Thermochimica Acta, 126 (1988) 199–203
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THE PREPARATION OF BISMUTH(III) SULFIDE FROM AMMONIUM THIOCYANATE AND THIOUREA

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(Received 30 June 1987)

ABSTRACT

A novel method for the preparation at low temperatures of bismuth(III) sulfide from ammonium thiocyanate and its isomer, thiourea, is described. The sulfide was prepared at 110 ° C from thiourea and at 170 ° C from ammonium thiocyanate. The sulfide prepared was stable in nitrogen up to 440 ° C. At higher temperatures the sulfide decomposed in nitrogen to its elements.

INTRODUCTION

Bismuth(III) sulfide was reported to be prepared by a direct reaction of bismuth with sulfur at high pressures [1].

For catalytic uses it is important to obtain powders prepared at low temperatures.

A method for the preparation of nickel and cobalt sulfides has been recently published [2] in which monophasic sulfides were prepared by a direct reaction of the salts with ammonium thiocyanate. In addition, potassium thiocyanate was used to prepare tin(II) sulfide [3].

This paper reports a new synthetic method for the preparation of bismuth(III) sulfide at low temperatures, using as reactants ammonium thiocyanate and its isomeric compound thiourea.

EXPERIMENTAL

Bismuth(III) sulfide was prepared in the present study by three methods: (i) precipitation with hydrogen sulfide in acidic aqueous solutions; (ii) reaction with ammonium thiocyanate; (iii) reaction with thiourea. The

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0040-6031/88/$03.50

sulfides obtained by the three methods were checked for the presence of elemental sulfur by extraction with carbon disulfide.

The nitrogen used was Matheson pink grade. In all the reactions the nitrogen was passed over copper turnings heated at 400 ° C.

X-ray analysis and characterization

Powder diffraction patterns were obtained with a Philips PW-1050 using Cu K_α radiation. The scans were performed on the samples without further annealing except for the samples obtained by hydrogen sulfide precipitation.

Infrared (IR) runs

These were carried out in order to check for the presence of residual reactants or products obtained by their conversion. The IR runs were performed on 1 mg samples pressed in a disc of 200 mg KBr. The majority of measurements were performed on a Perkin–Elmer 597 IR spectrophotometer. A Brucker FTIR model IFS 113V was used in a few cases.

Precipitation with hydrogen sulfide

The sulfides were precipitated from 0.1 M acidic solutions of bismuth (III) subnitrate pentahydrate (Mallinckrodt, purity, 99.97%) prepared by dissolving the solid in 100 ml of 1 : 6 hydrochloric acid. Hydrogen sulfide (Matheson, minimum purity, 99.5%) was bubbled into the solution until complete precipitation. The samples were rinsed four times with 25 ml portions of triply-distilled water, air dried and subsequently dried at 110 ° C in a stream of nitrogen.

Ammonium thiocyanate

Mixtures of solid ammonium thiocyanate (Riedel de Haan AR) and bismuth(III) subnitrate (Baker AR) (5.74 g and 2.36 g, respectively) were ground in an agate mortar. For each reaction, portions weighing 1 g were used. The reactions were carried out at temperatures from 110 ° C to 300 ° C in a reactor (under nitrogen flow). The samples were reacted in unglazed aluminum or silica boats.

In each experiment the temperatures were slowly elevated to a predetermined value. The samples were held at this temperature for 5 h , and in some cases overnight. The termination of the reaction was determined when the down-stream flow did not show the presence of acidic, basic or sulfide traces. The sample was gradually cooled under nitrogen flow to room temperature. When the sulfide was prepared at temperatures higher than 170 ° C, the reaction time was decreased in some experiments to 2 h, although reactions were also performed for 5 h. Reactions were also carried out at temperatures higher than 300 ° C (up to 700 ° C), and the samples were held at this temperature for prolonged periods of time.

Thiourea

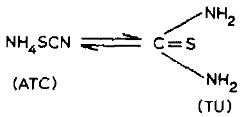
Mixtures of bismuth(III) subnitrate (2.36 g) and thiourea (5.74 g) (Riedel de Haan AR) were used. An identical procedure as described for the ammonium thiocyanate was used. Reactions were performed at temperatures from 110 to 300 ° C, at 10 ° C intervals. Reaction times were 5 h. At 110 ° C reactions were also performed for shorter times of 2, 1 and 0.5 h.

RESULTS AND DISCUSSIONS

Bismuth(III) sulfide was obtained in the present study from ammonium thiocyanate only at temperatures higher than 170 ° C. The sulfide was not obtained at lower temperatures even under prolonged heating of 24 h with ammonium thiocyanate, although the color of the solid mixture changed from white or yellow to orange. Products obtained from ammonium thiocyanate at temperatures higher than 170 ° C did not show residues of reactants in the IR region. The X-ray diffraction pattern was identical (Table 1) to the pattern obtained by the reaction of bismuth and sulfur [4] and also to the pattern obtained in the present work by hydrogen sulfide precipitation (Table 1).

The reaction of bismuth(III) subnitrate with thiourea gave pure bismuth(III) sulfide even at temperatures as low as 110 ° C and was completed within 15 min.

We propose that under our experimental conditions the reaction to form bismuth(III) sulfide proceeds via the sulfur atom of the thiourea. (The same applies in the reaction with ammonium thiocyanate.) Ammonium thiocyanate (ATC) isomerizes at 170 ° C to thiourea (TU) [5]



$$\underset{\text{(ATC)}}{NH_4SCN} \rightleftharpoons \underset{\text{(TU)}}{C(=S)(NH_2)_2} \qquad (1)$$

At temperatures lower than 170 ° C only ATC is present in the reaction and therefore no bismuth sulfide is obtained. However, at temperatures higher than 170 ° C, i.e. the isomerization temperature of ATC to TU, the reaction takes place with the TU which has been formed in situ. The formation of bismuth(III) sulfide reduces the amount of TU, and so reaction (1) shifts towards the formation of more TU. When TU is used as the reactant, bismuth(III) sulfide is formed at very low temperatures (110 ° C)

TABLE 1

X-ray diffraction results (bismuth(III) sulfide)—d values and relative intensities

Hydrogen sulfide precipitation		Ammonium thiocyanate		Thiourea		Literature values [4]	
d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0
3.569	100	3.569	100	3.569	100	3.565	100
3.118	80	3.118	80	3.118	80	3.118	80
3.530	80	3.530	80	3.530	80	3.530	60
2.821	50	2.821	50	2.821	50	2.821	50
3.967	40	3.967	35	3.967	30	3.967	40
2.521	30	2.521	25	2.521	25	2.521	40
1.953	40	1.953	40	1.953	40	1.953	40
1.738	30	1.738	25	1.738	25	1.738	35
2.258	25	2.258	20	2.258	25	2.258	30
1.945	30	1.945	35	1.945	30	1.945	30
1.884	10	1.884	10	1.884	10	1.884	25
5.654	20	5.654	20	5.654	20	5.654	20
5.040	20	5.040	20	5.040	20	5.040	20
2.305	20	2.305	20	2.305	10	2.305	20
3.748	20	3.748	20	3.748	20	3.748	18
2.641	20	2.641	20	2.641	15	2.641	18
1.990	20	1.990	25	1.990	20	1.990	18
1.919	20	1.919	20	1.919	15	1.919	18
1.480	15	1.480	15	1.480	15	1.480	18
3.253	15	3.253	20	3.253	15	3.253	16

and the reaction is completed in a very short time (15 min). In addition, the X-ray pattern showed a complete conversion of bismuth(III) sulfide (Table 1).

The X-ray patterns of the powders obtained by the three methods ((i), (ii) and (iii)) showed sharp reflections and a long-range order in the sulfide obtained. Even for the sulfide prepared from TU at low temperatures, the patterns were well defined.

The thermal stability of bismuth(III) sulfide

Bismuth(III) sulfide is stable in nitrogen or helium up to 440 °C. At higher temperatures it is decomposed and the X-ray diffractogram shows the presence of elemental bismuth.

Heating the bismuth(III) sulfide prepared by the above-mentioned methods at 700 °C for 5 h results in a complete decomposition. In all these experiments sulfur is deposited on the cool reactor wall.

The effect of oxygen

The reaction between ammonium thiocyanate and bismuth(III) subnitrate in air at 300 °C resulted in the production of bismuth(III) sulfide. However, the solid also contains species giving the diffraction pattern of bismuth(III) oxide.

ACKNOWLEDGMENTS

The authors extend their thanks to Prof. I.P. Mayer and Mr. S. Schneider from this department for help in X-ray runs. Thanks are extended to Prof. G.W. Keulks of the Chemistry Department, the University of Wisconsin, for helpful discussions. Mrs. M. Nechama is thanked for technical assistance.

This work was supported by the U.S.–Israel Binational Fund (contract 84-00185).

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