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Sublimation-Controlled Oxidation of Antimony Trioxide

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Previous investigators noted that a mixture of dimorphic Sb_2O_3 oxidizes to orthorhombic Sb_2O_4 more rapidly than each dimorph separately. It was hypothesized that Sb_2O_3(c) sublimes to low-energy nucleation sites on Sb_2O_3(o) to oxidize. In this study thermodynamic calculations indicated that the driving force for oxidizing a sublimed species is much greater than that for nonsublimed Sb_2O_3. The hypothesis was validated experimentally using small-particle-size (10–20 μm) Sb_2O_3 to achieve appreciable sublimation rates. It was found that the oxidation rates of both Sb_2O_3(c) and Sb_2O_3(o) are linearly correlated to the equilibrium sublimation pressure of each dimorph. Also, the apparent activation energy of oxidation was determined to be 42.6–45.9 kcal/mole, approximating the enthalpy of sublimation for Sb_2O_3 (~43–47 kcal/mole). These observations strongly support the hypothesis that Sb_2O_3 oxidation is sublimation controlled.

Introduction

Antimony trioxide forms both cubic and orthorhombic structures. Senarmontite, Sb_2O_3(c), is transformed to valentinite, Sb_2O_3(o), at about 829 K with a melting point of 929 K. Valentinite is metastable at ambient temperature, and both forms are found naturally. The product of oxidation of each form is orthorhombic Sb_2O_4 under all but the most extreme conditions (*1*).

Kinetic studies of the oxidation of antimony trioxide have been reported by Gopalakrishnan and Manohar (*2, 3*), Agrawal *et al.* (*4*), Cody *et al.* (*1*), Golunski *et al.* (*5*), and Trofimov *et al.* (*6*). Gopalakrishnan and Manohar (*2, 3*) studied the oxidation kinetics of single and polycrystalline Sb_2O_3(o). It was reported that the oxidation to Sb_2O_4(o) was topotactic in single-crystal experiments. For polycrystalline Sb_2O_3(o), it was reported that oxidation occurred in reasonable times over the temperature range 743–793 K under 140 Torr O_2. The apparent activation energy for oxidation was reported to be 41.6 kcal/mole which was attributed to the breakage of selected antimony–oxygen bonds in the valentinite crystal, permitting movement of oxygen atoms from site to site. They concluded that a diffusion process controls the rate of oxidation.

Thermal investigations of each dimorph under air or inert atmosphere (*1, 4, 5*), employing thermal gravimetric (TG) and differential thermal analytical (DTA) methods, have been reported. An inconsistency was the reporting of a DTA oxidation peak as endothermic (*4*). This and other observations were fully addressed (*1, 5*) by proving that finely ground Sb_2O_3(o) oxidizes at a lower temperature than does Sb_2O_3(c).

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Sb_2O_3(o) oxidation results in a weight gain of about 1%, while Sb_2O_3(c) loses approximately 20 wt% during oxidation. These differences in behavior were attributed to concurrent sublimation and oxidation of Sb_2O_3(c), while Sb_2O_3(o), with a lower sublimation pressure (*7, 8*), was thought to oxidize before significant sublimation.

Trofimov *et al.* (*6*) found in a high-temperature X-ray diffraction study that mixtures of Sb_2O_3(c) and Sb_2O_3(o) do not oxidize additively. In their work, when finely divided Sb_2O_3(c) was oxidized in air, Sb_2O_4 was produced at 733 K. Under similar conditions, Sb_2O_3(o) oxidized at 673 K. Mixtures of the dimorphs oxidized at 653 K, with much more rapid oxidation being found at 693 K where in 30–40 min all Sb_2O_3(c) was oxidized to α-Sb_2O_4 with the concentration of Sb_2O_3(o) remaining constant until all Sb_2O_3(c) was reacted. Those authors hypothesized that Sb_2O_3(o) acts as a low-energy nucleation site for the oxidation of sublimed Sb_2O_3(c). The low-energy nature of the reaction was attributed to epitaxial formation of α-Sb_2O_4 on Sb_2O_3(o) because Sb_2O_3(o) and α-Sb_2O_4 have nearly identical orthorhombic structures. In another oxidation study, Gopalakrishnan and Manohar (*2*) described the topotactic growth of α-Sb_2O_4 on Sb_2O_3(o) in detail, supporting the observations of Trofimov *et al.* These observations suggest a hypothesis that sublimation is critical in the oxidation of Sb_2O_3. To determine the validity of the hypothesis, an isothermal oxidation study of Sb_2O_3 was undertaken.

Theory

Trofimov's hypothesis is supported by calculation of the free energies for oxidation of the sublimed species of Sb_2O_3, i.e., Sb_4O_6, as compared with oxidation of solid Sb_2O_3. The reactions are as follows:

$$Sb_2O_3(s) + \tfrac{1}{2}O_2 \rightarrow Sb_2O_4(s) \qquad (1)$$

$$Sb_4O_6(g) + O_2 \rightarrow Sb_4O_8(s) \qquad (2)$$

Values of $\Delta G°$, the free energy, may be calculated using the equilibrium constant, K_{eq}. For a reaction at 726 K under 140 Torr O_2 and Sb_2O_3(o) sublimation pressure of 0.01648 Torr, $\Delta G°$ is -1.2 kcal/mole for Eq. (1) and -17.9 kcal/mole for Eq. (2). Therefore, oxidation is much more favorable for sublimed rather than solid species.

Quite likely, sublimation of Sb_2O_3 controls its rate of oxidation, such as occurs in the oxidation of antimony (*9*). The rate of sublimation of Sb_2O_3 can be expressed by Langmuir's relationship (*10*)

$$\dot{m} = P_e\alpha\left(\frac{2\pi RT}{M}\right)^{-1/2} \qquad (3)$$

where $\dot{m}$ = rate of sublimation of mass per unit surface area
P_e = equilibrium sublimation pressure
α = accommodation coefficient
M = molecular weight of subliming species
R = gas constant
T = reaction temperature

Thus, if sublimation is rate controlling, the oxidation reaction rate will be proportional to P_e, and since $\dot{m}$ is expressed per unit area, particle size will strongly influence the oxidation rate.

Rutner (*11*) has shown that $\dot{m}$ can also be expressed similarly to an Arrhenius rate constant relationship as

$$\dot{m} = Ae^{-\Delta H_s/RT} \qquad (4)$$

where A = a constant and ΔH_s = enthalpy of sublimation. Therefore, if the oxidation reaction rate is equal to $\dot{m}$, the activation energy for the reaction will be equivalent to ΔH_s.

Experimental

Sb_2O_3 (Alfa, Danvers, MA, 99.999% pure on metal basis) was heat treated in a platinum cylinder in a quartz tube under argon to form each dimorph. For Sb_2O_3(c) heat treatment was approximately 798–803 K for 1–2 h, and Sb_2O_3(o) was prepared by heating to about 898–913 K for similar periods. On removal from the furnace, the tube was air quenched. The purity of each dimorph was determined using a Raman method (*1*), in which a coherent argon laser (4880 Å) excited the sample (~150 mW incident) mounted in a glass capillary with 90° scattered radiation being detected by a photomultiplier tube. The Raman method is preferred over X-ray diffraction, because it is faster and provides an unambiguous spectrum of each dimorph. Each sample proved to contain the desired pure dimorph, with no trace of contamination.

Because large crystalline samples of Sb_2O_3(o) were not significantly oxidized prior to melting in preliminary DTA studies, Sb_2O_3(o) was ground and sieved through 20-μm and collected on 10-μm nickel screens (ATM Corp., Milwaukee, WI). Sb_2O_3(c) was sieved to the same size.

After sample preparation, each dimorph was oxidized at four temperatures in a closed glassware system modeled after that of Gopalakrishnan and Manohar (*3*) under 140 Torr O_2. A new quartz reaction tube was attached to the system prior to each experiment, because it was found that the presence of Sb_2O_4 produced in previous reactions influenced the rate of oxidation of Sb_2O_3(c); however, the oxidation rate of Sb_2O_3(o) was not similarly affected.

The oxidation procedure consisted of flushing the system three times with oxygen (99.995%), bringing the system to 140 Torr O_2, equilibrating the reaction tube at the desired temperature (±1 K), and then dropping the sample from the cold zone into the reaction tube. During the reaction, small amounts of oxygen were periodically added to the system to closely approximate isobaric conditions. O_2 was supplied from a gas buret by which it was possible to measure oxygen consumption. After completion of the reaction, products were analyzed using the Raman procedure (*1*).

Results and Discussion

Oxygen consumption as a function of reaction time for the oxidation of Sb_2O_3(o) from 729 to 795 K is presented in Fig. 1. For Sb_2O_3(c) similar data are given in Fig. 2. The data indicate that Sb_2O_3(c) oxidizes at a much higher temperature than Sb_2O_3(o) as found by others (*1*, *5*). In contrast to work reported earlier (*3*), it was also found that the time for the reaction to begin appears to be a function of the time it takes the sample to reach reaction temperature. Oxidation of both Sb_2O_3(o) and Sb_2O_3(c) appears to be linear over major portions of the reactions; however, some regions appear to suggest parabolic diffusion kinetics.

Theoretical yield for oxidation was not achieved for either dimorph, probably because the reactant becomes covered with

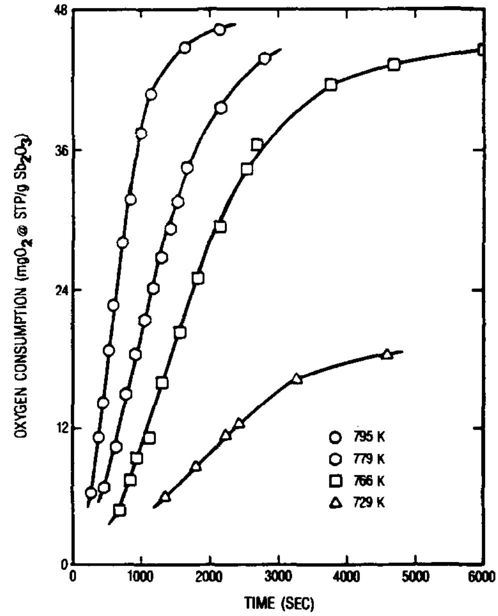

FIG. 1. Isothermal oxidation of Sb_2O_3(o).

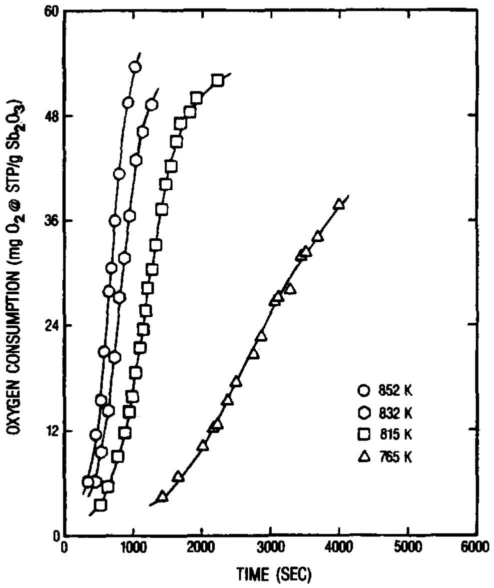

FIG. 2. Isothermal oxidation of Sb_2O_3(c).

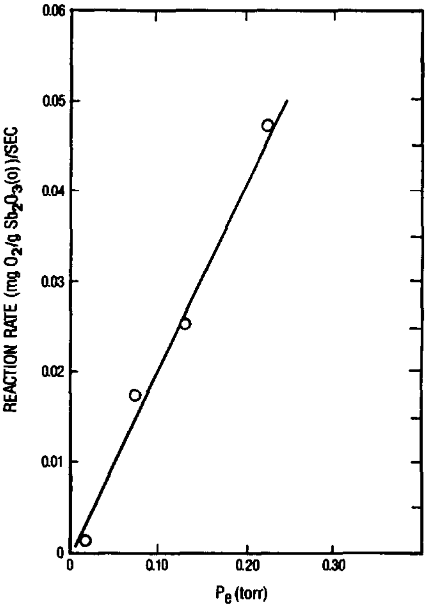

FIG. 3. Oxidation rate of Sb_2O_3(o) as a function of equilibrium sublimation pressure.

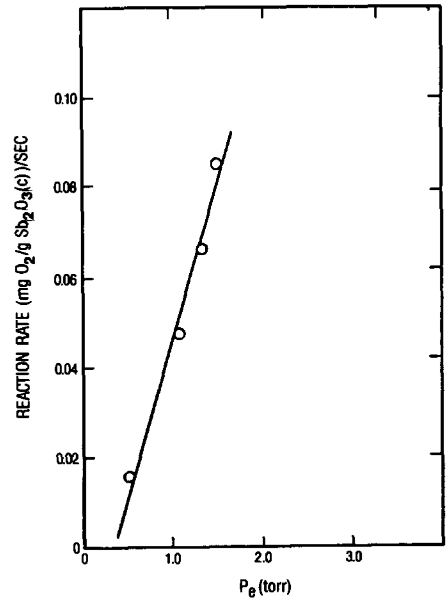

FIG. 4. Oxidation rate of Sb_2O_3(c) as a function of equilibrium sublimation pressure.

Sb_2O_4 which progressively retards sublimation. Such a process would be more effective at lower temperatures; in fact, at lower reaction temperatures oxidation appears to terminate at much less than the theoretical limit.

As confirmation that the rate of sublimation of Sb_2O_3 controls the rate of oxidation, rates of reaction are presented in Figs. 3 and 4 as a function of the equilibrium sublimation pressure, employing the Jungermann and Plieth (7) relationships. For Sb_2O_3(c) the oxidation temperature of 832 K is 3 K above the Sb_2O_3(c)-to-Sb_2O_3(o) transition, so the mean of Sb_2O_3(c) and Sb_2O_3(o) sublimation pressures was employed. The Sb_2O_3(c) reaction at a temperature of 852 K is 23 K above the transition temperature; therefore, the sublimation pressure for Sb_2O_3(o) was used. Data for each dimorph show a linear relationship between equilibrium sublimation pressure and oxidation rate (correlation coefficient = 0.995) for both Sb_2O_3(c) and Sb_2O_3(o), as

TABLE I

ACTIVATION ENERGIES (E_a) AND PREEXPONENTIAL FACTORS (A) FOR THE ISOTHERMAL OXIDATION OF Sb_2O_3(o) AND Sb_2O_3(c)

Reactant:	Sb_2O_3(o)					Sb_2O_3(c)				
% theoretical completion:	10	30	50	65	Mean	10	30	50	65	Mean
E_a (kcal/mole)	43.2	42.2	42.8	42.0	42.6 ± 0.6	43.4	44.3	46.7	49.3	45.9 ± 2.6
A (s^{-1})	3.06×10^9	8.41×10^8	7.89×10^8	3.50×10^8	9.18×10^8	6.09×10^8	6.74×10^8	2.49×10^9	1.08×10^{10}	1.82×10^9

expected if sublimation controls the oxidation rate.

Finally, the apparent Arrhenius activation energy and preexponential factor are as given in Table I. For 50% theoretical oxidation, Arrhenius plots are shown in Fig. 5. As predicted, the calculated oxidation activation energies over 10–65% reaction completion of 42.6–45.9 kcal/mole are quite close to the enthalpy of sublimation of the Sb_2O_3 dimorphs reported variously as 43–44 kcal/mole (*7*) and 44.1–47.3 kcal/mole (*8*). They are slightly higher than the activation energy of 41.6 kcal/mole reported in a previous oxidation study of Sb_2O_3(o) (*3*). The similarity between the activation energy of oxidation and enthalpy of sublimation further supports the hypothesis that sublimation controls the oxidation of Sb_2O_3.

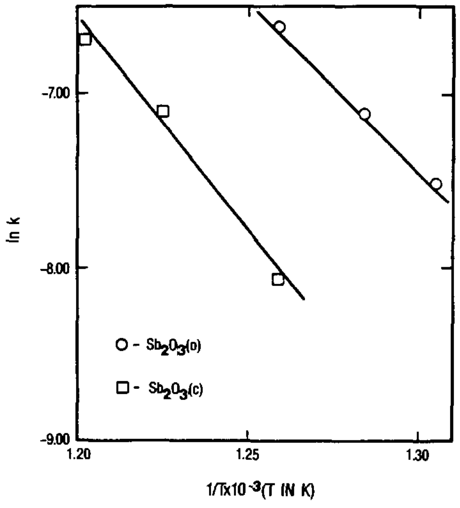

FIG. 5. Arrhenius plot for Sb_2O_3 oxidation at 50% theoretical reaction completion.

Conclusions

Free energy calculations indicate that the oxidation of Sb_2O_3 would occur more favorably for the sublimed species rather than for solid Sb_2O_3. Sublimation was shown to be rate controlling for Sb_2O_3 oxidation by linear correlations of the oxidation rate of each dimorph with its respective equilibrium sublimation pressure and comparison of the activation energy of oxidation with the enthalpy of sublimation. Sublimation of antimony trioxide prior to oxidation aids in rationalizing the data of Trofimov *et al.*, which suggest that sublimed Sb_2O_3(c) oxidizes to α-Sb_2O_4 at an orthorhombic surface site such as Sb_2O_3(o), providing a surface similar to α-Sb_2O_4.

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