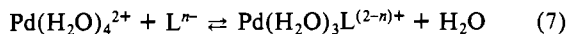
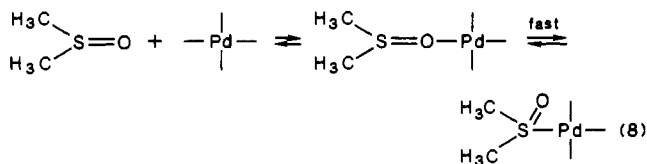


a five-coordinate intermediate.³³

In the case of palladium, rate constants for reaction 7 are listed in Table II for a series of entering ligands L. The large spread



in the k_1 values speaks in favor of an associative mode of activation. The replacement of a water molecule by Me_2SO is much slower than the rate of substitution of water for halides, which is contrary to the expectation for a sulfur-bonded ligand. A mechanism similar to that proposed for the formation of Me_2SO complexes of platinum(II)³³ might be operating (eq 8), with the rate-de-



termining formation of an oxygen-bonded form, followed by a rapid intramolecular isomerization to the thermodynamically more stable sulfur-bonded complex. The experiments so far give no conclusive support of such a mechanism, however. The rate constant for substitution with Me_2SO is ca. 12 times smaller than the water-exchange rate constant, without taking possible statistical factors into account. From the above discussion, it follows that Me_2SO is an even poorer nucleophile in the case of palladium than in the case of platinum.

The activation entropies for both forward and reverse processes, listed in Table I, have large negative values, in accord with the attribution of the associative mode of activation anticipated. The two corresponding volumes of activation are negative also. However, the large value of ΔV^\ddagger_1 cannot be immediately interpreted as a support for a strong associative character of reaction 1. For unsymmetrical reactions, the partial molar volumes of the

reactants and products can be very different. A closer inspection of the volume profile of the overall reaction is necessary before definite mechanistic conclusions can be drawn. In the present case, the volume profile of Figure 6 shows that the volume of the transition state is much smaller than the volume which would result from a smooth change along the reaction coordinate (Figure 6, dashed line), suggesting a strongly associative reaction. This is even more so, since formation of a fifth bond in a trigonal-bipyramidal transition state is expected to be accompanied by some axial bond lengthening, which will produce a positive contribution to the volume of activation. If the reaction takes place via an intermediate O-bonded complex, however, the interpretation of the volume changes will be even more complicated.

In conclusion, although an associative mode of activation can undoubtedly be assigned to the forward as well as to the reverse process of reaction 1, an evaluation of their degree of associative character must be postponed until more volumes of activation are collected for similar simple reactions of square-planar complexes.

Acknowledgment. I. Lind and Dr. P. J. Nichols are gratefully thanked for experimental assistance. We also warmly thank Dr. L. Helm for the NMR part of this study. Financial support for the *Swedish Natural Science Research Council* and the *Swiss National Science Foundation* (Grant No. 2.854-0.85) is gratefully acknowledged.

Registry No. $\text{Pd}(\text{H}_2\text{O})_4^{2+}$, 22573-07-5; $\text{Pd}(\text{Me}_2\text{SO})(\text{H}_2\text{O})_3^{2+}$, 107913-44-0; $\text{Pd}(\text{Me}_2\text{SO})_2(\text{H}_2\text{O})_2^{2+}$, 107913-45-1; Me_2SO , 67-68-5.

Supplementary Material Available: Spectrophotometric equilibrium measurements at 298 K and ambient pressure (Table SI) and at variable pressure (Table SII), NMR measurements at variable temperature (Table SIII), observed rate constants at ambient pressure for excess palladium at 298 K (Table SIV), for excess Me_2SO at various temperatures (Table SV), and for excess Me_2SO at various pressures (Table SVI) (6 pages). Ordering information is given on any current masthead page.

Contribution from the Institut de Chimie Minérale et Analytique, Université de Lausanne, CH-1005 Lausanne, Switzerland

Variable-Temperature, -Pressure, and -Frequency Oxygen-17 NMR Study of Water Exchange on Hexaaquatitanium(III): A Limiting Associative Mechanism?^{1,2}

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Water exchange on hexaaquatitanium(III) has been studied as a function of temperature (249–369 K) and pressure (up to 235 MPa, at several temperatures) by oxygen-17 FT-NMR spectroscopy at 1.4, 4.7, and 8.4 T. The samples, in up to 20% ¹⁷O-enriched H₂O, contained Ti³⁺ (~0.3 m), H⁺ (2.0–3.0 m), and trifluoromethanesulfonate as noncoordinating counterion. The following kinetic parameters were obtained: $k_{\text{ex}}^{298} = (1.81 \pm 0.03) \times 10^5 \text{ s}^{-1}$, $\Delta H^\ddagger = 43.4 \pm 0.7 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = +1.2 \pm 2.2 \text{ J K}^{-1} \text{ mol}^{-1}$, $\Delta V_0^\ddagger = -12.1 \pm 0.4 \text{ cm}^3 \text{ mol}^{-1}$, and $\Delta\beta^\ddagger = -(1.9 \pm 0.4) \times 10^{-2} \text{ cm}^3 \text{ mol}^{-1} \text{ MPa}^{-1}$. This volume of activation is the most negative value measured so far for a water-exchange reaction on a hexaaqua ion and is close to the value of $-13.5 \text{ cm}^3 \text{ mol}^{-1}$ suggested by Swaddle⁴ for a limiting associative A mechanism. These results are discussed together with available data for complex formation reactions involving hexaaquatitanium(III).

Introduction

The study of the effect of pressure on the rate of a chemical reaction has become an important aid in mechanistic elucidation in recent years.^{4,5} It has been shown to be particularly useful for a better understanding of the dynamics of exchange at solvated metal ions, the ubiquitous precursors of metal complexes in so-

lution. For example, the high-pressure oxygen-17 NMR study of water exchange on divalent metal ions across the first-row transition-metal series allowed us to demonstrate the unpredicted changeover from associative interchange I_a to dissociative interchange I_d mechanisms along the series.^{6,7} This changeover has been rationalized in terms of steric effects due to changes in ionic radius and of filling of d orbitals: increasing e_g antibonding electron population favors dissociation, and increasing t_{2g} "between-bond" electron population disfavors association.

- (1) High Pressure NMR Kinetics. 29. For part 28, see ref 3.
- (2) This work was presented at the XXIIIrd International Conference on Coordination Chemistry, Boulder, CO, July 1984.
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For trivalent first-row transition-metal hexaqua ions, high-pressure data have also been published recently. For water exchange on V^{3+} , Cr^{3+} , and Fe^{3+} , the volumes of activation are all negative and I_a mechanisms were assigned in the three cases.⁸⁻¹⁰ Ti^{3+} is a relatively large ion with only one electron in the t_{2g} orbitals, which would make it an ideal candidate for a limiting associative mechanism A. In this work we report a full variable-temperature, -pressure, and -frequency oxygen-17 NMR study of water exchange on Ti^{3+} . The experimental difficulties associated with the variable-temperature NMR work are such that the early results of Chmelnick and Fiat¹¹ obtained at low magnetic field can only be taken as rough estimates. To overcome some of these limitations, we have used higher magnetic fields, replaced chloride by the noncoordinating trifluoromethanesulfonate as counterion, and extended the study to variable-pressure experiments.

Experimental Section

Chemicals and Solutions. Titanium trifluoromethanesulfonate, $Ti(CF_3SO_3)_3$, was prepared in an oxygen-free glovebox by mixing 3.04 g of $TiCl_3$ (Alfa, purum) with 9.56 g of freshly degassed trifluoromethanesulfonic acid, CF_3SO_3H (Fluka, purum; hereafter called triflic acid). Degassed water (5.4 g) was vacuum-distilled onto that mixture and then, after homogenization of the solution, distilled off together with the hydrochloric acid formed by the reaction. A second portion of 5.6 g of degassed water was again distilled onto and off the mixture, to eliminate the residual HCl. Finally, the grayish blue salt was dried by heating to 359 K under vacuum (3×10^{-4} mmHg). Anal. Found (calcd): Ti, 9.85 (9.67); F, 34.28 (34.54); S, 19.20 (19.43); Cl, 0.26 (0.00). This corresponds to the formula $Ti(CF_3SO_3)_{2.96}Cl_{0.04}$.

Three solutions for NMR measurements were prepared in the glovebox by dissolving weighed quantities of titanium triflate in suitable amounts of freshly degassed triflic acid aqueous solutions, which were set to the desired acid concentrations by adding together the appropriate weights of pure triflic acid and ^{17}O -enriched water (normalized in 1H , Yeda). The solutions had the following compositions: 0.291 *m* $Ti(CF_3SO_3)_3$, 1.99 *m* CF_3SO_3H , 20% ^{17}O ; 0.303 *m* $Ti(CF_3SO_3)_3$, 2.01 *m* CF_3SO_3H , 14% ^{17}O ; 0.298 *m* $Ti(CF_3SO_3)_3$, 3.03 *m* CF_3SO_3H , 20% ^{17}O .

Samples for variable-temperature measurements were introduced into spherical glass cells that were then flame-sealed and placed into 10 mm o.d. NMR tubes,⁸ and the variable-pressure sample was contained in a thin glass tube fitted with a PTFE separator, as previously described.¹²

NMR Measurements. The variable-temperature work was performed at three different magnetic fields, with Bruker WP-60 (1.4 T, electromagnet), CXP-200 (4.7 T, cryomagnet), and WH-360 (8.4 T, cryomagnet) spectrometers. A ^{19}F external lock was used on the first one, while no lock was necessary with the other two for ^{17}O NMR, due to the high stability of the field produced by cryomagnets. The field homogeneity was checked by 1H NMR, by using the proton signal of an acidified water sample. The sample tubes were thermostated with a flux of nitrogen (below 310 K) or air, regulated by a Bruker B-VT 1000 unit. The temperature was measured with a 100- Ω Pt resistor, by using a previously described substitution technique.¹³

The variable-pressure work was performed on the CXP-200 spectrometer with a home-built high-pressure probe.¹² The pressure, generated by a Nova pneumatic pump, was measured with a Heise Bourdon gauge (0-700 MPa, ± 0.1 MPa). Temperature control was provided by a flux of ethanol, using a MGW-Lauda SK80 cryostat. A 100- Ω Pt resistor placed in the pressure bomb allowed the determination of the temperature, by use of a standard $T = f(\Omega, P)$ conversion table.¹⁴ At each temperature chosen for variable-pressure measurements, the experiments were run from ambient pressure to ca. 225 MPa, and then back to ambient pressure. No hysteresis was observed. Throughout the work, the spectra were computer-fitted to a Lorentzian function.

Data Treatment and Results

Variable Temperature. Immediately before or after each measurement of a titanium solution, a reference sample having identical triflic acid concentration but free of paramagnetic cation

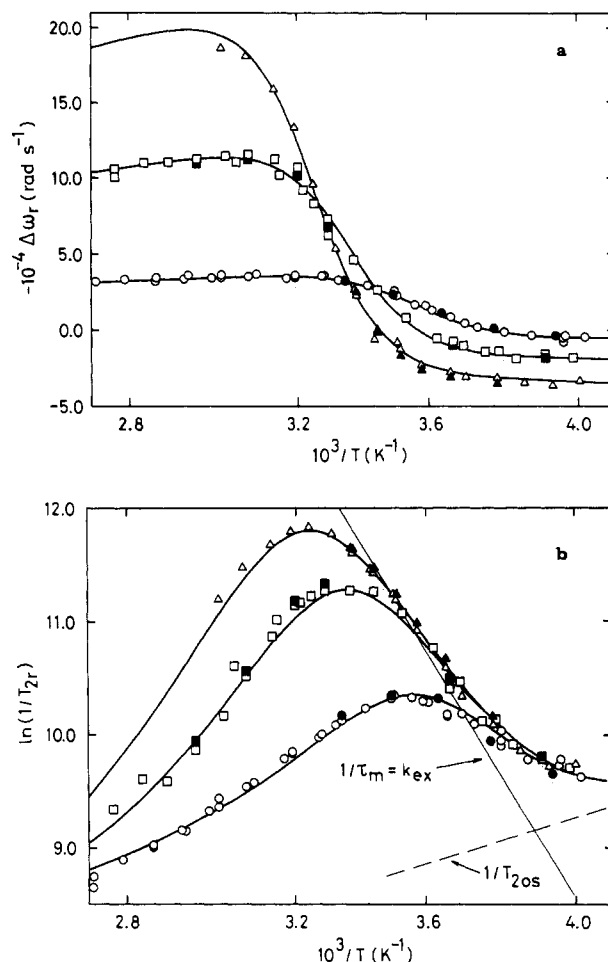


Figure 1. Variable temperature ^{17}O NMR data for $Ti(CF_3SO_3)_3$ in water, showing $\Delta\omega_r$ and $\ln(1/T_{2r})$ vs. inverse temperature. The curves are the result of a simultaneous fit of all the data ($[Ti^{3+}] = 0.30$ *m*; $[H^+] = 2.0$ *m* (open symbols) and 3.0 *m* (filled symbols): \circ and \bullet at 1.4 T; \square and \blacksquare at 4.67 T; \triangle and \blacktriangle at 8.4 T. The solid and dashed fine lines of Figure 1b show the contributions of $1/\tau_m$ and $1/T_{2os}$, respectively, to $1/T_{2r}$.

was measured at the same temperature. The fitted parameters 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 the following equations:

$$\frac{1}{T_{2r}} = \frac{1}{P_m} \left(\frac{1}{T_2} - \frac{1}{T_{2A}^0} \right) \quad (1)$$

$$\Delta\omega_r = \frac{\omega - \omega_A^0}{P_m} \quad (2)$$

P_m is the molar fraction of bound solvent molecules, assuming a coordination number of 6,¹⁵ $1/T_{2A}^0$ and ω_A^0 are the ^{17}O transverse relaxation rate and resonance frequency of water in the reference sample, and $1/T_2$ and ω are the corresponding values from the paramagnetic sample. Figure 1 shows the $\Delta\omega_r$ and $\ln(1/T_{2r})$ data as a function of reciprocal temperature. These data were analyzed by means of the slightly modified Swift and Connick equations:¹²

$$\frac{1}{T_{2r}} = \frac{1}{\tau_m} \left[\frac{T_{2m}^{-2} + (T_{2m}\tau_m)^{-1} + \Delta\omega_m^2}{(T_{2m}^{-1} + \tau_m^{-1})^2 + \Delta\omega_m^2} \right] + \frac{1}{T_{2os}} \quad (3)$$

$$\Delta\omega_r = \frac{\Delta\omega_m}{(\tau_m/T_{2m} + 1)^2 + \tau_m^2 \Delta\omega_m^2} + \Delta\omega_{os} \quad (4)$$

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Table I. Kinetic and NMR Parameters Derived from Relaxation and Chemical Shift Data as a Function of Temperature^a

$10^{-3}k^{298}$, s ⁻¹	1.81 ± 0.03	E_m , kJ mol ⁻¹	11.65 ± 3.26
ΔH^* , kJ mol ⁻¹	43.38 ± 0.67	A_{os} , s ⁻¹	181 ± 273
ΔS^* , J K ⁻¹ mol ⁻¹	+1.19 ± 2.23	E_{os} , kJ mol ⁻¹	8.45 ± 3.21
A/h , MHz	-4.19 ± 0.03	10 ² C	-4.49 ± 0.11
A_m , s ⁻¹	85 ± 118		

^a Reported errors are ±1σ.

The residence time τ_m is related to the pseudo-first-order reaction rate constant for solvent exchange, k , and its temperature dependence may be obtained from transition-state theory:

$$k = \frac{1}{\tau_m} = \frac{k_B T}{h} \exp\left(-\frac{\Delta H^*}{RT} + \frac{\Delta S^*}{R}\right) \quad (5)$$

ΔH^* and ΔS^* are the activation enthalpy and the activation entropy, respectively. The relaxation rate of the bound solvent ¹⁷O nucleus in absence of exchange, $1/T_{2m}$, is the sum of quadrupolar, scalar, and dipolar relaxation rates, but for the present purpose, it may be described by a simple Arrhenius equation:¹⁶

$$1/T_{2m} = A_m \exp(E_m/RT) \quad (6)$$

Similarly for the outer-sphere contribution:

$$1/T_{2os} = A_{os} \exp(E_{os}/RT) \quad (7)$$

In some recent solvent-exchange studies,^{12,17} the temperature dependence of $\Delta\omega_m$, the chemical shift between bound and free solvent in absence of exchange, was found to be well described by a power series of $1/T$. In the present case however, no direct measurement of $\Delta\omega_m$ was possible, and it appeared wiser to consider only a simple Curie behavior, according to Bloembergen's equation:¹⁸

$$\Delta\omega_m = -\frac{\omega_l[S(S+1)]\gamma_e}{3\gamma_l} \frac{A}{k_B T} \quad (8)$$

where ω_l is the Larmor frequency of the nucleus, S is the electron spin quantum number, γ_e and γ_l are the magnetogyric ratios of the electron and the nucleus, and A is the scalar coupling constant.

Finally, the outer-sphere chemical shift term was assumed to be related to $\Delta\omega_m$ by¹²

$$\Delta\omega_{os} = C \Delta\omega_m \quad (9)$$

The experimental $1/T_{2r}$ and $\Delta\omega_r$ data at three different magnetic fields were simultaneously treated by a nonlinear-least-squares computer program using eq 3-9 with eight adjustable parameters: ΔS^* (or k^{298}), ΔH^* , A_m , E_m , A_{os} , E_{os} , A , and C (weighting scheme: $W(y_i) = y_i^{-2}$). The fitted curves are plotted in Figure 1 together with the experimental data, and the adjusted parameters are given in Table I. Note that the standard deviations of the $1/T_{2m}$ and $1/T_{2os}$ parameters are very large; furthermore, the correlation coefficient matrix of the computer fit indicates a strong correlation between these parameters. This is not surprising if we consider Figure 1b: $1/T_{2os}$ contributes to $1/T_{2r}$ only at low temperature, and the fast-exchange region, in which $1/T_{2m}$ is effective,¹⁹ is hardly reached in the accessible temperature range. $1/T_{2m}$ would be better defined if bound water line widths were measured, but even at very low temperature no bound water signal is observable.²⁰

(16) It will be seen later that $1/T_{2m}$ is badly defined in the accessible temperature range, so there is no point in using the full equations corresponding to each relaxation mechanism.^{8,17}

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(20) In the case of V^{3+} , the line width of the bound water signal allowed the definition of $1/T_{2m}$ at low temperatures, using the equation $1/T_{2b} = 1/\tau_m + 1/T_{2m}$.⁸ In this case, however, no bound water signal was observed, even at very low temperature where the exchange rate constant is quite small ($\sim 5 \times 10^3$ s⁻¹ at 250 K), because of its expected broadness and the small value of $\Delta\omega_m$: from the fitted parameters in Table I, one can estimate that the bound water signal would have, at 250 K, a width at half-height of about 15 kHz and would lie at about 8 kHz from the bulk water signal.

Thus, the adjusted values of the $1/T_{2m}$ and $1/T_{2os}$ parameters have little significance, since they are so badly defined. Fortunately, this does not apply to the kinetic and chemical shift parameters, which are well characterized in our temperature domain. As a check, we artificially fixed the value of E_{os} to 25 kJ mol⁻¹ (approximately 3 times the fitted value),²¹ and repeated the fitting procedure: the kinetic and chemical shift parameters of both analyses agree within their standard deviations.

Another result deserving some discussion at this stage is the negative value of the outer-sphere chemical shift parameter C (eq 9). In the experimental spectra, the free water signal effectively stands at higher frequency than the pure acidified water signal at low temperature; as the exchange rate increases with temperature, it comes closer to the reference signal and finally resonates at much lower frequency. Thus the inner-sphere chemical shift is opposite in sign to the outer-sphere chemical shift, as was postulated by Golding and Stubbs:²² in their theoretical study on NMR shifts in paramagnetic systems, they considered a d^1 ion in a strong crystal field of octahedral symmetry, with six ligands all 0.2 nm from the central atom, which incidentally is the situation encountered with $Ti(H_2O)_6^{3+}$. Ab initio calculations lead to isoshielding diagrams that show the contours of equal chemical shift in the xy plane. It appears from their approach that the chemical shift is not isotropic around the central ion but that it depends strongly on the position of the observed nucleus with respect to the central ion and to the six ligands. For instance, if one assumes the water molecules of the second coordination sphere of Ti^{3+} to lie about 0.35 nm from the central ion, on the faces of the octahedron, they will experience, as we effectively observed, a chemical shift opposite in sign to that of the water molecules in the first coordination sphere.

Variable Pressure. The pressure dependence of the rate constant of a reaction is derived from transition-state theory, and it is usually²³ assumed to be a quadratic function of P :

$$\ln k_p = \ln k_0 - \frac{\Delta V_0^* P}{RT} + \frac{\Delta\beta^* P^2}{2RT} \quad (10)$$

where k_0 is the rate constant at zero pressure, ΔV_0^* is the activation volume of the reaction at zero pressure, and $\Delta\beta^*$ is the compressibility coefficient of activation. We must also take into account the pressure dependences of other parameters, since the NMR experiments do not provide k , but $1/T_2$.

First, the pressure dependence of $1/T_{2A}^\circ$ is to be considered. Variable-pressure ¹⁷O NMR measurements of a 0.05 M HClO₄ solution have been performed between 308 and 317 K by Ducommun et al.²³ From 0.1 to 225 MPa, the water linewidth narrows by about 7% of its ambient-pressure value. We repeated the experiment with a 2.0 *m* triflic acid solution at 299 K, and we observed also a 7% narrowing between 0.1 and 200 MPa. The largest $1/T_{2A}^\circ$ contribution to $1/T_2$ occurs for the variable-pressure experiment performed at the lowest temperature (273 K), where it constitutes about 14% of $1/T_2$ at 200 MPa, so the small variation of $1/T_{2A}^\circ$ with pressure will represent less than 1% of the observed $1/T_2$. This is well below the experimental uncertainty on $1/T_2$ measurements; therefore, we consider $1/T_{2A}^\circ$ to be pressure independent.

Second, even though we performed the variable-pressure measurements in a temperature range where the main contribution to $1/T_{2r}$ is k (273-298 K), the nonkinetic parameters $1/T_{2m}$, $1/T_{2os}$, and $\Delta\omega_m$ cannot be ignored, and their variations with pressure, if any, can influence the determination of the activation volume. No independent measurements of these pressure dependences are feasible, but reasonable predictions can be made on the basis of theoretical considerations. In the first coordination sphere of a tripositive ion, solvent electrostriction results in a large

(21) ¹⁷O NMR studies of comparable systems, but where the outer-sphere contribution is well-defined, yielded E_{os} values of 20.4 kJ mol⁻¹ for $V(H_2O)_6^{2+}$ and 26.6 kJ mol⁻¹ for $V(H_2O)_6^{3+}$.⁸

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(23) Ducommun, Y.; Earl, W. L.; Merbach, A. E. *Inorg. Chem.* **1979**, *18*, 2754.

Table II. Kinetic and NMR Parameters Derived from Relaxation and Chemical Shift Data as a Function of Pressure

fitting procedure ^a	ΔV_0^* , cm ³ mol ⁻¹	$10^2 \Delta \beta^*$, cm ³ mol ⁻¹ MPa ⁻¹	ΔV_{os}^* , cm ³ mol ⁻¹	$10^4 B_\omega$, MPa ⁻¹
I	-10.48 ± 0.13		-6.06 ± 0.35	
	-12.08 ± 0.38	-1.86 ± 0.42	-5.66 ± 0.32	
II	-11.99 ± 0.41	-1.74 ± 0.46	-6.52 ± 0.31	
III	-12.37 ± 0.27	-1.62 ± 0.30	-5.58 ± 2.11	
IV	-12.41 ± 0.24	-1.79 ± 0.27	-3.52 ± 2.32	1.38 ± 0.35

^aFits I and II were performed with relaxation data only, while fits III and IV used also chemical shift data. In all fits, the function of $\ln k$ with pressure was quadratic, except for fit I, where a linear equation was also used. The details of each procedure are given in the text.

compression, typically of the order of gigapascals.²⁴ Thus, an externally added pressure of about 200 MPa will not produce noticeable changes in bond lengths, and the scalar coupling constant, A , which depends on the distance between the metallic cation and the oxygen nucleus, is not expected to vary much during a variable-pressure experiment. Consequently, $\Delta\omega_m$ should show a very small pressure dependence, as will be demonstrated later. Further, changes in $1/T_{2m}$ and $1/T_{2os}$ can be ascribed to variations of reorientational correlation times, due to viscosity changes. As electrostriction is less severe in the second coordination sphere, $1/T_{2os}$ is expected to be more sensitive than $1/T_{2m}$ to the externally applied pressure. Effectively, $1/T_{2m}$ merely increased with pressure in the systems where it could be independently observed,^{12,17} while the variation of $1/T_{2os}$ was significant enough, in the study of Me₂SO and DMF exchanges on Fe³⁺, to be treated by the equation

$$\ln(1/T_{2os}) = \ln(1/T_{2os})_0 - \Delta V_{os}^*(P/RT) \quad (11)$$

The values of ΔV_{os}^* obtained for these exchanges were respectively -7.6 and -7.5 cm³ mol⁻¹.²⁵

Our variable-pressure experiments were performed at 1.4 T with a 0.3 *m* Ti(CF₃SO₃)₃ and 2.0 *m* CF₃SO₃H solution, at four different temperatures. The relaxation data are presented in Figure 2b; quite obviously the pressure dependence of $1/T_{2r}$ is different at each temperature and is not simply related to the rate constant. Thus, an overall analysis is necessary, using the full Swift and Connick equation (eq 3), and considering at least k and $1/T_{2os}$ to be pressure dependent, via eq 10 and 11 (a simpler treatment where only k varies with pressure could not fit the experimental data). In this analysis, at each temperature, $\Delta\omega_m$, $1/T_{2m}$, k_0 , and $(1/T_{2os})_0$ were fixed to their values found with the parameters given in Table I. The adjustable parameters were then ΔV_{os}^* and either ΔV^* if a linear equation for the pressure dependence of k is used or ΔV_0^* and $\Delta \beta^*$ with a quadratic equation. Both sets of results are given in Table II, fit I. Since the fitted $\Delta \beta^*$ value is significantly different from zero, the quadratic equation was then used throughout the rest of this analysis.

A variation of $1/T_{2m}$ with pressure of +0.1% MPa⁻¹, similar to that observed for the formyl proton in Ln(DMF)₈³⁺¹² (the largest known for comparable systems), was then introduced in the computer program. The adjusted kinetic parameters (fit II) are practically identical with those obtained in the previous fit, as could be expected considering that $1/T_{2m}$ has little effect on $1/T_{2r}$ in the chosen temperature range. It is thus justified to consider $1/T_{2m}$ as pressure independent for our kinetic analysis.

On the other hand, $1/T_{2r}$ depends strongly on $\Delta\omega_m$ at temperatures around that of coalescence. To determine to what extent $\Delta\omega_m$ varies with pressure, we found it necessary to consider also the $\Delta\omega_r$ data at variable pressure and to treat them simultaneously with the relaxation data (eq 3 and 4). As the $\Delta\omega_r$ data are determined in a less direct manner than the $1/T_{2r}$ data,²⁶ we had first to verify that they do not produce systematic errors in the fit. Hence, the same procedure as for fit I was applied, that is

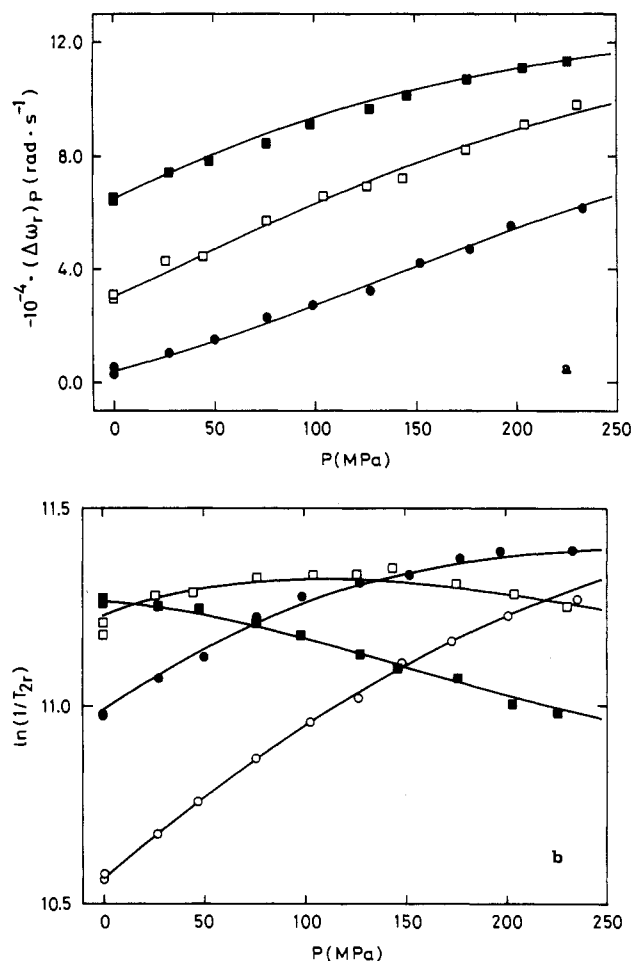


Figure 2. Variable-pressure ¹⁷O NMR data for Ti(CF₃SO₃)₃ in water, showing $\Delta\omega_r$ and $\ln(1/T_{2r})$ vs. pressure (0.30 *m* Ti³⁺, 2.01 *m* H⁺): ○ at 273.1 K; ● at 282.1 K; □ at 289.8 K; ■ at 297.6 K.

with only k and $1/T_{2os}$ as pressure-dependent variables. The adjusted parameters (fit III) agree with the results of fit I within their standard deviations, and we may thus be confident that the $\Delta\omega_r$ data added to the fit are coherent with the $1/T_{2r}$ data.

Then we allowed $\Delta\omega_m$ to vary with pressure, but since the second coordination sphere is more compressible than the first one, $\Delta\omega_{os}$ should vary at least as much as $\Delta\omega_m$. To simplify, we assumed the same pressure dependence for $\Delta\omega_m$ and $\Delta\omega_{os}$:

$$(\Delta\omega_i) = (\Delta\omega_i)_0(1 + B_\omega P) \quad (i = m, os) \quad (12)$$

Again, $(\Delta\omega_m)_0$, $(\Delta\omega_{os})_0$, $1/T_{2m}$, k_0 , and $(1/T_{2os})_0$ were set to their ambient pressure value, and the adjustable parameters were ΔV_0^* , $\Delta \beta^*$, ΔV_{os}^* , and B_ω (fit IV). The fitted $\Delta\omega_r$ curves are plotted in Figure 2a, together with the experimental data. The allowance for a pressure dependence of the chemical shifts induces a marked diminution of ΔV_{os}^* , but this parameter is in any case poorly defined and is of little importance; as for the variable-temperature study, we consider this outer-sphere term mainly as a corrective one. On the other hand, the kinetic parameters are almost identical with those of fit III, and as the fitted value of B_ω is indeed very small, ca. 0.01 % MPa⁻¹,²⁷ it is justified to consider $\Delta\omega_m$ as pressure

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(26) The detailed procedure for the obtention of $\Delta\omega_r$ is available in the supplementary material.

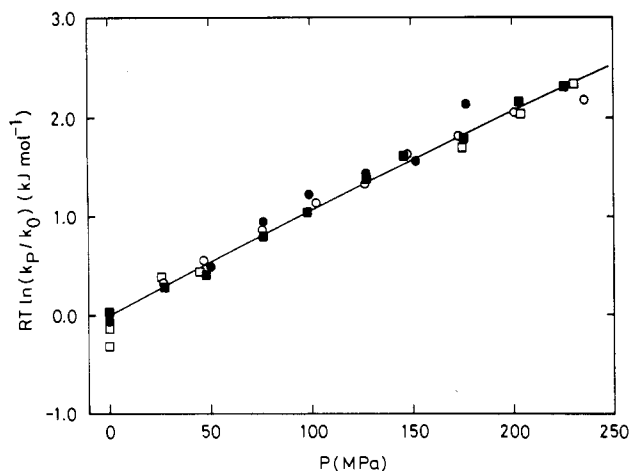


Figure 3. Calculated and experimental $RT \ln(k_p/k_0)$ as a function of pressure (0.30 m Ti^{3+} , 2.01 m H^+): \circ at 273.1 K; \bullet at 282.1 K; \square at 289.8 K; \blacksquare at 297.6 K.

independent for the determination of ΔV_0^* .

As pointed out earlier, the variable pressure $\Delta\omega$ data may be less accurate than the corresponding $1/T_{2r}$ data. Since we demonstrated that $1/T_{2m}$ and $\Delta\omega_m$ can both be assumed to be independent of pressure, the results of fit I, $\Delta V_0^* = -12.1 \pm 0.4$ cm^3 mol^{-1} and $\Delta\beta^* = -(1.9 \pm 0.4) \times 10^{-2}$ cm^3 mol^{-1} MPa^{-1} , appear to us as the most reliable ones.

Figure 2b does not make clear the effect of pressure on the exchange rate, and we therefore calculated the k_p values from the experimental $1/T_{2r}$ data, using the Swift and Connick equation. The $RT \ln(k_p/k_0)$ values are shown in Figure 3, together with the calculated curve. The points show no trend with the temperatures of the four variable-pressure experiments; that is, the activation volume is independent of the temperature, at least in the small experimental temperature range used. Furthermore, the data present a curvature with pressure, showing the necessity of a quadratic equation for the pressure dependence of k .

Discussion

Although our main goal in this study is the determination of the volume of activation for water exchange on $Ti(H_2O)_6^{3+}$, a detailed knowledge of the temperature dependence of the kinetic and NMR parameters involved is needed to analyze the variable-pressure results, obtained at several temperatures. The water-exchange rate on $Ti(H_2O)_6^{3+}$ is rather fast, as compared to other trivalent first-row transition-metal ions, while the scalar coupling constant and the spin quantum number, hence $\Delta\omega_m$, are comparatively small (as pointed out before, this explains why the bound signal cannot be observed). This prevents any simplification in the analysis of the relaxation rate as a function of temperature: at low temperatures, the outer-sphere relaxation rate and the exchange rate contributions to $1/T_{2r}$ are of similar importance; then, with increasing temperature, the outer-sphere contribution decreases, but the exchange rate becomes comparable to $\Delta\omega_m$; i.e., relaxation occurs also via a change in precession frequency. Thus, the full Swift and Connick equation (eq 3) must be used throughout, and each parameter of this equation is strongly correlated to the others.

Analysis of the chemical shift data together with the relaxation data permits a more accurate determination of $\Delta\omega_m$ and $1/\tau_m$. One obtains a still better characterization of these terms from a simultaneous analysis of results obtained at different magnetic

Table III. Complex Formation Rate Constants, k_f ($M^{-1} s^{-1}$), for the Reaction of $Ti(H_2O)_6^{3+}$ with Various Ligands in Water

ligand	pK_a	k_f	ref
$ClCH_2COOH$		0.7×10^3 (288 K)	32
CH_3COOH		1×10^3 (288 K)	32
NCS^-	-1.84	8×10^3 (281–282 K)	30
H_2O	-1.74	8.6×10^3 (285 K) ^a	this work
Cl_2CHCOO^-	1.25	1.1×10^5 (288 K)	32
$ClCH_2COO^-$	2.46	2.1×10^5 (288 K)	32
CH_3COO^-	4.47	1.8×10^6 (288 K)	32
$HOCCOO^-$	1.23	3.9×10^5 (283 K)	31
$HOOCCH_2COO^-$	2.43	4.2×10^5 (288 K)	33
$HOOCCH(CH_3)COO^-$	2.62	3.2×10^5 (288 K)	33

^aThis rate constant corresponds to the exchange of one of the six coordinated water molecules and is converted to second-order units, i.e. $6k^{285}$ (s^{-1})/55.5 (M).

fields, because $\Delta\omega_m$ is proportional to the field strength, while $1/\tau_m$ is independent of it.

For obvious technical reasons, neither multifrequency measurements nor an overall computer analysis was feasible two decades ago, and this accounts for the differences between our results (Table I) and those obtained by Chmelnick and Fiat¹¹ ($k^{298} = 1.0 \times 10^5$ s^{-1} ; $\Delta H^* = 26$ kJ mol^{-1} ; $\Delta S^* = -63$ J K^{-1} mol^{-1}). It is clear from Figure 1b that the simplified equation they used, assuming $1/T_{2r} = 1/\tau_m$ before coalescence, leads to a $\ln(k/T)$ slope less steep than it should, thus yielding values of ΔH^* and ΔS^* that are too small. It should also be emphasized that we used $CF_3SO_3^-$ instead of Cl^- as counterion, to avoid any complexation that may occur with halides at high concentration. It has been shown that these anions form complexes with V^{3+} , whereas triflate does not.⁸

The strongly negative ΔS^* value found by Chmelnick and Fiat was used as an argument for an associative activation mode; this is no longer evident with our value, apart from the fact that ΔS^* is not a very reliable parameter in this kind of study.¹⁷ Another approach to determine the activation mode for ligand substitution on a metal ion is to compare complex formation rate constants, k_f , obtained with various ligands (including water-exchange rate). For early first-row trivalent ions, it has been done with V^{3+} ,²⁸ Cr^{3+} ,⁹ and Fe^{3+} ,²⁹ and the large variations of k_f with the basicity of the incoming ligand, about 3 orders of magnitude, has been interpreted as the sign of an associative activation mode for substitution on these ions. This conclusion was corroborated by markedly negative activation volumes found for water exchange on these aqua ions.^{8–10} For Ti^{3+} , Chaudhuri and Diebler^{30–33} performed several complex formation studies (Table III). The obtained k_f values span 3 orders of magnitude as well and show a general increase with the ligand basicity, as expressed by their pK_a 's. Moreover, the k_f value for acetate is about 18 times larger than the water-exchange rate constant at 288 K. Such a difference cannot be explained by electrostrictive or outer-sphere association constant effects and supports the associative activation mode concluded for Ti^{3+} .

These variable-ligand studies, however, give only a qualitative answer and do not quantify the relative degree of associative character of substitution reactions on a given metal ion. Also, the comparison between ions is delicate. First, the lists of ligands chosen with different ions do not always overlap (for instance, there is only one ligand studied with both Ti^{3+} and Cr^{3+} : SCN^-). Second, metal ions have widely different reactivities, because of crystal field stabilization effects (about 10 orders of magnitude between substitution rates on Ti^{3+} and on Cr^{3+}); it is thus very hazardous to compare selectivities, because a series of fast reactions usually exhibits less selectivity than a comparable set of slow ones.⁴ Still, it is worth noticing that Ti^{3+} is a little more selective than

(27) The largest known B_0 was found for the exchange of DMF on lanthanide ions, where the fitted values averaged 0.05% MPa^{-1} .¹² However, these exchanges were studied by 1H NMR, on the formyl proton. Since the distance between this proton and the lanthanide ion is larger than the oxygen-titanium distance in our study, and since the proton and the lanthanide ion are not bound together, it is understandable that the pressure dependence of $\Delta\omega_m$ is smaller in our case. See also: Nielson, R. M.; Dodgen, H. W.; Hunt, J. P.; Wherland, S. E. *Inorg. Chem.* **1986**, *25*, 582.

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Fe³⁺, although substitution rates on Ti³⁺ are about 2 orders of magnitude faster than on Fe³⁺.²⁹

A quantitative way to appreciate the dissociative or associative character of a given reaction is to determine its activation volume, ΔV^\ddagger . This approach is particularly well suited to solvent-exchange reactions, because there is no significant development of charge or dipole during the process; hence, solvent electrostriction does not vary. Therefore, ΔV^\ddagger is essentially the result of changes in internuclear distances within the reactants upon going to the transition state, and its sign is an immediate diagnostic of the activation mode: dissociative when ΔV^\ddagger is positive, associative when ΔV^\ddagger is negative.

However, in the absence of a method to detect an intermediate of increased or reduced coordination number in solvent-exchange studies, it is not obvious to distinguish between interchange and limiting mechanisms. Over the years, some theoretical models have been used to predict the extreme values ΔV^\ddagger could reach, based on simple geometrical approaches.^{34,35} More recently, Swaddle^{24,36} presented a model inspired from the semiempirical equation (13), in which the "absolute"³⁷ partial molar volume \bar{V}_{abs}^0

$$\bar{V}_{\text{abs}}^0 = 2.523 \times 10^{-6}(r + 238.7)^3 - 18.07n - 417.5z^2/(r + 238.7) \quad (13)$$

(in cm³ mol⁻¹) of an aqueous metal ion is related to its effective ionic radius r (pm), its coordination number n , and its charge z . The three terms on the right-hand side of eq 13 represent respectively the volume of the solvated ion $M(\text{H}_2\text{O})_n^{z+}$, the loss of the contribution of n water molecules to the volume of the free solvent, and the electrostrictive effect of $M(\text{H}_2\text{O})_n^{z+}$ on solvent beyond the first coordination sphere, treated as a continuous dielectric (Born-Drude-Nernst equation). The term added to r in the parentheses, 238.7 pm, represents the effective "thickness" of the first coordination sheath and was determined by fitting eq 13 to a large number of experimental \bar{V}_{abs}^0 , obtained with aqueous metal ions of various charges ($z = 1-4$) and coordination numbers ($n = 4, 6, 8, \text{ or } 9$).³⁶

According to Swaddle's model, partial molar volumes can be calculated with eq 13 for a given aqua ion and for the corresponding intermediate of reduced or increased coordination, and the difference between these values yields then the limiting ΔV^\ddagger for a dissociative or associative process, respectively. The key feature of this model is to account for the increase of r with the coordination number, in accordance with Shannon's compilation³⁹ of ionic radii (for hexaaqua ions, e.g., $\delta r \approx \pm 6$ pm when n changes to 7 or 5). Among some interesting aspects pointed out by Swaddle²⁴ about $|\Delta V_{\text{lim}}^\ddagger|$ values calculated this way, the most pertinent to our results is that $|\Delta V_{\text{lim}}^\ddagger|$ depends so little on r that it has about the same value, 13.5 ± 1.0 cm³ mol⁻¹, for all first-row trivalent hexaaqua ions. Thus, the actual ΔV^\ddagger 's observed with these ions can be directly compared, a possibility that was not obvious a priori and a significant advantage over complex formation studies. Notice also that our experimental value for Ti³⁺, -12.1 cm³ mol⁻¹, is very close to the limiting value calculated above.

Kinetic parameters of water-exchange reactions obtained with early first-row trivalent hexaaqua ions are presented in Table IV.

Table IV. Kinetic Parameters for Water Exchange on Trivalent First-Row High-Spin Hexaaqua Ions

	electronic confign			
	t_{2g}^1	t_{2g}^2	t_{2g}^3	$t_{2g}^3e_g^2$
cation	Ti(III)	V(III) ^b	Cr(III) ^c	Fe(III) ^d
r_i , pm ^e	67	64	61	64
ΔH^\ddagger , kJ mol ⁻¹	43.4	49.4	108.6	64.0
ΔS^\ddagger , J K ⁻¹ mol ⁻¹	+1.2	-27.8	+11.6	+12.1
ΔG_{298}^\ddagger , kJ mol ⁻¹	43.0	57.7	105.1	60.4
k_{298} , s ⁻¹	1.8×10^5	5.0×10^2	2.4×10^{-6}	1.6×10^2
ΔV_0^\ddagger , cm ³ mol ⁻¹	-12.1	-8.9	-9.6 ^e	-5.4 ^e
$10^2 \Delta \beta^\ddagger$, cm ³ mol ⁻¹ MPa ⁻¹	-1.9	-1.1		

^aReference 39. ^bReference 8. ^cReference 9. ^dReferences 29 and 10. ^eLinear function of k .

Before focusing on the activation volumes, it is interesting to examine briefly some other parameters with respect to mechanistic interpretation. A fair correlation has been found between the labilities of octahedral ions, i.e. k_{298} or ΔG_{298}^\ddagger , and the crystal field activation energies,⁴⁰ but this correlation is equally good whether the CFAE's are calculated for an associative or a dissociative mechanism;⁴¹ therefore, the activation mode cannot be inferred from these parameters. Activation entropy, ΔS^\ddagger , has often been used for mechanism assignment.^{11,42} Indeed, among the water-exchange reactions on divalent and trivalent hexaaqua ions that have been investigated, ΔS^\ddagger happens to be smaller for those shown independently to have an associative activation mode than for those with a dissociative one.⁵ However, the imprecision of ΔS^\ddagger determination from NMR data of paramagnetic systems¹⁷ and the difficulty in interpreting the magnitudes of experimental values hamper the use of ΔS^\ddagger as a versatile diagnostic tool for mechanisms.

By contrast, activation volumes are accurately measurable, and simple models exist to interpret the results (see above). The sequence of ΔV^\ddagger 's for water exchange on the early first-row trivalent ions shows a definite trend in activation mode, from strongly associative (Ti³⁺) to moderately associative (Fe³⁺). This trend is most likely attributable to the same steric and electronic effects invoked for the divalent ion series mentioned in the Introduction.

To conclude, the associative character of Ti(H₂O)₆³⁺ substitution reactions had already been established by complexation kinetic studies prior to this work. Our variable-pressure study of water exchange on this ion yielded the most negative ΔV^\ddagger measured so far for a hexaaqua ion, -12.1 cm³ mol⁻¹. This result not only confirms the former conclusion but also comes quite close to the estimated limiting value calculated with Swaddle's model. This persuades us that the mechanism for substitution on Ti(H₂O)₆³⁺ is A or nearly A.

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Supplementary Material Available: Relaxation and chemical shift data as a function of temperature (Tables SI and SII) and pressure (Tables SIII and SIV) and correlation coefficient matrix of the variable-temperature computer fit (Table SV) (14 pages). Ordering information is given on any current masthead page.

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