

Rates and Activation Parameters for Dimethyl Sulphoxide Exchange with Hexakis(dimethyl sulphoxide)-nickel(II), -cobalt(II), and -iron(III) Ions

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Natural-abundance ^{17}O n.m.r. at 54.24 MHz has been used to measure the rates of dimethyl sulphoxide (dmsO) exchange with $[\text{M}(\text{dmsO})_6]^{2+}$ ($\text{M} = \text{Co}$ or Ni) ions, and 90-MHz stopped-flow ^1H Fourier-transform n.m.r., and 22.63-MHz ^{13}C n.m.r. line broadening, to measure the rate of dmsO exchange with $[\text{Fe}(\text{dmsO})_6]^{3+}$ ion. At 298.2 K the rate constants and associated activation parameters for the exchange of a single solvent molecule are: $10^{-3}k_{\text{ex}}/\text{s}^{-1} = 445 \pm 12$, 16.5 ± 0.3 , and 0.026 ± 0.002 ; $\Delta H^\ddagger/\text{kJ mol}^{-1} = 49.0 \pm 1.5$, 49.2 ± 0.4 , and 52.1 ± 0.7 ; $\Delta S^\ddagger/\text{J K}^{-1} \text{mol}^{-1} = 28 \pm 5$, 0.9 ± 1.1 , and -43 ± 3 for Co^{II} , Ni^{II} , and Fe^{III} respectively. A systematic method is proposed for adjusting the relative weights of data sets when simultaneously fitting $\ln(T_{2r}^{-1})$ and $\Delta\omega_r$ data to the Swift–Connick equations.

This work is an extension of our previous studies of dimethyl sulphoxide (dmsO) and *NN*-dimethylformamide exchange with aluminium(III) and gallium(III) ions,^{1,2} and acetonitrile exchange with Co^{2+} ,^{3,4} We demonstrate the suitability and advantages of natural-abundance ^{17}O n.m.r. line-broadening studies using a high-field (9.4 T) spectrometer, and the further use of stopped-flow Fourier-transform ^1H n.m.r. to investigate the rate of dmsO exchange with Fe^{III} . A comparison is made with previous studies of these systems by ^1H and ^{13}C n.m.r. line broadening.

Results

^{17}O N.M.R. Line-broadening Studies.—Natural-abundance ^{17}O n.m.r. spectra were recorded at 54.24 MHz in 10-mm tubes. Typically, 10^5 free-induction decays were taken, and averaged, over a period of 45 min at each temperature. Line-widths were measured by fitting the Fourier-transformed and carefully phased data to the equation for a Lorentzian line. For pure dmsO the full linewidth at half-maximum height ($v_{\frac{1}{2}}^0$) decreases from 167 Hz at 295 K to 55 Hz at 370 K, and a plot of $\ln(v_{\frac{1}{2}}^0/\text{Hz})$ versus $1/T$ (T = absolute temperature) is linear as shown in Figure 1. Linear least-squares analysis of these data gives equation (1).

$$\ln(v_{\frac{1}{2}}^0/\text{Hz}) = (1\,551 \pm 35)/T - (0.16 \pm 0.11) \quad (1)$$

$[\text{Co}(\text{dmsO})_6]^{2+}$ Ion.—Addition of a small amount of $[\text{Co}(\text{dmsO})_6][\text{ClO}_4]_2$ to dmsO, such that the mole fraction of bound solvent molecules, $P_m = 1.157 \times 10^{-3}$, causes the observed ^{17}O linewidth ($v_{\frac{1}{2}}^{\text{obs}}$) to increase by 171–722 Hz in the temperature range 295–370 K, as shown by the data in Table 1. Values of T_{2r}^{-1} were calculated from equation (2).

$$T_{2r}^{-1} = \pi(v_{\frac{1}{2}}^{\text{obs}} - v_{\frac{1}{2}}^0)/P_m \quad (2)$$

The chemical shift of the ^{17}O resonance was measured in the presence ($\omega^{\text{obs}}/\text{Hz}$) and absence (ω^0/Hz) of metal ion, and the reduced shift parameter ($\Delta\omega_r/\text{rad s}^{-1}$) calculated from equation (3) (data in Table 1). The Co^{II} produces a downfield shift of the ^{17}O resonance.

$$\Delta\omega_r = 2\pi(\omega^{\text{obs}} - \omega^0)/P_m \quad (3)$$

Plots of $\ln(T_{2r}^{-1})$ and $\Delta\omega_r$ as a function of T^{-1} are shown in Figures 2 and 3, together with the computer-calculated fits of the data to the modified Swift–Connick equations.⁵ Corrections for outer-sphere line broadening were not necessary, as found in related ^{13}C work (outer-sphere line broadening is

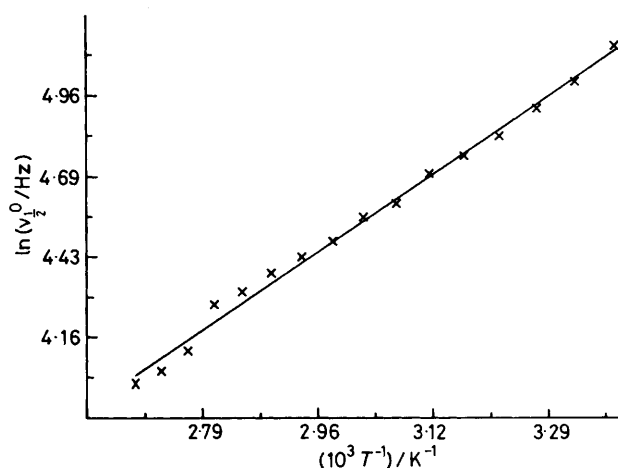


Figure 1. Variation of the logarithm of the natural linewidth $[\ln(v_{\frac{1}{2}}^0/\text{Hz})]$ of the ^{17}O n.m.r. resonance of dmsO with inverse temperature (T^{-1})

Table 1. Variation of $\ln(T_{2r}^{-1})$ and $\Delta\omega_r$, oxygen-17 n.m.r. data with temperature for $[\text{Co}(\text{dmsO})_6]^{2+}$ ($P_m = 1.157 \times 10^{-3}$) in dmsO solution

T/K	298.7	303.6	308.5	313.3	318.1
$\ln(T_{2r}^{-1}/\text{s}^{-1})$	13.048	13.318	13.614	13.942	14.148
$10^{-5}\Delta\omega_r/\text{rad s}^{-1}$	0	2.172	4.564	4.616	7.657
T/K	323.0	328.0	332.7	337.7	342.5
$\ln(T_{2r}^{-1}/\text{s}^{-1})$	14.330	14.512	14.475	14.530	14.446
$10^{-5}\Delta\omega_r/\text{rad s}^{-1}$	11.68	15.43	21.18	24.33	31.50
T/K	347.5	352.4	357.2	362.4	367.0
$\ln(T_{2r}^{-1}/\text{s}^{-1})$	14.414	14.256	14.065	13.959	13.769
$10^{-5}\Delta\omega_r/\text{rad s}^{-1}$	34.76	35.57	37.53	41.81	37.91

more important in ^1H n.m.r. studies).^{3,4} The equations used are summarised in (4)–(8). A weighted non-linear regression

$$\frac{1}{T_{2r}} = \frac{1}{\tau_m} \left[\frac{T_{2m}^{-2} + (T_{2m}\tau_m)^{-1} + \Delta\omega_m^2}{(T_{2m}^{-1} + \tau_m^{-1})^2 + \Delta\omega_m^2} \right] \quad (4)$$

$$T_{2m}^{-1} = A_m \exp(E_m/RT) \quad (5)$$

$$\Delta\omega_m = B_0 + B_1/T \quad (6)$$

$$\Delta\omega_r = \Delta\omega_m / [(\tau_m/T_{2m} + 1)^2 + \tau_m^2 \Delta\omega_m^2] \quad (7)$$

$$\tau_m^{-1} = (kT/h) \exp[(\Delta S^\ddagger/R) - (\Delta H^\ddagger/RT)] \quad (8)$$

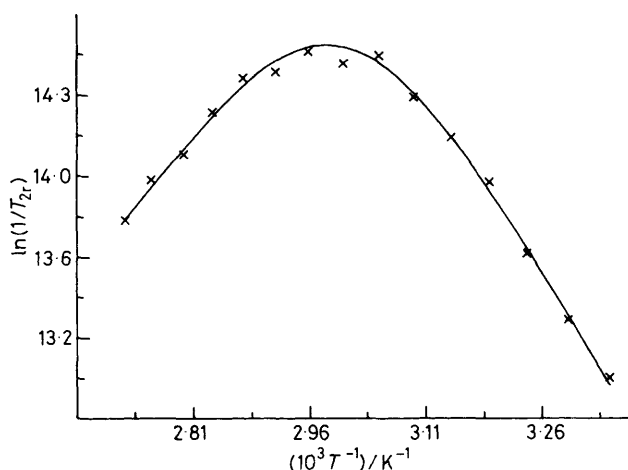


Figure 2. Plot of $\ln(T_{2r}^{-1})$ data (X) versus inverse temperature, together with the computer-calculated least-squares Swift-Connick curve (—), for $[\text{Co}(\text{dmsO})_6]^{2+}$ ion in dmsO solution

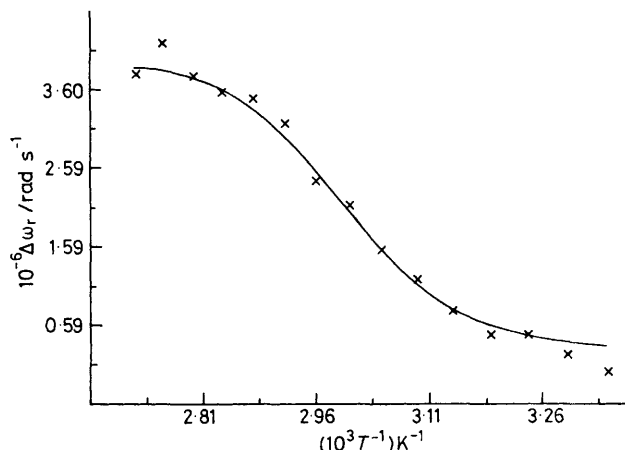


Figure 3. Plot of $\Delta\omega_r$ data (X) versus inverse temperature, together with the computer-calculated least-squares curve (—), for $[\text{Co}(\text{dmsO})_6]^{2+}$ ion in dmsO solution

analysis was employed to fit values of $\ln(T_{2r}^{-1})$ and $\Delta\omega_r$ at different temperatures to these equations, taking ΔH^\ddagger , ΔS^\ddagger , B_0 , B_1 , and A_m as the unknown parameters. A value of E_m of 4 kJ mol $^{-1}$ was used, as in previous ^{13}C and ^{15}N work^{3,4} (values of E_m in the range 1–4 kJ mol $^{-1}$ had negligible effect on estimated values of ΔH^\ddagger and ΔS^\ddagger).

One problem to be faced in simultaneously fitting the two data sets [$\ln(T_{2r}^{-1})$ and $\Delta\omega_r$] to these equations is the need to adjust the relative weights of the two data sets. This problem has been discussed previously.³ In this work we adopted the following method of adjusting the relative weights. First the weights of the $\ln(T_{2r}^{-1})$ data were set to unity, and an arbitrary small weight applied to the $\Delta\omega_r$ data such that the significance of either of the two data sets was not dominant (an initial value of 10^{-8} was used for the $\Delta\omega_r$ weights). After initial convergence the standard deviation (σ_i) of each data set, i ($i = 1$ or 2), was calculated from equations (9) and (10),

$$\sigma_i^2 = \left[\sum_{j=1}^{j=n_i} (y_{\text{obs.}} - y_{\text{calc.}})^2 - n_i(\bar{r}_i)^2 \right] / (n_i - 1) \quad (9)$$

$$\bar{r}_i = \sum_{j=1}^{j=n_i} (y_{\text{obs.}} - y_{\text{calc.}}) / n_i = \text{mean residual} \quad (10)$$

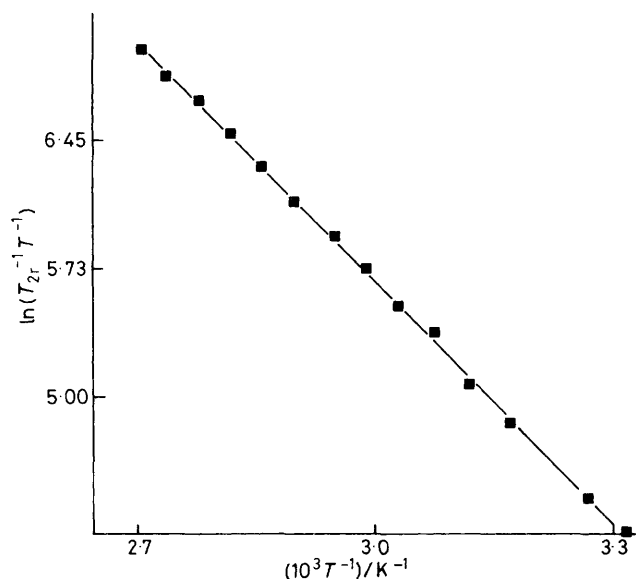


Figure 4. Plot of $\ln(T_{2r}^{-1}T^{-1})$ versus inverse temperature (T^{-1}) for $[\text{Ni}(\text{dmsO})_6]^{2+}$ ion in dmsO solution

where n_i is the number of observations for a given set, i , and the residuals ($y_{\text{obs.}} - y_{\text{calc.}}$) refer to either $\ln(T_{2r}^{-1})$ or $\Delta\omega_r$ data.

Next, the weights, W , of the $\Delta\omega_r$ data were adjusted according to equation (11) [σ_1 = standard deviation of $\ln(T_{2r}^{-1})$ data, σ_2 = standard deviation of $\Delta\omega_r$ data], and the whole process repeated until the weights did not vary significantly

$$W = (\sigma_1/\sigma_2)^2 \quad (11)$$

between successive cycles. Final convergence was reached after three or four cycles of least-squares refinement, with a final relative weighting, W , of 4.7×10^{-14} in this case. The estimated parameters [\pm one estimated standard deviation (e.s.d.)] were found to be $\Delta H^\ddagger = 49.0 \pm 1.5$ kJ mol $^{-1}$, $\Delta S^\ddagger = 27.7 \pm 4.8$ J K $^{-1}$ mol $^{-1}$, $B_1 = (2.23 \pm 0.03) \times 10^8$ s $^{-1}$ K $^{-1}$, $B_0 = 329.6 \pm 62.5$ s $^{-1}$, and $A_m = (9.9 \pm 2.2) \times 10^4$ s $^{-1}$, and the calculated curves using these parameters are shown in Figures 2 and 3. To obtain a value of the rate constant at 298.2 K (k_{298}), and its standard deviation, equation (8) was replaced by the related equation (12), and the parameter ΔS^\ddagger

$$\tau_m^{-1} = (k_{298}T/298.2) \exp\{(-\Delta H^\ddagger/R)[(1/T) - (1/298.2)]\} \quad (12)$$

replaced by k_{298} in the data analysis. This gave the rate constant for the exchange of a single solvent molecule at 298.2 K; $10^{-5}k_{\text{ex}}/\text{s}^{-1} = 4.45 \pm 0.12$.

$[\text{Ni}(\text{dmsO})_6]^{2+}$ Ion.—A similar ^{17}O n.m.r. study of this ion was undertaken for comparison with the recent ^{13}C n.m.r. line-broadening results.⁶ Whereas in the case of the ^{13}C study most of the T_{2r} data were obtained in the 'fast-exchange' region of the Swift-Connick curves, for ^{17}O n.m.r. because the value of the bound shift, $\Delta\omega_m$, is much larger, all of the T_{2r} data relate to the extreme slow-exchange region of the curve, and the approximations $\Delta\omega_m^2 \gg T_{2m}^{-2}$ and $\Delta\omega_m^2 \gg \tau_m^{-2}$ apply. In this situation equation (4) simplifies to $T_{2r} = \tau_m$, and so from equation (8) a plot of $\ln(T_{2r}^{-1}T^{-1})$ against T^{-1} is expected to be linear. Such a plot is shown in Figure 4 (data in Table 2), and from a linear least-squares analysis the activation parameters are calculated to be $\Delta H^\ddagger = 49.2 \pm 0.4$ kJ mol $^{-1}$

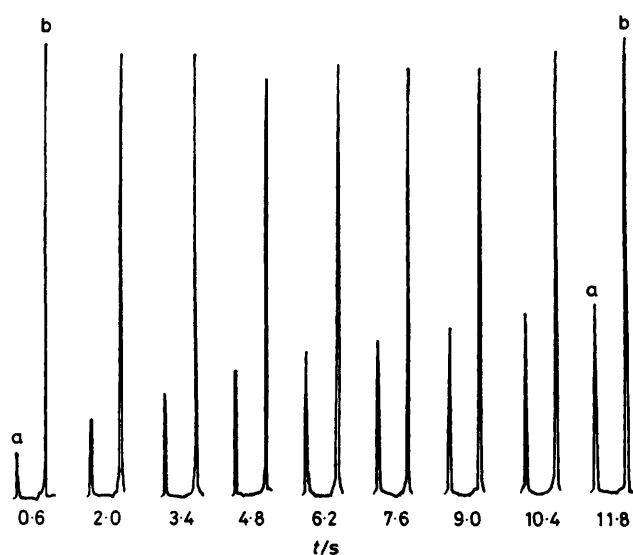


Figure 5. Parts of successively recorded ^1H n.m.r. spectra obtained by stopped-flow n.m.r. after mixing $[\text{Fe}(\text{dmsO})_6]^{3+}$ ion with $[\text{H}_3]\text{-dmso}$ in $[\text{H}_3]\text{nitromethane}$ solution at 243.4 K ($[\text{Fe}^{3+}] = 10^{-2}$ mol dm^{-3} ; $[\text{H}_3]\text{dmso} = 1.0$ mol dm^{-3}). Resonances: a = dmso; b = SiMe_4 .

Table 2. Variation of $\ln(T_{2r}^{-1})$ oxygen-17 n.m.r. data with temperature for $[\text{Ni}(\text{dmsO})_6]^{2+}$ ion ($P_m = 1.397 \times 10^{-3}$) in dmso solution (Values of $\Delta\omega$, are negligibly small in this temperature range and were omitted from the data analysis)

T/K	300.8	305.6	315.2	320.1	325.1
$\ln(T_{2r}^{-1}/\text{s}^{-1})$	9.9438	10.179	10.828	11.097	11.480
T/K	330.0	334.7	339.3	344.6	349.6
$\ln(T_{2r}^{-1}/\text{s}^{-1})$	11.718	12.007	12.251	12.534	12.822

and $\Delta S^\ddagger = 0.9 \pm 1.1 \text{ J K}^{-1} \text{ mol}^{-1}$. Using equation (12) gave the rate constant at 298.2 K; $10^{-4} k_{\text{ex}} = 1.65 \pm 0.03 \text{ s}^{-1}$.

$[\text{Fe}(\text{dmsO})_6]^{3+}$ Ion.—Since the dmso exchange rate with this tripotivite ion is much slower than those reported for most bivalent metal ions, it is possible to investigate the exchange by stopped-flow Fourier-transform ^1H n.m.r. at low temperatures (ca. -20°C), as we described previously for aluminium(III) and gallium(III) ions.^{1,2} In the case of $[\text{Fe}(\text{dmsO})_6]^{3+}$, mixing with excess of $[\text{H}_3]\text{dmso}$ in $[\text{H}_3]\text{nitromethane}$ solution causes exchange of the proteo- and deuterio-dmso molecules, and since the ^1H resonance of co-ordinated dmso is very broad, successively recorded ^1H n.m.r. spectra reveal a single resonance for the unco-ordinated dmso molecule, which grows with time as the exchange reaction occurs. A typical set of spectra is shown in Figure 5. A plot of $\ln(h_\infty - h_t)$ versus time (h_∞ and h_t are the heights of the resonance at the end of the reaction and at time t , respectively) is shown in Figure 6, and from a linear least-squares analysis of such data the rate constants in Table 3 were obtained.

The system was also investigated by ^{13}C n.m.r. line broadening in dmso solution at much higher temperatures, and values of T_{2r}^{-1} as a function of temperature are collected in Table 4. Because the solutions tend to decompose at the high temperatures required to produce significant line broadening, fresh solutions were used over short periods of time. A further ^{13}C study has recently been reported.⁷ Our ^{13}C data were recorded in the slow-exchange region where the approxi-

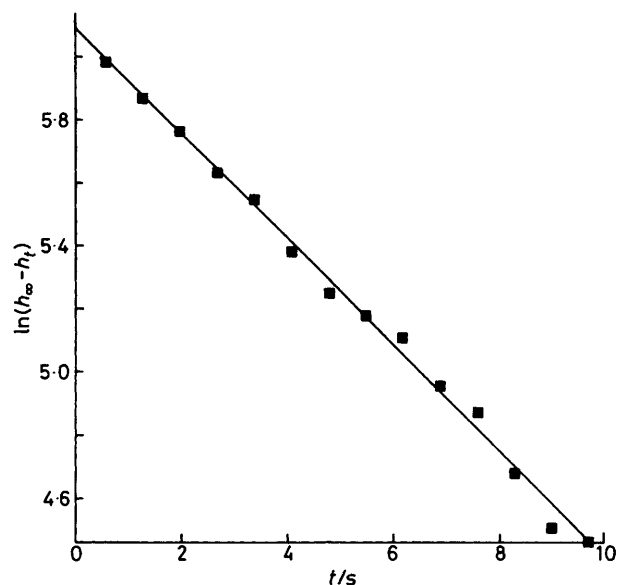


Figure 6. Kinetic plot showing the first-order growth of the released proteo-dmso molecules from the data shown in Figure 5 (h_∞ and h_t are the final height and the height at time t , of the proteo-dmso resonance)

Table 3. Rate constants for the exchange of a single solvent molecule with $[\text{Fe}(\text{dmsO})_6]^{3+}$ ion ($5 \times 10^{-3} - 10^{-2}$ mol dm^{-3}) obtained at low temperatures by stopped-flow Fourier-transform ^1H n.m.r. in $[\text{H}_3]\text{nitromethane}$ solution containing $[\text{H}_3]\text{dmso}$ (0.5–1.0 mol dm^{-3})

T/K	235.2	238.0	238.6	242.8	243.0
$k_{\text{ex}}/\text{s}^{-1}$	0.108 ^a	0.112 ^b	0.135 ^a	0.212 ^a	0.125 ^b
T/K	243.4	248.3	248.7	253.6	
$k_{\text{ex}}/\text{s}^{-1}$	0.168 ^a	0.274 ^b	0.396 ^a	0.294 ^b	

^a $[\text{Fe}^{3+}] = 10^{-2}$, $[\text{dmso}] = 1.0$ mol dm^{-3} . ^b $[\text{Fe}^{3+}] = 5 \times 10^{-3}$, $[\text{dmso}] = 0.5$ mol dm^{-3} .

Table 4. Variation of $\ln(T_{2r}^{-1})$ ^{13}C n.m.r. data with temperature for $[\text{Fe}(\text{dmsO})_6]^{3+}$ ion in dmso solution

T/K	348.3	351.0	356.3	358.2	358.6
$\ln(T_{2r}^{-1}/\text{s}^{-1})$	6.491 ^a	6.501 ^b	6.976 ^c	6.932 ^a	7.221 ^a
T/K	360.5	365.7	368.2	369.4	369.7
$\ln(T_{2r}^{-1}/\text{s}^{-1})$	6.894 ^b	7.317 ^c	7.538 ^a	7.599 ^a	7.315 ^b

^a $P_m = 7.33 \times 10^{-2}$. ^b $P_m = 5.31 \times 10^{-2}$. ^c $P_m = 4.66 \times 10^{-2}$.

^d $P_m = 4.75 \times 10^{-2}$.

mations made for the nickel(II) ^{17}O data apply, and combination of the high-temperature values of $\ln(T_{2r}^{-1}T^{-1})$ in dmso (Table 4) with the low-temperature $\ln(k/T)$ values in nitromethane solution (Table 3) gives the Eyring plot of Figure 7. From this figure, covering the temperature ranges 235–254 and 348–366 K, linear least-squares analysis gives $\Delta H^\ddagger = 52.1 \pm 0.7 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -43.4 \pm 2.4 \text{ J K}^{-1} \text{ mol}^{-1}$, and $k_{\text{ex}} = 25.7 \pm 1.4 \text{ s}^{-1}$ at 298.2 K.

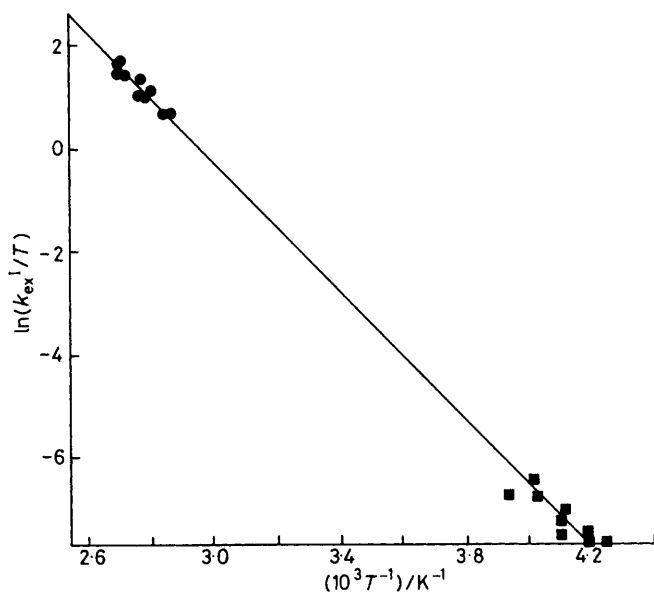
Discussion

Previous studies of the rates of dmso exchange with metal ions have been made by ^1H and/or ^{13}C n.m.r. line broadening,^{6–15} and the results of the more recent studies are compared with those from the present study in Table 5. Bearing in mind

Table 5. Comparison of rates and activation parameters at 298.2 K for dmsO exchange with $[M(\text{dmsO})_6]^{n+}$ ions

M^{n+}	$10^{-2}k_{\text{ex}}/\text{s}^{-1}$	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{J K}^{-1} \text{mol}^{-1}$	Solvent	Method ^a	Ref.
Ni^{2+}	98 ± 46	50 ± 2	0 ± 4	dmso	^{13}C f.t.	6
	165 ± 3	49.2 ± 0.4	$+0.9 \pm 1.1$	dmso	^{17}O f.t.	This work
	110	51 ± 3	$+5 \pm 6$		^1H f.t.	8 ^b
	32	54	+5	CD_3NO_2	^1H c.w.	9
Co^{2+}	42			dmso	^1H c.w.	14
	$4\,450 \pm 120$	49.0 ± 1.5	$+28 \pm 5$	dmso	^{17}O f.t.	This work
	3 100	51.1	+41	CD_3NO_2	^1H c.w.	9
	$3\,450 \pm 300$				^{13}C f.t.	8 ^b
Fe^{2+}	10 000	47.2	+28.9	dmso- CD_3NO_2	^1H c.w.	14
Mn^{2+}	27 000	37.2	+2.9	dmso	$^1\text{H}, ^{13}\text{C}$ f.t.	10
	63 000	31.0	-10.0	dmso	^1H	10
Be^{2+} ^c	2 300	25	-110	dmso	^1H	11
	1 400	51.1	-32.3	CD_3NO_2	^1H	12
Fe^{3+}	0.26 ± 0.02	52.1 ± 0.7	-43 ± 3	dmso- CD_3NO_2	$^{13}\text{C}, ^1\text{H}$ s.f.f.t.	This work
	0.093 ± 0.016	62.5 ± 1.9	-16.7 ± 5.2	dmso	$^1\text{H}, ^{13}\text{C}$ f.t.	7
Al^{3+}	0.0030 ± 0.0002	82.6 ± 1.2	$+22.3 \pm 3.7$	CD_3NO_2	^1H f.t.	3
Ga^{3+}	0.0187 ± 0.005	72.5 ± 0.5	$+3.5 \pm 1.6$	CD_3NO_2	^1H f.t.	3
Cr^{3+}	1.91×10^{-9} ^d	96.7 ± 2.1	-49.5 ± 6.3 ^d	dmso	Classical	13

^a f.t. = Fourier transform, c.w. = continuous wave, s.f.f.t. = stopped-flow Fourier transform. ^b Rather different results have been reported by this group: for Ni^{2+} , $\Delta H^\ddagger = 56.1 \pm 2.5 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = +22 \pm 6 \text{ J K}^{-1} \text{mol}^{-1}$, and for Co^{2+} , $\Delta H^\ddagger = 38.1 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -10 \text{ J K}^{-1} \text{mol}^{-1}$ (J. C. Bouble, J. J. Delpeuch, and A. A. Peguy, *Chem. Abs.*, 1976, **84**, 141293u; J. C. Bouble, J. J. Delpeuch, and G. Mathis, *Mol. Phys.*, 1977, **33**, 1729). ^c Four co-ordinate. ^d The value of k_{ex} quoted in ref. 13 has been multiplied by a factor of 6, since the authors erroneously divided by 6, for the reason explained in our previous paper (see Appendix I of ref. 1). ΔS^\ddagger is increased by $R \ln 6 = 14.9 \text{ J K}^{-1} \text{mol}^{-1}$.

**Figure 7.** Eyring plot of the combined data from Tables 3 and 4

the different methods used, and in some cases the different solvent diluents, the agreement between the recent results is remarkably good. Particularly encouraging is the agreement of the 'slow-exchange' ^{17}O results for Ni^{2+} with those obtained in the 'fast-exchange' region by ^{13}C n.m.r. Both the ^{17}O and ^{13}C results are believed to be more reliable than some of the earlier ^1H n.m.r. studies, since the bound (contact) shifts decrease markedly for nuclei further from the metal ion (*i.e.* $\Delta\omega_m$ for $^{17}\text{O} > ^{13}\text{C} > ^1\text{H}$). This makes it far easier to obtain data in the important 'slow-exchange' region of the Swift-Connick curves using ^{17}O rather than ^1H n.m.r. It also means that much faster exchange rates will be measurable in the future by ^{17}O paramagnetic line broadening. Another advantage is that outer-sphere effects are less of a problem

using paramagnetic ^{13}C or ^{17}O n.m.r. rather than ^1H n.m.r. line broadening. For example, in the case of $[\text{Fe}(\text{dmsO})_6]^{3+}$ ion, outer-sphere line broadening dominates the proton T_2 data.⁷

There can be little doubt that an I_d mechanism applies for solvent exchange with hexakis(solvents) of Ni^{2+} and Co^{2+} . The positive values of ΔV^\ddagger recently determined for solvent exchange with Ni^{2+} and Co^{2+} ions are among the best indicators of this conclusion.^{5,16,17} Use of ΔS^\ddagger values as a guide to mechanism is far less reliable, largely because of the difficulty of determining ΔS^\ddagger with the same precision as ΔV^\ddagger . This is why in previous studies, whenever possible, we have used flow n.m.r. coupled with n.m.r. line broadening to obtain exchange rates over a wide temperature range, in order to improve the accuracy of ΔS^\ddagger values.^{1,18} Nevertheless, the conclusions reached from variable-temperature studies are often less certain than those from variable-pressure work. For example, in a recent study of $[\text{Ga}(\text{dmsO})_6]^{3+}$ ion over a 113 K temperature range, ΔS^\ddagger was found to be $+3.5 \pm 1.6 \text{ J K}^{-1} \text{mol}^{-1}$, and the mechanism of the solvent exchange could not be established with certainty.¹ However, a subsequent variable-pressure study revealed $\Delta V^\ddagger = +13.1 \pm 1.0 \text{ cm}^3 \text{mol}^{-1}$, and a dissociative (probably I_d) mechanism was established.² Therefore, although the value of ΔS^\ddagger determined for $[\text{Ni}(\text{dmsO})_6]^{2+}$ ion is close to zero, we favour an I_d mechanism for solvent exchange with this ion. Only high-pressure studies will reveal if this prediction is correct. Complex-formation reactions in dmso have indicated both I_d ⁶ and I_a ¹⁹ mechanisms.

For $[\text{Co}(\text{dmsO})_6]^{2+}$ ion, ΔS^\ddagger is significantly positive and an I_d mechanism is more firmly established. Comparison of the $[\text{Co}(\text{dmsO})_6]^{2+}$ and $[\text{Ni}(\text{dmsO})_6]^{2+}$ activation parameters reveals that the greater lability of the Co^{2+} ion arises largely from the more positive ΔS^\ddagger value. This result is unexpected since in aqueous solution the values of $\Delta H^\ddagger/\text{kJ mol}^{-1}$ are 46.9 and 56.9, and the values of $\Delta S^\ddagger/\text{J K}^{-1} \text{mol}^{-1}$ are +37.2 and +32, for $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ respectively.¹⁶ A more positive ΔH^\ddagger value for Ni^{2+} compared with Co^{2+} is expected because of the greater crystal-field activation energy for a $3d^8$ compared with a $3d^7$ metal ion. We conclude, therefore, that the behaviour of $[\text{Ni}(\text{dmsO})_6]^{2+}$ ion is somewhat

anomalous, as noted in our previous studies of metal-complex formations.¹⁹ The possibility of an octahedral \rightleftharpoons square planar (or five-co-ordinate) equilibrium, well known for other nickel(II) systems, could account for the unusual behaviour of $[\text{Ni}(\text{dmso})_6]^{2+}$ ion,* even if the equilibrium lies well to the side of the six-co-ordinate species. However, there is no experimental evidence to suggest that a significant concentration of a reduced co-ordination number species exists.²⁰ An octahedral \rightleftharpoons tetrahedral equilibrium has been observed for the $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ion at elevated temperatures.²¹ Such equilibria would be favoured by bulkier solvent molecules such as dmso.

Because the rate of dmso exchange with $[\text{Fe}(\text{dmso})_6]^{3+}$ ion is quite slow, paramagnetic line-broadening studies require the use of high temperatures to produce significant exchange-broadening effects. At the high temperatures required, our solutions were observed to decompose slowly with time, becoming progressively more yellow. Therefore, we used several fresh solutions over short periods of time, and did not extend to the very high temperatures used in a recent study.⁷ We found this system much easier to examine at low temperatures in $[\text{H}_3]\text{nitromethane}$ solution using flow-Fourier transform n.m.r. The solutions are quite stable at low temperatures, and the relaxing effect of the paramagnetic ion prevents saturation of the spin system, even when using fairly rapid radiofrequency pulses. The absence of a co-ordinated dmso resonance from the spectra (Figure 5) makes the system very easy to study by flow n.m.r., and we believe these results are more reliable than the high-temperature ^{13}C data. Combining the two data sets gave the activation parameters shown in Table 5. The agreement with the recent study at elevated temperatures⁷ is not very good, and this could arise either because of the different solvent used in our flow n.m.r. study, or because of the decomposition noted earlier. The use of nitromethane as a diluent has not been observed to have much effect on solvent-exchange rates in the past,^{9,14} and we believe that decomposition at elevated temperatures is more likely to be the cause of the discrepancy. In any case, both studies reveal a significantly negative ΔS^\ddagger value, in line with an associative, I_a , mechanism. The value of ΔV^\ddagger of $-3.1 \pm 0.3 \text{ cm}^3 \text{ mol}^{-1}$ is further strong evidence in support of this conclusion.⁷ The isoelectronic Mn^{2+} and Fe^{3+} ions have both been found to undergo solvent exchange with an I_a mechanism.^{7,16,22}

Experimental

Materials.—Dimethyl sulphoxide was dried by refluxing under vacuum over calcium hydride for 1 h, followed by vacuum distillation and storage over pre-activated 3A molecular sieves. The sieves were activated by drying in a slow stream of dry N_2 at 623 K for 5 h. A fairly dry sample of each hydrated metal perchlorate was converted into the hexakis(dimethyl sulphoxide) salt by stirring with triethyl orthoformate (25 cm^3) for 2 h under dry N_2 , followed by the addition of dry dmso (2 cm^3) to precipitate the product. Stirring of the suspension was continued for 1 h, followed by filtration under dry N_2 . The products were washed with dry diethyl ether containing ca. 10% triethyl orthoformate ($5 \times 10 \text{ cm}^3$) and dried *in vacuo* for 2 h. They can be recrystallised from dry nitromethane containing 10% dmso. They were stored in sealed bottles under N_2 in a dry-box, and the iron(III) and nickel(II) salts analysed for metal content by ethylenediaminetetra-acetate titration {Found: Fe, 6.7. $[\text{Fe}(\text{dmso})_6]$

$[\text{ClO}_4]_3$ requires Fe, 6.8. Found Ni, 8.1. $[\text{Ni}(\text{dmso})_6][\text{ClO}_4]_2$ requires Ni, 8.1%}. The cobalt complex was analysed by oxidation to Co^{3+} followed by iodometric titration {Found: Co, 7.5. $[\text{Co}(\text{dmso})_6][\text{ClO}_4]_2$ requires Co, 8.1%}. Absence of water in the samples was confirmed by i.r. spectra, and by ^1H n.m.r. in $[\text{H}_3]\text{nitromethane}$.

N.M.R. Measurements.—Oxygen-17 n.m.r. spectra were recorded in 10-mm tubes at 54.24 MHz with a Bruker WH400 spectrometer, and ^1H (90 MHz) and ^{13}C (22.63 MHz) n.m.r. with a Bruker WH90, both spectrometers operating in the Fourier-transform mode. Temperatures were measured with a calibrated Comark thermocouple, using a separate tube containing an equal volume of the same solvent used in the n.m.r. measurements.

Non-linear Least-squares Analyses.—A program was written in BASIC for a Hewlett-Packard 9845 B minicomputer, using the methods described previously.²³

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* A referee has pointed out that a switch from *O*- to *S*-co-ordination by dmso could also account for the differences between these two metal ions. However, there is no experimental evidence to support this proposal.