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Enthalpies of formation of adducts of antimony(III) iodide with pyridine and methyl-pyridines

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Abstract

Solid adducts of formula $SbI_3{\cdot}L$ (L = pyridine or 2-, 3- or 4-methylpyridine abbreviated as Py, 2MPy, 3MPy or 4MPy) were synthesized and characterized by elemental analysis, IR spectroscopy and thermal analysis. IR data showed that coordination to antimony is through nitrogen. Thermal degradation of adducts starts at 431, 423, 413 and 411 K for Py, 2MPy, 3MPy and 4MPy, respectively. Reaction-solution calorimetry was used to evaluate the enthalpy change of reaction: $SbI_3(cr) + L(l) = SbI_3{\cdot}L(cr)$, 61.13 ± 1.75, -82.60 ± 1.55, -67.50 ± 0.97 and $-74.10 \pm 1.19\,kJ\,mol^{-1}$, respectively. Enthalpy change values for decomposition of adducts, lattice enthalpies and enthalpies of the Lewis acid–base reaction in the gas phase were calculated through appropriate thermochemical cycles. Mean Sb─N bond enthalpies were estimated as 134 ± 3, 154 ± 3, 140 ± 3 and $147 \pm 4\,kJ\,mol^{-1}$, for Py, 2MPy, 3MPy and 4MPy, respectively.

Keywords: Antimony(III) iodide; Aromatic amines; Adducts; Pyridines; Enthalpy

1. Introduction

A recent article described the preparation, characterization and kinetic study of adducts of antimony(III) halides with methyl-substituted pyridines [1]. The activation energy and pre-exponential factor for decomposition of these adducts were reported [1]. Several studies of adducts of 2-methylpyridine, 3-methylpyridine and 4-methylpyridine with transition metal salts have been reported [2–5], in which the main interest was the synthesis and structure with some data on thermal decomposition of the complexes. Adducts of antimony(III) halides with ligands containing nitrogen as the donor atom are reported in literature [6–9] but there is no information on the enthalpies of the Sb─N bond with pyridine and its methyl derivatives. The main focus of this paper is the synthesis of the adducts of antimony(III) iodide with pyridine and methyl-pyridines to obtain the enthalpies for formation of adducts.

2. Experimental

The solvents used in all preparations were distilled through an efficient column and stored over Linde 4 Å molecular sieves. The 2-, 3-, 4-methylpyridines and pyridine (Merck) were used without further purification. The antimony triiodide (Merck) was sublimed and stored in vacuum. All preparations and manipulations were performed under dry condition in a nitrogen atmosphere.

Adducts were prepared by mixing an equimolar amount of both reactants in carbon disulfide with stirring. The liquid amine was added to the SbI_3 solution. Stirring was maintained for 3 h. After solvent removal by filtration, the solids were washed with carbon disulfide and dried in vacuum. The yield was about 80%.

Iodide was determined by potentiometric titration with standard $0.1\,mol\,dm^{-3}$ $AgNO_3$ solution after dissolution of the adducts in water. Carbon, nitrogen and hydrogen contents were determined on a Perkin-Elmer model 2400 analyzer. The melting points of all the compounds were measured between PVC windows on Microquimica model MQAPF-301 apparatus. Infrared spectra at room temperature were made on adduct samples

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Table 1
Analytical data (calculated (experimental)) for $SbI_3 \cdot L$ adducts

Adduct	%C	%H	%N	%I	ΔT[a] (K)
$SbI_3 \cdot Py$	10.32 (10.42)	0.87 (0.95)	2.41 (2.47)	65.47 (65.40)	431–540
$SbI_3 \cdot \alpha$-Pic	12.08 (11.95)	1.31 (1.23)	2.35 (2.38)	58.32 (58.43)	423–538
$SbI_3 \cdot \beta$-Pic	12.08 (11.88)	1.31 (1.22)	2.35 (2.30)	58.32 (58.06)	413–515
$SbI_3 \cdot \gamma$-Pic	12.08 (11.96)	1.31 (1.30)	2.35 (2.37)	58.32 (58.76)	411–414

[a] With decomposition.

in KBr disks and films of the liquid between NaCl plates on a Bomem spectrometer MB series in the frequency range of 4000–400 cm^{-1} at a resolution of 4 cm^{-1} with 30 scans. Thermogravimetric curves were obtained with Shimadzu TG-50 thermo-balance with dynamic nitrogen atmosphere with a flow of 50 $cm^3\,min^{-1}$ with sample masses of 5.0 ± 0.5 mg and a heating rate of 10 K min^{-1}. DSC curves were obtained with a Shimadzu DSC-50 in nitrogen atmosphere (heating rate at 10 K min^{-1} and gas flow of 50 $cm^3\,min^{-1}$).

Calorimetric measurements were performed in a Hart Scientific isoperibol solution calorimeter. Ampoules containing 5–50 mg of reactant were prepared in a dry-box and broken in the glass reaction vessel charged with 25 cm^3 of calorimetric solvent at 298.15 ± 0.02 K. The accuracy of the calorimetric measurements was checked by measuring the thermal effect of dissolution of Tris-(hydroxymethyl)aminomethane in 0.1 mol L^{-1} standard hydrochloric acid solution. The value obtained, -29.70 ± 0.10 kJ mol^{-1}, agrees with the value of -29.736 ± 0.002 kJ mol^{-1} reported elsewhere [10,11].

3. Results and discussion

Elemental analyses of the solid adducts are in good agreement with the proposed general formula, Table 1.

The TG curves of the adducts are shown in Fig. 1. Decomposition followed similar processes, with the loss of 97–99% of mass, in a single step. This same behavior has also been observed for arsenic tri-chloride adducts [6], containing the ligands 2-, 3- or 4-methylpyridine in the same molar ratio of 1:1. Temperature ranges for the thermal adducts' decomposition are given in Table 1. The melting point measurements indicated that the compounds did not melt and the DSC curves confirmed they decompose.

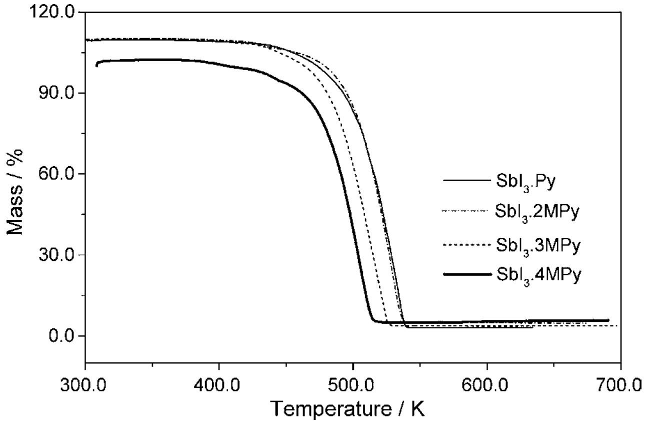

Fig. 1. Thermogravimetric data of the adducts $SbI_3 \cdot L$ containing pyridine and methyl-pyridines.

The infrared spectra assignments were based on previous reports [12,13]. The main vibrational absorption bands for adducts are listed in Table 2. Some bands were shifted when compared with the corresponding bands of the free ligand spectra. However, the pattern of the adducts spectra are similar to those of the free ligand spectra.

The enthalpy of reaction ($\Delta_r H_m^\theta$) of the reaction in condensed phase,

$$SbI_3(cr) + L(l) = SbI_3 \cdot L(cr), \qquad \Delta_r H_m^\theta \tag{1}$$

was obtained from enthalpies of solution ($\Delta_i H_m^\theta$) of each reagent and the product dissolved sequentially in 2-ethoxyethanol by applying the thermochemical cycle

$$SbI_3(cr) + \text{solvent} = \text{Sol A}, \qquad \Delta_1 H_m^\theta$$

$$\text{Sol A} + L(l) = \text{Sol B}, \qquad \Delta_2 H_m^\theta$$

$$SbI_3 \cdot L(cr) + \text{solvent} = \text{Sol C}, \qquad \Delta_3 H_m^\theta$$

$$\text{Sol B} = \text{Sol C}, \qquad \Delta_4 H_m^\theta$$

$$\Delta_r H_m^\theta \text{ was calculated by } \Delta_r H_m^\theta = \Delta_1 H_m^\theta + \Delta_2 H_m^\theta - \Delta_3 H_m^\theta \tag{2}$$

Since the solutions A and C are thermochemically equivalent, $\Delta_4 H_m^\theta = 0$. The dissolution enthalpy values are listed in Table 3. The values $\Delta_f H_m^\theta$ (adducts solid phase) were obtained with the data in Table 4 by reaction (3). Results are shown in Table 5.

$$\Delta_f H_m^\theta(\text{adduct (cr)}) = \Delta_r H_m^\theta + \Delta_f H_m^\theta(SbI_3)(cr) + \Delta_f H_m^\theta(\text{ligand})(l) \tag{3}$$

The molar enthalpies of decomposition ($\Delta_D H_m^\theta$) and the lattice molar enthalpies ($\Delta_M H_m^\theta$) of adducts are related to the following reactions:

$$SbI_3 \cdot L(cr) = SbI_3(cr) + L(g), \qquad \Delta_D H_m^\theta$$

$$SbI_3 \cdot L(cr) = SbI_3(g) + L(g), \qquad \Delta_M H_m^\theta$$

Table 2
Infrared data (cm^{-1}) for adducts and free ligands

Compound	υ_{CC}	$\upsilon_{CC,CN}$	$\upsilon_{CC,CN}$	δ_{CH}	X-sens	β_{CH}	ϕ_{CH}
Py	1575s	1460s	1421s	1288m	1108w	1146s	718s
SbI_3·Py	1599m	1530s	1481m	1235m	1048w	1161s	736s
2MPy	1594s	1478s	1377w	1295m	1101w	1150m	754s
Sbl_3·2MPy	1607m	1461w	1384w	1277w	1097w	1165w	751s
3MPy	1579s	1479s	1414m	1191m	1031w	1126m	790s
Sbl_3·3MPy	1601s	1536s	1466m	1229m	1112m	1127m	773m
4MPy	1608s	1498w	1418m	1213m	1002m	1059m	802s
SbI_3·4MPy	1536m	1595m	1500w	1241m	1048w	1196w	751s

υ, stretch; δ, bending in plane; ω, ring bending out of plane; β, bending out of plane; ϕ, ring bending in plane; X-sens, sensitive to substitution, X = CH_3; intensity of bands: s, strong; m, medium; w, weak.

Table 3
Molar enthalpies (kJ mol^{-1}) for dissolution reactions* in 2-ethoxyethanol

Adduct	$\Delta_1 H_m^\theta$	$\Delta_2 H_m^\theta$	$\Delta_3 H_m^\theta$
SbI_3·Py	−15.88 ± 0.82[a]	−48.91 ± 1.50[a]	−3.66 ± 0.41[a]
SbI_3·2MPy	−15.88 ± 0.82	−62.50 ± 1.22	4.22 ± 0.52
SbI_3·3MPy	−15.88 ± 0.82	−48.02 ± 0.41	3.60 ± 0.32
SbI_3·4MPy	−15.88 ± 0.82	−54.44 ± 0.80	3.78 ± 0.33

[a] Data based on four measurements.

These enthalpy values can be calculated by the expressions

$$\Delta_D H_m^\theta = -\Delta_r H_m^\theta + \Delta_l^g H_m^\theta \tag{4}$$

$$\Delta_M H_m^\theta = -\Delta_D H_m^\theta + \Delta_{cr}^g H_m^\theta(SbI_3) \tag{5}$$

The values of $\Delta_D H_m^\theta$ and $\Delta_M H_m^\theta$ were derived from the molar enthalpies of vaporization of ligands [14] and the enthalpy of sublimation of SbI_3 [15], The results are presented in Table 5. To evaluate the metal–nitrogen bond enthalpy of the adducts, information about the acid–base reaction in the gaseous phase, $\Delta_r H_m^\theta(g)$ [16–20], obtained from the reaction

$$SbI_3 \cdot L(g) = SbI_3(g) + L(g), \qquad \Delta_r H_m^\theta$$

and $\Delta_r H_m^\theta(g) = \Delta_M H_m^\theta + \Delta_{cr}^g H_m^\theta$, where the last term is the sublimation enthalpy of the adduct. The Sb–N bond enthalpy is equal to $\Delta_r H_m^\theta(g)$ because there is only one monodentate ligand coordinated to antimony [21]:

$$\langle D\rangle(\text{Sb–L}) = \Delta_r H_m^\theta(g) \tag{6}$$

The mean antimony–nitrogen bond enthalpy, $\langle D\rangle$(Sb–N), depends on the enthalpy of sublimation of the compound, but attempts to measure this were unsuccessful due to difficulties in subliming the adducts. To solve this problem, we can assume the enthalpy $\Delta_{cr}^g H_m^\theta$ as being equal (a) $\Delta_l^g H_m^\theta$ (ligand), (b) $[n\,\Delta_l^g H_m^\theta(\text{ligand})] + \Delta_{cr}^g H_m^\theta(SbI_3)/(n+1)$, (c) $\{[\Delta_l^g H_m^\theta(\text{ligand})]^n \cdot [\Delta_{cr}^g H_m^\theta(SbI_3)]^n\}^{1/(n+1)}$ and (d) $\Delta_{cr}^g H_m^\theta(SbI_3)$ [16–21]. The hypothesis "a" is reasonably valid within ±10 kJ mol^{-1} for some sublimed adducts and can be measured [22–24]. The equation we previously established [25] was adopted here

$$\Delta_f H_m^\theta(g) = 1.002\,\Delta_f H_m^\theta(s) + 73.874 \tag{7}$$

This relationship relates data of standard molar enthalpy of formation in solid state with data in gaseous state for a series of compounds with sublimation enthalpy in the range of 64–90 kJ mol^{-1} [26]. The values of molar enthalpy of formation in gaseous state for adducts described in literature [14] were estimated by each of the four hypotheses and Eq. (7). In some cases, the regression generated values that agreed with data obtained from the first hypothesis 'a'. However, for other adducts, the regression generated values that agreed with the ones obtained from hypothesis 'b' [27]. This behavior suggests that the hypotheses 'a' and 'b' would be appropriate only in some cases. Therefore, to estimate the molar enthalpies of formation for the adducts in the gas phase by Eq. (7) and the four hypotheses, the following methodology was adopted: (i) firstly, formation enthalpies of adducts in the gaseous phase were estimated by means of each of the hypotheses; (ii) each value was substituted in Eq. (7) for calculating the formation enthalpies of adducts in the solid state; (iii) the enthalpies of formation of the adducts in the solid state obtained from Eq. (7) were compared with the values obtained for $\Delta_r H_m^\theta$ (solid) (Eq. (3)); (iv) finally, the most adequate hypothesis supplies a formation standard

Table 4
Supplementary enthalpies (kJ mol^{-1}) for ligands and antimony(III) iodide at 298 K

Compounds	$\Delta_f H_m^\theta$(cr, l)	$\Delta_{cr}^g H_m^\theta$	$\Delta_l^g H_m^\theta$(ligand)	$\Delta_f H_m^\theta$(g)
SbI_3	−100.40 ± 0.70[a]	101.7 ± 1.50[a]		1.30 ± 1.66
Pyridine	100.17 ± 0.50[b]		40.24 ± 0.71[b]	144.56 ± 0.50[b]
2-Methylpyridine	56.69 ± 0.75[b]		42.46 ± 1.07[b]	99.16 ± 0.75[b]
3-Methylpyridine	61.92 ± 0.59[b]		44.43 ± 0.83[b]	106.35 ± 0.59[b]
4-Methylpyridine	56.82 ± 1.30[b]		45.31 ± 1.93[b]	102.13 ± 1.42[b]

[a] Reference [15].
[b] Reference [14].

Table 5
Standard molar enthalpies (kJ mol^{-1}) for the antimony adducts

Measurement	SbI_3·Py	SbI_3·2MPy	SbI_3·3MPy	SbI_3·4MPy
$\Delta_r H_m^\theta$	−61.13 ± 1.75	−82.60 ± 1.55	−67.50 ± 0.97	−74.10 ± 1.19
$\Delta_f H_m^\theta$(cr)	−61.57 ± 1.95	−123.96 ± 1.86	−107.19 ± 1.33	−111.08 ± 1.90
$\Delta_D H_m^\theta$(g)	101.37 ± 1.80	125.06 ± 1.88	119.55 ± 1.28	112.81 ± 2.27
$\Delta_M H_m^\theta$	−203.07 ± 2.41	−226.76 ± 2.41	−221.25 ± 1.97	−214.51 ± 2.72
$\Delta_f H_m^\theta$(g)^b	11.68 ± 2.93	−54.18 ± 3.03	−32.87 ± 2.61	−44.21 ± 3.65
$\langle D\rangle$(Sb–N)^a	162.83 ± 2.51	184.3 ± 2.63	169.20 ± 2.14	175.80 ± 2.98
$\langle D\rangle$(Sb–NN)^b	134 ± 3	154 ± 3	140 ± 3	147 ± 4

Parameters assigned with ‘a’ and ‘b’ were estimated using the first and second hypotheses, respectively.

molar enthalpy for the adduct, $\Delta_f H_m^\theta$(solid) that is neared to the value derived from Eq. (3).

The values of $\Delta_f H_m^\theta$(solid), $\Delta_f H_m^\theta$(g) and $\langle D\rangle$(Sb–N) of adducts are shown in Table 5. The $\langle D\rangle$(Sb–N) bond enthalpies were estimated based on two hypothesis The $\langle D\rangle$(Sb–N) bonding enthalpies by using hypothesis ‘a’ and hypothesis ‘b’ are shown in Table 5. The difference (a − b) equals to 28.65, 29.62, 28.63 and 28.19 kJ mol^{-1} for the adducts with Py, 2MPy, 3MP and 4MPy, respectively. According with item (iv), hypothesis ‘b’ was considered as the best route for estimating the standard molar enthalpy of sublimation of the adducts.

The molar enthalpies of formation of the adducts in the condensed phase showed a substantial difference between the adduct with pyridine as a ligand and those with methyl-pyridines. This suggests the substitution of one hydrogen atom by a methyl group increased the ligand basicity.

The mean antimony–nitrogen bond enthalpies for arsenic adducts AsI_3·3MPy and AsI_3·4MPy were 155 and 167.7 kJ mol^{-1} [28], respectively. $\langle D\rangle$ values in antimony adducts were lower than in the arsenic series, in agreement with the higher acidity of the arsenic(III) iodide.

For a series of adducts with the same stoichiometry, ΔS^θ values can be considered constant and a direct correlation between ΔG^θ and ΔH^θ values can be obtained. Based on this assumption, the stability order of the adducts is 2MPy > 3MPy > 4MPy > Py. The standard molar enthalpies of formation of the adducts in condensed phase ($\Delta_r H_m^\theta$) can be used to order the donor strength of the ligands [28]. The same sequence was observed in relation to $\Delta_M H_m^\theta$, $\Delta_D H_m^\theta$, $\Delta_f H_m^\theta$ and $\langle D\rangle$. This order is the same order obtained from pK_a of the ligands [29].

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