

## Solvent Effects in the Reaction of 2-Thiophenesulfonyl Chloride with Aniline

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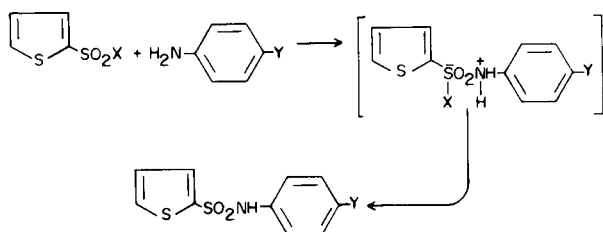
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The second order rate constants  $k_2$  and the activation parameters for the reaction of 2-thiophenesulfonyl chloride with aniline together with solution enthalpies of the reactants have been measured in methanol, ethanol, 2-propanol, acetonitrile and acetone. The reaction rates are slower in dipolar aprotic solvents than in protic ones due to a remarkable activation negative entropy. The rate constants  $k_2$  are correlated with empirical solvent polarity parameters. The data seem in accord with a  $S_{AN}$  reaction mechanism.

The rates of bimolecular nucleophilic substitution depend on the change from polar to dipolar aprotic solvents, particularly when the nucleophile is an anion (1-4). The remarkable rate increases found in dipolar aprotic solvents have been attributed both to increments of energy for the change of reactants from the aprotic solvent to the protic one, and to the increased solvation of the transition state in the dipolar aprotic solvent (5,6); in every case the energy gap between the reactants and the transition state as well as the enthalpy of activation diminishes with the solvent change.

Recently two different reaction mechanism for nucleophilic substitutions at tetracoordinate sulphur have been proposed:  $SN_2$  and  $S_{AN}$  (7-12). Previous work on the reactions of 2-thiophenesulfonyl halides with anilines (11, 12) let us hypothesize the  $S_{AN}$  mechanism as the more probable (Scheme I).



The solvent effect on the kinetics of these reactions was investigated in order to obtain further information about the structure and the electron distribution of the

transition state in order to discriminate between the two mechanisms.

In order to separate solvent effects on  $\Delta H^\ddagger$  into initial state and transition state effects, the heats of solution of the reactants were measured in various solvents. By combining differences in enthalpy of solution with differences in enthalpy of activation, the enthalpy of transfer of the transition state from one solvent to another could be calculated.

#### Results and Discussion.

The reaction between 2-thiophenesulfonyl chloride and aniline takes place quantitatively in all the solvents, as reported in previous papers (11,12).

The second order rate constants  $k_2$ , measured at different temperatures, are listed in Table 1, together with the activation parameter values at 25°; three to seven kinetic runs, at different aniline concentrations, were carried out at the established temperature. The heats of solution of aniline and 2-thiophenesulfonyl chloride in the solvents examined (see Table 2) were calculated by Dickinson's method (13).

Table 1 shows that the reaction rate is surprisingly faster in the protic solvents than in dipolar aprotic solvents.

The ratio of rate constants at 25° (Table 3) for the methanol-acetonitrile pair is *ca.* 5 and rises to *ca.* 22 for the methanol-acetone pair, while for methanol-ethanol and methanol-2-propanol it is *ca.* 2 and *ca.* 3, respectively.

Table 1

Rate Constants  $k_2$  and Activation Parameters for the Reaction of 2-Thiophenesulfonyl Chloride with Aniline

Solvents	$k_2 \cdot 10^3, \text{ l mol}^{-1} \text{ sec}^{-1}$ (a)					$\Delta H^\ddagger$ Kcal mol <sup>-1</sup>	$\Delta S^\ddagger$ cal mol <sup>-1</sup> K <sup>-1</sup>	
	15°	20°	25°	30°	35°			
Methanol	2.62		5.62		11.05	20.80	11.91 ± 0.13 (b)	-28.70 ± 0.42
Ethanol			3.15		6.53	11.35	11.50 ± 0.73	-31.38 ± 2.4
2-Propanol			1.83		2.68	4.93	9.93 ± 0.75	-38.04 ± 2.4
Acetonitrile			1.20		1.93	2.60	6.85 ± 0.86	-48.91 ± 1.4
Acetone		0.189	0.260	0.364	0.465		10.30 ± 0.42	-40.38 ± 1.4

(a) The estimated accuracy is ± 5% or better. (b) Standard deviations.

Table 2

Heats of Solution and Enthalpies of Transfer at 25° of 2-Thiophenesulfonyl Chloride and Aniline Relative to Methanol

Solvents	Aniline		2-Thiophenesulfonyl Chloride	
	$\Delta H_s$ Kcal mol <sup>-1</sup>	$\delta \Delta H_s$ Kcal mol <sup>-1</sup>	$\Delta H_s$ Kcal mol <sup>-1</sup>	$\delta \Delta H_s$ Kcal mol <sup>-1</sup>
Methanol	-0.60 ± 0.01 (a)	0	4.54 ± 0.13 (a)	0
Ethanol	-0.12 ± 0.01	+0.48	4.75 ± 0.14	+0.21
2-Propanol	+1.25 ± 0.01	+1.85	5.96 ± 0.06	+1.42
Acetone	-1.25 ± 0.01	-0.65	4.03 ± 0.08	-0.51
Acetonitrile	+0.025 ± 0.001	+0.625	5.24 ± 0.18	+0.70

(a) Standard deviations.

Table 3

Rate Constant Ratios for the Reaction of 2-Thiophenesulfonyl Chloride with Aniline in Various Solvents

Methanol/Ethanol	2	2	2
Methanol/2-Propanol	3	4	4
Methanol/Acetonitrile	5	6	8
Methanol/Acetone	22	24	-

Table 4

Enthalpies of Transfer of Reactants,  $\delta \Delta H_s^r$ , and Transition States,  $\delta \Delta H^\ddagger$ , and Differences in Enthalpy of Activation,  $\delta \Delta H^\ddagger$ , relative to Methanol, for the Reaction of 2-Thiophenesulphonyl Chloride with Aniline

Solvents	$\delta \Delta H_s^r$ Kcal mol <sup>-1</sup>	$\delta \Delta H^\ddagger$ Kcal mol <sup>-1</sup>	$\delta \Delta H^\ddagger$ Kcal mol <sup>-1</sup>
Methanol	0	0	0
Ethanol	+0.69	-0.41	+0.28
2-Propanol	+3.27	-1.98	+1.29
Acetonitrile	+1.33	-5.06	-3.73
Acetone	-1.16	-1.61	-2.77

Besides, these ratios rise with temperature when the protic-dipolar aprotic change is considered.

Table 4 shows that in the transfer from methanol to acetonitrile the reactants are desolvated by 1.3 Kcal mol<sup>-1</sup> in the dipolar aprotic solvent while the transition state is more solvated by 3.7 Kcal mol<sup>-1</sup> in the same solvent. Thus the activation energy is *ca.* 5 Kcal mol<sup>-1</sup> lower in acetonitrile with respect to methanol.

However the reaction rate is slower in acetonitrile owing to a dominating contribution from an unfavorable entropy ( $T\Delta S^\ddagger = \text{ca. } 6 \text{ Kcal mol}^{-1}$ ). In acetone the activation enthalpy is smaller than in methanol, due to a prevailing contribution of the transition state solvation (the reactants are less reactive owing to their increased solvation). Also in acetone the rate is slower than in methanol because of an unfavorable change in  $\Delta S^\ddagger$ . In 2-propanol  $\Delta H^\ddagger$  is lower than in methanol, due to a remarkable desolvation of reactants, but  $\Delta S^\ddagger$ , more negative, determines the reaction rate, as in dipolar aprotic solvents. The ethanol behaviour is similar to that of methanol.

The negative entropy changes accompanying the transfer from methanol to the other solvents might be

explained in terms of orientation of solvent molecules around the incipient ions in the transition state. In a strongly polar liquid such as methanol the molecules are already frozen due to remarkable intermolecular forces (hydrogen bonding, etc.) (14). When these molecules hold the transition state ions, they suffer a relatively small loss in entropy. Nonpolar liquids, on the other hand, being less associated, are quite free in the liquid state. When a strongly polar transition state is formed, their molecules suffer a remarkable reorientation accompanied by a great loss of rotational and translational freedom. Hence the entropy of activation decreases. Also the highly negative entropy values might be ascribed to a tighter transition state in the dipolar aprotic solvent, a medium that cannot solvate the leaving group (Cl) by hydrogen bonding (5).

Table 4 shows the heats of solution of the transition state ( $\delta\Delta H^\ddagger$ ) obtained from the relationship (15)  $\delta\Delta H^\ddagger = \delta\Delta H_s^\ddagger + \delta\Delta H^\ddagger$ .

If we assume methanol as the reference solvent ( $\delta\Delta H^\ddagger = 0$ ), then for ethanol and 2-propanol the transfer processes are endothermic while for acetone and acetonitrile they are exothermic.

There is no correlation between  $\delta\Delta H^\ddagger$  and the dielectric constant or empirical polarity solvent parameters. However a correlation between  $\delta\Delta H^\ddagger$  and  $E_t$  values was found (16) only for protic solvents, the transition state being better solvated in the most polar solvent in accord with the Hughes-Ingold concept (17).

The attempts to correlate second order rate constants with the dielectric constants for all the solvents were successful only for the alcohol series, presumably owing to specific interactions between solutes and dipolar aprotic solvents.

Good correlations were obtained with empirical solvent polarity parameters such as  $Z$ ,  $E_t$  or  $\log K_{\text{ION}}$  (16). However the correlations are better by using the kinetic model parameters  $\log K_{\text{ION}}$  or  $Y$  ( $r = 0.992$ ), rather than the spectroscopic model parameters  $Z$  or  $E_t$  ( $r = 0.97$ ). Presumably during the electronic transition, the solvent molecules around the solute have no time to change their positions and orientations to adjust to the excited state structure. Hence such an arrangement of solvent molecules certainly is not the optimum for the new arrangement of charges (18).

#### EXPERIMENTAL

##### Materials.

2-Thiophenesulfonyl chloride was obtained as described previously (12). Aniline is a Carlo Erba RPE-ACS commercial product, purified by several distillations over potassium hydroxide.

The solvents used are all commercial products. Methanol, before using, was dried by distillation from magnesium. Absolute ethanol and 2-propanol were dried with molecular sieves and fractionally distilled. Acetonitrile was purified as described (19); acetone was left on potassium carbonate overnight, distilled and

then refluxed on phosphorus pentoxide for half an hour and then distilled again (20).

##### Rate and Calorimetric Measurements.

The reaction rates were measured by the procedure described in previous papers (11,12).

For the heats of solution measurements, a LKB 8700-1 precision calorimeter, equipped with a "419 A.D.C. null voltmeter" electronic galvanometer connected to a L. and N. Speedomax W recorder, was used.

The measurements were performed by breaking 1 ml. LKB 8727-1 glass bulbs, containing the solute at the same concentration of kinetic runs into 100 ml. of solvent. The calorimeter was tested by measuring the solution heat of potassium chloride in water at 25°. The value of  $4.198 \pm 0.005$  Kcal mol<sup>-1</sup> obtained, is in good agreement with the literature (21,22).

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