Such a ΔE_a value is consistent with a bimolecular process, and the activation entropy value is remarkably similar to the value reported for the oxidation of $Ru(NH_3)_6^{2+}$ to $Ru(NH_3)_6^{4+}$ with oxygen at 25 °C ($\Delta S^{\ddagger} = -10$ eu).[15]

A rate law (eq 6) for sulfide loss that is consistent with our

$$-d[SR_2]/dt = \frac{k_1k_3[Ru]_{tot}[O_2][ROH]}{k_1[O_2] + k_3[ROH]} \qquad (6)$$

observations was derived by using a steady-state approximation for [peroxide] and the assumption that k_{-2} and k_{-3} are vanishingly small, where $[Ru]_{tot} = [Ru(IV)] + [Ru(II)]$ and where the term $k_{-1}[Ru^{IV}]/k_2[SR_2][ROH]$ is small.[10,16] The linear plot of $[Ru]_{tot}$/Rate vs. $[O_2]^{-1}$ is consistent with the rate expression of eq 6. The values of k_1 and k_3 for the oxidation of decyl methyl sulfide at 108 °C in methanol, derived from the slope and intercept of such a plot, are 5.1×10^{-4} atm^{-1} s^{-1} and 2.1×10^{-3} M^{-1} s^{-1}, respectively. This rate law correctly predicts the less than unity order for the oxygen dependence, as well as the profound effect of solvent. Thus, the kinetic expression derived from eq 2, 3, and 5 is in excellent agreement with experimental results and provides kinetic support for the proposed catalytic mechanism of this facile and selective sulfide oxidation utilizing molecular oxygen.

Registry No. Decyl methyl sulfide, 22438-39-7; dimethyl sulfide, 75-18-3; dibutyl sulfide, 544-40-1; tetrahydrothiophene, 110-01-0; phenyl methyl sulfide, 100-68-5; *cis*-$Ru(Me_2SO)_4Cl_2$, 64376-67-6.

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The Procter & Gamble Company **Dennis P. Riley**
Miami Valley Laboratories
Cincinnati, Ohio 45247

Received April 14, 1983

Does $CeSbO_3$ Exist?

Sir:

The synthesis of a new defect cubic pyrochlore, $CeSbO_3$, was recently reported.[1] Several aspects of this report seemed rather unusual, and since then the preparation has been carefully repeated and the conclusion drawn that the product is not a new compound but rather a mixture of the starting materials, one crystalline and the other amorphous.

Our attention was drawn to this report for the following reasons:

First, according to the formula, one must assume trivalent oxidation states for both cerium and antimony. This seemed somewhat unusual, since the authors reported a closed-system preparation expressed by the equation

$$2CeO_2 + Sb_2O_3 \rightarrow 2CeSbO_3 + {}^1/_2O_2$$

which would have produced an endogenous oxygen pressure. In such an oxidizing atmosphere, one would not expect to obtain relatively reduced forms of cerium and antimony.

Second, the existence of the pyrochlore structure with either the Ce(III)/Sb(III) or the Sb(III)/Ce(IV) combination would be unusual from a crystal chemical point of view. The pyrochlore structure, ${}^{VIII}A_2{}^{VI}B_2O_7$, consists of a rather open BO_3 framework of octahedra sharing all vertices. The seventh oxygen, nonessential to the structure, resides in a large cavity formed by the octahedral framework. The eight-coordinate A cation resides in a hexagon of anions from surrounding framework octahedra. Each hexagon joins two of the large cavities, the anions therein bringing the coordination to eight in a bicapping fashion. Thus, even in the defect pyrochlore, $A_2B_2O_6$ (ABO_3), where the large cavities are not occupied by oxygens and the coordination number of both cations is formally 6, the geometry of the cation sites is quite different and requires a "larger" A cation for structural stability. Substantial empirical data have accrued in the literature outlining stability fields for this structure according to the relative cation sizes,[2,3] considerable extension having been obtained with high-pressure techniques.[4] Cerium/antimony combinations fall either outside of known stability regions or near boundaries.

Third, the interpretation of the crystallographic data, in which oxygen was randomly distributed among both the (f) positions (essential framework octahedra) and the (a) positions (within the large cavities), is disturbing since in the defect pyrochlore ABO_3 the cavity sites are not occupied by anions.

Fourth, it was eventually realized that the X-ray powder diffraction pattern given by the authors for $CeSbO_3$ was essentially identical with that of CeO_2,[5] one of the reactants, except for the (111) reflection at $d = 6.18$, which, at a relative intensity of 1%, could well be spurious. CeO_2 has the fluorite structure with a unit cell parameter of 5.4110 Å. The authors reported that the X-ray data for $CeSbO_3$ could be indexed on the basis of a cubic cell of the fluorite type with a cell edge of 5.4123 Å.

It was decided to carefully repeat the preparation as reported.[1] Reagent grade starting materials were used, and a green-white mass with a glassy texture was obtained. Optical inspection revealed orange streaks in regions of the mass. The product was very hard and difficult to grind to a powder, and the Debye–Scherrer X-ray powder photograph gave a diffraction pattern identical with that of CeO_2. Although qualitative analysis with sulfide ion was positive for antimony, no trace of the oxide was evident in the X-ray diffraction pattern. The melting point of Sb_2O_3 is 656 °C, and thus at the reaction temperature of 690 °C, this compound is molten. To determine if quenching in liquid nitrogen would produce an amorphous solid, Sb_2O_3 alone was treated according to the $CeSbO_3$ preparation procedure. At 690 °C, Sb_2O_3 is a clear orange liquid. After quenching in liquid nitrogen, a yellow-orange glass is obtained, which is very hard and difficult to grind. Before the heat treatment, the X-ray diffraction pattern corresponded to that of the Sb_2O_3 polymorph, senarmontite. After quenching from the molten state, the powdered glassy product gave no diffraction pattern.

In an effort to separate the two presumed phases, CeO_2 and Sb_2O_3, the product from the $CeSbO_3$ preparation procedure was heated at 700 °C under flowing argon. A white cloudy ring was deposited on a cooler section of the quartz tube. The white substance gave an X-ray diffraction pattern corresponding to that of Sb_2O_3, senarmontite. Examination of the "$CeSbO_3$" product using electron microscopy also indicated the presence of two types of particles, one amorphous and the other crystalline. The diffraction patterns of crystalline particles could be indexed on the basis of the unit cell of fluorite-type CeO_2.

These results seem to indicate rather conclusively that CeO_2 and Sb_2O_3 do not react under the given conditions to form a new defect pyrochlore: "$CeSbO_3$" consists of a mixture of crystalline CeO_2 embedded in a glassy Sb_2O_3 matrix.

Registry No. $CeSbO_3$, 81642-86-6; CeO_2, 1306-38-3; Sb_2O_3, 1309-64-4.

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Department of Chemistry **T. A. Hewston**
The University of Connecticut
Storrs, Connecticut 06268

Received February 25, 1983