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THERMAL DECOMPOSITION OF STRONTIUM NITRITE MONOHYDRATE

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ABSTRACT

Thermogravimetry and differential thermal analysis in N_2 and mass spectrographic evolved gas analysis in vacuum were performed on $Sr(NO_2)_2 \cdot H_2O$. The results in N_2 indicate a single step loss of water at around 150°C followed by a $\text{solid}_1 \rightarrow \text{solid}_2$ phase transition in the anhydrous $Sr(NO_2)_2$ at around 265°C and subsequent melting at about 365°C. There is a very slight decomposition commencing even before melting which becomes more significant at 500°C and very rapid above 650°C. The final product is cubic SrO as identified by powder X-ray diffraction. EGA studies of the decomposition in a vacuum were consistent but indicated lower temperatures of dehydration and particularity of decomposition. The quantities of product gases evolved during the complex decomposition region followed the order $NO \gg NO_2 \approx O_2 > N_2 > N_2O$. $Sr(NO_3)_2$ is a probable intermediate species during the decomposition.

INTRODUCTION

The thermal stability of $Sr(NO_2)_2 \cdot H_2O$ is of interest because of its piezoelectric and pyroelectric properties [1]. Thermogravimetry (TG), differential thermal analysis (DTA), and mass spectrographic evolved gas analysis (EGA) are used to investigate the thermal decomposition of the powder. Earlier work describes the structure and nature of the $\text{solid}_1 \rightarrow \text{solid}_2$ phase transition in the anhydrous material [2].

EXPERIMENTAL PROCEDURES AND RESULTS

Fine crystals of $Sr(NO_2)_2 \cdot H_2O$ were prepared by recrystallization from aqueous solution. Reagent grade $Sr(NO_3)_2$ was used.

A Perkin-Elmer furnace (Model TGS-2) and controller (System 4) were used in conjunction with a Cahn (Model 1000) electrobalance. The digital data acquisition/computer system, was a Fluke (Model 2450). The heating rate was 10°C min^{-1} in a flow of N_2 at 40 ml min^{-1}. Figures 1 and 2 present

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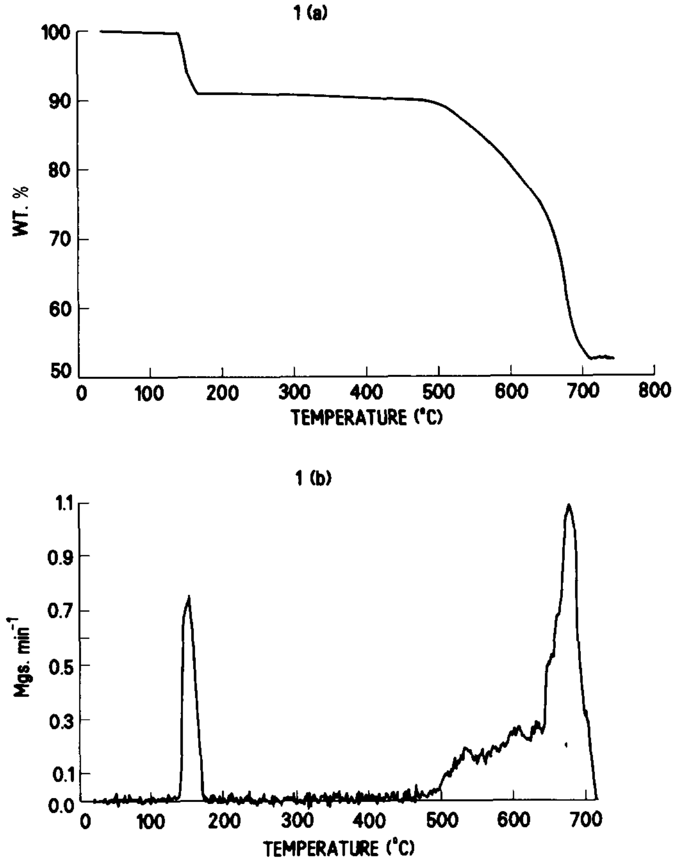

Fig. 1. Thermogravimetric and differential thermogravimetric curves for 18.42 mg of $Sr(NO_2)_2 \cdot H_2O$ heated in N_2 at 10°C min^{-1}.

thermograms and their calculated derivative (DTG), for $Sr(NO_2)_2 \cdot H_2O$ and $Sr(NO_3)_2$, respectively. The derivative was calculated by taking each digital point, except for the first and last, and the point on either side; fitting a parabola to these three points ($mg = a_1(s)^2 + a_2(s) + a_3$); and determining the derivative analytically, $d(mg)/d(s) = 2a_1(s) + a_2$.

A Perkin-Elmer (Model DTA-1700) was used for the DTA study. A flow of 50 ml min^{-1} of N_2 was maintained and the heating rate was 10°C min^{-1}. The Pt sample cups were used and Al_2O_3 was the reference material. The same digital data acquisition/computer was used as above. The resulting DTA curve for $Sr(NO_2)_2 \cdot H_2O$ is shown in Fig. 3.

The apparatus used for EGA has been described elsewhere [3]. A subsequent addition was a UTI programmable peak selector which allowed the frequent monitoring of selected atomic mass units (AMU) and storage of the data along with temperature and total pressure in a digital format for

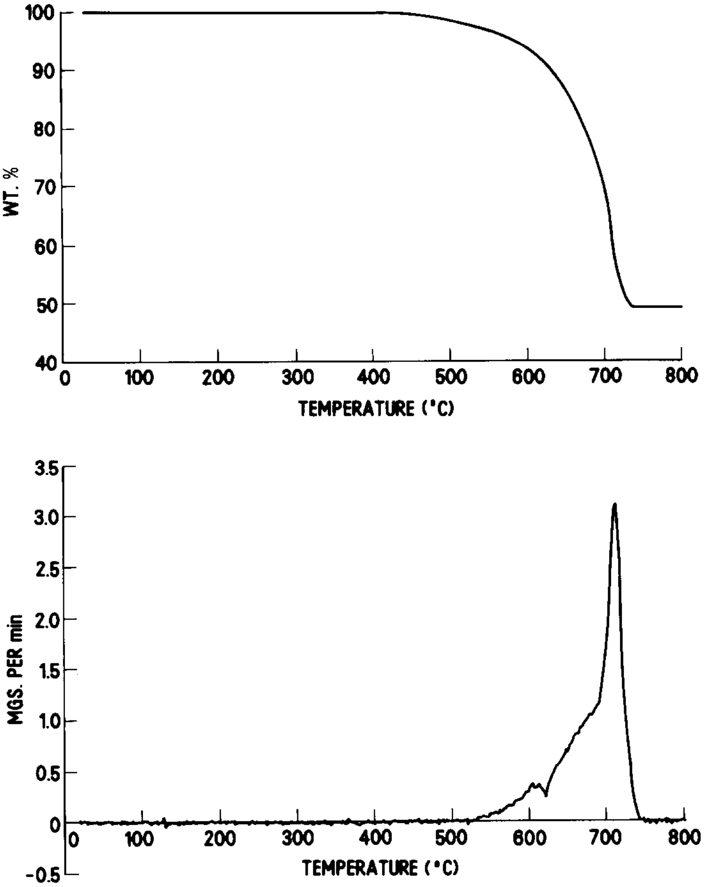

Fig. 2. Thermogravimetric and differential thermogravimetric curves for 30.2 mg $Sr(NO_3)_2$ heated in N_2 at 10°C min^{-1}.

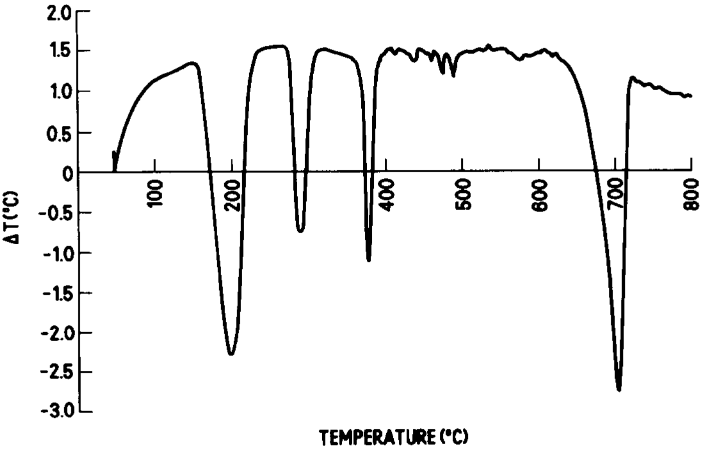

Fig. 3. Differential thermal analysis curve for 42.24 mg of $Sr(NO_2)_2$ H_2O heated in N_2 at 10°C min^{-1}.

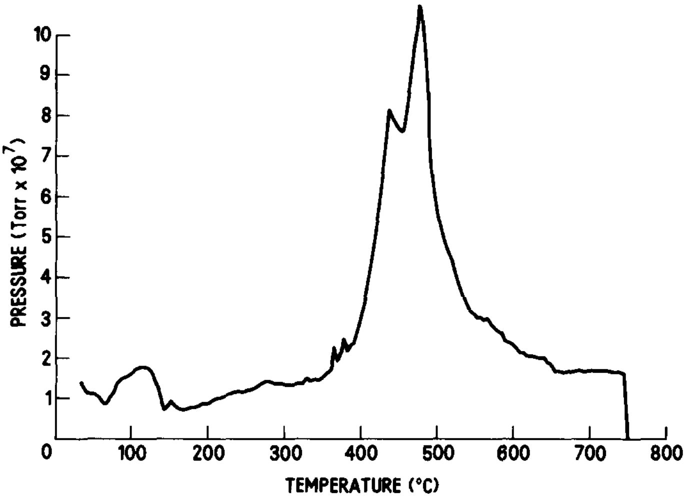

Fig. 4. Total pressure during evolved gas analysis of 2.74 mg of $Sr(NO_2)_2 \cdot H_2O$ heated in a vacuum at 10°C min^{-1}.

subsequent processing by the data acquisition/computer system. A general cyclic scan was made over the range of 1–100 AMU using conventional analog recording during a linear temperature program of 10°C min^{-1} to 1000°C. This provided information for selection of the relevant peaks to investigate in the digital programmed mode. Two scans at 10°C min^{-1} using nearly identical sized samples were necessary to obtain the desired information. Selected results are plotted in Figs. 4–6.

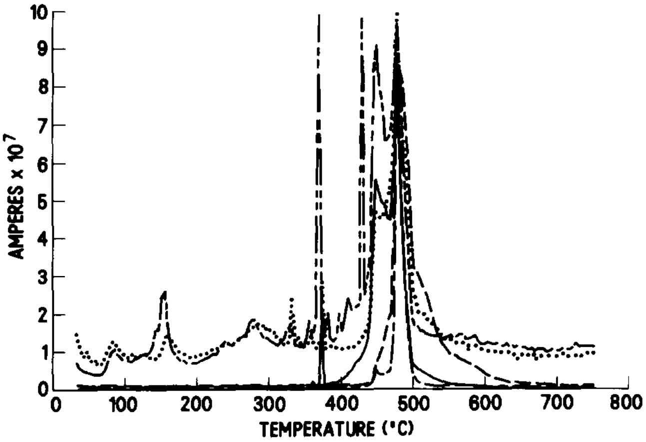

Fig. 5. Selected curves for evolved gas analysis of 2.74 mg of $Sr(NO_2)_2 \cdot H_2O$ heated in a vacuum at 10°C min^{-1}. (————) AMU = 30; (– – – – –) AMU = 46(×14); (— — —) AMU = 32(×14); (-----) AMU = 28(×40); (· · · · · ·) AMU = 44(×80).

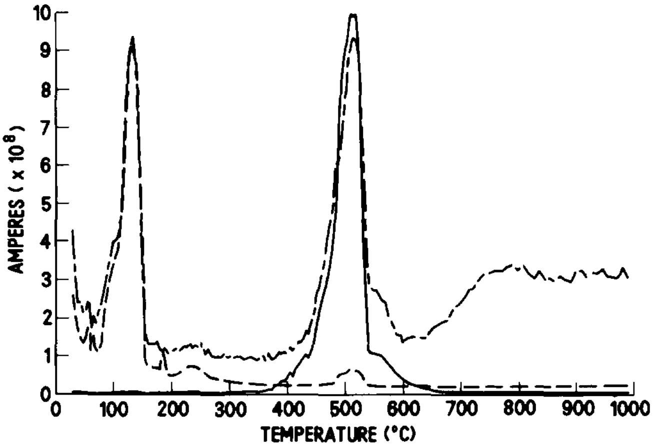

Fig. 6. Selected curves for evolved gas analysis of 2.73 mg of $Sr(NO_2)_2 \cdot H_2O$ heated in a vacuum at 10°C min^{-1}. (————) AMU = 14; (- - - - -) AMU = 2(×12); (— — —) AMU = 18(÷4).

X-ray diffraction results were obtained using a Philips APD 3600 system and Cu K_2 radiation. The composition of the residue from the DTA experiment was verified by comparison with data from the JCPD files. A computer generated comparison is presented in Fig. 7. The file (6-520) used for the comparison is that of cubic (NaCl structure) SrO.

DISCUSSION

The dehydration is straightforward with an apparent single step loss of water at around 150°C. The solid state phase transition in the anhydrous

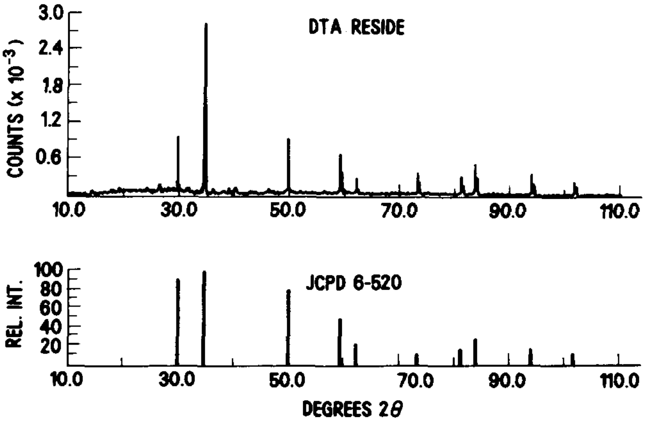

Fig. 7. Powder X-ray diffraction data of the product at 800°C compared with JCPD pattern for cubic SrO(Cu K_2 radiation).

nitrite at around 265°C is from an orthorhombic to a cubic structure and has been extensively discussed in previous work [2]. The temperatures of the two events reported here are in excellent agreement with the observations of Warrington, et al. [4].

The complexity of the decomposition of anhydrous alkaline earth nitrites has been well recognized [4–6]. A single decomposition scheme such as eqn. (1) can be conceived

$$Sr(NO_2)_2 \rightarrow SrO + NO + NO_2 \qquad (1)$$

However, the data in Fig. 1 obviously indicate that the process is not a smooth continuous one and the results of the EGA in Figs. 4–6 clearly do not support a simple mechanism as indicated by eqn. (1). Oxidation and reduction processes must be involved since substantially more NO is evolved then NO_2 and other species such as N_2, N_2O and O_2 are formed at times and in amounts completely inconsistent with mass spectrographic cracking patterns as their source. The reduced species of N_2 and N_2O seem more prevalent at earlier stages while O_2 is evolved last.

Stern [5] in his extensive review of nitrate and nitrite decompositions suggests ways in which $Sr(NO_3)_2$ may be formed as an intermediate in the decomposition of the nitrite. These speculations are based upon the reaction of product gases with the starting nitrite, eqns. (2) and (3), or oxide product, eqn. 4

$$Sr(NO_2)_2 + 2\ NO_2 \rightarrow Sr(NO_3)_2 + 2\ NO \qquad (2)$$

$$Sr(NO_2)_2 + 2\ NO \rightarrow Sr(NO_3)_2 + N_2 \qquad (3)$$

$$SrO + 3\ NO_2 \rightarrow Sr(NO_3)_2 + NO \qquad (4)$$

Equations (5) or (6) are written

$$2\ Sr(NO_2)_2 \rightarrow Sr(NO_3)_2 + SrO + NO + \tfrac{1}{2}\ N_2 \qquad (5)$$

$$2\ Sr(NO_2)_2 \rightarrow Sr(NO_3)_2 + SrO + N_2O \qquad (6)$$

to produce the nitrate and reduced species of nitrogen directly. The product gases would certainly be swept away rapidly in the vacuum present during the EGA and hence some form of direct formation as suggested by eqns. (5) or (6) seems more probable. However, if eqns. (2)–(4) are favorable it is not clear why the nitrate should not form directly. The great thermal instability of SrO_2 makes it a highly improbable intermediate [7].

The thermal decomposition of $Sr(NO_3)_2$ is seen in Fig. 2 to occur at a slightly higher temperature than that observed for the nitrite. Because any nitrate formed as an intermediate during the decomposition of the nitrite would be in a highly reactive, finely dispersed stage, a slight lowering of the observed temperature of decomposition would be completely consistent.

Clearly there are competing pathways or mechanisms during the decomposition of $Sr(NO_2)_2$ which give rise to a variety of product gases. It would, however, require a considerably more detailed study than that performed herein to completely elucidate this process. Under such circumstances the nature and concentration of intermediate species would be highly dependent upon the experimental parameters, particularly those which control the concentration of gaseous products in the immediate environment of the solid products and reactants, i.e., heating rate, gas flow, packing density, etc.

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