Identification of Antimony(III) Thiocyanato Species in the Mass Spectra of Antimony Trifluoride and Ammonium Thiocyanate Mixtures

G. ALONZO*, M. CONSIGLIO, F. MAGGIO

Dipartimento di Chimica Inorganica, Università di Palermo, via Archirafi 26, 90123 Palermo (Italy)

P. AGOZZINO

Dipartimento di Chimica e Tecnologie Farmaceutiche, Università di Palermo, via Archirafi 32, 90123 Palermo (Italy)

and N. BERTAZZI

Istituto di Chimica Generale, Inorganica ed Analitica, Universita di Cagliari, via Ospedale 72, 09100 Cagliari (Italy)

(Received May 11, 1989)

Antimony trifluoride readily interacts with thiocyanates like KNCS or NH_4NCS, as shown by the bright yellow–orange colour which develops after the first steps of the mechanical grinding of the reactants. We have also observed that SbF_3 can be dissolved in the above melted thiocyanates (providing there is an NCS^-/SbF_3 ratio larger than about 2) and the resulting yellow solutions, because of their relatively low thermal stability, have been characterized after quick freezing by vibrational and Mössbauer spectroscopy [1]. These investigations, besides revealing the different behaviour of SbF_3 in the two matrices, gave evidence of the formation of antimony fluorothiocyanato mixed species, the precise nature of which still remains uncertain.

Here we report on the mass spectrometric results obtained for $ANCS/SbF_3$ mixtures in different molar ratios ($A = K^+$ or NH_4^+; molar ratios ranging from 2:1 to 5:1), recorded at increasing temperature, including values well above the melting point of each thiocyanate salt (177° and 140 °C for KNCS and NH_4NCS, respectively). This study has been undertaken in consideration that, notwithstanding the inherent complexity of the inhomogeneous condensed phases, as well as, for example, the possible occurrence in the melts of complexation equilibria [2], mass spectrometric experiments could provide evidence of antimony-containing molecular ions related to species actually formed in the spectrometer probe. The measurements were also of potential use in giving information on the antimony species resulting from the thermal decomposition of thiocyanate systems containing antimony salts [3].

Mass spectra were taken on a JEOL JMS-01SG-2 double-focussing spectrometer operating at 75 eV. Runs at lower ionization potential, 13–15 eV, were also performed in order to differentiate the metal-containing molecular ions. Antimony species were easily identified from the characteristic patterns due to the metal isotopic composition.

In a typical experiment, weighed amounts of SbF_3 (Merck) and the appropriate thiocyanate salt (Janssen) were carefully ground together just before measurements and allowed to warm up in the direct inlet system of the spectrometer probe. The 50–210 °C temperature range was normally investigated and, as a general trend, the ionic current was found to reach its maximum immediately after the mixture melting point.

The mass spectrum of SbF_3 alone has also been obtained at 75 eV and related ions are listed in Table 1. For the mixtures, we do not report complete spectra and restrict our attention to observed main trends concerning the antimony-containing species.

SbF_3^+ and its fragments are always present in the mass spectra of the mixtures and, up to about 140 °C, dominate the fraction of metal-containing ions. At this temperature, the mixed-ligand molecular ion $SbF_2(NCS)^+$ is detected in both systems as a rather intense peak, providing evidence that ligand-exchange reactions can occur at antimony. Although at this stage only the ammonium samples are close to the melting point, the overall behaviour of the two systems shows only minor differences as, for instance, the appearance of Sb_4^+ peaks in the potassium samples with the lowest SbF_3 content.

Among the thiocyanate-containing fragments of the $SbF_2(NCS)^+$ molecular ion, $SbF(NCS)^+$ is detected with a rather low intensity and in no case were peaks corresponding to $Sb(NCS)^+$ observed. This indicates that a possible fragmentation pathway involves the loss of a fluorine ligand and, at the same time, points to the easier dissociability of the Sb–thiocyanate bond.

When the temperature is allowed to increase above 140–150 °C, one observes in both systems the appearance of various antimony sulfide species, the

TABLE 1. The mass spectrum of SbF_3

Ions	Intensity (%)[a]
Sb^{2+}	11
SbF^{2+}	6
Sb^+	51
SbF^+	30
SbF_2^+	100
SbF_3^+	11

[a] Only data for the ^{121}Sb isotope are reported.

---

*Author to whom correspondence should be addressed.

0020-1693/89/$3.50

relative abundance of which increases with the temperature. The most important peaks correspond to the ions SbS^+, $Sb_3S_3^+$, $Sb_4S_3^+$ and $Sb_4S_4^+$. Their formation can be reasonably ascribed to decomposition reactions occurring in the spectrometer probe since they are often the only metal-containing species found in spectra taken at high temperatures. The observed antimony/sulfur stoichiometries correspond to higher antimony sulfides not actually known, although compounds with these stoichiometries are well known in the chemistry of the lighter Group V elements As and P.

As far as the antimony thiocyanate species are concerned, the two systems show more substantial differences at increasing temperatures. In fact, while for the potassium thiocyanate mixtures, $SbF_2(NCS)^+$ remains the only molecular ion usually observable up to rather high temperatures, distinctive behaviour is found with the ammonium systems which, just after melting and up to about 180 ℃, provides evidence also of $SbF(NCS)_2^+$ and $Sb(NCS)_3^+$, together with all fragments deriving from simple Sb–ligand breakage. Representative data for a spectrum obtained in the above temperature range are reported in Table 2. Different spectra always showed relative intensities in the order $SbF_2(NCS)^+ > SbF(NCS)_2^+ > Sb(NCS)_3^+$ and each species reached a maximum value within the above cited temperature range. A slow temperature scanning rate and a low SbF_3 content favour the detectability of these new thiocyanato species.

Inspection of the spectra in the low *e*/*m* range reveals that the appearance of HF^+ ions slightly precedes and then accompanies the detection of $SbF(NCS)_2^+$ and $Sb(NCS)_3^+$. This suggests that, just after melting, a reaction between SbF_3 and the ammonium cation occurs causing the effective removal of fluoride ligands from the medium as volatile products, thus promoting the formation of thiocyanato species. Particularly interesting appears to be the identification of $Sb(CNS)_3^+$, since the pure antimony tris-thiocyanate has never been isolated. Under the conditions of the present experiments, these thiocyanates appear to undergo a thermal decomposition reaction ending with the formation of antimony sulfides although, below 170 ℃, this process is still slow enough to allow their detection.

TABLE 2. Relevant metal-containing ions in the mass spectra of SbF_3/NH_4CNS mixtures, molar ratio 1:5, at 170 ℃

Ions	Intensity (%)[a]
Sb^+	65
SbN^+	5
SbF^+	87
$SbNC^+$	25
SbS^+	92
SbF_2^+	98
$SbF(NC)^+$	27
$SbFS^+$	8
SbF_3^+	100
$Sb(NCS)^+$	60
$SbF(NCS)^+$	86
$SbF_2(NCS)^+$	95
$Sb(NCS)_2^+$	28
$SbF(NCS)_2^+$	78
$Sb(NCS)_3^+$	12
$Sb_3S_3^+$	6
Sb_4^+	3
$Sb_4S_3^+$	7
$Sb_4S_4^+$	10

[a] Only the most intense peak is reported.

Acknowledgement

We thank the Italian Ministero della Pubblica Istruzione for financial support.

References

1 N. Bertazzi and G. Alonzo, *J. Fluorine Chem.*, in press.
2 R. E. Hester and K. Krishnan, *J. Chem. Phys.*, *48* (1968) 825.
3 D. H. Kerridge, in *Advances in Molten Salt Chemistry*, Vol. 3, Plenum, New York/London, Ch. 5.