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OBSERVATIONS ON THE THERMAL DECOMPOSITION OF SOME DITHIONATES AND SULFITES

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ABSTRACT

The thermal decomposition of sodium and calcium dithionates has been studied in air and in vacuum. Calcium sulfite and sodium hydrogen sulfite were studied in vacuum. In vacuum, simultaneous thermogravity (TG) and effluent gas analysis (EGA) were carried out. For the dithionates, higher activation energies were observed in air than in vacuum, and only one activation energy was observed in vacuum in each case. The results suggest that SO is a fairly common product of the decomposition of sulfur oxy-acids and their salts.

INTRODUCTION

There is a paucity of literature on the thermal decomposition of dithionate salts, and it is generally considered that decomposition proceeds with the evolution of SO_2. In 1932, Tammann and Boehme[1] determined dehydration and decomposition temperatures of several dithionates. In 1934, Schreiber[2] carried out a similar study with emphasis on dehydration.

Recently, it has been shown[3] that thermal decomposition of aluminum and hafnium sulfates proceeds with the evolution of SO as a primary product. Therefore, it is of interest to inquire as to whether SO evolution is peculiar to sulfate decompositions. Observations on the thermal decomposition of dithionates of sodium and calcium, in air and in vacuum, are presented here. Somewhat less detailed observations on the decomposition of sodium hydrogen sulfite and calcium sulfite are also included.

EXPERIMENTAL

The sodium dithionate ($Na_2S_2O_6 \cdot 2H_2O$) used was the Fisher Scientific's Purified Grade, and it was further purified by recrystallization. Calcium dithionate ($CaS_2O_6 \cdot 4H_2O$) was prepared from the sodium salt. The sodium hydrogen sulfite ($NaHSO_3$) used was Merck's Reagent Grade. Calcium sulfite ($CaSO_3 \cdot 2H_2O$) was prepared by addition of calcium hydroxide solution to a solution of sodium sulfite.

Simultaneous thermal analysis and effluent gas analysis (EGA) was carried out using a system and methods previously described[3,4].

RESULTS

Calcium dithionate

In air, dehydration begins near 50 °C and is completed by 125 °C. The calculated weight loss is 26.4% and the observed value was 26.1%. In vacuum, dehydration takes place at ambient temperature.

The calculated weight loss for the decomposition of the anhydrous salt to the sulfate is 32.0%. The observed value in air was 30.9%, and in vacuum it was 31.8%. In vacuum the salt begins to decompose almost immediately upon dehydration with rapid decomposition (as noted by DTG) beginning at 215 °C. Decomposition is completed by 275 °C. In air the dithionate is more stable. Decomposition begins near 230 °C with rapid decomposition near 255 °C, and it is completed by 300 °C.

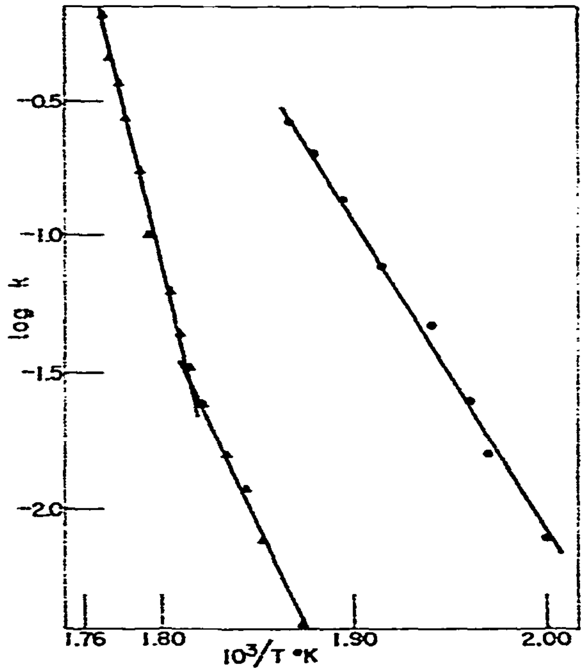
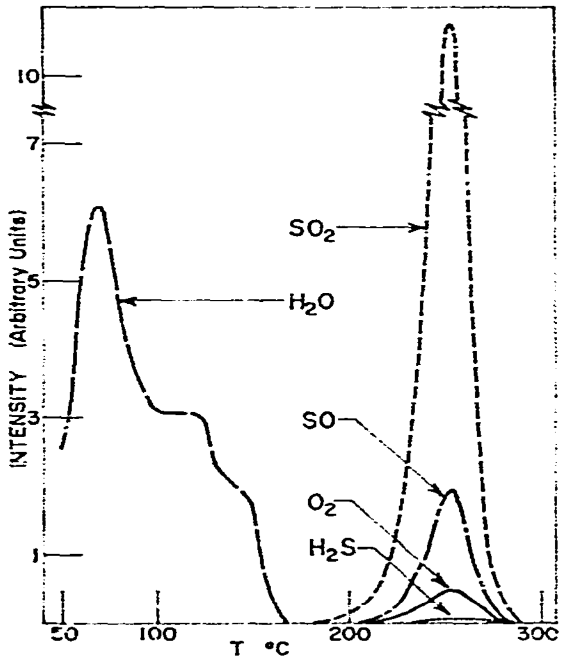


Fig. 1. Arrhenius relations in air and in vacuum for CaS_2O_6: ●—●, in vacuum; ▲—▲, in air.

The differences in stability are apparent in the Arrhenius relationships shown in Fig. 1. Both curves encompass about 80% of weight loss and are of apparent order 1. In vacuum, the activation energy is 52 kcal mole^{-1}. In air, there are two activation energies; 74 kcal mole^{-1} and, at higher temperatures, 131 kcal mole^{-1}.

During decomposition in vacuum, effluent gas analysis (EGA) was carried out. The EGA is shown in Fig. 2, where the results for SO and O_2 have been corrected for the cracking pattern of SO_2. The results are similar to those for the sulfate decompositions reported earlier[3]. However, a trace amount of H_2S is observed here, whereas in the sulfate work no H_2S was observed.



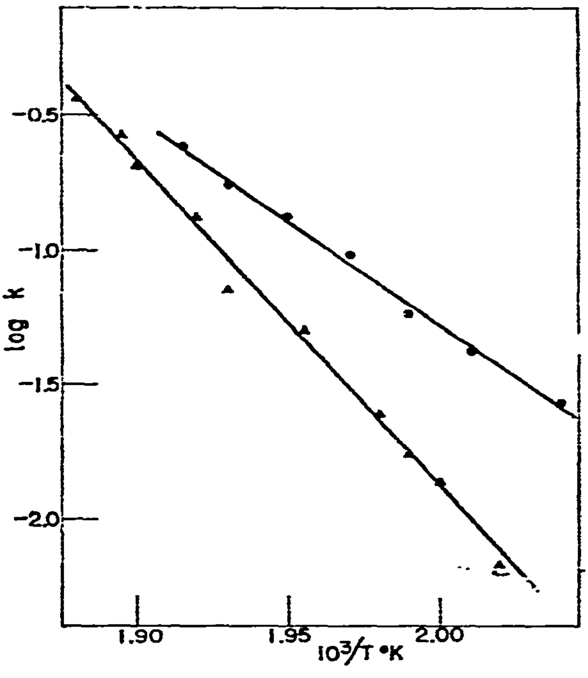


Fig. 2. Effluent gas analysis of CaS_2O_6.

Fig. 3. Arrhenius relations in air and in vacuum for $Na_2S_2O_6$: ●—●, in vacuum; ▲—▲, in air.

In both air and in vacuum, DTA indicates a small exotherm during the decomposition of the anhydrous salt.

Sodium dithionate

In air, dehydration begins near 40°C and is completed by 110°C. The calculated weight loss is 14.9% and the observed value, 14.7%. As with the calcium salt, in vacuum, dehydration begins at ambient temperature; however, in contrast to the calcium salt the last vestiges of water are removed with the beginning of decomposition of the dithionate (see Fig. 4).

The calculated weight loss for the decomposition of the anhydrous salt to the sulfate is 31.0%. The observed value in air was 30.2%, and in vacuum it was 30.7%. In both air and in vacuum, rapid decomposition begins near 190°C and is completed by 270°C. The Arrhenius relationships are shown in Fig. 3. Both curves encompass about 85% of weight loss and are of apparent order 1/2. In vacuum, the activation energy is 39 kcal $mole^{-1}$, and in air, it is 54 kcal $mole^{-1}$.

The EGA is shown in Fig. 4 where, as for Fig. 2, the results for SO and O_2 have been corrected for the contributions from SO_2. As with the calcium salt, a small amount of H_2S is observed.

In contrast to the calcium salt, DTA indicates an endotherm during decomposition of the anhydrous sodium dithionate.

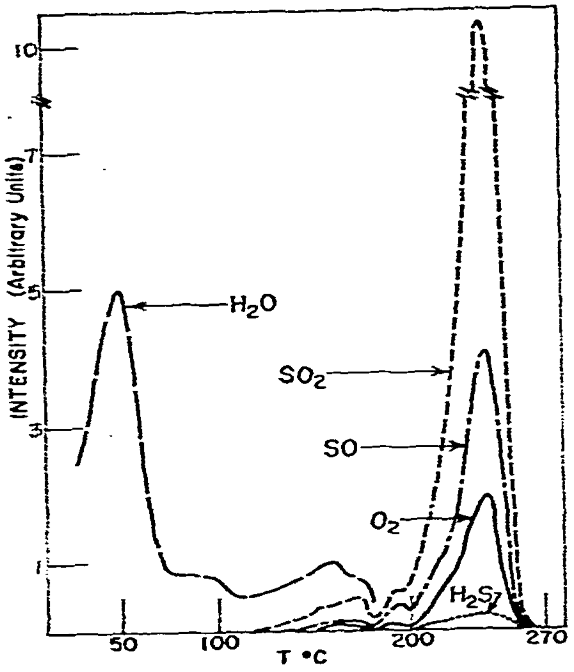
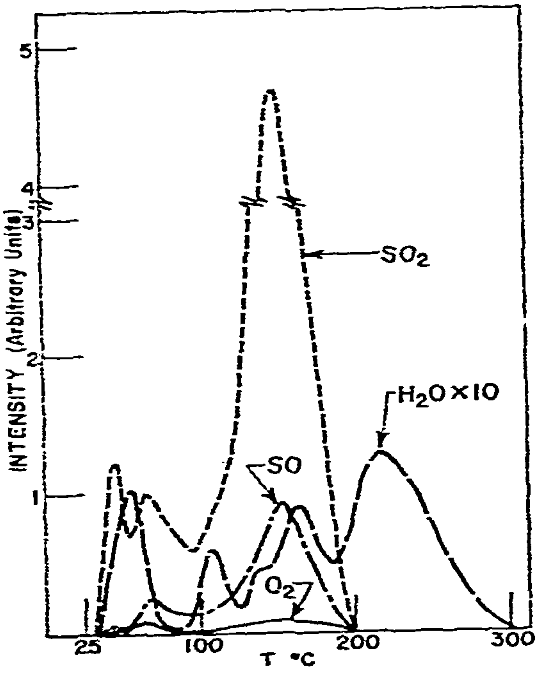


Fig. 4. Effluent gas analysis of $Na_2S_2O_6$.



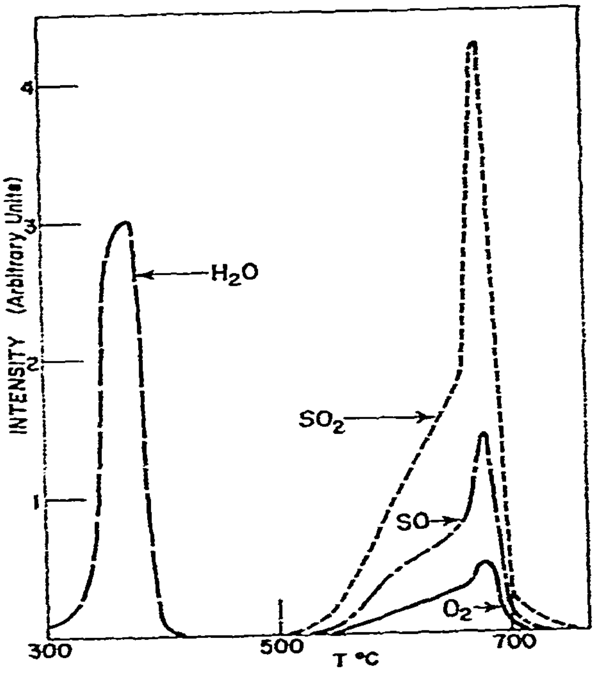


Fig. 5. Effluent gas analysis of $NaHSO_3$.

Fig. 6. Effluent gas analysis of $CaSO_3$.

Calcium sulfite and sodium hydrogen sulfite

The two materials were examined in vacuum, mainly to determine whether SO was a decomposition product.

Sodium hydrogen sulfite begins to decompose almost immediately upon initiation of heating. The EGA is shown in Fig. 5. Clearly, the decomposition is very complex. At the end of the decomposition (200°C), the weight loss is 27.9%, and further dehydration of the product (Fig. 5) accounts for 1.1% additional weight loss. The resulting product or product mixture begins to decompose near 780°C and this decomposition is not complete at the temperature limit of the furnace (1000°C). The EGA of this decomposition contains SO_2, SO, O_2, and H_2S. The H_2S peak intensity is about equal to the SO. The peak intensities for SO_2 and SO are about 15% of the peak intensities at 150°C for the precursor.

Fig. 6 shows the EGA for calcium sulfite. Dehydration begins near 300°C and is completed by 425°C. The anhydrous salt begins to decompose near 500°C and is completed near 750°C. The decomposition is complex; the DTG and EGA suggest that four steps are probably involved.

DISCUSSION

If the decomposition behavior of the dithionates studied here is compared with that of the sulfates investigated earlier[3], certain differences can be observed. For both dithionates higher activation energies were observed in air than in vacuum, while for the sulfates, the activation energies in air and vacuum were comparable. For both dithionates, only one activation energy was observed in vacuum. While a single activation energy was observed for the decomposition of hafnium sulfate, two values were observed in the case of aluminum sulfate.

The principal difference between the results observed for sulfates and those for the various sulfur oxy-acid salts studied here is concerned with H_2S evolution. Hydrogen sulfide can come from the reaction of SO with water according to the equation

$$3SO + H_2O \rightarrow H_2S + 2SO_2.$$

If this is the source of the H_2S observed, then it appears that for the salts studied here, dehydration is completed only after the onset of decomposition of the partially dehydrated salt. Since the anhydrous sulfates decompose at considerably higher temperatures than the other sulfur oxy-acid salts studied here, there is no overlapping of the dehydration and decomposition processes, and thus, no water available for reaction with SO. This explanation, however, does not account for the presence of significant amounts of H_2S at temperatures above 700°C in the EGA of sodium hydrogen sulfite.

From the EGA results for all four salts studied here, it appears that the decomposition mechanisms involved are more complex than for sulfates, and the decomposition of sodium hydrogen sulfite is obviously the most complex.

There is evidence in the literature[5] that SO is a product of the decomposition of several types of compounds—thionyl halides (SOX_2), polysulfur- and polysulfane-oxides, and polythionic acids. The indirect nature of the evidence has, in some cases, been the cause of considerable doubt. The results of the present study, along with those of the earlier work on sulfates[3], indicate that SO is a far more common product of the decomposition of sulfur oxy-acids and their salts than is generally assumed.

REFERENCES

1 G. Tammann and W. Boehme, *Z. Anorg. Chem.*, 204 (1932) 143.
2 J. Schreiber, *Ann. Chem.*, 1 (1934) 129.
3 H. A. Papazian, P. J. Pizzolato, and R. R. Orrell, *Thermochim. Acta*, 4 (1972) 97.
4 H. A. Papazian, P. J. Pizzolato, and J. A. Patrick, *J. Amer. Ceram. Soc.*, 54 (1971) 250.
5 P. W. Schenk and R. Steudel, *Angew. Chem. Int. Ed. Engl.*, 4 (1965) 402.