MODEL CALCULATIONS OF SECONDARY DEUTERIUM ISOTOPE EFFECTS IN
# HYDROGEN BRIDGED CARBONIUM IONS[1]

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Hydrogen bridged cations have been proposed as transition states (or intermediates) in solvolytic reactions proceeding with hydrogen migration[2]. The relatively large (k_H/k_D 2.0-2.2) secondary β-deuterium isotope effects observed in these reactions were consistent with bridging in the transition state[2] but could equally well be rationalized on the basis of a rate determining hydrogen (deuterium) elimination[3a]. Recent studies in these laboratories[3b] have shown that the larger than normal β-effect (k_H/k_D 2.39) observed in the solvolysis of neomenthyl tosylate was not due to partial elimination — the migrating deuterium survives in the olefinic product. In view of this finding it was considered to be of interest to perform numerical calculations to see if the observed effect was consistent with the structure assigned to the transition state. Semiquantitative considerations[4] have suggested that the loss of the bending frequency of the β-hydrogen in passing to a bridged activated complex could give rise to an isotope effect of the correct magnitude ($k_H/k_D = 3.6$). In this paper are reported the results of a model calculation that considers several additional degrees of freedom that are directly involved in the formation of the transition state.

As the first model system the bridged ethyl cation was chosen for simplicity, the semi-empirical MINDO/2[5] scheme was used because of its known success in the calculations of force constants[5a]. The structure of the transition state was assumed to have C_2 symmetry, with the four basal carbon-hydrogen distances of 1.201 Å (MINDO/2 calculations overestimate C-H distances by 0.1 Å[6]. The four nonmigrating hydrogens and the carbon atoms were assumed to be coplanar. The migrating hydrogen, H_{mig}, was placed at 1.198 Å above the basal plane, the energy minimum found from MINDO/2 calculations.

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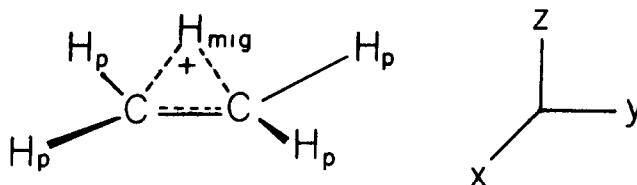
From the second derivative of the energy of the symmetrically bridged cation as a function of the distance $\underline{z}$ above the plane of the rest of the molecule of the migrating hydrogen (H_{mig}), the perpendicular force constant $k_z = 3.95 \times 10^5$ dyn/cm (A_1 motion of H_{mig}) was obtained. According to this calculation the symmetrically bridged species is stable with respect to motion of H_{mig} in the direction of the reaction coordinate $\underline{y}$. However, the potential energy curve in this direction has such a shallow minimum that the force constant is close to zero, as it would be if the bridged structure corresponded to a transition state. The motion of H_{mig} in the $\underline{x}$ direction corresponds to a B_1 rocking motion of the four coplanar hydrogens. The force constant calculated for this bending motion is $k_x/\ell^2 = 0.11 \times 10^5$ dyn/cm. Finally, the A_2 twisting motion of the four coplanar hydrogens was calculated to be $k_{twist}/\ell^2 = 0.98 \times 10^5$ dyn/cm.

The Table below lists the calculated frequencies corresponding to the four motions described together with the estimated ground state frequencies[8] from which they are derived. The last column of the Table lists the calculated multiplicative contributions[9] of these vibrations to the overall isotope effect.

Table Frequencies and Calculated Isotope Effects for the Formation of the Ethyl Cation

| | Frequencies (cm^{-1}) | | Contribution to |
	G.S. (est.)	T.S. (calc.)	k_H/k_D
H_{mig} (stretch)	2900	2635	1.22
H_{mig} (bend)	1375	0	2.64
H_{mig} (bend)	1375	432	1.95
H_p (internal rot.)	0	1303	0.40
		Total	2.50

Similar calculations have been carried out for the transition state bearing _trans_ 1,2-dimethyl substituents. The force constants obtained were remarkably similar and thus indicate that the simply bridged ethyl cation is an adequate model for the considerably more complex species used in the solvolytic studies.

From these exploratory calculations the conclusion can be drawn that the loss of the bending motion in the transition state is a major contributor to the total isotope effect, as suggested by Wiberg, but that the other motions described here play equally important roles. The loss of the degree of freedom associated with the internal rotation of the methyl group in the ground state contributes an equivalently large inverse isotope effect. The out-of-plane bending motion of H_{mig} also makes a large contribution. The stretching motion of H_{mig} makes only a small contribution to the isotope effect, and indicates that vertical stabilization[10] is insufficient to account for the observed total effect. It is interesting to note that this calculated partial isotope effect is almost identical with the observed β-isotope effect due to hyperconjugation[11] in nonbridging systems

Extrapolation of these exploratory calculations to cyclohexyl systems,[2b-d,3b] requires that several additional factors be taken into account. In cyclohexyl systems such as neomenthyl tosylate, the free internal rotation is replaced by the somewhat restricted rocking motion of the methylene groups. This would increase the calculated isotope effect. However, the rigidity of the cyclohexane ring would partially persist in the transition state[12], and tend to attenuate the contributions of both the out-of-plane bending and rocking motions, so that the full effect would not be observed. An additional factor is that in the neomenthyl system, the hydrogen atom migrates from a tertiary center to a secondary cation. In accordance with Hammond's postulate[13], in such a rearrangement the transition state would come earlier along the reaction coordinate implying that the observed isotope effect should be smaller than that calculated for the symmetrical ion.

References

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