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Adducts of Antimony(V) Pentachloride with Neutral Lewis Bases. Part II. Kinetics and Reaction Mechanism: a Variable Temperature and Variable Pressure Proton NMR Study*

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Abstract

The ligand exchange reaction $SbCl_5 \cdot L + {}^*L \rightleftharpoons SbCl_5 \cdot {}^*L + L$ has been studied in CH_2Cl_2 and $(CHCl_2)_2$ as a function of temperature and of pressure by using ^1H NMR. First order rate laws, positive activation entropies ranging from +9.8 to +37.3 cal K^{-1} mol^{-1}, positive activation volumes from +18.2 to +30.0 cm^3 mol^{-1} and a linear free energy relationship of slope -1.09 ± 0.06 have been observed for a series of L including nitriles, ethers, amides and –PO donor ligands. It is concluded that a limiting dissociative, D, mechanism exists for the whole series of ligand exchange reactions studied.

Introduction

In the preceding article [2], vibrational and NMR spectroscopy were used to demonstrate that the adducts of $SbCl_5 \cdot L$ (L = RCN, $R_{3-n}R'_nPO$, ethers and various other oxygen donors) may be assigned to the C_{4v} symmetry point group in both the solid form and in solution in inert solvents. The presence of ionic species, resulting from auto-ionisation reactions, was shown to be minimised by using nonpolar solvents and ligands whose adducts with $SbCl_5$ have relatively low stability constants. In the light of these observations, sample conditions may be optimised to permit kinetic measurements. This paper deals with the determination of parameters helpful in assigning the mechanism of ligand exchange for the reaction:

$$SbCl_5 \cdot L + L^* \rightleftharpoons SbCl_5 \cdot L^* + L \qquad (1)$$

Since there exists a magnetic inequivalence between the protons at the bound and free ligand sites, and since the rate of exchange falls in a domain amenable to ^1H NMR measurement, a series of variable concentration, variable temperature and variable pressure NMR measurements was undertaken in order to provide a complete mechanistic assignment for such a reaction. We have thus established that a first-order rate law holds for all the ligands studied, and that the activation parameters ΔH^*, ΔS^* and ΔV^* are large and positive for these ligands. These criteria are accepted [3] as being of primary importance in establishing the reaction mechanism, indicating in this case that the reaction proceeds via a limiting dissociative, D, mechanism (according to the classification of Langford and Gray [4]).

Experimental

Sample Preparation

All the samples used were prepared as described in the preceding article [2]. Relatively low polarity solvents, either CH_2Cl_2, CH_3Cl or $(CHCl_2)_2$ (or their deuterated analogs) were used in all cases. For the concentration dependence studies, the concentration of $SbCl_5$ was maintained at 0.050 m (m = mol kg^{-1}), whilst that of the ligand was varied from a minimum of 0.012 m to a maximum of 0.204 m, depending on the particular solution studied. Samples used in the variable temperature and variable pressure work were 0.05 m and 0.10 m in $SbCl_5$, respectively, with the exception of the THF and $POCl_3$ solutions, which had $SbCl_5$ concentrations of 0.40 m and 0.30 m, respectively. The $[SbCl_5]$ to [ligand] ratio was 1:2 throughout.

NMR Measurements

The spectrometer operating conditions have been described previously [2]. The variable pressure NMR studies made use of the purpose-built high pressure NMR probe head described elsewhere [5]. It is designed for use with a Bruker WP 60 FT spectrometer, and is capable of reaching pressures of 500 MPa. Temperature variation is achieved by circulating

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*Part 26 of the series 'High-Pressure NMR Kintetics', for Part 25, see ref. 1. Taken, in part, from the *Ph.D. Thesis* of J.E.K.

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gaseous N_2 or methylcyclohexane through a double helicoidal groove cut into the walls of the high pressure bomb, the temperature being measured via a platinum resistance. The sample is contained in a 1.5 mm external diameter glass capillary tube, fitted with a Teflon liquid/liquid separator. The ^1H resolution thus obtainable is *ca.* 1 Hz. The field was frequency locked using the ^{19}F signal of an external sample.

Data Treatment

In the slow exchange region the rate constants are obtained from the spectral line-widths. In the cases of intermediate and rapid exchange, least-squares curve fitting of theoretical (program derived from EXCNG [6]) to experimental spectra were performed. The magnetic field inhomogeneity and instability were taken into account in the data treatment using the solvent signal.

Results

In solution in a low polarity solvent, $SbCl_5 \cdot L$ adducts undergo the ligand exchange reaction described in eqn. (1) as shown in a preliminary report [7]. At low temperatures, the exchange is slow on the NMR time scale, and the ^1H NMR spectra exhibit two well separated signals, the high frequency resonance being due to the coordinated ligand. The ^1H NMR chemical shifts are listed in the preceding article in Table III. As the temperature is raised, both signals broaden and eventually coalesce, as a result of the increase in the rate of chemical exchange between the bound and free ligands. In such a situation, the dependence of the exchange rate on ligand concentration allows the rate law for the ligand exchange reaction to be determined. Furthermore, the activation parameters ΔH^*, ΔS^* and ΔV^* may be obtained for this reaction from the temperature (for ΔH^* and ΔS^*) and pressure (for ΔV^*) dependence of the ligand exchange rate, as indicated below.

Rate Law

If the ligand exchange reaction is dissociatively controlled, the rate determining step is

$$SbCl_5 \cdot L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SbCl_5 + L \qquad (2)$$

and the reaction is first order, $1/\tau_c$ (the inverse residence time of the coordinated ligand) being related to the kinetic law by:

$$1/\tau_c = -d[SbCl_5 \cdot L]/([SbCl_5 \cdot L]dt) = k_1 \qquad (3)$$

If the reaction is associative, the rate determining step is:

$$SbCl_5 \cdot L + L^* \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} SbCl_5 \cdot LL^* \qquad (4)$$

This displays a second order rate law, and

$$1/\tau_c = -d[SbCl_5 \cdot L]/([SbCl_5 \cdot L]dt) = k_2[L]_F \qquad (5)$$

where $[L]_F$ is the concentration of the free ligand. If both associative and dissociative pathways occur, then

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

In this work, the rate law has been determined for 11 adducts at a given temperature by varying the concentration of the free ligand and recording the ^1H NMR spectrum of the solutions. The results are given in Table I. Figure 1 illustrates the results of such a variable concentration study for the adducts of $SbCl_5$ with dimethylether and diethylether. As with all other ligands considered, a first order rate law was observed, the lifetime of the bound and free ligands being independent of the free ligand concentration.

Activation Parameters

The temperature dependence of the rate constant k may be expressed by the Eyring equation:

$$\ln(k/T) = \ln(k_B/h) + (\Delta S^*/R) - (\Delta H^*/RT) \qquad (7)$$

where k_B is the Boltzmann constant, h is Planck's constant, and R is the ideal gas constant. By recording the NMR spectra as a function of temperature, the temperature dependence of the rate constant k may be obtained, and hence the activation parameters ΔH^* and ΔS^*. An example of this is shown in Fig. 2, for the $SbCl_5 \cdot L$ adducts of dimethylether and diethylether and tetrahydrofuran, the best straight line having been determined by a least-squares analysis. The results for seventeen of the adducts studied in the previous article [2] are listed in Table I.

When pressure, P, is considered as a variable, it is related to the rate constant k by [8, 9]:

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = \frac{-\Delta V^*}{RT} \qquad (8)$$

where ΔV^* is known as the volume of activation of the reaction. Another parameter, $\Delta\beta^*$, the compressibility of activation, is often taken into account. It is defined as minus the pressure derivative of ΔV^*,

$$\Delta\beta^* = -\left(\frac{\partial \Delta V^*}{\partial P}\right)_T \qquad (9)$$

and describes the pressure dependence of ΔV^*, representing the excess compressibility coefficient of the transition state over that of the reactant species. Several data processing methods have been proposed to obtain the volume of activation from the rate constant [10]. After comparison of different methods, it was concluded [11] that the quadratic function, eqn. 10, below,

TABLE I. Order of Reaction and Activation Parameters for the Ligand Exchange Reaction $SbCl_5{\cdot}L + {}^*L \rightleftharpoons SbCl_5{\cdot}{}^*L + L$ in CH_2Cl_2 (except where stated).[a] The Concentration of $SbCl_5$ was 0.05 m Except when L = THF (0.40 m) and when L = $POCl_3$ (0.30 m). The $[SbCl_5{\cdot}L]:[L]$ Ratio was 1:1 Throughout

Ligand (L)	Order of reaction	ΔH^* (kcal mol^{-1})	ΔS^* (cal K^{-1} mol^{-1})	ΔG^* (298 K) (kcal mol^{-1})	Temperature range (K)
TMU[b]	1st	28.89 ± 1.63	21.75 ± 4.19	22.40 ± 0.39	367 to 414
DMA[b]	1st	30.05 ± 0.94	25.76 ± 2.43	22.37 ± 0.21	367 to 404
DMF[b]	1st	29.79 ± 1.39	23.93 ± 3.62	22.65 ± 0.32	367 to 404
$Cl((CH_3)_2N)_2PO$[b]	1st	26.63 ± 1.09	17.57 ± 2.86	21.39 ± 0.23	356 to 403
$(CH_3O)_3PO$[b]	1st	27.19 ± 0.58	21.34 ± 1.57	20.83 ± 0.11	347 to 394
THF[b]		24.12 ± 0.21	25.46 ± 0.65	16.52 ± 0.02	298 to 368
$Cl(CH_3O)_2PO$[c]	1st	17.74 ± 0.53	9.82 ± 1.82	14.81 ± 0.03	265 to 325
$Cl_2((CH_3)_2N)PO$		16.91 ± 0.47	9.78 ± 1.71	13.99 ± 0.04	261 to 298
$(CH_3)_2O$	1st	18.03 ± 0.26	16.97 ± 0.26	12.97 ± 0.03	243 to 293
$(CH_3)_2CO$	1st	16.71 ± 0.57	13.94 ± 2.17	12.55 ± 0.09	242 to 283
$Cl_2(CH_3O)PO$		14.36 ± 0.26	7.33 ± 1.08	12.17 ± 0.06	224 to 273
$(CH_3CH_2)_2O$	1st	22.98 ± 0.54	37.25 ± 2.05	11.87 ± 0.08	242 to 285
$(CH_3)_3CCN$	1st	16.74 ± 0.74	21.27 ± 3.11	10.40 ± 0.19	214 to 260
CH_3CN	1st	15.89 ± 0.42	18.41 ± 1.82	10.40 ± 0.13	214 to 251
CH_3SCN		13.63 ± 0.89	10.89 ± 3.98	10.38 ± 0.29	211 to 238
$POCl_3$		13.59 ± 1.40	14.48 ± 6.10	9.27 ± 0.43	208 to 254
ICH_2CN		13.49 ± 0.21	15.62 ± 1.01	8.84 ± 0.10	187 to 225

[a] By ^1H NMR, except when L = THF, ($^{13}C\{^1H\}$ NMR used). [b] In $(CHCl_2)_2$ solution. [c] In $CHCl_3$ solution.

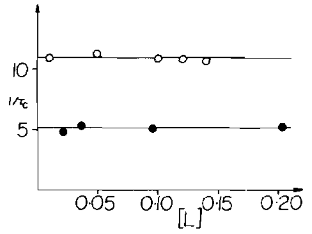

Fig. 1. The inverse mean lifetime, $1/\tau_c$, as a function of ligand concentration for the adducts of $SbCl_5$ with: $(CH_3)_2O$ (○) and $(CH_3CH_2)_2O$ (●) at 257 K and 249 K, respectively. The concentration of $SbCl_5$ was maintained at 0.05 m in both cases, and $1/\tau_c$ was determined using the slow exchange approximation in the case of $(CH_3)_2O$ and by computer simulation for $(CH_3CH_2)_2O$.

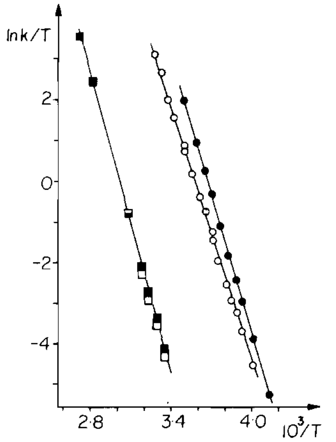

Fig. 2. Eyring plots for the ligand exchange reactions of the adducts of $SbCl_5$ with $(CH_3CH_2)_2O$ (●); $(CH_3)_2O$ (○) and THF (carbons α to oxygen: ■; carbon β to oxygen: □). In the case of $(CH_3)_2O$ and $(CH_3CH_2)_2O$ the concentration of $SbCl_5$ was 0.40 m, and that of THF was 0.80 m. The computer program EXCHIT was used to calculate the rate constants involved. The THF results were derived from $^{13}C\{^1H\}$ NMR spectra at 50.3 MHz.

$$\ln k = \ln k_0 - (\Delta V_0{}^*/RT)P + (\Delta\beta^*/2RT)P^2 \qquad (10)$$

(where $\Delta V_0{}^*$ and k_0 are the activation volume and the rate constant, respectively, at zero pressure) is the most appropriate for the experimental data and pressure range covered. This treatment assumes that $\Delta\beta^*$ is non-zero but that $(\partial\Delta\beta^*/\partial P^2)_T = 0$, and it must be stressed that there exists no physical justification for the use of such a quadratic function [11]. ΔV^* was determined for six $SbCl_5{\cdot}L$ adducts by variable pressure ^1H NMR and the results are listed in Table II, along with those of some comparable $NbCl_5{\cdot}L$ and $TaCl_5{\cdot}L$ adducts. In the curve fitting procedure, $\ln k_0$, $\Delta V_0{}^*$ and $\Delta\beta^*$ were treated as separately adjustable parameters. Figure 3 shows the observed and calculated ^1H NMR spectra of the methyl protons in bound and free diethylether as a function of pressure. It is clear that the rate of reaction decreases with an increase of the applied pressure, it being possible to resolve both triplets at pressures in excess of 200 MPa. Figure 4 illustrates the pressure dependence of the rate constant k for the adducts of $SbCl_5$ with both dimethylether and diethylether.

TABLE II. Volumes of Activation (ΔV_0^*) and Compressibility Coefficients of Activation ($\Delta\beta^*$) for the Ligand exchange Reactions of Octahedral $MX_5 \cdot L$ Adducts with Several Representative Ligands, L, in CH_2Cl_2 (except where stated)

$MX_5 \cdot L$	Temperature (K)	ΔV_0^* ($cm^3\ mol^{-1}$)	$\Delta\beta^*$ ($10^2\ cm^3\ mol^{-1}\ MPa^{-1}$)
$SbCl_5 \cdot Cl_2((CH_3)_2N)PO$	274.1	23.0 ± 0.6	
$SbCl_5 \cdot (CH_3)_2O$	273.3	27.2 ± 1.4	5.9 ± 1.0
$SbCl_5 \cdot (CH_3)_2CO$	264.5	28.1 ± 2.0	8.1 ± 1.9
$SbCl_5 \cdot (CH_3CH_2)_2O$	263.0	30.0 ± 1.5	3.8 ± 1.4
$SbCl_5 \cdot (CH_3)_3CCN$	236.2	18.2 ± 0.9	3.2 ± 0.6
$SbCl_5 \cdot CH_3CN$	253.6	24.7 ± 1.7	4.1 ± 1.8
$NbCl_5 \cdot (CH_3)_2O$[a]	286.3, 303.2	28.7 ± 1.1[c]	6.6 ± 1.2[c]
$NbCl_5 \cdot (CH_3)_3CCN$[a,b]	287.4	15.2 ± 1.7	2.0 ± 1.5
$NbCl_5 \cdot CH_3CN$[a,b]	286.2	19.5 ± 1.6	0.7 ± 1.6
$TaCl_5 \cdot (CH_3)_2O$[a]	310.1	27.8 ± 1.2	8.3 ± 1.3
$TaBr_5 \cdot (CH_3)_2O$[a]	283.8	30.5 ± 0.8	6.5 ± 0.7

[a] Ref. 8. [b] In $CHCl_3$ solution. [c] Arithmetic mean of two experiments at different temperatures.

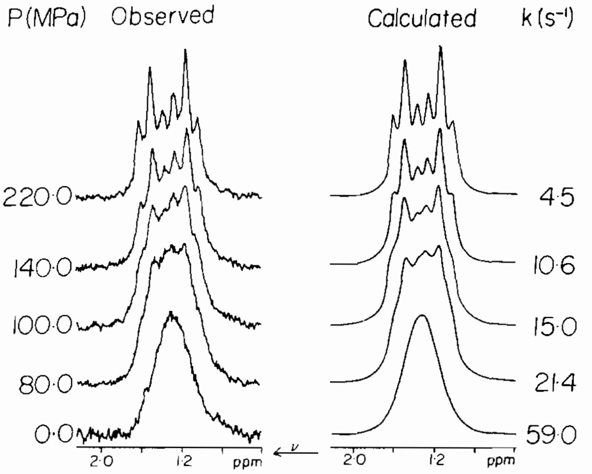

Fig. 3. Observed and calculated ^1H NMR spectra at 60 MHz and 263 K showing the pressure dependence of the ligand exchange reaction of the adduct of $SbCl_5$ with $(CH_3CH_2)_2O$ in $CHCl_3$. The methyl region of the spectrum is illustrated, the bound ligand resonating to high frequency of the free ligand. The solution contained 0.10 m $SbCl_5$ and 0.20 m $(CH_3CH_2)O$.

Discussion

The assignment of a mechanism to a substitution reaction relies on the results of various kinetic tests, some of which are detailed above. A first order rate law, together with large, positive values of the activation parameters ΔH^* and ΔS^*, are clear indications of a dissociative, D, mechanism [3, 4]. To test this mechanism we can also use the stability constants of the adducts determined in the preceding article [2] and see if when combined with the kinetic data they would fit to a linear free energy relationship. In Fig. 5 we show the free energies of activation as a function of the free energy of formation of the adducts (relative to $SbCl_5 \cdot CH_3CN$), where data are available, at 193 K. The linear correlation is excellent, except for diethylether, and the slope of -1.09 ± 0.06 is near to minus one, as expected for a D mechanism. Moreover, the observation of the large, positive values of ΔV^* listed in Table II is of particular relevance, since the volume of activation has been shown to be invaluable in confirming a mechanistic assignment [8]. The negative slope of the curves in Fig. 4 implies a positive volume of activation for both adducts. This is to be expected for a reaction involving bond elongation or bond breaking in the transition state. Such an observation is, in itself, indicative of a dissociative mode of activation. Taken together with the observed first-order

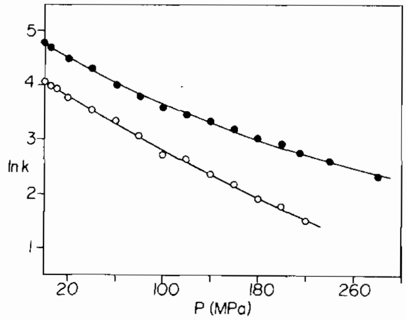

Fig. 4. The pressure dependence of the rate constant for the ligand exchange reactions of the adducts of $SbCl_5$ with $(CH_3)_2O$ (●) and $(CH_3CH_2)_2O$ (○) at 274 K and at 263 K, respectively. The concentration of $SbCl_5$ was 0.10 m and that of the ligand was 0.20 m in both cases. The $(CH_3)_2O$ solution was in CH_2Cl_2, whilst the $(CH_3CH_2)_2O$ solution was in CH_3Cl. The solid lines represent a quadratic fit to the data, and analysis yielded ΔV_0^* values of 27.2 ± 1.4 $cm^3\ mol^{-1}$ for $(CH_3)_2O$ and 30.0 ± 1.5 $cm^3\ mol^{-1}$ for $(CH_3CH_2)_2O$.

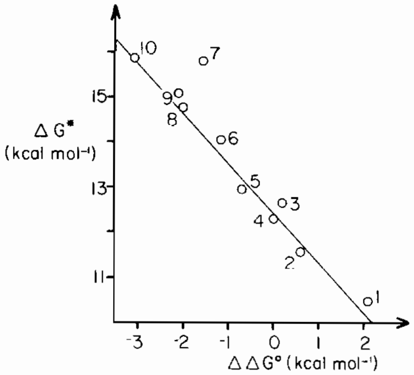

Fig. 5. Linear free energy relationship for reaction (1) in dichloromethane at 193 K. Numbered points correspond to the adducts $SbCl_5{\bullet}L$ with the following ligands, L: 1 = ICH_2CN; 2 = CH_3SCN; 3 = $(CH_3)_3CCN$; 4 = CH_3CN; 5 = $Cl_2(CH_3O)PO$; 6 = $(CH_3)_2CO$; 7 = $(CH_3CH_2)_2O$; 8 = $(CH_3)_2O$; 9 = $Cl_2((CH_3)_2N)PO$; 10 = $Cl(CH_3O)_2PO$.

rate law and the activation parameters, these results provide very convincing evidence that ligand substitution reactions on $SbCl_5{\cdot}L$ adducts proceed via a limiting dissociative, D, mechanism for all the ligands studied in the work. Such a conclusion must be viewed in the light of the few kinetic observations reported for comparable octahedral metal halide systems. Table II lists activation volumes and compressibility coefficients measured for six $SbCl_5{\cdot}L$ adducts, together with those for some analogous $NbCl_5{\cdot}L$ and $TaCl_5{\cdot}L$ adducts. It is clear from these values, as well as from the previously reported activation parameters and rate laws [8, 12], that $NbCl_5{\cdot}L$ and $TaCl_5{\cdot}L$ adducts also undergo dissociative substitution reactions. However, both Nb and Ta pentachloride adducts are known [8] to exhibit a dissociative–associative mechanistic crossover on going from so called 'hard' ligands, such as those reported in this study, to 'soft' ligands like $(CH_3)_2S$, $(CH_3)_2Se$ and $(CH_3)_2Te$. Adducts formed between the latter and Nb and Ta pentahalides react indubitably via an associative mechanism displaying second order rate laws and negative activation parameters [8]. From the results presented herein, it is impossible to predict whether such a crossover occurs with $SbCl_5{\cdot}L$ adducts with 'soft' ligands. A crossover is not expected for a d^{10} system like Sb^V, and does not occur for Sn^{IV}, for example.

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