

Importance of repulsion of lone electron pairs in the enhanced reactivity of 1,8-naphthyridine and the large α -effect of hydrazine in the aminolyses of *p*-toluenesulfonyl chloride¹

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This paper is dedicated to Professor Arthur N. Bourns

SHIGERU OAE and YOSHIHITO KADOMA. Can. J. Chem. **64**, 1184 (1986).

The rates of aminolyses of *p*-toluenesulfonyl chloride with primary and tertiary amines have been determined both in acetonitrile and in ethanol. The Brønsted plots of $\log k_{\text{rel}}$ against $\text{p}K_{\text{a}}$ values of amines (except hydrazine and 1,8-naphthyridine in acetonitrile) gave a good correlation when the aminolyses were carried out in acetonitrile. In ethanol, however, although Brønsted plots with all tertiary amines show a good correlation, less basic hydrazine shows a higher reactivity than *n*-butylamine. The abnormal rate enhancement found with hydrazine is undoubtedly due to the α -effect, while that with 1,8-naphthyridine in acetonitrile is considered to be due to the repulsion of two lone electron pairs on the two nitrogen atoms in 1,8-naphthyridine.

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On a déterminé les vitesses d'aminolyse du chlorure de *p*-toluènesulfonyle par des amines primaires ainsi que tertiaires, tant dans l'acétonitrile que dans l'éthanol. Lorsque les aminolyses sont effectuées dans l'acétonitrile, il existe une bonne corrélation pour les courbes de Brønsted du $\log k_{\text{rel}}$ vs. les valeurs de $\text{p}K_{\text{a}}$ des amines (excepté dans les cas de l'hydrazine et de la naphthyridine-1,8 dans l'acétonitrile). Dans l'éthanol, les courbes de Brønsted des amines tertiaires présentent toutes une bonne corrélation; toutefois, l'hydrazine qui est moins basique présente une réactivité qui est supérieure à celle de la *n*-butylamine. La vitesse de réaction anormalement élevée qui a été observée avec l'hydrazine est sans doute due à un effet α , alors que l'on considère celle de la naphthyridine dans l'acétonitrile comme étant due à une répulsion des deux paires libres d'électrons des deux azotes de la naphthyridine-1,8.

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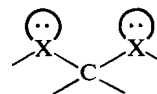
The enhanced reactivity of nucleophiles containing one or more lone electron pairs adjacent to the reacting center has been known as the α -effect (2–4). Among the following three major factors responsible for the α -effect, namely, (1) destabilization of the ground state of the α -nucleophile by repulsion between the adjacent lone electron pairs (5), (2) stabilization of the transition state by the extra pair of electrons, and (3) reduced solvation of the α -nucleophile by the adjacent lone electron pair, the last two factors have been fairly well substantiated by both theoretical (6–9) and experimental studies (10–13). Stabilization of the transition state by the α -nucleophile, namely the second factor, has recently been considered quite important and possibly the major factor for the enhanced reactivity in the nucleophilic attack of the α -nucleophile on the electropositive reacting center, especially in solution. Evidence supporting the third factor has become especially convincing now, since no α -effect was observed in the reaction of HOO^- with methyl formate in the gas phase (13), where HOO^- shows a strong α -effect in solution.

Not much significance has been given to the first factor, i.e., destabilization of the ground state of the α -nucleophile by repulsion between the lone pairs on adjacent atoms, and practically no convincing evidence has yet been shown, although repulsion between lone electron pairs on adjacent heteroatoms is considered to be quite substantial in view of the well-known "rabbit ear effect" (14) of lone electron pairs on nonadjacent atoms.

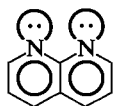
A nonbonding unshared electron pair, namely, a lone

electron pair, is large and takes up more space than a bonding pair (15). Therefore, if there is no electron pair other than a lone electron pair, the unshared pair of electrons would occupy a "s" type spherical orbital, spreading widely on the surface of the particular heteroatom (16). Even when the central heteroatom is bound to other atoms, the lone electron pair on the heteroatom tends to spread out, as exemplified by the decrease in the bond angle in the following three representative compounds: CH_4 , which has no lone electron pair on the central atom, has a bond angle, $\angle \text{C} = 109.5^\circ$; NH_3 , in which there is one lone electron pair on the central atom, has $\angle \text{N} = 107.3^\circ$; while H_2O , which has two lone electron pairs, is more angular, i.e., $\angle \text{O} = 104.7^\circ$. When bonding pairs are replaced succes-

sively by a lone electron pair, the bond angle between the bonding pairs decreases, since the lone electron pair takes up more space than the bonding electron pair. Since the lone electron pair engenders an electronic dipole, two lone electron pairs placed in proximity or in parallel must create a considerable electrostatic, and also even some steric, repulsion. The "rabbit ear effect" is caused by such a repulsion between two vicinal lone electron pairs on heteroatoms placed at the β -position to disfavor the conformations in which lone electron pairs on nonadjacent atoms are placed at parallel or at the *syn-axial* position (14), as shown below.

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In 1,8-naphthyridine two lone electron pairs on the two nitrogen atoms of the heterocyclic compound are placed in parallel, as shown below.



Therefore, due to the repulsion, this compound should have a considerable internal strain. However, if one of the nonbonding lone electron pairs is used for bonding, such a repulsion would be released, since one of repulsive dipoles would disappear and the steric requirement of a bonding electron pair is less than that of a nonbonding electron pair. Hence, if 1,8-naphthyridine is used as a nucleophile in the nucleophilic reaction and the conventional Brönsted plot of logarithm of rate constant against pK_a 's of attacking nucleophiles, 1,8-naphthyridine would show a positive deviation from the plotted line, since the release of repulsion between the two lone electron pairs would occur in the transition state by forming a new σ -bond between the nucleophile and the substrate, thus lowering the energy of activation. One earlier report (5*b*) suggested, based on others' work, that 1,8-naphthyridine would show fourfold rate acceleration in the reaction with methyl iodide. One might propose, however, that protonation of one of the two lone electron pairs would result in the release of this unfavorable repulsion, which in turn would result in the increase of the pK_a value of 1,8-naphthyridine. These two opposing effects, i.e., lowering of the activation energy and increasing pK_a value, should cancel out much of the anticipated positive deviation from the Brönsted slope. However, this consideration has been suggested to be not very significant in nucleophilic displacements (17), since the lone electron pairs are more fully removed in the transition state than when perturbed by protonation. The result of our SCF MO calculation also supports this argument (6).

Therefore, if one finds a substantial positive deviation from the Brönsted slope for 1,8-naphthyridine, similar to that for some α -nucleophiles, e.g., hydrazine, it may serve as supporting evidence that repulsion between lone electron pairs is at least partially responsible for the rate enhancement in the nucleophilic reactions. An observation by Zoltewicz and Deady (5*b*) seems to show the possibility of the above argument. However, in order to substantiate the argument, further data such as the solvent effect on the α -nucleophile and 1,8-naphthyridine, as well as quantitative measurements of deviations of both nucleophiles from the slope, should be necessary. Meanwhile, since 1,8-naphthyridine has a low pK_a value, it does not react readily with ordinary esters and hence a more reactive *p*-toluenesulfonyl chloride was used as substrate for the nucleophilic reaction. Thus, we have carried out a kinetic study on the reaction of *p*-toluenesulfonyl chloride with 1,8-naphthyridine, its isomer, 1,5-naphthyridine, hydrazine, and other amines in both ethanol and acetonitrile, observing substantial rate enhancements with both 1,8-naphthyridine and hydrazine in acetonitrile.

Results and discussion

In the reaction of *p*-toluenesulfonyl chloride with amines, the following two reaction paths, i.e., (a) and (b), are conceivable. However, the product analysis indicates the absence of *p*-toluenesulfinate ion and only the presence of the sulfonate ion in the reaction mixture. Thus, path (b) has been ruled out and the reaction is purely a nucleophilic substitution on the sulfonyl S atom.

Earlier, Kice and Legan (18) observed a marked α -effect in the nucleophilic substitution on the sulfonyl sulfur atom with hydroperoxide ion, and hence a substantial rate enhancement has been expected in the nucleophilic substitution of arenesulfonyl chloride with the α -nucleophile. Thus, we have carried out a kinetic study on the nucleophilic substitution of *p*-toluenesulfonyl chloride with various amines.

Although *p*-toluenesulfonyl chloride is quite reactive as compared to ordinary esters, the amines used for this study have a wide range of basicity from low basic 1,5-naphthyridine to highly basic piperidine, the rate of the reaction was found to vary widely in the range of $10^{7.5}$. Therefore, two different analytical procedures were necessary for kinetic measurements in order to compare all the rates. For the reaction with amines of low basicities, such as naphthyridines, quinolines, and pyridine, the reactions were carried out so that the amine concentration was maintained usually 100 times higher than that of the substrate in the reaction cell, and pseudo-first-order rate constants thus obtained were divided by the amine concentration to obtain bimolecular rate constants. In this case, the rate measurement was followed by monitoring the amount of chloride ion liberated in the reaction by conductometry. In the reactions with amines of high basicities from pyridine to piperidine, the conventional uv measurement of the absorption of *p*-toluenesulfonyl chloride was quite applicable, and concentrations of both the amine and the substrate can be kept nearly equal in this procedure. In both procedures, pyridine was used as the reference base and practically identical rate constants were obtained.

Since the repulsion between the vicinally situated lone electron pairs is expected to change considerably, both sterically and in dipole interaction, due to the possible change of solvation, the reaction was carried out in both protic and polar aprotic solvents, i.e., ethanol and acetonitrile. *p*-Toluenesulfonyl chloride is stable in both solvents at these kinetic temperatures and kinetic concentrations for over 10 days, while the concentrations of amines were not affected by these solvents. Thus, the rate constants obtained in acetonitrile are listed in Table 1.

In Fig. 1, the values of $\log k_{rel}$ in Table 1 were plotted against the pK_a values of amines used. Apparently, there is a good correlation and the β -value, 0.89, obtained from the Brönsted slope seems to suggest that the reaction is highly dependent on basicity, while there is a high degree of bond formation in the transition state.

The rate constants obtained with 1,8- and 1,5-naphthyridines

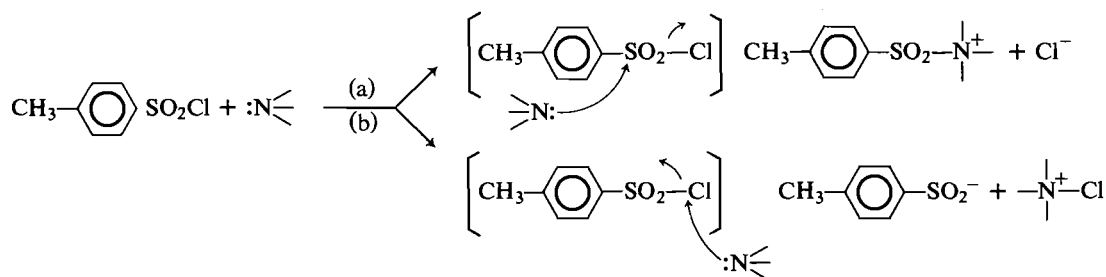


TABLE 1. Second-order rate constants for the reaction of *p*-toluenesulfonyl chloride with amines in acetonitrile at 20°C

Amine	k_2	$\log k_{rel}$	pK_a^a
Piperidine ^b	101 ± 3	7.69	18.92
<i>n</i> -Butylamine ^b	64.4 ± 0.5	7.49	18.26
Monoethanolamine ^b	20.4 ± 0.3	6.99	17.53
Hydrazine ^b	74.0 ± 0.5 ^c	7.55	16.61
Ammonia ^b	(8.73 ± 0.1) × 10 ⁻¹	5.62	16.46
Isoquinoline ^d	4.3–2.0 × 10 ⁻⁴	2.0–2.35	12.50 ^e
Pyridine ^{b,d}	(2.34 ± 0.06) × 10 ⁻⁴	1.20	11.98 ^e
1,8-Naphthyridine ^d	(2.08–7.04) × 10 ^{-4c}	2.5–3.0	10.44 ^e
1,5-Naphthyridine ^d	(2.08 ± 0.3) × 10 ⁻⁶	0.0	9.92 ^e

^a pK_a values are taken from Coetzee and Padmanabhan (19).

^bRate constant was obtained by conductometry.

^cObtained rate constant was divided by 2 because these amines have two nucleophilic centers.

^dRate constant was obtained by uv spectrophotometry.

^eEstimated value from a linear plot of pK_a' in water vs. pK_a' in acetonitrile.

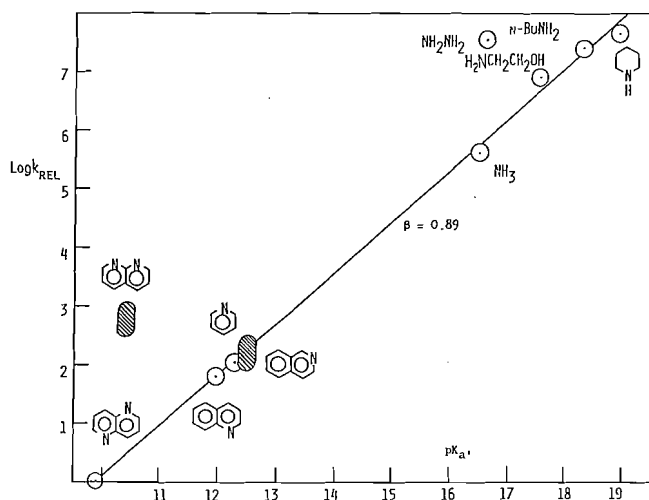


FIG. 1. Brønsted plot for the reaction of *p*-toluenesulfonyl chloride with amines in acetonitrile.

are divided by 2, since these amines have two nucleophilic centers (20). The plot for 1,5-naphthyridine lies well on the slope; however, hydrazine and 1,8-naphthyridine exhibit considerable deviations from the slope. The deviation of the plot with hydrazine is undoubtedly due to the α -effect, while that with 1,8-naphthyridine cannot be assigned to the α -effect but is obviously due to the repulsion of the two lone electron pairs, very likely in the ground state, since vicinally situated lone electron pairs, particularly in parallel positions, would result in a considerable repulsion. In this connection, it is interesting to see the first pK_a' values of substituted diamionaphthalenes (21); namely, 4.61 for 1,8-diamionaphthalene, 5.6 for 1,8-bis(monomethylamino)naphthalene, 6.43 for 1-dimethylamino-8-monomethylaminonaphthalene, and 12.34 for 1,8-bis(dimethylamino)naphthalene. The first pK_a' value for 1,8-bis(dimethylamino)naphthalene is thus higher than those of normal aliphatic amines. This compound is apparently a highly strained molecule in which the conjugative resonance between the amino group and the naphthalene ring is considerably inhibited and, despite the high van der Waals repulsion, both dipolar repulsion and the strain would be effectively relieved by protonation. Since the unfavorable strain produced by repulsion is expected to be relieved more by forming a σ -bond at the transition state of

TABLE 2. Second-order rate constants for the reaction of *p*-toluenesulfonyl chloride with tertiary amines in absolute ethanol at 21°C, by conductometry

Amine	k_2 (L mol ⁻¹ s ⁻¹)	$\log k_{rel}$	pK_a^a in water
Pyridine	(4.88 ± 0.04) × 10 ⁻³	2.58	5.25
Isoquinoline	(1.14 ± 0.04) × 10 ⁻²	2.95	5.42
Quinoline	(5.84 ± 0.06) × 10 ⁻⁴	1.64	4.90
1,8-Naphthyridine ^b	(7.83 ± 0.07) × 10 ⁻⁵	0.79	3.36
1,5-Naphthyridine ^b	(1.27 ± 0.15) × 10 ⁻⁵	0.00	2.84

^a pK_a' values are taken from Perrin (23).

^bObtained rate constants were divided by 2 because these amines have two nucleophilic centers.

TABLE 3. Second-order rate constants for the reaction of *p*-toluenesulfonyl chloride with primary amines in absolute ethanol at 21°C, by ultraviolet spectrophotometry

Amine	k_2 (L mol ⁻¹ s ⁻¹)	$\log k_{rel}$	pK_a^a in water
Hydrazine ^b	1.63 ± 0.05	1.89	7.96
<i>n</i> -Butylamine	0.860 ± 0.03	1.61	10.59
Monoethanolamine	0.605 ± 0.03	1.46	9.50

^a pK_a' values are taken from Perrin (23).

^bObtained rate constant was divided by 2 because these amines have two nucleophilic centers.

nucleophilic substitution than when perturbed by protonation, 1,8-bis(dimethylamino)naphthalene is considered to be more reactive than anticipated from its basicity. However, because of the sterically crowded center of the amino groups, it is not a good nucleophile for substitution.

As for 1,8-naphthyridine, the repulsion of lone electron pairs is considered to be effectively reduced at the transition state; thus the compound is 100-fold more reactive than anticipated from its basicity. The rate enhancement observed with 1,8-naphthyridine seems to indicate that the σ -bond formation is nearly complete at the transition state. This is also a favorable condition for hydrazine to exhibit its α -effect, as observed by the markedly positive deviation from the Brønsted slope, the rate enhancement being 40-fold (see Fig. 1).

Our earlier data (22)⁴ revealed that the α -effect was not observed in the aminolyses of alkyl, allyl, and benzyl iodides, nor in the hydrolyses of benzylic bromides with hydroperoxide ion, although the aminolyses of allyl and benzyl iodides give nearly identical Brønsted values (0.60 and 0.55, respectively) to that (0.54) obtained with *p*-nitrophenyl acetate. This lack of α -effect in the aminolyses on the sp^3 carbon atom and also in the S_N2 reaction of benzylic bromides with hydroperoxide ion may be explained on the basis of the inability to form tight σ -bonds at the transition state of these S_N2 processes. The tight σ -bond formation, as observed in the formation of a tight tetrahedral intermediate in the ester hydrolysis, seems to be quite essential in releasing repulsion between lone electron pairs, thus enhancing the rate and exhibiting a marked α -effect.

Since large rate enhancements can be observed in the aminolyses of *p*-toluenesulfonyl chloride with 1,8-naphthyridine and hydrazine in such an aprotic solvent as acetonitrile, it is interesting to see how the change of solvent from acetonitrile to

⁴Also, S. Oae and Y. Kadoma, unpublished results.

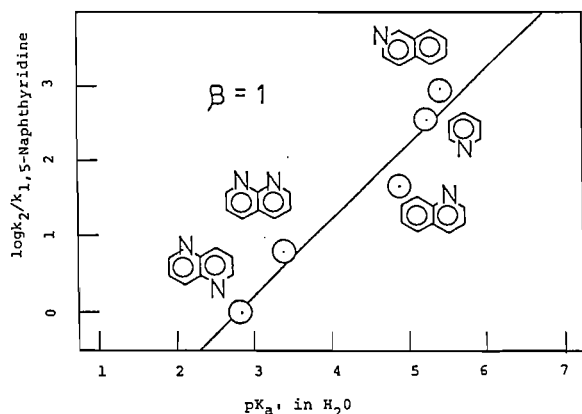


FIG. 2. Brønsted plot for the reaction of tertiary amines to *p*-toluenesulfonyl chloride in ethanol.

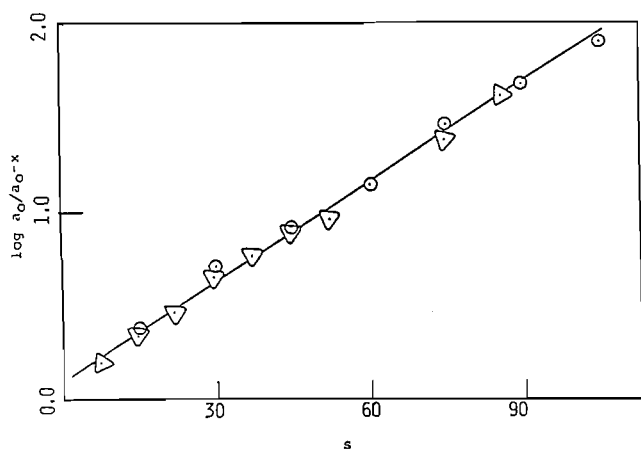


FIG. 3. Kinetic plots of the rates of aminolysis of *p*-toluenesulfonyl chloride with pyridine in ethanol. The $\log a_0/(a_0 - x)$ values are obtained by the plot of $[Cl^-]$ vs. conductivity of the reaction cell; \odot by uv spectrophotometry; \triangle by conductivity.

a protic solvent such as ethanol would affect the rate of the reaction. Thus, a kinetic study on the aminolyses of *p*-toluenesulfonyl chloride with tertiary as well as primary and secondary amines has been carried out and the results are summarized in Tables 2 and 3, respectively. The Brønsted plot for aminolysis with tertiary amines is also illustrated in Fig. 2. Since it has been known that the relative basicities are little affected by the change of solvent from water to alcohol (24), the rate constants are plotted against pK_a values of amines used in water.

In the aminolyses of *p*-toluenesulfonyl chloride with tertiary amines in ethanol (see Table 2 and Fig. 2), there is also a good correlation between the rate constants and pK_a values of amines used, and the Brønsted β -value of ≈ 1 indicates that the bond formation between the nucleophile and the substrate is nearly complete at the transition state, very likely expanding the valence shell of the central sulfur atom. However, in the aminolyses in ethanol, 1,8-naphthyridine does not show any positive deviation from the Brønsted slope, due mainly to solvation, since the lone electron pairs on two nitrogen atoms in the heterocycle are substantially solvated in ethanol by strong hydrogen bonding. Because of this solvation, orbitals of the lone electron pairs would be so contracted that the size of lone electron pairs would be reduced, thus reducing the unfavorable

steric interaction, while the unfavorable dipolar repulsion would also be reduced substantially. These repulsive interactions are considered to be removed by formation of a σ -bond between the sulfur atom and the nucleophile. However, the reacting center of 1,8-naphthyridine has vicinally situated lone electron pairs on the two nitrogen atoms, which would be solvated by ethanol molecules, far more in number than in the aminolyses with other tertiary amines. Hence this sterically unfavorable condition created by the strong hydrogen bonding would cancel out any positive deviation from the slope.

In general, the α -effect seems to be somewhat larger in protic solvents than in aprotic media, while it is also considered to be affected markedly by the change of solvent (20). However, there are not many data to substantiate the argument. Therefore, aminolyses of *p*-toluenesulfonyl chloride with primary amines have been carried out, just to see if the α -effect would depend on the solvent change as was observed with 1,8-naphthyridine. The results are shown in Table 3.

One finds in Table 3 that hydrazine reacts faster than other more basic primary amines, due obviously to the α -effect. In the reaction in ethanol the transition state would be well solvated by the solvent ethanol, and further solvation by the vicinally situated lone electron pair will not increase the stability, whereas the presence of the vicinal lone electron pair would rather decrease the solvation at the transition state by repelling some ethanol molecules. Thus in ethanol the ground state destabilization would be cancelled out by the transition state destabilization; the net result is no rate enhancement. The α -effect is solvent independent, while the lone pair - lone pair repulsion is solvent dependent. These observations suggest that while the lone pair - lone pair repulsion is an important factor, it is not the sole cause of the α -effect.

Experimental

Preparation of materials

1,8-Naphthyridine was prepared by the Skraup reaction (25). Five repeated sublimations at 80°C (0.2 Torr; 1 Torr = 133.3 Pa) gave glassy colorless needles, mp 99.5°C (lit. (25) mp 98–99°C). 1,5-Naphthyridine was prepared similarly (26); mp 75°C (lit. (26) mp 75°C). Other amines were prepared by distillation (19), or by recrystallization.

Product analysis

One gram of a given amine (pyridine or 1,8-naphthyridine) was added into the solution containing 1 g of *p*-toluenesulfonyl chloride in 20 g of acetonitrile. After keeping the solution for 5–30 min at room temperature, the reaction mixture was poured onto ice-water, acidified with HCl, and extracted with ether. In the ether solution, there was no *p*-toluenesulfinic acid present and only a trace of the unreacted sulfonyl chloride was detected. *p*-Toluenesulfonic acid in the remaining water layer was identified by adding a solution of *S*-benzylthiuronium chloride to obtain the crystalline *S*-benzylthiuronium salt of *p*-toluenesulfonic acid. After recrystallization from ethanol, the salt gave mp 178°C (lit. (27) mp 178°C).

Product analyses for the reaction of *p*-toluenesulfonyl chloride with primary and secondary amines in ethanol were also carried out using the same method as described above. In the case of a primary amine, the corresponding sulfonamide was isolated quantitatively, while the reaction product with a tertiary amine was the *p*-toluenesulfonic acid ester, which was also obtained quantitatively. The lack of the sulfonic acid ester among the products in the reaction with primary amines in ethanol suggests that at the rate-determining step the unfavorable influence of ethoxide anion can be neglected.

Kinetic measurements

Since a wide variety of amines were used, the rate constant changed widely over the range of $10^{7.5}$. Therefore, two kinetic procedures have

been applied. For the aminolyses with reactive primary and secondary amines, the reactions have been followed by uv spectrophotometry using the absorption of *p*-toluenesulfonyl chloride at 245 nm, while for the tertiary amines, the rates of the reactions have been followed by conductometry, by monitoring the conductivity change in the reaction cell that is caused by the change of chloride ion, liberated during the aminolysis. In the latter method, the concentration of the amine was usually maintained 100 times higher than that of the sulfonyl chloride. Thus, the pseudo-first-order rate constants obtained were divided by the concentration of the amine used, to estimate the second-order rate constant of the aminolysis. For all the kinetic measurements both in ethanol and in acetonitrile, the concentration range of the amine for conductometry was in the range of 1–0.5 mol/L, while *p*-toluenesulfonyl chloride was kept between 0.01 mol/L and 0.005 mol/L; also for the uv spectrophotometry the concentration of amine was between 0.5 mol/L and 5×10^{-4} mol/L, while the concentration of *p*-toluenesulfonyl chloride was between 0.2 mol/L and 1×10^{-4} mol/L. A typical run is shown in Fig. 3. The apparatus used for the conductivity is the same as that used previously (28). Meanwhile, the rate of the reaction with pyridine was measured by both uv spectrophotometry and conductometry and there was a good agreement in both.

In the aminolysis of sulfonyl chloride with pyridine in ethanol, ΔE^\ddagger and ΔS^\ddagger values are calculated to be 14.7 kcal/mol (61.61 kJ) and -15.9 eu, respectively, while ΔE^\ddagger and ΔS^\ddagger for the reaction with 1,8-naphthyridine are 17.2 kcal/mol (72.2 kJ) and -15.6 eu, respectively.

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