262. Adducts of Niobium (V) and Tantalum (V) Halides. XV[1]). Ligand Exchange of the Adducts with Some Phosphoryl Compounds[2])

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Summary

The ligand exchange $MX_5 \cdot L + {}^*L \rightleftarrows MX_5 \cdot {}^*L + L$ for the octahedral adducts $MX_5 \cdot L$, in an inert solvent (CH_2Cl_2 or $CHCl_3$) with neutral ligands, proceeds *via* a dissociative D mechanism when M = Nb, X = Cl and L = phosphoryl compound. A dissociative interchange I_d mechanism is suggested when M = Nb or Ta, and X = F. A first order rate law and positive values for ΔS^* (+4 to +14 cal K^{-1} mol^{-1}) are observed for the exchanges on the pentachloride adducts. However, a second order rate law and large negative values for ΔS^* (−15 to −24 cal K^{-1} mol^{-1}) are found for the intermolecular neutral ligand exchange (measured by ^1H-NMR.) and for the intramolecular fluorine exchange (measured by ^{19}F-NMR.) reactions on the pentafluoride adducts. The fluorine exchange is 2 to 5 times faster than the ligand exchange. The exchanges, on the pentachloride and on the pentafluoride adducts, are slowed down with increasing donor strength of the phosphoryl compound.

1. Introduction. - In dilute solution in inert organic solvents, dimeric niobium (V) and tantalum (V) chlorides and bromides, as well as tetrameric fluorides, react quantitatively with *Lewis* bases L to form, in general, monomeric non-electrolyte adducts $MX_5 \cdot L$ [1-6]. In solutions of these halides with an excess of L the ligand exchange (eq. 1) occurs. In the adducts of the niobium (V) and tantalum (V)

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

chlorides and bromides studied previously, the ligand exchange, followed by ^1H- or ^{31}P-NMR., occurs through a dissociative D mechanism when L = nitrile [7], ether [8], phosphorus oxychloride [4], and through an associative interchange I_a mechanism when L = dialkylsulfide, -selenide and -telluride [8]. The exchange between the equatorial and axial fluorine of $TaF_5 \cdot Me_2O$ in dichloromethane was studied by *Brownstein & Farrall* [9] by ^{19}F-NMR.; they favour an intramolecular process for a 1:1 mixture of tantalum pentafluoride and dimethyloxide. An excess of TaF_5 does not give any new species, but the exchange then occurs *via* an intermolecular route.

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[1]) Part XIV: [1].

[2]) Abstracted, in part, from the Ph. D. Thesis of *C. M. P. Favez*, University of Lausanne, 1976.

When dimethyloxide is in excess the new signals observed were attributed to the formation of ionic species with 1:2 stoichiometry, having the general formula $TaF_4L_n^+$. *Moss* [10] has shown that all 1:1 complexes of TaF_5 with Et_2O, Et_2S, and MeCN are soluble in an excess of ligand and give one sharp line in their ^{19}F-NMR. spectrum owing to rapid exchange.

Phosphoryl compounds R_3PO with R = Cl, OMe, NMe_2 are ideal *Lewis* bases for comparison of the mechanistic behaviour of the fluoride and chloride adducts. These adducts have a 1:1 stoichiometry in the presence of an excess of ligand, and the rate of exchange can easily be varied to fit the NMR. kinetic window by a proper choice of the substituents R in the phosphoryl compounds. In our study, carried out with an excess of phosphoryl compound, the rate of the intermolecular exchange process is obtained from ^1H- or ^{31}P-NMR., and the rate of the fluorine equatorial-axial exchange from ^{19}F-NMR.

2. Experimental Part. - The preparation and purification of the chemicals are described in [1]. Samples for the exchange reactions were prepared in a drybox (*Kewaunee Scientific Equipment* 2C2411) by weighing the metal halide, the solvent, and the ligand. The humidity, measured with a *Dupont* 26-303 Moisture Analyser, is about 6 ppm of water. Concentrations are expressed as molality (m). ^1H-NMR. spectra were recorded on a *Bruker* WP-60 FT spectrometer. ^{19}F- and ^{31}P-NMR. spectra were obtained on a *Bruker* HX-90 spectrometer operating in the pulsed *Fourier* transform mode, at 36.44 and 84.67 MHz, respectively. Temperature was stabilized with a *Bruker* BST-100/700 unit. Temperature measurements were made with the *Varian* methanol and ethyleneglycol samples, or by the substitution technique with a *Hewlett-Packard* 2802A digital thermometer. Chemical shifts downfield from the reference signal have been assigned positive signs.

The rate constants have been obtained by using the *Bloch* equations as modified by *McConnell* [11] (see also [8]) and by visual comparison of experimental spectra and calculated spectra using the DNMR3 [12] program or the EXCHNG [13] program, which is based on the *Kubo-Sack* stochastic theory, with *Bloch's* modified equations. In the latter program an exchange probability matrix, which represents the fraction of nuclei exchanging between the different sites, has to be introduced. This matrix is defined for each type of exchange, and obeys precise rules [14]. The chemical shifts and coupling constants have been tabulated previously [1].

3. **Results.** - 3.1 *Intermolecular ligand exchange.* In a solution containing a free phosphoryl compound L and its corresponding adduct $MX_5 \cdot L$, an exchange of the free and complexed ligand L occurs (eq. 1). At low temperature, in CH_2Cl_2 or $CHCl_3$, the ^1H-NMR. spectra show two separated doublets and the lower field doublet corresponds to the coordinated ligand. As the temperature is raised, the individual lines broaden and coalesce into a single doublet. The rate dependence of the ligand exchange has been determined for several adducts at fixed temperatures by varying the concentration of free ligand.

If the ligand exchange is a *first order process*, the mean lifetime τ_C of the ligand on the complex, determined by NMR., is related to the rate law by equation (2). If the reaction obeys a *second order process* the corresponding equation is (3). Two examples of rate law determinations

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

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

are given in *Figure 1*. The $(MeO)_3PO$ exchange follows a first order law in the $NbCl_5$ adduct and a second-order law in the NbF_5 adduct. The results of reaction order determinations are summarized in *Table 2*.

3.2 *Equatorial-axial fluorine exchange.* As an example, the ^{19}F-FT-NMR. spectrum of a 1:2 mixture of TaF_5 and $(MeO)_3PO$ in CH_2Cl_2 at −102° is given in *Figure 2.* At this low temperature, the spectrum is composed of one decet and one doublet in a 1:4 intensity ratio, characteristic of an AM_4X spectrum with $J(M,X)=0$. The axial fluorine is coupled to four equatorial fluorines, the resulting quintet being further split by coupling with the phosphorus (see [1]). This spectrum

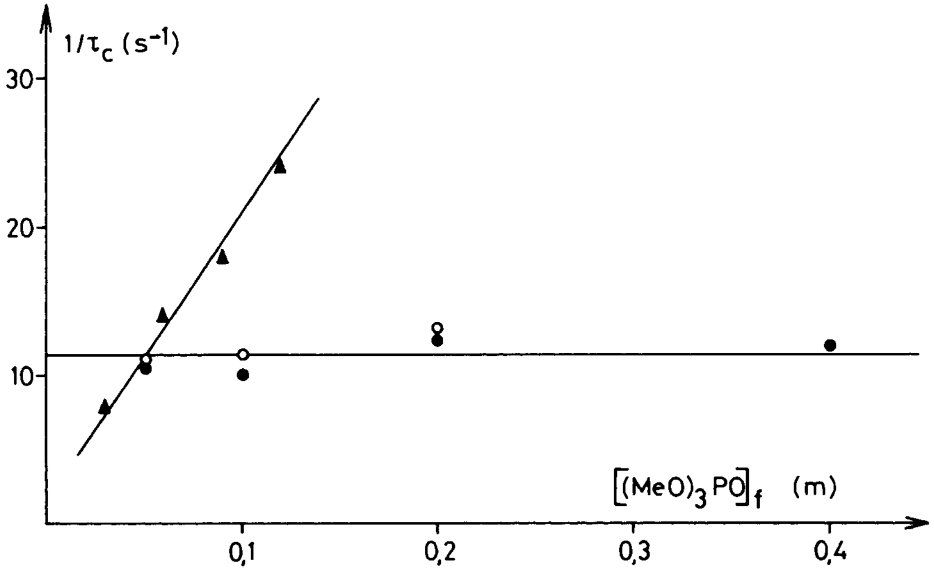

Fig. 1. *Ligand exchange reactions $NbX_5\cdot(MeO)_3PO+{}^*(MeO)_3PO \rightleftarrows NbX_5\cdot{}^*(MeO)_3PO+(MeO)_3PO$.* ○ and ● represent $1/\tau_C$ calculated from the coordinated and free ligand, for the $NbCl_5$ adduct in $(CHCl_2)_2$ at 112°. ▲ represents $1/\tau_C$ calculated with the DNMR3 program for the NbF_5 adduct in CH_2Cl_2 at −108°.
$[NbCl_5\cdot(MeO)_3PO]=0.10$ m and $[NbF_5\cdot(MeO)_3PO]=0.03$ m.

Table 1. *Transition probability matrix for the intramolecular exchange between axial and equatorial fluorine of $TaF_5\cdot L$.* Sites 1 to 10: axial decet, sites 11 and 12: equatorial doublet.

	1	2	3	4	5	6	7	8	9	10	11	12
1	−1	0	0	0	0	0	0	0	0	0	1/2	1/2
2	0	−1	0	0	0	0	0	0	0	0	1/2	1/2
3	0	0	−1	0	0	0	0	0	0	0	1/2	1/2
4	0	0	0	−1	0	0	0	0	0	0	1/2	1/2
5	0	0	0	0	−1	0	0	0	0	0	1/2	1/2
6	0	0	0	0	0	−1	0	0	0	0	1/2	1/2
7	0	0	0	0	0	0	−1	0	0	0	1/2	1/2
8	0	0	0	0	0	0	0	−1	0	0	1/2	1/2
9	0	0	0	0	0	0	0	0	−1	0	1/2	1/2
10	0	0	0	0	0	0	0	0	0	−1	1/2	1/2
11	1/128	1/128	1/32	1/32	3/64	3/64	1/32	1/32	1/128	1/128	−1/4	0
12	1/128	1/128	1/32	1/32	3/64	3/64	1/32	1/32	1/128	1/128	0	−1/4

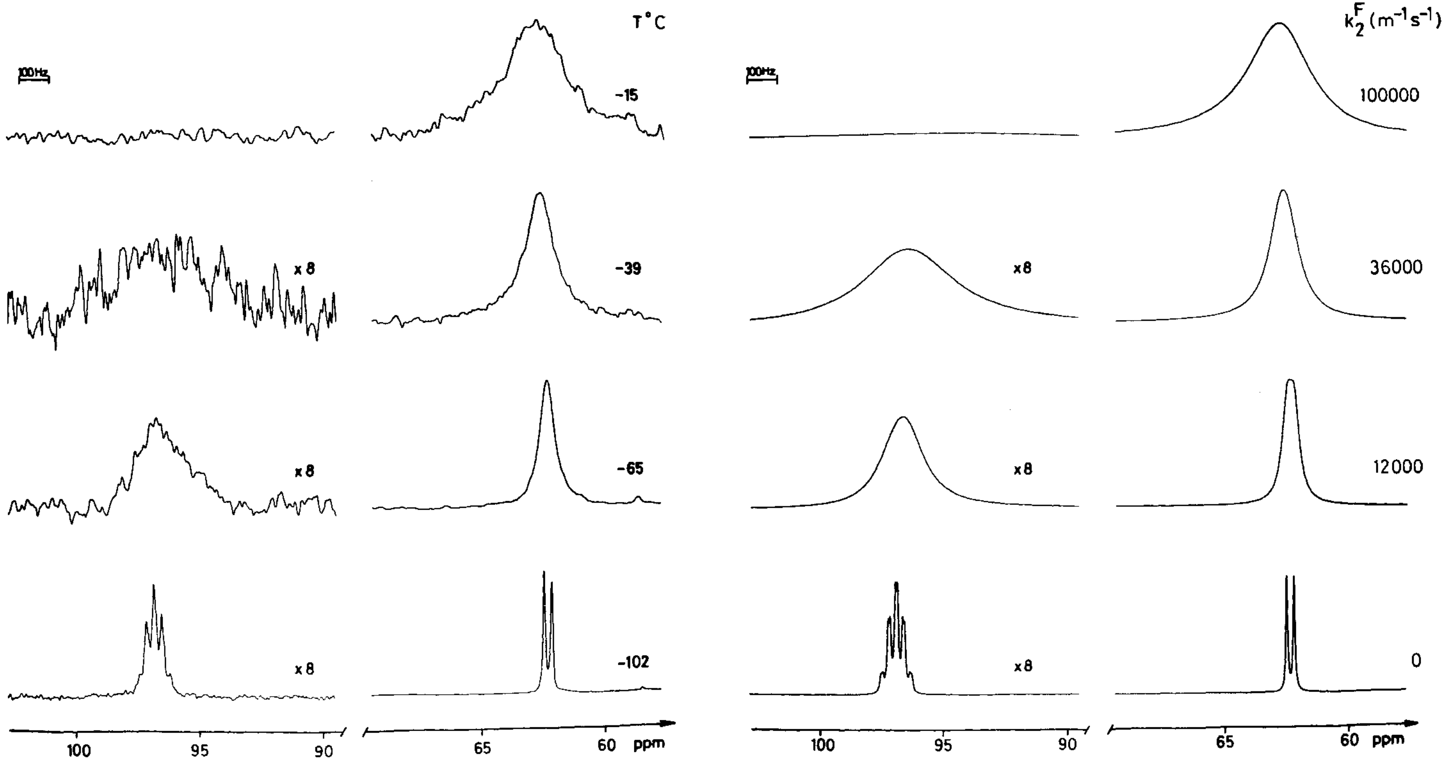

Fig. 2. *Observed, at T(°C), and calculated,* $k_2^F(m^{-1}s^{-1})$, *^{19}F-NMR. spectra for the intramolecular fluorine exchange in* $TaF_5 \cdot (MeO)_3PO$ *in* CH_2Cl_2. Internal reference: $CFCl_3$.

$[TaF_5 \cdot (MeO)_3PO] = 0.03$ *m* and $[(MeO)_3PO] = 0.03$ *m* is a good demonstration of the existence of the octahedral adduct $TaF_5 \cdot (MeO)_3PO$ in solution. As shown in the *Figure*, the fluorine signals broaden when the temperature is raised. At constant temperature, a similar broadening is observed when the concentration of free ligand is increased; however, no new signals appear in the spectrum, as previously observed for other *Lewis* bases [9] [10].

Two possible mechanisms for the fluorine exchange have been considered: firstly, an intramolecular exchange (the mean lifetime of an axial fluorine will be one quarter that of an equatorial fluorine), secondly, an intermolecular exchange involving, for example, free TaF_5 (the mean lifetimes of axial and equatorial fluorines will be equal [9]). For our solutions, with free ligand in excess, a good fit of the calculated with the experimental spectra has been obtained by postulating an intramolecular process. Typical spectra are given in *Figure 2.* The transition probability matrix used to calculate the spectra is reported in *Table 1.* By varying the concentration of free ligand, we have determined a second order dependence for this fluorine exchange (eq. 4).

$$1/\tau_{F_{axial}} = -d[MF_5 \cdot L]/([MF_5 \cdot L]dt) = k_2^F[L] \qquad (4)$$

The rates of ligand exchange and fluorine exchange have been measured over the widest temperature range allowed by the solvent and the NMR. kinetic window. The activation parameters reported in *Table 2* were obtained by least-squares analysis of *Arrhenius* plots.

Table 2. *Order of reaction, enthalpy ΔH^* (kcal mol^{-1}), entropy ΔS^* (cal K^{-1} mol^{-1}), and free energy ΔG^* (kcal mol^{-1}) of activation for the ligand exchange reaction $MX_5 \cdot L + {}^*L \rightleftarrows MX_5 \cdot {}^*L + L$, determined in CH_2Cl_2 by ^1H-NMR.*

MX_5	L	Order of reaction	ΔH^*	ΔS^*	$\Delta G^*_{0°}$	Temp. range[a]	$[MX_5 \cdot L]$	[L]
NbF_5	$(Me_2N)_3PO$	-	8 ±1	−15±5	12.2±0.3	− 57 to +32	0.022	0.033
	$(MeO)_3PO$	2nd	4.1±0.6	−20±3	9.7±0.2	−108 to −38	0.030	0.030
TaF_5	$(Me_2N)_2(MeO)PO$	-	5.7±0.6	−22±2	11.8±0.1	− 70 to +32	0.020	0.040
	$(Me_2N)(MeO)_2PO$	2nd	4.3±0.4	−24±2	11.0±0.1	−100 to 0	0.028	0.032
	$(Me_2N)(MeO)_2PO$[b]	-	4.4±1.0	−22±4	10.3±0.1	− 40 to +23		
	$(MeO)_3PO$	2nd	4.3±0.4	−20±1	9.7±0.1	−100 to +30	0.030	0.030
	$(MeO)_3PO$[b]	2nd	4.4±0.3	−18±1	9.4±0.1	− 70 to +32		
$NbCl_5$	$(MeO)_3PO$[c]	1st	-	-	-			
	$Cl(MeO)_2PO$[d]	1st	20 ±1	+11±4	17.5±0.2	+ 28 to +85	0.10	0.10
	$Cl_2(MeO)PO$[d]	1st	15.3±0.1	+ 4±2	14.2±0.1	− 19 to +43	0.10	0.10
	Cl_3PO[d][e]	-	16 ±1.5	+14±6	11.8±0.1	− 30 to +23	0.10	0.10
	$(Me_2N)_3PS$	1st	14 ±2	− 6±5	15.6±0.1	+ 5 to +40	0.05	0.05

[a] Experimental conditions for the determination of the activation parameters: temperature in °C, and concentration in molality.

[b] Data obtained by ^{19}F-NMR. for the axial fluorine and the equatorial fluorine exchange in $TaF_5 \cdot L$. The same samples were used for the ^1H and ^{19}F-NMR. measurements.

[c] In $(CHCl_2)_2$ at 112°: $[NbCl_5 \cdot (MeO)_3PO] = 0.10$ m and $[(MeO)_3PO] = 0.05$ to 0.40 m.

[d] In $CHCl_3$.

[e] By ^{31}P-NMR.

4. **Discussion.** The results summarized in *Table 2* show that the intermolecular ligand exchange for the niobium(V) chloride adducts with phosphoryl compounds follows a first order rate law with positive entropies of activation. This suggests a dissociative D mechanism (eq. 5).

$$\begin{aligned} &NbCl_5 \cdot R_3PO \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} NbCl_5 + R_3PO \\ &\qquad\qquad NbCl_5 + {}^*R_3PO \underset{k_1}{\overset{k_{-1}}{\rightleftarrows}} NbCl_5 \cdot {}^*R_3PO \end{aligned} \tag{5}$$

A correlation between the relative stability constants of the niobium(V) chloride adducts with their dissociative ligand exchange rate constants in a Linear Free Energy Relationship (LFER) was reported previously [7] [8]. In *Figure 3* the data for the adducts with $Cl_2(MeO)PO$ and Cl_3PO have been added (relative stability constants taken from [1]). The fact that such a variety of different ligands can fit a LFER[3]) of slope near unity (approximately 0.75) is a good indication for a D mechanism[4]) [16]. Thus, with increasing stability of these adducts, the ligand exchange rate decreases. The large increase in stability due to the conjugative effect in substituting Cl, by OMe and even more by NMe_2 in the phosphoryl compound

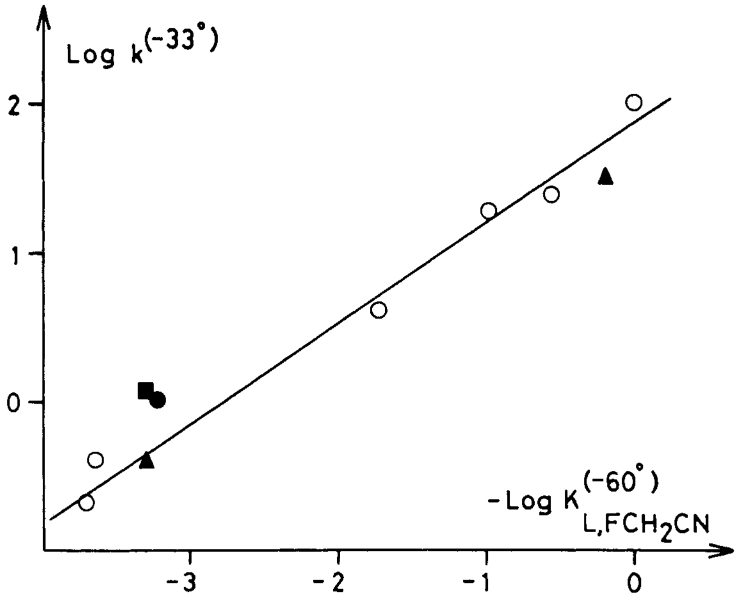

Fig. 3. *Linear free energy relationship for the reaction* $NbCl_5 \cdot L + {}^*L \rightleftarrows NbCl_5 \cdot {}^*L + L$ *in* $CHCl_3$, with the following ligand L (from left to right): ○ represents RCN, with $R = (CH_3)_3$, CH_3, ICH_2, $BrCH_2$, $ClCH_2$, FCH_2 [7]; ● represents Me_2O [8]; ■ represents MeSCN [15]; ▲ represents $Cl_2(MeO)PO$ and Cl_3PO.

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[3]) Rigorously, the stability and kinetic data should be given for the same temperature.

[4]) For an associative ligand exchange the slope would have the opposite sign.

is reflected in the free enthalpy of activation ΔG^*. The extrapolated ligand exchange rate constant for the $Cl(MeO)_2PO$ adduct at −33° is only $0.3 \cdot 10^{-3} s^{-1}$; for the $(MeO)_3PO$ adduct it is necessary to work at +112° in 1,1,2,2-tetrachloroethane to observe an NMR. line-broadening; and for the $(Me_2N)_3PO$ adducts no kinetic effect could be detected by NMR. even at +120°. At this point it is interesting to recall that *Good & Merbach* [8] have observed a dissociative-associative crossover for the ligand exchange mechanism on going from the niobium(V) chloride adduct with dimethyloxide to the more stable analogue with dimethylsulfide. One may have thought that the trimethylphosphate adduct, which is about 10^3 times more stable than that of dimethylsulfide, would also exchange through an associative mechanism owing to its better donor strength in these adducts. This is not the case; the observed first order rate law implies a D mechanism also.

The adduct $NbCl_5 \cdot (Me_2N)_3PS$, which is at least 10^{10} times less stable than its $(Me_2N)_3PO$ analogue [1], follows a first order rate law. For this thiophosphoryl adduct we also suppose a D mechanism despite the low value of the entropy of activation. The replacement of the oxygen phosphoryl donor atom by a sulfur atom does not produce a dissociative-associative mechanism crossover in this case.

The ligand exchange reaction for the niobium(V) and tantalum(V) pentafluoride adducts are much faster than for their pentachloride analogues. The observation of a second order rate law immediately rules out a dissociative D mechanism. This leads us to consider a heptacoordinated transition state or intermediate consistent with the large negative values of the activation entropies ΔS^* (−15 to −24 cal K^{-1} mol^{-1}). The second-order rate constants reported in *Table 3* show that the ligand exchange is slowed down when the ligand's nucleophilic strength increases. This can be explained by assuming that the formation of the new bond is energetically less important in the transition state than the breaking of the old one, which is the case for a dissociative (d) activation mode. We therefore, suggest a dissociative interchange I_d mechanism, involving the formation of an outer sphere complex followed by a dissociative ligand exchange between the first and the second coordination sphere (eq. 6 and 7). If the concentration of the outer sphere complex is small ($K_{os} \cdot [R_3PO] \ll 1$) the rate law is given by (8). The results show a second order rate law *(Figure 1)* with no curvature at the highest free ligand concentration. This implies a small preequilibrium constant K_{os}.

$$MF_5 \cdot R_3PO + {}^*R_3PO \overset{K_{os}}{\rightleftarrows} \{(MF_5 \cdot R_3PO)^*R_3PO\} \tag{6}$$

$$\{(MF_5 \cdot R_3PO)^*R_3PO\} \overset{k}{\rightleftarrows} \{(MF_5 \cdot {}^*R_3PO)R_3PO\} \tag{7}$$

$$-d[MF_5 \cdot R_3PO]/dt = k \cdot K_{os} \cdot [MF_5 \cdot R_3PO][R_3PO] = k_2^1[MF_5 \cdot R_3PO][R_3PO] \tag{8}$$

The intramolecular axial-equatorial fluorine exchange and the intermolecular ligand exchange are closely related. The ^{19}F-NMR. measurements also indicate a second order rate law, and the activation parameters are approximately equal.

Table 3 shows that fluorine exchange rate constants k_2^F exceed the ligand exchange rate constants k_2^L by a factor of 2 to 5. This can be explained by a decrease in the activation energy for fluorine exchange due to the ligand present in the outer sphere complex.

Table 3. *Ligand exchange rate constants* $k_2^L (m^{-1}s^{-1})$ *and fluorine exchange rate constants* $k_2^F (m^{-1}s^{-1})$ *for the adducts* $TaF_5 \cdot L$ *in* CH_2Cl_2 *at* −20°.

L	$k_2^L \cdot 10^{-3}$	$k_2^F \cdot 10^{-3}$	k_2^F/k_2^L
$(Me_2N)_2(MeO)PO$	0.82 ± 0.09	4 ± 1	5 ± 2
$(Me_2N)(MeO)_2PO$	4.7 ± 0.9	15 ± 3	3 ± 1
$(MeO)_3PO$	43 ± 6	89 ± 11	2.1 ± 0.5

The change from a D to an I_D mechanism observed from pentachloride to pentafluoride adducts can be accounted for by steric arguments; fluorine, being smaller than chlorine atoms, favours the coordination in a second sphere. In addition, the increase of the effective charge on the reaction centre going from a metal chloride to a metal fluoride allows a better stabilisation of a higher coordinated transition state in the case of the fluoride adducts.

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