Reactions Between the Oxides of Antimony and Vanadium

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Received June 4, 1983

Vanadium(III) and Vanadium(V) oxides react with antimony tetroxide in an atmosphere of flowing dry oxygen-free nitrogen to give biphasic products composed of non-stoicheiometric vanadium antimonate, $VSb_{1-y}O_{4-2y}$ $(0 < y < 0.1)$ *and antimony tetroxide. Antimony(III) oxide reacts with vanadium(IV) oxide under similar conditions at 670 °C to give a material of formula* $VOSb_2O_4$. *Reactions between antimony tetroxide and vanadium(V) oxide in air, although incomplete, give rise to the formation of oxidised vanadium antimonate,* $V_{1-y}Sb_{1-y}O_4$ $(0 < y < 0.1)$. *A material of formula* $Sb_2V_2O_9$ *has not been identified. The results are discussed within the context of the mechanism of solid state reactions between antimony– and vanadium–oxides.*

Introduction

The nature of the compounds which may be formed in the vanadium–antimony–oxygen ternary system have been the subject of some uncertainty for several years [1–6]. We have recently reported on the conditions [7, 8] under which non-stoicheiometric vanadium antimonates of composition $VSb_{1-y}O_{4-3/2y}$, $VSb_{1-y}O_{4-2y}$ and $V_{1-y}Sb_{1-y}O_4$ $(0 < y < 0.1)$ may be formed from solid state reactions between antimony(III) oxide and vanadium(V) oxide. We have also investigated the structural properties of these rutile-type vanadium antimonates and the β-form of antimony tetroxide containing small concentrations of vanadium [9], and have examined the oxidation state of vanadium in these materials by e.s.r. [10].

Our studies of the preparation of the vanadium antimonate phases [7, 8] demonstrated a high sensitivity of the vanadium-antimony-oxygen system to the presence of oxygen and revealed that under some conditions the rutile-type phases are formed in the presence of antimony tetroxide. Given that vanadium(V) oxide is amenable to reduction [11] it is possible that the formation of these biphasic products from the reaction between antimony(III) oxide and vanadium(V) oxide is related to the liberation of oxygen from vanadium(V) oxide and subsequent oxidation of antimony(III) oxide to antimony tetroxide. We have therefore investigated the reactions between different oxides of antimony- and vanadium-to identify the nature of the products and elucidate the possible influence which reduction and oxidation phenomena may have on the course of the solid state reaction between antimony(III) oxide and vanadium(V) oxide. We have also conducted additional investigations of the compound $Sb_2V_2O_9$ which has been reported [3] to arise from the reaction between antimony tetroxide and vanadium(V) oxide.

Experimental

Equimolar quantities of high purity oxides of vanadium- and antimony- were thoroughly mixed, ground and heated in silica crucibles in either air or in flowing nitrogen (BOC oxygen-free grade) which had been dried at 77 K and by passage over phosphorus pentoxide. Residual oxygen was removed from the nitrogen gas flow by passage over manganese(II) oxide supported on Celite [12]. The reactant mixtures were heated at temperatures described in Table I.

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

Results and Discussion

The results are summarised in Table I.

The reactions of antimony tetroxide with either vanadium(III) oxide or vanadium(V) oxide in purified nitrogen at 750 °C gave biphasic products containing non-stoicheiometric vanadium antimonate,

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0020-1693/84/$3.00

TABLE I. Reactions Between Some Oxides of Antimony and Vanadium.

Antimony Oxide	Vanadium Oxide	Conditions	Product
Sb_2O_3	V_2O_3	$25\,^{\circ}\mathrm{C} \xrightarrow[\text{12h}]{\text{Nitrogen}} 600\,^{\circ}\mathrm{C}$ (12h)	No reaction
Sb_2O_3	V_2O_4	$25\,^{\circ}\mathrm{C} \xrightarrow[\text{15 min}]{\text{Nitrogen}} 670\,^{\circ}\mathrm{C}$ (24h)	$VOSb_2O_4$ + V_3O_5
α-Sb_2O_4 α-Sb_2O_4	V_2O_3 V_2O_5	$25\,^{\circ}\mathrm{C} \xrightarrow[\text{11h} \quad 540\,^{\circ}\mathrm{C}(14\mathrm{h}) \quad \text{6h}]{\text{Nitrogen}} 750\,^{\circ}\mathrm{C}$ (6h)	$VSb_{1-y}O_{4-2y}$ + α-Sb_2O_4
α-Sb_2O_4	V_2O_4	$25\,^{\circ}\mathrm{C} \xrightarrow[\text{12h} \quad 650\,^{\circ}\mathrm{C} \quad \text{14h}]{\text{Nitrogen}} 740\,^{\circ}\mathrm{C}$	No reaction
α-Sb_2O_4	V_2O_5	$25\,^{\circ}\mathrm{C} \xrightarrow[\text{4h}]{\text{Air}} 780\,^{\circ}\mathrm{C}$	$V_{1-y}Sb_{1-y}O_4$ (impure)

$VSb_{1-y}O_{4-2y}$ $(0 < y < 0.1)$ and antimony tetroxide. Hence, despite the rigorous exclusion of oxygen which might be expected [7, 8] to lead to the monophasic rutile-type antimony-deficient vanadium antimonate of composition $VSb_{1-y}O_{4-3/2y}$ $(0 < y < 0.1)$, the products resemble those obtained [7, 8] from the reaction between antimony(III) oxide and vanadium(V) oxide in commercial nitrogen which contains trace quantities of oxygen. The formation of these biphasic products from the reaction between antimony(III) oxide and vanadium(V) oxide in commercial nitrogen was tentatively associated [8] with the premature oxidation of Sb_2O_3 by the residual oxygen in the impure nitrogen gas flow to antimony tetroxide and the subsequent involvement of the Sb_2O_4 in the labilisation of oxygen from remaining vanadium(V) oxide. The observation reported here of the formation of a similar biphasic product from the reaction of antimony tetroxide with vanadium(V) oxide, possibly involving further loss of oxygen, is quite consistent with the proposed mechanism. In this respect it is also relevant that the reduced form of vanadium(V) oxide, vanadium(III) oxide, reacted with antimony tetroxide to give a similar biphasic product containing the non-stoicheiometric vanadium antimonate and antimony tetroxide.

The results therefore suggest that the critical feature in the formation [7, 8] of the monophasic vanadium antimonate, $VSb_{1-y}O_{4-3/2y}$ $(0 < y < 0.1)$, from the reaction between antimony(III) oxide and vanadium(V) oxide in a strictly oxygen-free atmosphere is vested in the prevention of the initial formation of antimony tetroxide. Furthermore, given that antimony tetroxide failed to produce an identifiable product by reaction with vanadium(IV) oxide under similar thermal conditions in purified nitrogen, it seems that in the reaction between antimony(III) oxide and vanadium(V) oxide any reduction of the vanadium(V) oxide by antimony tetroxide leads to the formation of vanadium(III) oxide. Similarly, and in view of the considerable sublimation, the lack of reactivity between antimony(III) oxide and vanadium(III) oxide suggests that initial reactant antimony(III) oxide is rapidly oxidised in the reaction mixture containing Sb_2O_3 and V_2O_5 to antimony tetroxide.

The proposed reduction in the reaction mixture containing antimony(III) oxide and vanadium(V) oxide of the V_2O_5 to vanadium(III) oxide is also supported by the reactivity observed here of antimony(III) oxide with vanadium(IV) oxide in pure nitrogen at 670 °C which gives rise to the formation of green $VOSb_2O_4$ [6] as opposed to a vanadium antimonate phase. The presence in this material of vanadium(IV) and antimony(III) [6, 10] reveals an absence of those reduction and oxidation phenomena which occur in reactions between the other oxides of vanadium and antimony and which lead to the formation of the vanadium antimonate phases. The presence of black V_3O_5 in the $VOSb_2O_4$ product appears to reflect an incomplete reaction which may be related to the sublimation of antimony(III) oxide which occurs during the course of the reaction. It is also relevant to record that the reaction between antimony(III) oxide and vanadium(IV) oxide at higher temperature (*ca.* 750 °C) resulted in substantial sublimation of antimony(III) oxide which condensed in mainly the cubic form to leave a black residue containing a mixture of V_4O_7 and V_3O_5. It seems likely that at such temperatures the $VOSb_2O_4$ phase undergoes decomposition.

It is interesting to note that the reaction of antimony tetroxide with vanadium(V) oxide in air at 750 °C gave oxidised vanadium antimonate, $V_{1-y}Sb_{1-y}O_4$ ($0 < y < 0.1$), which, although contaminated with unreacted starting material, showed evidence of increasing purity when the reaction was performed at the higher temperatures over longer periods of time.

Finally, we would report that our investigations have failed to confirm the preparation [3] of vanadium antimonate '$VSbO_4$' at 600 °C. We have also been unable to confirm the formation of the compound of composition $Sb_2V_2O_9$ which has been reported [3] to result from the solid state reaction between antimony tetroxide and vanadium(V) oxide or by oxidation of vanadium antimonate. The examination by X-ray diffraction of the products from reactions performed during this work or of our other recent [7–10] investigations of the vanadium–antimony–oxygen system have produced no evidence for the formation of a compound of composition $Sb_2V_2O_9$ [3]. Given the close similarities reported [3] for '$VSbO_4$' and '$Sb_2V_2O_9$' it seems possible that both materials consisted of different non-stoicheiometric rutile-type vanadium antimonate phases with different concentrations of antimony tetroxide.

Acknowledgement

We thank the S.E.R.C. for the award of a Studentship (to M.E.B.).

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