# 254. High Pressure $^{17}$O-FT-NMR. Evidence for the Associative Nature of Substitution Reactions on $Mn^{2+}$ in Water[1])

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## *Summary*

The water exchange on $[Mn(H_2O)_6](ClO_4)_2$ in aqueous solution has been studied as a function of pressure (up to 250 MPa), measuring $^{17}$O-FT-NMR. linewidths of the free water resonance at 8.13 MHz. A pressure independent volume of activation, $\Delta V^{\neq} = -6.2 \pm 0.2$ cm$^3$ mol$^{-1}$ is obtained, producing a clear evidence that, contrary to general belief, the mechanism for solvent exchange on $Mn^{2+}$ is an associative interchange ($I_a$).

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**Introduction.** - For many years, the accepted mechanism for the formation of complexes from aquo-metal ions assumed the fast formation of an outer sphere complex followed by the rate-determining dissociative interchange ($I_d$) between the leaving water molecule and the incoming ligand [2]. This mechanism developed by *Eigen & Wilkins* [3] derives from observations of similar rates for the interchange step on a given metal ion and for the water exchange on it. More recently, it has been suggested that for some trivalent ions, like $Ti^{3+}$ and $V^{3+}$, the interchange step has some associative character [4], whereas for divalent ions, the dissociative nature of this step has not been questioned [5]. For $Ni^{2+}$ and $Co^{2+}$, where there is a wealth of data on complex formation rates, a dissociative interchange has been undoubtedly proved, but for $Fe^{2+}$ and $Mn^{2+}$, the available data are very sparse [6].

The study of the effect of pressure on the rate of chemical reactions is a recognized tool for assigning reaction mechanisms [7]. The pressure dependence of the rate constant $k$ yields the volume of activation $\Delta V^{\neq}$ according to equ. 1.

$$\left(\frac{\partial \ln k}{\partial P}\right)_{T} = -\frac{\Delta V^{\neq}}{RT} \tag{1}$$

$\Delta V^{\neq}$ is a direct measure of the change in partial molar volume between the reactants and the transition state. For solvent exchange reactions, the interpretation of $\Delta V^{\neq}$ is straightforward: reactions occurring *via* dissociative activation modes

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[1]) High pressure NMR. kinetics, part 9. For part 8 see [1].

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yield positive values of $\Delta V^{\neq}$ and those occurring *via* associative activation modes yield negative values [8] [9] [1].

Until recently, solvent exchange studies as a function of pressure have been limited to non-labile trivalent ions using isotopic labelling. With the advent of high-pressure NMR. fast exchanging systems have also become accessible. We have reported the volumes of activation for the water exchange on $Ni^{2+}$ observed by $^{17}O$-NMR. [10], and for various non-aqueous solvents on $Ni^{2+}$, $Co^{2+}$, $Fe^{2+}$ and $Mn^{2+}$ using $^{1}H$-NMR. [1] [11] [12]. All the results are summarized in the *Table*. The results for $Ni^{2+}$ and $Co^{2+}$ in each of the solvents are well in accord with a dissociative interchange ($I_d$). In the case of methanol exchange, the almost zero value of $\Delta V^{\neq}$ for $Fe^{2+}$ and the clearly negative value of $\Delta V^{\neq}$ for $Mn^{2+}$ led us to the controversial conclusion of a mechanistic changeover from $I_a$ to $I_d$ along the first row divalent transition metal ions series [2]. The purpose of this study is to ascertain whether this changeover also occurs for other solvents and particularly water, the solvent in which the evidence supporting the *Eigen-Wilkins* mechanism was founded.

Table. *Comparison of the volumes of activation* ($\Delta V^{\neq}$, $cm^3\ mol^{-1}$) *for various solvent exchanges on divalent metal centres*

| | $Mn^{2+}$ | $Fe^{2+}$ | $Co^{2+}$ | $Ni^{2+}$ |
|---|---|---|---|---|
| DMF | – | – | +6.7 (296 K)[a] | + 9.1 (297 K)[a] |
| $CH_3CN$ | – | – | +9.9 (260 K)[a] | + 9.6 (294 K)[a] |
| $CH_3OH$ | −5.0 (279 K)[b] | +0.4 (255 K)[b] | +8.9 (279 K)[a] | +11.4 (307 K)[a] |
| $H_2O$ | −6.2 (279 K)[c] | – | – | + 7.1 (313 K)[d] |

[a] See [12]. [b] See [1]. [c] This work. [d] See [10].

**Experimental Part.** - Variable temperature $^{17}O$-FT-NMR. transverse relaxation times were obtained from linewidths measurements at 8.130 MHz [10] in order to obtain the NMR. parameters needed for the variable pressure work [13]. Two $Mn(ClO_4)_2$ solutions ($1.1 \times 10^{-3}$ molal and $4.31 \times 10^{-3}$ molal) were used. They were made up using 25.3 atom % enriched $^{17}O$-water (*Yeda R. & D. Co. Ltd.*, Rehovoth, Israel) and acidified with a 60% $HClO_4$-solution (0.06 and 0.1 molal, respectively).

For $Mn^{2+}$, it may be readily shown that the *Swift-Connick* equation reduces to equ. 2 [14], where $P_m$ is the mole fraction of water bound to the metal, $T_2$ and $T_{2s}$ are the $^{17}O$ transverse relaxation

$$\frac{1}{T_{2r}} = \frac{1}{P_m}\left(\frac{1}{T_2} - \frac{1}{T_{2s}}\right) = \left[\tau_m + \frac{1}{C}\left(\frac{1}{\tau_m} + \frac{1}{T_{1e}}\right)\right]^{-1} \qquad (2)$$

times of the solution and of pure acidified water respectively, $\tau_m$ is the lifetime of bound water, C is a temperature independent term proportional to the scalar coupling constant. The electron transverse relaxation time, $T_{1e}$, is given [14] by equ. 3 where $\Delta$ is a parameter measuring the amplitude of modulation of the zero-field splitting, $\tau_v$ is the correlation time for this modulation and $\omega_e$ is the electron *Larmor* frequency.

$$\frac{1}{T_{1e}} = \frac{32}{25}\Delta^2\left[\frac{\tau_v}{1+\tau_v^2\omega_e^2} + \frac{\tau_v}{1+4\tau_v^2\omega_e^2}\right] \qquad (3)$$

The data were analyzed using a non-linear least-squares routine and yielded results closely similar to those reported by *Zetter et al.* [14]. They will be discussed in greater detail in a subsequent paper [13]. The values of the parameters in equ. 3, at the mean temperature of the high pressure NMR. study, are: $1/\tau_m = 1.43 \times 10^{-7} s^{-1}$, $1/C\tau_m = 2.20 \times 10^{-9} s^{-1}$, $1/CT_{1e} = 1.03 \times 10^{-8} s^{-1}$.

High pressure $^{17}$O-FT-NMR. measurements were performed twice up to 250 MPa at two similar temperatures (277.9 and 279.1 K) using a high pressure bomb similar to those previously described [10] [15]. The data were analyzed using equ. 2 with C and $T_{1e}$ kept at their ambient pressure values. The pressure dependence of the rate constant ($= 1/\tau_m$) was allowed to vary according to equ. 4, where $k_P$ and $k_0$ are the rate constants at pressure P and zero respectively. In this quadratic equation,

$$\ln k_P = \ln k_0 - \frac{\Delta V^{\ddagger} P}{RT} + \frac{\Delta\beta^{\ddagger} P^2}{2RT} \qquad (4)$$

$\Delta V^{\ddagger}$ is now the zero pressure volume of activation and $\Delta\beta^{\ddagger}$ is the compressibility coefficient of activation. The suppression of this latter term did not alter the quality of the fit and the derived value was negligible compared with its standard deviation. For this reason, $\Delta\beta^{\ddagger}$ was set equal to zero. The *Figure* shows the variation of RT $\ln(k_P/k_0)$ with pressure. The derived values of the volume of activation and its standard deviation are $\Delta V^{\ddagger} = -6.2 \pm 0.2$ cm$^3$ mol$^{-1}$. Fuller details of the curve fitting approach will be found in reference [13].

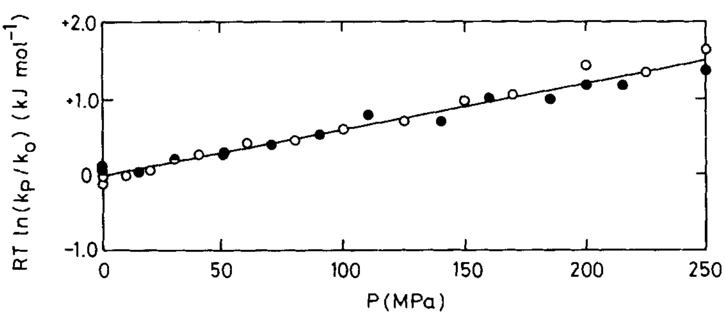

Figure. *Experimental and calculated values of RT* $\ln(k_P/k_0)$ *as a function of pressure for the water exchange on* $Mn^{2+}$ ($P_m = 1.2 \times 10^{-4}$); ● T = 277.9 K, ○ T = 279.1 K

**Discussion.** - *For a dissociative* D-*mechanism* for solvent exchange on $MS_6^{n+}$, it is generally assumed that the structure of the five-coordinate intermediate is close to that of the transition state. For any thermodynamic quantity X:

$$\Delta X^{\ddagger} \simeq X^0_{MS_5} + X^0_S - X^0_{MS_6} \qquad (5)$$

where $X^0_{MS_5}$, $X^0_S$ and $X^0_{MS_6}$ are the partial molar quantities relating to $MS_5^{n+}$, S and $MS_6^{n+}$ respectively. The value of $X^0_S$ is generally readily available since it is simply a thermodynamic quantity for a pure solvent and the problem of predicting $\Delta X^{\ddagger}$ revolves around estimating the difference $X^0_{MS_5} - X^0_{MS_6}$. When $X = V$, the partial molar volume (and this is also true for the compressibility coefficient, $\beta = (\partial V/\partial P)_T$), $V^0_{MS_5}$ and $V^0_{MS_6}$ are conventionally separated each into two components, according to equ. 6. $V_{int}$ is the intrinsic volume and $V_{elec}$ the contribution caused by the

$$V^0 = V_{int} + V_{elec} \qquad (6)$$

electrostrictive interaction between the solvated metal ion and the surrounding medium.

The intrinsic contribution $V_{\text{int}}$ can be estimated for both $MS_5^{2+}$ and $MS_6^{2+}$ utilizing a simple potential energy function composed of contributions arising from permanent dipolar attraction, repulsion and crystal field effects, as discussed in detail by *Stranks* [8]. He concludes that the compressibilities of metal-ligand bonds are extremely small for both $Ni(NH_3)_5^{2+}$ and $Ni(NH_3)_6^{2+}$ and that the ion-ligand bond lengths of the two species are closely similar. Assuming that these bond lengths are identical, *Stranks* further concludes that the volume swept out by five and six coordinate species is identical. This last assumption is probably not totally exact, but the difference in volume must be small. The above approach can be readily extended to other divalent and trivalent metal ion complexes leading to similar conclusions. Direct experimental evidence on the magnitudes of $(X^0_{MS_5} - X^0_{MS_6})$ is difficult to obtain. However, high-pressure UV. studies on transition metal ion complexes in both solid state and solution (where it is possible to measure the change in crystal field splitting parameter with pressure) lead to the conclusion that metal-ligand bonds in octahedral complexes are very incompressible. This gives us confidence that the bonds in $MS_5^{2+}$ must also be only slightly compressible.

The electrostrictive contribution $V_{\text{elec}}$ varies with the square of the ionic charge and inversely with the radius of the solvated ion and for divalent ions in water is estimated to be less than 6 cm$^3$ mol$^{-1}$ [8]. Thus, because the difference in radius is negligible between $MS_6^{2+}$ and $MS_5^{2+}$, there will be a totally negligible change in $V_{\text{elec}}$. In principle, the dipolar or multipolar distribution of charges is different in $MS_6^{2+}$ and $MS_5^{2+}$, but in view of the small size of $V_{\text{elec}}$, this latter effect must also be negligible. We are thus confident that for dissociative *D*-solvent-exchange reactions $\Delta V^{\ddagger}$ and $\Delta\beta^{\ddagger}$ should be close to $V^0_S$ and $\beta^0_S$ respectively.

*For an associative* A-*mechanism*, analogous arguments may be applied, but it should be noted that the potential function used does not attempt to include the effect of steric crowding. It is likely that the 7-coordinate transition state is highly crowded and some expansion may be expected in order to release the steric strain. We thus expect that the absolute value of $\Delta V^{\ddagger}$ should be less than or equal to $V^0_S$ and $\Delta\beta^{\ddagger}$ equal to minus the compressibility of the solvent.

*For an interchange* I-*mechanism*, as discussed earlier [1], symmetry arguments require that, at the transition state, there should be equal bonding to both leaving and entering groups and one may thus envisage a whole spectrum of transition state structures ranging from highly associative interchange ($I_a$), with considerable bonding of both groups, to highly dissociative interchange ($I_d$) with very weak bonding to both. One does not have a convenient model for the transition state as in the case of *D*- or *A*-mechanisms. At the transition state, for a highly associative $I_a$-process, the interchanging solvent molecules will lie very close to the metal centre, whereas for a highly dissociative $I_d$-process, they will be found out in the second coordination sphere. A formalistic separation into $V_{\text{int}}$ and $V_{\text{elec}}$ is therefore not necessarily useful. Notwithstanding this, $\Delta V^{\ddagger}$ and $\Delta\beta^{\ddagger}$ for interchange mechanisms must lie between the *D*- and *A*-limits. From a structural viewpoint, the only difference between $I_a$ and $I_d$ is the degree of expansion of the transition state which is precisely the information available from $\Delta V^{\ddagger}$. Therefore, in the same solvent, the volumes of activation for the different hexasolvated metal ions should reflect directly their tendency towards associative behaviour.

An inspection of the values in the *Table* for both water and methanol exchange clearly shows a change in sign of $\Delta V^{\ddagger}$ going from $Mn^{2+}$ to $Ni^{2+}$. The positive values for $Ni^{2+}$, smaller than the solvent partial molar volumes, have been shown [10] [12] to be well in accord with an interchange process with considerable dissociative character whereas the negative values for $Mn^{2+}$ can only be interpreted in terms of an interchange process with considerable associative character. For methanol exchange on $Mn^{2+}$, we had been forced to conclude to an associative interchange [1]. With the result for the water exchange, we have now enough insight to affirm that solvent exchange on $Mn^{2+}$ proceeds *via* an associative interchange ($I_a$). The values of $\Delta V^{\ddagger}$ for the methanol exchange on $Fe^{2+}$ and $Co^{2+}$ suggest that this change of mechanism occurs gradually along the series [1]. One may attempt to rationalize this trend towards increasing dissociative behaviour in two possible ways:

1) The ionic radii decrease monotonously from $Mn^{2+}$ to $Ni^{2+}$ and it may be that steric effects are important in determining the structure of the transition state.

2) The occupancy of the $t_{2g}$-orbitals increases continously from $Mn^{2+}$ to $Ni^{2+}$, and these orbitals being non-bonding in the absence of $\pi$-bonding, do not point towards the ligands but between adjacent ligands. Naively, one may suppose that an increased occupancy of these orbitals makes the approach of a seventh molecule towards the face of the octahedron less and less electrostatically favourable. Evidence has been accumulating that the early members of the trivalent first row series substitute also *via* associative mechanisms [4] [16] and it may be that *this trend away from associative to dissociative behaviour, going from left to right along the first transition metal series, is the norm for both divalent and trivalent ions.*

As briefly mentioned in the introduction, mechanistic evaluation of complex formation reactions is generally made by comparing the rates of the interchange step for different ligands and the solvent exchange rate. For $Ni^{2+}$ in water, complex formation rates have been studied with a very wide variety of ligands and it has been shown that the rate of the interchange step in the *Eigen-Wilkins*-mechanism exhibits very little dependence on the incoming ligand and is also very similar to the rate of solvent exchange. Furthermore, the volumes of activation for the interchange step are similar for different ligands, and similar to that of solvent exchange. They are also of the correct sign and size predicted for a dissociative interchange. All this evidence thus gives overwhelming weight to the mechanistic evaluation. For $Mn^{2+}$, according to a recent tabulation, there are only three variable temperature studies of complexation reactions with monodentate ligands [6], and no variable pressure studies, so a realistic examination of the mechanism is impossible. It is therefore to be hoped that many more studies of complex formation rates on $Mn^{2+}$ will become available in the future, in order to see if for this metal entering group effects are important. In this regard, the high pressure stopped flow technique, recently developed by *Heremans* [17], could be an important tool to obtain the evidence sought.

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[5] See [4a], p. 7 and [4b], p. 352-369.

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## Erratum

Helv. *62,* 1089, communication No. 110, *Riedo, Th. J.* and *Kaden, Th. A.*: page 1091, *Table 1.* The first line should read: **1** 10.94 ± 0.02 7.24 ± 0.02 15.84 ± 0.05 10.69 ± 0.05 15.05 ± 0.06.