

벤질 할라이드의 할로겐 교환반응(제 III 보)

아세톤 중에서의 열화 및 브롬화 벤질과 브롬화 및 요오드화 이온간의 교환반응

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HALOGEN EXCHANGE REACTIONS OF BENZYL HALIDES

Part III- Kinetics of Reactions of Bromide and Iodide Ions with Benzyl Chloride and Bromide in Absolute Acetone.

by

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ABSTRACT

Halogen exchange reactions of benzyl halides have been studied in absolute acetone. Rate constants were calculated using an integrated rate expression derived for the reaction involving ion-pair association.

The order of nucleophilicity of halide ions in acetone was found to be a reverse of the order in 90% aqueous ethanol solvent. This was interpreted by means of HSAB principle and solvation of halide ions.

Net increase in rate of reaction in acetone compared with the rate in protic solvent resulted from large increase in ΔS^\ddagger rather than decrease in ΔH^\ddagger . The solvation of the transition state also contribute to the net increase in rate.

요 약

할로겐화 벤질의 할로겐 교환반응을 무수 아세톤에서 연구하였으며 반응속도상수 계산에는 새로 유도

한 적분식을 사용하였다.

아세톤 용매 속에서의 할로젠 이온들의 친핵반응성은 90%에탄올 용매 속에서의 것과 정반대 순서이며 이것은 HSAB 원리와 할로젠 이온의 solvation 으로 설명할 수 있었다.

아세톤 용매 속에서의 반응속도의 증가는 ΔH^\ddagger 의 감소보다는 ΔS^\ddagger 의 증가에 기인되며 또 전이상태의 solvation 현상도 그 원인이 될 수 있음을 논의하였다.

INTRODUCTION

In the previous reports⁽¹⁾ of this series, we have reported halogen exchange reactions of benzyl halides in a protic medium, 90% ethanol water solution, showing that the relative nucleophilicity of halide ions was in the order $I^- > Br^- > Cl^-$.

We have now chosen a typical dipolar aprotic solvent, acetone, to study the same reactions to see whether the above order of the nucleophilicity for halide ions still hold or not as is well known that the order reverses in soft solvents such as acetone.

For the solvent medium, acetone, the equilibrium between ion pairs and the separated ions.



is not displaced completely to the right.⁽²⁾ For the halogen exchange reactions of benzyl halide, in which both ions and ion pairs are involved, the rate of exchange may be represented by the equation⁽³⁾⁽⁴⁾

$$\text{Rate} = k_i \alpha [A][C] + k_p (1-\alpha) [A][C] \dots \dots \dots (1)$$

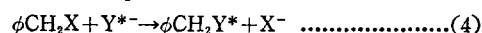
where k_i and k_p are second-order rate constants for the reactions of ions and ion-pairs respectively, α is the degree of dissociation of the salt, and $[A]$ and $[C]$ are the concentrations of benzyl halide and the total concentration of the salt, respectively. As recent work indicates the ion pairs are relatively unreactive⁽²⁾⁽³⁾⁽⁴⁾⁽⁵⁾ and thus the eq. (1) is reduced to eq. (2).

$$\text{Rate} = k_i \alpha [A][C] \dots \dots \dots (2)$$

Therefore the observed rate constant is given by⁽⁵⁾

$$k_{\text{obs.}} = k_i \alpha \dots \dots \dots (3)$$

In this work k_i is evaluated by means of a new integrated rate expression for the reaction;



in acetone.

EXPERIMENTAL

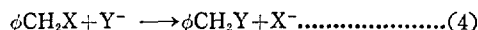
1). Material; benzyl chloride was prepared by photochlorination of toluene and benzyl bromide by

bromomethylation of benzene, as reported previously.

⁽¹⁾ Acetone (G. R.) was purified by drying over calcium chloride, distilling fractionally, and flowing through the aluminum oxide column. This treatment reduces the water content to 0.08% or less. ⁽²⁾ Radioactive bromine was obtained in ammonium bromide form from the Radioisotope Production Group of the Atomic Energy Research Institute. Ammonium bromide was converted to lithium bromide by adding equivalent amount of lithium hydroxide and evaporating the solution to dryness, which was diluted to suitable activity of Bromine 82. ⁽³⁾ Iodine 131 radioisotope used was supplied by the Radio Chemical Company in NaI form. Anhydrous acetone solutions were prepared at room temperature and protected from the moisture of the air.

2). Kinetic runs; A weighed amount of benzyl halide was dissolved in 50 ml of prepared acetone solution, quenched by means of liquid air and transferred to the ampoules. After sealing they were maintained in the thermostat at desired temperature. The extraction of benzyl halide and removal of residual salts were performed with 10 ml benzene and 5 ml distilled water for 5 ml sample. The bromine activities were measured in a well-type scintillation counter. The decay correction was made at each counting. ⁽⁶⁾

3). Determination of Rate Constants; For the exchange reaction (neglecting the reverse reaction)



from eq. (2), the rate is

$$\frac{dX}{dt} = k_i (a-x) \alpha (b-x) \dots \dots \dots (5)$$

where a and b are the initial concentration of benzyl halide and salt respectively, and x is the amount reacted at time t .

The degree of dissociation of salts, α , was substituted for by successive approximation from the mass-action law.

$$K = \frac{a^2(b-x)^2}{1-\alpha}, \text{ or } \alpha = \frac{-K \pm \sqrt{K^2 + 4K(b-x)}}{2(b-x)} \dots \dots \dots (6)$$

where K is ion-pair dissociation constant and γ is the activity coefficient, which can be considered as unity when concentration is low.

Taking plus sign of the square root,

$$\begin{aligned} \frac{dx}{dt} &= k_i (a-x) \frac{1}{2} [-K + \sqrt{K^2 + 4K(b-x)}] \\ &= \frac{k_i}{2} (a-x) \frac{1}{4K(b-x)} \frac{1}{K + \sqrt{K^2 + 4K(b-x)}} \\ &= \frac{2K k_i (a-x) (b-x)}{K + \sqrt{K^2 + 4Kb} \left(1 - \frac{4Kx}{K^2 + 4Kb}\right)^{\frac{1}{2}}} \\ &= \frac{2K k_i (a-x) (b-x)}{K + \sqrt{K^2 + 4Kb} \left(1 - \frac{1}{2} \frac{4Kx}{K^2 + 4Kb} + \frac{1}{4} \left(\frac{4Kx}{K^2 + 4Kb}\right)^2\right.} \\ &\quad \left. x^2 \dots \dots \dots\right) \end{aligned} \quad (7)$$

$$\text{As } \frac{1}{2} \left(\frac{4K}{K^2 + 4Kb}\right) x \gg \frac{1}{4} \left(\frac{4K}{K^2 + 4Kb}\right)^2 x^2,$$

rearranging the eq. (7),

$$\frac{dx}{dt} = \frac{k_i (a-x) (b-x) \sqrt{K^2 + 4Kb}}{[\sqrt{K^2 + 4Kb} + K + 4b - x]} \quad (8)$$

$$\text{let } \sqrt{K^2 + 4Kb} = D, \quad D + \frac{D^2}{K} = C,$$

$$\frac{dx}{dt} = \frac{k_i D (a-x) (b-x)}{(c-x)} \quad (9)$$

Integrating the eq. (9),

$$\begin{aligned} \left(\frac{a-c}{a-b}\right) \ln \left(\frac{a-x}{a}\right) + \left(\frac{c-b}{a-b}\right) \ln \left(\frac{b-x}{b}\right) \\ = -Dk_i t \dots \dots \dots (10) \end{aligned}$$

In case, $a \gg b$ therefore $a \gg x$, eq. (10) is simplified into⁽⁶⁾

$$\left(\frac{c-b}{a-b}\right) \log \left(1 - \frac{x}{b}\right) = -\frac{Dk_i t}{2.303} \quad (11)$$

$$\text{or } k_i = -\frac{2.303}{Dt} \left(\frac{c-b}{a-b}\right) \log (1-F) \quad (12)$$

where F is equivalent to $\left(\frac{x}{b}\right)$ in eq. (11).

Rate constants were determined using eq. (10) and (12), and early results⁽⁹⁾ were recalculated accordingly.

Ion pair dissociation constants in acetone were taken from the literature.⁽¹⁰⁾ Temperature dependence of K was neglected⁽⁴⁾⁽¹¹⁾ since it is within the accuracy of experiments when the temperature range is small as in the present work.

RESULTS AND DISCUSSION

The rate constant, k_i , for a reaction in which both ions and ion pairs are involved, is usually determined from equation (3) using an α value estimated with

salt concentration at a certain intermediate reaction time, normally at 50% completion of the reaction⁽⁵⁾ Sometimes, k_i is determined from equation⁽²⁾ with initial rate and α value calculated at initial salt concentration.⁽³⁾⁽⁴⁾ None of these methods, however, use an integrated rate expression but use a differential rate, and consequently determination of the rate constant is rather inconvenient. On the other hand, calculation of k_i with the integrated rate expression (10) derived in this work is no more complicated than the others and no unreasonable assumptions are involved in its derivation.

TABLE 1. ION PAIR DISSOCIATION CONSTANTS, K , OF VARIOUS SALTS AT 25°C⁽¹⁰⁾

Salt	$K \times 10^4$
LiCl	0.033 ± 0.001
LiBr	2.19 ± 0.07
KI	55.7 ± 0.3

TABLE 2. SUMMARY OF RATE CONSTANTS FOR THE REACTION; $\phi\text{CH}_2\text{X} + \text{Y}^- \rightarrow \phi\text{CH}_2\text{Y} + \text{X}^-$ IN ACETONE

X	Y	Temp °C	$k_i \times 10^4$ [l mole ⁻¹ sec ⁻¹]
Cl	Cl	18.6	6.11 ^(a)
Cl	Cl	25.0	26.5 ^(a)
Cl	Br	25.0	18.0*
Cl	Br	30.0	37.4
Cl	Br	40.0	163
Cl	I	24.8	16.2
Cl	I	30.0	34.0
Br	Br	-17.0	308
Br	Br	-14.8	321
Br	Br	0.0	400*
Br	I	-18.5	66.4
Br	I	-13.0	108
Br	I	0.0	330*

(a) Ref (9); Recalculated using eq. (12).

* Calculated value from the linear plot of $\log k$ vs. $\frac{1}{T}$.

Table 2 shows that the rate of halogen exchange in benzyl halide in acetone is 25 to 2500 times faster than that in 90% aqueous ethanol; ⁽¹⁾⁽⁶⁾⁽⁷⁾ benzyl chloride-chloride exchange rate increases 2500 times and benzyl bromide-iodide exchange rate increases

~25 times. These are consistent with the general rule that the rate of nucleophilic displacement reaction in a dipolar aprotic solvent is faster than that in a protic solvent. ⁽⁴⁾⁽¹²⁾⁽¹³⁾⁽¹⁴⁾⁽¹⁵⁾⁽¹⁶⁾

Comparison of activation parameters for aprotic solvent, acetone, with those of protic solvent, 90% aqueous ethanol, ⁽¹⁾ (Table 3) shows that the rate is largely controlled by the entropies of activation. Thus for exchanges in benzyl chloride ΔH^\ddagger is greater by 12 to 20 kcal in acetone while ΔS^\ddagger is also greater by about 40 e. u., which is more than enough to compensate for the unfavorable ΔH^\ddagger effect resulting net increase of rate in acetone. For exchanges in benzyl bromide, however, there is no change in ΔH^\ddagger , but there is an increase in ΔS^\ddagger of about 15. e. u. in acetone resulting also the rate increase. These findings are in direct contradiction to the result of Parker et al. ⁽¹⁵⁾⁽¹⁶⁾ Their result indicated that in bimolecular substitution reaction there was no change in ΔS^\ddagger when reaction medium was varied from protic to dipolar aprotic, and the net increase in rate accompanied with the medium change was mostly due to the decrease in ΔH^\ddagger .

TABLE 3. SUMMARY OF ACTIVATION PARAMETERS
FOR THE REACTION: $\phi\text{CH}_2\text{X} + \text{Y}^- \rightarrow \phi\text{CH}_2\text{Y} + \text{X}^-$
(A) IN ACETONE,
(B) IN 90% AQUEOUS ALCOHOL ⁽¹⁾

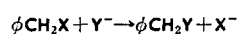
(A)			
X	Y	ΔH^\ddagger [Kcal]	ΔS^\ddagger [e. u.]
Cl	Cl	39.0 ^(a) (18.1) ^(b)	24.5 ^(a) (-18.5) ^(b)
Cl	Br	30.9	10.1
Cl	I	24.6	0.7
Br	Br	14.2	-9.7
Br	I	11.2	-15.7

(a) Ref. (9), Recalculated from the rate constants using eq. (10).

(b) Ref. (9), Value obtained without correction for ion-pair association of salt

(B)			
X	Y	ΔH^\ddagger [kcal]	$-\Delta S^\ddagger$ [e. u.]
Cl	Cl	20.2	21.6
Cl	Br	17.3	26.8
Cl	I	12.7	36.3
Br	Cl	19.4	16.8
Br	Br	15.7	24.5
Br	I	11.7	28.8

TABLE 4. RELATIVE NUCLEOPHILICITY OF HALIDE ION
FOR THE REACTION



		k_Y/k_{Br}		
X \ Y		Cl	Br	I
Cl		1.47 ^(a)	1 ^(a)	0.90 ^(a)
Br		—	1 ^(b)	0.83 ^(b)

(a) at 25°C

(b) at 0°C

They, however, seemed to have overlooked the possibility of ion-pair association of salts in dipolar- aprotic solvents, ⁽²⁾⁽³⁾⁽⁴⁾⁽⁵⁾ and this may have been the cause of the contradictory conclusion. In fact the neglect of this ion-pair association effect in the rate constant determination results erroneous ΔH^\ddagger and ΔS^\ddagger values as can be seen from Table 3 where we have listed two values for comparison.

Large increase in activation enthalpy for exchanges in benzyl chloride as compared to benzyl bromide is an indication that bondbreaking has large influence on ΔH^\ddagger in acetone solvent. ⁽¹⁾⁽¹⁴⁾⁽¹⁷⁾

Relative nucleophilic reactivity of halide ions in acetone is reported to decrease in the sequence, $\text{Cl}^- > \text{Br}^- > \text{I}^-$, ⁽¹²⁾⁽¹³⁾⁽¹⁴⁾⁽¹⁷⁾⁽¹⁸⁾⁽¹⁹⁾ an exact reverse of the order of nucleophilicity in protic solvents. Table 4 shows that the results of this work are consistent with the trend expected for acetone, i. e., the order of nucleophilicity for halide ions in exchanges of benzyl chloride is $\text{Cl}^- > \text{Br}^- > \text{I}^-$ and the order for benzyl bromide is $\text{Br}^- > \text{I}^-$.

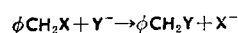
Dipolar aprotic solvents are much less structured than protic solvents and are highly polarizable. ⁽¹⁵⁾⁽¹⁶⁾ According to HSAB (Hard and Soft Acids and Bases) principle, ⁽¹²⁾⁽¹³⁾⁽¹⁸⁾ soft (dipolar aprotic) solvents should solvate strongly large, soft anions through strong dipole-dipole interactions and the London dispersion forces, while hard (strong hydrogen-bonding, protic) solvents should solvate preferentially small, hard anions. This means that in dipolar aprotic solvent Cl^- will be less solvated than I^- at the initial state and reactivity will decrease in the order $\text{Cl}^- > \text{Br}^- > \text{I}^-$ due to desolvation energies required in the formation of the transition state.

Another interesting feature to be noted in Table 4

is that the relative nucleophilic reactivity differences for halide ions are quite small compared with the differences in protic solvent reported in the previous paper.⁽¹⁾

It is known that the relative reactivity order of halide ions does not change in change of solvent from protic to dipolar aprotic if the softness of reaction center is sufficiently great.⁽¹³⁾ Very small reactivity differences observed in this work means therefore the medium softness (or borderline case) of benzyl carbon as we have correctly assumed previously.⁽¹⁾

TABLE 5. RELATIVE LEAVING ABILITY OF HALOGEN FOR THE REACTION:



$k_{\text{X}}/k_{\text{Cl}}$		
$\text{Y} \backslash \text{X}$	Cl ^(a)	Br ^(b)
Br	1	22.2
I	1	20.2

(a) at 25°C

(b) at 0°C

Table 5 shows that the relative leaving ability of bromide is about 20 times greater than that for chloride irrespective of nucleophiles. The relative insensitiveness of the leaving ability to the nucleophiles provides a good contrast with the degree of susceptibility of the leaving ability to the nucleophiles in protic solvents.⁽¹⁾

Hard solvents have the basicity leveling effect on halide ions while soft solvents have no such effect.⁽¹²⁾ But the results shown in Table 5 indicate that soft solvents have polarizability leveling (symbiotic) effect and the basicity difference becomes important in determining the reactivity difference.⁽²⁰⁾ This conclusion is of course true at the temperature studied, and the susceptibility may change at other temperatures.

Change of solvents also influences the solvation of the transition state.⁽¹⁵⁾⁽¹⁶⁾ General increase in rates of halide exchanges in acetone compared with 90% aqueous ethanol may be partly due to the increase in the transition state stabilization by increased solvation of the soft transition state by the soft solvent. For an example, in spite of the strongest solvation of I⁻ in acetone in the initial state, ΔS^\ddagger observed was the

least positive value for benzyl chloride series (Table 3A). Since ΔS^\ddagger is the difference in entropies between the transition state and the initial state, $\Delta S^\ddagger = \bar{S}_T - \bar{S}_I$, we would expect larger ΔS^\ddagger if the \bar{S}_I is smaller (or solvated stronger) as for I⁻. However, the transition state formed by the three-center overlap⁽¹⁾ including the entering I⁻ becomes softer by the symbiotic effect of the soft I⁻. This will increase the solvation of the transition state resulting smaller $-\bar{S}_T$ and ΔS^\ddagger . This type of solvent stabilization of the transition state will be absent in polar protic solvent.

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