ROOM TEMPERATURE SYNTHESIS IN LIQUID AMMONIA OF TIN SULFIDE

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Abstract

Reaction of elemental tin with sulfur in liquid ammonia at room temperature affords an intimate mixture of X-ray amorphous metal sulfides (SnS, SnS_2) and a trace of tin metal. Thermolysis of this material at 300-350°C for 2 hrs. produced crystalline tin (II) sulfide (SnS - Herzenbergite). Products were characterised by elemental analysis, FT-IR and Raman spectroscopy, ^{119}Sn NMR, X-ray powder diffraction, Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Analysis (EDXA).

Introduction

Synthetic routes to binary tin sulfides have been the focus of ever increasing attention over the past decade due to their mounting array of commercial applications. These include their uses in mosaic golds, pigments and semiconductors[1]. Traditionally, tin sulfide has been prepared by precipitation of the metal cation from aqueous media by a source of the S^{2-} anion[2], action of H_2S directly on the metal oxide[3], or by direct combination of the composite elements at high temperatures for prolonged periods of time[4]. Other preparatory techniques include self-propagating high temperature synthesis between lithium sulfide and tin (IV) iodide to produce crystalline SnS_2[5], as well as pyrolysis of organotin precursors to produce microcrystalline SnS[6]. More involved preparations include direct organic-template-mediated combination of the elements to form novel tin sulfide structures[7]. Here we report a convenient one step, room temperature synthetic route to an intimate mixture of amorphous tin(II) and tin(IV) sulfides, and their facile conversion to pure SnS.

Results and Discussion

The reaction of elemental tin with sulfur in liquid ammonia at room temperature (*ca* 6 Atm. pressure), using 1:2 molar ratios yielded a precipitate whose colour was characteristic of the binary metal sulfide commonly known as "mosaic gold" (SnS_2). The material had the expected strong infrared absorption band at 450-300 cm^{-1} corresponding to an M-S stretch. Elemental analysis showed the product to contain trace amounts of carbon and hydrogen (< 0.5%), as well as small amounts of nitrogen (*ca* 1.5%). Weak absorptions in the infrared corresponding to N-H vibrations (3200 cm^{-1} and 1450 cm^{-1}) were also observed. However, use of the Raman microscope showed the product to be a composite of three distinct phases, whose colours and relative abundance suggested the presence of *ca* 60% SnS (black), *ca* 35% SnS_2 (gold), and *ca* 5% unreacted tin (silver). The Raman signatures of each of the coloured materials supported this theory, with only the black and gold phases showing strong absorption bands at 450-300 cm^{-1} (characteristic of binary metal sulfides). X-ray powder diffraction patterns of the unthermolysed material showed the product to be a mixture of amorphous material and tin metal. Scanning electron microscopy (SEM) studies showed three phases of particles with typical dimensions of 3-8 microns, with the sulfides showing an aggregated structure. Compositional analysis of the bulk material using electron probe analysis confirmed the presence of tin (II) sulfide. The ^{119}Sn NMR spectra confirmed the presence of two separate tin nuclear environments with chemical shift values of 6871 ppm and 7220 ppm, corresponding to tin (II) and tin (IV).

This information taken together suggests that a mixture of amorphous tin sulfides are formed directly from the reaction of the metal and sulfur in liquid ammonia (Eqn.1):

$$Sn_{(s)} + S_{(s)} \xrightarrow{NH_{3\,(l)}\ /\ 25^{o}C} SnS_{(s)} + SnS_{2\,(s)} \qquad (1)$$

Heating of the X-ray amorphous metal sulfides at 300-350^{o}C *in vacuo* induces crystallinity, with the degree of crystallinity a function of temperature and thermolysis time. During the heat treatment, the whole product turned black with the sublimation of some elemental sulfur. The X-ray powder diffraction showed a single phase material which was identified as the Herzenbergite form of tin (II) sulfide (figure 1). This sample was further analysed by Raman microscopy and SEM/EDAX which were also consistant with the formation of a single phase of material SnS. It should be noted that heating intimate mixtures of Sn, SnS and SnS_2 produces SnS.

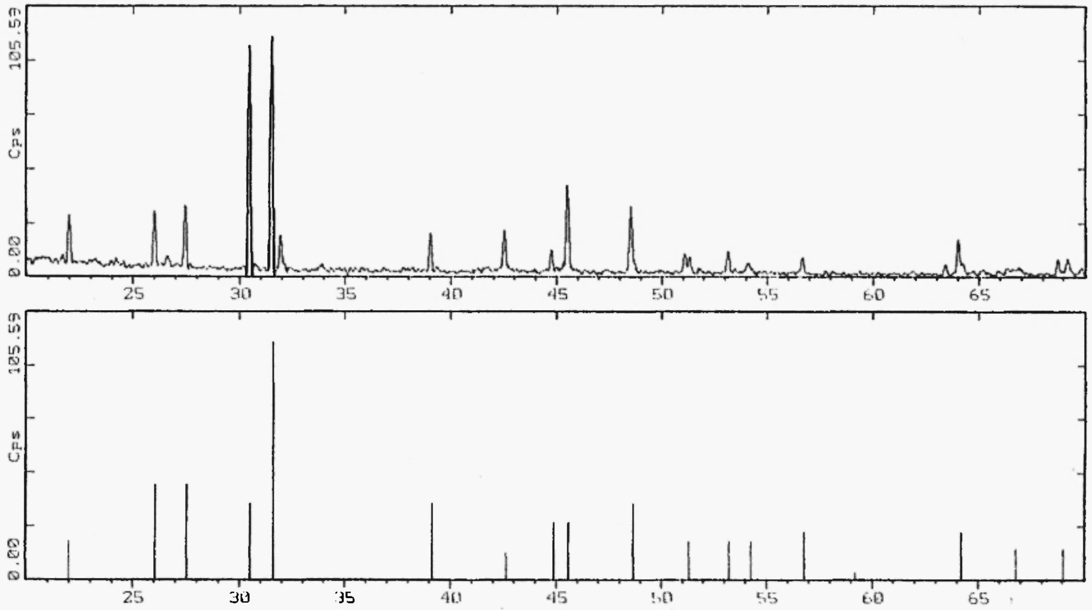

Fig. 1. X-ray powder diffraction pattern for thermolysed product (upper trace). Lower trace, obtained from data base[8], shows expected peak positions for orthorhombic Herzenbergite.

The lattice parameters derived from the powder pattern[9] closely correlate with literature values[10] for Herzenbergite. The values obtained were **a** = 3.98 (lit. 3.99), **b** = 4.33 (lit. 4.34), **c** = 11.20 (lit. 11.20), and the crystal system was defined as orthorhombic.

Sulfur is known to dissolve in liquid ammonia within a few hours to form highly coloured solutions (blue, green, or red) containing a variety of neutral and anionic chain and cyclic sulfur-nitrogen species.[11-13] Group IVb metals are insoluble in liquid ammonia, and so do not form solvated electrons / metal cations typical of the dissolution of elements from Groups Ia and IIa. In the reaction studied here, the ease of combination of the elements is facilitated by the excellent contact between dissolved sulfur and the metal. It is also probable that the ammonia also acts as a surface cleaning reagent that scrubs and removes the surface oxide layer from the metal that would otherwise prevent reaction.

The role of the liquid ammonia in the mechanism is crucial, since the reaction does not seem to occur when the solvent was varied (water, carbon disulfide, toluene, acetone, benzene, methanol and THF were each tried in turn). Also, the reaction observed is time dependent - i.e. no reaction occurs until the sulfur has dissolved into the liquid ammonia, and then 36 hours was required for appreciable amounts of product to precipitate. Since sulfur / ammonia solutions can take up to 1000 hours to fully establish the equilibria[13] one can reason that some of the sulfur species first generated play an important mechanistic role. The product also showed trace amounts of nitrogen and hydrogen content, but this was consistent with the presence of residual ammonia. This was not found to be the case in past work involving the reactions between sulfur and the group IIb metals[14] which reacted stoichiometrically (1:1) to form, in the case of zinc, cubic ZnS with small quantities of zinc amide. Interestingly, it has been shown that the reaction between zinc / copper and sulfur at the refluxing temperatures of strongly coordinating solvents such as pyridine and N-methylimidazole, form M-S_6-*solv* $_2$ complexes which can be decomposed at 500^{0}C to form, in the case of zinc, cubic ZnS[15].

The presence of tin exclusively in the +II oxidation state *after* thermolysis, suggests that the conditions during the heat treatment enabled the tin metal present to comproportionate with SnS_2 to form SnS[10]. Furthermore, the excess SnS_2 is thermally decomposed to sulfur and SnS. Given that the relative proportions of the oxidation states of tin in the pre-thermolysed mixture were Sn (II) > Sn (IV) > Sn (0), one can therefore rationalise the complete conversion of tin (IV) to tin (II) sulfide during thermolysis, with the removal of all tin metal and the formation of free (sublimed) sulfur. This mechanism can be jusified given the increase in thermal stability obtained by the conversion of SnS_2 to SnS. Studies into the formation of other binary metal sulfides by this process are in progress.

Conclusions

Sulfur-ammonia solutions offer a convenient route to the formation of tin sulfide, with the metal occuring in both the +II and +IV oxidation states. The reaction occurs at room temperature by direct combination of the elements, using a medium in which only one of the elements is soluble. The metal chalcogenides produced are X-ray amorphous and of high purity, with the only impurity detected being small, but appreciable, amounts of tin metal. Upon thermolysis (300-350^{0}C for 2 hrs) the reaction product is converted exclusively to tin (II) sulfide (Herzenbergite) with the sublimation or elemental sulfur.

Experimental

All reagents were of 99.9% purity or greater and purchased from Aldrich Chemical Company. The tin metal used was used as *ca* 325 mesh powder. Reagents were used without further purification. The ammonia was purchased from BOC and used without further drying. Manipulations and weighing were carried out in a dinitrogen-filled glove box. The reaction was carried out in a sealed thick-walled (3-4 mm) Teflon-in-glass Youngs-type Sclenk tube surrounded by safety netting. The tube was stored at 400^{0}C for at least six hours prior to use, in order to ensure the removal of water vapour. Raman spectroscopy was carried out using a Dilor XY spectrometer, with the 514.2 nm line of an argon laser (50 mW) being used as the excitation source; the slit width being 300 μm. Infra-red spectra were obtained on a Nicolet 250 spectrometer using pressed KBr discs. X-ray powder diffraction patterns were obtained on a Siemens D5000 transmission powder diffractometer using germanium monochromated Cu$K_{\alpha 1}$ radiation (λ=1.504 Å). ^{119}Sn NMR spectra were obtained within the expected chemical shift range for binary tin sulfides at room temperature for two different spin rates (10 kHz and 13 kHz), using a Bruker 300 MHz spectrometer. The sample was referenced against $C(SnMe_3)_4$, whose chemical shift was taken to be 48.2 ppm. SEM / EDXA analysis was carried out on a Joel

JXA-8600 Superprobe. A wavelength dispersive technique was utilised using a focused beam (charging energy 25 KV). Iron (II) sulfide and tin metal were used as standards (the tin crystals were picked with respects to the l-line of tin, and the SnS crystals with respects to the k-line of sulfur).

Reaction of Tin with Sulfur

A Teflon-in-glass, dual-seal, thick-walled Schlenk tube was cooled to -78^{0}C and*ca* 7 cm^3 of ammonia condensed directly into the tube under a steady stream of nitrogen. Powdered tin metal (850 mg, 8.27 mmol.) and sulfur (530 mg, 16.53 mmol.) was then added. The system was sealed, allowed to warm to room temperature, and stirred for 36 hours. During the course of the reaction, the solution changed from colourless to dark blue, to green, and finally to red with the progressive formation of a yellow precipitate. Within 1 hour of warming to room temperature, all the sulfur had dissolved into the solution. The tin metal could be seen in the reaction, but it had all been consumed within 30 hours. The precipitate was collected by cooling the solution back to -78^{0}C and evaporating the ammonia under a stream of nitrogen. The precipitate was dried *in vacuo* at room temperature for 10 min. and triturated with CS_2 (2 x 20 ml). The precipitate was collected and analysed, and half of the material thermolysed at 300-350^{0}C for 2 hours in order to induce crystallinity. The unthermolysed and thermolysed samples were analysed by microanalysis, X-ray powder diffraction, FT-IR, and Raman spectroscopy. The unthermolysed sample underwent analysis by solid-state NMR and SEM/EDAX (utilising an electron probe).

Acknowledgements

The University of London and Royal Society are thanked for equipment grants. Dr. D. Ciomartin is thanked for his help in acquiring Raman spectra, and A. Aliev for obtaining the solid state NMR spectra.

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Received: April 17, 1996 - Accepted: April 24, 1996 -
Received in revised camera-ready format: May 3, 1996