Positive Volumes of Activation and a Dissociative Mechanism for Solvent Exchange with [Mn(solvent)$_6$]$^{2+}$ Ions

Lee Fielding and Peter Moore*

Department of Chemistry, University of Warwick, Coventry CV4 7AL, U.K.

Volumes of activation ($\Delta V^\ddagger$) determined by high-pressure ^1H n.m.r. spectroscopy for the exchange of the solvents N,N-dimethylthioformamide (dmtf) and N,N-dimethylformamide (dmf) with the corresponding [MX$_6$]$^{2+}$ (X = solvent) ions are, for X = dmtf, +11.5 cm^3 mol^{-1} (302 K) and +20.6 cm^3 mol^{-1} (251 K) for M = Mn and Ni, respectively, and for X = dmf and M = Mn, +4.2 cm^3 mol^{-1} (318 K); the significantly positive values of $\Delta V^\ddagger$ for Mn^{2+} contrast with the negative values obtained previously for this metal ion when X is water, methanol, or acetonitrile, indicating a mechanistic change from I_d to I_a for the less bulky solvent molecules.

The volume of activation, $\Delta V^\ddagger$, for solvent exchange with solvated metal ions [reaction (1), M^{n+} = metal ion, X = solvent] is regarded as one of the best indicators of exchange mechanism. A positive value of $\Delta V^\ddagger$ indicates an expanded transition state and a dissociative (I_d or D) mechanism, and a negative $\Delta V^\ddagger$ indicates a decrease in volume in going from reactants to transition state and an associative (I_a or A) mechanism.[1,2]

$$[MX_m]^{n+} + {^*X} \rightleftharpoons [MX_{m-1}{^*X}]^{n+} + X \qquad (1)$$
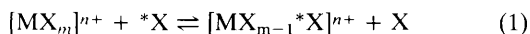
For divalent first-row d-block metal ions, values of $\Delta V^\ddagger$ for reaction (1) (X = H$_2$O, MeOH, or MeCN) change steadily from positive to negative in going from Ni^{2+} to Mn^{2+}. This is due to a gradual change in mechanism from I_d to I_a, and is ascribed to the regular decrease in the population of the non-bonding t_{2g} orbitals. The reduction in the number of electrons in the t_{2g} orbitals from six (Ni^{2+}) to three (high-spin Mn^{2+}) enables the incoming solvent molecule to approach, and an associative ligand exchange to occur with metal ions like Mn^{2+} possessing less than four t_{2g} electrons [$e.g.$ Mn^{2+} and Fe^{3+} ($t_{2g}{^3}e_g{^{*2}}$), V^{2+} ($t_{2g}{^3}$), and Ti^{3+} ($t_{2g}{^1}$)].[1,2]

For the Mn^{2+} ion, values of $\Delta V^\ddagger$ are -7.0 (X = MeCN), -5.0 (X = MeOH), and -5.4 cm^3 (mol^{-1} X = H$_2$O), as

Table 1. Comparison of rate constants and activation parameters for solvent (X) exchange with $[MX_6]^{2+}$ ions (M = Mn, Ni). Data from ref. 1 unless specified.

Solvent	V^{0a} /cm³ mol⁻¹	M	k_{ex}/s⁻¹ at 298 K	$\Delta H^{\ddagger}$ /kJ mol⁻¹	$\Delta S^{\ddagger}$ /J mol⁻¹ K⁻¹	$\Delta V^{\ddagger}$ /cm³ mol⁻¹ (T/K)	Nucleus[b]
H₂O	18.0	Mn	2.1 × 10⁷	32.9	+5.7	−5.4 (298)	¹⁷O
MeOH	40.5	Mn	3.7 × 10⁵	25.9	−50.2	−5.0 (279)	¹H
MeCN	52.2	Mn	1.4 × 10⁷	29.6	−8.9	−7.0 (256)	¹⁴N
dmf[c,e]	77.4	Mn	6.3 × 10⁵	17.5	−75.1	+4.2 (318)	¹H
			2.7 × 10⁶	35.8	−2	+1.6[d] (310)	¹⁷O
dmtf[c,f]	85.2	Mn	3.9 × 10⁷			+11.5 (302)	¹H
H₂O	18.0	Ni	3.2 × 10⁴	56.9	+32.0	+7.2 (298)	¹⁷O
MeOH	40.5	Ni	1.0 × 10³	66.1	+33.5	+11.4 (307)	¹H
MeCN	52.2	Ni	2.8 × 10³	64.3	+37.0	+9.6 (286)	¹H
						+7.3 (319)	¹⁴N
dmf	77.4	Ni	3.8 × 10³	62.8	+33.5	+9.1 (297)	¹H
dmtf[c,g]	85.2	Ni	8.7 × 10⁶	57.4	+80.5	+20.6 (251)	¹H
						+21.8 (282)	¹H

[a] Molar volume of the solvent. [b] N.m.r. nucleus used. [c] Ref., this work. [d] Ref. 3. $10^{-6} k_{ex}$/s⁻¹ = 2.7 ± 0.2, $\Delta H^{\ddagger}$/kJ mol⁻¹ = 35.8 ± 0.6, $\Delta S^{\ddagger}$/J K⁻¹ mol⁻¹ = −2 ± 2, $\Delta V^{\ddagger}$/cm³ mol⁻¹ = 1.6 ± 0.5. [e] $10^{-5} k_{ex}$/s⁻¹ = 6.3 ± 0.8, $\Delta H^{\ddagger}$/kJ mol⁻¹ = 17.5 ± 1.0, $\Delta S^{\ddagger}$/J K⁻¹ mol⁻¹ = −75.1 ± 4.5, $\Delta V^{\ddagger}$ cm³ mol⁻¹ = 4.2 ± 0.7. [f] $10^{-7} k_{ex}$ s⁻¹ = 3.9 ± 0.8, $\Delta G^{\ddagger}$/kJ mol⁻¹ = 29.7 ± 0.5, $\Delta V^{\ddagger}$/cm³ mol⁻¹ = 11.5 ± 1.5. [g] $10^{-6} k_{ex}$/s⁻¹ = 8.7 ± 0.8, $\Delta H^{\ddagger}$/kJ mol⁻¹ = 57.4 ± 1.1, $\Delta V^{\ddagger}$/cm³ mol⁻¹ = 20.6 ± 0.5 (251 K) and 21.8 ± 0.9 (282 K).

expected for an I_a mechanism.[1,2] However, in a recent ¹⁷O n.m.r. study of the $[Mn(dmf)_6]^{2+}$ ion (dmf = *N,N*-dimethyl-formamide), $\Delta V^{\ddagger}$ was found to be +1.6 cm³ mol⁻¹ at 309.5 K. This positive value of $\Delta V^{\ddagger}$ indicates that a dissociative, I_d, mechanism is possible for Mn^{2+} with bulkier solvent molecules, where steric crowding will disfavour a seven-co-ordinate transition-state.[3]

We have been studying the effect of changing the size and donor atom type upon the rate and mechanism of solvent exchange with Ni^{2+} and Mn^{2+} ions. Table 1 summarises our findings for the two closely related ligands, *N,N*-dimethylthio-formamide (dmtf) and *N,N*-dimethylformamide (dmf), from studies by variable temperature and variable pressure ¹H n.m.r.† For comparison, included in Table 1 are the rate data

† The dmtf and dmf complexes were obtained from the hydrated metal perchlorates using the method adopted previously.[4] Elemental analyses showed the products to be $[MX_6][ClO_4]_2$ (M = Ni, X = dmtf; M = Mn, X = dmf), and $[Mn(dmtf)_4(ClO_4)_2]$. The visible spectra of the complexes dissolved in the corresponding neat solvent are as expected for octahedral complexes. Solutions for variable pressure and variable temperature ¹H n.m.r. experiments were prepared by dissolving weighed amounts of each complex in a weighed amount of the corresponding solvent, and the molar fraction of bound solvent (P_m value) was calculated assuming a co-ordination number of six. Variable temperature studies were made in 5 mm n.m.r. tubes at several P_m values in the ranges 1.59—6.95 × 10⁻² for $[Ni(dmtf)_6]^{2+}$, 0.7—15.0 × 10⁻³ for $[Mn(dmtf)_6]^{2+}$, and 4.8—10.7 × 10⁻³ for $[Mn(dmf)_6]^{2+}$, and in the temperature ranges 240—377 K for dmtf, and 217—375 K for dmf complexes. Variable pressure studies were made in 1.9 mm non-spinning n.m.r. tubes between 0.1 and 200 MPa, using equipment built for a Bruker WH90 Fourier-transform spectrometer to the design of Merbach and co-workers.[1] Linewidths and shifts of the uncomplexed solvent formyl proton were measured at 90 MHz relative to that of the neat solvent. Digitised data from the spectrometer were downloaded to an IBM PC-AT microcomputer for data analysis, and the linewidths estimated by fitting selected regions of the spectra by non-linear least-squares to the equation for a Lorentzian lineshape, as described previously.[5] The linewidths and shifts were then fitted simultaneously to the modified Swift–Connick equations, with appropriate weighting as described in our previous studies,[4] to obtain the lifetime for solvent exchange (τ_m) and the activation parameters.

and activation parameters obtained previously from variable temperature and pressure studies of these two metal ions with other solvents.

Typical variable temperature results for $[Ni(dmtf)_6]^{2+}$ ion are shown in Figure 1 and the variable pressure results for Mn^{2+} ion are compared with literature data for $[Mn(MeOH)_6]^{2+}$ ion in Figure 2. Because of the very rapid exchange rate for $[Mn(dmtf)_6]^{2+}$, variable temperature data obtained down to the freezing point of the solvent were found to be in the fast exchange region of the Swift–Connick curve, and in this case only $\Delta G^{\ddagger}$ and $\Delta V^{\ddagger}$ were estimated. For the other systems it was possible to measure $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ as well as $\Delta V^{\ddagger}$ (Table 1). Values of k_{ex} at 298 K for $[Mn(dmf)_6]^{2+}$, obtained by ¹H n.m.r., compare reasonably with those values obtained by ¹⁷O n.m.r., although the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are not in such good agreement. Since the ¹⁷O n.m.r. data are in the slow exchange region of the Swift–Connick curve, whereas the ¹H n.m.r. data are largely in the fast exchange region, the activation parameters obtained by ¹⁷O n.m.r. are believed to be the more reliable.‡ The values of $\Delta V^{\ddagger}$ for $[Mn(dmf)_6]^{2+}$ obtained by both ¹H and ¹⁷O n.m.r. are small and positive, and the ¹H n.m.r. results confirm the conclusion reached in the ¹⁷O n.m.r. study.[3]

As is evident from Figure 2, for Mn^{2+} there is a gradual mechanistic changeover in going from the relatively small solvent methanol to the bulkier dmf, and even larger dmtf. Including the data for water and acetonitrile, a plot of $\Delta V^{\ddagger}/V^0$ vs. V^0 (the molar volume of the solvent) is reasonably linear for Mn^{2+} as shown in Figure 3. We interpret this trend towards a more positive fractional increase in the volume of activation with increasing molar volume of the solvent to be due to increased steric crowding in the inner sphere of the metal ion, which will make a dissociative mechanism more likely for the bulkier solvents. It would appear, therefore, that Mn^{2+} can only increase its co-ordination number in the transition state

‡ *Note added in proof.* This has been confirmed by a further study of $[Mn(dmf)_6]^{2+}$ by ¹³C n.m.r. spectroscopy; $\Delta V^{\ddagger}$ = 2.4 ± 0.2 cm³ mol⁻¹, $\Delta H^{\ddagger}$ = 34.6 ± 1.3 kJ mol⁻¹, $\Delta S^{\ddagger}$ = −7.4 ± 4.8 J K⁻¹ mol⁻¹, $10^{-6} k_{ex}$ = 2.2 ± 0.2 s⁻¹; C. Cossy, L. Helm, and A. E. Merbach, *Helv. Chim. Acta*, 1987, **70**, 1516.

Figure 2. Variation of the rate constants for reaction (1) (k_{ex}) with presssure, relative to the rate constant at atmospheric presssure (k_0), for $[MnX_6]^{2+}$ ions in the respective solvents MeOH, Me_2NCHO, and Me_2NCHS.
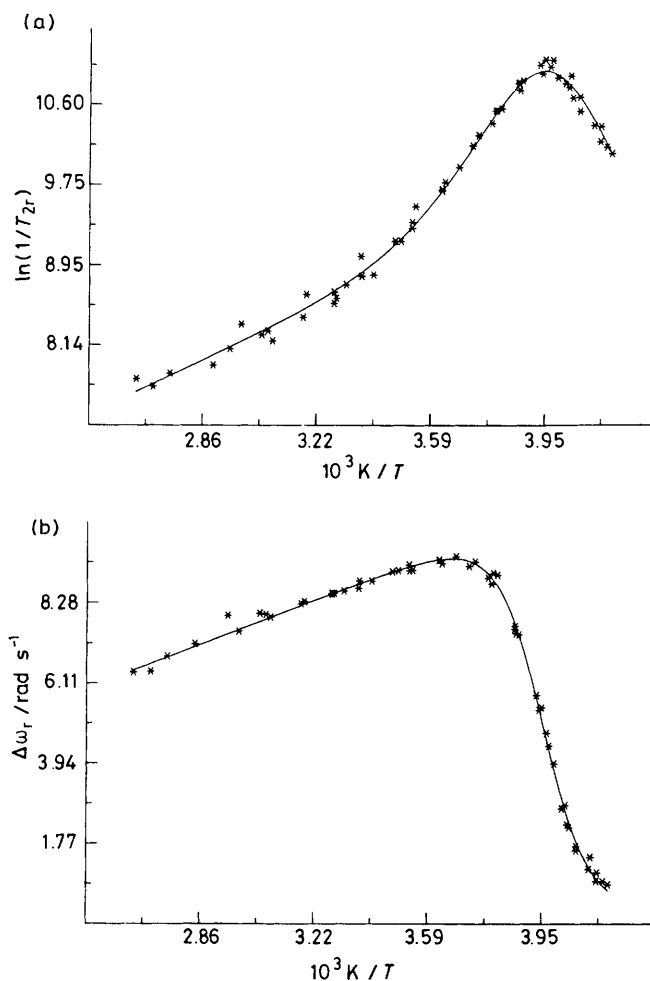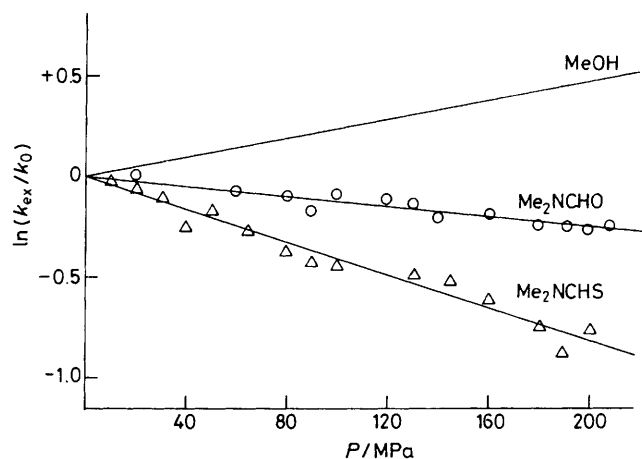

Figure 1. Plots of (a) $\ln(1/T_{2r})$ and (b) $\Delta\omega_r$ vs. $10^3K/T$ for $[Ni(dmtf)_6]^{2+}$ ion in dmtf solution. $T_{2r}^{-1} = \pi[\Delta v_{obs} - \Delta v_{ref}]/P_m$ and $\Delta\omega_r = 2\pi[v_{obs} - v_{ref}]/P_m$, for the unco-ordinated solvent formyl proton resonance, where P_m is the molar fraction of co-ordinated solvent molecules, Δv is the full linewidth (Hz) at half maximum height, and v is the chemical shift (Hz), in the presence (obs.) and absence (ref.) of Ni^{2+} ion. The continuous curves are from simultaneous fits of the two data sets to the Swift–Connick equations, neglecting any outer-sphere contribution, using non-linear least-squares.
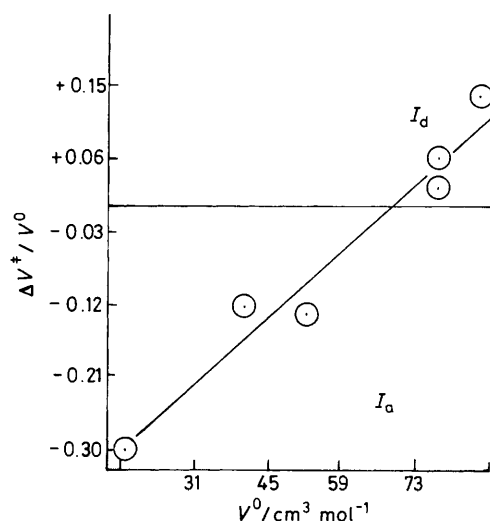
Figure 3. Plot of $\Delta V^{\ddagger}/V^0$ vs. V^0 for $[MnX_6]^{2+}$ ions, showing the mechanistic changeover from an I_a to an I_d mechanism with bulkier solvent molecules.

when co-ordinated to relatively small solvent molecules. From Figure 3, for $[MnX_6]^{2+}$ ions, $\Delta V^{\ddagger}$ can be expected to be negative for solvents with molar volumes below ca. 68 cm³ mol⁻¹. With even larger solvents than those studied so far, the possibility of a reduced co-ordination number in the ground state is also likely. Complexation of Mn^{2+} by the bulky ligand $(Me_2NCH_2CH_2)_3N$ (Me_6tren) does give a five-co-ordinate complex ion, $[Mn(Me_6tren)(dmf)]^{2+}$, and interestingly this reduced co-ordination number species can accommodate a second dmf molecule in the transition state, as shown by the significantly negative volume of activation for solvent exchange ($\Delta V^{\ddagger} = -6$ cm³ mol⁻¹).[6]

The trend for Ni^{2+} is similar to that for Mn^{2+}, with a much larger value of $\Delta V^{\ddagger}$ for dmtf compared with dmf exchange. Interestingly, the value of $\Delta V^{\ddagger}$ for $[Ni(dmtf)_6]^{2+}$ (+20.6 cm³ mol⁻¹ at 251 K) is significantly larger than that obtained previously for dmtf exchange with trans-$[MeCo(dmg)_2(dmtf)]$ ($\Delta V^{\ddagger} = 13.6$ cm³ mol⁻¹; H_2dmg = dimethylglyoxime) where a D mechanism could be expected.[7] We conclude that a D mechanism is operating for dmtf exchange with $[Ni(dmtf)_6]^{2+}$,

a conclusion supported by the observed formation of a reduced co-ordination number species in nitromethane solution. When the green $[Ni(dmtf)_6]^{2+}$ ion is dissolved in the non-co-ordinating solvent nitromethane, it dissociates to give purple-blue solutions, whose visible spectrum shows increased molar extinction coefficients, as expected for the formation of five- or four-co-ordinate species; addition of a small excess of dmtf to the purple-blue nitromethane solutions immediately gives a spectrum identical to that of the green six-co-ordinate complex observed in neat dmtf. Previous studies of $[Ni(dmf)_6]^{2+}$ in nitromethane did not show evidence for loss of a co-ordinated solvent molecule in the ground state, although the independence of the variable temperature n.m.r. linewidth data with solvent composition led to the conclusion that a D-mechanism also operates for this ion.[8] The values of $\Delta V^{\ddagger}$ for dmf exchange with $[Ni(dmf)_6]^{2+}$ and $[Fe(dmf)_6]^{2+}$ ($\Delta V^{\ddagger} = +8.5$ cm³ mol⁻¹)[1] are significantly more positive than for $[Mn(dmf)_6]^{2+}$, a trend that parallels the behaviour found for water, methanol, and acetonitrile exchange, but it would appear that with the bulkier ligand dmf, it is not possible for Mn^{2+} to undergo associative ligand exchange.

In conclusion, we have shown that for dmtf and dmf, although $\Delta V^{\ddagger}$ does decrease from Ni^{2+} to Mn^{2+}, in line with the trend towards an associative, I_a mechanism, the changeover to an I_a mechanism observed previously for Mn^{2+} when undergoing solvent exchange with smaller solvent molecules may not be complete, and the mechanism may remain I_d, if the solvent is bulky.

Received, 9th September 1987; Com. 1315

References

1 Y. Ducommun and A. E. Merbach, 'Inorganic High Pressure Chemistry, Kinetics and Mechanisms,' ed. R. van Eldik, Elsevier, Amsterdam, 1986, ch. 2.
2 T. W. Swaddle, *Adv. Inorg. Bioinorg. Mechanisms*, 1983, **2**, 95.
3 M. Ishii, S. Funahashi, and M. Tanaka, *Chem. Lett.*, 1987, 871.
4 C. H. McAteer and P. Moore, *J. Chem. Soc., Dalton Trans.*, 1983, 353.
5 P. Moore, *J. Chem. Soc., Faraday Trans. 1*, 1976, 826.
6 S. F. Lincoln, A. M. Hounslow, B. G. Doddridge, J. H. Coates, A. E. Merbach, and D. Zbinden, *Inorg. Chem.*, 1984, **23**, 1090.
7 P. Moore, *Pure Appl. Chem.*, 1985, **57**, 347.
8 L. S. Frankel, *Inorg. Chem.*, 1971, **10**, 2360.