Tetrahedron. Vol. 27, pp. 5921 to 5931. Pergamon Press 1971. Printed in Great Britain

A CALORIMETRIC AND PMR STUDY OF PROTONATION REACTIONS IN AN INERT SOLVENT

THE INTERACTION BETWEEN SOME WEAK ORGANIC BASES AND HCl–SbCl$_5$ IN 1,2-DICHLOROETHANE SOLUTION

Q. APPLETON,* L. BERNANDER and G. OLOFSSON†
Thermochemistry Laboratory, Chemical Center, University of Lund, S-220 07 Lund, Sweden

(*Received in the UK* 30 *April* 1971; *Accepted for publication* 12 *July* 1971)

Abstract—Protonation of dimethylacetamide (DMA), tetramethylurea (TMU), ethyl acetate (EtOAc) and dimethylsulphoxide (DMSO) by the complex acid HCl–SbCl$_5$ in 1,2-dichloroethane has been studied. Enthalpy changes for the interaction between the donor compounds (D) and excess HCl–SbCl$_5$ to give the protonated complexes $[DH]^+SbCl_6^-$ have been determined calorimetrically. From NMR experiments it was found that the acidic proton in the $[DH]^+SbCl_6^-$ complexes was in slow exchange on the NMR time scale with excess acid at 37°C. The observed chemical shift values of the acidic proton in the $[DMAH]^+$ and $[EtOAcH]^+$ complexes were in close agreement with values reported for the protonated bases in HSO_3F or HSO_3F–SbF_5, which indicates that complete proton transfer takes place in the hexachloroantimonate complexes.

In solutions containing the donor compounds in excess, half-protonated complexes $[D_2H]^+SbCl_6^-$ were formed. The acidic proton chemical shifts in these complexes were found at 8–9 ppm lower field than in the monoprotonated complexes indicating strong hydrogen bonding in the $[D_2H]^+$ cations. Exchange between complexed and excess donor was found to be rapid on the NMR time scale.

D·SbCl$_5$ donor–acceptor adducts have also been studied. Protonation and adduct formation are considered to take place at the C=O and S=O oxygen atoms.

INTRODUCTION

COMPLEX ACIDS of the general formula HX–MX$_n$, e.g. HCl–AlCl$_3$, HF–BF$_3$ and HF–SbF$_5$, act as catalysts in many types of Friedel–Crafts reactions.[1] The acids are not known to exist in the form HMX_{n+1} but in the presence of proton accepting substances, D, they form stable complexes of the composition $[D_iH]^+MX_{n+1}^-$ ($i \geq 1$).[2–4] The catalytic properties of the acids are related to their ability to supply protons.

Klages *et al.* have prepared and characterized a number of salts of organic cations, mainly of the composition $[DH]^+SbCl_6^-$.[2,5] D represents weak organic bases such as alcohols, ethers, aldehydes, carboxylic acids, amides, etc. The salts were prepared either directly by mixing the reactants at low temperature or by first preparing the electron donor–acceptor adduct D·SbCl$_5$ which was then treated with HCl in solution. Some salts of the composition $[D_2H]^+SbCl_6^-$ were also prepared.

It is obvious that when a complex acid HX–MX$_n$ interacts with an electron pair donor compound there is competition between protonation and adduct formation. To obtain information about the catalytic action of these systems it is therefore of interest to study both protonation reactions involving the complex acid and adduct formation reactions of the metal halide.

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* Present address: Chemical Science Dept., Hatfield Polytech, POB 109, Hatfield, Herts, England.

† To whom correspondence should be addressed.

In a series of reaction calorimetric experiments the enthalpies of formation have been determined for a number of molecular adducts between $SbCl_5$ and molecules containing the carbonyl group.[6] Here we report results of a calorimetric and NMR study on the protonation of dimethylacetamide (DMA), tetramethylurea (TMU), ethylacetate (EtOAc) and dimethylsulphoxide (DMSO) by $HCl-SbCl_5$.

RESULTS

Calorimetric measurements. The same enthalpy of solution value ($-1{\cdot}80 \pm 0{\cdot}10$ kJ.mol^{-1}) was found when $SbCl_5$ was dissolved in 1,2-dichloroethane or in 1,2-dichloroethane solution containing 0·06 mol.l^{-1} of HCl. The concentration of $SbCl_5$ was 0·03 mol.l^{-1}; half of the amount of $SbCl_5$ had been added to the calorimetric liquid prior to the experiment to scavenge water present in the solvent.

Results of the calorimetric measurements of dissolving the donor compounds in 1,2-dichloroethane solution containing an excess of HCl and $SbCl_5$, reaction 1, are summarized in the second column of Table 1.

$$D(1) + HCl(soln) + SbCl_5(soln \rightarrow [DH]^+SbCl_6^-(soln)\,\Delta H_1 \qquad (1)$$

The concentrations (in mol.l^{-1}) of the reactants were: 0·005–0·017 of D, 0·10–0·11 of HCl and 0·02–0·05 of $SbCl_5$.

Results of calorimetric measurements of addition of HCl in 1,2-dichloroethane solution to a solution containing a donor–acceptor adduct, $D{\cdot}SbCl_5$, and excess D, reaction 2, are summarized in column 3 of Table 1.

$$HCl(soln) + D{\cdot}SbCl_5(soln) + D(soln) \rightarrow [D_2H]^+SbCl_6^-(soln)\,\Delta H_2 \qquad (2)$$

TABLE 1. RESULTS OF CALORIMETRIC MEASUREMENTS OF INTERACTION BETWEEN DONOR COMPOUNDS (D) AND EXCESS $HCl-SbCl_5$ (ΔH_1) AND OF ADDITION OF HCl TO $D{\cdot}SbCl_5$ ADDUCTS IN THE PRESENCE OF EXCESS D (ΔH_2) IN 1,2-DICHLOROETHANE SOLUTION AT 25°C

Donor	$-\Delta H_1$/kJ.mol^{-1}	$-\Delta H_2$/kJ.mol^{-1}
DMA	173·3 ± 0·6	100·0 ± 0·9
TMU	181·0 ± 0·4	92·3 ± 1·0
EtOAc	89·1 ± 0·2	82·7 ± 1·3
DMSO	134·8 ± 0·8	70·3 ± 1·3

The experiments were performed with two sets of total concentrations of the reactants *viz.* HCl 0·004, $SbCl_5$ 0·02 and D 0·05 mol.l^{-1} and HCl 0·015, $SbCl_5$ 0·085 and D 0·20 mol.l^{-1} with DMA and EtOAc. Equal ΔH_2 values were observed. In the experiments with TMU and DMSO the total concentrations were: HCl 0·012–0·015, $SbCl_5$ 0·05–0·10 and D 0·20–0·25 mol. l^{-1}, respectively. For these donors the reactions became too slow to be measured in more dilute solutions.

The water present (less than 0·0015 mol.l^{-1}) is believed not to have influenced the measured ΔH_1 and ΔH_2 values. The values given in Table 1 are the mean values of three to five experiments.

The following values (in kJ.mol^{-1}) for the enthalpies of solution of the donor compounds (reaction 3) have been reported previously: DMA $-3{\cdot}81$,[7] TMU $-4{\cdot}39$[7] and EtOAc $-1{\cdot}00$.[8]

$$D(1) + \text{solvent} \rightarrow D(\text{soln}) \quad \Delta H_3 \tag{3}$$

A ΔH_3 value of DMSO of $(-1{\cdot}45 \pm 0{\cdot}02)$ kJ.mol^{-1} was found in the present study.

The hypothetical reaction 4 with reactants and reaction product in 1,2-dichloroethane solution is obtained by subtracting reaction 3 from reaction 1.

$$D(\text{soln}) + HCl(\text{soln}) + SbCl_5(\text{soln}) \rightarrow [DH]^+SbCl_6^-(\text{soln}) \quad \Delta H_4 \tag{4}$$

$$\Delta H_4 = \Delta H_1 - \Delta H_3$$

The formation of the $[D_2H]^+SbCl_6^-$ complex from the reactants in solution, reaction 5, is obtained by addition of the adduct formation reaction 6 to reaction 2:

$$2D(\text{soln}) + HCl(\text{soln}) + SbCl_5(\text{soln}) \rightarrow [D_2H]^+SbCl_6^-(\text{soln}) \quad \Delta H_5 \tag{5}$$

$$D(\text{soln}) + SbCl_5(\text{soln}) \rightarrow D \cdot SbCl_5(\text{soln}) \quad \Delta H_6 \tag{6}$$

$$\Delta H_5 = \Delta H_2 + \Delta H_6$$

The ΔH_4 and ΔH_5 values are shown together with the previously reported ΔH_6 values in Table 2.

TABLE 2. ENTHALPIES OF FORMATION OF THE $[DH]^+SbCl_6^-(\Delta H_4)$, $[D_2H]^+SbCl_6^-(\Delta H_5)$ AND $D\cdot SbCl_5$ (ΔH_6) COMPLEXES IN 1,2-DICHLOROETHANE SOLUTION AT 25°C

Donor	$-\Delta H_4$/kJ.mol^{-1}	$-\Delta H_5$/kJ.mol^{-1}	$-\Delta H_6$/kJ.mol^{-1}
DMA	$169{\cdot}5 \pm 0{\cdot}6$	$216{\cdot}3 \pm 1{\cdot}1$	$116{\cdot}3 \pm 0{\cdot}6$[a]
TMU	$176{\cdot}7 \pm 0{\cdot}4$	$216{\cdot}3 \pm 1{\cdot}1$	$124{\cdot}0 \pm 0{\cdot}4$[a]
EtOAc	$88{\cdot}1$[b]	$154{\cdot}2 \pm 1{\cdot}4$	$71{\cdot}5 \pm 0{\cdot}4$[c]
DMSO	$133{\cdot}4$[b]	$195{\cdot}2 \pm 1{\cdot}4$	$124{\cdot}9 \pm 0{\cdot}6$[d]

[a] Ref. 7.

[b] See Discussion.

[c] Ref. 8.

[d] Gutmann *et al.* give 124·7 kJ.mol^{-1} without stating the uncertainty of the measurement.[9]

It is assumed that the enthalpy values given in Table 2 approximate the enthalpy changes for reactions 4–6 in the gaseous state.

Error limits given in Tables 1 and 2 indicate random errors expressed as twice the standard deviation of the mean.

The enthalpy of formation of the $[DMAH]^+SbCl_6^-$ complex was checked by measuring the enthalpy change when liquid $SbCl_5$ was added to a solution containing DMA and HCl. A ΔH value of $(-99{\cdot}4 \pm 2{\cdot}8)$ kJ.mol^{-1} was found from experiments with $SbCl_5$ concentration of 0·013–0·018 mol.l^{-1}, total DMA concentration 0·003 mol.l^{-1} higher than that of $SbCl_5$ and HCl concentration of 0·12 mol.l^{-1}. An enthalpy value of $(-171{\cdot}5 \pm 2{\cdot}9)$ kJ.mol^{-1} was found after addition of the enthalpy of interaction between DMA and HCl[*] and subtraction of the enthalpy of solution of $SbCl_5$. The found value is in satisfactory agreement with the value reported in Table 2. With increased excess of DMA in the calorimetric liquid higher $-\Delta H$ values were observed, due to secondary interactions in the solution.

NMR. In the PMR study, systems involving DMA have been treated more thoroughly than systems involving the other donor compounds. The system *DMA–HCl–SbCl$_5$*. Figure 1a shows the spectrum of DMA in solutions containing an excess of HCl and $SbCl_5$ and the observed chemical shift values are given in Table 3. A signal of δ 9·37 (37°) ascribed to the acidic proton in protonated DMA was also observed in the spectrum. The relative intensities of the resonance signals as estimated from the peak integrals were consistent with the formation of $[DMAH]^+SbCl_6^-$. The chemical shifts of the protons in DMA are shifted to lower field on protonation and the long range proton coupling across the C—C(O)—N moiety is increased so that the peak of the *trans* N-Me group[†] is a resolved quartet. In neat DMA $^5J_{H-H}(trans)$ has been found to be 0·5 Hz, and no coupling was resolved between the acetyl- and *cis*-aminomethyl protons.[11]

Table 3. Chemical shifts and coupling constants in DMA and its adducts in 1,2-dichloroethane solution at 37°. The chemical shifts were measured relative that of the solvent and recalculated to δ in ppm relative internal TMS

	C—Me	N—$(Me)_2$ mean value	peak separation in $N(Me)_2$	$^5J_{H-H}(cis)$/Hz	$^5J_{H-H}(trans)$/Hz
DMA	1·98	2·90	0·11	unresolved	
$[DMAH]^+SbCl_6^-$	2·78	3·44	0·06	~ 0·3	1·0
$[(DMA)_2H]^+SbCl_6^-$[a]	2·41 ± 0·04	3·25 ± 0·04	—	—	—
$DMA \cdot SbCl_5$	2·70	3·39	0·06	~ 0·3	1·0

[a] derived values, see text.

The spectrum including the peak of the acidic proton did not vary with sample composition as long as HCl and $SbCl_5$ were present in excess; for instance a sample of composition DMA 0·19, HCl 0·28 and $SbCl_5$ 0·46 mol.l^{-1} gave the same results as a sample of DMA 0·26, HCl 0·73 and $SbCl_5$ 0·42 mol.l^{-1}. The peak of the acidic proton was fairly broad, about 4 Hz at 37°. The acidic proton is obviously in slow exchange with excess HCl, otherwise a shift value averaged over $[DMAH]^+$ and a high field shift of molecular HCl would have been observed.[12]

Spectra of solutions in which the relative concentrations of the reactants were $\frac{1}{2}DMA > SbCl_5 > HCl$ showed quite different features. A very narrow peak was observed at δ 18·67 (37°) and the chemical shift did not vary with the excess of DMA. On cooling to $-20°$ the shift was changed to 19·04 ppm but the peak did not broaden.

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[*] An enthalpy value of ($-73·9 \pm 0·6$) kJ/mol DMA was found at the DMA and HCl concentrations used in the above mentioned experiments (to be published).

[†] The N-Me group showing the largest coupling constant $^5J_{CH_3-CH_3}$ is ascribed to the position *trans* to the Ac group in the present paper in accordance with the interpretation of NMR spectra of the neutral amide.[10]

The DMA part of the spectra showed two poorly resolved peaks from the dimethylamino groups and one somewhat broadened peak of the acetyl methyl group. The chemical shifts of these signals varied with the composition of the sample due to rapid exchange between complexed and excess DMA. The low field signal is ascribed to the acidic proton in the $[(DMA)_2H]^+SbCl_6^-$ complex. The chemical shifts of the acetyl and aminomethyl protons in the complex have been calculated under the presumption that the exchange between protonated and excess DMA was rapid and that donor in the donor–acceptor adduct DMA · SbCl$_5$ present in the solution did not take part in that exchange. The found values are given in Table 3 and the random errors are expressed as twice the standard deviation of the mean. Six experiments were done with varying composition of the samples, five of the concentrations DMA 0·42–1·48, HCl 0·21 and SbCl$_5$ 0·28 mol.l^{-1}, and one of the composition DMA 0·51, HCl 0·05 and SbCl$_5$0·08 mol.l^{-1}. The shift values used for DMA were observed in spectra of dilute 1,2-dichloroethane solutions of DMA and are given in Table 3. The PMR spectral parameters did not vary in the concentration range 0·02 to 0·33 mol.l^{-1}.

DMA · SbCl$_5$. A PMR spectrum of the molecular adduct between DMA and SbCl$_5$ is shown in Figure 1b. Values of the chemical shifts and long range proton-proton coupling contants are given in Table 3. It can be noted that in the adduct, quite contrary to what was observed for pure DMA and for $[DMAH]^+SbCl_6^-$, the *trans* aminomethyl group absorbed at lower field than the *cis* Me group. In samples containing adduct and DMA in excess the donor–donor exchange was slow on the NMR time scale at 37°.

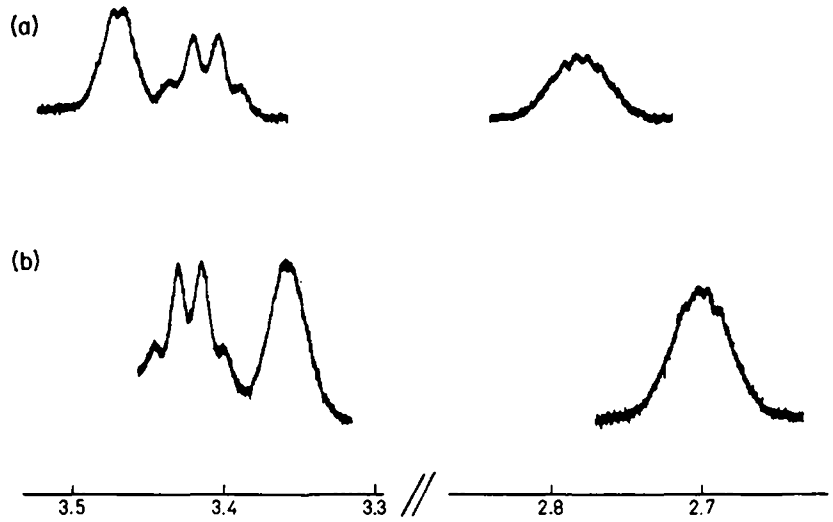

Fig 1. 60 MHz NMR spectra of (a) $[DMAH]^+SbCl_6^-$, (b) DMA · SbCl$_5$ in 1,2-dichloroethane solution. The chemical shift parameter is expressed in δ (ppm) relative internal TMS.

Results of NMR experiments on systems containing the donor compounds TMU, EtOAc and DMSO resembled those found for the DMA systems.

Systems D—HCl—$SbCl_5$. In spectra recorded at 37° of solutions containing close to equimolar amounts of donors and HCl (about 0·10 mol.l^{-1}) and with $SbCl_5$ in excess (0·17 mol.l^{-1}) the following observations were made: For TMU, a singlet peak from the $N(Me)_2$ groups was observed at δ 3·20 and in addition a somewhat broadened peak at δ 7·72 ascribed to the acidic proton in the $[TMUH]^+SbCl_6^-$ complex. The spectrum of the EtOAc solution showed a triplet centered at δ 1·50 from the $CH_2—CH_3$ group and a quartet from the $—CH_2—$ group centred at δ 4·68. The peak arising from the acetylmethyl protons, centered at δ 2·82, clearly revealed a triplet structure due to long range coupling with the methylene protons, coupling constant estimated about 0·3 Hz. A peak at δ 12·8 was observed at −20°, and assigned to the acidic proton in the $[EtOAcH]^+SbCl_6^-$ complex. A singlet peak from DMSO was observed at δ 3·19. No signal from the acidic proton was seen at 37 or −30°.

Spectra recorded at 37° of solutions containing the donors in excess (D 0·8, HCl 0·09 and $SbCl_5$ 0·17 mol.l^{-1}) showed narrow singlet peaks at low field from the acidic proton in the $[D_2H]^+SbCl_6^-$ complexes and averaged signals between D bound in the $[D_2H]^+$ complexes and excess D. Separate signals were observed from the D · $SbCl_5$ adducts. The acidic proton chemical shift values are shown in Table 4. At −20° the peaks of the acidic proton in the $[(TMU)_2H]^+$ and $[(EtOAc)_2H]^+$ complexes had broadened and were found at 0·6 and 0·9 ppm lower field, respectively.

TABLE 4. CHEMICAL SHIFTS OF THE ACIDIC PROTON IN THE HCl–$SbCl_5$ COMPLEXES IN 1,2-DICHLOROETHANE SOLUTION AT 37°. THE CHEMICAL SHIFTS WERE MEASURED RELATIVE THAT OF THE SOLVENT AND RECALCULATED TO δ IN PPM RELATIVE INTERNAL TMS

Donor	$[DH]^+SbCl_6^-$	$[D_2H]^+SbCl_6^-$
DMA	9·37	18·67
TMU	7·72	16·22
EtOAc	12·80[a]	19·67
DMSO	not observed	14·63

[a] At −20°

D · $SbCl_5$. The PMR spectra of the donor–acceptor adducts showed a close similarity to the spectra of the $[DH]^+SbCl_6^-$ complexes. The observed chemical shifts of the donors in the D · $SbCl_5$ adducts differed only a few Hz from those of the $[DH]^+SbCl_6^-$ complexes, the latter giving the larger shift change.

The following values were observed for the chemical shifts of the donor compounds in dilute 1,2-dichloroethane: TMU δ 2·73 (singlet; EtOAc $CH_3—CH_2$ δ 1·22 (triplet), $—CH_2—$ δ 4·07 (quartet), CH_3CO δ 1·99 (singlet); DMSO δ 2·50 (singlet).

DISCUSSION

In the presence of porton accepting substances the system HCl–$SbCl_5$ acts as a strong acid. Klages *et al.*[2] found from electric conductivity measurements that the complex salts $[R_2OH]^+SbCl_6^-$ and $[(R_2O)_2H]^+SbCl_6$ (R = alkyl) were completely dissociated in SO_2 solution. It was recently observed that HCl–$SbCl_5$ protonates sulpholane (tetramethylenesulphone, pK$_a$ (BH$^+$) = $-12{\cdot}9$) and acts as a strong acid in this solvent whereas acids like HClO$_4$ and HSO$_3$F were found to be incompletely ionized.[13] The great acidity of the HCl–SbCl$_5$ system can be considered a consequence of the high chloride ion affinity of SbCl$_5$. The acid is not known to exist as HSbCl$_6$ and no indications were found by calorimetry of an interaction between HCl and SbCl$_5$ in 1,2-dichloroethane. We prefer therefore to represent the acid as HCl–SbCl$_5$.

TABLE 5. CHEMICAL SHIFTS OF THE ACIDIC PROTON IN VARIOUS PROTONATED COMPOUNDS

Protonated species	acid system or solvent	temp.	δ OH$^+$/ppm	Lit. ref.
MeNH(H)COH$^+$	HSO$_3$F	−85	10·5	14
Me$_2$N(H)COH$^+$	HSO$_3$F	−80	10·0	15
Me$_2$N(Me)COH$^+$	HSO$_3$F	−79	9·8	15
EtO(Me)COH$^+$	HSO$_3$F–SbF$_5$	−75	12·8	16
EtO(Me)COH$^+$	HSO$_3$F–SbF$_5$–SO$_2$	−60	12·5	17
Me$_2$SOH^{+a}	HSO$_3$F–SbF$_5$–SO$_2$ClF	−80	6·8	18
Et$_2$OH$^+$	HSO$_3$F–SbF$_5$–SO$_2$	−60	8·6	19
[Et$_2$OH]$^+$SbCl$_6^-$	CH$_2$Cl$_2$	ambient ?	8·7	3
[(Et$_2$O)$_2$H]$^+$SbCl$_6^-$	CH$_2$Cl$_2$	ambient ?	16·4	3

[a] Interpreted as sulphur protonation by the original authors.

In a number of cases of interest here chemical shift values have been reported for the acidic proton in protonated oxygen compounds, Table 5. The close agreement between the acidic proton chemical shifts found for the [DH]$^+$SbCl$_6^-$ complexes (D = DMA and EtOAc see Table 4) and the corresponding shifts observed in HSO$_3$F or "magic acid" shows that there is complete proton transfer in the hexachloroantimonate complexes and that there is no specific interaction between the proton and the anion. In solvents of weak ionizing power like 1,2-dichloroethane and CH$_2$Cl$_2$, dissociation of the complexes into separate ions seems unlikely. Consequently we assume that ion pairs [DH]$^+$SbCl$_6^-$ and [D$_2$H]$^+$SbCl$_6^-$ are formed which are held together mainly by Coulombic forces.

The chemical shifts of the acidic proton in the [D$_2$H]$^+$SbCl$_6^-$ complexes are found at 8–9 ppm lower field than in the[DH]$^+$SbCl$_6^-$ complexes. The drastic change indicates the formation of strong, probably symmetrical hydrogen bonds in the cations.[3] Evidence for symmetrical hydrogen bonds has also been obtained from IR spectroscopic studies.[3, 20]

In the complexes studied here we consider protonation and adduct formation to occur through the C=O or S=O oxygen atoms. NMR studies have shown that protonation is on the carbonyl oxygen in EtOAc[17] and in Lewis acid adducts of alkyl esters bonding is at the C=O group.[6] It is evident from structural studies of the (NH$_2$)$_2$COH$^+$NO$_3^-$ and NHCH$_3$(NH$_2$)COH$^+$NO$_3^-$ salts that the carbonyl oxygen is the most basic atom in urea and alkyl ureas.[21, 22] The close similarity of the donor properties of DMA and TMU strongly suggests that both compounds interact through the C=O group. Protonation of amides in aqueous and non-aqueous solutions and in the solid state has been extensively studied during the last ten years. It is now generally agreed that protonation mainly occurs on the carbonyl oxygen.[10, 23] The spectrum of the $[DMAH]^+SbCl_6^-$ complex shows two non-equivalent aminomethyl groups and increased long range proton coupling compared to that in free DMA, indicative of increased conjugation across the C(O)—N bond in the complex. The spectrum is consistent only with protonation at the oxygen atom.

In donor–acceptor adducts between sulphoxides and the Lewis acids BF_3, $SbCl_5$ and $SnCl_4$, oxygen functions as the electron pair donor atom.[24] Olah *et al.*[18] observed singlet signals at δ 6·5 to 6·8 ppm for the acidic proton in protonated alkylsulphoxides in HSO_3F–SbF_5–SO_2ClF solution at $-80°$. They concluded that sulphoxides are protonated on the sulphur atom and not on the oxygen, the sole argument being that these chemical shifts were in the region for S–H^+ chemical shifts in protonated thiols and sulphides. We do not find the coincidence in chemical shifts sufficient evidence of sulphur protonation. The chemical shifts for $=OH^+$ in monoprotonated carbonyl compounds vary about 8 ppm from δ 7·7 found for protonated TMU to δ 15–16 for protonated aldehydes.[23] A quantitative description of this variation has not been given. The observed S–H^+ chemical shifts refer to compounds in which the sulphur atom is bound to two other atoms, carbon–carbon or carbon–hydrogen, and the change in the SH^+ chemical shift upon addition of oxygen directly at the sulphur atom will accordingly be difficult to predict. It can be noticed that no coupling was observed between the acidic proton and the Me group although the corresponding proton–proton coupling has been found to be strong, about 8 Hz, in protonated thiols and sulphides.[23]

The difference of 7·8 ppm between the acidic proton chemical shifts of DMSO observed in "magic acid" and in 1,2-dichloroethane solution of HCl–$SbCl_5$ containing excess base is the same as the differences in OH^+ chemical shifts between the monoprotonated bases and the $[D_2H]^+$ complexes found for the other bases in this study and for diethyl ether. We ascribe the low field DMSO peak to the acidic proton in a strongly hydrogen bonded $[(DMSO)_2H]^+$ cation where bonding most probably is between the oxygen atoms.

The stabilities of the protonated complexes $[DH]^+MX_{n+1}^-$ and $[D_2H]^+MX_{n+1}^-$ relative to the donor–acceptor complexes $D\cdot MX_n$ are of crucial importance for the acidic properties of the HX–MX_n system. The relations of interest in the present study are represented by reaction 2 and reaction 8.

$$D\cdot SbCl_5(\text{soln}) + HCl(\text{soln}) \rightarrow [DH]^+SbCl_6^-(\text{soln}) \qquad (8)$$

$$\Delta H_8 = \Delta H_4 - \Delta H_6$$

The $-\Delta H_8$ values (in $kJ.mol^{-1}$) are as follows: DMA 53·2; TMU 52·7; EtOAc 16·6; and DMSO 8·5.

The $\Delta G°$ values for the reactions are not known but it can be assumed that the ΔH values will give information about the relative stabilities of complexes of various donors as the entropy changes are not expected to fluctuate widely within the series of donors in the present study. The observed ΔH_2 values, ranging from -70 to -100 $kJ.mol^{-1}$, indicate a considerable stability of the $[D_2H]^+$ complexes over that of the $D\cdot SbCl_5$ adducts. Complete conversion to protonated complexes can be expected to take place in HCl–$SbCl_5$ solutions containing the donor compounds in excess. The addition of HCl to the DMA·$SbCl_5$ and TMU·$SbCl_5$ adducts is exothermic by more than 50kJ.mol^{-1}, which implies that also the $[DMAH]^+$ and $[TMUH]^+$ complexes are fairly stable. The derived $-\Delta H_8$ values are considerably lower for EtOAc and particularly for DMSO which means that the differences between the stabilities of the $[DH]^+SbCl_6^-$ and D·$SbCl_5$ complexes may be quite small for these donors. It is therefore uncertain whether the found ΔH_1 values refer to reaction 1 with complete conversion to protonated complexes or whether the equilibrium concentrations of the donor–acceptor adducts were significant under the conditions of the calorimetric experiments. No special investigation was carried out to elucidate this point. Accordingly the given values represent minimum values of $-\Delta H_8$ for EtOAc and DMSO.

It is evident that the stabilities of the protonated complexes relative to the donor–acceptor adducts are higher for DMA and TMU than for DMSO. The lower basicity of DMSO in the interaction with Brönsted acids is also seen when comparing the $pK_a(BH^+)$ values found for DMSO (−1·8 to −2·0)[25, 26] and DMA (−0·4).[27] Towards the electron pair acceptor $SbCl_5$ they show similar donor strength, the $-\Delta H$ values for the formation of the $SbCl_5$ adducts being the same for DMSO and TMU and slightly lower for DMA (Table 2). This reveals a difference in donor properties exhibited towards Brönsted and Lewis acids between on one side DMA and TMU and on the other DMSO.

The strong interaction in the $[DH]^+SbCl_6^-$ and D·$SbCl_5$ complexes causes a fairly large increase in conjugation across the C(O)—N and C(O)—O bonds in the donors. This is seen in the spectra as increased long range proton coupling in the DMA complexes and the appearance of coupling between the acetylmethyl and methylene protons in the EtOAc complexes. The latter coupling was not resolved in dilute 1,2-dichloroethane solution of EtOAc but has been reported to be 0·20 Hz in the neat liquid.[28]

EXPERIMENTAL

Materials. N,N-Dimethylacetamide, N,N,N′,N′-tetramethylurea (Fluka AG) and DMSO (Fisher, analytical grade) were distilled under reduced pressure on a Nester/Faust Auto Annular Spinning Band Distillation Column. EtOAc (Merck) was distilled at atmospheric pressure on the same column. The purity of the samples was checked by analytical GLC and NMR analysis and judged to be better than 99·9%. The donor samples were dried over 4A molecular sieves and the water content checked separately by GSC.[29] The sample of EtOAc contained 0·02% by volume of water and the other samples less than 0·01%.

$SbCl_5$ was treated as reported.[30] It was transferred by suction in an atmosphere of dry N_2 to one ml glass pippettes and sealed. For experiments where $SbCl_5$ determined the stoichiometry of the reaction and for estimation of the water content of the solvent it was found convenient to transfer Merck's $SbCl_5$ (chromatographic grade) from the delivery ampoules directly to the reaction calorimetric ampoules in an atmosphere of dry N_2 in a glove-bag. 1,2-Dichloroethane (Fisher Certified Reagent) was distilled immediately before use and dried further in a column containing dust free beads of 4A molecular sieves. No impurities could be detected by analytical GLC using dioctylphthalate as stationary phase. Water content of samples treated in this way was found by GSC to be about 10 ppm by volume. The solutions of HCl in this solvent were prepared by passing gaseous HCl (Fluka AG) through a drying agent, Sicapent (Schuckardt), into 1,2-dichloroethane until a solution of desired molarity was obtained. The HCl interfered with the GSC determination of water so instead the water content of the samples used as calorimetric liquid was estimated by measuring the enthalpy change when breaking an ampoule containing about $1{\cdot}5.10^{-3}$ mol of $SbCl_5$ in 100 ml of soln. The molar enthalpy change for interaction between water and $SbCl_5$ has been found to be −(77·8 ± 1·5) kJ.mol^{-1}.[31, 32] HCl and $SbCl_5$ do not interact to give any measureable enthalpy change in 1,2-dichloroethane soln (see results). The water content determined in this way was found to be between

14 and 30 ppm. HCl concentration was determined by treating a known amount of soln with water followed by acidimetric titration.

For the calorimetric experiments on the $[D_2H]^+$ complexes 1 ml thin-walled glass ampoules were filled with 1,2-dichloroethane containing about 0·3 mol.l^{-1} of HCl. Three to four ampoules were taken at random from the batch of 16 filled at each time and the concentration determined by acidimetric titration.

Apparatus and measurements. NMR spectra were obtained using a Varian A-60 A spectrometer equipped with a variable temperature probe and V-6040 temperature controller (temperatures known to ±3°). Teflon plugs with Viton O-rings were used to seal the NMR tubes, in which samples were prepared by mixing known amounts of stock solns of reactants. Sample preparations were carried out in an atmosphere of dry N_2. Chemical shift values were determined relative to solvent with the usual side band technique using a HP 200 CD Audio Oscillator and a HP 5216 A Electronic frequency counter, values were recalculated to δ-values relative to internal TMS using a δ-valve of 3·76 ppm for 1,2-dichloroethane. The value was determined from a soln of TMS in 1,2-dichloroethane and it is assumed that the chemical shift of the solvent did not vary with the composition of samples.

The calorimetric measurements on the formation of the $[D_2H]^+$ complexes were carried out in an LKB 8721 Reaction Solution Calorimeter. The calorimeter is of the constant-temperature-environment type and a thermistor used as temperature sensor. A modified LKB 8721 type calorimeter with digital output of time, temp and calibration voltage was used for the other experiments. Data were recorded on an Addo X printer. Incremental time was measured using the timer unit in the LKB 10746 Control Unit, temperature with a quartz crystal oscillator thermometer (Hewlett Packard 2801 A) and the voltage across the standard resistor in series with the calibration resistor with a DVM (Solartron LM 1867). The apparatus was operated with the quartz thermometer set with a counting period of 100 s. Unfortunately it was not possible to work with a negligible "dead time" between the measuring periods owing to a short time lag necessary for the system to print out the data and a display period of about 2·5 s was used. Glass reaction vessels of 25 (only the first mentioned calorimeter) and 100 ml volume were used. The calorimeter was charged with either pure 1,2-dichloroethane or a HCl soln of 1,2-dichloroethane and suitable amount(s) of $SbCl_5$ and/or the donor compound. After equilibration the reaction was started by breaking the sealed thin-walled glass ampoule containing the reactant that determined the stoichiometry of the reaction. Reaction took place immediately, the period was about 4 min in all cases except in the experiments with $[(DMSO)_2H]^+SbCl_6^-$ where it was about 8 min. In experiments where the thermistor was used, the corrected resistance values (R_i and R_f) were evaluated by extrapolating the fore and after periods to the time corresponding to 0·63 of the resistance change (Dickinson's extrapolation method). For the electrical calibrations, which were performed on the systems before the reaction took place, extrapolations were taken to the time corresponding to 0·50 of the temperature change. The Regnault–Pfaundler method was used in addition for $[(DMSO)_2H]^+SbCl_6^-$ but gave the same result as the extrapolation method. The expression $R_i - R_f/R_i + R_f$ was used as being proportional to the temperature change. When the quartz thermometer was used the corrected temperature change was calculated by the Regnault–Pfaundler method with the assumption that the temperature corresponding to the middle of each display period was the mean of the integrated mean temperatures of the preceding and following measuring periods. The method for calculating the corrected temperature change when a quartz crystal thermometer is used as temperature sensor has been discussed.[33]

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

Acknowledgement—The authors are grateful to Professor S. Forsén, Division of Physical Chemistry, Lund Institute of Technology, for putting the NMR spectrometer at our disposal. A grant from the *Swedish Natural Science Research Council* is gratefully acknowledged.

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