DAEHAN HWAHAK HWOEJEE
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HALOGEN EXCHANGE REACTIONS OF BENZYL HALIDES

Part II-Kinetics of Reactions of Iodide Ion with Benzyl Chloride and Bromide in 90% Ethanol-water

by

Bon-su Lee, Myung-hwan Whangbo and Ikchoon Lee

Department of Applied Chemistry, College of Engineering
Seoul National University

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벤질 할라이드의 할로겐 교환반응(제 II 보)

90% 에탄올 용액에서의 염화 및 브롬화 벤질과 요오드화 이온 간의 교환반응 속도

서울대학교 공과대학 응용화학과

이 본수 · 황보 명환 · 이 익춘

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요 약

전보에 이어 90% 에탄올 용액에서의 염화 벤질 및 브롬화 벤질과 요오드화 이온 간의 교환 반응을 연구하였다. HSAB 이론을 도입하여 할로겐화 이온의 *pd* 혼합 궤도가 서로 겹치는 전이 상태로써 실험 결과를 설명하였다.

INTRODUCTION

In the previous paper,[1] we have reported that bond-formation step in the SN2 reaction was more important than bond-breaking step, confirming the general trend that the rate of SN2 reaction is largely controlled by the nucleophilicity of nucleophiles and the leaving ability of leaving groups contribute less to the rate of reaction.

The nucleophilic reactivity has been expressed as functions of both basicity and polarizability of the nucleophiles by Edward,[2][3] whose attempt to generalize the nucleophilic reactivity has been extended by Pearson [4][5] to the principle of HSAB (hard and soft acid and base).

In this work, we are reporting the kinetics of iodide

exchange reactions in benzyl halides in 90% ethanol water mixture.

$$\phi CH_2Cl + I^{*-} \longrightarrow \phi CH_2I^* + Cl^- \quad (1)$$

$$\phi CH_2Br + I^* \longrightarrow \phi CH_2I^* + Br^- \quad (2)$$

Results are analyzed in the light of HSAB principle and a new transition state model has been presented.

EXPERIMENTAL

1. Materials; Same as reported previously except the following. [1][6]

Radioisotope I^{131}; About 1μc of I^{131} was used in NaI form for each run. The concentration of radioactive iodine incorporated into benzyl iodide by substitution was determined by γ counting with welltype seintillation counter. [1] Since half-life of 8 days was long enough as compared with the period of kinetic run, the decay during the run was ignored.

2. Kinetic runs and determination of rate constants: Procedures adopted were the same as described previously. [1][6] Distribution coefficient of benzyl iodide between *n*-heptane and 90% ethanol was assumed to be the same as that for benzyl bromide, i. e., K= 0.84. [1]

RESULTS AND DISCUSSION

The reaction is overall second-order, first-order with respect to each reactant. Rate constants determined are listed in Table1. Activation parameters, $\triangle H^{\neq}$ and $\triangle S^{\neq}$, were calculated using equations (3) and (4), (7) and are summarized in Table 2 with other relevant data.

$$k = \left(\frac{kT}{h}\right) \exp(-\triangle H^{\neq}/RT) \cdot \exp(\triangle S^{\neq}/R) \quad \ldots\ldots(3)$$

$$\triangle H^{\neq} = \frac{2.303RT_1T_2}{T_2 - T_1} \log(k_2T_1/k_1T_2) \quad \ldots\ldots(4)$$

TABLE 1. RATE CONSTANTS FOR THE REACTIONS:

(A) $\phi CH_2Cl + I^- \longrightarrow \phi CH_2I + Cl^-$

Temp [°C]	$k_2 \times 10^5$ [l mole^{-1} sec^{-1}]
30	5.22
40	10.6

(B) $\phi CH_2Br + I^- \longrightarrow \phi CH_2I + Br^-$

Temp [°C]	$k_2 \times 10^5$ [l mole^{-1} sec^{-1}]
0	300
10	135

TABLE 2. SUMMARY OF ACTIVATION PARAMETERS FOR THE REACTION:

$\phi CH_2X + Y^- \longrightarrow \phi CH_2Y + X^-$ at 50°C

X	Y	$\triangle H^{\neq}$ [kcal]	$-\triangle S^{\neq}$ [e. u]
[a] Cl	Cl	20.2	21.6
[a] Cl	Br	17.3	26.8
[b] Cl	I	12.7	36.3
[a] Br	Cl	19.4	16.8
[a] Br	Br	15.7	24.5
[b] Br	I	11.7	28.8

(a) Yong Ja Park and Ikchoon Lee, This Journal 2, 148 (1965)
(b) Present work.

From this table, we note two different trends that when nucleophiles are varied in the sequence Cl^-, Br^- and I^-, both enthalpy and entropy of activation decrease, while there is an increase in $\triangle S^{\neq}$ and decrease in $\triangle H^{\neq}$ when leaving group is changed from Cl^- to Br^-. This indicates that in the case of variation of nucleophiles the rate increase is entirely due to favorable $\triangle H^{\neq}$, but in the case of change in leaving group, the rate increase is partly due to favorable $\triangle S^{\neq}$. It appears that $\triangle S^{\neq}$ is an important factor determining leaving ability of the leaving group. The entropy of activation has indeed been correlated to the electronegativity of the leaving group. The larger negative $\triangle S^{\neq}$ observed for the leaving group Cl^- as compared to that for Br^- supports this view and this is also in accord with the result of Fife et al. [8]

According to Table 3, the relative nucleophilicity[9] of nucleophiles increases in the order $Cl^- < Br^- < I^-$, which is exactly the order predicted by the principle of HSAB. [2][4][5] In their attempt to generalize nucleophilic reactivity, Pearson and coworkers found that polarizability and basicity contribute independently in determining reactivities of nucleophiles. [2] They classified all the Lewis acids and bases into two classes, [4] soft and hard, according to whether they are polarizable or non-polarizable, and then generalized a principle[5] that soft acids are more reactive toward soft bases and so are hard acids with hard bases.

Large halide ions have low-lying excited states and therefore they are easily polarizable, i. e., they are soft bases. Softness is the greatest with the most

TABLE 3. RELATIVE NUCLEOPHILICITY OF HALIDE ION FOR THE REACTION:

$\phi CH_2X + Y^- \longrightarrow \phi CH_2Y + X^-$

X \ Y	K_Y/K_{Cl}* Cl	Br	I
Cl	1	6.6	7.2
Br	1	4.8	45.1

* Calculated value at 50°C from the linear plot of log k vs. $\frac{1}{T}$

polarizable I^- ion and decreases in the order $I^- > Br^- > Cl^-$. On the other hand, a methyl carbonium ion, CH_3, is known to be a medium soft acid. [5] Substitution of one hydrogen atom by phenyl group would not change the softness of the carbonium ion greatly, and thus benzyl ion is also expected to be on the soft side. If this is so, HSAB principle requires that reactivities of halides to benzyl carbon should increase with the softness of halide, i. e., in the order $I^- > Br^- > Cl^-$, which was in fact what we have found in this work. Thus the reactivity order obtained in this work for halide ions is consistent with the HSAB principle. [4][5][10][11]

We can also see from Table 3 that the relative nucleophilicity is more sensitive to the softness of the nucleophiles when the leaving group is changed from Cl^- to Br^-. This has been called the symbiotic effect, [5] which is in essence a preference for a soft substituent near the reaction center by a soft nucleophile. A soft substituent increases the softness of reaction center and thus increases the reactivity of soft nucleophile toward the reaction center. On the other hand the same effect is also observed for the leaving ability when we increase the softness of nucleophiles, as can be seen from Table 4.

TABLE 4. RERATIVE LEAVING ABILITY OF HALOGEN FOR THE REACTION

$\phi CH_2X + Y^- \longrightarrow \phi CH_2Y + X^-$

Y \ X	K_X/K_{Cl} Cl	Br
Cl	1	36.4
Br	1	26.3
I	1	228

For the nucleophile, Cl^-, relative leaving ability is $Br^- > Cl^-$, but it becomes accentuated to $Br^- \gg Cl^-$. for the nucleophile I^-. Thus it is also true that when the softness of nucleophile increases, leaving ability of the leaving group increases resulting an increase in rate. This type of effect was explained by Pitzer[13] in terms of the transition state stabitization due to the London or dispersion force proportional to the product of polarizabilities and $1/r^6$. Pearson and coworkers presented the symbiotic effect simply as a consequence of their HSAB principle without giving any detailed analysis.

We propose a model for the symbiotic stabilization of the transition state as follows. Large halides highly polarizable due to their low-lying excited (d) states, which will readily form hybrid orbitals with p srates of the following types.

$$\Psi^+_{hal} = \frac{1}{\sqrt{1+\lambda^2}}(\Psi_p + \lambda\Psi_d) \quad \text{.....(5)}$$

$$\Psi^-_{hal} = \frac{1}{\sqrt{1+\lambda^2}}(\Psi_p - \lambda\Psi_d) \quad \text{.....(6)}$$

These two pd hybrid orbitals are as shown in Fig. 1, and only one of these two is occupied as long as the halide ion is not participating in any reaction. However, when halide ion attacks the reaction center of the benzyl halide it will be easy for the empty hybrid orbital to approach the reaction center and form an orbital overlap rather than the occupied orbital approaching the reaction center. This type of overlap avoids the Pauli repulsion and improves interpenetration. The situation is essentially the same as that proposed by Edward et. al., [2] for the reaction of iodide ion with a peroxide. What is different in this case is that the leaving group can also have two pd hybrids which will also form a orbital overlap with the central p orbital as shown in Fig. 2. As reaction proceeds, the electron in the entering halide will shift to the empty orbital pushing the electron in leaving halide into its empty orbital. Now the role of the two pd hybrids in each halide has changed in the three center overlap, i. e. originally empty orbitals are now occupied. The transition state, i. e., the three-center molecular orbital will be stabilized by more polarizable, or softer, nucleophile or/and leaving group, and when both nucleophile and leaving

group are soft, stabilization of transition state by three center orbital overlap will be most effective. This will of course result increase in the rate of reaciton.

with the simple conventional type of NS2 transition state.

The present model does not change the argument concerning the Walden inversion involved in SN2

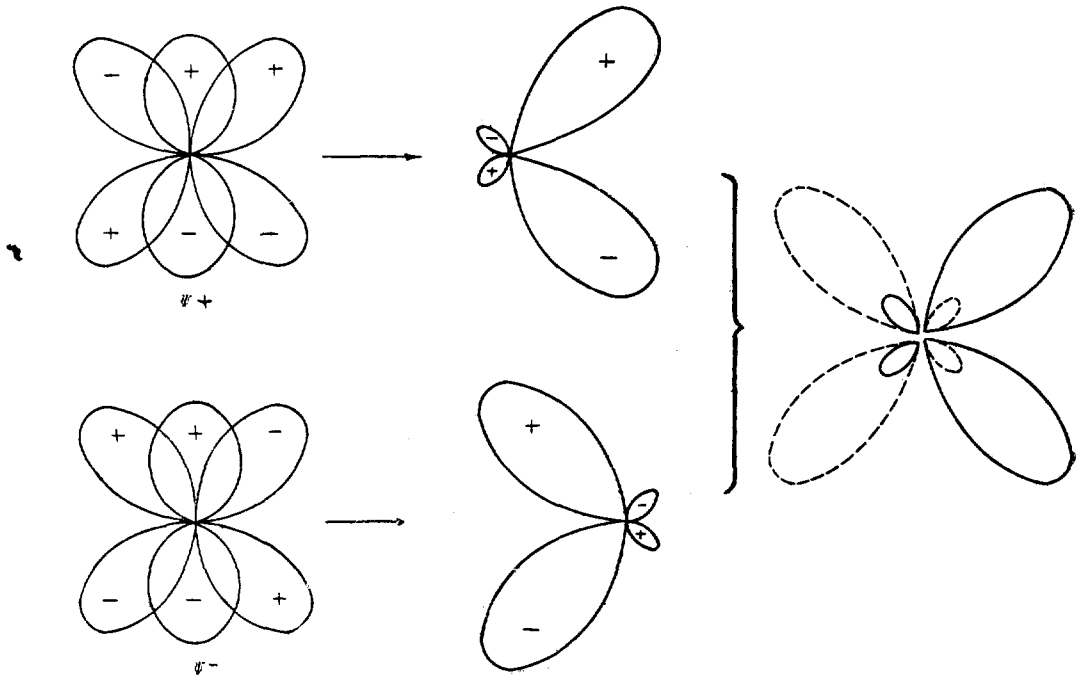

Fig 1. Schematic diagram of pd hybrid .....empty orbital, ——filled orbital.

The SN2 transition state model proposed above is quite different from the conventional one, (Fig. 3B), [12][14] since the incoming and outgoing groups use pd hybrids.

Notable consequences of this model will be; (a) two π-type lobes formed by the three-center overlap are exactly above the corresponding π-lobes of benzene ring. This will increase the inter-overlapping of π-orbitals and therefore the effect of ring substituent will be greater than we would expect from the conventional model. (b) stereochemical role of peri-hydrogens or -substituents will be more important, since the entering and leaving groups will interfere more with them. (c) symbiotic effect can be nicely explained by ease of formation of three-center molecular orbital. It will be difficult to explain this effect mechanism since the fact that nucleophile must approach from the opposite side to the leaving group has not changed. On the other hand the increased reactivity of allyl, benzyl and phenacyl halides are easily understood by the transition state stabilization by increased overlap of the three-center orbital with the p orbital on the adjacent sp^2 carbon atcm.

In this respect, Dougherty's PMO (Perturbation Molecular Orbital) approach[15] to displacement reactions is very interesting. He proposed two types of transition states for displacement with and without inversion at carbon. These two transition states A and B are approximated by the cyclopropenyl and allyl MO systems as shown in Fig. 3. The transition state B is not exactly the allyl system but the one with phase inversion at the central carbon. With the tran-

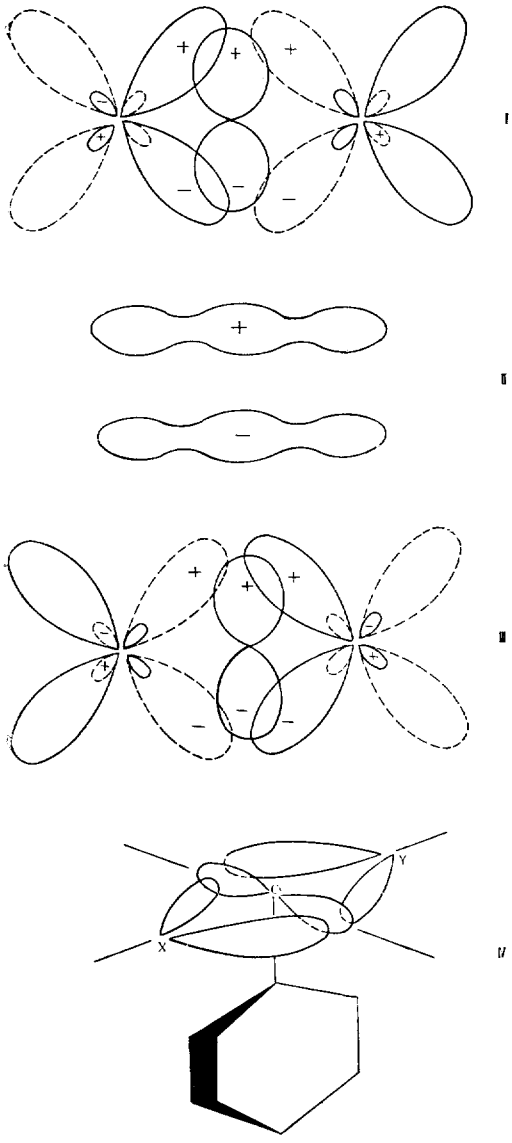

Fig 2. Transition State model
I. Bond formation stage
II. Transition state (Top view)
III. Bond breaking stage
IV. perspective view

sition state model proposed in the present work, however, we no longer need this type of phase inversion and moreover the above two MO models, A and B, are actually combined in one accommodating

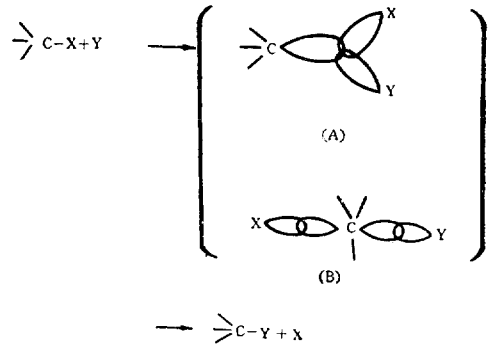

Fig 3. (A) Pseudo cyclopropenyl transition state
(B) Pseudo allyl transition state

the both MO characteristics. As Dougherty proposed, our model of the three-center M. O. transition state requires negative 1-3 β, i. e., bonding overlap of the 1-3 MO′ s, and the degree of 1-3 overlap determins the degree of stabilization of the transition state.

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