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Variations of Heavy-Atom Kinetic Isotope Effects in SN2 Displacement Reactions[1]

Sir:

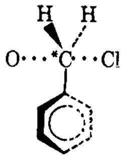
The primary hydrogen isotope effect has been widely utilized as a mechanistic probe of hydrogen-transfer reactions. Theoretical calculations[2-5] involving transfer of H from A to B using three center models A–H–B for the transition state indicate that the isotope effect should go through a maximum when H is symmetrically bonded to atoms A and B, when asymmetric motion of H from A to B is taken as the reaction coordinate. These results have been criticized,[6] since the calculations neglect effects of bending vibrations and of proton tunneling, but recent experimental results[7] support this behavior for a number of reactions. The concept is of considerable mechanistic usefulness, since it provides at least a qualitative correlation of the magnitude of the primary hydrogen isotope effect and transition state structure.

Several years ago, Fry[8] suggested that the carbon-14 (*C) kinetic isotope effect in an SN2 displacement reaction should exhibit similar behavior, whereas the isotope effect for labeled X should increase monotonically as F_1, the stretching force constant for bond 1, decreases. Experimental isotope effects for carbon-14 labeling at *C and chlorine-37 labeling at X have been obtained[9] for the benzyl chloride system, with Y = H_2O, CN^-, or $S_2O_3^{2-}$ and with R = para-substituted phenyl, p-Z-C_6H_4, with Z = CH_3O, CH_3, H, Cl, and NO_2. Recently, we have carried out a large number of calculations of the isotope effects expected for labeling at various positions in these systems for numerous models of the transition state for both SN1 and SN2 reactions. We present here some results from the calculations for the SN2 reactions of benzyl chloride.

$$Y + R{*}CH_2X \longrightarrow [Y\cdot\overset{2}{\cdot}\cdot R{*}CH_2\cdot\overset{1}{\cdot}\cdot X]^{\ddagger} \longrightarrow R{*}CH_2Y + X \qquad (1)$$

Carbon-14 and chlorine-37 isotope effects (k/k^*) were calculated using the complete transition state theory expression.[4,10] Moments of inertia and vibration frequencies were determined from complete vibrational analyses of the reactant and transition state models assumed. Extensive calculations have shown that in some cases one can extend the "cutoff" procedures of Stern and Wolfsberg[11] to include cutting through aromatic rings to conserve computer time. The validity of this cutoff procedure is indicated by the results in Table I for the complete models (**1**) of the reactants and complexes and for two cutoff models (**2**, **3**) of them. Force constants for the complex were calculated from the assumed bond orders for the *C···Cl bond (n_1) and for the Y···*C bond (n_2) in a manner similar to that used recently by other workers[5,12]

Table I. Calculated Kinetic Isotope Effects at 30° for Reaction 1 of Text[a]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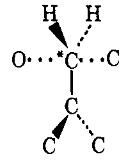
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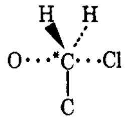
3

n_1	Complete model **1**	Cutoff model **2**	Cutoff model **3**
0.9	1.03764	1.03894	1.04531
	1.00348	1.00208	1.00048
0.7	1.05576	1.05750	1.06907
	1.01077	1.00924	1.00607
0.5	1.05473	1.05619	1.06788
	1.01702	1.01582	1.01265
0.3	1.03922	1.04022	1.04939
	1.02123	1.02064	1.01784
0.1	1.01090	1.01158	1.01689
	1.02451	1.02386	1.02493

[a] Values in the table correspond to the nucleophile Y in reaction 1 of text taken as oxygen, as in hydrolysis: upper entries, k^{12}/k^{14}; lower entries, k^{35}/k^{37}. Reactant models corresponding to those shown for the complex in **1–3** were employed. A zero reaction coordinate frequency $\nu_L^{\ddagger}$ was produced in these calculations as explained in the text.

$$\text{stretching of bond ab:} \quad F_{ab} = n_{ab}F^0_{ab}$$

$$\text{bending of angle abc:} \quad F_{abc} = n_{ab}n_{bc}F^0_{abc}$$

where the F^0's refer to reactant (or product) force constant values. The present calculations have assumed $n_1 + n_2 = 1$, which corresponds to constant total bonding during the course of the reaction.

The calculated k/k^* values were not sensitive to geometrical parameters of the complex, but to render the model realistic, bond distances for Y···*C and *C···Cl were adjusted from the assigned bond orders by Pauling's rule,[13] and the geometry about *C was varied

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systematically from a tetrahedral reactant-like transition state for $n_1 \sim 1$ to trigonal bipyramidal for symmetric models ($n_1 \sim 0.5$) to a tetrahedral product-like model for $n_1 \sim 0$. All other variables were taken equal to reactant (or product) values selected from standard sources.[14] A zero or imaginary reaction coordinate frequency $\nu_L^{\ddagger}$ was obtained by introducing an interaction constant F_{12} equal to or greater than $(F_1F_2)^{1/2}$, respectively.[15]

The calculated carbon-14 and chlorine-37 isotope effects for reaction 1 are shown in Figure 1 for Y equals O (I), Cl (II), and S (III). As can clearly be seen, the carbon isotope effect goes through a maximum as n_1 decreases. The results support the qualitative suggestion[8] that an S$_N$2 reaction can be viewed as an "RCH$_2$ group" transfer from X to Y, with mechanistic implications similar to those of hydrogen-transfer reactions.

Compared to the symmetric chlorine exchange reaction, where the maximum isotope effect occurs for $n_1 = 0.5$ (Figure 1, curve II), one can see that the transition state corresponding to the maximum isotope effect becomes more reactant-like, $n_1 > 0.5$ (curve I) as the forming bond (C–O) becomes stronger than the rupturing C–Cl bond, or more product-like, $n_1 < 0.5$ (curve III), as the forming bond (C–S) becomes weaker than the rupturing C–Cl bond. This trend is consistent with the Hammond postulate.[16]

The chlorine isotope effect, on the other hand, increases continuously as one goes from a reactant-like to a product-like transition state (*i.e.*, as n_1 decreases). The chlorine isotope effect for a forming O–C bond (curve I) is calculated to be somewhat larger than for a forming S–C bond (curve III), in contrast to the recent experimental results of Grimsrud and Taylor.[17] However, the calculated isotope effects for these two cases are not significantly different, and solvation of the leaving group and/or nucleophile may appreciably affect the chlorine isotope effect but would not be expected to alter the trends in the carbon isotope effect.

The experimental[9] isotope effects for solvolysis (curve I, Y = O) are: $k/k^* \sim 1.08$ for carbon-14 and 1.008 for chlorine-37. The results in Table II show that a more realistic reaction coordinate frequency ($\nu_L^{\ddagger}$ imaginary rather than zero) yields calculated carbon-14 and chlorine-37 isotope effects in better agreement with experiment. Details of the calculations, including cutoff procedures and comparisons with available experimental data, will be published subsequently.

Table II. Effect of Reaction Coordinate Frequency on Calculated Kinetic Isotope Effects at 30° for Reaction 1 of Text[a]

$\nu_L^{\ddagger}$	k^{12}/k^{14}	k^{35}/k^{37}
0	1.05911	1.01289
139i	1.07310	1.01087
204i	1.08159	1.00926
264i	1.08686	1.00825

[a] Cutoff model **2** (see Table I) was used with $n_1 = 0.6$ and $n_2 = 0.4$.

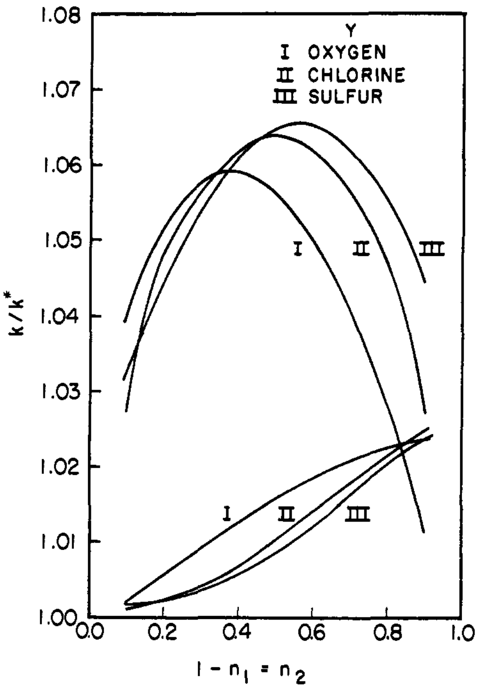

Figure 1. Calculated carbon-14 (upper curves) and chlorine-37 (lower curves) isotope effects as a function of bond order for reaction 1 using cutoff model 1.

To our knowledge, no heavy-atom kinetic isotope effect results have been reported which illustrate the bell-shaped behavior shown in Figure 1. Experiments are being carried out in this laboratory to test this concept.

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Synthesis and Chemistry of α-Lactones[1]

Sir:

Synthesis of α-lactones poses a long-standing challenge. α-Lactones have been invoked as intermediates in such diverse transformations as nucleophilic displacements,[2] free-radical processes,[3] thermal eliminations,[4] and photochemical reactions.[5] A variety of in-

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