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N,*N*-Dimethylformamide Exchange on Hexakis(*N*,*N*-dimethylformamide)titanium(III): A Variable-Temperature and -Pressure ^1H and ^{17}O NMR Study[1,2]

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Dimethylformamide (DMF) exchange on $[Ti(DMF)_6]^{3+}$ has been studied as a function of temperature (192–355 K) and pressure (up to 200 MPa, at two temperatures) by proton and oxygen-17 NMR spectroscopy at 4.7 and 9.4 T. The following kinetic parameters were obtained: $k_{ex}^{298} = (6.6 \pm 0.1) \times 10^4$ s^{-1}, $\Delta H^{\ddagger} = 23.6 \pm 0.3$ kJ mol^{-1}, $\Delta S^{\ddagger} = -73.6 \pm 1.1$ J K^{-1} mol^{-1}, $\Delta V^{\ddagger} = -5.7 \pm 0.6$ cm^3 mol^{-1}, and $\Delta\beta^{\ddagger} = -(1.3 \pm 0.6) \times 10^{-2}$ cm^3 mol^{-1} MPa^{-1}. The negative volume of activation suggests an associative interchange, I_a, mechanism for the DMF exchange on titanium(III), and confirms the mechanistic changeover (from I_a to I_d) along the hexasolvated trivalent first-row transition-metal ions previously observed in water, dimethyl sulfoxide, and trimethyl phosphate.

Introduction

Solvent exchange on metal ions is a 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 spectroscopy. Therefore, the volume of activation[3-5] has become an important criterion for determining the mechanisms of these reactions.

For the trivalent high-spin first-row octahedral transition-metal ions, activation volumes indicate that the mechanism for water exchange progressively changes from an associative activation mode for the early elements to a dissociative activation mode for the later ones. It has been shown that a solvent sterically governed mechanistic crossover is taking place for some metal ions. In the case of beryllium(II),[6] a very small tetrahedrally solvated metal ion, water exchange occurs through an A mechanism, and tetramethylurea exchange through a D mechanism, whereas both pathways are observed in the case of *N*,*N*-dimethylformamide (DMF). For manganese(II),[7] an octahedrally solvated metal ion in the middle of the divalent high-spin first-row transition-metal series, the activation volumes are -5.4 cm^3 mol^{-1} in water and $+2.4$ cm^3 mol^{-1} in DMF, again indicating a mechanistic change from an associative to a dissociative activation mode.

Up till now, DMF exchange on the trivalent high-spin first-row octahedral transition-metal ions has been studied under pressure only on the chromium(III),[8] iron(III),[9] and gallium(III)[10] ions. Here too, the activation volumes for DMF exchange on chromium(III) (-6.3 cm^3 mol^{-1}) and iron(III) (-0.9 cm^3 mol^{-1}) compared to the activation volumes for water exchange on these two ions, -9.6 and -5.4 cm^3 mol^{-1}, respectively, suggest that DMF exchange occurs via an activation mode less associative than that of water exchange.

For this reason we became interested in studying the steric incidence of DMF exchange on titanium(III), the earliest trivalent first-row transition-metal ion for which water-exchange data were available for comparison ($\Delta V^{\ddagger}(H_2O) = -12.1$ cm^3 mol^{-1}).[11] The solvent exchange on $Ti(DMF)_6^{3+}$ was performed in neat DMF, by multinuclear NMR spectroscopy, ^1H and ^{17}O, both as a function of temperature and pressure, making use of two magnetic fields (4.7 and 9.4 T).

Experimental Section

Chemicals and Solutions. DMF (Fluka, puriss pa) and deuterated DMF (DMF-d_7) (Ciba-Geigy, >99.5% D) were dried overnight on a mixture of 3- and 4-Å molecular sieves and then distilled on a vacuum line. ^{17}O-enriched DMF was prepared using the method described by Ott,[12] replacing $H_2{}^{18}O$ by $H_2{}^{17}O$. The resulting product was dried and distilled as described above.

$[Ti(DMF)_6](CF_3SO_3)_3$ was prepared by dissolving 1.42 g of anhydrous titanium(III) trifluoromethanesulfonate (triflate) (prepared as described previously)[11] in 5 mL of triethylorthoformate (Fluka, purum). A 5-mL aliquot of DMF was then added, and the resulting oil was precipitated with 50 mL of dry Et_2O. The deep blue crystals were collected by filtration, washed with dry ether (20 mL), and dried in vacuum. Anal. Calcd (found): C, 27.01 (26.91); H, 4.54 (4.50); N, 9.00 (8.96); S, 10.30 (10.13); F, 18.31 (18.04); Ti, 5.13 (5.10); Cl, 0.00 (0.28).

Five $[Ti(DMF)_6]^{3+}$ solutions for ^1H NMR measurements (0.0491, 0.0497, 0.0499, 0.0499, and 0.0526 mol kg^{-1}, containing 1% of tetramethylsilane as chemical shift reference, $I = 0.3$ mol kg^{-1}) and two for ^{17}O NMR measurements (0.0972 and 0.0999 mol kg^{-1}, $I = 0.6$ mol kg^{-1}) were prepared in a glovebox by dissolving weighed quantities of triflate salt in suitable amounts of 25% DMF-d_7 and 75% DMF (^1H NMR analysis), or ^{17}O-enriched DMF (^{17}O NMR analysis).

Samples for ^{17}O NMR variable-temperature measurements were introduced into spherical glass cells that were then flame-sealed and placed into 10-mm NMR tubes.[13] For ^1H NMR variable-temperature experiments, 5-mm tubes were used. Both variable-pressure ^1H and ^{17}O NMR samples were contained in a special cell described previously.[14]

NMR Measurements. Variable-temperature ^1H NMR measurements were performed at two different magnetic fields (4.7 and 9.4 T), with Bruker CXP-200 and AM-400 spectrometers. A total of 16 384 points was recorded, resulting from 30 scans using a frequency window of 3 kHz. Variable-temperature ^{17}O NMR measurements were performed at 54.24 MHz on the Bruker AM-400 spectrometer. A total of 2048 or 4096 points was recorded, resulting from 1000–5000 scans using a frequency window of 25–100 kHz. DMF-d_7 was used as an internal field lock for ^1H NMR spectroscopy, while no lock was necessary for ^{17}O NMR spectroscopy, due to high stability of the field produced by cryomagnets. The temperature was controlled within ±0.2 K by gas circulation through the probe and was measured by substitution of the NMR tube for a 100-Ω Pt resistor.[15] Both variable-pressure ^1H and ^{17}O NMR experiments were carried out on the AM-400 spectrometer with a previously described homebuilt probehead,[14] using the variable-temperature acquisition parameters.

Data Treatment and Results

Variable Temperature. In the ^1H and ^{17}O NMR spectra of titanium(III) solutions in neat DMF, the bound DMF signal is not visible, even at very low temperature, because of its broadness:

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this was also the case in aqueous solutions of titanium(III).[11] The Swift and Connick approach[16] was used to determine the kinetic parameters for reaction 1. Immediately before or after each

$$[Ti(DMF)_6]^{3+} + 6{*}DMF \overset{k_{ex}}{\rightleftharpoons} [Ti({*}DMF)_6]^{3+} + 6DMF \quad (1)$$

NMR measurement of a titanium solution, a reference sample containing pure DMF was measured at the same temperature. The full width at half-height, $\Delta\nu_{1/2}$ ($1/T_2 = \pi\Delta\nu_{1/2}$), and the chemical shift, ν ($\omega = 2\pi\nu$), of the free DMF NMR signal of both spectra were then used for the determination of the reduced transverse relaxation rate, $1/T_{2r}$, and the reduced chemical shift, $\Delta\omega_r$, via eqs 2 and 3. P_m is the mole fraction of coordinated solvent

$$\frac{1}{T_{2r}} = \frac{1}{P_m}\left[\frac{1}{T_2} - \frac{1}{T_{2A}}\right] \quad (2)$$

$$\Delta\omega_r = \frac{\omega - \omega_A}{P_m} \quad (3)$$

molecules, assuming a coordination number of 6, $1/T_{2A}$ and ω_A are the ^{17}O or ^{1}H (formyl proton in this work) transverse relaxation rate and resonance frequency of DMF in the reference sample, and $1/T_2$ and ω are the corresponding values for the paramagnetic sample. The reduced relaxation rate and chemical shift are dependent on various parameters, as shown below.[17] The relaxation rate of bound solvent in the absence of exchange, $1/T_{2m}$ in eqs 4 and 5, was set equal to zero in the data treatment since our study

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

$$\Delta\omega_r = \frac{\Delta\omega_m}{(\tau_m/T_{2m} + 1)^2 + \tau_m^2\Delta\omega_m^2} + \Delta\omega_{os} \quad (5)$$

does not reach the high temperatures at which it becomes important. Direct measurement of $1/T_{2m}$ via the observation of the bound DMF resonance signals was not possible, as already mentioned before. The residence time, τ_m, is related to the pseudo-first-order rate constant for the exchange of a particular solvent molecule, k_{ex}, whose temperature dependence is assumed to obey the Eyring equation (eq 6) where ΔS^* and ΔH^* are the

$$k_{ex} = 1/\tau_m = k_B T/h \exp(\Delta S^*/R - \Delta H^*/RT) \quad (6)$$

activation entropy and the activation enthalpy, respectively. The outer-sphere contribution, $1/T_{2os}$, may be described by a simple Arrhenius equation (eq 7), and the reference temperature is taken

$$1/T_{2os} = (1/T_{2os})^{200} \exp[(E_{os}/R)(1/T - 1/200.0)] \quad (7)$$

at 200 K, because this parameter is significant only at low temperatures in this study. The temperature dependence of $\Delta\omega_m$, the chemical shift between free and coordinated solvent in the absence of exchange, has been found[17,18] to be well described as a power series of $1/T$. In the present case however, only the first term will be considered (eq 8), where B_1 is a parameter proportional

$$\Delta\omega_m = B_1/T \quad (8)$$

to the Larmor frequency of the nucleus, and hence to the magnetic field of the spectrometer. Finally, the outer-sphere chemical shift, $\Delta\omega_{os}$, was also described as a function of $1/T$, where C is the outer-sphere parameter proportional to the Larmor frequency and $\Delta\omega_{os,0}$ is the value of $\Delta\omega_{os}$ at $1/T = 0$.

$$\Delta\omega_{os} = \Delta\omega_{os,0} + C/T \quad (9)$$

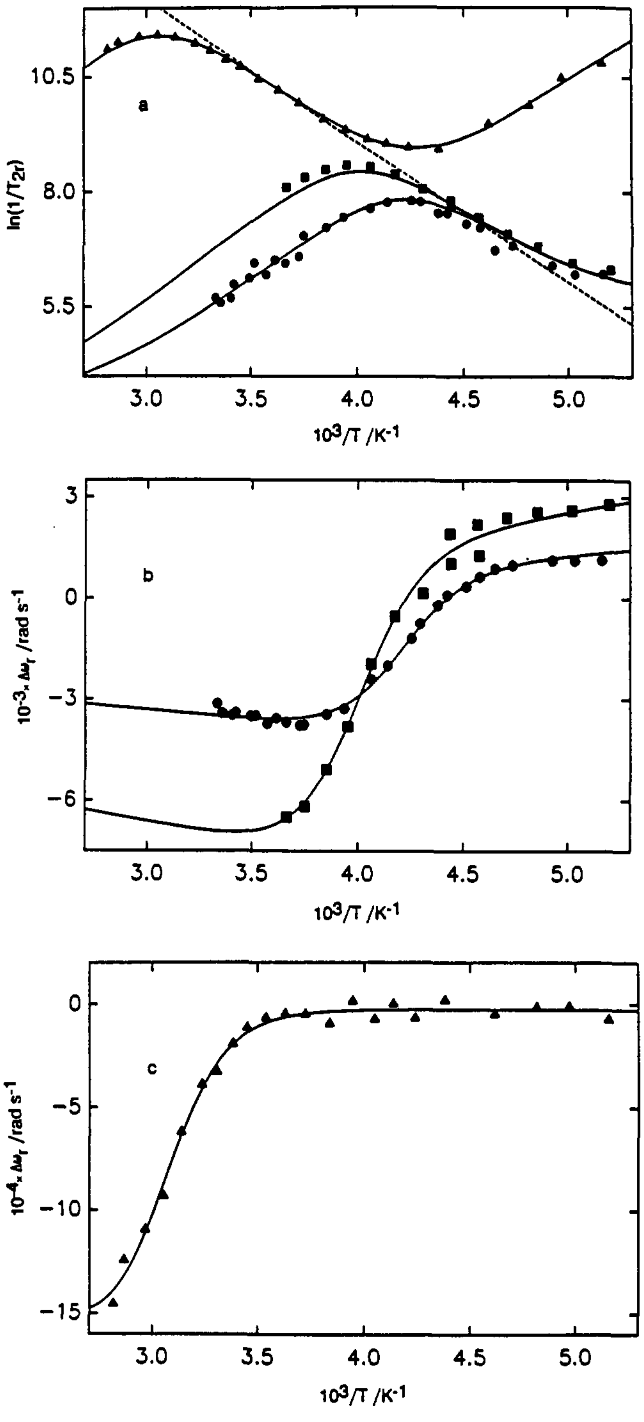

Figure 1. Variable-temperature ^{17}O NMR and ^{1}H NMR data for [Ti(DMF)$_6$](CF$_3$SO$_3$)$_3$ in DMF, showing ln ($1/T_{2r}$) and $\Delta\omega_r$ vs inverse temperature. The curves are the result of a simultaneous fit of all the data ([Ti^{3+}] = 0.05–0.1 mol kg^{-1}): (●) ^{1}H NMR at 4.7 T; (■) ^{1}H NMR at 9.4 T; (▲) ^{17}O NMR at 9.4 T. The dashed fine line of Figure 1a shows the contribution of $1/\tau_m$ to $1/T_{2r}$.

The ^{1}H NMR (at 4.7 and 9.4 T) and ^{17}O NMR (at 9.4 T) experimental $1/T_{2r}$ and $\Delta\omega_r$ sets of data were first treated independently by a nonlinear least-squares computer program using eqs 4–9 with seven (six for ^{17}O NMR: $C = 0$) adjustable parameters: ΔS^* (or k_{ex}^{298}), ΔH^*, $(1/T_{2os})^{200}$, E_{os}, B_1, C, and $\Delta\omega_{os,0}$. The kinetic parameters obtained from the two data analyses are given in Table I, and they are in excellent agreement. Thus, the three experimental $1/T_{2r}$ and $\Delta\omega_r$ sets of data were treated simultaneously, again using eqs 4–9. The new adjusted parameters are also reported in Table I, and the fitted curves are plotted in Figure 1 together with the experimental data. In this study, the kinetic and chemical shift parameters are particularly well determined because they were characterized in a large temperature

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Table I. Kinetic and NMR Parameters Derived from Relaxation and Chemical Shift Data as a Function of Temperature for $[Ti(DMF)_6](CF_3SO_3)_3$ Solutions in DMF

	^{1}H NMR	^{17}O NMR	simultaneous fit
$10^{-4}k_{ex}^{298}/s^{-1}$	6.8 ± 0.5	6.6 ± 0.3	6.6 ± 0.1
$\Delta H^\ddagger$/kJ mol^{-1}	23.9 ± 0.8	23.6 ± 1.2	23.6 ± 0.3
$\Delta S^\ddagger$/J K^{-1} mol^{-1}	−72.2 ± 3.4	−73.6 ± 3.6	−73.6 ± 1.1
E_{os}/kJ mol^{-1}	5.9 ± 2.3	24.1 ± 4.3	6.4 ± 2.9, 24.1 ± 2.9
$(1/T_{2os})^{200}/s^{-1}$	216 ± 55	33936 ± 5709	204 ± 55, 33933 ± 4365
$10^{-6}B_1$/rad K s$^{-1\,a}$	−2.30 ± 0.06	−59 ± 2	−2.30 ± 0.07, −59 ± 1
$10^{-6}C$/rad K s$^{-1\,a}$	1.1 ± 0.2	0^b	1.1 ± 0.2, 0^b
$\Delta\omega_{os,0}$/rad s$^{-1\,a}$	−3058 ± 837	−2783 ± 826	−3124 ± 946, −2773 ± 600

^{a}At 9.4 T. ^{b}Fixed value.

domain (163 K) due to the use of both ^{1}H and ^{17}O NMR spectroscopy.

Variable-Pressure ^{1}H NMR Spectroscopy. The pressure dependence of the rate constant of a reaction is derived from transition-state theory, and it is usually assumed to be a quadratic function of P

$$\ln(k_{ex}) = \ln(k_{ex})_0 - P\Delta V_0^\ddagger/RT + P^2\Delta\beta^\ddagger/2RT \quad (10)$$

where $(k_{ex})_0$ is the rate constant at zero pressure, $\Delta V_0^\ddagger$ is the activation volume of the reaction at zero pressure, and $\Delta\beta^\ddagger$ is the compressibility coefficient of activation. We must also take into account the pressure dependences of the other parameters appearing in eqs 2–5.

First, to calculate $1/T_{2r}$ and $\Delta\omega_r$ at every pressure, the pressure dependences of $1/T_{2A}$ and ω_A are to be considered. However, $1/T_{2A}$ constitutes less than 7% of $1/T_2$ at ambient pressure, and therefore we consider it, together with ω_A, to be pressure independent.

Second, at the temperature chosen for the variable-pressure measurements (T = 242.4 K), $1/T_{2os}$ contributes only about 2% to $1/T_{2r}$ and can be considered to be pressure independent. By contrast, $\Delta\omega_m$ cannot be ignored, but its pressure dependence is difficult to predict theoretically. Therefore, the data were first analyzed using the full eqs 4 and 5 as a function of pressure, keeping $\Delta\omega_m$ at its ambient pressure value and allowing τ_m ($=1/k_{ex}$) to vary according to eq 10, and the results are shown in Table II (fit A). The fitted $1/T_{2r}$ and $\Delta\omega_r$ curves are plotted in Figure 2, together with the experimental data. We then allowed $\Delta\omega_m$ to vary with pressure according to eq 11,[18] where $(\Delta\omega_m)_0$

$$\Delta\omega_m = (\Delta\omega_m)_0(1 + B_\omega P) \quad (11)$$

is the value at zero pressure and B_ω a constant. The data were treated using eqs 4, 5, 10, and 11, and the results are shown in Table II (fit B). It is evident, from Table II, that B_ω is not statistically significant and the two data analyses are identical. The even smaller contribution of $\Delta\omega_{os}$ to the observed shift $\Delta\omega_r$ was therefore also assumed to be pressure independent.

Variable-Pressure ^{17}O NMR Spectroscopy. We performed our variable-pressure ^{17}O NMR experiment at 270.3 K, in the slow-exchange region where $1/T_{2r}$ is practically identical to $1/\tau_m$. We used the variable-pressure ^{17}O NMR $1/T_{2A}$ measurements of pure DMF performed by Furrer[19] to calculate $1/T_{2r}$ (cf. eq 2) at each pressure. Keeping $1/T_{2os}$ (it contributes less than 4% to $1/T_{2r}$) and $\Delta\omega_m$ at their ambient pressure values, we fitted $\ln(1/T_{2r})$ values to the full eq 4 with the pressure dependence of τ_m ($=1/k_{ex}$) given by eq 10 and with $(k_{ex})_0$, $\Delta V_0^\ddagger$, and $\Delta\beta^\ddagger$ as fitted parameters. The results are shown in Figure 3 and Table II.

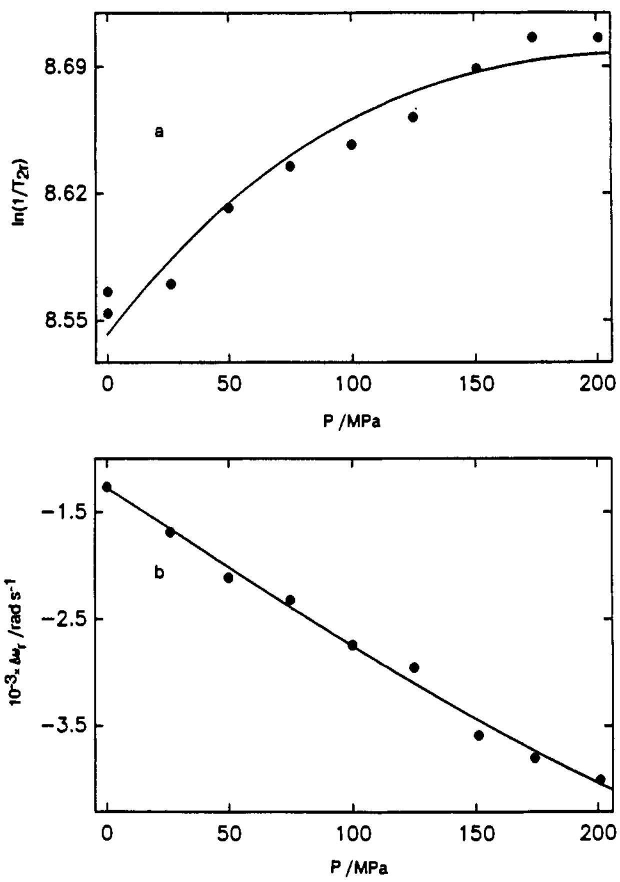

Figure 2. Variable-pressure ^{1}H NMR data for $[Ti(DMF)_6](CF_3SO_3)_3$ in DMF, showing $\ln(1/T_{2r})$ and $\Delta\omega_r$ vs pressure (0.05 mol kg^{-1} of Ti^{3+}) at 242.4 K and 9.4 T.

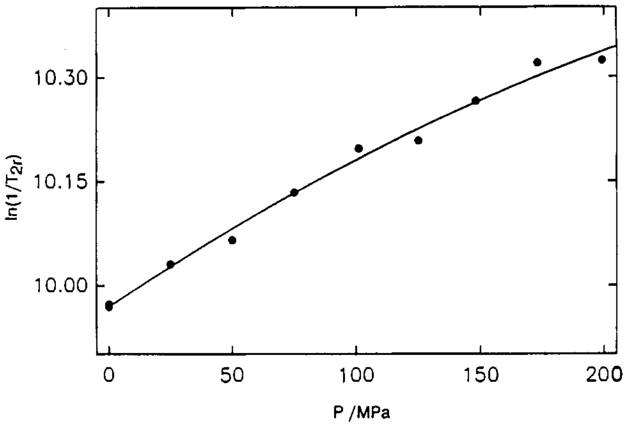

Figure 3. Variable-pressure ^{17}O NMR data for $[Ti(DMF)_6](CF_3SO_3)_3$ in DMF, showing $\ln(1/T_{2r})$ vs pressure (0.1 mol kg^{-1} of Ti^{3+}) at 270.3 K and 9.4 T.

The activation volume obtained from the ^{1}H NMR data (−6.8 cm^3 mol^{-1}) is slightly more negative than that determined by ^{17}O NMR analysis (−5.7 cm^3 mol^{-1}) (Table II). This difference is small, if we consider the standard deviations and the assumptions used in treating data for two different NMR nuclei. It is generally accepted that the determination of $\Delta V^\ddagger$ is subject to an experimental uncertainty of 10% or ±1 cm^3 mol^{-1}, whichever is the greatest.[13]

In the Discussion the ^{17}O NMR value will be quoted for two reasons. First, variable-pressure ^{17}O NMR measurements were performed at a temperature where the main contribution to $1/T_{2r}$ is k_{ex} (in Figure 1a, the $1/T_{2r}$ curve and the k_{ex} line are superposed at 270.3 K). Second, the temperature of the ^{17}O NMR experiment

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Table II. Kinetic and NMR Parameters Derived from Relaxation and Chemical Shift Data as a Function of Pressure for $[Ti(DMF)_6](CF_3SO_3)_3$ Solutions in DMF

	^1H NMR[a] (fit A)	^1H NMR[a] (fit B)	^{17}O NMR[b]
$\Delta V_0^\ddagger/cm^3\ mol^{-1}$	-6.8 ± 0.4	-7.0 ± 1.2	-5.7 ± 0.6
$\Delta\beta^\ddagger/cm^3\ mol^{-1}\ MPa^{-1}$	$(-1.5 \pm 0.4) \times 10^{-2}$	$(-1.6 \pm 0.8) \times 10^{-2}$	$(-1.3 \pm 0.6) \times 10^{-2}$
$(k_{ex})_0/s^{-1}$	6598 ± 184	6563 ± 346	20780 ± 205
B_ω/MPa^{-1}	0^c	$(1.4 \pm 12.6) \times 10^{-4}$	

[a] At 242.4 K. [b] At 270.3 K. [c] Fixed value.

Table III. Rate Constants and Activation Parameters for Solvent Exchange on Trivalent First-Row Octahedral Transition-Metal Ions[a]

$[M(solvent)_6]^{3+}$	r_i/pm	electronic configuration	k_{ex}^{298}/s^{-1}	$\Delta H^\ddagger/kJ\ mol^{-1}$	$\Delta S^\ddagger/J\ K^{-1}\ mol^{-1}$	$\Delta V^\ddagger/cm^3\ mol^{-1}$ (T/K)	ref
$[Sc(TMPA)_6]^{3+}$	75	t_{2g}^0	1207	37.4	−60.5	−20.1 (238–350)	20
$[Ti(H_2O)_6]^{3+}$	67	t_{2g}^1	1.8×10^5	43.4	+1.2	−12.1 (273–298)	11
$[Ti(DMF)_6]^{3+}$			6.6×10^4	23.6	−73.6	−5.7 (270)	*b*
$[V(H_2O)_6]^{3+}$	64	t_{2g}^2	500	49.4	−28.0	−8.9 (336–338)	13
$[V(DMSO)_6]^{3+}$			13.1	38.5	−94.5	−10.1 (311–349)	21
$[Cr(H_2O)_6]^{3+}$	61	t_{2g}^3	2.4×10^{-6}	108.6	+11.6	−9.6 (318)	22
$[Cr(DMSO)_6]^{3+}$			3.1×10^{-8}	96.7	−64.5	−11.3 (348)	23
$[Cr(DMF)_6]^{3+}$			3.3×10^{-7}	97.1	−43.5	−6.3 (338)	8
$[Fe(H_2O)_6]^{3+}$	64	$t_{2g}^3e_g^2$	160	64.0	+12.1	−5.4 (383)	24
$[Fe(DMSO)_6]^{3+}$			9.3	62.5	−16.7	−3.1 (308–378)	9
$[Fe(DMF)_6]^{3+}$			61	42.3	−69.0	−0.9 (255–399)	9
$[Ga(H_2O)_6]^{3+}$	62	$t_{2g}^6e_g^4$	400	67.1	+30.1	+5.0 (295–343)	25
$[Ga(DMSO)_6]^{3+\,c}$			1.87	72.5	+3.5	+13.1 (334)	10
$[Ga(DMF)_6]^{3+\,c}$			1.72	85.1	+45.1	+7.9 (314)	10
$[Ga(TMPA)_6]^{3+\,c}$			6.4	76.5	+27.0	+20.7 (319)	26

[a] By NMR analysis except for Cr^{3+} by isotopic labeling. [b] This work. [c] In CD_3NO_2 as diluent.

(270.3 K) is closer to ambient temperature than that of the ^1H NMR experiment (242.4 K) and is therefore better for making comparisons.

Discussion

The available kinetic parameters for solvent exchange on trivalent hexasolvated first-row transition-metal ions in water and in nonaqueous solvents are reported in Table III. The results for DMF exchange on titanium(III) confirm the gradual change of mechanism across the series observed in water, dimethyl sulfoxide, and trimethyl phosphate. For water exchange on $[Ti(H_2O)_6]^{3+}$, an A or nearly A mechanism was proposed on the basis of the strongly negative volume of activation (-12.1 cm^3 mol^{-1}).[11] By contrast, the activation volume for DMF exchange on $[Ti(DMF)_6]^{3+}$ is less negative (-5.7 cm^3 mol^{-1}), but it is consistent, together with the very negative value of $\Delta S^\ddagger$, with an associative activation mode. The results obtained in this study therefore suggest an associative interchange, I_a, mechanism for the DMF exchange on titanium(III). In water, complex formation studies on Ti^{3+} show a definite ligand dependence of the formation rate constants.[11] Unfortunately, such studies have not been performed in DMF: they would be very useful to characterize the complex formation mechanism, most probably I_a, of Ti^{3+} in this solvent.

Table III also allows us to compare the $\Delta S^\ddagger$ and k_{ex}^{298} values. Even though $\Delta S^\ddagger$ is not a very reliable parameter in this kind of study due to its inaccuracy,[17] it is interesting to note that the trend of the values is not inconsistent with that of the $\Delta V^\ddagger$ values. Note that the activation entropy values of nonaqueous solvent exchange are generally much more negative than those of water exchange.

When a comparison is possible in Table III, the sequence of solvent exchange rate constants is the same for almost all the metal ions: $H_2O > TMPA > DMF > DMSO$. Water exchange is 62 (Ga^{3+}) times faster than TMPA, between 2.6 (Fe^{3+}) and 232 (Ga^{3+}) times faster than DMF, and between 17 (Fe^{3+}) and 214 (Ga^{3+}) times faster than DMSO.

As discussed above, the sequence of $\Delta V^\ddagger$ for water and nonaqueous solvent exchange on the first-row trivalent transition-metal ions shows a definite trend in mechanism, from I_a (A for water exchange on Ti^{3+}) to I_d (D for nonaqueous solvent exchange on Ga^{3+}). However, it is worthwhile considering further DMF exchange on these ions. The $\Delta V^\ddagger$ values obtained in this solvent are always less negative than those obtained in water. The difference is largest in the case of Fe^{3+} and Ti^{3+} and suggests that DMF exchange occurs via a less associative activation mode than water exchange.[27] This mechanistic singularity can be explained by steric effects: DMF is bulkier than H_2O, and thus the associative character of the reaction is less favored. The plausibility of this explanation is reinforced by the observations made for solvent exchange on the small tetrahedrally coordinated Be^{2+} (water exchanges via an A mechanism whereas DMF exchanges via two parallel pathways, D and I_a)[6] and on Mn^{2+} (H_2O, MeOH, and MeCN exchange via an I_a mechanism and DMF via an I_d mechanism).[7] Moreover, the more pronounced dissociative character of reactions in DMF, when compared to water, has also been outlined for solvent exchange on trivalent lanthanide ions[30] and for complex formation reactions on nickel(II)[31] and iron(III).[32]

To conclude, this DMF solvent exchange study on titanium(III) not only confirms the mechanistic changeover (from I_a to I_d) along the hexasolvated trivalent first-row transition-metal cations previously observed in water and in dimethyl sulfoxide but also confirms that solvent exchange in DMF proceeds through a less associative activation mode than in water.

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Supplementary Material Available: Tables of ^1H and ^{17}O NMR relaxation and chemical shift data as a function of temperature (Tables SI and SII) and pressures (Tables SIII and SIV) (5 pages). Ordering information is given on any current masthead page.

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(27) It is not easy to make a comparison between solvents unless one can estimate what the limiting $\Delta V^\ddagger$ values for A and D processes should be for each solvent. These values can readily be estimated in water from a semiempirical model developed by Swaddle:[28,29] +13.5 and −13.5 cm^3 mol^{-1} for D and A exchange processes for the trivalent transition-metal ions. It seems reasonable to assume that these limiting values are greater for a larger solvent molecule like DMF than for the small H_2O solvent molecule. This has been shown clearly by experimental results for the $\Delta V^\ddagger$ values for trimethyl phosphate exchange around the following diamagnetic trivalent metal ions: +22.5 cm^3 mol^{-1} for Al^{3+} (D),[26] +20.7 cm^3 mol^{-1} for Ga^{3+} (D),[26] and −20.1 cm^3 mol^{-1} for Sc^{3+} (A or I_a).[20]

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