Ligand Nuclear Hyperfine Coupling Constants in the Vanadyl(IV)–Aquo Complex. Evidence for Metal–Ligand π Bonding

By JACQUES REUBEN and DANIEL FIAT

Ligand hyperfine coupling constants in the vanadyl(IV)–aquo complex have been determined from nmr chemical shift studies. The values obtained are $(A/h)_{^{17}O} = +(4.4 \pm 1.5) \times 10^6$ Hz and $(A/h)_{2H} = +(4.9 \pm 0.8) \times 10^5$ Hz. From the latter the proton hyperfine coupling is calculated to be $(A/h)_{1H} = +(3.2 \pm 0.5) \times 10^6$ Hz corresponding to a spin density of $(2.3 \pm 0.3) \times 10^{-3}$ on the hydrogen atoms. The results are interpreted in terms of currently accepted schemes of unpaired electron delocalization in transition metal–aquo complexes. It appears that metal–ligand π bonding is the major path of spin delocalization to the four equatorial water molecules in the vanadyl(IV)–aquo complex and that the effective charge of the VO^{2+} ion with respect to the ligands is greater than that of divalent transition metal ions.

Introduction

Considerable effort has been devoted to the elucidation of the structure and properties of vanadyl(IV) complexes in solution.[1] Particularly fruitful appear to be recent nuclear magnetic resonance studies.[2-6] Thus, it has been possible to characterize four tightly bound water molecules, apparently the equatorial ones, in the first coordination sphere of vanadyl(IV) in solution.[2] The exchange between these four molecules and the water in the bulk of the solution seems to be the main relaxation mechanism for the oxygen-17 nuclei of the solvent in the temperature range 25–120°.[2,3] A small downfield shift observed at room temperature is probably due to fast-exchanging water molecules in the axial position and in a second hydration shell.[2] Above 120° an apparent contribution of the transverse relaxation time, T_{2M}, of oxygen-17 in the hydration shell has been observed by Wüthrich and Connick.[3] This relaxation arises from the scalar hyperfine coupling between the ^{17}O nuclei and the unpaired electron of the central vanadyl(IV) ion and is given by[3,7]

$$1/T_{2M} = (1/3)S(S+1)(A/h)^2 \tau_e \qquad (1)$$

where S is the resultant electronic spin angular momentum (in $\hbar$ units), A/h is the hyperfine coupling constant (in frequency units, Hz), and τ_e is the correlation time for the interaction, which in this case may be identified with the electron relaxation time. Thus, from the value of T_{2M}, obtained from the experimental results, and using 1.0×10^{-8} sec for the electron relaxation time, Wüthrich and Connick have calculated an absolute value of 3.8×10^6 Hz for the ^{17}O hyperfine coupling constant of the four water molecules.[3] These

authors[3] have also estimated the proton hyperfine coupling constant, $|A/\hbar| = 1.6 \times 10^6$ Hz, from a reinterpretation of the proton relaxation data of Hausser and Laukien.[8]

Both the sign and magnitude of the hyperfine coupling constants are of importance for elucidation of the mechanism of spin delocalization. These are usually obtained from nmr chemical shift studies.[9] The frequency shift of a nucleus in a paramagnetic complex is given by[10]

$$\Delta \nu_M / \nu_0 = -A(\gamma_e/\gamma_N)[S(S+1)/3kT] \qquad (2)$$

where ν_0 is the Larmor frequency, γ_e and γ_N are the electronic and nuclear magnetogyric ratios, respectively, k is the Boltzmann constant, and T the absolute temperature. We note that the frequency shift is related to the field shift by $-\Delta \nu_M / \nu_0 = \Delta H/H_0$ and that γ_e is negative. Therefore a shift to higher field, observed in the respective spectrum, indicates positive $A_{^{17}O}$ since $\gamma_{^{17}O}$ is negative, but negative A_{1H} and A_{2H} since both γ_{1H} and γ_{2H} are positive. The hyperfine coupling constant is related to the amplitude of the wave function at the nucleus by

$$A/h = -(4/3)\gamma_e \gamma_N \hbar |\psi(0)|^2 \qquad (3)$$

It has been shown that the main path of spin transfer to the hydrogen atoms in transition metal–aquo complexes is *via* the π bonds between the suitable water molecular orbitals and unpaired d electrons of b_2 symmetry.[11] In the energy level scheme of Ballhausen and Gray the unpaired electron of VO^{2+} is placed in a purely nonbonding b_2 orbital.[12] Vanadium–ligand π bonding involving this b_2 orbital has been considered by Selbin, Holmes, and McGlynn in their discussion of the ligation effects on the V=O stretching frequency.[13]

(1) The reader is referred to the review articles: (a) J. Selbin, *Chem. Rev.*, **65**, 153 (1965); (b) J. Selbin, *Coord. Chem. Rev.*, **1**, 293 (1966).

(2) J. Reuben and D. Fiat, *Inorg. Chem.*, **6**, 579 (1967).

(3) K. Wüthrich and R. E. Connick, *ibid.*, **6**, 583 (1967); **7**, 1377 (1968).

(4) R. K. Mazitov and A. I. Rivkind, *Dokl. Akad. Nauk SSSR*, **166**, 654 (1966).

(5) T. J. Swift, T. A. Stephenson, and G. R. Stein, *J. Am. Chem. Soc.*, **89**, 1611 (1967).

(6) R. B. Jordan and N. S. Angerman, *J. Chem. Phys.*, **48**, 3983 (1968).

(7) I. Solomon, *Phys. Rev.*, **99**, 559 (1955); I. Solomon and N. Bloembergen, *J. Chem. Phys.*, **25**, 261 (1956); N. Bloembergen, *ibid.*, **27**, 572 (1957).

(8) R. Hausser and G. Laukien, *Z. Physik*, **153**, 394 (1959).

(9) The magnitude of the hyperfine coupling may in principle be obtained from the esr spectrum provided that it exceeds the line width. However for metal–ligand interactions this is rarely the case.

(10) N. Bloembergen, *J. Chem. Phys.*, **27**, 595 (1957).

(11) (a) Z. Luz and R. G. Shulman, *ibid.*, **43**, 3750 (1965); (b) B. B. Wayland and W. L. Rice, *Inorg. Chem.*, **5**, 54 (1966).

(12) C. J. Ballhausen and H. B. Gray, *ibid.*, **1**, 111 (1962).

(13) J. Selbin, L. H. Holmes, Jr., and S. P. McGlynn, *J. Inorg. Nucl. Chem.*, **25**, 1359 (1963).

We present here the results of an attempt to obtain the electron–nuclear hyperfine coupling constants of the nuclei of the equatorial ligands in the vanadyl(IV)–aquo complex from chemical shift measurements. Preliminary calculations using the A_{HO} value of Wüthrich and Connick[3] have shown that measurable shifts could become evident at temperatures above 100°. Published data[4,5,8] and our own results[14] on proton and deuteron relaxation have shown that conditions of relatively slow hydrogen exchange exist in neutral VO^{2+} solutions at ambient temperature. The exchange reaction is, however, acid catalyzed.[5,14] We have used deuteron resonance to determine the chemical shift in an acidified $VOSO_4$ solution at elevated temperature. Deuteron resonance as compared to pmr offers improvement of spectral resolution and permits conditions of fast exchange to be reached at relatively lower temperatures.[14]

Experimental Section

The nmr measurements were performed using a Varian DP-60 spectrometer operating at a fixed frequency of 8.13 MHz and equipped with the Model V-4340 variable-temperature probe accessories. The static magnetic field was adjusted to correspond to the resonance conditions for oxygen-17 or for deuterium, respectively.

Oxygen-17 shifts were measured in the following manner. The sample containing the $VOSO_4$ solution was brought to the desired temperature and its ^{17}O resonance was recorded. Then, with the magnetic field still sweeping in the appropriate direction, it was dismounted from the probe and replaced by a sample of pure water. The magnetic field was swept until the absorption of a suitably chosen audiofrequency side band was recorded. Thus a spectrum of two signals was obtained, the distance between them corresponding to the chemical shift plus the audiofrequency. The latter was monitored by an electronic counter. During the manipulations the probe temperature reached that of the room (24 ± 1°). In calculating the isotropic shift, the temperature dependence of the chemical shift of pure water was taken into account using the data of Florin and Alei.[15] Deuteron chemical shifts were referred to the resonance of $(CD_3)_2SO$, a small amount of which was added to the sample. Other experimental details are similar to those reported previously.[2]

Results

Oxygen-17 isotropic shifts in an acidified 0.975 *m* solution of $VOSO_4$ were measured in the temperature interval 110–150°. The results are plotted against the inverse absolute temperature in Figure 1. The shifts are toward higher field and increase in magnitude with increasing temperature. Under conditions of fast chemical exchange and complete averaging of the nmr absorptions of the coordinated and noncoordinated water molecules, the shift is expected to obey the Curie law predicted by eq 2. The results, however, show that even at 150° the exchange is relatively slow, as expected,[23] and the rate constant has to be taken into account in evaluating the chemical shift of a nucleus in the first coordination sphere. The apparent isotropic shift, δ, is given by the following formula of Swift and Connick[16]

(14) J. Reuben and D. Fiat, *J. Am. Chem. Soc.*, **91**, 4652 (1969).
(15) A. E. Florin and M. Alei, Jr., *J. Chem. Phys.*, **47**, 4268 (1967).
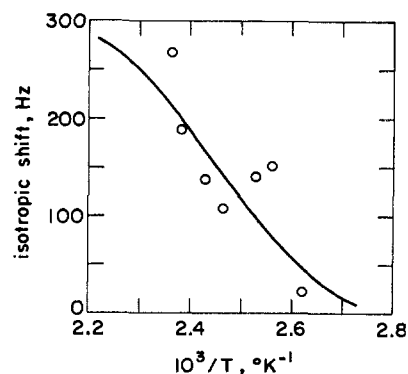(16) T. J. Swift and R. E. Connick, *ibid.*, **37**, 307 (1962).

Figure 1.—The water oxygen-17 isotropic shift at 8.13 MHz *vs.* $1/T$ in a 0.975 *m* solution of $VOSO_4$. The fit to eq 4 is represented by the curve.

$$\delta = \frac{\Delta\nu_{\mathrm{M}} n m_{\mathrm{M}}}{m_{\mathrm{L}} \tau_{\mathrm{M}}^2 [(1/T_{2\mathrm{M}}) + (1/\tau_{\mathrm{M}})^2 + (2\pi\Delta\nu_{\mathrm{M}})^2]} \quad (4)$$

where n is the coordination number, m_{M} is the number of millimoles of metal ions, m_{L} is the total number of millimoles of ligand (water) molecules, and τ_{M} is the mean residence time of a nucleus in the coordinate sphere. The mean residence time, τ_{M}, and its temperature dependence are known from the previously reported ^{17}O relaxation studies.[2] The transverse relaxation time, $T_{2\mathrm{M}}$, is obtained from line-width measurements. The experimental $P_{\mathrm{M}} T_{2\mathrm{p}}$ values, where $P_{\mathrm{M}} = n m_{\mathrm{M}}/m_{\mathrm{L}}$ and $1/\pi T_{2\mathrm{p}}$ is the line broadening, are plotted *vs.* $1/T$ in Figure 2. Anticipating the result that $1/T_{2\mathrm{M}} > |2\pi\Delta\nu_{\mathrm{M}}|$, one can show that[14,16]

$$P_{\mathrm{M}} T_{2\mathrm{p}} = T_{2\mathrm{M}} + \tau_{\mathrm{M}} \quad (5)$$

From the experimental results and extrapolated values of τ_{M}, the transverse relaxation time $T_{2\mathrm{M}} = (5.6 \pm 0.2) \times 10^{-6}$ sec was obtained. This value should be regarded as an average over the temperature interval studied owing to the temperature dependence of the correlation time governing the transverse relaxation time as shown in another publication.[14] However the variation is relatively small and moreover the contribution of $1/T_{2\mathrm{M}}$ to $\Delta\nu_{\mathrm{M}}$ calculated from eq 4 is sufficiently small relative to the other contributions and to the experimental uncertainties to justify the calculation of the chemical shift, $\Delta\nu_{\mathrm{M}}$, using the average value. The fit of the theoretical values calculated by means of eq 4 to the experimental values is represented in Figure 1 by the solid line. The hyperfine coupling constant calculated from eq 2 is $(A/h)_{\mathrm{HO}} = +(4.4 \pm 1.5) \times 10^6$ Hz. This value is in good agreement with the absolute value obtained by Wüthrich and Connick.[3] The large uncertainty in magnitude is due to the relatively small shifts and large line broadening in this temperature range.

The electron relaxation time was calculated using eq 1 and found to be $(0.9 \pm 0.4) \times 10^{-9}$ sec. Electron relaxation times in dilute solutions of VO^{2+} are much longer. Our finding conforms with the observation that electron relaxation is enhanced in concentrated
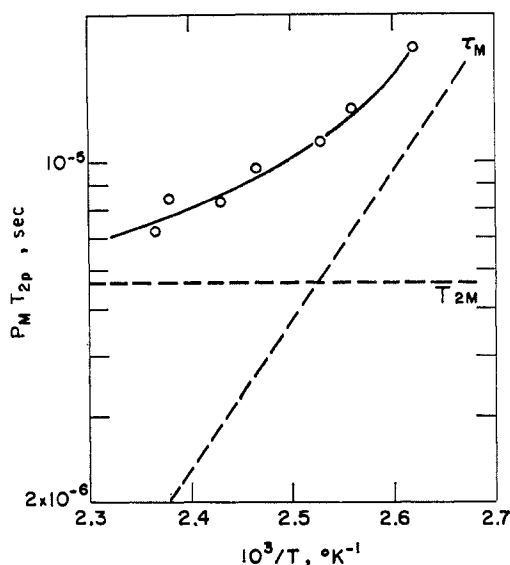
Figure 2.—The normalized oxygen-17 transverse relaxation time *vs.* $1/T$ in a 0.975 *m* solution of $VOSO_4$. The solid curve represents the fit to eq 5.

(>0.1 *m*) solutions,[17] probably owing to electron spin-exchange interactions.

The deuteron chemical shift was measured in an acidified (0.61 *m* $HClO_4$) 0.48 *m* solution of $VOSO_4$ in D_2O. A small quantity (about 1 mol %) of $(CD_3)_2SO$ was added as an internal standard. It may be assumed that the small amounts of $(CD_3)_2SO$ are not subject to chemical shift owing to the presence of the paramagnetic ions. This would require a very large equilibrium constant for the formation of $(CD_3)_2SO–VO^{2+}$ complex relative to that of the aquo complex and a very short mean residence time, which in view of the results for water exchange seems inconceivable. The chemical shift at $92.3 \pm 0.5°$ is 28.5 ± 2.5 Hz downfield from $(CD_3)_2SO$ and represents an average of 11 spectra. The chemical shift of pure water at the same temperature is 12.6 ± 0.5 Hz downfield from the same reference and has been obtained by linear interpolation from chemical shifts measured in the temperature range 25–100°. The isotropic shift is therefore -16 ± 3 Hz. The hyperfine coupling constant is $(A/h)_{2H} = +(4.9 \pm 0.8) \times 10^5$ Hz and has been obtained by a procedure similar to that used for ^{17}O. In this case, however, the effects of τ_M and T_{2M} are smaller. (The results of the proton and deuteron relaxation studies will be published shortly.)

Multiplying the deuteron hyperfine coupling constant by γ_{1H}/γ_{2H} (see eq 3) one obtains $(A/h)_{1H} = +(3.2 \pm 0.5) \times 10^6$ Hz, where isotope effects on $|\psi(0)|^2$ are neglected.

Discussion

Fermi-contact interaction between an unpaired electron and a nucleus takes place only if there is a finite probability of finding an electron spin on an atomic s orbital. Other orbitals have a node at the nucleus.

By a direct mechanism, a fraction of an electronic (parallel) spin is delocalized to an s orbital, and as a result a positive hyperfine coupling constant is observed (or negative for ^{17}O since γ_{17O} is negative). On the other hand, a fraction of an unpaired electron in p orbitals effectively polarizes the electrons in the s orbital leaving behind a negative (antiparallel) spin. This spin-polarization mechanism is expected to be less effective. It leads to a negative proton (or positive oxygen-17) hyperfine coupling.

The pertinent molecular orbitals of water are schematically represented in Table I. They are listed in the order of increasing energy.

TABLE I
SCHEMATIC REPRESENTATION OF WATER MOLECULAR ORBITALS

Orbital[a]	Sym-metry	Orbital[a]	Sym-metry
$2s + (h_1 + h_2)$	a_1, σ	$2p_z + (h_1 + h_2)$	a_1, σ
$2p_y + (h_1 - h_2)$	b_2, π	$2p_x$	b_1, π

[a] 2s and 2p are oxygen atomic orbitals; h_1 and h_2 are hydrogen 1s orbitals.

The oxygen-17 hyperfine coupling constant of water in most of the transition metal–aquo complexes hitherto studied is negative, corresponding to a positive spin density and leading to downfield shifts.[16] This finding suggests that σ bonding is important in these complexes. The greatest ^{17}O hyperfine coupling constants are observed in the aquo complexes of nickel(II)[18] and copper-(II)[19] (see Table II) in which the unpaired electrons are

TABLE II
OXYGEN-17 HYPERFINE COUPLING CONSTANTS IN
SOME TRANSITION METAL–AQUO COMPLEXES

Ion	$(A/h)_{17O}$, Hz	Ref
Ni^{2+}	-3.0×10^7	18
Cu^{2+}	-5.0×10^7	19
Ti^{3+}	$+4.4 \times 10^6$	20
VO^{2+}	$+(4.4 \pm 1.5) \times 10^6$	

confined in e_g orbitals suitable for σ bonding. For vanadyl(IV) we find a smaller magnitude and an opposite sign. This result could be anticipated since the only unpaired electron is in a t_{2g} (b_2) orbital. Clearly here the spin-polarization mechanism has the major contribution suggesting that vanadium–oxygen π bonding plays an important role in the ion–ligand binding. An oxygen-17 coupling constant of similar magnitude and sign has previously been obtained in our laboratory for the aquo complex of titanium(III), which also has only one d electron in a b_2-type orbital.[20]

The value of the proton hyperfine coupling constant may be rationalized within the same frame. Here π bonding places directly unpaired spin on the hydrogen orbitals leading to a large coupling constant.

In Table III are listed values of proton hyperfine coupling constants of some transition metal aquo com-

(17) (a) D. C. McCain and R. J. Myers, *J. Phys. Chem.*, **71**, 192 (1967); (b) G. P. Vishnevskaya and P. G. Tishkov, *Dokl. Akad. Nauk SSSR*, **142**, 841 (1962).

(18) R. E. Connick and D. Fiat, *J. Chem. Phys.*, **44**, 4103 (1966).
(19) W. B. Lewis, M. Alei, Jr., and L. O. Morgan, *ibid.*, **44**, 2409 (1966).
(20) A. M. Chmelnick and D. Fiat, *ibid.*, in press.

Table III

Proton Hyperfine Coupling Constants in
Some Transition Metal–Aquo Complexes

Ion	$(A/h)_{1H}$, Hz	Ref
Fe^{2+}	5.0×10^5	11b
Fe^{3+}	1.2×10^5	11a
VO^{2+}	$(3.2 \pm 0.5) \times 10^6$	
V^{3+}	3.2×10^6	21
Ti^{3+}	4.8×10^6	20

plexes.[21] It has been observed[11] that $(A/h)_{1H}$ in complexes of trivalent ions is much greater than that of divalent ions. The result obtained for the vanadyl(IV)–aquo ion and the comparison with values given in

(21) The value of $(A/h)_{1H}$ in the aquo complex of vanadium(III) is taken from F. Röhrscheid, R. E. Ernst, and R. H. Holm, *Inorg. Chem.*, **6**, 1315 (1967). It should be regarded as a lower limit until the temperature effects on either the chemical shifts or the line broadenings are investigated and the assumption of rapid exchange is verified.

Table III suggest that the effective charge of VO^{2+} with respect to the equatorial ligands may be greater than that of divalent transition metal ions.

The ligand hyperfine coupling constants of the equatorial water molecules in the VO^{2+} aquo ion provide convincing evidence that metal–ligand π bonding is the major pathway of spin delocalization in this complex and it has to be taken into account in the interpretation of other physical data and in molecular orbital calculations.[22,23]

(22) While this paper was in its final stages of preparation, a note by Vigee and Selbin intended to provide proton nmr evidence for π bonding in vanadyl-(IV) complexes appeared in the literature.[23] These authors observed small shifts in solutions of $VOSO_4$ at 43°. They, however, interpreted the results using the limit of fast exchange, although it is well established[3–5,8] that at this temperature the rate of hydrogen exchange of the four equatorial molecules is slow. It seems that the shifts observed by Vigee and Selbin[23] result from the small hyperfine couplings of the fast-exchanging axial molecule and molecules beyond the first coordination sphere[2,3] and are irrelevant to the problem of the nature of bonding of the equatorial ligands.

(23) G. Vigee and J. Selbin, *J. Inorg. Nucl. Chem.*, **30**, 2273 (1968).

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Proton Magnetic Resonance Line Broadening of Methanol and Trichloro- and Trifluoroethanol by Vanadyl Complexes

By N. S. Angerman and Robert B. Jordan

The line broadening of the methyl and hydroxy protons of solvent methanol caused by $VO(CH_3OH)_6{}^{2+}$ shows typical chemical exchange control above 0° with the OH protons exchanging faster than the CH_3 protons. The results are interpreted in terms of proton dissociation from the coordinated hydroxy group ($\Delta H^{\ddagger} = 10.9$ kcal mol^{-1}, $\Delta S^{\ddagger} = -5.3$ cal mol^{-1} deg^{-1}) and solvent methanol molecule exchange ($\Delta H^{\ddagger} = 9.46$ kcal mol^{-1}, $\Delta S^{\ddagger} = -14.2$ cal mol^{-1} deg^{-1}). Bis(acetylacetonato)-vanadyl ($VO(acac)_2$) causes chemical exchange control of the hydroxy proton line broadening only in methanol ($\Delta H^{\ddagger} = 11.79$ kcal mol^{-1}, $\Delta S^{\ddagger} = 3.1$ cal mol^{-1} deg^{-1}) and trichloroethanol ($\Delta H^{\ddagger} = 6.41$ kcal mol^{-1}, $\Delta S^{\ddagger} = -11.5$ cal mol^{-1} deg^{-1}). This complex in trifluoroethanol shows no chemical exchange behavior. The hydroxy proton exchange rate is obtained for bis(trifluoroacetylacetonato)vanadyl ($VO(tfac)_2$) in methanol ($\Delta H^{\ddagger} = 11.1$ kcal mol^{-1}, $\Delta S^{\ddagger} = -2.6$ cal mol^{-1} deg^{-1}). The mechanism for proton exchange is discussed. The kinetic results and the interpretation of the dipole–dipole interaction line broadening observed at low temperatures show that the vanadyl complexes are six-coordinate in these alcohol solvents.

Introduction

Increasing interest has been demonstrated recently in the exchange kinetics of ligands bound to the vanadyl ion.[1–4] As part of a general study of nonaqueous solvent exchange on VO^{2+} the nmr line broadening of protons in solvent methanol caused by the solvated vanadyl ion, by bis(acetylacetonato)vanadyl (VO-(acac)$_2$), and by bis(trifluoroacetylacetonato)vanadyl (VO(tfac)$_2$) have been studied. A similar study has been made on VO(acac)$_2$ in trichloro- and trifluoro-ethanol.

Both the rate of methanol molecule exchange and the rate of proton dissociation from coordinated methanol have been measured in the vanadyl ion–methanol system. When VO(tfac)$_2$ is dissolved in methanol,

only the solvent hydroxy proton shows chemical exchange controlled line broadening. Similar behavior is shown by VO(acac)$_2$ in CCl_3CH_2OH, while this complex in CF_3CH_2OH shows no chemical exchange. Analysis of the hydroxy proton exchange rates indicates that a solvent molecule in the coordination position *trans* to the vanadyl oxygen is involved but the detailed path for the exchange remains in question.

Experimental Section

Hydrated vanadyl perchlorate was prepared by mixing stoichiometric amounts of vanadyl sulfate (Fisher reagent) and barium perchlorate in aqueous solution. The barium perchlorate was prepared in solution by adding a slight excess of perchloric acid to a weighed amount of barium carbonate. The barium sulfate was removed by filtration and the solvent was distilled from the filtrate at 60–70° under reduced pressure. The aquated vanadyl perchlorate was treated with excess reagent grade methanol, which had been vacuum distilled twice from Linde Molecular Sieves, and with 2 molar equiv of dimethoxypropane. The solution was stirred for 2 hr at room temperature and then

(1) J. Reuben and D. Fiat, *Inorg. Chem.*, **6**, 579 (1967).

(2) K. Wüthrich and R. E. Connick, *ibid.*, **6**, 583 (1967).

(3) T. J. Swift, T. A. Stephenson, and G. R. Stein, *J. Am. Chem. Soc.*, **89**, 1611 (1967).

(4) F. A. Walker, R. L. Carlin, and P. H. Reiger, *J. Chem. Phys.*, **45**, 4181 (1966).