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+}	1.2×10^6	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 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]

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[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.

[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).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ALBERTA,
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Proton Magnetic Resonance Line Broadening of Methanol and Trichloro- and Trifluoroethanol by Vanadyl Complexes

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The line broadening of the methyl and hydroxy protons of solvent methanol caused by $VO(CH_3OH)_5^{2+}$ 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 trifluoroethanol.

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

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[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).

the solvent was removed by vacuum distillation. The resultant green crystals were analyzed for carbon and hydrogen. *Anal.* Calcd for $VO(CH_3OH)_5(ClO_4)_2$: C, 14.05; H, 4.73. Found: C, 13.91; H, 4.70.

Bis(acetylacetonato)vanadyl, obtained from Aceto Chemical Co. Inc., was recrystallized twice from reagent grade chloroform and stored under vacuum. *Anal.* Calcd for $VC_{10}H_{14}O_5$: C, 45.3; H, 5.32. Found: C, 44.9; H, 5.23.

Bis(trifluoroacetylacetonato)vanadyl was prepared by mixing stoichiometric amounts of vanadyl perchlorate and trifluoroacetylacetone (Peninsular ChemResearch Inc.) in slightly acidic redistilled water. The solution was slowly neutralized with sodium carbonate. The green precipitate which separated during neutralization was extracted into chloroform and recrystallized from this solvent. *Anal.* Calcd for $VC_{10}H_8O_5F_6$: C, 32.2; H, 2.16. Found: C, 32.7; H, 2.22.

Tris(acetylacetonato)vanadium(III) was prepared under vacuum, by the slow addition of dilute aqueous ammonia to a solution containing vanadium trichloride and acetylacetone. The product was extracted into chloroform and recrystallized from this solvent. *Anal.* Calcd for $VC_{15}H_{21}O_6$: C, 51.7; H, 6.06. Found: C, 50.1; H, 5.96.

The methanol, trifluoroethanol, and trichloroethanol solvents used for the nmr samples were purified by two vacuum distillations from molecular sieves, collecting the middle fraction of each distillation. The solvents were stored over molecular sieves and vacuum distilled onto the vanadyl complex in a suitable container for preparation of the nmr samples. Concentrations were determined by weighing the solvent and vanadyl complex. Metal ion concentrations were adjusted to give line broadenings of at least 10 Hz.

The nmr spectra were obtained on HA-60, HA-100, and A56-60 Varian spectrometers, equipped with Model V-4343 temperature controllers and standard variable-temperature probes. Frequency shifts from an internal standard (cyclopentane) and line widths were reproduced to ±2 Hz on all machines. No chemical shift of the solvent peaks caused by the paramagnetic ion was observed under any of the experimental conditions studied. Temperatures were checked by comparing the separation in hertz between the methyl and hydroxy peaks in pure methanol to a standard calibration curve published by Varian Associates.

The visible and ultraviolet spectra of the complexes were recorded on a Cary Model 14 spectrophotometer.

Results

The visible spectrum of $VO(ClO_4)_2$ in methanol shows a typical absorption at 13,000 cm^{-1} (ϵ 17.0), with a shoulder at 15,500 cm^{-1} and an additional band at 27,400 cm^{-1} (ϵ 117). The molecular orbital diagram given by Ballhausen and Gray[5] for the $VO(H_2O)_5^{2+}$ ion can be used to assign the spectral transitions observed in $VO(CH_3OH)_5^{2+}$. The 13,000- and 15,500-cm^{-1} absorptions are identified as the $b_2 \rightarrow e_\pi^*$ and $b_2 \rightarrow b_1^*$ transitions and the 27,400-cm^{-1} absorption is assigned to the $b_2 \rightarrow a_1^*$ transition. The value of Dq obtained directly from the $b_2 \rightarrow b_1^*$ transition is 1500 cm^{-1} and may be compared to the value of 1600 cm^{-1} for $VO(H_2O)_5^{2+}$.

The value for the transverse relaxation time in a hypothetical molal solution, T'_{2p}, is obtained from the nmr spectrum by using the relationship

$$(T'_{2p})^{-1} = \frac{\pi(\Delta\nu_{ob} - \Delta\nu_{sol})}{m} \tag{1}$$

where $\Delta\nu_{ob}$ is the full width at half-height of the solvent resonance in the presence of vanadyl complex, $\Delta\nu_{sol}$ is this line width in the absence of metal ion, and m is the molal concentration of metal ion.

The observed variation of $(T'_{2p})^{-1}$ with temperature in the systems studied is typical of that observed in a number of other nonaqueous solvents. When chemical exchange and T_{2m} relaxation are occurring from two kinetically different sites, a situation which is found to apply for the vanadyl systems studied, then $(T'_{2p})^{-1}$ at any temperature may be represented by the equations

$$(T'_{2p}{}^{-1}) = P_m\tau_m^{-1} + C\tau_c \tag{2}$$

$$(T'_{2p})^{-1} = P_m\left(\frac{kT}{h}\right)\exp\left(-\frac{\Delta H^{\ddagger}}{RT} + \frac{\Delta S^{\ddagger}}{R}\right) + C_1\exp\left(\frac{E_a}{RT}\right) \tag{3}$$

The first term on the right in eq 2 results from limiting conditions 10a or 10c of the general equation developed by Swift and Connick.[6] This term predominates when chemical exchange controls the nuclear relaxation. It appears that condition 10c actually applies because the solvent protons which show chemical exchange controlled line broadening probably have a short relaxation time in the coordination sphere of the vanadyl ion due to the hyperfine or contact relaxation mechanism (eq 4). This mechanism is very effective in this case because of the long electron spin-relaxation time (τ_e) of the vanadyl complexes. The second term in the above equation gives a general expression for outer-sphere T_{2m}-controlled relaxation, where τ_c is the correlation time for the interaction of the outer-sphere solvent protons and the unpaired electron of the vanadyl complex (T_{2m} is the transverse relaxation time of the solvent protons due to interaction with the paramagnetic ion). The correlation time is expected from Debye theory to vary directly as the viscosity of the solvent. Since viscosities generally show an exponential temperature dependence, the result is an exponential variation of τ_c with $(T°K)^{-1}$. In cases where both terms in eq 3 control $(T'_{2p})^{-1}$ at different temperatures a least-squares fit of the data (IBM Share Library Program, SDA 3094, 1964) to this equation was obtained by treating $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, C_1, and E_a as adjustable parameters. When only a linear decrease of $-\log(T'_{2p})$ with $(T°K)^{-1}$ was observed, the best straight line, as judged by eye, was used to obtain C_1 and E_a.

It should be possible to determine the mechanism for the T_{2m} relaxation by comparing the value of C_1 in eq 3 to the theoretical expressions for the three types of electron–nucleus interactions which usually govern T_{2m}. The electron–nuclear hyperfine contribution to T_{2m} is given by[7]

$$(T_{2m})^{-1} = \frac{1}{3}S(S+1)\left(\frac{A}{\hbar}\right)^2\left(\tau_e + \frac{\tau_e}{1 + \omega_s^2\tau_e^2}\right) \tag{4}$$

where $A/\hbar$ is the hyperfine coupling constant, ω_s is the electron Larmor frequency, and τ_e is the electron spin-

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(5) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).

(6) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).

(7) I. Solomon and N. Bloembergen, *ibid.*, **25**, 261 (1956).

TABLE I

INNER- AND OUTER-SPHERE PARAMETERS FOR VARIOUS VANADYL COMPLEX–ALCOHOL SYSTEMS AT 25°[d]

		Complex				
		$VO(ClO_4)_2$	$VO(acac)_2$	$VO(tfac)_2$	$VO(acac)_2$	$VO(acac)_2$
		Solvent				
		CH_3OH	CH_3OH	CH_3OH	CCl_3CH_2OH	CF_3CH_2OH
Hydroxy proton	(r_i), Å	2.95	2.95[a]	3.38	3.22	2.83[c]
	(r_o), Å	4.00	4.00[a]	6.00	4.30	4.16[c]
	$(T'_{2p})^{-1}{}_{obsd}$, sec^{-1}	275	256	260	4350	2200
Methyl or methylene protons	(r_i), Å	3.90	3.90[a]	4.33	4.17	3.78[c]
	(r_o), Å	4.80	4.80[a]	6.80	5.10	4.96[c]
	$(T'_{2p})^{-1}{}_{calcd}$, sec^{-1}	107	96	98	1350	580
	$(T'_{2p})^{-1}{}_{obsd}$, sec^{-1}	100	97	102	1360	583
$10^{11}\tau_c$, sec		4.10	3.60	9.35	27.0	10.8
E_a,[b] kcal mol^{-1}		2.91 ± 0.30	2.60 ± 0.21	3.01 ± 0.29	8.15 ± 1.27	6.50 ± 1.00

[a] Since no epr work was done on this system, the same values as those for $VO(CH_3OH)_5^{2+}$ were assumed. [b] Errors are quoted as standard errors from the nonlinear least-squares fit to the data. [c] The values of $(r_i)_{OH}$ and $(r_i)_{CH_3}$ will be too short and $(r_o)_{OH}$ and $(r_o)_{CH_3}$ too long, if there is fast hydroxy proton exchange with some hyperfine contribution to the observed T_{2m} relaxation. [d] One rapidly exchanging inner-sphere molecule was assumed in all cases.

relaxation time. The dipole–dipole relaxation time for solvent molecules in the first coordination sphere of the paramagnetic ion is given by[8,9]

$$(T_{2m})^{-1} = \frac{1}{15}\,\frac{S(S+1)\gamma_I^2g^2\beta^2}{r_I^6}\left\{7\tau_c + \frac{13\tau_c}{1+\omega_s^2\tau_c^2}\right\} \tag{5}$$

Luz and Meiboom[10] have calculated the dipole–dipole interaction of the electron with solvent nuclei outside of the first coordination sphere by integrating eq 5 from r_0 (the radius of the solvated paramagnetic ion) to infinity. The expression obtained is

$$(T_{2p})^{-1} = \frac{4\pi\rho Nm}{45\times10^3}\left(\frac{S(S+1)\gamma_I^2g^2\beta^2}{r_0^3}\right)\times \left\{7\tau_c + \frac{13\tau_c}{1+\omega_s^2\tau_c^2}\right\} \tag{6}$$

where ρ is the solvent density and N is Avogadro's number.

In the present work the distance r_0 was taken to be the distance of closest approach of the outer-sphere solvent molecules if molecules in the second coordination sphere aways had the same orientation toward the ion as the first coordination sphere molecules. This assumption implies a specific orientation in the second coordination sphere but retains the continium approximation implicit in the integration used to obtain eq 6. The results indicate that these approximations do not lead to any gross inconsistencies.

Unfortunately it is not possible to give an exact test of the theoretical eq 4–6 by comparison to the experimental value of C_1 because each equation contains at least two unknowns. Although $(A/\hbar)$ in eq 4 may be determined from shift measurements, no chemical shift was observed in any of the systems studied.

In Table I, the correlation time τ_c was determined from the epr line widths of the vanadyl complex in the appropriate solvent using the theory developed by Kivelson.[11,12] The method is described in a previous publication.[13] The values for τ_c were used to calculate the hydrodynamic radius of the ion (a_0) from the Debye formula $\tau_c = 4\pi a_0^3\eta/3kT$ (η is the viscosity). The outer-sphere hydroxy and methyl distances were arbitrarily taken as $a_0 + 0.5$ Å and $a_0 + 1.3$ Å, respectively. This procedure at least gives a consistent method of treating all of the systems. Studies of the epr line widths of $VO(acac)_2$ in various alcohols have shown that the Debye formula predicts the temperature and viscosity dependence of τ_c and gives generally consistent a_0 values. The inner-sphere interaction distance for the hydroxy proton was calculated from the observed broadening after subtracting off the outer-sphere contribution. The methyl proton line broadening was then calculated from eq 5 and 6 using $(r_i)_{CH_3} = (r_i)_{OH} + 0.95$ Å. The distance of 0.95 Å between the methyl and hydroxy protons is derived from models of methanol. It can be seen that the calculated and observed values of $(T'_{2p})_{CH_3}{}^{-1}$ are in good agreement. Therefore it is concluded that only the inner- and outer-sphere dipolar interactions are contributing significantly to the low-temperature line broadening.

I. Solvent Proton Relaxation in a Methanol Solution of $VO(ClO_4)_2$.

—The temperature dependence of $(T'_{2p})^{-1}$ for the methyl and hydroxy methanol protons is shown in Figure 1. The general features of the curve in Figure 1 are consistent with eq 2, the high-temperature portion being due to the P_m/τ_m term and the low-temperature region to the $C\tau_c$ term. It is apparent from the high-temperature region that the hydroxy and methyl protons are exchanging at different rates. The kinetic parameters for the exchange processes are given in Table II.

The methyl protons must be exchanging with the whole methanol molecule, whereas the hydroxy proton

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(8) I. Solomon, *Phys. Rev.*, **99**, 559 (1955).
(9) N. Bloembergen, *J. Chem. Phys.*, **27**, 572 (1957).
(10) Z. Luz and S. Meiboom, *ibid.*, **40**, 2686 (1964).
(11) D. Kivelson, *ibid.*, **44**, 154 (1966).
(12) R. Wilson and D. Kivelson, *ibid.*, **44**, 154 (1966).
(13) R. B. Jordan and N. S. Angerman, *ibid.*, **48**, 3983 (1968).

TABLE II

RATE PARAMETERS FOR SOLVENT PROTON EXCHANGE WITH VANADYL COMPLEXES

Vanadyl complex	Solvent	Exchanging protons	$10^{-3}k$,[b] $\sec^{-1}$ (25°)	$\Delta H^{\ddagger}$,[a] kcal mol^{-1}	$\Delta S^{\ddagger}$,[a] cal mol^{-1} deg^{-1}
VO^{2+}	CH_3OH	OH	4.35	10.90 (±0.73)	−5.39 (±2.3)
		CH_3	0.565	9.46 (±0.68)	−14.2 (±2.1)
$VO(acac)_2$	CH_3OH	OH	66.6	11.79 (±0.72)	3.1 (±1.7)
$VO(tfac)_2$	CH_3OH	OH	12.0	11.12 (±0.70)	−2.6 (±2.1)
$VO(acac)_2$	CCl_3CH_2OH	OH	401	6.41 (±1.49)	−11.5 (±4.2)

[a] Errors are quoted as the standard errors from the nonlinear least-squares fit to the data. [b] $k = \tau_m^{-1}$, where τ_m was calculated from the nmr line broadening assuming a coordination number of 4 for the solvated vanadyl ion and 1 in all other cases.

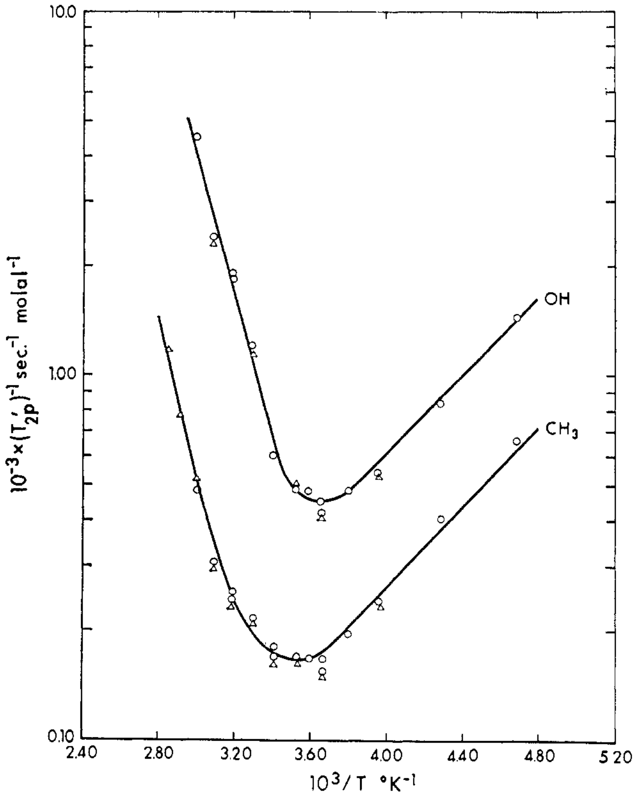

Figure 1.—Temperature dependence of $(T'_{2p})^{-1}$ for the hydroxy and methyl protons in methanol solutions of $VO(CH_3OH)_5(ClO_4)_2$.

can also exchange by proton dissociation from coordinated methanol or possibly by protonation of the vanadyl oxygen. For the latter mechanism two paths have been considered

$$CH_3OH_2^+ + O{=}V^{2+} \rightleftharpoons CH_3OH + HO{=}V^{3+} \quad (7)$$

$$CH_3OH + O{=}V^{2+} \rightleftharpoons CH_3O^- + HO{=}V^{3+} \quad (8)$$

If proton exchange occurs by reaction 7, then $(T_{2p})_{OH}^{-1}$ should show a first-order dependence on hydrogen ion concentration. This assumes that $HO{=}V^{3+}$ is a strong acid as indicated by the study of Rossotti and Rossotti.[14] The acid dependence of $(T_{2p})_{OH}^{-1}$ was investigated in the vanadyl acetylacetonate–methanol system. The system also shows only hydroxy proton chemical exchange, and because of the reduced charge of $VO(acac)_2$ compared to $VO(CH_3OH)_5^{2+}$ reaction 7 should be more favored for $VO(acac)_2$. Four solutions were prepared containing 0.096 *m* $VO(acac)_2$ and 0.0, 0.01, 0.05, and 0.10 *m* 2,4-dinitrobenzenesulfonic acid. No significant variation in the line widths in the four solutions was observed, proving that the hydroxy proton exchange rate in the $VO(acac)_2$ system and also in the $VO(CH_3OH)_5^{2+}$ system does not occur by reaction 7.

In reaction 8 it is expected that the rate constant for the reverse reaction will be diffusion controlled ($\sim 10^{10}$ $\sec^{-1}$) because it is the reaction of a strong acid $HO{=}V^{3+}$ and a strong base CH_3O^-. With this assumption and the rate constant of the forward reaction determined from the nmr line broadening, a value for the equilibrium constant of 5×10^{-8} is calculated for reaction 9. This result implies that the vanadyl ion has the same basicity as the acetate ion[15] in methanol, again inconsistent with the lack of basicity in aqueous solution.[14]

Based on the study of VO^{2+} in water by Swift, *et al.*,[3] a probable mechanism for hydroxy proton exchange in methanol is represented by the reaction

$$CH_3OH + O{=}V(HOCH_3)_4^{2+} \rightleftharpoons O{=}V(HOCH_3)_3(OCH_3)^+ + CH_3OH_2^+ \quad (9)$$

The rate constant for proton dissociation by reaction 9 is 4.35×10^3 $\sec^{-1}$ at 25°.

The inner–outer-sphere interpretation of the low-temperature line broadening is based on several observations which will be discussed with particular reference to the $VO(CH_3OH)_5^{2+}$–methanol system. Similar arguments apply to the other systems and will not be discussed in detail subsequently. In the low-temperature region the ratio of $(T'_{2p})_{OH}^{-1}/(T'_{2p})_{CH_3}^{-1}$ is 2.62. For transition metal ions dissolved in methanol this ratio is expected to be approximately constant since these ions have similar ionic radii and the orientation of the solvent in the outer coordination sphere is probably the same. For Ni^{2+},[16] Co^{2+},[16] and V^{2+} [17] in methanol this ratio is 1.64, 1.62, and 1.70, respectively. The apparently anomalous ratio for the vanadyl ion may be explained by the usual outer-sphere dipolar relaxation (eq 6) plus one rapidly exchanging solvent molecule with proton relaxation by the inner-sphere dipole–dipole interaction (eq 5). The rapid exchange of a fifth solvent molecule, presumably in the coordination position *trans* to the vanadyl oxygen, is consistent with the coordination number of 4 found for the vanadyl ion in water,[1] the recent structure determination of $[VO(OH_2)_4SO_4]\cdot$

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(14) F. J. C. Rossotti and H. S. Rossotti, *Acta Chem. Scand.*, **9**, 1177 (1955).

(15) T. Shedlovsky and R. L. Kay, *J. Phys. Chem.*, **60**, 151 (1956).

(16) Z. Luz and S. Meiboom, *J. Chem. Phys.*, **40**, 2686 (1964).

(17) N. S. Angerman and R. B. Jordan, unpublished results.

H_2O,[18] and the H_2O^{17} nmr work on various vanadyl chelates.[19] If the parameters given in Table I, as discussed previously, are used, then the inner- and outer-sphere contributions to $(T'_{2p})_{CH_3}^{-1}$ are 33 and 74 sec^{-1} m^{-1}, respectively. The sum of these contributions is reasonably close to the observed value of 100 $sec^{-1}\,m^{-1}$.

II. Solvent Proton Relaxation in a Methanol Solution of VO(acac)$_2$.—The variation of the solvent proton relaxation time with temperature is shown in Figure 2.

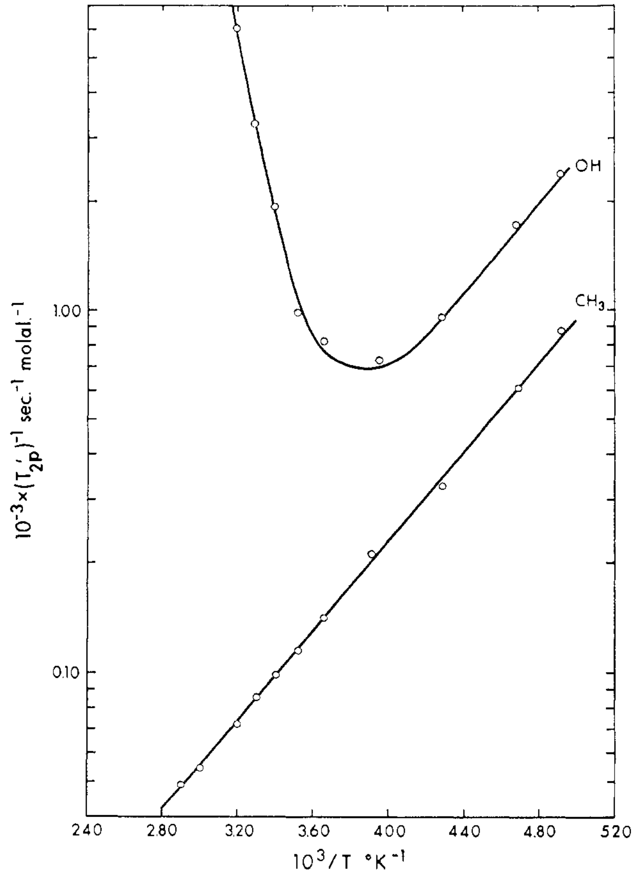

Figure 2.—Temperature dependence of $(T'_{2p})^{-1}$ for the hydroxy and methyl protons in methanol solutions of bis(acetylacetonato)-vanadyl.

In this system only the hydroxy protons show a chemical exchange controlled nuclear relaxation.

The relative values of the methyl and hydroxy line broadenings at low temperature may be explained by a combination of inner- and outer-sphere dipolar relaxation as discussed previously. The parameters used and the results are given in Table I.

The same considerations used previously may be applied to the vanadyl acetylacetonate complex to show that reaction 7 or 8 cannot explain the hydroxy proton exchange. There is the additional possibility that the CH proton of coordinated acetylacetonate may exchange with methanol. This possibility was tested by measuring the line width of the CH proton of tris(acetylacetonato)vanadium(III) dissolved in chloroform (no exchange) and in methanol. The spectrum in both solvents recorded at 100 MHz exhibited two peaks due to the CH and CH_3 resonances at 3948 and 4492 Hz, respectively, downfield from internal TMS. The CH resonance was broadened by less than 10 Hz in methanol, indicating an exchange rate of less than 62 sec^{-1} at 40°. Therefore, this type of exchange is too slow to account for the solvent hydroxy proton exchange.

Partial dissociation of one of the acetylacetonate ligands and substitution of a solvent molecule could also explain the results. The equilibrium constant is 10^2 for the reaction analogous to (10) in aqueous

$$VO(acac)_2 + 2CH_3OH + H^+ \rightleftharpoons VO(acac)(CH_3OH)_2^+ + Hacac \quad (10)$$

solution.[20] Hydroxy proton exchange may occur by proton dissociation from $VO(acac)(CH_3OH)_2^+$ by a process analogous to reaction 9. If the proton dissociation constant from coordinated methanol in the latter species is assumed to be 10^{-6}, then there is about 10% of the dissociated species present. The addition of up to 0.10 m acid should cause about 50% dissociation and, therefore, about a fivefold increase in $P_m(\tau_m)^{-1}$ and in turn in $(T'_{2p})^{-1}$. It was noted in the previous section that the line widths did not change on addition of 0.01, 0.05, or 0.10 m 2,4-dinitrobenzenesulfonic acid. Therefore, this mechanism cannot explain the exchange broadening except in the unlikely event that the complex is largely dissociated even in pure methanol solutions.

Partial dissociation of one of the chelate rings would also produce a species which would undergo hydroxy proton dissociation. Pearson and Moore[21] have found evidence for such species as intermediates in the hydrolysis of vanadyl acetylacetonate. It is not possible to estimate realistically the equilibrium constant for reaction 11. As part of a general epr line

$$VO(acac)_2 + CH_3OH + H^+ \rightleftharpoons VO(acac)(acacH)(CH_3OH)^+ \quad (11)$$

broadening study[22] the coupling constants $\langle A\rangle$ and g for VO(acac)$_2$ have been determined in a number of alcohols. In the series of alcohols including methanol, trichloroethanol, and trifluoroethanol the value of $\Delta g = g_x - g_y$ is constant at 0.0100 and the value of $\Delta A = A_x - A_y$ is also constant at 6.5 ± 0.5 G. The temperature dependencies of the line widths up to the boiling point of the respective alcohols show no anomalies and are quantitatively consistent with the presence of only one vanadyl species. The epr results of Wüthrich and Connick[19] indicate that it should be possible to observe a separate signal for a new species if it constitutes about 10% of the total species. Therefore, our epr study established that there can only be a

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[18] C. J. Ballhausen, B. F. Djurinskig, and K. J. Watson, *J. Am. Chem. Soc.*, **90**, 3305 (1968).

[19] K. Wüthrich and R. E. Connick, *Inorg. Chem.*, **7**, 1377 (1968).

[20] A. E. Martell and L. G. Sillén, Ed., "Stability Constants of Metal Complexes," Special Publication No. 17, The Chemical Society, London, 1964.

[21] R. G. Pearson and J. W. Moore, *Inorg. Chem.*, **5**, 1528 (1966).

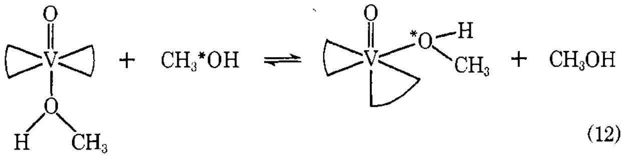
[22] R. B. Jordan and N. S. Angerman, results to be submitted for publication.

small concentration of the dissociated vanadyl acetylacetonate in the alcohol solution. This conclusion, combined with the lack of acid dependence of the line broadening, makes it very unlikely that there is a partially dissociated species undergoing chemical exchange.

Several other points argue against a partially dissociated exchanging species. The study of Wüthrich and Connick indicates that water exchange is about 10^3 times faster for various vanadyl chelates than for $VO(H_2O)_4^{2+}$. If a similar factor holds for the acetylacetonate chelates, then the observed chemical exchange might be due to whole methanol molecule exchange from $VO(acac)(CH_3OH)_2^+$. It is then necessary to explain the lack of chemical exchange controlled line broadening for the methyl protons. Considering arguments given previously it seems likely that the limiting conditions for the hydroxy protons are $T_{2m}^{-1} \gg \tau_m^{-1}$, $\Delta\omega_m$. If the hyperfine coupling constant for the methyl protons is 30 times less than for the hydroxy protons then $\tau_m^{-1} \gg T_{2m}^{-1}$ for the CH_3 protons and no chemical exchange would be observed. However the results for $VO(CH_3OH)_5^{2+}$ do not indicate any such large difference in the coupling constants, and it seems unlikely that the acetylacetonate would drastically change the relative values of the coupling constants.

It should also be noted that the line broadening in the chemical exchange controlled region is greater for $VO(acac)_2$ than for $VO(CH_3OH)_5^{2+}$. Since P_m is larger for the latter system, the hydroxy protons are exchanging more rapidly from $VO(acac)_2$ than from $VO(CH_3OH)_5^{2+}$. This result is the opposite of that expected when the higher charge on $VO(CH_3OH)_5^{2+}$ is considered. These relative rate considerations and especially the lack of acid dependence of the exchange rate all argue against a partial dissociation mechanism for the hydroxy proton exchange.

Another exchange mechanism[23] may be described by



(12)

I II

The detailed mechanism may be either a direct substitution as implied in reaction 12 or an intramolecular interchange of species I, since direct exchange of methanol in species I with bulk solvent is fast. The latter condition is based on the results for the solvated vanadyl in water[1] and methanol. The transverse relaxation time of the hydroxy protons in species II (T_{2II}) is assumed to be short owing to a hyperfine interaction.

The solvent proton T_2 will then be controlled by the rate of the I → II interchange of the hydroxy proton. It is necessary to assume that T_{2II} for the methyl protons is longer than the exchange lifetime. As noted previously this conclusion does not seem very probable in view of the results on VO^{2+} in methanol.

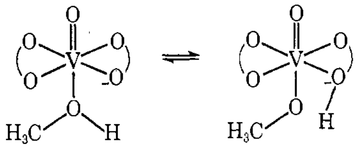
If the I → II interchange is slower than $(T_{2II})_{OH}$ but faster than $(T_{2II})_{CH_3}$, then hydroxy proton dissociation from II may control the solvent hydroxy proton relaxation

(13)

II III

The previous comparison of expected and observed proton dissociation rates from the chelated and solvated vanadyl ions again seems to make this an unlikely possibility.

A mechanism which does seem to be consistent with the observations is described by the reaction



(14)

I IV

In this case bulk solvent exchange with I is again assumed to be very fast. The hydroxy proton line broadening will be controlled by the I–IV exchange rate if $(T_{2I})_{OH}$ is longer and $(T_{2IV})_{OH}$ is much shorter than the I–IV exchange rate. Since the unpaired electron is in the d_{xy} orbital in the plane of the complex along with the acetylacetone ligands, there will be very little interaction with solvent protons in I and $(T_{2I})_{OH}$ will be governed by the dipolar interaction. However, a hyperfine interaction is expected with the proton in IV and this will cause the $(T_{2IV})_{OH}$ for this proton to be much shorter. The T_{2IV} for the methyl protons will still be due to the dipolar interaction. Therefore the solvent hydroxy proton transverse relaxation time is controlled by the I–IV exchange rate. The theory for this three-site case is given in the Appendix.

The proton transfer I–IV is considered to be to one of the electron pairs in an sp^2 hybrid orbital on the acetylacetonate oxygen. The bonding of acetylacetonate to the metal in IV would certainly be weakened because of the reduced charge, but neither the metal–ligand σ bonds nor the ligand π bond is broken during the proton-transfer process.

Several predictions of rate trends can be made on the basis of reaction 14. If the rate of internal proton transfer follows the normal pattern for intermolecular proton transfer,[24] then increasing the acidity of the alcohol and the basicity of the acetylacetone should increase the rate of proton transfer. The results described in the following sections show that these predications do correspond to the observations.

III. Solvent Proton Relaxation in Methanol Solution of $VO(tfac)_2$.

—The temperature dependence of the solvent proton relaxation time for this system is shown

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(23) The authors wish to acknowledge one of the referees for suggesting this possibility.

(24) L. De Maeyer and K. Kustin, *Ann. Rev. Phys. Chem.*, **14**, 5 (1963);

in Figure 3. It can be seen by comparison to Figure 2 that the line broadening behaviors of VO(acac)$_2$ and VO(tfac)$_2$ are similar.

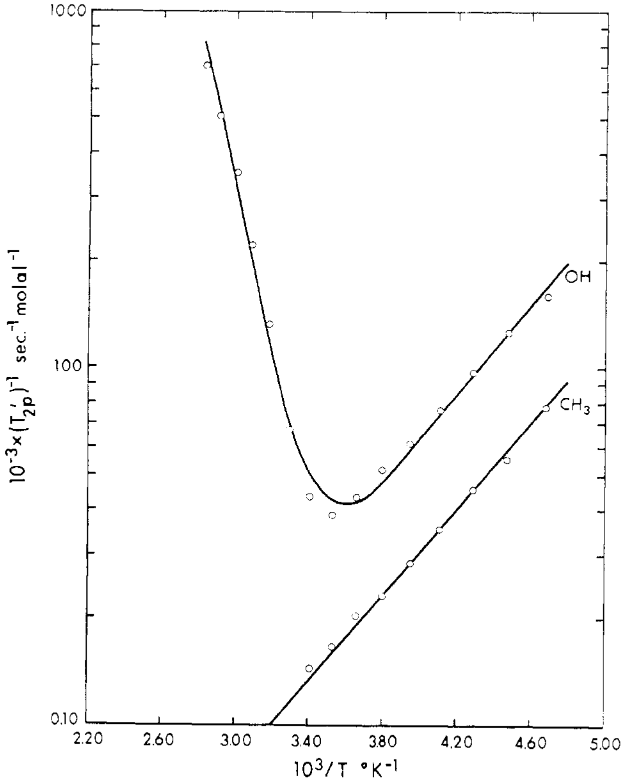

Figure 3.—Temperature dependence of $(T'_{2p})^{-1}$ for the hydroxy and methyl protons in methanol solutions of bis(trifluoroacetylacetonato)vanadyl.

The low-temperature broadening of the hydroxy and methyl protons is attributed again to inner- and outer-sphere dipolar relaxation. The unusually long outer-sphere interaction distance results from the longer tumbling time found for this complex which in turn gives a greater hydrodynamic radius from the Debye formula. If there is hydrogen bonding between the trifluoromethyl groups and solvent methanol, then VO(tfac)$_2$ may be a sticky rather than a hard sphere, and the Debye theory may not apply. Alternatively, if the hydrogen bonds have a lifetime longer than 10^{-10} sec, then the hydrogen-bonded solvent molecules may be tumbling with the VO(tfac)$_2$ and the molecule would then have a larger hydrodynamic radius.

It should also be noted that the inner-sphere distances $(r_i)_{OH}$ and $(r_i)_{CH_3}$ are longer in this system than for VO(acac)$_2$. This change is in the opposite direction to that expected on electrostatic grounds since the CF_3 groups should leave more positive charge on vanadium in VO(tfac)$_2$ relative to that in VO(acac)$_2$ and therefore give a stronger bond to the methanol. However, it must be remembered that the acetylacteone ligands in VO(acac)$_2$[25] and probably in VO(tfac)$_2$ are below the vanadium atom and the planes of each acac ligand intersect at an angle of 163° in VO(acac)$_2$.[25] The factors affecting this type of distortion are not well understood, but if it is greater in VO(tfac)$_2$ than in VO(acac)$_2$, then steric crowding may result in a longer bond length to methanol in VO(tfac)$_2$.

As mentioned previously, the slower hydroxy proton exchange observed in this system compared to VO(acac)$_2$ is as expected on the basis of the proton-transfer mechanism because the trifluoroacetylacetonate oxygens will be less basic than those in acetylacetonate.

IV. Solvent Proton Relaxation in Trichloroethanol Solution of VO(acac)$_2$.—The temperature dependences of $(T'_{2p})^{-1}$ for the hydroxy and methylene protons of trichloroethanol solutions of VO(acac)$_2$ are shown in Figure 4. The low-temperature hydroxy and all of the methylene proton broadening may be explained by the inner- and outer-sphere dipolar processes as discussed previously. The interaction distances and correlation time used are given in Table I. The interaction distances generally show the expected changes when compared to the VO(acac)$_2$–methanol system. The high value for E_a appears unusual but actually corresponds closely to that expected from the temperature dependence of the viscosity of trichloroethanol (8.5 kcal).[22]

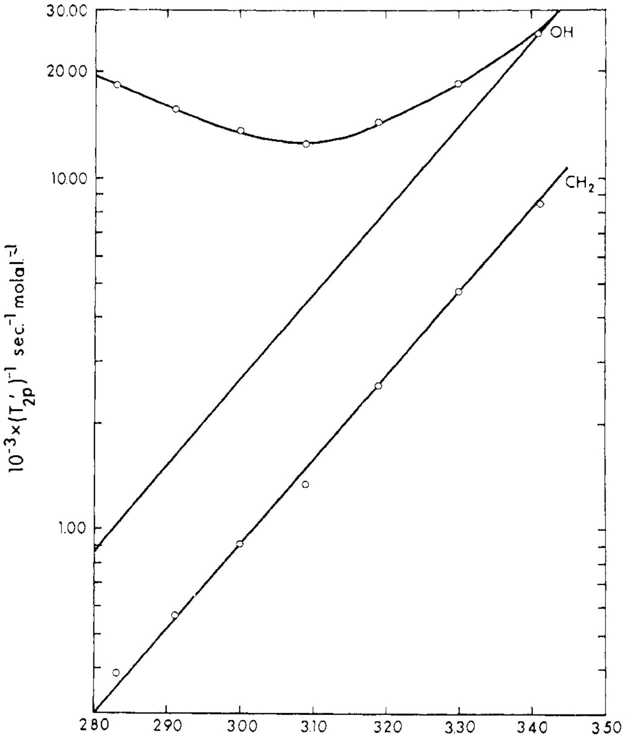

Figure 4.—Temperature dependence of $(T'_{2p})^{-1}$ for the hydroxy and methylene protons in trichloroethanol solutions of bis(acetylacetonato)vanadyl.

Chemical-exchange control of the hydroxy proton $(T'_{2p})^{-1}$ is again observed at high temperature, but there is no exchange control of the nuclear relaxation of the methylene protons. The faster exchange in this system is consistent with either hydrolysis (eq 11),

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[25] R. P. Dodge, D. H. Templeton, and A. Zalkin, *J. Chem. Phys.*, **35**, 55 (1961).

interchange (eq 12 and 13), or intramolecular proton transfer (eq 14). Since trichloroethanol is a stronger acid than methanol, it is expected to show faster proton transfer. Although the equilibria would not be so favorable for hydrolysis or interchange, the faster proton transfer might compensate for the smaller concentration of exchanging species.

V. Solvent Proton Relaxation in Trifluoroethanol Solution of VO(acac)$_2$.—It is apparent from the temperature dependence of $(T'_{2p})^{-1}$ in this system (Figure 5) that no chemical exchange controlled line broadening is observed for either the hydroxy or methylene protons.

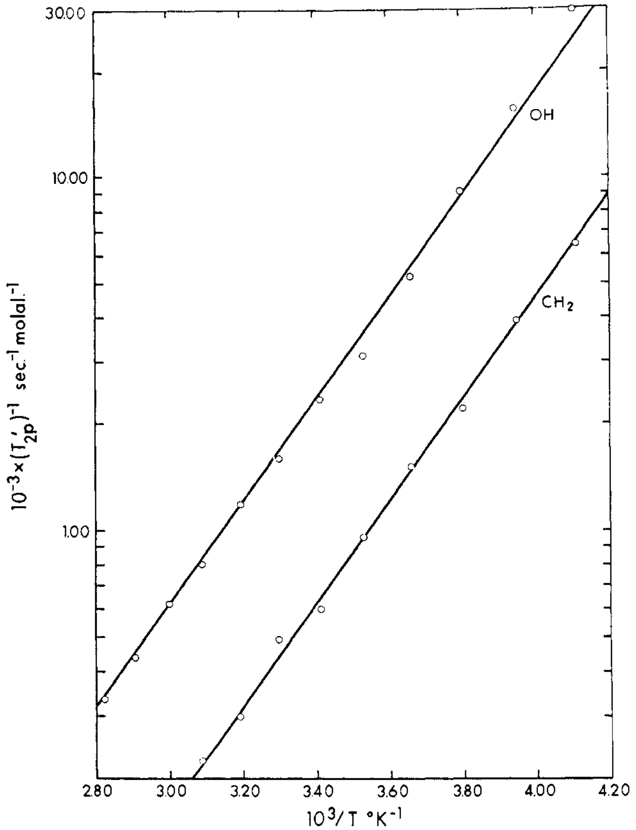

Figure 5.—Temperature dependence of $(T'_{2p})^{-1}$ for the hydroxy and methylene protons in trifluoroethanol solutions of bis(acetylacetonato)vanadyl.

Examination of the interaction distances given in Table I reveals some rather unexpected values. The inner-sphere interaction distances are shorter than the values for $VO(CH_3OH)_5^{2+}$, exactly the reverse of the expected trend as discussed for VO(acac)$_2$ in Cl_3CCH_2OH. The large errors given in the structural determination of CF_3CH_2OH,[26] by electron diffraction, do not preclude the possibility that the bond angles are rather different from those in methanol, and, therefore, the relative interaction distances of the OH and CH$_2$ protons may be different. Extrapolation of the results from CCl_3CH_2OH would indicate that the hydroxy proton exchange lifetime may be shorter than T_{2m} and there may be some hyperfine contribution to the hydroxy proton broadening as well.

Conclusions

The nmr line broadening of solvent alcohol protons by various vanadyl complexes indicates that there is a rapidly exchanging solvent molecule in the coordination position *trans* to the vanadyl oxygen. This conclusion rests primarily on the unusual ratio of hydroxy to methyl or methylene proton line broadenings. It is found that this ratio can be quantitatively explained by assuming one rapidly exchanging inner-sphere solvent molecule plus the usual outer-sphere molecules all interacting with the unpaired electron spin by a dipole–dipole mechanism.

Chemical exchange control of the nmr line broadening has been observed for the hydroxy alcohol proton in all systems except VO(acac)$_2$ in CF_3CH_2OH. The methyl or methylene proton line broadening was controlled by chemical exchange only for $VO(CH_3OH)_5^{2+}$ in CH_3OH. In the latter system the methyl proton broadening is associated with whole solvent molecule exchange from the four coplanar positions. The faster hydroxy proton exchange is caused by proton dissociation from the coordinated methanol molecules, analogous to that observed for $VO(H_2O)_5^{2+}$ in water.

Several mechanisms have been considered to explain the hydroxy proton exchange in the various vanadyl–acetylacetonate chelate systems. Protonation of the vanadyl oxygen is not consistent with the expected low basicity of this site. A partially solvolyzed species undergoing exchange is not consistent with the lack of acid dependence of the hydroxy proton exchange rate. This mechanism also requires that the inner-sphere relaxation time for the hydroxy protons is 30 times greater than that for the methyl protons for VO(acac)$_2$ in methanol if whole solvent molecule exchange is much faster than in $VO(CH_3OH)_5^{2+}$, as predicted from the results of Wüthrich and Connick.[19] Proton dissociation from a solvent molecule *trans* to the vanadyl oxygen is eliminated because the whole solvent molecule exchange rate from this site is much greater than the observed rates. Finally two mechanisms designated "interchange" and "intramolecular proton transfer" have been considered and both are found to be reasonably consistent with the observations.

The interchange mechanism proposes that normal proton dissociation occurs from a species with one end of an acetylacetonate in the position *trans* to the vanadyl oxygen and alcohol molecule in the position vacated by the end of the acetylacetone. The lack of chemical exchange controlled methyl or methylene proton line broadening requires that the hyperfine coupling constant for these protons is 10 times less than that for the hydroxy protons. This mechanism does not seem consistent with the low and more favorable $\Delta S^{\ddagger}$ and faster exchange in the VO(acac)$_2$–methanol system compared to the $VO(CH_3OH)_5^{2+}$–methanol system but is otherwise consistent with the results.

The results may also be explained by an intramolecular proton transfer from the solvent molecule *trans* to vanadyl oxygen to one of the acetylacetone

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[26] R. L. Livingston and G. Vaughan, *J. Am. Chem. Soc.*, **78**, 2711 (1956).

oxygen atoms. This mechanism requires that proton relaxation in the *trans* position is slower than chemical exchange but that relaxation of the proton on the acetylacetone oxygen is faster than chemical exchange. This condition seems reasonable since the electron nuclear hyperfine coupling constant is expected to be much greater for protons in the *xy* plane of the complex. This mechanism is consistent with the greater exchange rate and more favorable entropy for $VO(acac)_2$ in CH_3OH compared to $VO(CH_3OH)_5^{2+}$ in CH_3OH. The less favorable entropy for methanol hydroxy proton exchange with $VO(tfac)_2$ compared to $VO(acac)_2$ also is compatible with this mechanism.

An estimate of the relative basicity of solvent methanol and a coordinated acetylacetone oxygen may be made by comparing equilibrium constants for the reactions

$$VO(acac)_2CH_3OH + CH_3OH \xrightleftharpoons{K_{15}} VO(acac)_2CH_3O^- + CH_3OH_2^+ \quad (15)$$

$$VO(acac)_2CH_3OH \xrightleftharpoons{K_{16}} VO(acac_2H)CH_3O^- \quad (16)$$

Reasonable estimates based on the assumption that the reverse reactions are diffusion controlled would indicate that $K_{15} \approx 10^{-8}$ and $K_{16} \approx 5 \times 10^{-6}$. With due account for the difference in concentration of the bases this result indicates that coordinated acetylacetone is from 10 to 100 times stronger a base than a solvent methanol molecule. This result does not seem intuitively reasonable but is too approximate to constitute a strong argument against the intramolecular proton-transfer mechanism. More knowledge on the charge distribution in these complexes and the acidity of coordinated ligands is obviously required.

The solvent-exchange rates summarized in Table III do not show any regularity. In fact the higher $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for methanol exchange with Co^{2+} and Ni^{2+} compared to water is exactly opposite to the change observed in the vanadyl systems. The generality and mechanistic implications of these differences must await further exchange studies in other solvents.

Table III

Rate Parameters for Solvent Molecule Exchange of Water and Methanol

Metal ion	$10^{-3}k$, sec^{-1} (25°) Methanol	Water	$\Delta H^{\ddagger}$, kcal mol^{-1} Methanol	Water	$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1} Methanol	Water
VO^{2+}	0.57	0.50	9.5	13.5	−14.2	−1.5
Co^{2+}	270	1100	13.8	8.0	12.5	−4.1
Ni^{2+}	1.0	27	15.8	11.6	8.0	+0.7

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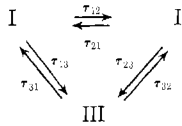
Appendix

The results of this work have required the use of a general expression for the transverse relaxation time of a nucleus exchanging between three sites. Swift and Connick have treated this situation previously but their development neglects exchange between minor species. Such an approximation was not possible in the present case. Although the results can be anticipated for certain limiting conditions by essentially phenomenological arguments, it seems worthwhile to give the complete expression for $(T_{2p})^{-1}$ for the three-site problem and discuss some of the simplifying limiting conditions.

The exchanging system may be designated as



where τ_{ij} represents the lifetime of the nucleus in species i as controlled by the $i \rightarrow j$ site exchange. The general development is based on the Bloch equations, as modified by McConnell, and follows the method used by Swift and Connick, except that all of exchanges are considered. It is assumed that the nucleus in site I only is being observed and that II and III are minor species which will not contribute to the nmr signal of site I. The usual slow-passage, steady-state assumption is also used. After considerable algebraic manipulation, it is found that

$$(T_{2p})^{-1} = (T_2)_{\text{obsd}}^{-1} - (T_{21})^{-1} = \frac{\begin{gathered}\left\{\left(\frac{1}{T_{22}} + \frac{1}{\tau_{21}}\right)\lambda_3 + \frac{1}{\tau_{23}}\left(\frac{1}{T_{23}} + \frac{1}{\tau_{31}}\right)\right\}\left\{\frac{1}{\tau_{12}}\left(\frac{\lambda_3}{T_{22}} + \frac{1}{\tau_{23}T_{23}}\right) + \frac{1}{\tau_{13}}\left(\frac{\lambda_2}{T_{23}} + \frac{1}{\tau_{32}T_{22}}\right)\right\} + \frac{1}{\tau_{12}}\left\{(\lambda_3^2 + \Delta\omega_3^2)\Delta\omega_2^2 + \right. \\ \left.\left(\frac{1}{T_{22}} + \frac{1}{\tau_{23}}\right)\Delta\omega_3^2\lambda_2 + \left(\frac{2}{\tau_{32}} + \frac{1}{\tau_{31}}\right)\frac{\Delta\omega_2\Delta\omega_3}{\tau_{23}}\right\} + \frac{1}{\tau_{13}}\left\{\left(\lambda_2^2 + \Delta\omega_2^2\right)\Delta\omega_3^2 + \left(\frac{1}{T_{23}} + \frac{1}{\tau_{32}}\right)\Delta\omega_2^2\lambda_3 + \right. \\ \left.\left(\frac{2}{\tau_{23}} + \frac{1}{\tau_{21}}\right)\frac{\Delta\omega_2\Delta\omega_3}{\tau_{32}}\right\}\end{gathered}}{\begin{gathered}\left\{\left(\frac{1}{T_{22}} + \frac{1}{\tau_{21}}\right)\lambda_3 + \frac{1}{\tau_{23}}\left(\frac{1}{T_{23}} + \frac{1}{\tau_{31}}\right)\right\}^2 + \\ \lambda_2^2\Delta\omega_3^2 + \lambda_3^2\Delta\omega_2^2 + \frac{2\Delta\omega_2\Delta\omega_3}{\tau_{23}\tau_{32}} + \Delta\omega_2^2\Delta\omega_3^2\end{gathered}} \quad (1A)$$

where $\lambda_i = (T_{2i}^{-1} + \tau_{ij}^{-1} + \tau_{ik}^{-1})$; T_{2i} is the transverse relaxation time of the nucleus in the ith site and $\Delta\omega_i$ is the chemical shift of the nucleus in the ith site from that in site I in the absence of exchange. The relationship $\tau_{12}\tau_{23}\tau_{31} = \tau_{13}\tau_{32}\tau_{21}$ has also been used to obtain eq 1A.

The equation developed by Swift and Connick can be obtained from (1A) simply by setting $(\tau_{32})^{-1} = (\tau_{23})^{-1} = 0$ and collecting terms.

With specific reference to the $VO(acac)_2$–methanol system the I, II, and III sites for the methanol protons are the bulk solvent, $VO(acac)_2CH_3OH$, and VO(acac)-(acacH)OCH_3, respectively. It was assumed that there is fast I–II exchange and that $(T_{22})^{-1}$ is small but $(T_{23})^{-1}$ is large owing to effective hyperfine interaction in III. That is $(\tau_{21})^{-1} \gg (T_{22})^{-1}$, $(\tau_{23})^{-1}$ and $(\tau_{32})^{-1} \gg (\tau_{31})^{-1}$.[27,28] If it is also assumed that all $\Delta\omega_i$ terms are small, then

$$(T_{2\mathrm{p}})^{-1} = \frac{\tau_{21}}{\tau_{21}}\left\{\frac{1}{T_{22}} + \frac{\tau_{32}}{\tau_{23}(T_{23} + \tau_{32})}\right\} \tag{2A}$$

If $T_{23} \ll \tau_{32}$ because of the hyperfine interaction, then

$$(T_{2\mathrm{p}})^{-1} = \frac{\tau_{21}}{\tau_{12}}\left(\frac{1}{T_{22}} + \frac{1}{\tau_{23}}\right) = P_{\mathrm{m}}(\tau_{23})^{-1} \tag{3A}$$

where $P_{\mathrm{m}} = [\mathrm{VO(acac)_2CH_3OH}]/[\mathrm{CH_3OH}]$. The initial condition that $(T_{22})^{-1}$ is small has been applied to the center expression of (3A).

It is also possible in the present system that only $\Delta\omega_2$ and $(T_{22})^{-1}$ are small relative to the other values in (1A), but that $\Delta\omega_3$ cannot be ignored. This would be more consistent with the condition that T_{23} is short due to a hyperfine interaction since this interaction requires a finite electron–nuclear coupling constant and therefore some finite value for $\Delta\omega_3$. If terms in $\Delta\omega_2$ and $(T_{22})^{-1}$ are dropped and noting that $\lambda_3(\tau_{21})^{-1} + (\tau_{23})^{-1}((T_{23})^{-1} + (\tau_{31})^{-1}) \approx \lambda_3((\tau_{21})^{-1} + (\tau_{23})^{-1})$ since $\lambda_3((\tau_{21})^{-1} + (\tau_{23})^{-1}) \gg (\tau_{32}\tau_{23})^{-1}$, then

$$(T_{2\mathrm{p}})^{-1} = \frac{\left\{\dfrac{1}{\tau_{12}\tau_{23}} + \dfrac{1}{\tau_{13}}\left(\dfrac{1}{\tau_{21}} + \dfrac{1}{\tau_{23}}\right)\right\}\left(\dfrac{\lambda_3}{T_{23}} + \Delta\omega_3{}^2\right)}{\left(\dfrac{1}{\tau_{21}} + \dfrac{1}{\tau_{23}}\right)(\lambda_3{}^2 + \Delta\omega_3{}^2)} \tag{4A}$$

The right-hand terms of the numerator and denominator will cancel under either of the probable conditions $(T_{23})^{-1} \gg (\tau_{32})^{-1}$, $(\tau_{31})^{-1}$ or $\Delta\omega_3{}^2 > \lambda_3{}^2$. If it is also assumed[28] that $(\tau_{21})^{-1} > (\tau_{23})^{-1} > (\tau_{13})^{-1}$, then

$$(T_{2\mathrm{p}})^{-1} = \frac{\tau_{21}}{\tau_{12}}\left(\frac{1}{\tau_{23}}\right) = P_{\mathrm{m}}(\tau_{23})^{-1} \tag{5A}$$

The various limiting conditions which have been discussed correspond to easily recognized situations. If $(T_{23})^{-1}$ is short, then nuclear relaxation in site III is very fast and the rate-limiting step for the relaxation in site I is the exchange into III. This might be either I–III or II–III exchange, and under the present circumstances it seems most likely that II–III exchange is faster. Then, as long as I–II exchange is faster than II–III exchange, the nuclear relaxation in site I is controlled by the II–III exchange. Similar considerations apply when $\Delta\omega_3$ is large but then the relaxation occurs through the change in precessional frequency or dephasing of nuclei from site I.

[27] Values for the exchange lifetimes may be estimated from ref 3, 4, and 28 and the present results on $\mathrm{VO(CH_3OH)_5{}^{2+}}$ in methanol.

[28] E. Grunwald, C. F. Jumper, and S. Meiboom, *J. Am. Chem. Soc.*, **84**, 4664 (1962).

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Spectral and Magnetic Studies on Thiourea Complexes of Some Metal Thiocyanates

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Infrared and electronic spectra and magnetic measurements are reported for the compounds $\mathrm{M(tu)_2(NCS)_2}$ (M = Mn, Fe, Co, Ni, Cd; tu = thiourea). Mössbauer results for the iron compound are also presented. The electronic spectrum of the iron compound is interpreted in terms of a strongly tetragonal ligand field, but for the other compounds too few bands were observed to permit a satisfactory analysis. The manganese compound shows negative and the nickel one positive magnetic interactions but the temperature dependence of the susceptibilities cannot be accounted for by the one-dimensional Ising model. The origin of the magnetic interactions is discussed in terms of the electron configuration of the ions.

Introduction

In the isomorphous[2] series of compounds $\mathrm{M(tu)_2(NCS)_2}$ (M = Mn, Fe, Co, Ni, Cd), the coordination polyhedron of the metal ion approximates to D_{4h} symmetry, with infinite chains of bridging sulfur atoms from the thiourea in the plane and nitrogen-bonded thiocyanate groups in the axial positions.[3] The nickel–thiocyanate bond distance (1.99 Å) is one of the shortest known, whereas the nickel–sulfur distances (2.56 and 2.53 Å) are appreciably longer than in $\mathrm{Ni(tu)_4Cl_2}$ (2.46 Å).[4] As a part of a study of the spectral and magnetic properties of the complexes of sulfur-donor ligands, we now report the electronic and infrared spectra and the magnetic properties of this interesting series of compounds.

Experimental Section

Preparation of Compounds.—The following general method was used except as stated below. The calculated quantity of thiourea was added to a solution of the metal thiocyanate in water, heated to dissolve the solid, filtered, and cooled (for cobalt and cadmium) or evaporated until crystallization commenced (for nickel and manganese). After filtration the complexes were dried at 50° *in vacuo*. For manganese, only about

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[3] M. Nardelli, G. F. Gasparri, G. G. Battistini, and P. Dominio, *Acta Cryst.*, **20**, 349 (1966).

[4] A. Lopez-Castro and M. R. Truter, *J. Chem. Soc.*, 1309 (1963).