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Note

MASS SPECTRA OF SnI_2

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The tin(II) halides, because of their continuum radiation in the visible spectrum, have been of interest in the development of electric discharge lamps [1]. Of particular interest in this application are $SnBr_2$ and SnI_2. Pertinent to the understanding of the arc phenomena are the thermodynamic and electrical properties of the vapor. As part of a study on the vaporization and thermodynamic properties of systems which contain these halides, we have determined the mass spectra of SnI_2(g). The positive ion mass spectra of $SnCl_2$ [2] and $SnBr_2$ [3] have been reported previously by Knowles and co-workers but that for SnI_2 has not been reported.

EXPERIMENTAL

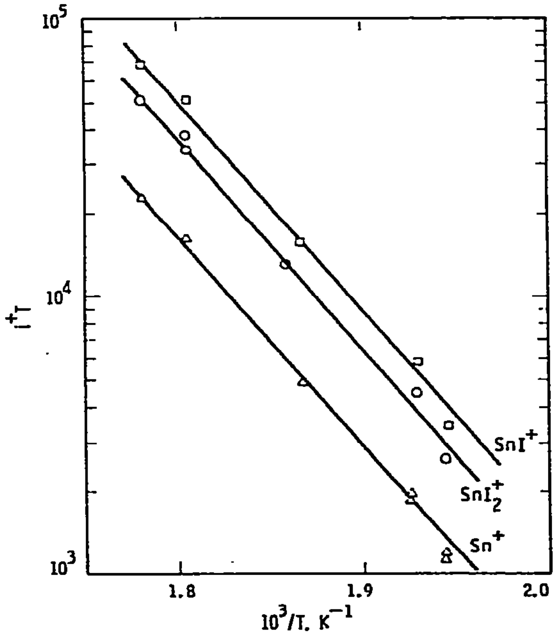
The SnI_2 was prepared by the direct reaction of iodine with six times the stoichiometric quantity of tin. Both materials were of at least 99.99% purity. To effect the reaction, the tin and iodine were sealed into a silica reaction tube under a vacuum of better than 10^{-4} torr. The silica tube had a short side arm in which the iodine was first loaded. The tube with the tin chips was placed into a tube furnace which was maintained at 600°C; the top of the tube with the side arm which contained the iodine was outside of the furnace. The iodine vapor pressure over the tin was maintained below one atmosphere by keeping the temperature of the exposed tube at approximately 200°C. The iodine completely reacted with the tin after 24 h of heating in this manner. The side arm was subsequently sealed off, and the reaction tube was then heated for an additional 48 h at 600°C in a horizontal furnace. The SnI_2 was then separated from the tin by sublimation within the reaction tube. Chemical analysis, whereby the SnI_2 was oxidized with HNO_3 and converted to SnO_2, showed the complete conversion of the product to SnI_2.

The mass spectrometric measurements were made on a Bendix Model 12-101 Mark IV spectrometer. Measurements were made with tantalum Knudsen cells with and without a platinum liner with identical results. There was no reaction of the SnI_2(c) with the tantalum at the low measurement temperatures. Sample temperatures were measured with a Pt—Pt10%Rh thermocouple which was in contact with the base of the cell. The cell was heated by radiation, and at the low temperatures herein the measured temperatures may be in error by as much as ±5°C relative to the actual sample temperature.

The mass spectrum was visually scanned on the oscilloscope, at an electron accelerating energy of 20—30 eV, while the cell was slowly heated. When a shutterable species emanating from the Knudsen cell was detected, the temperature was maintained constant while the spectrum was recorded on a strip chart. The relative intensity as a function of temperature was made at 23 eV by focusing on a given peak, and recording the intensity over a period of 1—5 min to determine if there was a time dependence of the ion intensity. The ion efficiency curves were determined for all shutterable species, and those of H_2O^+ and N_2^+ were also determined as standards. The latter ions were always present as a background in our spectra.

RESULTS

The shutterable species in the mass spectrum over the solid SnI_2 were Sn^+, SnI^+, SnI_2^+, and I^+ in the relative intensity ratios 40 : 124 : 91 : 120. The temperature dependence of the ion intensities, measured at 23 eV, is shown in Fig. 1 in the usual semi-log plot of i^+T against $1/T$, where i^+ is the ion intensity and T is the absolute temperature; the data for I^+ are not shown because they very nearly overlapped with those for SnI^+. The data in Fig. 1 show that the ions all originate from a single parent, i.e., SnI_2. It is interesting to note the high relative intensity of the I^+ ion. Knowles and co-workers did not report the presence of Br^+ and Cl^+ in the mass spectra over $SnCl_2$ and $SnBr_2$, respectively [2,3].



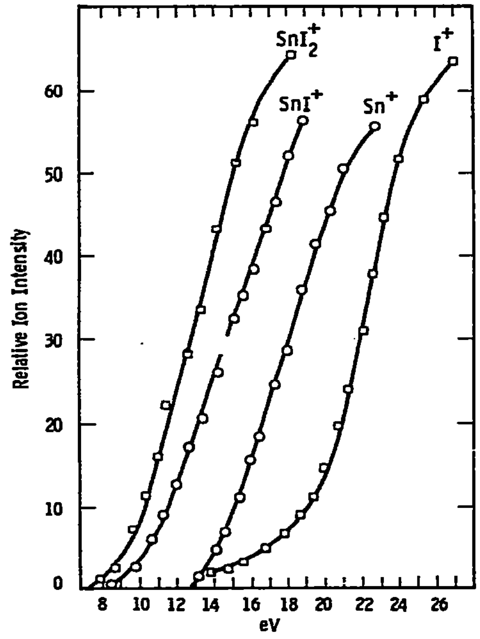


Fig. 1. Semi-log plot of i^+T against $1/T$ for positive ions from SnI_2.

Fig. 2. Efficiency curves for ions from SnI_2.

TABLE 1

Appearance potentials of positive ions from SnI_2

Ion	Reaction	AP (eV)	
		Calcd.	Measd.
Sn^+	(1) $SnI_2 + e \rightarrow Sn^+ + 2\,I + 2\,e$	$\geqslant 12.7$	13.6 ± 0.5
SnI^+	(2) $SnI_2 + e \rightarrow SnI^+ + I + 2\,e$		10.1 ± 0.5
SnI_2^+	(3) $SnI_2 + e \rightarrow SnI_2^+ + 2\,e$		9.3 ± 0.5
I^+	(4) $SnI_2 + e \rightarrow I^+ + Sn + I + 2\,e$	$\geqslant 16$	18.5 ± 1
	(5) $SnI_2 + e \rightarrow I^+ + Sn + I^- + e$	$\geqslant 12.8$	

The efficiency curves for the ions are shown in Fig. 2, and the appearance potentials (AP) obtained by the linear extrapolation method are shown in Table 1. The curve for the I^+ ion shows a long leg in the low electron energy region. This low energy process is probably an ion pair process, such as that shown by reaction (5) in Table 1. Also, there is a very small contribution from HI^+.

The AP of the Sn^+ ion was calculated from the relation AP $(Sn^+) \geqslant$ IP (Sn) + $D(SnI_2)$, where the ionization potential of Sn was obtained from Franklin et al. [4] and the atomization energy of SnI_2 was taken from Feber [5]. It is assumed in the calculations of the AP that there is no excess kinetic energy of the ground state species. The measured AP of 13.6 ± 0.5 eV for Sn^+ is in fair agreement with the calculated value of $\geqslant 12.7$ eV; the AP values of Sn^+ from $SnBr_2$ [3] and $SnCl_2$ [2] are 14.5 and 15.8 eV, respectively, for the reactions analogous to reaction (1).

The appearance potential of 10.1 ± 0.5 eV for SnI^+ compares with 11.0 and 11.3 eV, respectively, for $SnBr_2$ and $SnCl_2$. The ionization potential (IP) of SnI was estimated from the AP and the atomization energies [5] of SnI_2 and SnI. The upper value for the IP estimated here is $\leqslant 7.9$ eV; this value is nearly identical to the 7.8 eV reported for SnBr [3].

The IP of SnI_2 of 9.3 ± 0.5 eV is lower than the 11.0 and 10.1 eV reported for the IP of $SnBr_2$ [3] and $SnCl_2$ [2], respectively.

The AP of 18.5 ± 1 eV for I^+ is attributed to reaction (4). The estimated AP of $\geqslant 16$ eV from this reaction was obtained by using the enthalpy of formation of $SnI_2(g)$ from Feber [5], that of I^+ from Franklin et al. [4], and those of Sn(g) and I(g) from Stull and Sinke [6]. The experimental AP is appreciably higher than the calculated value because of the uncertainty incurred by the linear extrapolation of the efficiency curve. However, reaction (4) is the process which requires the highest energy for the formation of the I^+ ion from the electron impact ionization of SnI_2.

The efficiency curves for Sn^+, SnI^+ and SnI_2^+ (Fig. 2) show only a single source for these ions; the reactions for the formation of these ions are shown in Table 1. Knowles and co-workers, on the other hand, showed that there was also a contribution of the reaction

$$SnX_2 + e \rightarrow Sn^+ + X_2 + 2\,e$$

towards the formation of Sn^+ from $SnBr_2$ and $SnCl_2$. We do not observe any obvious contribution of the latter reaction in the case of SnI_2.

A least squares fit made to the limited data shown in Fig. 1 yielded an enthalpy of sublimation of 34 ± 3 kcal $mole^{-1}$ for the reaction

$$SnI_2(c) \rightarrow SnI_2(g)$$

at 533 K. Feber, based on the data of Fischer and Gewehr [7], reports a value of 32.5 kcal $mole^{-1}$ for the enthalpy of sublimation at 298 K. Our value of 34 kcal $mole^{-1}$ at 260°C is too high, and we attribute this discrepancy to the difficulty in accurate temperature measurement in our system.

DISCUSSION

The mass spectral data show that SnI_2 sublimes congruently as the monomer. This observation agrees with that of Karpenko [8] who found from vapor pressure measurements of the liquid SnI_2 that the vapor near the melting point consists primarily of the monomer.

Hastie and Margrave [9] had earlier predicted, on the basis of an ionic model, that the ionization potentials of the SnX would be around 8 eV, with IP increasing slightly with increasing atomic weight of the anion from F^- to I^-. Knowles et al. [3] confirmed the IP predictions of Hastie and Margrave, but the former authors concluded that the SnX are largely covalently bonded rather than ionically. The IP of 7.9 eV for SnI is also in accordance with the prediction of Hastie and Margrave, and as indicated by Knowles et al. [3] the ionized electron comes mainly from an atomic orbital of tin which is mainly covalently bonded to the iodine. The relatively high ionization cross-section of reaction (4), as compared to the very low cross section of the analogous reaction for the other SnX_2, is most probably related to the AP for this reaction. The calculated AP for the formation of I^+ was 16 eV, whereas those for the formation of Br^+ and Cl^+ are 19 and 21 eV, respectively. The latter values show that appreciably more energy is required for the formation of Br^+ and Cl^+ in the ionization process.

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