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Oxygen-17 FT NMR Study of the Effect of Pressure on the Exchange of Water on Nickel(II)¹

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The solvent exchange of [Ni(H₂O)₆](ClO₄)₂ in water has been studied as a function of temperature and pressure (up to 225 MPa) by measuring oxygen-17 FT NMR chemical shifts and line widths of the free water resonance at 8.133 MHz. A volume of activation ΔV^* of $+7.1 \pm 0.2$ cm³ mol⁻¹ is obtained by using the full Swift and Connick equation and is found to be independent of pressure. The activation parameters ΔH^* and ΔS^* are very sensitive to the method of analysis used. The three activation parameters are in accord with a dissociative-interchange (I_d) mechanism. The temperature and pressure dependences of pure acidified water T₂'s have also been studied by oxygen-17 FT NMR. The relaxation rate decreases with compression, suggesting that the effect of pressure is to destroy some of the water structure.

Introduction

Traditionally, the entropy of activation has been considered the parameter most useful for deciding whether a solvent-exchange reaction is associative or dissociative, a positive entropy indicating a dissociative process. The predictive power of ΔS^* is good only when the entropy is sufficiently positive or negative, but for values of ΔS^* near zero, the nonrandom errors associated with its determination often make the diagnosis highly dubious, and, additionally, the factors that affect ΔS^* are but poorly understood.

Advances in experimental techniques in the past decade have led to the increasing use of volumes of activation for the diagnosis of reaction mechanisms. The volume of activation ΔV^* is simply the difference between the partial molar volumes of the reactants and the transition state. It is considered the resultant of two contributions.³ The first arises from volume changes due to molecules not directly involved in the formal reaction scheme and is mainly due to changes in electrostriction of the surrounding solvent in going from reactants to transition state. For solvent exchange this term may ordinarily be neglected. The second contribution is due to bond making and breaking occurring during the activation process, and thus a positive volume of activation indicates an expansion of the reactants in forming the transition state (a bond has stretched or broken) and implies a dissociative activation mode (D or I_d).

The effect of compression on the rate constant of aqueous reactions has been almost exclusively confined to slow reactions, but a few fast ligand complexation rates have been measured by *T* jump.⁴ Early on, Connick and co-workers⁵ showed that NMR could be a useful tool to study solvent exchange in transition-metal solutions and especially that ¹⁷O NMR is the method of choice in studying water-exchange processes. The exchange of water molecules between the primary solvation shell of a cation and the bulk solvent is an important first step in the understanding of aqueous reaction mechanisms, especially complex formation and some redox reactions.

There are several reported studies on water exchange between the first coordination sphere of Ni(II) and the bulk solvent,^{6,7} with a wide variety of values of the activation parameters, the most recent one being a careful ¹⁷O CW NMR variable-temperature study reported by Bechtold et al.⁸ In order to clarify the mechanism of this exchange reaction, we have chosen to study it by ¹⁷O FT NMR as a function of pressure. Before attempting this variable-pressure study, we undertook a variable-temperature FT NMR study at 8.133 MHz to obtain the NMR parameters required for the accurate analysis of the variable-pressure data at this frequency as well as checking by Fourier transform techniques earlier results⁷ obtained by continuous wave NMR.

Experimental Section

Preparation of Materials and Samples. Oxygen-17 enriched water (11.3 atom %, normalized in ¹H) was obtained from Yeda R+D Co. Ltd., Rehovoth, Israel. It was distilled three times in vacuo for purification before each use. Nickel perchlorate hexahydrate (Ni(ClO₄)₂·6H₂O, Fluka, purum) was used without further purification. Sample solutions of aqueous nickel ion were prepared by direct dissolution of the weighed nickel salt in suitable amounts of weighed enriched water. The solutions and the blanks were acidified with 60% perchloric acid (HClO₄, Merck, pro analysi). Two solutions of Ni(H₂O)₆²⁺ were prepared. Solution I was 0.0195 *m* in nickel and 0.0520 *m* in HClO₄. Solution II was 0.0601 *m* in nickel and 0.0850 *m* in HClO₄ (*m* = mol of solute/kg of solvent).

NMR Measurements. Line-broadening measurements were performed on a Fourier transform Bruker WP-60 spectrometer, interfaced to a Nicolet BNC-12 computer with 8K of data memory, operating at 8.133 MHz and using an external fluorine lock.

Ambient pressure measurements were made without spinning, with a Bruker 8-14 MHz multinuclear probe, the temperature being controlled by a Bruker ST 100 unit. The $\pi/2$ pulse length was 14 μ s; sweep widths were either 10 or 25 kHz. The spectrometer frequency was adjusted to give the observed peak in the center of the sweep range. The pulse-repetition rate was between 0.2 and 2 s and the number of scans between 100 and 10 000, depending upon the relaxation times for the particular sample and the temperature. The delay between the pulse and the start of data acquisition was 1-4 dwell times, adjusted to give a flat base line. The low-temperature line width

measurements at ambient pressure were made in 10-mm tubes and the high-temperature measurements in short 10-mm sealed tubes to prevent distillation. For chemical shift measurements, 9-mm spheres were used to eliminate bulk susceptibility corrections. The chemical shift measurements of the bulk water resonance for nickel were made relative to pure acidified water by substitution of the samples by using solution II.

Variable-pressure measurements were made up to 225 MPa with a high-pressure NMR bomb similar in principle to the one previously built in our laboratory.⁹ For our studies in aqueous solutions, the temperature range of interest is restricted to temperatures above 273 K. Therefore, a noninductively wound resistance heater could be used for varying the temperature. The high-pressure probe was built from IMI titanium 550, a high tensile strength alloy. The coil and matching circuits have been changed for resonance at 8.133 MHz. The temperature was measured with a 100- Ω platinum resistor within the pressure bomb and regulated with a Bruker VT-1000 unit. The stability was better than ± 0.3 K. The spectrometric parameters were the same as for the ambient pressure measurements, except the number of scans which had to be increased to 30 000 due to the small sample size in the bomb.

All line widths and positions were measured by plotting the peaks followed by measurement with a ruler. It is estimated that the line widths and shifts are accurate to ± 5 Hz.

Data Treatment. The water exchange as a function of temperature was studied by methods outlined previously.^{5,7} The reduced bulk water relaxation time T_{2r} is related to the observed relaxation time T_2 by eq 1, where T_{2s} is the contribution to the bulk water relaxation time

$$\frac{1}{T_{2r}} = \frac{1}{P_m T_{2p}} = \frac{1}{P_m} \left(\frac{1}{T_2} - \frac{1}{T_{2s}} \right) \quad (1)$$

due to the pure solvent, T_{2p} is the contribution arising from the presence of the paramagnetic ion, and P_m is the ratio of the moles of waters in the bound site to the total moles of water. In the case of aqueous nickel ion, the coordination number of the nickel is 6 with all waters equally bonded.^{7,10} The relaxation time T_{2r} is given by eq 2,⁶ where

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

T_{2m} is the relaxation time due to the bound waters in absence of exchange, τ_m is the residence time of the solvent molecule in the first coordination sphere, and $\Delta\omega_m$ is the shift between bulk and bound water resonances when no exchange occurs.

The reduced chemical shift of the bulk water resonance has been shown⁷ to obey eq 3, where $\Delta\omega_s$ is the chemical shift of the bulk water

$$\Delta\omega_r = \frac{\Delta\omega_s}{P_m} = \frac{\Delta\omega_m}{(\tau_m/T_{2m} + 1)^2 + \tau_m^2 \Delta\omega_m^2} + \Delta\omega_{os} \quad (3)$$

relative to pure water. $\Delta\omega_{os}$ is a correction to the observed shift due to outer sphere interaction, which is assumed to follow simple Curie behavior.

For nickel, we expect the isotropic shift to have negligible contribution from pseudocontact interaction, so we have assumed that the resonance of the bound water will follow Bloembergen's equation¹¹ (eq 4), where ω is the precessional frequency of oxygen-17, $g_{eff}\beta$ and

$$\Delta\omega_{m-s} = \omega S(S+1) \frac{g_{eff}\beta}{\hbar \gamma_i} \left(\frac{A}{3kT} \right) \quad (4)$$

γ_i are the gyromagnetic ratios of the unpaired electrons and of the oxygen-17 nuclei, S is the electron spin quantum number, which is equal to 1 for nickel, and A is the scalar coupling constant in joules. Other symbols have their usual meanings.

From transition-state theory, the oxygen-17 dependence of the residence time τ_m and its relation to the pseudo-first-order reaction rate constant for solvent exchange has the form shown in eq 5, where

$$k_m = \frac{1}{\tau_m} = \frac{kT}{h} \exp(\Delta S^*/R - \Delta H^*/RT) \quad (5)$$

ΔS^* and ΔH^* are the entropy and enthalpy of activation for the exchange reaction.

The relaxation of the oxygen-17 nuclei of waters bound to the paramagnetic nickel ion is due to scalar coupling between the magnetic

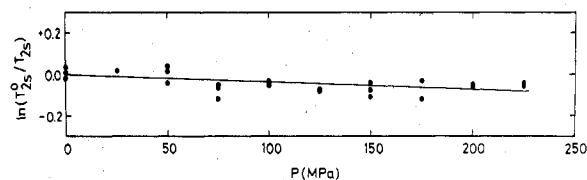


Figure 1. Experimental values of $\ln(T_{2s}^0/T_{2s})$ for pure acidified water as a function of pressure. The solid line through the points is a linear fit of all the data (T_{2s}^0 = zero-pressure relaxation time).

moment of the oxygen-17 and the unpaired electrons of the nickel ion and is described by eq 6,¹² where τ_e is a correlation time for electron

$$\frac{1}{T_{2m}} = \frac{S(S+1)}{3} \left(\frac{A}{\hbar} \right)^2 \left(\tau_e + \frac{\tau_e}{1 + \tau_e^2 \omega_e^2} \right) \quad (6)$$

relaxation and ω_e is the Larmor frequency of the electron. Following Neely and Connick,⁷ we have assumed an Arrhenius behavior for τ_e (eq 7), where E is the activation energy for the electronic relaxation.

$$\tau_e = \tau_e^0 \exp(E/RT) \quad (7)$$

As discussed in previous papers,^{2,13} the volume of activation can be defined according to transition-state theory as in eq 8, and the

$$\Delta V^* = -RT(\partial \ln k / \partial P)_T \quad (8)$$

pressure dependence of the rate constant k can be expressed by the polynomial in eq 9, where k_0 is the rate constant at zero pressure,

$$\ln k_p = \ln \frac{1}{\tau_m} = \ln k_0 - \Delta V^*_0 P / RT + \Delta\beta^* P^2 / 2RT \quad (9)$$

ΔV^*_0 is the volume of activation extrapolated to zero pressure, and $\Delta\beta^*$ is the pressure-independent compressibility of activation.

Results and Discussion

Relaxation of Pure Water. The pure water relaxation serves only as a blank in the determination of $1/T_{2r}$, but it is also interesting to look at the specific relaxation behavior of water with pressure. The water line widths in acidified water are in good agreement with those published by Neely and Connick.⁷ It is generally believed that for acidified solutions of pure water, the quadrupole mechanism predominates the relaxation of the ¹⁷O nucleus.¹⁴ If this is the case, T_1 should equal T_2 which is confirmed by the good agreement between the most recently published T_1 's reported by Hindman and co-workers¹⁵ and our values of T_2 . The transverse relaxation rate will therefore follow eq 10,¹² where η is the asymmetry

$$\frac{1}{T_2} = \left(\frac{3}{40} \right) \frac{2I+3}{I^2(2I+1)} \left(1 + \frac{\eta^2}{3} \right) \left(\frac{e^2 q Q}{\hbar} \right) \tau_e \quad (10)$$

parameter and $e^2 q Q / \hbar$ is 2π times the quadrupole coupling constant in hertz. Both terms are probably independent of pressure in the range studied here. The correlation time, τ_e , can be associated with the tumbling of the water molecule and should be pressure dependent. Simple volume arguments would predict an increase in volume with molecular rotation. An increase in the applied pressure would reduce the volume available for rotation and therefore cause τ_e to increase. This argument would predict an increase in relaxation rate with compression. These arguments have been confirmed by variable-pressure studies of the deuteron longitudinal relaxation time in CDCl_3 .¹⁶

Jonas et al.¹⁷ have measured the proton and deuteron longitudinal relaxation rates of water as a function of pressure. They have calculated the rotational contribution to the relaxation rate and found that it decreases with compression, contrary to predicted behavior. Figure 1 shows our results for the normalized $1/T_2$ of water plotted against the applied pressure. The data are plotted in this way in order to remove any temperature dependence. The line widths clearly narrow with increasing pressure, in agreement with Jonas' results.¹⁷

Table I. Kinetic and NMR Parameters Derived from Relaxation and Chemical Shifts of the $\text{Ni}(\text{ClO}_4)_2$ Bulk Water as a Function of Temperature and Pressure^a

	Neely ^g	Bechtold ^h	this work	Bechtold ^h and this work ^b
ΔH^* , kJ mol ⁻¹	58.1	56.8 ± 0.4	52.3 ± 0.6	56.9 ± 0.8
ΔS^* , J mol ⁻¹ K ⁻¹	41.8	32.2 ± 1.6	17.2 ± 2.1	32.0 ± 3.0
$k_m^{298.1}$, s ⁻¹ × 10 ⁻⁴		3.14 ± 0.06	3.37 ± 0.09	3.15 ± 0.08
A/h , MHz	24.0	22.23 ± 0.07	20.4 ± 0.2	21.3 ± 0.6, ^d 19.9 ± 0.6 ^e
E , kJ mol ⁻¹	2.5 ^c	8.8 ± 0.8	2.5 ^c	7.7 ± 3.0
τ_e^0 , s × 10 ¹²	3.8	1.23 ^f	3.6 ± 0.5	1.1 ± 0.9, ^d 0.9 ± 0.8 ^e
$\Delta\omega_{os}^{273.1}$, s ⁻¹ × 10 ⁻⁴		2.0 ± 0.1	1.7 ± 0.1	1.7 ± 0.4, ^d 1.4 ± 0.3 ^e
ΔV^* , cm ³ mol ⁻¹			+7.1 ± 0.2	+7.1 ± 0.2
ΔV_o^* , cm ³ mol ⁻¹			+7.3 ± 0.3	+7.3 ± 0.3
$\Delta\beta^*$, cm ³ mol ⁻¹ MPa ⁻¹ × 10 ²			+0.1 ± 0.4	+0.1 ± 0.4

^a Errors quoted are standard deviations. ^b Nine-parameter fit; see text. ^c Fixed values. ^d For Bechtold's data at 11.5 MHz. ^e For our 8.133-MHz data. ^f Personal communication from J. P. Hunt. This value corrects the published one. ^g Reference 7. ^h Reference 8.

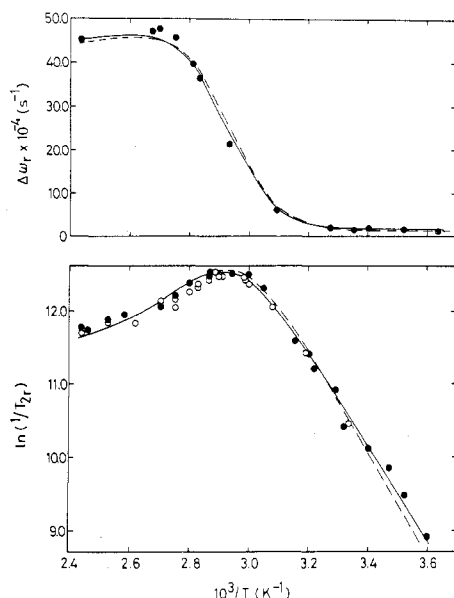


Figure 2. $\Delta\omega_r$ and $\ln(1/T_{2r})$ for $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ bulk water as a function of reciprocal temperature: (—) calculated from a simultaneous computer fit of all the data points; (---) calculated from a simultaneous computer fit of all the data together with the data of Bechtold et al.⁸ at 11.5 MHz; (O) solution I, $P_m = 0.002113$; (●) solution II, $P_m = 0.006540$.

It should be pointed out that many dynamic properties of water show anomalous pressure behavior, most notably the freezing point which lowers with compression, whereas in most other liquids the opposite effect is observed. This anomalous behavior implies that the water molecule reorients faster with increasing pressure. Water is a highly associated liquid with extensive hydrogen bonding. The effect of pressure is to destroy some of the tetrahedral open structure and distort the hydrogen bonds. This allows the water molecule to rotate faster, thus narrowing the lines.

Variable-Temperature Relaxation and Shifts for Ni(II) Solutions. The chemical shifts and line widths as a function of reciprocal temperature are shown in Figure 2. The solid lines are the result of a simultaneous nonlinear least-squares curve fit of all the data. The parameters obtained from the curve fitting are given in Table I, with the equivalent values from Bechtold's⁸ and Neely's⁷ published results. The reported values of ΔS^* are very different, but in fact, as discussed in an earlier publication,¹³ this parameter is exceedingly sensitive to small systematic errors¹⁸ and even to the exact method of analysis used. Further, as the exchange-controlled region occurs over a larger temperature range at higher field strength, the kinetic parameters derived will be better defined. Therefore, Bechtold et al.,⁸ working at 11.5 MHz, probably have the most accurate values of ΔH^* and ΔS^* , but a vari-

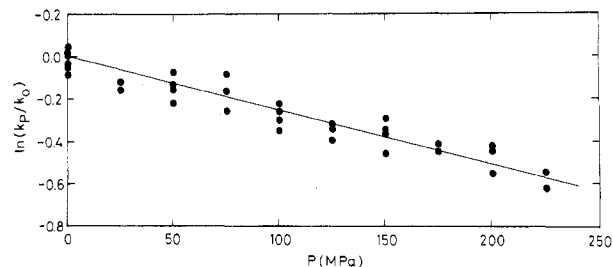


Figure 3. Experimental values of $\ln(k_p/k_0)$ for $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ in water as a function of pressure. The solid line is calculated from a computer fit of the data by using the full Swift and Connick equation.

able-field, variable-temperature study over a larger frequency range would be necessary to extend the relaxation information. In order to illustrate this point, we have fitted the 11.5-MHz data of Bechtold et al.⁸ together with our 8.133-MHz data. ΔH^* , ΔS^* , and E were common parameters for the two sets of data, and τ_e^0 , A/h , and $\Delta\omega_{os}$ were taken as different parameters for each of the two sets, to take into account any frequency dependence of these parameters. The results of this nine-parameter fit are shown in Table I. The dashed line in Figure 2 shows the calculated curve using these parameters.¹⁹ In the exchange-controlled region, although the difference in slope is not large, the extrapolated values of ΔS^* are very different. All other 11.5-MHz parameters are very close to those of Bechtold et al.⁸ Since the nine-parameter fit gives the best definition of the kinetic parameters, these results will be used in interpreting the variable-pressure data below, although any of our two sets of parameters from Table I could have been used.²⁰

Variable-Pressure, Constant-Temperature Measurements for Ni(II) Solutions. The results of the variable-pressure study are shown in Figure 3. We have measured the line width as a function of pressure in four separate experiments at four temperatures between 308 and 317 K. ΔV_o^* and $\Delta\beta^*$ were obtained as discussed elsewhere¹³ by a nonlinear least-squares curve fit to all four sets of data simultaneously, where k_0 was a different parameter for each set of data. In this analysis, the values of $1/T_{2m} = 1.9 \times 10^5 \text{ s}^{-1}$ and $\Delta\omega_m = 5.7 \times 10^5 \text{ s}^{-1}$ required in eq 2 were calculated by using the NMR parameters from the last column in Table I²⁰ and kept at their ambient pressure values.²¹ This treatment assumes that the volume of activation, ΔV_o^* , and the compressibility of activation, $\Delta\beta^*$, are independent of temperature. This assumption is surely correct over the small temperature range covered. When the compressibility term $\Delta\beta^*$ is equal to zero within experimental error, it can be neglected, and eq 9 reduces to a linear expression. We have used the symbol ΔV^* in the latter case to distinguish from ΔV_o^* , the volume of activation obtained by using quadratic expression (9).

The results of curve fitting are shown at the bottom of Table I. We clearly obtain no compressibility of activation within

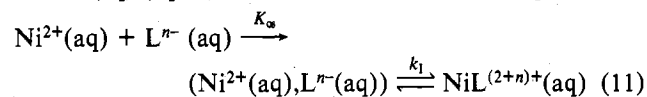
Table II. Experimental Values of the Activation Volumes for Solvent Exchange and Complex Formation Reactions of Ni²⁺(aq)

ligand	ΔV^* , cm ³ mol ⁻¹	ref	method
water	7.1 ± 0.2	this work	¹⁷ O NMR
ammonia	6.0 ± 0.3	27	T jump
Pada ^a	7.7 ± 0.3	27	T jump
glycinate	10 ± 1	28	T jump
murexide	12.2 ± 1.5	29	T jump
imidazole	11.0 ± 1.6	30	T jump

^a Pyridine-2-azodimethylaniline.

experimental error. Therefore, we could set $\Delta\beta^*$ equal to zero in eq 9 and fit ΔV^* with the linear equation. The value obtained is $\Delta V^* = +7.1 \pm 0.2$ cm³ mol⁻¹. The error quoted is the standard deviation, but it is clear that, due to possible nonrandom errors, volumes of activation can only be determined to within 1–2 cm³ mol⁻¹. This positive value for the volume of activation is an indication of a dissociative activation mode. For a dissociative mechanism (D) in octahedral complexes, it is usually assumed²² that the five-coordinate activated complex occupies the same volume in solution as the six-coordinate reactant. Thus, the partial molar volume V^0 of water represents the upper limit for the volume of activation; a value of $\Delta V^*/V^0$ equal to 1.0 implies a completely dissociated complex at the transition state. The partial molar volume of water is 18.15 cm³ mol⁻¹ at the mean temperature where the measures were performed. The value of $\Delta V^*/V^0 = 0.39$, notably smaller than 1.0, leads to the conclusion that the water exchange from Ni(II) follows an interchange mechanism (I_d). This is also supported by the negligible value of the compressibility of activation.²² In previous studies from this laboratory,^{2,13,23} three nonaqueous solvent exchanges from Ni(II) have been reported. The volumes of activation (ΔV^*) are² 11.4 ± 0.6 cm³ mol⁻¹ ($\Delta V^*/V^0 = 0.28$) for methanol exchange, 9.6 ± 0.3 cm³ mol⁻¹ ($\Delta V^*/V^0 = 0.18$) for acetonitrile exchange, and 9.1 ± 0.3 cm³ mol⁻¹ ($\Delta V^*/V^0 = 0.12$) for dimethylformamide exchange. All three results are in accord with an I_d mechanism. The $\Delta V^*/V^0$ in the case of water exchange is larger than any of the three $\Delta V^*/V^0$ values found for nonaqueous solvent exchanges, which suggests that the activation process follows a slightly more dissociative path when water is the exchanging solvent.

According to Eigen and Wilkins,²⁴ the rate of complexation of Ni²⁺(aq) (eq 11) is related to the water-exchange rate. In



the first step, rapid formation of an outer sphere complex occurs with equilibrium constant K_{os} . The second step is the interchange of a water molecule with the incoming ligand in the first coordination sphere. The activation mode for this step is dissociative, and the leaving rate of the water molecule determines the rate. The measured volume of activation ΔV^* for reaction 11 is therefore the sum of two contributions: first, the volume of formation of the outer sphere complex ΔV^0_{os} and second, the volume of activation for the interchange (I) step, ΔV^*_1 . For ion pairing, a positive value of ΔV^0_{os} is expected. Hemmes²⁵ has derived an equation from the Eigen–Fuoss treatment²⁶ which gives reasonable values for ΔV^0_{os} . When the complexation reaction involves only neutral ligands, the ΔV^0_{os} contribution is assumed to be negligibly small,²⁷ and the volume of activation then reflects only the breaking of the cation–water bond.

A few variable-pressure kinetic studies of complexation reactions with Ni(II) in water are reported in the literature. They are summarized in Table II together with their corresponding volumes of activation. Caldin and co-workers²⁷ have studied two complexation reactions with neutral ligands,

ammonia and pyridine-2-azodimethylaniline (Pada). In order to provide comparison between substitution by an anion and by neutral ligands, Grant²⁸ has extended the work to the reaction of glycinate anion with Ni(II). Following Hemmes,²⁵ this author has used the Eigen–Fuoss equations²⁶ to derive a value of $\Delta V^0_{\text{os}} = 3.2$ cm³ mol⁻¹, suggesting that ΔV^*_1 should be 7 ± 1 cm³ mol⁻¹. A similar procedure led Jost,²⁹ studying nickel(II)–murexide complex formation, to a value of $\Delta V^0_{\text{os}} = 3.5$ cm³ mol⁻¹, which produces a ΔV^*_1 of 8.7 cm³ mol⁻¹. All these ΔV^*_1 values are very similar to the ΔV^* for water exchange. Yu et al.³⁰ have reported a volume of activation for nickel(II)–imidazole complex formation, but the surprisingly large value obtained with this uncharged ligand is not discussed. Caldin et al.,²⁷ Grant,²⁸ and Jost²⁹ have all assumed that the rate of substitution is not affected significantly by the nature of the incoming ligand and conclude that considerable stretching of the nickel–water bond is likely to be responsible for the volume changes at the transition state. Our work shows clearly that their hypothesis that water exchange is the rate-determining step in these substitution reactions is correct, implying that the Eigen–Wilkins mechanism²⁴ operates well in aqueous nickel complex formation.

As shown in this work, volumes of activation for water exchange from metal ions are useful for the assignment of substitution mechanisms. Until now, the only reported value was -9.3 ± 0.3 cm³ mol⁻¹ for the associative interchange (I_a) on chromium(III).³¹ In order to obtain further insight into these fundamental exchange reactions, we are extending our high-pressure oxygen-17 NMR work to other +(II) and +(III) ions.

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Supplementary Material Available: Experimental data for (a) the temperature dependence of pure acidified water relaxation rate (Figure SI and Table SI) and of Ni(ClO₄)₂ bulk water relaxation rate (Table SII) and shift (Table SIII) and (b) the pressure dependence of the relaxation rates of pure acidified water (Table SIV) and Ni(ClO₄)₂ bulk water (Table SV) (11 pages). Ordering information is given on any current masthead page.

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- (18) For example, our FT NMR $1/T_2$ values are 1–21% narrower than the CW line widths measured by Neely and Connick at the same frequency.
- (19) Since τ_c^0 and E are strongly correlated, a decrease in E will cause τ_c^0 to increase, but, in any case, the choice of E will not significantly affect

- the magnitude of the residuals. For example, if E is fixed at 2.5 kJ mol^{-1} in the nine-parameter fit, a value of $\tau_e^0 = (4.2 \pm 0.5) \times 10^{-12} \text{ s}$ is obtained at 8.133 MHz and of $\tau_e^0 = (5.0 \pm 0.3) \times 10^{-12} \text{ s}$ at 11.5 MHz, which means that the NMR parameters derived in this way are compatible with those derived from the 8.133-MHz results alone.
- (20) The two different sets of parameters lead to $\Delta\omega_m = 5.8 \times 10^5 \text{ s}^{-1}$ and $1/T_{2m} = 1.2 \times 10^5 \text{ s}^{-1}$ for the five-parameter fit and to $\Delta\omega_m = 5.7 \times 10^5 \text{ s}^{-1}$ and $1/T_{2m} = 1.9 \times 10^5 \text{ s}^{-1}$ for the nine-parameter fit. To account for possible error in the evaluation of these two parameters, we have let $\Delta\omega_m$ vary by $\pm 10\%$ and $1/T_{2m}$ by $\pm 50\%$ around their value from the nine-parameter fit and introduced the extreme values in the computation of ΔV^* . The limiting values obtained are 6.7 and $7.3 \text{ cm}^3 \text{ mol}^{-1}$.
- (21) The effect of the pressure dependence of $\Delta\omega_m$ and $1/T_{2m}$ was examined by allowing each term to vary linearly by $+0.1\%/ \text{MPa}$. The change in ΔV^* is less than $+0.1 \text{ cm}^3 \text{ mol}^{-1}$ in both cases. See also ref 13.
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High-Pressure NMR Evidence for the Dissociative–Associative Crossover in the Ligand Substitution Mechanism of Octahedral Adducts of Niobium(V) and Tantalum(V) Halides¹

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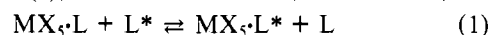
The ligand-exchange reaction $\text{MX}_5\text{L} + \text{L}^* \rightleftharpoons \text{MX}_5\text{L}^* + \text{L}$ ($M = \text{Nb, Ta}$; $X = \text{Cl, Br}$) has been studied in CH_2Cl_2 and CHCl_3 as a function of pressure by using ^1H FT NMR. Positive volumes of activation ranging from $+15.2 \pm 1.7$ to $+30.5 \pm 0.8 \text{ cm}^3 \text{ mol}^{-1}$ have been determined for dissociative (D) reactions when $L = \text{Me}_2\text{O, MeCN, Me}_3\text{CCN, (MeO)Cl}_2\text{PO, and (Me}_2\text{N)}_3\text{PS}$. Negative volumes of activation ranging from -10.7 ± 0.8 to $-19.8 \pm 0.9 \text{ cm}^3 \text{ mol}^{-1}$ have been determined for associative-interchange (I_a) reactions when $L = \text{Me}_2\text{S, Me}_2\text{Se, Me}_2\text{Te}$. The ΔV^*_{soln} can be neglected, and a model for the estimation of ΔV^*_0 (volume of activation extrapolated to zero pressure) is used for the D mechanism. It satisfactorily accounts for the changes in ligand, halide, and metal sizes. For the I_a reactions the ΔV^*_0 is difficult to predict quantitatively due to two opposing effects: the negative and positive contributions due to association and steric expansion in the highly crowded seven-coordinate transition state.

Introduction

During recent years a large number of high-pressure kinetic studies of inorganic systems have been reported.^{3,4} Most of them deal with ligand substitution reactions on octahedral or square-planar transition-metal complexes.⁵ For kinetically inert compounds, the reactions are sufficiently slow to be followed by conventional methods such as spectrophotometry or isotopic dilution. However, for performance of experiments under high pressure in kinetically labile systems, special instrumentation is required. Nowadays most of the important rapid reaction techniques have been adapted for use in high-pressure kinetics:⁶ pressure and temperature jump, and stopped flow. Recently we have built a high-pressure NMR probe head with the high spectral resolution and the good stability and accuracy of the temperature necessary for kinetic applications.^{7,8} We are presently using this technique for the mechanism elucidation of solvent exchange on metal ions and ligand exchange on transition-metal coordination compounds.^{2,9–13}

Usually the assignment of a mechanism to a substitution reaction (e.g., associative, interchange or dissociative, according to the classification of Langford and Gray¹⁴) is accomplished on the basis of different mechanistic tests: the order of the rate law, the entropy and enthalpy values obtained from a variable temperature study, steric effects of the reaction center and the reacting ligands, rate variations with changes in the ligand nucleophilicity, free energy relationship, etc. In some cases these tests cannot be applied or are difficult to interpret. The pressure effect on the reaction rate may then be very useful. It leads in transition-state theory to the volume of activation whose interpretation is simple and conclusive when electrostriction effects can be neglected, i.e., when there is no important development of charges or dipole moments from the

initial to the transition state. This is the case when the leaving and entering groups are uncharged as, for example, in solvent exchange on metal ions.^{2,10,11,13} In order to test the applicability of high-pressure NMR to chemical kinetics, we have chosen to study the pressure effect on the well-known¹⁵ ligand-exchange reaction (1), where $M = \text{Nb}$ or Ta , $X = \text{Cl}$ or Br , and



L (ligand) is a neutral Lewis base, with CH_2Cl_2 or CHCl_3 as solvent. This reaction shows an interesting ligand-controlled dissociative–associative crossover for the substitution mechanism and presents complete neutrality along the reaction profile, allowing the neglect of electrostriction effects.

The exchange reaction proceeds via a dissociative (D) mechanism when $L = \text{Me}_2\text{O, MeCN, Me}_3\text{CCN, (MeO)Cl}_2\text{PO, and (Me}_2\text{N)}_3\text{PS}$ ¹⁷ and via an associative interchange (I_a) mechanism when $L = \text{Me}_2\text{S, Me}_2\text{Se, Me}_2\text{Te}$.¹⁵ A different rate law is observed in each case; the NMR-determined mean lifetime of the complexed ligand τ_c is related to the kinetic laws by eq 2 and 3, where k_1 and k_2

$$1/\tau_c = -d[\text{MX}_5\text{L}]/([\text{MX}_5\text{L}]dt) = k_1 \quad (2)$$

$$1/\tau_c = -d[\text{MX}_5\text{L}]/([\text{MX}_5\text{L}]dt) = k_2[\text{L}] \quad (3)$$

are the first- and the second-order rate constants. On going from the first set of ligands to the second one, the activation parameters ΔH^* and ΔS^* decrease abruptly, with a change in sign for the latter. The dissociative and associative reactions are respectively accelerated and slowed down when the ligand and the reaction center are sterically hindered.¹⁵ The dissociative reactions fit to a linear free energy relationship of slope near unity,¹⁷ whereas for the associative reactions the reaction center exerts discrimination between the various nucleophiles.¹⁵