

THE ELUCIDATION OF SOLVENT EXCHANGE MECHANISMS BY HIGH-PRESSURE NMR STUDIES

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Abstract - High pressure multinuclear magnetic resonance with electro- and superconducting magnets has been used to study the effect of pressure on the rates of fast solvent exchange reactions on tetrahedral, square-planar and octahedral metal complexes in aqueous and non-aqueous solvents. The most striking results were obtained for the divalent and trivalent high spin first row hexasolvated transition metal ions: for both series a gradual changeover in substitution mechanism occurs, with the early members showing I_a behaviour and the later ones I_d behaviour, the change in activation mode occurring after the d^5 configuration.

INTRODUCTION

During recent years a large number of high pressure kinetic studies of inorganic systems have been reported [74.2][79.5][81.8]. Most of them deal with ligand substitution reactions on octahedral or square planar transition-metal complexes. For kinetically inert compounds, the reactions are sufficiently slow so as to be followed by methods such as conventional spectrophotometry or isotopic dilution, but for kinetically labile systems, which are the rule in inorganic chemistry, special instrumentation is required. Nowadays, most of the important fast reaction techniques have indeed been adapted for use in high pressure kinetics: stopped flow, temperature jump, pressure jump and nuclear magnetic resonance [78.4].

We have recently built high pressure multinuclear magnetic resonance probe heads, for electro- [78.5][78.6] and superconducting [80.1] magnets, with the high spectral resolution ($2 \cdot 10^{-9}$ and $0.5 \cdot 10^{-9}$ ppm, respectively) and the good stability (± 0.2 K) and accuracy in temperature required for kinetic applications. This technique has been used to study the effect of pressure on the exchange rate of solvent molecules between the first coordination sphere of a metal ion or complex, and bulk solvent.

In this paper the results for solvent exchange on tetrahedral, square-planar and octahedral complexes, obtained from high pressure studies, will be reviewed.

HIGH PRESSURE KINETICS DATA TREATMENT

The effect of pressure on the rate of a chemical reaction is now a well-accepted approach in elucidating reaction mechanisms [78.7]. The results are usually interpreted in terms of the transition state theory which assumes the transition state M in true equilibrium with the reactants A and B (Equation 1). The volume of activation ΔV^* is related to the pressure



derivative of $\ln k$ by equation 2, where ΔV^* is the difference between the partial molar

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\frac{\Delta V^*}{RT} \quad (2)$$

volumes of the transition state and the reactants evaluated at the reaction conditions. ΔV^* may be positive or negative, depending if the reaction is slowed down or accelerated with pressure. Another parameter, the compressibility of activation $\Delta \beta^*$, defined as minus the pressure derivative of ΔV^* , is also often introduced (Equation 3). This parameter describes the

$$\Delta \beta^* = -\left(\frac{\partial \Delta V^*}{\partial P}\right)_T \quad (3)$$

pressure dependence of ΔV^* and represents the excess of the compressibility coefficient of the transition state over that of the reactant species. The problem of finding a suitable equation to fit the $\ln k$ versus pressure data has been treated by various researchers [78.4]. The quadratic function (4), where $\Delta V_0^* = -bRT$ and $\Delta\beta^* = 2cRT$, is most commonly adopted;

$$\ln k = a + bP + cP^2 \quad (4)$$

treatment recognizes $(\partial\Delta V^*/\partial P)_T \neq 0$ and assumes $(\partial^2\Delta V^*/\partial P^2)_T = 0$, but it must be added that there is no physical justification for the use of a quadratic function [81.8].

CLASSIFICATION OF SUBSTITUTION REACTION AND SOLVENT EXCHANGE MECHANISMS

It is conventional to discuss the mechanism of ligand substitution reactions (5) in terms of



the classification proposed by Langford and Gray [65.2]. Their approach is operational and relies on kinetic tests that may be applied. If a mechanistic test is able to detect the presence of an intermediate of increased or decreased coordination number the mechanism is associative (A) or dissociative (D), respectively. Otherwise, it is assigned as an interchange (I) process. This last class can be further subdivided into two groups: associative interchange (I_a), when there are important entering group effects, or dissociative interchange (I_d), when there are none. For solvent exchanges (6), however, very few kinetic tests may be



applied unless one is working in an "inert" diluent, and recourse has to be made to the activation parameters. In this regard, the volume of activation is of supreme importance.

Bond stretching in a simple dissociative step gives rise to an increase in volume which is manifested in a decrease in the rate of reaction with increasing pressure, i.e. ΔV^* is positive. Conversely, bond formation occurring in a simple associative process will lead to an increase in the rate constant with increasing pressure, i.e. ΔV^* is negative. For substitution reactions, the solvent electrostrictive effect when ions or dipoles are formed or neutralized at the transition state represents another important contribution in determining the sign and magnitude of ΔV^* . Therefore the measured volume of activation ΔV_{exp}^* is usually considered the combination of an intrinsic contribution ΔV_{int}^* resulting from changes in internuclear distances within the reactants during the formation of the transition state and an electrostrictive contribution ΔV_{elec}^* . Unfortunately, for substitution reactions involving charged species, the observed ΔV_{exp}^* may be dominated by the effect of electrostriction ΔV_{elec}^* , to the extent that even the sign of ΔV_{exp}^* may differ from ΔV_{int}^* .

For solvent exchange, as discussed by Swaddle [74.3], the interpretation of ΔV_{exp}^* is simplified due to the absence of electrostrictive changes (i.e. $\Delta V_{exp}^* \approx \Delta V_{int}^*$). Therefore, the sign of ΔV^* is immediately diagnostic of the activation mode. Also the symmetrical nature of solvent exchange requires that the forward reaction coordinate must be symmetrical to the reverse one [79.4]. For an A mechanism where there is a reactive intermediate of increased coordination number and hence two transition states, they must necessarily have identical structures. Similar arguments apply to a D mechanism. For an interchange mechanism where there is no reactive intermediate, symmetry arguments require that, at the transition state, bonding to both entering and leaving solvent molecules must be identical. Thus, for an I_d mechanism, where there is little bonding to the entering group, there must of necessity be little bonding to the leaving group. Conversely, for an I_a mechanism, both entering and leaving groups must have considerable bonding to the metal (Fig. 1). From a structural point of view, the only difference between I_d and I_a mechanisms for solvent exchange is the degree of expansion of the transition state. The volume of activation, the difference between the volumes of transition state and reactants, can thus yield a direct measure of this expansion and hence of the dissociativity of a reaction. In the limiting cases of D and A mechanisms, the activation volumes cannot exceed + or - the partial molar volume V_S^0 of the exchanging solvent, the limits depending also on the relaxation or expansion of the non-exchanging metal-solvent bonds at the transition state. Intermediate values are indicative of interchange processes, being positive for I_d and negative for I_a mechanisms. One may envisage a continuous spectrum of transition states characterized by their degree of expansion ranging from highly associative to highly dissociative, with a changeover of mechanism arbitrarily defined when ΔV^* equals zero.

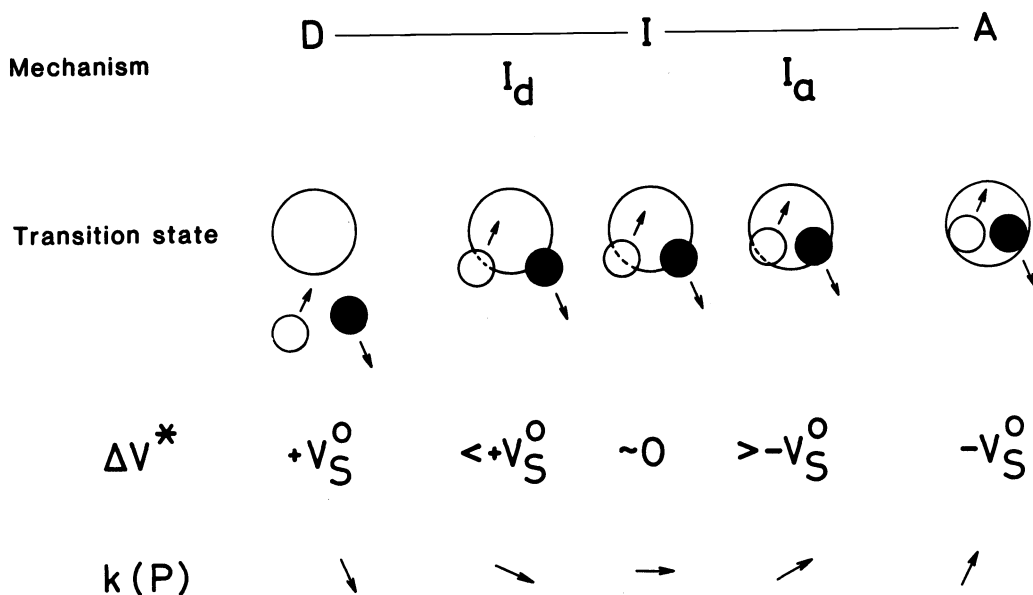


Fig. 1. Schematic view of solvent exchange mechanism classification

SOLVENT EXCHANGE ON TETRACOORDINATED COMPLEXES

To our knowledge the only exchange reactions studied under high pressure to date, are one ligand exchange on a tetrahedral complex and a second on a square planar complex.

Tetrahedral complexes

The triphenylphosphine (TPP) exchange with pseudotetrahedral $\text{CoBr}_2(\text{TPP})_2$ has been studied by variable pressure $^1\text{H-NMR}$ in deuteriochloroform [79.7]. A quadratic analysis of the rate constant data at 303 K, up to 265 MPa yielded: $\Delta V_0^* = -12.1 \pm 0.5 \text{ cm}^3 \text{ mol}^{-1}$ and $\Delta S^* = -(3.3 \pm 0.5) \cdot 10^{-2} \text{ cm}^3 \text{ mol}^{-1} \text{ MPa}^{-1}$. An earlier variable temperature study showed a second order kinetic law and yielded the following activation parameters: $\Delta H^* = 32 \pm 2 \text{ kJ mol}^{-1}$ and $\Delta S^* = -80 \pm 13 \text{ J K}^{-1} \text{ mol}^{-1}$ [68.1]. The rate law and the negative volume (and entropy) of activation suggest an associative process, proceeding through a pentacoordinate transition state (I_a mechanism) or intermediate (A mechanism). The proportionally small value of ΔV_0^* may result from a loosening of the complex that must occur in order to accommodate the bulky incoming triphenylphosphine, thus cancelling out some of the volume decrease due to bond formation.

Square-planar complexes

It has been shown in a preliminary kinetic study that the Me_2S exchange with $\text{trans-Pd}(\text{Me}_2\text{S})\text{-Cl}_2$ obeys a second-order kinetic law in chloroform [73.2]. A recent variable temperature and pressure $^1\text{H-NMR}$ study in the same solvent yielded: $\Delta H^* = 38.5 \pm 1.4 \text{ kJ mol}^{-1}$, $\Delta S^* = -75.5 \pm 4.5 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\Delta V^* (308 \text{ K}) = -10.8 \pm 0.7 \text{ cm}^3 \text{ mol}^{-1}$ (linear fit) [82.6]. A large number of substitution reactions have been studied under pressure, and they confirm the general picture of an A mechanism involving a trigonal-bipyramidal intermediate [81.8]. The second order rate-law and negative ΔS^* and ΔV^* values for the dimethylsulfide exchange reaction are also consistent with this general picture.

SOLVENT EXCHANGE ON OCTAHEDRAL ADDUCTS OF METAL PENTAHALIDES IN AN INERT DILUENT

The solvent exchange reactions (7), where $M = \text{Nb, Ta, Sb}$, $X = \text{Cl, Br}$ and L is a neutral Lewis



base, have been studied in CH_2Cl_2 or CHCl_3 as an inert diluent by $^1\text{H-NMR}$ [75.2][79.6][81.9].

These reactions show an interesting ligand-controlled dissociative-associative crossover for the substitution mechanism. The complete neutrality along the reaction profile allows the neglect of electrostriction effects. Moreover, an unusually large number of kinetic facts are available for mechanistic assignments : rate laws, ΔH^* and ΔS^* , ΔV^* and $\Delta\beta^*$, steric effects, free energy relationships and nucleophilic sequence. The exchange reactions proceed via a D mechanism when L is a nitrile, ether or phosphoryl ligand and via an I_a or A mechanism when L is a dimethylsulfide, -selenide or -telluride (see Table 1). Going from the first set of ligands to the second, the activation parameters ΔH^* and ΔS^* decrease abruptly, with a change in sign for the latter parameter. The dissociative and associative reactions are respectively accelerated and slowed down when the ligand and the reaction center are sterically hindered. The dissociative reactions fit to linear free energy relationships of slope near unity (0.8 for $NbCl_5 \cdot L$ and 1.2 for $SbCl_5 \cdot L$), whereas for the associative reactions, the reaction center exerts discrimination between the various nucleophiles (order of reactivity : $Me_2S < Me_2Se < Me_2Te$). Interestingly, the exchange on the $TaBr_5 \cdot Me_2S$ adduct can proceed via both mechanistic paths. For this exchange, the rate law is second order below 300 K, but a first order term appears at higher temperatures. This temperature dependent mechanism crossover is not surprising if one considers the large differences in ΔH^* between the two paths.

The results of the high pressure studies clearly confirm this ligand controlled dissociative-associative mechanistic crossover. The ΔV_O^* are positive for the D reactions, as expected for an expanded transition state. Conversely, they are negative for the A- I_a reactions. The volumes of activation for the D reactions are estimated using the following conditions. ΔV_{elec}^* is considered negligible, $\bar{V}(MX_6)$ equals $\bar{V}(MX_5)$ and can be estimated by regarding the molecule as a solid sphere whose radius is determined by the Van der Waals radius of the halide ligand and the metal-halide bond length. The estimated volume of activation ΔV_{estd}^* is then equivalent to the volume within the first coordination sphere that is filled by the exchanging ligand. The agreement between ΔV_{estd}^* and ΔV_O^* is very good considering the simplicity of the model. Unfortunately, for the associatively activated exchange, the evaluation of ΔV_{estd}^* is impractical. Considering the highly crowded complex, it would not be logical to consider the addition of a seventh ligand without any modification of the bond lengths and angles of the non-exchanging ligands. Application of the molecular model to an A mechanism would give an absolute value of ΔV_{estd}^* at least equal to that observed for the dimethyloxide D reaction. The relatively small ΔV_O^* , -11 to -20 $cm^3 mol^{-1}$, instead of $> -30 cm^3 mol^{-1}$, would tend to suggest an I_a mechanism. However, an A mechanism could as well take place with an elongation of the five M-X bonds in the heptacoordinate intermediate. This effect would give a positive contribution to ΔV_O^* and could be the reason for a less negative ΔV_O^* .

Because D and A mechanisms involve transfer of solvent between regions of high and low compressibility, finite values of $\Delta\beta^*$ are expected, positive and negative respectively. Whereas I mechanisms, characterized by solvent transfer between regions of similar compressibility, should yield negligible $\Delta\beta^*$ values. The finite positive $\Delta\beta^*$ values confirm the D mechanism for the first series of ligands, and the finite negative $\Delta\beta^*$ values may suggest an A mechanism for the second series of ligands.

SOLVENT EXCHANGE ON OCTAHEDRAL METAL IONS

Trivalent ions

The non-aqueous solvent exchange around the diamagnetic octahedral trivalent ion Al^{3+} , Ga^{3+} , Sc^{3+} and In^{3+} has been studied by 1H -NMR (Table 2). For higher accuracy in line-broadening kinetic determinations, nitromethane was used as diluent, with concentrations of free and coordinated solvent arranged to be approximately equal. For accurate ΔS^* determinations the temperature range could be extended to cover more than 100 K, using combined line-broadening and stopped-flow FT-NMR for Al^{3+} and Ga^{3+} , with DMSO and DMF. The mechanistic picture is clear. For Al^{3+} and Ga^{3+} , the two smallest ions (Note a), the rate law is first order and the activation entropies and volumes are both positive allowing to conclude to a dissociative activation mode. This is convincingly illustrated by the variable pressure spectra for the TMPA exchange on Al^{3+} shown in Fig. 2. At high pressure, the doublet at high field is due to free TMPA and the doublet at low field is due to the six trimethylphosphate molecules coordinated to Al^{3+} . With decreasing pressure at constant temperature, one observes a coalescence of the signals, in other words, an increase in exchange rate. This retardation of the ligand exchange reaction with increasing pressure can be related to the hindrance of the bond breaking process at the transition state of the dissociatively activated exchange. For $In(TMPA)_6^{3+}$ the change in spectra with pressure is the contrary : the acceleration of the ligand exchange indicates a bond making controlled mechanism. For In^{3+} and Sc^{3+} , the two largest ions, the rate law is second order, both the activation entropies and volumes are

Note a : In this paper reported ionic radii r are from the review of R.D. Shannon [76.3].

TABLE 1. Kinetic parameters for the solvent exchange $\text{MX}_5 \cdot \text{L} + \text{L}^* \rightleftharpoons \text{MX}_5 \cdot \text{L}^* + \text{L}$ in CH_2Cl_2

	Order of reaction	ΔH^* (kJ mol ⁻¹)	ΔS^* (J K ⁻¹ mol ⁻¹)	ΔV^\ddagger (cm ³ mol ⁻¹)	ΔV_{estd}^*	$\Delta \beta^*$ (10 ² cm ³ mol ⁻¹ MPa ⁻¹)
NbCl ₅ ·Me ₂ O MeCN ^{b)}	1st	77 ± 5	+65 ± 19	+28.7 ± 1.1 (286.3, 303.2 K)	+26.8	+6.6 ± 1.2
	1st	71 ± 3	+46 ± 8	+19.5 ± 1.6 (286.2 K)	+13.3	+0.7 ± 1.6
	1st	72 ± 2	+42 ± 8	+15.2 ± 1.7 (287.4 K)	+13.3	+2.0 ± 1.5
(MeO)Cl ₂ P(O) ^{b)}	-	64 ± 2	+18 ± 8	+20.5 ± 0.7 (284.7, 297.6 K)	+17.3	+3.7 ± 0.7
	-	59 ± 8	-25 ± 21	+17.7 ± 1.4 (307.6 K)	+17.0	c)
TaCl ₅ ·Me ₂ O	1st	83 ± 5	+59 ± 15	+27.8 ± 1.2 (310.1 K)	+26.8	+8.3 ± 1.3
	1st	74 ± 3	+62 ± 12	+30.5 ± 0.8 (283.8 K)	+31.0	+6.5 ± 0.7
SbCl ₅ ·MeCN	1st	67 ± 3	+82 ± 14	+24.7 ± 1.7 (253.6 K)	+14.1	+4.1 ± 1.8
	1st	66 ± 3	+70 ± 10	+18.2 ± 0.9 (236.2 K)	+14.1	+3.2 ± 0.6
Me ₂ O Et ₂ O ^{b)}	1st	75 ± 3	+70 ± 9	+27.2 ± 1.4 (273.7 K)	+30.1	+5.9 ± 1.0
	1st	96 ± 5	+157 ± 19	+30.0 ± 1.5 (263.0 K)	+30.1	+3.8 ± 1.4
Me ₂ CO (Me ₂ N)Cl ₂ P(O)	1st	70 ± 5	+58 ± 20	+28.1 ± 2.0 (264.5 K)	+26.9	+8.1 ± 1.9
	-	71 ± 4	+41 ± 15	+23.0 ± 0.6 (274.1 K)	+20.4	c)
TaCl ₅ ·Me ₂ S	2nd	22 ± 1	-108 ± 4	-19.8 ± 0.9 (283.8 K)	-	-5.3 ± 0.8
	2nd	24 ± 1	-96 ± 5	-18.7 ± 1.0 (287.5 K)	-	-5.9 ± 1.0
Me ₂ Te	2nd	24 ± 1	-95 ± 4	-10.7 ± 0.8 (284.7 K)	-	c)
	2nd	18 ± 1	-99 ± 5	-12.1 ± 1.0 (279.9 K)	-	-4.2 ± 1.0
NbBr ₅ ·Me ₂ S TaBr ₅ ·Me ₂ S	2nd ^{d)}	29 ± 2	-102 ± 6	-12.6 ± 0.8 (285.6, 294.2 K)	-	-0.3 ± 0.7
	2nd	33 ± 3	-76 ± 9	-13.6 ± 0.8 (285.2 K)	-	c)
Me ₂ Se Me ₂ T ₂	2nd	32 ± 4	-75 ± 13	-16.4 ± 0.7 (307.0 K)	-	-3.1 ± 0.7

a) See Ref. [75.2] for M = Nb, Ta and Ref. [81.9] for M = Sb

b) In CHCl₃

c) A linear fit was used

d) Above 300 K, a first order term appears in the rate law

TABLE 2. Kinetic parameters for the solvent exchange $MS_6^{3+} + 6^*S \rightleftharpoons M^*S_6^{3+} + 6S$ (M = Al, Ga, Sc, In) obtained by 1H -NMR in the diluent CD_3NO_2 .

	r (Å)	k_1^{298} (s^{-1})	k_2^{298} ($s^{-1} mol^{-1}$)	ΔH^* ($kJ mol^{-1}$)	ΔS^* ($J K^{-1} mol^{-1}$)	ΔV^* ($cm^3 mol^{-1}$)	$10^2 \Delta \rho^*$ ($cm^3 mol^{-1} MPa^{-1}$)	$\Delta V^*/V_S^0$	Ref.
Al(DMSO) $_6^{3+}$	0.53	0.30 ^{a)}	-	82.6	+22.3	+15.6 ± 1.4 (358.5 K)	+4.8 ± 1.4	0.22	[80.4], [80.5]
Al(DMF) $_6^{3+}$		0.05 ^{a)}	-	88.3	+28.4	+13.7 ± 1.2 (354.5 K)	+5.4 ± 1.2	0.18	[80.5]
Al(TMPA) $_6^{3+}$		0.78 ^{j)}	-	85.1	+38.2	+22.5 ± 0.6 (341.3 K)	- ^{b)}	0.20	[80.3]
Ga(DMSO) $_6^{3+}$	0.62	1.87 ^{a)}	-	72.5	+3.5	+13.1 ± 1.0 (334.6 K)	+5.5 ± 0.9	0.18	[80.4], [80.5]
Ga(DMF) $_6^{3+}$		1.72 ^{a)}	-	85.1	+45.1	+7.9 ± 1.6 (313.8 K)	+2.6 ± 2.7	0.10	[80.5]
Ga(TMPA) $_6^{3+}$		6.4 ^{f)}	-	76.5	+27.0	+20.7 ± 0.3 (319.0 K)	- ^{b)}	0.18	[80.3]
Sc(TMPA) $_6^{3+}$	0.75	-	39 ^{g)}	21.2	-143.5	-18.7 ± 1.1 (299.0 K)	-2.4 ± 1.2	-0.16	[81.3]
Sc(TMPA) $_6^{3+}$ e)		736	85 ⁱ⁾	34.1	-75.6	-23.8 ± 2.7 (240-350 K)	- ^{b)}	-0.21	[82.4]
In(TMPA) $_6^{3+}$	0.80	-	7.6 ^{h)}	32.8	-118	-22.8 ± 1.1 (322.5 K)	-3.9 ± 1.1	-0.20	[80.3] ^{c)}
						-20.0 ± 1.7 (335.0 K)	-5.9 ± 1.0	-0.17	[81.3] ^{d)}

a) Combined line-broadening and stopped-flow NMR studies b) Linear fit c) At 60 MHz d) At 200 MHz

e) In neat TMPA, by ^{34}Sc -NMR at 14.57 MHz f) First order rate law, see ref. [77.1] g) Second order rate law, see ref. [81.3]

h) Second order rate law, see ref. [77.1] i) Calculated with a molality of 8.66 for free TMPA j) First order rate law, see ref. [72.1]

Note: In this paper the reported rate constants k are for the departure of a particular solvent molecule from the first coordination sphere.

The rate constants for the exchange of any molecule k' in a hexasolvate equals 6 k .

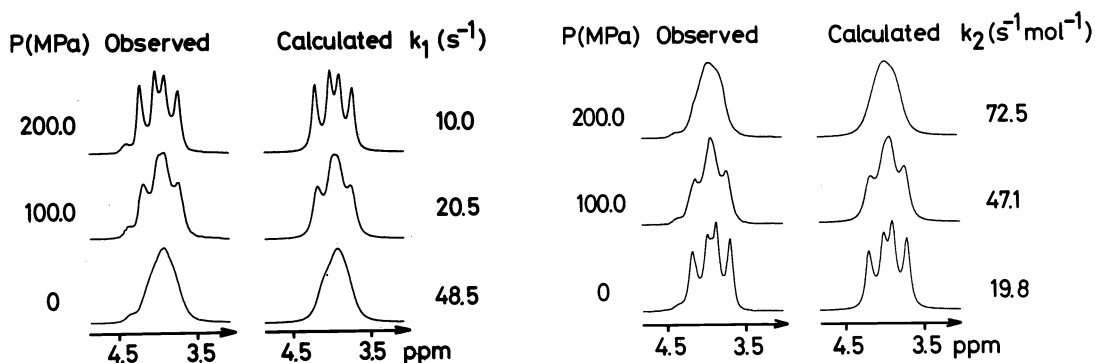


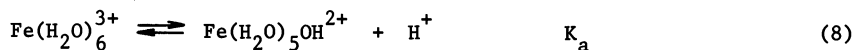
Fig. 2. Observed and calculated $^1\text{H-NMR}$ spectra at 60 MHz for $\text{M(TMPA)}_6^{3+} + *TMPA \rightleftharpoons \text{M(TMPA)}_5(*TMPA)^{3+} + TMPA$ in CD_3NO_2 as a function of pressure, with $\text{M} = \text{Al}$ at 341.3 K (left) and $\text{M} = \text{In}$ at 322.5 K (right).

negative, consistent with an associative activation mode. The exchange on Sc(TMPA)_6^{3+} has been studied in the diluent nitromethane and in neat solvent. The study in the neat solvent was performed by variable temperature and pressure $^{45}\text{Sc-NMR}$, taking advantage of the $^2J_{\text{Sc-p}}$ coupling (36.5 Hz). The similarity of the kinetic results of both experiments indicates that the diluent nitromethane has no effect on the mechanism.

For solvent exchange, high pressure studies allow a clear cut between dissociative and associative activation modes. They do not however always allow an easy distinction between the interchange mechanisms (I_d , I_a) and the limiting mechanisms (D , A). For the reactions in Table 2, the finite but small values of the compressibility coefficient of activation $\Delta\beta^*$, for instance, would suggest limiting mechanisms [74.2], but the interpretation of this parameter is not well understood in a diluent. When data are available for a series of similar compounds, it can be more instructive to look at the ratios of the activation volumes to the partial molar volumes of the solvent molecules, $\Delta V^*/V_s^0$. For instance, these ratios are around 0.2 for Al^{3+} and Ga^{3+} (except Ga(DMF)_6^{3+}), compared to around 0.1 for Ni^{2+} and Co^{2+} (Table 6), ions for which I_d mechanisms have been well established. For Al^{3+} , the much higher ratios indicate a far more dissociative activation mode, possibly approaching that of a limiting D mechanism. For Ga^{3+} , however, the ratios are consistently smaller than for Al^{3+} , and hence suggest an I_d mechanism. For Sc^{3+} and In^{3+} the distinction between A and I_a mechanisms is difficult to make since at the present time, no values of ΔV^* are available for known A -mechanisms involving the solvents used in these studies. The similarity between the ΔV^* 's for TMPA exchange on Sc^{3+} and In^{3+} and the volume of reaction ($\Delta V^0 = -23.8 \pm 1.5 \text{ cm}^3 \text{ mol}^{-1}$) for the addition of TMPA into Nd(TMPA)_6^{3+} ($r = 0.98 \text{ \AA}$) suggests that limiting A mechanisms may apply to the two exchanges [82.7].

A similar effect of decreasing ΔV^* values with increasing ionic radii is also apparent for the low spin t_{2g}^6 trivalent transition metal ions on going from the first row to the third row (Table 3). The first exchange reactions studied involved these ions since the reactions are slow and could therefore be followed by isotopic labelling techniques. Despite the small positive ΔV^* values, a dissociative mechanism D has been assigned to the exchanges on Co^{3+} . The argument is that the pentacoordinate cobaltamine intermediate has a partial molar volume about $17\text{--}20 \text{ cm}^3 \text{ mol}^{-1}$ smaller than the hexacoordinate cobaltamine complex [81.6]. Small ΔV^* 's, between $+2$ and $+4 \text{ cm}^3 \text{ mol}^{-1}$, have also been obtained recently for the aquation of pentaamminecobalt(III) complexes with neutral ligands [81.7]. The larger Rh^{3+} and Ir^{3+} ions produce small negative ΔV^* 's which can be ascribed to I_a exchange processes.

The only other studies on trivalent ions reported have been for V^{3+} , Cr^{3+} and Fe^{3+} . According to the small negative ΔV^* values the solvent exchange on the $t_{2g}^3 \text{Cr}^{3+}$ ion takes place through an I_a mechanism. The pattern of rates of substitution of water by other ligands in aqueous $\text{Fe(H}_2\text{O)}_5\text{OH}^{2+}$ and $\text{Fe(H}_2\text{O)}_6^{3+}$ is consistent with dissociative activation in the former case, but associative in the latter [74.1]. The recent variable temperature study by Grant and Jordan [81.5] yielded a much larger water exchange rate on $\text{Fe(H}_2\text{O)}_5\text{OH}^{2+}$ than on $\text{Fe(H}_2\text{O)}_6^{3+}$, which is also consistent with this assignment (Table 4). The observed total water exchange rate constant k for the two species in equilibrium (8) is given by the two term equation (9)



$$k = k_1 + k_{\text{OH}} \cdot K_a \quad (9)$$

TABLE 3. Kinetic parameters for the solvent exchange reaction $ML_5S^{3+} + S \rightleftharpoons ML_5^*S^{3+} + S$ obtained by isotopic labelling techniques for M = Co, Rh, Ir (t_{2g}^6) and M = Cr (t_{2g}^3).

ML_5S^{3+}	r (Å)	k_{ex}^{298} (s^{-1})	ΔH^* (kJ mol $^{-1}$)	ΔS^* (J K $^{-1}$ mol $^{-1}$)	$\Delta V^{\ddagger a}$ (cm 3 mol $^{-1}$)	$\Delta V^{\ddagger}/V_0^{\ddagger}$	Ref.
Co(NH $_3$) $_5$ (H $_2$ O) $^{3+}$	0.54	$6.0 \cdot 10^{-6}$	111 ± 1	$+28 \pm 4$	$+1.2 \pm 0.2$ (298 K)	+0.07	[74.1]
trans-Co(en) $_2$ (H $_2$ O) $_2^{3+}$	-	-	-	-	$+5.9 \pm 0.2$ (308 K)	+0.33	[76.1]
Co(NH $_3$) $_5$ (DMSO) $^{3+}$	0.66	$2.7 \cdot 10^{-6}$	123 ± 2	$+61 \pm 6$	$+10.0 \pm 1.2$ (318 K)	+0.14	[76.2]
Co(NH $_3$) $_5$ (DMF) $^{3+}$	0.68	$1.4 \cdot 10^{-6}$	113 ± 1	$+22 \pm 4$	$+3.2 \pm 0.1$ (329 K)	+0.04	[78.1]
Rh(NH $_3$) $_5$ (H $_2$ O) $^{3+}$	0.66	$9.0 \cdot 10^{-6}$	103 ± 1	$+3 \pm 5$	-4.1 ± 0.4 (308 K)	-0.22	[74.1]
Rh(NH $_3$) $_5$ (DMF) $^{3+}$	0.68	$2.5 \cdot 10^{-6}$	99 ± 2	-20 ± 6	-1.4 ± 0.2 (318 K)	-0.02	[78.1]
Ir(NH $_3$) $_5$ (H $_2$ O) $^{3+}$	0.68	$4.9 \cdot 10^{-8}$	118 ± 1	$+11 \pm 4$	-3.2 ± 0.1 (344 K)	-0.18	[74.1]
Cr(H $_2$ O) $_6^{3+}$	0.61	$2.8 \cdot 10^{-6}$	110 ± 1	$+16 \pm 4$	-9.3 ± 0.3 (318 K)	-0.52	[75.1]
Cr(NH $_3$) $_5$ (H $_2$ O) $^{3+}$	0.61	$6.3 \cdot 10^{-5}$	97 ± 1	0 ± 7	-5.8 ± 0.2 (298 K)	-0.32	[74.1]
Cr(DMSO) $_6^{3+}$	0.61	$1.9 \cdot 10^{-7}$	97 ± 2	-50 ± 6	-11.3 ± 1.0 (348 K)	-0.16	[75.1]
Cr(DMF) $_6^{3+}$	0.61	$3.3 \cdot 10^{-7}$	97 ± 1	-43 ± 3	-6.3 ± 0.2 (338 K)	-0.08	[75.1]

a) Linear fit

TABLE 4. Kinetic parameters for the solvent exchange on Iron(III) ($r = 0.64 \text{ \AA}$) obtained by NMR

	k_{ex}^{298} (s^{-1})	ΔH^* kJ mol^{-1}	ΔS^* $\text{J K}^{-1} \text{ mol}^{-1}$	$\Delta V^{\ddagger(a)}$ $\text{cm}^3 \text{ mol}^{-1}$	$\Delta V^{\ddagger}/V_S^0$	Nuclei	References
$\text{Fe}(\text{H}_2\text{O})_6^{3+}$	$1.6 \cdot 10^2$	64.0 ± 2.5	$+12.1 \pm 6.7$	-5.4 ± 0.4	-0.30	^{17}O	[81.5] ^b [81.1] ^c
$\text{Fe}(\text{DMF})_6^{3+}$	$6.1 \cdot 10^1$	42.3 ± 4	-69.0 ± 13	-0.9 ± 0.2	-0.01	^1H	[73.1] ^b [82.1] ^c
$\text{Fe}(\text{DMSO})_6^{3+}$	9.3	62.5 ± 1.9	-16.7 ± 6.2	-3.1 ± 0.3	-0.04	$^1\text{H}^{\text{b,c}}$ $^{13}\text{C}^{\text{b}}$	[82.5] ^b [82.1] ^c
$\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^{2+}$	$1.4 \cdot 10^5$	42.4 ± 1.5	$+5.3 \pm 4.0$	$+7.0 \pm 0.5$	+0.39	^{17}O	[81.5] ^b [81.1] ^c
$\text{Fe}(\text{CH}_3\text{OH})_5(\text{OCH}_3)^{2+}$	$2.4 \cdot 10^3$	44.7	- 29	$+6.4 \pm 0.2$	+0.16	^1H	[69.1] ^b [82.1] ^c

a) Linear fit

b) Latest variable temperature study

c) Variable pressure

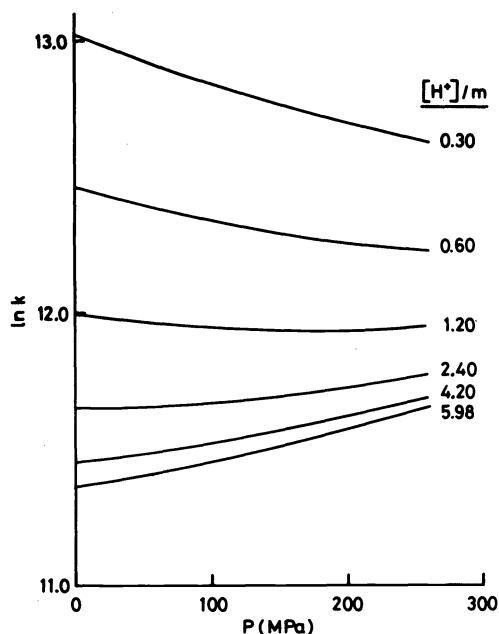


Fig. 3. Pressure dependence of $\ln k$ for the water exchange on Fe(III) at various acidities.

where k_1 is the rate for exchange of water on $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, k_{OH} is the rate for exchange on $\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}$ and K_a is the equilibrium constant for the acid dissociation equilibrium above. The effect of pressure on $\ln k$ for different perchloric acid concentrations is shown in Fig. 3. The change in slope with acidities clearly shows that a change in mechanism is occurring. In strongly acidic media the exchange rate increases with pressure, indicating an associatively activated process for $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, whereas in less acidic medium the rate decreases, favoring a dissociatively activated process for $\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}$. At intermediate acidities the upward curvature shows that pressure favors the associative pathway and disfavors the dissociative pathway. The small negative ΔV^* obtained in the non-aqueous solvents that do not hydrolyse, DMF and DMSO, confirms that the exchange on FeS_6^{3+} obeys to an interchange mechanism with a small associative character. On the other hand, in methanol solutions of $[\text{Fe}(\text{CH}_3\text{OH})_6](\text{ClO}_4)_3$, iron(III) is almost entirely in the hydrolysed form $\text{Fe}(\text{CH}_3\text{OH})_5(\text{CH}_3\text{O})^{2+}$ and produces a positive ΔV^* indicative of an I_d mechanism as found in not too acidic water solutions.

A comparison of the ΔV^* values for octahedral trivalent high spin ions (Table 5) shows a general trend across the transition metal series from an associative activation mode for the early elements to a dissociative activation mode for the d^{10} element Ga^{3+} . At both ends of the

TABLE 5. ΔV^* for solvent exchange on high spin MS_6^{3+} ions by NMR ^{a,b)}

Solvent	Sc^{3+} d^0	V^{3+} d^2	Cr^{3+} d^3	Fe^{3+} d^5	Ga^{3+} d^{10}
H_2O		-10.1 ^{c)}	- 9.3	-5.4	
DMF			- 6.3	-0.9	+ 7.9
DMSO			-11	-3.1	+13.1
$(\text{CH}_3\text{O})_3\text{PO}$	-20.7				+20.7
Mechanisms	A, I_a	I_a	I_a	I_a	I_d

a) Except Cr^{3+} by isotopic labelling

b) See table 2, 3, and 4 for references

c) Provisional value, ref. [81.4]

series, however, it is difficult to decide whether the limiting mechanisms are reached or not. For Sc^{3+} , as discussed above, the data are insufficient to decide between I_a and A . For Ga^{3+} , the case is clear in the non-aqueous solvents studied: an I_d mechanism is taking place. However, in water, it is believed that complex formation on Ga^{3+} takes place through an associative activation mode [78.2]; the ΔV^* for water exchange on $\text{Ga}(\text{H}_2\text{O})_6^{3+}$ would be welcome to confirm or not the difference in mechanism for this ion in aqueous and non-aqueous solvent.

Divalent ions

The rate constants as a function of pressure for water exchange on the divalent cations from V^{2+} to Ni^{2+} are shown in Fig. 4. Ni^{2+} shows the expected behaviour for a dissociatively activated mechanism, that is a decrease of the exchange rate with pressure. However, on going to the earlier elements of the series, V^{2+} and Mn^{2+} , one observes a reversed pressure effect. The slopes in Fig. 4 are now negative, characteristic of an associatively activated exchange. Simple complex formation reactions on divalent cations of the first-row transition series were generally thought to have dissociative activation modes. For complex formation

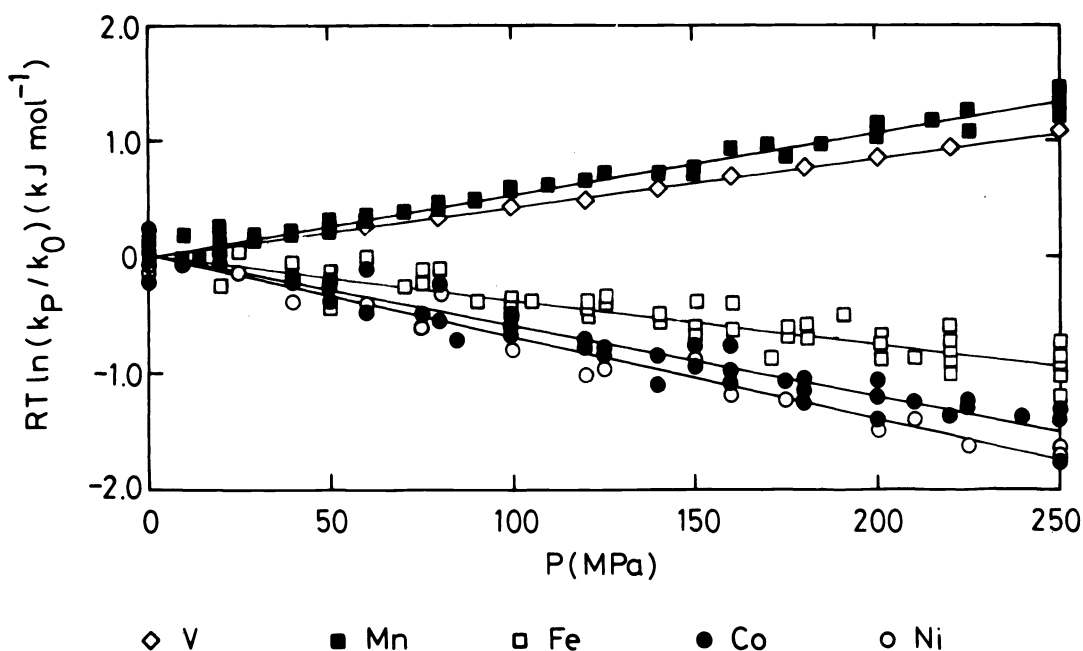


Fig. 4. Effect of pressure on the water exchange rates for the divalent ions

reactions on Ni^{2+} , such a behaviour has been clearly established by Eigen and Wilkins [60.1] [65.1][70.1], and further extended to the other metal ions of this series [78.3][78.2]. The value of ΔV^* $+7.2 \text{ cm}^3 \text{ mol}^{-1}$ for Ni^{2+} agrees well with the ΔV^* values ($+6.0$ to $+8.7 \text{ cm}^3 \text{ mol}^{-1}$) obtained for the interchange step in Ni^{2+} complex formation reactions in aqueous solution [79.3] (Table 6).

Along the series the results for non-aqueous exchange are similar to those obtained in water. The low values of the $\Delta V^*/V_S^0$ ratios in all solvents are clearly in accord with interchange processes. It has been suggested [80.7] that the volume loss on coordination can be expected to be a much smaller fraction of V_S^0 for the aprotic solvents DMF, DMSO and CH_3CN than it is for water, a solvent with anomalously open structure due to extensive hydrogen-bonding. Methanol, being partially H-bonded, should be intermediate between water and the aprotic solvents.

A change in activation mode along the series, should also be reflected by a systematic variation in activation entropies. This is not evident from the ΔS^* values in Table 6, and there is no simple correlation with the corresponding activation volumes. It should however be recalled that the ΔS^* values for solvent exchange with paramagnetic ions obtained by variable temperature NMR are sometimes subject to large systematic errors which restrict their usefulness in mechanistic assignments [79.1]. A good illustration of this point, are the reported values of ΔS^* for the acetonitrile exchange on Ni^{2+} , spread between -33 and $+50 \text{ J K}^{-1} \text{ mol}^{-1}$ [79.1]. ΔV^* determinations are not prone to such systematic errors: at appropriate temperatures, the changes in the NMR experimental data with pressure are simply related to the changes in rate constants, leading to accurate ΔV^* 's, without, for example, the risk of sign errors [79.1]. The values of ΔV^* obtained for the acetonitrile exchange on Co^{2+} are a good example: $+9.6$ for ^1H study (the proton is far from the paramagnetic center), $+6.7$ for ^{14}N (low sensitivity and solvent quadrupolar correction necessary) and $+7.7 \text{ cm}^3 \text{ mol}^{-1}$ for ^{13}C enriched nitrile (good sensitivity and advantage of spin $\frac{1}{2}$). The three values are in good agreement, although obtained using three different nuclei.

For the exchanges in neat solvent, the proposed assignment of interchange mechanisms is also borne out by the extremely small $\Delta\beta^*$ values. Since these values are negligible within experimental error, we shall restrict our discussion to the results obtained with $\Delta\beta^*$ set equal to zero. An overall view of the ΔV^* results for solvent exchange on the high spin divalent ions of the first row transition series is given in Table 7. The ΔV^* values for Co^{2+} are always slightly less than for Ni^{2+} , but I_D mechanisms can be assigned for both ions. For Fe^{2+} , one could argue that the small values of ΔV^* do not arise from a single interchange process, with slightly expanded transition state, but from the simultaneous existence of two kinetic pathways (e.g., the water exchange on Fe^{3+}). Should this crossover effectively be taking place, it would be reflected by an important variation of the volumes of activation

TABLE 6. Kinetic parameters for the solvent exchange $MS_6^{2+} + 6^*S \rightleftharpoons M^*S_6^{2+} + 6S$ obtained by NMR in neat solvent

	r (Å)	k_{ex}^{298} (s ⁻¹)	ΔH^* (kJ mol ⁻¹)	ΔS^* (J K ⁻¹ mol ⁻¹)	ΔV^* (cm ³ mol ⁻¹)	$10^2 \Delta \beta^*$ (cm ³ mol ⁻¹ MPa ⁻¹)	$\Delta V^*/V_0^O$	Nuclei	Ref.
$V(H_2O)_6^{2+}$	0.79	87	61.8 ± 0.7	- 0.4 ± 1.9	-4.1 ± 0.1 (350 K)	-0.0 ± 0.1	-0.23	¹⁷ O	[81.4] [82.2]
$Mn(H_2O)_6^{2+}$	0.83	2.1·10 ⁷	32.9 ± 1.3	+ 5.7 ± 5.0	-5.4 ± 0.1 (298 K)	-0.4 ± 0.4	-0.30	¹⁷ O	[80.2]
$Mn(CH_3OH)_6^{2+}$		3.7·10 ⁵	25.9	-50.2	-5.0 ± 0.2 (279 K)	-1.5 ± 0.5	-0.12	¹ H	[69.2] ^a [79.4] ^b
$Mn(CH_3CN)_6^{2+}$		1.4·10 ⁷	29.6 ± 0.5	- 8.9 ± 2.0	-7.0 ± 0.4 (252-260 K)	-	-0.13	¹⁴ N	[82.3]
$Fe(H_2O)_6^{2+}$	0.78	4.4·10 ⁶	41.4 ± 1.2	+21.2 ± 4.8	+3.8 ± 0.2 (298 K)	0.0 ± 0.6	+0.21	¹⁷ O	[80.2]
$Fe(CH_3OH)_6^{2+}$		5.0·10 ⁴	50.2	+12.6	+0.4 ± 0.3 (250-260 K)	+1.9 ± 0.9	+0.01	¹ H	[69.2] ^a [79.4] ^b
$Fe(CH_3CN)_6^{2+}$		6.6·10 ⁵	41.4 ± 0.7	+ 5.3 ± 2.5	+3.0 ± 0.5 (259-264 K)	-	+0.06	¹⁴ N	[82.3]
$Co(H_2O)_6^{2+}$	0.74	3.2·10 ⁶	46.9 ± 1.2	+37.2 ± 3.7	+6.1 ± 0.2 (298 K)	+0.6 ± 0.8	+0.34	¹⁷ O	[80.2]
$Co(CH_3OH)_6^{2+}$		1.8·10 ⁴	57.7	+30.1	+8.9 ± 0.3 (279 K)	+2.0 ± 0.7	0.22	¹ H	[64.1] ^a [79.2] ^b
$Co(CH_3CN)_6^{2+}$		3.4·10 ⁵	49.5 ± 0.7	+27.1 ± 2.3	+9.9 ± 0.7 (260 K)	-1.7 ± 2.2	0.20	¹ H a,b) ¹⁴ N a)	[79.2]
					+6.7 ± 0.4 (265-272 K)	-	0.13	¹⁴ N b)	[80.6] ^b
		2.6·10 ⁵	48.8 ± 1.1	+22.2 ± 3.7	+7.7 ± 1.7 (286 K)	-	0.15	¹³ C	[81.2]
$Co(DMF)_6^{2+}$		3.9·10 ⁵	56.9 ± 2.1	+52.7 ± 8.4	+6.7 ± 0.3 (296 K)	+1.4 ± 0.7	0.09	¹ H	[66.1] ^a [79.2] ^b
$Ni(H_2O)_6^{2+}$	0.69	3.2·10 ⁴	56.9 ± 0.8	+32.0 ± 3.0	+7.2 ± 0.3 (298 K)	+0.7 ± 0.8	0.40	¹⁷ O	[79.3] ^a [80.2] ^b
$Ni(CH_3OH)_6^{2+}$		1.0·10 ³	66.1	+33.5	+11.4 ± 0.6 (307 K)	+2.0 ± 2.0	0.28	¹ H	[64.1] ^a [79.2] ^b
$Ni(CH_3CN)_6^{2+}$		2.8·10 ³	64.3 ± 0.9	+37.0 ± 2.8	+9.6 ± 0.3 (294 K)	+1.8 ± 1.0	0.18	¹ H	[79.1] ^a [79.2] ^b
					+7.3 ± 0.3 (308-330 K)	-	0.14	¹⁴ N	[80.6] ^b
$Ni(DMF)_6^{2+}$		3.8·10 ³	62.8 ± 2.1	+33.5 ± 8.4	9.1 ± 0.3 (297 K)	+1.0 ± 1.0	0.12	¹ H	[66.1] ^a [79.2] ^b

a) Latest variable temperature study

b) Variable pressure

c) Linear fit

TABLE 7. ΔV^* for solvent exchange on high spin MS_6^{2+} ions by NMR a)

Solvent	V^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}
	d^3	d^5	d^6	d^7	d^8
H ₂ O	-4.1	-5.4	+3.8	+6.1	+7.2
CH ₃ OH		-5.0	+0.4	+8.9 ^{b)}	+11.4 ^{b)}
CH ₃ CN		-7.0	+3.0	+7.7 ^{b)}	+9.6 ^{b)}
DMF				+6.7	+9.1
Mechanisms	I_a	I_a	I	I_d	I_d

a) See Table 6 for references

b) Most reliable values

with temperature and pressure. The thermal expansivity of activation $\Delta\alpha^*$ and the compressibility of activation $\Delta\beta^*$, describing the pressure and temperature dependences of ΔV^* respectively, have been shown to be very small. We can therefore reject the idea of a crossover and assign an almost pure interchange I mechanism for Fe^{2+} . Both Mn^{2+} and V^{2+} are reacting according to I_a mechanisms.

Mechanistic trends

Both divalent and trivalent high spin first row transition metal ions show a gradual mechanism changeover along the series. In the two series, only the later members substitute via I_d mechanisms while the early members show I_a behaviour with the change in activation mode after the d^5 configuration (Fig. 5). A trend towards more associative mechanisms also occurs down

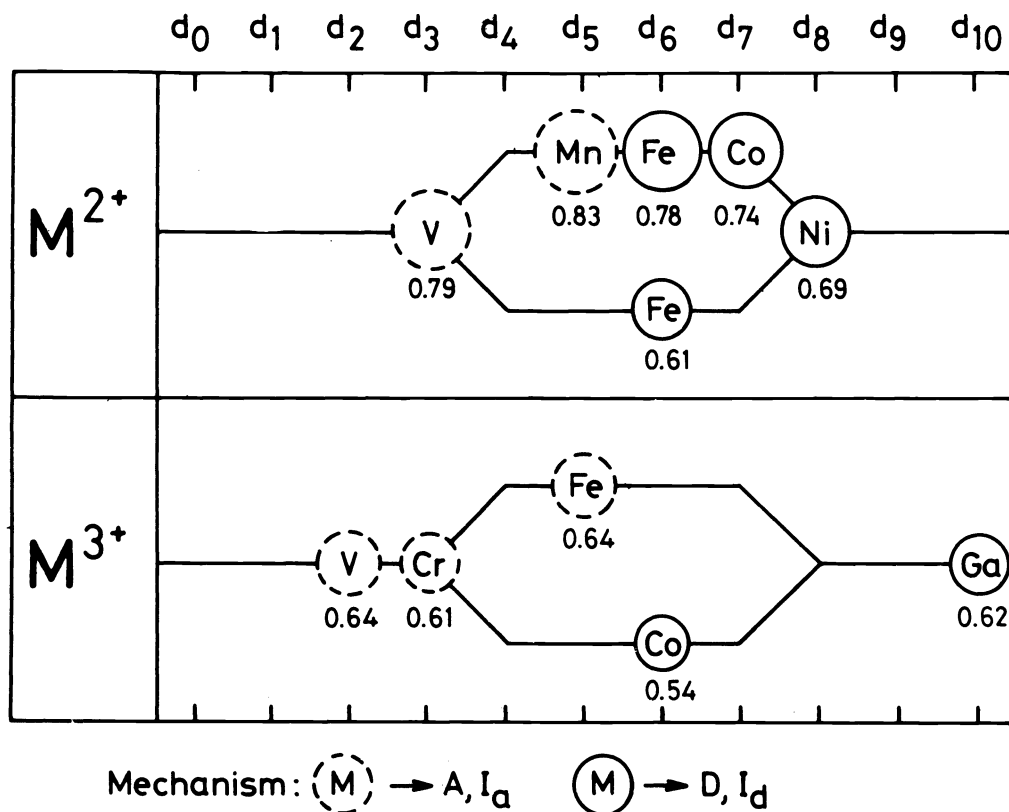


Fig. 5. First row octahedral transition metal ions (high and low spin) solvent exchange mechanisms.

the groups in the periodic table. These trends can be rationalized according to the following complementary and somewhat naïve ideas [79.4][80.2] :

- 1) A decrease of the ionic radii will increase the dissociative character due to steric crowding at the transition state. This explains the changeover along the transition series, as well as the changes down the groups Co^{3+} , Rh^{3+} , Ir^{3+} and Al^{3+} , Ga^{3+} , In^{3+} .
- 2) For an octahedral complex, in the absence of π bonding, the t_{2g} orbitals are nonbonding and the e_g orbitals σ^* antibonding. From Mn^{2+} to Ni^{2+} , the e_g orbitals occupancy remains constant, whereas the t_{2g} orbitals are gradually filled. This increased occupancy makes the approach of a seventh molecule towards the face of the octahedron less and less electrostatically favorable and could explain the tendency towards less and less associative behaviour. Similarly, along the trivalent series, Cr^{3+} (t_{2g}^3) reacts via an I_a mechanism, whilst Ga^{3+} ($t_{2g}^6 e_g^4$) reacts via an I_d mechanism (non-aqueous solvents), as does the low spin Co^{3+} (t_{2g}^6) ($r = 0.53 \text{ \AA}$). In accord is the assignment of D mechanisms for low spin Fe^{2+} (t_{2g}^6) ($r = 0.61 \text{ \AA}$) substitution reactions for which ΔV^* values of around $+20 \text{ cm}^3 \text{ mol}^{-1}$ have been found [77.2].
- 3) The above two arguments alone, do not predict the less associative character, less negative ΔV^* , for water exchange on V^{2+} over that for Mn^{2+} . This apparent anomaly can be explained by considering the changes in e_g orbital occupancy. These orbitals are σ^* antibonding, and it can be supposed that their filling will produce an increasing dissociative character. Considering the volumes of activation obtained for Mn^{2+} and V^{2+} , we can conclude that the steric effect (a seven coordinate transition state is less favorable for a smaller central ion) totally compensates this electronic effect or even slightly predominates over it.

CONCLUSION

The results reviewed in this paper vividly illustrate the power of high pressure multinuclear magnetic resonance in ascribing activation modes, and even in deciding between interchange and limiting mechanisms, for exchange processes. The technique has proven invaluable in the study of solvent exchanges on metal ions, reactions which are fundamental to the understanding of substitution and redox reactions in inorganic chemistry. The most striking result is that, for both divalent and trivalent high spin first row transition metal ions, and contrary to previous mechanistic assignments based on the sensitivity of the rates of complex formation reactions to the nature of the incoming ligand [65.2], the ΔV^* available for solvent exchange lead to the conclusion that only the later members of the series substitute via an I_d mechanism. It is worthwhile to note that the most studied substitution reactions are those of Ni^{2+} and the small low spin Co^{3+} , which show marked dissociative character, whereas much less attention has been paid to the early elements. The exchange mechanisms are also clearly controlled by the properties of the metal ion rather than by the nature of the solvent. In this respect, the ionic radius and the electronic configuration, two properties closely related for transition metal ions, are of supreme importance for the rationalization and the prediction of exchange mechanisms. As such, the results are a challenge and will provoke intense work in this area at the benefit of a better general understanding of inorganic substitution reactions.

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