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Thermochemical Splitting of Sulfur Dioxide with Cerium(IV) Oxide

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Abstract: $Ce_2(SO_3)_2SO_4{\cdot}4H_2O$ thermally decomposes in several steps to yield H_2O, sulfur, SO_2, and O_2 as gaseous products, plus $Ce_2O(SO_4)_2$, $Ce_2O_2SO_4$, $CeOSO_4$, and CeO_2 as intermediate products. The terminal solid product above 1250 K is CeO_2. Reaction pathways are described in detail. A thermochemical cycle for splitting SO_2 into sulfur and oxygen with CeO_2 is described, in which sulfur and/or oxygen and/or cerium all change valence in four different reactions.

The thermochemistry of cerium compounds and sulfur compounds is currently of interest because of the proven capability of the cerium(III)–cerium(IV) couple in splitting water thermochemically[1-3] and the propensity of metal sulfates to evolve oxygen on thermal decomposition.[4,5] Sulfur dioxide chemistry as related to environmental pollution is also of considerable interest.

We report here an assessment of the stoichiometry of a thermochemical cycle for splitting of sulfur dioxide into sulfur and oxygen that resulted from thermal decomposition studies. The heat stored by SO_2 splitting is about the same as that stored by water splitting. The standard enthalpy of formation of SO_2[6] is -296.8 kJ mol^{-1}, and that of H_2O[6] is -285.8 kJ mol^{-1}.

Experimental Section

Preparation and characterization of $Ce_2(SO_3)_2SO_4{\cdot}4H_2O$ have been described previously,[7] except for infrared and X-ray studies that are discussed below. Analytical techniques have been described in detail.[7]

Thermal decompositions were done in a quartz tube with the gases constrained as described for carbonate compositions.[8] Evolved gases were measured quantitatively by pressure change, except for sulfur, which was determined by weighing. SO_2 was separated from O_2 in a trap cooled with an isopropyl alcohol–CO_2 slush. The oxygen was identified with a gas chromatograph.

The dehydration product of $Ce_2(SO_3)_2SO_4{\cdot}4H_2O$ at 625 K was amorphous, but X-ray powder patterns showed two phases in the product at 800–850 K. One was identified to be $Ce_2O_2SO_4$ by comparison of X-ray diffraction peak positions and intensities with those of the $La_2O_2SO_4$ compound.[9] This identification was corroborated by the infrared spectrum of the 850 K product, which showed absorptions identical with absorptions of other rare earth dioxymonosulfates. The second phase was taken to be $Ce_2O(SO_4)_2$ from the chemical analyses and gas analyses and mass balance requirement. At 850–1000 K, CeO_2 was present along with a second unidentified phase that was projected to be $CeOSO_4$ to match the oxygen evolution measurement and sulfate analysis. At 1200 K the product was >98% CeO_2 as shown by weight loss and analyses for sulfur. Only CeO_2 lines were observed in the powder patterns.

Infrared spectra were taken of the decomposition products with a Perkin-Elmer spectrometer using standard techniques. No absorptions were observed that were atypical of sulfites or sulfates.

Results

A graph of the decomposition of $Ce_2(SO_3)_2SO_4{\cdot}4H_2O$ is shown in Figure 1. Water of hydration was removed first, then a small amount of SO_2. At 800 to 850 K, sulfur vapor and SO_2 were evolved. At 1000 to 1200 K, SO_2 and O_2 were evolved. There were no physical manifestations of SO_3 evolution such as liquid condensation and sulfuric acid formation on exposure to moisture.

The variation of sulfite and sulfate anions in the solid phase on decomposition is shown in Figure 2. Sulfite decreased with increasing temperature and was absent at 850 K. Sulfate first increased as a result of disproportionation and sulfur formation and subsequently decomposed at higher temperatures. It was completely decomposed above 1250 K with no measurable sulfur remaining in the solid phase.

The variation of the valence of cerium with increasing temperature in Figure 3 shows that Ce(III) predominated below 850 K and Ce(IV) predominated above 1000 K where O_2 also was present.

Table I gives yields of sulfur and oxygen. The relative amounts of each correspond to the thermal decomposition of SO_2.

Discussion

The decomposition reactions for SO_2 splitting are as follows:

400–800 K

$$Ce_2(SO_3)_2SO_4{\cdot}4H_2O \rightarrow Ce_2(SO_3)_2SO_4 + 4H_2O \qquad (1)$$

$$Ce_2(SO_3)_2SO_4 \rightarrow Ce_2O_X(SO_3)_{2-X}SO_4 + XSO_2 \qquad (2)$$
$$(X < 0.1)$$

800–850 K

$$Ce_2(SO_3)_2SO_4 \rightarrow Ce_2O(SO_4)_2 + {}^1/_4S_2 + {}^1/_2SO_2 \qquad (3)$$

800–850 K

$$Ce_2(SO_3)_2SO_4 \rightarrow Ce_2O_2SO_4 + 2SO_2 \qquad (4)$$

850–1000 K

$$Ce_2O(SO_4)_2 \rightarrow CeOSO_4 + CeO_2 + SO_2 \qquad (5)$$

850–1000 K

$$Ce_2O_2SO_4 \rightarrow 2CeO_2 + SO_2 \qquad (6)$$

1000–1200 K

$$CeOSO_4 \rightarrow CeO_2 + SO_2 + {}^1/_2O_2 \qquad (7)$$

Dehydration occurs first as shown in reaction 1, and then a small amount of SO_2 is evolved in reaction 2. Reaction 3 is a combination of two parallel reactions with sulfur formation predominating in a ratio of three to one. Reaction 4 is an SO_2 evolution reaction to give an undesirable product. All three figures show

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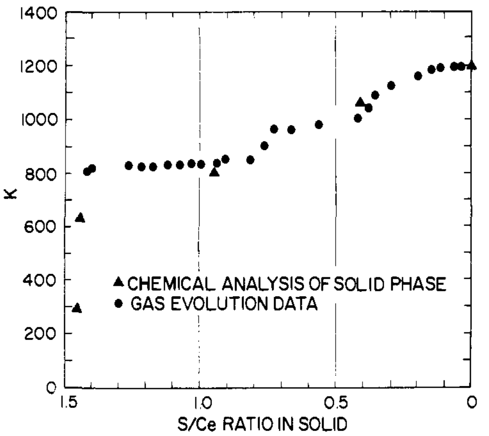


Figure 1. Change in sulfur content of the solid phase.

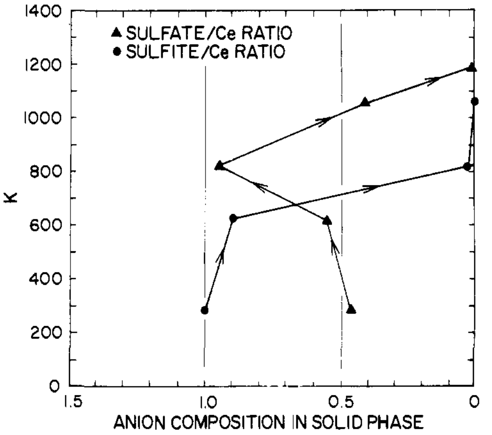


Figure 2. Variation of anion composition on sulfur removal from the solid phase.

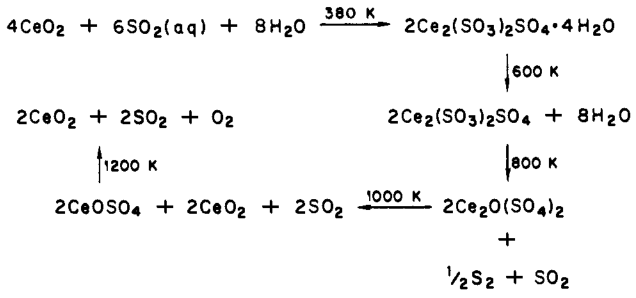
Table 1. Yields of Sulfur and O_2 per Mole of $Ce_2(SO_3)_2SO_4{\cdot}4H_2O$

T, K	mol of sulfur	mol of O_2
800–850	0.308	
800–850	0.410	
800–850	0.320[a]	
1000–1200		0.308[a]

[a] Same experiment.

the offset anion stoichiometry. Reactions 5 and 6 explain the SO_2 evolution and CeO_2 formation between 850 and 1000 K. The formation of $CeOSO_4$ in (5) is necessary to explain the stoichiometry and to account for concomitant evolution of SO_2 and O_2 above 1000 K in (7), and to account for the second phase in the X-ray analysis.

The thermochemical cycle for splitting SO_2, as shown below, includes synthesis of the initial insoluble compound. This cycle yields 1 mol of products by starting with 4 mol of CeO_2:



net reaction: $SO_2 \longrightarrow \frac{1}{2}S_2 + O_2$

Part of the cycle includes regeneration of CeO_2 and SO_2 from sulfate by oxidation of Ce(III) at 850 to 1000 K in reaction 5.

The measured yield of sulfur and O_2 is about one-third less than that predicted by the cycle stoichiometry. This deficiency results from reaction 4 in which SO_2 is evolved without a sulfur valence change. This reaction pathway, according to Lau, Cubiocciotti, and Hildenbrand, is preferred mechanistically to sulfur formation.[10] Thus, heating at a slower rate at 800 to 850 K and/or increasing SO_2 pressure could possibly improve the cycle efficiency by increasing the sulfur yield and simultaneously increasing the coupled O_2 yield.

The lack of thermochemical data for the various cerium sulfates precludes any reasonable estimate of cycle heat efficiency.

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Registry No. $Ce_2(SO_3)_2SO_4$, 87566-84-5; $Ce_2O(SO_4)_2$, 87566-83-4; $Ce_2O_2SO_4$, 12432-39-2; $CeOSO_4$, 77812-31-8; CeO_2, 1306-38-3; SO_2, 7446-09-5; O_2, 7782-44-7; S, 7704-34-9.

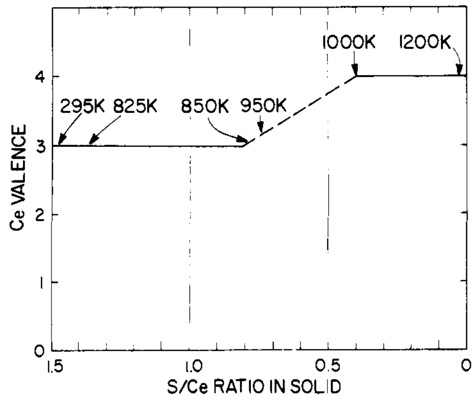

Figure 3. Variation of Ce valence.

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