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MASS SPECTRA OF VAPORS OVER Tl_3AsS_4

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ABSTRACT

The mass spectrometric study of the vapors over Tl_3AsS_4 shows that this sulfosalt decomposes to yield sulfur vapor at relatively low temperatures. From around 300 °C the equilibrium vapor also contains $TlAsS_2(g)$. The partial vapor pressure of the latter salt was determined over part of the solid and liquid range. The enthalpy of formation of $TlAsS_2(g)$ is $\leqslant 41$ kcal mol^{-1}.

INTRODUCTION

The sulfosalt crystals have been reported to be useful acousto-optic materials [1], and thallium arsenic sulfide (Tl_3AsS_4) recently has been reported to be of especial interest for acousto-optic devices [2].

Roland et al. [3] made a detailed phase equilibria study of the Tl–As–S system and showed that their phase diagram had little resemblance to the earlier one reported by Canneri and Fernandes [4]. The former authors showed that the Tl_3AsS_4 and $TlAsS_2$ melt congruently at 417 and 286 °C, respectively.

As part of a study of the vaporization chemistry of Tl_3AsS_4, we determined the mass spectrum of the vapors over this salt to better understand the vapor-condensed phase equilibria.

EXPERIMENTAL

A single crystal of Tl_3AsS_4 was grown in a silica tube by the method which has been described previously [5]. This compound is stable in air and is non-hygroscopic. For the mass spectrometric measurements, the crystal was easily crushed with an agate mortar and pestle prior to loading into the graphite Knudsen cell. The cylindrical cell was constructed with a tightly fitting lid with a thin, conical orifice of 0.078 cm diameter. Approximately 1.5 g of the crushed salt was used in each measurement.

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The mass spectrometric measurements were made on a Nuclide, Model HT-90, 90° magnetic sector instrument. Details of the instrumental arrangement and operation have been described previously [6]. The molecular beam was modulated by a beam chopper at 3600 Hz and the spectrum of the chopped beam was obtained through a lock-in amplifier and recorded on a two-pen recorder; the electrometer signal for the total ion current was also recorded simultaneously with the signal from the lock-in. The spectra and relative intensities were recorded at an electron accelerating potential of 30 eV, emission current of 4.0 mA, and ion accelerating potential of 8 kV. All instrument settings were kept the same for the measurement of the relative intensities as a function of temperature. The reproducibility of the relative intensities, as determined on zinc vapor, was within ±3% at the higher measured intensities, while that at the lower intensities was no better than ±10%. The pressure in the ionization chamber was in the range 10^{-7} to 10^{-8} Torr. The rectangular spectral peaks were clearly resolved and the ionic species assignment was made from the isotopic distribution for the different elements.

For each sample, the spectrum was scanned frequently while the sample was being heated to the temperatures at which measurements were made. The time dependence of the intensity of selected peaks was determined by observing the intensity at constant temperature over periods of up to 15 min. The detailed temperature dependence of the ion current for Tl^+ and $TlAsS_2^+$ was determined at increasing and decreasing temperatures for the peaks at $m/e = 203$ and 344, respectively. For the latter measurements the temperature was constant to within ±3°C.

RESULTS

The mass spectrum showed that the Tl_3AsS_4 started to decompose, with the vaporization of sulfur, at temperatures below 150°C. The evolution of sulfur at such low temperatures is most probably the result of the presence of a slight excess of sulfur in the crystal [5]. The vaporization of sulfur increased rapidly with the temperature, as shown by the rapid increase in the mass spectral intensities of the sulfur species, especially of S_2^+, as the temperature was raised. However, the ion current intensities of the sulfur ions at a fixed temperature were time dependent and decreased fairly rapidly with time. The time dependence persisted over the complete measured temperature range. The sulfur species observed in the spectra were S^+, S_2^+, S_3^+, S_4^+, S_6^+ and S_8^+, with S_2^+ being the dominant species.

The Tl^+ was first seen in the spectrum at approximately 300°C, and the ion-current intensities of the ions which contained Tl and As were constant at a fixed temperature. Table 1 shows the relative intensities of these ions from the lock-in amplifier spectrum determined at 492°C. The ratio of the

TABLE 1

Relative intensities and appearance potentials at 492° C

Ion	Rel. int.	*AP* (eV)
As^+	8.5	$\geqslant 15$
AsS^+	15	$\geqslant 12$
Tl^+	347	8.5 ± 0.3
TlS^+	20	12.5 ± 0.5
$TlAs^+$	13	$\geqslant 15$
$TlAsS^+$	10	$\geqslant 12$
$TlAsS_2^+$	84	7.5 ± 0.3
Tl_2S^+	4	9.0 ± 0.5
$Tl_2S_2^+$	0.7	
$TlAsS_3^+$	0.7	
S_2^+	[a]	

[a] Very strong and decreasing fairly rapidly with time.

maximum ion intensity of S_2^+ to that of Tl^+ increased with temperature from 360 at 365 °C to 1839 at 407 °C.

Table 1 also summarizes the appearance potentials (*AP*) determined by the linear extrapolation method; the *AP*s were calibrated with that of H_2O^+ which was used as the internal standard. Figure 1 shows the efficiency curves for Tl^+ and $TlAsS_2^+$. The curve for the latter ion shows a single source for the formation of this ion at an *AP* of 7.5 ± 0.3 eV. The low value for this molecular ion suggests that the parent is $TlAsS_2$. The linear extrapolation of the curve for Tl^+ yields an *AP* of 8.5 ± 0.3 eV, but there is a broad leg of approximately 1.5 eV for this ion with the ionization threshold at approximately 7.2 eV. The appearance potential of Tl^+ is significantly higher than the ionization potential of 6.1 eV [7] for Tl. Therefore, the Tl^+ is formed by fragmentation of a molecular species. The broad leg near the ionization threshold for Tl^+ suggests the possibility of a

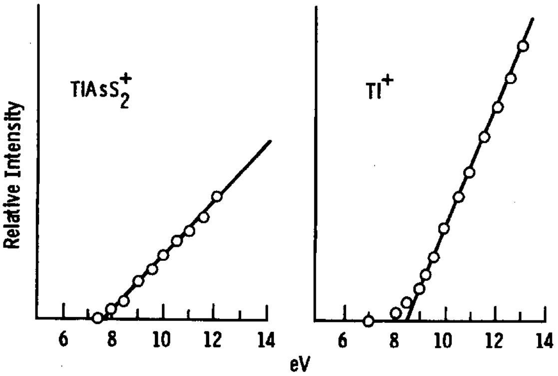

Fig. 1. Efficiency curves for $TlAsS_2^+$ and Tl^+.

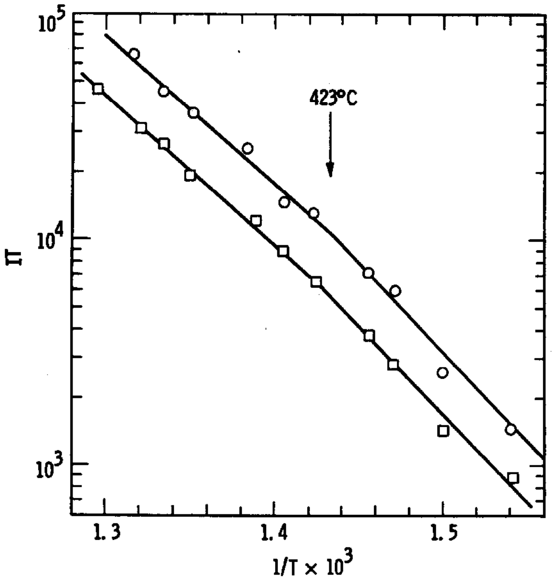

Fig. 2. Log (IT) vs. T^{-1} for (○) Tl^+ and (□) $TlAsS_2^+$.

second, minor species source for this ion. The *AP*s for most of the other species were also determined, but the probable error for these species is relatively high because of the low intensities for these ions. The relatively high *AP*s for the low-intensity ions show that these ions are formed by fragmentation upon electron impact of a larger molecule.

Figure 2 shows the temperature dependence of the intensities for Tl^+ ($m/e = 203$) and $TlAsS_2^+$ ($m/e = 344$), where I is the ion current, T the absolute temperature, and IT is proportional to the partial pressure of the ionized species. The parallel curves for Tl^+ and $TlAs_2^+$ show that these ions both have the same parent, i.e., $TlAsS_2$. The data at increasing and decreasing temperatures were indistinguishable. The temperature dependence for the minor ionic species which contain Tl and As were not determined because of their low intensities. Also, the temperature dependence of the sulfur species were not determined because of the strong time dependence of their ion currents. Figure 2 shows inflections in the curves at approximately 423°C. The inflection point is attributed to the melting of Tl_3AsS_4; Roland et al. [3] determined congruent melting points of 417°C for Tl_3AsS_4 and 286°C for $TlAsS_2$.

$TlAsS_2$ vapor pressure

The isotopic abundance of ^{203}Tl is 29.52% [8] while that for the $m/e = 344$ peak for $TlAsS_2$ was determined from the spectrum to be 67%. The data in Fig. 2 were fitted by the following least squares equations:

$TlAsS_2^+$

$$\log(IT) = 14.63 - (7600 \pm 36)/T \tag{1}$$

$$\log(IT) = 13.02 - (6453 \pm 12)/T \tag{2}$$

Tl^+

$$\log(IT) = 16.08 - (8409 \pm 29)/T \tag{3}$$

$$\log(IT) = 14.00 - (6985 \pm 28)/T \tag{4}$$

Equations (1) and (3) are for the solid phase while eqns. (2) and (4) are for the liquid phase. To obtain the total intensities, eqns. (1) and (2) were multiplied by 1.5 while eqns. (3) and (4) were multiplied by 3.39.

The partial vapor pressure of $TlAsS_2(g)$ was calculated by utilizing the following relationship [9]

$$P_u = (IT)_u \frac{P_s}{(IT)_s} \frac{\sigma_s}{\sigma_u} \frac{\gamma_s}{\gamma_u} \frac{\Delta E_s}{\Delta E_u} \tag{5}$$

where s refers to the calibrating species and u to the sample vapor species; σ is the ionization cross section taken from Mann [10] and the additivity principle was assumed; I is the ion current; T is the absolute temperature; $\Delta E = E - AP$, where $E = 30$ eV in our measurements; and $\gamma = \text{constant} \times M^{-1/2}$ where M is the molecular weight of the ion. For calibration, the ion currents of ^{64}Zn (48.87% abundance [8]) were fitted by the equation

$$\log(IT) = 15.45 - 6350/T \tag{6}$$

The data of Hultgren et al. [11] were fitted by the equation, where P is pressure in atmospheres

$$\log P = 6.06 - 6745/T \tag{7}$$

to calculate P_u in eqn. (5). For the calculation of the partial pressure of Tl^+ and $TlAsS_2^+$ by eqn. (5), the *AP*s of the ions were 8.5 and 7.5, respectively, and it was assumed that the ionization cross section for Tl^+ was the same as that for $TlAsS_2^+$, i.e., 20×10^{-16} cm^2. The P_u calculated for Tl^+ and $TlAsS_2^+$ were combined to obtain the partial vapor pressure of $TlAsS_2(g)$ over the solid and liquid phases. As shown in Table 1, the relative intensities of As^+, AsS^+, TlS^+, $TlAs^+$ and $TlAsS^+$ constitute 13% of the total including the ions Tl^+ and $TlAsS_2^+$. For our computation of the partial pressure of $TlAsS_2(g)$ it was assumed that these ions are all formed by electron impact of $TlAsS_2(g)$. Therefore, the sum of the partial pressures from Tl^+ and $TlAsS_2^+$ was multiplied by 1.15 to obtain the equilibrium partial pressure of $TlAsS_2(g)$. The following least squares equations summarize the partial vapor pressure, in atmospheres, of $TlAsS_2(g)$

$$\log P = 8.57 - 10321/T;\ \text{solid at 649–711 K} \tag{8}$$

$$\log P = 7.54 - 9810/T;\ \text{liquid at 711–733 K} \tag{9}$$

The enthalpy of vaporization from the solid and liquid phases calculated from eqns. (8) and (9) are 47.2 and 44.9 kcal mol^{-1} at 680 and 742 K, respectively; the enthalpy of fusion of Tl_3AsS_4 is 2.3 kcal mol^{-1}.

The assumption of 20×10^{-16} cm^2 for the ionization cross section is probably too high in our vapor pressure calculation. Piacente and Malaspina [12], for example, reported a cross section of 8.5×10^{-16} cm^2 for $TlAs^+$, whereas the sum of the cross sections for Tl^+ and As^+ is 12.0×10^{-16} cm^2. Our assumption of 20×10^{-16} cm^2 for the cross section of $TlAsS_2^+$ would result in a vapor pressure for $TlAsS_2(g)$ which is too low by the ratio of $\sigma/20 \times 10^{-16}$.

The enthalpy of formation of $TlAsS_2(g)$ was estimated from the following equations

$$TlAsS_2(g) + e \rightarrow TlAs^+ + 2S(g) + 2e \qquad AP \geqslant 15 \text{ eV} \qquad (10)$$

$$TlAs(g) + e \rightarrow TlAs^+ + 2e \qquad IP = 9 \pm 1 \text{ eV} \qquad (11)$$

$$TlAs(g) \rightarrow Tl(g) + As(g) \qquad D^\circ_{298} = 2 \text{ eV} \qquad (12)$$

$$TlAsS_2(g) \rightarrow 2S(g) + Tl(g) + As(g) \qquad D^\circ_{298} \geq 8 \text{ eV} \qquad (13)$$

The data for eqns. (11) and (12) were those of Piacente and Malaspina [12]. The ΔH^0_{f298} for S(g), Tl(g) and As(g) are 2.9 eV [13], 1.9 eV [14] and 2.1 eV [14], respectively. From eqn. (13), $\Delta H^0_{f298} \leqslant 1.8$ eV (41 kcal mol^{-1}) for $TlAsS_2(g)$. This enthalpy of formation is only the upper limit because of the uncertainty of the data used in its calculation.

DISCUSSION

Tl_3AsS_4 vaporizes dissociatively, with sulfur being the dominant vapor species. The dissociation also results in the vaporization of $TlAsS_2(g)$ as the predominant gaseous sulfosalt in equilibrium with the solid and liquid Tl_3AsS_4. The mass spectral presence of the ions Tl_2^+, $Tl_2S_2^+$, $TlAsS_3^+$ and Tl_2^+ suggests the existence of other vapor species, but the concentration of these species is very low in the measured temperature range. The exact dissociative reaction cannot be conjectured at present, but it is clear that there is a rapid depletion of sulfur as the Tl_3AsS_4 is heated. The total quantity of material which was vaporized was only a small fraction of the original sample, and the $TlAsS_2$ vaporization was congruent. It is not possible to conclude whether or not this sulfosalt is formed in the condensed phase. Roland et al. [3] determined the congruent melting points of $TlAsS_2$ and Tl_3AsS_4 to be 286 and 417°C, respectively. The sample in our study was observed to melt at approximately 423°C in satisfactory agreement with Roland et al. for Tl_3AsS_4.

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