138. Dimethylformamide-Exchange Mechanism on Some First-Row Divalent Transition-Metal Ions1)2)3)

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The effect of temperature on the dimethylformamide exchange on $Mn(DMF)_6^{2+}$ and $Fe(DMF)_6^{2+}$ has been studied by ^{13}C- and ^{17}O-NMR, respectively, yielding the following kinetic parameters: $k^{298} = (2.2 \pm 0.2) \cdot 10^6$ s^{-1}, $\Delta H^{\neq} = 34.6 \pm 1.3$ kJ mol^{-1}, $\Delta S^{\neq} = -7.4 \pm 4.8$ J $K^{-1}mol^{-1}$ for Mn^{2+} and $k^{298} = (9.7 \pm 0.2) \cdot 10^5$ s^{-1}, $\Delta H^{\neq} = 43.0 \pm 0.9$ kJ mol^{-1}, $\Delta S^{\neq} = +13.8 \pm 2.8$ J $K^{-1}mol^{-1}$ for Fe^{2+}. The volumes of activation, $\Delta V^{\neq}$ in cm^3mol^{-1}, derived from high-pressure NMR on these metal ions, together with the previously published activation volumes for Co^{2+} and Ni^{2+} ($+2.4 \pm 0.2$ (Mn^{2+}), $+8.5 \pm 0.4$ (Fe^{2+}), $+9.2 \pm 0.3$ (Co^{2+}), $+9.1 \pm 0.3$ (Ni^{2+})) give evidence for a dissociative activation mode for DMF exchange on these high-spin first-row transition-metal divalent ions. The small positive $\Delta V^{\neq}$ value observed for DMF exchange on Mn^{2+} seems to indicate that a mechanistic changeover also occurs along the series, (probably from I_d to D), as for the other solvents previously studied (I_a to I_d, for H_2O, MeOH, MeCN). This changeover is shifted to the earlier elements of the series, due to more pronounced steric crowding for dimethylformamide hexasolvates.

1. Introduction. – The exchange of solvent molecules between the primary solvation shell of a metal ion and bulk solvent may be considered as the fundamental reaction for the understanding of complex formation and inner-sphere redox processes. An important aid in solvent exchange mechanistic elucidation in recent years has been the study of the effect of the pressure on the exchange rate, using high-pressure NMR [2]. For the first-row di- and trivalent high-spin transition-metal ions, activation volumes indicate that the mechanism for solvent exchange is not unique, but progressively changes from an associative activation mode for the early elements to a dissociative activation mode for the later ones. This changeover could be explained by the progressive filling of the d orbitals and the decrease in ionic radii along the series, both factors disfavouring bonding processes.

N,N-dimethylformamide (DMF) exchange on Co(II) and Ni(II) ions have already been studied under pressure [3]. For both ions, the activation volume is positive and the exchange reaction occurs *via* a dissociative activation mode. To test whether a change in mechanism will also occur for the DMF exchange on earlier transitions elements, we have performed a variable-temperature and -pressure NMR study on Mn(II) and Fe(II) ions.

2. Experimental. – DMF (*Fluka, puriss.*) was stirred for one day with 4-Å molecular sieve. After decantation, it was stirred for one more day with oven-dried BaO, then distilled at 8 mBar. All the purification procedure was done under Ar in the dark, in order to avoid photochemical decomposition. The resulting solvent was kept in the freezer and used shortly after preparation. ^{17}O-enriched DMF was prepared using the method described by *Ott* [4],

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1) Part 33 of the series 'High-Pressure NMR Study'. Part 32: [1].

2) Taken in part from the diploma work of *C. Cossy*, Université de Lausanne, 1983.

3) This work was presented in part at the 24th International Conference on Coordination Chemistry, Athens, Greece, August 1986.

replacing $H_2{}^{18}O$ by $H_2{}^{17}O$ (*Yeda*, 20 atom-% ^{17}O, ^1H-normalized). The resulting product was dried and purified as described above. Formyl-^{13}C-enriched DMF (*Stohler Isotope*, 90 atom-% ^{13}C) was purified by the same method.

Hydrated manganese perchlorate (*Fluka, p.a.*) was used without further purification. Hydrated iron and zinc trifluoromethanesulfonate were obtained by dissolving a slight excess of metal (*Merck, p.a.*) in aq. 40% CF_3SO_3H. Solns. were then filtered and evaporated at reduced pressure. The remaining solids were left overnight at 0.1 mBar. $[Mn(DMF)_6](ClO_4)_2$, $[Fe(DMF)_5](CF_3SO_3)_2$ and $[Zn(DMF)_6](CF_3SO_3)_2$ were prepared by the following procedure: 20 mmol of each hydrated metal salt were dissolved under Ar in 150 mmol of triethyl orthoformate (*Fluka, purum*) and 130 mmol of DMF. The solns. were evaporated under reduced pressure to oily mixtures and extracted with 150 ml of Et_2O. The precipitates were collected by filtration in a glove box, washed 2 times with 20 ml of Et_2O, and dried under vacuum. For Fe(II), all syntheses and workup described above were done in an O_2-free atmosphere, and all liquids used were degassed before use. Elementary analyses of the final products were in good agreement with the theoretical formulae.

Four possible nuclei (^{17}O, ^{13}C, ^{14}N, and ^1H) could be used to follow the DMF exchange on Fe^{2+} and Mn^{2+}. The ^{17}O nucleus is the closest to the paramagnetic centre in the solvento complex, giving rise to the largest coordinated *vs.* bulk DMF chemical shift, and, therefore, the largest kinetic window. However, it is known that Mn^{2+} is a very efficient NMR-relaxation agent, therefore, for this metal ion, the less close ^{13}C-formyl nucleus was preferred.

Five $Mn(DMF)_6^{2+}$ solns. ($2.64 \cdot 10^{-3}m$, $1.023 \cdot 10^{-2}m$, and $2.042 \cdot 10^{-2}m$ for variable-temp. study; $3.64 \cdot 10^{-3}m$, $9.25 \cdot 10^{-3}m$, 30% ^{13}C for variable-pressure study), four $Fe(DMF)_6^{2+}$ solns. ($4.83 \cdot 10^{-3}m$, $9.70 \cdot 10^{-3}m$, 1% ^{17}O for variable-temp. study; $9.14 \cdot 10^{-3}m$, $1.000 \cdot 10^{-2}m$, 2% ^{17}O variable-pressure study), and two $Zn(DMF)_6^{2+}$ solns. ($9.78 \cdot 10^{-3}m$, 1% ^{17}O for variable-temp. study; $9.24 \cdot 10^{-3}m$, 2% ^{17}O for variable-pressure study) were prepared by weight in a glove box. For the Fe(II) solns., the solvent used was previously degassed. Samples for the variable-temp. study were sealed in 10-mm o.d. NMR tubes.

Variable-temp. ^{17}O-NMR measurements were performed at 27.11 MHz on a *Bruker CXP-200* spectrometer. Sweep widths varied from 10 to 40 kHz, number of scans from 2000 to 36000, repetition rate from 26 to 110 msec. ^{13}C-NMR measurements without ^1H decoupling were performed at 50.31 MHz on the same spectrometer and at 100.6 MHz on a *Bruker AM-400* spectrometer. Sweep widths varied from 15 to 30 kHz, accumulation number from 500 to 25000, and repetition rate from 0.5 to 2 s. Variable-pressure measurements were achieved on the *CXP-200* spectrometer with a previously described probehead [5] tuned to the appropriate frequency. Sweep width for ^{17}O (^{13}C) varied from 10 to 20 kHz (15 kHz), number of scans from 5000 to 10000 (1000), and repetition rate from 60 to 110 msec (0.5 to 2 s).

^{17}O-transverse relaxation rates were calculated from the full width at half height, measured on the plotted peaks ($1/T_2 = \pi \Delta\nu_{1/2}$). To obtain ^{13}C-transverse relaxation rates of the formyl doublet, the signals were fitted to two identical *Lorentzian* curves, separated by the $^1J(^{13}C,^1H)$ coupling constant (30.6 Hz).

3. Data Treatment and Results. – 3.1. *Basic NMR Equations.* The solvent exchange was studied by methods outlined in [6] [7]. The relevant equations are repeated here for convenience. The reduced transverse NMR relaxation time T_{2r} for the free or coalesced DMF signal is related to the observed relaxation time T_2 by *Eqn. 1*, where T_{2A}^0 is the contribution to T_2 due to pure DMF, T_{2m} is the relaxation time of coordinated DMF in

$$\frac{1}{T_{2r}} = \frac{1}{P_m}\left(\frac{1}{T_2} - \frac{1}{T_{2A}^0}\right) = \frac{1}{\tau_m}\left[\frac{T_{2m}^{-2} + (T_{2m}\tau_m)^{-1} + \Delta\omega_m^2}{(T_{2m}^{-1} + \tau_m^{-1})^2 + \Delta\omega_m^2}\right] + \frac{1}{T_{2os}} \qquad (1)$$

the absence of exchange, T_{2os} is the outer-sphere contribution, P_m is the mole fraction of coordinated DMF (for Mn^{2+} and Fe^{2+}, coordination numbers are assumed to be six in solution), and τ_m is the residence time of a coordinated DMF molecule. Similarly the reduced chemical shift $\Delta\omega_m$ (rad s^{-1}) relative to pure DMF by *Eqn. 2*, where $\Delta\omega_m$ is the chemical shift between free and coordinated DMF in the absence of exchange, and

$$\Delta\omega_r = \frac{\Delta\omega_s}{P_m} = \frac{\Delta\omega_m}{(\tau_m/T_{2m} + 1)^2 + \tau_m^2\,\Delta\omega_m^2} + \Delta\omega_{os} \qquad (2)$$

$\Delta\omega_{os}$ is the chemical shift between bulk and pure DMF.

The temperature dependence of the various parameters can now be considered. The exact functional dependence of the transverse relaxation rates depends on the relaxation mechanism in operation (relaxation *via* interaction of the electric quadrupole moment with an electric field gradient, *via* dipole-dipole, or *via* scalar interaction with the electron spin of the metal ion are possible). Because the relaxation of ^{17}O in pure DMF is governed by the electric quadrupole interaction and furthermore because the 'extreme narrowing' condition $\omega_0\tau_c \ll 1$ is fulfilled, we can use a simple exponential to describe the temperature dependence of $1/T^0_{2A}$, as shown in *Eqn. 3*. As $1/T^0_{2A}$ is proportional to the molecular reorientation correlation time of DMF, E_A is also the activation energy for this process.

$$1/T^0_{2A} = (1/T^0_{2A})^{298} \exp\,[(E_A/R)\,(1/T - 1/298.15)] \qquad (3)$$

For inner- and outer-sphere relaxation, a separation of the various relaxation mechanisms is a difficult task, but in our case we can assume simple *Arrhenius* behaviour (*Eqn. 4* and *5*). For outer-sphere relaxation, the reference temperature is taken at 223.15 K, because this parameters is significant only at low temperatures in this study.

$$1/T_{2m} = (1T_{2m})^{298} \exp\,[(E_m/R)\,(1/T - 1/298.15)] \qquad (4)$$

$$1/T_{2os} = (1/T_{2os})^{223} \exp\,[(E_{os}/R)\,(1/T - 1/223.15)] \qquad (5)$$

The residence time, τ_m, is related to the pseudo-first-order reaction rate constant for solvent exchange of a particular coordinated DMF molecule, k, and its temperature dependence may be obtained from transition-state theory (*Eqn. 6*).

$$k = 1/\tau_m = \frac{k_B T}{h} \exp(\Delta S^{\neq}/R - \Delta H^{\neq}/RT) \qquad (6)$$

For Fe(II), we expect the isotropic shift to have a negligible contribution from pseudocontact interaction, so we have assumed that *Bloembergen*'s equation (*Eqn. 7*) is

$$\Delta\omega_m = -\,\omega_I \frac{S(S+1)\gamma_e}{3\gamma_I k_B T} A \qquad (7)$$

obeyed [8], where ω_I is the spectrometer operating frequency, γ_e and γ_I are the gyromagnetic ratios of the unpaired electrons and of the nucleus respectively, S is the electron-spin quantum number and A/h is the scalar coupling constant in Hz. Other symbols have their usual meaning.

The pressure dependence of the various NMR parameters is more difficult to predict theoretically, and their pressure variation will be discussed in relation to the determination of activation volumes. The volume of activation, $\Delta V^{\neq}$, is defined according the transition-state (*Eqn. 8*). For solvent exchange reactions, a linear relationship between

$$\Delta V^{\neq} = -\,RT\,(\partial \ln(k)/\partial P)_T \qquad (8)$$

$\ln(k)$ and P is usually used (*Eqn. 9*), where k_0 is the zero-pressure rate constant.

$$\ln(k) = \ln(k_0) - \Delta V^{\neq} P/RT \qquad (9)$$

3.2. *DMF Exchange on Fe(DMF)$_6^{2+}$ by ^{17}O-NMR. Relaxation of DMF.* The ^{17}O-NMR relaxation rate of free solvent in absence of chemical exchange, $1/T^0_{2A}$, is normally obtained by measuring the relaxation rate of pure solvent. To ensure that there is no quadrupolar influence from the ionic solute on $1/T^0_{2A}$, we measured the temperature dependence of the line width of neat, dried DMF, of 1% ^{17}O-enriched DMF and of a solution of $9.78 \cdot 10^{-3}m$ $[Zn(DMF)_6](CF_3SO_3)_2$ in 1%-enriched DMF, which corresponds

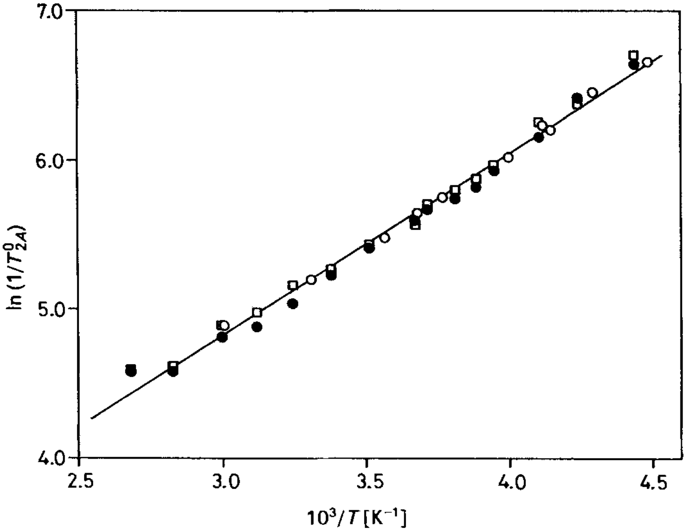

Fig. 1. *Logarithm of the transverse relaxation rate of ^{17}O of DMF* vs. *reciprocal temperature.* ((○) natural ^{17}O abundance; (●) 1% ^{17}O-enriched; (□) 1% ^{17}O-enriched, $9.78 \cdot 10^{-3}m$ $[Zn(DMF)_6](CF_3SO_3)_2$)

to the highest salt concentration used for the $[Fe(DMF)_6](CF_3SO_3)_2$. The relaxation rates are shown in *Fig. 1*. The three data sets coincide within experimental errors. The curve plotted in *Fig. 1* is the result of a nonlinear least-squares analysis with *Eqn. 3*, where all data points were used. The parameters obtained are $(1/T_{2A}^0)^{298} = 191 \pm 2\ s^{-1}$ and $E_A = 10.2 \pm 0.2\ kJ\ mol^{-1}$.

As no differences were detected between the results obtained from pure DMF and those from a solution containing a diamagnetic salt, we studied the influence of pres-

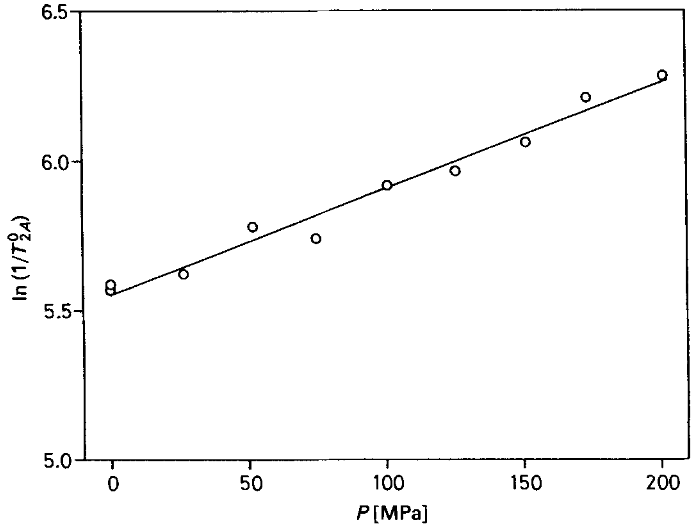

Fig. 2. *Logarithms of the ^{17}O relaxation rate of DMF* vs. *pressure in a 2% ^{17}O-enriched solution containing $9.24 \cdot 10^{-3}$m $[Zn(DMF)_6](CF_3SO_3)_2$*

sure on the quadrupolar relaxation rate of DMF in a solution containing Zn^{2+}. The measurements were done at 274.9 K and the results are shown in *Fig. 2*. Using *Eqn. 10* to describe the pressure dependence of the relaxation rate, a nonlinear least-squares fit gives

$$\ln(1/T_{2A}^{0}) = \ln(1/T_{2A}^{0})_0 - \Delta V_A^{\neq} P/RT \qquad (10)$$

$(1/T_{2A}^{0})_0 = 258 \pm 6\ s^{-1}$ and $\Delta V_A^{\neq} = -8.0 \pm 0.5\ cm^3\ mol^{-1}$. The quadrupolar relaxation rate is directly proportional to the reorientation correlation time, τ_c. Increasing pressure induces a decrease in the ease of molecular motion, and thus an increase in τ_c. This effect explains the fairly negative value of $\Delta V_A^{\neq}$ determined. The significant increase of $1/T_{2A}^{0}$ with pressure for DMF contrasts with the slight decrease of this parameter in H_2O [7]. However, H_2O is a highly structured solvent, with many H-bonds. The cleavage of these bonds has been postulated [9], in order to explain the decrease of τ_c with pressure.

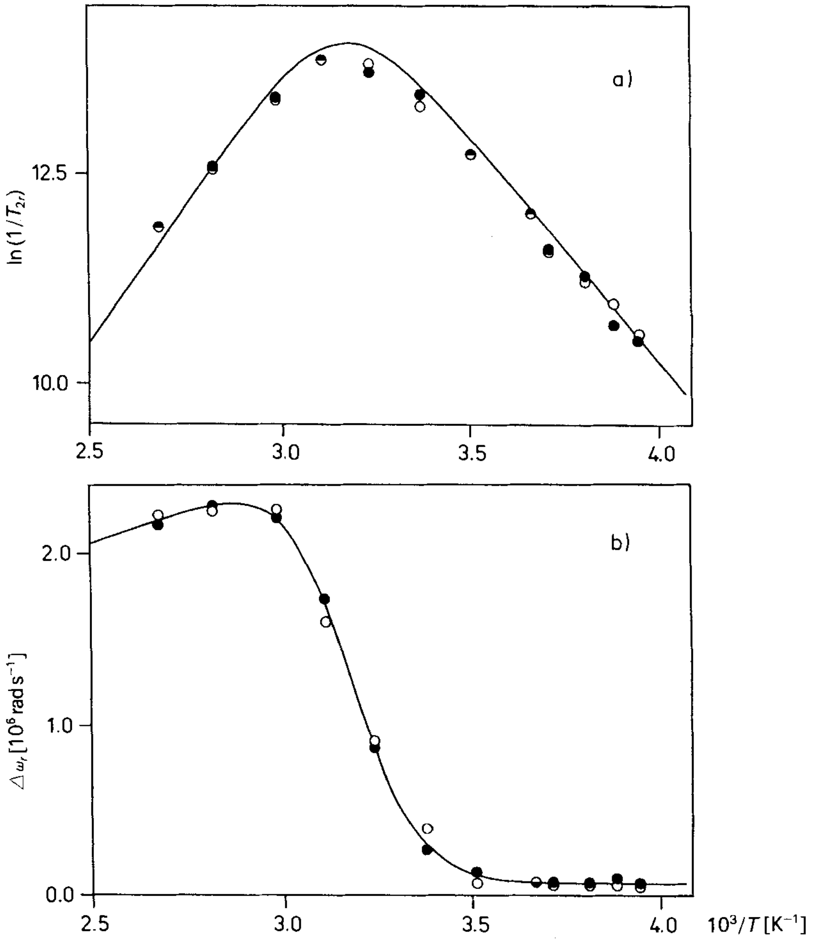

Fig. 3. *Experimental and calculated logarithms of* ^{17}O*-reduced relaxation rate* (a) *and reduced chemical shift* (b) *of DMF* vs. *reciprocal temperature in iron(II) trifluoromethanesulfonate solutions* ((○) $9.70 \cdot 10^{-3} m$ in Fe^{2+}; (●) $4.83 \cdot 10^{-3} m$ in Fe^{2+})

Fe^{2+} Solutions. The temperature dependence of the exchange rate of DMF on $Fe(DMF)_6^{2+}$ was obtained from the line width and the chemical shift of the ^{17}O-NMR signal (bulk or coalesced), measured between 253.4 K and 373.1 K, of two DMF solutions containing Fe^{2+} (see *Experimental*). The reduced relaxation rates and the reduced chemical shifts as calculated using *Eqn. 1* and *2* are shown in *Fig. 3* as a function of the reciprocal temperature. As can be seen from *Fig. 3a*, no significant deviation from a straight line is observed at low temperature, indicating that $1/T_{2os}$ is small compared with the line broadening due to exchange, therefore, we set it to zero.

Concerning the reduced chemical shift, a problem arises due to the unknown contribution of the magnetic susceptibility, χ, *to* $\Delta\omega_r$. The true chemical shift is connected to the observed one [10] *via Eqn. 11* where χ and χ_{ref} are the magnetic susceptibilities of the paramagnetic solution and the reference, respectively, S_f is the shape factor of the sample, and B_0 the external magnetic field strength. We have thus to add a third term to *Eqn. 2*. The temperature dependence of this term can be approximated by a simple *Curie* law, because $\chi \gg \chi_{ref}$. The outer-sphere contribution to the chemical shift should also obey a *Curie* law, and we added these two terms and used *Eqn. 12* to fit the data.

$$\Delta\omega = \Delta\omega_{obs} - 2\pi B_0 S_f(\chi - \chi_{ref}) \tag{11}$$

$$\Delta\omega_r = \frac{\Delta\omega_m}{(\tau_m/T_{2m} + 1)^2 + \tau_m^2\,\Delta\omega_m^2} + \frac{C}{T} \tag{12}$$

A nonlinear least-squares fit of $1/T_{2r}$ and $\Delta\omega_r$ *vs.* reciprocal temperature using *Eqns. 1, 4, 6, 7,* and *12* was unable to locate a minimum because of the small value calculated for $1/T_{2m}$ with respect to k and $\Delta\omega_m$. We repeated the calculations three times, fixing $(1/T_{2m})^{298}$ to 0, 14000 and 28000 rad s^{-1} and E_m to 3 kJ mol^{-1} (the value obtained for ^{17}O of water bound to Fe^{2+} [11]). The observed changes on the other parameters calculated ($\Delta H^{\neq}$, $\Delta S^{\neq}$, or k^{298}, A/h, and C) were small and within one standard deviation σ. The final results of the four parameters fitted are given in *Table 1*.

Table 1. *Kinetic and NMR Parameters Derived from Transverse Relaxation Rates and Chemical Shifts of Bulk (Coalesced) DMF in $Mn(DMF)_6^{2+}$ and $Fe(DMF)_6^{2+}$ Solutions*[a]

Metal ion	Mn^{2+} [this work][e]	Fe^{2+}	
		[this work]	[12]
Nucleus studied	^{13}C	^{17}O	^{1}H
k^{298} [10^5 s^{-1}]	22.2 ± 1.7	9.7 ± 0.2	17 ± 3
$\Delta H^{\neq}$ [kJ mol^{-1}]	34.6 ± 1.3	43.0 ± 0.9	48.9 ± 2.5
$\Delta S^{\neq}$ [J K^{-1} mol^{-1}]	–7.4 ± 4.8	+13.8 ± 2.8	+39 ± 8
$(1/T_{2m})^{298}$ [10^6 s^{-1}]	4.9 ± 0.6	0[b]	–
E_m [kJ mol^{-1}]	18.4 ± 1.3	–	–
$(1/T_{2os})^{223}$ [s^{-1}]	3280 ± 5430[c]	–	–
A/h [MHz]	–	9.11 ± 0.07	–
C [10^8 K s^{-1}]	–	1.77 ± 0.24	–
$\Delta V^{\neq}$ [cm^3 mol^{-1}]	+2.4 ± 0.2[d]	+8.5 ± 0.4	–

[a] Errors quoted correspond to one standard deviation. [b] Fixed value (see text). [c] Calculated with a fixed E_{os} value of 10 kJ mol^{-1} (see text). [d] Calculated with a fixed $\Delta V_m^{\neq}$ value of 0 cm^3 mol^{-1} (see text).

[e] **Note Added in Proof.** – An ^{17}O-NMR study yields very similar kinetic parameters: $k^{298} = (2.7 \pm 0.2) \times 10^6$ s^{-1}, $\Delta H^{\neq} = 35.8 \pm 0.6$ kJ mol^{-1}, $\Delta S^{\neq} = -2 \pm 2$ JK^{-1} mol^{-1} and $\Delta V^{\neq} = +1.6 \pm 0.5$ cm^3 mol^{-1} (M. Ishii, S. Funahashi, M. Tanaka, *Chem. Lett.* **1987**, 871).

The pressure dependence of $1/T_2$ was measured at 274.9 K and 292.0 K with two solutions of slightly different concentrations (see *Experimental*). Values of $1/T^0_{2A}$ at these two temperatures were calculated by introducing the value of $(1/T^0_{2A})_0$ extracted from the variable temperature results in *Eqn. 10* and by using the $\Delta V^{\neq}_A$ value of -8.0 cm^3 mol^{-1} determined above. $1/T_{2r}$ *vs.* pressure was fitted using *Eqn. 1* and *9*, with the same approximations used for the variable temperature data treatment ($1/T_{2m}$ and $1/T_{2os}$ negligible). $\Delta\omega_m$ was taken equal to its value determined from the variable-temperature study and was assumed to be pressure-independent. The three parameters calculated were $\Delta V^{\neq}$, $k_0^{274.9}$, and $k_0^{292.0}$. The results are illustrated in *Fig. 4* in a temperature-independent form.

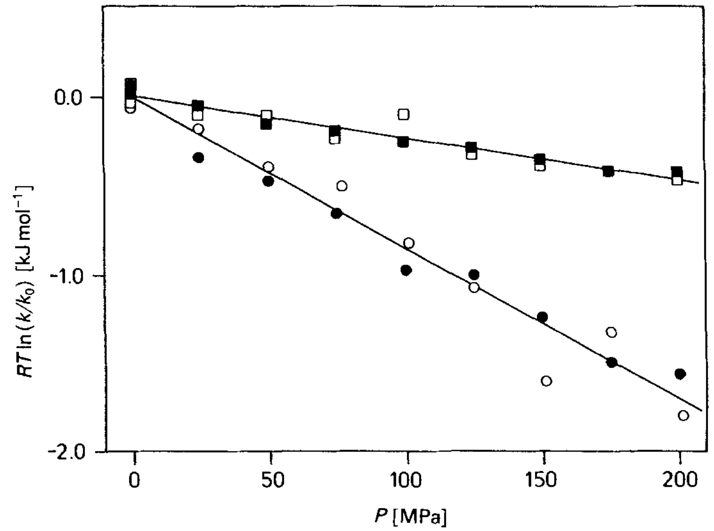

Fig. 4. *Experimental and calculated* RT *ln(*k/k$_0$*)* vs. *pressure for exchange of DMF on Mn(DMF)$_6^{2+}$* (squares) *and Fe(DMF)$_6^{2+}$*(circles) ((□) Mn^{2+} $3.64 \cdot 10^{-3}$*m* at 270.3 K; (■) Mn^{2+} $9.25 \cdot 10^{-3}$*m* at 262.7 K; (○) Fe^{2+} $1.000 \cdot 10^{-2}$*m* at 274.9 K; (●) Fe^{2+} $9.14 \cdot 10^{-3}$*m* at 292.0 K)

3.3. *DMF Exchange on Mn(DMF)$_6^{2+}$ by ^{13}C-NMR.* In pure DMF, we observed that the transverse relaxation rate of formyl-^{13}C increases from 33 s^{-1} to 38 s^{-1} between 219.3 K to 420.9 K, and is pressure-independent. These rather large relaxation values for ^{13}C are probably due to a coupling with the quadrupolar ^{14}N nuclei of the amide group. Anyway, except for the lowest temperatures investigated in this study, $1/T^0_{2A}$ values were small compared to $1/T_2$ of our Mn^{2+} solutions, thus we consider $1/T^0_{2A}$ as constant and equal to 35 s^{-1}.

The temperature dependence of the exchange rate of DMF on Mn(DMF)$_6^{2+}$ was obtained by measuring the transverse relaxation rate of the ^{13}C-formyl NMR doublet between 219.3 K and 420.9 K of three DMF solutions containing Mn^{2+} (see *Experimental*). Chemical shifts were not systematically measured, because the peaks are very broad and shifts small. At 403.1 K, a value of $4 \cdot 10^4$ rad s^{-1} for $\Delta\omega_m$ (equal to $\Delta\omega_r$ at this high temperature) was estimated. $\Delta\omega_m$ (see *Eqn. 7*) is, therefore, not greater than 10^5 rad s^{-1} in the whole temperature range studied, and can be neglected with respect to $1/T_{2m}$ and $1/\tau_m$ (*Eqn. 13* and *14*), leading to *Eqn. 15*, a simplified form of *Eqn. 1*.

$$\Delta\omega_m^2 \ll T_{2m}^{-2} \tag{13}$$

$$\Delta\omega_m^2 \ll (T_{2m}\tau_m)^{-1} \tag{14}$$

$$\frac{1}{T_{2r}} = \frac{(T_{2m}\tau_m)^{-1}}{\tau_m^{-1} + T_{2m}^{-1}} + \frac{1}{T_{2os}} \tag{15}$$

A nonlinear fit of $1/T_{2r}$ *vs.* reciprocal temperature using *Eqns. 4* to *6* and *15* was unable to define simultaneously $(1/T_{2os})^{223}$ and E_{os}. By fixing E_{os} to three reasonable values (0, 10, and 20 kJ mol^{-1}), the other calculated parameters ($\Delta H^{\neq}, \Delta S^{\neq}$ or k^{298}, $(1/T_{2m})^{298}$, E_m, and $(1/T_{2os})^{223}$) varied within 1 σ. The final values of the five parameters are given in *Table 1* and are illustrated in *Fig. 5*. Moreover, calculation of the terms T_{2m}^{-2}, $(T_{2m}\tau_m)^{-1}$, and $\Delta\omega_m^2$ at the extreme temperatures used in this study shows that inequalities *13* and *14* are fully respected.

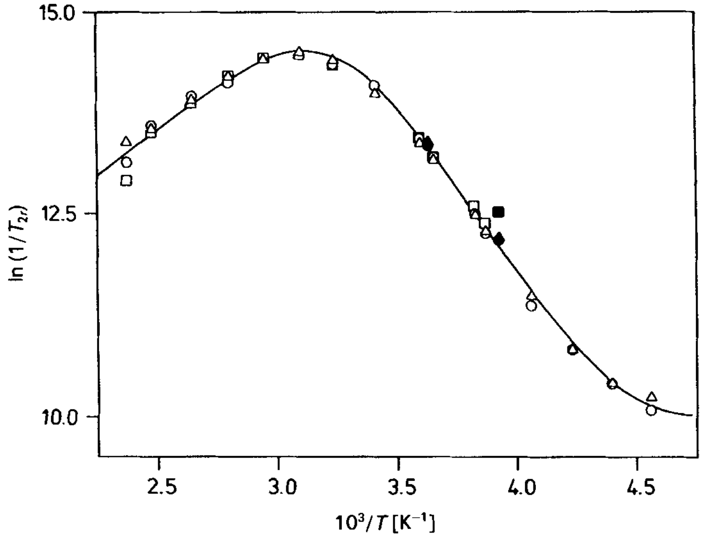

Fig. 5. *Experimental and calculated logarithms of formyl-*^{13}*C-reduced relaxation rates of DMF in Mn(II) perchlorate solutions* (squares: $2.64 \cdot 10^{-3} m$ in Mn^{2+}; triangles: $1.023 \cdot 10^{-2} m$ in Mn^{2+}; circles: $2.042 \cdot 10^{-2} m$ in Mn^{2+}; open symbols: measurements at 50.31 MHz; filled symbols: measurements at 100.6 MHz)

The pressure dependence of $1/T_2$ was measured at 262.7 K and 270.3 K with two solutions of different concentrations (see *Experimental*). At these temperatures, the contribution of $1/T_{2m}$ to $1/T_{2r}$ is small (1 % and 4 %, respectively), but cannot be neglected. Using *Eqns. 9, 15,* and *16*, fixing $(1/T_{2m})^0$ at values calculated with the parameters ex-

$$\ln(1/T_{2m}) = \ln(1/T_{2m})_0 - \Delta V_m^{\neq} P/RT \tag{16}$$

tracted from the variable temperature study, fixing $\Delta V_m^{\neq}$ to -10, 0 and 10 cm^3 mol^{-1}, we fitted $1/T_{2r}$ *vs.* pressure. $\Delta V^{\neq}$ varied from 1.86 to 2.55 cm^3 mol^{-1} with the various values of $\Delta V_m^{\neq}$ used, which is acceptable within experimental errors.

4. Discussion. – It is generally accepted, on the grounds of available activation volumes (see *Table 2*), that a gradual solvent-exchange mechanistic changeover occurs for divalent hexasolvates across the first-row transition-metal series, from the associa-

Table 2. *Volumes of Activation* [$cm^3\,mol^{-1}$] *for Solvent Exchange on Divalent First-Row d-Transition Hexasolvated Metal Ions*[a])

Solvent	V^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
H_2O	−4.1	−5.4	+3.8	+6.1	+ 7.2	
MeOH		−5.0	+0.4	+8.9	+11.4	+8.3
MeCN		−7.0	+3.0	+8.1	+ 8.5	
DMF		+2.4[b])	+8.5[b])	+9.2[c])	+ 9.1	
NH_3					+ 5.9	

[a]) From [2]. [b]) This work. [c]) Value at 253 K. At 296 K, $\Delta V^{\neq}$ = +6.7 $cm^3\,mol^{-1}$ [3].

tively activated V^{2+} to dissociatively activated Ni^{2+}, at least in H_2O, MeOH, and MeCN [2]. The small activation volume for Fe^{2+} in the later solvents are indicative of interchange *I* mechanism with almost as much associative as dissociative contributions to the transition state. Considering these solvents only, it appears that the electronic structure (filling of 3d orbitals) and the ionic radius of these metals ions are solely responsible for their exchange mechanisms.

However, a quite different behaviour is depicted for DMF exchange. The data obtained in this study show that the activation volumes remain positive on going from Ni^{2+} to Mn^{2+}. It is large and positive for Fe^{2+}, and slightly positive for Mn^{2+}, in accord with a dissociative activation mode for all four ions in this solvent. This mechanistic singularity, compared to the solvent studied, can be explained by steric effects. DMF is bulkier than H_2O, MeOH, and MeCN. An associative pathway is, thus, disfavoured and, therefore, DMF exchange occurs preferably *via* a dissociative pathway. The plausibility of this explanation is reinforced by the observations made for solvent exchanges on the small tetrahedrally coordinated Be^{2+} ion, where H_2O exchanges *via* an associative *A* mechanism, and DMF *via* two competitive I_a (or *A*) and *D* mechanisms [13]. Moreover, the pronounced dissociative character of reactions in DMF has also been outlined for complex formation reactions on Ni^{2+} [14], where a *D* mechanism with a five-coordinated intermediate has been postulated, in contrast with the I_d mechanism occurring for substitution on this ion in H_2O. A more dissociative substitution behaviour in DMF than in H_2O has also been noted for Fe^{3+}-solvent exchange [15] and complex-formation reactions [16]. The small positive $\Delta V^{\neq}$ value observed for DMF exchange on Mn^{2+} seems to indicate that a mechanistic changeover also occurs along the first-row divalent transition-metal ions (probably from I_d to *D*), like for the other solvents studied (I_a to I_d), but this changeover is shifted to the earlier elements of the series. In this respect, it would be interesting to study DMF exchange on the V^{2+} ion.

Even though $\Delta S^{\neq}$ [$J\,K^{-1}mol^{-1}$] is not a very reliable parameter in this kind of study [6], it is interesting to note that the trend of their values (−7 ± 5 for Mn^{2+}, +14 ± 3 for Fe^{2+}, +53 ± 8 [3] for Co^{2+}, and +34 ± 8 [3] for Ni^{2+}) is not inconsistent with that of the $\Delta V^{\neq}$ value.

The solvent-exchange rate constants for 3d divalent metal ions are reported in *Table 3*. It appears that the sequence of reactivity is independent on the exchange

$$Cu^{2+} > Mn^{2+} > Fe^{2+} > Co^{2+} > Ni^{2+} > V^{2+}$$

mechanism and on the solvent when a comparison is possible. This sequence agrees well with the predictions based on the use of crystal-field-activation energies [17] or

Table 3. *Solvent-Exchange Rate* [s^{-1}] *at 298.15 K on Divalent First-Row d-Transition Hexasolvated Metal Ions* a)

Solvent	V^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
H_2O	87	$2.1\cdot10^7$	$4.4\cdot10^6$	$3.2\cdot10^6$	$3.2\cdot10^4$	
MeOH		$3.7\cdot10^5$	$5.0\cdot10^4$	$1.8\cdot10^4$	$1.0\cdot10^3$	$3.1\cdot10^7$ b)
MeCN		$1.4\cdot10^7$	$6.6\cdot10^5$	$3.0\cdot10^5$ c)	$2.8\cdot10^3$	
DMF		$2.2\cdot10^6$ d)	$9.7\cdot10^5$ d)	$3.9\cdot10^5$	$3.8\cdot10^3$	
NH_3					$7.0\cdot10^4$ e)	

a) From [2]. b) From [19]. c) Average of the two values reported in [2]. d) This work. e) From [20].

MESQUAC MO calculations [18], nevertheless, these two theoretical approaches are unable to predict exchange mechanisms.

When a comparison is possible, the sequence of solvent-exchange rate constants is independent of the nature of the above metal ions:

$$NH_3 > H_2O > DMF > CH_3CN > CH_3OH.$$

The only exception is the MeCN exchange on Mn^{2+}, which is faster than expected. Neither obvious solvent macroscopic properties, like dielectric constant or donor number, nor microscopic properties, like steric hindrance or electric dipole moment, can be used to rationalize this sequence.

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