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# 유황의 친핵 치환반응(제 3 보). 아세톤 용매속에서의 Dimethylsulfamoyl Chloride 의 할라이드 교환반응에 관한 속도론적 연구

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# Nucleophilic Displacement at Sulfur Center (III). Kinetic Studies on Halide Exchange Reactions of Dimethylsulfamoyl Chloride in Dry Acetone

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요 약. Dimethylsulfamoyl chloride의 할라이드 교환반응을 무수 아세톤 용매속에서 방사성 할라이드 이온을 사용하여 두 온도에서 속도론적으로 연구하였다. 그 결과를 benzensulfony lchloride의 경우와 비교해 보면 친핵성에 있어서는 거의 비슷한 경향성을 나타내나, 반응속도는 dimethylsulfamoyl chloride쪽이 $10^{-2}$배 이상이나 느린 경향을 나타낸다. 또한 활성화 파라미터, $\Delta H^{\neq}$나 $\Delta S^{\neq}$는 benzensulfonyl chloride의 경우와는 반대로 dimethylsnlfamoyl chloride의 경우는 $Cl^- > Br^- > I^-$의 순서로 감소함을 나타낸다.

이 결과를 bond-breaking, bond formation, electronic requirment 및 HSAB 원리로 설명하였다.

**Abstract.** Kinetic study of halide exchange for dimethylsulfamoyl chloride in dry acetone by using radioisotopic halide ions has been carried out at two temperatures.

The result of the order of nucleophilicity, as compared with benzenesulfonyl chloride, shows a similar tendency but reaction rate is slower, more than $10^{-2}$ times, than benzenesulfonyl chloride.

The activation parameter, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ decrease in sequence $Cl^- > Br > ^-I^-$ in dimethylsulfamoyl chloride but it is the reverse order found for benzenesulfonyl chloride.

The results are interpreted with bond-breaking, bond-formation, and electronic requirments, and in the light of HSAB Principle.

## Introduction

Nucleophilic substitution at a saturated carbon atom and carbonyl carbon atom has been studied extensively.[1]

However, for sulfur centre atom, there are somereports presented, recentry, concerning solvo-lysis of sulfonyl halide,[2] while direct

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substitution of negative nucleophile has been studied by relatively few investigaters.[3]

The solvolysis of most aliphatic and aromatic sulfonyl chloride are supposed to occur by the $S_N2$ mechanism in water or in a mixture of water-organic solvent, but for dimethylsulfamoyl chloride, two types of mechanisms are proposed i.e. reacting by an $S_N1$ mechanism[4] and by the $S_N2$ mechanism with relatively loose transition state.[5]

On studing halide exchange of typical direct substitution, we discussed before timing of bond-breaking and bond-formation and also the electronic requirment at transition state.[6]

In this work, we carried out kinetic study of halide exchange for dimethylsulfamoyl chloride in order to gain more information of nucleophilic substitution at tetra-coordinate sulfur centre.

## Experimental

**1. Materials.** Dimethylsulfamoyl chloride was prepared from commercial sample and purified by distillation under reduced pressure. b. p. 53°C(5mm)

Acetone, $LiCl^{36}$, $LiBr^{82}$ and $NaI^{131}$ solutions were prepared as reported previously.[7]

**2. Kinetic Runs Were Conducted as Described Before.**[7] $Cl^{36}$ activity was counted using Aloka -1, 600 Liquid Scintillation Counter, and $Br^{82}$ and $I^{131}$ activities were measured using Well-type Scintillation Counter.

Exchange ratee were calculated by the equation

$$K=-\frac{1}{a+b}\cdot\frac{1}{\alpha\times t}\ln(1-F)$$

for chloride exchange, and

$$K=-\frac{c-b}{a-b}\cdot\frac{1}{Dt}\ln\left(1-\frac{x}{b}\right)$$

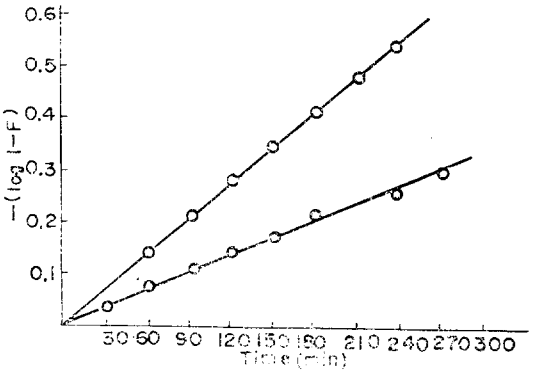



*Fig* 1. A typical plot of $-\log(1-F)$ *vs.* $t$ of chloride-chloride exchange at 40° C and 50° C

for bromide and iodide exchange reactions where a and bare inital concentration of dimethylsulfamoyl chloride and salt, respectively, and $c=\frac{1}{2}(D+K+4b)$, $D=(K^2+4Kb)\frac{1}{2}$ where $K$ is the ion pair dissociation constants in acetone, $F$ is the fraction reacted, $\alpha$ and $x$ are degree of dissociation of salt and radioactivity of organic layer at time $t$.

Activation parameter were calculated by general method based on absolute rate theory.

The plot of $\log(1-F)$ or $\log\left(1-\frac{x}{b}\right)$ versus $t$ was linear. A typical plot is given in *Fig.* 1.

The rate constant determined in this way reproducible to ± 5 %. Thus the accuracy of $\Delta H^{\mp}$ and $\Delta S^{\mp}$ were estimated ±1.0 Kcal/mole and ±2 e.u, respectively. The accuracy of $\Delta H^{\mp}$ and $\Delta S^{\mp}$ will not improve greatly even they were calculated with rate constant at more than two temperatures.

Thus we have calculated the activation parameters from rate constant $k$ at two temperatures since we are only concerned with general trends of the activation parameters in this work.

## Result and Discussion

The valules of the rate constants $k$ measured

*Table* 1. Summary of rate constants for halide exchange of dimethylsulfamoyl chloride in acetone.
$(CH_3)_2NSO_2Cl+Y^- \longrightarrow (CH_3)_2NSO_2Y+Cl^-$

| | Y⁻ | | |
|---|---|---|---|
| | $Cl^-$ | Br | $I^-$ |
| $K_{40°C}$ ($M^{-1}$. $Sec^{-1}$) | $1.49\times10^{-2}$ | $5.88\times10^{-4}$ | |
| $K_{50°C}$ ( 〃 ) | $3.39\times10^{-2}$ | $1.25\times10^{-3}$ | $1.38\times10^{-4}$ |
| $K_{60°C}$ ( 〃 ) | | | $2.16\times10^{-4}$ |
| *$K_{35°C}$ ( 〃 ) for $\phi SO_2Cl$ | 11.02 | $6.49\times10^{-2}$ | $1.96\times10^{-2}$ |

*Ref (7)

*Table* 2. Rate constants and activation parameters for hydrolysis of $YSO_2 \cdot Cl$

| Y | $k$25°C | $\Delta H^*$ (Kcal. $mole^{-1}$) | $\Delta S^*$ (e. u) | $\Delta Cp^*$ (cal $deg^{-1}$ $mole^{-1}$) |
|---|---|---|---|---|
| (*a*) $C_6H_5^-$ | $3.08\times10^{-3}$ | 17.2 | −12.3 | −56 |
| (*b*) $(CH_3)_2N^-$ | $3.85\times10^{-3}$ | 18.7 | −6.8 | −76 |

(*a*) R. E. Robertson *et al.*, *Can. J. Chem.*, 47. 4199(1969)
(*b*) E. C. F. Ko and R. E. Robertson, *J. Amer. Chem. Soc.*, **94**, 573, (1972)

at two temperatures are given in *Table* 1.

The value of the rate constant $k$ in *Table* 1 shows that the order of reaction rate coincide with the order of nucleophilisity of halide nucleophilie, $Cl^->Br^->I^-$, in dipolar aprotic solvent such as acetone,[8] as was expected.

Thus the order of reactivity of halide nucleophile on sulfur center is shown to have a similar tendency as on carbon center as described previously.[7]

*Table* 1 also ahows that the rate of halide exchange of dimethylsulfamoyl chloride is slower, more than $10^{-2}$ times, as compared to the rate for benzenesulfonyl chloride.

The rate constants and activation parameters for hydrolysis of dimethylsulfamoyl chloride are summerized in *Table* 2.

*Table* 2 shows that the rate of hydrolysis of dimethylsulfamoyl chloride is not different from that of benzensulfonyl chloride, but characterized by a large negative value of the heat capacity of activation, $\Delta Cp^*$, which is considered to have $S_N1$ character.

But Rogne presented evidence which raised doubts about such a conclusion based on isotope effect and activation parameters, $\Delta H^*$ and $\Delta S^*$, and strongly supported the conclusion that for dimethylsulfamoyl chloride as for the hydrolysis of most sulfonyl chloride, the $S_N2$ mechanism was operative.

The great difference of reaction rates between benzenesulfonyl chloride and dimethylsulfamoyl chloride, which are both tipical tetracoordinate sulfur center, suggest that the bond-formation is more important factor on determining reaction rate.

In other words, in the case of benzenesulfonyl chloride, there should be stabilization of the transition state by delocalization of the developing fractional positive charge on sulfur atom to the benzene ring as negative nucleophile approaches, while in the case of dimethylsulfamoyl chloride, which does not have benzene ring we do not expect this type of stabilization of the transition state.

The dimethylamine group is an electron relea-

*Table* 3. Activation parameters for halide exchanges of dimethylsulfamoyl chloride in acetone.
$(CH_3)_2N \cdot SO_2 \cdot Cl + Y^- \longrightarrow (CH_3)_2N-SO_2 \cdot Y + Cl^-$

| | $Y^-$ | | |
|---|---|---|---|
| | $Cl^-$ | $Br^-$ | $I^-$ |
| $\Delta H^{\neq}$ (Kcal/mole) | 16.0(11.7) | 14.5(14.8) | 8.5(17.3) |
| $\Delta S^{\neq}$ (e.u) | −15.9(−15.9) | −27.2(−16.4) | −50.0(−11.2) |

Ref(7) Values in parenthesis are the corresponding values for halide exchanges of benzenesulfonyl chloride, from

sing group and therefore will increase electron density on sulfur centre and decrease the positive charge, making it more difficult for a nucleophile to attack.

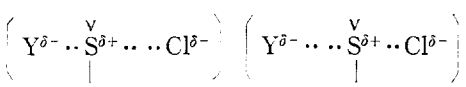
Accordingly, this should result in difficulty of the bond-formation and slower reaction rate.

On the other hand, it has been reported that the dimethylsulfamoyl chloride reacts with $S_N1$ character in strong ionizing power solvent, such as water, indicating relative easiness of bond-breaking.

It seems that this reaction is characterized for this compound by easy bond-breaking and difficult bond-formation.

*Table* 3 shows that the activation parameters, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ increase in the sequence $Cl^- < Br^- < I^-$ with various nucleophile for benzene-sulfonyl chloride[7] but decrease in the sequence $Cl^- > Br^- > I^-$ for dimethylsulfamoyl chloride.

It has been generally accepted that the magnitude of $\Delta H^{\neq}$ value is an indication of the degree of bond-breaking at the transition state.[9] Thus for a direct substitution reaction large $\Delta H^{\neq}$ value suggest the late transition state (I) where both bond-forming and-breaking have progressed relatively further along the reaction coordinate, while small $\Delta H^{\neq}$ suggests the early transition state (II) where bond-forming and-breaking are still the early state. (10)



(I) (II)

late transition state. early transition state.

The result shown in *Table* 3 implies that the transition state for dimethylsulfamoyl chloride is the type (II) while transition state for benzenesulfonyl chloride is the type(I).

This is in accord with the fact that sulfur atom of benzenesulfonyl chloride is more polarizable as compared with that of dimethylsulfamoyl chloride.

Therefore, a reasonable explanation can be given by comparing the softness of sulfur centre atom in dimethylsulfamoyl chloride and benzenesulfonyl chloride and invoking the HSAB principle.[11]

The sulfur atom in dimethylsulfamoyl chloride is harder than that of benzenesulfonyl chloride and forms early transition state (II) with the more polarizable, i.e, softer[5] nucleophile, while the trends is opposite for benzenesulfonyl chloride which has softer sulfur center.

However, it is appropriate here to note that there are many other factors than soutness which influence the rate of reaction and the rate is not controlled solely by the HSAB principle applied to the reaction center atom.

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