

# $\alpha$ -및 $\beta$ -염화나프탈렌술포닐과 $\alpha$ -나프틸아민과의 반응에 대한 용매효과

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Solvent Effect on the Reaction of  $\alpha$ -, and  $\beta$ -Naphthalene  
Sulfonyl chloride with  $\alpha$ -Naphthylamine

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## 요 약

$\alpha$ -, 및  $\beta$ -염화나프탈렌술포닐과  $\alpha$ -나프틸아민과의 반응에 대한 유사일차반응속도 상수를 여러 종류의 용매에서 구하고 그 결과로부터 반응성과 용매효과를 논의하였다. 순수 아세토니트릴용매 속에서의 반응속도상수는 양성자성용매계에서 보다 작게 관측되었다.

피리딘의 경우에는 유사일차 반응속도상수가 아세토니트릴용매계에서 크게 관측된 것과 비교해 볼 때 용매효과보다 친핵체의 영향이 크게 작용할 것으로 예상된다. Taft의 용매파라미터  $\alpha - \pi^*$  값과 좋은 직선관계가 성립됨을 볼 때 본 반응은 용매의 용질분자에 대한 수소결합성 능력과 극성이 동시에 작용함을 알 수 있었다.

## I. Introduction

The influence of solvation on the rate or direction of chemical reaction of reactivity and selectivity of the substitution reaction is generally well known.<sup>1,2,3,4,5</sup> A comparative study of data for the gas phase, the model solvent, and water make it possible to elucidate the influence of electrostatic solvation (nonspecific) and solvation via hydrogen

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bonding on the acid-base properties in an aqueous medium (specific).

During the last decade, the acid-base properties of a large number of organic compounds have been determined quantitatively in a series of aprotic polar solvents, which permit and approach to the solution of the problem under consideration.<sup>6,7,8,9,10,11,12)</sup>

Protic solvents are particularly good anion solvators due to their hydrogen bonding ability. This tendency is the more pronounced, the higher the charge density of the anion to be solvated, and its hardness according to the HSAB-principle. Therefore, in protic solvents, the strongest nucleophiles will be the ones with lower or more diffused charge density.<sup>13)</sup>

The relative nucleophilic reactivities and then solvent effects for SN2 reactions in various protic and dipolar aprotic solvents have been studied by kinetic methods.<sup>14)</sup> The solvent effects on nucleophilic substitution reaction of naphthalene sulfonyl chloride with the nucleophiles (pyridine, p-substituted anilines) were studied by I. Lee et al.<sup>21,22)</sup> But it has not investigated into for the nucleophilic substitution reaction of  $\alpha$ -, and  $\beta$ -naphthalene sulfonyl chloride with  $\alpha$ -naphthyl amine in various solvent mixtures.

The observed rate constants for these reactions have been measured and not only the electric static solvation and specific solvation by means of various solvent parameters but also the reaction mechanism for the transition state have been discussed.

## II. Experimental

### ① Materials

$\alpha$ -Naphthalene sulfonyl chloride ( $\alpha$ -NSC) and  $\beta$ -naphthalene sulfonyl chloride ( $\beta$ -NSC) were purchased from Tokyo Kasei Co., Japan and used after recrystallization with ether.  $\alpha$ -naphthylamine ( $\alpha$ -NA) was obtained from Tokyo Kasei Co., and used as received. The methanol (MeOH), ethanol (EtOH), 2-propanol (2-PrOH) 1-butanol (1-BuOH) and acetonitrile (MeCN) were purified by the method of the literature.<sup>16)</sup>

### ② Determination of rate constants

The nucleophilic substitution reactions for  $\alpha$ -, and  $\beta$ -NSC with  $\alpha$ -NA in various

pure solvents were carried out by the conductometric method that involved adding 0.1ml of 0.1M stock solution which was dissolved the substrate(1-NSC or 2-NSC) in acetone with 1.0ml of 0.5M, 0.75m, 1.0m stock solution which was also dissolved the nucleophile( $\alpha$ -NA) in acetone in each 20ml on pure solvents in thermostated cell compartment with equipped To-A CM 2-A digital conductmeter.

The cell constants of the electrode was  $0.985 \text{ cm}^{-1}$ . The reactions were followed by pseudo-first order, since the concentration of the nucleophile was very rich excess comparing with the substrate.

The pseudo-first rate constants of the reactions were calculated by Guggenheim equation<sup>17)</sup> and were given Table-1. The maximum error in the rate constant is estimated to be  $\pm 0.005$ .

### III. Results and Discussion

In the nucleophilic substitution reactions of  $\alpha$ - and  $\beta$ -NSC with  $\alpha$ -NA in various solvents, the higher concentration of  $\alpha$ -NA goes on, the observed rate constant( $k_{\text{obs}}$ ) shows higher and also the reaction temperature goes on higher, the second order rate constants( $k_2$ ) increases in Table-1.

The dependence on the concentration of  $\alpha$ -NA against the observed rate constants may have nothing to do, because the concentration of  $\alpha$ -NA is very rich compared with the concentration of the substrate,  $\alpha$ -NSC and  $\beta$ -NSC, but the results of Table-1 have shown that the observed rate constants depend on the concentration of  $\alpha$ -NA, and then this means  $\alpha$ -NA reacts as not only the nucleophile but also the catalyst. The nucleophilic substitution reaction of  $\alpha$ - and  $\beta$ -NSC with  $\alpha$ -NA in each pure solvent may be followed SN2 type mechanism, although the solvolysis takes place in the protic solvent, therefore the rate equation (1) is applicable.

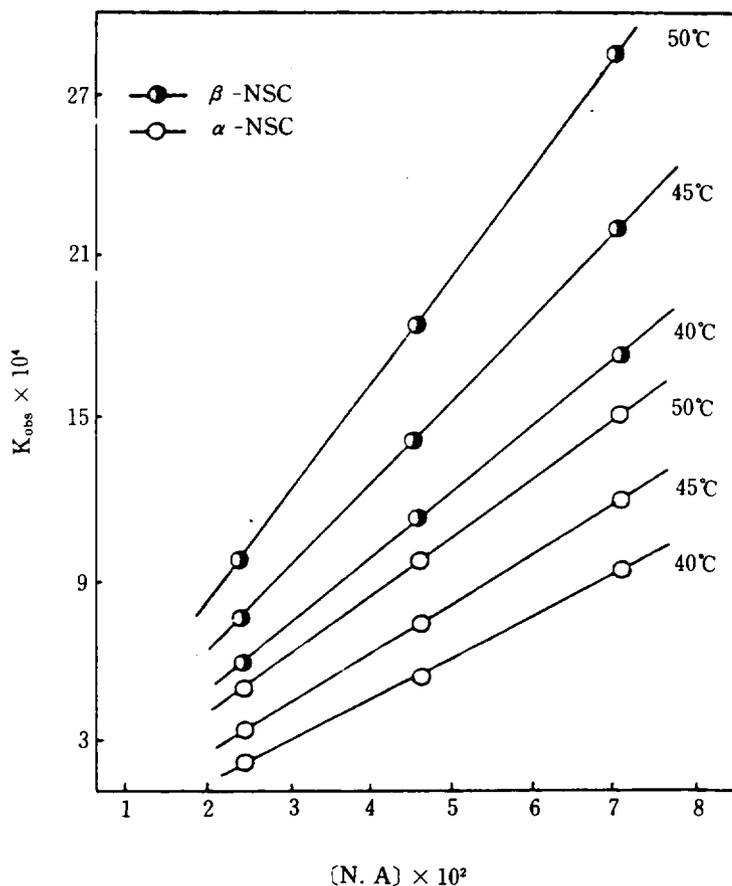
$$\text{rate} = k_2 [\alpha\text{-NA}] [\text{NSC}] \quad (1)$$

and the concentration of  $\alpha$ -NA is very excess comparing with the substrate NSC,

$$k_{\text{obs}} = k_s [\alpha\text{-NA}] \quad (2)$$

**Table-1. The observed pseudo-first order rate constants ( $k_{obs} \times 10^4 \text{ sec}^{-1}$ ) for the reaction of  $\alpha$  -, and  $\beta$  -naphthalenesulfonylchloride with  $\alpha$  -naphthylamine in various solvents.**

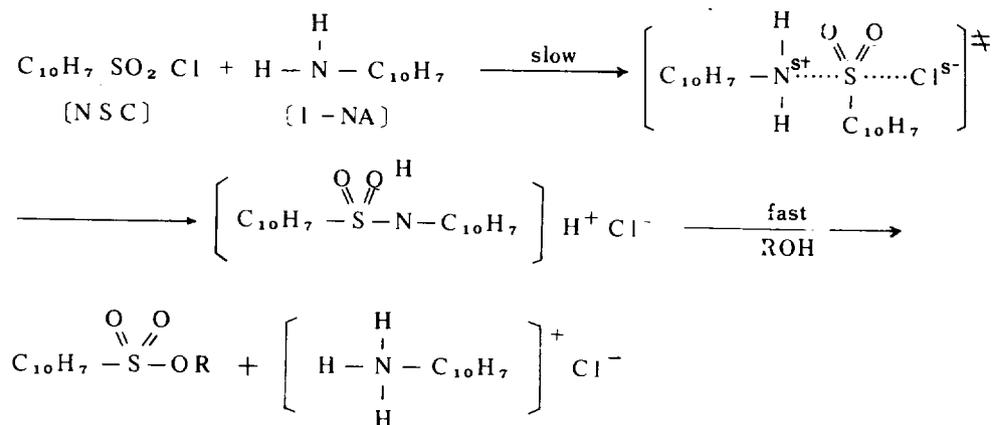
Solvent	Rate constant	[NA] $\times 10^2 \text{ M}$	$\alpha$ -NSC			$\beta$ -NSC		
			40°C	45°C	50°C	40°C	45°C	50°C
MeOH	$k_{obs}$	2.47	2.26	3.42	5.09	5.98	7.58	9.86
		4.73	5.25	7.36	9.81	11.1	14.1	18.4
		7.10	9.36	11.8	14.9	17.2	21.9	28.5
	$k_2$		15.4	18.1	21.2	24.3	31.0	40.3
EtOH	$k_{obs}$	2.47	0.41	0.58	0.85	1.34	1.78	2.00
		4.73	1.78	2.23	2.85	3.04	3.91	4.85
		7.10	2.78	3.40	4.26	5.44	6.57	7.76
	$k_2$		5.12	6.16	7.34	8.87	10.4	12.4
2-PrOH	$k_{obs}$	2.47	0.26	0.35	0.51	0.76	0.95	1.18
		4.73	0.57	0.74	1.04	1.49	1.82	2.19
		7.10	1.07	1.33	1.69	3.11	3.47	3.89
	$k_2$		1.76	2.11	2.55	5.08	5.45	5.86
1-BuOH	$k_{obs}$	2.47	0.34	0.42	0.49	0.68	0.83	1.02
		4.73	0.63	0.89	1.49	1.59	2.63	3.95
		7.10	1.50	1.79	2.18	4.66	5.38	6.34
	$k_2$		2.51	2.97	3.64	8.64	9.84	11.5
MeCN	$k_{obs}$	2.47	-	0.10	0.17	0.18	0.27	0.38
		0.24	0.24	0.30	0.43	0.37	0.52	0.71
		7.10	0.49	0.59	0.75	1.13	1.25	1.45
	$k_2$		-	1.05	1.24	2.05	2.12	2.31



**Fig. 1** Plot of  $k_{obs}$  against  $\alpha$ -naphthylamine concentration for the reaction of  $\alpha$ - and  $\beta$ -naphthalenesulfonylchloride in MeOH.

The second-order rate constants can be obtained from the plots that have shown in Fig. 1. Which have good linearities. These second-order rate constants have been shown also in Table-1.

As the good proportional to the concentration of  $\alpha$ -NA, it is convinced to be a second-order reaction for the total reaction, that is, a first-order for  $[\alpha\text{-NA}]$  and also a first-order for  $[\text{NSC}]$ . The reaction mechanism both for the hydrolysis catalysed by substituted pyridines and for the nucleophilic substitution by primary amines of benzenesulfonyl chloride has been discussed.



SCHEME I

In each case the first and slow step of the reaction is a nucleophilic displacement on sulfur yielding an unstable sulfonyl ammonium intermediate which can be a following fast step either lose a proton to give the corresponding sulfonamide (with primary of secondary amines) or be hydrolysed by water (with tertiary amines).

If the reaction of  $\alpha$ -, and  $\beta$ -NSC with  $\beta$ -NA in protic solvent follow a mechanism of the transition state for the nucleophilic displacement on sulfur yielding an unstable sulfonyl ammonium intermediate in the slow step, the reaction mechanism for the reaction of  $\alpha$ -, and  $\beta$ -NSC is in favor of SCHEME 1. In Table-1 the rate constants of protic solvents are observed higher than aprotic solvent, MeCN. This may be the protic solvents act as a electrophiles in the transition state and also be stabilized the transition state more than in aprotic solvent, therefore the leaving ability of chlorine accelerates. In protic solvents, the order of magnitude is MeOH > EtOH > 1-BuOH > 2-PrOH as shown Table-1.

Generally, the rate constants of solvolysis and the nucleophilic substitution reactions in protic solvents come to an agreement to the dielectric constants of the solven systems.

Fig. 2 says that the rate constants are proportional to dielectric constants in the solvents of the higher dielectric constants but go amiss in case of 1-BuOH. It is explainable as a specific solvation which is the phenomenon of isodielectric solvent each other.

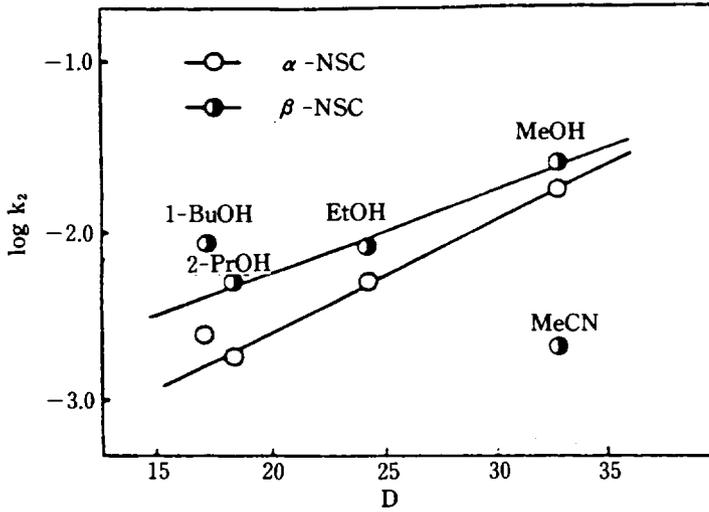


Fig. 2 Plot of  $\log k_2$  vs. dielectric constants of the solvents.

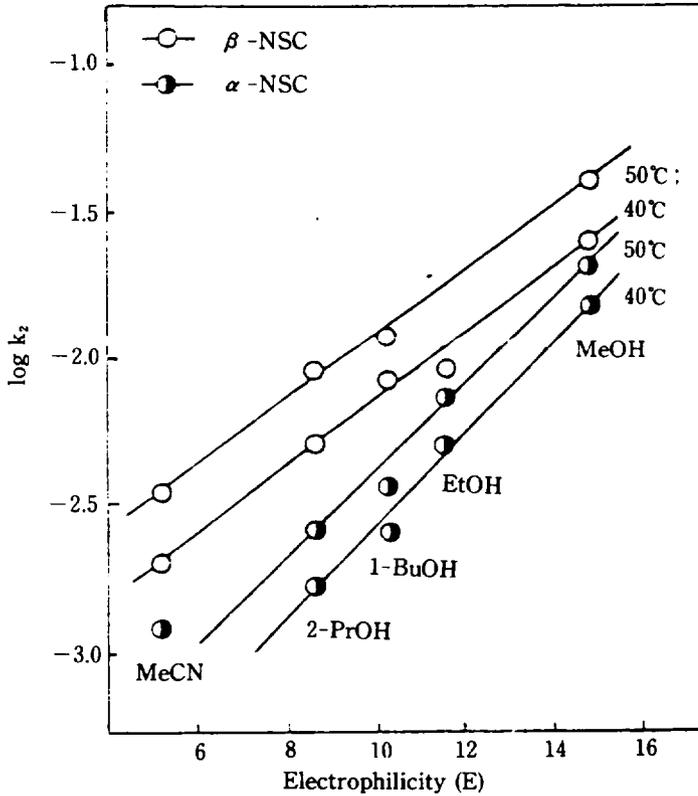


Fig. 3 Plot of electrophilicity vs.  $\log k_2$  for the reaction of  $\alpha$ - and  $\beta$ -NSC with  $\alpha$ -NA in various solvents.

While an aprotic solvent, MeCN secedes from the linearity. The solvent effect on the nucleophilic substitution reaction of  $\alpha$ -, and  $\beta$ -NSC with pyridine have been shown that the rate constants in MeCN are higher than other protic solvents as shown Table-2. That seems the reaction be controlled not by dielectric constant but by any other solvent parameter or by the variation of the nucleophiles. Good correlations were obtained with solvent electrophilicity and solvent polarity parameters such as  $E$ ,  $E_T$ ,  $Z$  in Fig. 3, Fig. 4 and Fig. 5.

The transition state might be explained in terms of orientation of solvent molecules around incipient ions, that is, the solvents react not only as the electrophile but also as the charge separator in this reaction series. However correlations are not good with Taft's HBD scale,  $\alpha^{33}$  in aprotic solvent, MeCN is severely deviated as shown Fig. 6.

**Table-2. \*) The observed pseudo-first order rate constants ( $k_{obs} \times 10^4 \text{sec}^{-1}$ ) and second order rate constants for the reaction of  $\alpha$ - and  $\beta$ -naphthalenesulfonylchlorides with pyridine in various solvents.**

Solvent	$k_{obs}$	Pyridine conc.	$\alpha$ -NSC			$\beta$ -NSC		
			25°C	30°C	35°C	25°C	30°C	35°C
MeOH	$k_{obs}$	0.05	7.21	9.48	12.6	11.3	14.2	17.0
		0.14	13.9	18.4	22.9	25.9	32.1	37.9
		0.23	21.2	27.4	32.2	37.9	48.6	56.6
	$k_2$		7.79	9.96	10.9	14.8	19.1	22.0
EtOH	$k_{obs}$	0.05	2.10	3.38	5.31	5.70	7.75	9.72
		0.14	4.88	7.14	9.87	12.2	15.5	20.0
		0.23	7.72	11.6	15.4	18.5	23.0	29.4
	$k_2$		3.12	4.57	5.61	7.11	8.47	10.9
MeCN	$k_{obs}$	0.05	9.48	11.3	13.0	24.5	27.3	30.0
		0.14	19.9	23.1	26.2	44.8	52.8	61.6
		0.23	29.9	34.0	38.0	65.7	77.9	90.1
	$k_2$		11.3	12.6	13.9	22.9	28.1	33.4
<i>n</i> -PrOH	$k_{obs}$	0.05	2.51	3.41	4.97	5.59	7.42	8.22
		0.14	4.17	5.98	8.23	9.40	12.8	15.9
		0.23	5.79	8.47	11.8	13.3	18.1	22.6
	$k_2$		1.81	2.81	3.89	4.28	5.93	7.99

\*) from ref. 21)

In order to obtain the correlations the rate constants with solvent parameters, applying the solvent parameters  $\alpha$  with  $\pi^*$ <sup>33)</sup> simultaneously to the rate constants Fig. 7 shows good linearity. Presumably during the electronic transition, the protic solvent molecules around the substrate ( $\alpha$ -NA) have no time to change their positions and orientations to adjust to the excited state,<sup>34)</sup> therefore we can not eliminate the transition state as shown SCHEME II.

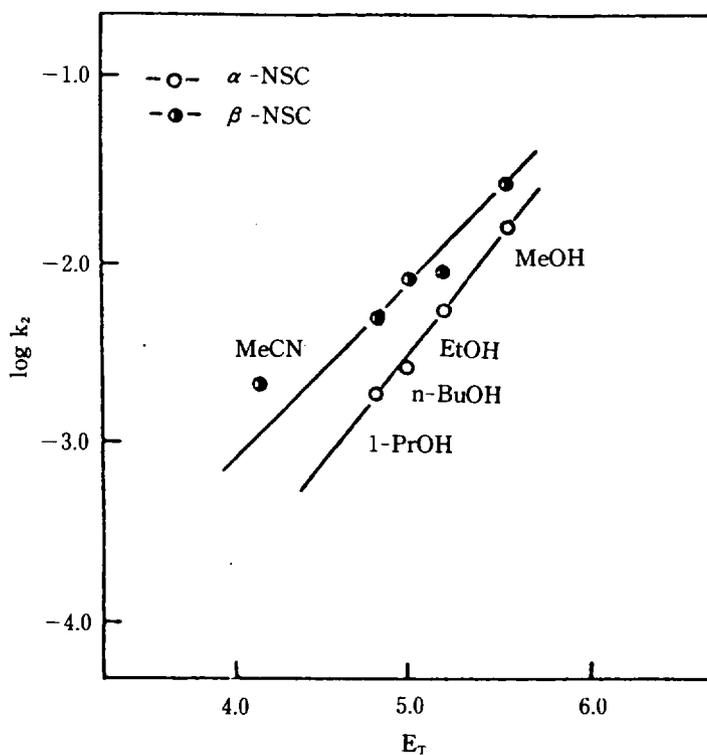


Fig. 4 Plot of  $\log k_2$  vs.  $E_T$  value for the reaction of  $\alpha$ - and  $\beta$ -NSC with  $\alpha$ -NA in various solvents at 40°C.

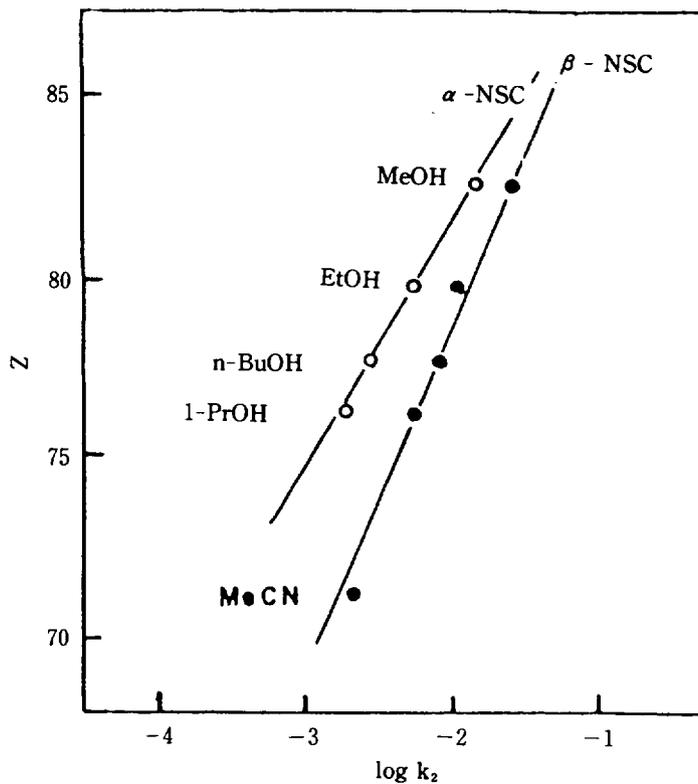


Fig. 5 Plot of  $\log k_2$  vs. Z value for the reaction of  $\alpha$ - and  $\beta$ -NSC with  $\alpha$ -NA at 40°C.

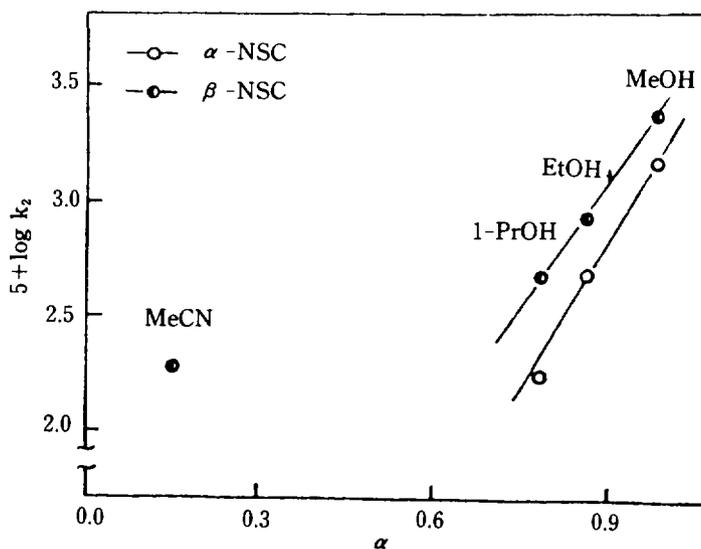


Fig. 6. Plot of  $\log k_2$  vs. Taft's HBD scale  $\alpha$  value for the reaction of  $\alpha$ - and  $\beta$ -NSC with  $\alpha$ -NA at 40°C.

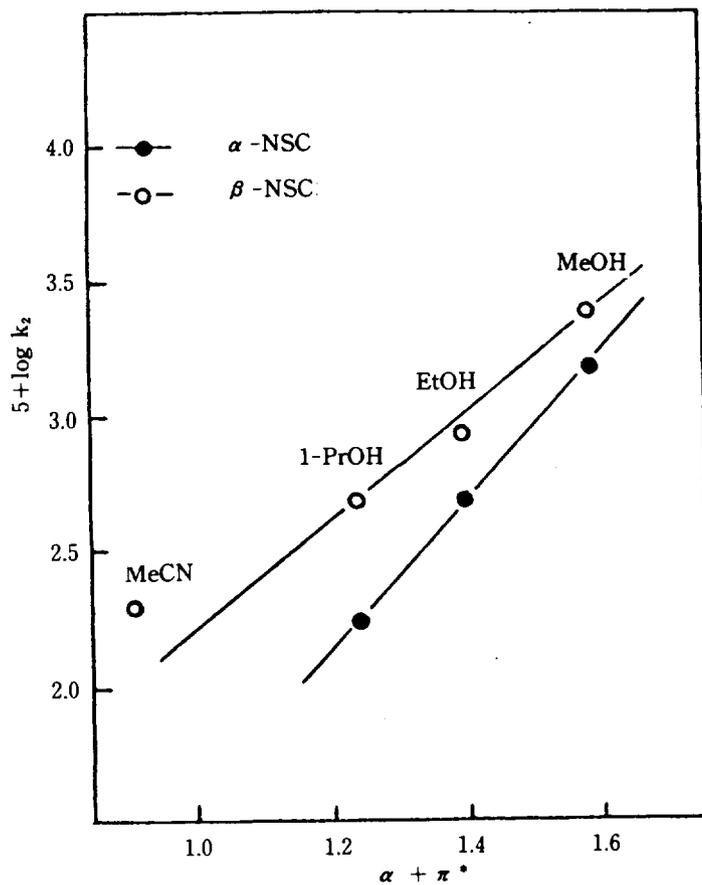
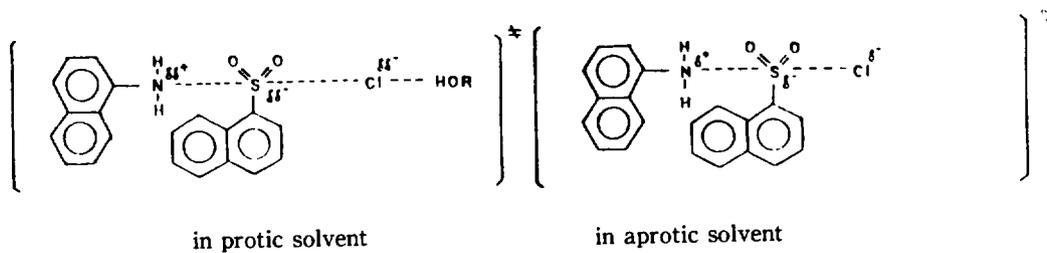


Fig. 7 Plot of  $\log k_2$  vs.  $\alpha + \pi^*$  for the reaction of  $\pi$ - and  $\beta$ -NSC with  $\alpha$ -NA at  $50^\circ\text{C}$ .



SCHEME II

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