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Oxidation States in "$VSbO_4$"

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Antimony Mössbauer studies show that compositions approaching $VSbO_4$ contain Sb only in the pentavalent state. Thus, contrary to earlier proposals, the oxidation states are best represented as $V^{III}Sb^{V}O_4$. Actually, stoichiometric $VSbO_4$ could not be prepared. Phases close to this composition have rutile-related structures, and they can be represented by formulas such as $V_{1-x}Sb_{1-x}O_4(M_{1-x}O_2)$ or $V_{1+y}Sb_{1-y}O_4(MO_2)$.

Introduction

The synthesis of $VSbO_4$ was first reported by Vernon and Milligan.[1] These authors observed a tetragonal rutile-type structure and indicated oxidation states of Sb^{3+} and V^{5+}. Roth and Waring[2] confirmed the rutile-like structure of $VSbO_4$, and they also suggested the existence of a high-temperature polymorph of $VSbO_4$. Schüer and Klemm[3] studied the magnetic properties of $VSbO_4$ and concluded that the oxidation states could not be Sb^{3+} and V^{5+}. However, Schüer and Klemm could not decide between $V^{IV}Sb^{IV}O_4$ and $V^{III}Sb^{V}O_4$. These two possibilities can easily be distinguished by means of ^{121}Sb Mössbauer spectroscopy, and our investigation of this system is reported here.

Experimental Section

The reactants were high-purity Sb_2O_3 and V_2O_5. Gold reaction containers were used since reactions with both platinum and silica were detected. Some preparations were carried out in air; others were in gold tubes which had been evacuated and welded shut.

X-ray powder patterns were obtained at 25 °C with a Hägg–Guinier camera using Cu $K\alpha_1$ radiation and an internal standard of high-purity KCl ($a = 6.2931$ Å). Cell dimensions were refined by least squares.

Mössbauer spectra were recorded on apparatus previously described.[4] Absorbers were prepared by intimately mixing the finely powdered sample with Apiezon grease and placing it between thin aluminum sheets in a copper holder. The samples contained 6 mg of Sb/cm^2. The source $BaSnO_3$ (^{121}Sb) was kept at room temperature (298 K) while the sample temperature was varied.[4] About 150000 counts per folded channel were accumulated using the escape peak from a Xe–CO_2 proportional counter. Isomer shifts were measured with respect to InSb at 4 K. Spectra were computer fitted to both a single Lorentzian[5] and an eight-line quadrupole spectrum.[6]

Results

When $VSbO_4$ is prepared in air at 800 °C according to the original synthesis given by Vernon and Milligan,[1] some oxidation occurs. Our analytical data indicate $VSbO_{4.35}$ or, more correctly, $V_{0.92}Sb_{0.92}O_4$. Our tetragonal cell dimensions for this oxidized $VSbO_4$ are given in Table I. Microprobe examination of this product indicates that it is homogeneous.

Table I. Cell Dimensions

a, Å	b, Å	c, Å	Y, deg	V, Å^3	Footnote
4.58		3.06		64.2	*a*
4.598		3.078		65.1	*b*
4.605	4.595	3.065	90.25	64.9	*c*
4.6085	4.6085	3.0839	90.20	65.50	*d*
6.5289	6.5061	3.0839		65.50	*e*
4.6241		3.0369		64.94	*f*

[a] Reference 1; really $V_{1-x}Sb_{1-x}O_2$. [b] Reference 2; really $V_{1+y}Sb_{1-y}O_2$. [c] Reference 3; however, monoclinic cell is changed from second setting to first setting and 3.595 Å is corrected to 4.595 Å. [d] This work; monoclinic cell, $V_{1.05}Sb_{0.95}O_4$. [e] This work; C-centered orthorhombic cell (V/2). [f] This work; $V_{0.92}Sb_{0.92}O_4$.

Preparations in sealed gold tubes did not give single-phase products when the heating temperature was in the range 700–800 °C. The products consisted primarily of a tetragonal rutile-type phase, but there were small amounts of Sb_2O_4 present. This indicates that the formula of the rutile phase was actually $V_{1+y}Sb_{1-y}O_4$ where y is of the order of 0.1. When this sample was quenched from 900 °C, the product appeared to be single phase by x-ray diffraction. However, microprobe studies showed small domains of an antimony oxide. These domains are amorphous. Their composition is not accurately known, but this glassy state may be stabilized by small amounts of vanadium. In any event, the vanadium-to-antimony ratio in the predominate rutile-related phase must be greater than 1. Based on a semiquantitative microprobe analysis, this phase will be referred to as $V_{1.05}Sb_{0.95}O_4$.

Four-probe electrical resistivity data for the very dense quenched product containing $V_{1.05}Sb_{0.95}O_4$ and amorphous antimony oxide showed semiconducting behavior with a room-temperature resistivity of 10^5 ohm-cm and an activation energy of 0.3 eV. These data should be reasonably representative of $V_{1.05}Sb_{0.95}O_4$ since the amorphous inclusions were clearly isolated from one another according to the microprobe studies.

The structure of $V_{1.05}Sb_{0.95}O_4$ quenched from 900 °C is clearly not tetragonal. We find that a C-centered orthorhombic cell will give an excellent account of the diffraction pattern. The cell dimensions are given in Table I, and the indexed pattern is in Table II. In this orthorhombic cell the tetragonal a has been increased by the factor of $2^{1/2}$. A

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Table II. Diffraction Pattern of $V_{1.05}Sb_{0.95}O_4$

I	h	k	l	d_{obsd}	d_{calcd}
w	1	1	0	4.622	4.608
s	2	0	0	3.267	3.264
s	0	2	0	3.259	3.253
w	0	0	1	3.066	3.085
s+	1	1	1	2.566	2.564
m	2	2	0	2.305	2.304
m−	2	0	1	2.241	2.242
m−	0	2	1	2.238	2.238
w	1	3	0	2.058	2.058
	3	1	0		2.064
s	3	1	1	1.714	1.715
s	1	3	1	1.712	1.712
m−	4	0	0	1.633	1.632
m−	0	4	0	1.626	1.626
m	0	0	2	1.542	1.543
m−	4	4	2	1.459	1.459
m−	2	4	0	1.456	1.456
m	0	2	2	1.394	1.394
	2	0	2		1.395
m+	3	3	1	1.375	1.375
w	2	2	2	1.285	1.282

Table III. Mössbauer Parameters for "$VSbO_4$"

	Temp, K	Isomer shift, mm s^{-1}	Quadrupole splitting, mm s^{-1}	Line width	Intens, %
$V_{1.05}Sb_{0.95}O_4$	298	8.02	−3.98	2.96	8.9
		8.10[a]		3.20	
	77	8.20	−5.70	2.96	15.2
		8.26[a]		3.51	
	4	8.20[a]		8.5[b]	
$V_{0.92}Sb_{0.92}O_4$	77	8.04	−6.29	2.94	19.3
		8.0		3.52	

[a] Fitted to a single Lorentzian.[4] [b] This spectrum could not be satisfactorily fitted to either a single Lorentzian or the eight-line quadrupole pattern. The spectrum is broadened due to the presence of a small magnetic hyperfine field.

monoclinic cell with $a = b$ and $\gamma \neq 90°$ could as well be used. However, we find no justification for this lower symmetry cell.

The quenched product containing $V_{1.05}Sb_{0.95}O_4$ plus antimony oxide was heated in air at 20 °C/min in a tga apparatus. Weight gain became noticeable at about 270 °C and ceased at about 750 °C. The total weight gain corresponded to an oxidation to $VSbO_{4.35}$ or $V_{0.92}Sb_{0.92}O_4$. This is in excellent agreement with the analysis of the air preparation.

The ^{121}Sb Mössbauer data are summarized in Table III and Figure 1. These data clearly indicate that the antimony is predominantly in the pentavalent state; no evidence for an Sb^{3+} resonance was found in either the quenched or the oxidized form of "$VSbO_4$".

Discussion

Stoichiometric $VSbO_4$ was not prepared. Instead, phases of the type $V_{1-x}Sb_{1-x}O_4(M_{1-x}O_2)$ and $V_{1+y}Sb_{1-y}O_4(MO_2)$ were apparently formed. Of course, combinations of these presumably occur, and this leads to even more complex situations. No attempt was made to determine the limits of x and y.

The Mössbauer studies show that these phases close to the $VSbO_4$ composition contain antimony predominantly in the pentavalent state. Thus, the formulas for nonstoichiometry may be rewritten as $V^{III}{}_{1-9x}V^{IV}{}_{8x}Sb^{V}{}_{1-x}O_4$ and $V^{III}{}_{1-y}V^{IV}{}_{2y}Sb^{V}{}_{1-y}O_4$. The latter formula maintains the ideal metal-to-oxygen ratio of the rutile structure. This phase may be considered to be a solid solution between VO_2 and $VSbO_4$. The oxidation states in $V_{1.05}Sb_{0.95}O_4$ would be $V^{III}{}_{0.95}V^{IV}{}_{0.1}Sb^{V}{}_{0.95}O_4$.

Nonstoichiometry is known in the rutile structure. Solid solutions in the TiO_2–Ta_2O_5 and TiO_2–Nb_2O_5 systems are reported[10,11] to give cation-deficient phases such as $Ti_{0.69}Nb_{0.24}O_2(M_{0.93}O_2)$ and $Ti_{0.82}Ta_{0.14}O_2(M_{0.96}O_2)$. Thus, these are analogous to $V_{0.92}Sb_{0.94}O_4$ found in this investigation. The oxidation states in this particular composition are $V^{III}{}_{0.28}V^{IV}{}_{0.64}Sb^{V}{}_{0.92}O_4$.

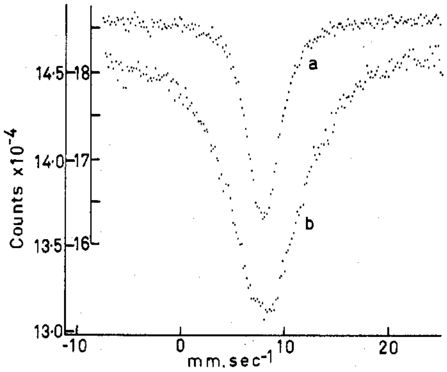

Figure 1. ^{121}Sb Mössbauer spectra of $V_{1.05}Sb_{0.95}O_4$ at (a) 77 K and (b) 4 K.

Some cell dimensions of various preparations close to the $VSbO_4$ composition are given in Table I. In view of the stoichiometry problems, the range in the cell dimensions is hardly surprising. It appears that the three previous investigations[1–3] actually had distinctly different phases. Vernon and Milligan[1] prepared their sample in air; thus, they presumably had a phase of the type $V_{1-x}Sb_{1-x}O_4$. Although we found x to be 0.08 for our air preparations, this value is likely to be somewhat sensitive to exact synthesis conditions.

Roth and Waring[2] prepared their samples at 700–800 °C in an evacuated tube. Thus, their products were presumably close to the $VSbO_4$ composition, but they were not single phase. The x-ray lines they attribute to a high-temperature polymorph of $VSbO_4$ actually are due to Sb_2O_4. Therefore, the tetragonal rutile phase reported by Roth and Waring presumably was of the type $V_{1+y}Sb_{1-y}O_4$. They also observed a glassy phase on quenching from above 800 °C.

Schüer and Klemm[3] prepared their sample at 1050 °C in a sealed tube. They obtained a phase with a rutile-related structure, but with symmetry lower than tetragonal. Although Schüer and Klemm indicated monoclinic symmetry (Table I), we find that an orthorhombic distortion is adequate to account for the diffraction pattern. It is not clear if Schüer and Klemm considered the possibility of this symmetry. The product of Schüer and Klemm almost certainly contained some amorphous second phase which they did not detect.

The Mössbauer parameters obtained for "$VSbO_4$" confirm Schüer and Klemm's conclusions, based on magnetic data,[3] that $V^{V}Sb^{III}O_4$ is not tenable. Furthermore, the presence of only an Sb^{5+} resonance clearly rules out $V^{IV}Sb^{IV}O_4$, which should show two ^{121}Sb Mössbauer resonances like Sb_2O_4,[7,8] therefore establishing the formula as $V^{III}Sb^{V}O_4$. The stability of the V^{3+} under the preparation conditions is rather remarkable since, at 900 °C, Sb_2O_5 undergoes reduction to the mixed oxide Sb_2O_4, and one might have expected Sb^{5+} to oxidize V^{3+} to V^{4+} or even V^{5+}. Of course, the oxidation states in "$VSbO_4$" at higher temperatures are not necessarily the same as those at room temperature.

Wooten, Long, and Bowen[9] have recently reported ^{121}Sb Mössbauer data for a number of metal antimonates with the rutile structure. Our data are in good agreement with theirs. There appears to be a trend of increasing isomer shifts (mm s^{-1}) from $VSbO_4$ (8.20) through $CrSbO_4$ (8.35) to $FeSbO_4$ (8.43). Quadrupole splittings are small and appear to be negative though computer fits to positive values were almost as good. Oxidized $VSbO_4$ has a larger quadrupole splitting than the stoichiometric compound, possibly due to a greater departure from ideal stoichiometry.

One further point of interest in $VSbO_4$ is the presence of magnetic ordering at 4 K. Figure 1 shows the effect on the spectrum of lowering the temperature from 77 to 4 K. This broadening can only be due to magnetic hyperfine splitting, which must arise from an ordering of the V^{3+} spins and be transferred to the antimony sites through the oxygen linkages in the structure. The magnetic data of Schüer and Klemm[3] also indicate that "$VSbO_4$" becomes magnetically ordered below 90 K.

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Registry No. $VSbO_4$, 58151-20-5; ^{121}Sb, 14265-72-6.

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Ring Closure in the Reaction of Metal Chelates. Formation of the Bidentate Oxovanadium(IV)–Glycine Complex

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The details of the rate of ring closure for the monodentate glycinatooxovanadium(IV) species have been studied by both stopped-flow and temperature-jump techniques. The rate corresponds to 35 s^{-1} at 25 °C and the values of the activation parameters are 13.6 kcal/mol for $\Delta H^{\ddagger}$ and –5.8 eu for $\Delta S^{\ddagger}$. Various potential mechanisms are discussed and the direct interaction between the nitrogen of the monodentate glycine and the trigonal face of the oxovanadium(IV) complex is presented as the most reasonable alternative. Appropriate rate constants are calculated in terms of this mechanism.

Introduction

The reactions between metal ions and various bidentate ligands are of considerable interest.[1–11] The rates and mechanisms of processes involving bidentate ligands have received particular attention.[8–11] Oxovanadium(IV) appears to be quite interesting in this context in that it has a d^1 electronic configuration and is readily amenable to studies of both oxidation–reduction[12,13] and substitution processes.[8–10] In this paper, we present a detailed study of the rate of ring closure for monodentate glycinatovanadium(IV) in which the final product is the bidentate complex. The system is characterized by equilibria 1–11 at 25 °C.

$$VO^{2+} + HGly \rightleftarrows VOHGly^{2+} \qquad K_1 = 2.88 \qquad (1)$$

$$VO^{2+} + Gly^- \rightleftarrows VO(Gly)^+ \qquad K_2 = 1.1 \times 10^6 \qquad (2)$$

$$VOHGly^{2+} \rightleftarrows VOGly^+ + H^+ \qquad K_3 = 5.3_0 \times 10^{-5} \qquad (3)$$

$$VOGly^+ \rightleftarrows VO(Gly)^+ \qquad K_4 = 1.8_1 \qquad (4)$$

$$VO(Gly)^+ + Gly^- \rightleftarrows VO(Gly)_2 \qquad K_5 = 5.4 \times 10^4 \qquad (5)$$

$$VO^{2+} + Gly^- \rightleftarrows VOGly^+ \qquad K_6 = 6 \times 10^5 \qquad (6)$$

$$VOHGly^{2+} \rightleftarrows VO(Gly)^+ + H^+ \qquad K_7 = 9.6 \times 10^{-5} \qquad (7)$$

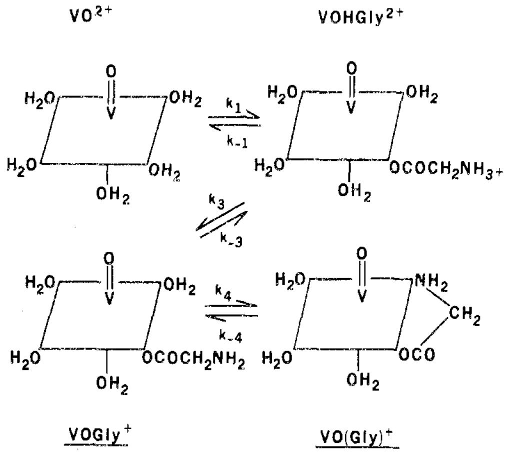
$$H^+ + HGly \rightleftarrows H_2Gly^+ \qquad K_8 = 2.18 \times 10^2 \qquad (8)^{15}$$

$$H^+ + Gly^- \rightleftarrows HGly \qquad K_9 = 3.98 \times 10^9 \qquad (9)^{15}$$

$$VO^{2+} + H_2O \rightleftarrows VOOH^+ + H^+ \qquad K_{M_1} = 1.0 \times 10^{-6} \qquad (10)^{14}$$

$$2VO^{2+} + 2H_2O \rightleftarrows (VO)_2(OH)_2^{2+} + 2H^+ \qquad K_{M_2} = 1.3_2 \times 10^{-7} \qquad (11)^{14}$$

Scheme I



For the purpose of convenience, the oxotetraaquovanadium(IV) ion will be written as VO^{2+} or oxovanadium(IV) and glycine will be abbreviated as HGly. When glycine is coordinated as a monodentate ligand, the complex is written as $VOHGly^{2+}$. The formula $VOGly^+$ represents the deprotonated form of $VOHGly^{2+}$. For glycine functioning as a bidentate ligand, the complex is specified as $VO(Gly)^+$. The structures and equilibrium[1,10] relationships between oxovanadium(IV) and the various monoglycinato complexes are shown diagrammatically in Scheme I.

The rate of water exchange in the equatorial position for oxovanadium(IV) has been reported[14,15] as 5.2×10^2 s^{-1} and the rate of $VOHGly^{2+}$ formation[10] from oxovanadium(IV) and HGly is 1.3×10^3 M^{-1} s^{-1}. The corresponding rate of dissociation is 4.6×10^2 s^{-1}.

Experimental Section

The stock solution of oxovanadium(IV) was prepared by electrolytically reducing a slurry of vanadium pentoxide in perchloric acid as has been described previously.[10,16] The stock solution gave negative tests[17] for both vanadium(III) and vanadium(V). The oxovanadium(IV) solutions were analyzed by titration with standard $KMnO_4$. The total acid concentration was determined by passing aliquots of the stock solution through a Dowex 50-X8 cation-exchange column and by titrating the eluent with standard NaOH to the phenolphthalein end point. The acid concentration was obtained by making corrections

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