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Studies of Antimony Oxides Formed by Dehydration of Antimony Suspensions in Nitric Acid

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The white solid formed by the addition of elemental antimony to concentrated nitric acid contains 'antimony oxide nitrate hydroxide', $Sb_4O_4(OH)_2(NO_3)_2$*, and orthorhombic antimony(III) oxide. Calcination of this material in air is accompanied by complete dehydration and decomposition to the orthorhombic antimony(III) oxide which is subsequently oxidised to α-antimony tetroxide. The products formed between 25 and 735 °C are different from those obtained by the thermal dehydration of hydrated antimony(V) oxide over a similar range of temperatures.*

Introduction

During recent investigations of catalytically active antimony-containing mixed metal oxides we have examined several materials prepared by the calcination of precipitates or evaporated suspensions [1, 2]. These, and other methods described in the patent literature for the preparation of antimony-containing mixed oxide catalysts, have frequently involved the initial addition of antimony to nitric acid. However, despite the attention which has recently been given to the solid state properties of the dehydrated and calcined mixed metal oxides, the nature of the products formed by the addition of pure antimony to nitric acid are unclear. Indeed, such materials have in the early chemical literature been reported [3] as antimony tetroxide, antimony(III) oxide or an antimony oxide nitrate, $(SbO)NO_3$, whereas more recent texts have described them as hydrated antimony(V) oxide (antimonic acid) [4] or 'antimony oxides' [5]. Furthermore, the course of the thermal dehydration of the separated solid component of the suspensions appears to have received little attention and consequently the nature of the materials formed during such processes is uncertain.

We have therefore conducted some investigations of the products formed by the addition of antimony to nitric acid and, by using X-ray diffraction, have attempted to identify the phase compositions of the dehydrated and calcined materials.

Experimental

Powdered antimony metal (24.6 g) was added to stirred concentrated nitric acid (118 cm^3, 69–71% HNO_3) at 80 °C, boiled and cooled. The white solid was removed by filtration, washed with water, and separate samples heated in air according to the conditions described in Table I.

'Antimonic acid' was prepared [6] by hydrolysing antimony(V) chloride in a mixture of ice and 30% hydrogen peroxide. The white precipitate was boiled for several hours, removed by filtration, washed, and dried in air at room temperature for five days. The material was subsequently heated in air according to the conditions described in Table I.

X-ray diffraction data were recorded with a Philips vertical goniometer (PW 1050/70) using CuK_α radiation.

Results and Discussion

The white precipitate obtained from the hydrolysis of antimony(V) chloride gave, following treatment at 25, 135, 220, 360 and 735 °C, X-ray diffraction patterns which were very similar to those previously [6] obtained by the calcination of antimonic acid at identical temperatures. Furthermore, and also in agreement with the previous study [6], calcination at temperatures below *ca.* 650 °C failed to give characterisable materials. Indeed, the first material to be identified was the antimony oxide

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TABLE I. Phases Identified in Products Formed by the Suspension of Antimony in Nitric Acid.

Sample	Thermal Treatment	Phase Composition
A	25 °C, air, 5 days	orthorhombic Sb_2O_3 and $Sb_4O_4(OH)_2(NO_3)_2$
B	135 °C, air, 2 hours	orthorhombic Sb_2O_3
C	220 °C, air, 50 hours	orthorhombic Sb_2O_3
D	360 °C, air, 20 hours	orthorhombic Sb_2O_3 and α-Sb_2O_4
E	735 °C, air, 25 hours	α-Sb_2O_4

Sb_6O_{13} which was formed by calcination of the antimonic acid at 735 °C.

In contrast, the white solid removed from the suspension of antimony in nitric acid produced materials which, when calcined at identical temperatures to those used for the hydration of antimonic acid, gave markedly different and characterisable X-ray diffraction patterns (Table I). Hence the material dried at room temperature for five days gave a well defined diffraction pattern which was interpreted in terms of a crystalline mixture containing orthorhombic antimony(III) oxide and the antimony oxide nitrate hydroxide of formula $Sb_4O_4(OH)_2(NO_3)_2$. The identification of the antimony oxide nitrate hydroxide suggests that antimony nitrates such as $Sb(NO_3)_3$ [7] ane $Sb(NO_3)_5$ [8] are susceptible to hydrolysis in the nitric acid media. It is also pertinent to record that the use of excess nitric acid in the preparation resulted in the nearly exclusive formation of $Sb_4O_4(OH)_2(NO_3)_2$ whereas the addition of larger quantities of antimony gave rise to the presence of additional peaks in the X-ray diffraction pattern which were characteristic of unreacted elemental antimony. It seems therefore that elemental antimony is initially oxidised in concentrated nitric acid to antimony(III) in the form of orthorhombic antimony(III) oxide which reacts with concentrated nitric acid to give the antimony oxide nitrate hydroxide [9].

The absence of peaks characteristic of $Sb_4O_4(OH)_2(NO_3)_2$ in the X-ray diffraction pattern recorded from the white solid when calcined at 135 °C suggests that mild thermal treatment induces the decomposition of antimony oxide nitrate hydroxide into orthorhombic antimony(III) oxide. Although prolonged calcination at 220 °C in air failed to change the orthorhombic antimony(III) oxide, heating to 360 °C for one day produced a material which gave a less well resolved X-ray diffraction pattern characteristic of a mixture of orthorhombic antimony(III) oxide and α-antimony tetroxide. The appearance of antimony tetroxide was unexpected since the calcination temperature is significantly lower than that previously [10] observed for the oxidation of antimony(III) oxide. In this respect it is pertinent to record that calcination of the white solid at 650 °C in purified nitrogen produced a mixture of α-antimony tetroxide and Sb_6O_{13} and that no evidence was found in the X-ray diffraction pattern for the presence of antimony(III) oxide which, given the inert atmosphere, might reasonably have been expected. The results suggest that phenomena other than simple atmospheric oxidation may operate during the calcination of the initial white solid and that the oxidation of antimony(III) oxide to antimony tetroxide may involve the decomposition of the antimony oxide nitrate hydroxide. Such processes would appear to facilitate complete oxidation of the orthorhombic antimony(III) oxide to α-antimony tetroxide at 735 °C in air.

The results of our investigations of the white solid formed by addition of antimony to nitric acid gave no evidence for the formation of antimonic acid as has been suggested in the past [4]. Hence the product is distinctly different from that formed by hydrolysis of antimony(V) chloride. Furthermore, the nature of the materials which may be formed by calcination of these products appear to depend on the conditions of calcination and reflect chemical processes which occur during the decomposition of the initial hydrated material. The results also suggest that the antimony bearing reactants used in the preparation of antimony-containing mixed oxide catalysts are antimony(III) oxide or α-antimony tetroxide.

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