A Proton Magnetic Resonance Study of SbCl₅·H₂O and SbCl₅·2H₂O Adducts in Solution

LARS BERNANDER and GERD OLOFSSON

Thermochemistry Laboratory, Chemical Center, University of Lund, S-220 07 Lund, Sweden

The interaction between H₂O and the Lewis acid SbCl₅ has been studied in CH₂Cl₂ solution with varying H₂O:SbCl₅ molar ratios by PMR at temperatures between −100 and +40°C. In solutions with H₂O:SbCl₅ ≤ 1 the monomeric adduct SbCl₅·H₂O is quantitatively formed. If 1 < H₂O:SbCl₅ ≤ 2 a second water molecule is added forming a stable, probably hydrogen bonded complex SbCl₅·2H₂O.

It is well known that a number of metal halides, MeXₙ, form stable complexes with water, which function as catalysts in a number of Friedel-Crafts reactions.¹ The only NMR spectroscopic study on such systems in non-aqueous solutions that to our knowledge has been reported concerns BF₃—H₂O in acetone solution.² As the MeXₙ·H₂O complexes are considered to behave as strong Brønsted acids a basic solvent like acetone might be expected to interact quite strongly with the complexes. It seemed therefore to be of interest to carry out a study in the weakly interacting solvent CH₂Cl₂. Due to the high solubility of SbCl₅—H₂O complexes in halogenated hydrocarbons this system was studied instead of the less soluble BF₃—H₂O system.

EXPERIMENTAL

Materials. SbCl₅ (Merck, chromatographic grade) was used without further treatment. CH₂Cl₂ (Fisher Certified Reagent) was distilled shortly before use and stored over dust free beads of 4A molecular sieves. No impurities were detected by analytical GLC using dinonyl phthalate as stationary phase. The water content was checked by GSC and found to be less than 10 ppm.

Samples. Stock solutions of SbCl₅ in CH₂Cl₂ were prepared by mixing weighed amounts of the components. Known amounts of solution were transferred to the NMR tubes and water was added from a calibrated Hamilton syringe. Whenever judged necessary the samples were prepared in a glove bag in an atmosphere of dry N₂. The composition of the samples was checked by determination of peak areas in the NMR spectra using the ¹²C-satellites of the solvent as an internal standard. The sample composition is considered to be known to within a few per cent. The samples were stable and could be kept at room temperature for days without showing changes in the NMR spectra.

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Apparatus and measurements. NMR spectra were recorded on a Varian A-60 A spectrometer equipped with a V-6040 temperature controller. Temperature calibration was carried out using sample substitution with a Varian methanol sample and is estimated to be accurate to within ±1°C.

Chemical shift values of SbCl₅ - H₂O in CH₂Cl₂ were determined either directly relative to the low field ¹⁹C-satellite of the solvent or relative to the solvent bulk peak with side band technique using an HP 200 CD Audio Oscillator and an HP Electronic Frequency Counter. The chemical shift values were recalculated to δ values relative to internal TMS using a value of δ 5.36 for the CH₂Cl₂ peak and a value of δ 6.84 for the low field ¹⁹C-satellite at 60 MHz. The reproducibility of the chemical shift values is estimated to be better than 0.01 ppm.

The spectra of SbCl₅.H₂O in C₂H₄Cl₂ and CCl₄ and of BF₃.H₂O in C₂H₄Cl₂ were recorded at the working temperature of the spectrometer, about 40°C. The shift values were measured relative to that of C₂H₄Cl₂ (a small amount of C₂H₄Cl₂ had been added to the CCl₄ sample) and recalculated to δ in ppm relative to internal TMS using a value of δ 3.76 for neat C₂H₄Cl₂ and of δ 3.69 for C₂H₄Cl₂ in CCl₄.

RESULTS

PMR spectra of samples containing SbCl₅ and H₂O in CH₂Cl₂ solution were recorded at temperatures ranging from −100 to +40°C and with varying SbCl₅: H₂O concentration ratios. Only one narrow peak was observed from the water protons in all cases indicating fast proton and/or water exchange between different species. The concentration of SbCl₅ was kept constant, 0.56 m.* In samples with water concentration below 0.56 m a proton chemical shift of δ 6.62 at 41°C was observed which is ascribed to the SbCl₅.H₂O adduct. The differences observed at constant temperature between proton shifts of samples containing SbCl₅.H₂O concentrations from 0.05 m to 0.56 m were less than 0.02 ppm (cf. below). This indicates that SbCl₅.H₂O is not associated in solution.

In NMR spectra recorded at 41°C of samples with water concentration between 0.56 to 1.03 m, i.e. molar ratios H₂O:SbCl₅ between 1.0 and 1.8, a steady change of the proton chemical shift to lower field with increasing water concentration was observed. Assuming quantitative formation of a 1:2 complex SbCl₅.H₂O + H₂O → SbCl₅.H₂O, the following eqn. (1) between the observed chemical shift δ and the concentrations of the reactants should be applicable:

\[ \delta = [2m(SbCl₅)(\delta₁ - \delta₂)/m(H₂O)] - \delta₁ + 2 \delta₂ \]  

where δ₁ and δ₂ denote the proton chemical shifts of the 1:1 and 1:2 complexes, respectively. A plot of observed chemical shift values against SbCl₅:H₂O concentration ratios is shown in Fig. 1 and as can be seen a linear relationship is observed. It can be concluded that the variation of δ can be ascribed to quantitative association of water with the 1:1 complex to form a 1:2 complex. Least squares fitting gives the values 6.61 and 7.02 for δ₁ and δ₂, respectively. The value of δ₁ is in good agreement with the chemical shift of the 1:1 complex observed in samples with SbCl₅ in excess.

Samples with H₂O:SbCl₅ molar ratios larger than 2 have not been studied.

The temperature dependence of the proton chemical shift was studied for four samples of SbCl₅ concentration 0.56 m and water concentration of 0.10 m (a), 0.31 m (b), 0.83 m (c), and 1.00 m (d), respectively. Samples (a) and (b)  

* Concentrations are expressed in mol/kg solvent and denoted by m.
thus contain the 1:1 complex while in samples (c) and (d) the two complexes are present in different proportions. The results are shown in Fig. 2 where the observed $\delta$ values are plotted against temperature. The results obtained with sample (a) differ slightly from those of (b), the differences being less than 0.02 ppm. The points obtained with samples (c) and (d) are equidistantly shifted to lower field from those of (a) and (b), the shift change being 0.25 ppm for sample (c) and 0.33 ppm for (d). The observed chemical shifts vary almost linearly with temperature and give an average temperature coefficient $\Delta \delta/\Delta T$ of $-4.1 \times 10^{-3}$ ppm/°C. Thus samples containing mixtures of the 1:1 and 1:2 complexes give the same temperature coefficient as samples containing only the 1:1 complex.

The chemical shift of water dissolved in CH$_2$Cl$_2$ was observed to be $\delta$ 1.59 in a $6.5 \times 10^{-3}$ m solution and $\delta$ 1.62 in a $39 \times 10^{-3}$ m solution at 20°C.

The proton chemical shift of SbCl$_5$H$_2$O in the presence of excess SbCl$_5$ was observed to be $\delta$ 7.0 in C$_2$H$_4$Cl$_2$ solution and $\delta$ 6.4 in CCl$_4$ solution at 40°C.

BF$_3$-H$_2$O. A signal from the water protons was observed at $\delta$ 8.2 in a sample containing BF$_3$ and H$_2$O in C$_2$H$_4$Cl$_2$. The sample was prepared by introducing BF$_3$ into a solution containing 0.10 % by weight of water. The solution was turbid at room temperature but became clear at 40°C. Further addition of BF$_3$ did not affect the proton resonance signal which is ascribed to the protons in the BF$_3$-H$_2$O adduct. Due to the low solubility in CH$_2$Cl$_2$ and C$_2$H$_4$Cl$_2$ the BF$_3$-H$_2$O system was not further studied.

**DISCUSSION**

The complexes SbCl$_5$H$_2$O and BF$_3$H$_2$O are considered to exist in weakly interacting solvents as molecular electron-pair donor-acceptor adducts. The
vibrational spectrum of (solid?) SbCl$_5$H$_2$O has been observed to be closely similar to that of SbCl$_5$.HOCN(CH$_3$)$_2$ in the range for the vibrational motions of the Cl$_3$SbO moiety.\textsuperscript{4} The latter complex is known from an X-ray crystallographic study to exist as a donor-acceptor adduct.\textsuperscript{9}

The donor strength of water towards SbCl$_5$ is about the same as that of alkyl ethers and alkyl ketones as judged from the enthalpies of formation of the adducts in C$_2$H$_4$Cl$_2$ solution.\textsuperscript{5-8} Adduct formation will increase the acidity of the water protons and thus make the adducts apt to interact with basic molecules either through protonation or through hydrogen bond formation.

Preliminary calorimetric experiments indicate that the association of the second water molecule to give the SbCl$_5$.2H$_2$O complex is less exothermic than the formation of the 1:1 adduct.\textsuperscript{9} The high solubility of both the 1:1 and 1:2 complexes in inert solvents like CH$_2$Cl$_2$ and C$_2$H$_4$Cl$_2$ indicates non-ionic structures for both complexes. The 1:2 complex may be described as a hydrogen bonded complex in which the second water molecule is held by hydrogen bonding to the 1:1 adduct.

The temperature coefficient of $-4.1 \times 10^{-3}$ ppm/°C of the water proton chemical shift in both the 1:1 and 1:2 complexes is larger than those usually observed for non-associated species; see e.g. Ref. 10. However, it does not seem likely that the shift changes are caused by changes in association equilibria within the SbCl$_5$–H$_2$O system. Solute-solvent interaction might be the reason for the large temperature coefficients. It is also possible that low frequency motions of the adduct molecules could give rise to the observed effect. Muller and Reiter\textsuperscript{10} have pointed out that in the case of hydrogen bonded species large temperature coefficients may arise from causes other than changes in association equilibria. They have shown that the chemical shift of hydrogen bonded protons depend quite strongly on the degree of excitation of the hydrogen bond stretching vibrational mode and that a large $\Delta \delta /\Delta T$ value would result from changes in population of excited states of this low frequency motion. Their discussion would be applicable to other types of low frequency motions that could affect the electrostatic field at the protons studied.

The large difference between the proton chemical shift of the BF$_3$.H$_2$O adduct in acetone, $\delta 12.46$,$^2$ and in C$_2$H$_4$Cl$_2$, $\delta 8.2$, indicates solute-solvent interaction in acetone solution. SbCl$_5$.H$_2$O has been found to interact with weak bases like ethers and ketones in C$_2$H$_4$Cl$_2$ solution to give stable ternary complexes of 1:1:1 composition.$^9$ The water proton chemical shifts are observed at lower field in the ternary complexes than in SbCl$_5$–H$_2$O. It is likely that the primary interaction between BF$_3$.H$_2$O and acetone is the formation of an analogous ternary complex and that therefore Gillespie and Hartman\textsuperscript{2} in their NMR study observed the behaviour of the ternary complex BF$_3$.H$_2$O.OC(CH$_3$)$_2$ instead of the binary adduct BF$_3$.H$_2$O as hitherto thought. Their statement that "...acetone is much inferior to water as an electron pair donor to BF$_3$" is not corroborated by comparison of donor strengths towards SbCl$_5$. The ex-

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* The enthalpy value for the formation of the SbCl$_5$.H$_2$O adduct referred to in Ref. 8 has been found to be in error. Later experiments have confirmed the value of $-18.0$ kcal mol$^{-1}$ given in Ref. 6.*

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change between acetone bound in the ternary complex and bulk acetone is expected to be rapid on the NMR time scale in accordance with observations on ternary complexes of SbCl₅H₂O⁹ and the complexation of acetone will therefore not be revealed by NMR.

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