

황의 친핵성 치환반응 (제 11 보).  
염화나프탈렌술폰닐과 아닐린과의 반응

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(1978. 1. 31 接受)

Nucleophilic Displacement at Sulfur Center (XI).  
Reaction of Naphthalenesulfonyl Chlorides with Anilines

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(Received Jan. 31, 1978)

요 약 1-염화 및 2-염화나프탈렌술폰닐과 아닐린과의 반응에서 그 반응의 유사 일차 반응속도상수( $k_{obs}$ )를 구하고 또한 2차 반응속도 상수  $k_2$  및 3차반응 촉매속도상수  $k_3$ 도  $k_{obs}$ 로부터 구하였다.

1-염화나프탈렌술폰닐과의 반응에서는 *Peri*-hydrogen 효과가 관측되었다. 또한 Brønsted 그림표에서는 큰 값의  $\beta$ 와 Hammett 그림표의 기울기로부터 큰 음의  $\rho$  값을 얻었다. 따라서 이 반응의 메카니즘은 매우 낮은 활성화파라미터의 값을 갖는 결과로  $S_{AN}$  반응메카니즘과 잘 일치되지만 associative  $S_N2$  메카니즘과으로도 동일하게 잘 설명될 수 있었다.

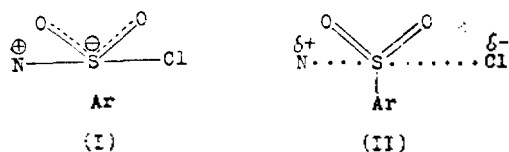
**ABSTRACT.** Pseudo-first order rate constants  $k_{obs}$  were determined for the reactions of naphthalenesulfonyl chlorides (1-NSC and 2-NSC) and alilines. The second order rate constant  $k_2$  and third order catalytic  $k_3$  were then determined from  $k_{obs}$ . For 1-NSC *peri*-hydrogen effect was observed. The large Brønsted  $\beta$  and large negative slopes  $\rho$  for the Hammett plots were obtained. These results with the unusually low values of activation parameters were consistent with the  $S_{AN}$ -elimination mechanism, but these can be equally well interpreted with the associative  $S_N2$  mechanism.

INTRODUCTION

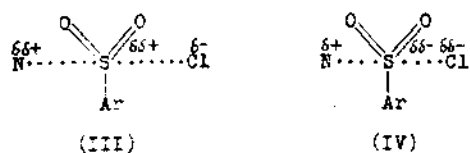
Reactions of nucleophilic substitutions at tetra-coordinate sulfur have been investigated extensi-

vely. However, most of these studies were concerned with substituted benzene,<sup>1</sup> aliphatic<sup>2</sup> and five-membered heterocyclic<sup>3</sup> sulfonyl chlorides. Two different reaction mechanism,  $S_N2$

and  $S_{AN}$ , for nucleophilic substitutions of these tetracoordinate sulfur compounds have been proposed. The  $S_{AN}$  mechanism is an addition-elimination type proceeding through an intermediate (I), whereas the  $S_N2$  is a single step mechanism with a transition state (II). The transition state can have a spectrum of



structures ranging from a "loose" type (III) to a "tight" (IV). An  $S_N2$  reaction involving type (III) transition state is called a dissociative



$S_N2$ , while an  $S_N2$  with (IV) an associative  $S_N2$  reaction.<sup>4</sup> In between these extremes there is a true synchronous push-pull type of mechanism with the transition state (II), in which bond-formation and -breaking occur to the same extent. This can also be either "early" or "late" depending on the extent of bond-formation and -breaking.<sup>5</sup> Recently we have reported the kinetics of solvolysis of 1- and 2-naphthalenesulfonyl chlorides (1-NSC and 2-NSC).<sup>6</sup> Main findings from these studies were (1) both compounds solvolyze in aqueous acetone and ethanol *via* the  $S_N2$  process, (2) 1-NSC solvolyzes slower than 2-NSC due to the *peri*-hydrogen effect in the transition state of the former, and (3) in general the solvolysis reactions are entropy controlled. In order to obtain further information about structure of the transition state, we have carried out the kinetic studies of reactions of NSC with anilines in dry acetone.

## EXPERIMENTAL

**Materials and Apparatus.** 1-Naphthalenesulfonyl chloride and 2-naphthalenesulfonyl chloride: Fischer reagents were used after recrystallization from ether and petroleum ether, m. p 68.0<sup>7</sup> and 79.0<sup>8</sup> respectively for 1-NSC and 2-NSC, agreed with the reported values.

**Alilines.** Tokyo Kasei reagents were used after recrystallization.

**Acetone.** Hayashi reagent was used after dehydration with anhydrous calcium sulfate and distillation.

Conductivity Bridge used was To-A electronics digital conductometer CM-2 A type, cell constant was 0.985 cm<sup>-1</sup>.

**Rate Measurements.** The reactions were followed by conductometric method. The temperature control was better than  $\pm 0.03$  °C. The substrate (NSC) concentration was  $2.330 \times 10^{-4} \sim 10^{-3}$  M and aniline concentration used was 0.02~0.4 M. Since aniline was in excess, the rate was pseudo-first order in all cases. The pseudo-first-order rate constant,  $k_{obs}$ , was determined using Guggenheim plots<sup>9</sup>.

$$\ln(\lambda' - \lambda) + k_{obs} \cdot t = \text{const.}$$

where  $\lambda$  and  $\lambda'$  are conductivities at time  $t$  and  $t + \Delta$ . The value of  $\Delta$  was taken normally as 2~3 times of half-life. A typical data is shown

Table 1. The reaction of 2-naphthalenesulfonyl chloride with aniline in acetone at 25 °C.

$(C_6H_5NH_2) = 0.164$  M.  $(2-ArSO_2Cl) = 2.33 \times 10^{-3}$  M

$t$ (min)	$\lambda$ ( $\mu$ mho/cm)	$t + \Delta$ (min)	$\lambda'$ ( $\mu$ mho/cm)	$\log(\lambda' - \lambda) + 2$
1.5	2.77	33.0	10.63	2.8954
3.0	3.86	34.5	10.78	2.8404
4.5	4.72	36.0	10.89	2.7903
6.0	5.48	37.5	11.01	2.7427
7.5	6.11	39.0	11.11	2.6994
9.0	6.66	40.5	11.22	2.6587
10.5	7.14	42.0	11.32	2.6215
12.0	7.55	43.5	11.42	2.5875

in Table 1 and Fig. 1.

**RESULTS AND DISCUSSION**

The reaction was first order with respect to NSC at 0.002~0.003 M concentration with pseudo-first-order constants ( $k_{obs}$ ), and in the case of *p*-anisidine it was also first order in the aniline (Fig. 2). In other cases the overall second-order constants  $k' = k_{obs}/[\text{aniline}]$  were linear in the aniline concentration. A typical plot is given for *p*-toluidine in Fig. 3. The pseudo-first-order rate constants,  $k_{obs}$ , are summarized in Table 2. This type of reaction is known to be catalyzed by various substances present in the reaction mixture.<sup>1</sup> Since the amount of products formed will be negligible compared with that of aniline, only catalytic path available in parallel with the usual noncatalyzed reaction is by the original aniline. Thus assuming an  $S_N2$  process (see Scheme 1 below).

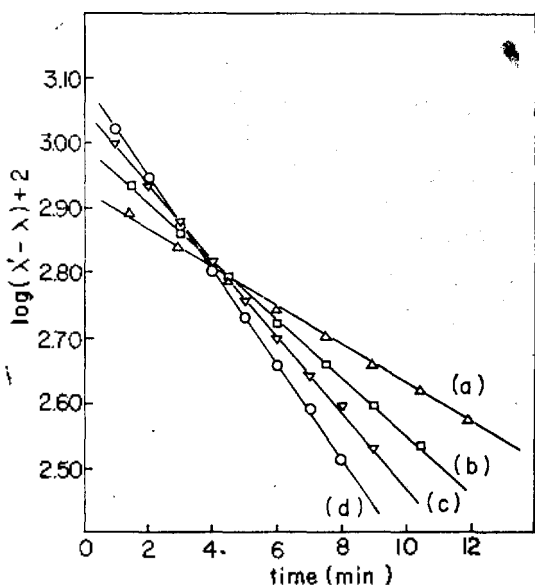


Fig. 1. Guggenheim plot for the reaction of 2-naphthalensulfonyl chloride with aniline in acetone at 25°C. aniline concentration: (a) 0.64 M, (b) 0.227 M, (c) 0.284 M, (d) 0.341 M.

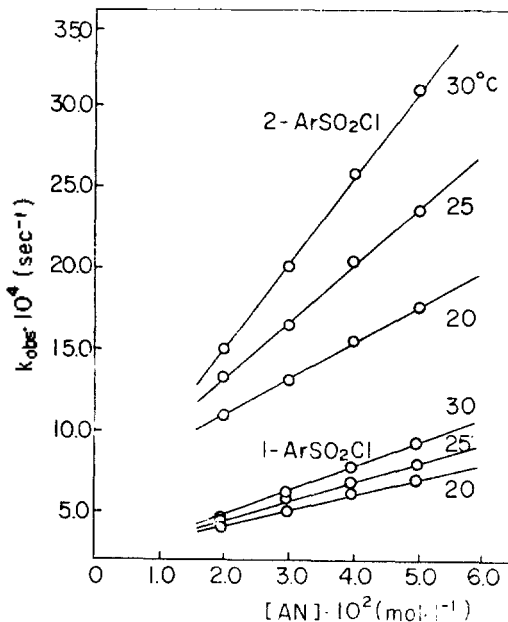


Fig. 2. Plot of the observed pseudo-first order rate constant ( $k_{obs}$ ) against the aniline concentration for the reactions of 1- and 2-naphthalenesulfonyl chloride with *p*-anisidine in acetone.

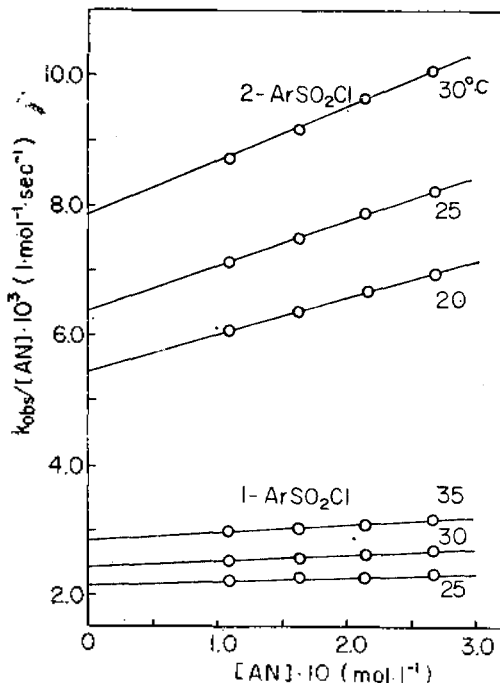
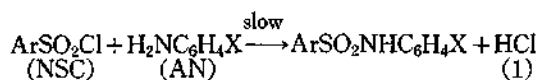


Fig. 3. Dependence of  $k_{obs}/[\text{AN}]$  against the aniline concentration for the reaction of 1- and 2-naphthalenesulfonyl chlorides with *p*-toluidine in acetone.

Table 2. Observed pseudo-first order rate constants ( $k_{obs}$ ) for the reactions of 1- and 2-naphthalenesulfonyl chlorides with *p*-substituted anilines in acetone. [substrate] =  $2.330 \times 10^{-4} \sim 10^{-3} M$ .

Anilines	[AN] × 10 (mole/l)	1-ArSO <sub>2</sub> Cl 10 <sup>5</sup> · $k_{obs}$ (sec <sup>-1</sup> )						2-ArSO <sub>2</sub> Cl 10 <sup>5</sup> · $k_{obs}$ (sec <sup>-1</sup> )					
		20°C	25°C	30°C	35°C	40°C	45°C	20°C	25°C	30°C	35°C	40°C	45°C
<i>p</i> -OCH <sub>3</sub>	0.200	42.3	46.2	47.7				110	133	155			
	0.301	53.2	57.6	62.1				132	166	203			
	0.350	—	63.8	—				—	—	—			
	0.402	63.4	69.3	78.8				157	205	260			
	0.501	71.2	81.1	94.2				178	238	312			
<i>p</i> -CH <sub>3</sub>	1.102		24.7	28.2	33.2			67.2	79.9	96.2			
	1.627		36.9	42.2	49.8			104	122	149			
	2.140		49.2	56.9	66.6			143	169	207			
	2.675		63.0	72.2	85.3			187	221	270			
<i>p</i> -H	1.636		—	—	—			92.9	113	133			
	2.272		18.6	22.4	25.4			138	170	199			
	2.840		—	—	—			182	220	263			
	3.408		29.3	34.3	39.7			223	277	328			
	4.545		40.2	47.6	56.3			—	—	—			
	5.680		51.8	61.6	72.6			—	—	—			
<i>p</i> -Cl	2.520				—	—	—			7.45	8.38	9.69	
	3.055				3.64	4.49	4.83			9.95	11.4	13.3	
	3.513				4.42	5.31	5.84			12.8	14.5	16.7	
	4.001				5.25	6.35	6.87						
<i>p</i> -NO <sub>2</sub>	3.513											0.587	0.706
	4.001											0.748	0.901



$$\text{Rate} = -\frac{d[\text{NSC}]}{dt} = k_{obs}[\text{NSC}] = k'[\text{AN}][\text{NSC}] \quad (2)$$

$$k_{obs} = k'[\text{AN}] = \{k_2 + k_3[\text{AN}]\}[\text{AN}] \quad (3)$$

$$k' = k_{obs}/[\text{AN}] = k_2 + k_3[\text{AN}] \quad (4)$$

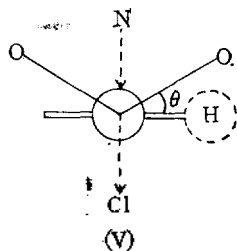
Values of noncatalyzed reaction rate constant  $k_2$  and the catalytic constant  $k_3$  were obtained from the linear plots (Fig. 3) of  $k'$  against [AN] and are summarized in Table 3. The Tables 2 and 3 show that  $k_{obs}$  and  $k_2$  are smaller for 1-NSC than for 2-NSC, as they were the case in solvolysis. According to the perturbation molecular orbital (PMO) theory<sup>10</sup> of Dewar, arenesulfonyl system is topologically equivalent

to, or isoconjugate with the arylmethyl system as a first approximation (*i. e.*, the first-order perturbation) since the arenesulfonyl system is formed from arylmethyl system by monocentric perturbation. Thus the PMO theory of alternant hydrocarbon is applicable to arenesulfonyl system as a first approximation. The theory predicts 1-NSC to be more reactive toward a nucleophile than 2-NSC since 1-naphthylmethyl which is isoconjugate with 1-naphthalene-sulfonyl has smaller nonbonding MO (NBMO) coefficient,  $a_{or}$ , at the methylene carbon than that for 2-naphthylmethyl. The results in Table 3 are therefore inconsistent with the prediction of the PMO theory. This is an indication that there is some steric inhibition, *i. e.*, *peri*-hydrogen

Table 3. Second order rate constants ( $k_2$ ) and aniline catalytic rate constants ( $k_3$ ) for the reactions of 1- and 2-naphthalenesulfonyl chlorides with anilines in acetone.

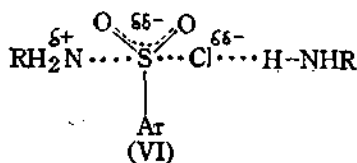
Anilines	Rate con. & $k_3/k_2$	1-ArSO <sub>2</sub> Cl						2-ArSO <sub>2</sub> Cl					
		20°C	25°C	30°C	35°C	40°C	45°C	20°C	25°C	30°C	35°C	40°C	45°C
<i>p</i> -OCH <sub>3</sub>	10 <sup>4</sup> · $k_2$	97	116	156				231	351	525			
	10 <sup>4</sup> · $k_3$	0	0	0				0	0	0			
	$k_3/k_2$	0	0	0				0	0	0			
<i>p</i> -CH <sub>3</sub>	10 <sup>4</sup> · $k_2$		21.6	24.6	28.8			54.8	63.9	79.1			
	10 <sup>4</sup> · $k_3$		6.89	9.17	11.5			56.6	69.2	87.3			
	$k_3/k_2$		0.32	0.37	0.40			1.03	1.08	1.21			
<i>p</i> -H	10 <sup>4</sup> · $k_2$		7.60	9.10	10.1			49.8	58.1	67.9			
	10 <sup>4</sup> · $k_3$		2.66	2.98	4.88			54.0	68.8	84.7			
	$k_3/k_2$		0.35	0.33	0.48			1.08	1.18	1.25			
<i>p</i> -Cl	10 <sup>4</sup> · $k_2$				0.91	1.07	1.13				1.22	1.29	1.57
	10 <sup>4</sup> · $k_3$				1.17	1.27	1.48				6.81	8.04	9.07
	$k_3/k_2$				1.28	1.19	1.31				5.58	6.23	5.78
<i>p</i> -NO <sub>2</sub>	10 <sup>4</sup> · $k_2$											0.027	0.031
	10 <sup>4</sup> · $k_3$											0.400	0.479
	$k_3/k_2$											14.81	15.5

effect, at the  $S_N2$  type transition state for 1-NSC<sup>10</sup>. A perspective view of the pentacoordinate transition state formation for 1-NSC along the S-C bond can be represented as V. (The horizontal bars represent the naphthalene ring) As the nucleophile, N, approaches the angle

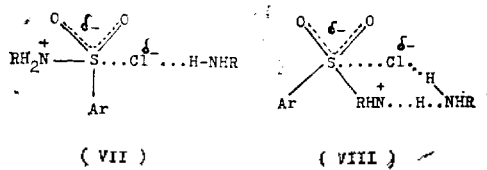


$\theta$  tends to zero degree to form a pentacoordinate transition state where an oxygen atom interferes sterically with *peri*-hydrogen. The presence of *peri*-hydrogen effect in 1-NSC transition state is compatible with associative  $S_N2$  mechanism with a pentacoordinate transition state, and also with the rate-determining formation of the intermediate (I). The contribution of the second-order

(aniline-catalyzed) route in the aniline increases from zero for *p*-OCH<sub>3</sub> to the greatest for *p*-NO<sub>2</sub> compounds as reflected by the  $k_3/k_2$  ratios of Table 3. The stronger catalytic activity with aniline with electron-withdrawing group, and hence with weaker base favors electrophilic catalysis *via*  $S_N2$ <sup>11</sup> with the transition state (VI). It also fits an electrophilic or bifunctio-



nal catalysis for chloride ion expulsion from the intermediate(I), with the transition state(VII) and (VIII).<sup>11</sup>



Thus a mechanistic possibility is an associative  $S_N2$  reaction where bond formation precedes bond cleavage. This is shown in in *Scheme 1*.

An alternative is a nucleophilic addition-elimination, *i.e.*,  $S_{AN}$ , via intermediate I with the rate-determining elimination. ( $S_{AN}$ -elimination). The transition state for the elimination step may be either noncatalyzed, base catalyzed or bifunctional catalyzed as shown in *Scheme 2*.

For *Scheme 2*, a steady-state treatment gives Eq. (7) for the rate expression.

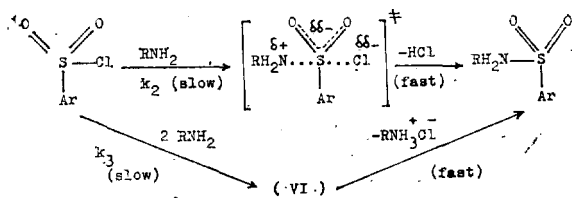
$$\text{Rate} = \left\{ \frac{k_2' k_4' [\text{AN}]}{k_{-2}' + k_4' + k_3' [\text{AN}]} + \frac{k_2' k_3' [\text{AN}]^2}{k_{-2}' + k_4' + k_3' [\text{AN}]} \right\} [\text{NSC}] \quad (7)$$

Assuming the rate-determining elimination, *i.e.*,  $k_4' + k_3' [\text{AN}] \ll k_{-2}'$ , the pseudo-first-order rate constant becomes as Eq. (8).

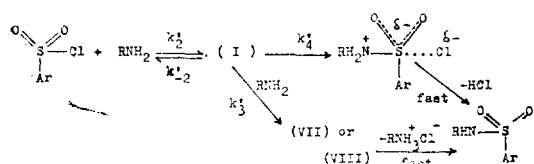
$$k_{\text{obs}} = \left\{ \frac{k_2' k_4'}{k_{-2}'} + \frac{k_2' k_3'}{k_{-2}'} [\text{AN}] \right\} [\text{AN}] \quad (8)$$

$$k' = \frac{k_2' k_4'}{k_{-2}'} + \frac{k_2' k_3'}{k_{-2}'} [\text{AN}] = K(k_4' + k_3' [\text{AN}]) \quad (9)$$

where  $K = \frac{k_2'}{k_{-2}'}$ . Therefore the ratio  $k_3'/k_4'$  in *Scheme 2* corresponds to  $k_3/k_2$  of *Scheme 1*,

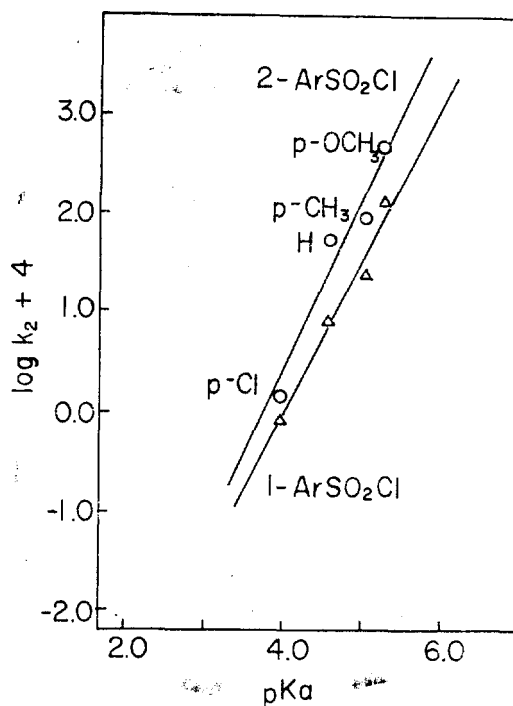


*Scheme 1.*



*Scheme 2.*

and *peri*-hydrogen effect will be reflected in the decrease of  $K$ , since  $k_2'$  will decrease due to the *peri*-hydrogen effect. *Table 3* shows that the ratio  $k_3/k_2 (=k_3'/k_4')$ , for  $S_{AN}$ -elimination, increases as  $k_2 (=k_4')$  decreases for a sulfonyl compound with varying nucleophile. However comparison of  $k_2$  for 1-NSC with that for 2-NSC shows that despite of low  $k_2$  for 1-NSC the ratio is small. This is nicely explained using Eq. (9). The small value of  $k_2 (=K \cdot k_4')$  is due to the small  $K$  as a result of *peri*-hydrogen effect, but the ratio  $k_3/k_2 (=k_3'/k_4')$  will be small for 1-NSC because of large  $k_2 (=k_4')$  as predicted by the PMO theory (see below). Any one mechanism, *Scheme 1* or 2 cannot be unequivocally excluded at the present stage. *Fig. 4* shows the Brønsted plot for the reactions of 1-NSC with substituted anilines in acetone. The slope,  $\beta=1.8$  and 1.6 for 2-NSC and 1-NSC



*Fig. 4.* Brønsted plot for the reactions of 1- and 2-naphthalensulfonyl chloride with *p*-substituted anilines. ( $\beta=1.8$  for 2- $\text{ArSO}_2\text{Cl}$ ,  $\beta=1.6$ , for 1- $\text{ArSO}_2\text{Cl}$ )

respectively, are rather large. Although the use of  $pK_a$  values in aqueous solution does not justify direct interpretation of the significance of  $\beta$  value, it seems appropriate to conclude that the degree of S-N bond formation in the transition state is very large indeed, if not complete as it will be in the  $S_N2$ -elimination mechanism.<sup>1c</sup> In aqueous mixtures  $\beta$  ranged from 0.4 to 0.8 for substituted benzenesulfonyl chlorides with anilines.<sup>1c</sup>

Another support for this view is provided by the Hammett plots, Fig. 5, which gave again large negative slopes,  $\rho = -4.6$  and  $-4.2$  for 2-NSC and 1-NSC respectively.<sup>1d</sup> Finally activation parameters determined from the temperature dependence of  $k_2$  (or  $K \cdot k_4'$ ) are collected in Table 4. Mechanistic interpretation of the activation parameters are complicated because of the parallel base catalyzed path. Values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  are in general low. The  $\Delta H^\ddagger$  value for 1-NSC with *p*-OCH<sub>3</sub>-aniline is smaller than that for 2-NSC, which is contrary to what we would have expected from the *peri*-hydrogen effect in 1-NSC if bond-formation were important. According to the PMO theory,<sup>10</sup> 1-naphthyl (1-N) and 2-naphthyl (2-N) groups are  $\pm E$  substituents which stabilize methylene carbon of the naphthylmethyl (*iso*-conjugate with naphthalene-sulfonyl) system equally in all three forms (anion, radical and cation). However as the NBMO coefficient,  $a_{or}$ , decrea-

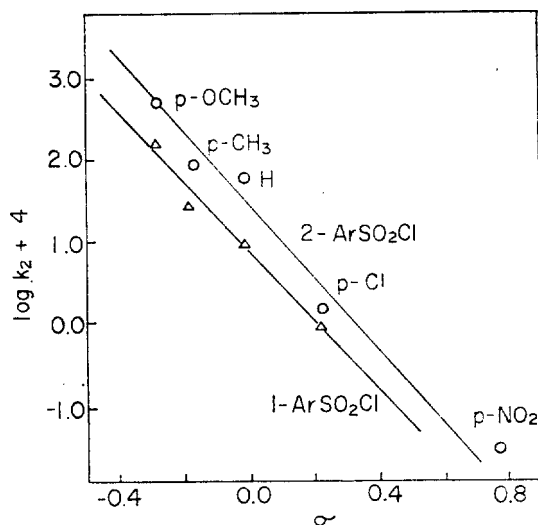


Fig. 5. Hammett plot for the reactions of *p*-substituted anilines with 1- and 2-naphthalensulfonyl chlorides in acetone at 30°C. ( $\rho = -4.6$  for 2-ArSO<sub>2</sub>Cl,  $\rho = -4.2$  for 1-ArSO<sub>2</sub>Cl).

ses with increasing electron-donating ability (*i. e.*,  $-E$  activity) of the aryl group, 1-N group is expected to stabilize the methylene cation (which is formed when chloride ion is expelled) more than 2-N group does, since the  $a_{or}$  values are 0.671 and 0.727 for 1-N and 2-N respectively.<sup>12</sup> Therefore chloride ion expulsion (or bond-breaking) will be easier with 1-NSC than with 2-NSC. This could be the reason why  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  values are smaller for 1-NSC. If this were true, then bond-breaking would be more important than bond-formation in the  $S_N2$

Table 4. Activation parameters for the reactions of *p*-substituted anilines with 1- and 2-naphthalensulfonyl chlorides in acetone.

Activation parameters	Substrate ArSO <sub>2</sub> Cl	Anilines				
		<i>p</i> -MeO	<i>p</i> -CH <sub>3</sub>	<i>p</i> -H	<i>p</i> -Cl	<i>p</i> -NO <sub>2</sub>
$\Delta H^\ddagger$ (kcal·mol <sup>-1</sup> )	1-naphthyl	7.7	4.9	4.6	4.2*	
	2-naphthyl	13.8	5.7	4.9	5.3	4.6**
$-\Delta S^\ddagger$ (e. u.)	1-naphthyl	41.3	54.4	57.4	58.9*	
	2-naphthyl	18.8	49.5	52.4	63.6	69.5

These values are calculated at 30°C. \*35°C, \*\*40°C.

mechanism, *i. e.*, a dissociative  $S_N2$  mechanism since there will be the *peri*-hydrogen effect if bond-formation were important. This does not fit with other experimental evidence presented above. In  $S_{AN}$ -elimination mechanism, however, this means that the temperature effect on  $k_4'$  is large than that on  $K$ , which is not inconsistent with the mechanism.

In this respect, therefore,  $S_{AN}$ -elimination mechanism accommodates better the trends in activation parameters than the  $S_N2$  does. In conclusion, all the mechanistic criteria fit bimolecular mechanism known as  $S_{AN}$ -elimination.

It is however difficult to exclude conclusively the associative  $S_N2$  mechanism since most of the experimental data can be accommodated with this mechanism equally well.

#### REFERENCES

1. F. E. Jenkins and A. N. Hambly, *Austral. J. Chem.*, **14**, 190, 205 (1961); (b) M. L. Tonnet and A. N. Hambly, *ibid.*, **24**, 703 (1971); (c) L. J. Stangeland, L. Senstore and E. Ciuffarin, *J. C. S. Perkin II*, 852 (1972); (d) A. R. Houghton, R. M. Laird and M. J. Spence, *ibid.*, 637 (1957); (e) O. Rogne, *J. Chem. Soc. (B)*, 1294 (1968); (f) L. M. Litvinenko, N. T. Maleeva, V. A. Savelova and T. D. Kovach, *J. Gen. Chem. USSR*, **41**, 2615 (1971).
2. (a) R. Foon and A. N. Hambly, *Austral. J. Chem.*, **24**, 713 (1971); (b) J. Lee and J. E. Yie, *J. Korean Nucl. Soc.*, **6**, 23 (1974).
3. (a) A. Arcoria, E. Maccarone, G. Musumarra and G. A. Tomaselli, *J. Org. Chem.*, **39**, 3595 (1974); (b) A. Arcoria, V. Librando, E. Maccarone, G. Musumarra and G. A. Tomaselli, *Tetrahedron*, **33**, 105 (1977); (c) A. Arcoria, E. Maccarone, G. Musumarra and G. A. Tomaselli, *J. Org. Chem.*, **39**, 1689 (1974).
4. R. Ta-Shma and Z. Rappoport, *J. Amer. Chem. Soc.*, **99**, 1845 (1977).
5. H. Giese, *Angew. Chemie, Internat. Ed.*, **16**, 125 (1977).
6. (a) T. S. Uhm, I. Lee and J. R. Kim, *J. Korean Chem. Soc.*, **20**, 358 (1978); (b) T. S. Uhm, I. Lee and E. S. Lee, *ibid.*, **21**, 262 (1977).
7. "Hand Book of Chemistry and Physics", 55th Ed., C-385 CRC Press, 1974~1975.
8. *ibid.*, 1974~1975.
9. E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).
10. M. J. S. Dewar and R. C. Dougherty, "The PMO Theory of Org. Chem.", Plenum, New York, 1975.
11. L. M. Litvinenko, A. F. Popov and V. A. Savelova, *Zh. O. Kh.* **36**, 47 (1966).
12. A. Streitwieser, Jr, "MO Theory for Org. Chemists", John-Wiley, New York, 1961.