Figure 2. Conformational dependence of $J^{199}\text{Hg}-^1\text{H}\beta$ in CH_3-$HgCH_2CH_3$. The asterisks mark approximate experimental values from ref 3.

down from values reported for organomercury chlorides to the data calculated for methylethylmercury.

The calculated curve resembles very strongly that for vicinal H–H coupling with an exaggerated value for the trans orientation. This curve appears to be at least qualitatively consistent with the experimental data.

Conclusions

These results with inclusion of changes in the effective nuclear change of the 6s orbital of mercury suggest strongly that all the major features of $^{199}\text{Hg}-^1\text{H}$ spin coupling in saturated organomercurials can be accounted for in terms of a dominant Fermi contact term and little use of mercury's 5d orbitals in bonding. The results may well be quantitative enough to aid in configurational studies of organomercurials or other heavy metal systems such as platinum-containing complexes.

Electron Spin Resonance Studies of Vinyl, Propargyl, and Butatrienyl Radicals Isolated in Argon Matrices

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Abstract: Electron spin resonance spectra of vinyl, propargyl, and butatrienyl radicals isolated in argon matrices at $\sim 4°K$ are obtained and analyzed. The analyses were made utilizing a spectrum simulation program which incorporates the effect of the forbidden transitions. An excellent agreement is noted between the spin density distributions assessed from the anisotropies of the hyperfine coupling tensors and those obtained by INDO molecular orbital calculations.

Electron spin resonance spectra of free radicals of the form $H_2C=(C)_n=C\cdot-H$ have been investigated by several groups.[1-7] The specific examples reported are vinyl ($n = 0$), propargyl ($n = 1$), and butatrienyl ($n = 2$) radicals. Fessenden and Schuler[1] obtained the isotropic or " the liquid state" spectra of vinyl and propargyl radicals generated in liquid ethylene and allene, respectively, by a high-energy electron beam. Kochi and Krusic[2] obtained the istropic spectrum of propargyl radicals by abstracting hydrogen from methylacetylene and allene using photochemically induced *tert*-butoxy radicals. Cochran, *et al.*,[3] ob-

tained the anisotropic or " the solid-state" spectrum of vinyl radicals by reacting hydrogen atoms with acetylene trapped within a solid argon matrix. The solid state spectra of propargyl radicals are observed from various organic matrices which had been irradiated with uv or γ-ray at 77°K.[4-6] As for butatrienyl radicals, only the solid-state spectrum obtained from an argon matrix is known.[7]

For a π-electron radical, when the isotropic coupling constant A_{iso} to an α proton is known, the spin density ρ at the p_π orbital of the carbon can be assessed using the relationship of McConnell and Chestnut[8]

$$A_{iso} = Q\rho \qquad (1)$$

The direct application of eq 1 to the present series of radicals is difficult, however, since the proportionality constant Q is known to vary substantially depending upon the type of hybridization of the carbon in question. The magnitude of Q has been shown to range from 23 G for a sp^2-hybridized carbon atom to 35 G

(1) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).
(2) J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **92**, 4110 (1970).
(3) E. J. Cochran, F. J. Adrian, and V. A. Bowers, *J. Chem. Phys.*, **40**, 213 (1964).
(4) D. H. Volman, K. A. Maas, and J. Wolstenholme, *J. Amer. Chem. Soc.*, **87**, 3041 (1965).
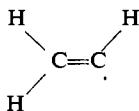(5) T. S. Zhuravleva and I. A. Misurkin, *Zh. Strukt. Khim.*, **5**, 656 (1964).
(6) C. P. Poole, Jr., and R. S. Anderson, *J. Chem. Phys.*, **31**, 346 (1959).
(7) P. H. Kasai, L. Skattebøl, and E. B. Whipple, *J. Amer. Chem. Soc.*, **90**, 4509 (1968).

(8) H. M. McConnell and D. B. Chestnut, *J. Chem. Phys.*, **28**, 107 (1958).

for a sp-hybridized system.[9] In the case of vinyl radicals which are known to have a bent structure

$$\begin{array}{c} H \\ \diagdown \\ \diagup \diagdown \\ H \end{array} C = C \diagup \begin{array}{c} H \\ \diagup \\ \cdot \end{array}$$
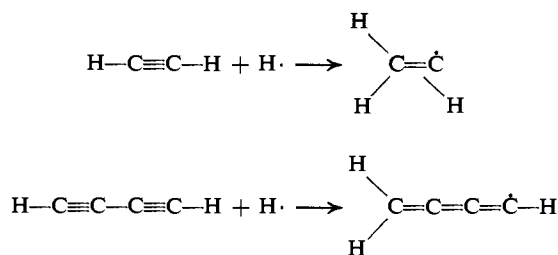
eq 1 cannot be applied at all.

An esr spectrum exhibited by an ensemble of rigidly held, but randomly oriented radicals is broad and often possesses extremely complicated features owing to the anisotropies of the **g** tensor and of the hyperfine coupling tensors. When the assignment of such a spectrum is made, however, the spin density at the p_π orbital of a carbon can also be assessed from the anisotropic, dipolar part of the coupling tensor to the α proton, circumventing the ambiguity associated with the usage of eq 1. The dipolar part of the hyperfine coupling tensor to an α proton is almost totally and directly related to the spin density at the p_π orbital of the carbon and is not sensitive to the type of hybridization of the carbon atom within the σ plane.

Reported in the following are the results of our analyses of the anisotropic spectra of vinyl, propargyl, and butatrienyl radicals generated and trapped within solid argon matrices at $\sim 4°K$. The assignment of the **g** tensors and the accurate assessment of both the isotropic and anisotropic parts of the hyperfine coupling tensors were done by utilizing a computer spectrum simulation program. In each case a satisfactory agreement between the computed and the observed spectra was obtained only when the effect of the forbidden transitions involving the acetylenic proton was included. The spectrum simulation program which allows the inclusion of the effect of such forbidden transitions is also described and demonstrated briefly.

Experimental Section

The design of the liquid helium dewar and an X-band esr spectrometer assembly which allows the trapping of reactive species in a rare gas matrix and measurement of their esr spectra has been described in an earlier report.[10]

Vinyl radicals and butatrienyl radicals were generated within a solid argon matrix by reacting hydrogen atoms (produced by the photolysis of HI) with acetylene and diacetylene, respectively.

$$H{-}C{\equiv}C{-}H + H\cdot \longrightarrow \begin{array}{c} H \\ \diagdown \\ \diagup \diagdown \\ H \end{array} C{=}\dot C \diagdown \begin{array}{c} \\ H \end{array}$$

$$H{-}C{\equiv}C{-}C{\equiv}C{-}H + H\cdot \longrightarrow \begin{array}{c} H \\ \diagdown \\ \diagup \end{array} C{=}C{=}C{=}\dot C{-}H$$

Propargyl radicals were produced by the photolysis of propargyl bromide trapped within an argon matrix. Unlike the cases where radicals are produced by vapor-phase pyrolysis prior to the deposition onto the matrix layer,[11] no effect attributable to preferential orientation was observed in these matrices.

The esr measurements were all made at $\sim 4°K$, and the spectrometer frequency locked to the loaded sample cavity was 9.435 GHz.

(9) M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960).
(10) P. H. Kasai, W. Weltner, Jr., and E. B. Whipple, *ibid.*, **42**, 1120 (1965).
(11) P. H. Kasai and E. B. Whipple, *J. Amer. Chem. Soc.*, **89**, 1033 (1967).

Forbidden Transition and Spectrum Simulation

Hyperfine structure of the esr spectra of oriented organic radicals has been discussed by several authors.[12-14] Features uniquely associated with the spectra of oriented radicals and not with their liquid-state counterpart are the orientation dependency of the spectra and the possibility of encountering the forbidden transitions.

Let us consider an organic radical in which all the magnetic nuclei giving rise to hyperfine structures are protons $(I = {}^1/_2)$. The Hamiltonian representing the interactions between the electron and nuclear spins and the externally applied magnetic field **H** is given by

$$\mathcal{3C} = -\beta_e \mathbf{S} \cdot \mathbf{G} \cdot \mathbf{H} + \sum_{i=1}^{n} \mathbf{S} \cdot \mathbf{A}_i \cdot \mathbf{I}_i + \sum_{i=1}^{n} g_p \beta_n \mathbf{I}_i \cdot \mathbf{H} \quad (2)$$

An analysis of this Hamiltonian shows that, even for a radical containing only one proton, four esr transitions are possible, and, as depicted in Figure 1, they can be classified into the outer doublet and the inner doublet. Assuming that the anisotropy of the **g** tensor is negligibly small in comparison to that of the hyperfine coupling tensor, McConnell, *et al.*, developed the following expressions for the resonance positions, $H_{\pm \text{out}}$ and $H_{\pm \text{inn}}$, and the transition probabilities, $T_{\pm \text{out}}$ and $T_{\pm \text{inn}}$, of these doublets.[13]

$$H_{\pm \text{out}} = H_0 \pm {}^1/_2(A_+ + A_-)$$
$$H_{\pm \text{inn}} = H_0 \pm {}^1/_2(A_+ - A_-) \quad (3)$$

and

$$T_{\pm \text{out}} = {}^1/_2(1 - \cos \tau)$$
$$T_{\pm \text{inn}} = {}^1/_2(1 + \cos \tau) \quad (4)$$

where

$$H_0 = h\nu/g_e \beta_e$$
$$H_p = (g_p \beta_n / g_e \beta_e) H_0$$
$$(A_\pm)^2 = (H_p \pm {}^1/_2 A)^2 \cos^2 \theta +$$
$$(H_p \pm {}^1/_2 B)^2 \sin^2 \theta \cos^2 \varphi +$$
$$(H_p \pm {}^1/_2 C)^2 \sin^2 \theta \sin^2 \varphi \quad (5)$$
$$\cos \tau = (4H_p{}^2 - A_0{}^2)/(4A_+ A_-)$$

and

$$A_0{}^2 = A^2 \cos^2 \theta + B^2 \sin^2 \theta \cos^2 \varphi +$$
$$C^2 \sin^2 \theta \sin^2 \varphi \quad (6)$$

In eq 5 and 6, A, B, and C are the diagonal elements of the principal hyperfine coupling tensor, and the angles θ and φ define, in the usual manner, the direction of the magnetic field relative to the principal axes. Inspection of these equations reveals (1) that the effect of forbidden transitions becomes significant (*i.e.*, $T_{\pm \text{out}} \cong T_{\pm \text{inn}}$) only when the magnitudes of A_0 and the anisotropy of the coupling tensor are both comparable to $2H_p$, and (2) that, when $A \approx B \approx C > 2H_p$, or $A \approx B \approx C < 2H_p$, only the two "normal" hyperfine components separated by A_0 are observed.

(12) N. M. Atherton and D. H. Whiffen, *Mol. Phys.*, **3**, 1 (1960).
(13) H. M. McConnell, C. Heller, T. Cole, and R. W. Fessenden, *J. Amer. Chem. Soc.*, **82**, 766 (1960).
(14) I. Miyagawa and W. Gordy, *J. Chem. Phys.*, **32**, 255 (1960).
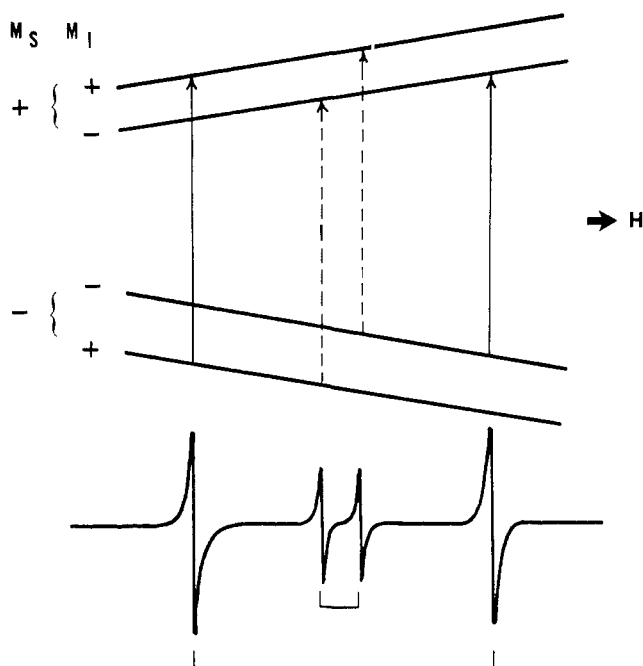
Figure 1. Energy levels of a radical with $S = I = \frac{1}{2}$ and its expected esr spectrum. Four transitions, the outer doublet, and the inner doublet are possible.

Figure 2. Powder pattern spectrum of $R_2 \cdot CH$ simulated with (solid line) and without (dotted line) the forbidden transitions.

Thus a radical containing n protons may exhibit as many as 4^n hyperfine components. The spectral pattern $S(H)$ exhibited by an ensemble of randomly oriented radicals containing n protons is, therefore, given by

$$S(H) = \sum_{M=1}^{4^n} \int_0^{2\pi} \int_0^{\pi} T_M(\theta,\varphi)D[H - H_M(\theta,\varphi)] \times \\ \sin\theta \, d\theta d\varphi \quad (7)$$

The angles θ and φ now define the direction of the magnetic field relative to the principal axes of the **g** tensor, and the summation M is performed over all the hyperfine components. $D[H - H_M(\theta,\varphi)]$ is the derivative of a line-shape function, and $H_M(\theta,\varphi)$ and $T_M(\theta,\varphi)$ represent, respectively, the resonance field and the transition probability of the Mth hyperfine component. Therefore

$$H_M(\theta,\varphi) = H_0 + \sum_{i=1}^{n} H_{i,m} \quad (8)$$

$$T_M(\theta,\varphi) = \prod_{i=1}^{n} T_{i,m} \quad (9)$$

where $m = 1 \sim 4$. $H_{i,m}$ and $T_{i,m}$ represent the contributions of the ith proton to the resonance position and the transition probability to the particular hyperfine component and are to be evaluated from the equations of the form 3 and 4, respectively. When the principal axes of a hyperfine coupling tensor do not coincide with those of the **g** tensor, the directional cosines of the applied field relative to the hyperfine axes can be best expressed in terms of the directional cosines of the field relative to the **g** tensor and the Eulerian angles relating the orientation of the hyperfine coupling tensor to that of the **g** tensor. A computer program was written which would simulate the powder pattern spectrum $S(H)$ in terms of the principal **g** tensor, the hyperfine
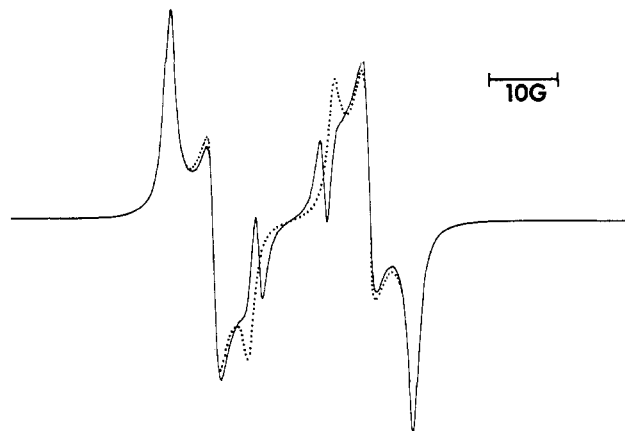
coupling tensors of the protons, and the Eulerian angles relating the orientations of these tensors. The program was written in such a way that the quadruplet splitting given by eq 3 and 4 is considered only for those protons so desired. For the remaining "normal" protons, only the normal doublet splitting with the unit transition probability and the separation of A_0 given by eq 6 is considered.

The diagonal elements of a principal hyperfine coupling tensor, A, B, and C, can be each considered in two parts, the isotropic part A_{iso} and the orientation dependent, dipolar part A_{dip}. McConnell and Strathdee[15] have made a detailed analysis of the dipolar part of the hyperfine coupling tensor to an α proton located within the σ plane of a π-electron radical. They have shown that A_{dip} in this case can be given by

$$A_{dip} = [\eta(3\cos^2\theta - 1) + \\ \zeta(1 - \cos^2\theta)\cos 2\varphi]\rho_\pi \quad (10)$$

where ρ_π represents the spin density of the unpaired electron at the p_π orbital of the α carbon. The angles θ and φ define, in the usual manner, the direction of the magnetic field relative to the C–H bond and the p_π orbital. The coupling tensor to an α proton has been accurately measured for several radicals for which $\rho_\pi \cong 1.0$.[16] The proportionality constants η and ζ in eq 10, therefore, can be determined empirically from these results. From the data compiled in ref 16, we obtained $\eta = 5.5$ G and $\zeta = 6.5$ G. Evaluation of eq 10 using these values gives the following expressions for the three cannonical orientations.

$$A_{dip}(\|) = +11.0\rho_\pi \text{ G}$$
$$A_{dip}(\perp,\|) = +1.0\rho_\pi \text{ G} \quad (11)$$
$$A_{dip}(\perp,\perp) = -12.0\rho_\pi \text{ G}$$

Here $A_{dip}(\perp,\|)$, for example, represents the dipolar part when the field is applied perpendicular to the C–H bond, but parallel to the p_π orbital.

Let us consider a disubstituted methyl radical $R_2 \cdot CH$ for which the spin density at the α carbon is unity, the isotropic coupling constant to the α proton is -23 G, and there is no coupling to the substituents R_2. The

(15) H. M. McConnell and J. Strathdee, *Mol. Phys.*, **2**, 129 (1959).
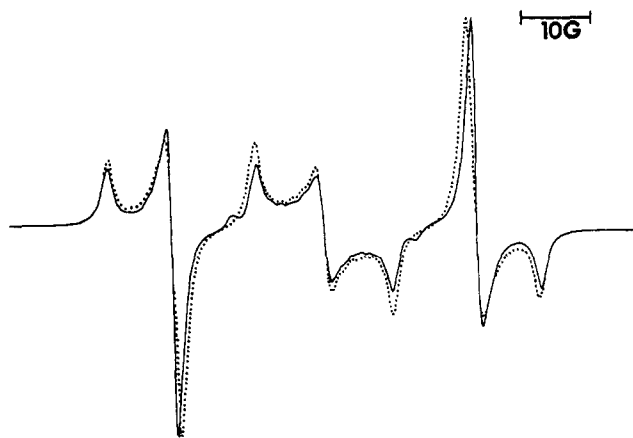(16) See, for example, a review article by J. R. Morton, *Chem. Rev.*, **64**, 453 (1964).

Figure 3. Powder pattern spectrum of R·CH₂ simulated with (solid line) and without (dotted line) the forbidden transitions.

hyperfine coupling tensor to the α proton, according to eq (11), would then be

$$A = A_{iso} + A_{dip}(||) = -12.0 \text{ G}$$

$$B = A_{iso} + A_{dip}(\perp,||) = -22.0 \text{ G} \qquad (12)$$

$$C = A_{iso} + A_{dip}(\perp,\perp) = -35.0 \text{ G}$$

Shown in Figure 2 is the powder pattern spectrum of this radical simulated by the program described earlier assuming the spectrometer frequency of 9.435 GHz and an isotropic g value of 2.0023. It is compared with the powder pattern simulated allowing only the normal doublet splitting by the α proton. The value of $2H_p$ for the assumed spectrometer frequency is 10.2 G. Thus, as expected, the effect of the forbidden transition is most conspicuous near the region corresponding to the A axis.

Figure 3 shows the powder pattern spectrum of a monosubstituted methyl radical R·CH₂ similarly computed using the same set of hyperfine coupling constants but taking cognizance of the fact that the orientations of the two coupling tensors differ from that of the g tensor by ±60° about the axis perpendicular to the molecular plane. In this case no significant difference was noted between the pattern computed allowing the forbidden transitions and that computed allowing only the normal doublet splitting. Apparently the effect of the forbidden transition is nullified in the powder pattern by the difference in the orientation of the two coupling tensors. This difference is also responsible for the extreme broadening, hence the loss of apparent intensity of the central component of the expected triplet.

Spectra and Assignments

The observed spectra of vinyl, propargyl, and butatrienyl radicals isolated in argon matrices are shown in Figures 4A, 5A, and 6A, respectively. In each case the spectrum was found to possess the effect of forbidden transitions involving only the acetylenic proton. Shown in Figures 4B, 5B, and 6B, respectively, are the spectra of these radicals simulated on the bases of the final assignments given in Table I, allowing the forbidden transitions only to the acetylenic proton. The spectra simulated based upon the same assignments but allowing only the normal doublet splitting to all the protons are also shown for comparison (Figures 4C, 5C, and 6C).
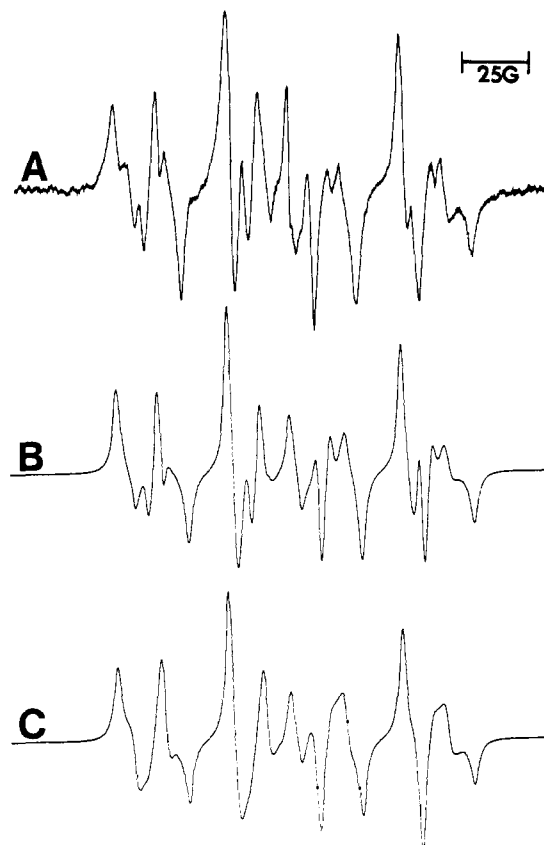

Figure 4. Esr spectrum of vinyl isolated in an argon matrix: (A) observed, (B) simulated allowing the forbidden transitions to the acetylenic proton, (C) simulated allowing only the normal transitions.

Table I. Assessed g and Hyperfine Coupling Tensors (in Gauss) of the Vinyl, Propargyl, and Butatrienyl Radicals

	x	y	z	A_{iso} (obsd)	$A_{iso}{}^a$ (INDO–MO)
		Vinyl			
g	2.0013	2.0023	2.0025		
H(acet)	26.7	11.3	4.0	13.8	12.3
H(meth)$_{tr}$	65.0	68.3	64.3	65.9	72.3
H(meth)$_{cis}$	42.3	38.5	38.0	39.6	30.7
		Propargyl			
	$|| = x$	$\perp = \frac{1}{2}(y + z)$			
g	2.0026	2.0022			
H(acet)	−7.0	−15.7		−12.8	−12.0
H(meth)	−23.3	−16.3		−18.6	−18.9
		Butatrienyl			
	x	y	z		
g	2.0008	2.0023	2.0028		
H(acet)	−6.7	−15.0	−19.0	−13.6	−12.7
H(meth)	45.3	42.5	42.0	43.3	61.6

^{a} The isotropic coupling constants predicted by INDO molecular orbital calculation (see Table II).

Depicted in Chart I are the principal valence-bond structures of these radicals. A general expression representing the dipolar part of the hyperfine interaction may be written as

$$A_{dip} = g_e\beta_e g_n\beta_n \left\langle \Phi \left| \frac{1 - 3\cos^2 \zeta}{r^3} \right| \Phi \right\rangle$$

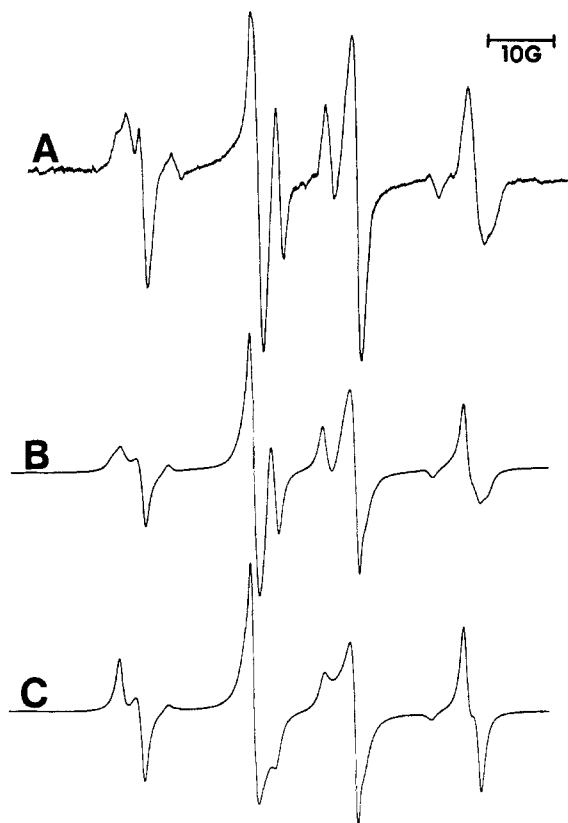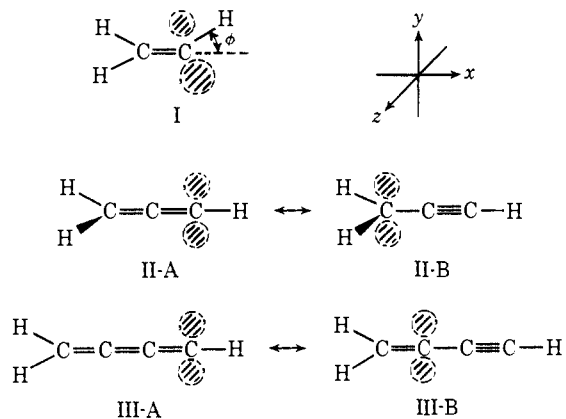$$\cong |g_e\beta_e g_n\beta_n|\langle 1/r^3\rangle(3\cos^2 \theta - 1)$$

Figure 5. Esr spectrum of propargyl isolated in an argon matrix: (A) observed, (B) simulated allowing the forbidden transitions to the acetylenic proton, (C) simulated allowing only the normal transitions.

Chart I

Here r is the distance between the unpaired electron and the magnetic nucleus concerned, and ζ is the angle between this line and the applied magnetic field. The latter approximate form applies when the electron can be considered localized at a point away from the nucleus; θ then defines the angle between the line connecting this point to the nucleus and the magnetic field. These equations then predict the following. Any proton in these radicals shown above should have the smallest coupling constant in the z direction if the sign of its isotropic coupling constant is positive, and the largest if it is negative. The coupling constant to the acetylenic proton should be the largest in the x direction if it has a positive isotropic coupling constant, and the smallest if it has a negative isotropic coupling constant. The establishment of the orientation of each principal coupling tensor relative to the
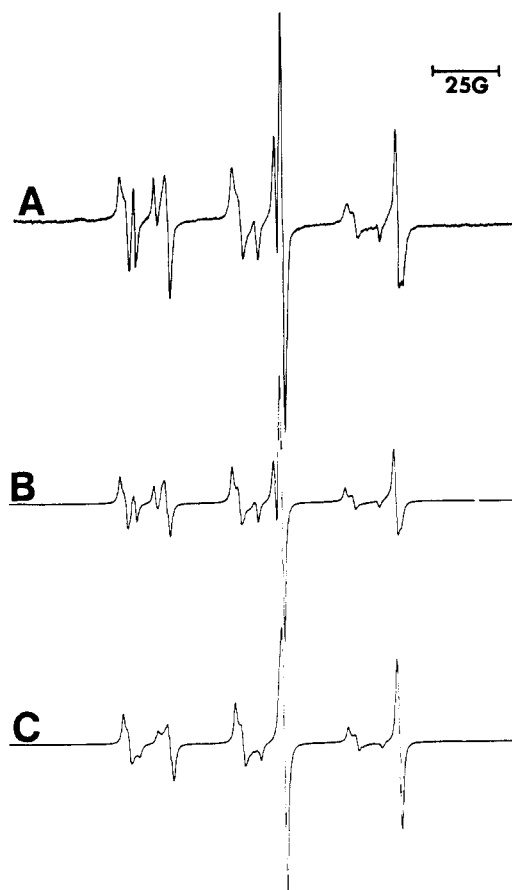

Figure 6. Esr spectrum of butatrienyl isolated in an argon matrix: (A) observed, (B) simulated allowing the forbidden transitions to the acetylenic proton, (C) simulated allowing only the normal transitions.

molecular geometry and the assessment of the signs of the isotropic coupling constants to the acetylenic protons (Table I) were made based upon these considerations together with the assertion that the isotropic coupling constant to the methylene protons should be positive for the vinyl and butatinenyl radicals and negative for the propargyl radical. In the case of vinyl radical the true orientation of the principal axes must be that the "x" axis is directed more along the bent C–H bond rather than the coordinate axis indicated in the figure. A brief discussion on each spectrum is given below.

Vinyl Radicals. The large isotropic coupling constants known for the β protons of this radical are mostly due to the direct overlap of the p_π orbital of the unpaired electron at the α carbon with the 1s orbitals of the β protons. The coupling tensors to the β protons are, therefore, expected to be positive and nearly isotropic. A reasonable estimate of the coupling tensor to the α proton can be made from the known isotropic coupling constant and the dipolar part estimated using eq 11. The spectrum simulated using these estimated coupling tensors possessed such a proximity to the observed spectrum that only several subsequent trial simulations were necessary before the final result (Figure 4B) was obtained.

Propargyl Radicals. The expected doublet-of-triplet pattern is readily recognized in the observed spectrum. The central component of each triplet, however, is much too prominent to be attributed to the two methylene

Table II. Experimentally Determined Spin Density Distributions in Vinyl, Propargyl, and Butatrienyl, and Those Given by INDO Molecular Orbital Calculations

| | Vinyl | | Propargyl | | Butatrienyl | |
	Expt	MO[a]	Expt	MO[a]	Expt	MO[a]
H(acet)	+0.026	+0.023	−0.024	−0.022	−0.025	−0.024
H(meth)	trans +0.122	+0.134	−0.034	−0.035	+0.080	+0.114
	cis +0.073	+0.057				
C(1)	+0.99	+0.97	+0.53	+0.49	+0.54	+0.52
C(2)	−0.21[b]	−0.18	−0.19[b]	−0.26	−0.19[b,c]	−0.26
C(3)			+0.75	+0.86	+0.70	+0.73
C(4)					−0.19[b,c]	−0.19

[a] The MO spin density given for each carbon atom is the sum of the spin densities at the four valence orbitals of that carbon. [b] Determined from the relation $\sum_{ao} \rho_{ao} = 1.0$. [c] Divided between C(2) and C(4).

protons held stationary in the matrix (see Figure 3, the spectrum simulated for R·CH₂ held stationary within a matrix). The prominence of the central component can be realized only when the two protons become magnetically equivalent. We are thus led to conclude that most of the propargyl radicals in this matrix are rotating about the C–C–C axis, making the two protons equivalent and rendering an axial symmetry to the system. Both the assignment and the simulation of the spectrum were made assuming the axially symmetric spin Hamiltonian indicated in the table. The small discrepancy between Figures 5A and 5B in the relative intensity of the central part is ascribed to noncompleteness of the averaging by the rotation.

Butatrienyl Radicals. The triplet-of-doublet feature is completely resolved. The orthorhombic g and hyperfine coupling tensors given in Table I were directly assessed from the spectrum and used for the simulation. The large triplet spacing is consistent with the resonance structure III-B where the two methylene protons are structurally equivalent and the hyperfine coupling interaction occurs through a direct overlap as in the case of vinyl radicals. The coupling tensors to these protons are, therefore, nearly isotropic, and the central component of each triplet possesses a prominent intensity normally expected for a liquid-state spectrum.

Spin Density and Structure

Table II shows the spin densities at various atoms of the radicals discussed above determined from the observed hyperfine coupling tensors. The spin density at the carbon-1 of each radical was determined from the observed anisotropy of the coupling constant $(A_{max} - A_{min})$ to the acetylenic proton using the relation derived from eq 11. In the case of vinyl radical which possesses the bent structure I, eq 11 should not be directly applicable. An INDO molecular orbital calculation[17] revealed, however, that the semifilled orbital at the α carbon is essentially a 2p orbital perpendicular to the C–H bond, thus justifying the usage of eq 11 for an approximate assessment of the spin density at this position. In the case of propargyl, eq 11 had to be transformed to represent the situation where the radical is rotating about the C–C–C axis. The spin density at the carbon-3 of this radical was also assessed from the anisotropy of the coupling tensor to the methylene protons assuming the H–C–H angle of 120° and the rota-

(17) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.
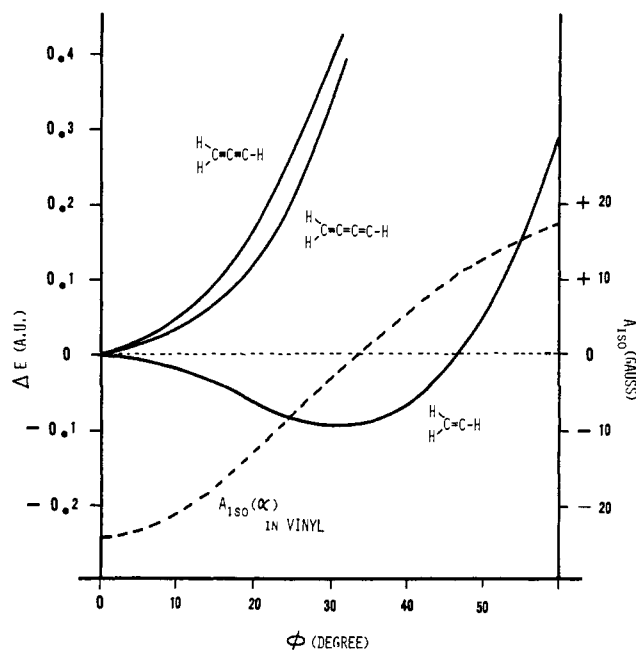

Figure 7. Dependency upon φ (the angle of bent at the acetylenic section –C–C–H) of the total energies of vinyl, propargyl, and butatrienyl, and A_{iso} (α) in vinyl given by INDO molecular orbital calculations.

tion about the C–C–C axis. The spin density at the carbon-3 of butatrienyl was estimated from the isotropic coupling constant to the methylene protons assuming that the structure III-B is responsible for the coupling and using the vinyl radical as a model case. The spin densities at various protons were assessed from the isotropic coupling constants using the relation, $A_{iso}(H) = 539\rho$ G, suggested by Pople, et al.[18]

Also shown in Table II are the spin density distributions in these radicals predicted by INDO molecular orbital calculations. The calculations were performed assuming a bent structure (φ = 50°) for vinyl and linear structures for the propargyl and butatrienyl radicals.[19]

(18) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Amer. Chem. Soc.*, **90**, 4201 (1968).

(19) Other structural parameters employed for the calculations are: for vinyl, C₁–C₂ = 1.34 Å; for propargyl, C₁–C₂ = 1.24 Å, C₂–C₃ = 1.38 Å; and for butatrienyl, C₁–C₂ = 1.24 Å, C₂–C₃ = 1.33 Å, C₃–C₄ = 1.31 Å. They were derived from the standard bond lengths given in ref 17. All the C–H bonds were taken to be 1.08 Å. φ = 50° was chosen for vinyl because of the best overall agreement of the calculated spin density distributions with the observed values. The calculations were performed utilizing an INDO program obtained from the Quantum Chemistry Program Exchange, Indiana University.

An excellent overall agreement is seen between the experimentally determined spin density distributions and those predicted by the molecular orbital calculations.

Several theoretical accounts have been reported concerning a bent structure, hence the nonequivalence of the β protons, of the vinyl radical,[20-22] and the sign of the isotropic coupling constant to its α proton.[3] The results of the present esr study show that, while the vinyl radical is bent, the propargyl and butatrienyl radicals possess a linear acetylenic section –C–C–H. This conclusion is not surprising since any bending of the latter radicals would have to occur at the expense of the optimum delocalization in the π-electron system. We have carried out INDO molecular orbital calculations of these radicals and examined the dependency of the total energy as well as those of the isotropic coupling constants of the protons upon the angle ϕ. The results

are depicted in Figure 7. The calculations clearly show the energy minimum for the vinyl radical at $\phi = 30°$. Also, although the calculated isotropic coupling constant to the α proton is still negative at this angle, the predicted dependency of the coupling constant upon ϕ provides a strong support to our experimental assignment of positive sign to this coupling. The dependency upon ϕ of the isotropic coupling constants to β protons is essentially the same as those given by valence bond or CNDO type calculations.[20,22]

As expected, no energy minima were found for the propargyl and butatrienyl radicals away from the linear configuration. Surprisingly the calculations also showed that, for these radicals, neither the isotropic coupling constant of the acetylenic proton nor those of the methylene protons change appreciably when the acetylenic section –C–C–H is bent.[23]

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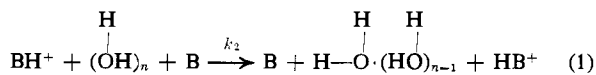
Quatermolecular Proton Transfer of 2,4-Lutidine and Its Conjugate Acid in Aqueous Solution[1a]

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Abstract: Symmetrical proton exchange between 2,4-lutidine and its conjugate acid in aqueous solution proceeds with participation of (on the average) 1.74 water molecules in H_2O and 1.8 water molecules in HOD–D_2O (5 atom % H). Within the experimental error both processes could be precisely quatermolecular; second-order rate constants at 25° are 1.05×10^8 sec^{-1} M^{-1} in H_2O and 0.26×10^8 sec^{-1} M^{-1} in HOD–D_2O. The high values of these rate constants, in spite of the quatermolecular nature of the reaction, indicate strong hydrogen-bonded solvation of at least one of the reactant solutes. The mechanism of acid dissociation of 2,4-lutidinium ion has been reexamined on the basis of kinetic HOD–D_2O solvent isotope effects and salt effects. The initial product of acid dissociation may be a lutidine molecule that is *not* hydrogen bonded to a water molecule at the nitrogen atom.

We wish to report a kinetic study, using nuclear magnetic resonance (nmr), of proton exchange in aqueous solutions of 2,4-lutidine (2,4-dimethylpyridine, B) and 2,4-lutidinium ion (BH+). We find that proton transfer involving BH+, B, and water is largely quatermolecular. For reaction 1 in H_2O at 25°, the (second-order) rate constant k_2 is 1.05×10^8 sec^{-1} M^{-1}, and $n = 1.74$.

$$\underset{H}{\overset{\underset{|}{H}}{BH^+}} + (OH)_n + B \xrightarrow{k_2} B + H-\overset{\underset{|}{H}}{O}\cdot(HO)_{n-1} + HB^+ \quad (1)$$

For reaction 2 in 5% HOD–D_2O (5 atom % H) at 25°, $k_2' = 2.6 \times 10^7$ sec^{-1} M^{-1} and $n = 1.8$.

$$\underset{D}{\overset{\underset{|}{D}}{BH^+}} + (OD)_n + B \xrightarrow{k_2'} B + HO\cdot(DO)_{n-1} + DB^+ \quad (2)$$
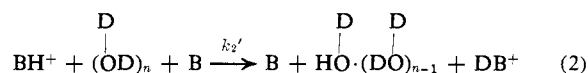
Within the experimental error, n could be precisely

2 in both cases. Our kinetic results in H_2O overlap in part with earlier work,[2] and the agreement is satisfactory.

For fast symmetrical proton-exchange reactions involving an acid, its conjugate base, and water or alcohol, previous *direct measurements* had led to the result that $n > 1$ only for the reaction of imidazolium ion with imidazole in water, where $n = 1.42 \pm 0.19$ at 25°.[3] There is indirect evidence (from reaction diameters and rate equations) that $n > 1$ for the reactions, in water, of H_3O^+ with OH$^-$, SO$_4^{2-}$, and $(CH_3)_3N$ and for the reaction of $H_2PO_4^-$ with HPO$_4^{2-}$.[4-7]

The participation of two or more water molecules in a fast proton-transfer reaction indicates that the hydrogen-bonded solvation of the reactants is strong.

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