

THE MASS SPECTRA OF VAPORS OVER SnI_2 , SnBr_2 , AND $\text{SnI}_2 + \text{SnBr}_2$, AND THE ENTHALPY OF FORMATION OF SnIBr

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ABSTRACT

The mass spectra of vapors over $\text{SnI}_2 + \text{SnBr}_2$ show that there is a rapid exchange of halides between the two salts, and that the SnIBr plays an important part in the mixture. The enthalpy of formation and ionization potential of SnIBr have been determined.

INTRODUCTION

The tin(II) halides, SnBr_2 and SnI_2 , have been of interest in the development of electric discharge lamps because of the continuum radiation in the visible [1]. Pertinent to the understanding of the arc phenomena are the thermodynamic and electrical properties of the vapor. We previously reported on the positive ion mass spectra of vapors over solid SnI_2 [2]. Knowles and co-workers earlier reported on the mass spectra of SnCl_2 [3] and SnBr_2 [4]. Because the tin halide discharge lamp usually contains both SnI_2 and SnBr_2 , the formation and properties of the mixed halide, SnIBr , must be considered in the study of the overall vapor composition. Earlier, unreported mass spectrometric studies in this laboratory showed that the SnIBr plays an important part in the vapor composition over the halide mixture. We have now completed this study with a high sensitivity Knudsen cell mass spectrometer, and report on the mass spectra of vapors over the mixture, as well as improved measurements of the vapors over SnI_2 and SnBr_2 .

EXPERIMENTAL

The SnI_2 was that prepared previously [2]. The SnBr_2 was prepared by first reacting 25 g of Sn turnings with approximately 12 g of liquid bromine in an argon atmosphere; the reactants were contained in a silica tube. After complete reaction of the bromine, the tube was sealed under a vacuum of 10^{-5} Torr; the product end of the tube was cooled with liquid nitrogen

during the evacuation. The tube was then inserted into an oven so that the lower end, which contained the excess Sn and molten salt, was heated at 500–550 °C for approximately 36 h. During the reduction process the cool end of the tube protruded from the furnace and was maintained at approximately 100 °C to avoid the buildup of excessive vapor pressure. The SnBr_2 was then purified by distillation. Mass spectrometric analysis showed only SnBr_2 in the product. The mixtures of SnBr_2 and SnI_2 were prepared by introducing nearly equimolar amounts of the halides into a glass tube (e.g., 1.1 g SnBr_2 and 1.4 g SnI_2) which was subsequently sealed under a vacuum of 10^{-5} Torr. The mixture was fused with a torch and continuously mixed while heating for a period of at least 10 min in the molten state. The handling of the halides was always done in a helium atmosphere in a polyethylene glove bag.

The mass spectrometric measurements were made on a Nuclide model HT-90 spectrometer, and the samples were vaporized from a tantalum Knudsen cell with a thin orifice of 0.0762 cm diameter. The temperature measurement was made with a W/5%Re–W/20%Re thermocouple which was inserted into a 0.15 cm diameter hole in the bottom of the crucible. The temperature was maintained constant to within ± 3 K during the measurements.

A Hewlett-Packard 9825B computer was interfaced with the spectrometer system to facilitate the measurements, and a Hewlett-Packard 9872A plotter was interfaced with the computer to automatically plot the data points for the ionization efficiency curves. For the latter measurements the data points were generally obtained at 0.1-eV intervals.

The molecular beam from the Knudsen cell was chopped at a frequency of 150 Hz, and the output signal of the intensities from the lock-in amplifier was recorded on a two-pen strip chart recorder for relative intensity measurements. The isotopic mass peaks were completely resolved for all species, and the relative intensities of the peaks agreed with calculated values based on the isotopic abundances of Sn and Br. All measurements of the relative intensities at various temperatures were made at identical instrumental settings, such as electron emission current and multiplier voltage, so that the relative intensities for the different measurements were directly comparable.

The ionization efficiency curves of Ag^+ , Au^+ , and H_2O^+ were determined to calibrate the appearance potentials. The ionization potentials measured with our instrument consistently agreed with the published values [5] to within ± 0.1 eV.

RESULTS

All of the species emanating from the Knudsen cell were shutterable, and the relative intensities of the different ions measured at 25 eV are shown in

Table 1. No evidence of the tetrahalides or dimers was observed over the solids. For SnI_2 , Karpenko [6] also found the vapor to consist of the monomer at the melting point of 593 K, while Murgulescu et al. [7] observed the presence of a few percent of the dimer at temperatures above 700 K.

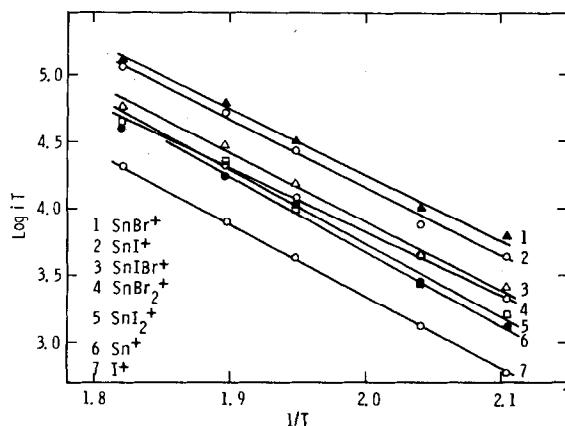
The temperature dependences of the ion intensities of the species from SnI_2 were parallel, as were the ion intensities for the species from SnBr_2 . This behavior shows that the ions originated from the same parent, i.e., from SnI_2 and SnBr_2 . The enthalpy of sublimation for SnBr_2 was 24 ± 5 kcal mol^{-1} at 480 K, while that for SnI_2 was 25 ± 5 kcal mol^{-1} at 500 K. These enthalpies of sublimation are too low by approximately 5 kcal mol^{-1} when compared to the values obtained from the vapor pressure measurements of Fischer and Gewehr [8]. The low values in the present work are attributed to temperature measurements which were too low; i.e., actual temperature was higher.

The temperature dependence of the ion intensities over the nearly equimolar mixture of $\text{SnI}_2 + \text{SnBr}_2$ is shown in Fig. 1. A least-squares fit to each of the curves resulted in the equations shown in Table 2. Although the scatter in the data points is quite high, the equations show that SnI_2^+ , SnI^+ ,

TABLE 1

Relative intensities of ions measured at 25 eV at indicated temperatures

Source	Ion	Rel. int.	Source	Ion	Rel. int.	Source	Ion	Rel. int.	Ion	Rel. int.
SnI (524 K)	Sn^+	100	SnBr ₂ (484 K)	Sn^+	100	SnI ₂ + SnBr ₂ (513 K)	Sn^+	100	SnI_2^+	106
	SnI^+	527		SnBr^+	430		SnBr^+	343	SnIBr^+	164
	SnI_2^+	394		SnBr_2^+	220		SnI^+	292	I^+	40
	I^+	101		Br^+	47		SnBr_2^+	126	Br^+	30

Fig. 1. $\text{Log } iT$ vs. $1/T$ for ions from $\text{SnI}_2 + \text{SnBr}_2$.

and I^+ have the steepest slope, while $SnBr_2^+$ and $SnBr^+$ have the lowest slope.

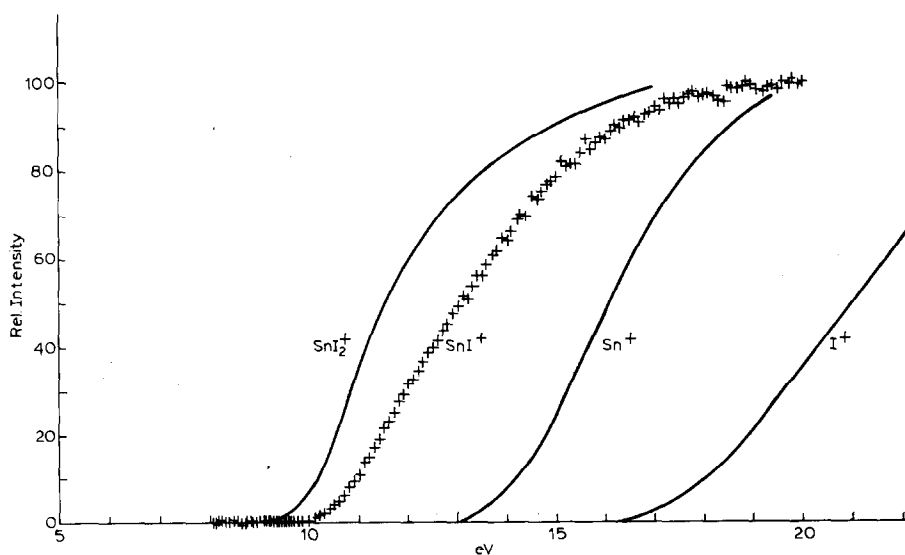
The ionization efficiency (IE) curves for the ions from SnI_2 , $SnBr_2$, and $SnI_2 + SnBr_2$ are shown in Figs. 2-4. Each of these figures shows the original data from the HP 9872A plotter for one of the ions; the curves without the data points were traced onto the plotted sheet from the data sheet for each ion which was plotted on an identical scale. The scatter in the data points for the latter curves was nearly identical to that for the points shown for the particular ion in each figure. In Fig. 4, for the ions from the halide mixture, the data points for $SnBr^+$ are shown, but the data points for SnI^+ superposed nearly identically over those for $SnBr^+$. The IE curve for SnI^+ , therefore, was not plotted in Fig. 4 because the curves for SnI^+ and $SnBr^+$ were indistinguishable.

As the IE curves show, SnI_2^+ , $SnBr_2^+$, and SnI_2Br^+ are parent ions formed by the electron impact ionization of the dihalides. All of the other ions from SnI_2 and $SnBr_2$, in Figs. 2 and 3, are formed by the dissociative ionization of the parents as indicated by the reactions in Table 3. This table also summarizes the appearance potentials (AP) determined from the IE curves

TABLE 2

Least squares equations, $\log iT = A - B/T$, for ions from $SnI_2 + SnBr_2$

Coefficient	Sn^+	$SnBr^+$	SnI^+	$SnBr_2^+$	SnI_2Br^+	SnI_2^+	I^+
A	13.79	13.74	14.57	13.26	13.82	14.38	14.28
B	5037	4734	5210	4717	4959	5332	5471

Fig. 2. Ionization efficiency curves for ions from SnI_2 . Initial $T = 586$, final $T = 586$.

by the method of linear extrapolation. By comparison with the data for SnI_2 in Table 3, we previously reported [2] APs of 13.6 ± 0.5 , 10.1 ± 0.5 , 9.3 ± 0.5 , and 18.5 ± 1 eV for Sn^+ , SnI^+ , SnI_2^+ , and I^+ , respectively. For SnBr_2 , Knowles et al. [4] reported APs of 10.0 ± 0.4 , 11.0 ± 0.4 , and 14.5 ± 1.0 for SnBr_2^+ , SnBr^+ and Sn^+ , respectively. These workers did not report the presence of Br^+ in their mass spectra. As shown in Figs. 2 and 3, the IE curves for I^+ and Br^+ show a long leg in the low electron energy region. This low energy process is probably an ion-pair process, e.g., $\text{SnI}_2 + e \rightarrow \text{I}^+ + \text{Sn}$

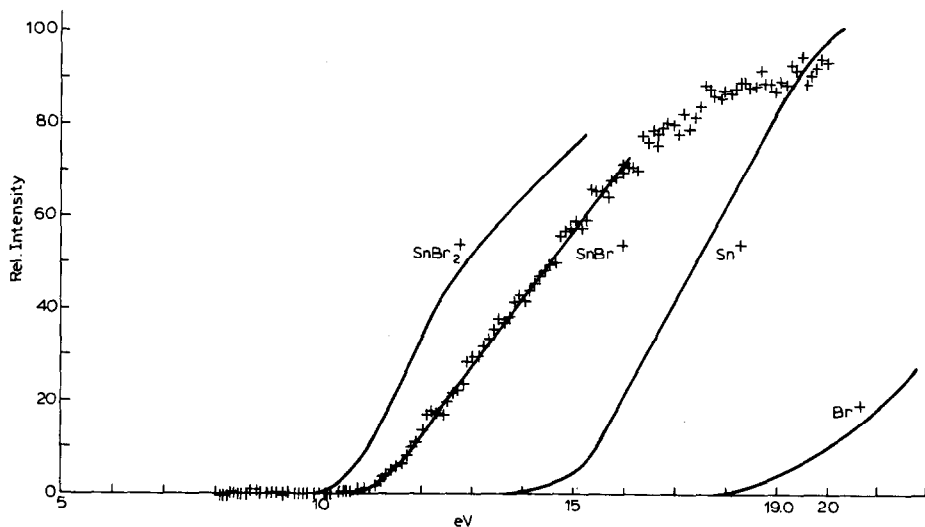


Fig. 3. Ionization efficiency curves for ions from SnBr_2 . Initial $T = 481$, final $T = 482$.

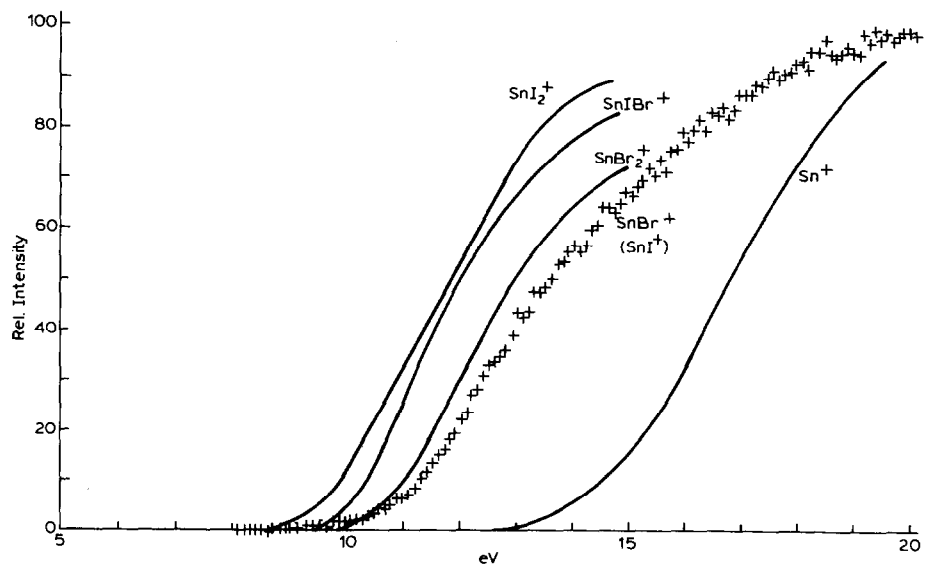


Fig. 4. Ionization efficiency curves for ions from $\text{SnI}_2 + \text{SnBr}_2$. The curve for SnI^+ was indistinguishable from that for SnBr^+ . Initial $T = 552$, final $T = 553$.

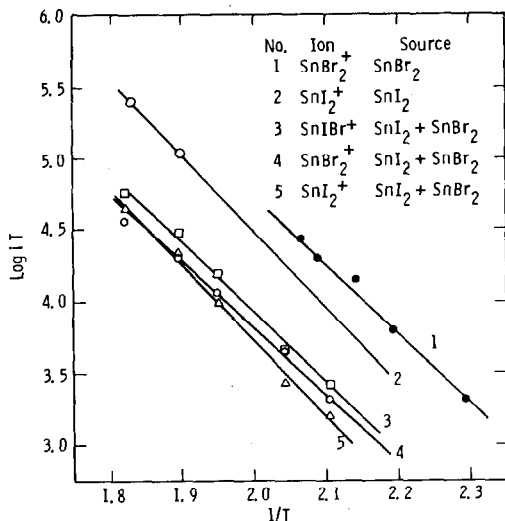
Fig. 5. Log iT vs. $1/T$ of parent ions.

TABLE 3

Appearance potentials (AP) of positive ions by electron impact

Ion		AP calcd. (eV)	AP measured (eV)
<i>Source: SnI₂</i>			
Sn ⁺	SnI ₂ + e → Sn ⁺ + 2I + 2e	≥ 12.7	13.8 ± 0.3
SnI ⁺	SnI ₂ + e → SnI ⁺ + I + 2e		10.5 ± 0.2
SnI ⁺	SnI + e → SnI ⁺ + 2e	≥ 7.8	
SnI ₂ ⁺	SnI ₂ + e → SnI ₂ ⁺ + 2e		9.8 ± 0.2
I ⁺	SnI ₂ + e → I ⁺ + Sn + I + 2e	≥ 16	17.0 ± 0.5
<i>Source: SnBr₂</i>			
Sn ⁺	SnBr ₂ + e → Sn ⁺ + 2Br + 2e	≥ 14.1	14.9 ± 0.3
SnBr ⁺	SnBr ₂ + e → SnBr ⁺ + Br + 2e		11.2 ± 0.2
SnBr ⁺	SnBr + e → SnBr ⁺ + 2e	≥ 7.7	
SnBr ₂ ⁺	SnBr ₂ + e → SnBr ₂ ⁺ + 2e		10.6 ± 0.2
Br ⁺	SnBr ₂ + e → Br ⁺ + Sn + Br + 2e	≥ 18.6	18.5 ± 0.5
<i>Source: SnI₂ + SnBr₂</i>			
Sn ⁺	SnI ₂ + e → Sn ⁺ + 2I + 2e		13.6 ± 5
	SnBr ₂ + e → Sn ⁺ + 2Br + 2e,		14.4 ± 0.5
	SnIBr ₂ + e → Sn ⁺ + I + Br + 2e		
SnI ⁺	SnI ₂ + e → SnI ⁺ + I + 2e		10.3 ± 0.5
	SnIBr + e → SnI ⁺ + Br + 2e		10.9 ± 0.5
SnBr ⁺	SnIBr + e → SnBr ⁺ + I + 2e		10.2 ± 0.5
	SnBr ₂ + e → SnBr ⁺ + Br + 2e		10.9 ± 0.5
SnI ₂ ⁺	SnI ₂ + e → SnI ₂ ⁺ + 2e		9.6 ± 0.2
SnBr ₂ ⁺	SnBr ₂ + e → SnBr ₂ ⁺ + 2e		10.6 ± 0.2
SnIBr ⁺	SnIBr + e → SnIBr ⁺ + 2e		10.0 ± 0.2

+ I⁻ + e, AP ≥ 12.8 eV. The calculated values of the APs shown in Table 3 were made by the usual method using the dissociation energies and enthalpies of formation for SnI₂, SnBr₂, SnI and SnBr from Feber [9]; the ionization potential (IP) for Sn and the enthalpy of formation of I⁺ from Franklin et al. [5]; and the enthalpy of formation of Sn(g) and I(g) from Stull and Sinke [10].

The IE curves for SnBr⁺, SnI⁺ and Sn⁺, in Fig. 4, for the ions from SnI₂ + SnBr₂ clearly show that these ions are formed from more than one parent. As shown in Table 3, we estimate two values for the APs for these ions. There are three dihalides in the vapor in comparable concentrations, as shown by the relative intensities shown in Table 1. Therefore, the IE curve for Sn⁺ should be a composite of ionization from three parents, and there should be three breaks in the IE curve. We estimate only two APs for Sn⁺, and the lower value of 13.6 eV should be that from the ionization of SnI₂. The AP for Sn⁺ from the ionization of SnIBr should be between those for the ionization of SnI₂ and SnBr₂; the higher AP of 14.4 eV must be a composite for the ionization from SnIBr and SnBr₂. The IE curves for SnI⁺ and SnBr⁺ should be composites of ionization from two parents, and the APs for the reactions are so indicated in Table 3. As shown in the table, the relative error in the AP for the fragment ions is appreciably greater than those for the parents because of the curvature in the low electron energy region of the IE curves.

For any molecule, the fragmentation pattern by electron impact should be independent of temperature in the region of our measurements. This is clearly indicated by the parallel temperature dependence of ion intensities for each ion from a given parent. Because the vapor pressure of a given compound is proportional to the product of the ion current and absolute temperature, i.e., $P_{\text{rel}} \propto iT$ where i is the ion current, the relative equilibrium constant for the reaction



may be represented by

$$K_{\text{rel}} = \frac{i_{\text{SnIBr}^+}^2}{i_{\text{SnI}_2^+} i_{\text{SnBr}_2^+}} \quad (2)$$

The ion currents in eqn. (2) are those for the parent ions. Figure 5 shows the log iT against $1/T$ plot for the parent ions from the SnI₂ + SnBr₂ mixture. Also shown in this figure are the data for SnBr₂⁺ and SnI₂⁺ from pure SnBr₂ and SnI₂. The latter data were obtained under identical instrumental conditions as those for the halide mixture, so that the curves should represent a comparison of the relative vapor pressures for the three different materials. We used the equations in Table 2 for SnI₂⁺, SnBr₂⁺ and SnIBr⁺, and substituted the calculated ion intensity values at 476 and 540 K into eqn. (2). The K_{rel} obtained were 0.528 and 0.574, respectively, for the two tempera-

tures, and the enthalpy of formation of SnIBr(g) from the dihalides was 330 cal mol^{-1} at 508 K. Because $\Delta C_p \approx 0$ for reaction (2), the enthalpy of reaction (1) at 298 K should be nearly identical to that at 508 K. Using the ΔH_{f298}^0 for $\text{SnI}_2(\text{g})$ and $\text{SnBr}_2(\text{g})$ from Feber [9], i.e., -1.9 and $-31.9 \text{ kcal mol}^{-1}$, respectively, we obtain $\Delta H_{f298}^0 = -16.8 \pm 5 \text{ kcal mol}^{-1}$ for SnIBr(g) . The enthalpy of sublimation of SnBr_2 and SnI_2 are 31.7 and $32.5 \text{ kcal mol}^{-1}$, respectively [8], at 298 K; we estimate $\Delta H_{s298}^0 = 32 \text{ kcal mol}^{-1}$ for SnIBr , and $\Delta H_{f298}^0 = -49 \pm 5 \text{ kcal mol}^{-1}$ for SnIBr(c) .

DISCUSSION

The mass spectra of the vapors over the halide mixture show that SnIBr is readily formed by halide exchange between SnI_2 and SnBr_2 , and that the reaction takes place with a low enthalpy of reaction. All of the thermodynamic properties of SnIBr are intermediate between those for SnI_2 and SnBr_2 , as expected. However, as suggested by the data presented in Fig. 5, there appears to be a suppression of the vapor pressure over the mixture as compared to pure SnI_2 and SnBr_2 .

The appearance potentials for the ions formed by the electron impact ionization of SnI_2 reported here are in generally good agreement with earlier measurements made on a time-of-flight spectrometer [2]. However, the present measurements are more accurate than the earlier results. Our APs for the ions formed by electron impact of SnBr_2 are also in generally good agreement with those reported by Knowles et al. [4]; the only significant difference is our IP of $10.6 \pm 0.2 \text{ eV}$ for SnBr_2 as compared to $10.0 \pm 0.4 \text{ eV}$ reported by Knowles et al. The latter authors also report an IP of 10.2 eV for SnCl_2^+ , while that for SnF_2^+ is reported to be 11.5 eV [11]. Recent photoelectron spectra and CNDO calculations for SnCl_2 and SnBr_2 [12] support the earlier extended Hückel analyses of Hastie and Margrave [11], that the ionization potential of the tin dihalides arises from the ionization of an electron from the tin lone-pair orbital. The increase in the IP of the tin dihalides with decreasing atomic weight of the halogen suggests that the Lewis basicity of these halides also increases with increasing IP. In view of the measured and calculated IP for all of the tin dihalides, it appears that the IP for SnCl_2 should be higher than the 10.2 eV reported by Knowles et al.

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