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High Pressure Nuclear Magnetic Resonance Kinetics. 3. Proton Nuclear Magnetic Resonance Study of the Effect of Temperature and Pressure on the Exchange of Acetonitrile on Nickel(II)

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Abstract: The effect of temperature and pressure (up to 200 MPa) on the solvent exchange of $[Ni(CH_3CN)_6](ClO_4)_2$ in acetonitrile has been studied utilizing ^1H FT NMR chemical shifts and T_2 measurements of both free and bound resonances at 60 MHz. It is found that, in order to obtain reliable values of ΔH^* and ΔS^*, the full Swift-Connick equation must be used, whereas for ΔV^* a simplified analysis may be adopted. Values of the exchange parameters are $k_{298.1} = 2840 \pm 50\ s^{-1}$, $\Delta H^* = +64.3 \pm 0.9$ kJ mol^{-1}, $\Delta S^* = +37.0 \pm 2.8$ J mol^{-1} K^{-1}, $\Delta V^*_{294\ K} = +9.6 \pm 0.4$ cm^3 mol^{-1}. They are in accord with a dissociative interchange mechanism I_d.

I. Introduction

Ever since the pioneering work of Eigen and Wilkins,[1] which showed that, for aqueous solutions, the rates and activation parameters for ligand substitution were closely similar to those of solvent exchange, the study of the latter process has assumed fundamental importance. The correlations have since been extended to nonaqueous solutions[2] and, although deficiencies in the theory have been discussed in terms of solvent structure,[3] a basic tenet of all such ideas is that the mechanism usually has a dissociative activation mode. Direct evidence as to this point is by no means easy to obtain since, in such studies, the solvent concentration cannot be varied at will. As discussed by Swaddle,[4] although there are severe theoretical limitations in regarding the entropy of activation as a measure of "the increase in randomness", comparisons of ΔS^* for closely related systems such as solvent exchange for different ions and/or solvents should give useful mechanistic information. The fast exchange of solvent bound to a transition ion with bulk solvent has been widely studied ever since the work of Swift and Connick[5] using NMR line broadening, i.e., T_2 (sometimes coupled with chemical shift and T_1) measurements, but it is disappointing to note that the precision and reproducibility of such results is considerably less than those obtained using classical techniques. Particularly disturbing is the fact, not infrequently mentioned, that the experimental data obtained by different researchers are often closely similar and yet the derived activation parameters are often so different.[6]

The pressure dependence of a reaction rate may be discussed in terms of transition-state theory through ΔV^*, the volume of activation. Stranks[7] has discussed how this parameter should also yield useful diagnostic information. For reactions involving no charge separation or neutralization going from reactants to the transition state and hence, when electrostriction changes should be negligible, ΔV^* can be directly related to the partial bond formation, rupture, or stretching during the activation process. In principle, the volume of activation defined as

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

should be considerably less prone to error than ΔS^* since increasing rate with increasing pressure implies a negative ΔV^* and vice versa.

No such simple relation applies for ΔS^*, but it is readily shown that

$$\Delta S^*/R = \underbrace{\ln (k/T) - \ln (k_B/h)}_{-\Delta G^*/RT} \; \underbrace{-(1/T)\, \partial \ln (k/T)/\partial(1/T)}_{+\Delta H^*/RT} \qquad (2)$$

Errors in k produce only very small errors in ΔG^* owing to the logarithmic relationship. However, a reliable estimate of ΔH^* requires the knowledge of a differential term which is more difficult. This term is usually large and never changes sign. Furthermore, ΔS^*, a small term which may be of either sign, is obtained as the difference of two terms of similar magnitude and this accounts for the important error problem associated with ΔS^* determinations.

An alternative way of looking at the error problem on ΔS^* is to note that the first and last terms on the right-hand side of eq 2 represent the extrapolation of the tangent to the ln (k/T) vs. $1/T$ curve to $1/T = 0$. For "ideal" Eyring behavior, they simply represent the extrapolation of the straight line plot to

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$1/T = 0$. This extrapolation will in general be very long and prone to error.

Experimentally, it is usually found that errors in ΔV^* are less than those in ΔS^*[7] where similar experimental approaches have been used.

Until now, ΔV^* for solvent exchange from metal ions have only been available for the nonlabile +III transition metal ions.[7] However, recently we have reported from this laboratory a high pressure, high resolution probe head designed for ready attachment to a commercial FT NMR spectrometer[8] together with some preliminary results on ligand and solvent exchange reactions.[9] In this paper, we report a study of the temperature and pressure dependence of the solvent exchange reaction

$$\mathrm{Ni(CH_3CN)_6^{2+} + {}^*CH_3CN \rightleftharpoons Ni(CH_3CN)_5{}^*CH_3CN^{2+} + CH_3CN}$$

a system widely studied previously (although there is by no means accord as to the exchange parameters) together with a detailed analysis of the factors necessary to obtain reliable values of k, ΔH^*, ΔS^*, and ΔV^*.

2. Theory

The detailed expressions for the effect of solvent exchange on T_2, the transverse NMR relaxation time, and $\Delta\omega$,[10] the chemical shift (relative to that of pure solvent) for the free or coalesced signal were first given by Swift and Connick:[5]

$$\frac{1}{T_2} - \frac{1}{T_{2\mathrm{A}}} = \frac{P_\mathrm{m}}{\tau_\mathrm{m}}\left[\frac{T_{2\mathrm{m}}^{-2} + (T_{2\mathrm{m}}\tau_\mathrm{m})^{-1} + \Delta\omega_\mathrm{m}^2}{(T_{2\mathrm{m}}^{-1} + \tau_\mathrm{m}^{-1})^2 + \Delta\omega_\mathrm{m}^2}\right] \quad (3)$$

$$\Delta\omega = \frac{P_\mathrm{m}\Delta\omega_\mathrm{m}}{(\tau_\mathrm{m}/T_{2\mathrm{m}} + 1)^2 + \tau_\mathrm{m}^2\Delta\omega_\mathrm{m}^2} \quad (4)$$

where T_2 is the observed relaxation time, $T_{2\mathrm{A}}$ is the relaxation time of bulk solvent, P_m is the mole fraction of bound solvent, $T_{2\mathrm{m}}$ is the relaxation time of the bound solvent in the absence of exchange, τ_m is the residence time of a bound solvent molecule, and $\Delta\omega_\mathrm{m}$ is the chemical shift between bound and free solvent in the absence of exchange. Swift and Connick[5] assumed that $T_{2\mathrm{A}}$ could be equated with the transverse relaxation time of pure solvent, but subsequent work on more slowly exchanging systems has shown that, even in the absence of exchange broadening, the two are not necessarily equal.[11] This has been ascribed to the fact that one of the paramagnetic relaxation processes, dipolar relaxation, exhibits a long-range dependence (r^{-6}) and relaxation effects in the second and subsequent solvation shells may not be negligible. Since this effect is expected to be proportional to P_m we may write

$$\frac{1}{T_{2\mathrm{A}}} = \frac{1}{T_{2\mathrm{A}}^0} + \frac{P_\mathrm{m}}{T_{2\mathrm{os}}} \quad (5)$$

where $T_{2\mathrm{A}}^0$ is the relaxation time of pure solvent and $T_{2\mathrm{os}}$ is the outer sphere contribution. Since measurements were made at varying values of P_m, it is convenient to normalize our data by dividing through by P_m. Thus, defining

$$\frac{1}{T_{2\mathrm{r}}} = \frac{1}{P_\mathrm{m}}\left(\frac{1}{T_2} - \frac{1}{T_{2\mathrm{A}}^0}\right) \quad (6)$$

we obtain from eq 3 and 5

$$\frac{1}{T_{2\mathrm{r}}} = \frac{1}{\tau_\mathrm{m}}\left[\frac{T_{2\mathrm{m}}^{-2} + (T_{2\mathrm{m}}\tau_\mathrm{m})^{-1} + \Delta\omega_\mathrm{m}^2}{(T_{2\mathrm{m}}^{-1} + \tau_\mathrm{m}^{-1})^2 + \Delta\omega_\mathrm{m}^2}\right] + \frac{1}{T_{2\mathrm{os}}} \quad (7)$$

Similarly defining

$$\Delta\omega_\mathrm{r} = \Delta\omega/P_\mathrm{m} \quad (8)$$

we obtain from eq 4

$$\Delta\omega_\mathrm{r} = \frac{\Delta\omega_\mathrm{m}}{(\tau_\mathrm{m}/T_{2\mathrm{m}} + 1)^2 + \tau_\mathrm{m}^2\Delta\omega_\mathrm{m}^2} \quad (9)$$

The temperature dependences of the various parameters can now be considered. The exact functional dependence of $1/T_2$ depends on the relaxation mechanism operating but, for both dipolar and scalar relaxation, it depends on the product of the square of an interaction energy and a correlation time.[12] The interaction energy is expected to show negligible temperature dependence and the correlation time Arrhenius behavior. Thus

$$1/T_{2\mathrm{m}} = A_\mathrm{m}\exp(E_\mathrm{m}/RT) \quad (10)$$

Similarly for the outer-sphere correction

$$1/T_{2\mathrm{os}} = A_\mathrm{os}\exp(E_\mathrm{os}/RT) \quad (11)$$

The residence time τ_m may be related to the pseudo-first-order reaction rate constant for solvent exchange, k, and its temperature dependence may be obtained from transition-state theory. Thus

$$k \equiv 1/\tau_\mathrm{m} = \frac{k_\mathrm{B}T}{h}\exp(\Delta S^*/R - \Delta H^*/RT) \quad (12)$$

The temperature dependence of $\Delta\omega_\mathrm{m}$ was first discussed by Bloembergen[13] in terms of the electron-nucleus coupling constant and he concluded that a $1/T$ temperature dependence should be obeyed. However, as frequently mentioned before, such simple behavior is often not observed and we shall use an equation of the form[14]

$$\Delta\omega_\mathrm{m} = B_1/T + B_2/T^2 \quad (13)$$

where B_1 and B_2 are constants. We may assign the first term on the right-hand side of eq 13 with the Bloembergen equation.[13] Thus

$$B_1 = \frac{\omega g_\mathrm{eff}\beta AS(S+1)}{g_\mathrm{N}\beta_\mathrm{N}3k_\mathrm{B}} \quad (14)$$

where ω is the spectrometer operating frequency, g_eff and g_N are the effective g values of electron and nucleus, respectively, β and β_N are the electron and nuclear Bohr magnetons, respectively, A is the electron-nucleus coupling constant (in joules), S is the electron spin, and k_B is the Boltzmann constant.

The pressure dependences of the various NMR parameters are more difficult to predict theoretically and where possible it is probably more reliable to measure them. Provided that complex geometry and bond lengths do not change significantly with pressure,[21] then $\Delta\omega_\mathrm{m}$ should show negligible pressure dependence and, further, all changes in $T_{2\mathrm{m}}$ and $T_{2\mathrm{os}}$ can be ascribed to changes in correlation times. Regardless of the mechanism operating, all likely relaxation processes should involve reorientational or translational motion and one would expect an approximate relationship of correlation time with viscosity. Indeed, Jonas[22] has found a very good correspondence between viscosity and translational correlation times for simple liquids. As will be shown below, the pressure dependences of the NMR parameters have a negligible effect on the derived exchange parameters.

The pressure dependence of $\tau_\mathrm{m}(=1/k)$ can be related to the integrated form of eq 1. It is conventional to express ΔV^* as

$$\Delta V^* = \Delta V_0^* - \Delta\beta^* P \quad (15)$$

where ΔV_0^* is the zero pressure volume of activation and $\Delta\beta^*$ is the pressure independent compressibility of activation. It is thus readily shown from eq 1 and 15 that

$$\ln k = \ln k_0 - \Delta V_0^* P/RT + \Delta\beta^* P^2/2RT \quad (16)$$

where k_0 is the rate constant at zero pressure.

3. Experimental Section

A. Preparation of [Ni(CH$_3$CN)$_6$](ClO$_4$)$_2$ and of Solutions for NMR Study. Acetonitrile (Fluka, puriss.) was purified by distillation at least

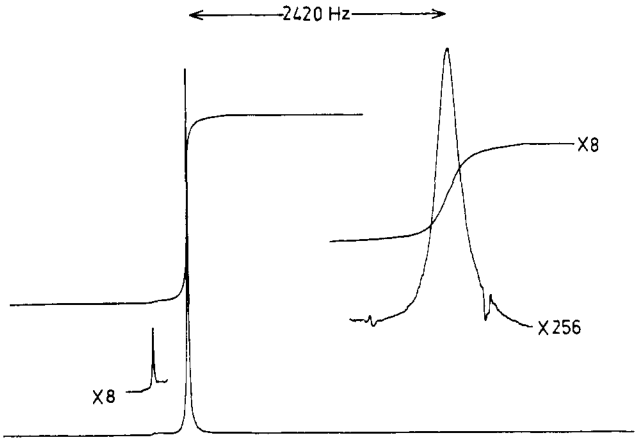

Figure 1. 60-MHz ^1H FT NMR spectrum with integral of $[Ni(CH_3CN)_6](ClO_4)_2$ in CH_3CN at 250.9 K. The resonances are (in order of increasing field) 1% internal benzene, free solvent, bound solvent. Mole fraction complex = 6.23×10^{-3}, sweep width = 8000 Hz, number of scans = 400, measured ratio bound/free = 3.57×10^{-2}, derived coordination number = 5.7.

twice from P_2O_5 and was stored over previously activated 4-Å molecular sieves (Merck). Benzene (Merck, pro analysis) was stored similarly. The complex was prepared according to the method of Wickenden and Krause.[18] The water content of the complex, as shown by Karl Fischer titration was $<5 \times 10^{-3}$ mol of water/per mol of metal ion. In the solution for NMR study, the water content was less than the sensitivity of the titration which corresponds to a water mole fraction of $<3 \times 10^{-5}$.

Solutions for NMR study were prepared by weight in a glove box (water <6 ppm). The solutions contained ~1% by weight benzene as internal reference.

B. Measurements. Variable Temperature. FT NMR spectra were obtained on a Bruker WP 60 spectrometer operating at 60 MHz using an internal deuterium lock. T_2 measurements were obtained from the full width at half-height of the NMR absorption resonance, $\Delta\nu_{1/2}$ in Hertz by means of the relationship $1/T_2 = \pi\Delta\nu_{1/2}$. Precision bore coaxial cells[23] were used. The 2-mm-o.d. inner tube contained the sample with the deuterium lock substance ($CDCl_3$ or D_2O) within the annular region. Inhomogeneity corrections were estimated from the width of the residual proton resonance of the lock substance. In virtually all cases this correction was <1 Hz. Chemical shifts were measured relative to the internal benzene resonance but are referenced to pure acetonitrile. The results are corrected for the small temperature dependence of the acetonitrile-benzene shift.

The observation of separate bound and free solvent peaks was performed using an external ^{19}F lock in order that 5-mm tubes could be used for the sample in view of the poor sensitivity. Figure 1 shows a typical spectrum of free and bound acetonitrile.

Variable Pressure. ^1H NMR shifts and line widths were measured up to 200 MPa using a high pressure probe head for a Bruker WP 60 similar to that previously described.[8] The temperature stability over several hours as measured by a 100-Ω platinum resistance within the pressure cell was better than ±0.1 K. An ^{19}F external lock was incorporated into the high pressure probe head to obviate the need for a lock substance. Its stability was better than 3 Hz over periods of several hours. All line widths were corrected for magnet inhomogeneity and instability by subtracting the width of the benzene reference and adding the width of the ambient pressure benzene resonance as determined using a coaxial cell (typically 4-7 Hz). This procedure neglects to take into account fully the effect of pressure on this line width. However, the pressure correction must be less than the accuracy of the data.

4. Results and Treatment of Data

A. Variable Temperature. The first requirement in the analysis of the data is to ascertain the number of solvent molecules exchanging from each nickel ion at the NMR accessible rate. Figure 2a and Table I show the temperature dependence of the bound shifts (using the linearized form of eq 13). It may be noted that the B_2 term is clearly nonzero. Also shown are the $\Delta\omega_r$, free solvent shifts normalized as discussed above by dividing by P_m (cf. eq 8 and 9). In this figure the coordination number has been chosen as 6. In the limit of very fast exchange, $\Delta\omega_r = \Delta\omega_m$ and thus the correct evaluation of P_m should make the bound peak and normalized free peak shifts collinear. A nonlinear least-squares curve fitting analysis,[24] fitting either the two or four highest temperature free solvent shifts and the bound solvent shifts simultaneously to two equations with B_1, B_2, and the coordination number as unknowns, yielded values of 5.91 ± 0.20 and 6.07 ± 0.12, respectively, for the number of exchanging solvent molecules. Digital integration of bound and free solvent peak areas (see Figure 1) in the temperature range −20 to −40 °C yielded a value of 5.4 ± 0.4 in spite of difficulties associated with comparing the areas of a very large narrow and a very small broad peak. Clearly the results are in accord with an octahedral complex and throughout the data analysis a value of 6.0 will be used.

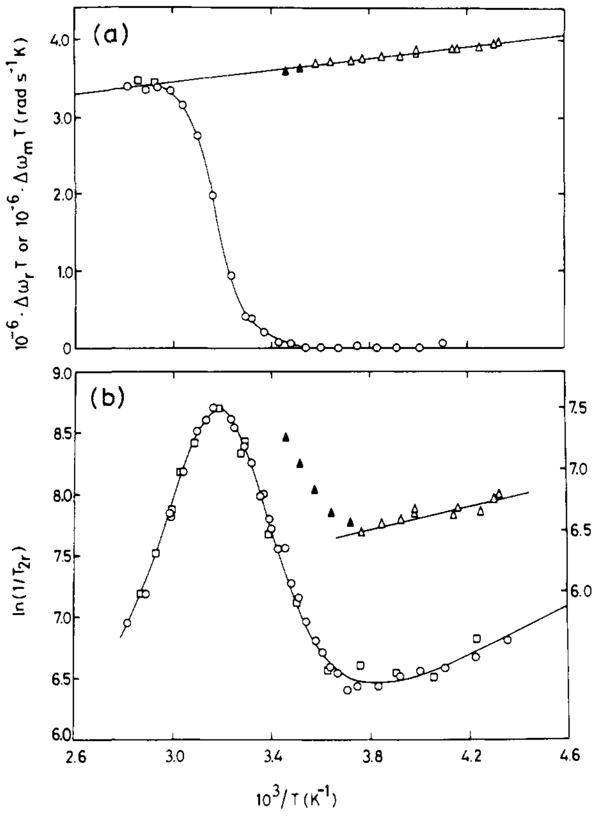

Figure 2. Variable-temperature ^1H NMR data for $[Ni(CH_3CN)_6](ClO_4)_2$ in CH_3CN. (a) Bound and free solvent chemical shifts as a function of temperature: ○, free solvent normalized shifts $\Delta\omega_r$ (P_m = 0.02521); □, free solvent normalized shifts $\Delta\omega_r$ (P_m = 0.03146); △, bound solvent shifts $\Delta\omega_m$ (P_m = 0.03739); ▲, bound solvent shifts $\Delta\omega_m$ showing exchange broadening contribution (P_m = 0.03739). (b) Bound and free solvent T_2 values as a function of temperature: ○, free solvent normalized T_{2r} (P_m = 0.02521); □, free solvent normalized T_{2r} (P_m = 0.03146); △, bound solvent T_{2m} (P_m = 0.03739); ▲, bound solvent T_{2m} showing exchange broadening contribution (P_m = 0.03739).

Figure 2b and Table I show the T_{2m} values for the bound peak and T_{2r} for the free peak as a function of temperature. Below 265 K exchange effects are small and reasonable estimates for A_m, E_m, A_{os}, and E_{os} can be readily obtained. Using the temperature dependence of T_{2m}, T_{2os}, and $\Delta\omega_m$ thus determined, the T_{2r} data were fitted to eq 7 by a nonlinear least-squares procedure to obtain ΔH^* and ΔS^*. Finally, free shifts, bound shifts (below 280 K), free T_{2r}, and bound T_{2m} (below 265 K) were fitted simultaneously using an eight parameter, four-equation nonlinear least-squares curve fitting procedure. Since there are eight parameters to optimize, B_1,

Table I. Experimental $1/T_2$ and Chemical Shifts as a Function of Temperature and P_m

free resonance									bound resonance		
$P_m = 0.03146$			$P_m = 0.02521$			$P_m = 0.02521$			$P_m = 0.3739$		
T, K	$1/T_2$, s^{-1}	δ, Hz[a]	T, K	$1/T_2$, s^{-1}	δ, Hz[a]	T, K	$1/T_2$, s^{-1}	δ, Hz[a]	T, K	$1/T_2$, s^{-1}	δ, Hz[a]
236.4	28.7		229.7	22.6		294.0	56.5		230.9	892	2719
246.4	21.0		236.9	19.8		295.1	61.2		232.1	867	2695
256.2	21.8		244.0	18.1	0.4	296.8	74.7	2.7	235.4	779	2624
265.9	23.1		249.5	17.75	−0.1	298.2	74.0		240.3	792	2559
275.5	22.4		255.2	17.0	0.3	301.3	97.1	4.8	241.2	754	2553
285.5	38.4		261.0	15.6	0.0	303.9	110.6	5.6	250.9	782	2421
295.2	67.0		266.9	15.6	0.5	308.0	128.9		251.0	760	2425
303.6	144.1		269.9	15.2		309.0	138.4	12.8	254.6	729	2362
305.1	129.6		272.7	17.3	0.1	316.2	151.2	24.9	259.9	704	2311
313.7	188.0		275.0	18.1		319.1	137.0		265.3	644	2240
324.4	141.8		277.5	20.6	0.3	322.5	125.7	34.1	268.4	707	2203
329.7	112.8		279.6	22.7		328.9	90.3	38.2	274.6	767	2141
334.9	81.5		282.3	26.4	0.2	334.8	64.3		278.9	927	2100
341.7	57.8	50.2	284.9	32.1		335.4	62.3	39.8	284.2	1140	2028
348.7	41.9	49.6	287.4	36.2	0.7	341.0		39.7	288.6	1420	1970
			289.2	48.2		346.2	33.1	38.8			
			291.8	48.2	1.1	355.2	26.2	28.2			

[a] Shift upfield from that of pure solvent.

Table II. Derived NMR and Kinetic Parameters (Together with Their Standard Deviations)

$k_{298.1}$, s^{-1}	2840 ± 50
ΔH^*, kJ mol^{-1}	64.33 ± 0.9
ΔS^*, J mol^{-1} K^{-1}	36.97 ± 2.8
A/h, Hz[a]	$(2.81 \pm 0.05) \times 10^5$
B_2, K s rad^{-1}	$(3.3 \pm 0.1) \times 10^8$
A_m, s^{-1}	103 ± 32
E_m, kJ mol^{-1}	4.1 ± 0.6
A_{os}, s^{-1}	12.8 ± 4.8
E_{os}, kJ mol^{-1}	8.2 ± 0.7

[a] Calculated from eq 14 using the value of $g_{eff} = 2.23$[18] ($g_{eff} = \mu_{eff}/\sqrt{S(S+1)}$).

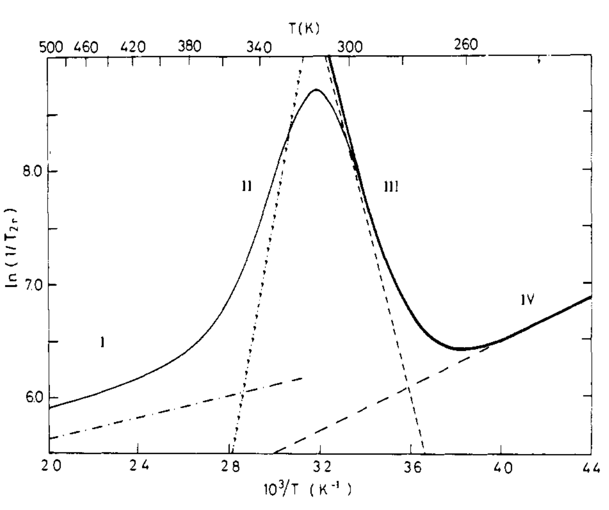

Figure 3. Calculated temperature dependence of ln $(1/T_{2r})$ for the four different exchange regions (I-IV) using various approximations to the full equations: —, full Swift-Connick equation including outer sphere contribution; —, $1/T_{2r} = 1/T_{2os} + k$; - -, $1/T_{2r} = 1/T_{2os}$; - · -, $1/T_{2r} = 1/T_{2m}$; - - -, $1/T_{2r} = k$; · · · ·, $1/T_{2r} = \Delta\omega_m^2/k$.

B_2, A_m, E_m, A_{os}, E_{os}, ΔH^*, and ΔS^*, the initial guesses required by the curve fitting routine needed to be fairly accurate in order to obtain convergence. Throughout the fitting the absolute values of the shifts were used since to a first approximation their absolute errors should be equal, whereas T_2 values were fitted in logarithmic form since their fractional errors should be similar. Table II gives the final values of the parameters and the continuous curves of Figures 2a and 2b show the calculated temperature dependences of shifts and $1/T_{2r}$ values.

B. Comparison with Earlier Results. In their celebrated paper, Swift and Connick[5] introduced certain simplifications of eq 3. In particular, they identified three different exchange regions: (I) at high temperatures, where exchange is faster than the NMR time scale

$$1/T_{2r} = 1/T_{2m} \tag{17}$$

(II) at lower temperatures where the coalesced signal is exchange broadened

$$1/T_{2r} = \tau_m \Delta\omega_m^2 \tag{18}$$

(III) at still lower temperatures where two well-resolved but exchange broadened signals may be observed, for the free solvent resonance

$$1/T_{2r} = 1/\tau_m \tag{19}$$

As discussed in the theory section, Swift and Connick did not explicitly consider an outer sphere contribution, but subsequent authors identified a fourth region: (IV) at temperatures where the exchange rate is much slower than the NMR time scale

$$1/T_{2r} = 1/T_{2os} \tag{20}$$

The regions of the four approximations are shown in Figure 3. Before the advent of high speed computer, curve fitting procedures, it was normal practice to delineate the ln $(1/T_{2r})$ vs. $1/T$ curve into four straight lines corresponding to the four limiting expressions, eq 17-20.[25] Figure 3 shows the temperature dependence of the four limiting expressions calculated using the parameters from our full data analysis together with the calculated temperature dependence using the full equation. It is immediately apparent that the linearization into four straight lines and the identification of such lines with equations 17-20 will yield highly erroneous kinetic parameters. It is interesting to note that, fortuitously, the ln k line crosses the curve of the full equation close to 298.15 K and thus the error in k should be small for this exchange reaction. Table III gives the results of previous studies for this system in chronological order. With but one clearly erroneous exception, the values of ln k show remarkable constancy.

Table III. Comparison of Kinetic Results for $[Ni(CH_3CN)_6](ClO_4)_2$ in CH_3CN

year	$10^{-3}k_{298}$, s^{-1}	ΔH^*, kJ mol^{-1}	ΔS^*, J mol^{-1} K^{-1}	nucleus	ref
1967[a]	2.8	49	−15	^1H	26
1967[b]	3.9	46	−37	^1H	27
1967[a,c]	2.1	49	−16	^1H	28
1971[d,e]	2.9	67	+43	^1H	29
1971[e,f]	3.0	63.2	+41.8	^{14}N	29
1973[f]	2.0	68	+50	^{14}N	30
1973[g]	3.6	60	+23	^1H	30
1973[h]	14.5	39.5	−32.6	^{14}N	31
1978[i]	2.9	64.6	+37.9	^1H	this work

[a] $\Delta\omega_m$ obtained from high temperature free solvent shifts. Kinetic parameters obtained from simplified Swift–Connick equations. [b] Kinetic parameters and $\Delta\omega_m$ obtained from simplified Swift–Connick equations. [c] k and ΔS^* recalculated using our definition of k. BF_4^- counterion. [d] $\Delta\omega_m$, kinetic parameters and various relaxation parameters obtained from combination of T_1 and T_2 measurements as a function of frequency and temperature using full Swift–Connick equations. [e] k and ΔS^* recalculated using coordination number of 6 instead of 4. [f] Kinetic parameters obtained from low temperature simplified Swift–Connick equation. [g] $\Delta\omega_m$ obtained from high temperature free solvent shifts. Kinetic parameters obtained from full Swift–Connick equations. [h] $\Delta\omega_m$ and kinetic parameters obtained from combination of free solvent shifts and T_2 measurements using full Swift–Connick equations. Details not given. [i] See text for details of data analysis.

Table IV. Derived ΔH^* and ΔS^* Values and Their Standard Deviations Using the Simplified Eq 21. T_{max} refers to the Maximum Temperature to Which Fitting Was Performed

T_{max}, K	ΔH^*, kJ mol^{-1}	ΔS^*, J mol^{-1} K^{-1}
316.2[a]	48 ± 3	−19 ± 9
305.1	58 ± 3	+17 ± 11
298.2	64 ± 5	+36 ± 17
294.0	72 ± 7	+62 ± 23
285.5	84 ± 14	+105 ± 48
277.5	96 ± 54	+148 ± 195

[a] Error distribution highly nonrandom and convergence very poor.

Table V. Chemical Shifts and $1/T_2$ Values for the Bound Resonance as a Function of Pressure[a] (T = 250.1 K, P_m = 0.03670)

P, MPa	δ, Hz[b]	$1/T_2$, s^{-1} [c]
0.1	2420	740
50.0	2410	750
75.0	2420	750
100.0	2430	790
150.0	2445	790

[a] 3000 scans, 8000-Hz sweep width, 8K FID data points. [b] Chemical shift upfield from free solvent resonance, estimated uncertainty ±10 Hz. [c] Estimated uncertainty ±5%.

However, the values of ΔH^* and more particularly ΔS^* show wide variations, although the more recent data analyzed generally using the full equations appear to be in general agreement. It is clear from Figure 3 that the major effect of the limiting eq 19 is to seriously underestimate $\partial \ln (k/T)/\partial(1/T)$ and this term is directly proportional to ΔH^* and also has a critical effect on ΔS^* (see eq 2). Mathematically, eq 19 is obtained from the limiting condition $\Delta\omega_m^2 \gg 1/\tau_m^2$ and thus the larger the shift, i.e., the higher the magnetic field, the more reliable will be the results. Further, nuclei other than protons generally give larger shifts and, as discussed by Lincoln and West,[30] the ^{14}N line widths for this system are well represented by this limiting equation. In general, however, reliable values of ΔH^* and ΔS^* will require the use of the full Swift and Connick equations and hence require the values and temperature dependences of $\Delta\omega_m$, T_{2m}, and T_{2os}.

As demonstrated above, the sensitivity and sweep width flexibility of current Fourier transform spectrometers means that bound resonances may be readily studied for ^1H NMR, and, when such observation is feasible, it is probably the best way of obtaining the temperature dependences of $\Delta\omega_m$ and T_{2m}. Where such results are not obtainable either owing to solvent properties or poor sensitivity, the free solvent T_2 and shift values need to be obtained over as wide a temperature range as possible in particular to characterize T_{2m}.

A more accurate limiting equation for low temperatures may be derived from eq 7 for the limiting condition $\Delta\omega_m^2 \gg 1/\tau_m^2$:

$$1/T_{2r} = 1/\tau_m + 1/T_{2os} \tag{21}$$

As may be seen from Figure 3, eq 21, using parameters obtained from the full analysis, is remarkably accurate up to 295 K. However, this equation is not good enough to yield reliable values of ΔH^* and ΔS^* since the value of $\partial \ln (k/T)/\partial(1/T)$ is only poorly defined. Table IV shows the derived values of ΔH^* and ΔS^* using this simplified equation (A_{os} and E_{os} treated as variables to optimize as well) as a function of the maximum temperature to which the data were fitted.

C. Variable Pressure. A full study of the effect of pressure on the rate of reaction might be expected to require a full T_2 and shift vs. temperature analysis at different pressures in order to obtain rate constants k as a function of pressure. Clearly this approach would be prohibitively time consuming and a more simplified approach is required. The expected pressure dependences of the various NMR parameters have been discussed in the theoretical section and the experimental values of $\Delta\omega_m$ and $1/T_{2m}$ are shown in Table V. In accord with expectation, $\Delta\omega_m$ exhibits negligible temperature dependence and the very small increase of $1/T_{2m}$ with pressure goes in the direction predicted from an increase of viscosity with pressure. A similar behavior should be expected for $1/T_{2os}$.

Thus we would plan to work at a fixed temperature as a function of pressure since the NMR parameters show such small pressure dependence. Furthermore, in the slow exchange region III, the value of $1/T_{2r}$ depends only very slightly on the NMR parameters; i.e., eq 21 is independent of $\Delta\omega_m$ and $1/T_{2m}$, and $1/T_{2os}$ is generally only a small contribution. Table VI shows $1/T_2$ values for the free resonance for two different complex concentrations at two similar temperatures chosen in this exchange region. These data were analyzed using the full eq 7 as a function of pressure keeping $\Delta\omega_m$, $1/T_{2m}$, and $1/T_{2os}$ at their ambient pressure values and allowing $\tau_m(=1/k)$ to vary according to eq 16, and the results are shown in Table VII. The effect of the pressure dependences of $\Delta\omega_m$, $1/T_{2m}$, and $1/T_{2os}$ were examined by allowing each term to vary linearly by +0.1 %/MPa (more than observed experimentally). ΔV^* changes are of only +0.1, 0 and +0.4 cm^3 mol^{-1} which are within its standard deviation.

This analysis is not entirely satisfactory since it requires the

Table VI. Experimental $1/T_2$ Values and Corresponding Values of k as a Function of Pressure

expt 1[a]				expt 2[b]			
no.[c]	P, MPa	$1/T_2$, s^{-1}	$10^{-3}k$, s[d]	no.[c]	P, MPa	$1/T_2$, s^{-1}	$10^{-3}k$, s[d]
1	0.1	80.1	2.17	1	0.1	53.3	1.74
11	0.1	75.3	2.02	10	0.1	54.3	1.78
2	40.0	68.2	1.79	11	20.0	53.3	1.47
10	60.0	61.6	1.58	2	40.0	44.9	1.41
3	80.0	59.0	1.50	12	60.0	45.8	1.44
9	100.0	57.1	1.44	3	80.0	42.0	1.29
4	120.0	53.7	1.33	9	100.0	39.9	1.21
8	140.0	48.8	1.18	4	120.0	35.2	1.02
5	160.0	47.7	1.14	8	140.0	34.9	1.01
7	180.0	44.9	1.06	5	160.0	33.2	0.94
6	200.0	42.4	0.97	7	180.0	32.7	0.92
				6	200.0	30.7	0.84

[a] $T = 294.5$ K, $P_m = 0.03146$, $1/T_{2os} = 373$ s^{-1}. [b] $T = 293.9$ K, $P_m = 0.02521$, $1/T_{2os} = 375$ s^{-1}. [c] Order in which experiments were performed. [d] Calculated from eq 21, ΔV^* assumed independent of pressure.

Table VII. Activation Volumes and Compressibilities at 294 K (Together with Their Standard Deviation)

	ΔV^*, cm^3 mol^{-1}	ΔV_0^*, cm^3 mol^{-1}	$10^2\Delta\beta^*$, cm^3 mol^{-1} MPa^{-1}
derived from full eq 7			
expt 1	9.6 ± 0.4	10.8 ± 1.2	1.2 ± 1.2
expt 2	9.6 ± 0.5	11.9 ± 1.8	2.4 ± 1.9
av	9.6 ± 0.4	11.3 ± 1.5	1.8 ± 1.5
derived from simplified eq 21			
expt 1	9.3 ± 0.3	10.2 ± 1.1	0.9 ± 1.1
expt 2	9.3 ± 0.5	11.5 ± 1.7	2.3 ± 1.7
av	9.3 ± 0.4	10.8 ± 1.4	1.6 ± 1.4

values of $\Delta\omega_m$, $1/T_{2m}$, and $1/T_{2os}$ and, in general, such parameters would require a full temperature analysis to be performed. However, as discussed above, the low temperature limiting form the Swift-Connick equation which includes the outer-sphere correction, i.e., eq 21, represents the temperature dependence of the free solvent, $1/T_{2r}$ values, well below 295 K (see Figure 3) and thus the high pressure data were also analyzed using this equation with the outer-sphere correction equal to its ambient pressure value. The results are also shown in Table VI. It is evident that, within experimental error, the data analyses are identical. We thus believe we are justified in using the simplified analysis in this exchange region and, furthermore, in future studies we shall restrict ourselves to single-temperature, variable-pressure studies.

The compressibility term, $\Delta\beta^*$ is very small and it can be neglected within experimental error. The random error in ΔV^* is about two times 0.4 cm^3 mol^{-1}, the standard derivation, but must be increased to 1-2 cm^3 mol^{-1} to include possible effects due to nonrandom errors. Figure 4 shows the calculated and observed values of ln k as a function of pressure using the simplified analysis with ΔV^* independent of pressure.

5. Discussion

In this paper, we have reported the effect of temperature and pressure on the solvent exchange reaction on nickel(II) and the activation parameters are summarized in Table VIII. The large positive values of both ΔV^* and ΔS^* are in accord with a dissociative activation mode d. For a dissociative mechanism D, the partial molar volume, $V°$, of the solvent represents an upper limit to the volume of activation assuming that the partial molar volumes of both hexasolvated ion and pentacoordinated transition state are equal. The measured ΔV^* is considerably smaller than $V°$ for acetonitrile, strongly suggesting a dissociative interchange mechanism I_d. A previous high pressure NMR study of methanol exchange on Ni(II) has shown similar behavior.[9b] Caldin and co-workers[32] have measured ΔV^* for the complex formation of Ni(II) and Co(II) with ammonia and pyridine-2-azodimethylaniline in water using a high pressure, laser T-jump apparatus. The values obtained show little specificity for ligand and are similar for both metals. They conclude that the transition state involves considerable stretching of the cation-water bond, as postulated in the Eigen-Wilkins mechanism.[1] One would thus expect a close similarity between the activation parameters for this system

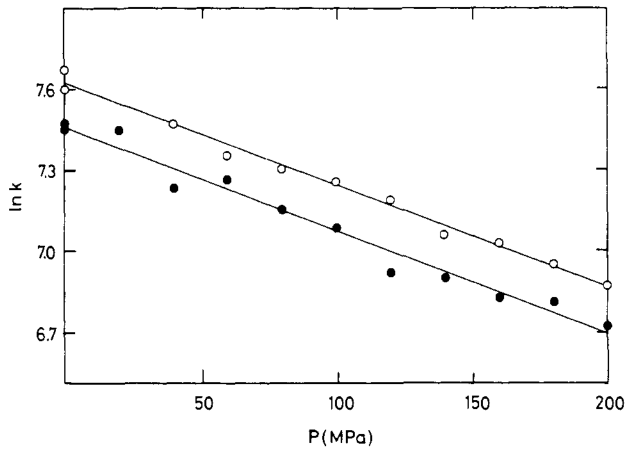

Figure 4. Calculated and experimental values of ln k as a function of pressure using eq 21 with ΔV^* independent of pressure: ○, experiment 1; ●, experiment 2.

Table VIII. Activation Parameters for Solvent Exchange and Ligand Substitution Reactions on Ni(II)

reaction	ΔH^*, kJ mol^{-1}	ΔS^*, J mol^{-1} K^{-1}	ΔV^*, cm^3 mol^{-1} [b]	$V°$, cm^3 mol^{-1}	ref
$Ni(CH_3CN)_6^{2+} + CH_3CN$	64.3 ± 0.9	+37.0 ± 2.8	+9.6 ± 0.4 (294 K)	52.8	this work
$Ni(CH_3OH)_6^{2+} + CH_3OH$	66.0	+33.4	+10.8 ± 0.6 (307 K)	40.5	9b
$Ni(H_2O)_6^{2+} + NH_3$	41.8	−25.4	+6.0 ± 0.3 (303 K)	18.0	32
$Ni(H_2O)_6^{2+}$ + PADA[a]	56.8 ± 4.2	+4.2 ± 8.4	+7.7 ± 0.3 (303 K)	18.0	32

[a] PADA = pyridine-2-azodimethylaniline. [b] Temperature given in parentheses.

and that of water exchange. Table VIII summarizes the available ΔV^* data for ligand and solvent exchange on Ni(II).

For the nonlabile +III transition metal ions,[7] the small negative volumes of water exchange, as obtained using isotopic labeling, on Cr(III), Rh(III) and Ir(III) strongly suggest an associative interchange, I_a, mechanism, whereas the data for Co(III) suggest an I_d mechanism. To obtain further insight into the solvent exchange process, further high pressure NMR work is in progress with other labile +II and +III ions in a variety of nonaqueous solvents and water.

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Hydrolysis of Benzaldehyde *O,S*-Acetals[1]

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Abstract: The acid-catalyzed breakdown of benzaldehyde *O*-ethyl *S*-ethyl acetal proceeds with initial C–O bond cleavage, whereas the *S*-phenyl acetal gives C–S cleavage in 90% methanol/water. Electron-withdrawing substituents on the thiol increase the amount of C–S cleavage and electron-donating substituents on the benzaldehyde increase C–O cleavage. The directions of cleavage are analyzed in terms of the *pull* exerted by the leaving group and the *push* exerted by the remaining groups. Increased electron donation by substituents on the benzaldehyde leads to decreased electron donation by substituents on the thiol for C–O cleavage. A limiting Brønsted coefficient of $\alpha_{min} = 0.84$ was determined for benzaldehyde *O*-ethyl *S*-phenyl acetal. The absence of detectable general acid catalysis is attributed to the poor hydrogen-bonding ability of thiols. The ratio of the rate constants for the acid-catalyzed and "water" reactions of this compound gives a ratio of $k_{RS^-}/k_{RSH} = 40$ for the attack of PhS^- and PhSH on an intermediate oxocarbonium ion in the reverse direction. This ratio and the large effects of polar substituents on the thiol and the benzaldehyde suggest that the rate-determining step of the "water" reaction is the diffusional separation of RS^- from the oxocarbonium ion.

The experiments described here were carried out in order to characterize further the position of bond cleavage, transition-state structures, and mechanisms of catalysis for the hydrolysis of *O,S*-acetals. Previous studies of the position of initial bond cleavage have given different conclusions for different compounds and the available data do not permit generalizations on this question.[2-5] The interpretation of transition-state structures from the available kinetic data has been hampered by the absence of definitive evidence for the position of bond cleavage, except for the reactions of benzaldehyde *O*-methyl *S*-aryl acetals.[3,6-10] An interesting and incompletely explained property of these reactions is that they do not exhibit general acid catalysis, although general acid catalysis is easily detected in the hydrolysis of the analogous oxygen acetals with OAr

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