SECONDARY DEUTERIUM ISOTOPE EFFECT IN CHLORINE ISOTOPIC

EXCHANGE REACTIONS IN ACETONITRILE[1]

Nobuo TANAKA, Aritsune KAJI, and Jun-ichi HAYAMI[2]

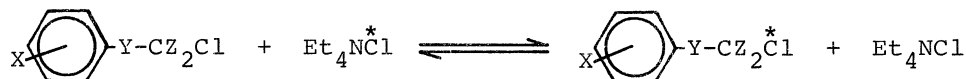Department of Chemistry, Faculty of Science, Kyoto University, Kyoto

Secondary deuterium isotope effects of about 12% were observed for reactions of chloromethyl aryl ethers or sulfides with radioactive chloride ion in CH_3CN.   2-Arylethyl chlorides gave about 3% of the isotope effect.   Magnitude of the isotope effect can also be a diagnostic of the looseness of the S_N2 transition state.

The recent publication by Willi and his co-workers on a large secondary deuterium isotope effect for the S_N2 reaction of p-methylbenzyl chloride with cyanide ion in aqueous methyl cellosolve[3] prompted the present authors to report the result of their isotope effect study in a preliminary form.

Leffek had reported an extensive work on solvolytic S_N2 reactions and other displacement reactions.[4]   The definite existence of isotope effect for the S_N2 reactions has also been substantiated by the works by Seltzer[5] and by Elias.[6] However, there is no systematic study of secondary isotope effect in which the electronic requirement of the S_N2 reaction center was examined.

In the course of the study of Finkelstein reactions, the present authors already reported a definite rate enhancing effect of an α-heteroatom in chloromethyl aryl ethers and sulfides.[7]   In a Hammett type analysis, they suggested that these rate enhancing effects can be attributed to the stabilization of the transition state by the electron-donating conjugation of oxygen or sulfur atom. Such a conjugation should give rise to a loose transition state where significant secondary deuterium isotope effect is anticipated.

In the present communication, the authors present examples of the significant deuterium isotope effect in a clean S_N2 reaction system.   The reaction studied is Finkelstein reaction with a symmetric transition state as is shown in the following scheme.

$$X-\!\!\left\langle\bigcirc\right\rangle\!\!-Y-CZ_2Cl \ + \ Et_4N\overset{*}{C}l \ \rightleftharpoons \ X-\!\!\left\langle\bigcirc\right\rangle\!\!-Y-CZ_2\overset{*}{C}l \ + \ Et_4NCl$$

Z; H, D.   I.   Y; CH_2 X; a)H, b)p-Cl

          II.   Y; O   X; a)p-Cl, b)m-Cl

          III. Y; S   X; a)p-OCH_3, b)H, c)p-Cl, d)m-Cl, e)p-NO_2

Chlorine-chlorine isotopic exchange reaction was undertaken in dry acetonitrile with tetraethylammonium chloride-^{36}Cl, utilizing ampoule technique.

As are shown in Table, normal isotope effects of about 12--14% were observed for chloromethyl aryl sulfides. The magnitude of the isotope effect is essentially

constant for all substituents examined. This is the strong support of the common reaction mechanism which is also anticipated by the good linear free energy relationship (ρ=-0.92, r=0.997).[7]

Similar isotope effects were also observed for chloromethyl aryl ethers. The isotope effect amounting about 11% is considerably large for an S_N2 displacement reaction, although Thornton had shown an example where 24% of the secondary isotope effect was observed for a solvolytic S_N2 reaction of methyl chloromethyl ether.[8] Significant isotope effect observed in the present study should imply a loose transition state where a conjugative stabilization would play an important role.

On the contrary, 2-arylethyl chlorides which gave a linear Hammett relationship with the positive ρ (ρ=0.57, r=0.991)[7] were shown to give about 3% of the isotope effect. Smaller effects and positive ρ imply that the transition state for this class of compounds is rather tight where the approach of a nucleophile plays an important role.

Provided that such indirect evidences as the constancy of second-order rate coefficients in a dilute solution, small values of ρ, and the inadequacy of σ^+,[7] validly indicate the S_N2 reaction,[9] the present results show that the secondary isotope effects reflect the looseness of the transition state and that the effect serves as a diagnostic of the transition state.

Table. Second-Order Rate Coefficients and Isotope Effects

Y	X	T (°C)	$k \times 10^2$ 1/mol·min H	D	k_H/k_D (per D)
CH_2	H	60	0.523	0.489	1.035
	p-Cl	60	0.889	0.836	1.031
O	p-Cl	-20	20.0	16.2	1.112
	m-Cl	-20	11.6	9.46	1.108
S	p-OCH$_3$	20	6.49	5.27	1.120
	H	20	3.10	2.44	1.128
	p-Cl	20	1.99	1.57	1.124
	m-Cl	20	1.60	1.23	1.141
	p-NO$_2$	20	0.652	0.519	1.121

References

1) S_N2 Reactions in Dipolar Aprotic Solvents. IV.

2) To whom the correspondence should be addressed.

3) A. Willi, C-K. Ho, and A. Ghanbarpour, J. Org. Chem., 37, 1185 (1972).

4) K. T. Leffek and A. F. Matheson, Can. J. Chem., 50, 986 (1972).

5) S. Seltzer and A. A. Zavitsas, ibid., 45, 2023 (1967).

6) H. Strecker and H. Elias, Chem. Ber., 102, 1270 (1969).

7) J. Hayami, N. Tanaka, S. Kurabayashi, Y. Kotani, and A. Kaji, Bull. Chem. Soc. Japan, 44, 3091 (1971).

8) T. C. Jones and E. R. Thornton, J. Amer. Chem. Soc., 89, 4863 (1967).

9) However, the intervention of an ion pair with a varying degree of tightness or looseness can hardly be excluded at this stage of the study.