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# Nucleophilic Displacement of Sulfur Center, Part VI.

## Halide Exchange Kinetics of Methanesulfonyl Chloride in Acetone, Acetonirile and Methanol.

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### Abstract

The rates and activation parameters for the halide exchange reactions of methanesulfonyl chloride in dry acetone, acetonitrile, and methanol have been determined.

It was found that nucleophilic order is $Cl^->Br^->I^-$. The rate of chloride exchange with methanesulfonyl chloride decreases in the order of solvent; $(CH_3)_2CO>CH_3CN\gg MeOH$.

Results are interpreted in terms of easiness of the initial state desolvation and solvation stabilization of the transition state.

### 요        약

염화 메탄 슬포닐의 할로겐 교환반응을 무수아세톤, 아세토니트릴, 메타놀 용매중에서 행하여 반응속도상수와 활성화파라메터를 구하였다.

친핵성도는 $Cl^->Br^->I^-$ 순서로 감소하였으며, 용매변화에 따른 염소이온과의 반응속도는 $(CH_3)_2CO>CH_3CN\gg CH_3OH$ 의 순서로 감소하였다.

실험결과를 초기상태 탈용매화의 용이함과 천이상태 용매화의 안정성으로 설명하였다.

## 1. Introduction

In a previous work, we reported that nucleophilic substitution at tetracoordinate sulfur proceeds via the simple $S_N2$ mechanism. The difference of reactivity from that of saturated carbon atom was attributed to the d-orbital participation in the reaction of sulfur center.

Several reports have since appeared on the reactivity of sulfur center through studies of various nucleophilic substitution reactions supporting the $S_N2$ mechanism[2]. Recently, however, points have been raised as to the importance of initial *v.s.* transition state contributions in determining the reactivity especially when solvent is varied from protic to aprotic.

In order to shed some lights on elucidation of detailed mechanism of $S_N$ reaction at sulfur center, we have investigated the

halide exchangse of methanesulfonyl chloride in dry acetone, acetonitrile and methanol.

## 2. Experimental

### 1) Materials

a) Methanesulfonyl chloride was obtained from Aldrich Chem. Co. Inc., and purified by redistillation (b. p. $161\pm1°C$ at 730mm Hg).

Acetone was purified as described before[1].

Acetonitrile; Reagent grade $CH_3CN$(WAKO) was shaken with potassium hydroxide pellets, dried with phosphorous pentoxide, and distilled fractionally in a column. The boiling fraction of 79-80°C was collected[2].

Methanol; Reagent grade methanol(WAKO) was dried with calcium oxide and fractionally distilled.

Stock solutions of LiCl, LiBr, KI containing tracer activities were prepared as described previously[1].

### 2) Kinetic runs.

Kinetic measurements were carried out as described previously. Rate constants for the halide exchange reactions were calculated by the following equation[1].

$$k=-\frac{1}{a+b}\cdot\frac{1}{at}\ln(1-\frac{x}{x\infty})$$

(for $Cl^-$ exchange)

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

(for $Br^-$, $I^-$ exchange)

where $a$ and $b$ are the initial concentrations of the substrates and salts respectively, $\alpha$ is the degree of dissociation of the salts in dipolar aprotic solvents, and $c=\frac{1}{2}(D+K+4b)$, $D=(K^2+4Kb)^{\frac{1}{2}}$ where $K$ is the dissociation constant of the salts in dry acetone. $x$ and $x\infty$ are radioactivities of organic layer at time and that at infinity time respectively.

In the kinetic runs in solvent $CH_3CN$ and $CH_3OH$, we measured the rate constants for the exchange systems composed of several different concentrations of LiCl and definite

concentration of methanesulfonyl chloride, instead of determining the dissociation constant of LiCl in the given solvents.

The precision of the rate constants is $\pm5\%$ or better, of $\Delta H^{\neq}$ ca. $\pm0.5$Kcal mole$^{-1}$ and of $\Delta S^{\neq}$ ca. $\pm2$ e. u.

## 3. Results and Discussion

The second order rate constants, $k$ and activation parameters for halide exchanges in methanesulfonyl chloride are summarized in Table I.

**Table 1.** Rate constants and activatoin parameters for the reaction of $CH_3SO_2Cl$ with $X^-$ in dry acetone.

| $X^-$ | $k_2$(mol$^{-1}$ sec$^{-1}$)$\times10^4$ | | | $\Delta H^{\neq}$ (Kcal/mol) | $-\Delta S^{\neq}$ (e. u.) |
|---|---|---|---|---|---|
| | 15°C | 25°C | 35°C | | |
| Cl$^-$ | 430 | 836*(56200) | | 10.7(11.7) | 27*(16) |
| Br$^-$ | 27.1 | 79.3(297) | | 17.7(14.8) | 9(16) |
| I$^-$ | | 4.85(73.4) | 10.1 | 11.9(17.3) | 35(11) |

\* Values in parentesis are for the reaction of $C_6H_5SO_2Cl$

Table 1. shows that the order of halide nucleophilicity is $Cl^->Br^->I^-$. This is precisely the $S_N2$ reactivity order expected for halides in aprotic solvents[3]. It has been shown that the nucleophilicity is determined primarily easiness of desolvation of nucleophiles while polarizabilities of both reaction center and nucleophile have secondary effect in determining the reactivity[2a,4] The order obtained in this work therefore provides further support to this contention. The present result is also consistent with the HSAB principle[5], since the sulfonyl sulfur is a hard center and hard-hard interaction with $Cl^-$ in the transition state has stabilizing effect while hard-soft interaction with e. g. $I^-$ has no such effect.

Rate constants for benzenesulfonyl chloride are also shown in Table 1. In all cases, rates for benzenesulfonyl chloride are faster than

**Table 2. Rate constants and activation parameters for the reaction of $CH_3SO_2Cl$ with $Cl^-$.**

| Solvent | $k_2(mol^{-1} sec^{-1}) \times 10^4$ | | | | | $\Delta H^{\neq}$ (Kcal/mol) | $\Delta S^{\neq}$ (e. u.) | $^*\varepsilon$ |
|---------|------|------|------|------|------|------|------|------|
| | 15°C | 25°C | 35°C | 45°C | 55°C | | | |
| Acetone | 430 | 836 | | | | 10.7 | 27 | 20.7 |
| Acetonitrile | | 15.2 | 23.1 | 34.5 | | 7.2 | 47 | 36.2 |
| Methanol | | | 0.0918 | 0.302 | 0.695 | 19.7 | 17 | 32.6 |

\* Dielectric constant at 25°C. Ref (9)

those for mathanesulfonyl chloride. This is not unexpected since stabilization of the transition state through dispersion of developing positive charge into benzene ring will accelerate the rate in the case of benzenesulfonyl chloride. In this respect it is interesting to note our molecular orbital(MO) analysis reported in the preceding paper[6]. According to the result of calculation using the Extended Hückel theory(EHT)[7], the lowest unoccupied (LU) MO's for the both compounds are sigma antibonding, and the frontier electron density of sulfur greater for $C_6H_5SO_2Cl(p_s^{LU} = 0.2744)$ as compared to that for $CH_3SO_2Cl$ ($p_s^{LU} = 0.1252$). Thus Fukui's forontier orbital theory[8] predicts the greater reactivity of $C_6H_5SO_2Cl$ than $CH_3SO_2Cl$. This MO analysis was based on the ground state properties of the molecules while charge dispersion occurs in the activation process. Both predictions at the initial and transition states therefore agree and they are in accord with the experimental findings.

Activation parameters for the reaction of $CH_3SO_2Cl$ in dry acetone are included in Table 1. The relatively large values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for $Br^-$ could reflect the unfavourable process of closer approach by the $Br^-$ to the sulfur center at the transition state since the $Br^-$ is neither highly polarizable nor easily desolvated.

Rate constants and activation parameters for chlorine exchange reactions of mathanesnlfonyl chloride in various solvents are given in Table 2.

Table 2 shows that the reaction of chlorine exchange in $CH_3SO_2Cl$ is generally faster in aprotic solvents at ordinary temperatures. Although acetone and acetonitrile are both aprotic, rate in acetone is greater than in acetonitrile. Since the dielectric constant of acetone is smaller than that of acetonitrile[9], this implies that the transition state is of the "tight" type( I ) rather than the "loose" type( II ),



$$Cl^-\delta \cdots S \cdots Cl^-\delta \qquad Cl^-\delta \cdots S \cdots Cl^-\delta$$

( I )                              ( II )
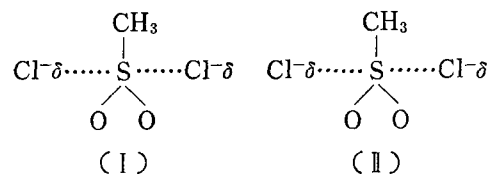
for in type( I ) the transition state has dispersed charge and hence will be better solvated by the dipolar aprotic solvent with smaller dielectric constant.

The rate constants in methanol are less than $10^{-2}$ times of values in acetonitrile. Activation parameters show that this is entirely due to the unfavorable effect of the enthalpy of activation. Since $\Delta S^{\neq}$ is more negative in acetonitrile than in methanol, the rate difference may be due largely to the better solvation of the transition state in the former through dipole-dipole and dispersion interactions between transition state and solvent. Similar suggestion has been made for the reaction of benzenesulfonyl chloride with imidazole[2b]. This of course is in good accord with the "tight" transition state as suggested above.

## References

1) J. E. Yie and I. Lee, J. Korean Chem. Soc., **17**. 154 (1973)

2) (a) J. Kim, J. Korean Nucl. Soc., **5**, 321 (1973)

   (b) O. Rogne, J. C. S. Perkin II, **823**, 1760(1973)

   (c) I. Lee and S. J. Kim, J. Korean Chem. Soc., **17**, 406 (1973)

3) A. J. Parker, Chem. Rev., **69**, 1 (1969)

4) J. H. Park, J. Korean Nucl. Soc., **5**, 20 (1973)

5) R. G. Pearson, J. Am. Chem. Soc., **85**, 3533 (1963)

6) I. Lee and E. R. Kim, Part V in this series. Submitted for publication.

7) R. Hoffmann, J. Chem. Phys., **39**, 1937 (1963)

8) K. Fukui, "MO in Chemistry, Physics and Biology" ed. by P. O. Lowdin and B. Pullman, Academic Press, New York, (1964)

9) R. A. Horne ed., "Water and Aqueous Solutions" Wiley-Interscience, New York, 1972. Chapter 4.