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A Proton Magnetic Resonance Study of $SbCl_5.H_2O$ and $SbCl_5.2H_2O$ Adducts in Solution

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The interaction between H_2O and the Lewis acid $SbCl_5$ has been studied in CH_2Cl_2 solution with varying H_2O:$SbCl_5$ molar ratios by PMR at temperatures between -100 and $+40$°C. In solutions with H_2O:$SbCl_5 \leq 1$ the monomeric adduct $SbCl_5.H_2O$ is quantitatively formed. If $1 < H_2O$:$SbCl_5 \leq 2$ a second water molecule is added forming a stable, probably hydrogen bonded complex $SbCl_5.2H_2O$.

It is well known that a number of metal halides, MeX_n, 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 BF_3-H_2O in acetone solution.[2] As the $MeX_n.H_2O$ 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 CH_2Cl_2. Due to the high solubility of $SbCl_5-H_2O$ complexes in halogenated hydrocarbons this system was studied instead of the less soluble BF_3-H_2O system.

EXPERIMENTAL

Materials. $SbCl_5$ (Merck, chromatographic grade) was used without further treatment. CH_2Cl_2 (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[3] and found to be less than 10 ppm.

Samples. Stock solutions of $SbCl_5$ in CH_2Cl_2 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 N_2. The composition of the samples was checked by determination of peak areas in the NMR spectra using the ^{13}C-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.

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 $SbCl_5-H_2O$ in CH_2Cl_2 were determined either directly relative to the low field ^{13}C-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 CH_2Cl_2 peak and a value of δ 6.84 for the low field ^{13}C-satellite at 60 MHz. The reproducibility of the chemical shift values is estimated to be better than 0.01 ppm.

The spectra of $SbCl_5.H_2O$ in $C_2H_4Cl_2$ and CCl_4 and of $BF_3.H_2O$ in $C_2H_4Cl_2$ were recorded at the working temperature of the spectrometer, about 40°C. The shift values were measured relative to that of $C_2H_4Cl_2$ (a small amount of $C_2H_4Cl_2$ had been added to the CCl_4 sample) and recalculated to δ in ppm relative to internal TMS using a value of δ 3.76 for neat $C_2H_4Cl_2$ and of δ 3.69 for $C_2H_4Cl_2$ in CCl_4.

RESULTS

PMR spectra of samples containing $SbCl_5$ and H_2O in CH_2Cl_2 solution were recorded at temperatures ranging from −100 to +40°C and with varying $SbCl_5$:H_2O 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 $SbCl_5$ 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 $SbCl_5.H_2O$ adduct. The differences observed at constant temperature between proton shifts of samples containing $SbCl_5.H_2O$ concentrations from 0.05 *m* to 0.56 *m* were less than 0.02 ppm (*cf.* below). This indicates that $SbCl_5.H_2O$ 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 H_2O:$SbCl_5$ 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 $SbCl_5.H_2O + H_2O \rightarrow SbCl_5.2H_2O$, the following eqn. (1) between the observed chemical shift δ and the concentrations of the reactants should be applicable:

$$\delta = [2\, m(SbCl_5)\, (\delta_1 - \delta_2)/m(H_2O)] - \delta_1 + 2\, \delta_2 \qquad (1)$$

where δ_1 and δ_2 denote the proton chemical shifts of the 1:1 and 1:2 complexes, respectively. A plot of observed chemical shift values against $SbCl_5$:H_2O 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 δ_1 and δ_2, respectively. The value of δ_1 is in good agreement with the chemical shift of the 1:1 complex observed in samples with $SbCl_5$ in excess.

Samples with H_2O:$SbCl_5$ molar ratios larger than 2 have not been studied.

The temperature dependence of the proton chemical shift was studied for four samples of $SbCl_5$ 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*.

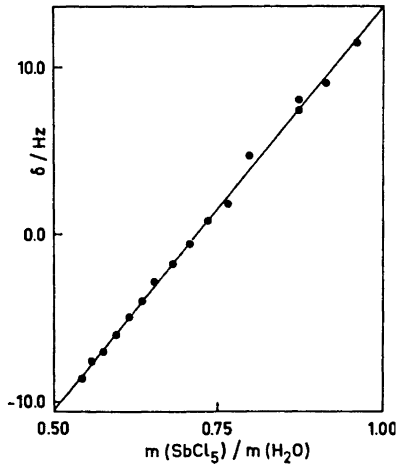

Fig. 1. Chemical shift of water protons against $SbCl_5$:H_2O molar ratio at 41°C. The chemical shifts are relative to that of the low field solvent ^{13}C-satellite.

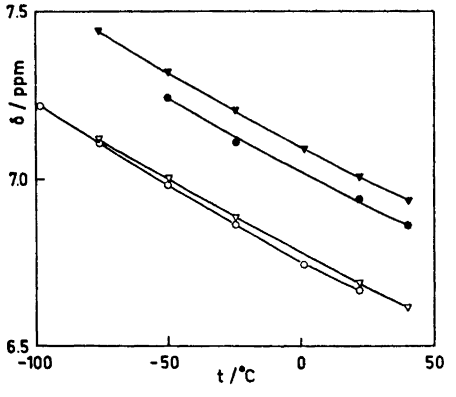

Fig. 2. Water proton chemical shifts of samples (a) – (d) against temperature. (a) ○, (b) ▽, (c) ●, (d) ▼. Chemical shifts are given in ppm relative to internal TMS.

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 δ 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 -4.1×10^{-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_2Cl_2 was observed to be δ 1.59 in a 6.5×10^{-3} *m* solution and δ 1.62 in a 39×10^{-3} *m* solution at 20°C.

The proton chemical shift of $SbCl_5.H_2O$ in the presence of excess $SbCl_5$ was observed to be δ 7.0 in $C_2H_4Cl_2$ solution and δ 6.4 in CCl_4 solution at 40°C.

$BF_3 - H_2O$. A signal from the water protons was observed at δ 8.2 in a sample containing BF_3 and H_2O in $C_2H_4Cl_2$. 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 $BF_3.H_2O$ adduct. Due to the low solubility in CH_2Cl_2 and $C_2H_4Cl_2$ the $BF_3 - H_2O$ system was not further studied.

DISCUSSION

The complexes $SbCl_5.H_2O$ and $BF_3.H_2O$ are considered to exist in weakly interacting solvents as molecular electron-pair donor-acceptor adducts. The

vibrational spectrum of (solid?) $SbCl_5.H_2O$ 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_5SbO moiety.[4] The latter complex is known from an X-ray crystallographic study to exist as a donor-acceptor adduct.[5]

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 $C_2H_4Cl_2$ solution.[6-8]* 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 $SbCl_5.2H_2O$ complex is less exothermic than the formation of the 1:1 adduct.[9] The high solubility of both the 1:1 and 1:2 complexes in inert solvents like CH_2Cl_2 and $C_2H_4Cl_2$ 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 -4.1×10^{-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 $SbCl_5-H_2O$ 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[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 $BF_3.H_2O$ adduct in acetone, δ 12.46,[2] and in $C_2H_4Cl_2$, δ 8.2, indicates solute-solvent interaction in acetone solution. $SbCl_5.H_2O$ has been found to interact with weak bases like ethers and ketones in $C_2H_4Cl_2$ 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 $SbCl_5-H_2O$. It is likely that the primary interaction between $BF_3.H_2O$ and acetone is the formation of an analogous ternary complex and that therefore Gillespie and Hartman[2] in their NMR study observed the behaviour of the ternary complex $BF_3.H_2O.OC(CH_3)_2$ instead of the binary adduct $BF_3.H_2O$ 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-

* The enthalpy value for the formation of the $SbCl_5.H_2O$ 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.[9]

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 $SbCl_5.H_2O$ [9] and the complexation of acetone will therefore not be revealed by NMR.

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