Element Effect Revisited.Variable and Inverse Element Effect in the S_NAr Reaction of Picryl Halide and 2,4-Dimethoxyaniline

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Kinetic studies were made of the S_NAr reaction of picryl halides (PicX, X=F, Cl) with 2,4-dimethoxyaniline in organic solvents. The element effect, $k_\psi^{PicF}/k_\psi^{PicCl}$, was found to be well-known large value at high [DMA], however, diminished continuously as the decrease of [DMA], and an inverse element effect was observed in CH_3CN. Variable/inverse element effect has not been suggested for S_NAr reaction and clearly shows that care must be exercised in using as the probe of reaction mechanism.

In bimolecular aromatic nucleophilic substitution reaction (S_NAr reaction), it is well known that the effect of a leaving group on its reaction rate is quite different from that of the aliphatic analogues. For example among aromatic halides ArX, while the rate decreases in the order for X as F >> Cl > Br > I for S_NAr reactions, the reverse is true for the aliphatic S_N2 and S_N1 reactions. Such effect of halogen nucleofuges is termed as "element effect."[1] The fact that fluorine, which has the largest bonding energy among the four, is far more easily substituted than the other halogenes, means breakage of C-X bond is not constituting a sole rate-determining-step.

The element effect has been taken as the proof that S_NAr reaction proceeds through a rate-determining addition of a nucleophile or through a multi-step mechanism involving an addition step and the succeeding step(s), the expulsion of the nucleofuge being one of them. The element effect is generally treated as a characteristic probe of the reaction system.[2]

In a study of solute-solute interactions, the present authors examined the S_NAr reaction between 2,4,6-trinitrofluorobenzene (PicF) or 2,4,6-trinitrochlorobenzene (PicCl) and 2,4-dimethoxyaniline (DMA) in acetonitrile. The kinetic studies were performed under pseudo-first-order conditions with large excess of the nucleophile (DMA) at 298 K.

Rate of the reactions were determined spectrophotometrically by following the increase of the absorbance at 390 nm, the absorption of the substitution product, ring-substituted diphenylamine. Pseudo-first-order rate constants were determined and were plotted against the nucleophile concentrations ([DMA]). Over two hundred data points were collected and a smooth curve was drawn to take a reading of k_ψ at a regular intervals of nucleophile concentration. The results are shown in Figures 1a (for PicF) and 2 (for PicCl).

For PicF, Fig 1a is suggesting a [nucleophile] dependency exceeding a first-order on DMA, k_ψ/[DMA] ratio was plotted against [DMA] and is shown in Figure 1b. A linear relationship at low [DMA] changes into curvilinear relationship concaving downward. Thus, in the reaction of PicF, pseudo-first-order rate constant is showing a second order dependency on the [DMA], accompanying a saturation kinetics approaching to a first order.

On the other hand, in the case of PicCl, pseudo-first-order rate constant shows an essentially first order dependency on [DMA] with only a minor contribution of second order term, $[DMA]^2$.

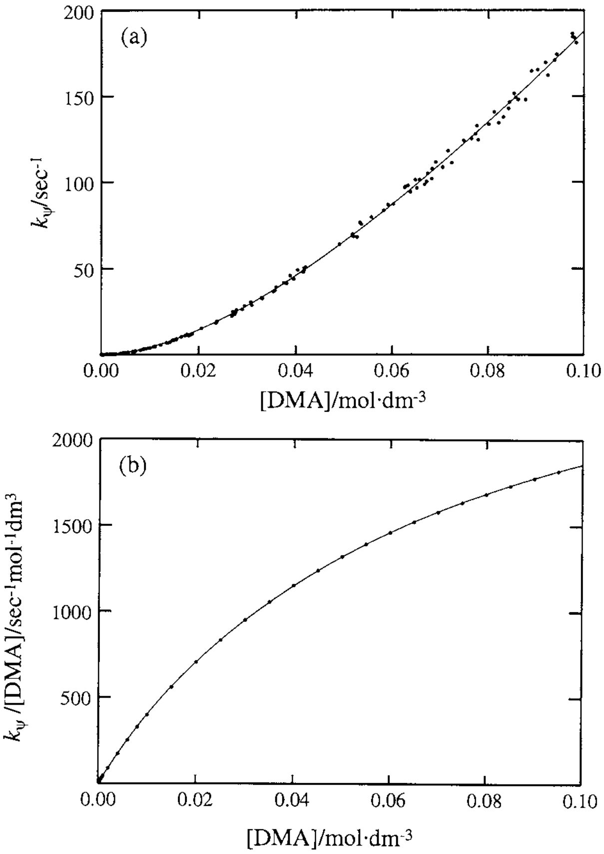

Figure 1. (a) The pseudo-first-order rate constant for the reaction of PicF and DMA in acetonitrile at 298 K. (b) Plot for the k_ψ/[DMA] against [DMA] for the reaction of picryl fluoride and DMA in acetonitrile at 298 K.

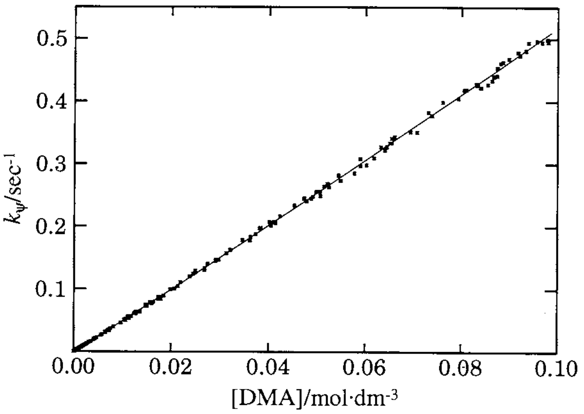

Figure 2. The pseudo-first-order rate constant for the reaction of PicCl and DMA in acetonitrile at 298 K.

Sheer difference in [DMA] dependency clearly shows a possibility that k^F/k^{Cl} ratio varies with change in [DMA]. Figure 3 gives the plot of the rate ratio of PicF to PicCl against the concentration of the nucleophile. The rate ratio was ca. 600 at the high DMA concentration, and it continuously diminished as [DMA] decreases. The plot suggests, in the low concentration range of [DMA], the rate ratio k^F/k^{Cl} can reach unity or below unity.

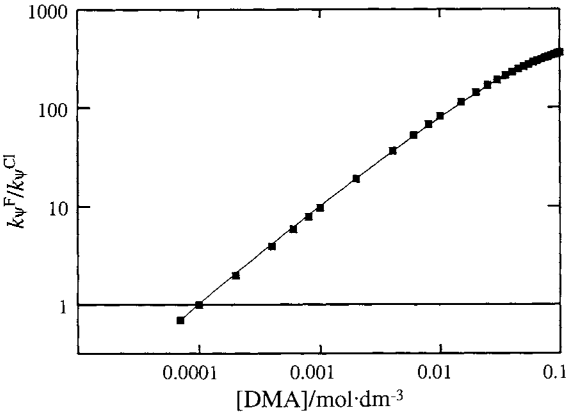

Figure 3. The rate ratio between PicF and PicCl in acetonitrile at 298 K.

Surprisingly enough, this was found to be the case. At [DMA] = 6.998 × 10^{-5} M, the rate ratio was $2.22\times10^{-4}/3.20\times10^{-4}$ = 0.69. The inverse element effect was substantiated. The variable element effect is not limited to the reaction in acetonitrile.

Similar kinetic studies were undertaken in varieties of common solvent, cyclohexane, methanol, 2,2,2-trifluoroethanol, and acetone. Data compiled in Table 1 shows the variable element effect in all these solvents, although the inverse element effect is not always observable mainly due to the experimental difficulties. In cyclohexane, k^F/k^{Cl} ratio for picryl halides reaches almost unity (7.832 × 10^{-4} /7.522 × 10^{-4}) at 2.057 × 10^{-5} M of [DMA].

Variable or an inverse element effect may be anticipated in the context of base catalysis in S_NAr reaction.[3] However, no such claim was suggested in the contemporary aspect of physical organic chemistry.

Table 1. Variable element effect in various solvents at 298 K

Solvent	10^3[DMA] /mol·dm^{-3}	k_ψ/sec^{-1}		k^F/k^{Cl}
		for PicF	for PicCl	
Cyclohexane	0.0206	0.000783	0.000752	1.04
	48.8	477	1.14	418
Ethanol	2.90	7.4	0.075	99
	29.0	150	0.82	183
TFE	0.0560	0.000480	0.0000690	6.96
	65.0	10.9	0.0777	140
Acetone	3.17	0.861	0.0180	47.8
	25.6	32.0	0.133	241

Care should be exercised as there is a definite possibility that no constant figure of an element effect is present, and a single figure of an element effect, which is derived from a limited range of reactant concentrations, should not be taken as a mechanistic probe in physical organic chemistry.

The authors are currently studying the implication of the multiple order dependencies observed in many S_NAr reaction in organic solvents. Results will be reported shortly.

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