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# SECONDARY ISOTOPE EFFECTS AND MASS-SENSITIVE AMPLITUDES OF VIBRATION

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In recent years secondary isotope effects in reactions involving carbonium ion transition states have been explored intensively by Lewis, Shiner, and others.[2] The retardation accompanying deuterium substitution at $\beta$ carbons is almost universally attributed to a hyperconjugative weakening of C-H or C-D bonds on the $\beta$ carbon atoms. The retardation associated with $\alpha$ substitution, on the other hand, is acknowledged to be entirely unrelated to hyperconjugation, and hence unrelated to the $\beta$ effect. It is the purpose of this communication to point out a factor, heretofore neglected, which seems to account for a substantial part of the $\beta$ effect without requiring that C-H bonds be weakened in the transition state. Further, it bridges the gap between the $\alpha$ and $\beta$ effects as it can be shown, in the $\alpha$ effect, to reduce essentially to the accepted explanation of Streitwieser *et al.*[3]

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[1] Research supported by the National Science Foundation.

[2] For reviews see E. S. Lewis, *Tetrahedron* **5**, 143 (1958); V. J. Shiner, *Tetrahedron* **5**, 243 (1958).

[3] Streitwieser, Jagow, Fahey and Suzaki, *J. Amer. Chem. Soc.* **80**, 2326 (1958).

The principle of the proposed argument is that the amplitudes of vibration of hydrogen atoms are larger than the amplitudes of the heavier deuterium atoms by a readily predictable amount. Nonbonded repulsions, averaged over the atomic vibrations, are greater for hydrogen atoms than deuterium atoms since, in the range of interest, the second derivative of the nonbonded potential function is positive. Moreover, there are more, and stronger nonbonded repulsions in the crowded tetrahedral reactant than in the carbonium ion transition state. Accordingly, the trigonal transition state is relieved of nonbonded repulsions to a greater extent when it contains hydrogen than when it contains deuterium. For a given nonbonded interaction the isotope effect is proportional to the mean-square of the mass-sensitive component of the relevant amplitude of vibration and to the second derivative of the potential function. Recent determinations of amplitudes from spectroscopic and electron diffraction data coupled with potential functions proposed elsewhere,[4] make it possible to estimate the numerical magnitude to be expected.

In preliminary calculations, for simplicity, the interactions of the solvent molecules and leaving group with the carbonium ion were ignored in the transition state. Unfortunately, the lack of structural data for the molecules considered made it necessary to resort to guesses. In the case of tosylate solvolyses the calculated isotope effect was found to be exceedingly sensitive to the assumed molecular configurations, and the

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[4] L. S. Bartell, J. Chem. Phys. (in press).

values calculated ranged from rather less than the observed value to considerably more. For the solvolysis of t-amyl chloride the calculated $\Delta\Delta E_a$ was roughly half the observed $\Delta\Delta F_a$[2]. In the analogous gas phase equilibrium[5]

$$Me_3B{:}NMe_3 = BMe_3 + NMe_3$$

where the structures of the molecules are much less speculative than in solvolysis reactions, the calculated isotope effect was approximately equal to the observed value. It is not possible to assess the accuracy of the assumed parameters at present. Nevertheless it is clear that the magnitude of the nonbonded effect is entirely comparable with that of the observed isotope effect. Therefore it would be injudicious to interpret isotope effects solely on the basis of hyperconjugation.

It is fitting to observe that nonbonded interactions obscure the role of hyperconjugation not only in studies of isotope effects, but also in studies of bond lengths and heats of formation of molecules in the ground state. According to evidence recently elicited,[4] nonbonded repulsions of the magnitude observed in Urey-Bradley analyses of vibrational spectra[6] are sufficient to account for variations of bond lengths and energies that are usually attributed to hyperconjugation and hybridization changes.

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[5] Love, Taft and Wartik, Tetrahedron 5, 116 (1959).

[6] T. Simanouti, J. Chem. Phys. 17, 245 (1949); J. W. Linnett, ibid 17, 801 (1949).

The Urey-Bradley analyses also indicate that nonbonded repulsions account for a substantial part of the potential energy of bond bending. To the extent that hydrogen atoms can be considered to be moving in harmonic nonbonded potential wells in bending motions, the present model can be reduced to Streitwieser's model for the $\alpha$ isotope effect. Calculations based on experimental amplitudes of vibration and the potential parameters of references (4) and (6) agree in magnitude with those of Streitwieser based on observed vibrational frequencies.[3]

Many implications broader than the present correlations are suggested by the nonbonded model. Discussions of kinetic isotope effects other than $\alpha$ or $\beta$ effects, and predictions of effects in rotational isomerization energies of hydrocarbons, spectra, and other observables will be presented along with the details of the present calculations in a forthcoming article.