

Vibrations" (McGraw-Hill, New York, 1955).

(9) This Eq. (4) is just the matrix expression of the chain rule for partial differentiation:

$$\frac{\partial P}{\partial S_i} = \sum_j \left(\frac{\partial P}{\partial Q_j} \right) \left(\frac{\partial Q_j}{\partial S_i} \right).$$

(10) J. F. Biarge, J. Herranz, and J. Morcillo, *Ann. R. Soc. Espan. Fis. Quim. (Madrid)* **A57**, 81 (1961).

(11) W. B. Person and J. H. Newton, *J. Chem. Phys.* **61**, 1040 (1974).

(12) E. U. Condon and H. Odishaw, eds., "Handbook of Physics" (McGraw-Hill, New York, 1967).

(13) L. E. Sutton, Ed., "Interatomic Distances" (The Chemical Society, London, 1958).

(14) E. A. Cohen and R. L. Poynter, *J. Mol. Spectrosc.*, **53**, 131 (1974).

(15) J. L. Duncan and I. M. Mills, *Spectrochim. Acta*, **20**, 523 (1964).

(16) P. Pulay and W. Meyer, *J. Chem. Phys.*, **57**, 3337 (1972).

(17) W. M. A. Smit and T. van Dam, *J. Chem. Phys.*, **72**, 3658 (1980).

(18) W. J. Hehre, W. A. Latham, R. Ditchfield, M. D. Newton, and J. A. Pople, *Quantum Chem. Program Exchange, QCPE*, **10**, 236 (1974).

(19) R. E. Bruns, A. B. M. S. Bassi, and P. M. Kuznesof, *J. Am. Chem. Soc.*, **98**, 3432 (1976).

(20) J. H. Newton and W. B. Person, *J. Phys. Chem.*, **82**, 226 (1978).

(21) D. F. Hornig and D. C. McKean, *J. Phys. Chem.*, **59**, 1133 (1955).

(22) D. C. McKean and P. N. Schatz, *J. Chem. Phys.*, **24**, 316 (1956).

(23) K. Kim and W. T. King, *J. Chem. Phys.*, **71**, 1967 (1979).

(24) K. Kim and W. T. King, *J. Chem. Phys.*, **80**, 983 (1984).

(25) K. Kim, *J. Phys. Chem.*, **88**, 2394 (1984).

Nucleophilic Substitution Reaction of Dansyl Chloride with Substituted Anilines¹

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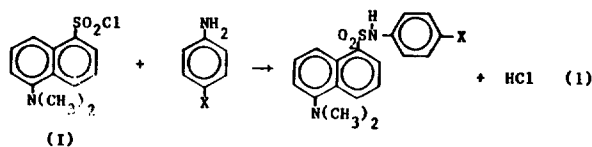
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Nucleophilic substitution reaction of dansyl chloride with anilines in various solvents have been investigated. The Brønsted β and Hammett ρ_N values indicated that the bond formation is advanced more than the bond breaking at the transition state. Solvatochromic correlations also predicted the importance of bond formation at the TS, showing a greater contribution of polarity (π^*) compared to hydrogen bond donor acidity (α). The effect of solvent on rate was found to violate the reactivity-selectivity principle.

The nucleophilic substitution at a sulfur atom has been a subject of long-standing interest for organic chemists. Studies on sulfonyl halides in particular have led to propose two types of mechanisms, S_N2^2 and S_N1^3 for this reaction, the former being preferred lately. 5-Dimethylaminonaphthalene-1-sulfonyl chloride (dansyl chloride) (I) is an important compound in determination of amino-terminal amino acid, since it can be advantageously used when only a small quantity of a polypeptide is available for analysis.⁴ In this type of reaction, NH_2 groups in a polypeptide displace chloride at the sulfur atom of dansyl chloride.

As an extension of our work on the nucleophilic substitution reaction at sulfur center,¹ we carried out kinetic studies

on the reaction of dansyl chloride with substituted anilines (1) in various solvents.



X = p-MeO, p-Me, H, p-Cl.

Experimental

Materials. Dansyl chloride and *para*-substituted anilines were obtained from Tokyo Kasei and used after purification by the

methods in the literature.⁵ Solvents, MeOH, 1-PrOH, 2-PrOH, 1-BuOH and MeCN, were purified by the known methods.⁶ Merck GR grade EtOH was used without further purification.

Kinetic Procedures. The rate was followed conductometrically. Other procedures and treatment of data to derive rate constants were similar to those reported, previously.^{2a} The reactions were carried out in a large excess of aniline and *pseudo*-first-order rate constants, were linearly correlated with aniline concentration, eq (2), to obtain second-order rate constant, k_2 . Good second-order kinetics were observed ($r > 0.999$) in all cases.

$$k_{\text{obs}} = k_2 [\text{aniline}] \quad (2)$$

Result and Discussion

Observed *pseudo*-first order rate constants, k_{obs} , and second order rate constants, k_2 , determined by eq. (2) are summarized in Table 1. The rate is seen to increase with the more electron donating substituent on the nucleophile, aniline, and with the increase in dielectric constants of protic solvents, alcohols. The rate in MeCN is smaller than those in MeOH and EtOH, but

TABLE 1: The Observed *Pseudo*-First Order Rate Constants ($k_{\text{obs}} \times 10^5 \text{ sec}^{-1}$) and the Second Order Rate Constants ($k_2 \times 10^4 \text{ l mol}^{-1} \text{ sec}^{-1}$) for the Reaction of Dansyl Chloride with *p*-Substituted Anilines in Various Solvent at 30.0°C.

Solvent	Rate constants	Aniline concentration ($\times 10^2 M$)	<i>p</i> -MeO	<i>p</i> -Me	<i>p</i> -H	<i>p</i> -Cl
MeOH	k_{obs}	1.92	338	101	55.6	6.36
		3.69	407	145	74.6	11.8
		5.34	476	188	92.2	17.3
		6.87	545	232	109	22.7
	k_2	418	264	107	33.0	
		1.92	175	60.0	12.3	4.36
		3.69	203	75.8	19.2	6.18
		5.34	230	91.6	25.3	8.00
EtOH	k_{obs}	6.87	258	107	31.0	9.82
		167	95.8	37.7	11.0	
		1.92	115	40.9	10.0	3.72
		3.69	119	43.7	11.3	4.32
	k_2	5.34	123	46.5	12.8	4.93
		6.87	127	49.3	14.3	5.52
		24.2	16.9	8.71	3.64	
		1.92	101	27.2	6.76	2.24
1-PrOH	k_{obs}	3.69	103	28.6	7.55	2.64
		5.34	105	30.0	8.45	3.05
		6.87	107	31.3	9.40	3.45
		12.1	8.30	5.33	2.45	
	k_2	1.92	107	29.5	8.20	2.75
		3.69	108	30.3	8.67	3.04
		5.34	109	31.0	9.22	3.33
		6.87	110	31.8	9.71	3.62
2-PrOH	k_{obs}	6.05	4.60	3.07	1.76	
		1.92	162	41.8	7.42	2.24
		3.69	170	46.7	9.20	3.02
		5.34	177	51.6	11.8	3.80
	k_2	6.87	185	56.5	14.1	4.58
		46.0	29.7	13.7	4.72	
		1.92	162	41.8	7.42	2.24
		3.69	170	46.7	9.20	3.02
1-BuOH	k_{obs}	5.34	177	51.6	11.8	3.80
		6.87	185	56.5	14.1	4.58
		1.92	162	41.8	7.42	2.24
		3.69	170	46.7	9.20	3.02
	k_2	5.34	177	51.6	11.8	3.80
		6.87	185	56.5	14.1	4.58
		1.92	162	41.8	7.42	2.24
		3.69	170	46.7	9.20	3.02
MeCN	k_{obs}	5.34	177	51.6	11.8	3.80
		6.87	185	56.5	14.1	4.58
		1.92	162	41.8	7.42	2.24
		3.69	170	46.7	9.20	3.02
	k_2	5.34	177	51.6	11.8	3.80
		6.87	185	56.5	14.1	4.58
		1.92	162	41.8	7.42	2.24
		3.69	170	46.7	9.20	3.02

is greater than those in other alcohols. This rate order of MeCN is in contrast with that for the reaction of benzenesulfonyl chloride (BSC) with aniline; the rate was smaller in MeCN than in all the other solvents studies in this work for the BSC reaction.⁷ The enhancement of rate in MeCN for dansyl chloride may be due to the formation of a bulky TS in the more polar (greater π^* values, *vide infra*) solvent; dansyl chloride is bulkier than BSC and MeCN has the greatest polarity scale as shown in Table 2. Relative contribution of polarity effect on the TS structure may be assessed by the ratio a/s of solvatochromic equation (3).

$$\log(k/k_0) = a\alpha + s\pi^* + B \quad (3)$$

where a and s are susceptibilities of rates to hydrogen bond donor (HBD) acidity (α) and polarity (π^*) of solvent, and B is a constant. The solvatochromic parameters, a and s , with a/s values are shown in Table 3. The correlation coefficients (r) determined by multiple regression analysis are seen to be satisfactory in all cases. Relatively small values of a/s is an indication that the effect of polarity (π^*) is more important than that of the HBD acidity of solvents. Furthermore according to our experience regarding solvent effects on transition state structure, the effect of polarity is reflected on the degree of bond formation at the TS of an S_N2 reaction; the dominant effect of polarity (π^*) is thus an indication that bond formation precedes bond cleavage.

Hammett ρ_N values obtained from the plots of $\log k_2$ vs σ for substituents on aniline are summarized in Table 4 together with β values determined from extended Brønsted treatments. The negative sign of ρ_N indicates that at the TS the N atom is positively charged as a result of charge transfer to dansyl chloride. Magnitudes of ρ_N and β in MeOH are comparable to those for the reaction of benzenesulfonyl chloride with anilines in MeOH^{2c}, -2.15 and 0.75 , respectively. These values indicate clearly that the bond formation is more advanced than the bond breaking at the TS. The magnitudes of $|\rho_N|$ and β are however

TABLE 2: Some Solvent Parameters

	Dielectric constants ϵ (25°C)	α	π^*
MeOH	32.6	0.98	0.60
EtOH	24.3	0.86	0.54
1-PrOH	20.1	0.80	0.51
2-PrOH	18.3	0.78	0.46
1-BuOH	17.1	0.79	0.46
MeCN	36.2	0.15	0.85

TABLE 3: Solvatochromic Correlations for the Reaction of Dansyl Chloride with X-Anilines at 30.0°C

	X = <i>p</i> -MeO	<i>p</i> -Me	H	<i>p</i> -Cl
a	3.60	3.49	3.06	2.62
s	7.55	7.30	6.28	5.16
a/s	0.48	0.48	0.49	0.51
r^\dagger	0.958	0.965	0.971	0.986

[†]Correlation coefficients.

TABLE 4: Hammett ρ_N and Brønsted β Values for the Reaction of Dansyl Chloride with Anilines at 30.0°C

	ρ_N	β
MeOH	-2.22	0.80
EtOH	-2.36	0.85
1-PrOH	-1.65	0.60
2-PrOH	-1.36	0.49
1-BuOH	-1.11	0.40
MeCN	-1.98	0.72

Correlation coefficients: $r > 0.998$.

considerably smaller than those for the reactions of 1- and 2-naphthalenesulfonyl chloride with anilines in acetone. ($\rho_N = -4.2$ and -4.6 , $\beta = 1.6$ and 1.8 respectively). Substitution of a dimethylamino group at the carbon 5 seems to reduce positive charge on the sulfur atom so that the degree of bond formation is decreased substantially compared with that for naphthalenesulfonyl chlorides. The size of both $|\rho_N|$ and β in various solvents decrease in the order EtOH > MeOH > MeCN > 1-PrOH > 2-PrOH > 1-BuOH. It is noteworthy that the $|\rho_N|$ and β values in MeCN are smaller than those in EtOH and MeOH while they are greater than those in other alcohols. Reference to Table 3 reveals that MeCN has the greatest values of ϵ and π^* but the smallest values of α among the solvent studied; polarity of solvent is not a sole factor in determining the TS, but HBD acidity (α) also contribute to the TS formation. This is clear from the relative importance of the two solvatochromic parameters, α and π^* , shown in Table 3.

According to the reactivity-selectivity principle (RSP)⁸, the greater the rate the less is the selectivity. Inspection of Tables 1 and 4 reveals that the RSP is not adhered in the present work, since a solvent of greater reactivity has also a greater selectivity (β and $|\rho_N|$).

We conclude that the reaction of dansyl chloride with anilines proceeds via an associative S_N2 mechanism, having somewhat similar TS structure with that of the benzenesulfonyl chloride reaction.

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Reference

- (1) Part 19 of the series "Nucleophilic Displacement at Sulfur Center". For part 18, see I. Lee and I. S. Koo, *Tetrahedron*, **39**, 1803 (1983).
- (2) (a) M. L. Tonnet and A. N. Hambly, *Aust. J. Chem.*, **24**, 703 (1971); (b) R. Foon and A. N. Hambly, *Ibid.*, **24**, 713 (1971); (c) I. Lee and I. S. Koo, *J. Korean Chem. Soc.*, **25**, 7 (1981); (d) I. Lee and I. S. Koo, *Bull. Korean Chem. Soc.*, **2**, 41 (1981); O. Rogne, *J. Chem. Soc. (P)*, 1294 (1968), *Ibid.*, 663 (1969), *Ibid.*, 1855 (1971), *Ibid.*, *Perkin* **2**, 472 (1972); (e) I. Lee and I. S. Koo, *Tetrahedron*, **39**, 1803 (1983).
- (3) (a) L. M. Litvinenko, A. F. Popov, and V. A. Savelova, *Ukr. Khim. Zr.*, **33**, 57 (1967); (b) L. M. Litvinenko, N. T. Maleeva, V. A. Savelova, and T. D. Kovach, *Zh. Obshch. Khim.*, **41**, 2615 (1971); (c) E. Ciuffarine, L. Senatore and, M. Isola, *J. Chem. Soc. Perkin* **2**, 468 (1972); (d) L. J. Stangeland, L. Senatore and E. Ciuffarin, *Ibid.*, 852 (1972); (e) A. Arcoria, E. Maccarone, G. Musumarra, and C. A. Tomaselli, *J. Org. Chem.*, **24**, 3595 (1974); (f) A. Arcoria, P. P. Ballistreri, G. Musumarra, and G. A. Tomaselli, *J. Chem. Soc. Perkin* **2**, 221 (1981).
- (4) F. B. Armstrong, "Biochemistry," 2nd Ed., p. 91. Oxford University Press, New York, 1983.
- (5) (a) K. Massie, *J. Org. Chem.*, **22**, 333 (1957); (b) H. F. Smith, *Amer. Ind. Hyg. Assoc. J.*, **23**, 95 (1962); (c) B. I. Ardashov, *J. Gen. Chem. (U.S.S.R)*, **21**, 1503 (1951); R. Weidenhagen and G. Train, *Ber.*, **75**, 1936 (1942).
- (6) (a) E. C. Evers and A. G. Knox, *J. Amer. Chem. Soc.*, **73**, 1739 (1951); (b) A. W. Stout and H. A. Schuette, *Ind. Eng. Chem. Anal., Ed.* **5**, 100 (1933); (c) R. J. Ozol and C. R. Materson, U. S. Pat. 2356689, Aug. 22, 1944 (Chem. Abs., **39**, 86 (1945)); (d) J. Clarke, R. Robinson, and J. C. Smith, *J. Chem. Soc.*, 2647 (1927); (e) J. Timmermans and Gillo, *Roetz. Chem.*, **18**, 812 (1938).
- (7) I. Lee, I. S. Koo, B. D. Chang, and D. H. Kang, *Bull. Inst. Basic Sci. Inha Uni.* **6**, in press.
- (8) See for example, (a) A. Pross, *Adv. Phys. Org. Chem.*, **14**, 69 (1977); (b) C. D. Johnson, *Chem. Rev.*, **75**, 755 (1975); (c) D. J. McLennan, *Tetrahedron*, **34**, 2331 (1978); (d) C. D. Ritchie, *Acc. Chem. Res.*, **5**, 348 (1972).

Fluorescence of Styrene and Acrylic Acid Copolymers Containing Eu^{3+} in Tetrahydrofuran Solution

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The fluorescence emission of polystyrene-acrylic acid copolymers containing Eu^{3+} in tetrahydrofuran solution was investigated by spectrofluorimetry. The excimer emission increased linearly with the polymer concentration up to approximately $5 \times 10^{-3}\text{M}$. Benzene and toluene collisionally quenched the excimer fluorescence and their rate constants of quenching were determined. Quenching efficiencies decreased in the order: naphthalene > toluene > benzene. Analyses of Rayleigh scattering and europium emission showed no measurable structural changes observed under the experimental conditions.