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Note

The fusion temperature of tin(II) bromide

R. A. DEANS, R. A. GEANANGEL AND W. W. WENDLANDT
Department of Chemistry, University of Houston, Houston, Texas 77004 (U.S.A.)
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During an investigation of amine adducts of tin(II) halides, we attempted to verify the purity of tin(II) bromide by its melting temperature and its X-ray powder diffraction pattern. It came to our attention in this regard that there are significant differences among the melting points cited for $SnBr_2$ and that the powder pattern listed in the ASTM powder diffraction file for that compound may be inaccurate. We wish to describe here our investigation of the melting temperature of tin(II) bromide.

EXPERIMENTAL

Preparation of $SnBr_2$

Tin(II) bromide was synthesized using an apparatus described elsewhere[1] in which hydrogen bromide gas is passed in a cyclical fashion over molten tin (280 °C) with the product subliming from the heated zone. The product was resublimed under a dynamic vacuum and the samples removed under a dry nitrogen atmosphere for characterization. Samples for melting point, DTA, and X-ray powder diffraction were sealed in glass capillary tubes of appropriate sizes.

Equipment

The melting temperature was measured on a Melt-Temp heated block apparatus. X-ray powder diffraction patterns were obtained by the Debye–Scherrer method employing a 114.6 mm diameter camera and a Norelco water-cooled X-ray generator with copper $K\alpha$ radiation (nickel filtered). The Mössbauer spectrum was obtained on an Austin Science Associates spectrometer. A laser interferometer was employed for velocity calibration. The source was $Ba^{119m}SnO_3$ and the isomer shift is expressed with respect to $BaSnO_3$. The absorber was maintained at 80 K and the source at about 300 K.

Sealed tube DTA apparatus

The sealed tube DTA apparatus has been previously described[2]. The temperature axis of the apparatus was calibrated by use of the fusion temperatures of naphthalene (80.2°C), benzoic acid (122.4°C), salicylic acid (159.1°C) and anthracene (216.2°C). The sample of $SnBr_2$ was sealed in a 1.8 mm glass capillary tube and placed in the sample heat transfer sleeve of the apparatus. A furnace heating rate of 11 °C min^{-1} was employed, at several different (T_s–T_r) axis sensitivities.

Discussion

A very early description[3] of the synthesis of tin(II) bromide noted a melting temperature of 232°C and this value was confirmed by other workers[4]. A number of other sources[5–7] quoted melting temperatures in the range 215.5 ± 0.5°C for $SnBr_2$. Presumably these secondary sources took the value from an earlier reference, which we have not been able to locate.

In order to prove the identity of our samples of tin(II) bromide, we undertook a full characterization of the substance, including especially its melting point. The synthesis of $SnBr_2$ was based on the method of Prasad et al.[8], employing a gas circulating system in which anhydrous HBr was continuously passed over molten tin at 280°C[1]. The product was sublimed under high vacuum before use and protected from exposure to oxygen and moisture at all times. Tin and bromine analyses were consistent with the formula $SnBr_2$[1]. The melting temperature observed in a sealed capillary tube was 228–229°C (decomposition). The DTA curves for several samples (Fig. 1) showed normal fusion behavior beginning at just below 230°C. The absence of T_s–T_r changes near 215°C makes it unlikely that a possible phase transition is responsible for the reported 215°C melting temperatures.

The *d* spacings from the X-ray powder diffraction pattern of our product did not resemble those reported in the ASTM Powder Diffraction File[9] for $SnBr_2$. A check of the original reference[10] cited in the ASTM File revealed that no melting point was reported for the $SnBr_2$ used to obtain the powder diffraction pattern. An X-ray crystallographic examination of tin(II) bromide[11] made it possible for us

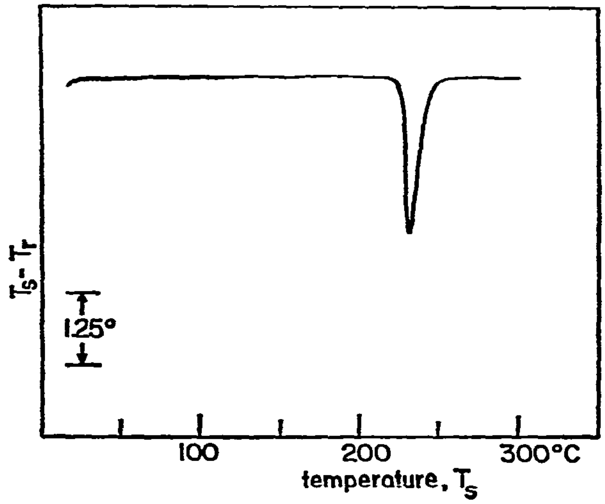

Fig. 1. DTA curve of $SnBr_2$ at a heating rate of 11 °C min^{-1} in a sealed tube.

to determine which powder pattern is correct. Using the reported group, *Pnma* or *Pna*2_1, and the cell dimensions, $a = 8.384$ Å, $b = 4.233$ Å, $c = 10.516$ Å, we calculated a set of interplanar spacings for allowed h, k, l combinations. Few, if any, coincidences between these values and those in the ASTM file were noted, but 20 of 22 of our d values fell within an average deviation of 0.05 Å from the calculated values. This finding appears to confirm the identity of our tin(II) bromide and its melting point of nearly 230°C.

Additional confirmation is provided by the ^{119}Sn Mössbauer spectrum of the tin(II) bromide. The isomer shift, 3.95 mm s^{-1}, compares well with the literature value[12] of 3.93 mm s^{-1}.

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