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GASEOUS THALLIUM (I) METABORATE AND THALLIUM (I) ALUMINUM FLUORIDE

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While all the thallium (I) halides have been studied,¹ only two gaseous ternary compounds of monovalent thallium, thallium (I) nitrate² and thallium (I) sulfate,³ have been reported so far. The purpose of this work was to extend the range of known gaseous ternary compounds of thallium (I) and to compare their mass spectrometric behavior to that of the corresponding alkali compounds. We have therefore examined the vapors above thallium (I) metaborate and an equimolar mixture of thallium (I) fluoride and aluminum fluoride.

Samples of thallium metaborate, thallium fluoride and aluminum fluoride were obtained from Research Organic/Inorganic Chemical Corporation. Mass spectra were run on an Atlas CH-4 mass spectrometer. The samples were contained in platinum-lined nickel effusion cells. Mass spectra obtained are shown in Tables 1 and 2.

The mass spectrum of thallium metaborate (Table 1) is similar to that of the alkali metaborates.⁴ Both thallium metaborate monomer, TlBO_2 , and dimer, $\text{Tl}_2(\text{BO}_2)_2$, are present in the vapor, the latter identified by means of the fragment ion Tl_2BO_2^+ . The different temperature dependence of Tl_2BO_2^+ and TlBO_2^+ showed the latter to be the monomer parent ion rather than a dimer fragment. The dimer parent ion $\text{Tl}_2(\text{BO}_2)_2^+$ was not found; it was present to the extent of less than one part in 400 of the fragment ion Tl_2BO_2^+ . It may be noted that for gaseous thallium nitrate

dimer the fragment ion Tl_2NO_3^+ was the only ion observed.² In this respect the two thallium pseudohalides resemble the alkali halides and pseudohalides, whose mass spectra only show dimer fragment ions M_2X^+ and differ from the thallium halides, whose mass spectra contain dimer parent ions Tl_2X_2^+ .² The monomer-dimer ratio in thallium metaborate vapor is difficult to establish since the thallium ion, which one would otherwise suppose to be a fragment of the monomer, had an appearance potential of 6 eV showing the presence of free thallium in the vapor.

Turning now to the mass spectrum of the vapor above the TlF-AlF_3 mixture, (Table 2), we see that the mixed thallium aluminum fluoride, TlAlF_4 , is indeed present. Its existence was in fact suggested by the observation of the corresponding indium compound, InAlF_4 , in work on the reduction of AlF_3 by indium.⁵ In addition, the presence of the ion $\text{Tl}_2\text{AlF}_4^+$ shows the existence of a higher polymer. In analogy with the assignment of the corresponding ions in the LiF-AlF_3 and NaF-AlF_3 systems,⁶ we are inclined to assign this ion to the double dimer $\text{Tl}_2(\text{AlF}_4)_2$. The presence of the mixed trimer, Tl_2AlF_5 , however, cannot be ruled out. In the case of TlAlF_4 , the parent ion, TlAlF_4^+ , is present in the mass spectrum, in contrast to LiAlF_4 and NaAlF_4 , in whose mass spectra only the fragments LiAlF_3^+ and NaAlF_3^+ are observed. The difference in behavior between the two sets of compounds may be explained by the recent work of Berkowitz.^{7,8} In interpreting the photoelectron spectra of TlCl and TlBr he concluded that the highest-lying orbital is a thallium s-orbital, in agreement with the calculations of Hastie⁹ and Cusachs.¹⁰ In Berkowitz's interpretation TlCl and TlBr are essentially ionic compounds, and removal of the thallium s-electron on ionization will actually

strengthen the ionic bond, the ion formed being effectively Tl^{++}X^- . Removal of a halogen p-electron (the next highest orbital, but with an appearance potential below that of the thallium s-orbital) removes the charge on the halogen and leads to the fragment ion Tl^+ .

This analysis may be extended to TlAlF_4 and the alkali aluminum fluorides if we assume that the mixed thallium halide has the same structure as NaAlF_4 , which has two bridging fluorine atoms between the sodium and aluminum atoms.¹¹ Removal of a thallium s-electron leads to the parent ion TlAlF_4^+ , whereas no such process is possible in the alkali compounds. Removal of a bridging fluorine p-electron, on the other hand, leads to the fragment ions MAlF_3^+ in both the thallium and the alkali compounds.

The general similarity of the thallium compounds to the corresponding alkali compounds suggests a bridge structure for the thallium halide dimers similar to that of the lithium halide dimers.¹² A linear structure X-Tl-Tl-X is unlikely if the constituent Tl-X units are ionic, and the fact the ion Tl_2^+ is observed in the mass spectrum may be due to simple rearrangement: it has been shown¹³ that the ion Cs_2^+ in the mass spectrum of cesium sulfate vapor arises from the dissociative ionization of Cs_2SO_4 , in which the cesium atoms are presumably located at opposite ends of the sulfate group.

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Table 1. Mass Spectrum of Vapor Above Thallium (I) Metaborate at 634C (70 volt ionizing electrons)

<u>Ion</u>	<u>Relative Intensity</u>
Tl^+	100
TlO^+	0.27
$TlBO^+$	0.48
$TlBO_2^+$	2.2
Tl_2^+	2.2
Tl_2O^+	21.3
$Tl_2BO_2^+$	17.5

Table 2. Mass Spectrum of Vapor Above an Equimolar Thallium (I) Fluoride-Aluminum Fluoride Mixture at 413C (70 volt ionizing electrons)

<u>Ion</u>	<u>Relative Intensity</u>
Tl^+	100
TlF^+	8.1
$TlAlF_2^+$	0.09
$TlAlF_3^+$	2.9
$TlAlF_4^+$	0.13
Tl_2^+	0.59
Tl_2F^+	3.9
$Tl_2F_2^+$	1.1
$Tl_2AlF_4^+$	1.3

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