1-염화안트라센 술포닐의 치환아닐린과의 친핵성치환반응의 속도론적 연구

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Kinetic Study on Nucleophilic Substitution of 1-Anthracenesulfonyl Chloride with Anilines

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요 약. 기질로 사용한 1-염화안트라센 술포닐(융점 124°C)을 안트라키논으로 부터 합성하여 확인한 결과, 그 융점이 문헌치(90°C)와 상당한 차이를 나타내었다. 이 기질과 치환아닐린이 무수 아세톤 속에서 일어나는 친핵성 치환반응의 메카니즘을 전기전도도법을 써서 속도론적으로 고찰하였다. 이 반응은 무촉매 과정과 아닐린류에 의한 촉매 과정이 병행하여 일어나며 촉매작용은 친전자 적임을 알았다. Brønsted β (0.77), Hammett ρ(−3.2) 및 무촉매반응 속도상수의 온도 의존성에서 결정한 활성화 파라미터로 부터 이 반응은 술포닐암모늄 중간체를 거치는 associative S_N2로 논의하는 것이 가장 적절하였다.

ABSTRACT. 1-Anthracenesulfonyl chloride used as a substrate has been prepared from anthraquinone, and its melting point (124°C) was confirmed to be considerably different from the literature value (90°C). Rates of nucleophilic substitution reactions of this substrate with some *p*-substituted anilines in dry acetone were determined by electroconductometric method, and their mechanism has been discussed. As a result, it has been found that these reactions proceed in parallel catalyzed by anilines together with noncatalyzed process, and that their catalytic activities are electrophilic. Judging from Brønsted β (0.77), Hammett ρ (−3.2), and activation parameters which were determined from the temperature dependence of noncatalyzed second order rate constants, it appears most appropriate that their mechanism should be discussed in terms of an associative S_N2 involving sulfonylammonium intermediate.

INTRODUCTION

Mechanistic investigations for nucleophilic substitution reactions at carbonyl and saturated carbon have been so extensively carried out as to defy enumeration. However, these studies of the reactions at sulfur, particularly at tetracoordinated one were comparatively limited. Most of these studies were concerned with aliphatic, substituted benzene, naphthalene[1], and five-me-

mbered heterocyclic[2] sulfonyl chlorides.

Applications of various mechanistic criteria to these nucleophilic substitutions have led different groups of investigators to propose mainly two types of mechanisms; S_N2 and S_AN, the former mechanism being more preferred by Lee[3] and Rogne[4], while the latter by Ciuffarin[5] and Arcoria[2d,e].

It has been known that the reactions of arylsulfonyl halides with primary or secondary amines[4b,6] in protic solvents take place quantitatively to produce the corresponding sulfonamides because of much less solvolysis rate and of high stability of the product to the solvents used, while the reactions with tertiary amines[7] in the protic solvents proceed by a nucleophilic catalysis or general base catalysis mechanism to produce the corresponding solvolysis products.

Litvinenko and his collaborators[8] found that the reactions between arylsulfonyl halides and amines proceed quantitatively and irreversibly even in nitrobenzene as well as in nonpolar solvents, and have suggested[9] that particularly in nonpolar solvents the processes may take place in parallel together with the usual noncatalyzed process catalyzed by original amines, their products and traces of water. The presence of such catalytic activities was actually confirmed for the reactions of substituted benzenesulfonyl bromides with p-anisidine in nitrobenzene-benzene mixture[10], and for the reactions of naphthalenesulfonyl chlorides with some anilines in acetone[1e].

However, the kinetic studies on the nucleophilic substitutions of tricyclo-aromatic sulfonyl halides are nearly nonexistent to our knowledge. In order to obtain, therefore, informations on the mechanism for reactions of 1-anthracenesulfonyl chloride (1-ASC) with anilines in a dipolar aprotic solvent, the rate constants and activation parameters were determined in dry

acetone, and the rate data were applied to Hammett and Brønsted equations.

EXPERIMENTAL

Materials. In respect to the preparation of anthracene-monosulfonyl chlorides from the corresponding sulfonate, some details of only 2-isomer are carried in literature[11]. 1-Anthracenesulfonyl chloride used as substrate has therefore been prepared from anthraquinone through its sulfonate according to a procedure similar to that of 2-isomer. Then the product (yellow crystal) was recrystallized several times from toluene, and identified by NMR and IR spectrometries as well as by elementary analysis. The results are as follows: the ^{1}H-NMR (DMSO-d_6, internal standard: Me_4Si), Varian EM-360A, $\delta9.33$ (s, 9-H), 8.43(s, 10-H), 7.87-8.02 (m, 2.4.5.8-H), 7.19-7.52 (m, 3,6,7-H); the IR (KBr), Simadzu IR-400, 1620 (cm^{-1}), 1535, 1435, 1395, 1367 (S=O), 1174 (S-Cl), 1158, 940, 885, 755, 730, 690 (C-S); elementary analysis, calcd. (found), C:60.76% (61.00), H:3.25 (3.39), Cl:12.84 (12.86), S:11.57 (11.35). To our surprise here, melting point of the product showed a great discrepancy between the observed value (124°) and literature one (90°)[12]. This is presumably ascribed to the poor means for identification at that time when the datum was reported.
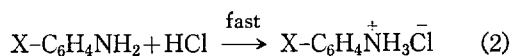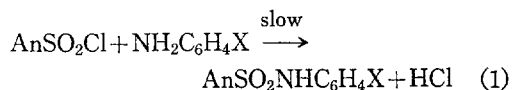
Aniline (Fisher GR grade) was distilled under reduced pressure from potassium hydroxide pellets. Recrystallization for the other anilines was performed as follows; p-anisidine (Hanawa Chemicals) and p-toluidine (Katayama Chemicals) from water, p-chloroaniline (Maruwaka Chemicals) from ethanol, and p-nitroaniline (Hanawa Chemicals) from acetone-water mixture (1:1 v/v). Acetone(Mallinckrodt AR) employed as solvent was distilled after dried over drierite,

and molecular sieve 3A was introduced into the distillate, which was redistilled immediately before use.

Rate Measurements. Reaction rates were determined by electric conductivity method using a digital conductometer To-A CM-2A type (cell constant $0.0995 cm^{-1}$). Observed rates of the reactions with anilines in large excess over sulfonyl chloride were of the first order(anilines; 0.01-0.4M, substrate; $1.8 \times 10^{-5} \sim 1.1 \times 10^{-4}$ M). The observed first order rate constants(k_{obs}) were obtained by Guggenheim method[13], and they were estimated to be accurate to $\pm 6\%$ or better. The temperature control by thermostat Haake FS type was better than $\pm 0.03°C$. Products were not isolated and identified since the well known formation of sulfonanilides from sulfonyl chlorides and anilines[14] was confirmed by Rogne[4b].

RESULTS AND DISCUSSION

Rate Analysis. It was demonstrated[8] that reactions between arylsulfonyl halides and amines proceed quantitatively and irreversibly in aprotic solvents. Accordingly the reactions of 1-anthracenesulfonyl chloride with substituted anilines in acetone can be, irrespective of their mechanism, expressed as the following eqn. (1) and (2);

$$AnSO_2Cl + NH_2C_6H_4X \xrightarrow{slow}$$
$$AnSO_2NHC_6H_4X + HCl \quad (1)$$

$$X-C_6H_4NH_2 + HCl \xrightarrow{fast} X-C_6H_4\overset{+}{N}H_3\overset{-}{Cl} \quad (2)$$

where An denotes anthryl group and X=p-OCH$_3$, p-CH$_3$, p-H, p-Cl and p-NO$_2$. And hence the overall reaction is as eqn. (3).

$$AnSO_2Cl + 2NH_2C_6H_4X \longrightarrow$$
$$AnSO_2NHC_6H_4X + X-C_6H_4\overset{+}{N}H_3\overset{-}{Cl} \quad (3)$$
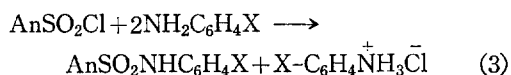
In *Table* 1 are given the pseudo-first order

rate constants at different temperatures for various concentrations of anilines. This type of reactions in protic solvents or protic-aprotic solvent mixtures have been found to show a linear correlation[4b,6] between k_{obs} and aniline concentration, indicating that the reactions are of the first order with respect to anilines. The kinetic data in this work did not show such a correlation, but a curve with an upward concavity except for p-anisidine. For interpretation of this nonlinearity an assumption was required that these reactions proceed by parallel processes involving catalytic activity of anilines (AN), 1-anthracenesulfonanilide (ASA) and anilinium chloride (ANC). Thereby the reaction rates are expressed by the following eqn.

$$Rate = -\frac{d[ASC]}{dt} = (k_2 + k_3[AN] + k_3'[ASA]$$
$$+ k_3''[ANC])[AN][ASC] \quad (4)$$

where k_2, k_3, k_3' and k_3'' are rate constants which characterize noncatalytic, AN-, ASA- and ANC- catalyzed processes, respectively. Since the aniline concentrations were used in large excess over the substrate, [ASA] and [ANC] are negligible relative to [AN] throughout the reaction. Consequently the rate eqn. is thus approximated;

$$Rate \simeq (k_2 + k_3[AN])[AN][ASC]$$
$$= k_{obs}[ASC] \quad (5)$$

therefore $k_{obs} = k_2[AN] + k_3[AN]^2 \quad (6)$

or $k_{obs}/[AN] = k_2 + k_3[AN] \quad (7)$

In fact eqn. (6) illustrates the kinetic data in which the plots of k_{obs} vs. [AN] were not linear as mentioned above. An exception for p-anisidine can be explicable as $k_3 = 0$. Correlations between $k_{obs}/[AN]$ and [AN] have however been found to be linear through all of anilines employed as examplified in *Fig.* 1 and 2. The values of k_2 and k_3 were calculated

Table 1. Pseudo-first order rate constants for the reactions of 1-ASC with *para*-substituted anilines in acetone. $[1-ASC] = (1.792\sim10.648)\cdot10^{-5}M$

Anilines	$[AN]\cdot10^2$ (mole·l⁻¹)	$k_{obs}\cdot10^4$ (sec⁻¹)				
		20°C	25°C	30°C	35°C	40°C
p-OCH₃	1.991	1.114	1.668	2.497		
	4.049	2.287	3.423	4.997		
	5.971	3.345	5.015	7.509		
	9.009	5.104	7.523	11.268		
p-CH₃	2.003		0.687	0.807	0.984	
	4.038		1.413	1.702	2.037	
	6.006		2.128	2.551	3.174	
	9.050		3.300	4.028	4.954	
p-H	3.924			0.398	0.454	0.510
	6.035			0.640	0.722	1.826
	8.274			0.913	1.042	1.185
	10.458			1.182	1.378	1.560
p-Cl	8.403			0.426	0.486	0.509
	10.494			0.611	0.664	0.727
	12.542			0.829	0.879	0.965
	14.980			1.069	1.195	1.311
p-NO₂	25.131				0.079	0.107
	30.077				0.110	0.151
	35.002				0.148	0.203
	39.965				1.901	0.262

Concentrations of anilines are mean values employed at two or three temperatures except for the upper case (1.991) of p-OCH₃.

from the intercept and slope by least square treatment respectively, and are summarized in *Table* 2 along with the ratio of k_3 to k_2. The ratio k_3/k_2 can be taken to indicate a true measure of the catalytic activity of anilines, which was checked in the reactions between naphthalenesulfonyl chloride and anilines in acetone by the stationary state treatment[1e]. Inspection of *Table* 2 reveals that the k_2 values increase with electron-donating substituents in *para*-position of aniline, whereas the ratios k_3/k_2 decrease to show zero for *p*-anisidine within experimental error. This is in accord with a consideration that the rate of noncatalyzed path is, as expected, accelerated with increasing the basicity of anilines, and the catalytic activity is enhanced with increasing the electrophilicity

of anilines. Therefore, Swain's push-pull mechanism might be claimed where the lower the nucleophilicity of attacking group, the greater the role of electrophilic assistance to leaving group. It should be noted that the k_3 values don't show a constant variation with a change in anilines. This appears due to the difference in the specific solvation of acetone for various anilines, which might allow a prediction that these reactions in vapor phase will exhibit a regular variation as expected.

Brφnsted Correlation. In *Fig.* 3 logarithm of the second order rate constants has been plotted in a Brφnsted fashion against the pK_a in water of the corresponding conjugate acid of anilines used. The relationship does not show a satisfactory linearity. This could be primarily
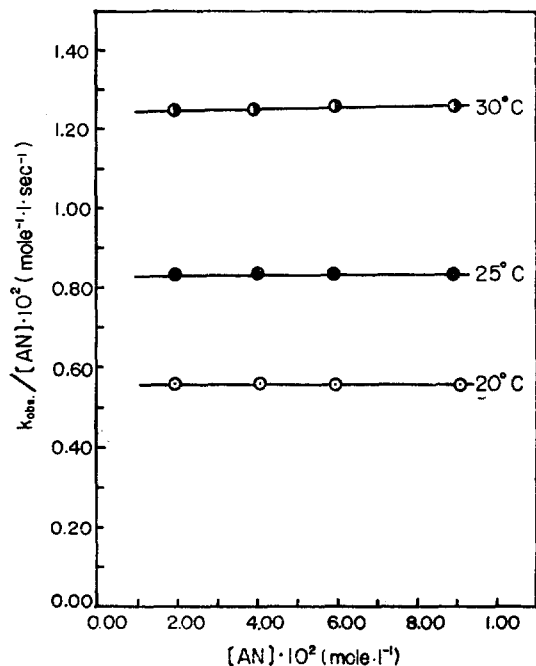
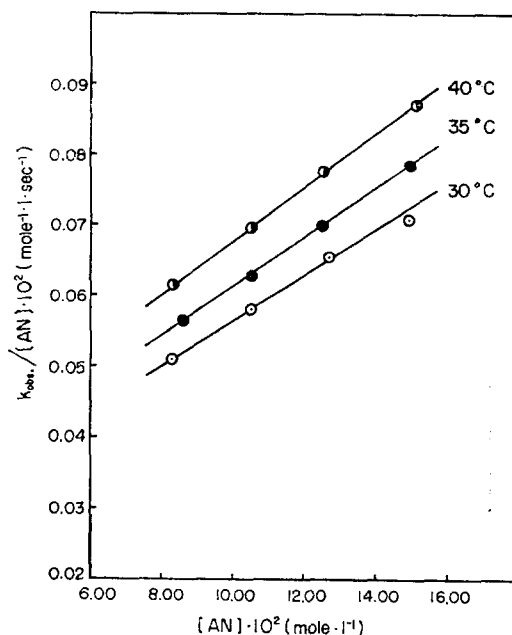*Fig.* 1. Plot of $k_{obs}/$[AN] *vs.* [AN] for the reaction of 1-ASC with *p*-anisidine in acetone.

Fig. 2. Plot of $k_{obs}/$[AN] *vs.* [AN] for the reaction of 1-ASC with *p*-chloroaniline in acetone.

Table 2. Second order rate constants and catalytic constants for the reactions of 1-ASC with anilines in acetone

Anilines	$k_2 \cdot 10^4$ (mole$^{-1} \cdot$l$\cdot$sec^{-1})					$k_3 \cdot 10^4$(mole$^{-2} \cdot$l$^2 \cdot$sec^{-1})					k_3/k_2 (mole$^{-1} \cdot$l)				
	20°C	25°C	30°C	35°C	40°C	20°C	25°C	30°C	35°C	40°C	20°C	25°C	30°C	35°C	40°C
p-OCH₃	55.9	83.7	125.3			1.38	2.71	5.37			0.02	0.03	0.04		
p-CH₃		33.6	39.5	47.4			33.8	52.7	81.6			1.01	1.33	1.72	
p-H		8.17*	9.30	10.7	12.0			19.1	24.1	28.9			2.05	2.25	2.41
p-Cl		2.20*	2.45	2.61	2.96			32.1	35.4	38.2			13.1	13.6	12.9
p-NO₂		0.031*	0.034*	0.037	0.040				1.10	1.54				29.6	38.3

*Extrapolated by Arrhenius plots.

due to the fact that pK_a values in water are related to reaction rates in acetone where the pK_a values of anilines are not known. For such nonhomogeneous comparisons, Leffler and Grunwald[15] pointed out that Brφnsted slopes are not largely affected by a change in solvent even though the absolute pK_a values are greatly changed by the solvent, and that the fit tends to deteriorate as the solvents in which rate constant and pK_a are measured become less alike. Brφnsted β in *Fig.* 3 is 0.77 in which linear correlation coefficient is 0.9869. In the case of omission of *p*-nitroaniline the linearity is considerably improved up to 0.9956, then the β value amounts to 1.2. Although such an improved fit may well indicate a marked deviation of *p*-nitroaniline from the linear correlation, the deviation could be attributed to a nonhomo-
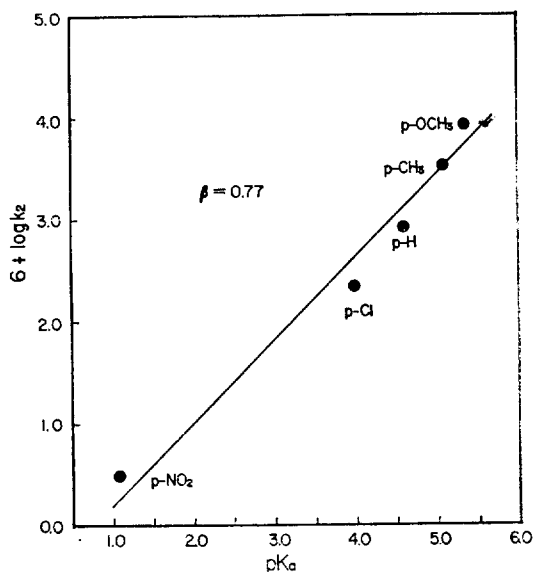
Fig. 3. Brønsted plot for the reactions of 1-ASC with *p*-substituted anilines in acetone at 25°C.

geneous pK_a variation by solvent change from water to acetone. It would be due to the superior ability[16] of a dipolar aprotic solvent, acetone, to solvate dispersed charge of *p*-nitroaniline hybrid resulted from its strong through-conjugation different from the other anilines, and could not be taken as a result caused by positive departure of the rate constant in view of a good linearity of Hammett plot (*Fig.* 4).

Brønsted β which provides a measure of sensitivity of a reaction to the basicity of nucleophile has been related to the degree of bond formation in the transition state of nucleophilic substitutions. In general, the β values ranging from 0.6 to 1.5 have been considered as an indication of large bond formation[17], while those from zero to *ca.* 0.3 have been related to little bond formation[5c, 18]. Intermediate values have also been reported and given a mechanistic significance. In the light of these considerations the bond formation in the transition state for

our reaction of 1-ASC is surely somewhat large.

The β values calculated using pK_a in water for the reactions of benzenesulfonyl chloride[4b, 6] (BSC) in methanol, 1-naphthalenesulfonyl chloride [1e] (1-NSC) in acetone, and 2-naphthalenesulfonyl chloride[1e] (2-NSC) in acetone with anilines were reported to be 0.75 (including *m*-nitroaniline), 1.6 and 1.8 (excluding *p*-nitroaniline) respectively. Although it is difficult to compare the bond formations in the transition state by β values for the three above reactions owing to the nonhomogeneous comparison[15] between rate constant and pK_a, it seems appropriate to conclude that the bond formation for 1-ASC is less advanced than that for the others, and hence incomplete.

For analogous reactions of *p*-methoxy- and *p*-nitrobenzenesulfonyl chloride with anilines in methanol, β values were also reported[4b] to be 0.65 and 0.93 respectively. The smaller β value for the former was interpreted to be ascribed to positive charge deficiency on sulfur in the ground state. This is also in agreement with predictions of substituent effect on S_N2 transition state structure[19]. In this context the β value for 1-ASC smaller than that for 1-NSC seems to be associated with higher electron-donating ability of 1-anthryl group by better π-conjugative effect. This is also consistent with the magnitude of Streitwieser's constant σ^+ (−0.56, −0.35)[20] and with reactivity number N_t (1.57, 1.81 respectively)[21] for each group.

Hammett Correlation. *Fig.* 4. shows a Hammett plot established from the correlation between logarithm of noncatalytic second order rate constant k_2 and ordinary substituent constant σ. As can be seen, this represents a very good linearity with correlation coefficient 0.9988, and its slope ρ is −3.22. Negative sign of the Hammett ρ with respect to substituent change in nucleophile indicates a positive charge deve-
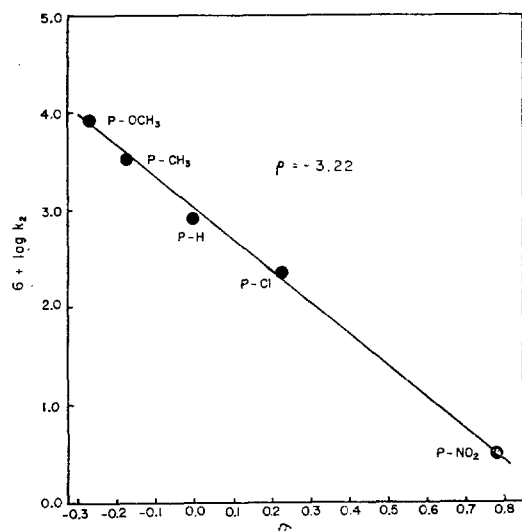
Fig. 4. Hammett plot for the reactions of 1-ASC with *p*-substituted anilines in acetone at 25°C.

lopment on the nucleophilic center N, and its magnitude indicates an amount of the charge developed and hence degree of bond formation in the transition state. Thus the relatively large values of $|\rho|$ and Brønsted β show that the reactions of 1-ASC with anilines in acetone are likely to be of an associative S_N2 or S_AN type. Moreover, a good linearity of the Hammett plot implies a constancy of the bond formation in the transition state irrespective of structural change in anilines. This is in accord with a prediction from More O'Ferrall diagrams[19a, 22] which have been recently used to examine the transition state variations for nucleophilic substitution reactions of benzyl halides[23] and benzenesulfonyl chlorides[3b]. In such a diagram presented by Lee *et al.*, supposing that in the reaction of 1-ASC with anilines the transition state lies at midway along the reaction coordinate of an associative S_N2 path, stabilization of the transition state by introducing electron-donating substituents in aniline leads to a movement of the transition state such that the bond formation

is nearly constant and the bond cleavage decreases. Similar effects were actually observed for benzenesulfonyl chlorides[4b]. Incidentally it could be considered that the transition state will lie at midway along the reaction coordinate provided that our reactions proceed *via* the associative S_N2. Even though the same amount of charge is transferred from aniline to substrate, negative charge development on sulfonyl sulfur for each reaction with anilines would not always be equal in the transition state. In the case mentioned above, since electron-withdrawing substituents in aniline will cause the bond cleavage to increase, electron density on the sulfur decreases, while that on the leaving group, and S-Cl bond polarization increases. Thus the increased negative charge on the leaving group will be capable of more electrophilic interaction with solvents or nucleophiles mainly by hydrogen bond. In protic solvents, interaction between the solvent and leaving group will generally predominate over that between nucleophile and leaving group, while in aprotic solvents interaction of the solvent with leaving group will be of little significance, particularly for small size of leaving groups[24]. Therefore it follows from this deduction that the electrophilic effect of nucleophile on the leaving group in protic solvents will hardly be observed separately, but will be done in aprotic solvents. In fact, the electrophilic catalysis of nucleophiles has not been found as yet in protic solvents at least in so far as sulfonyl halides are concerned. Accordingly it is firmly concluded that the catalytic activity found in our work is electrophilic as reflected by a trend of variations of the ratio k_3/k_2 as well.

The Hammett ρ values for the reactions of anilines were reported to be -2.15 with BSC in methanol[4b], -4.2 with 1-NSC in acetone[1e], and -4.6 with 2-NSC in acetone[1e]. Comparison

of these values with -3.2 for 1-ASC leads to the same conclusion for the degree of bond formation as that derived from the Brønsted β.

Mechanism Interpretation. We can assume for the present three types of reaction mechanisms as presented below (*Scheme* 1~3) : direct one step S_N2, *Scheme* 2; S_N2 *via* sulfonylammonium intermediate (1), *Scheme* 3; S_AN *via* a quinquecovalent intermediate (II). Here, difference between *Scheme* 1 and 2 can be considered to be due to the expulsion rate of hydrogen in aniline and leaving species Cl. For simplifying the description of these schemes, significant transition states possible involved in the aniline-catalyzed routes are also given below; [I] is for S_N2, [II] and [III] are for S_AN unifunctional and bifunctional, respectively. Of the three schemes, *Scheme* 1 would be inadequate for generalization of nucleophilic substitution reactions with extensive amines including tertiary amines since the tertiary amines in protic solvents such as water exert a nucleophilic catalysis to produce corresponding solvolysis products[7]. On the other hand, *Scheme* 3 appears accommodated provided that the rate-determining step is elimination of leaving group *via* intermediate (II). However, it might also be inadequate for interpretation of a progressive


Scheme I
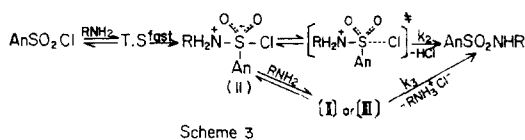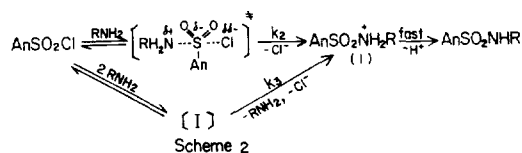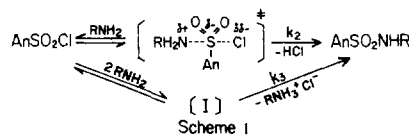
Scheme 2

Scheme 3

decrease in rates observed upon introduction of one and two *ortho*-methyl groups in aniline for the reaction of benzenesulfonyl chlorides[6]. Consequently *Scheme* 2 is favorable; giving a satisfactory illustration not only of greater bond formation in the transition state deduced from Brønsted β and Hammett ρ but also of the electrophilical catalytic activity. An alternative type of mechanism might be considered in which formation of intermediate (II) is the rate-determining step in *Scheme* 3. This appears impossible to explain the electrophilic catalysis.

Activation Parameters. Finally activation parameters determined from Arrhenius plot, temperature dependence of k_2, are collected in *Table* 3.

[I]

[II]

[III]

Table 3. Activation parameters for the reactions of 1-ASC with anilines in acetone at 30°C

Anilines	E_a (kcal·mole^{-1})	$\Delta H^{\ddagger}$ (kcal·mole^{-1})	$-\Delta S^{\ddagger}$ (eu·mole^{-1})
p-OCH$_3$	14.3	13.7	22.2
p-CH$_3$	6.3	5.7	50.8
p-H	4.8	4.2	58.5
p-Cl	3.6	3.0	65.3
p-NO$_2$	3.2*	2.5*	75.2*

*Values at 35°C.
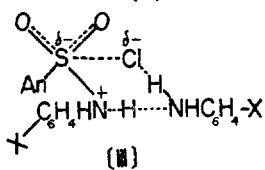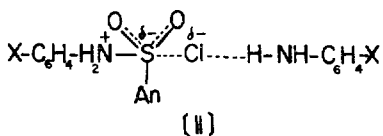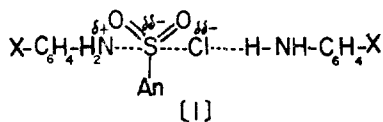
These parameters are, on the whole, much smaller than those for typical S_N2 except for p-anisidine. Although it is known that mechanistic interpretation of the activation parameters for reactions proceeding in parallel catalyzed by nucleophiles is in general complicated, it is quite likely that the typical values for p-anisidine imply a lack of catalytic activity, proceeding mainly by a noncatalytic route. The unusual smaller enthalpies of activation for reactions with the other anilines can be ascribed to reinforced interaction of leaving group with nucleophile, $i.e$, stabilization by electrophilic interaction; progressive decrease with electron-withdrawing substituents in aniline implies a gradual increase of the electrophilical catalytic activity, which is consistent with a deduction from the values k_3/k_2. On the other hand, the large negative entropies of activation for anilines with electron-withdrawing substituents seems to reflect highly polar transition state in which there could be relatively strong electrophilic interactions of leaving group not only with aniline but with positive end of dipole of acetone. Furthermore, the data show that in spite of the enthalpic advantage for anilines with electron-withdrawing substituents, the reaction rates (*Table* 1) become slower owing to a dominating contribution from unfavorable entropy.

Judging from the above discussions, we conclude that the reactions of 1-anthracenesulfonyl chloride with anilines in acetone proceed by an associative S_N2 mechanism catalyzed electrophilically by nucleophiles, in which formation of the corresponding sulfonylammonium intermediate is rate-determining step.

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REFERENCES

1. (a) Z. G. Linetskaya and N. V. Sapozhnikova, *Zh. Prickl. Khim. Mosk.*, **21**, 876 (1948); (b) Z. G. Linetskaya and N. V. Sapozhnikova, *C. R. Acad. Sci. USSR*, **86**, 763 (1952); (c) T. S. Uhm, I. Lee and J. R. Kim, *J. Korean Chem. Soc.*, **20**, 358 (1976); (d) T. S. Uhm, I. Lee and E. S. Lee, *ibid.*, **21**, 262 (1977); (e) T. S. Uhm, I. Lee and E. S. Lee, *ibid.*, **22**, 281(1978).

2. (a) A. Arcoria, E. Maccarone, G. Musumarra and G. A. Tomaselli, *J. Org. Chem.*, **38**, 2457 (1973); (b) *ibid.*, **39**, 1689, 3286, 3595 (1974); (c) A. Arcoria, E. Maccarone and G. A. Tomaselli, *J. Hetero. Chem.*, **12**, 333 (1975); (d) A. Arcoria, V. Librando, E. Maccarone, G. Musumarra, and G. A. Tomaselli, *Tetrahedron*, **33**, 105 (1977); (e) A. Arcoria, F. P. Ballistreri and G. A. Tomaselli, *ibid.*, **34**, 2545 (1978); (f) A. Arcoria, F. P. Ballistreri, G. Musumarra and G. A. Tomaselli, *J. Chem. Soc. Perkin II*, 221 (1981).

3. (a) W. K. Kim and I. Lee, *J. Korean Chem. Soc.*, **18**, 8 (1974); (b) I. Lee, I. S. Koo and H. K. Kang, *Bull. Korean Chem. Soc.*, **2**, 41 (1981).

4. (a) O. Rogne, *J. Chem. Soc. (B)*, 1294 (1968); (b) O. Rogne, *ibid.*, 1855 (1971).

5. (a) E. Ciuffarin, L. Senatore and M. Isola, *J. Chem. Soc. Perkin II*, 468 (1972); (b) L. J. Stangeland, L. Senatore and E. Ciuffarin, *ibid.*, 852 (1972); (c) L. Senatore, E. Ciuffarin, and A. Fava, *J. Amer. Chem. Soc.*, **92**, 3035 (1970).

6. O. Rogne, *J. Chem. Soc. Perkin II*, 472 (1972).

7. (a) O. Rogne, *J. Chem. Soc. (B)*, 727, 1056 (1970); (b) O. Rogne, *ibid.*, 1334 (1971).

8. (a) L. M. Litvinenko and A. F. Popov, *Dokl. Akad. Nauk SSSR*, **160**, 1124 (1965); (b) L. M. Litvinenko and V. A. Savelova, *Zh. O. Kh.*, **36**, 1524 (1966); (c) L. M. Litvinenko and A. F. Popov, *ibid.*, **36**, 1517 (1966).

9. L. M. Litvinenko, N. T. Maleeva, V. A. Savelova and T. D. Kovach, *J. Gen. Chem. USSR*, **41**, 2615 (1971).

10. L. M. Litvinenko, A. F. Popov and V. A. Savelova, *Ukr, Khim. Zh.*, **33**, 57 (1967).

11. Heffter, *Chemisch Berichte*, **28**, 2258 (1895).

12. (a) I. Heilbron, A. H. Cook, H. M. Bunbury and D. H. Hey, Ed., "Dictionary of Organic Compounds," 4th Ed., Vol. 1, p. 252, Oxford University Press, 1965; (b) J. Buckingham, Ed., "Dictionary of Organic Compounds," 5th Ed., Vol. 1, P. 383, Chapman and Hall, London, 1982.

13. E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

14. (a) C. M. Suter, "The Organic Chemistry of Sulfur," chapt. 5 and 6, John Wiley and Sons, New York, 1945; (b) A. I. Vogel, "Elementary Practical Organic Chemistry," Longmans, Green and Co., London, 1958.

15. J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," p. 242, John Wiley and Sons, New York, 1963.

16. A. J. Parker, *Chem. Rev.*, **69**, 1 (1969).

17. (a) R. F. Hudson, *Chimia*, **16**, 173 (1963); (b) W. P. Jencks and M. Gilchrist, *J. Amer. Chem. Soc.*, **90**, 2622 (1968); (c) E. Ciuffarin and L. Senatore, *J. Chem. Soc. (B)*, 1680 (1970); (d) E. Ciuffarin, L. Senatore, and M. Isola, *ibid.*, 2187 (1971); (e) J. R. Knowless, R. O. C. Norman and J. H. Prosser, *Proc. Chem. Soc.*, 341 (1961); (f) G. Biggi and F. Pietra, *J. Chem. Soc. (B)*, 44 (1971).

18. (a) R. F. Hudson and G. Klopman, *J. Chem. Soc.*, 1062 (1962); (b) R. F. Hudson and G. W. Loveday, *ibid.*, 1068 (1962); (c) H. J. Brass, J. O. Edwards, and M. J. Biallas, *J. Amer. Chem. Soc.*, **92**, 4675 (1970).

19. (a) E. R. Thornton, *J. Amer. Chem. Soc.*, **89**, 2915 (1967); (b) J. C. Harris and J. L. Kurtz, *J. Amer. Chem. Soc.*, **92**, 349 (1970).

20. A. Streitwieser, Jr., H. A. Hammond, R. H. Jagow, R. M. Williams, R. G. Jesaitis, C. J. Chang and R. Wolf, *J. Amer. Chem. Soc.*, **92**, 5141 (1970).

21. M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," p. 295, McGraw-Hill, New York, 1969.

22. (a) R. A. More O'Ferrall, *J. Chem. Soc. (B)*, 274 (1970); (b) D. A. Winey and E. R. Thornton, *J. Amer. Chem. Soc.*, **97**, 3102 (1975); (c) W. P. Jencks, *Chem. Rev.*, **72**, 705 (1972).

23. (a) P. R. Young and W. P. Jencks, *J. Amer. Chem. Soc.*, **101**, 3288 (1979); (b) J. M. Harris, S. G. Shafer, J. R. Moffatt and A. R. Becker, *ibid.*, **101**, 3295 (1979).

24. (a) A. J. Parker, *Quart. Rev. (London)*, **16**, 163 (1962); (b) R. Alexander, E. C. F. Ko, A. J. Parker and T. J. Broxton, *J. Amer. Chem. Soc.*, **90**, 5045 (1968).