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THERMAL STUDIES ON DITHIONATE COMPOUNDS. I. DITHIONATES OF CALCIUM, STRONTIUM AND BARIUM

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ABSTRACT

The decomposition of $CaS_2O_6 \cdot 4\ H_2O$, $SrS_2O_6 \cdot 4\ H_2O$ and $BaS_2O_6 \cdot 2\ H_2O$ was studied using TG and DTG. After dehydration, the decomposition of the anhydrous compounds involves the loss of sulfur dioxide to give the stable metal sulfates as the final products. Dehydration of $SrS_2O_6 \cdot 4\ H_2O$ takes place in two steps while that of calcium and barium dithionates takes place in one step. Kinetic and thermal parameters for these reactions are presented.

INTRODUCTION

Although Tammann and Boehone [1] determined the dehydration and decomposition temperatures of several dithionates as early as 1932, detailed studies on the decomposition of dithionates were not carried out until 1972. Decomposition studies on sodium, cesium and calcium dithionates show that the decomposition of dithionates proceeds with the evolution of sulfur dioxide [2,3]. However, these studies did not report any detailed information on the evaluation of the non-isothermal kinetic parameters. In the present report, the thermal behavior and the evaluation of non-isothermal kinetic parameters for the decomposition of calcium, strontium, and barium dithionates are described.

EXPERIMENTAL

The $CaS_2O_6 \cdot 4\ H_2O$, $SrS_2O_6 \cdot 4\ H_2O$ and $BaS_2O_6 \cdot 2\ H_2O$ used in this work were prepared as described by Pfanstiel [4] and were purified by recrystallization from aqueous solution. TG studies were carried out in a nitrogen atmosphere using a Perkin–Elmer thermogravimetric system Model TGS-2. The procedures employed were similar to those described previously [5].

Kinetic parameters were obtained by analyzing the TG data using the

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Coats and Redfern equations [6].

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right]=\ln\frac{AR}{E\beta}\left(1-\frac{2RT}{E}\right)-\frac{E}{RT} \tag{1}$$

and for the case where $n = 1$

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right]=\ln\frac{AR}{E\beta}\left(1-\frac{2RT}{E}\right)-\frac{E}{RT} \tag{2}$$

where α is the fraction of the reaction completed, E is the activation energy, β is the heating rate, T is the temperature (K), A is the frequency factor, and R is the molar gas constant. Calculations were carried out by computer using a FORTRAN program.

RESULTS AND DISCUSSION

Figures 1–3 show the TG and DTG curves for $CaS_2O_6 \cdot 4\ H_2O$, $SrS_2O_6 \cdot 4\ H_2O$ and $BaS_2O_6 \cdot 2\ H_2O$, respectively. The TG curves show that the

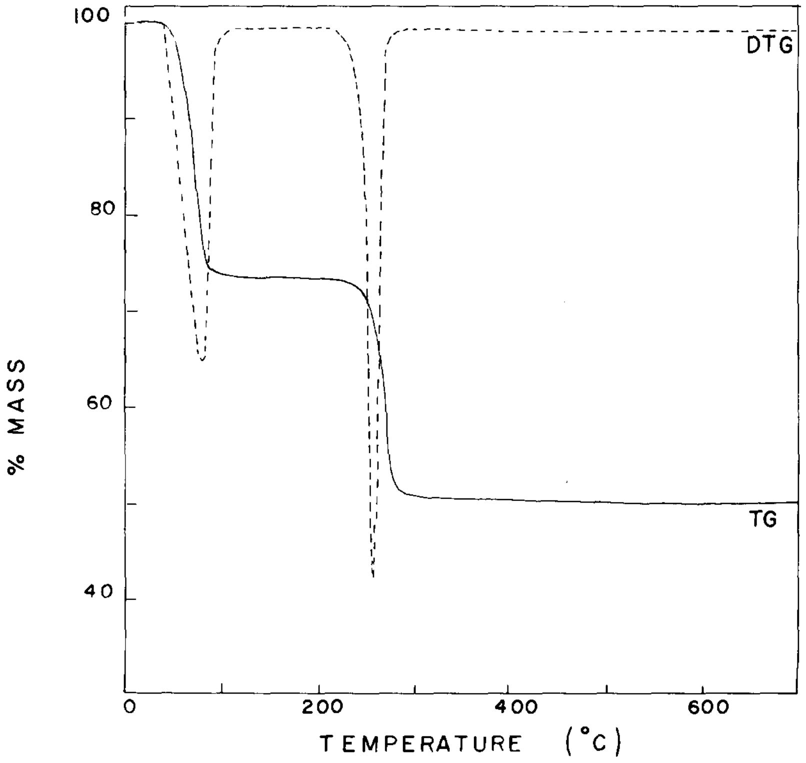

Fig. 1. TG and DTG curves for $CaS_2O_6 \cdot 4\ H_2O$.

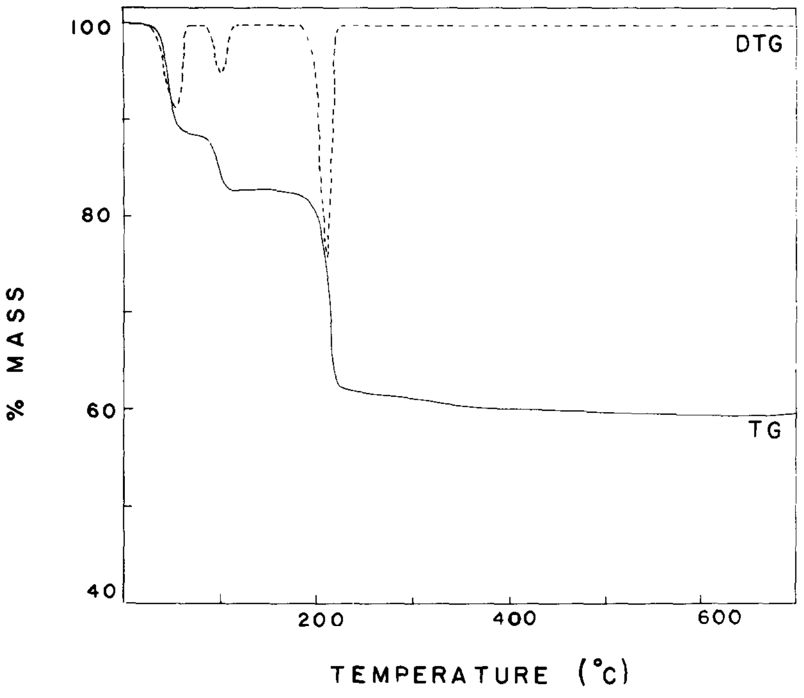

Fig. 2. TG and DTG curves for $SrS_2O_6 \cdot 4\ H_2O$.

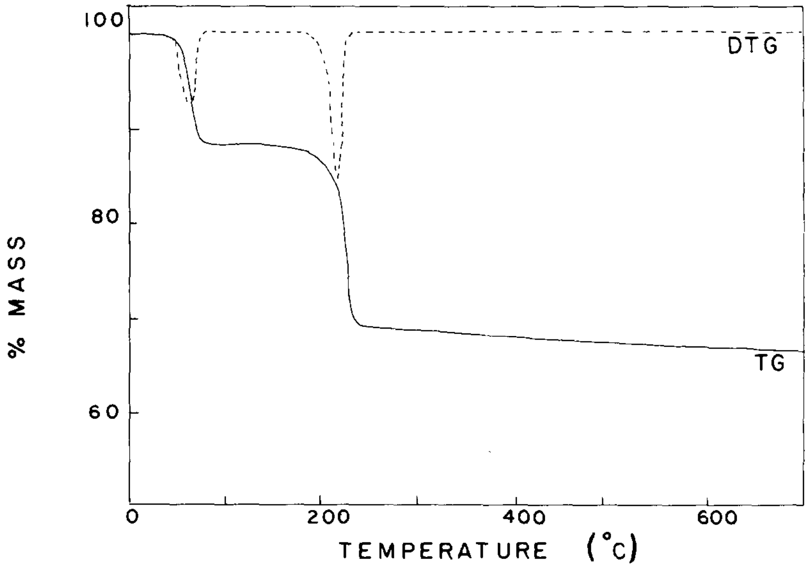

Fig. 3. TG and DTG curves for $BaS_2O_6 \cdot 2\ H_2O$.

decomposition of calcium and barium dithionates takes place in two distinct steps while that of strontium dithionate takes place in three distinct steps. In the case of $CaS_2O_6 \cdot 4\ H_2O$ and $BaS_2O_6 \cdot 2\ H_2O$, dehydration occurs completely in one step followed by a loss of sulfur dioxide leaving the stable metal sulfates as final products. These reactions can be represented by eqns. (3–6).

$$CaS_2O_6 \cdot 4\ H_2O(s) \rightarrow CaS_2O_6(s) + 4\ H_2O(g) \tag{3}$$

$$CaS_2O_6(s) \rightarrow CaSO_4(s) + SO_2(g) \tag{4}$$

$$BaS_2O_6 \cdot 2\ H_2O(s) \rightarrow BaS_2O_6(s) + 2\ H_2O(g) \tag{5}$$

$$BaS_2O_6(s) \rightarrow BaSO_4(s) + SO_2(g) \tag{6}$$

In each case, several individual samples were analyzed and the linear regression analysis of the data to fit the Coats and Redfern equations [eqns. (1) and (2)] indicated that the dehydration processes were first order reactions. The same analysis also showed that for $CaS_2O_6 \cdot 4\ H_2O$ and $BaS_2O_6 \cdot 2\ H_2O$, the activation energy for the dehydration reactions were 105.8 and 158.0 kJ mole^{-1}, respectively. Table 1 shows the thermal parameters for the decomposition of the dithionates of calcium and barium.

The dehydration of hydrated calcium dithionate begins near 35°C and is completed near 105°C. The equivalent reaction for BaS_2O_6 takes place between 45 and 80°C.

For $SrS_2O_6 \cdot 4\ H_2O$, the analysis of TG curves shows that the dehydration reaction takes place according to eqns. (7) and (8). Like the dithionates of calcium and barium, anhydrous strontium dithionate also loses sulfur dioxide in the final decomposition process between 175 and 230°C [eqn. (9)].

$$SrS_2O_6 \cdot 4\ H_2O(s) \rightarrow SrS_2O_6 \cdot H_2O(s) + 3\ H_2O(g) \tag{7}$$

TABLE 1.

Thermal parameters for the decomposition of $CaS_2O_6 \cdot 4\ H_2O$, $SrS_2O_6 \cdot 4\ H_2O$ and $BaS_2O_6 \cdot 2\ H_2O$

Eqn.	Temp. range (°C)	Mass loss		Order of reaction	E_a (kJ mole^{-1})	Corr. coeff.
		Calcd. (%)	Obsd. (%)			
$CaS_2O_6 \cdot 4\ H_2O$						
(3)	35–103	26.5	25.5	1	105.8	0.9990
(4)	220–290	23.5	24.4	2/3	301.4	0.9953
$SrS_2O_6 \cdot 4\ H_2O$						
(7)	35–85	16.9	16.7	1	104.9	0.9987
(8)	90–130	5.6	5.6	2/3	156.8	0.9929
(9)	174–230	20.0	19.6	2/3	293.0	0.9896
$BaS_2O_6 \cdot 2\ H_2O$						
(5)	46–82	10.8	10.5	1	158.0	0.9970
(6)	162–260	19.2	18.8	1/3	194.0	0.9940

$$SrS_2O_6 \cdot H_2O(s) \rightarrow SrS_2O_6(s) + H_2O \tag{8}$$

$$SrS_2O_6(s) \rightarrow SrSO_4(s) + SO_2 \tag{9}$$

Linear regression of the data using the Coats and Redfern equations showed that the first step of the dehydration reactions in $SrS_2O_6 \cdot 4\ H_2O$ follows a first order process and the energy of activation for this process was 104.9 kJ $mole^{-1}$. Kinetic parameters for dehydration and decomposition of the strontium compound are also shown in Table 1.

The results of this work show that the activation energy for the loss of sulfur dioxide from Group IIA metal dithionates decreases as the size of the cation increases. However, there is not a linear relationship between these parameters.

According to Papazian et al. [2], after dehydration the anhydrous CaS_2O_6 begins to decompose at 215°C in vacuum and at 230°C in air. In the present work, the results show that the anhydrous CaS_2O_6 starts to decompose at 220°C in a nitrogen atmosphere. Therefore, it can be concluded that the dithionate of calcium seems to be more stable in air than in vacuum or nitrogen atmosphere. The differences are slight, however, and may be the result of procedural differences.

The data obtained in this work were also analyzed by the Reich and Stivala iterative method to find the correct order and activation energy [7]. However, for some reason, the correlation coefficients obtained when the intercept reaches zero were extremely low and the values of n were unrealistically high. We have observed for other systems that the iterative method may produce an intercept near zero but as the intercept converges to zero, the correlation coefficient diverges. Thus, the iterative method produces an n value but the fit of the data is no longer close to linear. In the same cases, the Coats and Redfern method may give a nearly linear fit to the data with an entirely different value of n. It seems that there is some peculiar property of error magnification in the iterative method where ratios of the data are taken. We are currently examining the numerical properties of these data-treatment methods in detail. In the present case, the decomposition patterns of the dithionates were reproducible and the correlation coefficients obtained using the Coats and Redfern equations were in the range 0.990–0.999 for the correct value of n.

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