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Kinetic Studies on Halogen Exchanges of Substituted Benzenesulfonylbromides

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Abstract

The rates and activation parameters for the halide exchange reactions of substituted benzenesulfonylbromides ($R-C_6H_4SO_2Br$, $R=p-MeO$, $p-CH_3$, $p-H$, $p-NO_2$) in dry acetone at two temperatures were determined.

It was found that the nucleophilicity order of $Cl^- > I^- \gtrsim Br^-$ for strong electron withdrawing-, and mild electron donating group, and of $I^- \gtrsim Cl^- > Br^-$ for strong electron donating group.

Hammett plots showed slightly convexed characteristics which is similar to the plots of substituted benzenesulfonylchlorides, but contrary to the concaved nature for the halide exchange reactions of substituted benzyl chlorides.

The rate of halogen exchange between benzenesulfonylbromide and lithium bromide decreased in the order of solvent; $(CH_3)_2CO > CH_3CN \gg MeOH$.

The rates and activation parameters were also compared with those already known in the substituted benzenesulfonylchlorides. Theses were explained in terms of the structural properties of the transition state, and discussed the reaction mechanisms.

요 약

브롬화벤젠설포닐류($R-C_6H_4SO_2Br$, $R=p-MeO$, $p-CH_3$, $p-H$, $p-NO_2$ 등)의 할로겐 교환반응을 무수 아세톤중에서 행하고 두 온도에서의 반응속도항수를 구함으로써 활성화 파라메타들을 아울러 결정하였다.

친핵자의 강도는 강한 전자흡인 치환기를 가졌거나 약한 전자공여 치환기를 가진 유도체에 대하여는 $Cl^- > I^- \gtrsim Br^-$ 의 순위였으며, 강한 전자공여 치환기의 유도체에 대하여는 $I^- \gtrsim Cl^- > Br^-$ 의 순위임을 보았다.

하메트(Hammett)접시는 치환기를 가진 염화벤젠설포닐류에서와 유사하게 약간 위로 볼록한 특징을 보였는데 이것은 치환기를 가진 염화벤젠류의 할로겐 교환반응의 그것이 아래로 오목함을 보이는 것과는 대조적이었다.

한편 브롬화벤젠설포닐과 브롬화리튬 사이의 할로겐 교환반응 속도를 여러용매에서 측정한 결과 반응속도가 큰 순서는 $CH_3COCH_3 > CH_3CN \gg MeOH$ 이었다.

속도항수와 활성화파라메타들을 염화벤젠설포닐류에 대한 것과 비교하였으며 치환기효과, 용매효과등에서 얻은 결과들을 전이상태의 구조적 특징으로 설명하고 반응기구를 논의하였다.

1. Introduction

The S_N1 and S_N2 reaction paths at the reaction center of carbon had been much discussed by many workers¹⁻³⁾.

Investigations on the reaction centers of the second row elements such as silicon, phosphorus and sulfur have lately started with the interest of their adjacent d orbital participation on reactivity. Due to their great radii and thus their greater ability to disperse negative charge, and their polarizability, it is predicted that they pass the reaction path of S_N2 rather than S_N1 . The expected reluctance of the second row elements to react by S_N1 mechanism could be due to the favorable formation of electron deficient species. Conjugation between the reaction center and the alkyl and aryl moiety may be less-likely to occur due to the difference of atomic dimensions between the first and the second row elements with smaller orbital overlaps.

Even though some studies on the nucleophilic substitution reactions at di-⁴⁻⁷⁾ tri-⁸⁻¹¹⁾ and tetra-¹²⁻¹⁷⁾ co-ordinate sulfur were accomplished the evidence presented so far is still not conclusive, and more detailed investigation is desirable. For the tetra-co-ordinate sulfur center especially, some workers have endeavored themselves to the study of solvolytic reactions of alkyl and aryl sulfonylchlorides recently. They have performed the neutral and alkaline hydrolysis of sulfonyl derivatives and the results have been discussed in terms of S_N1 ¹²⁾, S_N2 ¹³⁻¹⁵⁾ or S_{AN} ^{16, 17)} mechanism.

The S_N1 mechanism was later discarded on various grounds. The S_{AN} mechanism was also abandoned because the sulfonyl oxygen atoms do not exchange with those of water during the hydrolysis and this was taken as a proof against the formation of an addition intermediate. Thus, the mechanism was mostly considered to involve a direct displacement on

sulfur, as recently emphasized by Rogne¹⁵⁾, since all the kinetic features of the reaction are, he insisted, in accord with the S_N2 mechanism. Rogne extended the investigation to a number of nucleophiles in aqueous media and the mechanism of the hydrolysis was identified as the reaction of nucleophile-catalyzed.

Ciuffarin¹⁸⁾ re-examined the abandoned S_{AN} mechanism with the study on the mobility of leaving group for the reactions of benzenesulfonylchlorides with aniline, n-butylamine and hydroxide ion. The leaving group effect for the tetra-co-ordinate sulfur was found to be in the order of $I^- > Br^- > Cl^- > F^-$. They have also reported a study on the element effect in nucleophilic substitutions at di-co-ordinate sulfur^{22, 23)}, at which the element effect or electronegativity effect, ie, the decrease of the $\pi(p-p)$ donating ability as $F^- > Cl^- > Br^- > I^-$, was related to the amount of bond breaking in the transition state, ie, leaving group effect which decreases in the order, $F^- > Cl^- > Br^- > I^-$. The leaving group ability at the tetra-co-ordinate sulfur¹⁸⁾ was discussed in terms of S_{AN} mechanism with bond forming or bond breaking as the rate determining step. Due to the different reactivity of sulfur in the two oxidation states, there is a different leaving group mobility. However, there are also some controversies in their discussion, and further research is necessary in order to establish reaction mechanisms of sulfur compounds. The results of the study on the isotopic exchange of benzenesulfonylchloride in dry acetone¹⁹⁾ indicated that the reaction proceeds via S_N2 mechanism on various grounds. However, to establish and to clarify the reaction mechanism, further study on the leaving group effect as well as the solvent effect will be helpful.

No detailed study on the structure of RSO_2X molecules was done, and the only available

evidence suggests that this class of molecules has a distorted tetrahedral shape^{20, 21}. This evidence gives an information about the structure of the benzenesulfonylbromide of which stereochemistry may be considered as a distorted tetrahedron but with shortened S-O bonds due to $p\pi-d\pi$ interactions. This initial structure gives some informations for the preliminary activation and how the resulting activated molecules will influence the approach of the displacing nucleophiles.

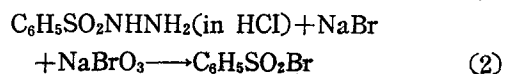
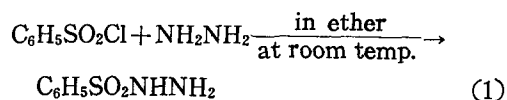
Much investigations have been performed to relate the structure and reactivity. Factors influencing the reactivity can be summarized as follow: 1) solvent effects both on the ground- and the transition state of the substrate and the nucleophile^{22, 23}, 2) polarizabilities of the substrate and nucleophile (HSAB principle)²⁴⁻²⁶, 3) basicity of the nucleophile^{1, 2}, 4) the structure of the transition state and the mechanism such as tight, and loose transition state²⁷⁻²⁹ etc. No single factor seems to be responsible but two or three factors cooperate in the reaction.

We have tried to find out an adequate factors which dominate the different phenomena of the tetra-co-ordinate sulfur compounds by halide exchange reactions of substituted benzenesulfonylbromides.

2. Experimental

1) Materials

(A) Benzenesulfonylbromide was prepared from benzenesulfonylchloride by the method reported by Poschus *et al*³⁰. According to the method the chloride was converted to the bromide via benzenesulfonylhydrazide;

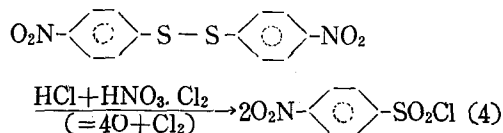
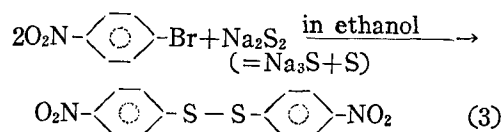


Finally the crude product was distilled under

reduced pressure (b. p. ; 121°C/5 mmHg).

(B) p-Methoxybenzenesulfonylbromide and p-toluenesulfonylbromide were, respectively obtained in the similar manner to that of benzenesulfonylbromide. p-Methoxybenzenesulfonylchloride and p-toluenesulfonylchloride were the commercial products of the Aldrich Chemical Co. The crude p-methoxy-, and p-toluenesulfonylbromides were purified by fractional recrystallization from petroleum ether, and the mp of the p-methoxy-, and p-methyl derivatives were identified to be 28-29°C(lit. ; 29-30°C)³⁰, and 94-95°C(lit., 95-96°C)³⁰, respectively.

(C) p-Nitrobenzenesulfonylbromide was synthesized as following; bromobenzene was subjected to nitration reaction and the p-isomer was separated by fractional recrystallization with ethanol. The m.p. of the purified nitrobenzene was identified as 127°C, which agrees well with that in the literature³¹. The p-nitrobromobenzene was treated with alcoholic sodium disulfide solution keeping the reaction temperature at 60°C to produce di-p-nitrophenyl disulfide³². The purified disulfide was subsequently treated with chlorine gas in strongly acidic medium, and the crude p-nitrobenzenesulfonylchloride was obtained.



The crude product was recrystallized from glacial acetic acid and washed with excess of water. The dried p-nitrobenzenesulfonylchloride was converted to p-nitrobenzenesulfonylbromide according to the afore-described method (m. p. ; 87-88°C).

(D) Dry Acetone; reagent grade acetone

(WAKO) was dried with anhydrous magnesium sulfate, and distilled fractionally in Todd column (reflux ratio; 10:1). The boiling fraction at 56–56.5°C was passed through activated alumina column (dia. ; 2.4cm, length; 30cm). The water contents after this treatment may be minimized to 0.8% or less³³.

(E) Acetonitrile; reagent grade acetonitrile (WAKO) was shaken with potassium hydroxide pellets, dried with phosphorus pentoxide, and distilled fractionally in column. The boiling fraction of 79–80°C was collected.

(F) Methanol; G. R. grade methanol (E. Merck) was dried with calcium oxide, and fractionally distilled.

(G) Lithium Chloride and Potassium Iodide; reagent grade chemicals were used without further purifications.

(H) Lithium bromide was prepared by treating lithium hydroxide solution with ammonium bromide. The slight excess of the added ammonium bromide was expelled by heating, and the product was recrystallized.

(I) Stock Solution of Lithium Chloride Containing Tracer Activity of Lithium Chloride-³⁶Cl; the radioactive chlorine-36, purchased

from Radiochemical Centre, Amersham, England, in hydrochloric acid form was converted to lithium chloride-³⁶Cl by adding equivalent amount of lithium hydroxide, and then evaporated to dryness. Definite amount of lithium chloride carrier salt and the radioactive lithium chloride were dissolved in the solvents.

(J) Stock Solution of Lithium Bromide; the radioactive bromine (⁸²Br) in ammonium bromide form was produced from TRIGA Mark III reactor via ⁸¹Br (n, γ) ⁸²Br reaction with high specific activity. It was converted to lithium bromide-⁸²Br by adding equivalent amount of lithium hydroxide, and subsequent heating to dryness. Definite amount of lithium bromide carrier salt and the radioactive lithium bromide-⁸²Br were dissolved in the solvents.

(K) Stock Solution of Potassium Iodide Containing Tracer Amount of Sodium Iodide-¹³¹I; the radioactive iodine in sodium iodide-¹³¹I form, the product of KAERI, was used after confirmation of radiochemical purity. Desired amount of potassium iodide carrier salt and the radioactive sodium iodide were dissolved in the solvents.

2) Determination of Radiochemical Purity

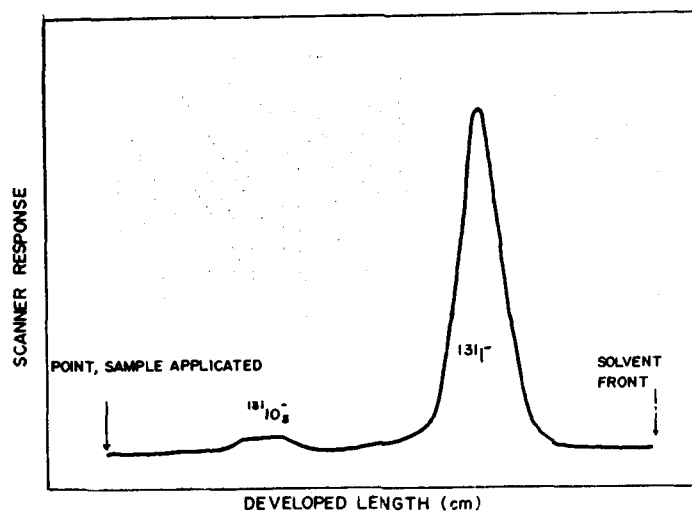


Fig 1. Typical radio-paperchromatogram scan for Na ¹³¹I (whatman No. 1 filter paper. Developing solvent=75 % MeOH)

of the Isotopic Solutions: since the oxidized forms of halide ions do not participate in the isotopic exchange reactions³⁴⁾, the radiochemical purities of the radiohalide solutions were checked by one dimensional paper chromatography using Whatman No. 1 filter paper and the developing solvent of 75% methanol. The developed chromatograms were scanned by using radiochromatogram scanner (Packard Model 702C). The radiochemical purities were calculated by measuring the relative peak areas on the chromatogram scan. A typical chromatogram scan is shown in Fig. 1.

The major impurity in sodium iodide solution was identified to be $^{131}\text{IO}_3^-$, however, its radioactivity was negligible showing upto 3% of the total radioactivity. The impurities in lithium chloride- ^{36}Cl , and lithium bromide- ^{82}Br were below detection limits.

3) Kinetic Runs

For the measurement of reaction rate, the following general procedure was adopted.

To a 30ml portion of the substrate solution in reaction flask, 30ml of the salt solution was added after thermal equilibrium in water bath. At timed intervals, 5ml aliquot of the reaction mixture was pipetted from the reaction flask to the benzene-water mixture in 250ml separatory funnel. Immediately the funnel was shaken vigorously, and left for 1 min. Two ml portion of the organic layer was used in determining the radioactivity. ^{131}I , and ^{82}Br activities were normally counted by using well type NaI(Tl) scintillation counter (Fujitsu Model EA14). ^{36}Cl activity was counted by using liquid scintillation counter (Aloka Model LSC 1600). Scintillator solution composed of 75% p-dioxane, 12.5% 1,2-dimethoxyethane, and 12.5% anisole, by volume as the solvent, and 7.0g/l P. P. O. and 0.5g/l dimethyl P. O. P. O. P. as solute, was used for the activity counting of aqueous samples. Four g/l P. P. O. and 0.05g/l P. O. P. O. P. in scintillation grade

toluene was used as a scintillator solution for counting of organic samples.

Exchange rates were calculated by the equations:^{19, 29)}

$$k = -\frac{1}{a+b} \cdot \frac{1}{at} \ln(1-F), \quad F = \frac{x}{x_\infty} \quad (5)$$

(for bromide exchange reactions)

$$k = -\frac{c-b}{a-b} \cdot \frac{1}{Dt} \ln\left(1 - \frac{x}{b}\right) \quad (6)$$

(for chloride and iodide exchange reactions)

In the above equations a and b are the initial concentrations of the substrates and salts, respectively, α is degree of dissociation of the salts, and $C = \frac{1}{2}(D+K+4b)$, $D = \sqrt{K^2+4Kb}$, where K is dissociation constant of the salts in dry acetone. x , and x_∞ are radioactivities of organic layer at time t and that at infinite time, respectively.

Activation parameters were determined by the general method which is based on absolute reaction rate theory³⁵⁾. Taking account for the precision problem in obtaining the thermodynamic data we used the precision measure for the rate coefficients, k_2 and k_1 as $\pm r_2$ and r_1 , respectively:³⁶⁾

$$\Delta H^\ddagger = \frac{RT_1T_2 \ln(k_2/k_1)}{T_2 - T_1} \pm \frac{RT_1T_2}{T_2 - T_1} \{(r_2/k_1)^2 - (r_1/k_2)^2\}^{1/2} \quad (7)$$

$$\Delta S^\ddagger = \frac{RT_2 \ln k_2 - RT_1 \ln k_1}{T_2 - T_1} - R(\ln k T/h + 1) \pm \frac{R}{T_2 - T_1} \sqrt{(T_2 r_2/k_2)^2 + (T_1 r_1/k_1)^2} \quad (8)$$

In the kinetic runs using solvent acetonitrile or methanol, we measured the rate constants in the exchange systems composed of several different concentrations of lithium bromide and definite concentration of benzenesulfonylbromide, instead of determining the dissociation constant of lithium bromide in the given solvents.

3. Results and Discussion

Since the dissociation of electrolyte in dipolar

aprotic solvent is not complete, the metal halide will be present in the form of both free ions and ion pairs in the solution. It is, however, reported that the reactivity of the ion pair form ($M^+ \cdots X^-$) is negligible toward the reaction center of saturated carbon in dry acetone^{37, 38}.

As it was shown by Yie¹⁹ that the rate equation may be given as

$$\text{Rate} = k_2(RSO_2Y)(X) + k'_2(RSO_2Y)(M^+ \cdots X^-) \quad (9)$$

in case of the ion pair form of the metal halide also taking part in the reactivity toward the tetra-co-ordinate sulfur center. The conclusion of his study was that the reaction center of the tetra-co-ordinate sulfur reacts only with free halide ion in dry acetone. Thus observed rate constant, k_{ob} , was

$$k_{ob} = k_2 \cdot \alpha \quad (10)$$

He also suggested that the criticism for Acree treatment may arise for the larger and the more polarizable anions.

The reaction was first order with substrate and with nucleophile. The plot of $-\log(1-F)$ vs. t of the halide exchange reaction systems at two temperatures were linear in accordance with the equations of (5) and (6). A typical plot is given in Fig. 2.

The linearity seemed to disappear after initial reaction stage probably due to the various side reactions.

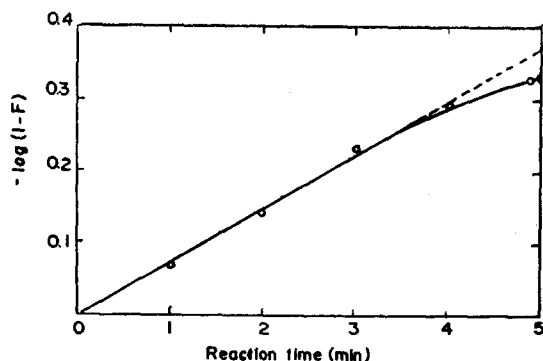
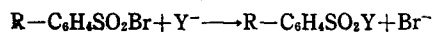


Fig 2. Typical plot of reaction time vs. $-\log(1-F)$ ($P-O_2NC_6H_4SO_2Br-Br^-$, $10^\circ C$)

Table 1. Summary of the rate constants for the reaction in dry acetone



R	Temp ($^\circ C$)	Cl^-	Br^-	I^-
p-H	0	6.30 ± 0.26	2.82 ± 0.08	4.42 ± 0.17
	10	9.32 ± 0.41	4.90 ± 0.19	9.10 ± 0.40
p-CH ₃	0	4.12 ± 0.14	0.33 ± 0.01	0.78 ± 0.02
	10	7.58 ± 0.34	0.54 ± 0.02	2.25 ± 0.05
p-CH ₃ O	0	0.73 ± 0.02	0.40 ± 0.01	1.10 ± 0.03
	10	2.10 ± 0.06	1.10 ± 0.03	2.91 ± 0.08
p-NO ₂	0	91.22 ± 10.92	15.54 ± 0.80	20.20 ± 1.25
	10	95.08 ± 13.30	22.60 ± 1.24	24.07 ± 1.50

Consequently the rate calculations were based on the initial reaction stages. The rate constants are summarized in Table 1.

Benzenesulfonylbromides underwent essentially no hydrolysis during extraction. The rate data were obtained by averaging results of 7 runs for each exchange reaction and the standard deviations were calculated. The specific rate constants did not possess the same degree of accuracy. The standard deviations of the rates were 3~4% except for the reaction of p-nitrobenzenesulfonylbromide at which the error was upto 15% due to the increased rate in given temperature and concentrations of the reagents. However, such errors in the rates do not seriously affect the discussion.

As Table 1 shows, the exchange rate for the electron donating substituent increases in the order, $I^- \gtrsim Cl^- > Br^-$, and that for the electron withdrawing substituent increases in the order $Cl^- > I^- \gtrsim Br^-$. The exchange rates for Br^- are always the smallest. The rates for the sulfonylbromide with no substituent, and those for p-toluenesulfonylbromide increase in the order, $Cl^- > I^- > Br^-$, which is consistent with that of the electron withdrawing substituent, but the rate differences between Cl^- and Br^- were not large. It is interesting to

note that the nucleophilicity order of halides for benzenesulfonylbromide with the electron withdrawing substituent is the same as that of benzenesulfonylchloride with the electron withdrawing substituent¹⁹).

Lee *et al.*³⁷⁾ argued that the nucleophilicity order of $\text{Cl}^- > \text{Br}^- > \text{I}^-$ in dry acetone is dictated by the easiness of desolvation of halide ion. However, both desolvation and polarizability are important in determining the nucleophilicity of anionic nucleophiles, and they are competitive. The nucleophilicity is also affected by the property of the reaction center. Thus, the order of nucleophilic reactivity found in this work seems to show the importance of both polarizability and the nature of the reaction center. If desolvation were the sole factor in determining the nucleophilicity order, we would expect the order to be, $\text{Cl}^- > \text{Br}^- > \text{I}^-$, while polarizability were the sole factor, $\text{I}^- > \text{Br}^- > \text{Cl}^-$ is expected. Since bromide is more polarizable than chloride, it is reasonable to expect that the polarizability of the sulfur center is increased in benzenesulfonylbromides as compared with in benzenesulfonylchloride. Therefore, according to the HSAB principle, soft-soft interaction will increase the rate and may well overwhelm the desolvation effect in determining the nucleophilicity order. This could result in the acceleration of I^- exchange rate and depending on the softness of reaction center, either I^- or Cl^- becomes the most reactive nucleophile of the three halides. At any rate, our result clearly show the importance of polarizability effect besides the desolvation effect in determining the nucleophilicity.

The Substituent Effect

Hammett plot (Fig. 3) shows that for all nucleophiles (Cl^- , Br^- , I^-) the electron donating substituent decreases the rates while the electron withdrawing substituent increases them.

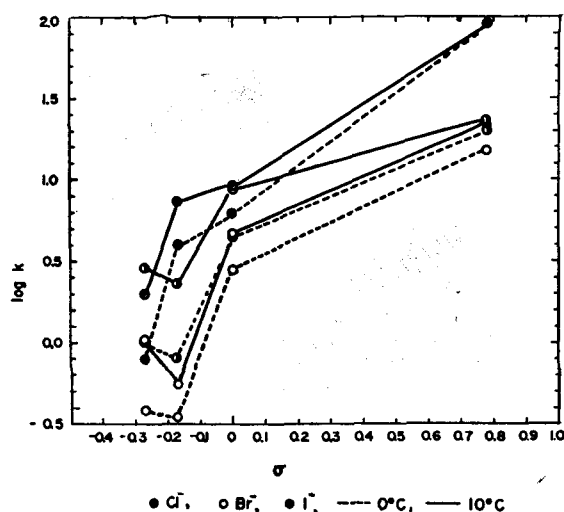


Fig 3. Hammett plot in this work

Rate decrease is extreme in case of p-CH_3 substituent for Br^- exchange, and the rate increase is the largest for p-NO_2 substituent in Cl^- exchange. The fact that the rate increases with electron withdrawing substituent and the rate decreases with electron donating substituent agrees with the generally known trend for $\text{S}_{\text{N}}2$ mechanism.

Roughly convex nature of the Hammett plot also agrees with the one obtained for isotopic exchange of substituted benzenesulfonylchlorides¹⁹), but quite different from the concave nature reported for reaction of benzyl halides in dipolar aprotic solvents^{37, 39}). Both reactions are considered to proceed via $\text{S}_{\text{N}}2$ mechanism.

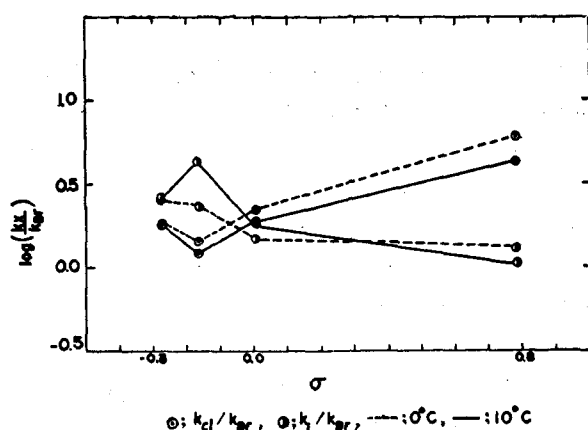
Slightly convex nature of our result may be considered as a characteristic for the benzenesulfonylhalide¹⁹) since it is common to both benzenesulfonylchlorides and benzenesulfonylbromides. For the former, Yie has concluded that the mechanism of halide exchange proceeds via $\text{S}_{\text{N}}2$ process.

Relative Rate Constants

The relative rate constants, $k_{\text{x}}/k_{\text{Br}}$, where $\text{x}=\text{I}$ or Cl , are given in Table 2, and $\log(k_{\text{x}}/k_{\text{Br}})$ vs. substituent constants are plotted

Table 2. Summary of relative rate constants in dry acetone

R	Temp. (°C)	k_{Cl}/k_{Br}	k_I/k_{Br}
p-H	0	2.24 ± 0.05	1.57 ± 0.05
	10	1.90 ± 0.06	1.87 ± 0.06
p-CH ₃	0	1.24 ± 0.05	2.36 ± 0.04
	10	1.40 ± 0.06	4.16 ± 0.04
p-CH ₃ O	0	1.82 ± 0.04	2.75 ± 0.04
	10	1.90 ± 0.04	2.64 ± 0.04
p-NO ₂	0	5.58 ± 0.13	1.30 ± 0.12
	10	4.20 ± 0.15	1.06 ± 0.08

Fig. 4. Hammett plot for kx/k_{Br}

in Fig. 4.

It can be seen from Fig. 4 that the electron donating substituent, p-MeO and p-CH₃, enhances rate of exchange with I⁻ while the electron withdrawing substituent, p-NO₂, enhances rate of exchange with Cl⁻. This is in accord with the HSAB principle since electron donating substituent makes the sulfur center softer while electron withdrawing substituent makes it harder as compared with the unsubstituted compound. Alternatively, we can rationalize the results as follows; the electron donating substituent makes the sulfur center sufficiently soft that soft-soft interaction becomes significantly large in the case of

I⁻ exchange, while for other compounds the rate of Cl⁻ exchange is larger simply due to the easiness of desolvation in the transition state formation.

The scrambling in the order of nucleophilicity is considerably more significant in benzenesulfonylbromide with electron donating substituent as compared with benzenesulfonylchloride since bromide is more polarizable than chloride as described above.

Leaving Group Mobility

The reactivity of benzenesulfonylbromide is generally higher than that of benzenesulfonylchloride¹⁹⁾ and much higher than that of benzyl chloride³⁹⁾. The fact may be attributable to the weakness of the S-Br bond comparing S-Cl or C-Cl bond⁴⁰⁾. The sulfur center of the benzenesulfonylbromide may interact with nucleophile rather strongly in the longer ranges than the carbon center of benzyl chloride does. Consequently, the bond formation between sulfur and nucleophile would be easier in the activated complex. The normal ratio of leaving group ability between Br and Cl, k_{Br}/k_{Cl} , for saturated carbon center is about 50⁴¹⁾. For the reaction of benzenesulfonylhalides with alkyl, and aryl amines k_{Br}/k_{Cl} ratio is reported to be upto 10¹⁸⁾. The ratio of leaving group mobility for halide exchanges in benzenesulfonylbromides in dry acetone is given in Table 3.

The value of k_{Br}/k_{Cl} is always greater than unity which is in general accord with the expected trend. The value is, however, quite

Table 3. The relative rate constants, k_X^Y *

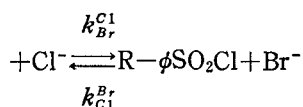
R	k_{Br}^{Cl}/k_{Cl}^{Cl}	k_{Br}^{Br}/k_{Cl}^{Br}	k_{Br}^I/k_{Cl}^I
p-H	173	4,000	14,700
p-CH ₃ O	7	130	2,200
p-NO ₂	925	2,590	1,050

* X is halogen on substrate, Y is halide nucleophile

large in some cases showing multiple factors are involved in determining reactivities. Among them, the following three are the most conceivable. Firstly, S-Br bond energy is small compared to that of S-Cl. Secondly, the sulfur center is made softer by Br atom (sympiotic effect) thereby increasing the soft-soft interaction with softer halides (Br^- and I^-). Thirdly, the transition state stabilization is greater in dipolar aprotic (soft) solvent (ie, in acetone).

The value of $k_{\text{Br}}/k_{\text{Cl}}$ is the smallest for *p*-MeO compound, which is a comparatively strong electron donating group. Since, the electron donating group will increase the electron density at sulfur center making the bond formation difficult, it may be concluded that the halide exchanges in benzenesulfonylbromide, bond formation is more important in the transition state.

Exchange Equilibrium; $\text{R}-\phi\text{SO}_2\text{Br}$



For this equilibrium, we have the rate constants for both forward and reverse reactions¹⁹⁾ and calculation of the equilibrium

constant, $K = \frac{k_{\text{Br}}^{\text{Cl}}}{k_{\text{Cl}}^{\text{Br}}}$, is now possible.

Using the k values at common temperature of 0°C the following equilibrium constants were obtained.

$\text{R} = \text{p-MeO}$	$K = 2.4 \times 10^2$
$\text{R} = \text{H}$	$K = 9 \times 10^3$
$\text{R} = \text{p-NO}_2$	$K = 1.5 \times 10^4$

In all cases, K values are greater than unity. This is in accord with our expectation since S-Cl bond is stronger than S-Br bond and therefore benzenesulfonylchloride will be more stable than benzenesulfonylbromide. *p*-Methoxybenzenesulfonyl system has the smallest K of the three listed above, and *p*-NO₂-

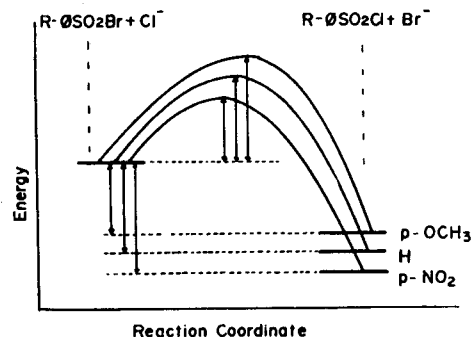


Fig. 5. Reaction energy profile

compound has the largest. The ratio of the two K values, $\frac{K_{\text{NO}_2}}{K_{\text{MeO}}}$, is approximately $\sim 10^2$, which is the approximate ratio of the rate constants for the forward reaction of the two compounds at the same temperature (0°C).

Thus, the energy profile can be roughly represented as shown in Fig. 5.

This figure gives us some important mechanistic implications. The forward reaction is exothermic, and therefore, according to the Hammond postulate^{42, 43)} the transition state has the structure more similar to the initial state (reactants) than to the products. Therefore, for the forward exchange reaction, which is, $\text{R}-\phi\text{SO}_2\text{Br} + \text{Cl}^- \rightarrow$, bond breaking and forming have not progressed to a significant degree at the transition state which may be called an "early" transition state. On the other hand, for the reverse reaction, ie, $\text{R}-\phi\text{SO}_2\text{Cl} + \text{Br}^- \rightarrow$, the transition state is similar to the products, and therefore the progress in bond-breaking and forming is relatively advanced, which may be called a "late" transition state. The latter conclusion agrees well with that of Yie¹⁹⁾. Since we are only concerned with the general trends, further detailed speculations are not warranted.

Activation Parameters

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

Table 4. Activation parameters in dry acetone

R	ΔH^\ddagger (Kcal/mole)			$-S^\ddagger$ (e. u.)		
	Cl ⁻	Br ⁻	I ⁻	Cl ⁻	Br ⁻	I ⁻
p-H	6.0 \pm 0.8(11.7)*	8.5 \pm 0.9(14.8)	10.9 \pm 1.2(17.3)	34.7 \pm 2.3	28.2 \pm 2.7	17.3 \pm 3.2
p-CH ₃	9.5 \pm 1.2	7.4 \pm 0.8	16.2 \pm 0.3	22.6 \pm 3.1	35.3 \pm 2.6	1.5 \pm 1.9
p-CH ₃ O	16.2 \pm 1.2(14.2)	15.5 \pm 1.1(13.9)	15.0 \pm 1.1(15.9)	1.7 \pm 1.6	6.2 \pm 2.0	6.0 \pm 2.1
p-NO ₂	0.6 \pm 0.4(11.1)	5.7 \pm 1.0(7.9)	2.8 \pm 0.8(10.2)	49.1 \pm 10.3	34.4 \pm 4.1	44.1 \pm 4.8

* ΔH^\ddagger for benzenesulfonylchloride¹⁹⁾

In general, ΔH^\ddagger values are small except for *p*-CH₃ compounds. Small ΔH^\ddagger values are consistent with the "early" transition state in the S_N2 mechanism. Electron donating substituent increases ΔH^\ddagger while electron withdrawing substituent decreases it. It is reasonable since the electron donating substituent makes partial bond formation difficult in transition state while the electron withdrawing substituent makes the bond formation easy. Also ΔH^\ddagger for nucleophile, Cl⁻, is generally smaller comparing those of other nucleophiles. It is in agreement with the preceding discussion. The activation entropy data show that for electron withdrawing substituent either the transition state may be more ordered or ground state more disordered, while for electron donating substituent either the transition state may be more disordered or the ground state more ordered. Thus, the partial bond formed between ArSO₂Br with electron withdrawing substituent and nucleophile in transition state is expected to be more tight than that formed between ArSO₂Br with electron donating substituent with nucleophile. This makes the leaving group ability enhancing in the transition state to get loose and disordered product. The activation parameters and the relative mobilities for the different leaving groups can be accounted for by S_N2 mechanism, and it is consistent with the preceding discussion.

Solvent Effect

The rate differences with the concentration of salt solutions were generally so small that

Table 5. Variation of rate constants and activation parameters with solvent transfer (Exchange System: C₆H₅SO₂Br+Li⁸²Br)

Solvent	Temp. (°C)	k_2 (1/mole·sec)	ΔH^\ddagger (Kcal/mole)	$-\Delta S^\ddagger$ (e. u.)
(Me) ₂ CO	0	2.8	8.5	28.2
	10	4.9		
CH ₃ CN	0	2.8 \times 10 ⁻²	10.5	27.0
	10	5.6 \times 10 ⁻²		
MeOH	0	1.4 \times 10 ⁻⁵	11.5	38.3
	10	3.2 \times 10 ⁻⁵		

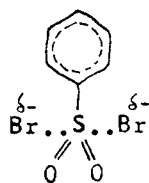
we concluded that the observed rates, k_{obs} , are not much different from the real rate, k_2 , in such dilute solutions. The measured rate constants and derived activation parameters are summarized in Table 5.

The solvent effect on rate is generally interpreted in terms of solvent activity coefficients for both reactants and transition state, in so far as the thermodynamic assumptions are valid. The solvent activity coefficients of Br⁻ with the reference solvent, methanol, at 25°C are known for various solvents⁴⁴⁾. According to the Parker's data, the *m*7CH₃CN Br⁻ is +4.2, and therefore Br⁻ is expected to react faster in CH₃CN than in MeOH. The solvation of small "hard" reactant anion decreases strongly in the order of solvent, as Parker has postulated; MeOH > CH₃CN, (Me)₂CO. It means that the rate of exchange in solvent, MeOH, will be very much slower than those in other solvent due to the high

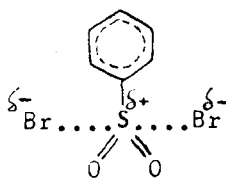
degree of solvation on nucleophile, Br^- , taking only the nucleophile into account. Methanol has structures involving hydrogen bond between rather small molecules, whereas, dipolar aprotic solvents have weaker structures and highly polarizable. Thus polar, polarizable large solutes are much more solvated by dipolar aprotic than by protic solvents.

According to the Parker's postulation, further, the solvation of polar reactants and uncharged transition states will increase in the order of solvent: $(\text{Me})_2\text{CO}$, $\text{CH}_3\text{CN} > \text{MeOH}$, and that of large polarizable $\text{S}_\text{N}\text{Ar}$ transition state anions decreases in the order; $\text{MeOH} > \text{CH}_3\text{CN}$, $(\text{Me})_2\text{CO}$.

As Table 5 shows, the rate increases with the order of solvents; $(\text{Me})_2\text{CO} > \text{CH}_3\text{CN} \gg \text{MeOH}$. This order suggests that the transition state is "tight"(I), rather than "loose"(II) in view of the transition state stabilization by solvation.



(I)



(II)

In the transition state(I), less charge is developed as compared to the transition state (II). Accordingly the solvation of the transition state will follow the order, $(\text{Me})_2\text{CO} > \text{CH}_3\text{CN} \gg \text{MeOH}$, which is precisely the order of rate constants. The extent of the change in chemical potential of bimolecular transition state, YRX^\ddagger (where R =benzenesulfonyl), with transfer from methanol to other solvents, depend on the nature of entering group, Y^- , the attacked group, R , the leaving group, X^- , the charge developed on these groups in the transition state, C , the solvent receiving the transition state from methanol, S , and

the geometry, G , of YRX^\ddagger . However, the effect of anyone of these variables can only be demonstrated if the others are hold constant, but R, C , and G are rather closely interrelated so that a rigorous treatment is difficult.

Table 6 shows differences in rates and activation parameters as the solvent is changed from methanol to dipolar aprotic solvents.

Table 6. Differences of activation parameters with solvent transfer

Solvent	$\log(k_s/k_m)$	$\frac{\Delta H_m^\ddagger - \Delta H_s^\ddagger}{(2.303)R \cdot 283}$	$\frac{\Delta S_m^\ddagger - \Delta S_s^\ddagger}{2.303R}$
$(\text{Me})_2\text{CO}$	5.3	2.3	-2.3
CH_3CN	3.3	0.7	-2.4

* ΔH_m^\ddagger , ΔS_m^\ddagger , and ΔH_s^\ddagger , ΔS_s^\ddagger are activation parameters in methanol, and in other solvents, respectively. The values are expressed in this way to be directly comparable with each other and with $\log k$; i.e., $\log k = (\Delta G^\ddagger / 2.303RT) = (\Delta H^\ddagger / 2.303RT) - (\Delta S^\ddagger / 2.303R)$

It is interesting to note that the solvent transfer from methanol to other solvents is accompanied by the decrease in activation enthalpy and the increase in activation entropy. This shows that the formation of the transition state in dipolar aprotic solvents is favored both energetically and entropically. Therefore, it can be concluded that the rate increase for the aprotic solvents is mainly due to the easiness of desolvation of the initial state, i.e., that of the attacking Br^- ion, since the transition state stabilization by solvation would involve positive $(\Delta S_m^\ddagger - \Delta S_s^\ddagger)$ values. This also indicates that the transition state structure is more similar to (I) than to (II), for in (I) desolvation of the attacking Br^- ion only is important while in (II) some degree of transition state stabilization by solvation must be involved.

We therefore conclude that bromide exchange of benzenesulfonylbromide proceeds via

S_N2 with tight transition state.

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References

- 1) J.L. Gleeve, E.D. Hughes and C.K. Ingold, *J. Chem. Soc.* 236 (1935)
- 2) A. Streitwieser, Jr., "Solvolytic Displacement Reactions", McGraw-Hill Book Co. Inc., N.Y. (1962), pp. 1-31
- 3) C.A. Bunton, "Nucleophilic Substitution at Unsaturated Carbon Atom", Elsevier Publishing Co., N.Y. (1963), pp. 1-76, and literatures cited therein.
- 4) A. Fava and A. Iliceto, *J. Am. Chem. Soc.*, **80**, 3478 (1958)
- 5) A. Fava and G. Pajaro, *ibid.*, **78**, 5203 (1956)
- 6) A. Fava, A. Iliceto and E. Camera, *ibid.*, **75**, 833 (1957)
- 7) E. Ciuffarin and A. Fava, *Progress in Phys. Org. Chem.*, **6**, 81 (1968)
- 8) W.A. Pryor, "Mechanism of Sulfur Reactions", McGraw-Hill Book Co., N.Y. (1962), p. 18
- 9) H. Phillips, *J. Chem. Soc.*, 2552 (1925)
- 10) C.R. Johnson and McCants, Jr., *J. Am. chem. Soc.*, **86**, 2935 (1964)
- 11) D.R. Rayner, E.G. Miller, P. Brickart, A.J. Gordon and K. Mislow, *J. Am. Chem. Soc.*, **88** 3138 (1966)
- 12) A.H. Fainberg and H. Winstein, *J. Am. Chem. Soc.*, **78**, 2770 (1956)
- 13) R. Foon and A.N. Hambly, *Austral. J. Chem.*, **15**, 668 (1962)
- 14) R.E. Robertson, B. Rossal, S.E. Sugamori, and L. Theindl, *Canad. J. Chem.*, **47**, 4199 (1969)
- 15) O. Rogne, *J. Chem. Soc. (B)*, 727 (1970)
- 16) H.K. Hall, Jr., *J. Am. Chem. Soc.*, **78**, 1450 (1956)
- 17) F.E. Jenkins and A.N. Hambly, *Austral. J. Chem.*, **14**, 90, 2505 (1961)
- 18) E. Ciuffarin, L. Senator, and Maruo Isolar, *J. Chem. Soc. Perkin II*, 468 (1972)
- 19) J.E. Yie and I. Lee, *J. Korean Chem. Soc.*, **17**, 154 (1973)
- 20) A.F. Cameron, G. Ferguson, and D.G. Morris, *J. Chem. Soc. (B)*, 1249 (1968)
- 21) D.M. Hawley, G. Ferguson, T.F.W. McKillop, and J.M. Robertson, *J. Chem. Soc. (B)*, 599 (1969)
- 22) R. Alexander, E.C.F. Ko, A.J. Parker, and J.T. Broxten, *J. Am. Chem. Soc.*, **90**, 5049 (1968)
- 23) R.F. Redewald, K. Mabendran, J.L. Bear, and R. Fuchs, *ibid.*, **90**, 6698 (1968)
- 24) R.G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963)
- 25) R.G. Pearson and J. Songstad, *ibid.*, **89**, 1827 (1967)
- 26) R.G. Pearson, *Science*, **151**, 172 (1966)
- 27) E.R. Thornton, *J. Am. Chem. Soc.*, **89**, 2915 (1967)
- 28) B.S. Lee, M.H. Whangbo, and I. Lee, *J. Korean Chem. Soc.*, **13**, 103 (1969)
- 29) E.R. Thornton, *J. Am. Chem. Soc.*, **90**, 1211 (1968)
- 30) A.C. Poschcus, J.E. Herweh, and F.A. Magnotta, *J. Org. Chem.*, **28**, 2766 (1963)
- 31) Charles D. Hodgman et al, "Handbook of Phys. and Chem.", 35th ed., Chemical Rubber Co., U.S.A. (1953), p. 757
- 32) Vogel, "Practical Org. Chem.", 3rd ed., Longmans Green and Co., London (1958), p. 587
- 33) E. Miller, "Methoden der Org. Chem.", 4th ed., Georg Thieme Verlag, Stuttgart (1958), p. 9163
- 34) J. Kim, *J. Korean Nuc. Soc.*, **3**, 3, 141 (1971)
- 35) Glasstone, Laidler, and Eyring, "Theory of the Rate Process", McGraw-Hill Publ. Co., (1964), p. 181
- 36) L.L. Schaleger and F.A. Long, "Advances in Phys. Org. Chem.", Vol. 1, ed. by V. Gold, Academic Press, London, (1963), p. 7
- 37) B.S. Lee, M.H. Whangbo and I. Lee, *J.*

- Korean Chem. Soc., **13**, 109 (1969)
- 38) R.A. Sneen and F.R. Rolle, J. Am. Chem. Soc., **91**, 2140 (1969)
- 39) T. Lee, B.S. Lee, and J.E. Yie, J. Korean Nuc. Soc., **3**, 198 (1971)
- 40) Gilman, "Org. Chem., Advanced Treatise". 2nd ed., Vol. 2, John Wiley and Sons Inc., N.Y. (1957)
- 41) E.M. Kosower, "Introd. to Phys. Org. Chem.", John Wile and Sons Inc., N.Y. (1968), p. 81
- 42) G.S. Hammond, J. Am. Chem. Soc., **77**, 334 (1955)
- 43) R.D. Gilliom, "Introd. to Phys. Org. Chem.", Adison Wiley Publ. Co., Reading, Mass. (1970), p. 206
- 44) A.J. Parker, Chem. Rev., **69**, 1, 1 (1969)