

Determination of Nucleophilic Reactivity by PMO Method (I)

Kinetic Studies on the Chloride Exchange Reactions of Arylmethylchlorides in Dry Acetone

by

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PMO법에 의한 친핵반응도 결정 (I) Arylmethylchloride의 Chloride 교환반응*

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ABSTRACT

Rate constants for the chloride exchange of some arylmethylchloride in dry acetone have been determined, and activation parameters have been evaluated.

The reactivities of substrates are explained with perturbational molecular orbital (PMO) method and HSAB principle. It was found that carbon-chlorine resonance integral at the transition state is about 67% of β , the carbon-carbon resonance integral.

요 약

Arylmethylchloride의 교환반응에 대한 반응속도 상수를 측정하고, 또한 활성화 파라메터를 결정하였다. Substrate의 반응도를 섭동분자궤도(PMO)법으로 설명하였으며 HSAB 원리를 이에 적용하였다. 또한 전이상태에서의 탄소-염소공명적분값이 탄소-탄소 공명적분값의 약 67%임을 밝혔다.

INTRODUCTION

Nucleophilic displacement reactions on saturated carbon atom have long been studied by many workers. (1)(2)(3)(4) For these types of reactions, the reaction mechanisms have generally been accepted as the duality

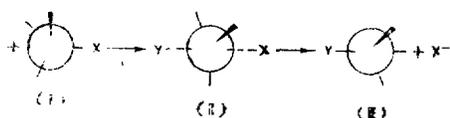
of SN_1 (unimolecular nucleophilic substitution) and SN_2 (bimolecular nucleophilic substitution) after Hughes and Ingold⁽⁵⁾.

The widely reported results for the halide exchange

* Material taken from master thesis of B. S. L. at Seoul National University

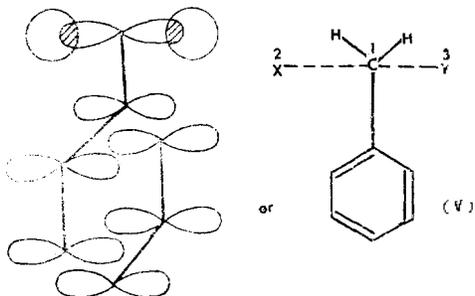
reactions of alkyl or arylmethyl halide showed that these reactions proceed by way of SN_2 path.⁽¹⁾⁽²⁾⁽³⁾

(4) The so called one-step mechanism, SN_2 , consists of a nucleophilic attacking of nucleophile(Y) at the rearward of displaced group(X) and inversion of configuration as shown in the following equation:



The first-order dependence upon both substrate and nucleophile provide the experimental evidence for the transition state(II). According to transition state theory, the reactivity of these reactions varies with the charge density of the reacting carbon center, nucleophilicity of nucleophile and the leaving ability of leaving group⁽²⁾⁽³⁾⁽⁴⁾. But, if the substrates are conjugated systems, for example, the high reactivity is not explained clearly with these factors.

Such rate enhancement was attributed to stabilization of the transition state by π -bond overlap as below (IV)⁽⁵⁾.



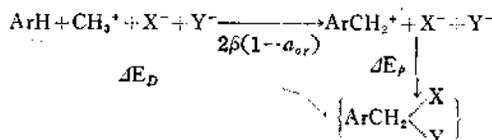
Other factors such as solvation of the ground and transition states⁽⁵⁾, steric inhibition, variations of charge density of the reaction center must also influence the reaction rate.

According to HSAB (Hard and Soft Acids and Bases) principle⁽⁷⁾ which was developed by Pearson, the softness of the exocyclic carbon atom and nucleophile may control the reactivity. When the aryl group changes from benzene to polynuclear aromatic ring it is expected that the softness of the exocyclic carbon should increase. Then the second order rate would be enhanced greatly from the ordinary reactivity.

But, at present, there is no way of explanation of

the reactivity quantitatively. Attempts have been made to correlate the simple MO (Molecular Orbital) calculations of Dewar⁽⁸⁾ with relative reactivity of the arylmethyl halide. Dewar and Sampson applied perturbation theory to a simple MO method. Dewar's method⁽⁸⁾ can be applied for the evaluation of the energy change of interaction (ΔE_D) between the nucleophile and the displaced group with the remainder of the system, $ArCH_2$, when the configuration of the transition state remains constant but the nature of Ar varies.

In order to get an approximate estimate of ΔE_D it can be simplified assuming that the electronegativities of all the atoms in the transition state are equal (introduction of differences in electronegativity by the perturbation methods has no gross effect). ΔE_D can be estimated by the following cycle:



Since the degenerate orbitals involved are the doubly occupied AOs of X and Y and the empty NBMO (non-bonding molecular orbital) of $ArCH_2$, perturbation energy, ΔE_p , can be found, using first order perturbation theory. On the usual notation the energies of the perturbed orbitals are related by the secular equation:

$$\det |H_{rs} - ES_{rs}| = 0 \quad \dots \dots \dots (1)$$

As usual $S_{12} = S_{23} = S_{13} = 0$; $H_{23} = 0$

From the previous approximation $H_{ii} = a$. Solving the secular equation, the following results are obtained.

$$a - E = 0 \quad \dots \dots \dots (2a)$$

$$a - E = \pm \sqrt{H_{12}^2 + H_{13}^2} \quad \dots \dots \dots (2b)$$

Expanding the NBMO, ψ_1 of $ArCH_2$ in terms of its AOs

$$\psi_1 = \sum a_{oi} \phi_i \quad \dots \dots \dots (3)$$

Hence,

$$H_{12} = \int (\sum a_{oi} \phi_i) \hat{H} \phi_2 d\tau \quad \dots \dots \dots (4)$$

Since only τ , the side-chain carbon atom, is adjacent to ϕ_2 , eq (4) reduces to

$$H_{12} = \int a_{or} \phi_r \hat{H} \phi_2 d\tau = a_{or} \beta_r \quad \dots \dots \dots (5)$$

Where β_r is the resonance integral between the side

chain carbon atom and the X group.

Similarly $H_{13} = a_{or}\beta_y \dots \dots \dots (6)$

Remembering that energies are reckoned relative to that (α) of a carbon 2p AO, the perturbed energies are:

$$+a_{or}(\beta_x^2 + \beta_y^2)^{1/2}, 0, -a_{or}(\beta_x^2 + \beta_y^2)^{1/2} \dots \dots \dots (7)$$

Two of the four electrons occupy the bonding orbital of the set, and two, the non-bonding orbital.

$$\text{Hence, } \Delta E_p = -2a_{or}(\beta_x^2 + \beta_y^2)^{1/2} \dots \dots \dots (8)$$

When the group X is same as Y,

$$\Delta E_p = +2\sqrt{2}a_{or}\beta_x$$

Then, $\Delta E_D = 2\beta(1 - a_{or}) + \Delta E_p$

$$\begin{aligned} &= 2\beta(1 - a_{or}) + 2\sqrt{2}a_{or}\beta_x \\ &= 2\beta - 2a_{or}(\beta - \sqrt{2}\beta_x) \\ &= 2\beta - 2a_{or}\beta_{eff} \dots \dots \dots (9) \end{aligned}$$

where β_{eff} is equal to $\beta - \sqrt{2}\beta_x$.

This leads to an expression for the rate constants:

$$-RT \ln k = C - 2a_{or}\beta_{eff} \dots \dots \dots (10)$$

Now, the slope of the plot of $\log k$ against $2a_{or}$ should, therefore, provide a method for estimating the degree of nucleophilic participation in the transition state by determining β_x from β_{eff} . The direct determination of β_x value is only possible for the system $X=Y$.

a_{or} , the coefficient of NBMO can be found without solving secular equation but with only a piece of paper and a pencil after Longuet-Higgins⁽⁹⁾.

RESULTS AND DISCUSSION

The rate constants and the activation parameters for the chloride exchange of arylmethyl chloride in acetone are summarized in Tables 1 and 2.

TABLE 1. Summary of Rate Constants for the Reaction of Chloride Exchange of Arylmethylchloride (ArCH_2Cl) in Dry Acetone.

Ar	$2a_{or}$	k at 25°C	k at 35°C
Phenyl	1.512	2.83×10^{-2}	6.41×10^{-3}
(a) 1-Naphthyl	1.342	4.29×10^{-3}	1.28×10^{-2}
9-Anthracyl	1.069	5.90×10^{-2}	1.20×10^{-1}
9-phenanthryl	1.336	7.16×10^{-2}	1.72×10^{-2}
10-(1,2-Benz)-Anthracyl	1.121	9.05×10^{-3}	1.87×10^{-2}

(a) recalculated value using eq. 16 from reference (11)

TABLE 2. Summary of Activation Parameters for the Chloride Exchange of Arylmethyl Chloride in Dry Acetone at 25°C

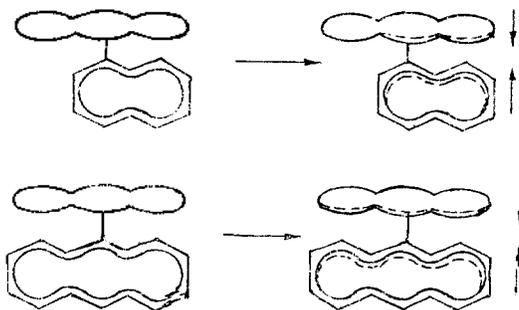
Ar	ΔH^\ddagger (kcal/mole)	ΔS^\ddagger (e. u)
phenyl	14.3	-21.9
1-Naphyl	19.3	-4.5
9-Anthracyl	12.3	-22.7
9-phenanthryl	15.4	-16.5
10-(1,2,-Benz)-Anthracyl	12.6	-25.3

The activation parameters for benzyl chloride obtained from our experiments are slightly smaller compared with de la Mare's results.⁽¹⁰⁾

As de la Mare *et al.* neglected the non-nucleophilicity of ion-pair, our results are considered to be more accurate.

Enthalpy and entropy of activation give some information about reactivity. For the halide exchange reactions of 1-naphthylmethylhalides, K. S. Lee⁽¹¹⁾ concluded that, in spite of the steric strain of perihydrogen in the transition state, the main effect contributing to the activation enthalpy is the electronic effect. This also applies to our results. Although the anthracyl or 1,2-benzanthracyl system has twofold perihydrogen effect, the activation enthalpies for both systems are lower than the 1-naphthyl or 9-phenanthryl substrate. Since the difference of solvation energy between those systems may be less than 2 kcal (calculated from solvent activity coefficient of large molecule reaction), the lowering of activation enthalpies of 9-anthracyl type substrates may be controlled by another electronic effect. If the transition state model proposed by Lee, *et al.*⁽¹²⁾ for the halogen exchanges of benzyl halide is adopted, this phenomenon is explainable very easily. The pseudo allyl type MO between Y-C-X may cause considerable interaction with substituted aryl group MO⁽¹²⁾. This intra MO-interaction stabilizes the 9-anthracyl type transition state more than the 1-naphthyl type. Then, this overcomes the twofold perihydrogen effect, and increases rate remarkably.

From Table 2, we can see that entropy decreases with increasing number of aromatic ring. The charge dispersal by the large aryl group increases solvation by



the soft aprotic solvent, acetone. So, the activation entropies may tend to have more negative values. The activation entropy of 1-naphthylmethyl chloride shows exceptional behavior, but it is not explicable at present. From the entropy of activation, it can safely be assumed that the transition state would be tight. In other words, the small anion, Cl^- which is more desolvated in soft solvent than in protic solvent, approaches nearer to the reacting carbon center, and forms C-Cl partial bond at the nearer distance^(6a,c).

It is the usual practice to relate the chemical reactivity of organic compounds to a particular MO index such as free valence, charge density, Z value, superdelocalizability and localization energy^{(9,c)(14)}.

The Dewar's PMO method explained in the previous section is most simple to treat the $\text{S}_{\text{N}}2$ -type reactivity. If we accept the transition state model adopted in PMO calculation, from eq. (10), $\log k$ against $2\alpha_{\text{or}}$ may give straight line.

The value of β_{eff} can be calculated from the slope

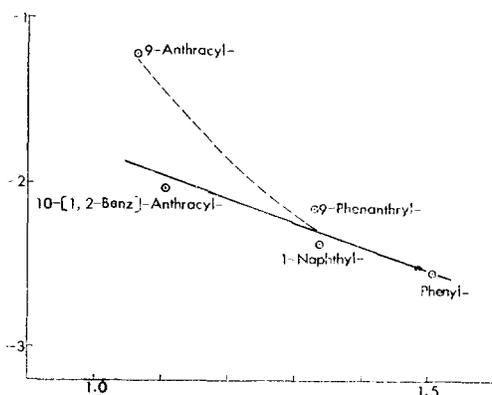


Fig. 1. Plot of $\log k$ against $2\alpha_{\text{or}}$ for the Chloride Exchange of Arylmethyl Chloride at 25°C

of the above relation, and β_x from this β_{eff} value. $\log k$ vs. $2\alpha_{\text{or}}$ plot for the chloride exchange reaction of some arylmethyl chlorides is shown in Fig. 1

This plot has a good linearity except for the case of 9-anthracylmethyl chloride. β_{eff} calculated from the slope of straight line in Fig. 1, is 1.8 kcal. Since $\beta_{\text{eff}} = \beta - \sqrt{2}\beta_x = 1.8$, this means that β_x is not very different from β which is carbon-carbon resonance integral. Assuming $\beta = 30 \text{ kcal}^{(9)}$, β_x is 20.0 kcal, which is about 67% of β value. On the other hand, the β_{eff} value for iodine exchange revealed in Dewar's review was 5 kcal^(2a). Although in the determination of rate constants for this reaction the non-nucleophilicity of ion-pair, was not considered, the slope should not change, and in this case, $\beta_x \neq \beta$ so that calculation of β_x value is not possible.

It can be concluded that the nucleophilic participation of Cl^- ion in the transition state is more extensive than that of I^- ion. The more solvated I^- ion may form loose transition state than the less solvated Cl^- ion. In other words, the ground state solvation controls the degree of nucleophilic participation in considerable part. This agrees well with solvation theory of Parker *et al.*⁽⁶⁾

The exceptional behavior of 9-anthracylmethyl chloride is surprising, but the similar behavior was reported for the solvolysis of arylmethyl chloride when the \log (relative rate) was related to the energy difference between carbonium-ion transition state and anthracene⁽¹⁵⁾.

Probable reasons for this deviation can be summarized as follows.

(1) The transition state model used in the PMO calculation is unjustifiable.

(2) Not only the first order but the second order perturbation should be taken into accounts.

The first of these has already been accounted for previously. The second reason may be explained as follows.

In Dewar's assumption, the energy level of the highest occupied MO of entering nucleophile is degenerate with that of the lowest unoccupied MO of the substrate NBMO. In practice, however, the relation may not hold exactly with certain nucleophiles ($\alpha_{\text{Cl}} = \alpha_c + 0.4\beta$ is occasionally used⁽¹⁶⁾). If the occupied energy

level of the nucleophile and that of unoccupied NBMO of the substrates have only near degeneracy, the stabilization is concerned with the second order perturbation according to the height of the other unoccupied energy level of substrate. 9-Anthracylmethyl chloride may be the case. Since the energy level of unoccupied MO for the 9-anthracylmethyl radical is remarkably low⁽¹⁷⁾, the stabilization energy by the second order perturbation cannot be neglected. HSAB principle, which is based upon the acid-base reaction of Lewis or Pearson⁽⁷⁾, is most powerful for the qualitative explanation of reactivity. According to this principle, the softer the nucleophile and the reaction center of substrate becomes, the faster the reaction proceeds. In such a discussion the softness of both reactants must be considered. It is evident that the softness of substrates increases with the increasing size and polarizability.

If the energy level of the unoccupied π^* -orbital is near to that of NBMO, it can safely be assumed that the unoccupied π^* -orbital will participate in the formation of partial bond in the transition state. Since the polarizability is inversely proportional to the excitation energy^{(7a)(18)}, the order of increasing polarizability, i. e., softness, must have the following order: 9-Anthracyl > 10-(1,2-benz)-Anthracyl > 9-phenanthryl > 1-Naphthyl > benzyl, while the excitation energies can be obtained from MO calculation in analogy with arylmethyl radical and indirectly from the quenching constants for liquid scintillator. Therefore, 9-anthracylmethyl chloride reacts faster than the other systems which have relatively high excitation energy for $n-\pi^*$ transition. Thus, the deviation of the substrate reactivity from the PMO treatment may be partially due to the polarizability effect of the 9-anthracyl system. The symbiotic effect,^(7b) or polarizability effect of leaving chlorine⁽¹⁹⁾ may also influence the polarizability of the systems.

EXPERIMENT

(1) Material

9-Anthraldehyde⁽²⁰⁾⁽²¹⁾ Formylation of anthracene gave 9-anthraldehyde. The bright yellow needles of aldehyde were obtained from the recrystallization in hot glacial acetic acid, after washing with 30 ml

of cold methanol. m. p. 105°C.

9-Anthracylmethanol:⁽²¹⁾⁽²²⁾ 9-Anthraldehyde is converted to alcohol by reduction with lithium aluminum hydride. After recrystallization from petroleum ether (30-90°C), pale yellow needles were obtained. m. p. 153°C.

9-Anthracyl methyl chloride:^{(7b)(22)} 9-Anthracyl methanol (2 g) was treated in hot benzene (50 ml) with thionyl chloride (3.2 ml) dropwise and refluxed for 2 hours. The solvent was distilled off and the recovered product was recrystallized from anhydrous benzene; yellow needle, m. p. 135°C, hydrolyzable chlorine 15.8% (calc. 15.7%).

10-(1,2-benz) anthracyl methyl chloride was prepared by the method of Badger and Cook⁽²³⁾. The recrystallized product from benzene was long pale yellow needles, m. p. 186°C, hydrolyzable chlorine 12.6% (calc 12.8%).

9-Phenanthryl methyl chloride was synthesized by the method of Badger *et al*⁽²⁴⁾. The directly chloromethylated product was separated by distillation under reduced pressure (150-170°C/4mmHg) and recrystallized from benzene-petroleum ether; colorless needle, m. p. 100°C hydrolyzable chlorine 15.5% (calc. 15.7%).

Benzyl chloride: Commercial benzyl chloride was purified by distillation under reduced pressure⁽²⁵⁾, 52°C/8 mmHg, $n_D^{20}=1.5419$. Dry Acetone was prepared as reported previously⁽¹²⁾⁽²⁶⁾

Stock solution of LiCl containing tracer activity LiCl³⁶.

The radioactive chlorine, Cl³⁶, which was purchased from the Isotope Center, Belgium, in HCl form in aqueous solution was converted to LiCl form by adding the equivalent amount of LiOH and then evaporated to dryness. LiCl carrier salt and radioisotopic LiCl was dissolved in anhydrous acetone.

Conc. of LiCl = $1.342 \times 10^{-3}M$

(2) Kinetic runs

Same as reported previously except the following. Cl³⁶ activity was measured using a scintillation counter type LS-100 manufactured by Beckman throughout these studies.

A scintillator solution containing 4 g per liter of PPO ((2,5 dipheyl oxazole)) and 100 mg per liter of

POPOP [2, 2-p-phenylene-bis-(5-phenyl oxazole)] in toluene was used⁽²⁷⁾.

Background counting was about 47 c. p. m. The quenching action of acetone for the counting sample was corrected for by the relationship⁽²⁸⁾

$$\log N = \log N_0 - q \cdot c / 2.303 \quad (11a)$$

where N_0 is the counting rate in the absence of acetone quenching. Quenching constant q was determined from the equation.

$$\log\left(\frac{N}{C}\right) = \log(s) - q \cdot c / 2.303 \quad (11b)$$

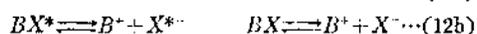
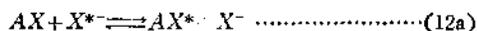
where c is the conc. of acetone in ml and S is the specific activity in the absence of acetone.

$$q \text{ of acetone} = 0.112/\text{ml}$$

The self quenching of the substrate, i. e., benzyl chloride, 9-phenanthrylmethyl chloride, 9-anthracylmethyl chloride and 10-(1, 2-benz) anthracylmethyl chloride was also corrected for as the above manner. Quenching constants obtained were 6.409×10^{-2} , 6.064×10^{-2} , 2.298, and 1.894 per mg respectively.

(3) Determination of rate constant

For the isotopic exchange reaction where ion-pair of salt is involved.



$$[AX] + [AX^*] = a, [BX] + [BX^*] = b$$

$$[X^-] + [X^*] = ab, [AX^*] = x$$

$$[BX^*] = y, [AX] = a - x$$

$$[X^*] = \alpha y, [BX] = b - y$$

$$[X^-] = \alpha(b - y)$$

where, α is the degree of dissociation of ion-pair. The conventional rate equation for isotopic exchange reaction can be modified.

$$\begin{aligned} \frac{dx}{dt} &= \alpha R \left(\frac{\alpha y}{ab} \left(\frac{a-x}{a} \right) - \alpha R \left[\frac{\alpha(b-y)}{ab} \right] \left(\frac{x}{a} \right) \right) \\ &= \alpha R \left(\frac{\alpha y - \alpha x}{ab} \right) \quad (13) \end{aligned}$$

where, R is constant rate $K \cdot a \cdot b$.

Since, $y - y_\infty = x_\infty - x$, and $\frac{x_\infty}{y_\infty} = a/b$

$$\frac{dx}{dt} = \frac{\alpha R}{ab} [(a+b)(x_\infty - x)] \quad (14)$$

This integrates into

$$-\ln(1-F) = \alpha \frac{R}{ab} (a+b)t \quad (15a)$$

or

$$-\ln(1-F) = \alpha k(a+b)t \quad (15b)$$

α is constant during the whole reaction time since no change of salt concentration occurs.

$$\text{Hence } k = \frac{-2.303 \log(1-F)}{\alpha(a+b)t} \quad (16)$$

The degree of dissociation of ion-pair can be calculated from the mass action law,

$$k = \frac{\alpha^2 b}{1-\alpha} \quad (17)$$

where K is the ion-pair dissociation constant of lithium chloride in acetone which is available from literature⁽²⁹⁾ 3.3×10^{-6} .

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