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REACTION OF ANTIMONY(III) HALIDES WITH LEWIS BASES

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ABSTRACT

The reaction of antimony(III) halides, SbX_3, with Lewis bases has been studied calorimetrically in 1,2-dichloroethane solution. The O-donors, Ph_3PO, Me_2SO and pyridine-*N*-oxide, form 1 : 1 adducts mostly of high stability but with small enthalpies of formation. Phosphines also form 1 : 1 adducts, though PBu_3 gives both $SbCl_3PBu_3$ and $SbCl_3(PBu_3)_2$; diphosphines are unidentate but some of the complex diphosphine $(SbCl_3)_2$ is formed when $SbCl_3$ is in excess. Aromatic amines form 1 : 1 adducts of moderate stability ($100 < K < 2500$ l mole^{-1}) with rather large enthalpies of formation, mostly about 100 kJ mole^{-1}. Heterocyclic bases form very stable 1 : 1 adducts ($K > 10^5$ l mole^{-1}) with enthalpies of formation around 90 kJ mole^{-1}; a second molecule of base can also be added with $K_2 < K_1$ and $-\Delta H_2^\circ < -\Delta H_1^\circ$. Enthalpies of formation of adducts with 2,2′-bipyridine and 1,10-phenanthroline are less than those of 1 : 1 adducts with pyridine.

Aliphatic amines and 2,4,6-trimethylpyridine form adducts of the type SbX_3B_3 of very high stability with enthalpies of formation about 250 kJ mole^{-1}. There is some evidence that in these adducts the base is coordinated to halogen rather than antimony.

INTRODUCTION

Although there have been many studies of the Lewis acidity of antimony pentachloride and addition compounds with a variety of bases have been isolated[1], there have been relatively few such studies of antimony(III) halides. Complex fluorides are known with the anions SbF_4^- [2] and SbF_5^{2-} [3] and crystal structures have been reported for the addition compounds SbF_3(4-methoxypyridine-*N*-oxide)$_2$ [4] and $SbF_3(Ph_3PO)_2$ [5], in both of which the antimony has square-pyramidal stereochemistry with an apical fluorine and the sixth octahedral site occupied by the "lone" pair of non-bonding electrons. A similar arrangement occurs in $SbCl_3$(1,4-dithiane), where two S atoms from different dithiane molecules complete a 5-coordinate square-pyramidal arrangement with the "lone" pair occupying the sixth site[6].

In the addition compound $(SbI_3)_2$ dithiane, on the other hand, the two S atoms of the dithiane are coordinated to two different Sb atoms, each of which becomes

4-coordinate; the geometry round the antimony is trigonal-bipyramidal with the S atom occupying an apical site and the "lone" pair occupying one of the equatorial sites[7]. This arrangement also occurs in $SbCl_3 \cdot PhNH_2$[8] and in the arsenic compound $AsCl_3 \cdot NMe_3$[9]. Various solid addition compounds of $AsCl_3$ and $AsBr_3$ with 2,2'-bipyridine, 1,10-phenanthroline and tetramethyl-*o*-phenylenediamine are known, but their structures remain undetermined[10]. In the addition compounds which $SbCl_3$ forms with the hydrocarbons phenanthrene[11] and pyrene[12] the pyramidal shape of $SbCl_3$ is preserved and the antimony appears to be coordinated to the side of the flat hydrocarbon, suggesting interaction with the aromatic π-system.

It is clear from the various reported structures that the antimony atom in the halides SbX_3 (X = Cl, Br or I) has Lewis acid properties, which may be exhibited either in the usual way by the formation of ligand → antimony σ-bonds, with accompanying increase in the coordination number of the metal atom to 5 or 6, or by interaction with the π-system of an aromatic hydrocarbon. Yet another form of behaviour is shown in the addition compound of antimony(III) iodide with elemental sulphur, $SbI_3(S_8)_3$. In this compound each of the S_8 molecules is bound to the SbI_3 molecule by the close approach of one S atom to each of I atoms[13]. Though the S–I distances are rather larger than would be expected for simple covalent bonds, there seems little doubt that this must be considered a Lewis acid–base complex in which the iodine atoms act as Lewis acid centres, possibly because the bulky S_8 molecules can not gain adequate access to the Sb atom.

In this paper we report calorimetric studies of the reactions of $SbCl_3$, $SbBr_3$ and SbI_3 with a variety of Lewis bases, including some O-donors, phosphines, heterocyclic bases and aromatic and aliphatic amines. All reactions were carried out in 1,2-dichloroethane as solvent, after conductivity experiments had shown that the solvent did not react with the bases under the experimental conditions used. The results show a wide range of reaction stoichiometries and suggest that some of the bases coordinate to the Sb atom and some to the halogens.

EXPERIMENTAL

Antimony(III) chloride was purified by distillation in vacuo, antimony(III) bromide by sublimation in vacuo and antimony(III) iodide by crystallisation from toluene. All operations involving handling of the halides were carried out in a dry bag filled with dry nitrogen. The methods of preparation and purification of phosphines have been described previously[14]; triphenylphosphine oxide was purified by crystallisation from ethanol, dimethylsulphoxide by distillation in vacuo and pyridine-*N*-oxide by sublimation in vacuo. Liquid nitrogenous bases were redistilled; 2,2'-bipyridine and 1,10-phenanthroline hemihydrate were recrystallised from ethanol and the hemihydrate was then dehydrated by azeotropic distillation with toluene before making up in solution. For use as solvent 1,2-dichloroethane was dried with anhydrous sodium sulphate, distilled and collected over a molecular sieve; it was used within two days, being stored in the dark and shaken immediately before use with anhydrous potassium carbonate to remove traces of HCl which might be present.

Conductimetric titrations were carried out using a Philips model PW 9504 conductivity bridge at 30.0 ± 0.2 °C with a conductivity cell specially adapted to exclude atmospheric moisture. Calorimetric titrations were carried out in a LKB 8700 tritation calorimeter, using the technique and precautions previously described[15]. Briefly, a solution of the base was added in increments to 100 ml of a solution of the antimony halide and the heat change measured after each addition. Control titrations were carried out to determine the heat of dilution of the titrant solution and thermograms constructed by plotting the corrected, cumulative heat of reaction against the total base concentration. When the reaction was quantitative and no further change occurred at the end of the titration, the enthalpy of reaction was calculated from the total, corrected heat change. When the reaction was incomplete at the end of the titration and a 1:1 adduct was formed, the adduct formation constant was calculated at each experimental point after the enthalpy of reaction had been estimated by extrapolation; the enthalpy was then refined iteratively until constant values of K were obtained throughout the titration. In cases where the reaction was incomplete and the data did not fit the expressions for formation of a 1:1 adduct, other possible stoichiometries were tried until a set of computed thermograms was obtained which fitted the experimental results.

For quantitative reactions the enthalpy was usually reproducible within ± 2%, though systematic errors probably make the thermodynamic data rather less accurate. In the tables of data uncertainties in ΔH° are mean deviations from the average of at least three determinations. For reactions in which a 1:1 adduct is formed incompletely, ΔH° is the average of at least three determinations; K is the average of at least three determinations and uncertainties in K are the sum of the mean deviation from the average and the average standard deviation in the individual titrations. Similar principles are applied to systems with other stoichiometries. Uncertainties in ΔG° and ΔS° are derived.

RESULTS AND DISCUSSION

The reaction of phosphines or amines with alkyl halides is known to lead to the formation of quaternary salts, but the reaction is slow compared with acid-base reactions. Conductimetric studies were carried out and showed that no significant conductivity could be observed in dilute solutions of any of the bases used in 1,2-dichloroethane or at any stage during the titration of these solutions into solutions of antimony(III) halides. This shows that under the experimental conditions not only is the formation of quaternary salts by reaction of bases with solvent too slow to interfere, but also that any free hydrogen halide, which might result from hydrolysis of antimony halide by traces of water, is too low in concentration to cause significant errors.

Oxygen donors

Titrations of solutions of the three oxygen donors, pyridine-*N*-oxide, triphenylphosphine oxide and dimethylsulphoxide, into solutions of antimony(III) halides in

1,2-dichloroethane showed successive formation of 1:1 and 2:1 adducts in distinct steps

$$B + SbX_3 \rightleftharpoons B\cdot SbX_3 \qquad (1)$$

$$B + B\cdot SbX_3 \rightleftharpoons B_2SbX_3 \qquad (2)$$

with $-\Delta H_2^\circ$ little less than $-\Delta H_1^\circ$ and $K_2 < K_1$. Data for these reactions are given in Table 1. A typical titration curve is shown in Fig. 1.

In view of the known structure of similar adducts with SbF_3 [4,5] it is reasonable to propose that these O-donors are coordinated to Sb, giving coordination numbers of four and five.

TABLE 1

THERMODYNAMIC DATA FOR SUCCESSIVE ADDITION OF TWO MOLECULES OF BASE TO SbX_3 IN 1,2-DICHLOROETHANE SOLUTION AT 30 °C
(ΔH° IN kJ MOLE^{-1}, K IN l MOLE^{-1})

Base	*X*	K_1	$-\Delta H^\circ_1$	K_2	$-\Delta H^\circ_2$
Ph_3PO	Cl	$> 10^4$	25 ± 1	184 ± 30	11 ± 2
	Br	$> 10^4$	15 ± 1	260 ± 35	19 ± 2
	I	260 ± 60	16 ± 1	81 ± 20	16 ± 2
Me_2SO	Cl	1150 ± 60	36 ± 2	24 ± 5	29 ± 3
	Br	625 ± 40	35 ± 3	23 ± 5	29 ± 3
	I	27 ± 5	45 ± 4	—	—
py-NO	Cl	$> 10^5$	49 ± 2	69 ± 8	47 ± 4
	Br	$> 10^4$	69 ± 2	139 ± 10	34 ± 4
	I	$> 10^4$	62 ± 2	53 ± 5	62 ± 5

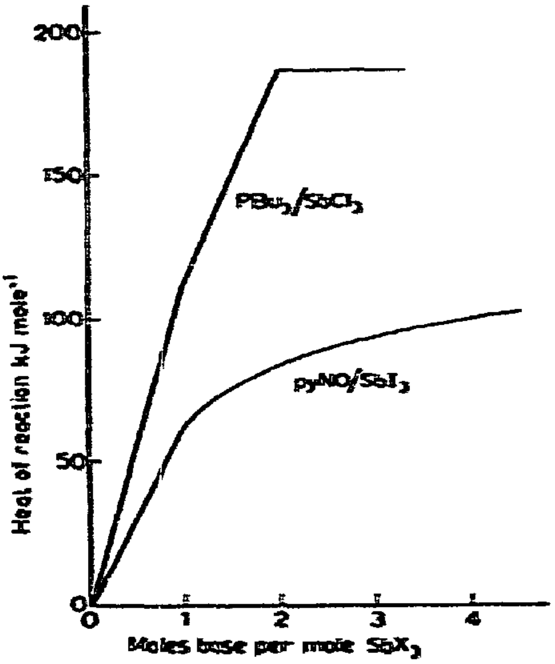

Fig. 1. Calorimetric titration of antimony(III) halides with Lewis bases in 1,2-dichloroethane solution at 30 °C.

Phosphines

Calorimetric titrations of solutions of tributylphosphine into solutions of antimony(III) chloride were similar to those of the above O-donors: first a 1:1 adduct was formed quantitatively, then a second molecule of PBu_3 added to form a 2:1 adduct of high stability (Fig. 1). When one or more of the butyl groups in PBu_3 was replaced by phenyl, addition of the second molecule of phosphine was no longer observed. As the number of phenyl groups increased the enthalpies of adduct formation and adduct stabilities both decreased. Data for these reactions are given in Table 2.

The considerable decrease in enthalpy of adduct formation as phenyl replaces butyl parallels that previously observed for reactions of tertiary phosphines with mercury(II) halides[14] and, to a lesser extent, organo-tin halides[16] and is evidently an inductive effect, which can be related to the Taft constants and basicities of the phosphines.

Titrations were also carried out with several bifunctional phosphines, including bis(diphenylphosphino)methane (PCP), 1,2-bis(diphenylphosphino)ethane (PCCP) and 1,3-bis(diphenylphosphino)propane (PCCCP), and with 1,2-diphenylphosphino-diphenylarsino-ethane (PCCAs). Enthalpies of formation of 1:1 adducts of $SbCl_3$ with all these compounds are similar to those of 1:1 adducts with Ph_2PBu, suggesting that the bifunctional bases behave only as unidentate donors. This is confirmed by the adduct stabilities: adducts with PCCP and PCCAs are of similar stability to that with Ph_2PBu; those with PCP and PCCCP are rather less stable. In no case is there any evidence for chelation and the data for PCCAs support coordination of phosphorus rather than arsenic.

TABLE 2

THERMODYNAMIC DATA FOR FORMATION OF 1:1 ADDUCTS OF SbX_3 WITH PHOSPHINES IN 1,2-DICHLOROETHANE SOLUTION AT 30 °C

(K IN l MOLE^{-1}, $\Delta H°$, $\Delta G°$ IN kJ MOLE^{-1}, $\Delta S°$ IN J K^{-1} MOLE^{-1})

Phosphine	X	K	$-\Delta H°$	$-\Delta G°$	$-\Delta S°$
PBu_3[a]	Cl	$> 10^4$	112.5 ± 0.1	> 23.2	< 295
$PhPBu_2$	Cl	4230 ± 1300	110.0 ± 2.3	21.1 ± 1.0	296 ± 1
Ph_2PBu	Cl	2740 ± 220	54.3 ± 1.0	20.0 ± 0.3	113 ± 4
Ph_2PPr	Cl	1930 ± 170	51.0 ± 2.5	19.1 ± 0.3	105 ± 9
Ph_3P	Cl	160 ± 2	26.0 ± 1.0	12.8 ± 0.1	44 ± 4
	Br	198 ± 24	35.8 ± 1.0	13.3 ± 0.3	54 ± 4
	I	83 ± 1	30.1 ± 1.0	11.1 ± 0.1	63 ± 4
PCP[b]	Cl	600 ± 100	50 ± 2	16.0 ± 0.5	112 ± 8
PCCP[b]	Cl	2000 ± 400	67 ± 3	19.1 ± 0.6	158 ± 12
PCCCP[b]	Cl	750 ± 150	49 ± 2	16.7 ± 0.6	117 ± 9
PCCAs	Cl	1830 ± 310	60.5 ± 2.8	18.9 ± 0.6	137 ± 11
PC–CP *cis*	Cl	845 ± 26	47.0 ± 3.0	17.0 ± 0.1	99 ± 10
PC–CP *trans*	Cl	912 ± 45	27.5 ± 2.7	17.1 ± 0.3	34 ± 10

[a] For PBu_3: $K_2 > 10^4$, $-\Delta H_2° = 74.2 \pm 1.0$.

[b] See text.

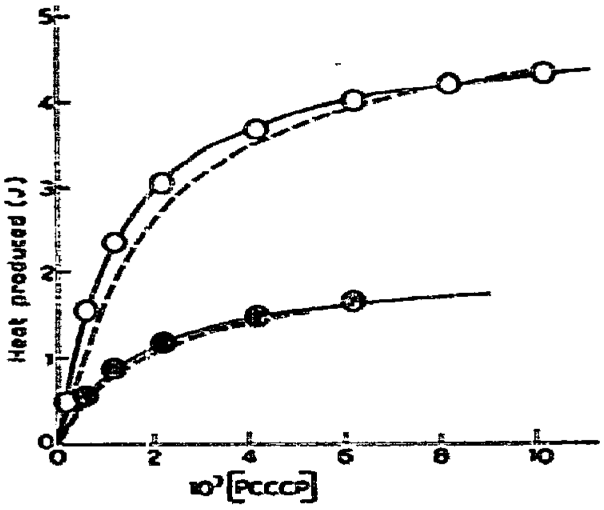

Fig. 2. Calorimetric titration of $SbCl_3$ with 1,3-bis(diphenylphosphino)propane in 1,2-dichloroethane solution at 30 °C. $[SbCl_3] = 1 \cdot 10^{-2}$ M (●) and $4 \cdot 10^{-3}$ M (○). Dotted lines calculated for 1:1 adduct formation, $K = 750$ l. mole^{-1}, $\Delta H^\circ = -49$ kJ. mole^{-1}; full lines for

$PCCCP + SbCl_3 \rightleftharpoons PCCCP \cdot SbCl_3$, $K = 750$, $\Delta H^\circ = 49$;
$PCCCP \cdot SbCl_3 + SbCl_3 \rightleftharpoons PCCCP(SbCl_3)_2$, $K = 750$, $\Delta H^\circ = 45$.

The stabilities of adducts with these bifunctional phosphines are sufficiently high that a significant proportion of the 1:2 adducts, such as $Cl_3Sb \leftarrow PCCP \rightarrow SbCl_3$, might be expected early in the calorimetric titrations when $SbCl_3$ is in excess. It was found that better fits of the calorimetric data to computed titration curves were obtained if allowance was made for this possibility (Fig. 2). The best-fit results for each diphosphine were as follows

$PCP + SbCl_3 \rightleftharpoons PCP \cdot SbCl_3$ $\quad K = 600$ $\quad -\Delta H^\circ = 50$
$PCP \cdot SbCl_3 + SbCl_3 \rightleftharpoons PCP(SbCl_3)_2$ $\quad K = 600$ $\quad -\Delta H^\circ = 50$
$PCCP + SbCl_3 \rightleftharpoons PCCP \cdot SbCl_3$ $\quad K = 2000$ $\quad -\Delta H^\circ = 67$
$PCCP \cdot SbCl_3 + SbCl_3 \rightleftharpoons PCCP(SbCl_3)_2$ $\quad K = 1400$ $\quad -\Delta H^\circ = 67$
$PCCCP + SbCl_3 \rightleftharpoons PCCCP \cdot SbCl_3$ $\quad K = 750$ $\quad -\Delta H^\circ = 49$
$PCCCP \cdot SbCl_3 + SbCl_3 \rightleftharpoons PCCCP(SbCl_3)_2$ $\quad K = 500$ $\quad -\Delta H^\circ = 48$

where K is in l mole^{-1} and ΔH° in kJ mole^{-1}.

Further confirmation of the failure of the arsenic atom in PCCAs to coordinate was provided by the absence of any indication of the formation of an adduct of the type $PCCAs(SbCl_3)_2$, even when $SbCl_3$ was in considerable excess. The results obtained for *cis*- and *trans*-1,2-bis-(diphenylphosphino)ethene (PC=CP) fall between those for PCCP and Ph_3P; there is no evidence for chelation or bifunctional behaviour with either ligand.

Aromatic amines

Aromatic amines are only slightly stronger proton bases than tertiary phosphines and there is little difference in pK_a between $PhNH_2$, PhNHMe and $PhNMe_2$.

TABLE 3

THERMODYNAMIC DATA FOR FORMATION OF 1:1 ADDUCTS OF SbX_3 WITH AROMATIC AMINES IN 1,2-DICHLOROETHANE AT 30 °C
(K IN l MOLE^{-1}, $-\Delta H^\circ$, $-\Delta G^\circ$ IN kJ MOLE^{-1}, $-\Delta S^\circ$ IN J K^{-1} MOLE^{-1})

Amine	*X*	*K*	$-\Delta H^\circ$	$-\Delta G^\circ$	$-\Delta S^\circ$
p-Et · $C_6H_4NH_2$	Cl	387 ± 39	153.2 ± 1.0	15.0 ± 0.3	456 ± 5
$PhNH_2$	Cl	118 ± 4	110.4 ± 1.3	12.0 ± 0.1	324 ± 5
PhNHMe	Cl	711 ± 38	99.4 ± 1.2	16.5 ± 0.2	274 ± 5
	Br	743 ± 8	128.4 ± 2.9	16.7 ± 0.1	368 ± 10
	I	213 ± 19	89.6 ± 4.9	13.5 ± 0.3	251 ± 17
$PhNMe_2$	Cl	2385 ± 76	108.1 ± 2.1	1.96 ± 0.2	292 ± 8
	Br	2090 ± 86	133.0 ± 3.0	19.3 ± 0.2	376 ± 11
	I	1258 ± 10	121.8 ± 1.3	18.0 ± 0.1	343 ± 5
$PhCH_2NHMe$	Cl	2160 ± 490	313 ± 2	19.4 ± 0.7	970 ± 10
	Br	1801 ± 105	334 ± 2	18.9 ± 0.2	1040 ± 8

Like phosphines these bases formed 1:1 adducts with antimony(III) halides in 1,2-dichloroethane solution; there was no evidence for the formation of adducts of the type $(SbX_3)_2$base, which have previously been reported to occur in solutions in diethyl ether[17]. Thermodynamic data for the formation of the 1:1 adducts are given in Table 3.

Enthalpies of adduct formation are considerably larger than those of analogous phosphines, suggesting that the antimony in SbX_3 is a relatively "hard" Lewis acid centre. There is little difference in the enthalpies of formation of adducts with $PhNH_2$, PhNHMe and $PhNMe_2$, though there is a marked increase in adduct stability as Me replaces H. This evidently is an entropy effect and may perhaps be attributed to restricted rotation about the Sb–N bond due to weak interaction between the N–H and Cl within the molecular adduct. Short intermolecular N–H···Cl distances occur in crystalline $SbCl_3PhNH_2$[8], indicating the possibility of weak hydrogen bonding, but the angles are not correct for any except the weakest intramolecular interaction of this type.

Substitution of *p*-ethylaniline for aniline increased both the enthalpy of adduct formation and adduct stability: this is presumably a direct result of increased base strength. The much weaker bases Ph_2NMe and Ph_3N gave no evidence of adduct formation.

Heterocyclic bases

Pyridine and the three picolines all reacted with SbX_3 in 1,2-dichloroethane in a similar manner; the calorimetric titration results (Fig. 3) are best interpreted as representing quantitative formation of 1:1 adducts ($K > 10^5$ l mole^{-1}), followed by addition of a second molecule of base to give 2:1 adducts of high stability

$$SbX_3 + B \rightleftharpoons SbX_3{\cdot}B$$

$$SbX_3{\cdot}B + B \rightleftharpoons SbX_3B_2$$

and thermodynamic data for these reactions are given in Table 4.

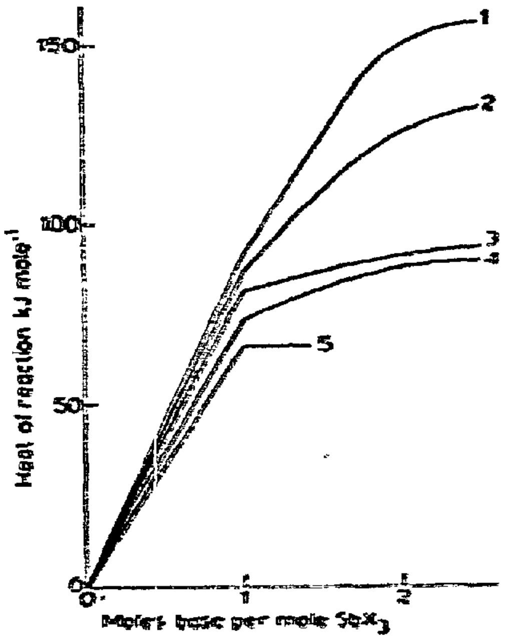

Fig. 3. Calorimetric titration of SbX_3 with heterocyclic bases in 1,2-dichloroethane solution at 30 °C: (1) SbI_3/4-mepy, (2) $SbCl_3$/2-mepy, (3) $SbCl_3$/py, (4) $SbBr_3$/phen, (5) $SbCl_3$/bipy.

TABLE 4

THERMODYNAMIC DATA FOR SUCCESSIVE ADDITIONS OF TWO MOLECULES OF HETEROCYCLIC BASE TO SbX_3 IN 1,2-DICHLOROETHANE SOLUTIONS AT 30 °C (K IS l mole^{-1}, $\Delta H'$ IS kJ mole^{-1}; $K_1 > 10^4$)

Base	*X*	$-\Delta H_1'$	$-\Delta H_2'$	K_2
Pyridine	Cl	51 ± 1	12 ± 1	3300 ± 300
	Br	94 ± 1	29 ± 1	1465 ± 220
	I	54 ± 1	15 ± 2	2330 ± 70
4-mepy	Cl	59 ± 4	35 ± 5	1360 ± 60
	Br	96 ± 1	59 ± 2	4460 ± 700
	I	91 ± 1	65 ± 3	5570 ± 1500
3-mepy	Cl	95 ± 1	36 ± 4	456 ± 3
	Br	97 ± 2	52 ± 1	1340 ± 50
	I	88 ± 2	60 ± 2	520 ± 30
2-mepy	Cl	86 ± 2	52 ± 3	1230 ± 220
	Br	93 ± 1	71 ± 1	$> 10^4$
	I	85 ± 2	66 ± 1	$> 10^4$
bipy	Cl	66 ± 1		
	Br	73 ± 2		
phen	Cl	73 ± 1		
	Br	72 ± 3	15 ± 3	2250 ± 25
	I	66 ± 3	30 ± 1	1410 ± 120

There are some unusual features of these results. While $\Delta H_1'$ is not much affected by change of either halide or base, $-\Delta H_2'$ is considerably increased by methyl substitution in the base, particularly by α-substitution. The considerable differences between $\Delta H_2'$ for pyridine and the picolines, the increase in $-\Delta H_2'$ from $SbCl_3$ to SbI_3

and the large values of K_2, even when associated with very small values of $\Delta H_2'$ for pyridine, suggest that the second molecule of base may not be coordinated to the antimony atom in the usual way.

Further methylation of the base brings about a complete change in reaction stoichiometry. When 2,4,6-trimethylpyridine (collidine) is titrated into SbX_3 solutions three molecules of base are added quantitatively at the one time

$$SbX_3 + 3B \rightarrow SbX_3B_3$$

Collidine is a slightly stronger base towards protons than is 4-methylpyridine[15], but is strongly sterically hindered by the two α-methyl groups and it is difficult to believe that the antimony atom could accommodate three collidine molecules more readily than one or two of 4-methylpyridine. A more probable explanation for the formation of a highly stable 3:1 adduct with collidine is that each molecule of base is associated with one of the three halogen atoms. This type of adduct is known in crystalline $SbI_3(S_8)_3$[13] and might be formed with heterocyclic bases if steric effects prevented close approach of N and Sb atoms. High adduct stability would result from the minimal steric interaction at the periphery of the SbX_3 molecule. Enthalpy data for the collidine adducts are included in Table 5.

When the bidentate bases, 2,2'-bipyridine and 1,10-phenanthroline, were titrated into solutions of SbX_3 1:1 adducts were formed quantitatively, followed in some cases by the addition of a second molecule of base with a much smaller enthalpy of reaction. Details are included in Table 4. The enthalpies of formation of these 1:1 adducts are smaller than those for adducts with pyridine or picolines. It is possible that bipyridine might give this result by behaving as a sterically hindered unidentate base.

TABLE 5

ENTHALPIES OF REACTION OF SbX_3 WITH THREE MOLECULES OF AMINE IN 1,2-DICHLOROETHANE SOLUTION AT 30 °C

(ΔH° in kJ (mole SbX_3)$^{-1}$)

Amine	*SbCl₃*	*SbBr₃*	*SbI₃*
Collidine	173 ± 1	190 ± 2	182 ± 1
Et_3N	256 ± 1	251 ± 2	286 ± 3
Bu_3N	257 ± 1	253 ± 1	276 ± 4
$CxNEt_2$[a]	264 ± 3	266 ± 1	271 ± 4
Et_2NH	283 ± 5	273 ± 2	306 ± 3
iPr_2NH	239 ± 4	250 ± 1	281 ± 1
Bu_2NH	268 ± 2	268 ± 1	270 ± 2
piperidine	330 ± 1	331 ± 1	331 ± 2
$PrNH_2$	275 ± 2	270 ± 4	267 ± 2
$iPrNH_2$	290 ± 1	293 ± 1	287 ± 2
$BuNH_2$	227 ± 2	305 ± 4	257 ± 1
$iBuNH_2$	316 ± 1	320 ± 2	317 ± 2
$tBuNH_2$	291 ± 1	277 ± 2	275 ± 2
$CxNH_2$[a]	285 ± 1	331 ± 1	331 ± 2

[a] Cx = cyclohexyl

but this is much less likely for phenanthroline and the similarity of the results for the two bases suggests that their adducts are structurally similar. The small enthalpies of formation of the adducts thus suggest that steric restraints make it difficult for these bulky bases to approach closely enough for Sb–N bonds to be formed as strong as those in pyridine adducts. These results thus provide further evidence for steric overcrowding close to the antimony atom and so some additional support for the proposition that in the 3:1 collidine adducts coordination may be to halogen rather than antimony.

Aliphatic amines

These were the strongest proton bases used in this study. A variety of primary, secondary and tertiary bases was used and all behaved in the same way: three molecules of base reacted almost quantitatively with one of SbX_3, as in the case of collidine. Enthalpies of reaction were large and in most cases close to the average of about -280 kJ(g-at.Sb)$^{-1}$; departures from this average did not appear to be systematic. Details are given in Table 5.

In most of these systems changes in the slope of the enthalpograms could be observed at stoichiometric ratios of 1:1 or 2:1 (Fig. 4) indicating small decreases in the enthalpies of addition of successive molecules of base. Since the differences are only small and the accuracy of the data only a little better, no attempt was made to analyse the data to give successive enthalpies of reaction.

The average enthalpy change for the addition of each molecule of base, about -87 kJ mole^{-1} for secondary and tertiary bases with $SbCl_3$ or $SbBr_3$, is comparable to that for the addition of the first molecule of a heterocyclic base. Even the most sterically hindered bases, such as $t\text{-}BuNH_2$, iPr_2NEt or diethylcyclohexylamine, show

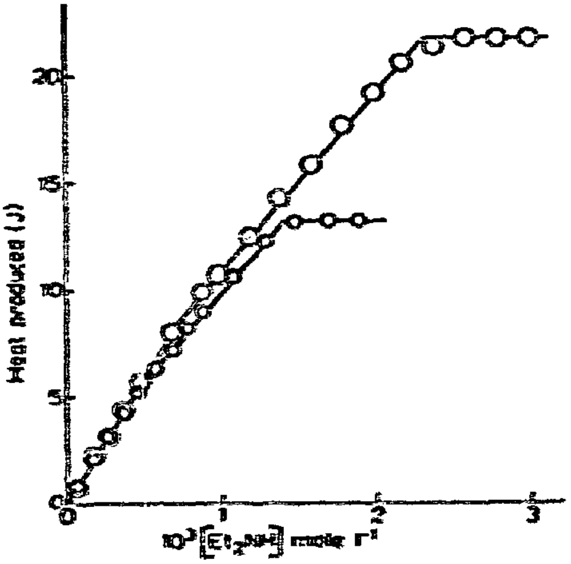

Fig. 4. Calorimetric titration of $SbBr_3$ with diethylamine in 1,2-dichloroethane solution at 30 °C. $[SbBr_3] = 4.75 \times 10^{-4}$ M (small circles), 7.97×10^{-4} M (large circles).

little evidence for steric interference, which could be expected to lead to lower enthalpies of adduct formation. It thus seems probable that in these adducts the three molecules of base are not coordinated to the antimony atom, but rather one to each halogen atom. However, this apparently occurs only with the strongest proton bases.

The quite different behaviour of aliphatic amines and collidine from other bases suggests that the antimony and halogen atoms may to some extent be able to act independently as alternative Lewis acid centres. Some studies were therefore made with mixed bases. After the addition of three equivalents of NBu_3 to a solution of $SbCl_3$ it was found that, although further NBu_3 gave no evidence of reaction, heat was still produced if PBu_3 was added. Conversely, after addition of rather more than one equivalent of PBu_3 to a solution of $SbCl_3$, the addition of NBu_3 liberated further heat, though further addition of PBu_3 did not. These results support the proposition that NBu_3 and PBu_3 react with different parts of the $SbCl_3$ molecule and that the chlorine atoms behave as Lewis acid centres to the stronger proton base.

There are good reasons why this might occur with antimony(III) halides: in isolated SbX_3 molecules the X–Sb–X angles are 97–99°[19]; this is usually taken to indicate that the Sb–X bonding depends mainly on the antimony *p*-orbitals, the non-bonding, "lone", pair of electrons being predominantly of *s*-character. Although the difference in electronegativities must lead to appreciably polar Sb–X bonds, the concentration of the "lone" pair in an antimony *s*-orbital will also lead to a high electron density close to the metal atom, which will tend to resist the coordination of a Lewis base. When coordination does occur and a 1:1 adduct is formed, rehybridisation takes place leading to a trigonal-bipyramidal arrangement of orbitals of which one, usually equatorial, is occupied by the "lone" pair. In the same way formation of an adduct with two molecules of base involves an octahedral set of orbitals, of which one is occupied by the "lone" pair, leading to a square-pyramidal stereochemistry. However, if steric hindrance were to prevent the formation of adducts of these types, the presence of the "lone" pair on the antimony atom could make the halogen atoms acceptable alternative Lewis acid centres.

In two of the systems studied, $SbI_3/PrNH_2$ and $SbI_3/BuNH_2$, reaction did not cease even after addition of three equivalents of base, but continued until three more equivalents had been added, giving overall enthalpies of reaction of −371 and −377 kJ mole^{-1} for the addition of six molecules of base. These reactions were virtually quantitative. There is no indication of likely structures for the products of the reactions.

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