

Vanadium Nuclear Spin-Lattice Relaxation in π -Tropyliumvanadium(-I) Tricarbonyl¹

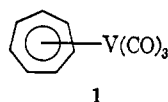
George M. Whitesides and H. Lee Mitchell²

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. Received October 7, 1968

Abstract: The ¹H nmr spectrum of π -tropyliumvanadium(-I) tricarbonyl (**1**) at 30° in nonviscous solutions is a broad doublet; in viscous solutions the spectrum is a relatively sharp singlet. The temperature dependence of this spectrum in toluene-*d*₆ and its viscosity dependence in mixtures of cyclooctane and Nujol establish that the observed spectral line shapes in nonviscous media are due to ⁵¹V-¹H spin-spin coupling. Combination of the value for the vanadium spin-lattice relaxation time inferred from the ¹H line shape of **1** in cyclooctane solution at 30° with an estimate of its rotational correlation time under these circumstances leads to an approximate value for the vanadium quadrupole coupling constant in **1** of $(e^2qQ/h) \cong 2.0 \pm 0.5$ MHz.

Nmr investigations of the dynamics of metal atom migration between carbon atoms in fluxional π - and σ -C_nH_n metal complexes have led to the discovery of a variety of new types of structurally significant molecular rearrangements.³ The spectral data on which these studies are based, although widely variegated, have normally shared one feature in common: *viz.*, the relatively complex "slow-exchange" spectra observed at low temperatures become simpler at higher temperatures, as the magnetic nonequivalences characterizing the static slow-exchange structures are averaged.

The temperature dependence of the nmr spectrum of π -tropyliumvanadium(-I) tricarbonyl⁴ (**1**) described by Fritz and Kreiter appeared to provide a notable exception to this general pattern of behavior:⁵ the single sharp peak observed for **1** at -50° in toluene



becomes progressively *more* complex at higher temperatures, ultimately becoming what appears to be a broadened doublet at room temperature and above. Since a single-crystal X-ray study of this complex had previously located the vanadium atom on the C₇ axis of the planar C₇H₇ ring,⁶ Fritz and Kreiter advanced the intriguing proposal to account for the nmr data that the symmetrical structure established by the X-ray work existed in temperature-dependent equilibrium in solution with one or more species in which the C₇ ring symmetry was not preserved. In this paper we wish to report evidence which establishes that the ¹H nmr line shape observed for **1** at ambient temperature is in fact due to ⁵¹V-¹H spin-spin coupling, and that the temperature dependence of the ¹H line shape reflects variations in the rate of ⁵¹V spin-lattice relaxation. The well-defined and rigid geometry of **1** permits a com-

parison between theoretical predictions concerning the influence of macroscopic solution viscosity on the rate of nuclear quadrupolar relaxation, and the experimental measurements of this rate as reflected in the ¹H spectrum, over more than two orders of magnitude in viscosity.

Results and Discussion

The ¹H nmr spectrum of **1** in toluene-*d*₆ solution at 30° is a broad doublet centered at 4.22 ppm from TMS having a peak width at half-height for the entire signal of 20.5 Hz; cooling the sample to -79° results in gradual collapse of this signal to a single line with half-width 4.7 Hz (Figure 1); the agreement between these observations and those reported earlier is good.⁵ Qualitatively similar changes are observed on varying the temperature of a cyclooctane solution of **1**; in this solvent the line width is 20.6 Hz at 30° and 8.0 Hz at -19°. The nmr spectrum of **1** in *n*-pentane solution at 30° is very similar to that observed in toluene and cyclooctane at the same temperature, again appearing as a broadened doublet with half-width 22.0 Hz (Figure 1). However, in contrast to the behavior observed in toluene and cyclooctane, cooling the pentane sample to -50° results in no significant change in the signal shape or line width. The line shape of **1** in several solvents does not change on decreasing the external magnetic field strength from 23 to 14 kG.

The magnetic field invariance of the spectrum of **1** indicates that all protons on the C₇H₇ ring have the same chemical shift, and strongly suggests that the observed structure in the room-temperature spectra of toluene and pentane solutions of this compound is not due to contributions to the spectra from isomers of **1** having an unsymmetrical C₇H₇ ring. The contrasting temperature dependence of the spectra from pentane, toluene, and cyclooctane solutions similarly indicates that the spectral changes observed on varying the temperature of, *e.g.*, the toluene solution are not due simply to an intramolecular conformational or structural change in **1**, but depend in a sensitive manner on the nature of the solvent. Taken together, these observations are incompatible with an explanation for the line shape observed in the ambient temperature spectra of **1** which presupposes a temperature-dependent equilibrium between magnetically nonequivalent isomers of **1**.

(1) Supported by the U. S. Army Research Office (Durham), Grants ARO(D) 31-124-435 and ARO(D)-31-124-G691. Computations were carried out in part at the MIT Computation Center, Cambridge, Mass.

(2) National Institutes of Health Predoctoral Fellow, 1966-1969.

(3) For examples, see F. A. Cotton, *Accounts Chem. Res.*, **1**, 257 (1968); G. M. Whitesides and J. Fleming, *J. Amer. Chem. Soc.*, **89**, 2855 (1967); F. A. L. Anet, H. D. Kaesz, A. Maasbol, and S. Winstein, *ibid.*, **89**, 2489 (1967); A. Davison and P. E. Rakita, *ibid.*, **90**, 4479 (1968).

(4) R. P. M. Werner and S. A. Manastyrsky, *ibid.*, **83**, 2023 (1961).

(5) H. P. Fritz and C. G. Kreiter, *Chem. Ber.*, **97**, 1398 (1964).

(6) G. Allegra and G. Perego, *Ric. Sci., A*, [2] **1**, 362 (1961).

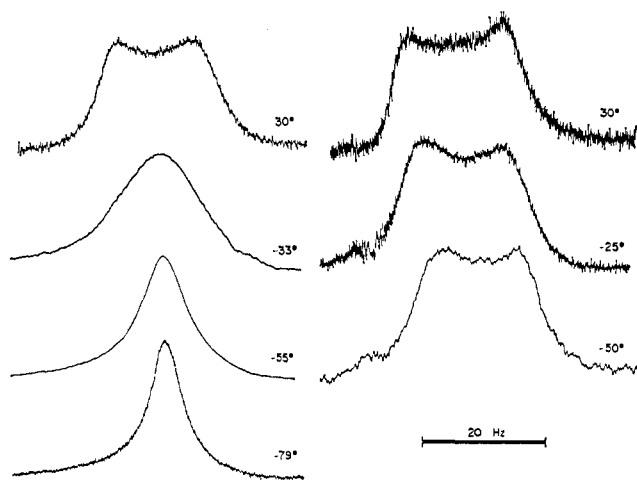


Figure 1. ^1H nmr spectra of π -tropliumvanadium tricarbonyl at 60 MHz in toluene- d_6 (left) and pentane (right) solutions as a function of temperature. Spectral measurement in pentane below -50° is prevented by crystallization of **1** from solution.

More than 99% of naturally occurring vanadium consists of the isotope ^{51}V , having $S = 7/2$ and electric quadrupole moment $Q \sim -0.3 \times 10^{-24} \text{ cm}^2$.⁷ Spin-spin coupling between protons and a nucleus with a quadrupole moment of this magnitude is normally not observed in solution, because rapid spin-lattice relaxation of the quadrupolar nucleus averages the coupling to zero. Nonetheless, since the variation in line shape of the proton spectrum of **1** with temperature is clearly *not* the result of a temperature-dependent equilibration between chemically distinct species, and since the structure observed in the ambient-temperature spectra of **1** is reminiscent of the spectra of other molecules characterized by coupling of fluorine to a nucleus of high spin,⁸ we thought it worthwhile to explore the possibility that this structure was in fact due to incompletely resolved vanadium-proton coupling.

The mechanism of spin-lattice relaxation of a quadrupolar nucleus is a well-understood and thoroughly documented phenomenon.^{9,10} In brief, the rotational and translational diffusion in solution of the molecule containing the quadrupolar nucleus, and of other molecules, gives rise to a fluctuating electric field gradient at that nucleus. The component of the Fourier spectrum of these fluctuations, $J(\omega)$, whose frequency coincides with the frequency ω_0 of a magnetic dipole transition of the quadrupolar nucleus, provides a spin-relaxation mechanism for this nucleus whose effectiveness depends both on the absolute magnitude of $J(\omega_0)$ and on the strength of the coupling between the nucleus and the fluctuating field. For neutral mole-

(7) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. I, Pergamon Press, Ltd., Oxford, 1965, p 590.

(8) K. J. Packer and E. L. Muettterties, *J. Amer. Chem. Soc.*, **85**, 3035 (1963); D. W. Aksnes, S. M. Hutchinson, and K. J. Packer, *Mol. Phys.*, **14**, 301 (1968); N. Bartlett, S. Beaton, L. W. Reeves, and E. J. Wells, *Can. J. Chem.*, **42**, 2531 (1964); R. J. Gillespie and J. W. Quail, *ibid.*, **42**, 2673 (1964); E. L. Muettterties and K. J. Packer, *J. Amer. Chem. Soc.*, **86**, 293 (1964); E. L. Muettterties and W. D. Phillips, *ibid.*, **81**, 1084 (1959).

(9) A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press, London, 1961, Chapters VII and VIII; C. P. Slichter, "Principles of Magnetic Resonance," Harper and Row, New York, N. Y., 1963, Chapters 5 and 6.

(10) H. G. Hertz, *Progr. Nmr Spectrosc.*, **3**, 159 (1967); R. A. Dwek and R. E. Richards, *Discussions Faraday Soc.*, **43**, 196 (1967).

cules, and particularly for those having less than cubic symmetry around the quadrupolar nucleus, the dominant motion contributing to nuclear quadrupole relaxation is the tumbling of the molecule containing this nucleus, rather than rotation or translation of neighboring solvent molecules.^{7,11,12} Further, if the rate of tumbling is characterized by a rotational correlation time τ_c , $J(\omega_0) \propto \tau_c$, provided that $\omega_0^2 \tau_c^2 \ll 1$.⁹ Thus, the rate of spin-lattice relaxation due to interaction of the vanadium nuclear quadrupole moment with fluctuating electric field gradients in solution of **1** is determined primarily by two factors: the strength of the coupling between the vanadium quadrupole moment and these fluctuations, measured by the magnitude of the nuclear quadrupole coupling constant (e^2qQ/h), and the amplitude of the component of the rotational motion having the frequency ω_0 , which in turn is determined by the rotational correlation time τ_c .

The structure of compound **1** is such that the electric field gradient at the metal atom might be expected to be weak; in consequence, despite a relatively large value of Q , the quadrupole coupling constant for **1** might be sufficiently small to permit observable ^1H - ^{51}V spin-spin coupling. In order to test the hypothesis that the structure observed in the ambient temperature spectra of **1** is due to vanadium-proton coupling, we have examined the dependence of the proton line shape on viscosity in hydrocarbon solutions. A significant contribution to this line shape from partially relaxed vanadium-proton coupling is expected to result in a characteristic inverse relationship between line width and viscosity;⁹ if the line shape is determined by the rate of a unimolecular chemical reaction, the line width should show little or no dependence on viscosity beyond that due to viscous broadening.

Following established precedures,^{13,14} the ^1H line shape of **1** was first calculated as a function of the rate of ^{51}V spin-lattice relaxation by a method which in effect treats the problem as one of exchange between eight equally populated sites corresponding to the $(2S + 1)m_S$ substates of a nucleus of $S = 7/2$, each having an "effective chemical shift" due to coupling with the vanadium of $m_S J_{V,H}$, relative to a frequency zero corresponding to the chemical shift of the protons in the absence of coupling. Under the influence of the fluctuating electric field gradient which results from the tumbling of **1**, the vanadium nuclei can undergo transitions from states of spin angular momentum m to those of $m \pm 1$ or $m \pm 2$. Making the assumptions that $\omega_0^2 \tau_c^2 \ll 1$ (extreme narrowing) and that the asymmetry parameter η is zero (axial symmetry of the electric field gradient tensor at the vanadium nucleus), the rates at which these transitions take place are related to the quadrupole coupling constant and to τ_c by eq 1-3;^{13,14} in these equations, T_{1V} is the spin-lattice relaxation time of the vanadium nucleus and is assumed to be determined entirely by the quadrupolar relaxation mechanism. The validity of the first of

(11) C. Deverell, D. J. Frost, and R. E. Richards, *Mol. Phys.*, **9**, 564 (1965); M. St. J. Arnold and K. J. Packer, *ibid.*, **10**, 141 (1966); W. B. Moniz and H. S. Gutowsky, *J. Chem. Phys.*, **38**, 1155 (1963).

(12) T. D. Alger and H. S. Gutowsky, *ibid.*, **48**, 4625 (1968).

(13) J. A. Pople, *Mol. Phys.*, **1**, 168 (1958); M. Suzuki and R. Kubo, *ibid.*, **7**, 201 (1964).

(14) H. S. Gutowsky, R. L. Vold, and E. J. Wells, *J. Chem. Phys.*, **43**, 4107 (1965).

these assumptions is established experimentally by the observation that the proton line shape, and by inference T_{1V} , is independent of the magnetic field strength.⁹ There is no simple way of checking the second assumption; however, on the basis of the structure of **1** in the solid state⁶ it is clearly physically reasonable.

$$\frac{1}{T_{1V}} = \left(\frac{3}{40}\right) \left(\frac{2S+3}{S^2(2S-1)}\right) \left(\frac{e^2qQ}{\hbar}\right)^2 \tau_c \quad (1)$$

$$k_{m,m\pm 1} = k_{m\pm 1,m} = \frac{(2m \pm 1)^2(S \pm m + 1)(S \mp m)}{2T_{1V}(2S-1)(2S+3)} \quad (2)$$

$$k_{m,m\pm 2} = k_{m\pm 2,m} = \frac{(S \mp m)(S \mp m - 1)(S \pm m + 1)(S \pm m + 2)}{2T_{1V}(2S-1)(2S+3)} \quad (3)$$

$$k_{m,m} = \sum_{m \neq m'} k_{m,m'} \quad (4)$$

With these equations, the calculation of the amplitude of the proton signal at frequency ω for any value of T_{1V} is reduced to the solution of eq 5,¹⁵ in which **R** is a

$$I(\omega) \propto \text{Re}[\mathbf{1} \cdot [i\omega + \mathbf{R} + \mathbf{K}]^{-1} \cdot \mathbf{1}] \quad (5)$$

diagonal matrix whose elements determine the line widths for the proton resonances in the absence of contributions from relaxation of the vanadium atom, ω is a diagonal matrix whose elements are the values $(m_S J_{V,H}) - \omega$ ordered in terms of increasing m_S , and **K**, the matrix describing the rates of transfer of magnetization between sites corresponding to different values of m_S due to vanadium spin-lattice relaxation, is calculated from eq 2-4.¹⁶

Using eq 5 and 6, spectra were calculated for a range of values of T_{1V} (Figure 2).¹⁷ In order to present the complete range of spectral behavior compactly, these spectra are represented in this figure by a surface rather than separately: a section through the surface perpendicular to the T_{1V} axis yields the ordinary spectral representation. The truncated appearance of the single peak calculated for values of T_{1V} less than ~ 0.004 sec

$$\mathbf{K} = (1/10T_{1V}) \begin{bmatrix} -28 & 21 & 7 & 0 & 0 & 0 & 0 & 0 \\ 21 & -52 & 16 & 15 & 0 & 0 & 0 & 0 \\ 7 & 16 & -48 & 5 & 20 & 0 & 0 & 0 \\ 0 & 15 & 5 & -40 & 0 & 20 & 0 & 0 \\ 0 & 0 & 20 & 0 & -40 & 5 & 15 & 0 \\ 0 & 0 & 0 & 20 & 5 & -48 & 16 & 7 \\ 0 & 0 & 0 & 0 & 15 & 16 & -52 & 21 \\ 0 & 0 & 0 & 0 & 0 & 7 & 21 & -28 \end{bmatrix} \quad (6)$$

($\log T_{1V} < -2.45$) is an artifact of the plotting routine used. The value of the elements of the matrix **R** used in these calculations was adjusted to correspond to a value of $T_2 = 0.455$ sec. This value was obtained from the ambient temperature line width of benzene used as an internal resolution standard in solutions of **1** in cyclooctane and carries with it the assumption that T_2 for benzene and T_2 for **1** were equal in the absence of line broadening due to vanadium relaxation. Although

(15) C. S. Johnson, Jr., *Advan. Magnetic Resonance*, **1**, 33 (1965).

(16) Analogous matrices for values of S less than $7/2$ are given in ref 14.

(17) Calculations were carried out using the program NMRCTL written by J. B. Lisle (cf. B.S. Thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1968). The surface graphics were produced using the routine PLOT3D.¹⁸

(18) D. L. Nelson, University of Maryland, Department of Physics and Astronomy, Technical Report 553, March 1966.

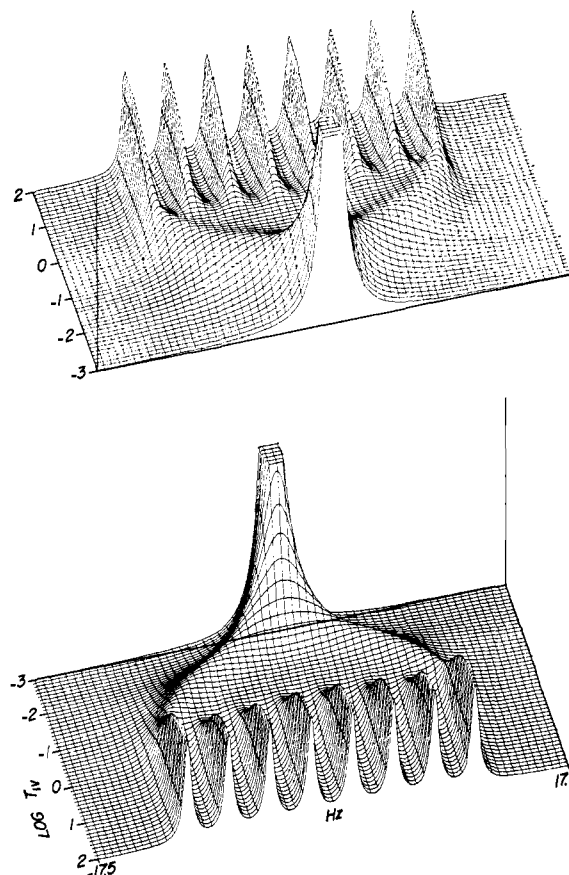


Figure 2. Surface representation of the calculated ^1H nmr line shapes for **1** as a function of T_{1V} . Two perspectives of the surface are given for clarity. A section through this surface perpendicular to the T_{1V} axis gives the spectrum at that value of T_{1V} . See the accompanying text for a description of the parameters used in calculating these spectra.

this assumption is reasonable on physical grounds, we were never successful in explicitly demonstrating its validity by finding conditions under which line widths

for benzene and **1** were equal;¹⁹ at best, using a sample of a mixture of **1** and benzene in Nujol cooled to 12° to increase the viscosity, we observed a line width of 2.3 Hz for the benzene resonance and of 4.5 Hz for the single line of **1**. However, it was clear that vanadium relaxation was still contributing to the difference in these line widths, and we believe that the correct value for T_2 for the protons of **1** in the absence of quadrupole

(19) An attempt to spin decouple the vanadium from the protons by double irradiation was unsuccessful. Over the range of decoupling frequencies examined, 15.50-16.08 MHz (^1H frequency 60 MHz), no decoupling was observed, although the ^{51}V resonance frequency would have been expected to fall near the center of this range (cf. O. W. Howarth and R. E. Richards, *J. Chem. Soc.*, 864 (1965); S. D. Gornostansky and C. V. Stager, *J. Chem. Phys.*, **46**, 4959 (1967)). However, the output power of the decoupler (an NMR Specialties HD-60A) varied so erratically with frequency that the absence of decoupling is not informative.

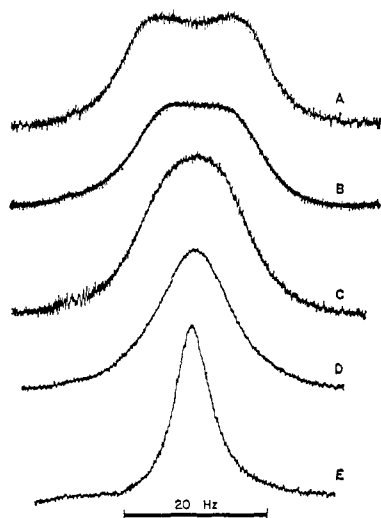


Figure 3. ^1H nmr spectra of **1** at 60 MHz and 30° in cyclooctane-Nujol solvents. Compositions (wt % Nujol) and viscosities (cP) of these solvents are: (A) 0, 2.05; (B) 10, 2.51; (C) 50, 11.1; (D) 68, 23.1; (E) 100, 165.

broadening is unlikely to differ from the estimated 0.455 sec by more than ~ 0.2 sec. The vanadium-proton coupling constant $J_{V,H}$ used in the matrix ω of eq 5 was set equal to 3.04 Hz, since this value, combined with the values of T_2 estimated as described above, resulted in calculated spectra whose width and shape fitted closely those observed at ambient temperature in the cyclooctane solution. This estimate is probably correct to within $\sim \pm 0.2$ Hz.

Comparison of the spectra calculated (Figure 2) with the spectra observed for compound **1** at 30° in cyclooctane-Nujol mixtures of different viscosity (Figure 3) permits a determination of the dependence of T_{1V} on η . By using only mixtures of saturated hydrocarbons to vary the viscosity, our intent was to minimize solvent-solute interactions. It is clear from Figure 3 that increasing the solution viscosity decreases the line width of the C_7H_7 resonance of **1**, and in consequence that an increase in η is accompanied by a decrease in T_{1V} . This result is of course qualitatively that expected if the ambient-temperature line shape of **1** is a reflection of quadrupole-broadened vanadium-proton coupling, since an increase in the viscosity of the solvent results in slower tumbling of **1**, larger values of τ_c , and smaller values of T_{1V} (eq 1).

The detailed form expected for this dependence of T_{1V} on viscosity is at present a subject of some controversy. Although the relationship $1/T_1 \propto \tau_c \propto \eta/T$ based on the Stokes hydrodynamic equation²⁰ has been observed to be followed experimentally in studies carried out over narrow ranges of viscosity, it is clear that the *absolute* values of the correlation times calculated from the Stokes equation are approximately one order of magnitude larger than those observed experimentally.^{10-12, 21, 22} A modification of the Stokes equation proposed by Gierer and Wirtz (eq 7) seems to provide the most satisfactory equation presently available for relating experimental values for rotational

(20) N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.*, **73**, 679 (1948).

(21) D. E. Woessner, *J. Chem. Phys.*, **40**, 2341 (1964).

(22) D. Herbison-Evans and R. E. Richards, *Mol. Phys.*, **7**, 515 (1964).

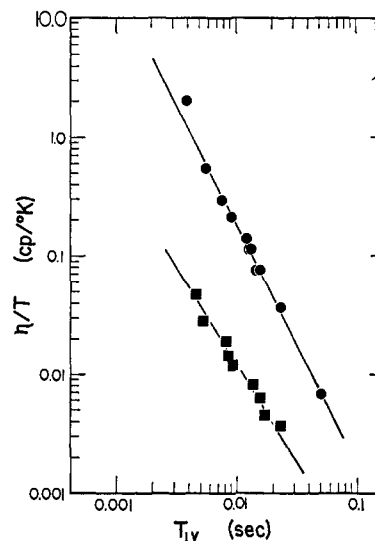


Figure 4. Plot of η/T vs. T_{1V} for **1**. Data in toluene- d_8 (■) were obtained over the temperature range -30 to -79° ; data in cyclooctane-Nujol mixtures (●) were obtained at 30° , with the exception of the point at $\eta/T = 2.02$ which was obtained at 12° .

correlation times to molecular size, macroscopic solution viscosity, and temperature.^{22, 23} Here r_{solute} and r_{solvent} are hard-sphere radii for solute and solvent

$$\tau_c = \frac{r_{\text{solute}} \tau_S}{6r_{\text{solvent}}} = \frac{(r_{\text{solute}})(V_{\text{solute}})\eta}{6kT(r_{\text{solvent}})} \quad (7)$$

molecules (cm), τ_S is the Stokes correlation time (sec), V_{solute} is the hard-sphere "volume" of the solute, and η is the macroscopic solution viscosity (poise). Both eq 7 and other, more complicated, equations which are ultimately based on the Stokes hydrodynamic approach relate τ_c to the molecular shape and rotational frictional coefficients characterizing the solute and solvent, but not to the rotational inertia of the solute molecules. A number of recent theoretical discussions of the relations between molecular shape and constitution and rotational motion in solution have taken inertial effects into consideration and have arrived at predictions concerning the dependence of rotational diffusion on temperature and macroscopic viscosity significantly different from those of the Stokes approach, particularly when applied to approximately spherical molecules which interact only weakly with the solvent.^{21, 24-26} However, in general, these treatments have shared with eq 7 the prediction that τ_c should depend on the mass or size of the solvent molecules, as well as on the bulk viscosity η . We were thus somewhat surprised to find that a plot of T_{1V} vs. η/T in the cyclooctane-Nujol mixtures yields a good straight line over a range of viscosities of approximately two orders of magnitude (Figure 4). In particular, this agreement is unexpected on the basis of eq 7, since the change in the magnitude

(23) A. Gierer and K. Wirtz, *Z. Naturforsch.*, **8a**, 532 (1953).

(24) For example, R. W. Mitchell and M. Eisner, *J. Chem. Phys.*, **33**, 86 (1960); W. A. Steele, *ibid.*, **38**, 2404, 2411 (1963); W. B. Monitz, W. A. Steele, and J. A. Dixon, *ibid.*, **38**, 2418 (1963).

(25) W. T. Huntress, Jr., *ibid.*, **48**, 3524 (1968); H. Shimizu, *ibid.*, **40**, 754 (1964).

(26) The few experimental studies which have provided data of sufficient quality to evaluate the relative merits of the hydrodynamic and free-rotator approaches to the calculations of rotational diffusion correlation times in solution suggest that both hydrodynamic and inertial effects are important; cf. T. T. Bopp, *ibid.*, **47**, 3621 (1967), and ref 21.

of the r_{solvent} term on going from pure cyclooctane ($\eta = 2.05$ cP, $\eta/T = 0.0068$ cP/°K) to Nujol ($\eta = 165$ cP, $\eta/T = 0.545$ cP/°K), although difficult to calculate exactly, should result in detectable nonlinearity in the plot of Figure 4. Regardless, this plot provides confirming evidence which establishes that the structure observed in the ambient temperature spectra of **1** is due to vanadium-proton spin-spin splitting, and suggests that the temperature dependence of the line shape in *toluene* solution is determined primarily by changes in the sample viscosity, rather than by a structural or conformational equilibrium involving **1** itself. This latter point in turn is confirmed by the linear relation between T_{1V} and η/T observed for the toluene solution (Figure 4).

The origin of the difference of approximately a factor of 4 observed for T_{1V} at the same value of η/T in toluene and the cyclooctane-Nujol mixtures is at present a matter of speculation. Some of this difference may be accounted for by the failure of eq 7 to describe correlation times precisely. However, two data suggest that the difference in T_{1V} in the aliphatic and aromatic solvents may be real. First, the chemical shift of the C_7H_7 protons of **1** displays a significant temperature dependence in toluene solution, shifting from δ 4.17 at 85° to δ 3.88 at -85°; the corresponding chemical shift change in a saturated hydrocarbon solvent is small. Second, **1** is five to ten times as soluble in toluene as in, e.g., cyclooctane. Both of these observations are consistent with the hypothesis that **1** forms a weak complex with toluene. Complex formation would clearly slow the tumbling of **1**, and correspondingly lengthen τ_c and shorten T_{1V} .²⁷ It might also affect T_{1V} by changing the quadrupole coupling constant. We have no way of distinguishing between these effects on the basis of the available experimental data.

The foregoing arguments establish that measurement of the line width of **1** provides a method of estimating T_{1V} . Combination of the estimated value for T_{1V} in cyclooctane solution with the X-ray structural data⁶ permits an approximate calculation of the vanadium quadrupole coupling constant of **1** in solution. Treating both **1** and cyclooctane as hard spheres, the terms r_{solute} and r_{solvent} of eq 7 can be estimated by calculating the molar volumes V_m for these species from their densities,²⁹ and assuming a closest packing relation between V_m and the hard-sphere radii ($0.74 V_m = 4\pi r^3/3$). On this basis, $r_{\text{solute}} \sim 3.53$ Å and $r_{\text{solvent}} \sim 3.42$ Å, and from the known²⁹ viscosity of cyclooctane at 30° the rotational correlation time for **1** in cyclooctane solution at this temperature can be estimated to be $\tau_c \sim 1.55 \times 10^{-11}$ sec from eq 7. Substituting this value and the measured value of the vanadium relaxation time $T_{1V} = 0.050$ sec into eq 1, the magnitude of the vanadium quadrupole coupling constant of **1** is estimated to be $|(e^2qQ/h)| \cong 2.0$ MHz. Although the error in this number due to uncertainty in

the magnitudes of the proton T_1 and T_2 in the absence of effects due to vanadium, and in the magnitude of the rotational correlation time, may be as much as ± 0.5 MHz, it is worthwhile explicitly pointing out that this type of nmr investigation in compounds for which the prerequisite structural information is available provides one of the most practical methods of estimating quadrupole coupling constants of this magnitude.

In conclusion, the data described in this paper establish that the observed nmr line shape of **1** is primarily determined by the magnitude of T_{1V} . The difference in the temperature dependence of the spectra of **1** in toluene and *n*-pentane (Figure 1) illustrates a point of practical importance: when varying the temperature of an nmr sample to determine if anomalous spectral line broadening is due to the effects of chemical exchange or quadrupole relaxation, it is useful to keep in mind the fact that temperature variations will produce large changes in the spin-lattice relaxation time of a quadrupolar nucleus only if they result in large changes in sample viscosity. The effect of *practically* attainable changes in temperature at constant viscosity on T_1 predicted by eq 7 is small. Thus, in the present study, the spectrum of **1** in *n*-pentane solution at 30° was obtained at the effective lower limit of solution viscosity. Although a further decrease in η/T would in principle have been desirable in order to increase T_{1V} and thus resolve directly the spectral fine structure expected to occur for $\log T_{1V} \lesssim -0.5$ (Figure 2), such a decrease could have been achieved in practice only by taking spectra of **1** in the vapor phase.

Experimental Section

General. Nmr spectra were taken on Varian HA-60 or HA-100 spectrometers equipped with a V-6040 variable-temperature probe and controller. Calibration of the temperature control unit was accomplished by measuring peak separations in methanol or ethylene glycol samples. Viscosities were measured with a Brookfield viscometer calibrated against literature values for the viscosities of cyclooctane ($\rho = 2.05$ cP at 30.0°),²⁹ Nujol ($\rho = 79.9$ cP at 45.0°),³⁰ and toluene ($\eta = 1.638$ cP at -40°).³¹ Literature values for the viscosities of *n*-pentane,³² neopentane,³³ and toluene³⁴ were used when applicable. Additional values of the viscosity of toluene were measured at temperatures below -40°, using samples protected from atmospheric condensation under a nitrogen atmosphere (temperature, viscosity, cP): -42.2°, 1.53; -63.6°, 5.0; -78.4°, 9.2; -95.1°, 19.6. Viscosities (cP) and compositions (wt % Nujol) at 30° for the cyclooctane-Nujol mixtures used in Figure 4 are: 2.51, 10%; 4.01, 25; 11.1, 50; 23.1, 68; 33.8, 75; 40.6, 80; 64.2, 86; 89.2, 90; 165, 100. The viscosity of Nujol at 12° was 577 cP. Toluene-*d*₈ (Diaprep) was used as received after deoxygenation.

Tropyliumvanadium(-I) tricarbonyl was prepared by a modification of the literature method.⁴ All operations were carried out in flame-dried glassware under nitrogen; liquids were transferred by forced siphon through stainless steel cannulas using a positive pressure of nitrogen. To a 300-ml round-bottomed flask fitted with a reflux condenser was added ~ 3.28 g (~ 15 mmol) of va-

(27) Analogous although smaller effects of association have been observed in previous studies of quadrupole^{12,26} and other motional relaxation rates.²⁸

(28) J. Crossley and S. Walker, *J. Chem. Phys.*, **48**, 4742 (1968), and references therein.

(29) The density ($\rho = 0.8284$ g/cm³) of liquid cyclooctane at 30° was obtained from E. Kuss, *Z. Angew. Phys.*, **7**, 372 (1955); the density of solid **1** ($\rho = 1.513$ g/cm³) was calculated from the unit cell parameters of ref 6.

(30) H. Kiefer and T. G. Traylor, *J. Amer. Chem. Soc.*, **89**, 6667 (1967).

(31) L. G. Belinskaya, *Uch. Zap. Mosk. Obl. Ped. Inst.*, **33**, 221 (1955); *Chem. Abstr.*, **52**, 821 (1958).

(32) "Selected Values of Properties of Hydrocarbons," NBS Circular C 461, U. S. Department of Commerce, National Bureau of Standards, Washington, D. C., 1947, p 109.

(33) Extrapolated from data of J. Lohrenz, *Petrol. Refiner.*, **35**, 169 (1956).

(34) "International Critical Tables," Vol. VII, McGraw-Hill Book Co., Inc., New York, N. Y., 1930, p 218.

adium(0) hexacarbonyl³⁵ and 9.3 g (0.1 mol) of freshly distilled cycloheptatriene in 100 ml of hexane.³⁶ Air (1 ml) was then injected into the reaction flask through a serum stopper by syringe,³⁷ and the solution was heated at reflux for 1 hr. The reaction mixture was cooled, transferred by cannula to a 250-ml centrifuge bottle, and centrifuged. Portions of the resulting dark green solution (~30 ml) were successively transferred into a 40-ml centrifuge tube capped with a serum stopper, and hexane and excess cycloheptatriene were removed at room temperature under vacuum until the entire solution was concentrated to ~5 ml. The residual oil was diluted with 10 ml of pentane and centrifuged and the supernatant solution again transferred to another stoppered centrifuge tube. Cooling this solution to -78° for 8-36 hr resulted in crystallization of **1** as green-black plates. The mother liquor was removed by cannula from these crystals at -78° and the resulting **1** dried in a slow stream of nitrogen at room temperature. Final purification of **1** before preparing nmr samples was effected by sublimation (42°, 0.05 Torr). The total yield of **1** is ~15%. Solid **1** reacts slowly with air; solutions of **1** oxidize very rapidly.

Sample Preparation. The preparation of samples in solvents of low viscosity was carried out with careful exclusion of oxygen and water, using unexceptional procedures. The preparation of solutions of **1** in solvents more viscous than cyclooctane required a

(35) R. Ercoli, F. Calderazzo, and A. Alberola, *J. Amer. Chem. Soc.*, **82**, 2966 (1960); R. P. M. Werner and H. E. Podall, *Chem. Ind.* (London), 144 (1961); R. B. King, "Organometallic Syntheses," Vol. I, Academic Press, New York, N. Y., 1965, p 82.

(36) Oxygen and olefins were carefully removed from the hexane before use by stirring with 96% H₂SO₄, followed by distillation from a suspension of sodium benzophenone ketyl under nitrogen.

(37) If this reaction is carried out with *strict* exclusion of oxygen, no **1** is formed. Presumably, traces of vanadium in higher oxidation states than V(0) or V(-I) are required as catalysts for the formation of **1**.

special procedure, since the rate of solution in these solvents was very slow. Ca. 40 mg. of freshly sublimed **1** was transferred in a nitrogen-filled glove bag to a 5-ml round-bottomed flask, 10 μl of deoxygenated benzene was added, and the mixture was ground into an oil. Then 0.25 ml of the desired solvent, previously degassed under vacuum by three freeze-thaw cycles (liquid nitrogen), was added with further stirring, a serum stopper placed on the flask, and the solution forced into a syringe using a positive pressure of nitrogen. The solution was transferred into an oxygen-free nmr tube through a serum stopper and the tube sealed under nitrogen. The presence of these small amounts of benzene in the sample had no significant effect on the spectral line shapes. Samples in toluene and cyclooctane were ~2.5-3.5 mol % **1**; samples in Nujol were ~1.5-3.0 wt % **1**. The viscosities of all solutions of **1** were assumed to be the same as the viscosities of the solvents themselves. Considering the low concentration of **1** in these samples, this assumption seems reasonable.

Values of T_{1V} were obtained by comparison of the shapes and half-height line widths of calculated (Figure 2) and observed spectra. The peak widths of **1** were corrected for viscous broadening unrelated to the vanadium quadrupole relaxation by the use of benzene as an internal line width standard in the hydrocarbon solvents and TMS in the toluene-*d*₃ sample. All of the data in Figure 4 have been so corrected.

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Production of Bromite and Perbromate Ions in Crystalline CsBrO₃ Irradiated with Cobalt-60 γ Rays and the Vibrational Spectrum of the BrO₄⁻ Ion¹

L. C. Brown, G. M. Begun, and G. E. Boyd

Contribution from the Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830. Received December 16, 1968

Abstract: The formation of *ca.* 30° by ⁶⁰Co γ rays of perbromate and bromite ions in CsBrO₃ was demonstrated by infrared absorption measurements on irradiated crystals and by ion-exchange column chromatographic separations on aqueous solutions of the radiolyzed solid. Vibrational spectra (infrared and laser-excited Raman measurements) were obtained for BrO₄⁻ ion in solution and in crystalline RbBrO₃ and (C₆H₅)₄AsBrO₄. The frequency assignments are ν₁ 801, ν₂ 331, ν₃ 878, and ν₄ 410 cm⁻¹. Force constants derived from these frequencies suggest that there is a close similarity in bonding between BrO₄⁻ and IO₄⁻ and that a significant decrease in the nonbonding interactions occurs in the series ClO₄⁻, BrO₄⁻, IO₄⁻ as the size of the central atom increases and the oxygens become less crowded. An unsuccessful search was made for ⁸²BrO₄⁻ ion formed in ⁷LiBrO₃ by thermal neutron capture. The yield of ⁸²BrO₄⁻ ion, if formed, was less than 0.05%.

A continuing objective in our researches on the decomposition of bromate ion in crystalline alkali-metal and alkaline-earth bromates² by energetic ionizing radiations has been to relate the species observed in an aqueous solution of the irradiated salt to those trapped in the crystal. It is by no means certain that these are always the same species; in at least one instance^{3a} there is evidence that they were

(1) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

(2) For a review see J. W. Chase and G. E. Boyd, "The Radiolytic Decomposition of Crystalline Alkali-metal and Alkaline-earth Bromates," ASTM Special Publication No. 400, 1966, p 17 ff.

quite different. On the other hand, recent studies^{3b} with crystalline KClO₃ irradiated with ⁶⁰Co γ rays have shown that within experimental error all the perchlorate ion found in aqueous solution was originally present as ClO₄⁻ in the crystal lattice. Evidence for stable products in radiolyzed CsBrO₃ crystals also has been obtained: cesium bromide in the lattice has been indicated by X-ray diffraction techniques,² and reflectance spectra² of solid samples show an absorption band in

(3) (a) L. J. Sharman and K. J. McCallum, *J. Am. Chem. Soc.*, **77**, 2989 (1955); (b) L. C. Brown and G. E. Boyd, *J. Phys. Chem.*, **73**, 396 (1969).