reactivity of the studied set of alkyl iodides, the

measuring was carried out mostly according to the method of initial rates (see, e.g.<sup>11</sup>). In case of the amines having high reactivity ( $\text{Me}_3\text{N}$ , piperidine) the process obeys the pseudofirst kinetic order (with the excess of amine). The rate was monitored by means of argentometric potentiometric titration of the forming iodide ion.

The elimination rate constants were obtained analogously, the only difference being that the olephine accumulation rate was measured. Its absolute concentrations were determined according to the g.l.c method. Either acetonitrile or toluene were used as the inner standard. The analysis was conducted in a 0.3 x 150 cm column stainless steel, containing 7.5 % 1,2,3-tert( $\beta$ -cyanetoxy)propane on Chromaton H which was previously treated with KOH solution in methanol.

In order to reduce the possible errors, measuring of the rate constants in the course of determining the kinetic isotope effect was carried out in identical conditions ( $k_{\text{H}}$  and  $k_{\text{D}}$  were determined by means of one and the same amine, the current optic density for the non-deuterated and deuterated substances was registered in parallel, etc.). The value of the secondary isotope effect was found by the averaged  $k_{\text{H}}/k_{\text{D}}$  ratio, obtained from a series of parallel measurements(5-6).

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NUCLEOPHILIC CATALYSIS WITH TERTIARY AMINES  
IN FORMATION REACTIONS OF AMIDES OF ARYLSULFONIC  
ACIDS. CATALYTIC ACTIVITY OF 4-DIMETHYLAMINOPYRIDINE

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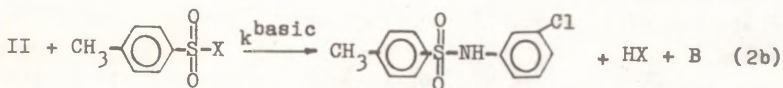
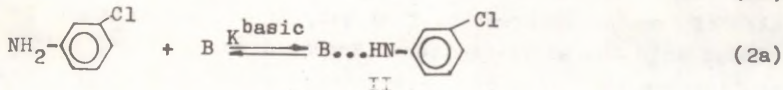
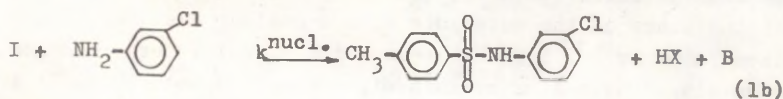
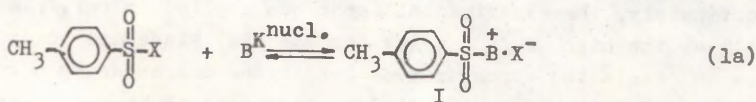
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The kinetics of 3-chloroaniline reactions with 4-toluenesulfochloride at 25°C in 50% nitrobenzene cyclohexane (B) mixture and with 4-toluenesulfo-bromide in benzene (C) catalyzed by means of 4-di-methylamino-, 3-methyl,3-bromopyridines and N-meth-yl- and N-(4-nitrophenyl)-imidazoles has been stud-ied in case of accumulation of the intermediates of the nucleophilic catalysis (the catalysis with 4-dimethylaminopyridine in reaction (B)) as well as in case of its absence. In these two series the catalytic activity ( $\log k_B$ ) obeys the Brønsted equation, including 4-dimethylaminopyridine ( $\beta=0.62$  (B) and 0.59 (C)). The comparison of the  $\log k_B$  for reactions B and C with the  $\log k_B$  for reaction A studied earlier (4-toluenesulfo-bromide with 3-chloroaniline in the 50% nitrobenzene and cyclo-hexane mixture at 25°C) enabled to calculate the catalytic rate constant value in reaction A, 4-di-methylaminopyridine being the catalyst. According to the Brønsted equation it correlates well with inclusion of data for a much larger set of pyridi-nes and imidazoles in reaction A (the total number of catalysts is 14,  $\beta=0.56$ ). In three reaction se-ries 4-dimethylaminopyridine whose nucleophilic

mechanism of catalysis has been proved by independent studies, has been used.

Our experiments have once more evidenced that this mechanism functions also in case of the N-substituted azoles and pyridines having weaker basicity. The insignificant role of the resonant stabilization effect in N-arylsulfonylpyridine or N-arylsulfonylimidazole intermediates in comparison with their carbonyl analogues was proved again.

Catalytic activity of N-aryl- and N-alkylimidazoles as well as the pyridines substituted in the nucleus has been studied earlier<sup>1-3</sup> during the arylaminolysis of the derivatives of arylsulfonic acids according to the model reaction of 4-toluenesulfobromide with 3-chloroamine in a 50% (volume) nitrobenzene (NB) - cyclohexane (CH) mixture at 25°C reaction A). For the majority of the examined catalysts 4 - dimethylaminopyridine included, the reaction has the first order for any reagent and catalyst. Such formal kinetics refers to the rapid formation of the unstable intermediate (I in case of the nucleophilic mechanism of catalysis, II in case of the general basic mechanism), which in the following slow stage ((1 b) or (2 b)) interacts with another reagent.



At that, within the studied concentration range, the equilibrium concentrations I or II are considerably smaller than those of the initial reagents' and catalysts' ones, i.e. no significant accumulation is observed in the mentioned intermediates.

As a result of this, the catalytic rate constant  $k_B$  ( $l^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$ ) is numerically equal to the product of the equilibrium constant and the second stage rate constant, i.e. to  $K^{\text{nucl.}} \cdot k^{\text{nucl.}}$  or  $K^{\text{basic}} \cdot k^{\text{basic}}$ . Thus, neither the formal kinetic regularities, nor the uniform Brønsted correlation  $\log k_B$  versus the catalysts'  $pK_a$  (the  $pK_a$  range is 1.4 - 7.0)<sup>2</sup> permit correctly to decide upon the use of the nucleophilic or general basic mechanism of catalysis, though we tended to prefer the former because of a number of yet unclear causes.

The omission of catalysts from the series under discussion is exemplified by 4-dimethylaminopyridine ( $pK_a$  9.60). It has been shown in<sup>4</sup> that the catalyzed model reaction A proceeds only according to the nucleophilic mechanism. In experimental conditions the quantitative accumulation of intermediate  $\bar{I}$  is observed ( $B = 4\text{-dimethylaminopyridine}$ ;  $X = \text{Br}$ ).

It refers to the entirely irreversible character of process (1a). Therefore, the information about the individual stage of nucleophilic catalysis (1b) has been got in<sup>4</sup>. Unfortunately, the experimental technique applied in ref.<sup>4</sup>, as well as the high  $K^{\text{nucl.}}$  value for the (1a) stage did not allow to create the concentration conditions guaranteeing a remarkable equilibrium shift (1a) to the left, as it might be in the cases of the catalysts with a smaller basicity, examined formerly<sup>1-3</sup>. For this reason the  $k_B$  value for reaction A catalyzed by 4-dimethylaminopiperidine was not found. It is also of immense interest to find out, if the constant is included into the above-mentioned Brønsted correlation, which would prove the unity of the mechanism of catalysis for the whole set of heterocyclic tertiary amines within the wide  $pK_a$  range.

With this goal in view we started the investigation into the formal kinetic regularities and catalytic activity of

4-dimethylaminopyridine, in two more series alongside the other amines (with a lower basicity) belonging to the set studied earlier in the course of reaction A. So, the interaction of 3-chloroaniline and 4-toluenesulfochloride in the 50% NB-CH mixture (reaction B) and 4-toluenesulfbromide in benzene (reaction C) was examined. There is ground to consider that the substitution of bromine for chlorine in a corresponding sulfohalogenide (see<sup>5</sup>) or a more polar solvent ( a 50% NB and CH mixture) for a non-polar (benzene) one allows to study process (1) with the participation of 4-dimethylaminopyridine in the conditions equalized with I, resulting from the decrease of the  $K^{\text{nucl}}$  value.

Reaction of 4-toluenesulfochloride with 3-chloroaniline in the 50% NB-CH Mixture (B).

The kinetics of non-catalytic interaction obeys the same regularities as the analogous processes observed earlier.<sup>6</sup> The effective second order rate constant calculated either from the integral formula or from the initial rates  $(dx/dt)_0$  depends linearly on the initial amine concentration  $b$  (a - initial concentration of acylating agent).

$$k_{\text{eff.}} = \frac{(dx/dt)_0}{a \cdot b} = k_2 + k_3 b \quad (3)$$

Constants  $k_2$  ( $l \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ ) and  $k_3$  ( $l^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$ ) characterize the bimolecular process and the catalysis of the second amine molecule.

The  $k_{\text{eff.}}$  values for different amine concentrations and the  $k_2$  and  $k_3$  values calculated according to eq.(3) are given in Table 1.

Table 1

The  $k_{\text{eff}}$ ,  $k_2$  and  $k_3$  Values for 4-Toluenesulfochloride  
Reaction with 3-Chloroaniline in the 50% NB-CH Mixture,  
at 25°C.

No	a mole . l <sup>-1</sup>	b mole . l <sup>-1</sup>	$k_{\text{eff}} \cdot 10^6$ l . mole <sup>-1</sup> . sec <sup>-1</sup>
1	0.6	0.05	0.68 ± 0.01
2	0.3	0.1	1.23 ± 0.06
3	0.1	0.2	2.31 ± 0.39
			$k_2 = (1.40 \pm 0.05) \cdot 10^{-7}$
			$k_3 = (1.084 \pm 0.004) \cdot 10^{-5}$

The catalysts used in reaction B were N-methylimidazole, N-(4-nitrophenyl)-imidazole, 3-methylpyridine and 4-dimethylaminopyridine. Comparison of the effective second order rate constants for reactions with the  $k_{\text{eff}}$  value in the presence of even the least active tertiary amine (Table 2) for the non-catalytic reactions according to eq. (3) speaks of the fact, that in all cases the rate of non-catalytic processes can be neglected. In case of the three catalysts the  $k_B$  values calculated by eq. (4):

$$k_B = \frac{(dx/dt)_0}{abm} = \frac{k_H}{m}, \quad (4)$$

remain constant, when changing the concentration of catalyst (m) and the initial concentrations of the reagents (a and b) (see Table 2, No 2-4). Consequently, there is no accumulation of intermediate product I under such concentration conditions.

However, for the 4-dimethylaminopyridine catalyzed reaction (Table 2, No 1) the kinetic law of rate (4) is observed within the range of values  $a \leq 12 \cdot 10^{-3}$  mole . l<sup>-1</sup> and  $m \leq 7 \cdot 10^{-3}$  mole . l<sup>-1</sup> only. At remarkably higher concentrations values a and m, the first order for the acylating agent and the catalyst is not valid. It may be conditioned by the intermediate accumulation in the reaction system, which can

Table 2

$k_H$  and  $k_B$  Values for 4-Toluenesulfochloride Reaction with 3-Chloroaniline  
Catalyzed by Tertiary Amines, in the 50% NB and CH Mixture at 25°C.

No	Concentration of reagents and catalysts, mole $\cdot$ l $^{-1}$			$k_H$	$k_B$
	a $\cdot$ 10 $^3$	b $\cdot$ 10 $^3$	m $\cdot$ 10 $^3$	l.mole $^{-1}$ . sec $^{-1}$	l $^2$ .mole $^{-2}$ .sec $^{-1}$
1	2	3	4	5	6
4 - dimethylaminopyridine					
				$k_H \cdot 10^3$	$k_B$
167	6.75	5.1	7.2	13.12 $\pm$ 0.52	1.82
	11.1	5.1	3.0	5.59 $\pm$ 0.35	1.86
	12.1	5.1	5.0	10.02 $\pm$ 0.22	2.00
	14.2	5.1	9.0	11.98 $\pm$ 0.52	1.33
	12.7	5.1	11.0	17.52 $\pm$ 0.46	1.59
	11.9	5.1	15.0	22.92 $\pm$ 1.06	1.53
	66.8	5.0	5.1	5.37 $\pm$ 0.29	1.05
	122.6	5.0	5.1	2.90 $\pm$ 0.08	0.57
N-methylimidazole					
2				$k_H \cdot 10^3$	$k_B \cdot 10^2$
	50	25	5	0.44 $\pm$ 0.02	8.8
	30	10	20	1.689 $\pm$ 0.002	8.4
	20	15	5	0.36 $\pm$ 0.03	7.2

$$\bar{k}_B = 1.90 \pm 0.06$$

Table 2 continued

1	2	3	4	5	6
	20	5	10	$0.66 \pm 0.04$	6.6
	10	20	15	$1.125 \pm 0.004$	7.5
					$\bar{K}_B = 7.7 \pm 0.4$
3	3 - methylpyridine				
				$k_H \cdot 10^4$	$k_B \cdot 10^3$
	100	10	20	$1.31 \pm 0.02$	6.6
	80	80	50	$3.54 \pm 0.92$	7.1
	20	20	80	$7.44 \pm 0.07$	9.3
					$\bar{K}_B = 7.7 \pm 0.8$
4	N - methylimidazole				
				$k_H \cdot 10^5$	$k_B \cdot 10^3$
	50	50	20	$5.21 \pm 0.07$	2.6
	50	5	10	$2.12 \pm 0.10$	2.1
	40	10	30	$7.62 \pm 0.10$	2.5
					$\bar{K}_B = 2.4 \pm 0.2$

be seen from curving of the charts and their entering the range separating the  $(dx/dt)_0/b$  values from a if  $m = \text{const}$  and  $(dx/dt)_0/b$  from  $m$  if  $a = \text{const}$  (fig. 1). For that reason the  $k_B$  value for reaction B catalyzed by 4-dimethylaminopyridine was estimated proceeding from the data for this concentration area, which had not undergone a considerable equilibrium shift (1a) towards I yet, thus, the law of rate (4) is observed.

4-Toluenesulfobromide Reaction with 3-Chloroamine in Benzene (C).

N-methylimidazole, 3-methylpyridine, 3-bromopiperidine and 4-dimethylaminopyridine were used as catalysts in reaction C. The  $k_H$  values as well as those of  $k_B$  calculated via them according to eq. (4) are presented in Table 3. Here the law of rate (4) is valid in all cases, 4-dimethylaminopyridine included. Thus, as to the reaction in benzene, no considerable accumulation of intermediate I takes place even in the last case.

The catalytic activity of the tertiary amines in reactions B and C is described by the Brønsted equations (5) and (6) respectively ( fig. 2, I, II)

$$\log k_B = (-5.62 \pm 0.27) + (0.62 \pm 0.04) pK_a \quad (5)$$

$$S = 0.13, \quad N = 4, \quad r = 0.996$$

$$\log k_B = (-5.12 \pm 0.56) + (0.59 \pm 0.08) pK_a \quad (6)$$

$$S = 0.4, \quad N = 4; \quad r = 0.98$$

As the given correlation equations are valid also if 4-dimethylaminopyridine whose nucleophilic mechanism of catalysis in reactions A<sup>4</sup> and B (the present paper) is proved kinetically, the latter concerns evidently also the weak N-heterocyclic bases, e.g. the N-substituted imidazoles and pyridines substituted in the nucleus.

The correlation between the  $\log k_B$  for reactions B and C, catalyzed by the tertiary amines versus the  $\log k_B$  used for the catalysis of reaction A by the same bases has been depict-

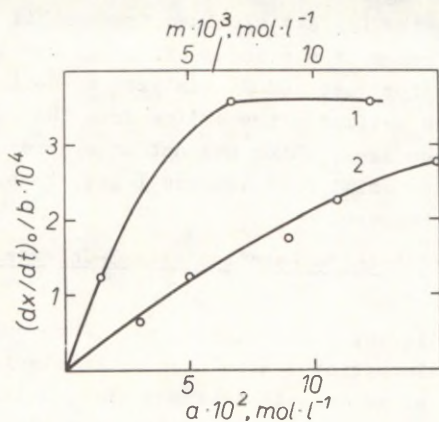


Fig. 1. Dependence of the  $(dx/dt)_0/b$  on  $a$  at  $m \approx 5 \cdot 10^{-3}$  mole.l $^{-1}$  (1) and on  $m$  at  $a \approx 1.2 \cdot 10^{-2}$  mole.l $^{-1}$  (2) for the 4-toluenesulfochloride reaction with 3-chloroaniline in the 50% NB and CH mixture, 4-dimethylaminopyridine being the catalyst, at 25°C.

Table 3  
 $k_H$  and  $k_B$  Values for 4-Toluenesulfochloride Reaction with 3-Chloroaniline in Benzene, Catalyzed by Tertiary Amines at 25°C

No	Concentration of reagents and catalyst mole.l $^{-1}$			$k_H$	$k_B$
	$a \cdot 10^3$	$b \cdot 10^3$	$m \cdot 10^3$	1.mole $^{-1}$ . sec $^{-1}$	1 $^2$ .mole $^{-2}$ . sec $^{-1}$
	1			4 - dimethylaminopyridine	
				$k_H \cdot 10^2$	
12	5.14	10	2.29 ± 0.08	2.29	
12	5.14	7.0	1.94 ± 0.05	2.77	
10,5	5.14	15.7	3.22 ± 0.09	2.05	
12	5.14	5.4	1.4 ± 0.05	2.59	
12	5.14	3.0	0.72 ± 0.04	2.41	
3	2.36	3.1	0.67 ± 0.02	2.16	
51.9	2.36	3.0	0.54 ± 0.01	1.79	
				$k_B = 2.29 \pm 0.12$	

Table 3 continued

2			N - methylimidazole	
			$k_H \cdot 10^2$	$k_B$
12.5	5	5	$0.18 \pm 0.02$	0.36
20	5	10	$0.28 \pm 0.04$	0.28
2.5	2.5	10	$0.28 \pm 0.04$	0.28
5.0	10.0	15	$0.32 \pm 0.03$	0.21
2.5	2.5	20	$0.57 \pm 0.03$	0.28
10.0	20	40	$1.1 \pm 0.2$	0.28
			$\bar{k}_B = 0.28 \pm 0.01$	
3			3 -methylpyridine	
			$k_H \cdot 10^4$	$k_B \cdot 10^2$
10	10	10	$1.0 \pm 0.3$	1.0
15	15.2	20	$1.2 \pm 0.3$	0.6
5	5.1	50	$5.0 \pm 0.2$	1.0
			$\bar{k}_B = (0.8 \pm 0.1) \cdot 10^{-2}$	
4			3-bromopyridine	
			$k_H \cdot 10^5$	$k_B \cdot 10^3$
10	20	40	$1.77 \pm 0.06$	0.44
10	24.6	60	$1.90 \pm 0.05$	0.32
5	16.1	80	$3.1 \pm 0.2$	0.39
			$\bar{k}_B = (0.38 \pm 0.04) \cdot 10^{-3}$	

ted in fig. 3. Supposing that 4-dimethylaminopyridine also satisfies these corrections, the  $k_B$  value of reaction A, catalyzed by this amine which had not been found earlier was calculated from the data for straight lines I and II in fig. 3;  $52 \pm 17 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$  (as the mean value from  $70 \pm 32 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$  and  $35 \pm 9 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$ , obtained, respectively, from the B and C reaction data).

According to the Brønsted equation this value correlates well with the inclusion of data concerning a wider pyridine set and imidazole<sup>1-3</sup> set in case of reaction A (see fig.2,

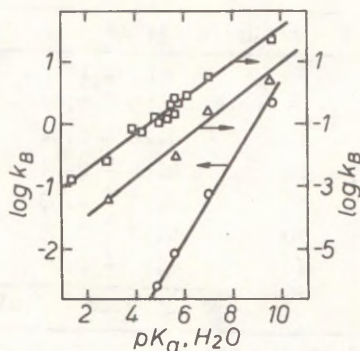


Fig. 2. Dependence of  $\log k_B$  on the  $pK_a$  of catalysts for the 3-chloroaniline reactions with 4-toluenesulfochloride (I) and 4-toluenesulfobromide (III)<sup>1-4</sup> in the 50% NB and CH mixture, as well as with 4-toluenesulfobromide in benzene (II) at 25°C.

Numeration of the I and II points corresponds to Tables 2 and 3; for III:

1. 4-dimethylaminopyridine; 2. N-methylimidazole; 3. 4-methylpyridine; 4. N-phenylimidazole; 5. 3-methylpyridine; 6. N-methylbenzeneimidazole; 7. isoquinoline 8. pyridine; 9. N-(4-nitrophenyl)imidazole; 10. 3-metoxypyridine; 11. N-phenylbenzeneimidazole; 12. N-(2,4-dinitrophenyl)imidazole; 13. 3-chloropyridine; 14. 3-cyanopyridine.

straight line III).

$$\log k_B = (-3.59) \pm 0.11 + (0.56 \pm 0.02)pK_A \quad (7)$$

$$S = 0.14; N = 14; r = 0.992$$

Thus, the present paper has established the following regularities: 1) the formation of arylsulfanylides of the unite Brønsted dependences in three reaction series while catalyzing with the N-substituted imidazoles and pyridines, substituted in the nucleus containing 4-dimethylaminopyri-

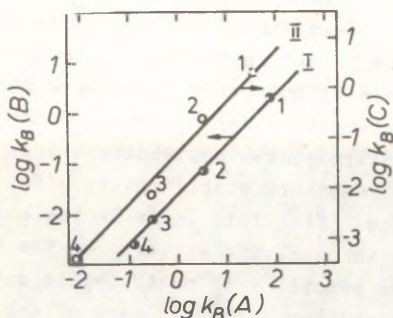


Fig. 3. Comparison of  $\log k_B$  values for the reactions catalyzed by tertiary amines.

A - 4-toluenesulfochloride reaction with 3-chloroaniline in the 50% NB and CH mixture at 25°C.

B - 4-toluenesulfochloride reaction with 3-chloroaniline in the 50% NB and CH mixture at 25°C. (I);

C - 4-toluenesulfochloride reaction with 3-chloroaniline in benzene at 25°C (II)

Numeration of points corresponds to Tables 2 and 3.

dine, (whose nucleophilic mechanism of catalysis was proved independently<sup>4,7,8</sup>) was observed; 2) close values of the Brønsted coefficients for all studied reactions (see eqs. (5) - (7)). These facts speak of the nucleophilic catalysis carried out by the *n*-heterolytic bases in the wide range of  $pK_a$  during the arylaminolysis of arylsulfonic acids in the aprotic atmosphere.

The data of the report prove the suppositions<sup>2</sup> about an insignificant role of the resonance stabilization effect of *N*-arylsulfonylimidazoles or -pyridines of the cation in intermediate I. The existence of the unite Brønsted correlation, containing *N*-alkyl- and *N*-phenylimidazoles, as well as pyri-

dines with electron-releasing substituents means that the connection of the  $\pi$ -systems of the heteroaromatic nucleus with the  $S=O^-$  bond is not realized. Its interaction with the vacant d-orbitals of sulphuric atoms does not either take place. Such interaction was observed in case of the analogous acyclic intermediates containing the carbonic acid residue, where the resonance stabilization effects are of essential importance.<sup>2,9,10</sup> This leads to the conclusion that the nucleophilic catalytic activity of the N-heterocyclic bases in the reactions of nucleophilic substitution at the sulphonylic sulphur atom, in case of approximately equal steric characteristics of the nucleophilic center, is determined by the basicity of the sulphur tertiary atom.

#### Experimental

4-toluenesulfobromide<sup>11</sup>, 4-toluenesulfochloride,<sup>12</sup> 3-chloroaniline<sup>13</sup>, 4-dimethylaminopyridine<sup>14</sup>, 3-methyl-<sup>15</sup>, 3-bromopyridine<sup>16</sup>, N-methylimidazole<sup>17</sup> and N-(4-nitrophenyl)imidazole<sup>18</sup> were synthesized and purified according to the known methods. Nitrobenzene and cyclohexane were purified as in<sup>6</sup>; benzene was dried over the metallic nitrogen and distilled over its fresh portion.

The reaction rate was monitored by the 3-chloroaniline decrease, which was registered using the potentiometric titration with the nitrogen nitrite<sup>13</sup>.

The intermediate constant values are characterized by the mean square duration; N denotes the number of points.

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NUCLEOPHILIC CATALYSIS WITH TERTIARY AMINES IN  
FORMATION REACTIONS OF AMIDES OF ARYLSULFONIC ACIDS.  
"ANOMALOUSLY" HIGH CATALYTIC ACTIVITY OF 1,4-DIAZA-  
BICYCLO- [2,2,2]- OCTANE

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Catalytic activity of 1,4-diazabicyclo -  
-[2,2,2]-octane (DABCO) in the formation re-  
actions of amides of arylsulfonic acids ex-  
emplified by 3-chloroaniline and 4-toluene-  
sulfobromide (A) and -chloride (B) in the  
50% (volume) nitrobenzene and cyclohexane mix-  
ture as well as with 4-toluenesulfobromide in  
benzene (B) at 25°C has been studied. The qui-  
nuclidone-3 catalysis in reaction A was also  
studied. It was shown that in a definite con-  
centration range of the reagents and the cat-  
alyst no accumulation of the intermediate prod-  
uct of the acylirating agent joining the catal-  
yst was observed. The DABCO catalytic activity  
in reaction A, B and C and quinuclidone-3 in  
reaction A turned out to be considerably great-  
er than had been expected according to the Brøn-  
sted " $\log k_B - pK_a$ " dependence for the  
studied reactions, the substituted pyridin-  
es N-alkyl- and N-phenylimidazoles being  
the catalysts. The  $\Delta \log k_B$  deviations for  
DABCO in case of reactions A, B and C  
are 1.59, 1.47 and 1.25, respectively. The  
observed behavior of DABCO differs from the

regularities characteristic to the similar reaction of benzoylchloride arylaminolysis in benzene, in case of which the activity of DABCO (quinuclidone-3 and quinuclidine) undergoes a negative shift from the analogous Brønsted correlation ( $\Delta \log k_B = 2.47$ ).

It has been established earlier<sup>1</sup> that 1,4-diazabicyclo - [2,2,2] - octane (DABCO) and quinuclidone-3 in the formation reaction of amides of arylsulfonic acids (in case of the interdependence of 4-toluenesulfobromide and 3-chloroaniline in the 50% (volume) nitrobenzene (NB) and cyclohexane (CH) mixture at 25°C (- reaction series A) are catalytically more active than follows from the Brønsted " $\log k_B - pK_a$ " dependence for a large set of heterocyclic tertiary amines as catalysts including substituted pyridines, N-alkyl- and N-phenylimidazoles<sup>1,2</sup>. Positive deviation from dependence  $\Delta \log k_B$  in case of DABCO is 1.6 according to the data<sup>1</sup>. This phenomenon is interesting as in the similar reaction of benzoylchloride arylaminolysis in benzene the mentioned amine as well as quinuclidone -3 and quinuclidine with close structures have a considerably lower catalytic activity than it follows from the analogous Brønsted dependence ( $\log k_B - 2.5$ )<sup>1,3</sup>.

In this connection the catalytic activity of DABCO in the sulfamide formation reactions is treated as anomalously high.

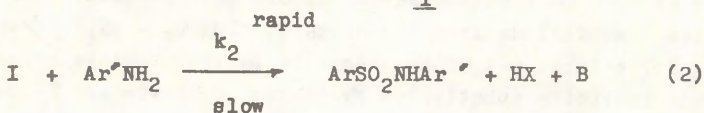
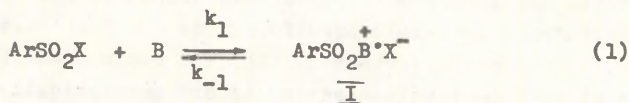
In Ref. 1 are presented the catalytic rate constants  $k_B$  for DABCO and quinuclidone - 3, obtained from a series of experiments with a slight variation of concentrations of reagents and catalysts. Consequently, the validity of the kinetic law in case of reactions A with participation of these catalysts should be established more firmly. In order to confirm the observed "anomaly", the effect on other reaction series should be found.

For that reason, in addition to<sup>1</sup> the data on catalytic activity of DABCO and quinuclidone-3 in reaction A as well as the results of the DABCO catalysis in the reactions of



3-chloroaniline with 4-toluenesulfochloride in the 50% NB and CH (B) mixture and 4-toluenesulfochloride in benzene (C) at 25°C are given.

### Results and Discussion

Proceeding from reasons given earlier<sup>1</sup> and arguments<sup>2,4,5</sup> it can be said that the nucleophilic mechanism of catalysis is most likely to occur in case of sterically uncomplicated tertiary amines.



In the present study: Ar = 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>;

Ar' = 3-ClC<sub>6</sub>H<sub>4</sub>; X = Br, Cl; B =  or 

In reactions with DABCO as a catalyst the high rate of the first stage  $k_1$  in (1) measured in chlorine methylene proved the validity of the scheme. This problem will be discussed in the next publication<sup>6</sup>. Unfortunately, it is methodically impossible to carry out the analogous measurements in the 50% NB and CH mixture. The results of comparison of the catalytic activities of DABCO ( $\log k_B \approx 2.9^1$ ) and 4-dimethylaminopyridine ( $\log k_B = 1.7^2$ ) with the  $pK_{BH}$  (2.2 and 2.81, p-fluorophenol, CCl<sub>4</sub><sup>7</sup>), characterizing the catalysts' ability of forming the hydrogen bond, are in correspondence with the catalysis mechanism.

In order to achieve a correct comparison of the catalytic activity of the aliphatic cyclic amines with the corresponding data for reactions A-C, given in<sup>2</sup>, we studied the rate when the accumulation of intermediate I was not observed. The most serious difficulties may crop up in case of

reaction A only, which is characterized by a good leaving group, and comparatively high solvent polarity. We tried to take it into consideration while determining the concentration range (the correlation between the concentrations of bromoanhydride and DABCO does not differ greatly from the stoichiometric one). In all other cases (reaction A, the catalysis with hinuclydine-3; reactions B and C, catalysis with DABCO) the possibility of the intermediate  $\text{I}$  accumulation sharply decreases (considerably lower basicity of quinuclidone-3; the worse leaving group in 4-toluenesulfochloride or the solvent (benzene) polarity is low).

The kinetic data were analyzed as in<sup>1</sup> proceeding from the initial rate  $(dx/dt)_0$ . It can be expressed as follows (if processes (1)-(2) go without the accumulation of intermediate  $\text{I}$ ):

$$(dx/dt)_0 = k_B a b m; \quad (3)$$

where  $k_B$  ( $\text{l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$ ), numerically equal to  $Kk_2$  (see schemes (1) - (2) is the rate constant of the catalytic process;  $a$ ,  $b$ ,  $m$  ( $\text{mole} \cdot \text{l}^{-1}$ ) denote the acylating agent, arylamine or catalyst concentration.

Later on we shall use the values of the second order effective rate constants.

$$k_H = (dx/dt)_0 / a \cdot b = k_B m \quad (4)$$

The  $k_H$  values for all studied reactions at various concentrations are presented in Table 1. Their analysis according to (4) shows that the law of rate (3) holds for reactions A and B (see Fig. 1, straight lines 1-3). At the same time, for the reaction in benzene (C) the  $k_H$  values curvilinearly depend on the catalyst concentration (Fig. 1, curve 4), indicating that the reaction order according to the catalyst exceeds unity. According to<sup>8</sup>, such formal - kinetical rate law enables to test the nucleophilic mechanism of catalysis in case of the processes like (1)-(2), which proceed under stationary conditions. If the order according to the catalyst exceeds the unity, stage  $k_2$  in scheme (2) can be realized by two parallel routes: bimolecular interaction of

intermediate  $\bar{I}$  with arylamine and general basic catalysis with the free basicity as a catalyst.

Usually, in such cases  $k_H$  is expressed

$$k_H = k_B m + k_B' m^2 \quad (5)$$

or

$$(k_H)/m = k_B + k_B' m \quad (6)$$

The experimental data (Table 1, Nos 19-23) can be satisfactorily described by this equation (Fig. 2).

The comparison of the  $\log k_B$  values (see Table 1) with those of Brønsted correlations for reactions A-B<sup>2</sup> catalyzed with heterocyclic tertiary amines, demonstrates that in all cases the positive deviation from the indicated straight lines of cyclic aliphatic amines is observed. The  $\Delta \log k_B$  values are 1.59 (A, DABCO), 0.97 (A, quinuclidone-3), 1.47 (B, DABCO) and 1.25 (C, DABCO).

Thus, there are no doubts about the fact that the anomalously high catalytic activity of DABCO (and, evidently, of similar cyclic aliphatic amines) is characteristic of the arylaminolysis of the halogenides of arylsulfonic acids in the protoinert atmosphere. Its manifestation in reactions A-B shows that it is not connected with the substrate's structure but with the nature of the medium. Evidently, this fact is the result of the higher nucleophilicity of nitrogen atom in the DABCO-type cyclic amines with respect to the electrophilic sulfonic center.

It is of interest, from this point of view to monitor the rate of individual stages  $k_1$  and  $k_2$  in schemes (1) - (2) including amines B of aliphatic and heterocyclic series. The results of these studies will be reported in the future.

#### Experimental

4-Toluenesulfobromide<sup>9</sup>, 4-toluenesulfochloride<sup>10</sup>, 3-chloroaniline<sup>11</sup> applied for kinetic measurements were purified according to the known methods. DABCO and quinuclidone were repeatedly sublimated in vacuum and kept in vacuum-desiccator at P<sub>2</sub>O<sub>5</sub>. Nitrobenzene and cyclohexane were purified as m<sup>12</sup>

Table 1

$k_H$  and  $k_B$  Values for Reactions of 3-Chloroaniline with 4-Toluenesulfobromide (A) and - Chloride (B) in the 50% Nitrobenzene and Cyclohexane Mixture and with 4-Toluenesulfobromide in Benzene (B), Catalyzed with Cyclic Aliphatic Amines, at 25°C.

No	$a \cdot 10^3$ mole $\cdot$ l $^{-1}$	$b \cdot 10^3$ mole $\cdot$ l $^{-1}$	$m \cdot 10^3$ mole $\cdot$ l $^{-1}$	$k_H \cdot 10^2$ l $\cdot$ mole $^{-1}$ .sec $^{-1}$	$k_B^*$ l $^2$ .mole $^{-2}$ .sec $^{-1}$
Reaction A, catalyst DABCO					
1.	5	0.25	0.3	34 $\pm$ 1	854 $\pm$ 57
2.	4	0.55	0.3	53 $\pm$ 1	S = 0.21;
3.	1	0.5	0.6	53 $\pm$ 1	N = 10;
4.	4	1.7	0.64	71 $\pm$ 7	r = 0.983
5.	1	0.45	0.73	84 $\pm$ 1	
6.	1	1.5	0.8	118 $\pm$ 12	
7.	1	0.64	0.83	81 $\pm$ 2	
8.	2.5	0.5	1	169 $\pm$ 2	
9.	2.5	0.24	1.5	238 $\pm$ 12	
10.	2.5	1	2.4	384 $\pm$ 12	
Reaction A, catalyst quinuclidone-3					
11.	3	3	0.83	2.73 $\pm$ 0.01	25.6 $\pm$ 0.1
12.	2	2	3	8.15 $\pm$ 0.25	S = 8 $\cdot$ 10 $^{-4}$ ;
13.	2.5	2.5	6.25	16.6 $\pm$ 0.2	N = 4;
14.	5	5	8	21.1 $\pm$ 0.6	r = 0.999
Reaction B, catalyst DABCO					
15.	11.4	5.2	2.9	11.0 $\pm$ 1.7	20.3 $\pm$ 0.5
16.	12.3	5.2	4.2	15.8 $\pm$ 1.2	S = 0.0042
17.	14.9	5.11	6.0	22.9 $\pm$ 5.0	N = 4;
18.	12.0	5.2	8.1	32.1 $\pm$ 1.4	r = 0.999
Reaction C, catalyst DABCO					
19.	1	2.5	0.6	4.0 $\pm$ 0.1	21 $^{\pm}$ 4;
20.	3	2.9	1.2	9.3 $\pm$ 0.2	$K_B$ = 17500 $\pm$ 2200
21.	2.5	1	2.2	24.3 $\pm$ 0.3	S = 3.6;
22.	20.9	2.4	2.4	31.6 $\pm$ 1.7	N = 4;
23.	11	2.4	2.5	32.6 $\pm$ 2.7	r = 0.978

\* statistical factor 2 has been taken into consideration when calculating the  $k_B$  of DABCO.

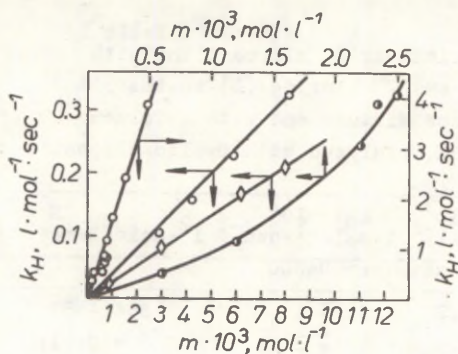


Fig. 1. Dependence of  $k_H$  (catalyst DABCO (1,3,4) and quinuclidone-3 (2)) on  $m$  for reactions of 3-chloroaniline with 4-toluenesulfobromide (1,2) and 4-toluenesulfochloride (3) in the 50% NB and CH mixture, and with 4-toluenesulfobromide in benzene (4) at 25°C.

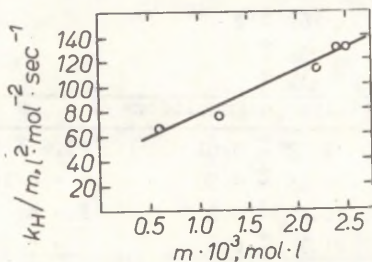


Fig.2. Dependence of  $k_H/m$  on  $m$  for the 4-toluenesulfobromide reaction with 3-chloroaniline in benzene (catalyst - DABCO), at 25°C.

Benzene was dried over metallic sodium and distilled over the fresh amount of the latter.

The reaction rate was monitored by the decrease of 3-chloroaniline which is determined according to the potentiometric titration with sodium nitrite in the medium of hydrochloric acid.

The integral values of constants are characterized by the mean square deviation;  $N$  denotes the number of points.

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NUCLEOPHILIC CATALYSIS WITH TERTIARY AMINES  
IN FORMATION REACTIONS OF AMINES OF ARYLSULFONIC  
ACIDS. FIRST STAGE KINETICS AND MECHANISM.

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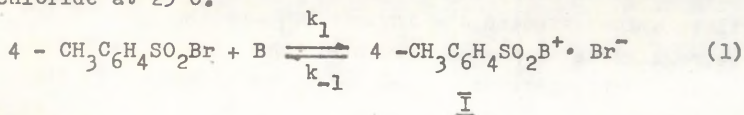
The interaction rate of 4-toluenesulfobromide with aliphatic amines (tertiary ones included) , pyridines, imidazoles and arylamines in methylene chloride at 25°C has been studied. The obtained data and the results published earlier concerning the process of aminolysis of the substrate in nitrobenzene were analyzed in terms of the Brønsted equation. It is shown that in case of equal basicity ( $pK_a$ ,  $H_2O$ ) and close steric characteristics ( $E_N$ ) amines of different classes form the following order of reactivity: cyclic aliphatic amines of quinuclidine series  $>$  imidazoles, pyridines  $>$  secondary aliphatic amines (piperidine)  $\geq$  arylamines  $\gg$  primary aliphatic amines (benzylamines). The observed order cannot be explained by the anomalies of nucleophilic reactivity of amines belonging to various classes but by the anomalies of their basicity in water. This standpoint refers to the existence of the united Brønsted correlation, including pyridines, N-substituted imidazoles and tertiary aliphatic amines,  $K_p$  denoting the equilibrium constant values for the processes under discussion. The reasons for the higher ( $\approx 10^7$  times) reactivity of pyridine N-oxides with regard to 4-toluenesulfobro-

mide in comparison with the pyridine bases of equal basicity in weakly solvating media have been discussed.

The first requirement of the nucleophilic mechanism of catalysis in the course of the aminolysis of arylsulfonic acids' derivatives in non-aqueous conditions in the wide range of the catalysts structure (tertiary aliphatic amines, N-substituted imidazoles, pyridines and their N-oxides) was satisfied.

It follows from some previous reports<sup>1,2</sup> that the catalytic activity of substituted pyridines N-alkyl- and N-phenylimidazoles obeys the united Brønsted equation in the arylaminolysis reactions of chloro- and bromoanhydrides of arylsulfuric acids in the conditions of low polarity. The reactions proceed without the accumulation of the nucleophilic catalysis intermediates, i.e. N-arylsulfonylammonium salts. At the same time cyclic aliphatic amines of the quinuclidine series are more active<sup>3</sup> in case of equal basicity. These regularities remarkably differ from those of the analogous arylaminolysis of benzoic acid chloroanhydride in benzene<sup>1</sup>. In the latter case various tertiary amines form separate Brønsted correlations. At equal basicity the following sequence is observed: N-phenylimidazole > N-alkylimidazole > pyridines > cyclic aliphatic amines.

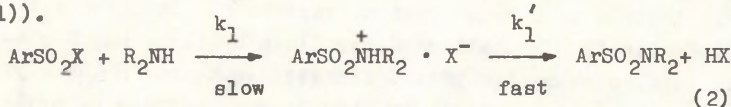
In order to find out the reasons for the difference, separate steps of the catalytic mechanism were studied. The present paper deals with the kinetics of the first stage of nucleophilic catalysis, exemplified by the interaction of 4-toluenesulfobromide and tertiary amines B in methylene chloride at 25°C.



4-dimethylaminopyridine (DMAP) N-methylimidazole, imidazole  
 In case of these amines the tertiary nitrogen atom in position 3 is attacked. Nevertheless, process (1) cannot be practically turned into the product's stabilization power via rapid separation of proton from the nitrogen atom in position 1 (see the products in Eq. (2)).

benzimidazole<sup>\*</sup>, quinuclidine, quinuclidone-3, 1,4-diaza-bicyclo- [2,2,2] -octane (DABCO), N-methylformoline, methyl-diethylamine and triethylamine were applied as B.

As the proton transfer in the aminolysis reaction of arylsulfonic acids' halogenhydrates is not included into the rate of determining the stage<sup>4</sup>, the data on the reactivity of primary and secondary amines ( $k_1$  in (2)) can be analyzed together with the corresponding results of tertiary ( $k_1$  in (1)).



For that reason also the kinetics of 4-toluenesulfobromide reactions with piperidine and benzylamine were studied.

#### Results of Kinetic Measurements

In all cases the reaction rate was studied under the pseudofirst order conditions at the amine excess.

The rate constant of pseudofirst order  $k_H$  ( $\text{c}^{-1}$ ) for reactions with participation of tertiary amines (Table 1, Nos 3, 4, 8-13) can be described by the equation<sup>5</sup>:

$$k_H^{(1)} = k_{-1} + k_1 [\text{B}], \quad (3)$$

where  $k_1$  ( $1 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ ) and  $k_{-1}$  ( $\text{sec}^{-1}$ ) are the rate constants of the direct and inverse processes; B ( $\text{mole} \cdot \text{l}^{-1}$ ) denotes the amine concentration.

It should be mentioned that in case of the majority of tertiary amines studied the inverse process ( $k_{-1}$ ) turns out to be negligible in the experimental conditions, i.e. the  $k_{-1}$  value is found with errors, observed already with the  $k_{-1}$  itself.

For practically irreversible reactions (Table 1, Nos 1, 2, 7, 14) the pseudofirst order rate constant  $k_H^{(1)}$  is found according to the following equation (cf.6):

$$k_H^{(1)} = k_1 [\text{B}] + k_2 [\text{B}]^2 \quad (4)$$

Table 1

Rate Constant of 4-Toluenesulfobromide Interaction with Various Amines in Methylene Chloride  
at 25°C

No	Amines	pK <sub>a</sub> H <sub>2</sub> O 25°C	Range [B] · 10 <sup>3</sup> mole · l <sup>-1</sup>	Σσ <sup>*</sup>	-E <sub>N</sub> <sup>7,9</sup>	k <sub>1</sub> , l · mole <sup>-1</sup> · sec <sup>-1</sup>	r <sup>a</sup>	S <sub>0</sub> <sup>a</sup>	N
1.	Benzimidazole	5.53	2-20	-	0.24 <sup>b</sup>	0.015 <sup>±</sup> 0.004 (2.30 <sup>±</sup> 0.32) <sup>c</sup>	0.962	0.005	6
2.	imidazole	7.00	1-100	-	0.24 <sup>b</sup>	0.58 <sup>±</sup> 0.03 (15.1 <sup>±</sup> 0.7) <sup>c</sup>	0.994	0.057	6
3.	N-methylimi- dazole	7.00	10-75	-	0.24 <sup>b</sup>	0.80 <sup>±</sup> 0.08	0.984	0.004	5
4.	DMAP	9.60	1-20	-	0.24	118 <sup>±</sup> 3	0.997	0.060	11
5.	3-chloroaniline	3.34		-	0.38 <sup>d</sup>	~2 · 10 <sup>-6</sup> <sup>e</sup>			
6.	4-methoxyaniline	5.29		-	0.38 <sup>d</sup>	~2 · 10 <sup>-4</sup> <sup>f</sup>			
7.	benzylamine	9.34	5-10	1.2	0.38 <sup>d</sup>	0.449 <sup>±</sup> 0.008	0.999	0.0003	3
8.	quinuclidone - 3	7.2	1-20	0.73 <sup>g</sup>	1.3	27.7 <sup>±</sup> 4.2	0.958	0.066	6
9.	DABCO	8.8	0.6-10	0.39	1.3	743 <sup>±</sup> 38 <sup>h</sup>	0.990	0.69	10
10.	quinuclidine	10.95	5-21	-0.35	1.3	4200 <sup>±</sup> 500	0.985	6.0	4
11.	N-methylmorpholine	7.38	1-50	0.69	3.0	0.229 <sup>±</sup> 0.026	0.980	0.001	5
12.	methyldiethylamine	10.43	5-57	-0.20	3.0	1.39 <sup>±</sup> 0.05	0.997	0.002	6
13.	triethylamine	10.65	5-22	-0.30	3.8	0.201 <sup>±</sup> 0.021	0.989	0.0003	4
14.	piperidine	11.22	0.6-17	0.31	0.79 <sup>d</sup>	220 <sup>±</sup> 4	0.999	0.07	7
15.	DMAP N-oxide	3.88			0.38 <sup>j</sup>	(2.47 <sup>±</sup> 0.16) · 10 <sup>4</sup> <sup>i</sup>			

- a) Correlation coefficients  $r$  and general dispersion  $S_0$  for Nos 1 and 2 belong to the data treatment according to Eq. (5), for Nos 7 and 14 to that according to Eq. (4) if  $k_2 \cdot [B]^2 = 0$  and in case of the rest of amines according to Eq. (3).
- b) Steric characteristics of the tertiary nitrogen atom in imidazole seem to be quite similar to those of pyridines. It follows from the united Brønsted correlation for the catalysis with pyridines and N-substituted imidazoles of the reaction under discussion<sup>2</sup>.
- c) Values  $k_2$  ( $l^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$ ) were calculated according to (5).
- d) Equal to the  $E_S$  value for isosteric radical<sup>8</sup>
- e) Calculated on the basis of  $k_1 \approx 2 \cdot 10^{-4}$  (Table 1, 6) and the  $\rho$  values by the arylamine structure  $-2.94$ <sup>10</sup>.
- f) Calculated from  $k_1 = 7.1 \cdot 10^{-4}$  for 4-nitrobenzenesulfo-bromide reactions with 4-metoxyaniline in  $\text{CH}_2\text{Cl}_2$  at  $25^\circ \text{C}$ ,  $\rho^0$  was calculated according to the substrate structure  $+0.6$ <sup>11</sup>.
- g) Calculated by equation  $\text{p}K_a = 9.55 - 3.23 \sum \sigma^* 12$ .
- h) Statistic correction 2 was taken into consideration.
- i) For reactions with benzenesulfo-bromide<sup>13</sup>.
- j) The  $E_N$  value for the DMAP N-oxide is evidently almost similar to the  $E_N$  value for "isosteric" benzene radical<sup>8</sup>.

where  $k_2$  ( $l^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$ ) is the rate constant of the process catalyzed by the second molecule of amine B. Constants  $k_1$  and  $k_2$  were then calculated as follows:

$$(2) \quad k_H = k_1 + k_2 [B], \quad (5)$$

where  $k_H$  ( $l \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ ) denotes the second order rate constant.

Member  $k_2[B]$  does not remarkably contribute to the total rate (5) within the concentration range studied in case of reactions with participation of benzylamine and piperidine.

Rate constants  $k_1$  calculated by Eqs. (3) and (5) are given in Table 1, as well as the  $k_1$  values for 4-toluenesulfo-bromide reactions with a number of arylamines (Nos 5, 6) and

#### 4-dimethylaminopyridine N-oxide (No 15).

#### Discussion

The reactivity of amines characterized by rate constant  $k_1$  is compared with their basicities in Fig. 1A. The comparison of the Brønsted straight lines in Fig. 1A with the results of analogous processes in nitrobenzene containing a wide range of N-substituted imidazoles, arylamines and benzylamines (Fig. 1B)<sup>14</sup> leads to the fact that the amines of different classes having practically equal steric characteristics form separate Brønsted correlations. In case of equal basicity their reactivity decreases as follows: cyclic aliphatic amines of quinuclidone series (quinuclidineamines;  $-E_N = 1.3$ ) > imidazoles, pyridines ( $-E_N = 0.24$ ) > secondary aliphatic amines (piperidine,  $-E_N = 0.79$ )  $\gg$  arylamines ( $-E_N = 0.38$ )  $\gg$  primary aliphatic amines (benzoyl- amines  $-E_N = 0.38$ ). High reactivity of quinuclidineamines was a surprising fact, as the situation in the similar aminolysis process of carbonic acids was quite different<sup>15,16</sup>.

From Fig. 2 one can see that in case of equal basicities the reactivity of different amines decreases as follows: imidazoles > pyridines > primary and secondary amines > quinuclidine amines. The comparison of data on the substitution at the carbonylic and sulfonylic centers suggests the anomalously high reactivity of cyclic aliphatic amines in the last case.

Still, treatment of the data on aliphatic amines, the sterically complicated ones included (Table 1, Nos 8-14<sup>\*</sup>) according to the equation of Bogatkov - Popov - Litvinenko<sup>17</sup>

$$\log k = \log k_0 + \rho^* \sum \sigma^* + \delta E_N \quad (6)$$

leads to the same correlation indicators (Table 2, No 1) as in case of the aminolysis reaction of other substrates, if the latter are to be included into the correlation data for quinuclidine amines (Table 2, Nos II - IX).

\* Benzylamine (Table 1, No 7) will not suit the correlation (6) ( $\Delta \log k_1 = -2.7$ ). There are references about the unsatisfactory correlation of the data on the benzylamine reactivity also in some other reaction series (see, e.g.<sup>17</sup>).

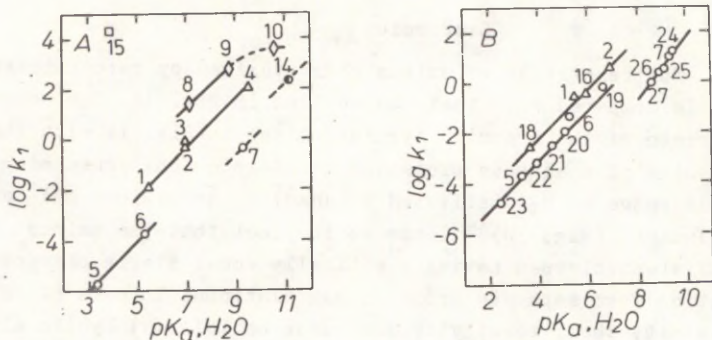


Fig. 1. Dependence of  $\log k_1$  on the  $pK_a$  of amines for the 4-toluenesulfobromide aminolysis reaction in methylene chloride (A) and in nitrobenzene (B) at 25°C. Numeration of points corresponds to Table 1. In addition to that: 16 - 5,6 - dimethylbenzimidazole, 17 - 4(5) - phenylimidazole, 18 - 4(5) - bromoimidazole; 19-23- $RC_6H_4NH_2$ : R =  $N(CH_3)_2$  (19), 4- $CH_3$  (20), H (21), 4-Cl (22), 3- $NO_2$  (23); 24-27 -  $RC_6H_4CH_2NH_2$ : R = 4- $OCH_3$  (24), 4-Cl (25), 3-Cl (26), 3- $NO_2$  (27).

Thus, the conclusion can be drawn that there are no anomalies in the reactivity of aliphatic amines relative to the sulfonyl sulphuric atom.

It is known<sup>12,22</sup> that the correlation of the amine basicities in water and in organic medium with parameter  $\sum \sigma^*$  characterizing the substituent inductive effect at the nitrogen atom results in the separate straight lines for the primary, secondary and tertiary amines. This is connected with different contributions of the ammonium cations solvation effect (the number of their N-H bonds differ) as well as some other effects, whose nature still remains unclear.

In the reaction series studied the primary aromatic

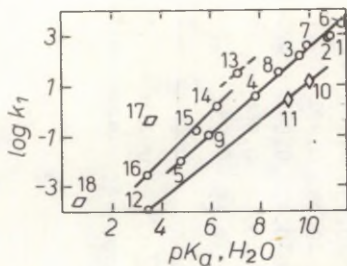


Fig. 2. Dependence of  $\log k_1$  on  $pK_a$  of amines for the 4-nitrophenylacetate aminolysis in water:  $\mu = 1$  (KCl) at  $25^\circ\text{C}$ <sup>16</sup>

- 1 - ethylamine, 2 - propylamine, 3 - methoxyethylamine, 4 - carboethoxyethylamine, 5 - aniline, 6 - piperidine, 7 - piperazine, 8 - morpholine, 9 - piperazine- $\text{H}^+$ , 10 - quinuclidine-3, 11 - DABCO, 12 - DABCO $\text{H}^+$ , 13 - imidazole, 14 - 4-methylpyridine, 15 - pyridine, 16 - nicotineamide, 17 - 4-aminopyridine, N-oxide, 18 - pyridine, N-oxide

amines' and tertiary heteroaromatic amines' (imidazoles, pyridines) reactivity has taken the intermediate position between the aliphatic amines of different classes (Fig. 1). Consequently, a suggestion can be made that the polarizability effect hardly contributes to the amines' reactivity. The conclusion made earlier<sup>14</sup> about the significance of the effect's contribution into the nucleophilic reactivity of arylamines and imidazoles, relative to the sulfonylic center should be considered somewhat doubtful. The existence of separate Brønsted correlations in Fig. 1 does not seem to be connected with the reactivity of different amines but with their anomalous basicity in water<sup>12,22</sup>.

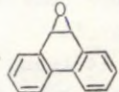
The sequence of the amines' reactivity during substitution at the carboxylic carbon atom (see Fig. 2) can be linked with<sup>(23, p.85)</sup> the resonant stabilization effect manifesting itself with aromatic and heteroaromatic amines due

Table 2

Correlation Parameters for Reaction Series Including Aliphatic and Other Amines  
According to Eq. (6)<sup>a</sup>

Reaction Series <sup>b</sup>	Amines, included into correlation <sup>B</sup>	log k <sub>o</sub>	$\rho^{\ddagger}$	$\sigma$	R	S <sub>o</sub>	S <sub>o</sub> , %	Ref.
I	8,14,15,18,20,21,23	4.64 $\pm$ 0.52	-1.42 $\pm$ 0.53	1.50 $\pm$ 0.21	0.963	0.567	13.4	
II <sup>c</sup>	12,15,20,21,23	3.42 $\pm$ 0.69	-2.49 $\pm$ 0.76	1.42 $\pm$ 0.32	0.956	0.605	15.4	18
III	2-5,8-11,22,23,25	6.50 $\pm$ 0.19	-1.12 $\pm$ 0.09	0.59 $\pm$ 0.18	0.977	0.159	8.0	16
IV	2-5,8-11,23,24,26	5.31 $\pm$ 0.28	-1.28 $\pm$ 0.15	0.57 $\pm$ 0.24	0.955	0.274	10.5	16
V	2-5,8-11,22-24	7.26 $\pm$ 0.60	-2.34 $\pm$ 0.27	4.63 $\pm$ 0.53	0.967	0.61	8.1	16
VI	2-5,8-11,22-24	3.81 $\pm$ 0.26	-1.96 $\pm$ 0.12	3.84 $\pm$ 0.23	0.991	0.27	5.0	16
VII	8,9,11,20,22,23	2.40 $\pm$ 0.55	-1.33 $\pm$ 0.24	2.98 $\pm$ 0.47	0.967	0.204	13.6	19
VIII	14,15,17-19,23	0.58 $\pm$ 0.36	-0.66 $\pm$ 0.26	0.79 $\pm$ 0.12	0.968	0.245	11.1	20
IX	1,2,6-8,12,16,20,22	1.61 $\pm$ 0.24	-1.81 $\pm$ 0.24	0.87 $\pm$ 0.15	0.952	0.254	15.2	21

<sup>a</sup> E<sub>N</sub> and  $\Sigma\sigma^{\ddagger}$  values are taken from references 7,8,9,17  $\Sigma\sigma^{\ddagger}$  for Nos 4,5,10,21,22,24 are calculated according to equations from 12 for the primary, secondary and tertiary amines

- b
- I.  $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{Br}$ ;  $\text{CH}_2\text{Cl}_2$ ,  $25^\circ\text{C}$ ;
- II.  $\text{C}_6\text{H}_5\text{C}(=\text{O})\text{Cl}$ ; reaction catalysis with 3-chloroaniline in benzene at  $25^\circ\text{C}$ ;
- III.  $\text{CH}_3\text{C}(=\text{O})\text{ON}^+\langle\text{C}_6\text{H}_4\rangle^-\text{OCH}_3$ ;  $\text{H}_2\text{O}$ ,  $\mu = 1.0$  (KCl),  $25^\circ\text{C}$ ;
- IV.  $\text{CH}_3\text{C}(=\text{O})\text{O}-\langle\text{C}_6\text{H}_3(\text{NO}_2)\rangle-\text{NO}_2$ ;  $\text{H}_2\text{O}$ ,  $\mu = 1.0$  (KCl),  $25^\circ\text{C}$ ;
- V.  $\text{CH}_3\text{C}(=\text{O})\text{O}-\langle\text{C}_6\text{H}_4(\text{NO}_2)\rangle-\text{NO}_2$ ;  $\text{H}_2\text{O}$ ,  $\mu = 1.0$  (KCl),  $25^\circ\text{C}$ ;
- VI.  $\text{CH}_3\text{C}(=\text{O})\text{O}-\langle\text{C}_6\text{H}_5\rangle$ ;  $\text{H}_2\text{O}$ ,  $\mu = 1.0$  (KCl),  $25^\circ\text{C}$ ;
- VII.  $\text{SO}_2-\text{SO}_2$ ; 60% hydrous dioxane,  $25^\circ\text{C}$ ;
- VIII.  $\text{Cl}-\text{C}(=\text{O})-\langle\text{C}_6\text{H}_4\rangle-\text{N}-\text{C}_6\text{H}_5$ ; acetone - water (6:4)  $45^\circ\text{C}$ ;
- IX. ;  $\text{H}_2\text{O}$ ,  $\mu = 1.0$  (KCl),  $30^\circ\text{C}$ ,

- B
- 1 - methylamine, 2 - ethylamine, 3 - propylamine; 4 - 2-methoxyethylamine, 5 - ethyleneamine- $\text{H}^+$ ; 6 - dimethylamine, 7 - benzylamine, 8 - piperidine, 9 - piperazine, 10 - piperazine- $\text{H}^+$ , 11 - morpholine, 12 - trimethylamine, 13 - dimethylethylamine, 14 - methyldiethylamine, 15 - triethylamine, 16 - N-methylpiperidine, 17 - N-ethylpiperidine, 18 - N-methylmorpholine, 19 - N-ethylmorpholine, 20 - quinuclidine, 21 - quinuclidone-3, 22 - quinuclidinole-3, 23 - 1,4 - diazabicyclo-[2,2,2] - octane (DABCO), 24 - DABCO- $\text{H}^+$ , 25 - pyridine, 26 - 4-methylpyridine.

to the  $p-\pi$ - interaction of the multiple  $\text{C}=\text{O}$  bond substrate and the  $\pi$ - system of the attacking nucleophile. Evidently, the effect's contribution depends on the transition state structure (of the type of reagent or product or similar to the tetrahedral intermediate).

The data of Fig. 1A show that the DMAP<sup>13</sup> N-oxide reacts  $\approx 10^9$  times faster than arylamine and  $10^7$  times faster than pyridine having similar basicity. According to this we might speak of the "supernucleophilicity" of pyridine N-oxides relative to the sulfonylic atom of sulphur in such solvents as methylene chloride. Unfortunately, there is no data on the reactivity of the pyridine N-oxides with the other substrates, particularly with the derivatives of carbonic acids in non-aqueous media. Literature gives only one result<sup>(23,p.79),24</sup> about the rate of the pyridine N-oxides reaction with 4-nitrophenylacetate in water. In case of the pyridine N-oxides and 4-aminopyridine the deviation of points from the Brønsted straight line is (according to the data for pyridine basicities) only  $\approx 1$  and  $\approx 2$  logarithmic units, respectively. If this result really refers to the nucleophilic attack of N-oxides and not to the general basic catalysis of hydrolysis, there is ground to presume that the "supernucleophilicity" of N-oxides in the reaction observed (Fig. 1A) can mainly be conditioned by the more substantial increase of the N-oxides' basicity during transition from water to chloromethylene as compared to the nitrogen basicities (e.g. piperidines). The authors of<sup>25,26</sup> have noticed the effect of the change of correlation of the basicities belonging to the above mentioned classes of bases and explained it with the greater desolvation of the N-oxide polar molecule in comparison with the pyridine base in proportion to the decrease of the solvating medium characteristics. Such effects as polarizability and good steric accessibility of the oxygen center also contribute to the high reactivity of N-oxides.

The data of Fig. 1A allows to draw some conclusions about the possibility of nucleophilic catalysis with tertiary amines of various classes in the arylaminolysis reactions of halogenanhydrides of arylsulfonic acids. First of all, they show that in case of equal basicity the reactivity of pyridines, imidazoles and cyclic amines is greater than that of aromatic amines. Thus, the first condition of nucleophilic catalysis<sup>(23,p.61)</sup> is satisfied for the model reaction of

4-toluenesulfobromide with 3-chloroaniline without the accumulation of the intermediate<sup>1-3,27</sup> in the whole variation range of  $pK_a$  of the catalysts studied, the pyridines' having weak basicity with the electronwithdrawing substituents.

The existence of separate Brønsted correlations for amines of various classes (Fig.1) should also be reflected in the corresponding rate dependences of the inverse process rate constant  $k_{-1}$  and the equilibrium constant  $K_p$  (1) on  $pK_a$ .

The equilibrium constants of N-toluenesulfonyl-(4-dimethylamino)pyridine and -(N-methyl)imidazole in methyl chloride have been measured earlier, using the IR-spectroscopy<sup>28</sup>. In the present report, the  $K_p$  values for the equilibrium process (1) with participation of tertiary aliphatic (Table 3, Nos 2,4,6) and heterocyclic amines (Table 3, Nos 3,5) were obtained by means of the UV-spectroscopy.

The dependence of  $\log K_p$  on  $pK_a$ , determined by the data of Table 3 is depicted in Fig.3. It is similar for the amines of different classes (pyridines, N-methylimidazole, tertiary aliphatic amines) and obeys the following equation:

$$\log K_p = (-3.92 \pm 0.60) + (0.79 \pm 0.07)pK_a \quad (7)$$

$$S_0 = 0.18 \quad r = 0.985$$

The existence of this correlation (7) means that the stabilization effects of the  $ArSO_2B^+$  cation'arylsulfonylammonium in such medium as methyl chloride are analogous to the  $BH^+$  ammonium cations in water. This corresponds to the aforesaid consideration about the formation causes of separate Brønsted straight lines while making difference between the reactivity and basicity of various amines (Fig. 1A).

It is known<sup>29</sup> that the  $K_p$  values for the formation of the cations' N-acetylimidazoles are much higher than those resulting from the Brønsted dependence for the formation of cations' N-acetylpyridines. This can be explained by the additional contribution of the resonance stabilization effect into the  $\log K_p$  values, unlike the  $pK_a$  values. We have already pointed out<sup>1</sup> the difference of resonance stabilization

of cations  $\text{ArSO}_2\text{B}^+$  and  $\text{ArCOB}^+$  (B - imidazole, pyridines), the fact has been proved experimentally now.

It should be noticed that the  $K_p$  value for the formation of intermediate I (N-oxide of DMAP<sup>13</sup> is B) is considerably higher than it follows from its basicity in water (Fig.3).

Table 3  
Spectroscopically Measured  $K_p$  Values for 4-Toluenesulfo-  
bromide Reaction with Amines of Different Classes in  
Methylene Chloride at 25°C.

No	Nucleophile	$\text{pK}_a$ $\text{H}_2\text{O}$	$K_p$ , l. mole <sup>-1</sup>
1.	N-methylimidazole	7.00	$41 \pm 3^{28}$
2.	N-methylmorpholine	7.38	$100 \pm 5$
3.	4-morpholinopyridine	8.53	$810 \pm 20$
4.	DABCO	8.80	$800 \pm 10$
5.	DMAP	9.60	$9400 \pm 580$
6.	N-methylpiperidine	9.86	$5700 \pm 70$

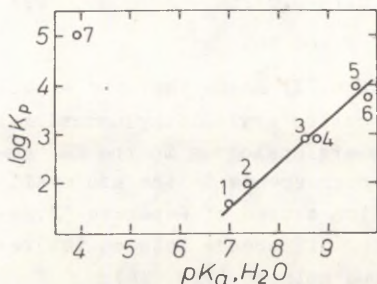


Fig. 3. Dependence of  $\log K_p$  on  $\text{pK}_a(\text{H}_2\text{O})$  for 4-toluenesulfo-bromide reaction with amines of different classes in methylene chloride at 25°C. Numeration of points corresponds to that of Table 3, No 7 - N-oxide of 4-dimethylaminopyridine<sup>13</sup>

In case of nitrogen bases the deviation from the Brønsted straight line is  $> 5$  logarithmic unites, which is approximately equal to the deviation of the corresponding straight line in case of its reactivity ( $\approx 7$  logarithmic unites, see Fig. 1A). This supports our supposition about the fact that the polarizability effect does not significantly contribute

to the N-oxide nucleophilic reactivity (Fig. 1A). Otherwise the equilibrium constant  $K_p$  would not depend that much on the base nature because of the polarizability effect's one-directional influence on the rate of the direct and inverse reactions. The polarizability effect is neither the basic nor the only cause for the greater catalytic activity of pyridine N-oxides in the reactions of the acyl group transition, proceeding without the intermediate accumulation, as it was postulated in a number of our previous contributions<sup>27,30</sup>.

The above-given considerations about the stabilization effects of final state I in reaction (1) for amines of different classes (Fig. 3) as well as about the existence of separate Brønsted correlations, correspond to the  $\log k_1$  behavior from  $pK_a$  (Fig. 4) in case of  $k_1$  (Fig. 1).

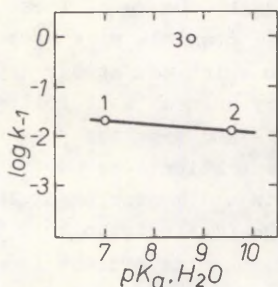


Fig. 4. Dependence of  $\log k_{-1}$  on  $pK_a(H_2O)$  for decomposition reactions of intermediate  $H_3CC_6H_4SO_2B^+ \cdot Br^-$  in methylene chloride at  $25^\circ C$ . B: 1-N-methylimidazole, 2-DMAP, 3-DABCO.

Remarkably higher reactivity of intermediate I where B-DABCO is in conformity with the above views about the smallest stabilization of the mentioned intermediates because of the solvation effects in the series of the other N-arylsulfonylammonium cations.

The analysis shows that considerably higher DABCO catalytic activity ( $k_B$ ) in comparison with the pyridine and imidazole bases in the arylsulfohalogenides' arylaminolysis in protoinert media<sup>1,3</sup> without the accumulation of intermediate I ( $k_B = K_p \cdot k_2$ ) cannot be explained by the difference in the stability of acylammonium salts (values  $K_p$ ) compared in Table 3, since the latter changes proportionally to the  $pK_a$  values. In this connection would be interesting to study the rate of the low stage of nucleophilic catalysis, i.e.

the arylaminolysis of intermediates I, characterized by the nature of leaving group B.

### Experimental

#### Preparation of Reagents and Solvent.

Methylene chloride was purified as described in<sup>31</sup>. Only freshly purified solvent was used before each series of experiments. Its quality was tested according to the absence of the DMAP hydrochloride absorption in the UV - spectrum of the DMAP ( $\approx 5 \cdot 10^{-5}$  mole  $\cdot$  l<sup>-1</sup>) solution. In case of amines with weak bases ( $\text{pK}_a \leq 7-8$ ) the amine solution of higher concentration was prepared. A number of other solutions were obtained via dilution. With stronger amines ( $\text{pK}_a \geq 8$ ) each kinetic experiment was carried out using an individual portion of amine solution immediately before measuring the rate. These precautions were taken in order to avoid possible side processes of the amine and solvent interaction which can appear especially clearly in case of cyclic tertiary amines<sup>32</sup>. It follows from the good reproductivity of results and from the observing of rate law (3) that the amine concentration does not change during the preparation of solvents and measuring of the rate. The only exception is quinuclidine (Table 1, No 10). The authors are not quite sure whether the side process is entirely included here (the reproductivity in a number of experiments was worse than usual), hence the  $k_1$  value for this reaction may be a bit lowered.

All operations concerning the preparation of strong amines and filling of the cells of the spectrometer were performed in dry ( $\text{P}_2\text{O}_5$ ) in the atmosphere of nitrogen.

4-Toluenesulfobromide was obtained and purified according to<sup>33</sup>. N-methylimidazole was synthesized by methods<sup>34</sup>. Imidazole was purified as in<sup>35</sup>. Quinuclidone-3, DABCO and quinuclidine were sublimated in vacuum at the metallic sodium. These amines were used directly after their sublimation. DMAP was prepared and purified as described in<sup>36</sup>.

Amines (piperidine, triethylamine, N-methylmorpholine ,

methyldiethylamine), previously kept at alkali, were distilled several times at normal pressure in the nitrogen current.

### Methods of Kinetic Measurements

The optic density decrease of 4-toluenesulfobromide at the excess of amine in the  $\lambda = 281$  nm range was registered. In case of the reaction with DMAP the rate was monitored via the forming product in the range  $\lambda = 308$  nm. With amines whose reaction rate is lower ( $k_1 \leq 1,1 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ ) the rate was measured on a spectrophotometer SF - 26. In other cases (Table 1, Nos. 4, 8-10, 14, 15) rate was registered applying the method of stopped flow on a rapid scan spectrophotometer SP - 176. The reaction with N-methylimidazole was used to show that the manual registration (low amine concentrations) and the method of stopped flow (high amine concentration) give coinciding results in the range of measuring errors. The pseudofirst order rate constant in case of the processes with participation of primary, secondary and some tertiary amines (Table 1, Nos. 3, 4), calculated by equation

$$k_H^{(1)} = \frac{2.303}{t} = \log \frac{D_\infty - D_0}{D_\infty - D_t} \quad (8)$$

remains constant in the course of the process. For a number of tertiary amines (Table 1, Nos 8-13)  $k_H^{(1)}$  decreases in the course of the process. This is, evidently, connected with the inaccuracy of determining the  $D_\infty$  value because of the instability of the forming N-arylsulfonylammonium salts. For that reason the calculations were carried out either by the method of initial rates or by means of the nonlinear regression type (8) restoration.

### Equilibrium constants

of intermediate I formation, where B is DABCO, N-methylmorpholine and N-methylpiperidine (concentration range  $1.3 \cdot 10^{-4} \frac{\text{mole}}{\text{l}} - 1 \cdot 10^{-3} \frac{\text{mole}}{\text{l}}$ ), was determined according to the optic density decrease of 4-toluenesulfobromide (concentration range  $1 \cdot 10^{-5} \frac{\text{mole}}{\text{l}} - 5.4 \cdot 10^{-4} \frac{\text{mole}}{\text{l}}$ ,  $\lambda$  is 286 nm,  $\epsilon = 3950 \pm 30$ ). If DMAP and 4-morpholinopyridine (con-

centration  $1 \cdot 10^{-4}$  mole  $\cdot$  l $^{-1}$ ) were used as B the constants were obtained by the appearance of the intermediate I optic density within the range of 320 nm and 310 nm, respectively. The molar extinction coefficients of intermediate I were registered earlier ( B = DMAP,  $\lambda = 320$  nm,  $\epsilon = 13200 \pm 450$ , B = 4-morpholinopyridine,  $\lambda = 310$  nm,  $\epsilon = 22860 \pm 580$ ) equilibrium (1) being shifted to the conditions of acylammonium salts formation (4-toluenesulfobromide concentration was  $(1.0 \frac{\cdot}{85}) \cdot 10^{-5}$  mole  $\cdot$  l $^{-1}$ , concentration B =  $B = 1 \cdot 10^{-3}$  mole  $\cdot$  l $^{-1}$ ).

Optical density was measured immediately after mixing reagent solutions ( in 1 min.). The interval between mixing of the solutions and the first measuring of parallel experiments were strictly synchronized, since the solution density does not remain constant during a longer period of keeping the reaction mixture. It is probably the result of hydrolytic destruction of the forming intermediate leading to the decrease of 4-toluenesulfobromide concentration.

Reaction Products. Primary and secondary amines form quantitatively the corresponding amines<sup>14</sup>.

The products of 4-toluenesulfobromide interaction with DMAP<sup>37</sup> and N-methylimidazole<sup>38</sup> have been obtained in the conditions similar to those described above. These are white crystal products which will disperse in the air. The measures of precaution were taken ( in the box with P<sub>2</sub>O<sub>5</sub>) in the quantitative acylation of acylamine<sup>39</sup>.

Acylammonium salts cannot be obtained on the bases of 4-toluenesulfobromide and tertiary aliphatic amines. It was shown by means of DABCO that the white precipitate forming after mixing of equimolecular solutions of amine and 4-toluenesulfobromide in dry benzene is the mixture of hydrobromide and the amine toluenesulfonate salt. These products could form during the hydrolysis of the forming acylammonium salt because of moisture in the course of synthesis, separation, and analysis of reaction product.

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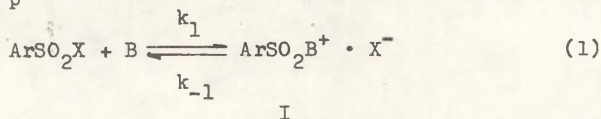
NUCLEOPHILIC CATALYSIS WITH TERTIARY AMINES IN FORMATION  
REACTIONS OF AMIDES OF ARYLSULFONIC ACIDS.  
KINETICS AND MECHANISM OF SECOND STAGE

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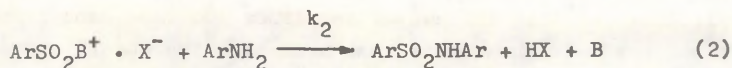
Bimolecular reaction rate of intermediates  
 $4\text{-ClC}_6\text{H}_4\text{SO}_2\text{B}^+ \cdot \text{SO}_3\text{C}_6\text{H}_4\text{Cl-4}$  (B: 1-4-dimethylaminopyridine;  
2-4-morpholinopyridine; 3-N-methylimidazole; 4-1,  
4-diazabicyclo-[2,2,2]-octane) with 3-nitroaniline in  
methylene chloride at 25°C was studied. The comparison  
of  $\log k_2$  with the  $\text{pK}_a$  of the splitting base  $\text{B}(\text{H}_2\text{O}$  at  
25°C) leads to the straight line where  $\beta = -0.51 \pm 0.07$   
for Nos 1-3 and No 4 deviates from it ( $\Delta \log k_2 = +3.3$ ).  
It was established that the stabilization of intermedi-  
ate 4 is smaller than that of intermediates 1-3 because  
of solvation effects. The causes of oxyridine inter-  
mediates ( $\beta$ -4-dimethylaminopyridine N-oxide) lower re-  
activity in comparison with the pyridine analogues  
( $\Delta \log k_2 = -2.6$ ) have been discussed.

In the previous report<sup>1</sup> was discussed the problem of the  
influence of tertiary amines' (B) nature on the rate ( $k_1$ ) and  
equilibrium ( $K_p$ ) of intermediate I formation:



In order to comprehend the peculiarities of the nucleophilic

catalysis mechanism in the aminolysis reactions of arylsulfonic acids, compared to the analogous substitution processes at the carbon carbonylic atom<sup>2</sup> the rate of low stage (2) and its dependence on the nature of group B in I were studied



It is known<sup>3</sup> that the arylaminolysis of intermediates  $\bar{\text{I}}$  (B = 4-dimethylaminopyridine, Ar = C<sub>6</sub>H<sub>5</sub>, X = Cl, Br) is a multichannel process. In addition to bimolecular interaction, it also includes such trimolecular routes as the catalysis with a free base and the anion of ionic pair intermediate I. Though, the contribution of catalytic routes into the total rate is negligible, if X = SO<sub>3</sub>C<sub>6</sub>H<sub>5</sub>.

Application of the anhydrides brings of arylsulfonic acids as the substrate about a considerable increase in the constant of equilibrium process (1). Thus, the estimation of K<sub>p</sub> according to<sup>1,4,5</sup> of salts  $\bar{\text{I}}$  (Ar = C<sub>6</sub>H<sub>5</sub>, X = SO<sub>3</sub>C<sub>6</sub>H<sub>5</sub>) formation yields the following values: B = 4-dimethylaminopyridine (DMAP) > 10<sup>5</sup>, 1,4-diazabicyclo-[2,2,2]-octane (DABCO) > 10<sup>4</sup>, N-methylimidazole > 400.

The interaction kinetics of intermediates  $\bar{\text{I}}$  where Ar = 4-ClC<sub>6</sub>H<sub>4</sub>, X = 4-ClC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>, B = DMAP, 4-morpholinopyridine, N-methylimidazole and DABCO, with 3-nitroaniline in methylene chloride at 25°C was studied. If the more reactive 4-chlorobenzenesulfonic anhydride<sup>6</sup> is used as substrate, the values of equilibrium constant K<sub>p</sub> are still higher than the above estimations for benzenesulfonic anhydride.

#### Results of Kinetic Measurements

Intermediates  $\bar{\text{I}}$  were obtained in situ, pouring together the 4-chlorobenzenesulfonic anhydride solutions and the corresponding base B. In case of the reagents' correlation 1 : 1 in the UV-spectrum of the anhydride mix and 4-dimethylamino- and 4-morpholinopyridine appears a long-wavelength band, belonging to the intermediate<sup>7</sup> spectrum. The mixing of anhydride solutions with N-methylimidazole and DABCO is not ac-

accompanied by the exact distribution of the reagents' and forming products' absorption bands, though remarkable changes take place in the spectrum. But it appears from the above evaluative  $K_p$  values ( $> 10^4$  for DABCO and  $> 400$  for N-methylimidazole)<sup>p</sup> that in case of anhydride and base concentrations used in the kinetic measurements, the quantitative accumulation of the intermediate is obtained.

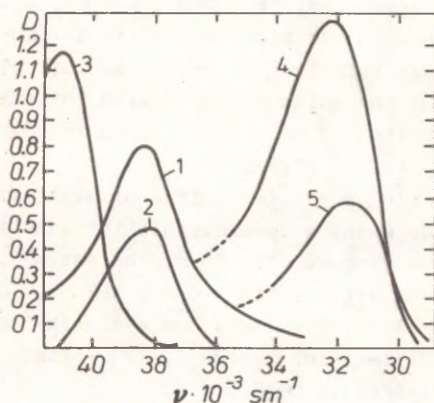


Fig. 1. UV-spectra of initial reagents and their interaction products obtained in situ,  $\text{CH}_2\text{Cl}_2$  at  $25^\circ\text{C}$ .

- 1 - DMAP,  $c \approx 6 \cdot 10^{-5}$  mole  $\cdot$  l $^{-1}$ ;
- 2 - 4-morpholinopyridine,  $c \approx 6 \cdot 10^{-5}$ , mole  $\cdot$  l $^{-1}$ ;
- 3 -  $(4\text{-ClC}_6\text{H}_4\text{SO})_2\text{O}$ ,  $c \approx 5 \cdot 10^{-5}$  mole  $\cdot$  l $^{-1}$ ;
- 4 -  $4\text{-ClC}_6\text{H}_4\text{SO}_2\text{N}(\text{C}_6\text{H}_4)\text{-N}(\text{CH}_3)_2 \cdot \text{SO}_3\text{C}_6\text{H}_4\text{Cl-4}$ ,  
 $c \approx 5 \cdot 10^{-5}$  mole  $\cdot$  l $^{-1}$ ;
- 5 -  $4\text{-ClC}_6\text{H}_4\text{SO}_2\text{N}(\text{C}_6\text{H}_4)\text{-N}(\text{C}_6\text{H}_4)\text{O} \cdot \text{SO}_3\text{C}_6\text{H}_4\text{Cl-4}$ ,  
 $c \approx 5 \cdot 10^{-5}$  mole  $\cdot$  l $^{-1}$

The rate of reaction I with 3-nitroaniline were studied according to the loss of the latter under pseudomonomolecular conditions (excess of I). Concentration relationships between anhydride and base B in case of I formation in situ are presented in Table 1.

In all cases the reaction rate is described as follows:

Table 1

Concentration Conditions for Studying Interaction of Intermediates  
 $4\text{-ClC}_6\text{H}_4\text{SO}_2\text{B}^+ \cdot \text{SO}_3\text{C}_6\text{H}_4\text{Cl-4 (I)}$  with 3-nitroaniline, and Rate  
 Constant  $k_2$  in Methylene Chloride at  $25^\circ\text{C}$

No	B	$[\text{ArSO}_2\text{X}] \cdot 10^3$ mole $\cdot$ l $^{-1}$	$[\text{B}] \cdot 10^3$ mole $\cdot$ l $^{-1}$	$[\text{I}] \cdot 10^3$ mole $\cdot$ l $^{-1}$	$k_H \cdot 10^4$ sec $^{-1}$	$k_2 \cdot 10^2$ l $\cdot$ mole $^{-1}$ $\cdot$ sec $^{-1}$
1	2	3	4	5	6	7
1.	4-dimethylamino- pyridine	6.25	6.25	6.25	0.283	0.463
		12.5	12.5	12.5	0.853	0.680
		14.3	14.3	14.3	1.12	0.781
		16.6	16.6	16.6	1.23	0.742
		30.5	30.5	30.5	1.77	0.580
						0.649 $\pm$ 0.061
2.	4-morpholino- pyridine	3.7	3.7	3.7	1.33	3.59
		7.4	7.4	7.4	2.88	3.89
		14.8	14.8	14.8	5.54	3.74
		29.7	29.7	29.7	8.75	2.95
						3.54 $\pm$ 0.21

Table 1 continued

1	2	3	4	5	6	7
3.	1,4-diazabicyclo- [2,2,2] -octane	1.52	1.52	1.52	716	4710
		5.35	1.52	1.52	800	5260
		10.7	1.52	1.52	532	3510
		15.0	1.52	1.52	632	4160
		21.4	1.52	1.52	756	4970
		25.0	1.52	1.52	494	3250
		30.0	1.52	1.52	434	2860
						4100 ± 300
4.	N-methylimidazole	15.0	15.0	15.0	26.7	17.8
		30.0	30.0	30.0	56.6	18.9
		5.0	30.0	5.0	6.41	12.8
		0.49	1.48	0.49	0.738	15.1
		0.50	20.0	0.50	0.665	13.3
		0.49	11.6	0.49	0.706	14.4
		0.49	29.2	0.49	0.833	17.0
		0.49	14.6	0.49	0.751	15.3
						15.6 ± 0.8

$$k_H = k_2 [I] \quad (3)$$

where  $k_H$  ( $\text{sec}^{-1}$ ) is the pseudofirst order rate constant;  $k_2$  ( $l \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ ) denotes the rate constant of  $I$  bimolecular interaction with the amine.

The analysis of the  $k_2$  values depending on the  $pK_a$  of group B entering  $I$  are given in Fig. 2.

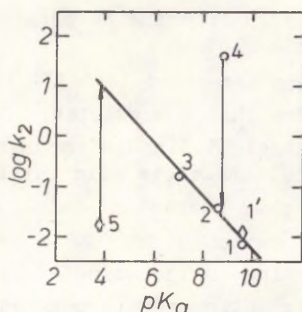


Fig. 2. Dependence of  $\log k_2$  values on  $pK_a$  ( $H_2O$  at  $25^\circ C$ ) for reactions of intermediates  $4-ClC_6H_4SO_2B^+ \cdot \bar{SO}_3C_6H_4Cl-4$  (Nos 1-4) and  $C_6H_5SO_2B^+ \cdot \bar{SO}_3C_6H_5$  (Nos 1,5) with 3-nitroaniline in methylene chloride at  $25^\circ C$ . B: 1 and 1'-DMAP, 2-4-morpholinopyridine, 3-methylimidazole, 4-DABCO, 5-DMAP N-oxide

Satisfactory correlation is observed when the pyridines and N-methylimidazole are used as B.

$$\log k_2 = (2.85 \pm 0.64) + (-0.52 \pm 0.08)pK_a \quad (4)$$

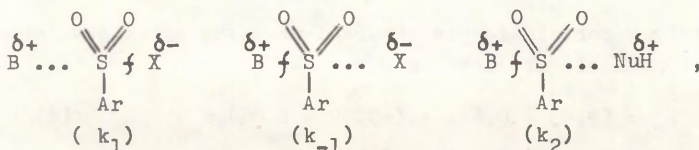
$$r = 0.990, S_0 = 0.141, N = 3$$

DABCO deviates 3.3 logarithmic unites from this straight line towards higher rates. Thus, in case of attacking the sulfonylic sulphur atom ( $k_1$  in (1))<sup>1</sup>, as well as in case of breaking from the intermediate in the inverse process ( $k_{-1}$  in (1))<sup>1</sup> and interaction process with arylamine ( $k_2$ , Fig. 2) at equal basicity, the cyclic aliphatic amines are more reactive than pyridines and imidazoles.

It was pointed out in<sup>1</sup> that unlike reactivity, the equilibrium constant of process (1)  $K_p$  is described with the united Brønsted straight line. The data for heteroaromatic

and tertiary aliphatic amines are located on the latter. Consequently, the effects stabilizing cation  $\text{ArSO}_2\text{B}^+$  are analogous to the stabilization effects of the  $\text{BH}^+$  cation. Thus, the comparison of  $\log k_2$  and  $\text{pK}_a$  values (Fig. 2) yields the same qualitative results as the comparison of  $\log k_2$  with  $\log K_p$ . It follows from the aforesaid and from the considerations given in<sup>1</sup> that the higher elimination rate of DABCO in processes  $k_2$  and  $k_{-1}$  is connected with the smaller stabilization of the corresponding intermediate  $\text{I}$  because of solvation effects in comparison with the cations formed from other amines, particularly from the heteroaromatic ones.

Thus, the data obtained here and excerpted from the previous report<sup>1</sup> lead to the conclusion that the existence of the separate individual Brønsted straight lines when comparing the attacking rates of  $k_1$  in (1) and their elimination rates  $k_{-1}$  in (1) and  $k_2$  in (2), is guaranteed mainly with the different solvation effects of cations  $\text{BH}^+(\text{pK}_a)$  or  $\text{ArSO}_2\text{B}^+$  ( $\log K_p$ ), the latter depending on the amine's nature (primary, secondary or tertiary, aromatic or heteroaromatic, etc.). The solvation differences considerably disappear in the transition states of the following types:

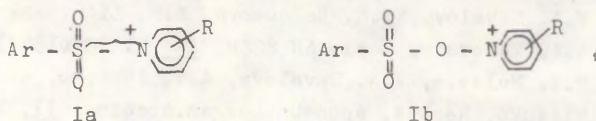


where the nitrogen atom in B has a partial positive charge only, differing, thus, from  $\text{BH}^+$  or  $\text{ArSO}_2\text{B}^+$ .

The data obtained in the present paper allow also to say that a remarkably higher catalytic activity of the  $k_B$  amines of quinuclidine series, compared to the pyridines and imidazoles of equal basicity in the arylaminolysis of halogenanhydrides of arylsulfonic acids proceeding without the accumulation of the nucleophilic catalysis ( $k_B = K_p \cdot k_2$ )<sup>2,11,12</sup> intermediates, is mainly explained by the different reactivity of the corresponding intermediates in the low stage of  $k_2(2)$ ,

and not by the difference in their thermodynamic stability  $K_p^{(1)}$ .

It is noteworthy that the 4-dimethylaminopyridine N-oxide breaks from the intermediate much slower than follows from the Brønsted correlation (4)\*. At the same time, as it was mentioned in<sup>1</sup>, in the stage of attacking 4-toluenesulfobromide, N-oxide is a great deal more reactive than pyridine and imidazole of equal basicity. The equilibrium constant of the oxypyridine intermediate<sup>1</sup> formation is also remarkably higher ( $> 10^5$  times). These facts prove that the effects responsible for the existence of separate Brønsted correlations in case of  $k_1$  and  $k_2$  for N-oxides do not coincide with those for the amines of different classes. So, the deviation of point 5 in Fig. 2 downwards from the Brønsted straight line can be caused by the greater basicity of the pyridine N-oxides as compared to the pyridine bases during transition from water into methyl chloride (cf.<sup>13</sup>). It is possible that there is also difference between the electronic stabilization effects of pyridine (Ia) and oxypyridine (Ib) cations which



is connected with the elimination of positive charge from the electrondeficient center in case of Ib.

### Experimental

Methylene chloride was purified as described in<sup>14</sup> 4-chlorobenzylsulfanehydride<sup>15</sup>, 4-dimethylaminopyridine<sup>16</sup>, and 1,4-diazabicyclo[2,2,2]-octane<sup>1</sup> were purified according

\* Intermediate  $[\text{C}_6\text{H}_5 - \text{SO}_2\text{O}^+\text{NC}_5\text{H}_4\text{N}(\text{CH}_3)_2 - 4] \cdot \text{SO}_3\text{C}_6\text{H}_5$  (Fig. 2, No 5), differs from the intermediates participating in Reactions 1-4 (Fig. 2) not only as to the nature of base B but also in the acyclic part and counter-anion's structure. Though, point 1 belonging to the corresponding pyridine intermediate (cf. with 1) show that the structural changes of the substrate and anion influence reactivity only slightly.

to the methods explained earlier. 4 - morpholinopyridine was synthesized as in<sup>17</sup>. In kinetic measurements, the decrease of 3 -nitroaniline optic density was registered in the range of  $\lambda = 365$  nm under pseudomonomolecular conditions on a spectrophotometer SF - 26. The observed rate constants are considered as those in<sup>1</sup>.

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INTERACTION OF BENZYL AND ALLYL ALCOHOLS WITH SOLVENTS

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The influence of solvents on the IR-spectrum of benzyl and allyl alcohols has been studied. Application of the LFER equation shows that the solvent basicity has some effect on the OH-band shift  $\Delta\nu_{OH}$  of alcohol. Slight influence of nonspecific solvation caused by the polarizability effect was also observed.

The interrelation of the IR-band shifts  $\nu_{X-H}$  for X - H acids in the same solvents is a well - established fact. The proportionality of  $\nu_{OH}$  changes under the influence of solvents has been stated quantitatively in<sup>1</sup>. The high values of correlation coefficients ( $R=0.98 \div 0.99$ ) were obtained, comparing the OH band shifts of alcohols and phenols with the standard changes of the phenol OH band in the  $CCl_4$  medium, i.e. with basicities "B":

$$\Delta\nu_{HX}^{CCl_4} = a + b \Delta\nu_{PhOH}^{CCl_4} = a + bB$$

This conclusion has been confirmed by several authors also for alcohols of diverse structure, including the fluorinated alcohols<sup>2,3</sup> as well as the hydroperoxides<sup>4</sup>.

The proportionality coefficient value "b" which charac-

terizes the OH sensitivity of the discussed compound to the solvent effect, is approximately proportional to the pK value of acidic dissociation of the corresponding X-H acids<sup>1,4</sup>.

The value of intercept "a" is near to zero in most cases. Though, the studies of a larger data set concerning the solvents' effect on the OH IR bands of various alcohols have shown that in a number of cases deviation from their linear bond with the medium basicity B, is observed, which results in a low relation degree of these values (R may drop to 0.91 - -0.97<sup>5</sup>). The deviations for the alcohols which have low acidity or are sterically complicated, as well as for those falling in the range of deformation deviations, are more remarkable.

The bond degree can be increased via the application of the LFER equation, taking into account also the other interaction types of the solvent with alcohol, first of all the non-specific solvation conditioned by the medium polarizability<sup>5</sup>. The latter should be proved by a greater number of examples.

Medium effect on the location of the OH IR-band of benzyl alcohol has not been studied yet. The aromatic nature of this compound leads to the increased values of polarizability and acidity, being the intermediate between the n-alcanoles and phenoles: the calculated pK is 15.6 in comparison with 16-17 for alcohols, 10- for phenoles, and 12.6 - 12.8 for hydroperoxides.

A sample of freshly distilled benzyl alcohol, its boiling point being 92.5 - 93.5 at 10 mm Hg,  $n_D^{20} = 1.5396$  was used. The solvents were freshly distilled. Their physico-chemical properties corresponded to the reference data. The spectra were taken in the range of 3700-3200  $\text{cm}^{-1}$  on a spectrophotometer IKS-14A with the LiF prism at 20-22°C. Its calibration was done according to the absorption spectra of polystyrene and water vapor.

The concentration of benzyl alcohol in solvents having strong basicity was 0.01 mole/l, the donor concentration being 10-25 times higher. The solutions were prepared in  $\text{CCl}_4$ . In the solvents with weak basicity the concentration of

Shifts OF IR BANDS  $\nu_{\text{OH}}^{\text{cm}^{-1}}$  OF BENZYL AND ALLYL ALCOHOLS IN SOLVENTS  
AND THEIR BASICITIES  $B_{\text{cm}^{-1}}$

Table

N°	Solvent	$\Delta \nu_{\text{OH}}$	$\Delta \nu_{\text{OH}}$	B	$\Delta \nu_{\text{OH}}$	$\Delta \Delta \nu_{\text{OH}}$
		$\text{PhCH}_2\text{OH}$	$\text{CH}_2=\text{CHCH}_2\text{OH}$		calcul.	
1.	$\text{C}_6\text{H}_5\text{Br}$	15		32	21.0	-6
2.	$\text{CHCl}_2\text{-CHCl}_2$	18		40	15.5	+2.5
3.	p-Chlorotoluene	23		41	21.4	+1.6
4.	m-Bromotoluene	28		53	31.4	-3.4
5.	$\text{C}_2\text{H}_5\text{Br}$	38		79	39.3	-1.3
6.	Toluene	41		58	30.9	+10.1
7.	$\text{C}_2\text{H}_5\text{SO}_2\text{N}(\text{CH}_3)_2$	88		158	92.4	-4.4
8.	Butylacetate	96		158	88.4	+7.6
9.	Ethylacetate	101		181	101.7	-0.7
10.	Acetone	123		224	128.5	-5.5
11.	Dioxane	145		237	142.0	+3.0
12.	Dibutyl ether	163		285	171.5	-8.5
13.	DMFA	168	169	291	177.7	-17.7
14.	THF	172	165	287	173.2	-1.2
15.	N-methylpyrrolidone	204		357	223.3	-19.3
16.	$(\text{BuO})_3\text{PO}$	222	209	336	206.6	+15.4
17.	DMSO	247	236	362	227.3	-19.8

PhCH<sub>2</sub>OH was 0.2 mole/l and the solutions were prepared in the solvent - CCl<sub>4</sub> 1:1 binary mixtures. For registration of the spectra, the donor solution of the same concentration was conducted into the comparison cuvette.

The obtained data of  $\Delta\nu_{OH}$  are given in the Table.

The comparison of the  $\Delta\nu_{OH}$  shifts of the PhCH<sub>2</sub>OH with the basicity of solvents shows a satisfactory linearity (Fig.). Only  $\Delta\nu_{OH}$  values for the solvents with the greatest basicity - (BuO)<sub>3</sub>PO and DMSO deflect significantly. The treatment of the results by the mean squares method gives the following equation with a high degree of freedom:

$$\Delta\nu_{OH} = -(6.93 \pm 4.88) + (0.632 \pm 0.022)B;$$

$$n = 17, R = 0.991, S = 10.65$$

The application of a five - parameter LFE equation which takes into account the specific and nonspecific solvation parameters of the Koppel-Palm equation<sup>6</sup> as well as the cohesion energy density<sup>4,5</sup> does not result in a significant increase in the bond degree, though it enables to evaluate the significance of different solvation factors' effect.

13 solvents, having the required characteristics, obey the equation where  $R = 0.993$ , in case of the partial correlation coefficient  $r_{OB} = 0.987$ . The factors of electrophilic solvation (due to the acidic nature of PhCH<sub>2</sub>OH) and the density of cohesion energy are negligible. Their exclusion from the regression equation permitted to repeat the calculations for those 17 points, which had proved to be negligible also from the point of view of the medium polarity. It was conclusively established that the value of  $\Delta\nu_{OH}$  is determined by the medium basicity, taking into consideration the influence of nonspecific solvation, connected with the polarization effect, although the corresponding partial correlation coefficient value is extremely insignificant ( $r = 0.430$ ).

$$\Delta\nu_{OH} = -48.11 + 141.1 (n^2-1)/(n^2 + 2) + 0.650 B$$

$$n = 17, R = 0.992 \quad S = 10.5$$

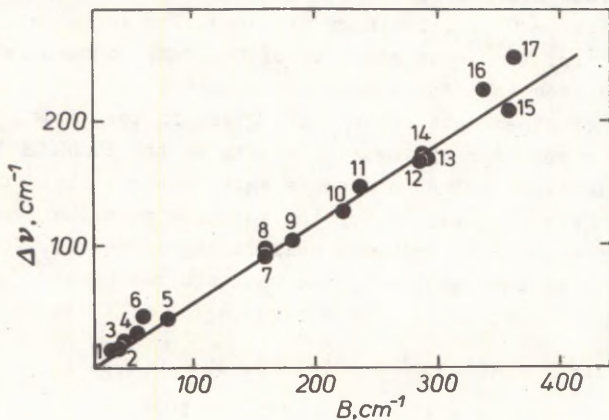


Fig. 1. The dependence of the IR-band shifts of the  $\text{PhCH}_2\text{OH } \Delta\nu_{\text{OH}}$  on solvent basicity  $B$ .

For comparison, the  $\Delta\nu_{\text{OH}}$  values calculated by means of the equation cited above and as well as their corresponding deviations from the experimental values are presented in the Table:

$$\Delta\Delta\nu_{\text{OH}} = \Delta\nu_{\text{exp.}} - \Delta\nu_{\text{calc}}$$

It can be seen that at generally good coincidence, the greatest deviations (up to  $20 \text{ cm}^{-1}$ ) are observed in case of a few solvents with a strong basicity. The value of coefficient of  $\nu_{\text{OH}}$  susceptibility to the basicity of one - parameter equation  $b = 0.632$  at  $\text{pK} = 15.6$  is satisfactorily close to the linear dependence  $b = f(\text{pK})^4$ .

We also studied the  $\nu_{\text{OH}}$  shifts in some solvents of allyl alcohol, whose electronic structure resembles that of benzyl alcohol.

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NON-ELECTROLYTE EFFECTS ON THE STRUCTURE OF LITHIUM  
CHLORIDE SOLUTIONS IN ISOAMYL ALCOHOL

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The results of the differential-conductometric measurements of the non-electrolyte influence on the electrical conductivity of lithium chloride solutions in iso-amyl alcohol are presented. The specific molar volumes  $V_g$  characterizing the structure reorganization effects in solution were calculated for these non-electrolyte molecules. A significant difference in the behavior of  $V_g$  of the hydroxylic and aprotic non-electrolytes has been established.

The results of the differential-conductometric investigation of non-electrolyte influence on the structure of aqueous and ethanolic electrolyte solutions were given in a number of recent publications.<sup>1-5</sup> In the present article, the effect of small additions of several hydroxylic and aprotic organic substances on the structure of the lithium chloride solution in iso-amyl alcohol is discussed.

As the result of the differential-conductometric measurements<sup>6</sup>, the change of the specific conductivity of 1 l electrolyte solution per 1 mole of added secondary non-electrolyte is found.<sup>\*</sup> Namely, this is the quantity

<sup>\*</sup> To avoid the non-linear addition concentration dependence of the specific conductivity change only very small amounts of the substance investigated ( $10^{-2}$ - $10^{-3}$  mol/l) are added to the solution

$$Y = \frac{k \cdot 10^3}{c_s} \left( \frac{1}{R_0 + \Delta R} - \frac{1}{R_x} \right), \quad (1)$$

which may be called the molar differential conductivity of the addition investigated in the given solution. In this formula  $k$  denotes the conductometric cell constant ( $\text{cm}^{-1}$ ),  $c_s$  is the molar concentration of the substance added ( $\text{mol/l}$ ), and  $R_0$  and  $R_x$  are the resistances ( $\Omega$ ) of the solution before and after adding this substance, respectively. Quantity  $\Delta R$  takes into account the change of the resistance of solution caused by the dilution in the process of non-electrolyte addition.

It was shown, that in the framework of the structural theory of electrolyte solutions<sup>2,7</sup> parameter  $Y$  is proportionally dependent on the specific conductivity of the pure electrolyte solution of the given concentration:

$$Y = V_s \cdot \quad . \quad (2)$$

Multiplier  $V_s$ , which has the dimension ( $1/\text{mol}$ ), is characteristic of the given non-electrolyte added to the solution. This parameter describes its influence on the structure of solvent and it is numerically equal to the statistically average volume in the vicinity of addition molecule where the solvent structure is fully perturbed (i.e. transformed either to the ideally ordered structure of pure solvent or to the entirely disordered form).

#### Experimental.

Methanol (grade "Pure") was distilled. The fraction used had b.p.  $65.0^\circ\text{C}$  (760 m.m Hg) density  $d_{25}^{25} = 0.7962 \text{ g/cm}^3$  and refraction index  $n_D^{20} = 1.3312$ .

Ethanol (grade "Pure for analysis") was dried on the CaO and distilled. The fraction used had b.p.  $78.4^\circ\text{C}$  (760 mm Hg) and  $d_{25}^{25} = 0.7898$

Isobutyl alcohol (grade "Pure") was distilled. The frac-

tion used had b.p. 107.5°C (760 mm Hg);  $d_{25}^{25} = 0.8019$  and  $n_D^{20} = 1.3960$ . Isoamyl alcohol (grade "Pure") was distilled. The fraction used had b.p. 130.5°C (760 mm Hg),  $d_{25}^{25} = 0.8123$  and  $n_D^{20} = 1.4080$

Dimethyl sulfoxide (grade "Pure for analysis") was dried on the BaO and bidistilled from the mixture with  $\text{CaH}_2$  in the argon atmosphere. The fraction used had b.p. 64.0°C (6 mm Hg) and  $d_{25}^{25} = 1.10105$

Acetonitrile (grade "Pure for analysis") was treated with KOH, distilled. The principal fraction was treated with  $\text{CaH}_2$  and fractionally distilled. The fraction used had b.p. 81.5°C (760 mm Hg) and  $d_{25}^{25} = 0.7791$

Dioxane (grade "Pure for analysis") was treated with HCl and KOH, dried and then boiled with sodium. Finally the fractional distillation was carried out. The fraction used had b.p. 101.5°C (760 mm Hg) and  $d_4^{20} = 1.0329$ .

The water used was deionized and bidistilled. The conductometric measurements were carried out on the apparatus described elsewhere<sup>6</sup>. All the measurements were made at temperature  $25.0 \pm 0.1^\circ\text{C}$ , hold constant with the precision of  $\pm 0.001^\circ\text{C}$ . The conductivity cell was isolated from the surrounding atmosphere with CaO tubes to prevent the absorption of water. The cell constant was  $19.40 \text{ cm}^{-1}$ . Constant resistance  $R_p = 9907.0$  was used in parallel joint to the conductivity cell in case of dilute solutions.

Dilution term  $\Delta R$  in Eq. (1) was calculated according to the procedure, described previously<sup>4</sup>.

### Discussion.

The numerical values of the molar differential conductivities  $Y$  are given in Table 1-4. The results of the least-squares treatment of these data according to the equation

$$Y = V_g \cdot x + a_0, \quad (2a)$$

where  $a_0$  is the small intercept allowed due to the self-conductivity of addition, are presented in Table 5. The examples of linear relationship (2a) for some non-electrolytes are given in Fig. 1.

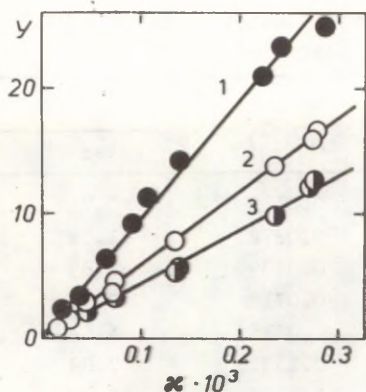


Fig. 1. The relationship between molar differential conductivities  $Y$  and specific conductivity of LiCl solution in isoamyl alcohol in the case of acetonitrile (1), water (2) and ethanol (3).

The overall statistical fitness of correlations (2a) is good (See Table 5.). The intercept is practically equal to zero (in limits of experimental error). The  $V_B$ -parameters are of negative sign for all non-electrolytes investigated. According to the structural theory of electrolyte solutions<sup>7</sup>, they are structure-breakers for the isoamyl alcohol. In the previous investigations<sup>1-5</sup>, the regularity between the  $V_B$ -parameters and intrinsic volumes of non-electrolyte molecules in the aqueous and ethanolic solutions was established. For the LiCl solutions in isoamyl alcohol, such a regularity may be obtained in the case of hydroxylic non-electrolyte additions. (See Fig. 2). In a good approximation this regularity is presented by the following linear relationship:

$$V_B = (-739.9 \pm 38.3) + (27.08 \pm 2.22) \sum R_D \quad (3)$$

$$r = 0.990 \quad s = 43.3 \quad s_0 = 0.081$$

Table 1  
Molar Differential Conductivities  $\Upsilon$  of Water and Ethanol  
in LiCl Solutions in Isoamyl Alcohol

$C_{\text{LiCl}}$ (mol/l)	$\kappa \cdot 10^3$ ( $\Omega^{-1}$ )	$-\Upsilon \cdot 10^2$	
		water	ethanol
0.00921	0.0163	0.71	0.76
0.0298	0.0272	1.34	1.20
0.0653	0.0439	2.83	1.91
0.118	0.0712	3.56	3.23
0.125	0.0716	4.64	3.18
0.257	0.1330	7.89	5.17
0.267	0.1398	10.20	5.74
0.503	0.2331	13.80	9.85
0.621	0.2702	15.90	12.80
0.727	0.2778	16.60	12.50
1.000	0.2616	16.60	12.10

Table 2  
Molar Differential Conductivities  $\Upsilon$  of Isobuthanol and  
Dioxane in LiCl Solutions in Isoamyl Alcohol.

$C_{\text{LiCl}}$ (mol/l)	$\kappa \cdot 10^3$ ( $\Omega^{-1}$ )	$-\Upsilon \cdot 10^2$	
		isobuthanol	dioxane
0.069	0.0468	0.04	-0.22
0.112	0.0705	0.72	0.70
0.170	0.0948	0.65	0.82
0.229	0.1180	1.23	0.99
0.481	0.2220	1.53	4.83
0.855	0.3331	3.66	8.99

Table 3  
Molar Differential Conductivities  $\Upsilon$  of Methanol and Dioxane  
in LiCl Solution in Isoamyl Alcohol.

$C_{\text{LiCl}}$ (mol/l)	$\kappa \cdot 10^3$ $\Omega^{-1}$	$-\Upsilon \cdot 10^2$	
		methanol	dioxane
0.0163	0.0193	1.20	-0.18
0.0189	0.0235	1.21	-0.18
0.0412	0.0347	2.33	-0.28
0.0674	0.0448	3.05	-0.28
0.0949	0.0644	4.04	-0.01
0.125	0.0716	4.98	0.27
0.207	0.1123	7.12	0.28
0.245	0.1288	7.48	1.15
0.261	0.1346	7.93	1.38
0.341	0.1622	9.42	4.78
0.431	0.2087	11.50	3.06
0.486	0.2222	12.40	4.83
0.708	0.2760	16.20	7.86
0.789	0.2911	16.30	8.83

Table 4  
Molar Differential Conductivities  $\Upsilon$  of Dimethyl Sulfoxide  
and Acetonitrile in LiCl Solution in Isoamyl Alcohol.

$C_{\text{LiCl}}$ (mol/l)	$\kappa \cdot 10^3$ $\Omega^{-1}$	$-\Upsilon \cdot 10^2$	
		dimethyl sulfoxide	acetonitrile
0.0189	0.0210	3.72	2.33
0.0430	0.0396	5.82	3.26
0.0877	0.0640	9.03	6.35
0.157	0.0894	14.6	9.37
0.210	0.1041	16.2	11.3
0.291	0.1385	19.9	14.1
0.488	0.2228	24.4	20.9
0.578	0.2425	29.2	23.3
0.735	0.2850	27.2	24.9

Table 5  
The Parameters of the Statistical Treatment of Molar  
Differential Conductivities in Isoamyl Alcohol According  
to Eq. (2a)

Non-electrolyte	$a_0 \cdot 10^{-3}$	$V_s \left( \frac{\text{cm}^3}{\text{mol}} \right)$	$r$	$s \cdot 10^3$	$\left( \frac{a}{s_0} \right)$
1. Water	$0.3 \pm 3.8$	$-610.8 \pm 22.3$	0.994	7.3	0.036
2. Methanol	$7.2 \pm 2.1$	$-510.2 \pm 13.6$	0.996	4.5	0.027
3. Ethanol	$2.0 \pm 2.3$	$-457.2 \pm 13.5$	0.996	4.4	0.029
4. Isobuthanol	$-3.3 \pm 2.9$	$-111.1 \pm 16.0$	0.961	3.9	0.139
5. Dioxane	$19.3 \pm 4.2$	$-326.5 \pm 27.0$	0.962	9.0	0.079
6. Acetonitrile	$9.4 \pm 4.5$	$-1194.0 \pm 38.0$	0.997	6.5	0.032
7. Dimethyl- sulfoxide	$-11.4 \pm 8.0$	$-1381.0 \pm 67.0$	0.993	11.4	0.048

(<sup>a</sup> The normalized standard deviation (see 7)).

where the intrinsic volumes of the non-electrolytes are calculated as the sum of the corresponding bond refractions in the molecule ( $\sum R_D$ )<sup>(8)</sup>. The slope of linear relationship (3) is significantly different from the analogous parameter for other hydroxylic solvents ( $11.50 \pm 0.32$  in water<sup>1</sup> and  $12.2 \pm 0.4$  in ethanol<sup>4</sup>). Therefore, different solvents seem to have different sensitivities towards the structure-making or structure-breaking effects by the other hydroxylic solvent additions. The aim of the further investigations should be the establishment of the theoretical description of such different sensitivity.

However, it is interesting to note, that in aqueous solutions the larger effects (and, namely, structure-making)

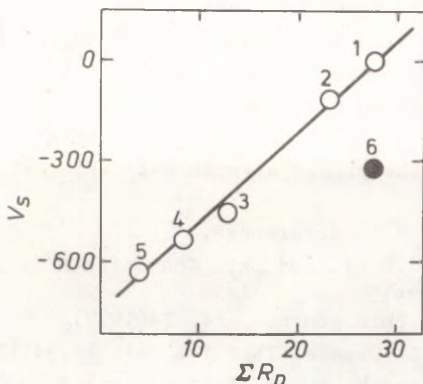


Fig. 2. The dependence of the characteristic volumes  $V_s$  on the intrinsic volumes ( $\Sigma R_D$ ) of some non-electrolytes in the LiCl solution of isoamyl alcohol.

- ( 1 - isoamyl alcohol (inner standard,  $V_s=0$  by definition)  
 2 - isobutyl alcohol  
 3 - ethanol  
 4 - methanol  
 5 - water  
 6 - dioxane ).

on solvent structure had the molecules with the bigger intrinsic volume<sup>1</sup>. In isoamyl alcohol the larger effects on the solvent structure (which is structure-breaking, in this case) are established for the molecules with smaller intrinsic volume (water, methanol). Consequently, there is a significant difference in the structure-making and structure-breaking abilities of addition molecules from the basic solvent.

The  $V_s$  of aprotic solvents investigated (dimethyl sulfoxide, acetonitrile and dioxane) have large deviations from the linear relationship (3). This behavior is analogous to that observed in ethanolic electrolyte solutions<sup>5</sup>. However, the deviations in the case of isoamyl alcohol are even bigger (cf. Table 5 and Fig. 2). All the aprotic solvents investi-

gated here are also structure-breakers for the isoamyl alcohol. In comparison with the hydroxylic molecules of the same volume, the aprotic molecules have stronger structure-breaking ability. This is in accordance with the results for the aqueous and ethanolic solutions, where the aprotic solvents were described by the bigger structure-breaking effects, too.

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NON-ELECTROLYTE EFFECTS ON THE STRUCTURE OF  
AMMONIUM RHODANIDE ACETONITRILE SOLUTIONS

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The results of differential-conductometric measurements of the non-electrolyte addition effects on the conductivity of the ammonium rhodanide solutions in acetonitrile are presented. The solution structure reorganization volumes  $V_s$  are calculated on the basis of these data for five non-electrolytes investigated (water, ethanol, isoamyl alcohol, dioxane and dimethylformamide).

In the previous communications<sup>1-4</sup> of this series of investigation, the results of differential-conductometric measurements of non-electrolyte effects in the electrolyte solutions of water, ethanol and isoamyl alcohol were published. The present article deals with the results of the study of similar effects in an aprotic solvent - acetonitrile. The electrolyte, whose conductivity changes were measured, was ammonium rhodanide. This choice was governed by its good solubility in acetonitrile, which allows to study solutions in the wide range of electrolyte concentration.

The molar differential conductivity<sup>5</sup>:

$$\gamma = \frac{k \cdot 10^3}{c_s} \left( \frac{1}{R_0 + \Delta R} + \frac{1}{R_x} \right) \quad (1)$$

is calculated on the basis of the differential-conductometric measurements. In this formula  $k$  denotes the conductometric cell constant ( $\text{cm}^{-1}$ ),  $c_s$  is the molar concentration of the substance added to the electrolyte solution ( $\text{mol/l}$ ), and  $R_0$  and  $R_x$  are the resistances ( $\Omega$ ) of the solution before and after adding this substance, respectively. Quantity  $\Delta R$ , added to the initial resistance, takes into account its change due to the dilution by the substance admixed to the electrolyte solution.

In the framework of the structural theory of solutions<sup>1,6</sup> the molar differential conductivity  $Y$  has to be proportional to the overall specific conductivity of the pure electrolyte solution of the given concentration ( $\kappa$ ):

$$Y = V_s \cdot \kappa \quad (2)$$

Multiplier  $V_s$  is a characteristic volume for a given substance investigated as an addition to the electrolyte solution. This parameter describes its influence on the structure of solvent and it is numerically equal to the statistically average volume in the vicinity of the admixture molecule, where the solvent structure is fully perturbed. In the case of positive values of  $V_s$ , this perturbation means the formation of ideally ordered structure of solvent, the negative values of  $V_s$  correspond to the entirely disordered form of the latter.

The amounts of the substance added to the solutions are small ( $c_s \sim 10^{-2}-10^{-3}$  mol/l) to avoid the higher order effects on the solvent structure.

#### Experimental.

Ethanol (grade "Pure for analysis") was dried on the CaO and distilled. The fraction used had b.p.  $78.4^\circ\text{C}$  (760 mm Hg) and the density  $d_{25}^{25} = 0.7898$ .

Isoamyl alcohol (grade "Pure") was fractionally distilled. The fraction used had b.p.  $130.5^\circ\text{C}$  (760 mm Hg),  $d_{25}^{25} = 0.8123$  and the refraction index  $n_D^{20} = 1.4080$ .

Acetonitrile (grade "Pure for analysis") was treated with KOH and distilled. The principal fraction obtained was treat-

ed with  $\text{CaH}_2$  and fractionally distilled. The fraction used as the basic solvent in experiments had b.p.  $81.5^\circ\text{C}$  (760 mm Hg) and  $d_{25}^{25} = 0.7791$ .

Dioxane (grade "Pure for analysis") was treated with HCl and KOH, dried and then boiled with sodium. Finally the fractional distillation of this product was made. The fraction used had b.p.  $101.5^\circ\text{C}$  (760 mm Hg) and  $d_4^{20} = 1.0329$ .

Dimethyl formamide (grade "Pure for analysis") was dried on the CaO and bidistilled. The fraction used had b.p.  $39.7-40.0^\circ\text{C}$  (20 mm Hg) and  $d_{25}^{25} = 0.9492$ .

The water used in experiments was deionized and bidistilled.

The conductometric measurements were carried out on the apparatus described elsewhere<sup>5</sup>. All the measurements were made at temperature  $25.0 \pm 0.1^\circ\text{C}$ , hold constant with the precision of  $\pm 0.001^\circ\text{C}$ . The conductivity cell was isolated from the surrounding atmosphere with CaO tubes to prevent the absorption of water. The cell constant was  $19.40 \text{ cm}^{-1}$ . Constant resistance ( $R_p = 9907.0 \Omega$ ) was used in parallel joint to the conductivity cell in case of dilute solutions.

The dilution term,  $\Delta R$  in Eq. (1) was calculated according to the procedure, described previously<sup>12</sup>.

### Discussion.

The numerical values of the molar differential conductivities are given in Tables 1.-3. The results of the least-squares treatment of these data according to equation

$$Y = V_g X + a_0, \quad (2a)$$

where  $a_0$  is the small intercept taking into account the self-conductivity of addition substance, are presented in Table 4. The example of linear relationship (2a) is illustrated by the data for dioxane in Fig. 1. Such linear relationships are valid also for water, isoamyl alcohol and dioxane additions. Dimethyl formamide is characterized by special behaviour of molar specific conductivity (see Fig. 2.). The Y values are close to -1 at all concentrations of electrolyte investigated, and the slope in Eq. (2) corresponds to the positive value

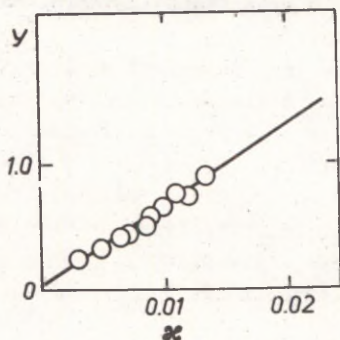


Fig. 1. The linear relationship between the molar differential conductivity  $Y$  of dioxane in the  $\text{NH}_4\text{SCN}$  solution of acetonitrile and the specific conductivity  $X$  in this solution.

( $34.5 \pm 3.7$ ) of the specific volume  $V_s$ . This linearity is characterized by a very large intercept ( $1.36 \pm 0.03$ ), which is much greater than the self-conductance of dimethyl formamide. Consequently, there has to be a substantial curvature of this relationship in the region of small electrolyte concentrations. The slope of the dependence in this region is obviously negative. Therefore, it should be concluded, that dimethyl formamide does not have a constant restructuring volume  $V_s$ , valid at all concentrations of electrolyte in acetonitrile. Moreover, the nature of the solvent structure reorganization by dimethyl formamide is different at various concentrations. In the dilute electrolyte solutions dimethyl formamide is substantially a structure-breaker, whereas in more concentrated solutions of electrolyte it acts as a structure-forming agent.

Water, ethanol and dioxane are characterized by a constant specific volume  $V_s$  at all electrolyte concentrations investigated. The negative sign of  $V_s$ -values indicates that all these three substances are structure-breakers in aceto-

Table 1.

Molar Differential Conductivities  $\chi$  of Water Additions  
to the  $\text{NH}_4\text{SCN}$  Solutions in Acetonitrile.

$C_{\text{NH}_4\text{SCN}} \left( \frac{\text{mol}}{\text{l}} \right)$	$\chi \cdot 10^3$	$-\chi$
0.018	1.36	0.980
0.036	2.54	1.33
0.068	3.13	1.46
0.131	4.76	1.90
0.184	6.05	2.10
0.194	6.15	2.39
0.259	7.45	2.49
0.381	9.70	2.99
0.486	11.5	3.29
0.599	12.9	3.63
0.626	13.6	3.68

Table 2

Molar Differential Conductivities  $\chi$  of the Ethanol  
and Isoamyl Alcohol Additions to the  $\text{NH}_4\text{SCN}$  Solutions  
in Acetonitrile.

$C_{\text{NH}_4\text{SCN}} \left( \frac{\text{mol}}{\text{l}} \right) \cdot 10^3$	$-\chi$	
	ethanol	isoamyl alcohol
0.082	1.23	0.02
0.088	1.24	- 0.04
0.135	1.46	- 0.01
0.205	1.58	0.09
0.256	1.60	- 0.10
0.298	1.78	- 0.04
0.319	1.81	0.03
0.412	1.99	- 0.07
0.446	2.04	0.08
0.504	2.29	0.00

Table 3.

Molar Differential Conductivities  $\Upsilon$  of the Dioxane  
and Dimethyl Formamide Additions to the  $\text{NH}_4\text{SCN}$   
Solutions in Acetonitrile.

$C_{\text{NH}_4\text{SCN}} \left( \frac{\text{mol}}{\text{l}} \right) \cdot 10^3$	- $\Upsilon$		
	dioxane	dimethyl formamide	
0.062	2.94	0.249	1.01
0.168	4.95	0.310	1.22
0.216	6.59	0.410	1.14
0.243	7.12	0.415	1.14
0.303	8.26	0.492	1.10
0.340	8.90	0.575	1.06
0.396	9.82	0.668	1.08
0.460	11.0	0.769	1.00
0.522	12.0	0.730	0.94
0.603	13.2	0.907	0.86

Table 4.

The Parameters of the Statistical Treatment of Molar  
Differential Conductivities Values in Acetonitrile  
According to Eq. (2a) .

Non-electrolyte	$a_0$	$v_s \left( \frac{\text{cm}^3}{\text{mol}} \right)$	$M^{(a)}$	$s^{(b)}$	$s_0^{(c)}$
1. Water	$0.809 \pm 0.063$	$-219.0 \pm 7.7$	0.994	0.103	0.035
2. Ethanol	$0.814 \pm 0.052$	$-117.5 \pm 6.5$	0.989	0.056	0.055
3. Isoamyl alcohol	$-0.023 \pm 0.050$	$-1.0 \pm 6.2$	$0.055^{(d)}$	0.054	0.353
4. Dioxane	$0.004 \pm 0.043$	$-65.7 \pm 4.8$	0.979	0.045	0.071

(<sup>a</sup> - correlation coefficient, (<sup>b</sup> standard deviation, (<sup>c</sup> the normalized standard deviations (See <sup>6</sup>). (<sup>d</sup> The  $\Upsilon$  value for isoamyl alcohol is practically zero at all electrolyte concentrations. Therefore, the linear regression correlation coefficient is also close to zero.

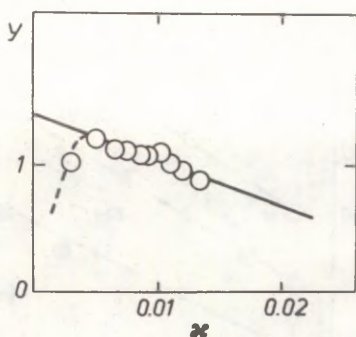


Fig. 2. The dependence of molar differential conductivity  $Y$  of dimethyl formamide on the specific conductivity of electrolyte  $(\text{NH}_4\text{SCN})$  solution in acetonitrile.

nitrile solutions (See<sup>1</sup> for  $V_s$ -analysis). The isoamyl alcohol has practically no effect on the structure of acetonitrile solutions, and therefore its  $V_s \approx 0$ . There is a satisfactory linear relationship between the volumes  $V_s$  and intrinsic volumes of non-electrolytes investigated in the present work. (See Fig. 3). The latter were estimated as the sum of molecular bond refractions ( $\sum R_D$ ) for a given substance<sup>7</sup>. This linear relationship is described by the following statistical parameters:

$$V_s = (-245.7 \pm 17.3) + (8.87 \pm 0.93) \sum R_D \quad (3)$$

$$r = 0.989 \quad s = 16.5 \quad s_0 = 0.104$$

The slope of this relationship is less than the corresponding slopes for aqueous, ethanolic and isoamyl alcohol solutions ( $11.50 \pm 0.32$ <sup>1</sup>,  $12.2 \pm 0.4$ <sup>2</sup>, and  $27.1 \pm 2.2$ <sup>4</sup>, respectively). The intercept of abscissa ( $V_s = 0$ ) does not correspond to the intrinsic volume of acetonitrile itself ( $\sum R_D(\text{acetonitrile}) = 11.112$ <sup>7</sup>), but has a much greater value. This fact means that all the substances investigated have bigger structure-break-

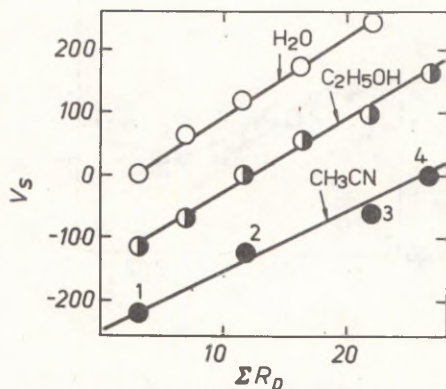


Fig. 3. The dependence of molar volumes of restructurization  $V_s$  on the intrinsic volume ( $\Sigma R_D$ ) of non-electrolyte additions to the electrolyte solutions in water, ethanol and acetonitrile (The additions: 1 - water, 2 - ethanol, 3-dioxane, 4- isoamyl alcohol).

ing volumes  $V_s$  on the liquid acetonitrile than those following their intrinsic volumes. This trend is analogous to the behaviour of  $V_s$ -values of aprotic solvents in hydroxylic solvents, where the aprotic additions do have a bigger structure-breaking effect in comparison with the hydroxylic additions of the same intrinsic volume<sup>1-4</sup>. Consequently, if to assume the division of all solvents into two classes - aprotic and hydroxylic, respectively, the following general conclusion can be made: The molecule of addition of different class has a bigger structure-breaking effect on the given solvent than the molecule of the same class with equal intrinsic volume.

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EFFECTS OF REACTION MEDIUM AND TEMPERATURE ON SOLVOLYSIS  
OF N,N-DIMETHYL-2-PHENYL-AZIRIDIUM ION.

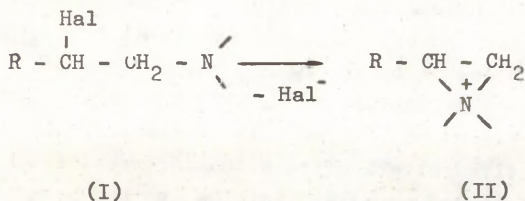
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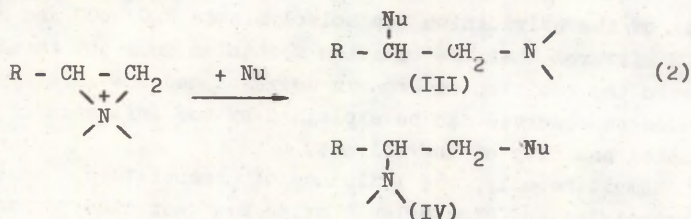
Kinetics of solvolysis of N,N-dimethyl-2-phenyl-aziridium ion has been studied in water, in the solutions of KCl and CsCl and in different water - organic solvent mixtures. Also the product analysis of the solvolytic reaction in water - ethanol and water - methanol mixtures has been made. On the basis of these data it has been shown that the reaction occurs according to the  $S_N1$  mechanism at neutral and acidic pH values, while this mechanism changes to  $S_N2$  in alkaline solution. Data on the temperature dependence of solvolysis rate at neutral pH and in different water - solvent mixtures were described by the isokinetic plot and the isokinetic temperature, calculated from this plot was  $494^\circ\text{K}$ .

Effect of solvents on the rate of the solvolysis at neutral pH has been described by a single - parameter version of the Koppel-Palm equation which took into account the general basicity of the solvent.

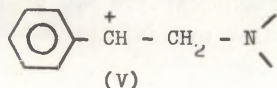
The aziridium ions (II) form from tertiary 2-halogenoethylamines (I) through the intramolecular nucleophilic displacement reaction<sup>1</sup>:



In reactions with external nucleophiles the aziridinium ion can yield two types of products (III and IV) of the nucleophilic displacement reaction depending upon the particular reaction mechanism



Secondary alcohols are formed from the aziridinium compound in water at neutral pH, if a phenyl group stands for substituent R in (III)<sup>1</sup>. This fact points to the S<sub>N</sub>1 mechanism of this reaction, which occurs through the carbonium ion (V) stabilized by the phenyl group<sup>1</sup>:



Formation of this carbonium ion is the rate-limiting step of the displacement reaction. It can be assumed in accordance with this reaction mechanism that the observed process rate is independent of the reactivity and nature of the nucleophilic reagent. Nevertheless, it was shown that the solvolysis rate of the N,N-dimethyl-2-phenylaziridinium ion can be remarkably increased in alkaline medium as well as in neutral medium in the presence of organic solvent (acetone)<sup>1</sup>.

In the first case it can be assumed that the monomolecu-

lar mechanism of hydrolysis transforms to the bimolecular substitution reaction of  $S_N2$  type<sup>1</sup>. Acceleration of the reaction in the presence of an organic solvent can be, however, explained also by solvent effects. With the purpose to elucidate the mechanism of this solvolytic reaction and to specify these putative solvent effects the decomposition kinetics of the N,N-dimethyl-2-phenylaziridinium ion has been studied at different temperatures in water and in mixtures of water with ethanol, 2-propanol, acetonitrile, 1,4-dioxane, dimethylformamide, dimethylsulphoxide as well as in the presence of neutral electrolytes KCl and CsCl. It has been established on the basis of this data and the results of the product analysis of the aziridinium ion solvolysis in  $H_2O/EtOH$  and  $H_2O/MeOH$  mixtures that the reaction mechanism does not change due to the addition of organic solvents and the acceleration phenomena observed can be explained by the influence of the general basicity of the solvent.

Simultaneously, the influence of temperature, neutral electrolytes and dimethylsulphoxide has been studied on the rate of decomposition of the N,N-dimethyl-2-phenylaziridinium ion in alkaline medium. The bimolecular  $S_N2$  mechanism of alkaline hydrolysis reaction of the N,N-dimethyl-2-phenylaziridinium ion has been established proceeding from these results.

The complex of results obtained allows a more detailed discussion of the reaction mechanism of aziridinium ions with different biopolymers, including receptors and enzymes. The latter reactions are responsible for the high biological activity of these compounds.

#### Experimental

Solvents were purified according to the recommendations in<sup>2</sup>. The salts (KCl, NaOH,  $KH_2PO_4$ ,  $Na_2HPO_4$ ,  $CH_3COONa$ ) of analytical grade from "Reakhim" were used without the additional purification. Buffer solutions (0.1 M acetate buffer, pH 3.7, 4.4, 5.2, 5.6; 0.1 M and 0.15 M phosphate buffer, pH=6.2 and 7.5) were made as described in<sup>3</sup>. The pH of buffer solutions was measured at a PHM 82 pH-meter, "Radiometer", Denmark. All solutions were made up in bidistilled water.

Synthesis and properties of *N,N*-dimethyl-2-chloro-2-phenylethylamine hydrochloride were described in<sup>4</sup>. Solutions of *N,N*-dimethyl-2-phenylaziridinium ion were prepared by the dissolution of *N,N*-dimethyl-2-chloro-2-phenylethylamine hydrochloride in a 0.15 M phosphate buffer pH 7.5 immediately before the experiments. Formation of the aziridinium compound occurs at pH 7.5 and 25°C with half-life of 12 s.<sup>4</sup> The aliquots of the aziridinium solution (0.1 ml) were taken after a 5-minute preincubation and mixed with 2.9 ml of the reaction solution, containing solvents, salts, NaOH or buffer. Concentration of *N,N*-dimethyl-2-phenylaziridinium ion in reaction mixture did not exceed 1 mM.

Decomposition kinetics of the aziridinium compound was followed spectrophotometrically by the decrease in the optical density of the reaction mixture at  $\lambda = 269.5$  nm. The UV-spectra of the initial compound (*N,N*-dimethyl-2-phenylaziridinium ion) and the product of its hydrolysis (*N,N*-dimethyl-2-hydroxy-2-phenylethylamine) are shown in Fig. 1.

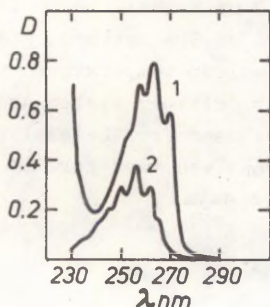


Fig. 1. UV-spectra of *N,N*-dimethyl-2-phenylaziridinium ion (1) and *N,N*-dimethyl-2-hydroxy-2-phenylethylamine (2) in 0.15 M phosphate buffer pH 7.5. Concentration of compounds 2 mM.

The changes observed in the spectrum of the initial compound at  $\lambda = 269.5$  nm were found to be independent of the composition of the reaction medium. Experiments were conducted in the temperature controlled cells on a Perkin Elmer 402 spectrophotometer. The solvolysis reactions were followed dur-

ing 5-6 half-lives. The observed first-order rate constants (k) were calculated by the differential method of Rudakov<sup>5</sup>:

$$\ln \dot{\psi} = \text{const} - k \cdot \tau \quad (3)$$

where  $\dot{\psi} = D_i - D_{i+1}$ ;  $D_i$  and  $D_{i+1}$  denote optical density of the solution at time moments  $t_i$  and  $t_{i+1}$ ;  $\tau = \frac{t_i + t_{i+1}}{2}$ .

Calculations of the first-order rate constants and statistical treatment of the experimental data by means of a linear least-squares regression programme were performed on an Iskra 1256 computer.

Four-parameter linear correlations were made, using a multilinear regression programme written by professor V. Palm in language "EXPER" for a modified "Elektronika 60" computer, designed in Institute of Physics, of the Academy of Sciences of the ESSR.

The HPLC equipment has been used for the analysis of products of solvolysis of N,N-dimethyl-2-phenylaziridinium ion in water and in the water - ethanol and water - methanol mixtures. Analyses were done on 4.6x250 mm Zorbax ODS (C 18) columns (Du Pont, USA). Eluent consisted of 90% methanol and 10% 0.05 M acetate buffer, pH 5,6. The column temperature was 50°C, the pressure 90 bar. A solvent delivery system and a UV-detector from "Bruker" (FRG) were used for the analysis. A SP 4100 integrator unit from Du Pont was used for the quantitative analysis of chromatographic data.

### Results

#### Influence of pH.

Decomposition of N,N-dimethyl-2-phenylaziridinium ion follows the first-order kinetics within the pH range from 1.1 (0.08 M HCl) up to 13.8. This allows the determination of the first-order rate constant (k). The plot of log k vs. pH is shown in Fig. 2.

It can be seen, that there is a remarkable increase in the k-values in alkaline solution. The slope of the log k vs. pH plot in this region is  $1.03 \pm 0.07$ . This agrees with

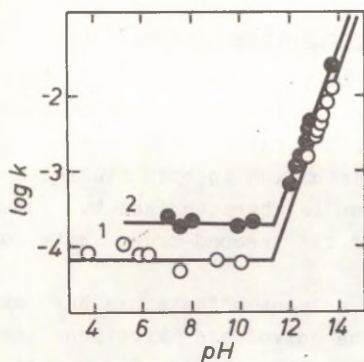


Fig. 2. Plot of  $\log k$  vs. pH for solvolysis of N,N-dimethyl-2-phenylaziridinium ion in water (1) and in 4.2 M DMSO solution in water at 25°C.

the bimolecular mechanism of the solvolysis reaction for which the second order rate constants ( $k_{OH}$ ) can be calculated from  $k$  vs.  $C_{OH}$  plot (Fig. 3):

$$k = k^0 + k_{OH} \cdot C_{OH} \quad (4)$$

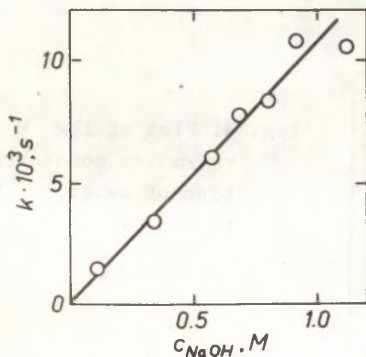


Fig. 3. Plot of  $k_{OH}$  vs. NaOH concentration for decomposition of N,N-dimethyl-2-phenylaziridinium ion in water at 25°C.

### Influence of organic solvents

There is also  $\log k$  vs. pH plot for the 4.2 M dimethylsulphoxide solution shown in Fig. 2. It can be seen that addition of this solvent increases the rate of solvolysis of the N,N-dimethyl-2-phenylaziridinium ion in both neutral and alkaline media where the reaction is characterized by the first-order rate constant  $k$  and the second-order rate constant  $k_{OH}$ , respectively.

A more detailed analysis of solvent effects has been made at neutral pH. In this case the solvolysis kinetics has been studied in mixtures of water with ethanol, 2-propanol, acetonitrile, 1,4-dioxane, dimethylformamide and dimethylsulphoxide. The rate constants obtained are listed in Table 1.

It can be seen from this Table that the addition of organic solvents into the reaction mixture and the decrease of water concentration in it leads, in general, to the increase in the solvolysis rate. This dependence can be formalized by the linearity between  $\log k$  and the molar concentration of water in the reaction mixture (Fig. 4):

$$\log k = \log k^S + \rho C_{H_2O} \quad (5)$$

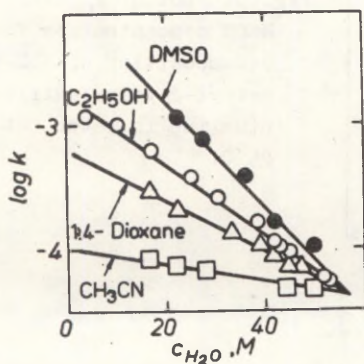


Fig. 4. Plot of  $\log k$  vs. molar concentration of water, 25°C, pH 7.5.

Table 1  
 Solvolysis of N,N-Dimethyl-2-phenyl-aziridinium Ion in  
 Water - Solvent Mixtures, 25<sup>o</sup>C, 0.01 M Phosphate Buffer  
 pH 7.5

$C_{\text{solv}}, M$	$10^4 \cdot k, c^{-1}$	$C_{\text{solv}}, M$	$10^4 \cdot k, c^{-1}$
		<u>C<sub>2</sub>H<sub>5</sub>OH</u>	
0.85	0.54 $\pm$ 0.07	8.35	2.56 $\pm$ 0.03
1.15	0.58 $\pm$ 0.03	10.0	3.85 $\pm$ 0.05
3.60	0.93 $\pm$ 0.03	12.4	6.18 $\pm$ 0.50
4.15	1.01 $\pm$ 0.03	13.95	10.1 $\pm$ 0.7
4.60	1.11 $\pm$ 0.01	16.2	11.5 $\pm$ 0.8
5.75	1.65 $\pm$ 0.05		
		<u>(CH<sub>3</sub>)<sub>2</sub>CHOH</u>	
1.30	0.81 $\pm$ 0.05	6.45	2.05 $\pm$ 0.05
2.57	0.99 $\pm$ 0.04	7.75	2.67 $\pm$ 0.09
3.85	1.34 $\pm$ 0.08	9.0	3.58 $\pm$ 0.08
5.17	1.65 $\pm$ 0.06	10.25	4.85 $\pm$ 0.14
		<u>CH<sub>3</sub>CN</u>	
1.91	0.462 $\pm$ 0.03	11.5	0.732 $\pm$ 0.05
3.85	0.468 $\pm$ 0.03	13.4	0.813 $\pm$ 0.04
9.55	0.643 $\pm$ 0.04		
		<u>1,4-Dioxane</u>	
1.76	0.724 $\pm$ 0.04	4.69	1.37 $\pm$ 0.06
2.35	0.714 $\pm$ 0.03	7.05	2.08 $\pm$ 0.09
2.93	0.872 $\pm$ 0.05	8.22	2.93 $\pm$ 0.13
3.52	1.07 $\pm$ 0.11		
		<u>DMFA</u>	
2.57	1.36 $\pm$ 0.03	7.7	6.48 $\pm$ 0.14
5.14	2.67 $\pm$ 0.12	10.3	22.3 $\pm$ 2.7
		<u>DMSO</u>	
1.41	1.05 $\pm$ 0.10	7.06	7.55 $\pm$ 0.37
3.52	1.61 $\pm$ 0.07	8.47	11.9 $\pm$ 0.7
4.94	3.92 $\pm$ 0.32		

Similar linearity can be obtained in the coordinates  $\log k - \text{molar concentration of organic solvent}$ . The results of treatment of the experimental data in Table 1 by means of equation (5) are given in Table 2. Constants  $\log k^B$ , calculated from equation (5), characterize the solvolysis rate in pure solvents.

Table 2.

Rate Constants for Solvolysis of N,N-Dimethyl-2-phenylaziridinium Ion in Pure Solvents ( $k^B$ ) and Parameters of Polarity (Y), Polarizability (P), General Acidity and Basicity (E and B) of Solvents Obtained from<sup>6</sup>.

Solvent	$\log k^B$	Y	P	E	B
H <sub>2</sub> O	-4.35	0.4907	0.27976	21.8	156
C <sub>2</sub> H <sub>5</sub> OH	-2.80	0.4698	0.29908	11.6	235
(CH <sub>3</sub> ) <sub>2</sub> CHOH	-3.08	0.4601	0.30961	8.7	236
CH <sub>3</sub> CN	-3.98	0.4803	0.28568	5.2	160
1,4-Dioxane	-3.23	0.2231	0.33845	4.2	237
DMFA	-2.38	0.4798	0.34143	2.6	291
DMSO	-1.96	0.4848	0.37212	3.2	362

These rate constants were further analyzed by means of the Koppel-Palm equation<sup>6</sup>:

$$\log k^B = \log k^{B0} + yY + pP + eE + bB \quad (6)$$

which takes into account the polarity and polarizability (Y, P) as well as the general acidity and basicity of solvents (E, B). y, p, e and b denote the appropriate intensity factors.

In the case of the N,N-dimethyl-2-phenylaziridinium ion, solvolysis, equation (6) can be remarkably simplified, as the statistically satisfactory description of experimental data can be obtained by using the B-parameters only:

$$\log k^B = \log k^{B0} + bB \quad (7)$$

The results of data fitting are as follows:

$$\log k^{B_0} = -5.82 \pm 0.35, \quad b = 0.0113 \pm 0.0014$$

$$s_0 = 0.319, \quad s = 0.249, \quad R^2 = 0.858$$

where  $s_0$  and  $s$  denote the standard deviation in normalized and natural scales. The plot of  $\log k^B$  vs.  $B$  is illustrated in Fig. 5.

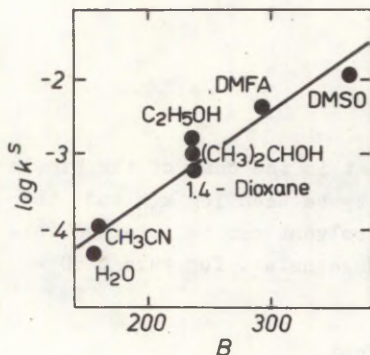


Fig. 5. Plot of  $\log k^B$  vs.  $B$ -parameter for general basicity of solvents.

In alkaline medium the second-order rate constants were measured in mixtures of water and dimethylsulphoxide (Table 3, Fig. 6).

Table 3.

Alkaline Hydrolysis of *N,N*-Dimethyl-2-phenylaziridinium Ion in Water-DMSO Mixtures at 25°C.

$C_{\text{DMSO}}, M$	$10^2 \cdot k_{\text{OH}}, M^{-1} s^{-1}$	$C_{\text{DMSO}}, M$	$10^2 \cdot k_{\text{OH}}, M^{-1} s^{-1}$
1.4	$1.30 \pm 0.13$	4.2	$2.79 \pm 0.59$
2.8	$2.02 \pm 0.29$	5.7	$4.10 \pm 0.25$

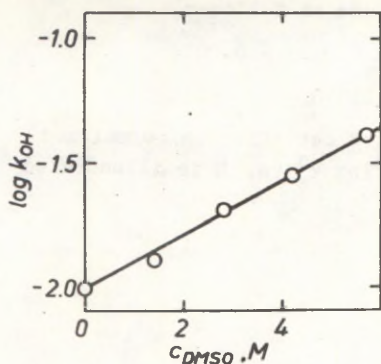


Fig. 6. Plot of  $\log k_{\text{OH}}$  vs. DMSO concentration at  $25^{\circ}\text{C}$ .

It can be seen in Fig. 6 that in the case of the bimolecular reaction also the linearity between  $\log k_{\text{OH}}$  and the molar concentration of organic solvent can be obtained. This allows also to estimate the rate constant for pure DMSO -  $k_{\text{OH}}^{\text{DMSO}} = 0.343 \text{ M}^{-1} \text{ sec}^{-1}$  ( $25^{\circ}\text{C}$ ).

#### Salt Effect

Neutral electrolytes added into the reaction medium show different influence on the decomposition reaction of aziridinium ion in neutral and alkaline media. In the former case there is no primary salt effect and a small decrease in the  $k$ -values in saturated KCl and CsCl solutions if compared with the reaction rate in pure water (Fig. 7), can be explained with salting effect<sup>7</sup>.

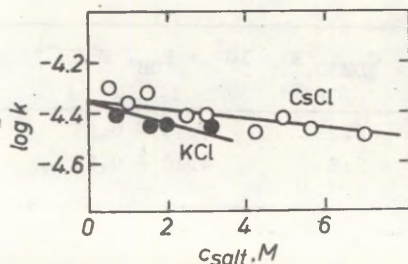


Fig. 7. Effect of KCl and CsCl on solvolysis rate of  $N,N$ -dimethyl-2-phenylaziridinium ion in water at pH 7.5 and  $25^{\circ}\text{C}$ .

In case of alkaline hydrolysis, a remarkable negative primary salt effect is revealed (Fig. 8) pointing to the participation of two ions of opposite charge in this reaction.

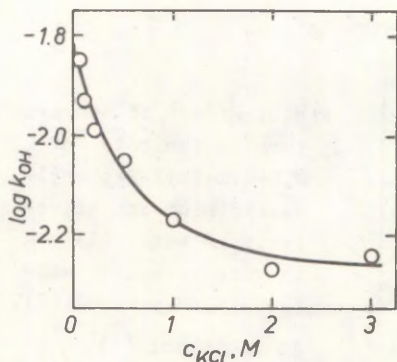


Fig. 8. Effect of KCl on rate of alkaline hydrolysis of N,N-dimethyl-2-phenyl-aziridinium ion, 25°C

#### Effect of Temperature

Thermodynamic parameters were calculated for the solvolysis reaction of N,N-dimethyl-2-phenylaziridinium ion in water and in water - solvent mixtures at pH 7.5, making use of the following equations:

$$\ln \frac{k}{T} = \text{const} - \frac{\Delta H^\ddagger}{RT} \quad (8)$$

$$\Delta F^\ddagger = -RT \ln \frac{k \cdot h}{k_B \cdot T} \quad (9)$$

$$\Delta S^\ddagger = \frac{\Delta H^\ddagger - \Delta F^\ddagger}{T} \quad (10)$$

where  $\Delta F^\ddagger$  stands for activation free energy,  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  denote the activation standard enthalpy and entropy changes, R - universal gas constant ( $8.31 \frac{J}{\text{mol} \cdot K}$ ),  $k_B$  - the Boltzmann constant ( $1.38 \cdot 10^{-23} \frac{J}{K}$ ), h - the Planck constant

$(6.62 \cdot 10^{-34} \text{ J.s.})$ .

The plot of  $\ln k$  vs.  $\frac{1}{T}$  are shown in Fig. 9.

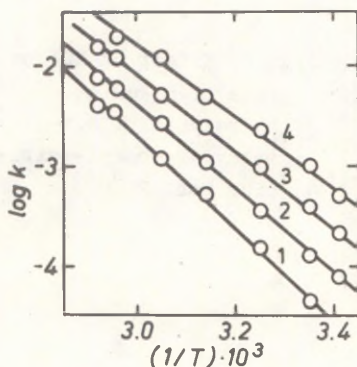


Fig.9. Effect of temperature on the rate of N,N-dimethyl-2-phenylaziridinium ion solvolysis in water (1) and in water-ethanol mixtures: 5.2M ethanol (2), 10 M ethanol (3), 13.9 M ethanol (4).

It can be seen that within the whole temperature interval investigated (from  $20^{\circ}$  to  $70^{\circ}\text{C}$ ), good linear relationships were obtained. The thermodynamic parameters calculated from Eqns. (7-9) are listed in Table 4.

Table 4

Thermodynamic Parameters for the Solvolysis of N,N-Dimethyl-2-Phenylaziridinium Ion in Water and in Water-Solvent Mixtures at  $\text{pH}=7.5$

	$\Delta H^{\ddagger}, \frac{\text{kJ}}{\text{mol}}$	$\Delta S^{\ddagger}, \frac{\text{J}}{\text{mol} \cdot \text{K}}$
$\text{H}_2\text{O}$	$82.95 \pm 5.07$	$-49.45 \pm 0.02$
5.2 M $\text{C}_2\text{H}_5\text{OH}$	$75.23 \pm 4.19$	$-66.64 \pm 0.02$
10.0 M $\text{C}_2\text{H}_5\text{OH}$	$70.54 \pm 2.60$	$-74.87 \pm 0.01$
13.9 M $\text{C}_2\text{H}_5\text{OH}$	$62.73 \pm 8.34$	$-93.03 \pm 0.03$
4.1 M DMSO	$75.60 \pm 5.66$	$-61.13 \pm 0.03$
6.8 M DMSO	$71.15 \pm 3.90$	$-66.62 \pm 0.04$
5.0 M DMFA	$74.01 \pm 6.29$	$-63.27 \pm 0.02$
9.9 DMFA	$66.16 \pm 5.64$	$-74.50 \pm 0.04$
Alkaline hydrolysis ( $\text{H}_2\text{O}$ )	$64.61 \pm 6.96$	$-64.87 \pm 0.03$

Eqns. (7-9) were used also for the analysis of temperature effects in the alkaline hydrolysis of *N,N*-dimethyl-2-phenylaziridinium ion (Fig. 10). The results of this analysis are given in Table 4, too.

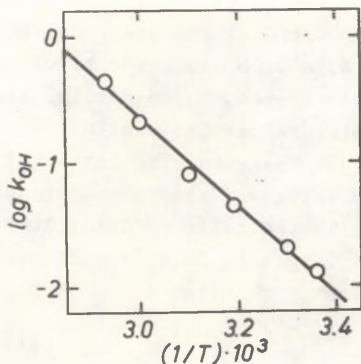


Fig. 10. Effect of temperature on the rate of *N,N*-dimethyl-2-phenyl-aziridinium ion alkaline hydrolysis.

#### Product Analysis

Solvolysis of *N,N*-dimethyl-2-phenylaziridinium ion in water (pH 7.5) yields a single product (Fig. 11A) which can be identified as *N,N*-dimethyl-2-hydroxy-2-phenylethylamine by HPLC. For the solvolysis product  $V_e = 3.39 \pm 0.06$  and for the standard compound obtained in<sup>4</sup>  $V_e = 3.41 \pm 0.05$ .

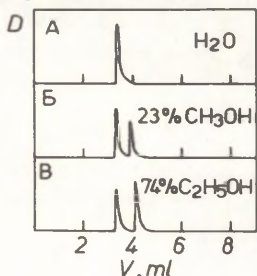


Fig. 11. HPLC analysis of solvolysis products for decomposition of *N,N*-dimethyl-2-phenyl-aziridinium ion in water (A), in water-methanol mixture (67:23w/w) (B) and in water-ethanol (26:74w/w) mixture (C).

In the presence of ethanol and methanol in the reaction mixture the solvolysis reaction yields two products (Fig. 11 B, C). In these both cases one of the products can be identified as the aminoalcohol formed through the hydrolysis of the aziridinium ion ( $V_e = 3.36 \pm 0.07$ ). Other products which formed in water-ethanol and water-methanol mixtures, had the  $V_e$  values  $3.98 \pm 0.08$  ml and  $V_e = 4.18 \pm 0.06$  ml, respectively. That points to their different structures. Consequently, alcohols, added into the reaction mixture, participate in the solvolysis reaction as nucleophilic reagents. The ratio of product concentrations formed by water and alcohol increase proportionally with the increase in the ratio of molar concentrations of water and alcohol (Fig.12). This proportionality can be formalized by the following equation :

$$\frac{[\text{Prod}^S]}{[\text{Prod}^{\text{H}_2\text{O}}]} = a + b \frac{C_S}{C_{\text{H}_2\text{O}}} \quad (11)$$

where a and b are the constants.

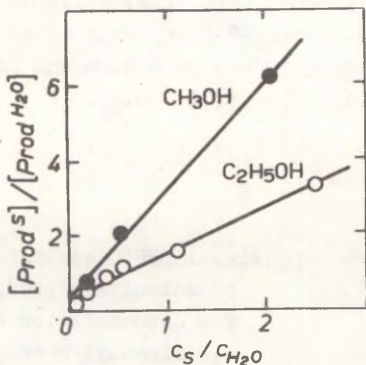


Fig. 12. Dependence of the ratio of N,N-dimethyl-2-phenylaziridinium ion hydrolysis and alcoholysis products ( $\text{Prod}^{\text{H}_2\text{O}}$  and  $\text{Prod}^S$ ) upon the ratio of water and alcohol molar concentrations in the reaction mixture.

The data treatment gave for water-methanol mixtures  $a = 0.39 \pm 0.82$ ,  $b = 2.88 \pm 0.67$  and for water - ethanol mixtures  $a = 0.29 \pm 0.23$ ,  $b = 1.21 \pm 0.20$

#### Discussion

The results obtained show that the decomposition of N,N-

-dimethyl-2-phenylaziridinium ion can occur through two reaction mechanisms. The second order reaction of  $S_N2$  type with the hydroxyl ion as a nucleophile takes place in alkaline medium. This conclusion can be drawn proceeding from the fact that the reaction is a first order one with respect to the concentration of alkali (Fig. 3). Consequently, the interaction between the ionic reagents with opposite charges takes place in the rate limiting step and the primary kinetic salt effect should manifest itself in this case. Indeed, this salt effect has been found in KCl solutions as shown in Fig. 8. Thus, the present results confirm the conclusion made in literature<sup>1</sup> about the incursion of the  $S_N2$  mechanism of decomposition of aziridinium ion in alkaline medium.

The second type of reaction mechanism of N,N-dimethyl-2-phenylaziridinium ion decomposition can be observed at neutral and acidic pH where water participates as a nucleophilic component of the solvolysis reaction. It has been shown in literature<sup>1</sup> by the establishment of the product structure for the hydrolysis reaction of N,N-dimethyl-2-phenylaziridinium ion that the most reliable solvolysis mechanism is  $S_N1$ , which involves monomolecular fission of CN bond on the **rate-limiting step** and the formation of the carbonium ion (V). However, it is impossible to prove such a  $S_N1$  reaction path by variation of water concentration in the reaction medium without changing other rate - determining factors.

Thereby, **alterations** in the structure and reactivity of the nucleophilic component may change the rate of aziridinium ion solvolysis. This phenomenon is connected with the change in the reaction mechanism. But, a remarkable increase in the rate of solvolysis can be achieved also by the addition of organic solvents into the reaction mixture. As these ingredients can as well participate in the solvolysis reaction as the nucleophilic reagent, the acceleration effect can also be connected with the change in reaction mechanism. However, there exists another possibility where the acceleration is connected with solvation effects on the carbonium

ion formation step.

With the purpose of differentiating between these two alternatives we have studied the solvolysis reaction of N,N-dimethyl-2-phenylaziridinium ion in water-ethanol mixtures. The addition of ethanol into the reaction mixture remarkably increases the reaction rate (Fig. 4) and the linearity between the logarithm of the apparent rate constant and molar concentration of water as well as ethanol can be observed. At the same time, the ratio of concentrations of two solvolysis products, formed in water-ethanol mixture is proportional to the ratio of molar concentrations of water and ethanol (Fig. 12). Thus, the acceleration of the reaction by ethanol and the formation of the alcoholysis product follow different regularities. For example, in 14 M ethanol solution in water the apparent reaction rate increases 22.6 times, while the ratio of the alcoholysis and hydrolysis is only 1.6. Hence, the acceleration of the N,N-dimethyl-2-phenylaziridinium ion decomposition by organic solvents can not be explained by bimolecular mechanism because in this case the ratio of the two products, formed by parallel reactions of hydrolysis and alcoholysis should change proportionally to the increase in the reaction rate.

Thus, it can be concluded that the decomposition of the aziridinium ion in water and in water-alcohol mixtures has a common  $S_N1$  mechanism. This conclusion is supported also by the analysis of temperature effects on the solvolysis reaction in water and water-solvent mixtures. The linearity between  $\log k^{45^\circ}$  and  $\log k^{20^\circ}$  shown in Fig. 13, corresponds to the isokinetic nature of this process in different reaction media and refers to a common reaction mechanism.

Isokinetic temperature  $\beta$ , calculated from equations (12) and (13)

$$\log k^{45^\circ} = \text{const} + \alpha \log k^{20^\circ} \quad (12)$$

$$\alpha = \frac{(T_2 - \beta)T_1}{(T_1 - \beta)T_2} \quad (13)$$

was found to be equal to  $494^\circ\text{K}$

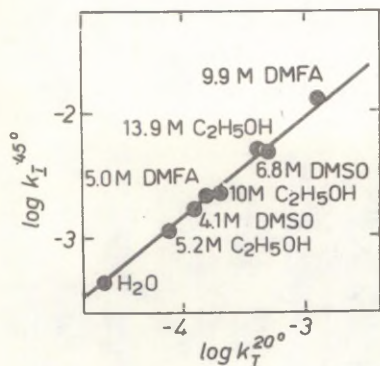
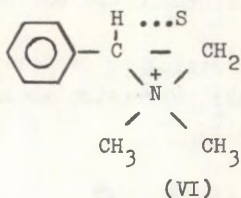


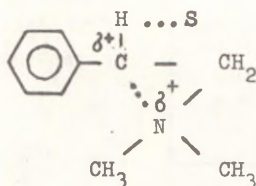
Fig. 13. Plot of  $\log k^{45^\circ}$  vs.  $\log k^{20^\circ}$  for N,N-dimethyl-2-phenylaziridinium ion decomposition in different water - solvent mixtures

Eqn. 6 takes into consideration four different solvation mechanisms. The statistical analysis of the experimental data revealed that only the general basicity is important for the solvolysis of N,N-dimethyl-2-phenylaziridinium ion. This type of specific solvation effect assumes the formation of donor-acceptor complexes between solvent molecules and the acidic (electrophilic) center of the reagent molecule. Such acidic centers in the molecule of N,N-dimethyl-2-phenylaziridinium ion which is the initial state for the reaction studied, is the hydrogen atom at the second carbon atom of the aziridinium cycle.



Formation of two acidic centers can be assumed in the structure of the activated complex which precedes the carbonium ion intermediate of the solvolysis reaction. Firstly, analogously with the initial state, acidic properties characterize the hydrogen atom at the second C-atom of the aziridinium cycle. Secondly, a new electrophilic center arises

through the formation of a free or partially free orbital at the carbon atom in the same position of the aziridinium cycle due to the dissociation of C-N bond. Interaction of a solvent molecule with the hydrogen atom, as shown in the following scheme (VII),



(VII)

seems to be more reliable for steric reasons. According to schemes (VI) and (VII), there is also no change in the structure of the solvated complex through the activation process. Moreover, scheme (VII) does not contradict the results of product analysis given above.

In order to further study the structure of the solvent - ligand interactions in the decomposition reaction of the aziridinium cycle, it would be interesting to deal with derivatives in which the hydrogen atom in the second position of the aziridinium cycle is replaced by deuterium or tritium atoms or by some other substituents which modify the ability of the aziridinium cycle to form complexes (VI) and (VII).

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