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 $\tau_e^0 = (4.2 \pm 0.5) \times 10^{-12}$ s is obtained at 8.133 MHz and of $\tau_e^0 = (5.0 \pm 0.3) \times 10^{-12}$ 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 $\Delta\omega_m = 5.8 \times 10^5$ s^{-1} and $1/T_{2m} = 1.2 \times 10^5$ s^{-1} for the five-parameter fit and to $\Delta\omega_m = 5.7 \times 10^5$ s^{-1} and $1/T_{2m} = 1.9 \times 10^5$ 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 ±10% and $1/T_{2m}$ by ±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 cm^3 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%/MPa. The change in ΔV^* is less than +0.1 cm^3 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) Halides[1]

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The ligand-exchange reaction $MX_5 \cdot L + L^* \rightleftarrows MX_5 \cdot L^* + L$ (M = Nb, Ta; X = Cl, Br) has been studied in CH_2Cl_2 and $CHCl_3$ as a function of pressure by using ^{1}H FT NMR. Positive volumes of activation ranging from +15.2 ± 1.7 to +30.5 ± 0.8 cm^3 mol^{-1} have been determined for dissociative (D) reactions when L = Me_2O, MeCN, Me_3CCN, $(MeO)Cl_2PO$, and $(Me_2N)_3PS$. Negative volumes of activation ranging from −10.7 ± 0.8 to −19.8 ± 0.9 cm^3 mol^{-1} have been determined for associative-interchange (I_a) reactions when L = Me_2S, Me_2Se, Me_2Te. The ΔV^*_{solv} 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 Gray[14]) 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-known[15] ligand-exchange reaction (1), where M = Nb or Ta, X = Cl or Br, and

$$MX_5 \cdot L + L^* \rightleftarrows MX_5 \cdot L^* + L \qquad (1)$$

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 = Me_2O,[15] MeCN,[16] Me_3CCN,[16] $(MeO)Cl_2PO$,[17] and $(Me_2N)_3PS$[17] and via an associative interchange (I_a) mechanism when L = Me_2S,[15] Me_2Se,[15] and Me_2Te.[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

$$1/\tau_c = -d[MX_5 \cdot L]/([MX_5 \cdot L]dt) = k_1 \qquad (2)$$

$$1/\tau_c = -d[MX_5 \cdot L]/([MX_5 \cdot L]dt) = k_2[L] \qquad (3)$$

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]

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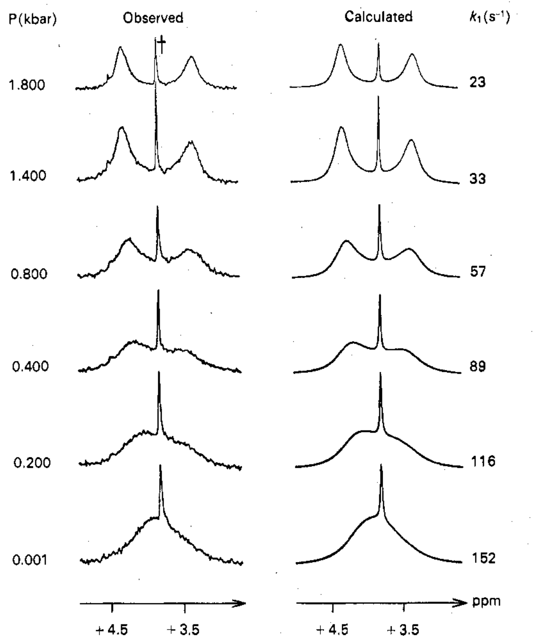

Figure 1. Observed and calculated ^{1}H NMR spectra for the D ligand exchange $TaBr_5 \cdot Me_2O + Me_2O^* \rightleftharpoons TaBr_5 \cdot Me_2O^* + Me_2O$ as a function of pressure in CH_2Cl_2 at 286.1 K. †: signal of the ^{13}C satellite of the solvent. $[TaBr_5 \cdot Me_2O] = 0.130$ *m* and $[Me_2O] = 0.114$ *m*.

Experimental Section

Sample Preparation. The metal halides were sublimed twice under vacuum. The preparation and the purification of the organic ligands have been described previously.[18-20] Dichloromethane was distilled twice from phosphorus pentoxide and stored over 4 Å molecular sieves. Nitrogen was bubbled through chloroform (IR grade, Fluka) before use. Samples for the ligand-exchange reactions were prepared in a glovebox by weighing the metal halide, the solvent, and the ligand. Concentrations were expressed as molalities, thus avoiding a correction for volume changes with pressure.

NMR Measurements. High-resolution ^{1}H FT NMR spectra were recorded on a Bruker WP-60 spectrometer. For the variable-temperature measurements, the temperature was stabilized with a Bruker BST-100/700 unit and measured with a 100-Ω platinum resistance attached to a Hewlett-Packard 2802 A digital thermometer by using a substitution technique. The variable-pressure measurements were performed with a high-pressure probe head described in detail elsewhere.[7,8] The temperature stability over several hours as measured by a 100-Ω platinum resistance[21] within the pressure cell was better than ±0.2 °C in the range −10 to +80 °C. The magnetic field inhomogeneity and instability were taken into account in the data treatment and assumed to be equal to the width of the solvent or the added tetramethylsilane signal (ca. 1 Hz).

Results and Data Treatment

The results of the kinetic measurements as a function of pressure for the ligand-exchange reactions (eq 1) are given in Table S-1 (supplementary material). The rate constants were derived from visual comparison of experimental spectra and calculated spectra obtained with the computer program ECHGNC of Delpuech et al.[22,23] The chemical shifts and the coupling constants required for these calculations have been tabulated previously.[24] The errors on the rate constants are estimated at 5–10%.

According to transition-state theory, the volume of activation ΔV^* is defined by eq 4, and its pressure dependence is given by eq 5, where $\Delta\beta^*$ is the compressibility coefficient of activation. Several data processing methods have been proposed to obtain the volume of activation from the rate constants.[25]

$$\Delta V^* = -RT(\partial \ln k/\partial P)_T \qquad (4)$$

$$\Delta\beta^* = -(\partial \Delta V^*/\partial P)_T \qquad (5)$$

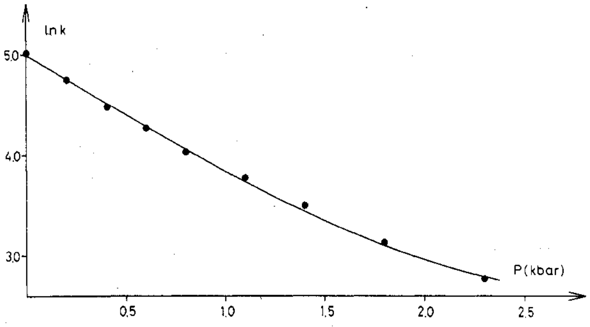

Figure 2. Pressure dependence of the rate constant for the D ligand exchange $TaBr_5 \cdot Me_2O + Me_2O^* \rightleftharpoons TaBr_5 \cdot Me_2O^* + Me_2O$ in CH_2Cl_2 at 286.1 K. $[TaBr_5 \cdot Me_2O] = 0.130$ *m* and $[Me_2O] = 0.114$ *m*. The solid line represents a quadratic fit to the data.

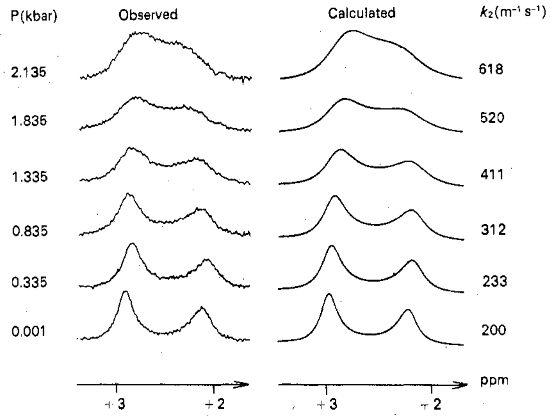

Figure 3. Observed and calculated ^{1}H NMR spectra for the I_a ligand exchange $TaBr_5 \cdot Me_2S + Me_2S^* \rightleftharpoons TaBr_5 \cdot Me_2S^* + Me_2S$ as a function of pressure in CH_2Cl_2 at 285.6 K. $[TaBr_5 \cdot Me_2S] = 0.160$ *m* and $[Me_2S] = 0.131$ *m*.

After comparison of different methods, we concluded that the quadratic function (eq 6) was well adapted to our experimental

$$\ln k = \ln k_0 - (\Delta V^*_0/RT)P + (\Delta\beta^*/2RT)P^2 \qquad (6)$$

data and our pressure range. This treatment recognizes that $(\partial \Delta V^*/\partial P)_T \neq 0$ and does assume that $(\partial^2 \Delta V^*/\partial P^2)_T = 0$, but it must be added that there is no physical justification for the use of a quadratic function. In the curve-fitting procedure $\ln k_0$, ΔV^*_0, and $\Delta\beta^*$ were treated as adjustable parameters. The same sign is expected for ΔV^*_0 and $\Delta\beta^*$, and only three exceptions are observed ($NbCl_5/(Me_2N)_3PS$, $TaCl_5/Me_2Te$, and $TaBr_5/Me_2Se$). In these three cases, standard errors with a confidence level of 95% on $\Delta\beta^*$ would include the zero value, and therefore a linear equation could be safely used. Figure 1 shows the observed and calculated spectra as a function of pressure for a ligand-exchange reaction with the dissociative (D) mechanism $TaBr_5 \cdot Me_2O + Me_2O^* \rightleftharpoons TaBr_5 \cdot Me_2O^* + Me_2O$. As expected for a reaction involving bond elongation or bond breaking at the transition state, the increase of pressure slows down the rate of ligand exchange. At ambient pressure a coalesced signal is indicative of a fast rate, and at high pressure one obtains two signals corresponding to the bound and free ligand, indicative of a much slower rate. The experimental rate constants are shown as a function of pressure in Figure 2. The negative slope of the curve gives a positive volume of activation consistent with a dissociative mechanism. For the same type of reaction, but with a different ligand, Figure 3 shows a quite different behavior. The associative-interchange (I_a) reaction $TaBr_5 \cdot Me_2S + Me_2S^* \rightleftharpoons TaBr_5 \cdot Me_2S^* + Me_2S$ involves the formation of a partial bond at the transition state, and the spectra display an opposite situation. The two resonances corresponding to the free and bound ligand for a slow exchange rate at normal pressure are

Table I. Exchange Reactions $MX_5{\cdot}L + L^* \rightleftarrows MX_5{\cdot}L^* + L$ with a D Mechanism[h]

$MX_5{\cdot}L$	T, K	ΔV^*_0	ΔV^*(estd)	$\Delta\beta^*$	ΔH^*	ΔS^*
$NbCl_5{\cdot}Me_2O$	286.3, 303.2	+28.7 ± 1.1[a]	+26.8	+6.6 ± 1.2[a]	18.4 ± 1.3[b]	+15.5 ± 4.5[b]
MeCN[c]	286.2	+19.5 ± 1.6	+13.3	+0.7 ± 1.6	17.0 ± 0.6[d]	+11 ± 2[d]
Me_3CCN[c]	287.4	+15.2 ± 1.7	+13.3	+2.0 ± 1.5	17.1 ± 0.5[d]	+10 ± 2[d]
$(MeO)Cl_2PO$[c]	284.7, 297.6	+20.5 ± 0.7[a]	+17.3	+3.7 ± 0.7[a]	15.3 ± 0.5[e]	+4 ± 2[e]
$(Me_2N)_3PS$	307.6	+17.7 ± 1.4[f]	+17.0	*f*	14 ± 2[e]	−6 ± 5[e]
$TaCl_5{\cdot}Me_2O$	310.1	+27.8 ± 1.2	+26.8	+8.3 ± 1.3	19.9 ± 1.1[g]	+14.0 ± 3.6[g]
$TaBr_5{\cdot}Me_2O$	283.8	+30.5 ± 0.8	+31.0	+6.5 ± 0.7	17.8 ± 0.8[g]	+14.7 ± 2.9[g]

[a] Arithmetic means of two experiments at different temperatures. [b] See supplementary material: Table S-2. [c] In $CHCl_3$. [d] Reference 16. [e] Reference 17. [f] Obtained from a linear fit; a quadratic fit gives +19.3 ± 6 and −3.4 ± 2.5, respectively. [g] Reference 15. [h] The following parameters have their units given in parentheses: volumes of activation ΔV^*_0 ($cm^3\ mol^{-1}$), compressibility coefficients of activation $\Delta\beta^*$ ($cm^3\ mol^{-1}\ kbar^{-1}$), enthalpies of activation ΔH^* ($kcal\ mol^{-1}$), and entropies of activation ΔS^* ($cal\ mol^{-1}\ K^{-1}$). The estimations of the volume of activation ΔV^*(estd) were obtained from the molecular model (see text). The solvent used was CH_2Cl_2. Errors quoted are standard deviations (ΔV^*_0, $\Delta\beta^*$) or standard errors with a confidence level of 95% (ΔH^*, ΔS^*).

Table II. Exchange Reactions $MX_5{\cdot}L + L^* \rightleftarrows MX_5{\cdot}L^* + L$ with an I_a Mechanism[f]

$MX_5{\cdot}L$	T, K	ΔV^*_0	$\Delta\beta^*$	ΔH^{*a}	ΔS^{*a}
$TaCl_5{\cdot}Me_2S$	283.8	−19.8 ± 0.9	−5.3 ± 0.8	5.2 ± 0.3	−25.6 ± 1.0
Me_2Se	287.5	−18.7 ± 1.0	−5.9 ± 1.0	5.7 ± 0.3[b]	−23.0 ± 1.1[b]
Me_2Te	284.7	−10.7 ± 0.8[c]	*c*	5.8 ± 0.2	−22.8 ± 0.9
$NbBr_5{\cdot}Me_2S$	279.9	−12.1 ± 1.0	−4.2 ± 1.0	4.2 ± 0.3	−23.6 ± 1.1
$TaBr_5{\cdot}Me_2S$	285.6, 294.2	−12.6 ± 0.8[d]	−0.3 ± 0.7[d]	6.9 ± 0.4	−24.3 ± 1.4
Me_2Se	285.2	−13.6 ± 0.8[e]	*e*	7.9 ± 0.6	−18.1 ± 2.2
Me_2Te	307.0	−16.4 ± 0.7	−3.1 ± 0.7	7.6 ± 0.9	−18.0 ± 3.2

[a] Reference 15. [b] See supplementary material: Table S-2. [c] Obtained from a linear fit; a quadratic fit gives −9.4 ± 0.8 and +1.5 + 0.9, respectively. [d] Arithmetic mean of two experiments at two different temperatures. [e] Obtained from a linear fit; a quadratic fit gives −12.2 ± 1.0 and +1.3 ± 0.9, respectively. [f] The following parameters have their units given in parentheses: volumes of activation ΔV^*_0 ($cm^3\ mol^{-1}$), compressibility coefficients of activation $\Delta\beta^*$ ($cm^3\ mol^{-1}\ kbar^{-1}$), enthalpies of activation ΔH^* ($kcal\ mol^{-1}$), and entropies of activation ΔS^* ($cal\ mol^{-1}\ K^{-1}$). The solvent used was CH_2Cl_2. Errors quoted are standard deviations (ΔV^*_0, $\Delta\beta^*$) or standard errors with a confidence level of 95% (ΔH^*, ΔS^*).

coalesced at high pressure. The rate constants are shown as a function of pressure in Figure 4 for comparison with the dissociative mechanism seen above. The slope is positive, leading to a negative volume of activation consistent with an associative mechanism. In this case the curvature is negligible, and a linear fit would give a similar ΔV^*_0 value.

The quality of the least-squares fits is excellent: $\overline{\Delta k/k}$ the arithmetic mean of the absolute value of $(k_{measd} - k_{calcd})/k_{calcd}$ is 0.6% in the best case and 4.0% in the worst one (Table I). This is far better than the believed accuracy in the determination of rate constants by NMR mentioned above. Following the habit of high-pressure kineticists, we have quoted the standard deviation for ΔV^*_0 and $\Delta\beta^*$. The mean standard deviation on the activation volumes is 1.2 $cm^3\ mol^{-1}$ in absolute value and 6% in relative value. The standard errors with a confidence level of 95% are obtained by multiplying the standard deviation by a Student's *t* value between 2 and 3, depending on the number of data points.

An important requirement before the comparison of the ΔV^*_0 values is to ascertain their temperature and solvent dependences. The temperature effect was studied in four cases: $NbCl_5{\cdot}Me_2O$ (in CH_2Cl_2; temperature difference 20.3 K), $NbCl_5{\cdot}Me_2O$ (in $CHCl_3$; 16.9 K), $NbCl_5{\cdot}(MeO)Cl_2PO$ (in $CHCl_3$; 12.9 K), and $TaBr_5{\cdot}Me_2S$ (in CH_2Cl_2; 8.6 K). The differences in the volume of activation are smaller than the standard errors (−0.4 ± 9.7, +3.1 ± 6.1, +0.8 ± 3.1, and −0.8 ± 4.6 $cm^3\ mol^{-1}$, respectively); moreover, these differences are sometimes negative and sometimes positive. According to these observations, we will admit that the temperature dependence can be neglected over the small range, 279.9–310.1 K, of our experiments. As it will appear later in the Discussion, it is of primary importance to know about a possible solvent dependence on ΔV^*_0. This effect was examined for three reactions: $NbCl_5{\cdot}Me_2O$ at two temperatures (284 and 302 K) and $NbCl_5{\cdot}Me_3CCN$ (287 K). The chloroform and the dichloromethane used as comparison solvents, with dielectric constants equal to 4.81 and 9.08 at 20 °C, did not give significant variations of the volume of activation (+3.0 ± 5.3, −0.5 ± 9.2, and 1.4 ± 7.3 $cm^3\ mol^{-1}$). Positive and negative ΔV^* variations within the standard errors enable us to consider the solvent effect negligible.

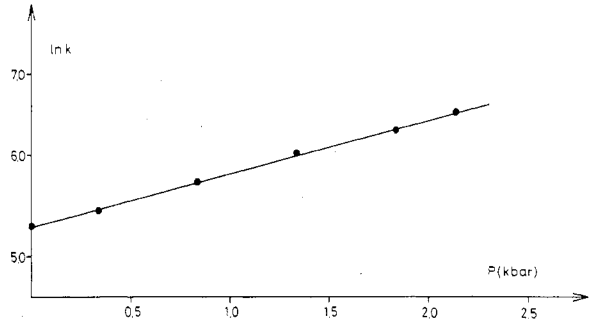

Figure 4. Pressure dependence of the rate constant for the I_a ligand exchange $TaBr_5{\cdot}Me_2S + Me_2S^* \rightleftharpoons TaBr_5{\cdot}Me_2S^* + Me_2S$ in CH_2Cl_2 at 285.6 K. $[TaBr_5{\cdot}Me_2S]$ = 0.160 *m* and $[Me_2S]$ = 0.131 *m*. The solid line represents a quadratic fit to the data.

Discussion

The activation parameters for the D and I_a ligand-exchange reactions on $MX_5{\cdot}L$ are summarized in Tables I and II, respectively. For the dissociative reactions both entropies[27] and volumes of activation are positive as expected for a transition state characterized by an increase in randomness and in volume. For all the associative-interchange reactions, the values of ΔV^*_0 and ΔS^* are negative in accord with the same arguments. It has been suggested[28] that for a given class of reactions, under similar conditions, a linear correlation between the volume and the entropy of activation should exist. However, inspection of Tables I and II shows that this is clearly not the case for this class of reactions.

The measured volume of activation ΔV^*_0 is usually considered[25] the combination of an intrinsic contribution ΔV^*_{int} and a solvation contribution ΔV^*_{solv}. The former results from changes in internuclear distances within the reactants during the formation of the transition state. In other words it reflects

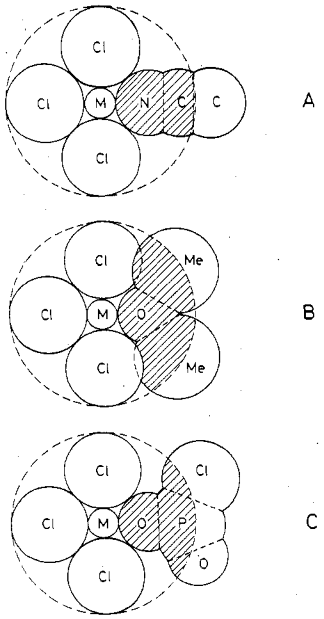

Figure 5. Molecular model used for the calculation of the volume of activation ΔV^*_0 in the dissociative mechanism. Only the three chlorides in the drawing plane are represented in the pentachloro complex: A, $MCl_5{\cdot}CH_3CN$; B, $MCl_5{\cdot}Me_2O$; C, $MCl_5{\cdot}(MeO)Cl_2PO$. Atoms of the exchanging ligand L situated entirely outside the first coordination sphere are not represented.

the bond stretching in a dissociative process or the bond formation in an associative one. The latter is due to the solvent electrostrictive effect when ions or dipoles are formed or neutralized at the transition state. The estimation of the solvation contribution is a major hindrance in the use of ΔV^*_0 for mechanism assignments, particularly in solvents of low polarity where the electrostriction effects are the largest. However, the exchange reactions we have studied involve neutral reactants and transition states and should lead to a negligible $\Delta V^*_{\mathrm{solv}}$ contribution. As mentioned above, no ΔV^*_0 differences could be detected between measurements made in chloroform and dichloromethane, enabling us to neglect $\Delta V^*_{\mathrm{solv}}$.

Several models have already been proposed for the estimation of the volumes of activation. They are mainly based on hard and incompressible spherical[3] or cylindrical[29] molecules. The lack of well-defined solvent coordination spheres and the volume difference between the metal and the exchanging ligands prevent us from using one of these previous models. For the reactions proceeding by a D mechanism, we have adapted the approach developed by Stranks.[3] Our model is based on the following hypotheses (see Figure 5).

(1) Each atom of the molecule $MX_5{\cdot}L$ is represented by a sphere with a dimension defined by its van der Waals radius. (2) In the ligand, L, the distance between the centers of two spheres is defined by the bond length, and the atoms are placed in agreement with the bond angles (see supplementary material). (3) The radius r of the first coordination sphere of the complex $MX_5{\cdot}L$ is defined by a sphere containing six halogens closely packed in octahedral symmmetry. In such an arrangement the central hole, 0.75 Å for six chlorides and 0.81 Å for six bromides, is sufficient to tolerate the niobium or the tantalum ions without a major distortion. (4) The $MX_5{\cdot}L$ representation is obtained by substituting one halogen with the exchanging ligand L and placing it in contact with the metal. This representation does not take into account a slight deformation of the octahedral symmetry, and an average value of 90° is always employed for the X–M–X angle. (5) The volume of $MX_5{\cdot}L$ is thus the volume of the first coordination sphere, $^4/_3\pi r^3$, plus the volume of the ligand that extends beyond the sphere. The volume of the intermediate MX_5 is assumed equal to the volume of the first coordination sphere. (6) The estimated volume of activation, which should be close to the volume of reaction $MX_5{\cdot}L \rightarrow \{MX_5 + L\}^*$, is readily seen to be the volume within the first coordination sphere that is filled with the exchanging ligand L. This volume is indicated by shading in Figure 5.

The molecular model does not include solvent participation at the transition state; i.e., the penetration of the solvent into the first coordination sphere synchronously with the departure of the leaving ligand is not considered.

Returning to Table I, several comparisons between ΔV^*_0 and ΔV^*(estd) must be underlined. First, according to the molecular model, the volume of activation is dependent on the leaving ligand atoms included in the first coordination sphere but should be independent of those in the following spheres. In other words, the molecular model predicts the same ΔV^*(estd) for the RCN series whatever R is considered (Figure 5A). Although the ΔV^*(estd) are smaller (13.3 cm^3 mol^{-1}) than the experimental ones, a larger ΔV^*_0 for MeCN (19.5 cm^3 mol^{-1}) than for Me_3CCN (15.2 cm^3 mol^{-1}) seems indicative of the independence of the alkyl substituent on the cyano group although the effect is not far above likely experimental error. Another example is the predicted ΔV^*(estd) similarity of $(MeO)Cl_2PO$ and $(Me_2N)_3PS$ in spite of the large differences in the substituents beyond the first coordination sphere, which is borne out experimentally.

The ligand-exchange reactions of Me_2O on $TaBr_5$ and $TaCl_5$ allow an interesting comparison between the nonexchanging halide ligands. The definition of the first coordination sphere is directly related to the diameter of X; therefore, for the same ligand L, a larger ΔV^*_0 is expected for the bromides. As it can be seen in Table I, the ΔV^*_0 values are in good agreement with the ΔV^*(estd), confirming the importance of the first coordination sphere in evaluating the volume of activation (Figure 5B).

Finally, the effect of the metal M is revealed in the Me_2O ligand exchange on $NbCl_5$ and $TaCl_5$. As mentioned above, the volumes of Ta^{5+} and Nb^{5+} are almost identical, and the two cations can be located in the octahedral complex without a major deformation. In this case, the volume of activation should be equal within the experimental errors, and this is totally confirmed by the experimental values.

The good agreement between ΔV^*_0 and ΔV^*(estd) implies that the ligand L is just leaving the first coordination sphere at the transition state. According to the molecular model, this corresponds to a bond stretching of about 150%. The bond is already completely broken before this point. Naively, we may consider that there are two energy-requiring processes. The first, occurring over a short range, is related to bond rupture and the second to transfer of the ligand to the second coordination sphere. It is possible that the second term may depend on the size of the solvent molecule. Experiments carried out with much larger (e.g., long alkyl chains) or smaller solvents (e.g., H_2O) would certainly provide interesting information. However, difficulties of dissolution or oxide formation made impossible the use of such solvents, and no solvent dependence has been observed with chloroform and dichloromethane. It must also be emphasized that the rearrangement of the complex to a possible distorted square pyramid may give a small negative contribution to ΔV^*_0, but in no way can it be compared to the hole left by the leaving ligand in the complex.

D and A mechanisms involve transfer of solvent between regions of high and low compressibility. Therefore, finite values of $\Delta\beta^*$ are expected, being positive and negative, respectively. I mechanisms characterized by solvent transfer between regions of similar compressibility yield negligible $\Delta\beta^*$

values. For metal–halide adducts it is also probable that the compressibility of the exchanging ligand is much less in the coordinate form than in the free form. Therefore, we should expect finite positive values for $\Delta\beta^*$ for the D reactions shown in Table I as is the case. However, we must stress that the interpretation and physical meaning of this parameter is still subject to discussion in the literature.[5]

The volumes of activation for the associative interchange reactions reported in Table II are all negative. Application of the molecular model to an A mechanism would give an absolute value of ΔV^*(estd) at least equal to the dimethyl oxide D reaction. However, considering the highly crowded complex, it would not be logical to consider the addition of a seventh ligand without any modification of the bond lengths and angles of the already present ligands. This observation shows the difficulty of using the molecular model for a ΔV^* estimation for associative reactions. The relatively small ΔV^*_0, −11 to −20 cm^3 mol^{-1}, instead of >−30 cm^3 mol^{-1}, would tend to suggest an I_a mechanism, with a predominant reaction step characterized by the formation of a partial bond between the entering ligand and the metal. However, it is important to point out that an A mechanism cannot be excluded only on the basis of the volume of activation. In fact a possible heptacoordinate intermediate may also be imagined with an elongation of the five M–X bonds. This effect would give a positive contribution to ΔV^*_0 and could be the reason of a less negative ΔV^*_0.

An inspection of Table II reveals that the volumes of activation for $NbBr_5{\cdot}Me_2S$ and $TaBr_5{\cdot}Me_2S$ are very similar as would be expected for the similar metal radii. The effect of the exchanging ligands for the tantalum chloride and bromide reactions exhibits opposite trends. The very negative value for $TaCl_5{\cdot}Me_2S$ is consistent with an associative interchange whose transition state must have short and equal bond lengths to leaving and entering ligands. The van der Waals radius of the bromide ion (1.95 Å) is not too different from that of the donor atom of the exchanging ligand (S 1.85 Å, Se 2.0 Å, Te 2.2 Å) unlike that of the chloride ion (1.8 Å) which is always smaller. Therefore, the positive contribution to ΔV^*_0 due to first coordination sphere expansion is expected to be similar for the pentachloride adducts, whereas it should increase in the pentabromide adducts in changing from Me_2S to Me_2Te ligands. For the pentabromide reactions we observe the reverse trend along the series which is not explained by the above argument. As pointed out above, the bond lengths of the exchanging ligands must be short and thus more or less equal in the three cases. The model predicts for such a picture that the most negative ΔV^*_0 values should be observed for the largest Me_2Te. For the pentachloride reactions it appears that first coordination sphere expansion determines the trend along the series. Thus the less negative value for $TaCl_5{\cdot}Me_2Te$ is explained by a short metal–chalcogen bond length but more expansion of the metal–halide bonds. It is interesting to note than an increase in the coordination sphere of 0.1 Å corresponds to a change of volume of 14 cm^3 mol^{-1}.

Some of the $\Delta\beta^*$ values are finite negative which, on the argument developed above, would suggest a A mechanism. However, for a crowded octahedral complex, the estimation of the volume of activation for an associative mechanism is almost impossible due to two opposing effects. The evidence for an A mechanism is not conclusive enough, and we will conclude with an interchange mechanism I_a with strong associative character.

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Registry No. $NbCl_5{\cdot}Me_2O$, 33726-50-0; $NbCl_5{\cdot}MeCN$, 21126-02-3; $NbCl_5{\cdot}Me_3CCN$, 25403-68-3; $NbCl_5{\cdot}(MeO)Cl_2PO$, 61277-07-4; $NbCl_5{\cdot}(Me_2N)_3PS$, 57965-43-2; $TaCl_5{\cdot}Me_2O$, 33772-76-8; $TaBr_5{\cdot}Me_2O$, 52757-74-1; $TaCl_5{\cdot}Me_2S$, 25403-69-4; $TaCl_5{\cdot}Me_2Se$, 52660-36-3; $TaCl_5{\cdot}Me_2Te$, 52660-37-4; $NbBr_5{\cdot}Me_2S$, 31200-84-7; $TaBr_5{\cdot}Me_2S$, 31113-20-9; $TaBr_5{\cdot}Me_2Se$, 52757-75-2; $TaBr_5{\cdot}Me_2Te$, 52757-72-9.

Supplementary Material Available: Pressure dependence of the rate constants (Table S-1), temperature dependence of the rate constants for the ligand-exchange reactions on $NbCl_5{\cdot}Me_2O$ and $TaCl_5{\cdot}Me_2Se$ (Table S-2), ionic, covalent, and van der Waals radii (Table S-3), bond lengths and bond angles (Table S-4) of atoms and molecules used in the molecular model, and molar volume of exchanging ligands (Table S-5) (6 pages). Ordering information is given on any current masthead page.

References and Notes

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