On the Conformational Dependence of Secondary β-Deuterium Isotope Effects

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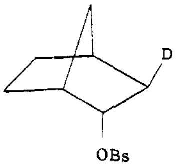
Abstract: The conformational dependence of secondary β-deuterium isotope effects on hypothetical reactions involving formation of the ethyl cation, ethyl radical, and ethyl anion from ethane has been investigated by means of ab initio molecular orbital theory. In all three systems the hyperconjugative component of the calculated secondary isotope effect is found to closely follow a $\cos^2 \alpha$ relationship, α being the dihedral angle which the β CH bond makes with the vacant (half-filled or filled) orbital at the cation (radical or anion) center.

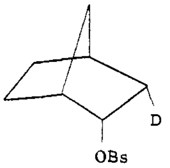
Introduction

It is well established that the magnitudes of β-secondary deuterium isotope effects on the rates of processes involving carbocation-like transition states or intermediates are strongly dependent on the detailed geometrical structures of those transition states or intermediates.[2a] For example, it has been observed that, while both *exo-* and *endo*-3-deuterio-*exo*-norbornyl brosylate (I and II) solvolyze noticeably slower than the parent (unlabeled) compound,[2b] the corresponding bridgehead deuterium compound (III) reacts at nearly an identical rate.[2c] A simple hyperconjugative picture provides the needed rationale. Thus, while the CD linkages in I and II are oriented so as to permit significant hyperconjugative interaction with the vacant p function of the solvolysis transition state, the bridgehead CD bond in III is nearly orthogonal to this empty orbital, seriously curtailing the possibility for such interaction. Analysis of rate data for rigid systems (i.e., those in which the geometrical relationship between the vacant p orbital at the carbocation center and the CD linkage is constrained to a certain value) has recently lead us to suggest that the angular dependence of secondary β-deuterium isotope effects follows a $\cos^2$ dependence:[3]



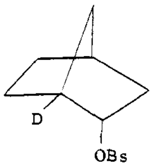
I

$k_H/k_D = 1.19$



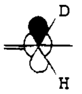
II

$k_H/k_D = 1.12$

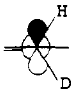


III

$k_H/k_D = 1.00$

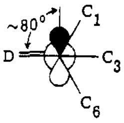


I



II

(C_2C_3 bond)

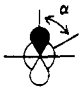


III

(C_2C_7 bond)

$$\log k_\alpha = \log k^1 + \log k_0 \cos^2 \alpha$$

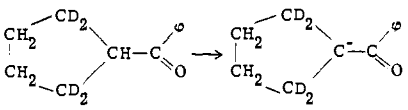
Here, k_α is the H/D rate ratio for a single linkage disposed at an angle α to the vacant p function, k_0 is the limiting rate ratio for a bond which is exactly parallel to the empty orbital, and k^1 is the conformationally independent (inductive) component of the rate effect. In practice k^1 has been assigned a value of 0.985, while k_0 is derived from the measurement of the secondary β-deuterium isotope effect incurred by a CD_3 rotor which in total (i.e., taking account of all three CD linkages and assuming free rotation) is independent of conformation.



Virtually no information is available experimentally on the conformational dependence of β-deuterium isotope effects for reactions proceeding through anion-like transition states or intermediates. Sizable secondary isotope effects have been observed in such situations, however, both on the rates of processes occurring in condensed media[5,6] (eq 1–3) and on the direction of equilibria for gas-phase ion–molecule reactions.[7]

$$\phi CD_2COOH \longrightarrow \phi CD_2COO^- \qquad (1) \quad k_H/k_D = 1.12^{5a}$$

$$(CD_3)_2CH_2NO_2 \longrightarrow (CD_3)_2\overset{-}{C}HNO_2 \qquad (2) \quad k_H/k_D = 1.14^{5b}$$



(3) $k_H/k_D = 1.24^{5c}$

$$CD_3NH^- + CH_3NH_2 \rightleftharpoons CD_3NH_2 + CH_3NH^- \qquad K_{eq} = 1.9 \quad (4)$$

$$CD_3O^- + CH_3OH \rightleftharpoons CD_3OH + CH_3O^- \qquad K_{eq} = 2.3 \quad (5)$$

$$CD_3S^- + CH_3SH \rightleftharpoons CD_3SH + CH_3S^- \qquad K_{eq} = 1.7 \quad (6)$$

If hyperconjugative factors are primarily responsible, as has been suggested[7] and recently supported by the results of quantitative molecular orbital calculations,[8] then the measured isotope effects should exhibit conformational dependence which is qualitatively similar to that encountered for the cation systems. That is to say, the hyperconjugative interactions here should be at a maximum when the CD linkage is parallel to the lone pair orbital at the anion center, and at a minimum (or zero) when the CD bond and the adjacent lone pair are orthogonal.

There seem to be few experimental determinations of β-secondary deuterium isotope effects for systems including a free-radical center. However, the notion of hyperconjugation in such systems is well established.[9,10] Electron spin resonance measurements show that in the ethyl radical, for example, there

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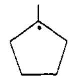
is a significant transfer of spin density to the β hydrogens. In addition, the hyperfine coupling constant for the β hydrogens, $a_{H\beta}$, has been shown to follow a $\cos^2 \alpha$ dependence, with α defined as above. For the radical IV in which four of the seven



IV

β hydrogens are conformationally constrained the relationship has been determined to be[9]

$$a_{H\beta}\,(G) = 0.92 + 42.60 \cos^2 \alpha$$

Such relationships have been used in the determination of the stable conformers of a number of β-substituted ethyl radicals.[11]

In this paper we provide theoretical evidence, in the form of ab initio molecular orbital calculations, supporting our previous suggestion regarding the form of the angular dependence of secondary β-deuterium isotope effects in reactions proceeding via a carbocation-like transition state or intermediate. In addition we also consider the form of the angular dependence of the isotope effect incurred by a carbon-deuterium linkage placed in the opposite environment, that is, alongside of a center on which a nonbonded electron pair is localized, as well as the effect when the adjacent grouping incorporates a half-filled orbital. For the present, we shall deal only with model systems, specifically the ethyl cation, radical, and anion. Later applications of the theory will concern themselves with systems which are more suitable for experimental investigation.

Methods, Results, and Discussion

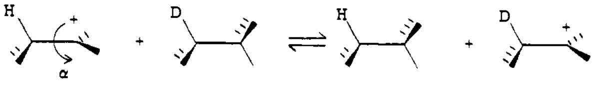
The angular dependence of the secondary isotope effect incurred by a single deuterium β to the vacant orbital in the open ("classical") ethyl cation, to the half-filled orbital in the ethyl radical, and to the filled lone pair in the ethyl anion has been evaluated by consideration of changes in CH stretching force constants alone.[12] These have been calculated using standard single-determinant ab initio molecular orbital theory at the split-valence-shell 4-31G level,[13] using a two-point approximation:[14]

$$k_{\mathrm{CH\ stretch}}\,(\mathrm{mdyn\ \AA^{-1}}) = 4.3593\,\frac{E^+ + E^- - 2E^0}{\Delta^2}$$

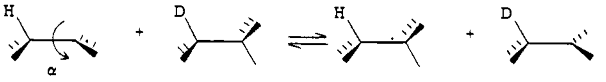
Here E^0 is the energy corresponding to the minimum in the theoretical CH stretching potential;[15] E^+ and E^- are energies corresponding to displacements of a single CH linkage by $+\Delta$ (+0.01 Å) and $-\Delta$ (−0.01 Å), respectively, and 4.3593 is the conversion factor from hartrees $\mathrm{\AA^{-2}}$ to mdyn $\mathrm{\AA^{-1}}$. All other geometrical parameters in the ethyl cation, radical, and anion have been assigned fixed values (r_{CC} = 1.54 Å; r_{CH} = 1.09 Å; methyl group HCH angles tetrahedral). The ethyl cation and ethyl radical have been constrained to a geometry in which the reactive center is planar trigonal ($\angle HC^+H = \angle HC{\cdot}H = 120°$), close to what is actually found for full calculations on the open forms of these systems. Two idealized geometries were considered for the ethyl anion, the first in which the carbanion center was constrained to be planar trigonal, the second, to be tetrahedral ($\angle HC^-H = 109.47°$). The latter model is, of course, the more realistic.

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

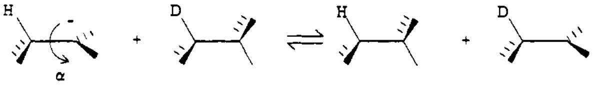
I. Planar Trigonal $-CH_2^+$, $-CH_2\cdot$, and CH_2^-. Considering changes in zero-point vibrational energy alone, the theoretically evaluated CH stretching force constants may be used to calculate equilibrium constants and reaction energies for the hypothetical ion-molecule processes (7), (8), and (9) as a function of the angle of torsion, α, of the methyl group about the planar trigonal carbonium ion, carbon radical, and carbanion centers. Our results are plotted in Figure 1 and have been fitted by least squares to the functions



(7)



(8)



(9)

reaction 7: ΔE (cal mol^{-1}) = $-32 + 58 \cos^2 \alpha$
correlation coefficient = 0.9997
reaction 8: ΔE (cal mol^{-1}) = $-9 + 24 \cos^2 \alpha$
correlation coefficient = 0.9969
reaction 9: ΔE (cal mol^{-1}) = $39 + 126 \cos^2 \alpha$
correlation coefficient = 0.9996

A number of points deserve special comment.

It is apparent that the $\cos^2$ function provides an excellent description of the calculated rotational potentials for the trigonal planar forms of all three molecules. It should again be emphasized that these are only model systems, constrained into highly idealized geometries. Whether our conclusions will hold up for chemically more realistic systems remains a matter for further study.

The coefficient of the $\cos^2 \alpha$ term in the function fitting the rotational potential in the trigonal planar ethyl anion is of the same sign as that for the corresponding cation, but roughly twice as large. One is tempted to suggest, therefore, that hyperconjugative interactions involving donation of charge from a nonbonded lone pair into the lowest vacant orbital of appropriate symmetry on the methyl group are of greater consequence energetically than are those operating in the opposite direction (i.e., charge transfer from a filled CH bonding orbital on methyl to the vacant p function at the carbocation center). Such a conclusion is somewhat surprising in view of our earlier comment that hyperconjugation in anions has long been presumed to be of lesser importance than the analogous interaction operating in cationic systems. It should be noted, however, that in the gas phase the largest secondary β-deuterium isotope effects which have been observed to date are those associated with the formation of anions.[7] The magnitudes of secondary isotope effects on ion-molecule equilibria involving gaseous carbocations are generally considerably smaller.[17]

The coefficient of the $\cos^2 \alpha$ term fitting the rotational potential in the trigonal planar ethyl radical is of the same sign as for the corresponding charged species but is roughly half as large as that for the cation.[18] According to perturbation molecular orbital theory, the half-filled orbital on the radical center is capable of accepting electron density from the filled methyl group orbital of π symmetry and of donating to the corresponding π^* orbital. Both interactions lead to weakening of the methyl carbon-hydrogen bonds and a preference for the light isotope. The energetic consequences of such one- and three-electron interactions are generally considered to be significantly smaller than those accompanying two-electron interactions, and it is not unreasonable to expect that the degree of charge transfer will parallel the energetic effects. That is to say, the small magnitude of the hyperconjugative component in the rotational potential is, after the fact, not at all surprising.

Finally, it should be pointed out that the conformationally independent term in the potential fitting function for the tri-

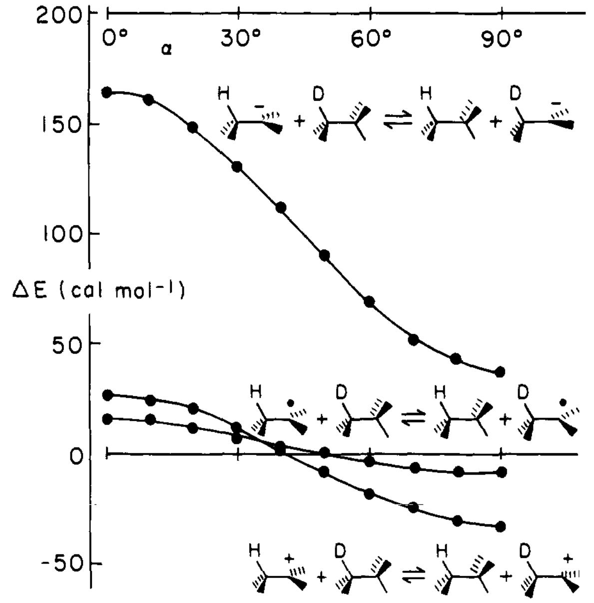


Figure 1. Theoretical energies for reactions 7, 8, and 9 as a function of torsion angle, α (α = 0° shown). Lines correspond to linear least-squares fits of functions $E(\alpha) = A + B \cos^2 \alpha$ to the theoretically calculated points.

gonal planar ethyl cation is of opposite sign (and of comparable magnitude) to that of the corresponding anion. The conformationally independent component for the ethyl free radical is in the same direction as that for the cation but considerably smaller. This suggests that, while inductive (or otherwise named conformationally independent) interactions involving a methyl group and a planar carbocation or radical center lead to the strengthening of the bonds in the former, those between a CH_3 rotor and a carbanion center act in the opposite direction. There is considerable evidence in (qualitative) support of our observations on the ethyl cation, arrived at from secondary isotope effect measurements in systems in which the vacant p function at the carbocation center is rigidly held orthogonal (or nearly orthogonal) to the CD linkage. It would appear, however, that the magnitudes of the inductive isotope effects noted in solution[3,20] are somewhat smaller than that calculated here for the ethyl cation. (k_H/k_D (inductive) calculated for the ethyl cation is 0.948, to be compared with an average solution-phase experimental value of 0.985.) It should be mentioned that the calculated total (CD_3) isotope effect associated with the formation of the open ethyl cation from the parent hydrocarbon is nearly zero

$$CH_3CH_2^+ + CD_3CH_3 \rightleftharpoons CH_3CH_3 + CD_3CH_2^+$$

$$\Delta E \text{ (theory)} = -8 \text{ cal/mol}$$

representing an almost complete cancellation between opposing hyperconjugative and inductive effects. Were it not for the latter contribution, the calculated β effect would be very close to that obtained experimentally, both in the gas phase[17] and in superacid media,[21] for the closely related process involving formation of the *tert*-butyl cation from the chloride. Whether the apparent failure of the theory here is due to an overestimation of the inductive effect (or alternatively an underestimation of the hyperconjugative contribution) or whether it implies that the ultimate resolution of the observed isotopic preference necessitates consideration of force constant changes beyond those directly associated with CH bond stretching motions, is a subject for further study.

Experimental evidence regarding the importance of inductive factors on the magnitudes of β-secondary isotope effects on free radical and anion forming reactions is unavailable.

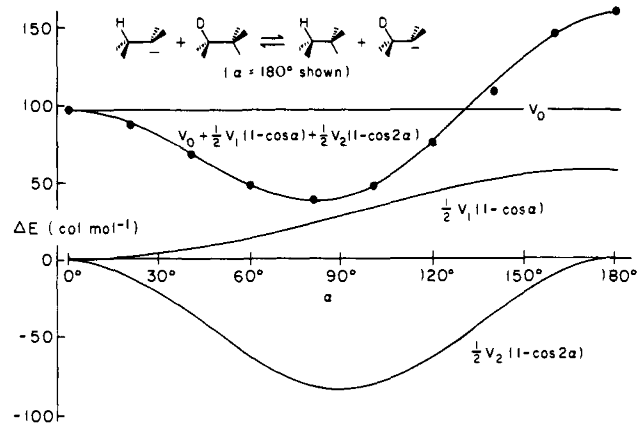


Figure 2. Theoretical energy for ion-molecule reaction 10 as a function of torsion angle, α (α = 0° shown). Line corresponds to nonlinear least-squares fit of function $E(\alpha) = A + B \cos^2(\alpha/2) + C \cos^2 \alpha$ to the theoretically calculated points.

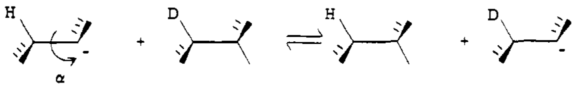
It is convenient to express the conformational dependence of the β-secondary deuterium isotope effect calculated for the ethyl cation, free radical, and anion in an alternative (but strictly equivalent) manner, in terms of a truncated Fourier series.[22]

$$V(\alpha) = V_0 + \frac{1}{2} V_1 (1 - \cos \alpha) + \frac{1}{2} V_2 (1 - \cos 2\alpha) + \frac{1}{2} V_3 (1 - \cos 3\alpha)$$

In the case of the model systems considered here, which incorporate strictly planar cation, free radical, and anion centers, only the V_0 and V_2 terms contribute to the fit.

for reaction 7	V_0 = 27 cal mol^{-1}
	V_2 = −58 cal mol^{-1}
for reaction 8	V_0 = 15 cal mol^{-1}
	V_2 = −24 cal mol^{-1}
for reaction 9	V_0 = 164 cal mol^{-1}
	V_2 = −126 cal mol^{-1}

II. Tetrahedral $-CH_2^-$. Although carbocations and free radicals are generally believed to prefer planar or nearly planar arrangements, unless otherwise constrained (i.e., the 1-adamantyl cation), the local geometries about centers of negative charge may range from planar trigonal in highly delocalized anions (i.e., benzyl) to nearly tetrahedral in systems where significant charge delocalization is not possible (i.e., the methyl anion).[23] We have, therefore, extended our calculations to include the conformational profile of the secondary β-deuterium isotope effect for the hypothetical ion-molecule process (10), involving the formation of a tetrahedral ethyl anion.[24]



(10)

Our theoretical data, presented in Figure 2, have been fitted by nonlinear least squares to a series in $\cos^2 \alpha$ and $\cos^2 \alpha/2$:

reaction 10: $\Delta E(\text{cal mol}^{-1}) = 70 + 86 \cos^2 \alpha - 58 \cos^2 \alpha/2$

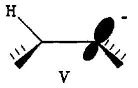
and equivalently to a truncated Fourier expansion including a V_1 component in addition to the V_0 and V_2 terms required for the description of the rotational potential in the planar carbanion.

$$V_0 = 98 \text{ cal mol}^{-1}$$

$$V_1 = 58 \text{ cal mol}^{-1}$$

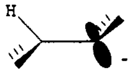
$$V_2 = -86 \text{ cal mol}^{-1}$$

The three individual Fourier components have been plotted in Figure 2, alongside of the total expansion. Interpretation of the calculated profile follows the same pattern as before. Thus, the V_0 term indicates that conformationally independent factors (inductive effects) lead to bond weakening in the ethyl anion relative to its neutral precursor, while the V_2 component provides a measure of the overall strength of the hyperconjugative interaction. The fact that the V_1 term contributes in a significant manner to the conformational profile reflects a strong difference in the hyperconjugative interaction energy for the $\alpha = 0$ (V) and $\alpha = 180°$ (VI) conformers. The effect is greater in the latter arrangement, in which the small back lobe of the lone-pair orbital points directly toward the CH bond, rather than in the former conformation where the larger front lobe points away.



V

$\alpha = 0°$

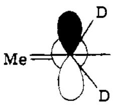


VI

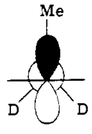
$\alpha = 180°$

Conclusion

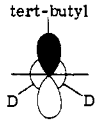
We have demonstrated, by means of ab initio molecular orbital calculations, that the magnitude of the hyperconjugative component of the secondary β-deuterium isotope effect originating from interaction of either a vacant, half-filled, or filled orbital and a CH linkage closely follows a $\cos^2 \alpha$ relationship, α being the angle which the CH bond makes with the empty or filled orbital. A number of interesting applications follow, the most important of which is perhaps the potential for experimentally determined secondary deuterium isotope effects to be employed as a means of determining the equilibrium conformations of both positive and negative ions. In fact, secondary kinetic isotope effects have already been employed to assign equilibrium conformations for such transition-state or intermediate species as the ethyl dimethyl (*tert*-amyl) and *tert*-butyl dimethyl cations in solution generated during the course of solvolysis of the corresponding alkyl chlorides.[3] In the former system, the measurements have been interpreted in terms of a predominance of conformation VII, in which all five carbons reside in a single plane, and each of the β deuteriums forms an angle of 30° with the vacant orbital at the carbocation center. The alternative arrangement, VIII, in which the ethyl group rises directly out of the plane made by the other four carbons, and which each of the CD linkages tends a 60° angle with the empty p orbital, would not give rise to the large secondary isotope effects which the experimental data suggest. A much smaller β-secondary kinetic isotope effect has been noted on the rate of solvolysis of 2,4,4-trimethyl-2-pentyl chloride, suggesting that the equilibrium conformation of the corresponding (*tert*-butyl dimethyl) cation is that in which the bulky *tert*-butyl group is suspended above the plane of the remaining four carbons, IX, rather than the sterically more crowded arrangement, X, in which it rests in this plane. It appears, therefore, that what these combined isotope effect measurements suggest is that, although the energetic stabilization resulting from the alignment of a CH linkage parallel to a vacant p orbital (CH hyperconjugation) is inherently greater than that associated with CC bond alignment (CC hyperconjugation), the two stabilization energies are of similar enough magnitude such that steric factors may also act to play an important role in dictating conformation. The use of equilibrium isotope effects as a means of assigning the conformation of stable ions in the gas phase has yet to be explored. Information on the structures of isolated ions, used in conjunction with solution-phase conformational data, should be of value in elucidating the effects of real media on structure.



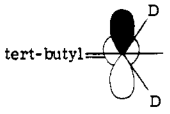
VII



VIII



IX



X

Knowledge of the angular dependence of β-deuterium isotope effects also allows for dissection into conformationally dependent (hyperconjugative) and independent (inductive) components. Such a decomposition should be invaluable in any detailed analysis of the effects which such factors as substituents and solvent system might have on the structures and stabilities of ions. Research in this direction is in progress.

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(1) (a) University of California; (b) University of Zagreb.

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$$\delta = \frac{\int \varphi_p H \varphi_\pi d\tau|^2}{|E_p - E_\pi|}$$

Introduction of the Wolfsberg-Helmholtz approximation[4] yields an expression for the energy of hyperconjugation which depends on the square of the overlap of the interacting orbitals.

$$\delta \approx \frac{[\int \varphi_p \varphi_\pi d\tau]^2}{|E_p - E_\pi|}$$

As the angular dependence of the overlap goes as the cosine of the angle between the interacting functions, the hyperconjugative energy should follow a $\cos^2$ relationship.

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(11) See ref 9, p 482 ff.

(12) For an assessment of the validity of such an assumption, see D. J. DeFrees, M. Taagepera, B. A. Levi, S. K. Pollack, K. D. Summerhays, R. W. Taft, M. Wolfsberg, and W. J. Hehre, *J. Am. Chem. Soc.*, submitted.

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(24) It should be noted that the actual (4-31G level) equilibrium structure for the ethyl anion incorporates a nearly tetrahedral carbanion center.

Oxygen-17 Nuclear Quadrupole Double Resonance Spectroscopy. 1. Introduction. Results for Organic Carbonyl Compounds[1]

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Abstract: The pure nuclear quadrupole resonance (NQR) spectra of ^{17}O in natural abundance in 23 substances containing carbonyl groups are reported. The spectra were obtained on powdered solids at 77 K, using the double resonance field cycling technique pioneered by Hahn and co-workers. The substances studied include $C_6H_5C(O)X$ (X = F, Cl, Br, CN), substituted benzaldehydes, phenyl benzoate, several acid anhydrides, phthalimide, $KHCO_3$, $NaHCO_3$, sodium formate, and potassium acid phthalate. An analysis of the carbonyl oxygen data in terms of a simple Townes-Dailey model shows that variation in carbon-oxygen π bond character among the compounds is the major source of variations in quadrupole coupling constant and asymmetry parameter. The atomic orbital populations on oxygen deduced from the NQR data are in accord with the limited physical data and theoretical results available for comparisons.

Introduction

Oxygen-17, the sole isotope of oxygen with nonzero spin ($I = 5/2$), occurs naturally in fractional abundance of only 3.7×10^{-4}. Although important NMR and ESR experiments involving ^{17}O have been performed, few observations have been made of ^{17}O nuclear quadrupole resonance (NQR) spectra in oxygen-containing substances. Quadrupole coupling constant data have been obtained from microwave spectra for gaseous, isotopically enriched SCO,[2] CO,[3] H_2O,[4] and H_2CO.[5] High-field NMR experiments have yielded quadrupole coupling constants in ^{17}O-enriched liquid water,[6] ice,[7] and chromium(III)-doped alumina.[8]

The double-resonance experiments pioneered by Redfield[9] and Hahn and co-workers[10,11] offer the possibility of very high sensitivity in observing pure quadrupole resonance spectra of any low-abundance spin system of half-integral spin $I \geq 3/2$. Despite their wide potential application, these techniques have not thus far been widely employed. The few ^{17}O systems that have been studied by double-resonance methods include the isotopically enriched substances KH_2PO_4,[12] ice,[13a,b] and $BaClO_3 \cdot H_2O$;[13c] NQR for natural abundance ^{17}O have been reported only for a series of eight organic solids,[11] and—using a slightly different technique—for two other organic compounds.[14] Most recently we have described several results from studies involving natural-abundance ^{17}O.[15]

Because oxygen is an important constituent of so many substances, particularly those of biological importance, a spectroscopic probe of the electronic environment about the oxygen nucleus would be of substantial and widespread utility. We have begun an extended series of studies of natural abundance level ^{17}O NQR spectra. The double-resonance experiment is adequately described elsewhere.[10,11,15,16] Briefly, it consists in cooling of the abundant *I* spin system (protons) by adiabatic demagnetization in the laboratory frame, followed by application of high-level rf intended to excite the pure quadrupole transitions of a rare spin *S* system, ^{17}O. When the rf frequency is at or near resonance with an *S* spin quadrupole transition, thermal contact is established between the "hot" *S* spin system and cold *I* spin system. However, even though temperature equilibration may occur, the *I* spin temperature is changed very little because it has a much higher heat capacity than the *S* spin system. Repeated heating of the *S* spin system is effected by application of 180° phase shifts at intervals on the order of 500 μs. After about 10^4 such intervals, the spin temperature of the *I* system is substantially increased. The sample is returned to high magnetic field, and the *I* spin magnetization that remains is measured by applying a 90° pulse and sampling the free induction decay. The *I* spin system is then saturated and allowed to remagnetize for a given time, and the cycle is repeated at a new, incremented *S* channel frequency. The displayed spectra show the variation in *I* spin magnetization as a function of *S* channel frequency.

In this paper, we describe a few details of the experimental method employed, and present data for a series of carbonyl compounds, mainly organic in character. The ^{17}O data are interpreted in terms of the classic Townes-Dailey model; the results are compared with other structural and spectroscopic data for the compounds studied.

Description of the Spectrometer

A block diagram of the instrument, which is similar to that described by Slusher and Hahn,[10b] is shown in Figure 1. The proton (*I* channel) transmitter operates at about 40 MHz. A single coil design, consisting of a parallel resonant LC circuit, is employed. A short section of coaxial cable is used as a capacitor. The induction coil is tapped to effect impedance

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