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Nucleophilic Displacement at Sulfur Center (I). Halogen Exchange in Benzenesulfonyl Chlorides*

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요 약. 치환된 염화벤젠슬포닐 $XC_6H_4SO_2Cl$ (X : *p*-MeO, H, *p*-Cl, *p*-Br, *p*-NO_2)의 할라이드 교환반응을 무수 아세톤 중에서 행하여 반응속도 상수와 활성화계수를 구하였다. 금속할라이드의 이온쌍 M^+X^-의 반응성은 할라이드 이온에 비하여 무시할 수 있음을 보았다. 또 친핵성도가 전자를 밀어내는 치환기를 가진 경우에 $Cl^->Br^->I^-$이고, 전자를 끌어주는 치환기를 가진 경우에는 $Cl^->I^->Br^-$이었다.

이들 결과와 Hammett 그림표가 위로 볼록한 것을 결합 약화과정이 크게 기여하는 단순 S_N2 메카니즘으로 설명하였다.

Abstract The rates and activation parameters for the halide (Cl^-, Br^-, I^-) exchange reactions of substituted benzenesulfonyl-chloride, $X\text{-}C_6H_4SO_2Cl$ (X : *p*-MeO, H, *p*-Cl, *p*-Br, *p*-NO_2) in dry acetone at two temepratures have been determined. It was found that the ion-pair of metal halide, M^+X^-, have negligible reactivity compared to free halide ions. It was also found that the nucleophilic order is $Cl^->Br^->I^-$ for electron-donating substituent, and $Cl^->I^->Br^-$ for electron-withdrawing substituents.

These results and convex nature of the Hammett plot are interpreted in the light of simple S_N2 mechanism with the bond breaking becoming important for compounds with the electron withdrawing substituents.

Introduction

Since Ingold and Hughes have suggested that the nucleophilic substitution reactions pass through either S_N1 (unimolecular displacement) or S_N2 (bimolecular direct displacement) path, their pioneering views are largely responsible for the interest in the substitution reactions of saturated carbon.

Recently, many investigators turned their

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interest from carbon reaction center to second row elements such as silicon, phosphorus and sulfur centers. These elements attract more interest on account of their adjacent vacant *d* orbital participation on reactivity. Due to their greater radius and thus greater ability to disperse a negative charge, and their polarizability, it has been predicted that they favor S_N2 mechanism rather than S_N1 mechanism. This could be due to a less favorable formation of electron-deficient species. Conjugation between the reaction center and the alkyl- or aryl-moiety may be less likely to occur due to the difference of atomic dimensions between first and second row elements with smaller orbital overlap.

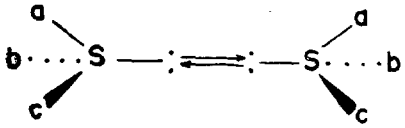
In this series of work we will investigate the nucleophilic substitution reactions at di-, tri-, and tetracoordinate sulfur using theoretical as well as experimental method. The geometry of the transition state[2] for substitution at dicoordinate sulfur has been reported to correspond to a trigonal bipyramid with axial entering and leaving groups while the equatorial positions are taken by the organic moiety and the lone electron pairs (I)



(I)

The bonding in these molecules can be described in terms of three sp^2 (equatorial) and two *pd* (axial) bonds. Alternatively an orbital defficient model can be used, omitting the *d* or ital and assuming that four orbitals of the central atom suffice three of them forming sp^2 equatorial hybrids while the fourth orbital extends over both axial groups in a three-center bond. In either picture the equatorial orbitals are the more electronegative (having greater s character) and will prefer the more electropositive substituents.

The structure of tricoordinate sulfur compound may be generally represented as shallow pyramids with sulfur as the apex. Angles between the bond can vary between 93° and 114°. Inversion of the pyramid occurs only at high temperatures (II)



(II)

Studies of the substitution reactions of tricoordinate sulfur compounds have been made much easier because of their susceptibility to the classical methods of stereochemistry. The stereochemical studies showed that substitution reactions on tricoordinate sulfur occurs with a Walden-like inversion of configuration suggesting a direct nucleophilic substitution involving the formation of intermedates similar to those formed in the hydrolysis of carboxylic esters or a multistage nucleophilic reaction path.[4] However, the evidence presented so far is not conclusive, and a more detailed investigation is desirable.

The amount of data concerning nucleophilic substitution at tetracoordinate sulfur had been very limited. Some workers have endeavoured themselves to the study of solvolytic reactions of alkyl-and aryl-sulfonyl chlorides recently. They have performed the neutral and alkaline hydrolysis of sulfonyl derivates and the results have been discussed in terms of S_N1, S_N2, or S_AN[7] (or addition-elimination) mechanisms.

Sulfamoyl chlorides are known to solvolyze by S_N1 mechanism. Majority of tetracoordinate sulfur compounds, however, pass through either S_N2 or S_NN mechanism in the nucleophilic substitution. It is a difficult problem to decide which of the two mechanisms is correct, and at present there are two contradicting views. Rogne favors simple concerted substitution i. e., S_N2 mechanism while Ciuffarin supports

the mechanism involving intermediate complex formation, i.e., S_AN.

In this work, we have studied the halogen exchanges of benzensulfonylchlorides and hope to shed some light in clarifying the mechanism involved in the nucleophilic substitution at the tetracoordinate sulfur.

Experimental

(1) **Materials.** (a): Benzenesulfonylchlorides were commercial compounds (Aldrich Chem. Co., Inc.) and purified by distillation under reduced pressure or by recrystalization. Their physical properties[9] are summarized in *Table* 1.

(b) Acetone: Technical acetone was dried over chloride and distillated fractionally in Todd column (reflux ratio, 10 : 1). The boiling fraction at 56–56.5 °C was passed through activated alumina column (Dia. 3cm, Length 20cm). The water content after this treatment may be minimized to 0.8 % or less[10].

(c) LiCl and KI: G.R. grade samples were used without further purification.

(d) LiBr was prepared by titrating LiOH solution with NH_4Br solution followed by recrystallization.

(e) Stock solution of LiCl: The radio active chrorine, Cl^{36}, which was purchased from the Radiochemical Center, Amersham, Buckinghamshire, England, in HCl^{36} form was converted to $LiCl^{36}$ by adding the equivalent amount of LiOH and then evaporated to dryness. Suitable amount of LiCl carrier salt and radio isotopic $LiCl^{36}$ was dissolved in anhydrous acetone.

f) Stock solution of LiBr: The radio active bromine, Br^{82}, which was supplied by A.E.R.I., Korea, in NH_4Br^{82} form is converted to $LiBr^{82}$ by adding the equivalent amount of LiOH and then evaporated to dryness. Suitable amount of LiBr carrier salt and radioactive LiBr was dissoloved in anhydrous acetone.

g) Stock solution of KI: The radioactive iodine, I^{131}, which was supplied by A.E.R.I., Korea, in NaI^{131} form is used as it was obtained. Suitable amount of KI carrier salt and radio isotopic NaI^{131} was dissoloved in anhydrous acetone.

(2) **Kinetic runs.** For measurment of rates, the following general procedure was adopted. To 20 ml substrate solution 15ml salt solution was added. At timed interval, 5 ml aliquot of the reaction mixture was pippeted from the flask to the benzene-watar mixture and shaking vigorousely. Cl^{36} activity was counted using Aloka-1600 liquid scintallation counter, and Br^{82} and I^{131} activities were measured using well-type scintillation counter.

Exchange rates were calculated by the equation[11]

$$k_2=\left(\frac{1}{a+b}\right)\left(\frac{1}{at}\right)\ln\left(x_\infty/x_\infty-x\right) \qquad (1)$$

for chloride exchange reactions, and by[12]

$$k_2=-\left(\frac{c-b}{a-b}\right)\left(\frac{1}{Dt}\right)\ln\left(1-\frac{x}{b}\right) \qquad (2)$$

for bromide and iodide exchange reactions where a and b are initial concentrations of substrate and salt, respectively, and $c=\frac{1}{2}(D+K+4b)$, $D=(K^2+4kb)^2$. x and x_∞ and radioactivity of organic layer at time t and infinite time respectively.

Shaking effect was investigated and found

Table 1. Physical constants of benzenesulfonyl chlorides

X	Mp°C (Bp °C/mmHg)	lit.[a]
p-MeO	37.5	38.5-40
H	(120°C/15 mm)	120 °C/15 mm
p-CI	51 °C	50-52 °C
p-Br	80 °C	78.5-79 °C
p-NO_2	81-82 °C	81-82 °C

[a]) Ref. 9

that benzenesulfonylchlorides underwent essentially no hydrolysis during extraction. Activation parameters were determined by general method based on absolute rate theory.

Results and Discussion

It is well known that dissociation of electrolytes in dipolar aprotic solvent is not complete, and the effect of ion association on rates cannot be neglected. It has been reported that metal halide (MX) is present as ion-pair form (M^+X^-) and free ions ($M^+ + X^-$) and the reactivity of ion-pair form(M^+X^-) is negligible toward saturated carbon centre in dry acetone. Acree treated this ion association effect on rates by simply assuming that ion pairs are unreactive. Thus,

$$k_{ob}=\alpha k_2 \tag{3}$$

where k_{ob} is apparent rate constant observed and k_2 is the rate constant at infinite dilution of metal halide (MX), and α is the degree of dissociation of MX.

Recently, Lee et. al., proposed reasonable method of calculation of rate constants for free halide ion exchange rections.

For isotopic exchange reaction, the method of Lee et. al., is the same as Acree treatment[14], but for heterolytic halide exchange reactions, their method has been proved to be adequate.

The reactivity of ion-pair form of metal halide toward tetracoordinate sulfur centre has not been reported. If ion-pair form is reactive, rate equation many be given as,

$$\text{Rate}=k_2[RSO_2Y][X^-]+k_2'[RSO_2Y][M^+X^-] \tag{4}$$

where k_2 and k_2' are the rate constants for free ion and ion-pair respectively, $[M^+X^-]$ and $[X^-]$ represesent the concentration of ion pairs and dissociated free anions respectively. Eq. (4) can be rearranged as,

$$\begin{aligned}\text{Rate}&=k_2[RSO_2Y]\alpha[MX]\\&\quad+k_2'[RSO_2Y](1-\alpha)[MX]\\&=(\alpha k_2+(1-\alpha)k_2')[RSO_2Y][MX]\\&=[(k_2-k_2')\alpha+k'_2][RSO_2Y][MX]\\&=k_{ob}[RSO_2Y][MX]\end{aligned} \tag{5}$$

where [MX] represents formal concentration of MX, whether present as ions or ion-pairs or both, and

$$k_{ob}=k_2'+(k_2-k'_2)\alpha \tag{6}$$

Rate constants obserbed for lithium chloride exchange reaction of benzenesulfonylchloride in dry acetone with various concentrations are given in *Table* 2. It can be seen that k_{ob} varies with LiCl concentration over a considerable range.

Equation (6) shows that plot of k_{ob} *v. s.* α will give k_2' as intercept and $\left(k_2-k_2'\right)$ as slope of the straight line. Such a plot using the data of *Table* 2 is shown in *Fig.* 1, where we

Table 2. Summary of rate constants with various salt concentrations.

[Subs]	[Salt]	α^a	k_{ob}	k_2
1.620×10^{-3}	2.446×10^{-4}	0.1096	6.146×10^{-1}	5.607
	7.076×10^{-4}	0.0664	3.744×10^{-1}	5.685
	11.793×10^{-4}	0.0515	2.923×10^{-1}	5.676
0.810×10^{-3}	7.076×10^{-4}	0.0664	4.149×10^{-1}	6.249
	3.538×10^{-4}	0.0920	5.058×10^{-1}	5.498

a; $\alpha=\dfrac{(K^2+4Kb)^{\frac{1}{2}}-K}{2b}$ $K=3.3\times10^{-6}$

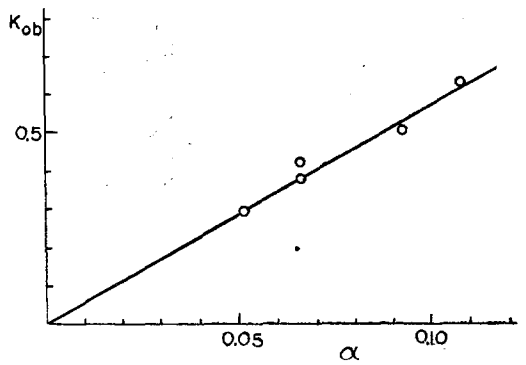


Fig. 1. polt of k_{ob} *vs.* α

obtained a straight line, whose intercept is zero. This indicates that $k_2'=0$ and k_2=slope, and shows nonnucleophilicity of LiCl ion-pair toward the tetracoordinate sulfur.

Thus we conclude that tetracordinate sulfur reacts only with free halide in dry acetone. We have therefore calculated k_2 using

$$k_2=k_{ob}/\alpha \tag{7}$$

Second order rate constants, k_2, for the halide exchange reactions of substituted benzenesulfonylchlorides are summarized in *Table.* 3 The reactivity of benzenesulfonylchlorides towards halide ions are higher than those of benzylchlorides. This owes primarily to the weakness of S–Cl bond compared with C–Cl bond[15].

This may also be attributed to the fact that the sulfur centre of benzenesulfonylchloride interacts with nucleophile rather strongly at the longer distance than carbon centre of benzylchloride does, and hence, partial bond formation between sulfur and nucleophile in activated complex would be casier. It can be seen that all the substituents decrease rates for Cl^- exchange while electron withdrawing substituents increase rates for Br^- and I^- exchange.

The nucleophilie reactivity order of the three halide ions are, $Cl^->Br^->I^-$ for electron donating substituents, and $Cl^->I^->Br^-$ for electron withdrawing substituents. Lee et. al., have argued that the nucleophilicity order of $Cl^->Br^->I^-$ in dry acetone is dictated by the easiness of desolvation halide ion in ground states. In general, both desolvation and polarizability are important in determining the nucleophilic reactivities of anionic nucleophile and they are competitive.

Since the results of this work show a similar tendency as benzyl-system, it can be concluded that nucleophilicity of halide ions is not affected by the change of reaction center from a saturated carbon to a tetracoordinate sulfur and ground state desolvation seems to play a dominant role in determining the reactivity of halide ions.

Majority of nucleophilic substitution on tetracoordinate sulfur is reported to take place by a concerted one-step process (III), S_N2, or by an addition mechanism, S_AN. involving a penta-coordinate intermediate (IV)

$$S_N2\ ;\ X^-+RSO_2Cl \xrightarrow{k_2} [X\cdots \underset{\displaystyle O\ \ O}{\overset{\displaystyle R}{\overset{|}{S}}}\cdots Cl]^- \quad \text{(III)} \xrightarrow{k_1} RSO_2X+Cl^- \tag{8}$$

$$S_AN\ ;\ X^-+RSO_2Cl \overset{k_2'}{\rightleftharpoons} [X\cdots \overset{\displaystyle R}{\overset{|}{S}}O_2Cl]^- \quad \text{(V)}$$

$$\rightleftharpoons [X-\underset{\displaystyle O\ \ O}{\overset{\displaystyle R}{\overset{|}{S}}}-Cl]^- \quad \text{(IV)} \overset{k_1'}{\rightleftharpoons} [X-\overset{\displaystyle R}{\overset{|}{S}}O_2\cdots Cl]^- \quad \text{(VI)}$$

$$\longrightarrow RSO_2X+Cl^- \tag{9}$$

Since Rogne was not able to find evidence for pentacoordinate intermediates in reaction of sulfonates[17], he abandoned S_AN mechanism for the reactions of sulfonylchlorides, which have a much better leaving group[18].

Robertson also claimed that the distorted

Table. 3. Summary of rate constant for the reaction $CX_6H_4SO_2Cl+Y^- \longrightarrow XC_6H_4SO_2Y+Cl^-$

X	Temp.	Cl^-	Br^-	I^-
p-MeO	25°C	0.387	0.00638	0.00381
	35°C	0.872	0.0141	0.00944
H	25°C	5.62	0.0279	0.00734
	35°C	11.02	0.0649	0.0196
p-Cl	25°C	1.26	0.0368	0.115
	35°C	2.13	0.0710	0.199
p-Brr	25°C	0.892	0.0474	0.119
	35°C	1.40	0.0889	0.200
p-NO_2	25°C	0.661	0.0224	0.101
	35°C	1.25	0.0356	0.182

tetrahedral form of the sulfonyl chloride with π bonding of oxygen $p\pi$-electrons into empty $d\pi$-orbitals on sulfur provides an empty d_{z^2} orbital for the approching nucleophile, thus in the activation process it is attractive to postulate a trigonal bipyramidal structure for the transition state with displacement of Cl from RSO_2 Cl and the nucleophile approching along the z axis.

But recently Ciuffarin reanalysed the leaving group mobility and emphasized the S_AN mechanism (9) for the reaction of benzenesulfonyl chloride, He showed that bond-breaking process, k_1' of (9), is dominant for more electronegative leaving group, e.g., F, and bond-formation process, k_2' of (9), is dominant for less electronegative one, e.g., Cl, Br and I. According to him only bond-formation, k_2', is important for substitution of benzenesulfonylchloride. This mechanism assumes that the leaving group, Cl in this case, is tightly bound to S and no loosening has occured at the transition state. However in contrast to this, S_N2 mechanism always accompanies certain amount of loosening of the leaving group at the transition state, (III).

If the S_AN mechanism applies to the symmetrical Cl-Cl exchange, i.e., X=Cl in (9), the the transition state structures (V) and (VI) will be identical, and it can be easily shown that only the bond forming k_2', is always important in the rate of exchange irrespective of the group R. This means that electron-attracting group on benzene e.g. *p*-NO_2, will accelerate the rate of exchange as compared with unsubstituted compound, since electron-attracting substituent form electron deficient center at sulfur and therefore favors bond-making but oppose bond breaking.

Our results in *Table* 3, however, are exactly opposite to this expectation, *p*-NO_2 benzenesulfonylchloride having lower k_2 value than that for unsubstituted one.

Thus bond streching and charging in the transition state of the S-Cl bond must be more important relative to the bond-forming process for compounds with electron attraction substiutents in Cl-Cl exchange. This is in agreement with predictions of substituent effects for a simple S_N2 displacement reaction. Similar conclusions have been obtained for the pyridine-catalyzed hydroysis of benzenesulfonyl chlorides[19].

An alternative explanation can be advanced by introducing *d*-orbital participation. According to Taft[21], $\pi(p$-$p)$ donating interaction ($Ar\leftarrow\ddot{S}$ and $\ddot{S}\rightarrow\ddot{X}$) is important for dicoordinate sulfur, while $\pi(p$-$d)$ accepting interaction ($Ar\rightarrow SO_2$ and $SO_2\leftarrow\ddot{X}$) is important for tetra-

coordinate sulfur. Thus electron density will be delocalized from the leaving group X to the *d*-orbital of sulfur for tetracoordinate sulfur compounds. Therefore sulfonyl sulfur with a strong electron attracting group attached will become more electron deficient compared with unsubstituted one and the empty *d*-orbital of S will overlap with *p* electrons of the leaving group X (in this case Cl) more efficiently and will result increase in the S-Cl bond strength.

Thus even if we assume the same degree of bond-breaking at the transition state for all the sulfonyl chlorides, the reduced rate of the compound with electron-attracting substituent can be explained as caused by the increase in this bond strength. This is also in good accord with the concerted S_N2 displacement mechanism.

We therefore support the simple S_N2 mechanism for nucleophilic substitution at tetracoordinate sulfur in view of the incapability of explaining our isotopic exchange results with S_AN mechanism.

The Hammett plots did not give simple linear correlations, and showed convex curves. Similar plots were obtained for the pyridine-catalyzed hydrolysis of benezenesulfonylchlorides .

From the Hammett plots shown in *Fig.* 2 it can be seen that every substituent decreases rate considerably for Cl-exchange, but for I-exchange, electron withdrawing substituents increase rate. This is rather unusal, since normally rate increases are accompanied by either the electron donating or the electron withdrawing substituent depending on the reaction type.

On the other hand, nonlinear Hammett plots have been reported for the S_N2 type reaction of benzylhalides in dipolar-aprotic or protic solvents, showing concave curve nature.

Therefore, the convex nature of our result may be considered as acharacteristics for the nucleophilic substitution reactions of benzene-

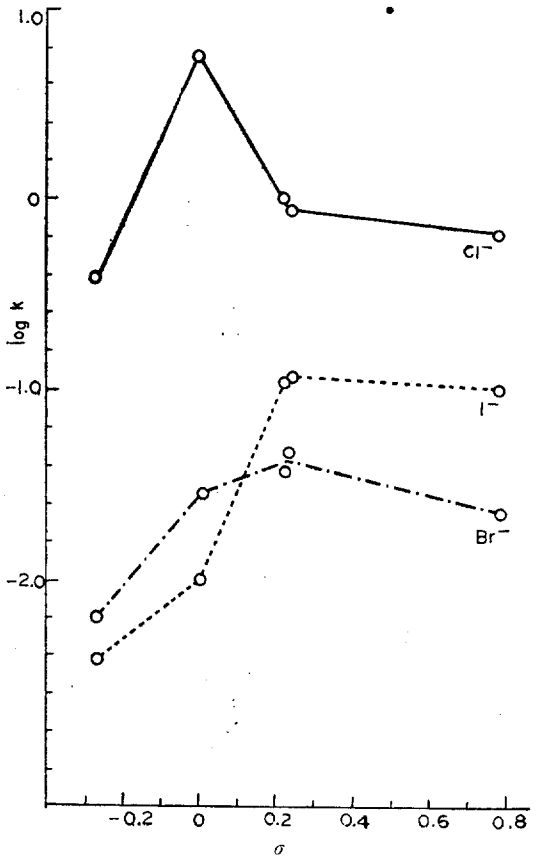


Fig. 2. Plot of log *k vs.* σ

sulfonylchlorides.

Another important feature is that convxe nature of the curve tends to revert to the more normal straight line plots as nucleophile changes from Cl^- to Br^- and I^-. This is an indication that the bond breaking becomes less important at the transition state as we change the nucleophile from Cl^- to Br^- and I^-. We can therefore conclude that the importance of bond breaking increases with the increase in the nucleophilicity of nucleophiles, since in acetone generally accepted order of nucleophilicity is $I^- < Br^- < Cl^-$.

This is again in good agreement with the simple S_N2 mechanism, since for the nucleophiles of low nucleophilicity the bond formation will be more difficult and important.

In the language of Pearson's HSAB[23] (Hard

Table. 4. Summary of activation parameters. ΔH (Kcal/mole) and $-\Delta S^{\neq}$ (e. u) (in parenthesis)

	Cl^-	Br^-	I^-
p-MeO	14.2 (11.3)	13.9 (22.1)	15.9 (16.4)
H	11.7 (15.9)	14.8 (16.4)	17.3 (11.2)
p-Cl	7.5 (33.0)	11.4 (26.9)	9.4 (31.5)
p-Br	7.6 (33.2)	10.9 (28.1)	8.9 (33.2)
p-NO_2	11.1 (22.3)	7.9 (39.8)	10.2 (29.3)

and Soft, Acid and Base) principle, sulfonyl sulfur is a hard acid center, while the softness of halide bases increases in the order, $Cl^- < Br^- < I^-$. Therefore the principle of HSAB predicts that Cl^- exchange will be faster than the others. Our results are in accord with this prediction, except that when sulfonyl sulfur was made harder with a strong electron attracting group rate decreases.

This is in contradiction to the principle, but either by assuming different degree of bond breaking at the transition state, or by assuming the increase in $\pi(p\text{-}d)$ accepting ability, this difficulty can easily be overcome.

Activation parameters for the halide exchange reactions of substituted benzenesulfonylchlorides in dry acetone are summarized in *Table* 4.

From the activation enthalpies in this Table, we can see the tendency that electron-donating substituent increases $\Delta H^{\neq}$, while electron-withdrawing substituents decreases it. These results show that electron-donating substituent makes partial bond formation difficult in transition state, while electron-withdrawing substituents make the bond formation easy. It is in agreement with the preceeding discussions.

The activation entropy data show larger negative values for electron-withdrawing substituent indicating more ordered transition state compared to compounds with electron-donating substituents. This is in accord with the greater degree of bond breaking at the transition state for these compounds.

Acknowledgement

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