

# A $^1\text{H}$ and $^{121}\text{Sb}$ NMR Study of Ionization Reactions in Antimony Pentachloride Donor—Acceptor Adduct Systems in Solution

P. STILBS<sup>a</sup> and G. OLOFSSON<sup>b</sup>

<sup>a</sup> Division of Physical Chemistry 2 and <sup>b</sup> Thermochemistry Laboratory, Chemical Center, University of Lund, S-220 07 Lund, Sweden

The occurrence of ionization reactions in the donor-acceptor adduct systems tetramethylurea (TMU)– $\text{SbCl}_5$  (I) and dimethyl sulphoxide (DMSO)– $\text{SbCl}_5$  (II) in 1,2-dichloroethane or dichloromethane solution and hexamethylphosphorotriamide (HMPT)– $\text{SbCl}_5$  in nitrobenzene solution (IV) has been established by direct observation of the  $\text{SbCl}_6^-$  ion by  $^{121}\text{Sb}$  magnetic resonance. Indirect evidence for the (donor)<sub>2</sub>– $\text{SbCl}_4^+$  ion is obtained from  $^1\text{H}$  magnetic resonance spectra. Fast exchange reactions involving antimony as well as the donors are indicated from both  $^{121}\text{Sb}$  and  $^1\text{H}$  resonance. While the weaker ethyl acetate  $\text{SbCl}_5$  adduct in 1,2-dichloroethane solution is shown to be nonionizing, the measured  $\text{SbCl}_6^-$ /adduct ratios in the systems, II, I, and IV are roughly 0.05, 0.1, and 0.3. Results from systems I and II can satisfactorily be interpreted in terms of the autoionization equation  $2(\text{donor})\text{SbCl}_5 \rightleftharpoons \text{SbCl}_6^- + (\text{donor})_2\text{SbCl}_4^+$ , but system IV shows more complex behaviour and the degree of ionization increases markedly with donor in excess of the ratio  $\text{HMPT}/\text{SbCl}_5 = 1.0$ .

Antimony pentachloride is a strong electron pair acceptor which forms numerous donor-acceptor adducts with electron-pair donating molecules. A number of adducts have been shown by X-ray diffraction studies to exist as discrete molecular adducts in the solid state.<sup>1–3</sup> Ionic salts containing the  $\text{SbCl}_6^-$  anion can result from interaction with acid chlorides which contain an easily ionizable chlorine atom.<sup>4</sup>

Evidence for the structure of the adducts in solution is less conclusive, but what is known is consistent with the assumption that they exist predominantly as molecular adducts in solvents of low dielectric constant.<sup>1,5,6</sup> Autoionization reactions resulting in the formation of  $\text{D}_2\text{SbCl}_4^+$

and  $\text{SbCl}_6^-$  ions \* have been deduced from conductometric measurements on, e.g.,  $\text{SbCl}_5$ – $\text{CH}_3\text{CN}$ ,<sup>7–10</sup>  $\text{SbCl}_5$ –HMPT in nitrobenzene solution,<sup>11</sup> and  $\text{SbCl}_5$ –2,2,6,6-tetramethylpiperidine-*N*-oxyl or  $(\text{C}_2\text{H}_5)_2\text{S}$  in 1,2-dichloroethane solution.<sup>12</sup> The conductometric measurements are very sensitive to contamination especially of water, which has been amply demonstrated in the work by Beattie and coworkers<sup>13</sup> on the  $\text{SbCl}_5$ – $\text{CH}_3\text{CN}$  system. These later measurements showed  $\text{SbCl}_5$  to be nonconducting in  $\text{CH}_3\text{CN}$ , thus invalidating the conclusions about autoionization reached in Refs. 7–10. Consequently, results of conductometric measurements in this kind of systems must be treated with great caution.

The only previous NMR work on  $\text{SbCl}_5$  adduct ionization seems to be Ref. 11 and the recent paper by Ahmed and Schmulbach.<sup>14</sup> In the latter publication it is stated that  $\text{SbCl}_5$  in acetonitrile solution is entirely or predominantly ionized to  $\text{SbCl}_6^-$  and (acetonitrile)<sub>2</sub> $\text{SbCl}_4^+$ . No real  $^1\text{H}$  NMR evidence for this is presented and the measurements can equally well be interpreted in terms of simple donor-acceptor adducts.

In a  $^1\text{H}$  NMR study of exchange processes in  $\text{SbCl}_5$ -alkylurea adducts,<sup>15</sup> varying chemical shifts of the donors present in excess were observed. Water contamination was suspected

\* The following abbreviations will be used in this article: TMU = tetramethylurea, DMSO = dimethyl sulphoxide, HMPT = hexamethylphosphorotriamide, EtOAc = ethyl acetate, D = donor, A =  $\text{SbCl}_5$  (acceptor), X = halogen and  $\text{MX}_n$  = metal halide. Concentrations are expressed in mol l<sup>-1</sup> (M).

to be the cause but subsequent studies on the ternary adduct systems  $\text{H}_2\text{O}-\text{SbCl}_5-\text{D}$ <sup>16</sup> and  $\text{HCl}-\text{SbCl}_5-\text{D}$ <sup>17</sup> have shown that this interpretation is not satisfactory. An alternative cause for the observed effect could be ionization reactions in the binary adduct system. The present  $^1\text{H}$  and  $^{121}\text{Sb}$  magnetic resonance study was undertaken to obtain a reasonable description of the  $\text{SbCl}_5$ -alkylurea systems and to gain some information about ionization reactions of  $\text{SbCl}_5$  adducts in solution.

During the study we learned about the careful work of Hartman and Schrobilgen<sup>18</sup> on the analogous  $\text{TMU}-\text{BX}_3$  systems in dichloromethane solution. These authors have, from  $^1\text{H}$ ,  $^{11}\text{B}$ , and  $^{19}\text{F}$  magnetic resonance studies, obtained direct evidence for the presence of  $(\text{TMU})_2\text{BF}_3^+$  and  $\text{BF}_4^-$ , arising from autoionization of the adduct.

## EXPERIMENTAL

**Samples.** The samples for the low-concentration study of the  $\text{TMU}-\text{SbCl}_5$ -dichloroethane system were prepared in a glove box in  $\text{P}_2\text{O}_5$ -dried air from stock solutions (0.2 M) of  $\text{TMU}$  and  $\text{SbCl}_5$ . The  $\text{TMU}$  solution was determined by a chromatographic method<sup>19</sup> to contain less than 0.01 % water by weight (2 mM). These solutions were dispensed with two Metrohm precision burets *via* an all glass-*teflon* tubing system. All other samples were prepared in a polyethylene glove bag in a dry  $\text{N}_2$  atmosphere. The neat donors were slowly dispensed from an all glass-*teflon* syringe into weighed amounts of 0.2–1.9 M  $\text{SbCl}_5$  solutions kept in the 10 mm i.d. *teflon* screwcap tubes used for the  $^{121}\text{Sb}$  NMR measurements. For the  $^1\text{H}$  NMR measurements 0.5 ml of these solutions were transferred to 5 mm o.d. tubes. The two sets of tubes were stored under identical conditions. All glassware had been dried at temperatures above 120 °C overnight. The presence of water or acidic impurities in the samples had been tested for in the low-field region of  $^1\text{H}$  NMR, where signals from these acidic protons would occur.<sup>16,17,20</sup> Within the sensitivity of the instrument no such signals could be seen in any sample. In analogy with the  $\text{BF}_3$  adduct systems,<sup>20</sup> signals from the D part of species such as  $\text{DH}^+\text{SbCl}_5^-$  would have been expected in the vicinity of the normal adduct signals in samples having acceptor in excess.<sup>17</sup>

The relatively high concentrations used and the methods of sample preparation employed were chosen to minimize water contamination effects.

Under conditions of rapid addition of  $\text{TMU}$  to the  $\text{SbCl}_5$  solution (the solution temperature rising to the boiling point) a small extra signal 0.05 ppm to low field of the adduct signal could be observed. No such signal was seen in samples prepared by mixing the two components under milder conditions as dilute solutions. The nature of this species has not been investigated further but it is probably a decomposition product derived from the adduct. No exchange with other species in solution with any sample composition is indicated in  $^1\text{H}$  NMR spectra at 40 °C.

**Reagents.** 1,2-Dichloroethane (Fisher Certified reagent), dichloromethane (BDH, redistilled) and nitrobenzene (BDH, Analar) were pure as judged from  $^1\text{H}$ NMR spectra and were dried with 4A molecular sieves prior to use. Tetramethylurea (Fluka) was vacuum distilled on a Nester-Faust spinning band column and was more than 99.5 % pure according to GLC. Hexamethylphosphorotriamide (BDH) was distilled from  $\text{CaH}_2$ . Ethyl acetate and dimethyl sulphoxide were dried at least 3 h with freshly regenerated 4A molecular sieves just prior to use and were pure as judged from  $^1\text{H}$  NMR.

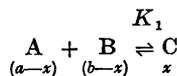
**Synthesis.** Triphenylmethylhexachloroantimonate was prepared according to Cowell *et al.*<sup>21</sup>

**Instrumentation.**  $^1\text{H}$  NMR spectra were recorded on a Varian Associates A-60A spectrometer equipped with a V-6040 temperature controller.  $^{121}\text{Sb}$  spectra were recorded on a V-4200 wide-line spectrometer from the same manufacturer. These spectra were registered as the derivative of the absorption signal at 14.98 MHz.

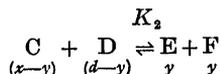
All quantitative measurements were made at 20 °C.

## CALCULATIONS

A numerical cyclic relaxation method has been used to solve the equations for coupled equilibria and simultaneously adjust equilibrium constants for best agreement with the conversion data. The procedure is best illustrated with an example. Consider the following coupled equilibria:



and



For each data point (with initial concentrations  $a$ ,  $b$ , and  $d$ ) three equations are obtained:

Table 1. Summary of quantitative measurements on systems I and IV.

SbCl <sub>5</sub> adduct/solvent	D <sub>tot</sub> /[M]	A <sub>tot</sub> /[M]	SbCl <sub>5</sub> <sup>-</sup> (obs) <sup>a</sup> /[M]	SbCl <sub>5</sub> <sup>-</sup> (calc) <sup>b</sup> /[M]	<sup>1</sup> H NMR shifts of the excess donor + cation signal $\nu_{\text{obs}}/\text{Hz}$	$\nu_{\text{calc}}/\text{Hz}$
TMU/CH <sub>2</sub> Cl <sub>2</sub> (Ia)	1.3	0.83	0.11	0.097	21.9	21.9
	1.1	0.85	0.10	0.099	16.5	17.2
	1.2	0.83	0.12	0.097	23.8	20.3
	1.4	0.80	0.11	0.092	25.3	23.7
	1.2	0.66	0.06	0.077	26.6	24.1
	1.4	0.64	0.05	0.075	27.2	26.6
	1.6	0.66	0.07	0.077	27.2	26.6
	2.3	0.58	0.06	0.068	28.6	28.7
	0.105	0.099	- <sup>c</sup>	0.0109	8.0	5.8
	0.111	0.097	-	0.0101	13.7	13.1
TMU/CH <sub>2</sub> ClCH <sub>2</sub> Cl (Ib)	0.115	0.097	-	0.0094	16.6	16.6
	0.120	0.079	-	0.0087	17.9	19.0
	0.124	0.074	-	0.0082	20.3	20.3
	0.127	0.070	-	0.0077	19.5	21.3
	0.130	0.066	-	0.0073	21.3	22.0
	0.135	0.059	-	0.0067	22.2	22.9
	0.137	0.057	-	0.0063	22.2	23.3
	2.7	1.5	0.20	0.16	27.6	-
	2.2	1.9	0.20	0.20	19.0	-
	HMP/ nitrobenzene (IV)	0.18	0.27	0.02	0.039	-
0.32		0.28	0.05 (0.05)	0.044	8.5	8.2
0.36		0.27	0.06 (0.05)	0.056	12.3	10.2
0.48		0.28	0.10 (0.07)	0.073	13.0	12.1
0.60		0.26	0.10 (0.08)	0.076	13.5	13.7
0.70		0.25	0.10 (0.08)	0.079	14.0	14.3
0.94		0.24	0.09 (0.08)	0.082	14.9	15.3
0.19		0.27	0.03	0.041	-	-
0.40		0.26	0.09 (0.06)	0.061	11.4	11.4
0.68		0.24	0.09 (0.08)	0.073	14.0	14.5
0.94	0.24	0.10 (0.08)	0.081	14.0	15.3	

<sup>a</sup> From intensity measurements in <sup>121</sup>Sb spectra. Values in parenthesis are from <sup>1</sup>H NMR spectra and have been calculated with the aid of eqn. (9). <sup>b</sup> Calculated from the experimentally estimated equilibrium constants (see the text) and the concentrations given in columns 2 and 3.  $K_2 = 0.023$  in the Ia system, 0.02 in the Ib system, and 0.14 in the IV system where  $K_2$  is also 3.3 l mol<sup>-1</sup>. <sup>c</sup> Shifts are expressed relative to the adduct <sup>1</sup>H NMR signal at 60 MHz. The averaged excess donor + cation signal is upfield. <sup>d</sup> Calculated with the aid of eqn. (7) and the ion concentrations shown in column 5. The assumed shifts are given in the text. <sup>e</sup> These concentrations are too low to be measured by <sup>121</sup>Sb magnetic resonance.

$$x - K_1(a-x)(b-x) = Q_1$$

$$y^2 - K_2(x-y)(d-y) = Q_2$$

$$(y_{\text{obs}} - y)^2 = Q_3$$

Totally there will be  $3n$  such equations for  $n$  samples and there will be  $2n$  parameters for the  $x$  and  $y$  and 2 parameters for the equilibrium constants. These  $2n+2$  parameters are then varied to make the sum of all ( $Q_1 + Q_2 + Q_3$ ) a minimum. The  $2n$  parameters are completely orthogonal to all other parameters so when the procedure has converged all  $Q_1$  and  $Q_2$  are zero.

The procedure outlined here is time consuming and tedious for a manual calculation, but it lends itself nicely to a computer treatment. The FORTRAN subroutine STEPIT<sup>22</sup> is ideally suited for this purpose and a calculation for 10 samples only takes a few seconds on a UNIVAC 1108 computer. The procedure may be extended to more complicated equilibria, and no complicated explicit concentration expressions have to be derived.

## RESULTS AND DISCUSSION

The following  $\text{SbCl}_5$  adduct systems were studied by  $^1\text{H}$  and  $^{121}\text{Sb}$  magnetic resonance spectroscopy: the adduct with TMU in  $\text{CH}_2\text{Cl}_2$  (Ia) and in  $\text{C}_2\text{H}_4\text{Cl}_2$  (Ib), the adduct with DMSO in  $\text{CH}_2\text{Cl}_2$  (II) and with EtOAc in  $\text{CH}_2\text{Cl}_2$  (III) and finally the adduct with HMPT in nitrobenzene (IV). System IV has previously been studied by Gutmann *et al.*<sup>11</sup>

The solvent properties of  $\text{CH}_2\text{Cl}_2$  and  $\text{C}_2\text{H}_4\text{Cl}_2$  are similar, the dielectric constants at 20 °C being 9.08 and 10.7, respectively, while the dielectric constant of nitrobenzene is appreciably higher (35.7).<sup>23</sup>

$^1\text{H}$  NMR spectra of solutions containing  $\text{SbCl}_5$  in excess show one set of signals ascribed to donor bound in the  $\text{DSbCl}_5$  adduct. In samples containing donor in excess, that is with concentration ratios  $D/A > 1$ , an additional set of donor signals appears at higher field. However, for the EtOAc system (III), the temperature must be lowered below 0 °C to give a separation of the signals. In this system both the adduct and excess donor chemical shifts are almost independent of the composition of the sample, and furthermore the excess donor signals coincide with the signals observed in samples of EtOAc in  $\text{CH}_2\text{Cl}_2$ . Thus  $^1\text{H}$  NMR spectra give

indications of only EtOAc-adduct molecules when  $D/A < 1$ , and only adduct molecules and unbound EtOAc molecules when  $D/A > 1$ , the donor exchange between the latter being slow on the  $^1\text{H}$  NMR time scale below 0 °C.

For systems I and II the chemical shifts of the adducts remained unchanged over the concentration ranges studied ( $D/A \geq 1$ ), while the shifts of the "excess" donors were observed to vary with the composition of the samples. Results for systems Ia, Ib, and IV are shown in column 6 of Table I. No quantitative  $^1\text{H}$  NMR shift measurements were made on system II. For concentration ratios  $D/A \geq 1$  the "excess donor" shifts approached the shifts observed for a solution of the donor. Thus in these systems there are indications of an additional species containing donor molecules in rapid exchange with unbound donors, but slowly exchanging with adducts.

The HMPT system (IV) shows more complex behaviour and some typical  $^1\text{H}$  NMR spectra from this system are shown in Fig. 1. These spectra show the effect of adding donor incrementally to a = 0.3 M solution of  $\text{SbCl}_5$  in nitrobenzene containing a small amount of 1,2-dichloroethane reference. The excess donor signal has a variable chemical shift (see column 6, Table 1), and in addition the intensities

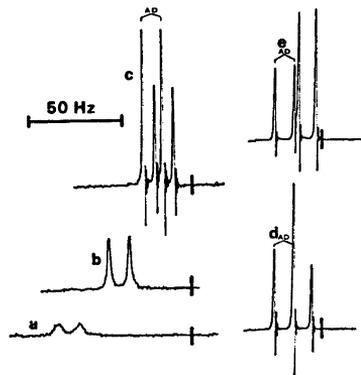


Fig. 1. Some representative 60 MHz  $^1\text{H}$  NMR spectra from the HMPT region of the HMPT -  $\text{SbCl}_5$  - nitrobenzene system (IV) at 40 °C. The solid line is 90 Hz upfield from an internal 1,2-dichloroethane reference signal. The  $D/A$  ratio increases in the series a - e, the a and b samples containing excess  $\text{SbCl}_5$  and the c - e samples excess donor. The 1:1 doublet structure arises from  $^1\text{H} - ^{31}\text{P}$  spin-spin coupling ( $J \approx 10$  Hz).

of the excess donor signals relative to the adduct signals differed markedly from the ratio  $([D]_{\text{init}} - [A]_{\text{init}})/[A]_{\text{init}}$ , which is the ratio expected for the simple adduct formation reaction. In samples with  $D/A < 1$ , the signal of the HMPT adduct was quite broad and the chemical shift was observed to vary with the excess of SbCl<sub>5</sub>. For samples containing  $D/A > 1$  the adduct signal is sharp and has a constant <sup>1</sup>H NMR shift.

Although there certainly must be small amounts of water or acidic impurities in the samples (which will cause similar effects in <sup>1</sup>H NMR spectra)<sup>16,17,20</sup> we are convinced that this only gives a minor contribution to the observed shift effects, even in the most dilute samples. Experiments have been made with additions of controlled amounts of water and were found to cause large changes in the spectra as well as the appearance of an "acid proton" signal<sup>16,17,20</sup> in the low field <sup>1</sup>H NMR region.

In <sup>121</sup>Sb NMR spectra of systems I and II no signals were observed for  $D/A < 1$ , while a narrow signal ascribed to SbCl<sub>6</sub><sup>-</sup> was observed in samples containing donor in excess. In the HMPT system the SbCl<sub>6</sub><sup>-</sup> signal was observed in samples with donor in excess but also in samples containing a slight excess of SbCl<sub>5</sub>.

<sup>121</sup>Sb spectra of samples of system III showed a broad signal ascribed to SbCl<sub>5</sub> in samples with concentration ratios  $D/A < 1$ , and no <sup>121</sup>Sb signal in samples containing EtOAc in excess. This confirms the findings from the <sup>1</sup>H NMR experiments that in this system there is quantitative formation of the molecular SbCl<sub>5</sub>-EtOAc adduct with no further reactions taking place in solution.

The assignment of the two <sup>121</sup>Sb signals has been made by comparison with signals from 1,2-dichloroethane solutions of SbCl<sub>5</sub> and (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>C<sup>+</sup>SbCl<sub>6</sub><sup>-</sup>, respectively. The SbCl<sub>6</sub><sup>-</sup> signal ( $\approx 0.075$  mT peak-to-peak linewidth on the derivative spectrum)\* is 380 ppm upfield from the SbCl<sub>5</sub> signal ( $\approx 1.8$  mT linewidth).

A few preliminary measurements have been made on the *N,N*-dimethylformamide and 1,3-dimethylurea adducts, and the results were in all respects similar to those found in the TMU systems.

The <sup>121</sup>Sb NMR linewidths will be determined

by two factors: the linewidth of individual species and the rates of exchange among all antimony-containing species in solution. Since the <sup>121</sup>Sb nucleus has an electric quadrupole moment, its linewidths will be dominated by the rate of quadrupolar relaxation.<sup>24</sup>

The relation between the transverse relaxation time ( $T_2$ ) and the derivative peak-to-peak linewidth ( $\Delta B$ ) for a Lorentzian bandshape<sup>24</sup> is given by (1).

$$\Delta B = 2/T_2 \sqrt{3} \quad (1)$$

When the product of the resonance frequency in rad/s ( $\omega$ ) and the rotational correlation time ( $\tau_c$ ) in s is  $\ll 1$ , (the so-called extreme narrowing case)  $T_2$  is approximately given by (2).<sup>24</sup>

$$\frac{1}{T_2} = \frac{24}{1000} \left( \frac{e^2 q Q}{\hbar} \right)^2 \tau_c = k q^2 \tau_c \quad (2)$$

This formula applies for a nucleus with  $I = 5/2$ , such as <sup>121</sup>Sb, under the conditions in the present work. In eqn. (2)  $e$  stands for the electron charge,  $q$  represents the electric field gradient at the nucleus and  $Q$  is the quadrupole moment of the nucleus.

$q$  is strongly correlated to molecular symmetry around the antimony atom and consequently sharp resonances are expected for the SbCl<sub>6</sub><sup>-</sup> ion and broader ones (perhaps undetectable) for the donor-acceptor adducts. The averaged linewidth of all species in fast exchange with each other will be given by eqn. (3).\*

$$\Delta B = \sum_i p_i \Delta B_i \quad (3)$$

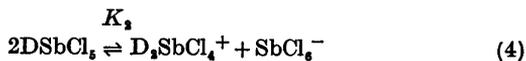
Here the  $p_i$  represent fractions of antimony content. In case of fast exchange among antimony compounds with very different linewidths, the linewidth will be of the order of that of the broadest line and in case of slow exchange only the sharpest line will be seen since it is difficult to observe broad lines superimposed on sharp lines.

For an accurate quantitative description of the ionization equilibria one must consider the possible importance of solvent separated ions, ion pairs, higher ion aggregates, the composition-dependent dielectric constants of the solutions and a whole spectrum of cations related

\* T stands for Tesla (1 Tesla = 10 000 Gauss).

\* See, e.g., Ref. 33.

to the  $D_2SbCl_4^+$  ion. To test if a description of the equilibria is possible with a minimum number of parameters the simple autoionization scheme (4) was assumed as a working hypothesis.



In conjunction with the equation for the normal donor-acceptor formation (5), this leads to expression (6), where  $x = [SbCl_6^-] = [D_2SbCl_4^+]$ , and which can be solved for  $x$ .



$$x^2 \frac{K_1(2\sqrt{K_2} + 1)^2}{\sqrt{K_2}} - x \left[ K_1([D]_{tot} + [A]_{tot})(2\sqrt{K_2} + 1) + 1 \right] + \sqrt{K_2}K_1[D]_{tot}[A]_{tot} = 0 \quad (6)$$

In the systems studied adduct formation is essentially complete so  $K_1$  is very large<sup>5</sup> and eqn. (6) leads to a constant adduct/ $x$  ratio irrespective of the donor/acceptor ratio, as illustrated in Fig. 2.

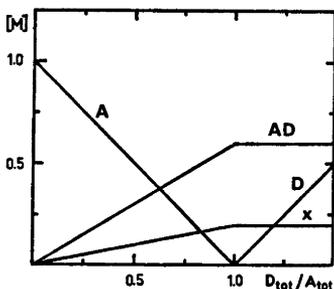


Fig. 2. Calculated concentration dependence of the autoionization reaction (4) for  $K_2 = 0.111$  and a large  $K_1$ .  $[A]_{tot} = 1$  M is constant.

When a  $^{121}Sb$  NMR signal from the species  $SbCl_6^-$  is observed measurements of the degree of ionization are straightforward. The concentration of this ion can be obtained by comparison with samples of known concentrations of hexachloroantimonate, assuming that the height  $x$  (linewidth)<sup>2</sup> of the peak is proportional to the intensity at constant spectrometer settings. Unless the signals are overmodulated or

the lineshape is different this quantity is proportional to the integrated area of the absorption signal. The relatively low signal to noise ratio in the  $^{121}Sb$  NMR spectra precluded a more accurate intensity measurement *via* numerical double integration of the derivative spectrum. The  $SbCl_6^-$  concentrations determined from  $^{121}Sb$  spectra are shown in column 4 of Table 1. From these ion concentrations equilibrium constants can be evaluated. The Ia system fits well with the simple autoionization scheme (4) with a value of 0.023 for  $K_2$ . This is also the case with the Ib and II systems and the corresponding values are 0.02 and 0.005, respectively. The latter values are, however, based on a small number of samples (4) and the determination is correspondingly less accurate.

The HMPT system (IV), however, does not fit into the simple scheme and, as further discussed below, another equilibrium process has to be considered. From the appropriate equilibrium constants "smoothed" values for the ion concentrations can be calculated. These are given in column 5 of Table 1.

A check on the self-consistency of the models can be made *via* the PMR spectra. The variable chemical shift of the "excess donor" signal in  $^1H$  NMR spectra is a result of the variable proportions of unbound donor and cation. The variation in the observed chemical shift  $\nu_{obs}$  relative to suitable reference can be simulated by the application of eqn. (7) under the assumption that the chemical shifts  $\nu_D$  and  $\nu_{ion}$  are constant.

$$\nu_{obs} = \frac{[D]\nu_D + 2[ion]\nu_{ion}}{[D] + 2[ion]} \quad (7)$$

$\nu_D$  should be close to the value observed for a solution of D in the same solvent and  $\nu_{ion}$  is an unknown which has to be adjusted to obtain the "best fit". The chemical shifts in column 7 of Table 1 have been calculated in this way from the calculated ion concentrations in column 5 of the same table. The agreement is reasonably good, considering the fact that  $\nu_D$  and  $\nu_{ion}$  are not necessarily constants over a larger concentration range and that acidic impurities may interfere. For the TMU adduct in 1,2-dichloroethane (Ib) a value of 0 Hz for the ion and 27 Hz upfield for unbound donor reproduces the  $\nu_{obs}$  values quite well.  $^1H$  NMR shifts are expressed

relative to the shift of the adduct. The donor shift is in good agreement with the shift observed in a solution of TMU in dichloroethane. Provided that there is an exchange process between TMU in cation and adduct when D/A < 1, the former value explains the initially confusing fact that the adduct <sup>1</sup>H NMR shift is the same under conditions of excess donor and excess acceptor and that no separate cation <sup>1</sup>H NMR signal is ever observed. Evidence for such an exchange process is indeed found in <sup>121</sup>Sb spectra as further discussed below. In the Ia and IV systems the shifts (cation/unbound donor) 0/31 and 4/18 Hz were found.

As a consequence of ionization the adduct will be consumed and converted to ions. This should affect the relative areas of the adduct signal and the "excess donor" + cation signal in samples having donor in excess. For each cation formed, two adduct molecules are required. Taking the D<sub>2</sub>SbCl<sub>4</sub><sup>+</sup> concentration to be x, the observed <sup>1</sup>H NMR signal intensity ratio, R, between the averaged signal of unbound donor + cation and the adduct signal will be given by (8).

$$R_{obs} = \frac{[D]_{init} - [A]_{init} + 2x}{[A]_{init} - 2x} \tag{8}$$

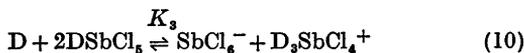
Rearranging leads to (9), from which the degree of ionization can be estimated.

$$x = \frac{R_{obs}[A]_{init} + [A]_{init} - [D]_{init}}{2(1 + R_{obs})} \tag{9}$$

Since only deviations are measured, fairly accurate values of the initial concentrations of donor and SbCl<sub>5</sub> are required if a reasonable precision of the determination is to be obtained. For this reason this method has only been used for the HMPT adduct (IV) where the conversion to ions is extensive. These results are shown within parenthesis in column 4 of Table 1. The observed degrees of ionization from <sup>121</sup>Sb spectra and from <sup>1</sup>H spectra (with the aid of eqn. (9)) agree satisfactorily considering the probable errors of these measurements.

It can be seen that the ionization data for system IV cannot be interpreted according to the simple autoionization scheme since the SbCl<sub>5</sub><sup>-</sup> concentration increases significantly with the D/A ratio. One model for this situation involves the assumption of a simultaneous induced autoionization as a result of solvation

effects of the excess donor. Formally this can be expressed as (10), where the third D in the ion is assumed to be more weakly bonded.

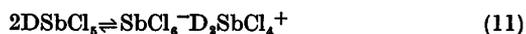


Values of K<sub>2</sub> (0.14) and K<sub>3</sub> (3.3 l mol<sup>-1</sup>) can be found which satisfactorily reproduce the ionizations in this adduct system, as shown in columns 5 and 7 of Table 1, which give the SbCl<sub>5</sub><sup>-</sup> concentrations and <sup>1</sup>H NMR shifts calculated using the above values for the equilibrium constants. The difference in ionization behaviour between the HMPT adduct system in nitrobenzene and the other systems may reflect the stronger donor-acceptor interaction in the adduct<sup>25</sup> and the higher dielectric constant of the solvent (35.7).<sup>25</sup> It is also known that HMPT is an effective solvent for organic ions.<sup>26</sup> As illustrated in Fig. 1 this adduct system also exhibits a variable <sup>1</sup>H NMR shift of the signal from the HMPT adduct with SbCl<sub>5</sub> in varying excess. This might be due to coordination of excess SbCl<sub>5</sub> to the nitrogen atoms in the donor molecule. The HMPT signal in this region is quite broad, revealing the existence of an exchange process, which has not been further investigated. Above a D/A ratio of unity the adduct signal suddenly sharpens and remains at a constant shift. Now instead the excess donor signal shows the same type of shift variation as the excess TMU signal.

It has not been possible to directly observe the D<sub>2</sub>SbCl<sub>4</sub><sup>+</sup> ions in solutions containing SbCl<sub>5</sub><sup>+</sup> in excess in any of the systems studied. However, it seems reasonable to assume that autoionization takes place and that donor in the cation is in rapid exchange with donor in the adduct below the ratio D/A = 1.0. In solutions with D/A > 1 the exchange between cation and excess donor is rapid while the donor exchange with the adduct is slow. The following experiment illustrates this point further. To a 0.5 M solution of SbCl<sub>5</sub> in CH<sub>2</sub>Cl<sub>2</sub> (showing a broad SbCl<sub>5</sub> signal in <sup>121</sup>Sb spectra), tetrabutylammonium chloride was added in order to make the solution 0.2 M with respect to SbCl<sub>5</sub><sup>-</sup>, (which should readily form). The <sup>121</sup>Sb signal observed after the addition was shifted upfield, but was as broad as the original SbCl<sub>5</sub> signal and no SbCl<sub>5</sub><sup>-</sup> signal was seen. Addition of a few mol % of TMU to this sample washes out the <sup>121</sup>Sb

signal completely. Combined with the observation that the weaker and probably nonionizing EtOAc adduct system shows a  $\text{SbCl}_5$  signal when  $\text{SbCl}_5$  is in excess but no  $\text{SbCl}_6^-$  signal when EtOAc is in excess, this suggests that the presence of  $\text{SbCl}_6^-$  and  $\text{D}_2\text{SbCl}_4^+$  in the solution provides an exchange pathway between these ions,  $\text{SbCl}_5$  and the adduct. The averaged linewidth will be given by (3) and should be of the order of the adduct linewidth. This is expected to be broad enough to make the line unobservable. The same argument explains the paradox that no  $^{121}\text{Sb}$  signal at all is seen in systems I, II, and IV when  $\text{SbCl}_5$  is in excess. Closely below the D/A ratio of unity in the HMPT adduct system a  $\text{SbCl}_6^-$  signal is, however, seen. This could be an effect of the above-mentioned coordination of excess  $\text{SbCl}_5$  to the HMPT nitrogens whereby the exchange pathway is interrupted.

The equilibria under consideration also include ion pairs, and an alternative to eqn. (4) is



An alternative to eqn. (10) is an equation which describes a separation of the ion pairs in (11) into ions whereby the equilibrium in (11) is driven further to the right. The available data can, however, be satisfactorily described with eqns. (4) and (10). For instance, eqn. (4) describes the Ib ionization data in Table 1 better than eqn. (11), which leads to a concentration dependent degree of ionization.

$^{121}\text{Sb}$  linewidths of the free  $\text{SbCl}_6^-$  ion and  $\text{SbCl}_6^-$  in an ion pair possibly differ due to distortions of the octahedron in the ion pair and the different rotation correlation times of the two species. This effect is noticeable for small ions such as the sodium ion.<sup>27</sup> Linewidth considerations could therefore be useful for the estimation of the relative abundances of free ions and ion pairs. The observed  $\text{SbCl}_6^-$  linewidths in the present work are essentially the same as in the triphenylmethylhexachloroantimonate reference samples. Bowyer *et al.* state that in 1,2-dichloroethane this salt is almost completely in the ion pair form.<sup>28</sup> On the other hand, the linewidths are smaller ( $\approx 50\%$ ) than those corresponding to  $T_2$  data for  $\text{SbCl}_6^-$  ions in 5 M HCl<sup>29</sup> where predominantly free ions should exist, so no conclusions can be drawn from these data.

The  $^{121}\text{Sb}$  spectra of  $\text{SbCl}_5$  deserve special comment since the linewidth of neat  $\text{SbCl}_5$  (0.75 mT) is smaller than in 1 M 1,2-dichloroethane solutions (1.8 mT p-p). Neat  $\text{SbCl}_5$  seems to have a greater viscosity than the solutions, so a change in  $\tau_c$  does not explain the difference. Possible explanations include rapid exchange between  $\text{SbCl}_5$  and small amounts of  $\text{SbCl}_5 - \text{H}_2\text{O}$ , which may be present as an impurity, and solute-solvent interaction. The enthalpy of solution of  $\text{SbCl}_5$  in 1,2-dichloroethane is  $-1.80$  kJ/mol.<sup>17</sup> Although  $\text{SbCl}_5$  is invariably reported as monomeric in the literature (solid, Ref. 30 and gas phase, Ref. 31), halogen bridges in related compounds such as  $\text{Al}_2\text{Cl}_6$  and  $\text{SbF}_5$  are well known.<sup>32</sup> If  $\text{SbCl}_5$  is to some extent dimeric or polymeric at higher concentrations, the electric field gradient factor  $q$  in eqn. (2) could be reduced, thereby making the lines sharper. A careful variable solvent study should provide conclusive evidence for the correct explanation.

*Added in proof:* Preliminary results indicate that the  $^1\text{H}$  NMR signal from the  $\text{D}_2\text{SbCl}_4^+$  ion can be observed in TMU- $\text{SbCl}_5$ - $\text{CH}_2\text{Cl}_2$  samples, where an initial excess of  $\text{SbCl}_5$  has been scavenged with EtOAc. The signal has the correct intensity ( $\approx 20\%$  of the adduct signal) and coalesces with the adduct signal above  $\approx 0^\circ\text{C}$  (composition dependent). The shift of this signal is  $\approx 3$  Hz (60 MHz) upfield from the adduct signal.

*Acknowledgements.* We wish to thank Professor J. S. Hartman for a stimulating and helpful discussion and for making results available to us prior to publication. We are also grateful for suggestions and helpful comments from Professors S. Forsén and I. Lindqvist.

Dr. R. E. Carter kindly helped to improve the language.

## REFERENCES

1. Lindqvist, I. *Inorganic Adduct Molecules of Oxo-Compounds*, Springer, Berlin 1963.
2. Brun, L. and Brändén, C.-I. *Acta Crystallogr.* 20 (1966) 749.
3. Binas, H. Z. *Anorg. Chem.* 352 (1967) 271.
4. Chevrier, B., Carpentier, J.-M. and Weiss, R. J. *Amer. Chem. Soc.* 94 (1972) 5718.
5. Olofsson, G. *Acta Chem. Scand.* 22 (1968) 377.
6. Gutmann, V. and Czuba, H. *Monatsh. Chem.* 100 (1969) 708.
7. Zuur, A. P. and Groenveld, W. L. *Rec. Trav. Chim. Pays-Bas* 86 (1967) 1089.

8. Kolditz, L. and Preiss, H. *Z. Anorg. Chem.* 310 (1964) 172.
9. Beattie, I. R. and Webster, M. *J. Chem. Soc.* (1963) 38.
10. Schmulbach, C. D. and Ahmed, I. Y. *J. Chem. Soc. A* (1968) 3008.
11. Gutmann, V. and Imhof, J. *Monatsh. Chem.* 101 (1970) 7.
12. Lim, Y. Y. and Drago, R. S. *Inorg. Chem.* 11 (1972) 202.
13. Beattie, I. R., Jones, P. J. and Webster, M. *J. Chem. Soc. A* (1969) 218.
14. Ahmed, I. Y. and Schmulbach, C. D. *Inorg. Chem.* 11 (1972) 228.
15. Olofsson, G., Stilbs, P., Drakenberg, T. and Forsén, S. *Tetrahedron* 27 (1971) 4583.
16. Olofsson, G. and Olofsson, I. *Tetrahedron* 29 (1973) 1711.
17. Appleton, Q., Bernander, L., and Olofsson, G. *Tetrahedron* 27 (1971) 5291.
18. Hartman, J. S. and Schrobilgen, G. J. *Inorg. Chem.* 13 (1974) 874.
19. Sellers, P. J. *Chem. Thermodyn.* 2 (1970) 211.
20. Hartman, J. S. and Schrobilgen, G. J. *Can. J. Chem.* 50 (1972) 713.
21. Cowell, G. W., Ledwith, A., White, A. C. and Woods, H. J. *J. Chem. Soc. B* (1970) 227.
22. Chandler, J. P., Program No. 66:2, Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University, Bloomington, Ind., U.S.A.
23. Maryott, A. A. and Smith, F. A. *Nat. Bur. Stand. (U.S.), Circ.* 514 (1951).
24. Abragam, A. *The Principles of Nuclear Magnetism*, Oxford Univ. Press, Oxford 1961.
25. Gutmann, V. *Chimia* 23 (1969) 285.
26. Fieser, L. F. and Fieser, M. *Reagents for Organic Synthesis*, Wiley, New York 1967.
27. Erlich, R. H. and Popov, A. I. *J. Amer. Chem. Soc.* 93 (1971) 5620.
28. Bowyer, P. M., Ledwith, A. and Sherrington, D. C. *J. Chem. Soc. B* (1971) 1511.
29. Kok, G. L., Morris, M. D. and Sharp, R. R. *Inorg. Chem.* 12 (1973) 1709.
30. Ohlberg, S. *J. Amer. Chem. Soc.* 81 (1959) 811.
31. Wilmshurst, J. K. *J. Mol. Spectrosc.* 5 (1960) 343.
32. Cotton, F. A. and Wilkinson, G. *Advanced Inorganic Chemistry*, 3rd Ed. Interscience, New York 1972.
33. Zimmermann, J. R. and Britten, W. E. *J. Phys. Chem.* 61 (1957) 1328.

Received February 21, 1974.