Table III. Reactions of Importance in the pH range 2.5–4.0

(1) $HNO_2 \rightleftharpoons H^+ + NO_2^- \quad pK_a = 2.95^a$
(2) $nH^+ + Mn^{II}CyDTA \rightleftharpoons Mn^{2+} + H_nCyDTA^b$
(3) $HNO_2 + H^+ + e^- \rightleftharpoons NO + H_2O \quad E^\circ = 1.00^c$
(4) $Mn^{III}CyDTA + e^- \rightleftharpoons Mn^{II}CyDTA \quad E^\circ = 0.81^d$
(5) $Mn^{II}CyDTA + HNO_2 + H^+ \rightleftharpoons Mn^{III}CyDTA + NO + H_2O^e$
(6) $2NO + O_2 \rightleftharpoons 2NO_2{}^f$
(7) $N_2O_4 + H_2O \rightarrow NO_2^- + NO_3^- + 2H^+ \quad k = 1.0 \times 10^3\ sec^{-1\ g}$
(8) $2NO_2 \rightleftharpoons N_2O_4 \quad K = 6.5 \times 10^{4\ g}$
(9) $2Mn^{III}CyDTA + NO_2^- + H_2O \rightleftharpoons 2Mn^{II}CyDTA + NO_3^- + 2H^+$

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after 1 day but the $Mn^{III}CyDTA$ could be regenerated by exposing the solution to air. This cycle could be repeated several times. These results suggest that, in the absence of oxygen, $Mn^{II}CyDTA$ simply catalyzes the disproportionation of nitrous acid, and, in the presence of oxygen, the overall reaction is the oxidation of nitrite to nitrate by molecular oxygen.

Acknowledgment. The authors are indebted to Dr. Mark Zetter for providing a copy of the Dye and Nicely computer program and to Professor Karl H. Pool for his helpful discussions.

Registry No. $Mn^{III}CyDTA^-$, 54182-32-0; NO_2^-, 14797-65-0; $Mn^{II}CyDTA^{2-}$, 14650-07-8.

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Dissociative–Associative Crossover for the Ligand-Substitution Mechanism in Octahedral Adducts of Niobium(V) and Tantalum(V) Halides[1,2]

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The neutral ligand-exchange reaction $MX_5 \cdot L + L^* \rightleftarrows MX_5 \cdot L^* + L$ for the octahedral adducts $MX_5 \cdot L$ (M = Nb, Ta; X = Cl, Br) proceeds *via* a dissociative mechanism when L = Me_2O and *via* an associative mechanism when L = Me_2S, Me_2Se, Me_2Te. A different rate law is observed in each case and on going from Me_2O to the other ligands, activation parameters change abruptly (ΔH^* decreases by 11 kcal/mol and ΔS^* by 30–40 eu). Reaction rates vary according to the change in effective charge on the metal and obey the following reactivity sequences: dissociative mechanism, $MCl_5 \ll MBr_5$; associative mechanism, $MF_5 > MCl_5 > MBr_5$. For the associative mechanism, the reaction center exerts discrimination between the various nucleophiles. The proposed dissociative and associative reactions are respectively accelerated and slowed down when the ligand is sterically hindered.

Introduction

Substitution processes on octahedral systems were believed for many years to be exclusively dissociative. However, a number of reactions were then investigated which seemed to be best explained by an associative mechanism.[3-14] For these reactions which have not eventually been explained by another mechanism, the conclusions often are based on one type of evidence only (*i.e.*, either activation parameters, or rate law, or steric effects, etc.), this being usually due to difficulties inherent to the system under study.

We wish to report here on a system for which it was possible to collect a wide variety of data which are consistent with an associative mechanism. If a change in ligand occurs however, the same system can react according to a dissociative mechanism.

In dichloromethane and in chloroform, the dimeric niobium(V) and tantalum(V) halides react quantitatively with Lewis bases to form monomeric nonelectrolyte[15,16] adducts with 1:1 stoichiometry.[17] The ligand-exchange reactions examined can be described by the equation

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

where M = Nb, Ta; X = Cl, Br; L = Me_2O, Me_2S, Me_2Se, Me_2Te, Et_2O, Et_2S. The two sites of free and complexed ligand are magnetically inequivalent and the rate of exchange is such that it can be determined by nmr methods.

Nucleophilic attack on octahedral ions with fewer than three d electrons was anticipated by Taube.[18] Using ligand-field theory, Orgel[19] arrived at the same conclusion by pointing out that an empty t_{2g} orbital facilitates the formation of a seventh bond. Niobium(V) and tantalum(V) are d^0 ions, and the occurrence of an associative mechanism would therefore not be surprising from a theoretical point of view.

Experimental Section

Materials. Dichloromethane was distilled twice from phosphorus pentoxide and stored over 4-Å molecular sieve. Nitrogen was bubbled through chloroform (IR grade, Fluka) before use. The metal halides were sublimed twice under vacuum. Dialkyl oxides and sulfides were purified and dried by standard methods. Dimethyl selenide and telluride were purchased as reagent grade materials (Strem) and were used without further purification.

Preparation of Complexes.[20] All preparative work was done in a drybox. The syntheses have been described.[17,21] All compounds gave excellent elemental analyses supporting the general formula $MX_5 \cdot L$.

Sample Preparation. Samples for the ligand-exchange reactions were prepared in the drybox by weighing the metal halide, the solvent, and the ligand. The molality units were transformed into molarity by use of the solvent densities at room temperature.

Nmr Spectra.[20] Spectra were obtained in CH_2Cl_2 solutions using a Varian A-60A spectrometer equipped with a variable-temperature probe. Temperature measurements were made with the Varian methanol and glycol samples. Line widths in absence of ligand exchange have been determined at low temperature, where the reaction is frozen on the nmr time scale. To minimize the effect of instrumental line broadening, the line width at half-height is given by

$$W = W^{\text{measd}} - W_{\text{TMS}}^{\text{measd}} \qquad \text{(I)}$$

where W^{measd} is the actual width on the spectrum.

The values of τ_C and τ_F, the mean lifetimes of the complexed and free ligands, were obtained from the Bloch equations as modified by McConnell.[22] In the slow-exchange region

$$1/\tau_C = \pi(W_C - W_C{}^0) \quad (\text{if } 1/\tau_C \leqslant (\pi/5)\Delta\nu_{CF}{}^0) \qquad \text{(II)}$$

where $W_C{}^0$ is the line width at half-height and $\Delta\nu_{CF}{}^0$ (Hz) the chemical shift difference between the signals, both in absence of exchange.

In the region of intermediate exchange

$$1/\tau_C = 1/\tau_F = \frac{\pi}{\sqrt{2}}[(\Delta\nu_{CF}{}^0)^2 - (\Delta\nu_{CF})^2]^{1/2} \qquad \text{(III)}$$

if the coordinated and free populations, P_C and P_F (with $P_C + P_F = 1$), are equal. Under these particular conditions, coalescence is observed when

$$1/\tau_C = 1/\tau_F = 2.222\Delta\nu_{CF}{}^0 \qquad \text{(IV)}$$

When $P_C \neq P_F$ in the region of intermediate exchange, $1/\tau_C$ was obtained by comparison of experimental spectra with calculated spectra. The program used was DNMR3.[23]

Above coalescence, in the fast-exchange region

$$1/\tau_C = \frac{4\pi P_C P_F{}^2(\Delta\nu_{CF}{}^0)^2}{W_{CF} - P_C W_C{}^0 - P_F W_F{}^0} \quad (\text{if } 1/\tau_C \geqslant 2\pi\Delta\nu_{CF}{}^0) \qquad \text{(V)}$$

$1/\tau_C$ and $1/\tau_F$ are related to the relative populations by

$$P_C\tau_F = P_F\tau_C \qquad \text{(VI)}$$

Results and Discussion

In a solution containing free dialkyl chalcogenide and its corresponding complex, an exchange of the free and complexed ligand takes place (eq 1). At low temperature, the nmr spectra show two well-separated signals and the signal situated at lower field corresponds to the coordinated ligand.[24] As the temperature is raised, the signals broaden and coalesce into a single one.

Rate Laws. If the ligand-exchange reaction is dissociatively controlled (first-order rate law), the rate-determining step is

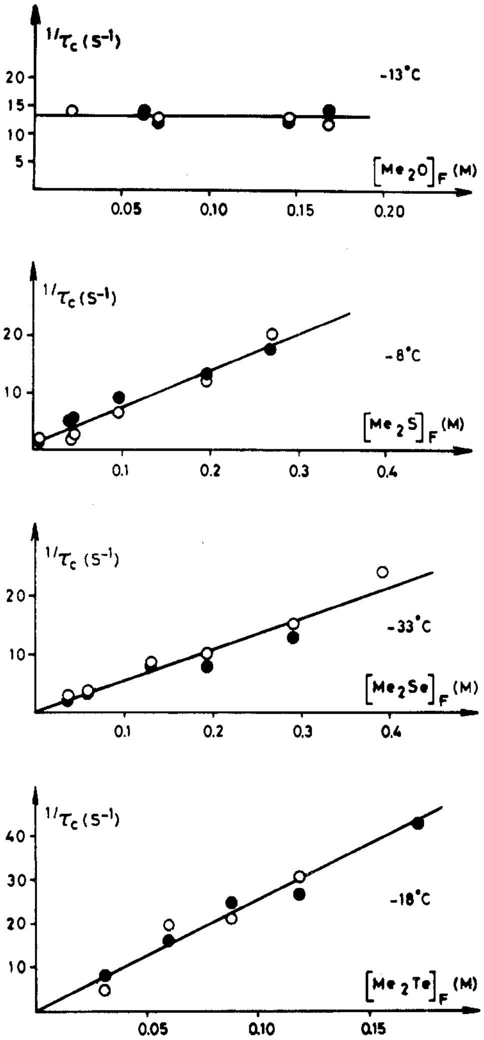

Figure 1. Ligand-exchange reactions $MX_5 \cdot L + L^* \rightleftarrows MX_5 \cdot L^* + L$ for $TaBr_5 \cdot L$ in CH_2Cl_2. $1/\tau_C$ calculated from the coordinated (○) and free (●) ligand *vs.* free ligand concentrations. $[TaBr_5 \cdot L]$ was between 0.05 and 0.07 *M*.

$$MX_5 \cdot L \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} MX_5 + L \qquad (2)$$

and $1/\tau_C$ is related to the kinetic law as in

$$1/\tau_C = -d[MX_5 \cdot L]/([MX_5 \cdot L]dt) = k_1 \qquad (3)$$

If the reaction is associative (second-order rate law), the rate-controlling step is

$$MX_5 \cdot L + L^* \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} MX_5 \cdot LL^* \qquad (4)$$

and

$$1/\tau_C = -d[MX_5 \cdot L]/([MX_5 \cdot L]dt) = k_2[L]_F \qquad (5)$$

If both associative and dissociative paths operate, the expression for $1/\tau_C$ is

$$1/\tau_C = k_1 + k_2[L]_F \qquad (6)$$

The rate law has been determined for every adduct at one or two fixed temperatures by varying the concentration of free ligand. The trivial supposition that the reaction is first order with respect to the complex has been checked.

The results in Figure 1 show that the adduct of $TaBr_5$ containing Me_2O exchanges ligand according to a first-order rate law, indicating a dissociative mechanism of reaction. In contrast, for adducts containing Me_2S, Me_2Se, and Me_2Te (henceforth called "soft dimethyl chalcogenides") there is a

Table I. Order of Reaction and Activation Parameters for the Ligand Exchange $MX_5 \cdot L + L^* \rightleftarrows MX_5 \cdot L^* + L$, in CH_2Cl_2

MX_5	L	Order of reacn[a]	ΔH^*, kcal mol^{-1}	ΔS^*, eu	$\Delta G^*_{0°}$, kcal mol^{-1}	Temp range, °C
$NbCl_5$	Me_2O	1st[b]	14.7 ± 0.6	4.0 ± 2.3	13.58 ± 0.06	−20 to +42[c]
	Me_2S	2nd	3.8 ± 1.0	−25.4 ± 4.2	10.72 ± 0.09	−57 to −7
$TaCl_5$	Me_2O	1st	16.8 ± 0.5	4.3 ± 1.5	15.68 ± 0.06	+2 to +82[c]
			19.9 ± 1.1	14.0 ± 3.6	16.12 ± 0.05	+3 to +73
	Me_2S	2nd	6.2 ± 0.2	−22.5 ± 0.7	12.30 ± 0.05	−70 to +65[c]
			5.2 ± 0.3	−25.6 ± 1.0	12.16 ± 0.04	−59 to +42
	Me_2Se	2nd	6.0 ± 0.3	−22.4 ± 1.3	12.09 ± 0.05	−63 to +70[c]
	Me_2Te	2nd	5.8 ± 0.2	−22.8 ± 0.9	12.00 ± 0.05	−67 to +41
$NbBr_5$	Me_2O	1st	15.9 ± 1.3	15.8 ± 5.3	11.55 ± 0.07	−52 to −2
	Me_2S	2nd	5.2 ± 0.3	−23.6 ± 1.1	11.67 ± 0.06	−78 to +37[d]
$TaBr_5$	Me_2O	1st	17.8 ± 0.8	14.7 ± 2.9	13.77 ± 0.08	−29 to +32
	Me_2S	2nd[e]	6.9 ± 0.4	−24.3 ± 1.4	13.50 ± 0.06	−22 to +30
	Me_2Se	2nd	7.9 ± 0.6	−18.1 ± 2.2	12.78 ± 0.06	−39 to +39
	Me_2Te	2nd	7.6 ± 0.9	−18.0 ± 3.2	12.51 ± 0.07	−29 to +27

[a] Full information about determination of rate laws is given in Figure 1 and Appendix 1 (supplementary material). [b] Reference 25. [c] In $CHCl_3$. [d] To avoid decomposition caused by direct attack of dimethyl sulfide, the metal halide is first dissolved in a 0.1 *M* solution of pivalonitrile in CH_2Cl_2. The exchange rate of dimethyl sulfide is not affected by this procedure. [e] Above 30°, a first-order term appears in the kinetic law.

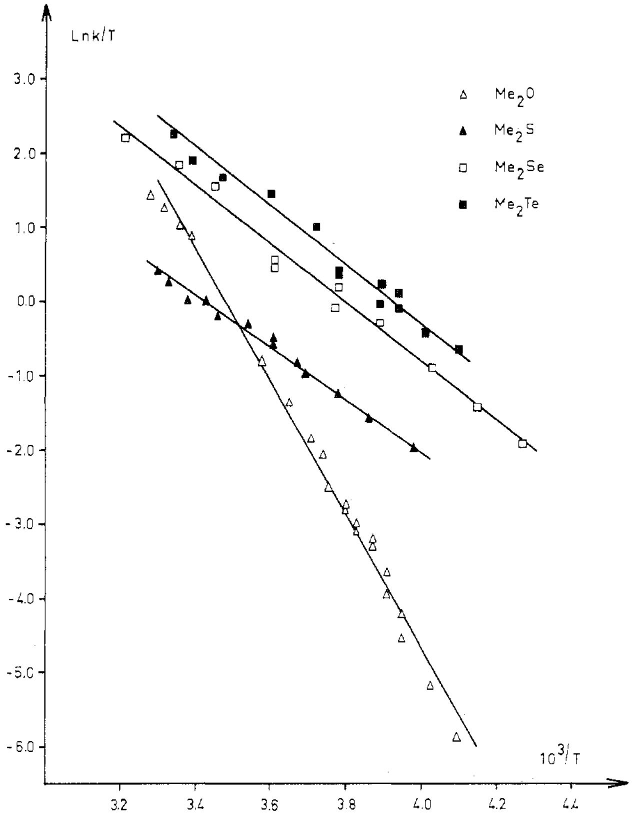

Figure 2. Arrhenius plots for ligand exchange in $TaBr_5 \cdot L$. [$TaBr_5 \cdot L$] was between 0.04 and 0.07 *M*, free ligand concentrations were between 0.04 and 0.20 *M*, and the solvent was CH_2Cl_2.

linear dependence of $1/\tau_C$ on the free ligand concentration. This can safely be accounted for by an associative mechanism, since pairing of reaction partners prior to exchange is not likely to be rate-determinant while it is absent in the case of Me_2O. The reaction orders observed for the adducts examined are listed in Table I and it can be seen that the behavior of $TaBr_5$ is shared by the other metal halides.

Activation Parameters. The rates of reaction as a function of temperature have been measured over the widest range allowed by solvents and $1/\tau_C$ equations. In the less favorable case, the temperature interval was still of 50°. The activation parameters in Table I were obtained from Arrhenius plots in which the best straight line has been determined by a least-squares analysis. A typical plot for the adducts of $TaBr_5$ is shown in Figure 2. For the other adducts, see Appendix 2 (supplementary material).

The activation enthalpy is lowered by 11 kcal/mol on going from the exchange of Me_2O to the reactions with soft dimethyl chalcogenides. Similarly, the activation entropy drops by 30 eu or more, to reach values typical of an associative mechanism with the soft dimethyl chalcogenides. As shown in Table I, this set of parameters parallels the pattern observed for the rate laws.

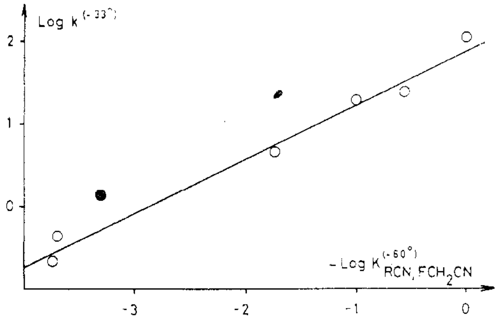

Figure 3. Linear free energy relationship for the reaction

$NbCl_5 \cdot RCN + RCN^* \rightleftarrows NbCl_5 \cdot RCN^* + RCN$

in chloroform. Open circles represent $NbCl_5 \cdot RCN$ with R = $(CH_3)_3$, CH_3, ICH_2, $BrCH_2$, $ClCH_2$, and FCH_2 from left to right. The filled circle represents $NbCl_5 \cdot Me_2O$.

Linear Free Energy Relationship (LFER). The relative stability constants of the adducts examined here have been reported earlier.[17] After the present kinetic study, it was possible to see if they would fit a LFER reported previously[26] for the adducts of $NbCl_5$ with various nitriles in chloroform. Figure 3 shows the position of the adduct with Me_2O. The agreement is quite good, considering the different type of ligand. Preliminary results from our laboratory[27] indicate that this relation will also be valid for ligands like MeSCN and $OP(OMe)Cl_2$. The fact that such a variety of different ligands can fit a LFER is a good confirmation for the dissociative nature of the reaction.

The situation changes completely, if we turn to Me_2S. An attempt to place the adducts formed by this ligand on the LFER plot fails completely. $1/\tau_C$ (measured in the same conditions as for Me_2O) is approximately three orders of magnitude larger than expected from the stability of the adduct, indicating a marked departure from the dissociative mechanism.

Nature of the Reaction Center. The effective charge on the metal is reduced on going from a pentachloride to a pentabromide, since bromide holds back its electrons less tightly than chloride. The dissociation of an electron-giving ligand therefore becomes easier, and as can be seen from Table II, the rate of reaction increases from MCl_5 to MBr_5 when the ligand is Me_2O. In the case of an associative reaction, we expect an

Table II. First- and Second-Order Rate Constants for the Ligand Substitution of Adducts Formed by Niobium(V) and Tantalum(V) Chlorides and Bromides in CH_2Cl_2 at 0°[a]

Ligand	$NbCl_5$	$NbBr_5$	$TaCl_5$	$TaBr_5$
Me_2O	80[b]	3200	0.7	54
Me_2S	15,000	2600	1000	90
Me_2Se			1200[a]	340
Me_2Te			1400	570

[a] k_1 (sec^{-1}) for Me_2O and k_2 ($M^{-1}\ sec^{-1}$) for the remaining ligands. [b] In $CHCl_3$.

opposite trend, since nucleophilic attack will be slower on a moderately charged atom. Table II shows that these predictions are verified when the ligand is a soft dimethyl chalcogenide.

Preliminary experiments on the adducts of the pentafluorides with Me_2S and Me_2Se are in agreement with the trends just mentioned and we have the reactivity sequences

dissociative mechanism: $MCl_5 << MBr_5$

associative mechanism: $MF_5 > MCl_5 > MBr_5$

These effects could also be accounted for by steric arguments: bromine atoms, being larger than chlorine atoms, favor dissociation and hinder nucleophilic attack. In fact, both explanations may be relevant and do not alter the conclusion. If the two opposite trends are to be explained, it is necessary to allow for an important participation of the entering ligand in the exchange reaction with the soft dimethyl chalcogenides.

Discrimination Exerted by the Reaction Center. The variation of reaction rate with nucleophilic strength of the entering ligand is a sought-for argument for an associative mechanism. In principle, this effect can only be measured if the leaving group remains the same. This is obviously not possible with an exchange reaction. However, if we assume that in the transition state the formation of the new bond is energetically more important than the breaking of the old one, the reaction rate should show some sensitivity to the nucleophilic strength of the entering ligand.

For the associative reactions of platinum(II), we known that Me_2Se is a stronger nucleophile than Me_2S. For our systems, we consider that the scales of relative stability of the adducts formed by the soft dimethyl chalcogenides[17] ($Me_2S < Me_2Se < Me_2Te$) give a good indication of nucleophilic strength for these ligands. Thus the more stable the complex, the faster should be the exchange reaction. Table II shows that this is indeed the case. The small effects observed can be ascribed to the small differences in nucleophilic strength for these ligands. It was unfortunately not possible to find other types of ligand which would exhibit an associative behavior.

In addition, the scale of relative stability for the adducts of $TaBr_5$ is expanded with respect to that of $TaCl_5$. It is therefore not surprising that the former reaction center shows a better differentiation between the various second-order rate constants than does $TaCl_5$.

Steric Effects. It was known from earlier measurements[17,28] that the stability of the adducts formed by niobium(V) and tantalum(V) halides is sensitive to a change in the alkyl groups of the dialkyl chalcogenide. In order to strengthen our proposition of an associative mechanism, we investigated the effect on reaction rates of replacing methyl by ethyl groups in the adducts of $TaCl_5$ with Me_2O and Me_2S. Two different mechanisms called for two different effects (while the effect on stability was a lowering of the latter in both cases). In both experiments, we determined the rate law for the exchange of diethyl chalcogenide at a fixed temperature. The rate constant thus obtained was compared with the rate constant for the corresponding dimethyl chalcogenide, as can be calculated for the same temperature from activation parameters.

In the case of $TaCl_5 \cdot Et_2O$, the reaction still shows a first-order rate law and the rate constant is 4.5 ± 0.3 sec^{-1} at −2.5°. This means that the reaction is about 3 times faster than for $TaCl_5 \cdot Me_2O$, where k_1 = 1.3 ± 0.3 sec^{-1}. This is the expected effect for a dissociative process. With $TaCl_5 \cdot Et_2S$, we also have conservation of rate law since the only modification with respect to Me_2S is a tiny first-order participation which possibly arises from experimental error. The second-order rate constant is 46 ± 4 $M^{-1}\ sec^{-1}$ at −23°. The reaction is thus approximately 25 times slower than for $TaCl_5 \cdot Me_2S$, where k_2 = 1170 ± 110 $M^{-1}\ sec^{-1}$. Such an effect indicates a crowded transition state and suggests an associative mechanism.

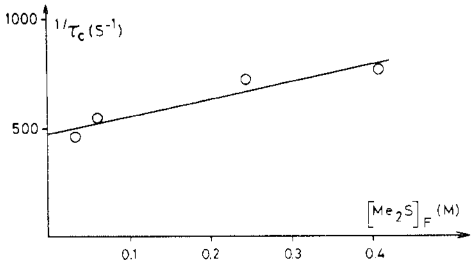

Figure 4. Ligand-exchange reaction for $TaBr_5 \cdot Me_2S$ in chloroform at 52°. $1/\tau_C$ calculated from the coalesced signal *vs.* free ligand concentration. $[TaBr_5 \cdot Me_2S] = 0.074\ M$. $1/\tau_C = k_1 + k_2 \cdot [Me_2S]$ with $k_1 = 320 \pm 130\ sec^{-1}$ and $k_2 = 740 \pm 670\ M^{-1}\ sec^{-1}$.

Temperature Dependence of the Rate Laws. If a reaction can proceed *via* two alternative paths, the activation energies for each of them can vary differently as a function of temperature. It is thus possible to favor one or the other mode of substitution. Examination of some activation parameters in Table I showed that such a behavior might be found for $TaBr_5 \cdot Me_2S$. The reasoning is based on the assumption that a possible dissociative reaction for this adduct would fit a linear free energy relationship[29] (taken here with an ideal slope of 1.0). We thus can calculate the activation free energy for this hypothetical dissociative process from known values

$$\Delta G^*_{Me_2S,diss} = \Delta G^*_{Me_2O,diss} + \Delta G^\circ_{Me_2S,Me_2O} \qquad (7)$$

where $\Delta G^*_{Me_2O,diss}$ is the activation free energy for the dissociative reaction of the adduct $TaBr_5 \cdot Me_2O$. $\Delta G^\circ_{Me_2S,Me_2O}$ is obtained from the relative stability constant[17] between the adducts formed by $TaBr_5$ with Me_2S and Me_2O.

Using eq 7 to calculate $\Delta G^*_{Me_2S,diss}$ at various temperatures ($\Delta G^\circ_{Me_2S,Me_2O}$ is assumed to be constant) we see that, at 50°, it becomes comparable in magnitude to $\Delta G^*_{Me_2S,assoc}$

$$\Delta G^*_{Me_2S,diss} = 13.0 + 2.0 = 15.0\ \text{kcal/mol} \qquad (8)$$

$$\Delta G^*_{Me_2S,assoc} = 14.7\ \text{kcal/mol} \qquad (9)$$

Therefore, the reaction could be partly dissociative in nature at this temperature. Figure 4 shows the result obtained at 52°. It can be seen from the graph that a first-order term has appeared and that two parallel mechanisms operate at that temperature.

Intermolecular Halide Exchange. Upon mixing two solutions containing respectively $TaCl_5 \cdot Me_2S$ and $TaBr_5 \cdot Me_2S$, intermolecular halide exchange occurs, leading to the formation of mixed compounds of general formula $TaCl_nBr_{5-n} \cdot Me_2S$ ($0 \leq n \leq 5$). The reason for conducting this experiment was to check that halide exchange does not influence ligand exchange.

Practically, the two solutions were prepared separately in dichloromethane and mixed at −80°. Figure 5 shows how the low-temperature spectra evolve after several rewarmings to 10°, finally displaying at least seven different species. This has been obtained previously[16] in more detail for a solution of $NbCl_5 + NbBr_5$ in acetonitrile by ^{93}Nb nmr. The time necessary for some appreciable halide exchange to occur at 10° has been estimated to 500 sec[30] from a series of spectra

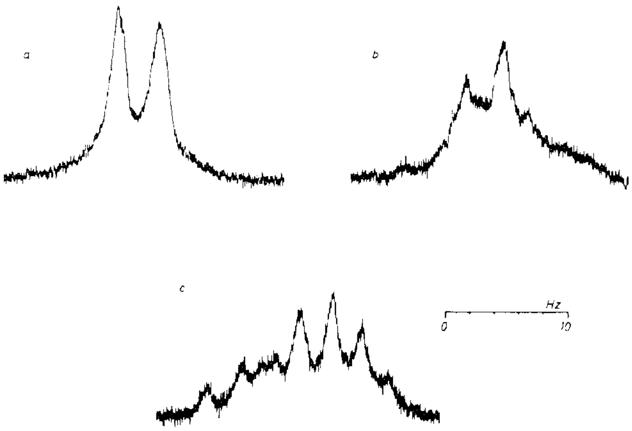

Figure 5. Intermolecular halide exchange in the system $TaCl_5$ + $TaBr_5$ + Me_2S in CH_2Cl_2. All spectra are measured at −80°: (a) immediately upon mixing components at −80°; (b) after warming for 500 sec at 10°; (c) after warming for 30 min at 10°. Original concentrations: $[TaCl_5] = 0.046\ M$, $[TaBr_5] = 0.046\ M$, $[Me_2S] = 0.186\ M$.

of the type shown in Figure 5. This has been compared to the half-life times of the slowest ligand-exchange reactions at that temperature. For a first-order reaction ($TaCl_5\cdot Me_2O$), $t_{1/2} = 0.4$ sec, and for a second-order reaction ($TaBr_5\cdot Me_2S$), $t_{1/2} = 0.1$ sec. We thus see that ligand exchange is approximately 10^3 times faster than halide exchange, which means that a participation of the latter in the ligand-exchange process can be excluded.

Conclusion

We believe that the ligand exchange in the octahedral adducts studied may occur through a penta- or a hepta-coordinated transition state. No information has been obtained about the respective reaction rates for the intramolecular halide rearrangement and the ligand exchange. It is therefore not possible to decide whether the entering ligand attacks in a cis or a trans position[31] with respect to the leaving group in the associative mechanism. Nonetheless, we hope to have well established the existence of ligand-controlled exchange mechanisms in a system which presents favorable characteristics: solvent–ligand[32] and solvent–metal halide interactions are weak compared to the interaction involved in the formation of an adduct, and charged species are absent in solution.[16] Moreover, we are not in the presence of a mechanism showing a progressive modification on changing ligands, and for example the smooth passage from an I_d to an I_a mechanism is not taking place in our system. The dissociative and associative substitution modes are basically different and operate independently.

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Registry No. $NbCl_5\cdot Me_2O$, 33726-50-0; $NbCl_5\cdot Me_2S$, 31113-18-5; $TaCl_5\cdot Me_2O$, 33772-76-8; $TaCl_5\cdot Me_2S$, 25403-69-4; $TaCl_5\cdot Me_2Se$, 52660-36-3; $TaCl_5\cdot Me_2Te$, 52660-37-4; $NbBr_5\cdot Me_2O$, 52757-78-5; $NbBr_5\cdot Me_2S$, 31200-84-7; $TaBr_5\cdot Me_2O$, 52757-74-1; $TaBr_5\cdot Me_2S$, 31113-20-9; $TaBr_5\cdot Me_2Se$, 52757-75-2; $TaBr_5\cdot Me_2Te$, 52757-72-9; $TaCl_5\cdot Et_2O$, 33772-75-7; $TaCl_5\cdot Et_2S$, 33772-77-9; Me_2O, 115-10-6; Me_2S, 75-18-3; Me_2Se, 593-79-3; Me_2Te, 593-80-6; Et_2O, 60-29-7; Et_2S, 352-93-2.

Supplementary Material Available. Detailed graphs used to determine rate laws and tables of numerical values for activation energies will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.50 for photocopy or \$2.50 for microfiche, referring to code number AIC40659S.

References and Notes

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