*Disulfonyl Transfer*

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# Reaction Intermediate of Organic Sulfur Compound
# II. Nucleophilic Substitution Reaction of Disulfonyl Chloride Compounds

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The nucleophilic substitution reactions of naphthalene-1,5-disulfonyl chloride and 4-fluorosulfonylbenzenesulfonyl chloride with *p*-substituted anilines and methyl substituted pyridines in methanol-acetonitrile mixtures and hydrolyses of those disulfonyl halides have been studied by means of conductometric and polarographic methods. A large difference in the selective parameter, $\rho_N$ between mono-sulfonyl chloride and disulfonyl halide can be taken as an evidence that the second $SO_2Cl$ group of naphthalene-1,5-disulfonyl chloride also takes part in the reaction in contrast to sulfonyl fluoride in 4-fluorosulfonylbenzenesulfonyl chloride, which only acts as a substituent in the nucleophilic substitution reaction.

## Introduction

The hydrolysis of sulfonyl chlorides[1] and the nucleophilic substitution reactions at a sulfonyl sulfur atom[2] have been studied on the basis of the sulfonyl transfer to nucleophiles extensively. Many of these reactions are essentially similar to attack at carbonyl halides[3], though sulfonyl chlorides are not as active as chlorides of carboxylic acids. Though many papers have been reported, less work has been done on these reactions than on those at an acyl carbon. The mechanism of the reaction of sulfonyl chlorides are not identical; for example, there is a contention[4] that the nucleophilic substitution to occur at tetracoordinate sulfur such as sulfonyl chloride proceeds through the concerted one-step $S_N2$ mechanism[2] or the route of addition-elimination ($S_AN$) mechanism *via* the pentacoordinate intermediate.[4]

It has been found that monosulfonyl chlorides hydrolyze according to the $S_N2$ mechanism, which involves a trigonal pyramidal transition state[5]. These papers have shown that at a constant concentration of the nucleophile, the reaction can be described by the pseudo-first-order rate constants for the solvolytic and nucleophilic substitution reactions of monosulfonyl chlorides.

The solvolytic and nucleophilic substitution reactions of bifunctional sulfonyl halides have been studied by Vizgert[6] and Sanecki *et al.*[7] In benzenedisulfonyl chlorides hydrolyses studied by a continuous polarographic method, the second step in the consecutive reactions, $-SO_2Cl$ and $-SO_3H$ groups influence the reactivity of the second group $-SO_2Cl$.[7]

Despite more detailed study of bifunctional sulfonyl chloride, there has not been, as far as we are aware, any kinetic observation of disulfonyl chloride of naphthalene ring and a little different bifunctional halides such as, $-SO_2Cl$ and $-SO_2F$ in the benzene ring.

In this paper we have determined the rate constants of the nucleophilic substitution reaction of naphthalene-1,5-disulfonyl chloride and 4-fluorosulfonylbenzenesulfonyl chloride and discussed possible changes of solvent effect according to a change of nucleophiles.

## Experimental

**Material.** Naphthalene-1,5-disulfonyl chloride (NDC) was synthesized and purified by classical method.[8] m.p. 181 °C (lit., 181-183 °C), IR(KBr) $cm^{-1}$: 3120, 1500, 1370, 1237, 1208, 1180, 1145, 1070, 800, 765, 645, 575, 550, 495; $^1$H-NMR (TMS, $C_6D_6$): 7.8-8.0 (s, 2H), 7.2-7.3 (s, 2H), 6.4-6.6 (m, 2H); $m/z$ Calculated for $C_{10}H_6S_2O_4Cl_2$: 325.18; Found 323.95 (relative abundance, 6.60) $m/z$ 126 [$(M-S_2O_4Cl_2)$]$^+$ (100) $m/z$ 225 [$(M-SO_2Cl)$]$^+$ (56). 4-Fluorosulfonylbenzenesulfonyl chloride (FBC) was purchased from Aldrich and used after identification of the physical constants $p$-Chloroaniline ($p$-Cl), $p$-nitroaniline ($p$-NO_2) and aniline ($p$-H) were commercial samples, which were used after purification as previously described.[9] Pyridine (py-H), $\alpha$-picoline (2-Me-py), $\beta$-picoline (3-Me-py), and $\gamma$-picoline (4-Me-py) were obtained from Tokyo Kasei and used after purification as the method of Ralph,[10] Kyte,[11] Coulson[12] and Krupicka[13] *et al.*, respectively. Acetic acid (HOAc) and sodium acetate (NaOAc) were obtained from Aldrich as the grade of A.C.S. reagent, Gold Label and were used without further purification. Solvents, methanol (MeOH) and acetonitrile (MeCN) were purified as described in the previous work.[14]

**Kinetic Methods.** The general kinetic method by means of conductometer has been described previously.[14] The $k_{obs}$ values were obtained by the Guggenheim equation.[15] The polarographic method enables us to observe the instantaneous concentration of the sulfonyl halides.

The rate of hydrolysis in HOAc containing water in the presence of NaOAc was determined by a polarographic method according to Sanecki's. The Polarograms were recorded with a EG & G Princeton Applied Research (PAR) Model 174A polarograph. A three electrode system using a PAR Model 174A was employed for all polarogram measurement. The cell was connected to an external reference electrode in the saturated aqueous acetate electrode by a reservoir filled with same solution as that used for dissolving the substrates. The solution of sulfonyl halides in HOAc were degassed and introduced into degassed solution of the other components in the polarographic cell and stirred with a stream of nitrogen gas at 25 ± 0.05 °C for 4 seconds.

Then, the polarographic circuit was closed and current intensity as a function of time was recorded. The concentration of substrates were always 3.50 × 10$^{-3}$M. The rates of hydrolysis by the polarogram were calculated from the Sanecki's equation[7],

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**Table 1.** The Observed Pseudo-First-Order Rate Constants ($k_{obs} \times 10^4 sec^{-1}$) and the Second-Order Rate Constants ($k_2 \times 10^3 L.mol^{-1}.sec^{-1}$) of the Reaction of 4-Fluorosulfonylbenzenesulfonyl Chloride with p-Substituted Anilines in MeOH-MeCN Binary Solvent Mixtures at -15 °C

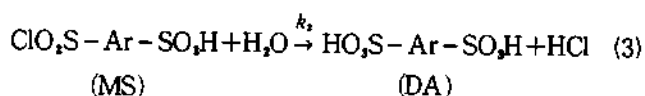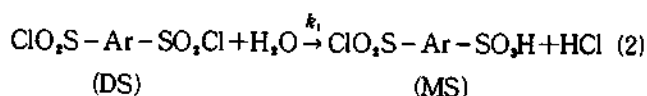| MeOH Content (v/v%) | Rate Constant | p-H [Nu]×10²M | | | | p-Cl [Nu]×10⁻²M | | | | p-NO₂ [Nu]×10²M | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 4.42 | 6.49 | 8.47 | 12.2 | 4.42 | 8.47 | 12.2 | 13.0 | 16.6 | 19.9 | 23.0 | 25.8 |
| 100 | $k_{obs}$ | 20.4 | 27.8 | 33.6 | — | 4.00 | 7.77 | 10.6 | 0.279 | — | 0.391 | 0.439 | — |
| | $k_2$ | | 32.6(r = 0.998) | | | | 8.50(r = 0.998) | | | | 0.160(r = 0.999) | | |
| 90 | $k_{obs}$ | 20.3 | 27.7 | 34.2 | — | 4.19 | 7.99 | 11.7 | 0.348 | 0.415 | — | 0.521 | — |
| | $k_2$ | | 34.3(r = 0.999) | | | | 9.65(r = 0.999) | | | | 0.172(r = 0.999) | | |
| 80 | $k_{obs}$ | 19.2 | 25.1 | 30.2 | 43.2 | 4.10 | 7.67 | 11.0 | 0.333 | — | 0.444 | — | 0.549 |
| | $k_2$ | | 30.8(r = 0.999) | | | | 8.87(r = 0.999) | | | | 0.169(r = 0.999) | | |
| 70 | $k_{obs}$ | 18.4 | 23.4 | — | 41.3 | 3.72 | 6.74 | 9.47 | 0.320 | — | 0.429 | — | 0.522 |
| | $k_2$ | | 29.8(r = 0.999) | | | | 7.39(r = 0.999) | | | | 0.158(r = 0.999) | | |
| 50 | $k_{obs}$ | 14.4 | — | 26.4 | 36.2 | 3.02 | 5.92 | 8.54 | 0.287 | — | 0.374 | — | 0.457 |
| | $k_2$ | | 28.0(r = 0.999) | | | | 7.20(r = 0.999) | | | | 0.153(r = 0.999) | | |
| 30 | $k_{obs}$ | 9.18 | 14.6 | 19.9 | — | 2.37 | 4.09 | 5.98 | — | — | — | — | — |
| | $k_2$ | | 26.5(r = 0.999) | | | | 4.63(r = 0.999) | | | | | | |

**Table 2.** The Observed Pseudo-First-Order Rate Constants ($k_{obs} \times 10^4 sec^{-1}$) and the Second-Order Rate Constants ($k_2 \times 10^2 L.mol^{-1}.sec^{-1}$) of the Reaction of 4-Fluorosulfonylbenzenesulfonyl Chloride with p-Substituted Pyridines in MeOH-MeCN Binary Solvent Mixtures at 0 °C

| MeOH Content (v/v%) | Rate Constant | Py-H [Nu]×10²M | | | 2-Me-py [Nu]×10²M | | | 3-Me-py [Nu]×10²M | | | 4-Me-py [Nu]×10²M | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 2.43 | 4.74 | 6.94 | 13.5 | 19.9 | 25.8 | 2.43 | 4.74 | 6.94 | 2.43 | 4.74 | 6.94 |
| 100 | $k_{obs}$ | 9.28 | 17.9 | 29.9 | — | — | — | 17.7 | 41.3 | 55.7 | 31.8 | 63.8 | 94.3 |
| | $k_2$ | | 4.58 | | | — | | | 8.44 | | | 13.8 | |
| 90 | $k_{obs}$ | 15.6 | 25.0 | 40.1 | 1.23 | 1.95 | 2.44 | 28.9 | 62.0 | 84.9 | 18.9 | 99.3 | 148 |
| | $k_2$ | | 5.41 | | | 0.0985 | | | 12.4 | | | 22.1 | |
| 80 | $k_{obs}$ | 22.9 | 37.8 | 52.2 | 1.51 | 2.34 | 2.81 | 35.2 | 85.4 | 22.9 | 64.7 | 144.3 | 189 |
| | $k_2$ | | 6.50 | | | 0.106 | | | 17.6 | | | 27.8 | |
| 70 | $k_{obs}$ | 26.1 | 41.8 | 79.6 | 2.03 | 2.83 | 3.79 | 61.2 | 107 | 162 | 85.3 | 182 | 252 |
| | $k_2$ | | 11.8 | | | 0.140 | | | 22.4 | | | 37.1 | |
| 60 | $k_{obs}$ | 31.1 | 56.2 | 92.1 | 2.56 | 3.42 | 4.61 | — | — | — | — | — | — |
| | $k_2$ | | 13.5 | | | 0.166 | | | — | | | — | |
| 50 | $k_{obs}$ | 41.7 | 78.1 | 113 | 3.12 | 4.16 | 5.35 | — | — | — | — | — | — |
| | $k_2$ | | 15.9 | | | 0.181 | | | — | | | — | |
| 40 | $k_{obs}$ | 54.3 | 92.6 | 131 | 3.58 | 4.69 | 5.89 | — | — | — | — | — | — |
| | $k_2$ | | 17.1 | | | 0.187 | | | — | | | — | |
| 30 | $k_{obs}$ | 62.9 | 117 | 127 | 4.02 | 5.16 | 6.38 | — | — | — | — | — | — |
| | $k_2$ | | 21.0 | | | 0.191 | | | — | | | — | |

$$i_1/i_{so} = \exp(-k_1 t) + \frac{\exp(-k_1 t) - \exp(-k_2 t)}{2(k_2/k_1)} \quad (1)$$

where $i_1$ was the limiting current measured at a given moment in the sum of limiting current of both forms of disulfonyl chlorides (DS) and monosulfonyl chloride (MS),

$$ClO_2S-Ar-SO_2Cl + H_2O \xrightarrow{k_1} ClO_2S-Ar-SO_3H + HCl \quad (2)$$
$$\text{(DS)} \qquad\qquad\qquad\qquad \text{(MS)}$$

$$ClO_2S-Ar-SO_3H + H_2O \xrightarrow{k_2} HO_3S-Ar-SO_3H + HCl \quad (3)$$
$$\text{(MS)} \qquad\qquad\qquad\qquad \text{(DA)}$$

and $i_{1,0}$ was the value, which was directly proportional to the initial concentration of DS in Ilkovic's equation[16].

## Results and Discussion

In MeOH-MeCN binary solvent, the reactions of NDC and FBC with the nucleophiles (p-substituted anilines and pyridines: Nu) were carried out at the pseudo-first-order condition with respect to the substrate. The pseudo-first-order rate constants ($k_{obs}$) were linearly correlated with the concentration of the nucleophiles, eq. (4), to obtain the second-order rate constants, $k_2$.

$$k_{obs} = k_2 [Nu] \quad (4)$$

Good second order kinetics were observed ($r > 0.9997$) in all cases. The observed pseudo-first-order rate constants ($k_{obs}$) and second-order rate constants are summarized in Tables 1,2 and 3.

**Effect of the Substituent of Nucleophile.** The reac-

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**Table 3.** The Observed Pseudo-First-Order Rate Constants ($k_{obs} \times 10^4 sec^{-1}$) and the Second-Order Rate Constants ($k_2 \times 10^2 L.mol^{-1}.sec^{-1}$) of the Reaction of Naphthalene-1,5-disulfonyl Chloride with $p$-Substituted Anilines in MeOH-MeCN at -15 °C

| MeOH Content (v/v%) | Rate Constant | $p$-CH$_3$ [Nu] × 10$^2$M | | | $p$-H [Nu] × 10$^2$M | | | $p$-Cl [Nu] × 10$^2$M | | | $p$-NO$_2$ [Nu] × 10$^2$M | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 2.43 | 4.74 | 6.94 | 2.43 | 4.74 | 6.94 | 9.05 | 13.0 | 16.6 | 9.05 | 13.0 | 16.6 |
| 100 | $k_{obs}$ | 22.0 | 40.9 | 52.9 | 6.27 | 6.74 | 7.19 | 4.04 | 5.14 | 6.15 | — | — | — |
| | $k_2$ | | 6.86 | | | 2.02 | | | 0.279 | | | | |
| 90 | $k_{obs}$ | 23.2 | 43.1 | 61.8 | 7.36 | 7.93 | 8.48 | 5.37 | 7.27 | 9.02 | 0.256 | 0.341 | 0.418 |
| | $k_2$ | | 8.54 | | | 2.48 | | | 0.483 | | | 0.0214 | |
| 80 | $k_{obs}$ | 24.0 | 45.3 | 63.1 | 7.56 | 8.22 | 8.85 | 6.25 | 7.69 | 11.5 | 0.317 | 0.416 | 0.507 |
| | $k_2$ | | 8.64 | | | 2.87 | | | 0.685 | | | 0.0252 | |
| 70 | $k_{obs}$ | 24.5 | 47.8 | 64.6 | 9.63 | 10.4 | 11.1 | 5.12 | 8.29 | 11.2 | 0.402 | 0.551 | 0.689 |
| | $k_2$ | | 8.89 | | | 3.24 | | | 0.805 | | | 0.0338 | |
| 60 | $k_{obs}$ | 24.6 | 46.6 | 63.3 | 8.54 | 9.27 | 9.96 | 6.48 | 8.22 | 12.3 | 0.411 | 0.516 | 0.612 |
| | $k_2$ | | 8.87 | | | 3.15 | | | 0.770 | | | 0.0266 | |
| 50 | $k_{obs}$ | 22.5 | 43.4 | 59.6 | 7.28 | 7.81 | 8.32 | 4.88 | 6.18 | 7.88 | — | — | — |
| | $k_2$ | | 8.22 | | | 2.30 | | | 0.436 | | | — | |

**Table 4.** Hammett $\rho_N$ Values and Brönsted $\beta$ Values for the Reaction of 4-Fluorosulfonylbenzenesulfonyl Chloride with $p$-Substituted Anilines and Pyridines in MeOH-MeCN Binary Solvent Mixtures at -15 °C

| MeOH Content (v/v%) | $\rho_N$ | | $\beta$ | |
|---|---|---|---|---|
| | Anilines | Pyridines | Anilines | Pyridines |
| 100 | -3.30 | -2.77 | 1.11 | 0.504 |
| 90 | -3.29 | -3.52 | 1.11 | 0.643 |
| 80 | -3.24 | -3.59 | 1.09 | 0.663 |
| 70 | -3.25 | -2.89 | 1.09 | 0.523 |
| 50 | -3.17 | — | 1.07 | — |

($r$>0.995)

**Table 5.** Hammett $\rho_N$ Values and Brönsted $\beta$ Values for the Reaction of Naphthalene-1,5-Disulfonyl Chloride with $p$-Substituted Anilines in MeOH-MeCN Binary Solvent Mixtures at -15 °C

| MeOH Content (v/v%) | $\rho_N$ | $\beta$ |
|---|---|---|
| 100 | -3.94 | 1.50 |
| 90 | -2.71 | 0.588 |
| 80 | -2.66 | 0.581 |
| 70 | -2.55 | 0.557 |
| 60 | -2.66 | 0.583 |
| 50 | -3.19 | 1.37 |

($r$>0.931)

tion of FBC and NDC with the series of anilines and pyridines show linear Hammett plots with large negative slopes, $\rho_N = -2.55 \sim -3.49$ and good Brönsted relationships with $\beta$ values of $0.5 \sim 1.5$ in various MeOH-MeCN mixtures as shown in Tables 4 and 5. These values indicate that at the transition state the $N$ atom becomes more positive relative to the ground state and bond formation is more advanced than the bond breaking.
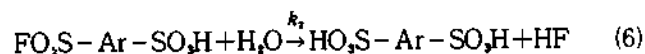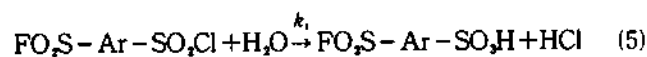
One observed here a large difference in the character of

**Table 6.** Pseudo-First-Order Rate Constants of Consecutive Hydrolysis ($k_1$ and $k_2 \times 10^{-5} sec^{-1}$) of Naphthalene-1,5-Disulfonyl Chloride and 4-Fluorosulfonylbenzenesulfonyl Chloride at 25 °C

| Substrate | $k_1 \times 10^5$ (sec$^{-1}$) | $k_2 \times 10^5$ (sec$^{-1}$) | $Q = k_2/k_1$ |
|---|---|---|---|
| NDC | 26.3 | 3.07 | $1.17 \times 10^{-1}$ |
| FBC | 12.4 | 0.00706 | $5.69 \times 10^{-4}$ |

these selective parameters between monosulfonyl chloride and disulfonyl halide. The $\rho_N$ values of the reaction of monosulfonyl chloride (benzenesulfonyl chloride) with anilines in MeOH-MeCN mixtures have been reported as $-2.0 \sim -2.9$[17] and these are considerably smaller than the values of $-3.2 \sim -3.3$ for the reactions of FBC with anilines.

Substitution of sulfonyl fluoride group at the 4-position of benzene seems to act as an electron-withdrawing substituent to the sulfur atom of sulfonyl chloride so that the degree of bond formation is increased substantially compared with that for monosulfonyl chloride. Whether the fluoride atom of the sulfonyl fluoride reacts as a leaving group or a simple substituent is an interesting aspect. It is expected that $k_1$ will be quite larger than $k_2$. If the fluoride atom of the sulfonyl fluoride reacts as a leaving group, the hydrolysis will obey the following eq. (5) and eq. (6).

$$FO_2S - Ar - SO_2Cl + H_2O \xrightarrow{k_1} FO_2S - Ar - SO_3H + HCl \quad (5)$$

$$FO_2S - Ar - SO_3H + H_2O \xrightarrow{k_2} HO_3S - Ar - SO_3H + HF \quad (6)$$

The data of consecutive hydrolysis from the polarographic method have been shown in Table 6 together with the rate constant ratio $Q = k_2/k_1$, which indicates that the reactivity of the second -SO$_2$F group, after the more reactive Cl$^-$ has left SO$_2$ group as a substituent, is very small and has a negligibly small leaving group ability.

On the other hand, the values of rate constant ratio, $Q$ in the hydrolyses of benzenedisulfonyl chlorides, are as large (0.28 ∼ 1.00) as shown in Sanecki's result[8] with the exception

of 2,4,6-trimethyl-1,3-benzenedisulfonyl chloride and 1,4-benzenedisulfonyl chloride.

For the hydrolysis of NDC in the same condition, the $Q$ value is three orders of magnitude higher than the corresponding values of $Q$ for FBC and has quite different $k_2$ values $(k_{2(NDC)}/k_{2(FBC)} = 435)$. This constitutes good evidence that two leaving groups of NDC partake in the reaction in contrast to sulfonyl fluoride of FBC which acts as a monosulfonyl chloride with $SO_2F$ as a substituents.

**Effect of Solvent.** The second-order rate constants in Table 1 show a maximum rate behavior at the composition of 90 (v/v)% MeOH. This result reflects that an anomaly is due to the physico-chemical properties of MeOH-MeCN mixtures. MeOH-MeCN mixture is well known as an isodielectric solvent mixture and appeared the physico-chemical anomalies at the composition of 80-90 (v/v)%, which are often associated with the broken down polymer chain structure of MeOH[18]. Table 1, shows a maximum rate phenomenon at 90 (v/v)% MeOH content in MeOH-MeCN mixtures as a trend of general physico-chemical anomalies which have been reported previously.[19]

In spite of this trend of anomalies for MeOH-MeCN, the plots of log $k_2$ vs. methanol content for the reaction of FBC with substituted pyridines show that the logarithms of second-order rate constants increase with MeCN content of solvent mixture gradually as shown Table 2. This may be due to lower $pK_b$ values of pyridines than those of anilines and the differences in $pK_b$'s counterbalances[20] the property of anomalies for MeOH-MeCN mixtures. Pyridine and methyl-substituted pyridines have $pK_b$ values in the range 7.87-8.80[21], while aniline and $p$-substituted anilines have $pK_b$ values in the range 8.88-12.10.[22] In case of $p$-substituted anilines, electron withdrawing substituents in the ring decrease the basicity, especially in case of $-NO_2$ substituent[23].

A wide range variation of basicity in $p$-substituted anilines would be affected by the same tendency of the variation of the solvent mixtures basicity[24] in the nucleophilic substitution reaction of FBC and NDC with $p$-substituted anilines in MeOH-MeCN binary solvent mixtures. While the nucleophilic substitution reaction of FBC with substituted pyridines could not be influenced by the basicity of solvent mixtures because the higher basicities of pyridines compensate the anomalies of solvent by basicities of solvent mixtures and MeCN accelerates desolvation effect with substituted pyridines in the rate determining step.

The shift of the maximum rate toward 70 (v/v)% is shown in Table 3 for the reaction of NDC with $p$-substituted anilines in MeOH-MeCN. This estimates that only one leaving group in FBC react mainly, in contrast with, two groups in NDC separating from the reaction center competitively, and then the transition state of NDC is stabilized at a bit of higher region of MeCN content which is caused by the effect of ascending the polarity of solvent comparing with the transition state of FBC. This trend is in accord with the $Q$ values of NDC in Table 6 and it can shift the region of maximum rate lower to 70 (v/v)%.

We conclude that the reactions of disulfonyl halides with various nucleophilies have proceeded with different solvent effects according to the $pK_b$'s of nucleophiles.

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