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Note

On the thermal decomposition of alkali persulfates by derivatograph

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Persulfates or peroxydisulfates are among the most powerful and useful oxidizing agents known and are used mostly as the sodium and potassium salt ($Na_2S_2O_8$ and $K_2S_2O_8$). They are also important in the polymerization catalysis. The thermal decomposition of the peroxydisulfate involves two main reactions. These are (1) the loss of an oxygen molecule per two molecules of the salt giving the pyrosulfate ($Na_2S_2O_7$ and $K_2S_2O_7$) and (2) the decomposition of the pyrosulfate into sulfates and sulfur trioxide as the gaseous product[1].

Lorant[2] has suggested a mechanism for the decomposition of potassium persulfate on the basis of thermogravimetric data and analysis of the gaseous products. In this mechanism the pyrosulfate decomposes partially between 780 and 850°C into $K_4S_3O_{12}$ as an unstable intermediate which decomposes at higher temperatures into the sulfate. On the other hand De Varies and Gellings[3] have claimed about the detection of K_2SO_5 as an intermediate by X-ray diffraction lines. They have also stated that the initial decomposition temperature and the decomposition range at which the pyrosulfate converts into the sulfate depends on the heating rate used. Burmakina and Kuprii[4] have studied the decomposition of the persulfate into pyrosulfate radio-isotopically and shown that it involves a cleavage of the oxygen–oxygen bond of the original peroxy group located between the two sulfur atoms. Cleghorn and Davies[5] have examined the IR spectrum of the potassium salt after being heated at 220°C to constant weight. The spectrum corresponds closely to that for sodium pyrosulfate with a small little exception.

Most of the previous work has been concerned mainly with mechanism of decomposition as well as the temperature at which the reactions took place. The present work is concerned with the kinetics of the decomposition reactions as well as their thermodynamic nature using the derivatographic method of investigation[6].

EXPERIMENTAL

The materials studied were analytical grade: $Na_2S_2O_8$ and $K_2S_2O_8$ (Hopkin & Williams Analar). The samples were powdered in an agate mortar and dried at 80°C

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for about 20 min. This was followed immediately by the simultaneous thermogravimetry (TG), differential thermogravimetry (DTG), and differential thermal analysis (DTA), between 20 and 1000 °C.

The analyses were carried out in a Paulik-Paulik-Erdey MOM derivatograph under static (air) and nitrogen atmospheres. Samples of about 200 mg of the predried compounds were placed in platinum crucibles preheated to 1050 °C for 1 h. Heating rates used were 10, 5.8 °C min^{-1}. α-Al_2O_3 was used as a reference material after being heated to 1500 °C. In order to study the effect of sample weight on the mode of decomposition, 200, 250 and 400 mg samples were considered for this investigation.

For DTA calibration and the evaluation of the heat of reaction silver nitrate was employed as a standard material for the temperature range of 200 °C.

RESULTS AND DISCUSSION

Decomposition of $K_2S_2O_8$ and $Na_2S_2O_8$

A sharp weight loss is noticed at 200 °C for $K_2S_2O_8$ and between 200 and 225 °C for $Na_2S_2O_8$; it corresponds to the complete conversion of the peroxydisulfate into pyrosulfate, $K_2S_2O_7$ and $Na_2S_2O_7$:

$$K_2S_2O_8 \rightarrow K_2S_2O_7 + \tfrac{1}{2}O_2 \qquad (1)$$

$$Na_2S_2O_8 \rightarrow Na_2S_2O_7 + \tfrac{1}{2}O_2 \qquad (2)$$

The conversion process is highly heat generating and a big exotherm was recorded at the DTA curve (Figs. 1 and 2). Mechanistically the reaction begins endothermic because it involves the cleavage of O–O bond[4], as the rate determining step; but as soon as the oxygen atoms are produced each two combine liberating a large amount of heat: (O–O bond energy 118 kcal mol^{-1}).

As a result of this heat a noticeable increase in the reference temperature was observed (Fig. 3) as a small hump above the straight line of the regular heating rate.

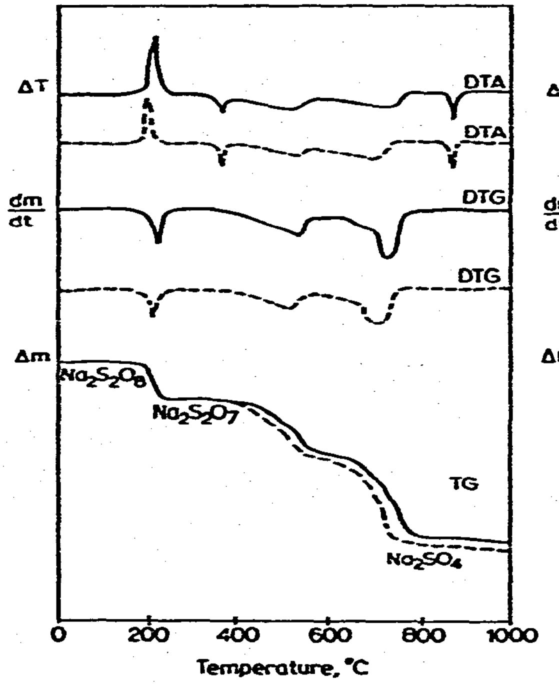
By utilizing the TG, DTG and T curves, E (activation energy) and n (reaction order) were estimated for the first stage of the decomposition reaction of sodium persulfate by means of the expression [7]

$$\Delta \log R_T = n\Delta \log W_r - (E/2.3\ R)\Delta(1/T) \qquad (3)$$

where R_T is the slope of the primary thermogram, TG which is simply the DTG; W_r is $W - W_c$, where W is the weight (mg) at time t, and W_c is the weight of sample at the end of the reaction. By keeping $\Delta(1/T)$ constant ($0.035\ 10^{-3}\ K^{-1}$), a linear relation was obtained from the plot of $\Delta \log R_T$ versus $\Delta \log W_r$, whose slope will give the value of n and whose intercept a value of E. By this method the values obtained for the decomposition of sodium persulfate into pyrosulfate are:

$$n = 2.15 \pm 0.15, \qquad E = 77\ \text{kcal mol}^{-1}$$

The heat of reaction was determined by measuring the DTA peak area and by referring to the heat of fusion of silver nitrate which occurs at 212 °C, i.e., at the same interval of temperature of the decomposition reaction[8]. The values obtained for the heats of decomposition of sodium and potassium persulfates into pyrosulfates are 81.1 and 79.0 kcal mol^{-1} respectively.



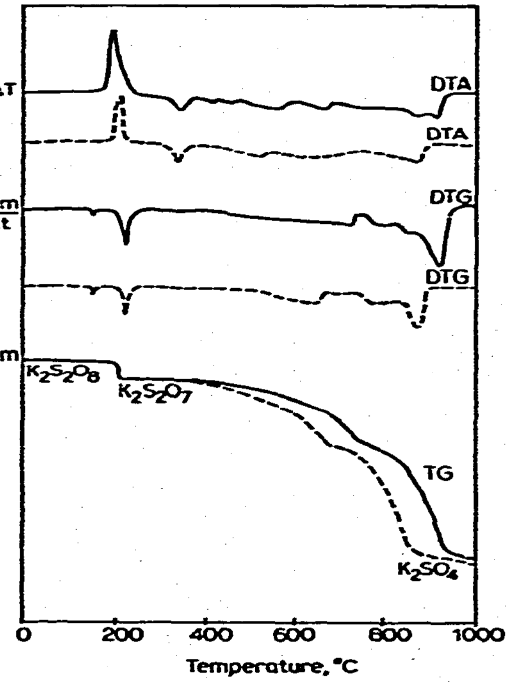


Fig. 1. Complex thermoanalytical curves of sodium persulfate. Full line at a heating rate of 10°C min^{-1}; broken line at 5.8°C min^{-1}.

Fig. 2. Complex thermoanalytical curves of potassium persulfate. Full line at 10°C min^{-1}; broken line at 5.8°C min^{-1}.

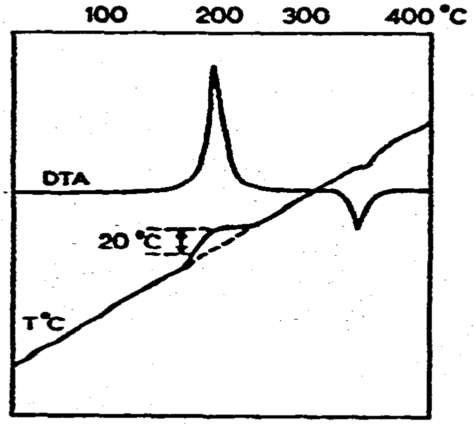


Fig. 3. The increase in the reference temperature due to heat evolved from the sample.

It is apparent that the values are close to each other which means that the reaction is characteristic of the persulfate group regardless of the character of the cation attached to it .The slight difference may be attributed to the difference between the lattice energies of the sodium and potassium salts.

Decomposition of $K_2S_2O_7$ and $Na_2S_2O_7$

Decomposition of pyrosulfates occurs in the melt. Potassium pyrosulfate melts at 340°C and sodium pyrosulfate at 380°C. For sodium pyrosulfate the decomposition follows the melting immediately at a considerable rate, while the initial decomposition of the potassium salt was noticed at 390°C, (50°C after melting) and proceeds slowly. During this 50°C interval the molten potassium pyrosulfate interacts with atmospheric oxygen and undergoes a 1.6% gain in weight. No such gain in weight was observed when nitrogen was allowed to flow in the reaction medium at a flow-rate of 20 ml $\min^{-1}$.

About 20% of potassium pyrosulfate decomposes into potassium sulfate between 390 and 640°C, while about 30% of sodium pyrosulfate decomposes between 380 and 540°C as partial surface decomposition. The remaining pyrosulfate decomposes at a rate twice as fast as the rate of the first stage for sodium pyrosulfate and four times for potassium pyrosulfate. The temperature ranges at which the decomposition takes place are listed in Table 1.

TABLE 1

THE TEMPERATURE RANGES OBTAINED FOR THE DECOMPOSITION OF SODIUM AND POTASSIUM PYROSULFATE[a]

Material	*Heating rate*	
	5.8°C $\min^{-1}$	*10°C $\min^{-1}$*
$K_2S_2O_7$	390–875°C	390–920°C
$Na_2S_2O_7$	380–750°C	380–790°C

[a] Each value is the mean of five determinations.

The process of pyrosulfate decomposition into sulfate and sulfur trioxide is almost reversible since smaller temperature ranges were recorded for the whole process at lower heating rates, i.e., at the low heating rate the gaseous product has greater chance to escape from the neighborhood of the product without accelerating the reverse reaction.

Thermodynamically the decomposition process is endothermic but kinetic measurements could not be performed on it because it takes a big interval of temperatures to complete and proceeds at varying rates.

As a correction on the Devaries–Gellings note[3] about the observation K_2SO_5 as an intermediate product in the pyrosulfate decomposition, we have found that the thermograms are not divided by the knee corresponding to K_2SO_5 formation. On the contrary the thermograms proceed very smoothly at the last stage of decomposition and this is a good evidence that no K_2SO_5 could be formed during the pyrosulfate decomposition. However, the diffraction line which led them to think of K_2SO_5 occurence may be ascribed to a certain phase. In this phase a physical interaction of some unevolved SO_3 (being embedded in the cooled product) with one of the principal species, sulfate or pyrosulfate.

CONCLUSION

The thermal decomposition of sodium and potassium persulfates into the corresponding pyrosulfates is exothermic by 81.1 and 79.0 kcal mol^{-1} respectively. The sample weight does not alter the shapes of the derivatograms greatly while the heating rate does. The pyrosulfates decompose straightly into the sulfate without any intermediate product formation.

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