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High Pressure Carbon-13 FT-NMR. Acetonitrile Exchange with $[Co(CH_3CN)_6](ClO_4)_2$*

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Modifications to a recently described high pressure, high resolution NMR probe-head to improve sensitivity and allow observation of carbon-13, are described. Variable temperature and pressure carbon-13 studies on the nitrile resonance of pure acetonitrile in the presence of $[Co(CH_3CN)_6](ClO_4)_2$ *yield the following parameters for the solvent exchange rate:* $k_{298.15} = (2.56 \pm 0.06) \times 10^5\ s^{-1}$, $\Delta H^* = 48.79 \pm 1.10\ kJ\ mol^{-1}$, $\Delta S^* = +22.2 \pm 3.7\ J\ K^{-1}\ mol^{-1}$, $\Delta V^* = +7.7 \pm 1.7\ cm^3\ mol^{-1}$. *The results are discussed in terms of the relative accuracy and reliability of* ΔS^* *and* ΔV^*, *the parameters most frequently used for solvent exchange mechanistic assignment.*

Introduction

Nuclear magnetic resonance is a unique tool for the study of fast symmetric chemical exchange processes, *i.e.* where there is no net chemical reaction [2]. In the area of mechanistic inorganic chemistry, some of the most important results to emerge over many years have been on solvent exchange with solvated paramagnetic ions [3]. These results are of vital interest in the interpretation of the mechanisms of complex formation and of electron transfer reactions. It was thus rather unfortunate that, for much of the early work, the discrepancies in the kinetic parameters obtained by different research groups for the same system were sometimes so large as to caste doubt on the entire approach. It frequently appeared that, whereas different authors agreed on the rate constant around room temperature, the values of ΔH^* and ΔS^* showed very large variation [4, 5]. This is particularly disturbing since changes in ΔS^*, for closely related systems, are often used as evidence for mechanistic changes. The causes of these discrepancies are complex but arise mainly because the relaxation times and chemical shifts depend not only on kinetic but also on several NMR parameters making the overall temperature dependence extremely complicated. In a recent article [4], we have shown that, for ^{1}H-NMR, the simplified equations frequently used in the past, are not valid and it is necessary to use the full equations which require computer curve-fitting techniques. However, there always remains the potentially serious problem of correlation of errors. As is well known, ΔS^* is obtained from the intercept at $1/T = 0$ of an Eyring plot whereas ΔH^* is obtained directly from the slope [4] and unless the Eyring plot extends over a very wide temperature range [6], the errors on ΔH^* and ΔS^* will always be strongly correlated.

Another activation parameter, the volume of activation ΔV^*, is increasingly used as an aid for mechanistic assignment. Since it is defined as $\Delta V^*/RT = -(\partial \ln k/\partial P)_T$, it does not suffer the error problems of ΔS^*; an increase of rate with pressure implies a negative ΔV^* and *vice versa* [4]. For substitution reactions which do not involve charge separation between reactants and transition state, the interpretation of ΔV^* is particularly simple, a positive ΔV^* implies a dissociative activation mode and a negative value an associative activation mode [7]. We have recently described the construction of a high pressure ^{1}H-NMR probe-head designed for ready interchangeability with the commercial probe-head of a Bruker WP 60 spectrometer [8, 9]. It has been used for the study of volumes of activation of non-aqueous solvent exchange with the transition metal ions, Mn^{2+} to Ni^{2+} [4, 7, 10].

The advantages of ^{1}H-NMR are obvious: its sensitivity is very high, it has a spin of ½ making the correction due to the relaxation rate of pure solvent very small and most solvents of interest contain protons. Its major disadvantages are that the proton is frequently far from the paramagnetic site thus giving rise to only a small electron nucleus hyperfine interaction and hence small chemical shift between 'free' and 'bound' solvent. This causes the 'kinetic window', the temperature range over which kinetic results may be obtained, to be relatively narrow. Furthermore, in some solvents, most notably water,

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the protons are very labile and study by ^{1}H-NMR leads to the proton exchange rate which is not necessarily the same as the 'whole' solvent exchange rate.

Both of these shortcomings of ^{1}H-NMR can be solved by choosing a different nucleus, one closer to the paramagnetic centre. With the aim of studying water exchange, we have recently reported modifications of our high pressure probe for ^{17}O [11], the only possible nucleus for this solvent, and have reported values for the volumes of activation for water exchange on the paramagnetic ions, Mn^{2+} to Ni^{2+} [1, 11, 12]. Due to its very low natural abundance (0.037%) and isotropic enrichment problems, high pressure ^{17}O-NMR will probably only ever be useful for water exchange.

For non-aqueous solvents, the choice of nuclei is much larger. Swaddle [13] has recently reported high pressure ^{14}N-NMR studies of acetonitrile exchange on Ni^{2+} and Co^{2+}. The obvious advantages of ^{14}N are that it is 99.6% abundant and that in this case the nitrogen atom will generally be very close to the paramagnetic ion. However, it is clearly limited to nitrogen-containing solvents, the nucleus has a spin of 1 giving rise to a large correction for the relaxation rate of pure solvent (^{17}O-NMR suffers similarly) and it has a low magnetogyric ratio which causes low sensitivity and small absolute values of the shift. ^{15}N has a spin of ½ and so gives rise to only a small correction for the relaxation rate of pure solvent but suffers all the other problems of ^{14}N and has very low natural abundance (0.365%) and hence isotopic enrichment problems.

Carbon-13 has a spin of ½, a much larger magnetogyric ratio than either ^{14}N or ^{15}N and most solvents of interest contain a carbon atom close to the paramagnetic centre. Its low natural abundance (1.1%) is more than offset by the fact that most common solvents are available with specified carbon atoms enriched up to 90%. In this paper, we report modifications of our high pressure NMR probe to improve sensitivity and to enable it to be used for ^{13}C together with a variable temperature and pressure study of the solvent exchange on $[Co(CH_3CN)_6](ClO_4)_2$ in CH_3CN in order to obtain ΔH^*, ΔS^* and ΔV^*.

Experimental

Preparation of Solvents, Complex and Solutions

Acetonitrile (Fluka, puriss) was refluxed for 24 hours over CaH_2 and distilled (water content by Karl-Fischer titration < 10 ppm). Dioxan (Fluka, purum) was shaken with $CaCl_2$ for 4 hours and distilled. Both solvents were stored over 4 Å molecular sieves (Merck). 90% enriched CH_3-^{13}CN (Stohler) contained 1% water and was dried by 3 successive distillations through P_2O_5 on a vacuum line. Water content was checked by ^{1}H-NMR and by Karl Fischer titration on a non-enriched sample which had been subjected to the same handling procedures. $[Co(CH_3CN)_6](ClO_4)_2$ was prepared according to the method of Wickenden and Krause [14]. The Co^{2+} content was analysed by EDTA titration and water content by Karl-Fischer titration (less than 0.01 mole water/mole salt). All solutions were prepared in a glovebox (water < 6 ppm). The solution for variable temperature study was prepared using normal acetonitrile and 9% dioxan by weight as internal reference. The solution for variable pressure study was prepared ten times too concentrated in normal acetonitrile and then diluted with enriched solvent. No internal reference was added.

NMR Measurements

Variable temperature spectra were obtained on a Bruker WP 60 spectrometer equipped with a multinuclear probe tuned to 15.08 MHz using broad-band ^{1}H decoupling and an external ^{19}F lock. Quadrature detection was employed (2K + 2K). Other spectrometer parameters were chosen to optimise signal to noise noting the wide variation of linewidth with temperature. Temperatures were measured before and after each spectral accumulation by substituting the sample with a calibrated Pt resistance contained in a 10 mm o.d. NMR tube. Temperature accuracy was better than 0.5 K. All spectra, after Fourier transformation and phasing, were transferred via floppy disc to a computer and both CH_3CN and dioxan resonances were fitted to Lorentzian functions using a non-linear least squares fitting procedure. In order to take into account magnet inhomogeneity, the contribution of the Co^{2+} ion to the broadening was taken as the difference between the computer fitted linewidths of the CH_3CN and the dioxan. The chemical shifts were measured relative to the dioxan but are referenced to the shift of pure CH_3CN.

Variable pressure measurements were performed up to 200 MPa on a high pressure probe designed for attachment to a Bruker WP 60 spectrometer. The overall design philosophy is the same as for earlier probes [8, 9] but the modifications made have produced a significant improvement in sensitivity. As before, the probe consists of an aluminium box the same size as the commercial probes. It contains the circuitry for the platinum resistance thermometer, an external ^{19}F probe and matching circuit as well as matching circuits for *both* ^{1}H and ^{13}C. A mechanical switch allows either of these circuits to be connected to the r.f. coil (the design of which is optimised for ^{13}C). The high pressure bomb consists of a beryllium-copper (Berylco 25) cylinder of the same dimensions as in the earlier design. Temperature regulation is achieved as before but thermal insulation is now achieved by surrounding

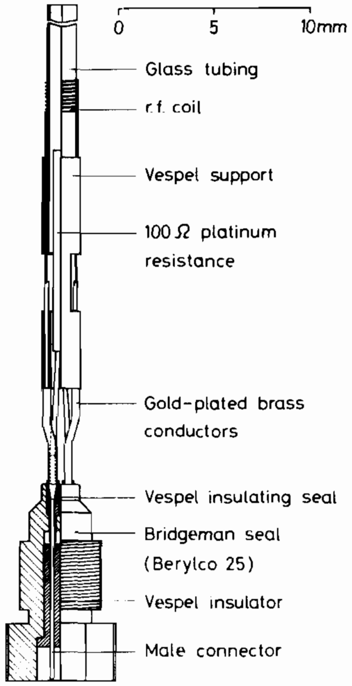

Fig. 1. High pressure NMR probe insert. Left hand side shows sectional view and right hand side external view.

the bomb with a silvered vacuum dewar. However, the major improvements have been made in the design of the bomb insert, *i.e.* the internal electrical components and pressure seal of the bomb. The new arrangement is shown in Fig. 1. The principal aim has been to reduce the resistance of the wires from the coil by using thick gold-plated brass conductors instead of the thin wires and reducing the soldered connections to one for each wire. In addition it was found that over a period of time, the polyimide (Vespel) Bridgeman seals of the original bombs, when run at high temperatures, gradually exuded through the cell, eventually breaking the connecting wires. The current design [15] obviates this problem by using only thin Vespel washers and insulating mantles. Changing the bomb insert in order to change nuclei is now a matter of minutes. The bomb assembly has been tested to 400 MPa between 120 and 420 K. The r.f. coil for carbon-13 consists of 36 turns of 0.05 mm diameter copper wire, the turns being separated by 0.05 mm and wound on a glass tube 3.0 mm o.d., 2.6 mm i.d. The adjustment of the homogeneity of the magnetic field may be performed by switching the coil matching circuitry to ^{1}H and observing the proton FID on either the sample of interest or a diamagnetic sample. In this way any homogeneity correction can be made negligible. As in the variable tempeature study the linewidth was obtained from the transformed and phased FID by fitting to a single Lorentzian function. Since we are working with proton-coupled spectra, the resonance of the pure solvent is never narrow but under the conditions of these experiments the proton coupling (~7 Hz) is never resolved and the overall envelope of the resonance was computer fitted to a single Lorentzian function whose width was calculated to be 28.1 Hz. This value was thus subtracted from the linewidth in the presence of Co^{2+}, in order to obtain the line-broadening contribution of the ion.

Data Treatment and Results

The detailed expressions for the effect of solvent exchange on both transverse relaxation time and chemical shift of the free or coalesced signal were first given by Swift and Connick [16] and have been summarised recently [4]:

$$\frac{1}{T_{2r}} = \frac{1}{P_m}\left(\frac{1}{T_2} - \frac{1}{T^0_{2A}}\right) =$$

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

$$\Delta\omega_r = \Delta\omega/P_m = \frac{\Delta\omega_m}{(\tau_m/T_{2m} + 1)^2 + \tau_m{}^2\Delta\omega_m{}^2} \quad (2)$$

$1/T_2$ is the observed relaxation rate, $1/T^2_{0A}$ is the relaxation rate of pure solvent and P_m is the fraction of bound solvent. Thus $1/T_{2r}$ is the contribution of the paramagnetic site (and exchange) to the relaxation rate. Since this contribution is proportional to the fraction of bound solvent, this term has also been normalized by dividing through P_m. τ_m is the residence time of the solvent molecule in the first coordination sphere. T_{2m} is the transverse relaxation rate of bound solvent in the absence of exchange and $\Delta\omega_m$ is the chemical shift (rad s^{-1}) between free and bound solvent in the absence of exchange. The observed chemical shift, $\Delta\omega$ (relative to that of pure solvent), is also normalized by dividing through by P_m to give the solute concentration-independent $\Delta\omega_r$. $1/T_{2os}$ is the relaxation rate contribution of solvent in the second coordination shell. The main relaxation mechanism for this process would be electron-nucleus dipolar interaction which is relatively long-range (r^{-6}). However, it is also proportional to the square of the magnetogyric ratio which explains why it is often observed for ^{1}H-NMR but rarely for other nuclei. In this work we see no effect of T_{2os} and thus set this term to zero. Similarly, we see no evidence of any contribution of $1/T_{2m}$ to the data and have set this parameter to zero also. The temperature and pressure dependences of the remaining parameters will now be considered. The residence time τ_m may be related to the pseudo-first order rate constant for solvent exchange and its temperature and pressure dependence may be obtained from transition state theory. Thus at zero pressure

$$k(T)_{P=O} = \frac{1}{\tau_m} = \frac{kT}{h} \exp\left(-\frac{\Delta H^*}{RT} + \frac{\Delta S^*}{R}\right) \qquad (3)$$

and at constant temperature

$$k(P)_T = \frac{1}{\tau_m} =$$

$$= \exp\left(\ln k(0)_T - \frac{\Delta V_0^* P}{RT} + \frac{\Delta\beta^* P^2}{2RT}\right) \qquad (4)$$

where $k(0)_T$ is the zero pressure rate constant, ΔV_0^* is the zero pressure volume of activation and $\Delta\beta^*$ is the pressure independent compressibility of activation. ΔV^* will refer to the volume of activation obtained assuming $\Delta\beta^* = 0$.

The temperature dependence of $\Delta\omega_m$ is normally assumed to obey Bloembergen's equation [17]:

$$\Delta\omega_m = \omega S(S+1) \frac{g_{eff}\beta}{\hbar\gamma_i} \frac{A}{3kT} \qquad (5)$$

where ω is the precessional frequency of carbon-13, $g_{eff}\beta/\hbar$ and γ_i are the magnetogyric ratios of the unpaired electrons and of the carbon-13 nuclei, S is the electron spin quantum number and A is the scalar coupling constant (in joules). Any changes in $\Delta\omega_m$ with pressure can only be due to changes in the coupling constant A. As is well known from high pressure UV studies of transition metal complexes in the solid state, changes in both metal-ligand bond length and covalency are very small in the pressure range 0–200 MPa [18]. We have recently measured the change of $\Delta\omega_m$ with pressure for the proton NMR of $[Ni(CH_3CN)_6](ClO_4)_2$ and it is negligible [4]. Therefore, the $\Delta\omega_m$ pressure dependence for this system can be neglected, particularly when one considers that the variable pressure measurements were made in the slow exchange region [4].

In previous studies we have always analysed the variable temperature data alone to obtain the various NMR parameters and then analysed the variable pressure data using as fixed values the NMR parameters. This procedure may be open to some criticism that by keeping the NMR parameters fixed, one is then unable to see how the errors in the volume of activation correlate with all the other parameters. In this work we thus fit the variable temperature $1/T_{2r}$ and $\Delta\omega_r$ values *and* the variable pressure $1/T_{2r}$ values together. Two points must be made. Firstly, since all $1/T_2$ values are measured approximately to the same *relative* accuracy, we fit the $1/T_{2r}$ values in logarithmic form with equal weights but since all the shifts have approximately a similar *absolute* accuracy we fit the absolute values of $\Delta\omega_r$. This causes a major problem since the relative magnitudes of the two data sets are so different, we have to give the $1/T_{2r}$ values a very much larger weighting. Objective criteria for this weighting are difficult to find but the choice has been made from a visual inspection of the data in graphical form. The relative weighting ($1 : 4.5 \times 10^{-10}$) chosen in this case is close to that which gives the optimum correlation matrix and also similar to that expected from order of magnitude considerations. The second problem concerns the comparison of the variable temperature and variable pressure data. In previous work, we have always treated the zero pressure data rate constant, $k(T)_{P=O}$, as a parameter to be optimised [4, 7]. This is because ΔV^* is related to $\partial \ln k/\partial P$ at zero pressure and any small differences between the variable temperature study at ambient pressure and variable pressure study at constant temperature could cause serious errors in the data analysis. These small differences can arise from several causes: they may be small differences in the temperature calibration of the two experiments, there may be some inconsistencies in the concentrations of the two solutions or there may be small errors in the magnet homogeneity corrections. This problem may be resolved by assuming there is some small constant error in either the variable pressure $1/T_{2r}$ values or the temperature. We adopt the latter approach, in effect treating the temperature of the variable pressure experiment as an unknown. Thus the two data sets were fitted to eqns. (1), (2), (3) and (4) with the following unknowns: ΔH^*, ΔS^*, A/h, ΔV^* and Δ. Δ is given by the expression

$$T_{cor} = T_{meas} + \Delta \qquad (6)$$

TABLE I. Carbon-13 Relaxation Rates, $1/T_{2r}$, and Chemical Shifts, $\Delta\omega_r$ of the Nitrile Resonance of CH_3CN in the Presence of $[Co(CH_3CN)_6](ClO_4)_2$ as a Function of Temperature ($P_m = 4.90 \times 10^{-3}$).

10^3 T^{-1}, K^{-1}	$\ln(1/T_{2r})$	10^{-5} $\Delta\omega_r$[a], rad s^{-1}
2.842	9.498	2.606
2.904	10.056	2.794
2.991	10.487	2.756
3.082	11.013	2.812
3.184	11.662	2.831
3.287	11.940	1.891
3.346	12.000	1.308
3.422	11.796	0.727
3.503	11.400	0.201
3.628	10.938	0.086
3.755	9.747	0.029

[a] Shifts measured relative to pure dioxan but referenced relative to pure CH_3CN ($\delta_{dioxan\text{-}CH_3CN} = 767.5$ Hz).

TABLE II. Carbon-13 Relaxation Rates, $1/T_{2r}$ of the Nitrile Resonance of CH_3CN in the Presence of $[Co(CH_3CN)_6](ClO_4)_2$ as a Function of Pressure at 285.9 K ($P_m = 5.05 \times 10^{-3}$).

P, MPa[a]	$\ln(1/T_{2r})$
0.1	11.507
40.0	11.398
80.0	11.284
120.0	11.171
160.0	11.050
200.0	10.927
180.0	10.980
140.0	11.100
100.0	11.212
60.0	11.335
20.0	11.433
0.1	11.501

[a] Data given in the order in which the experiments were performed.

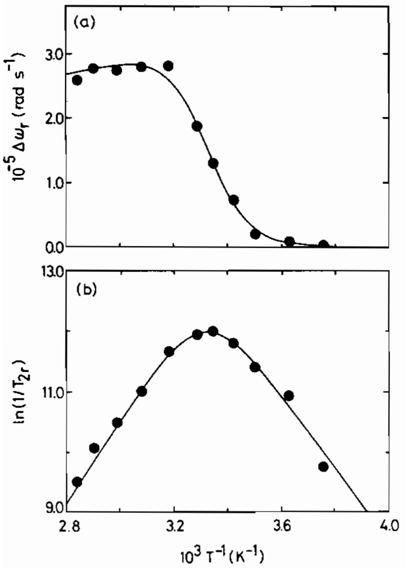

Fig. 2. Variable temperature ^{13}C-NMR data for the nitrile resonance of $[Co(CH_3CN)_6](ClO_4)_2$ in CH_3CN. (a) Free (or coalesced) solvent normalised chemical shifts, $\Delta\omega_r$ (rad s^{-1}). (b) Free (or coalesced) solvent normalised transverse relaxation rates, $1/T_{2r}$ (s^{-1}).

where T_{cor} is the corrected temperature of the high pressure experiment, T_{meas} is the nominal, measured value and Δ is the correction. The experimental data are given in Tables I and II and a comparison of observed and calculated values is given in Figs. 2 and 3. The values obtained together with their standard deviations are*: $\Delta H^* = 48.79 \pm 1.10$ kJ mol^{-1}, $\Delta S^* = +22.2 \pm 3.7$ J K^{-1} mol^{-1}, $A/h = 4.99 \pm 0.05$ MHz, $\Delta V^* = +7.7 \pm 1.7$ cm^3 mol^{-1}, $\Delta = 0.4 \pm 1.2$ K.

TABLE III. Error Correlation Coefficient Matrix.

	ΔS*	ΔH*	A/h	ΔV*	Δ
ΔS*	1.00	1.00[b]	0.05	0.01	0.27
ΔH*		1.00	0.05	0.01	0.28
A/h			1.00	−0.01	−0.01
ΔV*				1.00	0.78
Δ					1.00
$k_{298.15}$[a]	1.00	−0.24	−0.02	−0.01	−0.32

[a] Values obtained if $k_{298.15}$ and ΔH* are treated as for the temperature dependence of k instead of ΔS* and ΔH*. [b] >0.995, rounded up to 1.00.

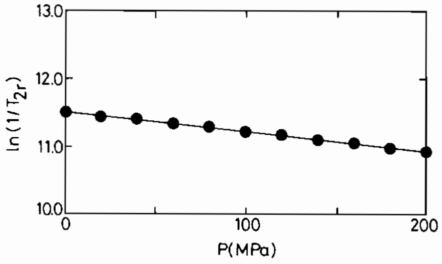

Fig. 3. Variable pressure ^{13}C-NMR normalised transverse relaxation rates, $1/T_{2r}$ (s^{-1}) for the nitrile resonance of $[Co(CH_3CN)_6](ClO_4)_2$ in CH_3CN at 285.9 K. (Drawn to same scale as Fig. 2).

The value of the rate constant is $k_{298.15} = (2.56 \pm 0.06) \times 10^5$ s^{-1}.

Discussion

In view of the past difficulties associated with the determination of reliable variable temperature activation parameters, it is interesting to compare the error problems associated with ΔS* and ΔV*. It is immediately clear from the error correlation coefficient matrix of our data analysis (Table III) that ΔS* and ΔH* are extremely correlated indeed which accounts for the very poor reliability which may be placed on ΔS*. $k_{298.15}$ on the other hand does not show serious correlation problems. ΔV* likewise shows no serious correlation with other parameters except possibly Δ. However, the value of Δ is very close to zero, *i.e.* the measured temperature is very close to the corrected one and if Δ is constrained to be zero, $\Delta V^* = +7.3 \pm 1.0$ cm^3 mol^{-1}. It is thus

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*If the full expression, eqn. (4) is utilized instead, $\Delta V_0^* = +7.8 \pm 5.9$ cm^3 mol^{-1} and $\Delta\beta^* = (+0.14 \pm 5.8) \times 10^{-2}$ cm^3 mol^{-1} MPa.

TABLE IV. Comparison of Kinetic and NMR Results for $[Co(CH_3CN)_6](ClO_4)_2$ in CH_3CN.

10^{-5} $k_{298.15}$ (s^{-1})	ΔH^* (kJ mol^{-1})	ΔS^* (J K^{-1} mol^{-1})	ΔV^* (cm^3 mol^{-1})	Nucleus	$A/h\gamma_i$ (T)	Reference
1.4	33.9	−31.4		^1H	-5.32×10^{-4} [a,b]	20
3.5	47.7	+21.8		^1H	-9.22×10^{-4} [a,c]	21
3.2	37.7	+20.9		^{14}N	2.71[d], 2.79[e]	21
3.57	49.7	+28.1		^{14}N	2.98	[f]
2.7	36.8	−17.6		^{14}N	3.09	21
3.38	49.5	+27.1	+9.9	^1H, ^{14}N	-4.15×10^{-4} [a,c], 2.98	10
			+6.7	^{14}N		13
2.57	48.8	+22.7	+7.7	^{13}C	0.466	This work

[a] ^1H shifts show non-Curie dependence. [b] No temperature quoted and thus not feasible to compare with other values. [c] At 25 °C using eqn. (5). [d] Obtained from $1/T_{2r}$ data. [e] Obtained from $\Delta\omega_r$ data. [f] Reanalysis of ^{14}N data of [21].

clear that the inclusion of Δ in the data analysis does not cause serious doubts about the reliability of ΔV^*. We are thus certain that, from a purely practical point of view ΔV^* is a very much superior parameter than ΔS^* for the elucidation of mechanisms. As discussed elsewhere, ΔV^* also is much more amenable to interpretation in terms of molecular models of bond length changes between reactants and transition state [7].

Returning to the problem of choice of relative weights between $\ln(1/T_{2r})$ and $\Delta\omega_r$, it appears that there are some small inconsistencies between the shift and linewidth data. Thus when one changes the weight from a value such that only the T_2 values are important to a value where only the shifts are fitted, the parameters change as follows:

	$\ln(1/T_{2r})$	$\Delta\omega_r$
10^{-5} $k_{298.15}$ (s^{-1})	2.46	2.57
ΔH^* (kJ mol^{-1})	48.7	55.6
ΔS^* (JK^{-1} mol^{-1})	+21.5	+45.1
A/h (MHz)	5.09	4.90

Strictly speaking, the correct way of dealing with the weighting of the data is to use the experimental standard deviations of the data which could be obtained, for example, by fitting the variable temperature spectra to the sum of two Lorentzians, one for the CH_3CN and one for the dioxan. Thus one could obtain the standard deviations of both T_2 values and the chemical shift between the two. However, such a procedure deals with the random errors only and it is clear that the inconsistencies in the data are due to non-random errors. These latter errors can cause serious faults in the determination of ΔH^* and ΔS^*.

It is also possible that some of the simplifications made in the equations are not correct. $1/T_{2m}$ has been fixed at zero. The relaxation mechanism involved is probably scalar and would thus obey eqn. [11]

$$\frac{1}{T_{2m}} = \left(\frac{A}{h}\right)^2 \frac{S(S+1)}{3} \tau_e \tag{7}$$

We have no knowledge about τ_e but a recent ^{17}O-NMR study of the analogous hexa-aquo complex gave 5×10^{-12} s^{-1} at 298.15 K [1]. Using this value, an order of magnitude estimate of 6×10^3 s^{-1} may be obtained from $1/T_{2m}$ and it is clear that a value of this size is not totally negligible in the data analysis. A more detailed analysis shows that a finite $1/T_{2m}$ would indeed make the shifts and widths more consistent. However, it should be added that this effect is very small indeed, much too small to give any sensible results using curve-fitting procedures without a proper estimate of τ_e (and its temperature dependence).

The outer sphere correction, $1/T_{2os}$ has also been set to zero. The relaxation mechanism in this case is probably dipolar and hence depends on the square of the magnetogyric ratio and the inverse sixth power of the metal-nucleus distance. As a rough calculation, we may guess that the ratio of ion-proton distance to ion-nitrile carbon distance in the outer sphere is close to one, definitely less than 1.5. With this value and taking into account the change of magnetogyric ratio, one may estimate that the outer sphere correction for ^{13}C is less than 70% of the proton value. It is thus clear from a comparison of West and Lincoln's [21] ^1H outer sphere correction that for this ^{13}C study the outer sphere term is completely negligible.

Table IV summarises the available kinetic and NMR parameters for CH_3CN exchange on $[Co(CH_3CH)_6](ClO_4)_2$ in acetonitrile. The scalar coupling constants are normalised by dividing through by the magnetogyric ratio and, as given, are directly proportional to the unpaired electron density at the nucleus

[19]. It should be noted that entries 2 to 6 all involve the data of West and Lincoln. As discussed in an earlier paper [10], our ^{1}H-NMR were not reliable enough to properly define the kinetic parameters due to very small line-broadening and limited solubility and so they were analysed together with West and Lincoln's ^{14}N data. This explains why these results are so close to the ^{14}N study alone. It is clear from Table IV that there is by no means agreement as to the value of ΔS^* although our experience with the Ni^{2+}-acetonitrile system would suggest the positive values are more correct. For ΔV^*, the situation is much less ambiguous and it seems clear that a value of the order of 7 cm^3 mol^{-1} is very reasonable, particularly since the ^{1}H-derived value of 9.9 cm^3 mol^{-1} was known to be the last reliable result we had obtained. It is now gratifying to note that for all the solvents we have so far studied, the ΔV^* values for Co^{2+} are always slightly smaller than for Ni^{2+}. This is in accord with the trend established for both H_2O and MeOH that going to earlier members of the first row divalent metal ion series from Ni^{2+}, the values become less and less positive until at Mn^{2+} they are negative. These results are only readily interpretable in terms of a mechanistic changeover for complex formation reactions from a dissociative interchange, I_d for Ni^{2+} to an associative interchange, I_a, for Mn^{2+}.

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