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DECOMPOSITION OF SOLID PEROXYDISULFATES

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ABSTRACT

Conversion of ammonium and potassium peroxydisulfates to the pyrosulfates has been studied using DSC and TG. The TG curves show that both of these compounds lose oxygen in a single step. Extensive fragmentation of the crystals occurs as oxygen is lost. For conversion of $K_2S_2O_8$ to $K_2S_2O_7$, $\Delta H = -57.2 \pm 6.3$ kcal mol^{-1} and $E_a = 86.4 \pm 6.2$ kcal mol^{-1}. The heat of fusion of the $K_2S_2O_7$ produced was found to be 12.4 ± 2.6 kcal mol^{-1}. For conversion of $(NH_4)_2S_2O_8$ to the pyrosulfate, $\Delta H = -82.8 \pm 8.3$ kcal mol^{-1} and $E_a = 65.4 \pm 6.7$ kcal mol^{-1}.

INTRODUCTION

Peroxydisulfates have been the subject of several investigations using thermal techniques. These compounds have several important synthetic uses, and at least some attention has been focused on the chemical storage of solar energy using a cycle based on partial decomposition of peroxydisulfates.

It has now been established[1] that when peroxydisulfates are heated the decomposition involves as the first step

$$S_2O_8^{2-} \rightarrow S_2O_7^{2-} + \tfrac{1}{2}O_2 \qquad (1)$$

Cleghorn and Davies[2] have shown that for $K_2S_2O_8$, the product has an infrared spectrum which is consistent with the product being $K_2S_2O_7$. Evidence exists which shows that rupture of the O–O bond is the first step in the process[3]. This is not unexpected in view of the fact that the O–O bond energy is about 34 kcal mol^{-1} while the S–O bond is stronger. Decomposition of the $K_2S_2O_7$ product is not as well understood.

Although several thermal studies have been conducted on peroxydisulfates, physical parameters for the decomposition reactions are still uncertain. In a recent study, Barbooti and Jasim reported the results of DTA experiments on peroxydisulfates[5]. The first reaction was found to be complete conversion to pyrosulfate, with the pyrosulfate being converted at higher temperatures to the sulfate by loss of SO_3. The conversion of sodium peroxydisulfate to the pyrosulfate was reported to liberate

81.1 kcal mol^{-1} and have an activation energy of 77 kcal mol^{-1}. For $K_2S_2O_8$ conversion to $K_2S_2O_7$, the reported ΔH is — 79.0 kcal mol^{-1}.

While estimates of the kinetic and thermodynamic parameters have been made for peroxydisulfate decomposition, reliable data are lacking. This report presents results of observations on ammonium and potassium peroxydisulfate decomposition.

EXPERIMENTAL

Reagent grade potassium and ammonium peroxydisulfates were used without further treatment.

DSC studies were carried out using a Perkin-Elmer differential scanning calorimeter Model DSC-1B. Procedures used were similar to those previously reported[6]. For studies on ammonium peroxydisulfate, gold sample pans were used owing to the reaction of the acidic ammonium ions with aluminum at the higher temperatures. Activation energies were determined using the procedures of Thomas and Clarke[7].

Thermogravimetric studies were carried out using a Perkin-Elmer thermogravimetric system Model TGS-2. Heating rates of 10 and 20 deg min^{-1} were used. Some TG runs were made with the samples enclosed in crimped aluminum pans as in DSC runs. This procedure was necessitated by the extensive fragmentation of crystals as oxygen is released. In all DSC and TG runs, the sample was maintained in a nitrogen atmosphere.

RESULTS AND DISCUSSION

The DSC curves for $K_2S_2O_8$ show a broad exotherm in the temperature range of 197–245°C. In this temperature range, the TG curves show a loss of mass of 5.19%. Weighing the DSC sample before and after heating past the exothermic transition shows that the weight loss is 6.6%. The reaction

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

corresponds to a mass loss of 5.92%. The data thus indicate that the reaction involves cleanly the loss of oxygen to produce the pyrosulfate. A ΔH value of — 57.2 ± 6.3 kcal mol^{-1} is found for this process and an apparent activation energy of 86.4 ± 6.2 kcal mol^{-1} was obtained.

The DSC curves for $(NH_4)_2S_2O_8$ show a broad endotherm in the range 170–212°C. TG curves for this compound show a mass loss of 7.38% from 180–210°C. The calculated mass loss for the reaction

$$(NH_4)_2S_2O_8(s) \rightarrow (NH_4)_2S_2O_7(s) + \tfrac{1}{2}O_2(g) \qquad (2)$$

is 7.01%. From the DSC curves, ΔH for the reaction represented by eqn (3) is determined to be — 82.8 ± 8.3 kcal mol^{-1} and the activation energy 65.4 kcal mol^{-1}.

In the case of $K_2S_2O_8$, an activation energy of about 86.4 kcal mol^{-1} is somewhat higher than expected since the O–O bond energy is typically around 34 kcal mol^{-1}. It would appear that decomposition of the peroxydisulfate ion could be initiated by breaking a bond of about that energy. However, the S–O bond must also be broken before oxygen can be liberated and that bond has an energy of about 65 kcal mol^{-1} (ref. 8). Thus, bonds totalling about 99 kcal mol^{-1} must be broken. For $K_2S_2O_8$, the conversion to $K_2S_2O_7$ has an activation energy of about 86.4 kcal

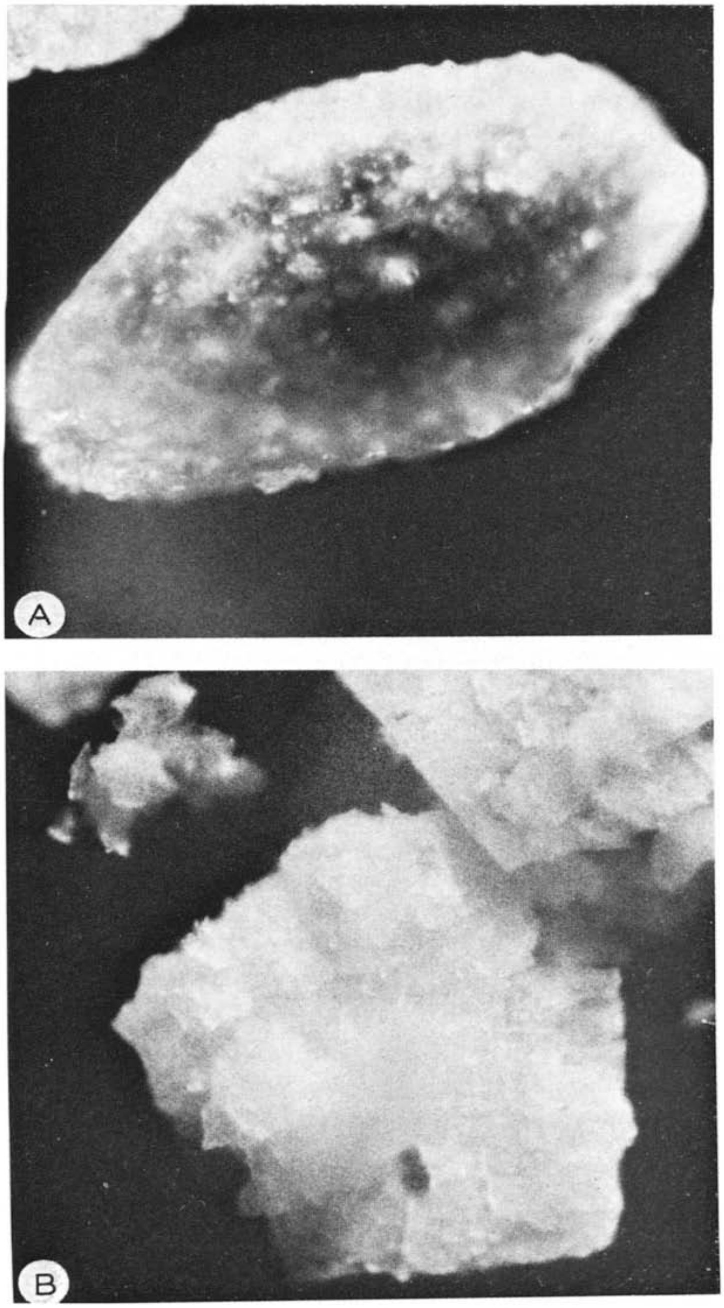

Fig. 1. Photomicrographs of $K_2S_2O_8$ (A) and $K_2S_2O_7$ (B) produced in the TG apparatus.

mol^{-1} while for the conversion of $(NH_4)_2S_2O_8$ to the pyrosulfate the activation energy found was 65.4 kcal mol^{-1}. Thus, the magnitude of the activation energies found is consistent with a process involving at least the breaking of the S–O bond as the rate determining step. Rupture of only the O–O bond (34 kcal mol^{-1}) cannot produce oxygen, so it appears that a minimum activation energy should be about 65 kcal mol^{-1}.

Rupture of the O–O bond to produce two SO_4^- groups would probably lead to extensive lattice rearrangement in the solid. As oxygen is liberated, it must escape from the crystal. During the TG experiments, samples heated in open platinum pans in a nitrogen atmosphere fragmented extensively with the fragments being propelled out of the container. Subsequent runs were made with the samples contained in aluminum DSC pans with a lid crimped in place to contain the sample. In this way, the mass loss curve gave a plateau at 280°C at a mass loss of 5.19% with the theoretical value for conversion of $K_2S_2O_8$ to $K_2S_2O_7$ being 5.92%.

Figure 1 shows photomicrographs of the $K_2S_2O_8$ and the $K_2S_2O_7$ produced after oxygen evolution has occurred in the TG apparatus. These photomicrographs show the extensive fracturing of the crystals caused by the escape of oxygen. The energy associated with this physical change could be considerable. Since the reaction leads to significant fragmentation of the crystals, the measured enthalpy change for oxygen evolution involves not only bond breaking and bond making steps, but also enormous physical changes. Thus, a direct interpretation of the ΔH value is not readily at hand.

Further heating of $K_2S_2O_7$ produces no mass loss in the TG but leads to an endotherm at 337–342°C. This peak is associated with fusion of the $K_2S_2O_7$, and the heat of fusion is 12.4 ± 2.6 kcal mol^{-1}. No fusion peak could be found for $(NH_4)_2S_2O_7$, neither could conversion to $(NH_4)_2SO_4$ be identified. This difference from $K_2S_2O_7$ probably arises from complicated redox reactions involving the cation in the case of the ammonium compound. Also, the heated ammonium compound was found to react with the aluminum pans used to contain the rupturing crystals.

In order to try to separate the kinetic and thermodynamic changes of these reactions from the physical changes, other studies are underway. In these, the influence and role of the cation and particle size will be studied.

REFERENCES

1 C. Duval, *Anal. Chim. Acta*, 20 (1959) 20.
2 H. P. Cleghorn and M. B. Davies, *J. Chem. Soc. A1*, (1970) 137.
3 V. A. Lunenko-Burmakina and V. Z. Kuprii, *Zh. Neorg. Khim.*, 15 (1970) 1806.
4 K. J. DeVaries and P. J. Gellings, *J. Inorg. Nucl. Chem.*, 31 (1969) 1307.
5 M. M. Barbooti and F. Jasim, *Thermochim. Acta*, 16 (1976) 402.
6 A. Akhavein and J. E. House, Jr., *J. Inorg. Nucl. Chem.*, 32 (1970) 1479.
7 J. M. Thomas and T. A. Clarke, *J. Chem. Soc. (A)*, (1968) 457.
8 E. A. V. Ebsworth, J. A. Connor and J. J. Turner, in J. C. Bailar, Jr., J. J. Emeleus, R. Nyholm and A. F. Trotman-Dickenson (Eds.), *Comprehensive Inorganic Chemistry*, Vol. 2, Pergamon Press, Oxford, 1973, p. 740.