sealed, and immersed in a thermoregulated oil bath at 74.0 ± 0.1°. The tubes were removed at various time intervals, quenched in ice, read in the spectrometer, and reimmersed in the bath. All rate plots were linear for three half-lives, and the rate constants were obtained by a least-squares treatment[21] of the experimental data. The rate constants were: in isooctane, $k = 1.77 \times 10^{-5}\ \text{sec}^{-1}$ and in paraffin oil, $k = 0.91 \times 10^{-5}\ \text{sec}^{-1}$.

Acknowledgment. We wish to express our appreciation to the National Science Foundation and the U. S. Army Research Office, Durham, for financial support of this work.

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A Semiempirical Molecular Orbital Method for Estimating the Hyperconjugative Contribution to β-Secondary Deuterium Isotope Effects

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Abstract: A semiempirical equation is derived to connect ω-SCF molecular orbital wave functions and eigenvalues with the hyperconjugative contribution to β-secondary deuterium isotope effects. The results of the application of this equation to a number of hydrocarbon systems are discussed.

Secondary deuterium kinetic isotope effects have been examined as mechanistic probes in relatively few radical reactions. The excellent work of Seltzer[2] in elucidating the detailed mechanisms of azo compound decompositions is the most outstanding example. These effects have also been determined for radical additions to olefins[3,4] but interpretation here is complicated by the simultaneous operation of opposing α and β effects. The β effect has been examined for the formation of the phenethyl radical from both the corresponding azo compound[5] and the corresponding *t*-butyl perester.[6] These values for k_H/k_D, as well as that for the formation of the *t*-butyl radical from *t*-butyl perpivalate,[7] indicate that the β effect for radical formation is much smaller in magnitude than that for formation of cations of the same formal structure.

When we began this work we did not expect that radical isotope effects would be so low. The only β effect for a radical process which had been measured, at that time, was in the autoxidation of cumene.[8] The observed value was comparable to an ionic reaction in that case. After more careful consideration of the general state of the theory of β effects, it was realized that there was little basis for any expectation of the magnitude of such isotope effects. The only factor which resembled a generalization was that these effects were in some way related to hyperconjugation. We therefore carried out a preliminary analysis of the magnitudes of the relative isotope effects in radical- and cation-forming processes predicted by molecular orbital methods. We used the formalism of Salem[9] in this preliminary analysis.[7] The result of this work was that the observed β effects were in good agreement with these preliminary calculations. We thus were encouraged to pursue this line of endeavor more carefully. The additional results are summarized below.

Results

The general formalism[9] used in the preliminary calculations begins with the assumption of a linear correlation of bond distance and π-bond order (eq 1)

$$r = A - BP \tag{1}$$

where r is the equilibrium bond length, P is π-bond order, A the intercept, and B the slope of the bond order–bond length proportionality. Also, it is assumed that the bond integral can be approximated as

$$\beta = ce^{-r/a} \tag{2}$$

where c and a are constants. The total bonding potential (V) is assumed to be the sum of π (E) and σ (Σ) parts which are separable (eq 3). With these assumptions one can

$$V = E + \Sigma \tag{3}$$

integrate the force condition $\delta V/\delta r = 0$ to obtain Σ in

$$\Sigma = \frac{2ce^{-r/a}}{B} - (r - A + a) \tag{4}$$

terms of π parameters (eq 4). The total potential for an isolated bond is then as shown in eq 5.

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(1) National Defense Education Act Predoctoral Fellow, 1965–1968.

(2) S. Seltzer and F. T. Dunne, *J. Am. Chem. Soc.*, **87**, 2628 (1965); S. Seltzer and S. E. Scheppele, *ibid.*, **90**, 358 (1968); S. Seltzer, *ibid.*, **85**, 14 (1963); S. Seltzer and S. Mylonakis, *ibid.*, **89**, 8598 (1967).

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$$V = \frac{2ce^{-r/a}}{B}(r - A + a) + 2Pe^{-r/a} \qquad (5)$$

The force constant (F) for stretching an isolated bond is the second derivative (V'') of (5) with respect to distance

$$F = V'' = \frac{1}{B} - \frac{\pi\beta}{a}2\beta' \qquad (6)$$

where π is the self-polarizability[10] of the bond and β' is the derivative of β with respect to distance. For the present problem, the ratio of force constants for the hyperconjugatively perturbed intermediate (cation, radical, or anion) to that for an isolated methyl in the ground state is required. To a good approximation, the bond order and self-polarizability of an isolated methyl group are determined by symmetry (as in ethylene, $P = 1$, $\pi = 0$). The required ratio is then given as

$$\frac{F}{F_0} = \frac{\beta'}{\beta_0'}\left(1 - \frac{B}{a}\pi\beta\right) \qquad (7)$$

where β' refers to the function evaluated at the equilibrium bond distance for the intermediate and β_0' refers to the function at the equilibrium distance for an isolated methyl group.

In our previous treatment[7,9] we neglected the β'/β_0' term ($\beta'/\beta_0' = 1$). However, using (2) and power series expansion gives

$$\frac{F}{F_0} = 1 - \frac{B}{a}[(1 - P) + \pi\beta] \qquad (8)$$

The bond order term that cancels in taking derivatives of V reenters the final expression due to the change in bond distance. This result is reminiscent of the general treatment of Halevi[11] for perturbation of an anharmonic potential with a nonlinear perturbing potential.

In the latter formalism, the initial potential is expressed in a power series

$$V - V_0 = \tfrac{1}{2}kx^2 + \tfrac{1}{6}gx^3 \qquad (9)$$

where k and g are constants and x is displacement distance. The perturbation potential can similarly be expressed as

$$\delta V = ax + \tfrac{1}{2}bx^2 \qquad (10)$$

where a and b are constants. The final force constant can be shown[11] to be

$$F = k + b + gx \qquad (11)$$

The potential function derived here (5) gives, in this formalism

$$V - V_0 = \frac{\tfrac{1}{2}(2\beta_0')x^2}{B} + \frac{\tfrac{1}{6}(4\beta_0')x^3}{B} \qquad (12)$$

and

$$\delta V = \delta V_0 - 2(1 - P)\beta_0'x + \frac{1}{2}\left[\frac{2(P - 1)\beta_0'}{a} - \frac{2\pi\beta_0\beta_0'}{a}\right]x^2 \qquad (13)$$

These two relationships (12 and 13) and (11) give (8) identically.

The force constant ratio for any system could be evaluated if B/a were known. For C–C bonds the slope of the empirical bond order–bond distance relationship gives B and other data can give a. No such data are available for methyl groups. However, one such force constant ratio has been published in connection with the normal mode analysis of *t*-butyl cation.[12] This allows the determination of B/a for methyl groups. The frequency shift for a vibration is given as

$$\Delta\gamma = \gamma_0(1 - \sqrt{F/F_0}) \qquad (14)$$

where $\Delta\gamma$ is the shift and γ_0 is the frequency of vibration of the effected group in the ground state. The isotope effect can be calculated using Streitwieser's[13] reduction of the total isotope effect formula.

$$\ln k_H/k_D = \frac{0.187}{T}\gamma_0(1 - \sqrt{F/F_0}) \qquad (15)$$

In the previous calculations,[7] we assumed γ_0 was an effective frequency and used the observed isotope effect on the formation of *t*-butyl cation to fix its value. Reparameterizing in this way, including the bond order term neglected in the previous calculations, gives γ_{eff} as 2600 cm^{-1}. The isotope effect for *t*-butyl radical formation is raised to 1.48. This is actually a more favorable result for the radicals than the previous value (1.24 calculated and observed for the decomposition of *t*-butyl perpivalate) since perester decompositions are probably exothermic and should therefore not experience all of their potential hyperconjugative interaction at the transition state.

Several criticisms can be raised about the advisability of using an experimental isotope effect to fix γ_{eff}. An alternative is to set γ_0 equal to the value of the stretching frequency of an isolated methyl (*ca.* 3000 cm^{-1}). This has the advantage of eliminating any additional assumptions about the response of other motions of the molecule to the change in C–H force constant. Using this parameterization would mean that the method was approximating the contribution of only the stretching force constant change to the equilibrium isotope effects. It is better from a purely theoretical standpoint. It has the disadvantage of missing the possibility of the usual Hückel-type internal compensation which comes with a more empirical method of parameterization. With γ_0 set equal to 3000 cm^{-1} and an F/F_0 of 0.885,[7,12] the calculated equilibrium isotope effect for *t*-butyl cation is 2.72 which is not in bad agreement with the observed value. We therefore chose to use these parameters in all subsequent calculations. It should be noted that an F/F_0 ratio of 0.900 reduces the calculated isotope effect for *t*-butyl cation to 2.38.

The next problem which we considered in more detail was the effect of variation of input parameters (β's, S's, α's, etc.) on the calculated isotope effects. As mentioned in the earlier report,[7] the large difference in the hyperconjugative contribution to the equilibrium isotope effects predicted for radicals and cations of the same formal structure was not very sensitive to such variations. However, the radicals, compared to themselves, were fairly sensitive to these changes.

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[10] C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.* (London), **A191**, 39 (1947).

[11] E. A. Halevi, *Progr. Phys. Org. Chem.*, **1**, 109 (1963).

[12] J. C. Evans and C. Y.-S. Lo, *J. Am. Chem. Soc.*, **88**, 2118 (1966).

[13] A. Streitwieser, R. Jagow, R. C. Fahey, and S. Suzuki, *ibid.*, **80**, 2326 (1958).

Table I. Calculated C–C Bond Distances and Overlaps

Compd	Bond	P	r^a	$r_{\text{exptl}}{}^b$	S^c	Slater^d S
$H_3\equiv CC\equiv H_3$	2,3	0.180^e	1.537	1.540	0.1935	0.1925
$CH_2=CHCH=CH_2$	1,2	0.960^f	1.343	1.337	0.2696	0.2670
	2,3	0.279^f	1.500	1.483	0.2151	0.2048
Benzene	1,2	0.667^g	1.396	1.397	0.2455	0.2455
Graphite	1,2	0.525^g	1.429	1.421	0.2320	0.2326
Ethylene	1,2	1.000^g	1.330	1.336	0.2758	0.2721

[a] Calculated using listed bond order and eq 16. [b] Reference 9. [c] Calculated using eq 17 and *r* (see footnote *a*). [d] Slater overlaps at r_{exptl}. [e] CNDO/2[15] bond order: this work. [f] SCF bond order: J. A. Pople, *Trans. Faraday Soc.*, **49**, 375 (1953). [g] By symmetry.

Table II. Comparison of Present and Advanced MO Results $(\overset{1}{H_3}\equiv\overset{2}{C}\overset{3}{C}<)$

Compd	P_{23}	Den. 1^a	Den. 2^a	Den. 3^a	$r_{12}{}^b$
$H_3\equiv CC\equiv H_3{}^c$	0.193	+0.049	−0.049		1.532
$H_3\equiv CC\equiv H_3{}^d$	0.183	−0.002	+0.002		1.539
$H_3\equiv CCH_2{}^{+c}$	0.652	+0.382	+0.082	+0.536	1.399
$H_3\equiv CCH_2{}^{+d}$	0.545	+0.319	−0.109	+0.499	1.428^e
$H_3\equiv CCH_2\cdot{}^c$	0.419	0.121	−0.049	0.929	1.457
$H_3\equiv CCH_2\cdot$	0.356^d	0.109^f	-0.014^f	0.919^f	1.468^e
$H_3\equiv CCH_2{}^-$	0.450	−0.132	−0.092	−0.777	1.448
$H_3\equiv CCH_2{}^{-d}$	0.411	−0.425	+0.146	−0.454	1.459

[a] Charge or spin density at the indicated position. Spin density is McLachlan spin density: A. D. McLachlin, *Mol. Phys.*, 233 (1960). [b] Calculated using eq 16. [c] Calculations using the present theory. [d] CNDO/2[15] results of this work. [e] CNDO/2 results of Wiberg.[17] [f] INDO results of Pople.[16]

The molecular orbital results needed in eq 8 are for the species at its equilibrium bond distances. The bond orders for the C–C bonds in ethyl radical and ethyl cation are rather different. The bond distances are also therefore different (1). Hence the bond integrals are different (2). Some sort of self-consistency in bond order is thus suggested.

The apparatus for inclusion of such a self-consistancy procedure is inherent in the formalism derived for the isotope effects except for the complication of hybridization which results from a *single* parameterization. A *linear* bond order–bond distance correlation, such as that given by Coulson,[14] indicates that a C–C bond of zero π-bond order should be 1.517 Å long. The methyl-ring C–C bond length in toluene is already longer than this while the π-bond order is not yet zero. This could be taken into account using a different bond order–bond length correlation for methyl carbon–sp^2 carbon bonds ($r = A' - B'P$). This would necessitate new parameters and would make the calculation more cumbersome.

It was then noted that the observed bond lengths from ethane to ethylene can be fit to a square-root dependence on bond order (eq 16). A comparison of the observed and calculated bond lengths for several compounds are

$$r = A - B\sqrt{P} \qquad (16)$$

$$A_{\text{C-C}} = 1.690 \qquad B_{\text{C-C}} = 0.360$$

$$A_{\text{H}_3\text{-C}} = 0.618 \qquad B_{\text{H}_3\text{-C}} = 0.188$$

listed in Table I. The agreement appears to be about as good as that given by other empirical bond distance–bond order relationships.[9] Using this relationship for *r* we assume that the overlap integrals can be approximated as

$$S_{ij} = Ce^{-r/a} \qquad (17)$$

i and *j* bonded, $a = 0.567$, $C_{\text{C-C}} = 2.843$, $C_{\text{H}_3\text{-C}} = 1.080$. The overlap integrals estimated in this way are within about 1% of Slater values. These data are also listed in Table I.

The self-consistency requirement is now easily met using eq 17, 18, and 19.

$$H_{ii} = H_{ii}{}^0 + \omega(1 - P_{ii}), \qquad \omega = 1.41 \qquad (18)$$

$$H_{ij} = S_{ij}/S_{\text{C}_6\text{H}_5\text{-H}}, \qquad i \text{ and } j \text{ bonded} \qquad (19)$$

The eigenvalues which result from this procedure are still in units of the coulomb and bond parameters of benzene. However, the distance variation refers to ethylene. A comparison of the results of calculations of this type with more advanced methods[15-17] is made in Table II.

The force constant ratio must be rederived, taking into account the change in the dependence of distance on bond order from first power to square root. The same derivative gives

$$\frac{F}{F_0} = \left(1 - \frac{B}{a}\right)P^{1/2} + \frac{B}{a}\left(P - \frac{\pi\beta}{2}\right) \qquad (20)$$

Using 0.885 for F/F_0 for the *t*-butyl cation and $\gamma_0 = 3000$ cm^{-1} one finally obtains

$$\ln\left(\frac{k_{\text{H}}}{k_{\text{D}}}\right) = \frac{561}{T}\left[\left(1 - \sqrt{0.656P^{1/2} + 0.344\left(P - \frac{\pi\beta}{2}\right)}\right)\right] \qquad (21)$$

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(14) C. A. Coulson and A. Golebiewski, *Proc. Phys. Soc.* (London), **78**, 1310 (1961).

(15) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966).

(16) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *ibid.*, **47**, 2026 (1967).

(17) K. B. Wiberg, *J. Am. Chem. Soc.*, **90**, 59 (1968).

Table III. Computed Equilibrium, Distances, and β Isotope Effects ($\overset{1}{H_3}\equiv\overset{2}{C}\overset{3}{C}<$)

Compd	ν_{23}[a]	k_H/k_D[b]	k/k'[c]	$(k/k')_{\text{exptl}}$[d]	Den. 3[e]
CD_3		1.0002	1.007		
CD_3CD_3	1.532	1.014			−0.049
$CD_3CH=CH_2$	1.506	1.027			−0.002
$CD_3CH=CHCH=CH_2$	1.501	1.032	1.099		0.000
$CD_3C_6H_5$	1.511	1.025	1.077		+0.002
$CD_3CH_2^+$	1.399	1.284	2.116		+0.531
$CD_3CH_2\cdot$	1.457	1.081	1.264		0.928
$CD_3CH_2^-$	1.449	1.083	1.272		−0.777
$(CD_3)_2CH^+$	1.432	1.166	2.507	2.20[f]	+0.429
$(CD_3)_2CH\cdot$	1.468	1.067	1.476		0.828
$(CD_3)_2CH^-$	1.465	1.064	1.452		−0.667
$(CD_3)_3C^+$	1.451	1.119	2.743	2.38[g]	+0.375
$(CD_3)_3C\cdot$	1.477	1.058	1.661	1.25[7]	0.740
$(CD_3)_3C^-$	1.476	1.053	1.598		−0.595
$CD_3CHC_6H_5^+$	1.456	1.107	1.356	1.224[h]	+0.308
$CD_3CHC_6H_5\cdot$	1.479	1.056	1.179	1.07[5,6]	0.649
$CD_3CHC_6H_5^-$	1.491	1.038	1.117	0.16[i]	−0.351
$(CD_3)_2CC_6H_5^+$	1.466	1.089	1.670		+0.293
$(CD_3)_2CC_6H_5\cdot$	1.485	1.050	1.343		+0.588
$(CD_3)_2CC_6H_5^-$	1.496	1.035	1.230		−0.340
$(CD_3)_2CC\equiv CH^+$	1.460	1.104	1.811	1.84[j,k]	+0.322
$(CD_3)_2CC\equiv N\cdot$	1.489	1.045	1.305	1.24[l,m]	+0.535
p-$CD_3C_6H_5CHCH_3^+$	1.493	1.022[n]	1.070	1.16[o]	+0.107
m-$CD_3C_6H_5CHCH_3^+$	1.513	1.000[n]	1.002	0.98[o]	+0.005
8-$CD_3C_8H_6CH_2^+$	1.508	1.001[n]	1.006	1.029[p]	+0.004
$D_2=C(C_4H_4)$	1.500	1.069	1.141		+0.026

[a] Calculated using (16) and the present theory. [b] Isotope effect per deuterium. [c] Total isotope effect for the compound shown. [d] Experimental kinetic isotope effect. [e] Charge on McLachlan [A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960)] spin density. [f] A. Streitwieser, private communication. [g] V. J. Shiner, B. L. Murr, and G. Heineman, *J. Am. Chem. Soc.*, **85**, 2413 (1963); G. J. Frisone and E. R. Thornton, *ibid.*, **90**, 1211 (1968); L. Haaka, A. Queen, and R. E. Robertson, *ibid.*, **87**, 1961 (1965). [h] V. J. Shiner, W. E. Buddenbaum, B. L. Murr, and G. Lamaty, *ibid.*, **90**, 418 (1968). [i] A. Streitwieser and D. E. Van Sickle, *ibid.*, **84**, 254 (1962). [j] V. J. Shiner, J. W. Wilson, G. Heineman, and N. Solliday, *ibid.*, **84**, 2408 (1962). [k] Calculated for the enic compound. [l] S. Rummel, H. Huebner, and P. Krumbiegel, *Z. Chem.*, **7**, 351 (1967). [m] Calculated using $\alpha_n = \alpha_0 + 0.5\beta$. [n] Corrected for IE in starting $H_3\equiv CAr$. [o] E. S. Lewis, R. R. Johnson, and G. M. Coppinger, *J. Am. Chem. Soc.*, **81**, 3140 (1959). [p] G. J. Karabatsos, G. C. Sonnichsen, C. G. Papaioannou, S. E. Schepple, and R. L. Shone, *ibid.*, **89**, 463 (1967).

Equilibrium isotope effects for a number of hydrocarbon species, calculated by these methods are listed in Table III.

Discussion

The data of Table II indicate that this simple procedure is a reasonably good approximation to the more advanced methods of calculation. This can be seen by comparing C–C bond orders which, for symmetry reasons have similar meaning by either method of calculation. The present theory overestimates the C–C bond orders slightly. The spin densities for ethyl radical are in very good agreement with recent INDO[16] results. The most obvious discrepancy between the two methods is the charge distribution in the ionic species. This overemphasis of charge leveling is inherent in the ω technique and has been pointed out elsewhere.[9,18]

This extra charge delocalization could contribute to the larger value of the calculated isotope effects for ionic compared to radical species but we do not believe it is of overriding importance. The large difference in the isotope effects calculated for radicals and cations is dependent on the nonneglect of differential overlap. The eigenvectors of the present method are reproduced reasonably well neglecting overlap. However the eigenvalue spacing is strongly perturbed and, since differences in these quantities are inherent in the polarizability computation, the self-bond polarizabilities can be quite different when overlap is neglected.

The particular method which we have used to eliminate this problem is due to Lowdin.[19] The atomic orbitals are orthogonalized in each iteration. The resultant eigenvectors can be used directly in Coulson[10] formulas for polarizabilities. The changes in bond order, at each iteration, cause changes in the *S* matrix and a new orthogonalization is thus required at each iteration.

The present molecular orbital method takes into account in a somewhat extreme way, the effect of hyperconjugation. Even ethane enjoys some hyperconjugative stabilization in the sense that the C–C π-bond order is not zero. This view is not really different from that of any of the recent generalized molecular orbitals (CNDO, EHT, and INDO) which take into account both π and σ electrons. There is probably no compound which has the nuclei arranged properly for C–C π interaction which is so strongly bonded elsewhere that the C–C π-bond order is zero. The implication of eq 16 is that such a compound would have a C–C bond distance of 1.69 Å, much longer than that of ethane.

The data of Table III include the predicted methyl-C trivalent C–C bond distances calculated using (16) and

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(18) J. A. Pople and A. Bristock, *Trans. Faraday Soc.*, **50**, 268 (1954).

(19) P. O. Lowdin, *J. Chem. Phys.*, **18**, 365 (1950); J. P. Colpa and E. de Boer, *Mol. Phys.*, **1**, 333 (1963); C. A. Coulson and D. H. Chirgwin, *Proc. Roy. Soc.* (London), **A191**, 188 (1947).

the converged bond orders. There does appear to be considerable variation in these numbers though they will be difficult to obtain experimentally. The variation in the H_3–C bond distances is too small to be significant within the series. We believe that the present method does give molecular orbital results which are a good approximation to those of the more advanced methods. The present type of calculation has an advantage over these more advanced methods in that an analytic connection between the eigenvectors and isotope effects is available. The computed isotope effects appear to us to be in reasonably good agreement with observed kinetic effects. The agreement is best in the cation series. However, the consideration just discussed raises additional problems with the quantitative interpretation of the computed values. As can be seen in Table III, the isotope effect on formation of ethane from two isolated methyls is appreciable (*ca.* 4% per methyl group). The isotope effects listed in Table III use a localized methyl for the reference state, yet the prediction of this molecular orbital method is that there can be considerable variation in the force constant of the ground state (even ethane). This variation has been neglected completely.

The next complication is the effect of solvent. The magnitudes of the calculated isotope effects for the cation series go as ones intuition would predict assuming hyperconjugative demand is a function of net positive charge at the α position. While this is a good result in one context, it makes the problem of the role of solvent more acute. To the extent that solvent molecules coordinate with the vacancy orbital, they also should reduce hyperconjugative demand and hence the *experimental* isotope effect. To the extent that solvent molecules provide a long-range attractive potential for the β protons in these cations, they should broaden (without necessarily affecting the depth) the potential for the stretching motion of the β-C–H_3 group. This would cause the observed isotope effects to be larger than calculated by the present method.

A third note of caution cannot be overemphasized. That is the Bigeleisen–Mayer formulation[20] for these isotope effects, which was simplified to eq 15, transcends the present theory in the sense that it is not connected in any way to the reason for a change in force constant but states that if force constant changes of a given magnitude in a reaction do occur, these will produce an isotope effect of a predictable magnitude. The present theory has picked one possible source of a change in β-C–H force constant and attempts to determine if that source is sufficient to explain the total effect. The results of Table III do seem to indicate, to us at least, that the hyperconjugative origin of these isotope effects is quite important. However, it should always be remembered that steric[21] changes in force constants can also enter into the total magnitude of the F/F_0 ratio.

Factors which have also been neglected in the present theory (which presently seem to be less important) are the temperature-independent term,[22] the inductive isotope effect[23] and the effects due to the differences in size of deuterio and protio molecules.[24] The no-force constant change isotope effects[22] have been demonstrated to be small enough in magnitude that they, by themselves, should not exert a significant perturbation on the quantitative numbers of Table III. However these, combined with the other small factors mentioned previously, do add up to an appreciable correction.

With these notes of due caution, the calculated deuterium isotope effects, given in Table III, can be examined. Several generalizations are immediately apparent. First the equilibrium β-secondary deuterium isotope effects due to hyperconjugative changes in β-C–H stretching force constants are predicted by the present molecular orbital method to be significantly smaller for radicals and anions compared to cations of the same formal structure. The difference between radicals and cations is not as large in the present theory as was estimated by our previous[7] more approximate method but the generalization still appears to be valid. It should be remembered that inclusion of a perturbation of the coulomb integral for the $D_3{\equiv}C$ group, such as the one proposed by Halevi and Pauncz, would reduce the calculated isotope effects for the cations.[25] The magnitude of this change in this coulomb integral is not obvious to us.

The calculated magnitudes of the isotope effects for the radical species are almost (with the exception of the cyanoisopropyl radical for which the input parameters for the nitrile group are a problem) always considerably larger than the observed kinetic isotope effects. This, we believe, is a point in favor of the present theory (in contrast to the previous approximation[7]) since all of the unit processes which are thought to be operative in the reactions which gave the measured values are exothermic. Less than 100% of the radical character potentially available to the incipient species should be present in the corresponding transition state. To the extent that the leaving group (carbon dioxide for peresters or nitrogen for azo compounds) remains "bonded" to the radical center at the transition state, the demand for hyperconjugation should be reduced.

The same complication holds for cation formation in the sense that the presence of the leaving group as well as solvent must strongly perturb the demand for hyperconjugation. This complication for carbonium ion processes becomes very serious after inspection of the range of per D β-isotope effects predicted for those species (2%/D for *p*-methyl group in a phenethyl cation to 28%/D for ethyl cation). While this trend in the magnitude of the β effect is fully predicted by simple physical organic principles, we did not expect the magnitude of the variation would be so large.[26] This variation in the per D effect suggests that such isotope effects are more sensitive to the detailed structure of the species (degree of solvation, fraction bond breaking, etc.) than was previously thought.

There is some variation in the magnitude of the calculated isotope effects (per D) within the series of radicals but it is much less pronounced than in the cation series.

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(26) We made one attempt to test the prediction of the large magnitude of the β effect in ethyl cation formation by studying the acid-catalyzed solvolysis of ethyl mercuric acetate and its β-trideuterated analog. The observed isotope effect in this reaction was 12% at 100° for three deuterium atoms. This small isotope effect suggest that the rate-determining transition state for this reaction probably does not resemble ethyl cation even ignoring the predictions of Table III.

The magnitudes of the calculated β effects in the anion series were surprising to us. In the simple alkyl series the values are very similar to the corresponding radicals. Our prejudice, when we began this work, was that there would be very little isotope effect for anions but large effects for radicals. Substitution by aryl groups reduces the calculated isotope effects for anions more than for radicals so that some of our prejudice is borne out by the calculated results.

As mentioned previously, this particular molecular orbital method emphasizes hyperconjugation in a rather extreme way. The β-isotope effects calculated for "formation" of propene, 2,3-pentadiene, and cyclopentadiene are correspondingly appreciable. A test of the predicted 14% isotope effect on the "formation" of cyclopentadiene from its hypothetical localized precursor could be a retro-Diels–Alder reaction or equilibration of 1,1-d_2-cyclopentadiene with a Diels–Alder adduct.

While the present method of estimating these hyperconjugative effects is by no means completely satisfactory, it does seem to offer encouragement to pursue this line of investigation with more advanced molecular orbital formalisms. It would be worthwhile having a similar method for estimating the magnitudes of changes in stretching force constants for nonrotating β (as well as γ, δ, etc.) C–H groups. We are presently attempting to develop such a method.

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Secondary Deuterium Isotope Effects in Radical-Forming Reactions. IV. Concerted Perester Decompositions

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Abstract: The secondary deuterium isotope effects on the rates of decomposition of *t*-butyl peresters of phenylacetic (**1**), hydratropic (**2**), α,α-dimethylphenylacetic (**3**), and pivalic acids have been determined by infrared, galvinoxyl, and double-labeling methods. The α effects for **1** and **2** are 1.03–1.06 per deuterium. The β effects for the series are 1.014–1.020 per deuterium. The implications of these effects with respect to the detailed mechanisms of the reactions are discussed.

Preliminary investigations[2] of secondary deuterium kinetic isotope effects on the decomposition of *t*-butyl perphenylacetate (**1**) and *t*-butyl perhydratropate (**2**) were carried out as control experiments to test the validity of our expectation that concerted decomposition rates would be sensitive to deuteration. This expectation was based on the idea that the benzylic carbon atoms of the peresters would approach sp^2 hybridization in the transition states. The bending frequencies associated with the α-hydrogen atoms might therefore be expected to be reduced.[3] The studies of Seltzer on the α effects in azo compound decomposition[4] as well as the β scission of cumyloxy radical[5] have indicated that these α effects are of the order of 1.10–1.15 per deuterium atom for these radical-forming reactions. The observed α effects in the preliminary studies were within this expected range while that for the decomposition of acetyl peroxide was much smaller. We therefore concluded that the small value for the latter reaction must be interpreted in terms of a nonconcerted process.

The β effect in the perhydratropate case was also examined and found to be much smaller than the value reported for the autoxidation[6] of cumene. Subsequently it was found that β effects in the formation of phenethyl[7] and cyanoisopropyl[8] radicals from the corresponding azo compound were also small. Similarly the β effect,[8] as estimated by direct kinetic methods, in the decomposition of *t*-butyl perpivalate was also small.[9] It has been demonstrated[9,10] that the ratio of the equilibrium β effects for the formation of radicals and cations of the same formal structure are in agreement with the predictions of molecular orbital theory.

During the course of these developments, the general picture for peroxide decompositions has been revolutionized by the demonstration of reversible oxy–oxy radical formation in a number of cases.[11,12] This perturbation of

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