

◀Original▶ Kinetic Studies on the Halide Exchange Reactions of Some Substituted Benzyl Chlorides

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Abstract

Kinetic studies on the halide exchange reactions of some substituted benzyl chlorides have been carried out using radioisotope tracer halide ions. Results are consistent with our previous conclusion that the rates of halide exchange reactions in acetone with arylmethy halides are dictated by the polarizabilities of both substrate and nucleophile.

요 약

방사성 동위원소로 표지된 할라이드 이온과 염화벤질간의 할로겐 교환반응을 아세톤 용액에서 반응속도론적으로 연구하였다. 결과로 전보에서 얻은 결론대로 교환반응속도가 기질과 할라이드 이온의 편극화율에 의하여 좌우됨을 알았다.

I. Introduction

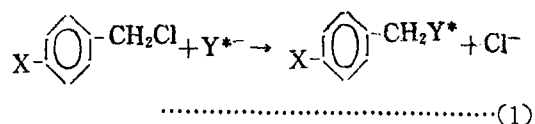
The nucleophilic substitution reaction of arylmethyl halides in various solvents has been studied extensively¹⁾, with the view to relate reactivities with structure and other external factors. Such structural and external parameters which are known to dictate reactivities are: (1) charge density at the reaction center, (2) basicity of nucleophile, (3) polarizabilities of both substrate and nucleophile, (4) steric hindrance, and (5) solvent effects involving solvations of the initial and transition states^{2, 3)}.

We have reported previously results of halide exchange reactions of arylmethyl halides

in dry acetone⁴⁾ and drawn conclusion that the solvation and the polarizabilities of halides in the ground state are the controlling factors determining relative reactivities of the nucleophiles. It has also been found that reactivities of a series of arylmethyl chlorides are linearly correlated with the nonbonding molecular orbital(NBMO) coefficients of the methyl carbon atom⁴⁾. This indicated that this type of reaction is frontier-controlled, or polarizability-controlled.

In this work we have investigated the substituent effect on the rate of halide exchange of benzyl chloride, (1), in order to gain further insights as to the structure-reactivity

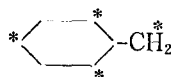
relations. Isotopically labelled halide ions were introduced in dry acetone solution and the exchanged benzyl halides were extracted and a portion of the extracts counted using a well-type or a liquid scintillation counter.



where $\text{Y}^* = \text{Cl}^{36}, \text{Br}^{82}, \text{and } \text{I}^{131}$ and
 $\text{X} = \text{p-CH}_3, \text{p-Cl}, \text{H}, \text{p-NO}_2, \text{o-CH}_3$
 and m-CH_3 .

II. Results and Discussion

Rate constants and activation parameters obtained for the three halide exchange reactions of substituted benzyl chlorides are summarized in Tables 1 and 2. Table 1 shows that substituents at active sites (starred position)⁵⁾ of benzyl system increases rates considerably while substituent at inactive site, e.g., m-Me, decreases rate. Substituents at



active site, whether they are electron-donating or electron-withdrawing groups, activate the exocyclic carbon center towards halide exchange.

Table 1. Summary of rate constants, k
 (1 mole⁻¹sec⁻¹ × 10³)

X \ Y	Temp.			Temp.		
	25°C			35.2°C		
	Cl ⁻	Br ⁻	I ⁻	Cl ⁻	Br ⁻	I ⁻
p-NO ₂	18.5	4.30	3.71	46.6	22.6	9.12
p-Cl	4.96	2.08	3.20	12.6	3.91	5.28
H	2.83 [†]	1.80 [†]	1.62 [†]	6.41 [*]	3.74 [*]	3.40 [†]
p-Me	4.52	1.95	3.02	9.82	4.95	8.07
m-Me	1.71	0.459	1.01	5.05	1.37	2.05
o-Me	10.3	2.67	4.83	23.9	10.3	8.79

conc. of substrate; $\sim 5 \times 10^{-2}$ M

conc. of salt; $\sim 5 \times 10^{-4}$ M

[†]24.8°C ^{*}30.0°C; M.H. Whangbo, B.S. Lee and I. Lee, *J. Korean Chem. Soc.*, **13**, 109(1969)

^{*}35.0°C; B.S. Lee and I. Lee, *ibid* **13**, 281 (1969)

Table 2. Summary of Activation Parameters

(A) Activation Enthalpies, ΔH^\ddagger
 (Kcal mole⁻¹)

X \ Y	Cl ⁻	Br ⁻	I ⁻
p-NO ₂	11.0	30.3	16.2
p-Cl	11.0	11.1	8.7
H	14.3 [*]	30.9 [†]	24.6 [†]
p-Me	9.1	16.7	17.7
m-Me	13.0	19.7	12.7
o-Me	10.0	24.6	12.7

(B) Activation Entropies, ΔS^\ddagger (e.u.)

X \ Y	Cl ⁻	Br ⁻	I ⁻
p-NO ₂	-29.6	32.4	-15.5
p-Cl	-32.1	-33.2	-40.7
H	-21.9 [*]	10.1 [†]	0.7 [†]
p-Me	-38.6	-14.9	-10.9
m-Me	-27.7	-7.7	-29.7
o-Me	-34.2	12.1	-26.9

^{*}B.S. Lee and I. Lee, *J. Korean Chem. Soc.*, **13**, 281(1969)

[†]M.H. Whangbo, B.S. Lee and I. Lee, *ibid*, **13**, 109(1969)

anges. This means that both electron-donating and electron-withdrawing groups at active sites stabilize the transition state and increase rates of exchanges.

This is rather unusual since normally rate increases are accompanied by either the electron-donating or the electron-withdrawing substituent depending on the types of reaction⁶⁾. Due to this abnormal substituent effect, the Hammett σ - ρ plots do not give a simple linear correlation but give a U-shaped curve as shown in Fig. 1.

The U-shaped Hammett plots were also found in other S_N2 reactions of para-substituted benzyl halides, such as reactions of benzyl chloride with thiosulfate anion in ethanol, acetone and diglym⁷⁾, and of benzyl bromide with thiophenols⁸⁾. In fact this behavior is a common and a general one for reactions of benzyl halides with anionic nucleophiles, and

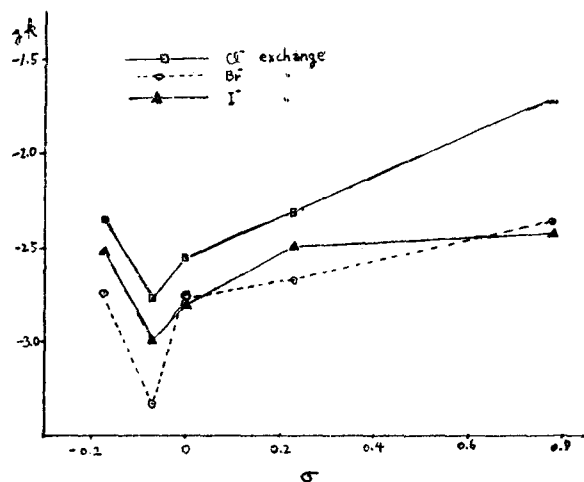


Fig. 1. Plot of $\log k$ against Hammett's σ -constants.

therefore we are not to expect a linear free energy relation for these reactions.

The relative nucleophilicities of the three halide ions are summarized in Table 3. The nucleophilicity order is $\text{Cl}^- > \text{I}^- > \text{Br}^-$ except for the unsubstituted and $p\text{-NO}_2$ compounds. For these the order is $\text{Cl}^- > \text{Br}^- > \text{I}^-$. We have already argued⁴⁾ that the nucleophilicity order $\text{Cl}^- > \text{Br}^- > \text{I}^-$ in dry acetone is dictated by the easiness of desolvation in ground states. In protic solvents on the other hand the large sized I^- is solvated less than the small Cl^- ion and the more polarizable I^- ion is the most reactive of the three anions giving the order of nucleophilicity, $\text{I}^- > \text{Br}^- > \text{Cl}^-$. In this case polarizability effect favors rate increase of the exchange reaction. Considering these two extreme

situations we might conclude that in general both desolvation and polarizability are important in determining the nucleophilic reactivities of anionic nucleophile and they are competitive

Klopman³⁾ pointed out that benzyl chloride systems correspond to the borderline case of softness, and therefore the reaction of benzyl chloride with halide ion can be considered as medium soft-medium soft interaction⁹⁾. Thus the relative nucleophilicity does not belong to either of the two above extreme cases but complicated giving scrambled order of $\text{Cl}^- > \text{I}^- > \text{Br}^-$ or $\text{I}^- > \text{Cl}^- > \text{Br}^-$ even in dipolar aprotic solvents.

From Table 1, it can be seen that the reactivity order of substrates varies slightly with varying nucleophile; the order being,

For Cl^- ; $p\text{-NO}_2 > o\text{-Me} > p\text{-Cl} \sim p\text{-Me} > \text{H} > m\text{-Me}$

For Br^- ; $p\text{-NO}_2 > o\text{-Me} > p\text{-Cl} \sim p\text{-Me} > \text{H} > m\text{-Me}$

For I^- ; $o\text{-Me} > p\text{-NO}_2 > p\text{-Cl} \sim p\text{-Me} > \text{H} > m\text{-Me}$

Methyl-substituents show markedly different effect on rate of exchange. Substitution at ortho and para position (active sites) increases the rate while substitution at meta position (inactive site) decreases the rate.

Activation enthalpy and entropy data show that the easiness of bond formation is in the order $\text{Cl}^- > \text{Br}^- > \text{I}^-$ and the easiness of transition state desolvation is in the order $\text{Br}^- > \text{I}^- > \text{Cl}^-$ for $o\text{-Me}$ substituted, which is the same trend as for $p\text{-NO}_2$ substituted. On the other hand, $p\text{-Me}$ substituted benzyl chloride exhibits the order of $\text{Cl}^- > \text{Br}^- > \text{I}^-$ and $\text{I}^- > \text{Br}^- > \text{Cl}^-$, respectively. This implies that modes of transition state stabilization for $o\text{-Me}$ and $p\text{-Me}$ substituted are different.

Meta-methyl substituent deactivates the reaction center in all cases. The activation enthalpy and entropy for meta-Me compound are somewhat lower than those for unsubstituted compound. This indicates that for the $m\text{-Me}$ compound either the transition state

Table 3. Relative Nucleophilicities, k_Y/k_{Cl}

X \ Y	Cl ⁻	Br ⁻	I ⁻
p-NO ₂	1.0	0.23	0.20
p-Cl	1.0	0.42	0.65
H	1.0	0.64	0.57
p-Me	1.0	0.43	0.65
m-Me	1.0	0.27	0.59
o-me	1.0	0.26	0.47

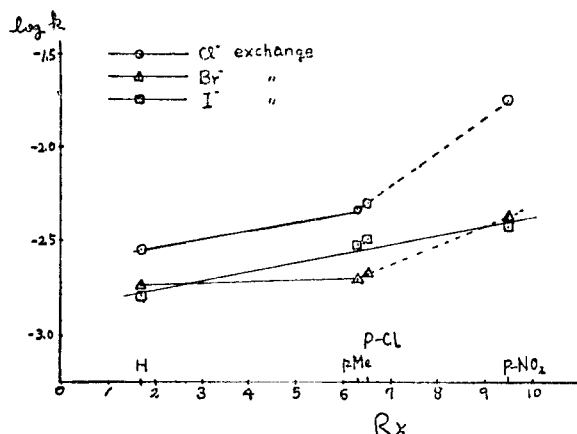


Fig. 2. Plot of $\log k$ against group refractivity of substituent, R_X

Bond refractivity data was taken from the literature; "Handbook of Chemistry and Physics", 45th ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1965.

solvation or the ground state desolvation is unfavorable for the reaction, although bond formation is easier.

In Fig. 2, \log (relative rate) is plotted against group refractivity for para substituent, which is defined by the sum of bond refractivity,¹⁰⁾ e. g., for Me-, $R_{Me} = R_{C-C} + 3R_{C-H}$. For I⁻ exchange reaction this plot gives good linear correlation, but for Br⁻ and Cl⁻ exchange reaction rates show slight deviation from linearity at p-NO₂ position.

Since refractivity can be assumed to be the measure of polarizability^{9, 10)}, our suggestion that the rate determining factor of benzyl chloride exchange with soft nucleophile is the polarizability of both substrate and nucleophile can be justified. But, in the reactions of benzyl chlorides with less polarizable (more hard) nucleophiles, the polarizability effect is again competitive with charge effect. In particular, p-NO₂ group makes charge development at reaction center rather strongly¹¹⁾, so that p-NO₂ compound will have strong charge interaction with hard nucleophile, leading to slight deviations for Cl⁻ or Br⁻ exchange

reactions.

In conclusion, the results of the present work are consistent with our previous argument⁴⁾ that rate of halide exchange in arylmethyl halides are dictated by the polarizabilities of both substrate and nucleophile.

III. Experimental

All substituted benzyl chlorides and alkali halides were purified by standard method.

Anhydrous acetone was prepared as reported previously⁴⁾.

Kinetic runs and isotope counting procedures were as described before.⁴⁾

Rate constants for Br⁻ and I⁻ exchange reactions were calculated by eq. (2), and for Cl⁻ exchange reaction by eq. (3).

$$\left(\frac{c-b}{a-b}\right)\log(1-F) = \frac{-Dkt}{2.303} \quad \text{.....(2)}$$

$$\left(\frac{1}{a+b}\right)\log(1-F) = \frac{-\alpha kt}{2.303} \quad \text{.....(3)}$$

where a and b are the initial concentrations of substrates and salts, respectively, $D = (K^2 + 4Kb)^{1/2}$, $C = \frac{1}{2}(D + D^2/K)$, K = ion pair dissociation constant of salt in dry acetone, and α = degree of dissociation of salt ion pair⁴⁾.

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