

## Kinetic Studies on Halogen Exchanges of 2-Naphthylmethyl Chloride

Ikchoon Lee, Jae Eui Yie, Wang Ki Kim\* and Kae Soo Lee\*

Department of Chemistry, Inha University, Incheon.

\*Department of Chemistry, Chon Nam University, Kwangju.

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### Abstract

The halogen exchange reactions of 2-naphthylmethyl chloride have been investigated in acetone and acetonitrile. The results were in good accord with PMO theory and HSAB principle.

### 요 약

염화 2-나프틸메틸의 할로젠 교환반응을 아세톤 및 아세토니트릴 용매내에서 실시하였다. 실험결과를 PMO 이론과 HSAB 원리로 잘 설명할 수 있었다.

Solvolytic displacement reactions of aryl-methyl halides have been studied extensively<sup>1)</sup>. Solvolysis reactions of arylmethyl compounds are especially valuable for studying the properties of  $\pi$  electron systems. According to the perturbational molecular orbital (PMO) theory developed by Dewar<sup>2)</sup>, it is possible to correlate the effect of structural variation on the relative reactivity with the nonbonding molecular orbital (NBMO) coefficient,  $a_{\sigma}$ , of the carbon center undergoing displacement. The slope of the linear correlation actually provide us with the measure of bond formation at the transition state. Dewar has shown that  $S_N2$  reaction can also be dealt with the PMO theory similarly as the solvolysis reactions<sup>2)</sup>.

The halogen exchange of substituted methyl halides is a typical  $S_N2$  process, where the bond-formation is progressed to a signi-

ficant degree at the transition state<sup>3)</sup>. Eventually we hope to correlate the  $S_N2$  reactivity with a PMO parameter and obtain a quantitative measure of bond-formation at the transition state.

As a part of our work in the study of  $S_N2$  reactions, we have now carried out the kinetic studies on halogen exchange of 2-naphthylmethyl chloride in acetone and acetonitrile.

### Results and Discussion

The reaction was essentially of second order, first order in the substrate and also in halide. Second order rate constants calculated were consistent within the experimental error of less than  $\pm 5\%$  for the change in halide ion concentration except for the case of iodide. For the iodide exchange the error increased to about two-fold and these rates

**Table 1. Effect of iodide ion concentration on the rate of  $2\text{-C}_{11}\text{H}_9\text{Cl} + \text{I}^- \rightarrow 2\text{-C}_{11}\text{H}_9\text{I} + \text{Cl}^-$** 

Solvent	°C	$[\text{I}^-]$ M	$k(1/\text{mol sec}) \times 10^3$
Acetone	35.0	$2.60 \times 10^{-3}$	2.13
		2.17 "	2.35
		1.93 "	2.52
		$8.66 \times 10^{-4}$	2.46
		1.73 "	2.12
		Average = $2.3 \pm 0.2$	
Acetonitrile	45.0	$4.12 \times 10^{-3}$	4.12
		3.09 "	4.77
		2.06 "	3.89
		Average = $4.3 \pm 0.4$	

**Table 2. Summary of rate constants for the reaction  $2\text{-C}_{11}\text{H}_9\text{Cl} + \text{X}^- \rightleftharpoons 2\text{-C}_{11}\text{H}_9\text{X} + \text{Cl}^-$** 

Solvent	X <sup>-</sup>	$k(1/\text{mol sec}) \times 10^3$			
		30.0°C	35.0°C	40.0°C	45.0°C
Acetone	Cl <sup>-</sup>	8.53	12.1(12.8)*		37.4
	Br <sup>-</sup>		2.19(6.98)	3.44	4.58
	I <sup>-</sup>		2.3 (8.84)		8.8
Acetonitrile	Cl <sup>-</sup>		0.557		1.52
	Br <sup>-</sup>		1.07	1.96	3.51
	I <sup>-</sup>		1.6		4.3

\* Value in ( ) are those for 1-naphthylmethyl chloride; Ref. (5)

are quoted to only two significant figures in Tables 1 and 2. The effect of iodide ion concentration on the rate of exchange is shown in Table 1. The rate constants obtained are summarized in Table 2.

Table 2 shows that the nucleophilicity of free halide ions in anhydrous acetone for the 2-naphthylmethylchloride increases in the order  $\text{Br}^- < \text{I}^- < \text{Cl}^-$ , while the order changes to  $\text{Cl}^- < \text{Br}^- < \text{I}^-$  in acetonitrile.

The scrambling in the order of nucleophilicity shown in acetone indicates that both desolvation and polarizability are important in determining the nucleophilicity of anionic

**Table 3. Effect of Groups Attached to the Reaction Center on Rates of Cl-Cl Exchanges in Acetone.**

Number	Compound	Relative Rate (35.0°C)	Nucleophilicity order	Reference
I	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{Cl}$	$<10^{-2}$	$\text{Cl}^- > \text{Br}^- > \text{I}^-$	6
II	$\text{C}_6\text{H}_5\text{CH}=\text{CHCl}$	0.7	$\text{I}^- > \text{Br}^- > \text{Cl}^-$	7
III	$\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$	1.0	$\text{Cl}^- > \text{Br}^- > \text{I}^-$	4
IV	$p\text{-ClC}_6\text{H}_4\text{CH}_2\text{Cl}$	1.9	$\text{Cl}^- > \text{I}^- > \text{Br}^-$	4
V	$2\text{-C}_{10}\text{H}_7\text{CH}_2\text{Cl}$	1.9	$\text{Cl}^- > \text{I}^- > \text{Br}^-$	this work
VI	$1\text{-C}_{10}\text{H}_7\text{CH}_2\text{Cl}$	2.0	$\text{Cl}^- > \text{I}^- > \text{Br}^-$	5
VII	$\text{C}_6\text{H}_5\text{COCl}$	$>10^3$	$\text{Cl}^- \gg \text{I}^-$	8

nucleophiles and they are competitive. Precisely the same trend was found for halide exchanges of substituted benzyl chloride in acetone<sup>(4)</sup>. In acetonitrile however polarizability effect seems to predominate as in water.

Rate constants for 1-naphthylmethyl chloride<sup>(5)</sup> are also included in Table 2 for comparison. The rates for 2-naphthylmethyl chloride are smaller than those for 1-naphthylmethyl chloride. This is in good agreement with the prediction of PMO theory<sup>(2)</sup>; the NBMO coefficient  $a_{or}$  for 2-naphthylmethyl carbon (0.727) is greater than that for 1-naphthylmethyl carbon (0.406) and therefore the former is less reactive than the latter.

Table 3 shows the effect of variation of groups attached to the reaction center on rates of chlorine-chlorine exchanges in acetone. Since in  $S_N2$  reaction bond formation is considered to have progressed significantly in the transition state, the relative rate shown in Table 3 may be considered an indication of relative easiness of bond-formation. According to relative rate values bond-formation is generally assisted by delocalization of  $\pi$  electrons to the reaction center. In the compound I which is the least reactive, the reaction center is relatively remote from the ring and therefore there is no delocalization

**Table 4. Activation Parameters for Halogen Exchanges of 2-Naphthylmethyl Chloride.**

Solvent	Halide	$\Delta H^*$ (kcal/mol)	$\Delta S^*$ (e. u.)
Acetone	Cl <sup>-</sup>	17.7	-9.6
	Br <sup>-</sup>	14.9	-22.4
	I <sup>-</sup>	18.6	-11.0
Acetonitrile	Cl <sup>-</sup>	19.0	-12.0
	Br <sup>-</sup>	22.5	+0.9
	I <sup>-</sup>	25.5	+4.9

of ring  $\pi$  electrons, while in **VII** the reaction center has a  $\pi$  electron which is directly conjugated with the ring  $\pi$  electrons and thus it is the most reactive one. It is interesting to note that reactivities of **IV** and **V** are about the same, which implies that p-chloro substituent is equivalent to a catacondensed ring at  $\beta$ -position. A catacondensed ring at  $\alpha$ -position seems somewhat more efficient in delocalizing  $\pi$ -electrons to the reaction center. This is of course what the PMO theory predicts as mentioned above<sup>2)</sup>.

Table 3 also shows the relative nucleophilicities of halide ions in acetone for various reaction centers. According to the HSAB principle of Pearson<sup>14)</sup>, hard nucleophile, e.g., Cl<sup>-</sup>, should react faster than the soft nucleophile, e.g., I<sup>-</sup>, with a hard reaction center. Thus reaction centers in **I** and **VII** are relatively hard since the order is Cl<sup>-</sup> > Br<sup>-</sup> > I<sup>-</sup>, while the reaction center in **II** must be soft since it is reversed to I<sup>-</sup> > Br<sup>-</sup> > Cl<sup>-</sup>. 2-naphthylmethyl center must be softer than benzyl center since now the nucleophilicity order becomes scrambled to Cl<sup>-</sup> > I<sup>-</sup> > Br<sup>-</sup>.

Activation parameters calculated are summarized in Table 4. The trends in variation of activation parameters as halides are changed from Cl<sup>-</sup> to I<sup>-</sup> in acetone are the same as for 1-naphthylmethyl chloride<sup>5)</sup>. In acet-

onitrile, however, both  $\Delta H^*$  and  $\Delta S^*$  tend to increase in the order Cl<sup>-</sup> < Br<sup>-</sup> < I<sup>-</sup>, which was precisely the order of reactivity. This means that the reaction is entropy controlled.

## Experimental

### 1) Materials

(A) 2-Naphthylmethyl chloride was purchased from Eastman Kodak Co., and purified by repeated recrystallization from absolute ethanol. m.p. 48-49°C<sup>9)</sup>.

(B) Acetone. Technical acetone was dried over calcium chloride and distilled fractionally in a Todd column (reflux reflux ratio, 10:1). The boiling fraction at 56-56.5°C was passed through activated Alumina column (Dia. 3 cm, Length 20 cm). The water content after this treatment may be minimized to 0.8% or less<sup>10)</sup>.

(C) Acetonitrile. Chemical pure acetonitrile was dried over P<sub>2</sub>O<sub>5</sub> and distilled fractionally in a Todd column<sup>11)</sup>.

(D) LiCl and KI. Commercial samples were used without further purification.

(E) LiBr was prepared by titrating LiOH solution with NH<sub>4</sub>Br solution followed by recrystallization.

(F) Cl<sup>36</sup>. The radioactive chlorine, Cl<sup>36</sup>, which was purchased from the Radiochemical Center, Amersham, Buckinghamshire, England, in HCl form was converted to LiCl by titration with LiOH.

(G) Br<sup>82</sup>. The radio active Br<sup>82</sup> which was supplied by A.E.R.I. in Korea, in NH<sub>4</sub>Br form was converted to LiBr by titration with LiOH.

(H) I<sup>131</sup>. The radioactive I<sup>131</sup> which was supplied by A.E.R.I. in Korea in NaI form was used.

2) Kinetic runs. Isotope tracer method was used to measure the reaction rates.

For measurement of rates, the following general procedure was adopted. To 20 ml substrate solution (ca.  $10^{-2}$ – $10^{-3}$ M) 15 ml salt solution (ca.  $10^{-4}$ M) was added. At timed interval, 5 ml aliquot of the reaction mixture was pipetted from the reaction vessel to the benzene-water mixture and shaking vigorously. 1 ml portion of organic layer was used in detecting radioactivity.

$\text{Cl}^{36}$  activity was counted using Aloka-1600 liquid scintillation counter, and  $\text{Br}^{82}$  and  $\text{I}^{131}$  activities were measured using a well-type scintillation counter.

Exchange rates were calculated by the equation

$$k = \frac{1}{a+b} \times \frac{1}{at} \times \ln\left(\frac{x_{\infty}}{x_{\infty}-x}\right)$$

for chloride exchange reactions<sup>(12)</sup>, and

$$k = -\frac{c-b}{a-b} \times \frac{1}{Dt} \times \ln\left(1 - \frac{x}{b}\right)$$

for bromide and iodide exchange reactions<sup>(13)</sup> where  $a$  and  $b$  are initial concentrations of substrate and salt, respectively, and  $c = \frac{1}{2}(D+K+4b)$ ,  $D = (K^2+4Kb)^{\frac{1}{2}}$ .

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