

# Halogen Exchange Reactions of Benzyl Halides (Part I)

## Kinetics of Reactions of Chloride and Bromide Ions with Benzyl Chloride and Bromide

by

Kyung Hoon Jung, Yeon Huh\* and Ikchoon Lee

Atomic Energy Research Institute, Seoul

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벤질 할라이드의 할로젠 교환 반응(第 1 報)

鹽化 및 臭化 벤질과 鹽素 및 臭素이온과의 反應速度

原子力研究所 化學研究室

鄭景薰·許淵\*·李益春

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### 要 約

Benzyl chloride 및 bromide 와 chloride 및 bromide ion 間의 反應을 90% ethanol 용액에서 反應속도론적으로 연구하였다. 반 정량적인 결과의 해석은 bond-formation 이 bond-breaking 보다 더 중요하고 또 결합형성 과정에서는 형성으로 얻은 energy 보다는 nucleophile 의 electron affinity 의 증가로 인한 차이가 더 중요함을 보여주고 있다.

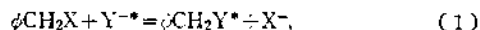
### Abstract

Kinetics of reactions of chloride and bromide ions with benzyl chloride and bromide have been investigated in 90% ethanol solution. Semi-quantitative analysis of the results shows that the bond-formation is more important than the bond-breaking and furthermore in bond-formation the energy gain due to bond-formation is less than the increase in electron affinity of the nucleophile.

### Introduction

A number of works on halogen exchanges both in alkyl<sup>1)</sup> and aryl<sup>2)</sup> systems have been reported. We have reported previously a preliminary work on chlorine exchange between benzyl chloride and radiochloride ion in 90% ethanol-water solution<sup>3)</sup>. Due to the complexities that may be resulted from the accompa-

nying solvolysis reaction, most of the previous works have been conducted in acetone solution. It is however known that acetone differs from other media of reaction due to its relatively low dielectric constant. We have chosen in this work 90% ethanol-water mixture, and the halogen exchanges have been investigated for the reaction,



where X and Y were Cl and Br.

\* Department of Chemistry, Pusan National University.

## Experimental

### 1. Materials:

Benzyl bromide was prepared by photobromination of toluene and purified by distillation under reduced pressure. B. p. 4 84°~86°C (lit. 198°C<sup>4</sup>),  $n_D^{20}=1.5742$ . Radioactive bromine was obtained ammonium bromide form from the radioisotope production group of this Institute. Ammonium bromide was converted to sodium bromide by adding equivalent amount of sodium hydroxide and evaporating the solution to dryness, which was then diluted to suitable activity of bromine-82. By cooling sufficient period short-lived activity of bromine-80 was eliminated. The decay of bromine-82 activity during the run was corrected for. Other materials used were as reported previously.<sup>3</sup>

### 2. Kinetic Runs:

Procedures were as described previously<sup>3</sup> except for the points noted below.

The extraction of benzyl bromide prior to titrations of halide ions in aqueous layer was carried out twice with 20ml. of *n*-heptane. This was found to be sufficient to remove interference caused by the solvolysis of benzyl bromide during titration. Bromine activity was counted with a well type scintillation counter. Counting rate was high enough so that the error could be kept to less than 1% with 1-2 minute counting. Distribution coefficient of benzyl bromide between *n*-heptane and 90% ethanol was determined by titration of solvolyzed bromide ion after extraction of known concentration of benzyl bromide in *n*-heptane and was found to be,

$$K = \frac{(\phi\text{CH}_2\text{Br})_{\text{eth.}}}{(\phi\text{CH}_2\text{Br})_{\text{hept.}}} = 0.84$$

### 3. Determination of Rate Constant:

For isotopic exchange reaction, i.e., X=Y, the same procedure was adopted as described previously<sup>3</sup>, using the expression,

$$k_x = -\frac{2.303 \log (1-F)}{(a+b)t} \quad (1)$$

where  $a$  and  $b$  are the initial concentrations of benzyl halide and halide ion, and

$$F = \frac{\text{Spec. Act. of } \phi\text{CH}_2\text{X at } t}{\text{Spec. Act. of Total X}}$$

For displacement reactions, i.e., for which X and Y differed, similar integrated rate equation as (1) was obtained from the standard second-order rate expression

$$k_2 = \frac{1}{(a-b)t} \ln \frac{b(a-x)}{a(b-x)} \quad (2)$$

where  $a$  and  $b$  are the initial concentrations of benzyl halide and halide ion. Since in all cases  $a \gg b$ , (about hundred-fold difference) and therefore  $a \gg x$ , equation (2) can be simplified into,

$$k_2 = -\frac{2.303}{a \cdot t} \log \left(1 - \frac{x}{b}\right) \quad (3)$$

where  $\frac{x}{b}$  represents the fraction reacted at time  $t$  and in this respect it is equivalent to  $F$  in equation (1). Since this quantity is a ratio, radioactivity can be used provided the condition be kept constant. In the case of reaction accompanying measurable side reactions, however, the observed counting rate does not represent the true value. The benzyl halides we have studied showed measurable but not too serious side effect due to solvolyses, and therefore in application of equation (3) this was corrected for as follows:

Let  $\rho$  be the concentration of benzyl halide solvolyzed at  $t$  and the observed value of  $x$  be  $x_0$  at this time. It is reasonable to assume that the loss of product due to  $\rho$  is proportional to  $\rho$  and may be approximated as  $x - x_0 = \left(\frac{x}{a}\right) \rho$ , giving  $x = \frac{a}{a-\rho} x_0$ , and  $1 - \frac{x}{b}$

$= 1 - \frac{x_0/a - \rho}{b/a} = 1 - f_t$ . At the initial stage of the reaction, up to about 30~50%, where we have ceased to follow the reactions, no serious error would be introduced by using this expression since  $\rho$  was small and  $x_0$  did not differ appreciably from  $x$ . That this is reasonable has been shown by excellent linearity of the plot  $\log (1-f_t)$  vs.  $t$ . In all cases we have used only the initial part of the rate curves in order to avoid complications due to the increase of the salt concentration. For the reaction of bromine isotopic exchange, we have varied the initial concentration of the salt,  $b$ , up to ten-fold, and found that  $k_x$  was constant to within the experimental error.

Rate constants and activation parameters were determined as reported previously<sup>3</sup> except that the least squares method was applied in the determination of activation energies.

A typical kinetic run is given in Table I and the rate constants are summarized in Table II. Activation parameters obtained in these studies are summarized in Table III. together with the data for chlorine isot-

opic exchange reaction.

Table I

Kinetic Run for  $\phi\text{-CH}_2\text{Br} + \text{Cl}^- \rightarrow \phi\text{-CH}_2\text{Cl} + \text{Br}^-$  at  $25^\circ\text{C}$  ( $\pm 0.05^\circ\text{C}$ ).

Reaction Period (hr.)	Counting Rate (cpm)	Total Halide Ion (M./l.) ( $\times 10^3$ )	$\phi\text{-CH}_2\text{Br}$ (M./l.)	$1-f_t$	$k_x$ (l/mole·sec.)
0	(7981)	—	—	—	—
1	490	6.16	0.236	0.912	$7.62 \times 10^{-5}$
2	959	7.58	0.236	0.826	
3	1401	8.38	0.234	0.746	
4	1605	9.29	0.2335	0.708	
5	1986	11.4	0.233	0.637	
6	2156	12.8	0.232	0.603	
8	2535	13.6	0.231	0.532	

Initial concentration of benzyl bromide: 0.336 M/l.

Initial concentration of sodium chloride:  $3.81 \times 10^{-3}$  M/l.

(a): Corrected for back ground, dead time loss and self absorption, cpm/10ml. Heptane.

(b): Total halide ion concentration,  $(\text{Br}^-) + (\text{Cl}^-)$ .

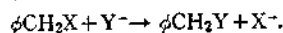
(c):  $\phi\text{-CH}_2\text{Br}$  in 10ml. of *n*-Heptane used in extraction.

(d):  $f_t = \frac{x_0/a - a}{b/a}$ ; see text.

(e): Original counting, which was corrected for back ground, dead time loss and self absorption. For cpm/5ml. EtOH.

Table II

Summary of Rate Constant for



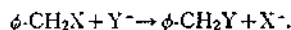
X	Y	$k_x$ (a)			$k_{50}$
Cl	Cl	—	—	—	$2.83 \times 10^{-5}$ (b)
Cl	Br	45°	55°	65°	$1.88 \times 10^{-4}$
		$1.21 \times 10^{-4}$	$2.92 \times 10^{-4}$	$6.48 \times 10^{-4}$	
		25°	35°	40°	
Br	Cl	25°	35°	40°	$1.03 \times 10^{-3}$
		$7.62 \times 10^{-5}$	$2.15 \times 10^{-4}$	$3.94 \times 10^{-4}$	
		30°	35°	40°	
Br	Br	$9.43 \times 10^{-4}$	$1.26 \times 10^{-3}$	$2.30 \times 10^{-3}$	$4.94 \times 10^{-3}$

(a): Calculated. Standard deviation was 3%.

(b): Taken from Ref. (3).

Table III

Summary of Activation Parameters for



X	Y	$\Delta H^\circ$ (Kcal) (a)	$-\Delta S^\circ$ (e. u.) (b)
Cl	Cl	20.2 (c)	21.6 (c)
Cl	Br	17.3	26.8
Br	Cl	19.4	16.8
Br	Br	15.9	24.5

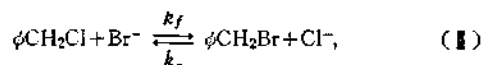
(a): Standard deviation was 0.06 Kcal.

(b): Standard deviation was 0.2 e. u.

(c): Taken from Ref. (3).

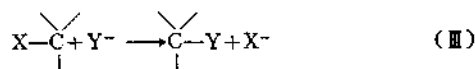
### Results and Discussion

Rates of reactions were first order with respect to each reacting species in all cases. The rate of exchange is fastest for the reaction between benzyl bromide and bromide ion, and slowest for that between benzyl chloride and chloride ion. To show the relative velocity of the reactions, we have calculated the reaction constant at  $50^\circ\text{C}$  and given in Table II. From these rate constants at a common temperature, we can obtain equilibrium constant  $K = k_f/k_r$  for the reaction, (I).



The calculated equilibrium constant was 0.18 at  $50^\circ\text{C}$ , which was comparable to that of Johnston et al.,<sup>5)</sup> for the reaction,  $\text{CH}_2\text{ClCOOH} + \text{HBr} \rightleftharpoons \text{CH}_2\text{BrCOOH} + \text{HCl}$ , in 95% dioxane solution, which was 0.209 at  $50.6^\circ\text{C}$ .

The data reported here are too limited for the quantitative analysis of the energies involved in the activation processes of bimolecular displacement at saturated centers but some semi-quantitative results may be deduced. Moelwyn-Hughes<sup>6)</sup> treated the activation energy of bimolecular displacement reaction between ion and polar molecule mainly with the energy needed for desolvation of nucleophile ion and the polar molecule. On the other hand Hudson<sup>7)</sup> gives the energy change in forming transition state for the same type of reaction, (II), by equation (4), for the fixed bond energy of C—X as  $\text{Y}^-$  was varied.



$$\Delta E^* = \alpha \Delta H_Y + \beta E_Y - D_{\text{C-Y}} + C, \quad (4)$$

where  $\Delta H_Y$  is the solvation energy of the nucleophile Y,  $E_Y$  is the electron affinity of Y,  $D_{C-Y}$  is the bond dissociation energy of C—Y bond  $\alpha, \beta, \gamma$  and C are the constants.

For the reactions between  $\phi\text{-CH}_2\text{X}$  and  $\text{Y}=\text{Br}$  and  $\text{Cl}$ , we can look at the energies needed by considering the various factors as listed in Table IV.

Table IV

Y <sup>-</sup>	$\Delta H_Y$ <sup>(8a)</sup> (Kcal)	$E_Y$ <sup>(8b)</sup> (Kcal)	$D_{C-Y}$ <sup>(8c)</sup> (Kcal)
Cl <sup>-</sup>	67	88	68
Br <sup>-</sup>	58	82	51
$\Delta(\text{Cl}^- - \text{Br}^-)$	9	6	17

Thus the activation energy difference for the reactions between fixed benzyl halide and varying nucleophile from Cl to Br can be expressed as

$$\Delta\Delta E^* = 9\alpha + 6\beta - 17\gamma, \quad (5)$$

Our experimental value gives  $\Delta\Delta E^* = 2.9$  Kcal for benzyl chloride and  $\Delta\Delta E^* = 3.5$  Kcal for benzyl bromide. This simply shows that for the reactions we have studied the contribution of  $D_{C-Y}$  to the activation energy is small compared to that of desolvation and electron affinity of Y<sup>-</sup>, i.e.,  $\gamma$  is small compared to  $\alpha$  plus  $\beta$ . This in turn can be expressed as the less gain in bond energy,  $D_{C-Y}$ , compared with the increase in electron affinity as Y is changed from Br to Cl. This has been correctly assumed by Hudson for reactions at saturated centres<sup>7</sup>.

On the other hand keeping Y<sup>-</sup> constant, we contain about 1 Kcal difference in  $\Delta E^*$  as X is changed from Cl to Br. i.e.,

$$\Delta\Delta E^* = \Delta E^*(\phi\text{CH}_2\text{Cl}) - \Delta E^*(\phi\text{CH}_2\text{Br}) = 1\text{Kcal.}$$

Thus the energy difference associated with the bond-breaking may not contribute to the activation energy,

$\Delta E^*$ , as much as the energy associated with the nucleophile Y<sup>-</sup> in bond-formation at the transition state. Entropies of activation are also mainly dictated by the loss of entropies of halide ions. Entropy of bromide ion in water is about 6 e. u. larger than that of chloride ion<sup>9</sup>, while about the same magnitude of  $\Delta S^*$  difference is shown as Y<sup>-</sup> is changed.

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