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A CALORIMETRIC STUDY OF THE INTERACTION OF $H_2O{\cdot}SbCl_5$ AND HCl–$SbCl_5$ WITH WEAK ORGANIC BASES IN 1,2-DICHLOROETHANE

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Abstract—The enthalpies of interaction between $H_2O{\cdot}SbCl_5$ and the oxygen bases DMA, n-Pr_2O, MePrCO, and EtOAc to form ternary complexes $D{\cdot}H_2O{\cdot}SbCl_5$ in 1,2-dichloroethane solution have been determined calorimetrically. Reaction of water with the binary adducts $D{\cdot}SbCl_5$ result in the formation of the same ternary complexes which has been confirmed by PMR spectroscopic experiments. The base molecules are considered to be strongly H-bonded to the $H_2O{\cdot}SbCl_5$ adduct in the complexes in solution.

The enthalpy of formation of $H_2O{\cdot}SbCl_5$ in 1,2-dichloroethane solution has been redetermined.

The enthalpies of formation of the $[DH]^+SbCl_6^-$ and $[D_2H]^+SbCl_6^-$ complexes from the complex acid HCl–$SbCl_5$ and Pr_2O, MePrCO and $(MeO)_2CO$ have been determined and estimates of the association constant for the formation of the $[DH]^+SbCl_6^-$ complexes from the $D{\cdot}SbCl_5$ adducts have been derived for D = MePrCO, EtOAc and $(MeO)_2CO$.

Measurements of the interaction between HCl–$SbCl_5$ and the protogenic ligands PrOH and H_2O were also made.

INTRODUCTION

Antimony pentachloride is a strong Lewis acid which forms numerous electron-pair donor-acceptor adducts with organic oxygen bases. In a series of reaction calorimetric experiments the enthalpies of formation have been determined for a number of 1 : 1 molecular adducts of $SbCl_5$ and oxygen bases, mostly carbonyl compounds.[1,2] The adducts are usually quite reactive and show a strong tendency to interact with proton-releasing substances like water and HCl. Interaction of the adducts with HCl leads to the formation of oxonium salts consisting of $SbCl_6^-$ anion and either the protonated base, DH^+, or the hydrogen bonded cation D_2H^+.[3–6] Results of a reaction calorimetric and PMR spectroscopic study on the formation of $SbCl_6^-$ complexes in 1,2-dichloroethane solution of DMA, TMU, DMSO and EtOAc has recently been reported.[7] Results of calorimetric experiments on complex formation of the donor compounds MePrCO, $(MeO)_2CO$, n-Pr_2O and PrOH with HCl–$SbCl_5$ are given in the present paper.

$SbCl_5$ interacts with water to give an adduct of 1 : 1 composition that is considered to exist as an electron-pair donor-acceptor adduct in solution.[8] Adduct formation is supposed to enhance the acidity of the water protons and make $H_2O{\cdot}SbCl_5$ a strong Brönsted acid. Formation of solid salts of the hydrate of $SbCl_5$ and diethyl ether and cineol has been reported.[9] The composition of the Et_2O salt was 2 : 1 : 1 and it may therefore be considered analogous to the $[D_2H]^+SbCl_6^-$ salts. The interaction between $H_2O{\cdot}SbCl_5$ and four nonprotogenic donors has been studied in 1,2-dichloroethane solution by reaction calorimetry to gain some information about the acidic properties of $H_2O{\cdot}SbCl_5$ in solution.

RESULTS

Calorimetric experiments were carried out by dissolving the donor compounds in 1,2-dichloroethane solutions containing both $SbCl_5$ and HCl in excess. The measured enthalpy change, ΔH(obs), can be regarded as the sum of enthalpy changes of three processes: dissolution of the liquid donor, ΔH(soln); quantitative formation of the $D{\cdot}SbCl_5$ adduct, $\Delta H(D{\cdot}SbCl_5)$; reaction of $D{\cdot}SbCl_5$ with HCl to give the oxonium salt, reaction (I).

$$HCl(soln) + D{\cdot}SbCl_5(soln) \rightarrow [DH]^+SbCl_6^-(soln) \qquad \Delta H(I) \quad (I)$$

If reaction (I) goes to completion it follows that

$$\Delta H(I) = \Delta H(obs) - \Delta H(D{\cdot}SbCl_5) - \Delta H(soln)$$

HCl and $SbCl_5$ do not give any measurable interaction enthalpy under the conditions of the calorimetric experiments.[7]

Values for $\Delta H(D{\cdot}SbCl_5)$ and ΔH(soln) for the donors used in the present study are given in columns 2 and 3 of Table 1.

The ΔH(obs) values were found to vary, however, with HCl concentration which is ascribed to changes in degree of conversion to ternary complex. The results are shown in Fig 1 where the difference between ΔH(obs) and the sum of ΔH(soln) and

Table 1. Enthalpies of solution of the donor compounds in 1,2-dichloroethane and enthalpy changes accompanying the formation of the D·$SbCl_5$ adducts in solution

D	$-\Delta H$(soln) kJ mol^{-1}	$-\Delta H$(D·$SbCl_5$) kJ mol^{-1}	Lit. ref.
DMA	$3·8 \pm 0·1$[a]	$116·3 \pm 0·6$	10
MePrCO	$1·2 \pm 0·1$	$73·2 \pm 0·2$	11
EtOAc	$1·0 \pm 0·1$	$71·5 \pm 0·4$	12
$(MeO)_2CO$	$0·6 \pm 0·1$	$63·5 \pm 0·3$	12
$(n\text{-}Pr)_2O$	$-2·6 \pm 0·1$	$74·6 \pm 0·2$	2
PrOH	$-14·6 \pm 0·2$	$82·0 \pm 0·6$	this study
H_2O	$-18·4 \pm 0·8$	$68·7 \pm 1·0$	this study

[a] Error limits given in the Tables indicate random errors expressed as twice the standard deviation of the mean.

Table 2. Enthalpy changes accompanying the formation of oxonium salts from the D·$SbCl_5$ adducts in 1,2-dichloroethane

D	$-\Delta H([DH]^+SbCl_6^-)$ kJ mol^{-1}	$-\Delta H([D_2H]^+SbCl_6^-)$ kJ mol^{-1}
DMA	53[a]	100 ± 1[a]
MePrCO	35[b]	81 ± 3
EtOAc	39[b]	83 ± 3
$(MeO)_2CO$	31[b]	71 ± 1
$(n\text{-}Pr)_2O$	40[b]	92 ± 3
n-PrOH	—	46 ± 2

[a] From ref. 7.
[b] See text.

ΔH(D·$SbCl_5$), denoted $\Delta H(I)_{app}$, are plotted against HCl concentration.* The concentration of the donor compounds were close to 0·010 mol l^{-1} and that of $SbCl_5$ 0·02 to 0·03 mol l^{-1}. The excess $SbCl_5$ is thought not to have any influence on the equilibrium of reaction (I). It is clear from the figure that only for Pr_2O is there close to complete conversion to the oxonium salt under the conditions of the calorimetric experiments. Estimates of $\Delta H(I)$ and the association constant, K, for the other donors can be obtained from an analysis of the variation of $\Delta H(I)_{app}$ with HCl concentration. From results of seven experiments with MePrCO and five with EtOAc and $(MeO)_2CO$ K-values of 13, 7 and 8 l mol^{-1}, respectively, were derived together with the $\Delta H(I)$ values shown in column 2 of Table 2. The uncertainties in the figures are quite large so it is not meaningful to discuss differences between the donors.

The enthalpy changes observed for the interaction between $SbCl_5$ and PrOH and H_2O, respectively, were not affected by the presence of 0·17 mol l^{-1} HCl. The stabilities of the $[PrOH_2]^+SbCl_6^-$ and $H_3O^+SbCl_6^-$ complexes in solution are apparently too low to give any noticeable conversion under the conditions of the calorimetric experiments.

Results of calorimetric measurements of addition of HCl in solution to a solution containing D·$SbCl_5$ and excess D, reaction (II), are summarized in column 3 of Table 2.

$$\begin{aligned}&HCl(soln) + D(soln) + D\cdot SbCl_5(soln)\\ &\rightarrow [D_2H]^+SbCl_6^-(soln) \quad \Delta H(II) \qquad (II)\end{aligned}$$

The values given are mean values of four experiments and the concentrations of the reactants were HCl 0·013, $SbCl_5$ 0·05–0·10 and D 0·10–0·20 mol l^{-1}.

To determine the enthalpy of interaction between H_2O·$SbCl_5$ and the donor compounds calorimetric experiments were carried out by dissolving the donor in 1,2-dichloroethane containing two different concentrations of H_2O·$SbCl_5$. The results of duplicate runs are shown in Table 3. The enthalpy values have been corrected for the dissolution of the donors and they refer to the following reaction:

$$\begin{aligned}&D(soln) + H_2O\cdot SbCl_5(soln) \rightarrow D\cdot H_2O\cdot SbCl_5(soln)\\ &\Delta H(III) \qquad (III)\end{aligned}$$

The concentration dependence of the found values for MePrCO and EtOAc is considered to be due to changes in degree of conversion to ternary complex while for DMA the reason for the slightly higher $-\Delta H(III)_{app}$ values observed in 0·20 mol l^{-1} H_2O·$SbCl_5$ also could be interaction with a second H_2O·$SbCl_5$ molecule, *cf* reference 13. The difference between the two values for Pr_2O is probably not significant.

In ternary systems D–H_2O–$SbCl_5$ there will be competitive formation of ternary complexes D·H_2O·$SbCl_5$ and binary adducts D·$SbCl_5$. The thermodynamic properties of the following reaction will be of interest in this connection:

$$\begin{aligned}&H_2O(soln) + D\cdot SbCl_5(soln) \rightarrow D\cdot H_2O\cdot SbCl_5(soln)\\ &\Delta H(IV) \qquad (IV)\end{aligned}$$

The enthalpy change $\Delta H(IV)$ can be obtained from $\Delta H(III)$ by addition of $\Delta H(H_2O\cdot SbCl_5)$ and subtraction of $\Delta H(D\cdot SbCl_5)$. Using the value of -69 kJ mol^{-1} for $\Delta H(H_2O\cdot SbCl_5)$ (see below) and values of $\Delta H(D\cdot SbCl_5)$ shown in Table 1, the

Table 3. Observed enthalpy changes accompanying the interaction between donor compounds and H_2O·$SbCl_5$ at a donor concentration of 0·01 mol . l^{-1} and H_2O·$SbCl_5$ concentrations indicated

D	$-\Delta H(III)_{app}$/kJ mol^{-1} c = 0·033	c = 0·20
DMA	88·4	91·3
MePrCO	35·3	41·0
EtOAc	31·3	37·2
$(n\text{-}Pr)_2O$	44·0	45·6

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*The subscript "app" is used in the following to indicate that given enthalpy values may refer to reactions with incomplete conversion to product.

$\Delta H(IV)_{app}$ values shown in Fig 1 were calculated from the $\Delta H(III)_{app}$ values given in Table 3.

Results of calorimetric measurements of addition of water to the $D\cdot SbCl_5$ adducts of DMA and Pr_2O in solution are shown in Table 4. The enthalpy values have been corrected for enthalpy of dissolution of water and thus refer to reaction (IV). The observed values for DMA vary with the concentration of the reactants and it is clear that the association constant is smaller in that system than in the Pr_2O system. The formation of the ternary complex is considered to be quantitative in the more concentrated solutions. Considering the uncertainties in the results it can be concluded that there are no indications of a significant difference between the $\Delta H(IV)$ values for DMA and Pr_2O determined according to reaction (IV) or the values derived from $\Delta H(III)$.

Calorimetric experiments in which $H_2O\cdot SbCl_5$ in solution was added to solutions containing donor compounds in excess gave slightly more exothermic enthalpy changes than those observed for the reactions with $H_2O\cdot SbCl_5$ in excess. The excess enthalpies observed were less than 15 kJ mol^{-1} except for Pr_2O for which it amounted to 22 kJ mol^{-1}. The concentrations were 0·015 mol l^{-1} of $H_2O\cdot SbCl_5$ and 0·10 mol l^{-1} of D. Experiments with smaller excess of D gave smaller excess enthalpies.

The secondary interactions in these solutions are interpreted as partial association of donor to the $D\cdot H_2O\cdot SbCl_5$ complexes. It can be noted that the enthalpy changes for the formation of the corresponding $[D_2H]^+SbCl_5^-$ complexes are between −70 and −100 kJ mol^{-1}, Table 2.

The enthalpy of formation of $H_2O\cdot SbCl_5$ has been redetermined.

$$H_2O(soln) + SbCl_5(soln) \rightarrow H_2O\cdot SbCl_5(soln) \quad \Delta H(H_2O\cdot SbCl_5) \qquad (V)$$

Results of measurements of breaking ampoules containing 1·5 to 2 mmol of water in 100 ml $C_2H_4Cl_2$ containing 3 mmol $SbCl_5$ were combined with results of measurements of dissolving water in pure $C_2H_4Cl_2$ (1 to 2 mmol water in 100 ml $C_2H_4Cl_2$) to give the enthalpy value for reaction V shown in Table 1. Within errors of measurements the same enthalpy value was found from experiments of addition of 50 μmol of water dissolved in 1 ml $C_2H_4Cl_2$ to 25 ml 0·02 mol l^{-1} $SbCl_5$ solution.*

Water is predominantly monomeric in $C_2H_4Cl_2$ at the concentrations used in the present study.[15]

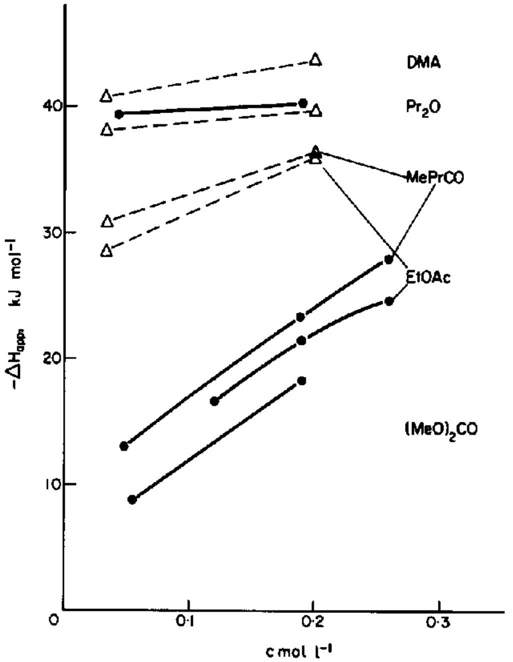

Fig 1. Apparent enthalpy changes for the formation of ternary complexes from $D\cdot SbCl_5$ adducts plotted against concentrations of HCl and $H_2O\cdot SbCl_5$, respectively.
● $HCl + D\cdot SbCl_5 \rightarrow [DH]^+SbCl_6^-$ (I)
△ $H_2O + D\cdot SbCl_5 \rightarrow D\cdot H_2O\cdot SbCl_5$ (IV)

Table 4. Observed enthalpy changes in experiments of addition of water to $D\cdot SbCl_5$ adducts in 1,2-dichloroethane

D	$c(H_2O)$ mol l^{-1}	$c(SbCl_5)$ mol l^{-1}	$-\Delta H(IV)_{obs}$ kJ mol^{-1}
DMA	0·020	0·025	33·1
	0·014	0·025	35·2
	0·081	0·113	38·7
	0·054	0·115	41·8
	0·052	0·116	42·8
$(n-Pr)_2O$	0·014	0·025	42·4
	0·014	0·027	43·3
	0·055	0·112	42·5
	0·055	0·121	44·8

The $-\Delta H(H_2O\cdot SbCl_5)$ value found in the present study is somewhat lower than the value of 75 kJ mol^{-1} reported by Gutman and Mayer.[16] There was no information given in their paper about experimental procedure and errors of measurements.

$H_2O\cdot SbCl_5$ has been found to interact with excess H_2O to give a complex $2H_2O\cdot SbCl_5$ in solution.[8] Calorimetric experiments in which 0·41 mmol $H_2O\cdot SbCl_5$ in solution was added to 25 ml $C_2H_2Cl_2$ containing a slight excess of H_2O gave an enthalpy change of −28 kJ mol^{-1}. Attempts to double the water content resulted in formation of a precipitate. It can be concluded, however, that the association of the second water molecule is less

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*An earlier reported value[14] is in error partly due to a systematic error in the determination of water concentration and partly due to the neglect of formation of ternary complex between $H_2O\cdot SbCl_5$ and ethyl propionate.

exothermic than the formation of $H_2O \cdot SbCl_5$ although it is probable that the association was not quantitative under the experimental conditions.

NMR spectra. PMR spectra of samples containing close to equimolar amounts of DMA, H_2O and $SbCl_5$ showed chemical shifts and long-range coupling constants as indicated in Table 5A. In addition a signal of the water protons was observed at δ 7·9. The relative intensities of the resonance signals as estimated from peak integrals were consistent with a DMA:H_2O ratio of 1:1. The samples were prepared either by addition of DMA to a solution containing $H_2O \cdot SbCl_5$ or addition of H_2O to a $DMA \cdot SbCl_5$ solution. Previously reported values for DMA and its $SbCl_5$ and HCl–$SbCl_5$ complexes are included in Table 5A.[7] The *trans* aminomethyl group, that is the group showing the larger long-range coupling, was found to absorb at higher field than the *cis* group in DMA and its ternary complexes while the opposite was observed for $DMA \cdot SbCl_5$, *cf* Fig 1 of reference 7. In samples containing DMA in excess rapid exchange was observed between complexed and unbound DMA at 37°C and the water proton peak was observed at lower field. Chemical shifts observed in samples containing EtOAc, H_2O and $SbCl_5$ in equimolar amounts are shown in Table 5B. The chemical shift of the water was δ 9·8. The same chemical shift values were observed for EtOAc in samples containing $H_2O \cdot SbCl_5$ in excess and the water proton shift was the weighted average of the shift in the ternary complex and in $H_2O \cdot SbCl_5$, δ 6·6.[8] In samples containing EtOAc in excess the water proton signal was shifted below δ 9·8. Results of PMR measurements on MeOPr and its complexes in $C_2H_4Cl_2$ are summarized in Table 5C. The given values of $^4J_{H-H}$ refer to coupling over the oxygen atom. A broadened peak at δ 11·1 was observed for the acidic proton in the HCl–$SbCl_5$ sample. The chemical shift of the water protons in samples of MeOPr, H_2O and $SbCl_5$ prepared to contain equimolar amounts of reactants was observed to vary a couple of tenths ppm between different samples, the mean value being δ 10·2.

DISCUSSION

It was concluded from the close agreement between the acidic proton chemical shifts observed for the protonated bases in HSO_3F or "magic acid" and in the corresponding $[DH]^+SbCl_6^-$ complexes that there is complete proton transfer in the oxonium salts without specific interactions between anion and cation.[7] The equilibrium constants for the association of HCl to the $D \cdot SbCl_5$ adducts of MePrCO, EtOAc and $(MeO)_2CO$ have been found to be about 10 l mol^{-1} showing that the stability of the $[DH]^+SbCl_6^-$ complexes is moderate in $C_2H_4Cl_2$ solution. The formation of the oxonium salts is thus accompanied by a large negative entropy change as the association enthalpies were −30 to

Table 5. Proton chemical shifts and coupling constants in DMA, EtOAc, and MeOPr and their respective adducts in 1,2-dichloroethane solution at 37°C. The chemical shifts were measured relative that of the solvent and recalculated to δ in ppm relative internal TMS

A.

	$C-CH_3$	$N-CH_3$ mean value	peak separation in $N(CH_3)_2$	$^5J_{H-H}(cis)$ Hz	$^5J_{H-H}(trans)$ Hz
DMA[a]	1·98	2·90	0·11	unresolved	
$DMA \cdot SbCl_5$[a]	2·70	3·39	0·06	~0·3	1·0
$[DMAH]^+SbCl_6^-$[a]	2·78	3·44	0·06	~0·3	1·0
$DMA \cdot H_2O \cdot SbCl_5$	2·67	3·38	0·08	unresolved	0·8

B.

	CH_2-CH_3	CH_2	$CO-CH_3$	$^5J_{H-H}$ Hz
EtOAc[a]	1·22	4·07	1·99	unresolved
$EtOAc \cdot SbCl_5$	1·49	4·65	2·78	~0·3
$[EtOAcH]^+SbCl_6^-$[a]	1·50	4·68	2·82	~0·3
$EtOAc \cdot H_2O \cdot SbCl_5$	1·41	4·52	2·54	indicated

C.

	$C-CH_3$	$C-CH_2-C$	$C-CH_2-O$	$O-CH_3$	$^4J_{H-}$ Hz
MeOPr	0·54	1·54	2·37	2·06	~0·3
$MeOPr \cdot SbCl_5$	1·05	1·91	3·07[b]	3·01[b]	1·0
$[MeOPrH]^+SbCl_6^-$	1·05	1·91	3·34	3·16	1·0
$MeOPr \cdot H_2O \cdot SbCl_5$	0·99	1·75	2·95	2·75	1·0

[a] From reference 7.

[b] Overlapping signals.

-40 kJ mol^{-1}. It can be noted that neither NMR nor calorimetry have given any indications of association of HCl in $C_2H_4Cl_2$ solution to the $SbCl_5$ adducts of PrOH and H_2O. However, the solid oxonium salts have been prepared.[3]

The $[DH]^+SbCl_6^-$ complexes show a pronounced tendency to add a second base molecule to form $[D_2H]^+SbCl_6^-$ complexes in which the cation is held together by a strong possibly symmetrical H-bond.[3,6] The formation of the $[D_2H]^+$ complexes from the $D\cdot SbCl_5$ adducts is accompanied by a considerable enthalpy change, -70 to -100 kJ mol^{-1} for the non-protogenic donors in this study. The formation of what is considered to be the analogous PrOH complex is less exothermic, -46 kJ mol^{-1}. The reason for the reduced tendency of PrOH and H_2O to form oxonium salt in solution is obscure. Klages *et al.*[3–5] have prepared a number of protonated complexes in solid state and studied their stability by measuring the vapour pressure over the salts as a function of temperature. The $[DH]^+SbCl_6^-$ salts showed a quite large HCl pressure at room temperature while the $[D_2H]^+$ salts were characterized by a low equilibrium pressure of HCl. Assuming the gas phase to consist of HCl they calculated the dissociation enthalpies of the salts. However, the dissociation products were not studied and it is uncertain to which reaction the ΔH values refer and they cannot therefore be compared with the enthalpy values found in the present study.

The donor strength of water towards $SbCl_5$ is about the same as that of alkyl ethers and ketones, *cf* Table 1. However, interactions in solutions containing $SbCl_5$ and the donor compounds H_2O and D in excess cannot be described as competitive formation of the binary adducts, $H_2O + D\cdot SbCl_5 \rightleftarrows H_2O\cdot SbCl_5 + D$. The results of the calorimetric and PMR experiments show that well defined complexes $D\cdot H_2O\cdot SbCl_5$ are formed under these conditions. The same complex is formed either from reaction of D with $H_2O\cdot SbCl_5$ or from reaction of H_2O with $D\cdot SbCl_5$. Interactions in the ternary system D–H_2O–$SbCl_5$ can therefore be regarded either as reaction of the $D\cdot SbCl_5$ adduct with water or interaction of the presumedly acidic $H_2O\cdot SbCl_5$ adduct with the basic compound D. The DMA part of the PMR spectrum of the ternary complex with $H_2O\cdot SbCl_5$ resembled that of the $[DMAH]^+SbCl_6^-$ complex and showed a pattern of the N–$(CH_3)_2$ group which differs from that observed of the $DMA\cdot SbCl_5$ adduct. Therefore, water is considered to coordinate at the Sb atom and not the carbonyl oxygen of DMA. It is clear from the calorimetric experiments of addition of $H_2O\cdot SbCl_5$ to solutions containing DMA in excess that the $DMA\cdot H_2O\cdot SbCl_5$ complex interacts only weakly with excess donor. This is contrary to what is observed for $[DMAH]^+SbCl_6^-$. Therefore we prefer to describe the complex as a ternary adduct in which DMA is held by strong H-bonding to water in the $H_2O\cdot SbCl_5$ adduct. The other ternary complexes studied are assumed to have similar structures. The smaller chemical shift changes of the protons in EtOAc and MeOPr accompanying the formation of the ternary complexes compared to the formation of the corresponding $D\cdot SbCl_5$ adducts are consistent with this assumption.

From Fig 1 it is obvious that the association enthalpies of water to the four $D\cdot SbCl_5$ adducts in the present study are closely similar. Thus the formation of the $D\cdot H_2O\cdot SbCl_5$ complexes shows a levelling effect as DMA generally acts as a stronger electron-pair donor and stronger base than the other three compounds. Results of the experiments of addition of H_2O to the DMA and Pr_2O adducts indicate indeed that the $Pr_2O\cdot H_2O\cdot SbCl_5$ complex is more stable in 1,2-dichloroethane solution than the DMA complex.

The enthalpy changes for the formation of the ternary complexes $[DH]^+SbCl_6^-$ and $D\cdot H_2O\cdot SbCl_5$ from $D\cdot SbCl_5$ and HCl and H_2O, respectively, are about the same for Pr_2O, MePrCO and EtOA. The difference between the enthalpy values found for DMA is small and might arise from secondary interactions with excess acid.[13] It will thus seem that HCl–$SbCl_5$ and $H_2O\cdot SbCl_5$ interact quite analogously with the oxygen bases studied to give ternary complexes of approximately equal enthalpies of formation. There is, however, the difference that while the $SbCl_6^-$ anion shows very weak hydrogen bonding tendency the $SbCl_5OH^-$ anion is strongly H-bonding. The strong tendency of the $[DH]^+SbCl_6^-$ complexes to form strongly H-bonded cations $[D_2H]^+$ is not observed for the $H_2O\cdot SbCl_5$ complexes which were found to interact only weakly with excess base in solution.

EXPERIMENTAL

Materials. The organic compounds were dried with molecular sieves 4A and fractionally distilled. The purity of the samples was better than 99·5% as judged from analytical GLC. The water content of the samples was checked separately using a GSC method[17] and found to be less than 0·01% except n-propanol which contained 0·18% by volume of water. $SbCl_5$ and 1,2-dichloroethane were treated as described previously.[7] The HCl solutions used in the experiments with $[DH]^+SbCl_6^-$ and $[D_2H]^+SbCl_6^-$ were prepared as described in reference 7 except that anhyd $AlCl_3$ was used as drying agent for HCl instead of Sicapent.

The samples of $SbCl_5\cdot H_2O$ were prepared by addition of a known amount of $SbCl_5$ dissolved in $C_2H_4Cl_2$ to a cooled sample of $C_2H_4Cl_2$ to which an appropriate amount of water had been added. The water which was added in slight excess dissolved on gentle shaking to give a clear, almost colourless soln. The solns of $DMA\cdot SbCl_5$ and $Pr_2O\cdot SbCl_5$ were prepared directly in the calorimetric vessel immediately before each experiment. The donor compounds were added in slight excess. The concentrations were considered to be known to within a couple of percent.

For the determination of $\Delta H(H_2O\cdot SbCl_5)$ two samples of $C_2H_4Cl_2$ containing about 0·1% by weight of water were prepared by adding known amounts of water to dry $C_2H_4Cl_2$ using a Hamilton syringe. The water concentra- was checked by GSC. The solutions were filled into 1 ml thin-walled ampoules.

The NMR samples were prepared directly in the NMR tubes by addition under cooling of the liquid donor compound from a Hamilton syringe to a weighed amount of $H_2O\cdot SbCl_5$ soln. Samples were also prepared by addition of water to cooled samples of $D\cdot SbCl_5$. The $SbCl_5$ concentration was about 1·3 mol l^{-1} in the samples. The MeOPr–HCl–$SbCl_5$ samples were prepared by introduction of gaseous HCl to MeOPr·$SbCl_5$ in soln.

Apparatus and measurements. The calorimetric measurements were made with an LKB 8721 Reaction Solution Calorimeter using glass vessels of 25 and 100 ml volume. The calorimetric experiments were performed as described elsewhere.[7] The reactions took place immediately and the reaction periods were less than 4 min except in the experiments in which the calorimetric ampoules contained pure water in which the slow dissolution of water gave reaction periods of about 30 min duration.

NMR spectra were recorded using a Varian A-60 A spectrometer. The chemical shifts relative to that of the solvent were determined directly from the calibrated charts. The values were recalculated to δ values relative to internal TMS using a δ value of 3·76 for 1,2-dichloroethane.[7]

Units of measurements. The results of the calorimetric experiments are expressed in absolute joules and refer to the isothermal process at 25°C.

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