I_{Me} of +0.011 is of the same order as that in the allenes and confirms that the electron donation through the bond is dominant.

IV. Conclusions

The following conclusions can be drawn about methyl groups.

1. They are electron attracting in alkanes but electron repelling in other systems.

2. Methyl groups in systems other than alkanes should be regarded as more polarizable than hydrogen though the major electron donation occurs through the bond.

This confirms Ingold's empirical ideas about methyl groups. However, partitioning of inductive residues by calculation does require a conventional boundary for not merely the carbon atom. In organic species it requires a boundary for carbon and hydrogen and we suggest spheres of radii 0.77 and 0.33 Å, respectively. This choice is arbitrary but does not affect the conclusions if the β position approach is followed. The exclusion of approximately 25% of the charge by using spheres is mediated by the increase in the calculated inductive effect with the radius of the sphere. A number of authors[13] have commented on the result that, in molecular orbital calculations, a methyl group can appear electron attracting relative to hydrogen. We suggest that this is an artifact of the Mulliken population analysis, in particular, the equal division of the overlap charge.

The use of sphere charges is at present being applied to an investigation of orientation in aromatic substitution.

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References and Notes

(1) S. M. Dean and W. G. Richards, *Nature* (*London*), **258,** 133 (1975).
(2) C. K. Ingold, "Structure and Mechanism in Organic Chemistry", 2nd ed., Cornell University Press, Ithaca, N.Y., 1969.
(3) See, for example, (a) R. F. W. Bader and A. D. Bandrank, *J. Chem. Phys.*, **49,** 1953 (1968); (b) R. F. W. Bader, P. M. Bedall, and J. Peslak, *ibid.*, **58,** 557 (1973); (c) P. Politzer and R. S. Mulliken, *ibid.*, **55,** 5135 (1971); (d) P. Politzer and A. Politzer, *J. Am. Chem. Soc.*, **95,** 5450 (1973); (e) B. J. Ransil and J. J. Sinai, *J. Chem. Phys.*, **46,** 4050 (1967); (f) A. Hinchliffe and J. C. Dobson, *Chem. Soc. Rev.*, **15,** 79 (1976).
(4) R. S. Mulliken, *J. Chem. Phys.*, **23,** 1833 (1955).
(5) The defects and subsequent modifications to the Mulliken scheme are the subject of many papers. See, for example, (a) D. Peters, *J. Chem. Soc.*, 2015 (1963); (b) P. Ros and G. A. C. Schuit, *Theor. Chim. Acta*, **4,** 1 (1966); (c) E. R. Davidson, *J. Chem. Phys.*, **46,** 3320 (1967); (d) M. Pollak and R. Rein, *ibid.*, **47,** 2045 (1967); (e) E. W. Stout and P. Politzer, *Theor. Chim. Acta*, **12,** 379 (1968); (f) C. A. Coulson and G. Doggett, *Int. J. Quantum Chem.*, **2,** 825 (1968); (g) G. Doggett, *J. Chem. Soc. A*, 229 (1969).
(6) W. G. Richards and J. Wallis, *Proc. R. Soc. London, Ser. B*, **199,** 291 (1977).
(7) J. Wallis, V. Sackwild, I. L. Wiseman, and W. G. Richards, to be published.
(8) K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Heden, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, "ESCA Applied to Free Molecules", North-Holland Publishing Co., Amsterdam, 1969.
(9) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51,** 2657 (1969).
(10) L. E. Sutton, "Tables of Interatomic Distances and Configurations in Molecules and Ions", *Chem. Soc., Spec. Publ.*, **No. 11** (1958); *Suppl.*, **No. 18** (1965).
(11) V. W. Laurie and J. S. Muenter, *J. Am. Chem. Soc.*, **58,** 2883 (1966); *J. Chem. Phys.*, **45,** 825 (1966).
(12) L. Radom, J. A. Pople, and P. von R. Schleyer, *J. Am. Chem. Soc.*, **94,** 5935 (1972).
(13) See: G. A. Olah and D. A. Forsyth, *J. Am. Chem. Soc.*, **97,** 3137 (1975).

Role of Hyperconjugation in Secondary β-Deuterium Isotope Effects

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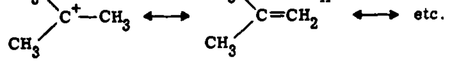
Abstract: The effect of hyperconjugation on the magnitudes of secondary β-deuterium isotope effects has been investigated by ion cyclotron resonance spectroscopy and ab initio molecular orbital theory. Isotope effects measured for ion-molecule equilibria involving formation either of a nonbonded pair of electrons or of a vacant orbital adjacent to a methyl probe have been compared to theoretical calculations which have been restricted to consideration of changes in CH stretching force constants alone. Although this simple theoretical model successfully mirrors the observed β effects in the former systems in which the methyl group acts to accept excess electron density, it fails to properly account for the observed effects in those systems where the methyl probe is adjacent to an electron-deficient center.

Introduction

The origin of β secondary deuterium isotope effects on the rates of solvolysis reactions proceeding through carbocation-like transition states has been ascribed to hyperconjugation.[2] Within the framework of transition-state theory, such isotope effects are interpreted similarly to those associated with purely equilibrium processes.[3] Thus, the observation that, in 60% ethanol, *tert*-butyl-d_9 chloride solvolyzes 2.4 times more slowly than the corresponding protio compound[4] demonstrates that the force constants involving the hydrogen positions in the transition state are smaller than those in the reactant.[5] This suggests that the structure of the *tert*-butyl cation, to which the solvolysis transition state is expected to be closely related, can be described in terms of hyperconjugative resonance structures of the form



$$(CH_3)_2C^+{-}CH_3 \longleftrightarrow (CH_3)_2C{=}CH_2\ H^+ \longleftrightarrow \text{etc.}$$

The molecular orbital analogue of hyperconjugation is the withdrawal of electrons from the filled π symmetry orbital of the methyl group into the vacant p function at the carbocation center.[6]

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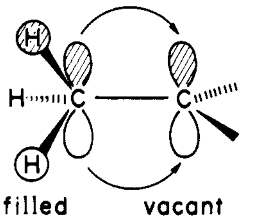
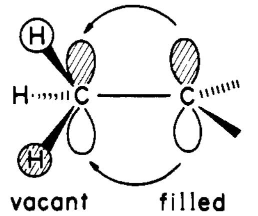


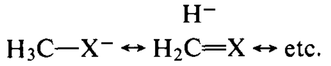
As the orbital from which electron density is removed is essentially C–H bonding, an increase in CH bond length and a reduction in the corresponding stretching force constants are expected, leading directly to the observed isotopic preference. The theoretical (STO-3G level) equilibrium geometry for the *tert*-butyl cation[6c,7] clearly shows the expected CH bond lengthening. The six out-of-plane CH linkages have lengthened to 1.093 Å (compared with 1.086 and 1.085 Å for the corresponding bonds in propane and propene, respectively[8]). The three in-plane CH linkages, which are orthogonal to the vacant p function, are calculated to be 1.086 Å. Theoretical equilibrium structures for other carbocations show similar effects.[7]

The molecular orbital picture also suggests that shifts in electron density between nonbonded atoms (i.e., the methyl group hydrogens) will lead to angular distortions in a methyl group attached to a carbocation center. Specifically, electron displacement away from the occupied methyl group orbital should lead to diminishment of the repulsive interaction between the pairs of out-of-plane hydrogens and a corresponding reduction in HCH bond angles. STO-3G calculations on *tert*-butyl cation concur,[6c,7] yielding HCH bond angles involving out-of-plane hydrogens which are 107.3°, significantly less than the corresponding bond angles in propane and propene (108.2 and 108.5°, respectively, at the STO-3G level, 107.7 and 109.0°, experimentally). Such changes in equilibrium bond angles will presumably result in changes in the magnitudes of the corresponding bending force constants. It is tempting to assume, however, that such differential effects are small, and that the observed secondary isotope effects might be due in total to changes in CH stretching force constants alone. Our goal at present is to test the limits of applicability in such an assumption.

Molecular orbital theory further suggests that a lowering of force constants involving the C–H bonds will occur if the methyl group acts (in the opposite manner) to accept electron density. This follows since the methyl group acceptor orbital of π symmetry is C–H antibonding.



A like result derives from resonance arguments



$$\mathrm{H_3C{-}X^- \leftrightarrow \overset{H^-}{H_2C{=}X} \leftrightarrow etc.}$$

and has been aptly termed "negative hyperconjugation".[9] The observation of nonnegligible secondary β-deuterium isotope effects for the gas-phase ion-molecule equilibria

$$\mathrm{CD_3NH^- + CH_3NH_2 \rightleftharpoons CD_3NH_2 + CH_3NH^-}, \quad K = 1.9 \pm 0.3 \quad (1)$$

$$\mathrm{CD_3O^- + CH_3OH \rightleftharpoons CD_3OH + CH_3O^-}, \quad K = 2.3 \pm 0.4 \quad (2)$$

$$\mathrm{CD_3S^- + CH_3SH \rightleftharpoons CD_3SH + CH_3S^-}, \quad K = 1.7 \pm 0.2 \quad (3)$$

has recently been cited as evidence for such an effect.[10] At present, there exists little evidence for or against the notion that negative hyperconjugative factors are important in reaction processes in solution.

Equilibrium constants for gas-phase isotope exchange reactions may be evaluated theoretically in the harmonic approximation[11] given only the equilibrium geometries and all quadratic force constants, quantities which may be calculated in a straightforward manner with standard single-determinant ab initio molecular orbital theory. Recent work from our laboratories[12] has shown that isotope effects for ion-molecule equilibria such as (1) and (2) above, calculated using complete quadratic force fields obtained at the split-valence-shell, 4-31G level of theory, are in good quantitative agreement with experimental gas-phase values. Unfortunately, the a priori evaluation of complete quadratic force fields is an extremely tedious and time-consuming matter, even for molecules as small as those involved in reactions 1 and 2. It is advantageous, therefore, that such complete studies be limited to a small number of prototype systems, and that more approximate models be sought for the calculation of isotope effects.

We present in this paper the results of our experimental and theoretical studies of β-secondary deuterium isotope effects on gas-phase ion-molecule equilibria. We have deliberately limited our theoretical work to the consideration of changes in CH stretching force constants. Thus, the calculations may be employed to provide a test of the notion that changes in stretching force constants rather than changes in bond angle deformation force constants or possibly torsional force constants play the dominant role in determining the magnitudes and directions of β-secondary deuterium isotope effects.

The examples chosen for study may be divided into two distinct categories. The first set of reactions has been selected to exemplify situations in which chemical reaction leads to the formation of a (formally) nonbonded pair of electrons at a site adjacent to that of the isotopic probe (in all cases a CD_3 group). The second set of processes considered typifies the other extreme, situations in which reaction leads to the generation of an electron-deficient center adjacent to the probe.

Methods, Results, and Discussion

Theoretical calculations of average CH stretching force constants have been carried out at three different levels of approximation.

(A) Equilibrium geometries have been fully optimized using the STO-3G minimal basis set,[13] and an average CH stretching force constant evaluated using the relationship[14]

$$k_{\mathrm{CH\ stretch}}\ (\mathrm{mdyn\ Å^{-1}}) = \frac{4.3593}{N_{\mathrm{CH}}} \frac{E^+ + E^- - 2E^\circ}{\Delta^2}$$

Here, E° is the energy at the theoretical equilibrium geometry in hartrees; E^+ and E^- are energies corresponding to displacement of *all* CH linkages by $+\Delta$ and $-\Delta$, respectively. N_{CH} is the number of CH bonds. Displacements, Δ, for all calculations have been chosen as 0.01 Å, a compromise between the desire to sample only the harmonic region of the potential curve and the necessity to maintain numerical significance in the calculated energy differences.

(B) CH bond lengths only have been reoptimized using the split-valence-shell 4-31G basis set.[15] An average value for the CH stretching force constant has been evaluated at the 4-31G level in the manner described above.

(C) Theoretical equilibrium geometries have been optimized completely using the 4-31G basis. An average CH stretching force constant has been calculated in the manner prescribed above.

All ab initio calculations have been carried out using the GAUSSIAN 77/UCI computer program[16] on a Harris Corp. Slash 6 digital computer.

Table I. Theoretical Force Constant and Bond Length Data

molecule	A		B		C	
	k_{CH}	r_{CH}	k_{CH}	r_{CH}	k_{CH}	r_{CH}
CH_3NH_2	7.22	1.090	5.89	1.082	5.80	1.084
CH_3NH^-	6.31	1.108	4.93	1.109	4.80	1.112
CH_3OH	7.15	1.094	5.90	1.081	5.96	1.080
CH_3O^-	5.61	1.132	4.55	1.123	4.56	1.122
CH_3SH	7.27	1.086	6.02	1.079	6.19	1.076
CH_3S^-	6.73	1.100	5.35	1.095	5.59	1.088
$CH_3NH_3^+$	7.41	1.091	6.15	1.076	6.15	1.076
$(CH_3)_2NH$	7.22	1.090	5.84	1.083		
$(CH_3)_2NH_2^+$	7.38	1.091	6.16	1.076		
$(CH_3)_3N$	7.22	1.090	5.84	1.084		
$(CH_3)_3NH^+$	7.40	1.090	6.12	1.077		
$(CH_3)_3CH$	7.32	1.086	5.85	1.084		
$(CH_3)_3C^+$	7.27	1.091	5.87	1.083		
CH_3CN	7.35	1.088	5.99	1.080		
CH_3CNH^+	7.25	1.094	5.98	1.081		
CH_3CHO	7.34	1.086	5.90	1.082		
CH_3CO^+	7.18	1.097	5.89	1.083		

Table II. Theoretical and Experimental Free Energy Changes ($\Delta G°$) for Isotope Exchange Reactions (kcal/mol)[a]

reaction	theory				exptl[c]
	A	B	C	D[b]	
(1) $CD_3NH^- + CH_3NH_2 \rightleftharpoons CD_3NH_2 + CH_3NH^-$	−0.27	−0.32	−0.33	−0.52	−0.37 ± 0.04
(2) $CD_3O^- + CH_3OH \rightleftharpoons CD_3OH + CH_3O^-$	−0.47	−0.46	−0.47	−0.63	−0.50 ± 0.05
(3) $CD_3S^- + CH_3SH \rightleftharpoons CD_3SH + CH_3S^-$	−0.16	−0.22	−0.19		−0.30 ± 0.04
(4) $CD_3NH_3^+ + CH_3NH_2 \rightleftharpoons CD_3NH_2 + CH_3NH_3^+$	0.05	0.08	0.11	0.13	0.09 ± 0.02[d]
(5) $(CD_3)_2NH_2^+ + (CH_3)_2NH \rightleftharpoons (CD_3)_2NH + (CH_3)_2NH_2^+$	0.05	0.10			0.12 ± 0.02[e]
(6) $(CD_3)_3NH^+ + (CH_3)_3N \rightleftharpoons (CD_3)_3N + (CH_3)_3NH^+$	0.05	0.09			0.11 ± 0.02[f]
(7) $(CD_3)_3C^+ + (CH_3)_3CH \rightleftharpoons (CD_3)_3CH + (CH_3)_3C^+$ [g]	−0.04	0.02			−0.10 ± 0.05[h]
(8) $CD_3CNH^+ + CH_3CN \rightleftharpoons CD_3CN + CH_3CNH^+$	−0.03	0.00			−0.05 ± 0.03
(9) $CD_3CO^+ + CH_3CHO \rightleftharpoons CD_3CHO + CH_3CO^+$ [i]	−0.05	0.00			−0.10 ± 0.03

[a] Per methyl group. [b] Reference 12. [c] Errors quoted correspond to one standard deviation. [d] A free energy of 0.1 kcal/mol for this equilibrium has previously been reported: D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Am. Chem. Soc.*, **98**, 311 (1976). [e] See also: T. B. McMahon and J. L. Beauchamp, *J. Phys. Chem.*, **81**, 593 (1977). [f] An isotope effect of 0.084 per methyl group has been obtained in aqueous solution. D. Northcott and R. E. Robertson, *J. Phys. Chem.*, **73**, 1559 (1969). [g] Experimental number corresponds to $\Delta G°$ (per methyl group) for the chloride transfer equilibrium $(CD_3)_3C^+ + (CH_3)_3CCl \rightleftharpoons (CD_3)_3CCl + (CH_3)_3C^+$. The energy for this reaction has been evaluated theoretically, with the use of force constants obtained at the level A approximation, and is very nearly identical with that evaluated in the same way for (7). [h] An equilibrium constant for the reaction in footnote *g* has been calculated on the basis of force constants deduced from solution-phase vibrational spectra.[25] The resulting free-energy change, 0.17 kcal mol^{-1}, is stated to arise primarily from differences in CH stretching modes. [i] Experimental number corresponds to $\Delta G°$ for the chloride transfer equilibria $CD_3CO^+ + CH_3COCl \rightleftharpoons CD_3COCl + CH_3CO^+$.

Theoretical stretching force constants calculated in the manners described above are presented in Table I for all molecules considered in this paper. The corresponding average CH bond lengths have also been provided. It has already been noted that at the 4-31G level (schemes B and C), CH stretching force constants, and bond lengths correlate linearly.[12] The tabulated data further support this observation. Experimental CH bond lengths and stretching force constants are available for the neutral molecules dealt with here. The former quantities are generally in good accord with the theoretical data;[17] the experimental stretching force constants are consistently smaller than the theoretical values.[18]

Theoretical and experimental data on standard free energies of isotopic exchange equilibria are presented in Table II.

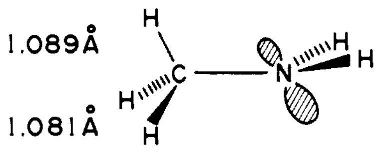
Through the application of perturbation theory to the vibrational problem[19] it has been demonstrated that isotope effects on equilibria can be approximated without explicit consideration of the normal vibrational modes. Rather the molecular vibrational motions are assumed to correspond to uncoupled stretch, bend, and torsion oscillators. In this approach, a zero-point energy $[h/4\pi(k_{CH}/m_C + m_H)^{1/2}]$, where h is Planck's constant and m_C and m_H are the masses of carbon and hydrogen, respectively, corresponds to each CH stretch. The contributions of the CH stretches to the isotopic exchange equilibria can then be approximated from a knowledge of the corresponding CH stretching force constants; the contribution to $\Delta G°$ for the reaction is, therefore, given simply by the changes in zero-point energies corresponding to CH stretching motions. The theoretical data in columns A, B, and C of Table II have been obtained by the use of average CH stretching force constants from the corresponding columns of Table I. The data in column D for reactions 1, 2, and 4 have been arrived at through the use of complete sets of quadratic force constants, obtained with the split-valence 4-31G basis set and evaluated at the corresponding theoretical equilibrium geometries. These results, which were obtained by direct calculation of normal mode frequencies, have previously been presented; the reader is referred elsewhere to a discussion of the computational methods involved.[12] They have been included to help in the assessment of the importance of changes in CH stretching vibrations in dictating the magnitude of the observed isotope effect. The experimental free energy data given in the table have been obtained by standard pulsed ion cyclotron resonance spectroscopy, the instrumentation[20] as well as the methods and procedures[21,22] for which have been described previously. Values for processes 1–3, involving formation of the methylamino, methoxy, and thiomethyl anions, have been previously published.[10]

Theoretical energies for reactions 1–6 are in qualitative agreement with free energies obtained experimentally by ion cyclotron resonance spectroscopy. Except for process 2, the theoretical reaction energies based on force constants calculated at level B are in better accord with the experimental data than are those arrived at using force constants obtained at level A. This is not surprising in view of the fact that the absolute values of force constants calculated using the split-valence-shell 4-31G basis are generally in better accord with experimental values than are those obtained from the minimal basis set STO-3G method.[18a] It should be emphasized, however, that equilibrium constants for isotopic exchange reactions reflect *changes in force constants* at the position of isotopic substitution much more strongly than they do the absolute values of the force constants.[5]

A limited number of calculations have been carried out at level C (i.e., utilizing CH stretching force constants based on structures which have been completely optimized at the split-valence-shell level). The results here (for reactions 1-4 are in almost perfect agreement with those obtained at the less costly level B in which only CH bond lengths have been optimized at 4-31G.

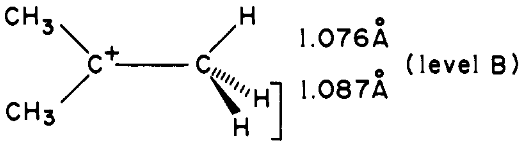
The high level of agreement between the theoretical and experimental free energies for the first six reactions seems to lend support to the suggestion of the simple molecular orbital and resonance models, that hyperconjugative interactions between the nonbonded lone pair(s) on the heteroatom and the methyl CH linkages act to weaken the latter. In the case of reactions 1-3, proton removal from the neutral species leaves behind a loosely bound heteroatom lone pair. This is turn interacts hyperconjugatively with the CH bonds on the adjacent methyl group, resulting in their weakening. The observed direction of equilibria (favoring formation of the light anion) follows. Reactions 4-6 involve proton transfer to neutral methyl-, dimethyl-, and trimethylamine, respectively. In each of these instances the loosely bound lone pair at the nitrogen center is replaced by a highly localized NH σ bond. Hyperconjugative interactions involving the methyl group linkages are, therefore, lessened, resulting in CH bond strengthening. The associated increase in CH stretching force constant will result in a favoring for formation of the heavy cation.

Calculated CH bond lengths also provide strong evidence in favor of the notion of hyperconjugation. Thus, the average CH bond length for each of the anions in reactions 1-3 is significantly longer than those for the corresponding neutral species (by 0.27, 0.042, and 0.016 Å, respectively, at level B). Similarly the average CH linkage in each of the ammonium ions in reactions 4-6 is noticeably shorter than those for the corresponding neutral amines (by 0.006, 0.007, and 0.007 Å, respectively, at level B). The angular dependence of hyperconjugative interactions has previously been discussed.[23] For example, in methylamine the CH bond which lies in the same plane as the nitrogen lone pair is oriented optimally to accept excess electron density into its antibonding orbital. Hence, it is lengthened by hyperconjugation to a greater extent than either of the two out-of-plane CH linkages. The theoretical 4-31G level equilibrium structure concurs. The detailed geometrical structures of methyl groups attached to other electron-rich centers as well as to electron-deficient sites show similar behavior.

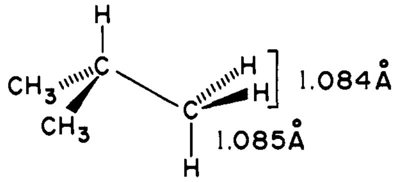


Finally, limited comparisons are possible between the theoretical calculations which have been restricted to changes in CH bond stretches alone, and those, previously published, in which all force constant changes have been explicitly considered (column D of Table II). In all cases considered, the results of the full theoretical calculations parallel those of the more restricted treatments, the effect of considerations of the additional force constant changes being one of enhancement of isotopic preference. However, in both methylamine-methylamino anion and methanol-methoxy anion equilibria, changes in force constants other than those associated with the methyl group CH stretching motions have not an insignificant effect on the theoretical results. Indeed, the calculated free energy of the methylamine-methylamino anion equilibrium (reaction 2) is increased by about 50% (from −0.33 to −0.52 kcal mol^{-1}); that for the methanol-methoxide anion equilibrium (reaction 2) is increased from −0.47 to −0.63 kcal mol^{-1}. For the remaining equilibrium examined at both levels C and D (that between neutral methylamine and the methylammonium positive ion) the overall effect of force constant changes associated with vibrational modes other than CH stretches is of less significance.

The theoretical result for reaction 7, involving formation of the *tert*-butyl cation from the hydride, is in poor agreement with the experimental measurement based on a chloride transfer equilibrium. Whereas the calculations, limited to consideration of changes in CH stretching force constants, predict an essentially zero β-secondary isotope effect, the measured preference for the gas-phase equilibrium is in the direction of favoring the formation of the light cation, consistent with the rate effects noted in solution.[2,4,25] Similarly, the theoretical free energies for reactions 8 and 9, involving proton transfer to acetonitrile and hydride removal from acetaldehyde, respectively, are in poor agreement with their corresponding gas-phase experimental quantities. Again the experimental data suggest a favoring for formation of the light cation, while the calculations indicate essentially no isotopic preference at all. In all three cases ion formation is paralleled by creation of a (partial) vacancy in the π system adjacent to the methyl probe. Thus, the simple molecular orbital and resonance pictures of hyperconjugation suggest the possibility for electron donation into this vacancy from the CH bonding orbitals of the attached methyl group(s). The calculations of molecular equilibrium geometry clearly indicate the occurrence of hyperconjugative interactions involving the methyl CH bonds. Thus, the two out-of-plane CH bonds of each methyl group in the *tert*-butyl cation are significantly longer than the corresponding in-plane linkages, which are orthogonal to the vacant p function at C$^+$ and hence may not directly interact with it.



Comparison of the theoretical (level B) CH bond lengths in the *tert*-butyl cation with those calculated for the neutral hydride reveal, however, that some additional factor is at work.



Specifically, not only does cation formation lead to lengthening of the (to be) out-of-plane CH linkages in isobutane, as is expected by the hyperconjugative model, but it also results in a significant shortening of the bonds which will eventually reside in the plane defined by the carbon skeleton. It is this increase in "in-plane" CH stretching force constant which acts to cancel the isotopic preference dictated on hyperconjugative grounds.

Conclusions

The results of the theoretical calculations and the associated gas-phase experiments described in this paper allow the following conclusions to be drawn.

(1) Secondary β-deuterium isotope effects for reactions leading to the creation of a nonbonded pair of electrons adjacent to a methyl probe (e.g., processes 1-6) are mirrored by simple levels of ab initio molecular orbital theory considering changes in CH stretching force constants alone. This result is consistent with previously advanced notions that such effects arise in great part because of hyperconjugation, that is, electron donation from the nonbonded lone pair into CH antibonding orbitals.

(2) The same theoretical model is not qualitatively successful in accounting for the observed β-secondary isotope effects associated with the generation of a vacant oribtal adjacent to a methyl probe. Although the quantitative calculations described here and previously[23b] yield clear evidence in favor of the existence of hyperconjugative interactions (i.e., donation of electrons from the filled CH bonding orbitals into the vacancy at the cationic center), they also suggest the importance of other contributions to the isotope effect. In particular they depict a conformationally independent (inductive) effect of the cation center acting, opposite to hyperconjugation, to strengthen the methyl CH bonds.[23b,24]

(3) The theoretical model appears to be more successful for reactions in which a lone pair of electrons is formed adjacent to the isotopic probe (reactions 1-6) than for those processes which lead instead to a vacant orbital in the β position (reactions 7-9). It should be emphasized, however, that the magnitudes of the β-deuterium isotope effects on these former reactions are considerably larger than those on the latter. This, we believe, is due to the fact that inductive and hyperconjugative components complement one another for reactions 1-6, while they act in opposite directions for reactions 7-9. The differences between the results of the full force field calculations (column D of Table II) and those of the simple CH stretching model (column C) for reactions 1, 2, and 4 are of the same order of magnitude as the differences between the model and experimental isotope effects for reactions 7-9. Thus explicit consideration of vibrational modes other than CH stretches (e.g., HCH and HCC bends) appears to be equally important for both sets of systems, and that fuller theoretical treatment (i.e., calculation of complete force fields) will be required in order to accurately calculate secondary β-deuterium isotope effects. Work in this direction is in progress.

Experimental Section

Commercial samples were used for all procedures with the exceptions of acetyl-d_3 chloride, which was prepared via reaction of acetic-d_3 acid-d_1 with thionyl chloride, and of dimethylamine-d_6, which was liberated from the commercially available amine hydrochloride salt. Standard instrumentation[20] and procedures[21] were employed in obtaining equilibrium measurements. The amine equilibria were run with neutral mixtures made up both on a vacuum line and in the ICR spectrometer. The method of mixture preparation had no effect on the equilibrium constants.

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References and Notes

(1) (a) Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pa. (b) Department of Chemistry, University of San Francisco, San Francisco, Calif.

(2) See, for example, V. J. Shiner, Jr., in "Isotope Effects in Chemical Reactions", C. J. Collins and N. S. Bowman, Eds., Van Nostrand-Reinhold, Princeton, N.J., 1970, p 90.

(3) S. R. Hartshorn and V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **94**, 9002 (1972).

(4) V. J. Shiner, Jr., B. L. Murr, and G. Heinemann, *J. Am. Chem. Soc.*, **85**, 2413 (1963).

(5) See, for example, M. Wolfsberg, *Acc. Chem. Res.*, **5**, 225 (1972).

(6) For discussions see: (a) R. Hoffmann, L. Radom, J. A. Pople, P. v. R. Schleyer, W. J. Hehre, and L. Salem, *J. Am. Chem. Soc.*, **94**, 6221 (1972); (b) R. F. Hudson, O. Eisenstein, and N. T. Anh, *Tetrahedron*, **31**, 751 (1975); (c) W. J. Hehre, *Acc. Chem. Res.* **8**, 369 (1975).

(7) W. J. Hehre in Modern Theoretical Chemistry," Vol. 4, H. F. Schaefer, Ed., Plenum Press, New York, 1977, p 277.

(8) W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 5339 (1971).

(9) For examples, see: (a) D. Holtz, *Prog. Phys. Org. Chem.*, **8**, 1 (1971); (b) W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry", W. A. Benjamin, New York, 1969, p 18 ff; (c) D. J. Cram, "Fundamentals of Carbanion Chemistry", Academic Press, New York, 1965, p 68 ff.

(10) D. J. DeFrees, J. E. Bartmess, J. K. Kim, R. T. McIver, Jr., and W. J. Hehre, *J. Am. Chem. Soc.*, **99**, 6451 (1977).

(11) J. Bigeleisen and M. G. Mayer, *J. Chem. Phys.*, **15**, 261 (1947).

(12) D. J. DeFrees, D. Z. Hassner, W. J. Hehre, E. A. Peter, and M. Wolfsberg, *J. Am. Chem. Soc.*, **100**, 641 (1978).

(13) (a) First-row atoms: W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969). (b) Second-row atoms: W. J. Hehre, R. Ditchfield, R. F. Stewart, and J. A. Pople, *ibid.*, **52**, 2769 (1970).

(14) In all cases calculated force constants correspond to the theoretical equilibrium geometry, and have been obtained in the manner suggested by Newton et al. (M. D. Newton, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **52**, 4064 (1970)). It has been suggested (R. H. Schwendeman, *ibid.*, **44**, 2115 (1966)) that theoretical force constants (second derivatives) be evaluated at the experimental rather than the theoretical equilibrium geometry. Without taking a position on this suggestion, our choice of using the theoretical geometry was clearly dictated by a lack of experimental structural data for the ions.

(15) (a) First-row atoms: R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971). (b) Second-row atoms: W. J. Hehre and W. A. Lathan, *ibid.*, **56**, 5255 (1972).

(16) D. J. DeFrees, B. A. Levi, S. K. Pollack, E. S. Blurock, and W. J. Hehre, to be submitted to QCPE.

(17) For a recent review of the performance of the 4-31G basis set with regard to the calculation of equilibrium geometries see: J. A. Pople in ref 7, p 1.

(18) This has been noted previously. See: (a) W. A. Lathan, W. J. Hehre, L. A. Curtiss, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 6377 (1971); (b) C. E. Blom, P. J. Slingerland, and C. Altona, *Mol. Phys.* **31**, 1359 (1976), and later papers in this series.

(19) (a) G. Singh and M. Wolfsberg, *J. Chem. Phys.*, **62**, 4165 (1975); (b) S. A. Skaron and M. Wolfsberg, *J. Am. Chem. Soc.*, **99**, 5253 (1977).

(20) (a) R. T. McIver, Jr., *Rev. Sci. Instrum.*, **41**, 555 (1970); (b) J. D. Baldeschwieler and S. S. Woodgate, *Acc. Chem. Res.*, **4**, 114 (1971); (c) R. T. McIver, Jr., and R. C. Dunbar, *Int. J. Mass Spectrom. Ion Phys.*, **7**, 471 (1971); (d) R. T. McIver, Jr., *Rev. Sci. Instrum.*, **49**, 111 (1978).

(21) (a) M. T. Bowers, D. H. Aue, H. M. Webb, and R. T. McIver, Jr., *J. Am. Chem. Soc.*, **93**, 4314 (1971); (b) J. F. Wolf, R. H. Staley, I. Koppel, M. Taagepera, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *ibid.*, **99**, 5417 (1977).

(22) For applications of ion cyclotron resonance spectroscopy to the determination of equilibrium constants for isotopic exchange reactions, see ref 10 and J. F. Wolf, J. L. Devlin, III, R. W. Taft, M. Wolfsberg, and W. J. Hehre, *J. Am. Chem. Soc.*, **98**, 287 (1976).

(23) (a) D. E. Sunko, I. Szele, and W. J. Hehre, *J. Am. Chem. Soc.*, **99**, 5000 (1977); (b) D. J. DeFrees, W. J. Hehre, and D. E. Sunko, *ibid.*, **101**, 2323 (1979).

(24) Solution-phase kinetic secondary β-deuterium isotope effects measured for systems in which the vacant p function at the carbocation center is rigidly held orthogonal (or nearly orthogonal) to the CD linkage suggest an inductive effect in the same direction as that proposed here. However, the magnitude of the inductive effect in solution is quite small. (a) V. J. Shiner, B. L. Murr, and G. Heinemann, *J. Am. Chem. Soc.*, **85**, 2413 (1963); (b) M. Tarle, S. Borčić, and D. E. Sunko, *J. Org. Chem.*, **40**, 2049 (1975).

(25) (a) N. C. Evans and G. Y. S. Lo, *J. Am. Chem. Soc.*, **88**, 2118 (1966); (b) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastein, *ibid.*, **86**, 1360 (1964); (c) G. A. Olah, A. Commeyras, J. DeMember, and J. L. Bribes, *ibid.*, **93**, 459 (1971).