have been obtained which show well defined carbonyl bands (5.7 μ). It seems most likely that these are acetoxy derivatives of hexamethylbenzene.

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The Role of Non-bonded Repulsions in Secondary Isotope Effects. I. Alpha and Beta Substitution Effects.[1]

BY L. S. BARTELL

Beta deuterium isotope effects in reactions involving carbonium ions have been attributed almost universally to hyperconjugative weakening of C–H or C–D bonds. In view of recent calculations which indicate that structural and thermochemical effects in ground states of molecules previously ascribed to hyperconjugation can be correlated semiquantitatively in terms of non-bonded interactions, the non-bonded model is now extended to the treatment of isotope effects. Its basis is that repulsions involving deuterium atoms, when averaged over stretching and bending vibrations, are smaller than those for hydrogen which has a characteristically greater amplitude of vibration. Results are found to be sensitive to assumptions made about molecular structures. Nevertheless, results for several typical reactions strongly indicate that the isotopic differences in relief of non-bonded repulsions experienced by molecules going from crowded tetrahedral configurations to trigonal transition states or products, are quite comparable to the observed isotopic free energy differences. The alpha deuterium isotope effect, previously regarded as unrelated to the beta effect, is found to be accounted for semiquantitatively by the same model.

Several years ago Lewis and Boozer,[2] and Shiner[3] found that rates of solvolyses may be retarded appreciably if hydrogen atoms are replaced by deuterium atoms on carbon atoms β to the site of the leaving group. This secondary isotope effect has been attributed almost universally to the hyperconjugation presumably encountered in the carbonium ion transition state.[4] The associated withdrawal of electrons from C–H bonds has been considered to weaken the bonds and, accordingly, to lower zero point vibrational energies. Since the lowering would be less for the heavier deuteriums than for the hydrogens, the activation energy would be greater for the deuterated molecules. The effect has been studied extensively since its discovery with a view to elucidating the role of hyperconjugation in trigonal molecules and complexes. Analogous secondary isotope effects have been studied in rates of free radical reactions,[5] and even in the equilibrium constants of reactions involving transformations from tetrahedral to trigonal configurations.[6]

Whereas hyperconjugation currently is acknowledged to be important in transition states of molecules, its significance in ground states has been questioned seriously in the last two years, especially by Dewar. Dewar and Schmeising[7] showed that if the difference in bond energy between trigonal and tetrahedral σ bonds is taken into account, it is

no longer necessary to invoke hyperconjugation to account for heats of hydrogenation and bond lengths. Dewar ascribed the distinction between bonds in trigonal and tetrahedral molecules to differences in hybridization, which is plausible but not, at present, susceptible of a definitive formulation of meaning. Very recently it has been pointed out that non-bonded repulsions provide an alternative scheme for correlating effects customarily attributed to hybridization and hyperconjugation.[8] The number of non-bonded repulsions varies in the molecules concerned, decreasing in just those cases where bond lengths are observed to become shorter and bond energies increase. Furthermore, the magnitudes of non-bonded repulsions, as inferred from vibrational spectra, seem to be quite sufficient to account for the magnitudes of the observed effects in *ground states* of molecules. It is appropriate to inquire, then, whether considerations of non-bonded repulsions can offer an alternative explanation to hyperconjugation in secondary isotope effects involving *transition states* of molecules.

Model

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. Non-bonded repulsions, averaged over the atomic vibrations, are greater for hydrogen atoms than for deuterium atoms since, in the range of interest, the second derivative of the non-bonded potential function is positive. Moreover, there are more and stronger non-bonded repulsions in a tetrahedral reactant than in a trigonal product or carbonium ion transition state. Accordingly, the relief of non-bonded repulsions associated with the transformation from a tetrahedral to a trigonal form is greater in molecules containing hydrogen than it is in those containing deuterium.

(1) (a) Research supported by the National Science Foundation; (b) presented at the 138th Meeting of the American Chemical Society, New York, N. Y., September 12, 1960.

(2) E. S. Lewis and C. E. Boozer, *J. Am. Chem. Soc.*, **74**, 6306 (1952); **76**, 794 (1954); **76**, 795 (1954).

(3) V. J. Shiner, Jr., *ibid.*, **75**, 2925 (1953); **76**, 1603 (1954).

(4) See, for example, E. S. Lewis, *Tetrahedron*, **5**, 143 (1959); V. J. Shiner, *ibid.*, **5**, 243 (1959).

(5) G. S. Hammond (private communication). In free radical reactions, however, the present "steric" arguments must be considered with greater reservation. In α substitution effects, at least, unshared electrons are sometimes considered to behave as if they are "bulkier" than adjacent bonded groups.

(6) P. Love, R. W. Taft, Jr., and T. Wartik, *Tetrahedron*, **5**, 116 (1959).

(7) M. J. S. Dewar and H. N. Schmeising, *ibid.*, **5**, 166 (1959).

(8) L. S. Bartell, *J. Chem. Phys.*, **32**, 827 (1960),

In order to reduce the argument to numerical results it is convenient to introduce several simplifications. Let us assume that the non-bonded interaction between a hydrogen atom and any given atom can be approximated by a potential function, $V(r)$, of the form discussed in reference (8), depending upon the distance, r, between the pair of atoms, but not upon any orientational factor,[9] or deformation of the remainder of the molecule to which the atoms are attached. Let us also assume that the mean distance, r_g, between non-bonded pairs is the same for deuterated molecules as for molecules with hydrogen atoms. This assumption, while not rigorously correct in view of the anticipated asymmetries of vibrations, does not alter greatly the present conclusions, according to preliminary calculations. Finally, we shall adopt a time-average probability distribution describing the separation of atoms of the form

$$P(x) = k \exp(-x^2/2l_t{}^2) \qquad (1)$$

where $x = r - r_g$ and $l_t{}^2$ is the mean-square amplitude of vibration of the atom pair. This distribution is theoretically reasonable for most intramolecular pairs, ignoring vibrational asymmetries, and is compatible with experimental electron diffraction studies which reveal the amplitudes, l_t, in simple molecules.

If the atoms involved are bonded to the same atom, l^2_t will vary inversely as the square root of the appropriate reduced mass of the oscillator. If the atoms are not bonded to the same atom we can subdivide l_t according to $l^2_t = l^2_m + l^2_s$, to a good approximation, where l_m is a mass-sensitive component arising from the zero point motion of the hydrogen with respect to the carbon atom to which it is bonded and l_s is an amplitude independent of the mass of the hydrogen but dependent upon the other skeletal vibrations. Representative magnitudes of l_m for $H \cdots X$ interactions are 0.08 Å. parallel to the C–H bond and 0.09 to 0.11 Å. perpendicular to the bond. For $H \cdots H$ interactions l_m is perhaps 0.12 to 0.15 Å. The l^2_m will vary inversely as the square root of the reduced mass, giving, approximately

$$l_m(H)/l_m(D) \simeq 1.17 \qquad (2)$$

If $V(r)$ is considered to be a weak interaction coupling the nearly independent oscillators, one of amplitude l_m and the other of amplitude l_s, the average non-bonded potential, per interaction, becomes

$$\bar{V}(r_g) \simeq \int \int V(r)P_m(x_m)P_s(x_s)dx_m dx_s \qquad (3)$$

The non-bonded potential of the whole molecule, $V = \Sigma V_{ij}(r)$, can be expanded in a Taylor's series about the mean separations, r_g, giving

$$V = \Sigma V_{ij}(r_g) + \Sigma x_{ij}(\partial V/\partial r_{ij})_{r_g} + \tfrac{1}{2}\Sigma\Sigma x_{ij}x_{rl}(\partial^2 V/\partial r_{ij}\partial r_{rl})_{r_g} + \cdots \qquad (4)$$

In our harmonic approximation with pairwise additive potentials, mean values of $x_{ij}{}^n$ with odd n and crossterms drop out so that the average over molecular vibrations becomes a simple sum of terms over the non-bonded interactions. Each term has the form

$$\bar{V}_{ij}(r_g) \simeq \{ V(r_g) + l_t{}^2 V''(r_g)/2 + l_t{}^4 V^{IV}(r_g)/8 + \cdots \}_{ij} \qquad (5)$$

A further simplification for $C \cdots H$ and $H \cdots H$ interactions in the present range of interest is that, according to the potentials of reference (8)

$$V^{IV}/2V'' \simeq 15 \times 10^{16} \text{ cm.}^2 \qquad (6)$$

We may now calculate the contribution of the non-bonded component to the activation energy (or reaction energy as the case may be) by considering the difference in non-bonded repulsions between the trigonal and tetrahedral forms, or

$$\Sigma \Delta V_{ij} = \Sigma\{ V_{ij}(r_g \text{ trig}) - V_{ij}(r_g \text{ tetr}) \} \qquad (7)$$

as a perturbation, and averaging it over the spatial distribution of the hydrogen atoms in the reference tetrahedral state. Since $V(r)$ decreases rapidly with increasing r, many terms can be neglected. Finally, the desired isotopic difference in energy, found by substituting eq. 1–6 into 7, reduces, very nearly, to

$$\Delta \Delta E = \Sigma \Delta \Delta E_{ij} \qquad (8)$$

where

$$\Delta \Delta E_{ij} \simeq 0.13_5 l_m{}^2 (H) \{ 1 + 15 \times 10^{16} l_t{}^2(H) \}_{ij} \{ V_{ij}''(r_g \text{ trig}) - V_{ij}''(r_g \text{ tetr}) \}$$

in which l_t is expressed in cm. Plots of the required second derivatives, $V_{ij}''(r)$, derived from the preliminary potential functions and estimates based on atomic radii of reference (8), and Shimanouchi's spectroscopic values[10] are given in Fig. 1. The parameters involved in the present calculations then reduce to the r_g, l_t, and l_m for the interacting pairs. The values for $l_m(H)$ presented above probably are correct to within about 10% for most molecules. Calculations of mean-square amplitudes from force constants, especially those by Morino, et al.,[13] and recent electron diffraction studies provide measures of l_t for the present purposes. Morino points out that amplitudes for given groups are likely to be quite constant from molecule to molecule. Structural data for molecules for which secondary isotope effects have been measured are meager, but reasonable guesses of the necessary r_g often can be made from known bond distances and angles.

Perhaps the most uncertain of the values used here are the $V_{ij}''(r)$, for which only the scantiest literature exists. Nevertheless, the $V_{HH}''(r)$ function which was devised to fit virial data and theoretical calculations[14] at distances of 2.6 Å. and above, predicted successfully the V_{HH}'' later determined in a modified Urey-Bradley analysis of methane[12] for which the equilibrium $H \cdots H$ distance is only 1.78 Å. It is not improbable that V'' in the range of greatest interest is adequately represented for the present purposes by the inter-

(9) Urey-Bradley analyses[10-12] of vibrational spectra suggest that atoms are not, after all, greatly "whittled down" on the side of covalent bonds as conjectured by L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1960, third edition, p. 264.

(10) T. Shimanouchi, J. Chem. Phys., 17, 245, 734, 848 (1949).

(11) J. W. Linnett, ibid., 19, 801 (1951).

(12) L. S. Bartell and K. Kuchitsu (to be published). See also K. Kuchitsu and L. S. Bartell, Abstract R7, Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, 1960.

(13) Y. Morino, K. Kuchitsu. A. Takahashi and K. Maeda, J. Chem. Phys., 21, 1927 (1953).

(14) J. de Boer. Physica, 9, 363 (1942).

polation between the extremes established above. Once one of the $V_{HX}''(r)$ has been determined on an absolute scale, the other $V_{ij}''(r)$ functions can be estimated. Therefore it seems likely that the $V_{ij}''(r)$ are in error by no more than, say, a factor of two, even at the closest distances involved in the present calculations.[15] If, however, the widely held view is correct that the non-bonded repulsion between two atoms at a given separation is less if the atoms are bonded to a common atom than otherwise, then the V_{ij}'' values used below probably are *too small.*

It is to be noted that the character of our perturbation approach is such that $\Delta\Delta E$ is not simply a difference in potential energy. It represents an estimate of the difference in total energy, including kinetic. Clearly, then, the model is directly relatable to Streitwieser's and Bigeleisen's formalism for secondary isotope effects[16] in terms of isotopic differences in vibrational energies—to the extent that $\Delta\Delta E$ results from non-bonded interactions. Furthermore, in its application to β effects it is essentially a harmonic model, and the difference in "effective size" between hydrogen and deuterium atoms is not to be confused with the familiar anharmonic shift in mean bond lengths. Inclusion of anharmonicity would require consideration of the terms in eq. 8 involving odd as well as even derivatives of V.[17] The vibrational parameter of the present harmonic model, l^2_m, the mean-square amplitude, depends upon mass in precisely the same way as does frequency, ν, in the conventional treatment. This necessarily follows from the properties of harmonic oscillators where, for zero-point vibrations, l^2 is proportional to ν. A novelty of the present model, apart from its assessment of the non-bonded contribution to isotope effects, is that it permits a numerical computation to be made from a knowledge of just one vibrational datum, the well-known amplitude of the hydrogen in the tetrahedral reactant.

Application to Beta Substitution Effects

The beta effect is associated with the reaction schematically illustrated below in which a tetrahedral reactant (I) with β-hydrogens as illustrated is converted to a trigonal molecule, ion, or radical (II) upon the withdrawal of the molecule, ion, or radical (III). The replacement of hydrogen by deuterium usually is found to decrease the equilibrium constant and/or rate constant for the forward direction. Of the numerous examples for

(15) While, in a sense, the $V_{ij}''(r)$ functions are the most speculative parameters of the present model, the uncertainties of the r_g values also may be expected to introduce substantial uncertainties in the result if the form of the present $V_{ij}''(r)$ functions is approximately correct. According to the proposed functions, $V_{ij}''(r)$ may change 30% in 0.05 Å. In view of the fact that the physical organic chemist's fancy has been the principal instrument brought to bear upon the structure elucidation of carbonium ions, it cannot be taken for granted that the present estimates of the r_g will all be correct to within 0.05 Å. Nevertheless it should be possible to test the plausibility of the present model.

(16) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey and S. Suzuki, *J. Am. Chem. Soc.*, **80**, 2326 (1958).

(17) In α effects the geometry is such that the influence of stretching anharmonicity on isotopic differences in the mean x_{ij} is quite obviously at its greatest. Here, as we shall see later, the anharmonic correction becomes large. Strictly, the small correction in eq. 8 derived from V^{IV} in eq. 5 and 6 is also anharmonic in origin.
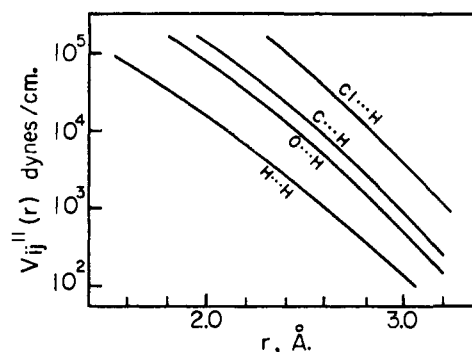

Fig. 1.—Estimated second derivatives of potential functions describing non-bonded interactions between pairs of atoms.

which results have been reported we shall consider only the solvolysis of t-alkyl chlorides and secondary tosylates, and the dissociation of the complex between trimethylborane and trimethylamine. No attempt will be made to present great detail in describing calculations since the tentative nature of the parameters assumed precludes accurate results. For simplicity we shall ignore the interactions of solvent molecules and leaving group with the carbonium ion in calculations for solvolyses.

$$(I) \qquad\qquad (II) \qquad\qquad (III)$$
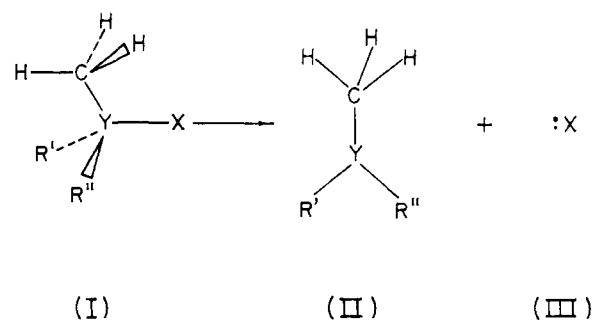
For gaseous t-butyl chloride several structural analyses have been reported,[18] and it will be assumed that the parameters are the same for the molecule in solution. No structural determinations exist, of course, for carbonium ions. If we take all C–C bonds to be 1.54 Å., all C–H bonds to be 1.10 Å., and all angles to be either 109.5° or 120°, as the case may be, we may calculate all of the essential r_g values for the anticipated conformations. If, further, we take the electron diffraction value from n-butane[19] of 0.18 Å. for l_t for the 2.8 Å. H· · ·C interactions and for the analogous H· · ·Cl interaction, and guess 0.23 Å. for the 2.5 Å. H· · ·H interactions, the effect of deuterium substitution on the activation energy of the solvolysis of t-butyl chloride can be calculated from eq. 8. The result, $\Delta\Delta E_a = 22$ cal. per mole of D, is insensitive to the guesses of l_t and is roughly half the $\Delta\Delta F_a$ observed for t-pentyl chloride by Lewis[4] and Shiner.[4] No study of t-butyl chloride was reported in the reviews referred to. It is to be noted, however,

(18) L. E. Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, London, 1958.

(19) R. A. Bonham and L. S. Bartell, *J. Am. Chem. Soc.*, **81**, 3491 (1959).

that Shiner has observed that $\Delta\Delta F_a$ increases very rapidly as the bulk of the alkyl groups increases, up to a point. It is possible that this effect is related to the present steric argument, and that the deuterium retardation is larger for t-pentyl chloride than for t-butyl chloride.

Of the 22 cal./D effect calculated according to the above model, 11 cal. result from relief of H$\cdots$Cl repulsions, 8 from H$\cdots$C repulsions, and 3 from H$\cdots$H repulsions. The latter two repulsions, of course, are not as fully relieved as the H$\cdots$Cl repulsion where the relief is complete (according to the model). If the H$\cdots$Cl interactions were included in calculations for the carbonium ion, considering a van der Waals separation of ions, the result would be changed by perhaps a calorie.

It is probable that the intramolecular increases in the non-bonded r_g values as (II) is formed from (I) are overestimated in the above calculations. It is likely that the C–C bond shortens, perhaps by 0.04 Å. or so, in the carbonium ion, instead of remaining at 1.54 Å. In the present scheme this would tend to reduce the H$\cdots$C and H$\cdots$H contributions to $\Delta\Delta E_a$, owing to the enhanced 2.2 Å. H$\cdots$C interactions with the α carbon in the carbonium ion. On the other hand we might expect, in our crude model, that the decrease in size of the positively charged α carbon in the carbonium ion would tend to offset the effect of the 0.04 Å. shrinkage in bond length.

In addition, and probably more importantly, it is not unreasonable to expect the hydrogens to share some of the positive charge. The consequent reduction of non-bonded repulsions and of covalent bond order would enhance the isotope effect. If it is assumed that these reductions are in proportion to the time average loss of charge by the hydrogens[20] it is possible to estimate $\Delta\Delta E_a$. Since the loss of one hydrogen electron would cause one V_{CH}'' and two V_{HH}'' to vanish, application of eq. 8, for the loss of n electrons (from hydrogens) per methyl group, gives

$$\Delta\Delta E_a\text{(non-bonded)} \sim 550n \text{ cal. per 3D} \sim 180n \text{ cal./D}$$

Similarly, if the C–H bond is represented by a Morse-like potential of fixed asymmetry constant a, it is easy to show that

$$\Delta\Delta E_a\text{(covalent)} \sim (n/6)[h(\nu_H - \nu_D)/2] \sim 190n \text{ cal./D}.$$

This treatment of charge delocalization is, of course, tantamount to invoking hyperconjugation. The implication that non-bonded relief accompanying charge delocalization may be as important as bond weakening is, however, new.

In the case of tosylate solvolyses the calculated isotope effect was found to be exceedingly sensitive to the assumed molecular configurations, and the values calculated ranged from rather less than the observed values to considerably more. The bulk of the tosylate group is such that normal staggered conformations about all of the single bonds cannot possibly be attained, and it is impossible to predict accurately, at present, the amount of distortion the molecule undergoes in achieving its equilibrium configuration. It ap-

pears, nevertheless, that the non-bonded repulsion contribution to the isotope effect must be appreciable.

It might seem that the gas phase equilibrium

$$\text{Me}_3\text{B:NMe}_3 = \text{Me}_3\text{B} + :\text{NMe}_3$$
$$\text{I} \qquad \text{II} \qquad \text{III}$$
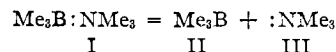
studied by Love, Taft and Wartik[6] would offer an ideal test of the model because not only are all of the molecules involved amenable to structural analysis (unlike carbonium ions, at present) but in fact, some structural data exist for each. A simple calculation based on the $V(r)$ functions of reference (8) soon reveals, however, that the complex (I) is severely strained across the B–N bond because of H$\cdots$H interactions and, to a lesser extent, C$\cdots$H interactions. The difficulty resembles that encountered with tosylates except that the symmetry of the amine-borane complex makes it possible to guess the configuration if not the precise stopping point of the strain. If interatomic distances are calculated for the complex, assuming bond angles and bond lengths characteristic of unstrained molecules, and if amplitudes are taken from their counterparts in n-butane, $\Delta\Delta E_a$ comes out to be about 66 cal. per D of the borane. Over half of this result stems from H$\cdots$H interactions across the B$\cdots$N bond. This may be compared with the experimental value estimated by Taft, *et al.*,[6] to be 22 cal. per D or somewhat larger. Spectroscopic evidence reported by Lide, Taft and Love[21] confirms the large strain across the B-N bond. Lide, Taft and Love, assuming normal angles and bond lengths in each half of the complex separately, deduce the extremely long B–N bond length of 1.80 $\pm$ 0.15 Å., on the basis of the measured moment of inertia, I_b. The $\Delta\Delta E$ calculated for their model of the structure falls severalfold below the value calculated for the "unstrained" structure above. The $V_{ij}(r)$ from which the present $V_{ij}''(r)$ values were derived, coupled with estimated force constants, suggest a deformation intermediate between the "unstrained" structure and Lide, Taft and Love's expanded structure, but with the methyls at each end somewhat more crowded together. The calculated value of $\Delta\Delta E$ associated with the intermediate structure turns out to be about 20 cal. per D of the borane but the corresponding moment of inertia, I_b, is slightly less than the microwave result. This implies that the $V_{ij}(r)$ and, consequently, the $V_{ij}''(r)$ both may be undercalculated somewhat by the present scheme. Presumably if the $V_{ij}(r)$ were increased the borane-amine distances and I_b would increase, tending to decrease the intracomplex ΔE_{ij}, but the increase in the $V_{ij}''(r)$ would compensate, leaving the calculated $\Delta\Delta E$ relatively unchanged from 20 cal.

On the basis of the foregoing results it seems likely that non-bonded interactions can account for an appreciable or possibly even a major fraction of the beta substitution secondary isotope effect without the invoking of a hyperconjugative weakening of C–H bonds in the trigonal configuration (II).[22]

(20) This simple relation between charge and covalent bonds is more or less compatible with the calculations of N. Muller and R. S. Mulliken, *J. Am. Chem. Soc.*, **80**, 3489 (1958).

(21) D. R. Lide, Jr., R. W. Taft, Jr., and P. Love, *J. Chem. Phys.*, **31**, 561 (1959).

(22) The fact that B(CH₃)₃ does not dimerize readily like BH₃ is

Alpha Substituted Effect

A secondary isotope effect in solvolyses has been found by Streitwieser, et al.,[16] in cases where hydrogens on the α carbon atom are replaced by deuterium. Whereas the retardation accompanying deuterium substitution at β carbons heretofore has been almost universally attributed to hyperconjugative effects, the retardation associated with α substitution has been acknowledged to be entirely unrelated to hyperconjugation, and hence unrelated to the β effect. The present model, in its approximation ignoring the charge on carbonium ions, treats the α and β effects on the same basis and provides an ample magnitude for the α effect. The bridge between the present model and the conventional treatment in terms of frequencies is emphasized by the fact that the second derivatives, V_{ij}'', of the principal interactions in the α effect are just the non-bonded force constants (Shimanouchi's F constants) of the Urey–Bradley type of force field.[10]

A numerical calculation for Streitwieser's original example, the solvolysis of cyclopentyl tosylate,[16] is simple for any assumed model of the transition state. Conformational uncertainties in the tosylate are not as important in the α effect as in the β effect because the α hydrogen interacts much more strongly with one atom of the tosylate group, the bonding oxygen atom, than with the others. We shall use normal bond lengths and angles with trigonal bonds 0.02 to 0.04 Å. shorter than tetrahedral bonds, and use butane-like amplitudes of vibrations. If we assume the carbonium ion is isolated the difference in activation energy is calculated, using eq. 8, to be $\Delta\Delta E_a \sim 240$ cal./mole, about half of which stems from the loss of H$\cdots$OTs interactions and half of which is associated with the non-bonded relief accompanying the (assumed) change from tetrahedral to trigonal configuration. The net result is in fortuitously close agreement with Streitwieser's estimate, based

commonly explained by a hyperconjugative stabilization of B(CH₃)₃. Since the non-bonded model provides an explanation for the secondary isotope effect alternative to that of hyperconjugation it is worthwhile examining whether it can account, in addition, for a significant part of the reluctance of B(CH₃)₃ to dimerize. A preliminary calculation with the potentials of reference 8 indicates that steric destabilization of the dimer is of the order of 7 kcal./mole more for the methyl compound than for the hydride. Although this seems appreciable it is possible that the difference between methyl and hydrogen bridges is also important. It is interesting to note that in Be(CH₃)₂, which polymerizes readily, the structure of the polymer is sufficiently different from that of the dimer of B(CH₃)₃ that the steric destabilization almost vanishes, according to the potentials of reference 8.

on empirical zero-point frequencies of model compounds, of 230 cal./mole.

Both values are much larger than the observed value of $\Delta\Delta F_a \sim 90$ cal./mole, perhaps partly for the reasons cited by Streitwieser. Clearly, however, the geometry is such that the effect of anharmonicity will be much more pronounced than in the β effect. The fact that mean hydrogen non-bonded distances are greater than their deuterium counterparts partially offsets the effect of the larger hydrogen amplitudes and reduces the isotope effect. In order to estimate the magnitude of the decrease we must evaluate the average of the previously neglected $x_{ij}V_{ij}'$ term of eq. 4. The first derivatives, evaluated from the same potential functions as the V_{ij}'' illustrated in Fig. 1, were calculated to be -0.14, -0.11, and -0.08 millidyne for tetrahedral H$\cdots$C and H$\cdots$O, and trigonal H$\cdots$C interactions, respectively. Analyses of methane[12] suggest that mean internuclear distances for these interactions are 0.004 Å. greater than the corresponding deuterium distances. The resultant correction of -140 cal./mole brings the calculated α isotope contribution down to the observed magnitude. The result of this simple treatment based on intramolecular non-bonded interactions alone is pleasing but serves as a sharp reminder of the sensitivity of the effect to commonly neglected factors. It is apparent that the quantitative deficiencies of these and other qualitatively understood interactions preclude the definitive deduction of the nature of the transition state from the magnitude of the α effect.

Conclusion.—Almost all discussions of secondary isotope effects to date have been in terms of molecular vibrational frequencies which have been interpreted within the framework of valence force fields. Shifts in valence force constants in the course of reaction have been rationalized by invoking specialized interactions (as hyperconjugation, hybridization, induction, etc.). The present work indicates that simple non-bonded components of the force field, which change dramatically as the degree of crowding in molecules is altered in reactions, can account qualitatively or semiquantitatively for many effects previously attributed to the more specialized interactions. A discussion of non-bonded contributions in isotope effects involving deuteriums more distant than the β carbon, in solvation energies, rotational isomerization energies, lengths of bonds adjacent to C–D bonds, and other steric effects will be discussed elsewhere in paper II of this series.