J. Chem. Eng. Data 1995, 40, 963−967

UV−Vis Vapor Absorption Spectrum of Antimony(III) Chloride, Antimony(V) Chloride, and Antimony(III) Bromide. The Vapor Pressure of Antimony(III) Bromide

Norman W. Gregory

Department of Chemistry, University of Washington, Seattle, Washington 98195

Molar absorptivities of $SbCl_3(g)$, $SbCl_5(g)$, and $SbBr_3(g)$ are reported at 10 nm intervals in the wavelength range 200−400 nm. Absorbances of $SbBr_3 + Br_2$ vapor mixtures, with a Br_2 concentration of 6.16 $mM{\cdot}L^{-1}$, give no indication of contributions from $SbBr_5$. Absorbances of $SbCl_3 + Br_2$ vapor mixtures are discussed. Equilibrium vapor pressures of antimony(III) bromide are derived from absorbance data and are compared with the results of previous researchers: liquid phase, $\ln(P/\text{bar}) = 7617(\pm1.5\%)/(T/\text{K}) + 13.96(\pm2.1\%)$, range 370−417 K; solid phase, $\ln(P/\text{bar}) = 8290(\pm2.9\%)/(T/\text{K}) + 15.83(\pm4.3\%)$, range 330−370 K.

No previous report of the UV−vis vapor phase absorbance spectra of the antimony chlorides or of antimony bromide has been found in the literature. In the present work spectral data have been obtained and used to derive vapor pressures for antimony(III) bromide. Mixtures containing bromide have been examined for spectrophotometric evidence for the presence of antimony(V) halide molecules containing bromine. The "nonexistence" of $SbBr_5$ has been discussed by a number of researchers (e.g., see Holmes (1961), Adams and Downs (1972), Breidung and Thiel (1992)) and is of particular interest since $SbCl_5$ is well-known and SbI_5 has been reported (Gmelins Handbook, 1949; Lefkowitz *et al.*, 1969; CRC Handbook, 1955−56, 1990−91).

Equilibrium vapor pressure data for antimony(III) bromide have been published in the CRC Handbook for many years. More recently values determined with a quartz diaphragm gauge by Sime (1963) and values derived from differential thermal analysis and tensiometric data by Ustinov and Petrov (1970) agree closely with each other but are appreciably higher than those in the CRC Handbook (1955−56, 1990−91) and those derived from argon transport studies by Gray and Sime (1965). Bourdon gauge values reported by Maeda (1973) agree well with the CRC pressures and, at temperatures near the melting point, are intermediate between those of Sime, Ustinov and Petrov, and Gray and Sime. Thermodynamic data published by Barin *et al.* (1989) give calculated vapor pressures much higher than a compilation by Knacke *et al.* (1991). The latter gives values close to those reported by Maeda. In the present study vapor pressures for antimony(III) bromide have been derived from absorbance data.

Absorbances have also been measured for vapor mixtures formed by antimony(III) bromide + bromine, antimony(III) chloride + bromine, antimony(III) chloride + antimony, and antimony(III) chloride + chlorine.

Experimental Section

Absorbances between 200 and 700 nm were measured with a Cary 14H spectrophotometer. Samples were isolated in cylindrical quartz cells, 2 cm diameter, with path length 1, 2, 2.5, 5, or 10 cm. A side arm, to permit introduction of the samples, was attached at the center of each cell, perpendicular to the cell axis. The cell and side arm were heated by separate clam-shell-type furnaces, in close contact in a T arrangement. Temperatures of the cell and side arm tip were controlled separately, ±1 K, and were measured with chromel−alumel thermocouples, calibrated at the freezing and boiling points of water and the melting point of tin. When a condensed phase was present, condensation on the windows was prevented by keeping the temperature of the vapor in the cell body, T_g, somewhat higher than that of the condensed phase in the tip of the cell side arm, T_c.

$SbBr_3$ Samples. Five samples of antimony(III) bromide were prepared by reaction of antimony metal and bromine (Bakers Analyzed Reagent) in a Pyrex tube attached to a vacuum system and, by graded seal, to a quartz absorbance cell. Bromine vapor, generated from liquid bromine at 273 K, reacted slowly with the metal at room temperature, forming a white solid. Reaction occurred rapidly when the metal was flamed gently, forming a clear liquid. The product was vaporized and condensed away from the reaction zone. The reaction tube was cooled with liquid nitrogen to condense any unreacted bromine and then sealed off. A small amount of the product was sublimed in vacuum into an absorbance cell and the cell isolated by flame seal-off of the side arm. Four of the five samples were prepared using an antimony granule (Aldrich Chemical, 99.9999%, 10 mesh). One, SN 1b (SN, an abbreviation for sample number), was prepared from antimony powder for which analysis was not available. All five gave the same absorption spectrum. The excess $SbBr_3$ from the SN 1b preparation was observed to melt at 369.8 K (literature values: 369.8 K (CRC Handbook, 1955−56, 1990−91; Maeda, 1973; Knacke *et al.*, 1991); 368.0 K (Barin, 1989).

Above 392 K, absorbances of SN 1b were measured over the full wavelength range with the sample completely vaporized. At lower temperatures for 1b, and at all temperatures for SN 2b, 3b, and 4b, a condensed phase was present. Bromine was added to SN 3b before the cell was sealed off. After measurements on SN 3b the $SbBr_3$ was condensed in the cell body and the side arm tip immersed in liquid nitrogen; the condensed bromine in the tip was sealed off, after which the cell contents were identified as SN 4b.

After measurements on SN 2b a small amount of the $SbBr_3$ in the side arm tip was sublimed into the cell body; the remainder in the tip was cooled with liquid nitrogen and sealed off, and the cell contents were then identified as SN 5b. Above 399 K, absorbances of 5b were measured with the sample completely vaporized.

0021-9568/95/1740-0963$09.00/0 © 1995 American Chemical Society

Table 1. Vapor Phase Molar Absorptivity Constants

	390–530 K	358–485 K	300–350 K
λ/nm	$\epsilon_{\lambda,T}(SbBr_3)/(L{\cdot}mol^{-1}{\cdot}cm^{-1})$	$\epsilon_{\lambda,T}(SbCl_3)/(L{\cdot}mol^{-1}cm^{-1})$	$\epsilon_{\lambda,T}(SbCl_5)/(L{\cdot}mol^{-1}cm^{-1})$
200	~ 10000	$18500 - 33.33(T/K)$	300
210	$6898 + 2.275(T/K)$	$15508 - 26.96(T/K)$	$1988 - 1.709(T/K)$
220	$6837 + 0.946(T/K)$	$14743 - 27.03(T/K)$	$5600 - 6.00(T/K)$
230	$8220 - 2.297(T/K)$	$7060 - 10.30(T/K)$	$7650 - 8.009(T/K)$
240	$6352 - 1.183(T/K)$	$1115 - 3.196(T/K) + 0.0077(T/K)^2$	$6500 - 6.00(T/K)$
250	$4900 - 0.760(T/K)$	$-130 + 1.755(T/K)$	$5520 - 4.40(T/K)$
260	$3725 - 0.599(T/K)$	$-1609 + 10.12(T/K) - 0.0121(T/K)^2$	$8100 - 11.0(T/K)$
270	$1872 + 0.944(T/K)$	$161 + 0.247(T/K)$	$7531 - 9.77(T/K)$
280	$688 + 1.796(T/K)$	$61.9 + 0.260(T/K)$	$5296 - 6.16(T/K)$
290	$471 + 1.303(T/K)$	$-83.4 + 0.337(T/K)$	$1700 + 1.00(T/K)$
300	$101 + 1.317(T/K)$	$-44.0 + 0.140(T/K)$	1170
310	$7.5 + 1.085(T/K)$	$-10.0 + 0.037(T/K)$	$1378 - 1.92(T/K)$
320	$-95.2 + 0.874(T/K)$	2.3	425
330	$-159 + 0.6659(T/K)$		275
340	75		150
350	40		$-44 + 0.45(T/K)$
360			$-57 + 0.44(T/K)$
370			60
380			60
390			50
400			$-88 + 0.33(T/K)$

Finally the contents of SN 1b and SN 5b were dissolved in 2% HNO_3 and amounts of antimony determined using an ICP atomic emission spectrometer, model 955, Plasmo Atomcorp. Intensities were compared against standards prepared by dissolving a known mass of antimony.

$SbCl_3$ Samples. SN 1c, 2c, and 3c. Two 1 cm quartz cells were attached to the Pyrex vacuum system, and approximately 0.015 g of granules of antimony (Aldrich, 99.9999%) was added to each cell. The system was evacuated. A small amount of chlorine, generated by heating a dehydrated sample of $CuCl_2{\cdot}2H_2O$ (Baker-Adamson Reagent, 99.0%) in an attached Pyrex tube, was condensed by cooling, in liquid nitrogen, in a U-tube. The U-tube provided a connection to the cell assembly. The Pyrex tube, which contained an excess of $CuCl_2$, was then sealed off. As the U-tube was allowed to warm, the chlorine reacted with the antimony at room temperature, forming a white solid. From visual estimate of the change in the size of the granules, about half of the antimony in each cell reacted with chlorine. The reaction appeared to form a mixture of $SbCl_3$ and $SbCl_5$. At room temperature the vapor pressure of $SbCl_5$ (Knacke *et al.*, 1991) is approximately 15 times larger than that of $SbCl_3$. $SbCl_5$ may largely be removed from the mixture by briefly evacuating the system. After evacuation at room temperature one of the cells, SN 1c, was sealed off, leaving the excess Sb in the cell with $SbCl_3$ to ensure that, after equilibration, the contribution of $SbCl_5$ to the absorbance would be negligible (Knacke *et al.*, 1991).

SN 2c. $SbCl_3 + Br_2$. After removal of SN 1c, the evacuated system was isolated by closing a stopcock and detached from the vacuum line at a connecting ball joint. The assembly was turned over so the remaining antimony granule rolled out of the cell into a Pyrex finger. The assembly was reconnected to the vacuum line and the finger with the excess antimony sealed off. On the vacuum side of the stopcock a tube containing bromine was attached and evacuated and a sample of bromine sublimed into the liquid nitrogen cooled U-tube. The bromine was then allowed to warm. When the bromine vapor color indicated a suitable amount in the cell, the cell was sealed off to give SN 2c.

After absorbance measurements on SN 2c, the contents were sublimed into the body of the cell and cooled with ice. With the tip immersed in liquid nitrogen to condense the bromine, the side arm between the cell and tip was sealed off to give SN 3c. Subsequent absorbance measurements showed the presence of a small amount of Br_2 in 3c, probably vaporized from the tip during the seal-off.

SN 4c, 5c, 6c, and 7c. After reaction of Sb and Cl_2, an assembly with two cells was evacuated at room temperature to remove excess chlorine and the more volatile $SbCl_5$. Then part of the $SbCl_3$ was sublimed into each cell, and different amounts of bromine were added to give SN 4c and SN 6c.

After measurements on SN 4c the $SbCl_3$ was sublimed from the tip into the body of the cell. The bromine was condensed in the tip with liquid nitrogen. The tip was allowed to warm slowly until the color of the bromine vapor was about half the initial value. Then both cell body and tip were immersed in liquid nitrogen, and side arm was sealed off, and the cell contents were identified as SN 5c.

After measurements on SN 6c the contents were condensed with liquid N_2 in the cell body. The tip was then immersed in a separate liquid N_2 bath and the cell body allowed to warm slowly. When about four-fifths of the bromine, estimated from the change in color of the deposit on the cell window, had been transferred into the tip, the tip and cell were again immersed in liquid nitrogen baths and the connecting side arm was sealed off to give SN 7c.

$SbCl_5 + Cl_2$ Sample. The product of a reaction of Sb and Cl_2 at room temperature was condensed in an absorbance cell by immersing the cell in liquid nitrogen. The reaction tube, which contained some $SbCl_3$ and unreacted Sb, was then sealed off. An additional amount of chlorine was generated and condensed in the cell and the cell sealed off.

Results and Discussion

Antimony(III) Bromide. $SbBr_3(g)$ did not contribute measurably to the absorbance at wavelengths, λ, above 350 nm. Absorbances of the fully vaporized samples 1b and 5b were used to derive molar absorptivities for $SbBr_3(g)$, $\epsilon_{\lambda,T}(SbBr_3(g)) = A_{\lambda,T}/c(SbBr_3(g))$, at 10 nm intervals for the range 200–350 nm; see Table 1. $A_{\lambda,T}$ represents the absorbance divided by the cell path length. The concentrations of $SbBr_3(g)$, $c(SbBr_3(g))$, were calculated from the amounts of antimony found in the cells and the cell volumes. To allow for variation with temperature, values of $\epsilon_{\lambda,T}$, Table 1, are expressed in empirical equations with constants determined by least squares at each selected wavelength. The spectrum, Figure 1, shows a maximum

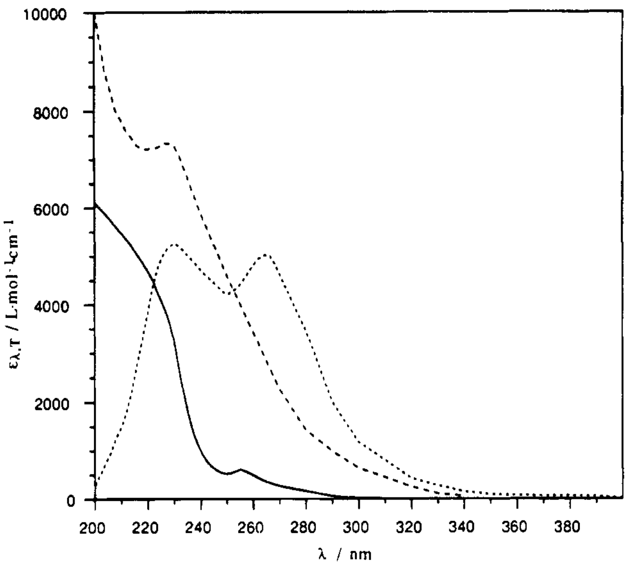

Figure 1. Molar absorptivities: - - -, $SbBr_3$(g) at 400 K; —, $SbCl_3$(g) at 372 K; · · ·, $SbCl_5$(g) at 298 K.

Table 2. Temperatures (*T*), Derived Concentrations (*c*), and Spectral Fit (SF) for $SbBr_3$

T_c/K	T_g/K	$c(SbBr_3(g))$/ (μM·L^{-1})	SF
	SN 1, 2.5 cm cell, $c(Br_2) = 0$		
334	351	4.14	0
361	369	26.8	0
390	397	90.1	2
347	349	8.95	0
381	386	75.7	1
387	392	90.1	1
372	385	46.7	0
356	367	20.5	0
350	360	14.4	0
333	353	4.41	1
466	413	90.1	0
466	469	90.1	0
520	530	90.1	0
	SN 2, 5 cm cell, $c(Br_2) = 0$		
352	374	14.6	0
360	363	25.5	1
373	386	49.6	0
383	392	86.1	0
369	375	40.2	0
360	374	23.8	0
345	356	9.41	0
382	544	63.8	0
	SN 3, 1 cm cell, $c(Br_2(g)) = 6.16$ mM·L^{-1}		
383	394	76.9	2
393	400	127	0
402	414	194	0
409	416	264	0
417	423	365	1
373	385	48.0	2
	SN 4, 1 cm cell, $c(Br_2) = 0$		
405	410	249	0
396	402	147	0
379	387	62.3	0
418	422	409	0
	SN 5, 5 cm cell, $c(Br_2) = 0$		
462	444	51.4	0
528	520	51.4	1
406	400	51.4	1
362	367	27.6	2

at approximately 230 nm and a shallow minimum at approximately 220 nm.

The molar absorptivity equations, extrapolated where necessary, were then used to predict values of $\varepsilon_{\lambda,T}(SbBr_3(g))$ at the temperatures at which vapors were in equilibrium with condensed phases. The concentration of the vapor for each scan was then selected to fit the observed absorbances. The concentration of bromine in SN 3b was calculated from absorbances in the range 380–500 nm, using molar absorptivities assigned by Passchier. The small contributions from bromine at wavelengths in the range 200–350 nm were subtracted from the total absorbances to derive the $SbBr_3$ absorbances. Derived concentrations, listed in the order in which scans were taken, are shown in Table 2. The spectral fit, abbreviated SF, represents the number of absolute values of DA, DA = $(A_{obsd} - A_{calcd})$(PL), greater than 0.016, taken as a reasonable uncertainty. PL is the cell path length. In the 200–350 nm range only 11 of the approximately 500 observations exceeded this uncertainty. Although the spectral fit suggests that the relative values of the molar absorptivities (Table 1) are reliable within a few percent, absolute values depend on the accuracy of the analysis, and must be given a larger uncertainty, estimated to be 5–10%.

Figure 2 shows the derived equilibrium vapor pressures, $P = c(SbBr_3(g))RT$, as a plot of ln P against $1000(K/T_c)$, along with the results of other researchers. Within experimental uncertainty, values for SN 3b, bromine present, cannot be distinguished from those of SN 4b, bromine removed, and are consistent with those of the other samples. Hence, with $c(Br_2(g)) = 6.16$ mM·L^{-1}, no evidence is seen from absorbances in the range 210–700 nm to suggest the presence of appreciable concentrations of $SbBr_5$.

Least-squares treatments of the absorbance vapor pressures give the equations (liquid) $\ln(P/\text{bar}) = -7617(\pm 1.5\%)/(T/\text{K}) + 13.96(\pm 2.1\%)$, range 370–417 K and (solid) $\ln(P/\text{bar}) = -8290(\pm 2.9\%)/(T/\text{K}) + 15.83(\pm 4.3\%)$, range 330–370 K. Standard deviations are shown in parentheses. In the overlapping temperature ranges the absorbance vapor pressures agree well with the results of Maeda (1973) and those given in the CRC Handbook (1955–56, 1990–91) and lie between the lines representing results given by Sime (1963), Ustinov and Petrov (1970), and Gray and Sime (1965). The latter appears to be the only previous experimental study of vapor pressures for the solid phase. The other solid-phase line in Figure 2 is based on an equation given by Knacke *et al.* (1991). The larger standard deviations for the absorbance sublimation data reflect the smaller absorbances and hence larger relative uncertainties. At lower temperatures the absorbance sublimation pressures are somewhat larger than those found by Gray and Sime and those projected from thermodynamic data given by Knacke *et al.*

Antimony Chlorides. $SbCl_3$(g). Using absorbances for SN 1c and concentrations of $SbCl_3$(g), $c(SbCl_3(g))$, calculated from equilibrium vapor pressures given by thermodynamic data tabulated by Knacke *et al.* (1991), molar absorptivities for $SbCl_3$(g), $\varepsilon_{\lambda,T}(SbCl_3(g)) = A_{\lambda,T}/c(SbCl_3(g))$, were assigned at 10 nm intervals in the wavelength range 200–320 nm. $A_{\lambda,T}$ represents the observed absorbance divided by the cell path length. No appreciable absorbance was detected in the range 330–700 nm. On the basis of work by Corbett *et al.* (1957), the solubility of antimony in $SbCl_3$ was assumed not to lower the vapor pressure of $SbCl_3$ appreciably.

$SbCl_5$(g). Molar absorptivities for $SbCl_5$(g), $\varepsilon_{\lambda,T}(SbCl_5(g))$, were assigned from absorbances observed for the mixture of $SbCl_5$ and chlorine; $\varepsilon_{\lambda,T}(SbCl_5(g)) = (A_{\lambda,T} - c(Cl_2(g))\varepsilon_{\lambda,T}(Cl_2(g)))/c(SbCl_5(g))$. The chlorine concentration, $c(Cl_2(g))$, was derived from absorbances around the chlorine maximum, 330 nm, where the $SbCl_5$ contribution is small. Literature values for the chlorine molar absorptivities, $\varepsilon_{\lambda,T}(Cl_2(g))$, derived by Rustad and Gregory (1991), using

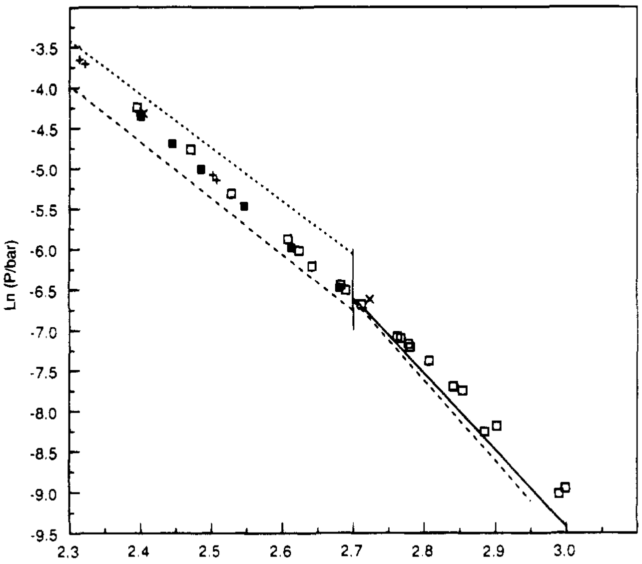

Figure 2. $SbBr_3$ equilibrium vapor pressures: □, absorbance data, SN 1b, 2b, 4b, and 5b; ■, absorbance data, SN 3b, with bromine present; +, Maeda (1973); ×, CRC Handbook (1955–56, 1990–91); - - -, Gray and Sime (1965); • • •, Sime (1963) (7), Ustinov and Petrov (1970); —, Knacke et al. (1991). The melting point is shown as a vertical line.

data of Seery and Britton (1964), Burns and Norrish (1963), and Gibson and Bayliss (1933), were used. Absorbances were measured with T_c in the range 270–315 K, with a condensed phase of $SbCl_5$ present. $c(SbCl_5(g))$ values were calculated from an equation based on equilibrium vapor pressures given in the CRC Handbook (1990–1991).

Values of $\epsilon(SbCl_5(g))$ and $\epsilon(SbCl_3(g))$, with temperature dependences expressed as empirical functions of T, are given in Table 1; spectra are shown, along with $SbBr_3$, in Figure 1. It was found that the absorptivities of these compounds at a given temperature could be reproduced by empirical selection of constants for a collection of Gaussians (three for $SbCl_5$; five each for $SbBr_3$ and $SbCl_3$) of the form used by Seery and Britton (1964) for diatomic molecules; however, the corresponding projected variations with temperature were not satisfactory.

Antimony(III) Chloride + Bromine Mixtures. With $\lambda > 400$ nm the absorbances of the antimony compounds are small. $c(Br_2(g))$ values in SN 2c–7c were initially approximated from bromine vapor molar absorptivities, $\epsilon_{\lambda,T}(Br_2(g))$, given by Passchier (1968) and absorbances around the bromine peak maximum, 410–420 nm. The quantities $Ax_{\lambda,T} = A_{\lambda,T} - c(SbCl_3(g))\epsilon_{\lambda,T}(SbCl_3(g)) - c(Br_2(g))\epsilon_{\lambda,T}(Br_2(g))$, with $c(SbCl_3(g))$ values corresponding to saturation vapor pressures of $SbCl_3$ in equilibrium with a pure $SbCl_3$ condensed phase, were found to be positive over the wavelength interval 200–400 nm. When compared at a selected temperature and wavelength, the ratios $Ax_{\lambda,T}/c(Br_2(g))c(SbCl_3(g))$ were different for the various samples, contrary to the expectation if the extra absorbance corresponds only to that of $SbCl_3Br_2$, as may be generated by reaction 1.

$$SbCl_3(g) + Br_2(g) \rightleftharpoons SbCl_3Br_2(g) \qquad (1)$$

In an initial trial it was found possible to predict the observed absorbances by assuming the vapors to be mixtures of $SbCl_3(g)$, $SbCl_5(g)$, and $Br_2(g)$. Required values of $c(SbCl_3(g))$ were at or near saturation values for equilibrium with a pure $SbCl_3$ condensed phase. Values of $c(SbCl_5(g))$ and $c(Br_2(g))$ were selected to match the observed absorbances. Thermodynamic properties (Knacke *et al.*, 1991) indicate that $SbCl_5$ produced by reaction of $SbCl_3$ and bromine is sufficient to account for that needed in SN 4c and 5c. However, in SN 2c and 3c, $c(SbCl_5(g))$ values were so large as to suggest that $SbCl_5$ was not completely separated from $SbCl_3$ when these samples were prepared. The following thermodynamic argument indicates that the mixed halide $SbBrCl_2$ should also be considered.

If $c(SbCl_3(g))$ and $c(SbCl_5(g))$ are assumed given by the absorbance data, thermodynamic constants (Knacke *et al.*, 1991) for reaction 2 may be used to calculate the chlorine

$$SbCl_3(g) + Cl_2(g) \rightleftharpoons SbCl_5(g) \qquad (2)$$

concentration, $c(Cl_2,g)$. The concentration of $SbBr_3(g)$, $c(SbBr_3(g))$, may then be derived from equilibrium constants (Knacke *et al.*, 1991) for reaction 3 and values of

$$SbCl_3(g) + 1.5Br_2(g) \rightleftharpoons SbBr_3(g) + 1.5Cl_2(g) \qquad (3)$$

$c(SbCl_3(g))$, $c(Br_2(g))$ and $c(Cl_2(g))$. For SN 2c–7c derived values of $c(Cl_2(g))$ and $c(SbBr_3(g))$ are too small for $Cl_2(g)$ and $SbBr_3(g)$ to make measurable contributions to the absorbance. However, values of $c(SbCl_3(g))$ and $c(SbBr_3(g))$ and an equilibrium constant of 3, estimated from statistical considerations, for reaction 4, give projected concentrations

$$(2/3)SbCl_3(g) + (1/3)SbBr_3(g) \rightleftharpoons SbBrCl_2(g) \qquad (4)$$

of $SbBrCl_2$, $c(SbBrCl_2(g))$, large enough in most of the samples to anticipate a significant contribution to the absorbance. Molar absorptivities of $SbBrCl_2(g)$ have not been found in the literature; estimated values, $\epsilon_{\lambda,T}(SbBrCl_2(g)) = (1/3)\epsilon_{\lambda,T}(SbBr_3(g)) + (2/3)\epsilon_{\lambda,T}(SbCl_3(g))$, were used. A similar treatment for $SbBr_2Cl$ gives very small absorbances, generally less than the uncertainty of the measurements.

Concentrations of $BrCl(g)$, $c(BrCl(g))$, calculated from $c(Cl_2(g))$ and $c(Br_2(g))$ and equilibrium constants (Chase *et al.*, 1986) for reaction 5, K_5, are large enough in two of the

$$0.5Cl_2(g) + 0.5Br_2(g) \rightleftharpoons BrCl(g) \qquad (5)$$

samples, 2c and 3c, to give measurable contributions to the absorbance. Molar absorptivities for $BrCl(g)$ have been published by Seery and Britton (1964).

The concentrations used in the initial trial fit were adjusted to include contributions expected from $SbBrCl_2$ and $BrCl$. $c(SbCl_3(g))$ values were reduced by amounts varying from 0% to 30%, as needed to explain the absorbances. Such a reduction is consistent with an anticipated lowering of the $SbCl_3$ vapor pressure if condensed phase solutions with $SbCl_2Br$ and $SbCl_5$ are formed. Absorbances observed for both SN 2c and SN 3c indicated relatively large amounts of both $SbCl_3$ and $SbCl_5$ in both vapor and condensed phases. Both $c(SbCl_3(g))$ and $c(SbCl_5(g))$ had to be increased markedly as T_c values were increased. For these samples $\ln P(SbCl_5)$ against K/T_c gave a linear plot, as expected for a solution of $SbCl_5$ in $SbCl_3$.

The bromine absorbance for SN 2c, 4c, and 5c also indicated dissolution of bromine from condensed phases as temperatures were increased. A similar effect was not observed in SN 3c, in which $c(Br_2(g))$ is only approximately 1/10 the value in SN 2. For SN 3c, and at the higher temperatures for SN 4c–7c, K_5 and the equation $c(Br_2(g))_o = c(Br_2(g)) + 0.5c(BrCl(g))$, with $c(Br_2(g))_o$ a different fixed constant (total amount of bromine) for each sample, were used to calculate values of $c(Br_2(g))$ and $c(BrCl(g))$. The concentrations of other bromine-containing compounds in the vapor phase are small compared to $c(Br_2(g))$.

Table 3. Vapor Concentrations, Derived at Three Selected Temperatures, Low, Intermediate, and High, for $SbCl_3$ + Br_2 Mixtures[a]

SN	*PL* cm	*Tg* K	*Tc* K	*c(Br₂)* mM·L⁻¹	*c(BrCl)* mM·L⁻¹	*c(SbCl₃)* μM·L⁻¹	*c(SbBrCl₂)* μM·L⁻¹	*c(SbCl₅)* μM·L⁻¹	SF
2c(15,4)	1	353	346	6.00	0.070	139	5.53	11.7	0
		389	385	6.97	0.184	819	32.6	32.6	0
		448	439	7.13	0.553	5104	201	65.7	0
3c(8,5)	1	367	356	0.756	0.018	259	7.05	4.13	3
		423	418	0.732	0.066	2845	64.5	17.7	0
		482	469	0.673	0.183	11720	214	39.0	0
4c(7,4)	1	348	321	7.36	0.0083	23.2	8.36	0.035	0
		391	378	7.90	0.063	482	66.5	1.73	0
		408	404	7.90	0.122	1378	136	6.73	3
5c(6,6)	1	346	324	4.41	0.0069	27.9	7.00	0.053	0
		387	379	4.56	0.048	549	52.8	2.56	0
		413	406	4.56	0.104	1644	120	7.58	1
6c(8,16)	10	303	299	1.09	0.0064	2.26	0.042	0.826	1
		345	320	1.09	0.0084	17.3	0.856	0.216	2
		376	367	1.09	0.015	126	7.59	0.464	2
7c(9,4)	10	304	294	0.172	0.0023	2.16	0.018	0.631	0
		359	344	0.172	0.0043	116	2.46	0.845	1
		392	378	0.172	0.0069	140	3.89	0.266	1

[a] The actual number of scans and total SF number are indicated in parentheses after each sample number.

To calculate concentrations of $SbCl_5$ expected from reaction of bromine and $SbCl_3$, for SN 4c and SN 5c, reactions 2–5 were combined to give the dependent equilibrium relationships 6–8. The equilibrium constants, K,

$$2SbCl_3(g) + Br_2(g) \rightleftharpoons 2SbBrCl_2(g) + Cl_2(g) \qquad (6)$$

$$3SbCl_3(g) + Br_2(g) \rightleftharpoons 2SbBrCl_2(g) + SbCl_5(g) \qquad (7)$$

$$SbCl_3(g) + Br_2(g) \rightleftharpoons SbBrCl_2(g) + BrCl(g) \qquad (8)$$

for the various reactions, with the reaction numbers shown as subscripts, are related in the following way: $K_6 = K_4{}^2K_3{}^{2/3}$; $K_7 = K_2K_6$; $K_8 = K_3{}^{1/3}K_4K_5$. If these reactions determine the relative concentrations, the relationship $c(SbBrCl_2(g)) = 2c(Cl_2(g)) + 2c(SbCl_5(g)) + c(BrCl(g))$ is projected. This equation, together with K_2, K_5, and K_6 and values of $c(SbCl_3(g))$ and $c(Br_2(g))$, fixed by the absorbance data, was used to calculate the separate concentrations. For SN 6c and 7c, it was necessary to assume that small amounts of $SbCl_5$, $c(SbCl_5(g))_0$, taken as a different constant for each sample, were in the initial Br_2 + $SbCl_3$ mixtures. In such a case $c(SbBrCl_2(g)) = 2c(Cl_2(g)) + 2(c(SbCl_5(g)) - c(SbCl_5(g))_0) + c(BrCl(g))$.

Effects suggesting dissolution of $SbCl_5$ from the condensed phases were not seen with SN 4c–7c. Amounts of antimony in these samples were small; SN 6c and 7c were completely vaporized for the scans at the two highest temperatures in each case. Some derived concentrations, taken as representative, are given in Table 3.

While the fit between observed and calculated absorbances is very good, less than 3% of the approximately 1500 observations have absolute DA values > 0.016, the complexity of the system and the required estimations indicate clearly that the composition of these mixtures cannot be derived with certainty from the absorbance data. The initial trial fit neglecting $SbBrCl_2$ was somewhat better (SF = 30) than the one using the revised concentrations (SF = 39). Antimony(V) bromide chlorides with one or two bromine atoms may be sufficiently stable to make a significant contribution. If so, however, their molar absorptivities do not differ sufficiently from those of $SbCl_5$ for the absorbance data to give evidence of their presence.

Suvorov and Martynov (1968) have examined a solution of Br_2 (0.02 M·L^{-1}) and $SbCl_3$ (0.02 M·L^{-1}) in chloroform at 296 K. They observe a maximum in the absorbance spectrum at 340 nm. Considering the reactions discussed above, it seems unlikely that a single species is responsible.

Literature Cited

Adams, C. J.; Downs, A. J. *J. Inorg. Nucl. Chem.* **1972**, *34*, 1829–1840.

Barin, I., Ed. *Thermochemical Data for Pure Substances*; VCH Verlagsgesellschaft mbH: Weinheim, Germany, 1989; Vol. 2, p 1292.

Breidung, J.; Thiel, W. *J. Comput. Chem.* **1992**, *13* (2), 165–176.

Burns, G.; Norrish, R. G. W. *Proc. R. Soc. London, A* **1963**, *271*, 289–295.

Chase, M. W., Jr.; Davies, C. A.; Downey, J. R.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *JANAF Thermochemical Tables*, 3rd ed.; American Chemical Society and American Institute of Physics: Washington, DC, and New York, 1986.

Corbett, J. D.; Winbush, S. V.; Albers, F. C. *J. Am. Chem. Soc.* **1957**, *79*, 3020–3024.

CRC Handbook of Chemistry and Physics; Chemical Rubber Publishing Co.: Cleveland, OH; 37th ed., 1955–56, p 2151; 71st ed, 1990–91, p 6–50.

Gibson, G. E.; Bayliss, N. S. *Phys. Rev.* **1933**, *44*, 188–192.

Gmelins Handbook of Inorganic Chemistry, Syst. 18; 1949; p 496.

Gray, G. A.; Sime, R. J. *J. Chem. Eng. Data* **1965**, *10* (2), 176–177.

Holmes, R. R. *J. Inorg. Nucl. Chem.* **1961**, *19*, 363–366.

Knacke, O.; Kubaschewski, O.; Hesselmann, K. *Thermochemical Properties of Inorganic Substances*, 2nd ed.; Springer-Verlag: New York, 1991; p 1759.

Lefkowitz, I.; Brodman, B.; Shields, M. A. *J. Cryst. Growth* **1969**, *6*, 13–18.

Maeda, K., *Sci. Pap. Inst. Phys. Chem. Res. (Jpn.)* **1973**, *67* (3), 143–147.

Passchier, A. A. Ph.D. Thesis, University of Washington, Seattle, WA, 1968.

Passchier, A. A.; Christian, J. D.; Gregory, N. W. *J. Phys. Chem.* **1967**, *71*, 937–942.

Rustad, D. S.; Gregory, N. W. *Polyhedron* **1991**, *10*, 633–643.

Seery, D. J.; Britton, D. *J. Phys. Chem.* **1964**, *68*, 2263–2266.

Sime, R. J. *J. Phys. Chem.* **1963**, *67*, 501–503.

Suvorov, B. A.; Martynov, Yu. M. *Zh. Neorg. Khim.* **1968**, *13* (12), 3192–3193.

Ustinov, A. I.; Petrov, E. S. *Isv. Sib. Otd. Akad. Nauk, SSSR, Ser. Khim. Nauk.* **1970**, No. 2, 36–43.

Received for review January 27, 1995. Accepted April 4, 1995.®

JE950030V

® Abstract published in *Advance ACS Abstracts*, June 1, 1995.