k_5, are listed in Table V along with the calculated concentrations of Hox^- and ox^{2-}.

In Figure 8, $k_5/[Hox]$ is plotted as a function of the $[ox]/[Hox^-]$ ratio. The straight line in this figure suggests the rate law

$$k_5 = k_{5,Hox}[Hox] + k_{5,ox}[ox] \qquad (13)$$

The values of $k_{5,Hox}$ and $k_{5,ox}$ were determined to be $7.0 \pm 1.3 \times 10^2$ M^{-1} s^{-1} and $1.29 \pm 0.06 \times 10^4$ M^{-1} s^{-1}, respectively.

It is interesting to compare these rate constants with the values of k_{Hox} and $k_{exptl,ox}$ from eq 3 and 4. For the oxalate-exchange process with $VO(ox)_2^{2-}$, $k_{exptl,Hox}$ was larger than $k_{exptl,ox}$, while $k_{5,ox}$ is much larger than $k_{5,Hox}$ for the formation of $VO(ox)_2^{2-}$. The larger value of $k_{5,ox}$ as compared to the value of $k_{5,Hox}$ can be explained by the assumption that the divalent negative oxalate ion–VO_2^{2+} reaction is primarily a Coulombic process and thus should be faster than the corresponding reaction with the monovalent Hox species. On the other hand, since the $VO(ox)_2^{2-}$ complex has a negative charge, the monovalent Hox^- exchange should be faster than the divalent ox^{2-} exchange with $VO(ox)_2^{2-}$. This is exactly what is observed experimentally.

This ratio of the formation rate constants $k_{5,ox}/k_{5,Hox}$ for reaction 5a corresponds to 18.4 ± 4.2. This value can be compared with the ratio of the theoretically calculated association constants from the Fuoss equation[16] for the reaction between $VO^{2+}(aq)$ and ox^{2-} or Hox^-

$$K_{os(ox)}/K_{os(Hox)} = 23.6$$

The agreement between the calculated and experimental values for these ratios suggests that ligand substitutions on $VO^{2+}(aq)$ are mainly controlled by the electrostatic forces between $VO^{2+}(aq)$ and the various ligands and that the corresponding chelation processes are associative controlled.

Conclusions

It was demonstrated in this paper that ^{13}C NMR spectrometry can be used effectively to determine the rate of ligand-exchange processes for oxovanadium(IV) complexes. These values compare well with the corresponding ^{19}F NMR measurements.

The experiments reported here support the earlier results[4-6] that indicate that ligand-substitution reactions on oxovanadium(IV) complexes are essentially associative. Furthermore, the charge of the entering ligands, $Hmal^-$ and ox^{2-}, is of particular importance in determining the rates for both the ligand-exchange reactions with $VO(ox)_2^{2-}$ and the rate of complex formation for $VO^{2+}(aq)$ to form $VO(ox)_2^{2-}$.

The chelation process starting with $VO(gly)glyF^-$ to form $VO(gly)_2$ is also consistent with the preliminary observations reported earlier,[6] and the results clearly show that the chelation process is associative and is not dissociation (water or anion) controlled.

A similar unidentate ligand complex for the reaction between VO^{2+} and oxalic acid was observed just as in the reactions of glycine[13] and malonic acid[14] with VO^{2+}. The stability constant for the $VOHox^+$ reaction is 10.1 M^{-1}, which is somewhat smaller than the value of 44.7 M^{-1} for the corresponding malonato complex, $VOHmal^-$. The difference between these stability constants can be readily explained from the different pK_2 values for these ligands in that $pK_2(H_2ox) = 1.12$ and $pK_2(H_2mal) = 2.80$.

Registry No. $VO(gly)glyF^-$, 80327-44-2; $VO(ox)_2^{2-}$, 17569-94-7; $VO(gly)_2$, 15283-90-6; F_2, 7782-41-4; $VO(H_2O)_5^{2+}$, 15391-95-4; H_2ox, 144-62-7.

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Nitrogen-14 Magnetic Resonance Studies of the Effect of Pressure and Temperature on the Rate of Exchange of Acetonitrile Solvent on Iron(II) and Manganese(II) Perchlorates

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The pressure and temperature dependences of ^{14}N NMR line widths yielded the following activation parameters for the exchange of acetonitrile solvent on iron(II) perchlorate: $\Delta H^* = 41._4$ kJ mol^{-1}, $\Delta S^* = +5._3$ J K^{-1} mol^{-1}, $k^{298} = 6.6 \times 10^5$ s^{-1}, and $\Delta V^*(259–264\ K) = +3._0$ cm^3 mol^{-1}. For acetonitrile exchange on manganese(II) perchlorate, the parameters were as follows: $\Delta H^* = 29._6$ kJ mol^{-1}, $\Delta S^* = -8._9$ J K^{-1} mol^{-1}, $k^{298} = 1.3_6 \times 10^7$ s^{-1}, and $\Delta V^*(252–260\ K) = -7._0$ cm^3 mol^{-1}. Problems concerning the mechanistic significance of these data, and inconsistencies with ΔH^* and ΔS^* values of some earlier reports, are discussed.

We have recently reported the results of a study of the effect of pressure on the rate of exchange of acetonitrile solvent on nickel(II) and cobalt(II),[2] using nitrogen-14 FT NMR line-broadening measurements. That study complemented those of Meyer, Newman, and Merbach[3,4] using proton FT NMR, which is not well suited to this purpose in the case of the cobalt(II) system because, at temperatures high enough to preclude freezing the solvent on application of pressure, the "slow-exchange" approximation of Swift and Connick[5] is no longer applicable; i.e., the ^1H line broadening due to the presence of the paramagnetic ion is not simply related to the solvent-exchange rate from the first coordination sphere.

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0020-1669/82/1321-1141$01.25/0

For iron(II) and manganese(II) in acetonitrile, the relatively fast solvent-exchange rates effectively preclude high-pressure kinetic measurements using ^1H NMR, and consequently ^{14}N (or possibly ^{13}C) NMR must be used, as in the present study. Even with ^{14}N NMR, however, low temperatures are needed to remain within the "slow-exchange" (Arrhenius or Eyring) region of the Swift–Connick equation,[5] and we have therefore been limited to pressure ceilings of 140 MPa for the iron(II) and 110 MPa for the manganese(II) solutions by the risk of freezing the solvent.[6-8] Nevertheless, adequately reliable values for the respective volumes of activation ΔV^* (eq 1) have

$$(\partial \ln k/\partial P)_T = -\Delta V^*/RT \qquad (1)$$

been obtained, and incidentally to this main purpose, the temperture dependence of ^{14}N line broadening in the title systems has been reexamined in an attempt to reconcile some differences among previous reports.[9-12]

Experimental Section

Materials. Acetonitrile (Baker Analyzed or Fisher Certified reagent grades were used, with identical results) was purified as described previously[2] and subsequently handled under a dry-nitrogen atmosphere after vacuum degassing.

Iron(II) perchlorate acetonitrile solvate was made by starting from iron wire (Baker Analyzed reagent) by the method of Lincoln and West,[10] except that Linde 3A molecular sieves, dried for over 12 h at 220 °C, were used. There was a significant loss of iron(II) into the sieve in this procedure. Analysis of the solid product indicated somewhat less than six acetonitriles per iron, and solutions of $[Fe(CH_3CN)_6](ClO_4)_2$ made up for NMR work were therefore analyzed individually for iron(II) by spectrophotometry using 1,10-phenanthroline.[13]

Hexaaquamanganese(II) perchlorate was made by treating an excess of MnO_2 with aqueous $HClO_4$ and 30% H_2O_2 and filtering and evaporating the solution on a steam bath until crystallization occurred. The product was recrystallized from water, dried under vacuum, and checked for purity by EDTA titration. Solutions of hexakis(acetonitrile)manganese(II) perchlorate for the NMR experiments were prepared by dehydrating solutions of the hexaaqua compound in doubly distilled acetonitrile under reflux (typically, for 6 h) in a modified Soxhlet extractor with 4A molecular sieves in the thimble. The final water content of these solutions, and those of $[Fe(CH_3CN)_6](ClO_4)_2$, was below the detection limit of Karl Fischer titrations ($\lesssim 10^{-5}$ mol L^{-1}, i.e., much less than the concentrations of the paramagnetic ions).

^{14}N NMR measurements at atmospheric pressure were made at 6.48 MHz (2.114 T) with a Bruker WH-90 Fourier transform spectrometer as previously described.[2] Temperatures were measured, before and after pulsing, with a copper–constantan thermocouple, which was calibrated against a standardized quartz thermometer. The temperature readings were unaffected by the magnetic field. Typically, 20 000 pulses of 35 μs were applied with a sweep width of 50 kHz and a delay time of 700 μs, with use of 2K data points and quadrature detection. Artificial line broadening of up to 10% of the peak width $\nu_{1/2}$ at half-height was applied to reduce noise and was subtracted before calculating the ^{14}N transverse relaxation times T_2 ($=1/\pi\nu_{1/2}$).

^{14}N NMR measurements at elevated pressures were conducted with use of the pressurizable probehead previously described[2] but now modified to include an evacuable thermally insulating jacket for the pressure vessel and provision for double-tuning the coil to 6.48 MHz (^{14}N) and 13.81 MHz (^2D). Optimum shim settings were established with use of the ^2D resonance of C_6D_6 in the sample tube, but with acetonitrile solutions it was necessary to use the external D_2O lock during observation of the ^{14}N signal. Temperatures, which were uniform to within ±0.2 °C over the length of the sample tube, were measured before and after pulsing with an internal copper–constantan thermocouple and were controlled with circulating methanol. Pressure was transmitted with hydraulic oil from a screw press. Spectrometer settings were as for atmospheric pressure measurements except that 40 000–60 000 pulses of 40-kHz sweep width were used.

Table I. Temperature Dependence of the Rate of Exchange of CH_3CN Solvent with $M(CH_3CN)_6{}^{2+}$

M	NMR	ΔH^*/kJ mol^{-1}	ΔS^*/J K^{-1} mol^{-1}	(A/h)/MHz (^{14}N)	k^{298}/s^{-1}
Fe	$^{14}N^a$	41.4 ± 0.7	5.3 ± 2.5	5.12 ± 0.11	6.6×10^5
	$^{14}N^b$	40.6 ± 2.9	1.3 ± 9.2	5.0	5.5×10^5
	$^1H^c$	36.4	−14.9		4.3×10^5
Mn	$^{14}N^{a,d}$	29.6 ± 0.5	−8.9 ± 2.0	3.60 ± 0.07	1.36×10^7
	$^{14}N^{d,e}$	30.3 ± 1.1	−7.5 ± 3.4	3.2	1.2×10^7
	$^1H,^{14}N^f$	15 ± 2	−63 ± 12	3.6 ± 0.4	0.85×10^7
	$^{14}N^{a,g}$	23.3 ± 4.0	−32 ± 14	3.24 ± 0.25	1.08×10^7
	$^1H^c$	35.9	19.0		3.1×10^7

[a] This work. Uncertainties cited are standard deviations in the nonlinear least-squares fit. [b] Reference 10. [c] Reference 11. [d] Assuming $T_{1e} = T_{2e}$ of eq 10. [e] Reference 9. [f] Reference 12. [g] Using τ_{A_1} values of ref 12; temperature range 298–343 K only.

Magnetic moment determinations were made with use of the ^1H NMR of the CH_3CN solvent taken with a Perkin-Elmer R-24B 60-MHz (^1H) spectrometer.[14]

Results

$[Fe(CH_3CN)_6](ClO_4)_2$ Solutions at Variable Temperature. Measurements of T_2 were made at temperatures T ranging from 249 to 335 K. Values[15] of the reduced transverse relaxation time $T_{2p}p_m$ due to the presence of the paramagnetic ion were calculated from

$$T_{2p}{}^{-1} = T_2{}^{-1} - T_{2s}{}^{-1} \qquad (2)$$

where T_2 and T_{2s} refer to the solution and the pure solvent,[2] respectively, and p_m is the mole fraction of solvent in the first coordination sphere, assuming a coordination number of 6.[10] At a given temperature, $T_{2p}p_m$ data over the range of p_m used (0.0036–0.0082) agreed well among themselves and with those obtained by West and Lincoln[10] at higher p_m (0.045–0.091), so that any influence of the perchlorate counterion on T_{2p} must be negligible. The full Swift–Connick equation[5]

$$\frac{1}{T_{2p}} = \frac{p_m}{\tau_m}\left[\frac{T_{2m}{}^{-2} + (T_{2m}\tau_m)^{-1} + (\Delta\omega_m)^2}{(T_{2m}{}^{-1} + \tau_m{}^{-1})^2 + (\Delta\omega_m)^2}\right] + \frac{1}{T_{2os}} \qquad (3)$$

(where T_{2m} is the relaxation time of ^{14}N in CH_3CN while coordinated to the paramagnetic ion, $\Delta\omega_m$ is the ^{14}N chemical shift of complexed CH_3CN relative to free solvent, τ_m is the time constant for exchange of CH_3CN between the first coordination sphere and bulk solution, T_{2os} is the contribution to T_2 from outer-coordination-sphere interactions, and the *electronic* longitudinal relaxation time T_{1e} of the central metal ion is taken to be negligibly short) reduces in this case to

$$T_{2p}p_m = \tau_m + 1/(\tau_m(\Delta\omega_m)^2) \qquad (4)$$

since $\tau_m T_{2m} >> (\Delta\omega_m)^{-2}$ and there was no discernible evidence for a contribution from outer-sphere effects at the lower temperatures (in contrast to the nickel(II)–CH_3CN case,[2] for which solvent exchange to the first coordination sphere is some 200-fold slower than for iron(II) at 298 K).

The rate coefficient k for inner-sphere solvent exchange is given by the Eyring equation

$$k = \tau_m{}^{-1} = 2.083 \times 10^{10} T \exp(\Delta S^*/R - \Delta H^*/RT) \text{ s}^{-1} \qquad (5)$$

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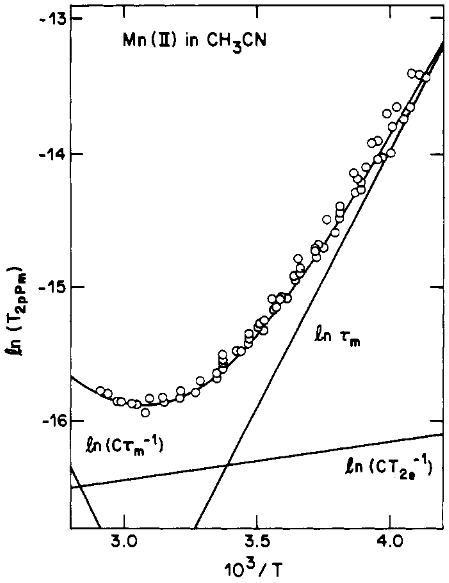

Figure 1. Temperature dependence of the reduced ^{14}N NMR line width $T_{2p}p_m$ for manganese(II) perchlorate in acetonitrile at 0.1 MPa.

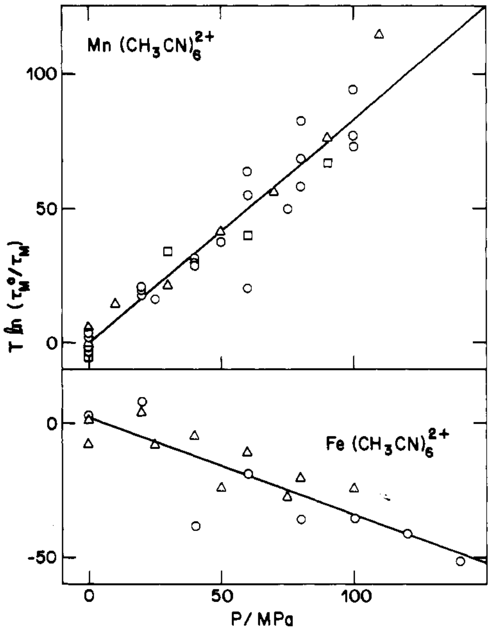

Figure 2. Pressure dependence of the relative rate coefficients for the exchange of acetonitrile solvent on $Mn(CH_3CN)_6^{2+}$ and $Fe(CH_3CN)_6^{2+}$. Upper frame: triangles, 255.9 K; circles, 252.3 and 252.5 K; squares, 259.5 K. Lower frame: triangles, 258.9 K; circles, 263.8 K.

and the chemical shift $\Delta\omega_m$ may be assumed to follow the Curie-law-based equation

$$\Delta\omega_m/\omega_0 = 2\pi(A/h)\mu_{eff}\mu_B[S(S+1)]^{1/2}/3kT\gamma_N \quad (6)$$

where the symbols have their usual meanings.[16,17] Combination of eq 4–6 permitted reduction of the $T_{2p}p_m$ data[15,18] to the activation parameters ΔH^* and ΔS^* and the scalar coupling constant A/h (Table I) through a nonlinear least-squares computation, with the measured magnetic moment $\mu_{eff} = 5.2 \pm 0.1$ μ_B of $Fe(CH_3CN)_6^{2+}$ in solution (cf. 5.4 ± 0.2 μ_B reported for solid $[Fe(CH_3CN)_6](PF_6)_2$[19]). Two significant points emerge: the results are in excellent agreement with the continuous-wave ^{14}N NMR data of West and Lincoln,[10] though less so with the ^{1}H data of Vigee et al.,[11] and the values of $T_{2p}p_m$ at the temperatures (−9.4, −14.3 °C) of the variable-pressure study described below differ from τ_m by negligible amounts (<0.8%, 0.4%).

$[Fe(CH_3CN)_6](ClO_4)_2$ Solutions at Variable Pressure. It was first established that the pressure dependence of the ^{14}N transverse relaxation time T_{2s} of pure acetonitrile was the same in the temperature regime of the present experiments as was previously reported[2] for higher temperatures, and T_{2p} values for the $Fe(CH_3CN)_6^{2+}$ solutions over the pressure range 0.1–140 MPa at 263.8 and 258.9 K were derived accordingly (eq 2). Putting $k = (T_{2p}p_m)^{-1}$ and assuming from experience[2,20] that ΔV^* for solvent exchange may be taken to be independent of pressure, we obtained representative values of k_0 (=k at pressure $P = 0$) for each variable-pressure data set from the integrated eq 1, and since ΔV^* will be sensibly constant over the narrow temperature range of the pressure experiments,[2] the unedited data have all been presented together as a plot of $T \ln (k/k_0)$ vs. P in Figure 2. From a least-squares determination of the slope, $\Delta V^* = +3.0 \pm 0.5$ cm^3 mol^{-1}; the correlation coefficient r seems rather poor (0.850) on account of the narrow pressure range available and the relatively small pressure effect, but the absolute value of ΔV^* is as reliable as most such data.

$[Mn(CH_3CN)_6](ClO_4)_2$ Solutions at Variable Temperature. Preliminary measurements of the temperature dependence of $T_{2p}p_m$ from 236 to 346 K (10^4p_m = 1.55–9.58) agreed well with those of Purcell and Marianelli[9] above 280 K, but the shortening of T_{2p} observed by these authors and by von Goldammer and Bassaris[12] below this temperature, and ascribed by them to outer-sphere interactions, was absent.[15] The definitive set of measurements[15] taken over the range 243–343 K in temperature and 0.524 × 10^4 to 3.037 × 10^4 in p_m, summarized in Figure 1, confirm this. Values of $T_{2p}p_m$ at a given temperature were independent of p_m, the source of the solvent, and the rigor of the dehydration procedure, so that the possibility that $T_{2p}p_m$ might have been influenced by ion pairing or by traces of water or other impurities can be discounted. Since acetonitrile exchange on Mn(II) is 4 × 10^3 times faster at 298 K than on Ni(II), it may well be that the outer-sphere effects discernible below 300 K (where $k \approx 3 \times 10^3$ s^{-1}) in the latter case remain unimportant for Mn(II) even at 240 K (where $k \approx 8 \times 10^5$ s^{-1}; see below), despite the anticipated influence[9] of the relatively long T_{1e} of Mn(II) on T_{2os} through a scalar coupling mechanism. Equation 3 can therefore be applied to our data without the final term, and since the longitudinal electronic relaxation time T_{1e} is relatively long for sextuplet Mn(II),[5,9] we have

$$(\Delta\omega_m)^2 << T_{2m}^{-2}, (T_{2m}\tau_m)^{-1} \quad (7)$$

and eq 3 reduces to

$$T_{2p}p_m = \tau_m + T_{2m} = \tau_m + C(T_{1e}^{-1} + \tau_m^{-1}) \quad (8)$$

where C is a constant given by[16]

$$C = 3/[4\pi^2(A/h)^2S(S+1)] \quad (9)$$

Direct measurements of T_{1e}, however, are not available. Purcell and Marianelli[9] reported measurements of the *tran-*

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sverse electronic relaxation time T_{2e}, which can be represented by

$$T_{2e}^{-1} = 4.5 \times 10^{7} \exp(292/T) \qquad (10)$$

and they assumed that $T_{1e} = T_{2e}$ to calculate ΔH^*, ΔS^*, and (A/h) from eq 5, 8 and 9, using the position of the minimum in the ln $(T_{2p}p_m)$ vs. T^{-1} plot to fix C. Our data[15,18] are well represented (Figure 1) by a nonlinear least-squares fit to the combined equations (5), (8), (9), and (10). The derived parameters (Table I) agree well with those of Purcell and Marianelli[9] from ^{14}N NMR and adequately with the ^{1}H data of Vigee et al.[11] These latter parameters[11] were derived under conditions where T_{1e} dominates eq 8 (the first term on the right-hand side of which was neglected accordingly) and consequently allow a good estimate of the asymptote

$$T_{2p}p_m = CT_{1e}^{-1} \qquad (11)$$

to be made, and this, together with the reported[11] (A/h) for ^{1}H, leads to an expression

$$T_{1e}^{-1} = 5 \times 10^{7} \exp(320/T) \qquad (12)$$

which is sufficiently close to eq 10 to indicate that T_{1e} and T_{2e} are the same, within the experimental uncertainty, up to 300 K at least.

Nevertheless, von Goldammer and Bassaris have concluded from their recent variable-frequency study[12] of ^{1}H and ^{14}N relaxation in acetonitrile solutions of $Mn(ClO_4)_2$ that T_{1e} and T_{2e} are *not* the same. Direct measurements of these times were not made, but the ^{1}H data gave values of $\tau_{A1}^{-1} = \tau_m^{-1} + T_{1e}^{-1}$, which can be applied to the solution of eq 8 for ^{14}N relaxation over the range 298–413 K. Application of the τ_{A1} values of von Goldammer and Bassaris[12] to our ^{14}N $T_{2p}p_m$ measurements[15,18] at $298 \leq T \leq 343$ K according to eq 5, 8, and 9 gave activation parameters (Table I) that were not in good agreement with the values cited by these authors.[12] Our parameters were used to estimate apparent values of T_{1e} from eq 5, 8, and 9;[15] ln T_{1e} was a nonlinear function of T^{-1} showing a maximum near 320 K such that T_{1e} became as short as T_{2e} just at the upper temperature limit of Purcell and Marianelli's measurements of T_{2e} (~350 K). The von Goldammer–Bassaris τ_{A1} data[12] are thus not necessarily inconsistent with the Purcell–Marianelli[9] measurements, although the latter give no hint of a faster T_{1e} at $T > 350$ K.

$[Mn(CH_3CN)_6](ClO_4)_2$ Solutions at Variable Pressure. The data obtained at 252.3, 252.5, 255.9, and 259.5 K, 0.1–110 MPa, were treated as described for the iron(II) pressure experiments, on two different bases. First, k was assumed to equal $(T_{2p}p_m)^{-1}$, in which case ΔV^* was found to be -6.0 ± 0.3 cm^3 mol^{-1}. This procedure, however, assumes that the factor $C(T_{1e}^{-1} + \tau_m^{-1})$ in eq 8 is negligible at the temperatures of the pressure experiments, whereas, as Figure 1 shows, the results of the variable-temperature study indicate that it constitutes 11–16% of $T_{2p}p_m$ over the relevant temperature range, mainly because of the T_{1e}^{-1} term. Alternatively, then, it was assumed that T_{1e} was equal to the T_{2e} of eq 10 and that the pressure dependences, like the temperature dependences, of C and T_{1e} were negligible for the purpose of extracting realistic values of τ_m from $T_{2p}p_m$, which was done for each temperature by solving the quadratic equation in τ_m obtained by combining eq 8 and 10. The results are summarized in Figure 2 and yield $\Delta V^* = -7.0 \pm 0.4$ cm^3 mol^{-1} ($r = 0.954$). We consider the assumption $T_{1e} = T_{2e}$ to be correct, at least at the relevant temperatures, but ΔV^* would not be greatly affected if this were not so, since T_{2e} cannot exceed T_{1e} and, in the limiting case where $T_{1e} >> \tau_m$, $C\tau_m^{-1}$ would constitute over 99.7% of $T_{2p}p_m$ in the pressure experiments. Thus, one can state conservatively that $-7.4 \leq \Delta V^* \leq -5.7$ cm^3 mol^{-1}, a value of -7.0 cm^3 mol^{-1} being most probable.

Discussion

The variable-temperature results summarized in Table I serve to emphasize once again[4,24] the sensitivity of the parameters ΔH^* and ΔS^* to the assumptions made in analyzing the $T_{2p}p_m$ data. For iron(II) perchlorate in acetonitrile, the incursion of the outer-sphere term T_{2os}^{-1} can be ignored for ^{14}N resonance, for which the chemical shift $\Delta\omega_m$ is large enough that the "Eyring region" of eq 3 extends to sufficiently high temperatures. For ^{1}H resonance, however, "fast-exchange" contributions (cf. last term of eq 4) and "outer-sphere" effects reduce the slope of eq 3 in the very limited Eyring region so that the apparent ΔH^* and ΔS^* for inner-sphere solvent exchange are lowered even though the derived rate coefficient k may be quite realistic. The susceptibility of enthalpy and entropy terms to mutually compensatory errors is inherent in any Eyring/Arrhenius (or van't Hoff) analysis of the temperature dependence of kinetic (or equilibrium) data generally[25] but emerges especially strongly in NMR line-broadening studies because of the problem of taking all possible contributions to the line width properly into account, the effect of oversight in this respect being usually to reduce the apparent values of ΔH^* and ΔS^*. From this standpoint, the agreement between the activation parameters from different sources for the Fe(II) acetonitrile exchange is actually quite good, the ^{14}N data being the more reliable.[11]

Definitive analysis of the temperature dependence of the relatively rapid Mn(II) acetonitrile exchange must await direct measurement of the unusually slow longitudinal electronic relaxation time T_{1e} of the $Mn(CH_3CN)_6^{2+}$ ion. In the meantime, we have shown that T_{1e} values can be extracted from the report of Vigee et al.[11] that are, in effect, equal to the T_{2e} measurements of Purcell and Marianelli,[9,26] and it will be clear from Figure 1 that our ^{14}N line-width data are well represented over the whole temperature range 243–343 K by a combination of these T_{2e} data with eq 4–6 and the parameters of Table I. In particular, this analysis can be applied with confidence over the temperature range of the high-pressure experiments, which was our primary concern.

The alternative approach of von Goldammer and Bassaris[12] to estimation of the bracketed term of eq 8 is applicable only above 298 K and so covers only part of our data with an inevitably poorer fit. The derived activation parameters are somewhat lower than found by the first method, but not nearly as low as those reported by von Goldammer and Bassaris.[12] The discrepancy may be due, all or in part, to the presence of an "outer-sphere" contribution in their low-temperature data (as in those of Purcell and Marianelli,[9] who evidently allowed for it in extracting ΔH^* and ΔS^*), which we sought but did not observe. The origin of this is a matter for speculation; as explained above, we do not consider it likely that true outer-sphere effects would be important in the very labile Mn(II)–CH_3CN system. We would also expect some hint of the marked acceleration of T_{1e}^{-1} (as derived from the τ_{A1} data of ref 12) above ~330 K to be reflected in the T_{2e} values of Purcell and Marianelli, but this is absent. We have therefore adopted the analysis based on eq 10 and the equality of T_{1e} and T_{2e} until such time as direct measurements of T_{1e} become available.

The effect of pressure on the ^{14}N line widths was small, especially since the pressure range was kept small to avoid

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(26) The purported T_{2e} data of Purcell and Marianelli[9] are, strictly speaking, *lower limits* to T_{2e}, since unknown factors could have contributed to the observed ESR line widths, but the close correspondence with the T_{1e} values recovered from the report of Vigee et al.[11] makes it highly probable that they actually do represent T_{2e} and that they equal T_{1e} within the ~10–15% uncertainty inherent in this analysis.

Table II. Volumes of Activation ΔV^*/cm^3 mol^{-1} (at Temperature/K) for the Exchange of Solvent on M(solvent)$_6^{2+}$

M	H_2O[a]	CH_3OH[b]	DMF[c]	CH_3CN
Mn	−5.4 (298)	−5.0 (279)		−7.0 (252–260)[d]
Fe	+3.8 (298)	+0.4 (255)		+3.0 (259–264)[d]
Co	+6.1 (298)	+8.9 (279)	+6.7 (296)	+6.7 (266–272)[e,f]
Ni	+7.2 (298)	+11.4 (307)	+9.1 (297)	+7.3 (308–330)[e,g]

[a] ^{17}O NMR, ref 21. [b] ^{1}H NMR, ref 22. [c] ^{1}H NMR, ref 3. [d] ^{14}N NMR, this work. [e] ^{14}N NMR, ref 2. [f] Monnerat et al.[23] obtained $\Delta V^* = +7.7 \pm 1.7$ cm^3 mol^{-1} at 286 K using ^{13}C NMR; an earlier determination[3] using ^{1}H NMR was subject to large uncertainties. [g] Meyer et al.[3] obtained $\Delta V^* = +9.6 \pm 0.3$ cm^3 mol^{-1} at 294 K using ^{1}H NMR.

freezing the sample, and consequently the data illustrated in Figure 2 show considerable scatter. By the same token, however, the systems remained within the regions where τ_m dominates $T_{2p}p_m$ very strongly, throughout the pressure cycle. Furthermore, although integration of eq 1 with constant ΔV^* gives eq 13, which is in principle a two-parameter equation,

$$\ln k = \ln k_0 - P\Delta V^*/RT \tag{13}$$

one parameter ($\ln k_0$), unlike the ΔS^* term of eq 5, represents a directly measurable quantity (in fact, one that is more precisely measurable than the high-pressure k values), and so the problem of compensatory errors that plagues ΔH^* and ΔS^* determinations does not affect ΔV^* significantly. One can therefore present ΔV^* values with the confidence expressed by the statistical uncertainty limits.

The most striking feature of the ΔV^* values for solvent-exchange reactions collected in Table II is that they are quite similar for a given metal in each of the four very diverse solvents covered but vary from strongly positive for Ni(II) to moderately strongly negative for Mn(II). In terms of the molar volume V^0_s of the solvent, the gain (loss) of volume on releasing (coordinating) a molecule of solvent on going to the transition state for solvent exchange by dissociative (associative) activation actually varies significantly from solvent to solvent for a given metal ion, e.g., for Ni^{2+}, $\Delta V^*/V^0_s = 0.40$, 0.28, 0.12, and 0.14 for water, methanol, DMF, and acetonitrile, respectively. This may reflect the openness of the H-bonded structure of liquid water, the lesser degree of H-bonding in methanol, and the absence of H-bonded structuring in the dipolar aprotic solvents, resulting in a somewhat fortuitous similarity in ΔV^*. Nevertheless, the general trend in ΔV^* from Mn(II) to Ni(II), which can be taken to indicate a progressive change from associative to predominately dissociative activation, is clearly controlled by properties of the metal ion rather than of the sovlent, so that emphasis on d-orbital occupancy in interpreting this trend seems justified.[21,22,27-29] The entropies of activation ($\Delta S^* = -9$, +5, +21,[24] and +38[4] J K^{-1} mol^{-1} for Mn(II), Fe(II), Co(II), and Ni(II), respectively) exhibit the same trend as ΔV^*, as is often the case,[30,31] and may be similarly interpreted, but the uncertainties inherent in evaluating ΔS^*, as discussed above, render detailed consideration of these numerical values inappropriate.

The proposition that substitution on Mn(II) in solution is associatively activated can be expected to evoke skepticism,[32,33] since the limited data that exist on net substitution reactions of Mn(II) show a lack of sensitivity to the nature of the incoming ligand,[21] and hence the mechanism would be operationally classified as "dissociative interchange" (I_d) in the Langford–Gray scheme.[34] As has been pointed out,[21,27,29,35] associative activation involving the attack of "hard" ligands such as molecules with O- or N-donor atoms on "hard" centers such as Cr(III), Fe(III), or Mn(II) is unlikely to display a very wide range of nucleophilicities of incoming ligands ("selectivity"). It should be added, however, that the faster an associatively activated process is, the less selective it will becomes; this is a well-established phenomenon in organic chemistry[36] and will be examined at greater length in the inorganic context in a forthcoming article. Thus, while ΔV^* data for solvent exchange on M(solvent)$_6^{n+}$ indicate substitution to be associatively activated for M^{n+} = Cr^{3+}, Fe^{3+}, and Mn^{2+},[27] selectivity is marked for Cr(III)[35,37] (time scale $\approx 10^5$ s), less for Fe(III)[35,38,39] ($\approx 10^{-2}$ s), and possibly very limited on Mn(II)[21] ($\approx 10^{-7}$ s).

The possibility that a reaction may be associatively activated (S_N2 in the older terminology) and yet be legitimately classified as I_d arises because of the limitations inherent in operationism.[27] Alternative operational definitions such as selectivity[34] and ΔV^*[27] in the present case may lead to somewhat different classifications of phenomena. It is perhaps unfortunate that the words "associative" and "dissociative" appear in the Langford–Gray operational classification of the interchange category of substitution mechanisms;[34] "selective" and "unselective" might have conformed more closely to the operational criterion. In any event, we recommend that the Langford–Gray classification scheme should be used only with reference to its original operational basis of selectivity, within the interchange category at least. With other mechanistic criteria, a reaction may be said to be *associatively* (or *dissociatively*) *activated.*

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Registry No. [Fe(CH$_3$CN)$_6$](ClO$_4$)$_2$, 65413-87-8; [Mn(CH$_3$CN)$_6$](ClO$_4$)$_2$, 40791-27-3.

Supplementary Material Available: Listings of ^{14}N NMR line broadening measurements and of T_{1e} values calculated from the τ_{A1} values of ref 12 and a graph of the temperature dependence of the reduced ^{14}N NMR line width for manganese(II) perchlorate in acetonitrile (4 pages). Ordering information is given on any current masthead page.

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