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THERMAL DECOMPOSITION OF $Cs_2S_2O_6$

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ABSTRACT

Thermogravimetric, differential thermal, and evolved gas analyses were used to study the thermal stability of $Cs_2S_2O_6$ in O_2 and N_2. No phase transitions were observed between room temperature and the onset of thermal decomposition. Primary loss of SO_2 and conversion of $Cs_2S_2O_6$ to Cs_2SO_4 occurs around 300°C, with a preliminary decomposition around 250°C in which SO_2 and H_2O are evolved, representing about 8% of the total weight loss. The source of the 250°C decomposition is not clear. Evolution of trace occluded or trapped water can be detected below 250°C. X-Ray diffraction results gave the cell dimensions as $a = 6.35658 \pm 0.00004$ Å and $c = 11.53907 \pm 0.00004$ Å for the hexagonal-symmetry starting material.

INTRODUCTION

The thermal stability of $Cs_2S_2O_6$ is of interest because of its piezoelectric and pyroelectric properties [1]. The possibility of a phase transition between room temperature and the melting point or thermal decomposition temperature is of particular interest. Differential thermal analysis (DTA), evolved gas analysis (EGA) and thermogravimetry (TG) were used both to determine the nature and onset of the decomposition and to search for possible solid state transitions.

EXPERIMENTAL PROCEDURES

The sample of $Cs_2S_2O_6$ was prepared as described in Brauer [2]. The material was slowly recrystallized twice from aqueous solution.

A Perkin-Elmer (model TGS-1) thermobalance, modified for digital data acquisition and processing [3] was used to obtain the TG data. Temperatures were based upon magnetic calibration [4]. DTA curves were obtained with a Du Pont (model 900) apparatus using the "DSC" cell. An empty Al pan served as the reference. Experiments were performed in both oxygen and nitrogen at a flow of 50 cm^3 min^{-1}. The heating rate was 10°C min^{-1}.

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The basic EGA apparatus has been described elsewhere [5] except for the following modifications. The temperature controller was changed to a Netzch model 411. A Fluke (model 2190A) digital thermometer with analog output coupled with a Spectrum (model 1021) filter/amplifier was used for temperature recording. Finally, a UTI (model 2054) programmable peak selector was used to control the mass spectrometer scan and provide data acquisition. The heating rate was 10°C min^{-1} and the vacuum ranged from about 1×10^{-7} torr to 1×10^{-6} torr, depending upon the extent of the decomposition.

RESULTS AND DISCUSSION

Table 1 is a summary of the X-ray diffraction data for the starting material. No additional lines were present. The TG and DTA curves in O_2 and N_2 were identical. TG, DTG, and DTA curves in N_2 are shown in Figs. 1 and 2. The general decomposition is

$$Cs_2S_2O_6 \rightarrow Cs_2SO_4 + SO_2 \tag{1}$$

presumed to be similar to that of the analogous sodium salt [6]. The weight loss according to eqn. (1) nicely fits the second or major step in the TG

TABLE 1

Experimental and calculated powder diffraction data *

2θ (deg.)	I/I_0	d_{exp} (Å)	*hkl*	$\Delta 2\theta$ ** (deg.)
23.976 ***	1	5.512	10.0	−0.029
26.629	33	4.971	10.1	−0.015
33.378	88	3.986	10.2	−0.032
42.217	100	3.179	11.0	−0.009
42.572	18	3.154	10.3	−0.010
46.756	61	2.885	00.4	−0.010
49.228 ***	2	2.749	20.0	0.074
50.636	33	2.677	20.1	0.004
53.224	21	2.556	10.4	−0.014
54.894	79	2.484	20.2	0.010
61.527	30	2.238	20.3	0.003
64.821	51	2.136	11.4	0.004
66.722 ***	3	2.082	21.0	−0.040
71.585	42	1.958	21.2	−0.011
77.201	26	1.835	30.0	−0.003
78.193	18	1.815	10.6	0.007

* Format used follows the recommendations of the American Crystallographic Association Committee on Criteria for Powder Diffraction Patterns. Data based on a Guinier-Hägg XDC-700 focussing camera powder photograph taken with $CrK\alpha_1$ = 2.28975 Å using Si (a = 5.431065 Å as internal standard).

** $2\theta_{\text{exp}} - 2\theta_{\text{calc}}$, a = 6.35658 ± 0.00004 Å, c = 11.53907 ± 0.00004 Å.

*** Very weak line, of reduced accuracy.

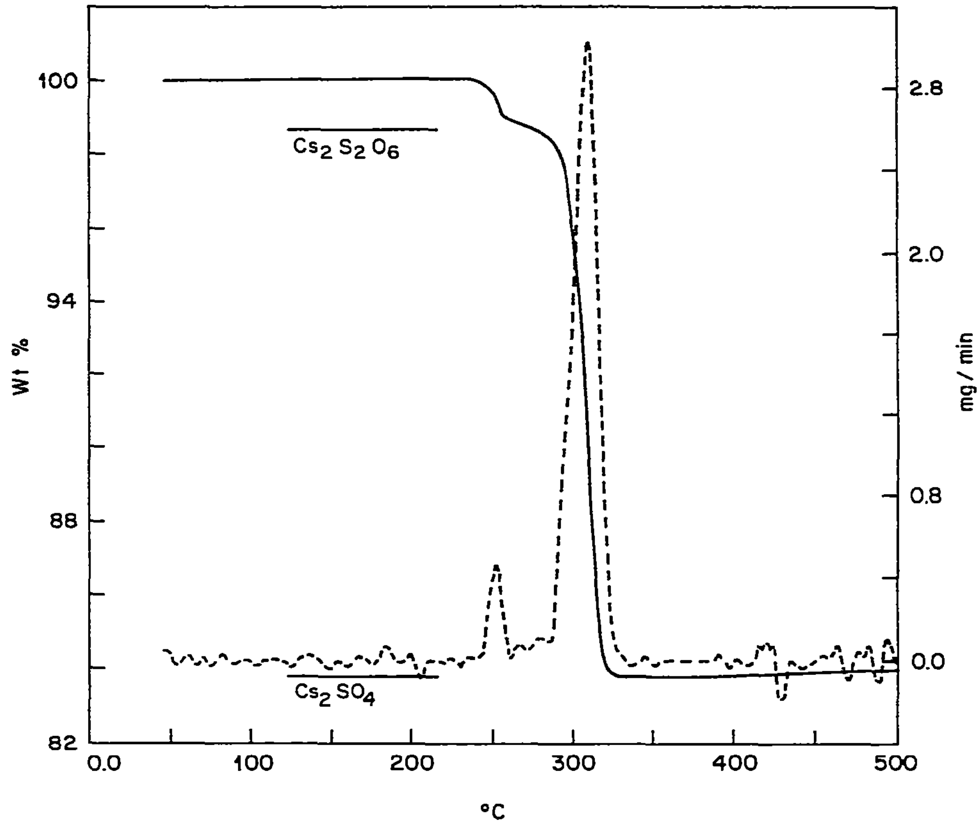

Fig. 1. Thermogravimetric curves for 4.02 mg of $Cs_2S_2O_6$ heated in N_2 at 10°C min^{-1}. (———) TG; (- - - - - -) DTG.

curve (see Fig. 1). However, there is an earlier weight loss at ~250°C (1.35 wt.% or 5.81 a.m.u.) which is not readily explainable based solely upon the observed weight change.

The DTA curve in Fig. 2 also indicates some decomposition prior to the major peak. The preliminary decomposition (250—300°C) appears to be composed of several processes, as seen from the cluster of small peaks in that temperature span. There are numerous smaller peaks or spikes in the curve below 250°C. These do not appear to be associated with significant weight loss (see Fig. 1). These spikes or peaks do not occur reproducibly from one DTA to another.

The EGA results are summarized in Figs. 3 and 4. Figure 3 shows a plot of the relative intensity of the mass 18 peak as a function of temperature for both heating and cooling. There are numerous short bursts of water vapor which occur upon heating the sample to 245°C but which are absent on cooling. This implies that the DTA "disturbances" below 250°C are due to the evolution of very small amounts of water which were trapped and occluded during crystallization.

The gaseous products evolved during the preliminary decomposition around 250°C are clearly shown from the EGA to be SO_2 and H_2O. The shape of the SO_2 profile given in Fig. 4 strongly resembles the DTG curve in

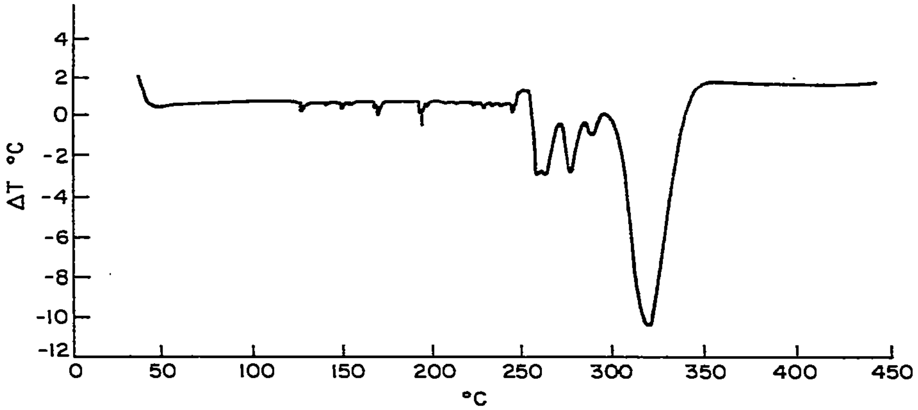

Fig. 2. Differential thermal analysis curve for 19.61 mg of $Cs_2S_2O_6$ heated in N_2 at 10°C min^{-1}.

Fig. 1. There were no observable peaks in the EGA curves for CO_2 or SO_3 in the temperature range investigated. Consequently, the early decomposition cannot be attributed to a carbonate or sulfate impurity. X-Ray fluorescence analysis did not detect any elements other than Cs and S, nor was there any indication of a second phase in the diffraction pattern (Table 1).

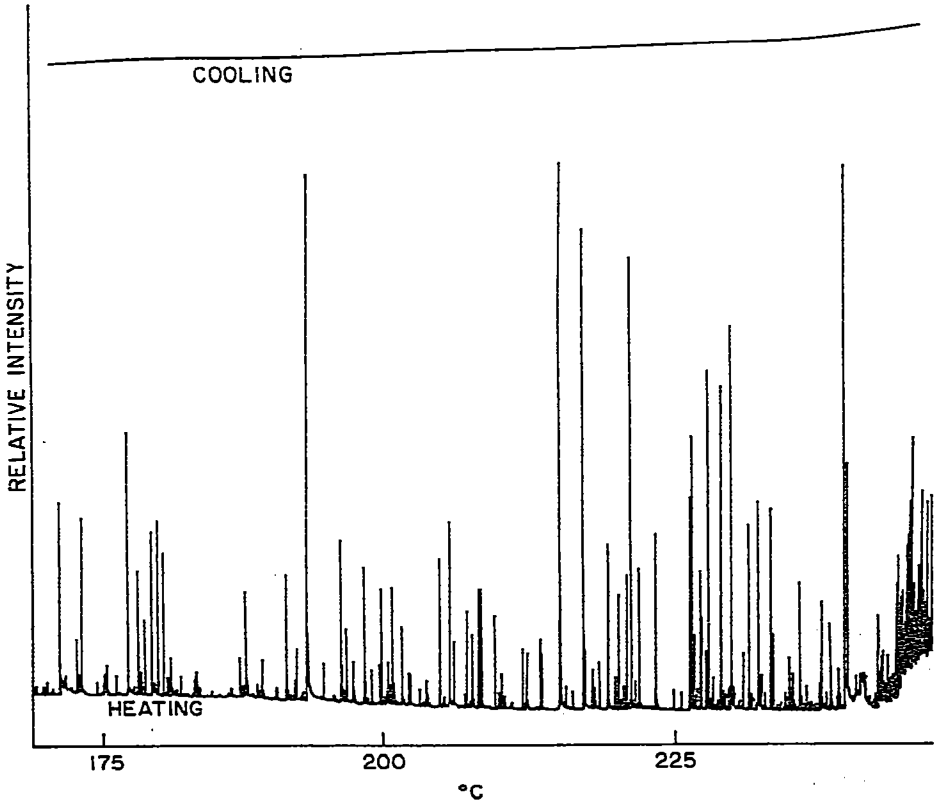

Fig. 3. Relative intensity of the mass 18 peak (H_2O^+) as a function of temperature for $Cs_2S_2O_6$ heated and cooled in vacuum.

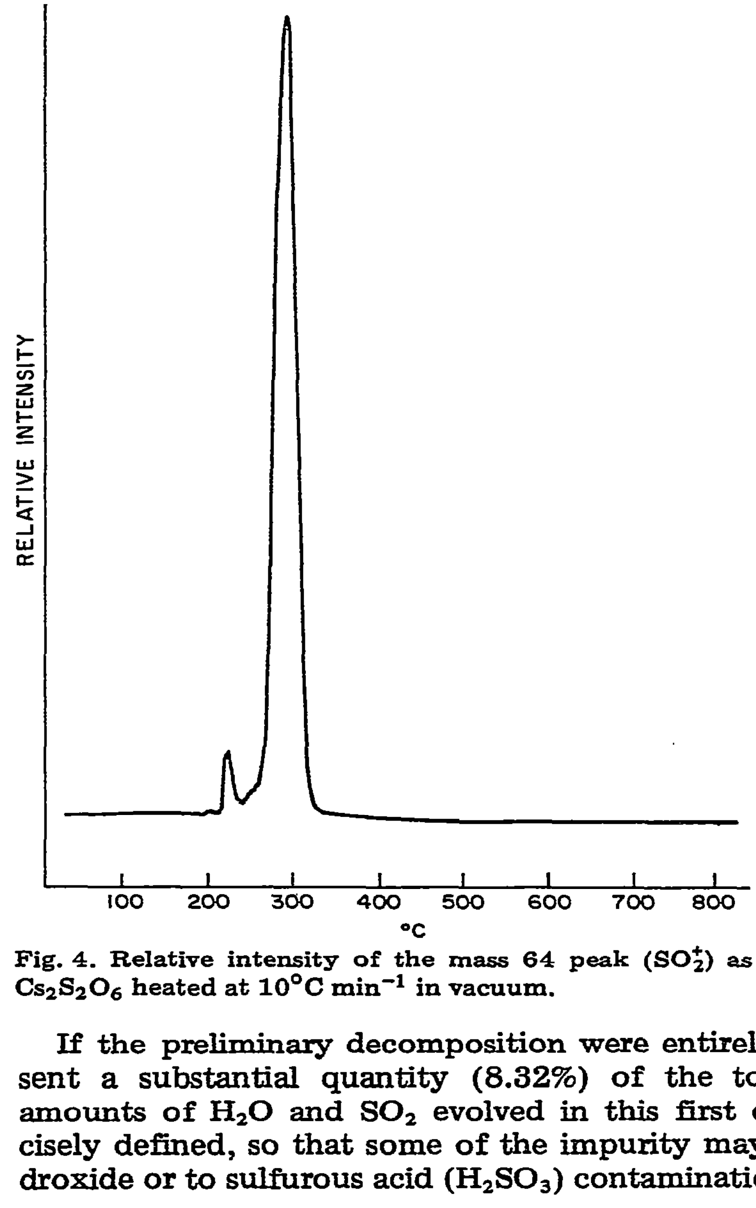

Fig. 4. Relative intensity of the mass 64 peak (SO_2^+) as a function of temperature for $Cs_2S_2O_6$ heated at 10°C min^{-1} in vacuum.

If the preliminary decomposition were entirely SO_2 then it would represent a substantial quantity (8.32%) of the total SO_2 lost. The relative amounts of H_2O and SO_2 evolved in this first decomposition are not precisely defined, so that some of the impurity may be due to a hydrate or hydroxide or to sulfurous acid (H_2SO_3) contamination.

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