

- (1981).
35. R. Belcher, S. L. Bogdanski, E. Henden, and A. Townshend, *Analyst*, **100**, 522 (1975).
36. J. Aggett and A. C. Aspell, *Analyst*, **101**, 341 (1976).
37. A. Dorneman and H. Kleist, *Fresenius' Z. Anal. Chem.*, **305**, 389 (1981).
38. C. J. Peacock and S. J. Singh, *Analyst*, **106**, 931 (1981).
39. C. Boamong, I. D. Brindle, X. Le, L. Pidwerbesky, and C. M. C. Ponzone, *Anal. Chem.*, **60**, 1185 (1988).
40. F. J. Flanagan, *Geochim. Cosmochim. Acta*, **37**, 1189 (1973).
41. S. Terashima, *Geostandards Newslett*, **8**, 155 (1984).
42. E. S. Gladney, C. E. Burns, and I. Roelandts, *Geostandards Newslett.*, **7**, 3 (1983).
43. E. Steinnes, *Pure and Appl. Chem.*, **53**, 903 (1981).
44. H. Heinrichs, *Fresenius' Z. Anal. Chem.*, **294**, 345 (1979).
45. J. S. Kane, *Anal. Chim. Acta*, **106**, 325 (1979).
46. D. S. Lee, J. M. Edmond, and K. W. Bruland, *Earth Planet. Sci. Lett.*, **76**, 254 (1985/86).

## The Salt Effect on The Nucleophilic Substitution Reaction

Hee Hyun Park, Young Seuk Hong, and Dae-Dong Sung\*

Department of Chemistry, Keimyung University, Taegu 704-200

\*Department of Chemistry, Dong-A University, Pusan 604-714. Received January 7, 1991

The nucleophilic substitution reactions of *p*-substituted benzenesulfonyl chlorides with *p*-substituted anilines were carried out in 1, 1, 1, 3, 3, 3-hexafluoro-2-propanol and 2-propanol mixtures. The salt effect was observed to be inhibited by the reaction of 1, 1, 1, 3, 3, 3-hexafluoro-2-propanol with nucleophiles. To investigate the effectiveness of the salt for the nucleophilic substitution reaction the relative salt effect was determined. According to the comparison with the inhibitive salt effect and the substituent effects for the substrates and nucleophiles, the reactions were predicted to be controlled by the salt effect more than substituent effect in HFP-PrOH mixtures.

### Introduction

The factors underlying ionizing power and nucleophilicity of solvents involved in  $S_N2$  reactions have long held the interest of mechanistic chemists.<sup>1</sup> These solvent effects on nucleophilic substitution reactions have presented as linear free energy relationships (LFER) as a major tool studying.<sup>2</sup>

In the discussion thus far, an attempt has been made to understand nucleophilicity by use of relatively well understood model reactions,<sup>3</sup> or by use of reaction conditions that reduce the number of variables affecting nucleophilicity.<sup>4</sup>

However, it seems now clear that the failure of nucleophilic substitution reactions from the use of LFER in unsuitable solvent systems such as poly fluorinated alcohols as which are well known to have a highly ionizing power and very poor nucleophilic assistant properties.<sup>4</sup>

An anomalous behavior, mainly from Schleyer *et al.*<sup>5</sup> proved that solvolysis of primary and simple secondary substrates involved nucleophilic solvent assistance (*ks*). Moreover, the magnitude of *ks* is significant, even in the case of weakly nucleophilic media such as 1, 1, 1, 3, 3, 3-hexafluoro-2-propanol (HFP).<sup>5</sup> Conductibility studies carried out on various electrolytes in HFP show that their solvating ability is strong towards anions and weak towards cations.<sup>7</sup>

In the study of the evaluation of the anomalous medium effect, McManus *et al.* showed that the binary solvent mixtures of HFP and 1, 3-propane-dithiol (PDT) were nonlinear with solvent nucleophilicity dropping off at high HFP concentrations. Nevertheless, HFP-PDT mixtures were surprisingly, 3 to 4 orders of magnitude more nucleophilic than HFP-H<sub>2</sub>O mixtures although pure PDT is estimated to be only 2.5

orders of magnitude more nucleophilic than pure water.

To explain these observations, they suggest that, at high concentrations of electrophilic solvents, hydrogen bonding to the oxygen or sulfur atom in the more nucleophilic solvent molecules reduces the nucleophilicity of these solvents.

Nucleophilic substitution reaction of arenesulfonyl halides with anilines are thought to have important effects upon substrate reactivity in highly ionizing power solvents as HFP or its mixtures.

A much discussed question arising in the direct displacement process concerns the timing of bond formation and breakage, that is, whether the rate determining step corresponds to a transition state or intermediate in the reaction of arenesulfonyl halides with aniline or pyridines.<sup>9</sup> For the reactions of arenesulfonyl chlorides with pyridine bases, Rogne<sup>10</sup> concluded that the amines function reveals as nucleophilic catalysts. But King *et al.*<sup>11</sup> observed a different kind in the reaction of 1-alkenyl arylsulfonyl chloride with pyridine. In this case the nucleophilic attacks the vinyllogous carbon to form the cationic sulfene which on subsequent reaction gives either the betylate or the simple overall substitution product.

Until it has been studied thoroughly for the nucleophilic substitution reaction of arenesulfonyl chloride with various bases, any conclusion is unjustified. One of the most interesting challenges for us is the design of reaction patterns that are catalytically controlled through noncovalent interactions in the reaction of arenesulfonyl chloride with *p*-substituted anilines. Control in a catalytic system should be limited by the relative rates of the catalyzed reaction such as in highly ionizing power solvent as HFP, and the uncatalyzed

**Table 1.** The Observed Pseudo-First Order Rate Constants ( $k_{obs} \times 10^4 \text{ sec}^{-1}$ ) and The Second Order Rate Constants ( $k_2 \times 10^3 \text{ l} \cdot \text{mol}^{-1} \cdot \text{sec}^{-1}$ ) of The Reactions of *p*-Methoxybenzenesulfonyl Chloride with *p*-Substituted Anilines in 1, 1, 1, 3, 3, 3-Hexafluoro-2-propanol and 2-Propanol Mixtures at 0°C

PrOH contents (v/v %)	Anilines Rate constants	<i>p</i> -CH <sub>3</sub>			<i>p</i> -H			<i>p</i> -Cl		
		[Nu] × 10 M			[Nu] × 10 M			[Nu] × 10 M		
		1.45	2.42	3.39	1.74	2.42	3.46	1.45	2.42	3.39
100	$k_{obs}$	42.5	50.4	58.3	31.2	34.8	40.3	12.5	15.5	18.6
	$k_2$		8.14			5.29			3.14	
99.873	$k_{obs}$	3.94	5.89	7.84	3.08	3.64	4.49	1.37	1.65	1.94
	$k_2$		2.01			0.817			0.294	
70	$k_{obs}$	3.20	4.58	5.87	2.15	2.58	3.28	1.09	1.36	1.61
	$k_2$		1.38			0.658			0.269	
50	$k_{obs}$	2.82	3.52	4.22	1.52	1.78	2.18	0.864	1.06	1.27
	$k_2$		0.721			0.383			0.209	
40	$k_{obs}$	1.76	2.20	2.73	0.950	1.13	1.43	0.719	0.892	1.08
	$k_2$		0.500			0.279			0.186	
30	$k_{obs}$	1.29	1.61	1.90	0.713	0.844	1.02	0.472	0.613	0.767
	$k_2$		0.314			0.179			0.152	

reaction such as in poor ionizing power solvent as 2-propanol (PrOH) or PDT.

We expect that the salt effect can be used to enhance the reactivity of substrates that are noncovalently attached to ionic host molecules while the reaction proceeds in the HFP and PrOH binary mixtures because it would be preferred that *p*-substituted anilines react with very acidic HFP molecules more than react with substrate molecules.

In order to facilitate evaluation of solvent effects in nucleophilic substitution reactions, we have begun to study protic solvent not ordinarily included in solvolytic studies. In the present article, we report studies of the nucleophilic substitution reaction for *p*-substituted benzenesulfonyl chlorides with *p*-substituted anilines in binary mixtures of two very different solvent—one a highly electrophilic but poorly nucleophilic solvent, HFP and the other a poorly electrophilic but comparative highly nucleophilic solvent, PrOH.

## Experimental

**Materials.** *p*-Substituted benzenesulfonyl chlorides, obtained commercially (Aldrich), were purified by repeated recrystallization or redistillation. *p*-Substituted anilines were purchased from Aldrich and purified. All nucleophiles and substrates were characterized, hence structures were verified by comparison of melting points, where appropriate, with literature values<sup>12</sup> and by characteristic IR and NMR spectra. HFP was obtained from Aldrich and was stored in the bottle of silicagel after dried over several times. PrOH was dried over 3A molecular sieves, purified by distillation, and stored in a desiccator.

**Kinetics.** Rates were determined conductimetrically as previously described<sup>13</sup> but using conductimetric cells with pressure seals of teflon to prevent solvent loss. Each kinetic sample contained about 5 ml of solvent *ca.*  $1 \times 10^{-1}$  M in nucleophile and *ca.*  $1 \times 10^{-3}$  M in substrate.

## Results and Discussion

Pseudo-first-order rate constants,  $k_{obs}$  and second order rate constants,  $k_2$  for the nucleophilic substitution reaction of *p*-substituted benzenesulfonyl chlorides with *p*-substituted anilines are summarized in Table 1-5.

The pseudo-first-order rate constants were linearly correlated with the concentration of the nucleophiles to obtain the second-order rate constants,

$$k_{obs} = k_2[\text{Nu}] \quad (1)$$

where [Nu] represents the concentration of *p*-substituted anilines. Good second order kinetics were observed ( $r \geq 0.9997$ ) in all cases.

At the very outset we hoped to study the reactions in pure HFP. However, rates for nucleophilic substitution reactions of the *p*-substituted benzene-sulfonyl chlorides with *p*-substituted anilines in pure HFP solvents could not be obtained by using our standard procedures. For example, conductivity in such solutions was found to be low and the reactions, monitored by GC/MS analysis, were also too slow. Assuming that the slow rates resulted from an interruption factor to accelerate the rates. HFP is known for its high electrophilicity and low nucleophilicity.<sup>14</sup>

The rate constants were increased with added PrOH, even though HFP had high ionizing power and low nucleophilicity. These data showed that the reactions may be inhibited by the solvent effect, which added PrOH into HFP solvent. The reactions must be expected that HFP molecules are reacted with the nucleophiles, *p*-substituted anilines and formed a kind of anilinium salt of hexafluoro-2-propionate before the nucleophile attacks to the substrate. The reaction were catalytically facilitated by the number of nucleophile's molecules were unrestricted form the salt formation.

McManus and his coworkers<sup>15</sup> have measured solvolytic rate constants for various alkyl tosylate and brosylates in

**Table 2.** The Observed Pseudo-First Order Rate Constants ( $k_{obs} \times 10^4 \text{ sec}^{-1}$ ) and The Second Order Rate Constants ( $k_2 \times 10^3 \text{ l} \cdot \text{mol}^{-1} \cdot \text{sec}^{-1}$ ) of The Reactions of *p*-Toluenesulfonyl Chloride with *p*-Substituted Anilines in 1, 1, 1, 3, 3, 3-Hexafluoro-2-propanol and 2-Propanol Mixtures at 0°C

PrOH contents (v/v %)	Anilines Rate constants	<i>p</i> -CH <sub>3</sub>			<i>p</i> -H			<i>p</i> -Cl		
		[Nu] × 10 M			[Nu] × 10 M			[Nu] × 10 M		
		1.45	2.42	3.39	1.74	2.42	3.46	1.45	2.42	3.39
100	$k_{obs}$	80.8	93.1	105	63.2	68.1	75.7	29.5	34.5	39.5
	$k_2$		12.5			7.27			5.15	
99.873	$k_{obs}$	7.22	10.2	13.2	5.00	6.11	7.81	2.49	3.19	3.89
	$k_2$		3.08			1.63			0.722	
70	$k_{obs}$	4.71	6.48	8.25	3.02	3.85	5.01	1.53	1.92	2.34
	$k_2$		1.82			1.15			0.417	
50	$k_{obs}$	2.87	3.86	5.01	1.80	2.50	3.18	0.910	1.14	1.42
	$k_2$		1.10			0.562			0.262	
40	$k_{obs}$	1.96	2.56	3.24	1.49	1.77	2.08	0.794	0.982	1.20
	$k_2$		0.659			0.339			0.211	
30	$k_{obs}$	1.58	2.00	2.43	0.974	1.14	1.38	0.542	0.697	0.872
	$k_2$		0.438			0.234			0.180	
20	$k_{obs}$	0.880	1.11	1.35	0.525	0.599	0.712	0.385	0.464	0.543
	$k_2$		0.242			0.109			0.0814	

**Table 3.** The Observed Pseudo-First Order Rate Constants ( $k_{obs} \times 10^4 \text{ sec}^{-1}$ ) and The Second Order Rate Constants ( $k_2 \times 10^3 \text{ l} \cdot \text{mol}^{-1} \cdot \text{sec}^{-1}$ ) of The Reactions of Benzenesulfonyl Chloride with *p*-Substituted Anilines in 1, 1, 1, 3, 3, 3-Hexafluoro-2-propanol and 2-Propanol Mixtures at 0°C

PrOH contents (v/v %)	Anilines Rate constants	<i>p</i> -CH <sub>3</sub>			<i>p</i> -H			<i>p</i> -Cl		
		[Nu] × 10 M			[Nu] × 10 M			[Nu] × 10 M		
		1.45	2.42	3.39	1.74	2.42	3.46	1.45	2.42	3.39
100	$k_{obs}$	—	—	—	121	156	210	20.4	27.5	34.6
	$k_2$	—	—	—		51.7			7.32	
99.873	$k_{obs}$	34.8	49.8	64.7	10.7	13.8	18.5	1.86	2.53	3.19
	$k_2$		15.4			4.53			0.686	
70	$k_{obs}$	12.8	21.1	29.4	4.94	6.17	8.00	1.40	1.76	2.20
	$k_2$		8.55			1.76			0.426	
50	$k_{obs}$	3.74	5.27	6.73	3.19	3.76	4.59	0.963	1.23	1.55
	$k_2$		1.45			0.812			0.304	
40	$k_{obs}$	2.02	2.72	3.46	1.630	1.93	2.35	0.800	0.994	1.26
	$k_2$		0.742			0.417			0.237	
30	$k_{obs}$	1.68	2.13	2.63	0.880	1.08	1.40	0.534	0.712	0.944
	$k_2$		0.489			0.309			0.211	
20	$k_{obs}$	0.957	1.20	1.45	0.512	0.637	0.828	0.363	0.505	0.641
	$k_2$		0.254			0.184			0.144	

HFP-PDT binary mixtures. They observed that the solvolytic rates in pure thiols are very low, but by mixing them with an electrophilic cosolvent like HFP, high reaction rates were obtained. These results are similar to these normally found for solvolysis in HFP-THF mixtures for limiting substrates.<sup>16</sup>

Unlike the solvolytic rates in HFP and its binary solvent mixtures for limiting substrates such as 2-adamantyl tosylate, the nucleophilic substitution reactions of arenesulfonyl chlorides with anilines were reversed over the entire range (Table 1-5). This may be attributed that the reactions would

be suppressed by increasing with the content of HFP in binary mixtures. These inhibitive action of HFP molecules may be caused to neutralize the effects of nucleophilic center and the rates may be inhibited by the salt effect.

The effects of the intramolecular salt that in reaction of 3-chlorobenzylamine with methyl propynoate in the presence of tetrabutylammonium tosylate were observed by Smith *et al.*<sup>17</sup> They reported that the reaction showed good overall second-order behavior, and the rate was shown to vary linearly with salt concentration.

**Table 4.** The Observed Pseudo-First Order Rate Constants ( $k_{obs} \times 10^4 \text{ sec}^{-1}$ ) and The Second Order Rate Constants ( $k_2 \times 10^3 \text{ l} \cdot \text{mol}^{-1} \cdot \text{sec}^{-1}$ ) of The Reactions of *p*-Chlorobenzensulfonyl Chloride with *p*-Substituted Anilines in 1, 1, 1, 3, 3, 3-Hexafluoro-2-propanol and 2-Propanol Mixtures at 0°C

PrOH contents (v/v %)	Anilines Rate constants	<i>p</i> -CH <sub>3</sub> [Nu] × 10 M			<i>p</i> -H [Nu] × 10 M			<i>p</i> -Cl [Nu] × 10 M		
		1.45	2.42	3.39	1.74	2.42	3.46	1.45	2.42	3.39
		100	$k_{obs}$	—	—	—	162	194	244	45.6
	$k_2$	—	—	—		47.7			12.5	
99.873	$k_{obs}$	19.1	32.8	46.6	12.8	15.4	19.5	3.78	4.66	5.53
	$k_2$		14.2			3.90			0.092	
70	$k_{obs}$	8.81	13.6	19.2	5.98	7.52	9.18	1.99	2.55	3.27
	$k_2$		5.36			1.86			0.660	
50	$k_{obs}$	4.40	6.42	8.61	3.32	4.08	5.36	1.02	1.36	1.76
	$k_2$		2.17			1.19			0.381	
40	$k_{obs}$	2.98	3.97	5.02	2.17	2.63	3.26	0.893	1.18	1.48
	$k_2$		1.05			0.631			0.304	
30	$k_{obs}$	2.03	2.76	3.49	1.72	2.04	2.53	0.573	0.781	1.03
	$k_2$		0.752			0.470			0.236	
20	$k_{obs}$	1.39	1.94	2.48	1.22	1.53	1.89	0.314	0.585	0.856
	$k_2$		0.562			0.386			0.279	

**Table 5.** The Observed Pseudo-First Order Rate Constants ( $k_{obs} \times 10^4 \text{ sec}^{-1}$ ) and The Second Order Rate Constants ( $k_2 \times 10^3 \text{ l} \cdot \text{mol}^{-1} \cdot \text{sec}^{-1}$ ) of The Reactions of *p*-Nitrobenzenesulfonyl Chloride with *p*-Substituted Anilines in 1, 1, 1, 3, 3, 3-Hexafluoro-2-propanol and 2-Propanol Mixtures at 0°C

PrOH contents (v/v %)	Anilines Constants	<i>p</i> -CH <sub>3</sub> Rate [Nu] × 10 M			<i>p</i> -H [Nu] × 10 M			<i>p</i> -Cl [Nu] × 10 M		
		1.45	2.42	3.39	1.74	2.42	3.46	1.45	2.42	3.39
		100	$k_{obs}$	—	—	—	184	224	284	65.3
	$k_2$	—	—	—		58.1			18.1	
99.873	$k_{obs}$	32.7	48.3	63.8	14.9	17.7	22.0	7.87	13.2	18.8
	$k_2$		16.0			4.13			5.63	
70	$k_{obs}$	16.3	22.4	28.5	8.61	10.6	13.7	4.17	7.69	10.6
	$k_2$		6.29			2.96			3.30	
50	$k_{obs}$	8.12	11.9	15.7	5.36	6.65	8.64	2.93	4.28	5.83
	$k_2$		3.91			1.91			1.49	
40	$k_{obs}$	4.79	7.88	11.5	3.97	4.93	6.41	1.03	1.56	2.08
	$k_2$		3.46			1.42			0.541	
30	$k_{obs}$	3.26	4.76	6.21	2.58	3.25	4.28	0.612	0.900	1.38
	$k_2$		1.52			0.988			0.396	
20	$k_{obs}$	1.91	2.54	3.18	1.23	1.92	2.19	0.102	0.365	0.611
	$k_2$		0.654			0.533			0.262	

To test the effectiveness of the salt in the reaction of arenesulfonyl chlorides with anilines the rate constants in the same concentration of HFP and *p*-substituted anilines, 0.242 M respectively were determined and showed in Table 1-5.

0.242 M of [HFP] corresponds with 99.873% (v/v) of PrOH. In comparison with 100% (v/v) and 99.873% (v/v) of PrOH there is significantly different in the rates from Table 1-5.

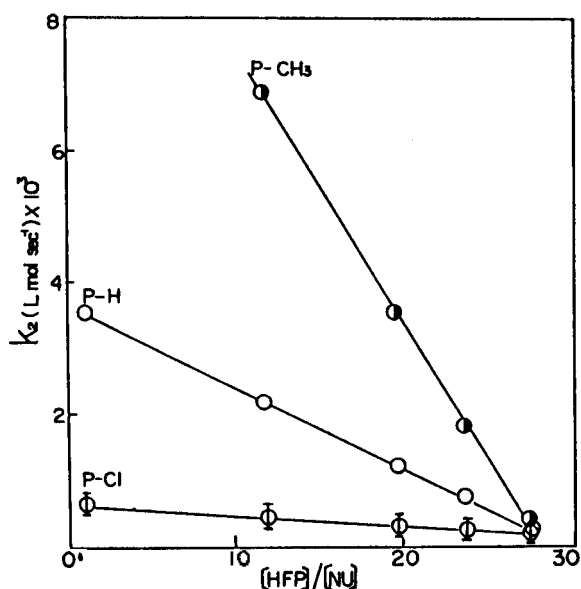
Below of the content 99.873% (v/v) of PrOH the reaction would be inhibited by the concentration of anilinium of hexa-

fluoro-2-propionate, then the second-order rate constant represents by the following equation.

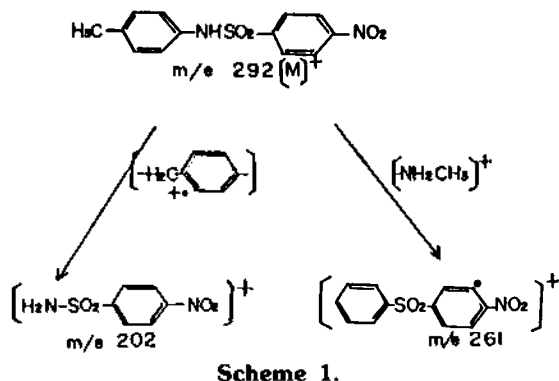
$$k_2 = k_2^0 - k'[\text{salt}] \quad (2)$$

where  $k_2^0$  is a rate constant which is not affected by salt effect,  $k'$  is a rate constant which is affected by ionic salt and [salt] is the concentration of anilinium of hexafluoro-2-propionate. If we assume a ratio of the concentration of HFP to anilines correlates with the concentration of salt,

$$a[\text{HFP}]/[\text{Nu}] = k'[\text{salt}] \quad (3)$$



**Figure 1.** The relative salt effect of anilinium hexafluoro-2-propionates upon the second-order rate constants of the reaction of benzenesulfonyl chloride with *p*-substituted anilines in HFP-PrOH mixtures.

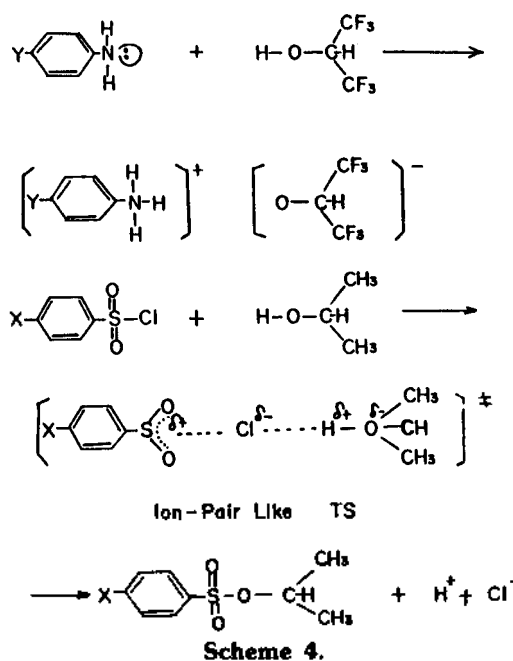
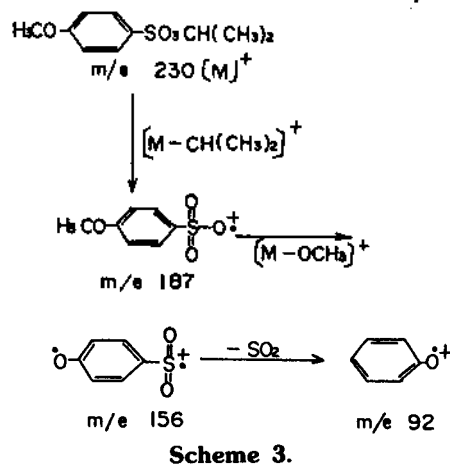
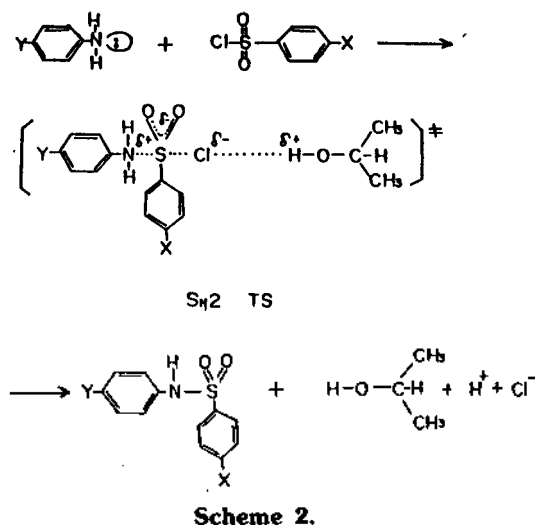


where  $[\text{Nu}]$  represents the concentration of anilines and  $a$  is constant. Hence, equation (2) becomes

$$k_2 = k_2^0 - a[\text{HFP}]/[\text{Nu}] \quad (4)$$

The relative salt effect on  $[\text{HFP}]/[\text{Nu}]$  in the rate of reaction of *p*-substituted benzenesulfonyl chlorides with *p*-substituted anilines are presented in Figure 1.

As shown Figure 1 the rate constant decreases with increasing the relative salt effect. On the other hand, above of the content 99.873% (v/v) of PrOH the reactions showed 10 times faster than the mixture of 0.242 M of  $[\text{HFP}]$  and  $[\text{Nu}]$  respectively in Table 1-5. The reaction mechanism in case of 100% PrOH would be certainly different from below of the content 99.873% (v/v) of PrOH. To be assured the mechanism GC/MS product analyses were carried out. The results were entirely consistent with solvent effect. In the reaction of *p*-toluidine with *p*-nitrobenzenesulfonyl chloride in 100% PrOH the product was found *p*-nitrophenyl sulfoanilide toluidine as shown Scheme 1. Therefore the reaction would be proceeded by a typical  $S_N2$  mechanism (Scheme 2). In contrast to the product was found *p*-methoxyphenyl 2-propyl sulfonate for the reaction of *p*-methoxybenzene-sul-



fonyl chloride with *p*-chloroaniline in below of the content of 99.873% (v/v) of PrOH as shown Scheme 3. It is predicted that the reaction should be controlled by the salt effect

**Table 6.** Hammett  $\rho_N$  Values for The Reactions of *p*-Substituted (X) Benzenesulfonyl Chlorides with *p*-Substituted (Y) Anilines in 1, 1, 1, 3, 3, 3-Hexafluoro-2-propanol and 2-Propanol Mixtures at 0°C

PrOH (v/v %)	X = $\phi$ -OCH <sub>3</sub>	$\phi$ -CH <sub>3</sub>	$\phi$ -H	$\phi$ -Cl	$\phi$ -NO <sub>2</sub>
100	-2.24	-2.36	-2.41	-2.52	-2.78
99.873	-1.79	-1.84	-1.87	-1.96	-2.64
70	-1.77	-1.80	-1.83	-1.94	-2.62
50	-1.34	-1.54	-1.78	-1.92	-2.53
40	-1.06	-1.23	-1.24	-1.35	-2.06
30	-0.772	-0.914	-0.923	-1.28	-1.48

**Table 7.** Brønsted  $\beta$  Values for The Reactions of *p*-Substituted (X) Benzenesulfonyl Chlorides with *p*-Substituted (Y) Anilines in 1, 1, 1, 3, 3, 3-Hexafluoro-2-propanol and 2-Propanol Mixtures at 0°C

PrOH (v/v %)	X = $\phi$ -OCH <sub>3</sub>	$\phi$ -CH <sub>3</sub>	$\phi$ -H	$\phi$ -Cl	$\phi$ -NO <sub>2</sub>
100	0.703	0.714	0.752	0.764	0.998
99.873	0.681	0.698	0.702	0.745	0.975
70	0.640	0.672	0.692	0.713	0.924
50	0.486	0.559	0.640	0.685	0.902
40	0.387	0.450	0.450	0.487	0.731
30	0.228	0.342	0.383	0.460	0.524

**Table 8.** Hammett  $\rho_S$  Values for The Reactions of *p*-Substituted (X) Benzenesulfonyl Chlorides with *p*-Substituted (Y) Anilines in 1, 1, 1, 3, 3, 3-Hexafluoro-2-propanol and 2-Propanol Mixtures at 0°C

PrOH (v/v) %	Y = $\phi$ -CH <sub>3</sub>	$\phi$ -H	$\phi$ -Cl
100	2.10	2.08	2.04
99.873	1.28	1.71	0.993
70	1.21	1.54	0.982
50	1.20	1.18	0.787
40	0.778	0.537	0.437
30	0.456	0.400	6.377

(Scheme 4).

The question still remains as to how contribute the substituent effect of the substrates and anilines to the reaction. The reactions of *p*-substituted benzenesulfonyl chlorides with the series of anilines show linear Hammett plots with negative slopes,  $\rho_N = -0.772 \sim -2.64$ , and good Brønsted relationships with  $\beta$  values of 0.288~0.975 in the below region of 99.873% (v/v) in HFP-PrOH mixtures as summarized in Table 6 and 7. The magnitude of  $\rho_N$  and  $\beta$  values are however considerably smaller than those for the reactions of *p*-substituted benzenesulfonyl chlorides with *p*-substituted anilines in methanol-acetonitrile mixtures.<sup>18</sup> This trend means the reactions in HFP-PrOH are affected by strong solvent effect more than the substituent effect. A similar

trend for Hammett  $\rho_S$  values in Table 8, for the reactions of the series of benzenesulfonyl chlorides with anilines showed 0.377~1.77 in the below region of 99.873% (v/v) in HFP-PrOH mixtures. But the  $\rho_S$  values in 100% (v/v) PrOH are shown significantly higher. This indicates that the N-S bond is formed weakly by the reaction of the nucleophiles with the more electron-withdrawing substituents in higher content of PrOH such as 100% (v/v).

This means that S atom is less negatively charged and the N-S bond must be longer in the transition state with the nucleophiles in 100% (v/v) PrOH as in case of ethanol-acetonitrile mixture.

According to the comparison with the inhibitive effect of the salt effect and the substituent effect, the reactions were predicted to be controlled by salt effect and the contribution of substituent effect to the reaction was shown relatively small in HFP-PrOH mixtures.

We conclude that the reaction of *p*-substituted benzenesulfonyl chlorides with *p*-substituted anilines proceeds to be controlled by the salt effect in the region of relatively high content of HFP in HFP-PrOH solvent mixtures.

## References

- (a) J. H. Marris, *Prog. Phys. Org. Chem.*, **11**, 89 (1974); (b) C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, 2nd, ed.,
- (a) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948); (b) F. L. Schadt, T. W. Bentley, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **98**, 7667 (1976); (c) M. H. Abraham, R. W. Taft, and M. J. Kamlet, *J. Org. Chem.*, **46**, 3053 (1981).
- (a) E. S. Lewis, S. Kukes, and C. D. Slater, *J. Am. Chem. Soc.*, **102**, 1619 (1980); (b) C. R. Wong, L. M. Jacksman, and R. G. Portman, *Tetrahedron Lett.*, 921 (1974); (c) C. D. Richie, C. Kubistz, and G. -Y. Ting, *J. Am. Chem. Soc.*, **105**, 279 (1983).
- (a) G. A. Dafforn and A. Streitwieser Jr., *Tetrahedron Lett.*, 3159 (1970); (b) B. Allard, A. Casadevall, E. Casadevall, and C. Largeau, *Nou. J. Chimie*, **3**(5), 335 (1978)
- (a) P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *J. Am. Chem. Soc.*, **92**, 2542 (1970); (b) J. L. Reich, A. Diaz, and S. Winstein, *J. Am. Chem. Soc.*, **91**, 5635 (1969); (c) D. J. Raber, J. M. Harris, R. E. Hall, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **93**, 4821 (1971).
- (a) F. L. Scott, *Chem. and Ind. (London)*, 224 (1959); (b) W. S. Trahanovsky, and M. P. Doyle, *Tetrahedron Lett.*, 2155 (1968); (c) D. J. Raber, M. D. Dukes, and J. Gregory, *Tetrahedron Lett.*, 667 (1974); (d) M. D. Bentley and J. A. Lacadie, *Tetrahedron Lett.*, 741 (1971).
- (a) M. A. Matesich, J. Knoefel, H. Feidman, and D. F. Evans, *J. Phys. Chem.*, **77**, 366 (1973); (b) D. F. Evans, J. A. Nadas, and M. A. Matesich, *J. Phys. Chem.*, **75**, 1708 (1971).
- S. P. McManus and A. Safavy, *J. Org. Chem.*, **51**, 3532 (1986).
- (a) R. V. Vizgert, *Russ. Chem. Rev. (Engl. Transl.)* **32**, 1 (1963); (b) J. L. Kice, *Adv. Phys. Org. Chem.*, **17**, 65 (1980).
- (a) O. Rogne, *J. Chem. Soc., B*, 727 (1970); (b) O. Rogne, *J. Chem. Soc., B*, 1334 (1971).

11. J. F. King and J. H. Hillhouse, *Can. J. Chem.*, **62**, 1977 (1984).
12. (a) R. Adams, C. S. Marvel, H. T. Clarke, C. R. Noller, J. B. Conant, and F. C. Whitmore, *Org. Syn. Coll.*, **1**, 84 John Wiley & Sons, New York (1941); (b) T. Curtius and G. Kraemer, *J. Prakt. Chem.*, **125**, 323 (1930); (c) *Beilsteins Handbuch der Organischen Chemie*, **11**, 55 (1972); (d) *Beilsteins Handbuch der Organischen Chemie*, **11**, 72 (1972); (e) A. I. Vogel, *Pract. Org. Chem. 3rd. Ed.*, Logmans, 564 (*Synth.*) (1959); (f) Cahours, *Ann.*, **74**, 298 (1850); (g) W. Windholz, ed., *The Merck Index* 690, Merck & Co., Rahway, N. J., U.S.A. (1983); (h) Sidgwick and Rubie, *J. Chem. Soc.*, **119**, 1013 (1921).
13. (a) I. Lee, H. W. Lee, T. S. Uhm, D. D. Sung, and Z. H. Ryu, *J. Korean Chem. Soc.*, **32**, 85 (1988); (b) I. Lee, D. D. Sung, T. S. Uhm, and Z. H. Ryu, *J. Chem. Soc. Perkin Trans. II*, 1697 (1989).
14. F. L. Schadt, P. v. R. Schleyer, and T. W. Bentley, *Tetrahedron Lett.*, 2335 (1974).
15. P. McManus and A. Safavy, *J. Org. Chem.*, **51**, 3532 (1986).
16. B. Allard, A. Casadevall, E. Casadevall, and C. Largeau, *Nouv. J. Chemie*, **3**, 335 (1979).
17. P. J. Smith and C. S. Wilcox, *J. Org. Chem.*, **55**, 5675 (1990).
18. I. Lee and I. S. Koo, *Tetrahedron Lett.*, **39**, 1803 (1983).

## Kinetic Studies on the Addition of Thiophenol to $\alpha$ , N-Diphenylnitron

Tae-Rin Kim\*, Kwang-Il Lee<sup>†</sup>, and Sang-Yong Pyun

Department of Chemistry, Korea University, Seoul 136-701

<sup>†</sup>Department of Chemistry, Kyong-Gi University, Suwon 440-760, Received January 23, 1991

The rate constants for the nucleophilic addition of thiophenol to  $\alpha$ , N-diphenylnitron and its derivatives (*p*-OCH<sub>3</sub>, *p*-Cl, *p*-NO<sub>2</sub>) were determined from pH 3.0 to 13.0 by UV spectrophotometry and rate equations which can be applied over a wide pH range were obtained. On the basis of rate equation, general base and substituent effect a plausible addition mechanism of thiophenol to  $\alpha$ , N-diphenylnitron was proposed: At high pH, the addition of sulfide ion to carbon-nitrogen double bond was rate controlling, however, in acidic solution, reaction was proceeded by the addition of thiophenol molecule to carbon-nitrogen double bond after protonation at oxygen of  $\alpha$ , N-diphenylnitron.

### Introduction

The nucleophilic addition of activated carbon-carbon and carbon-nitrogen double bond has been an important elementary process in organic chemistry.<sup>1-4</sup>

Nitron, having carbon-nitrogen double bond and oxygen attached to nitrogen atom is very reactive and a nucleophile such as Grignard reagent,<sup>5</sup> thiol<sup>6,7</sup> and HCN<sup>8-11</sup> easily react with nitron and used as intermediate in organic synthesis.<sup>12</sup>

In previous paper,<sup>13</sup> we described the hydrolysis mechanism of  $\alpha$ , N-diphenylnitron over a wide pH range. In the present paper, we discuss the kinetic behavior of thiophenol to nitron.

### Experimental

$\alpha$ , N-Diphenylnitron and its derivatives were prepared by condensation of N-phenylhydroxyamine and benzaldehyde.<sup>14</sup> All of the synthetic reagent used commercial grade without purification and the ionic strength of buffer solution was constant 0.1 M by adding sodium chloride. The absorbance of nitron and its derivatives were determined by Pye Unicam SP 500 UV spectrophotometer.

Kinetic runs were made in water at 25°C. Each nitron and thiophenol were introduced as 1 ml of  $2.0 \times 10^{-3}$  M methanolic solution in 100 ml aqueous buffer solution, which

was then analyzed spectrophotometrically at the absorption maxima of nitron.

### Results

The observed rate of reaction with excess thiophenol concentration were always of the pseudo-first order. Plots of the first-order rate constants against thiophenol concentration were also in all cases linear, showing the reaction are of the first order in nitron and thiophenol. Thus, the second-order rate constants simply can be calculated from the slope of the equal initial concentration ( $2.0 \times 10^{-7}$  M) of nitron and thiophenol against time (Figure 1). The second-order rate constants ( $k_2$ ) calculated from the slope at various pH are given Table 1 and Figure 2.

The relationship between acetate ion concentration and rate constant given by the point in Figure 3, was not catalyzed by general base.

As shown in Figure 4, the effect of substituent on the rate of addition was found to conform to the Hammett  $\sigma$ -constant with  $\rho$  is 0.77 at pH 4.0 and 1.25 at pH 10.0.

### Discussion

As shown in Figure 2, the rate of addition of thiophenol to  $\alpha$ , N-diphenylnitron is given by an expression of the