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THERMAL DECOMPOSITION OF OXALATES. PART 15. EFFECT OF CONTAINER MATERIAL ON DTA RESULTS FOR THERMAL DECOMPOSITION OF MAGNESIUM OXALATE

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ABSTRACT

During the study of the thermal decomposition of magnesium oxalate dihydrate certain anomalies were noted. It was found that even in the presence of oxygen the decarboxylation peak was endothermic except in the presence of a catalyst. In a platinum crucible results were found to be different from those in a porcelain crucible due to the platinum acting effectively as a catalyst.

INTRODUCTION

The thermal decomposition of oxalates proceeds by several routes. Some oxalates such as calcium oxalate decompose to a carbonate, others such as zinc oxalate decompose to an oxide. A further group of oxalates if decomposed in an inert atmosphere produce a metal as the solid product and this is observed in air to oxidise up to the metal oxide. The decomposition process has been studied using a thermogravimetric technique [1] and by a parallel differential thermal analysis investigation [2]. It has also been noted that the design and type of sample cell used in differential thermal analysis can have an important influence on the observed reaction [3]. It was noted in preliminary studies on the thermal decomposition of magnesium oxalate that different results were obtained according to the equipment used. The difference was at first attributed to the geometry of the sample holders but the investigation was extended to cover the effect that the materials used in the sample holder construction had upon the course of the reaction.

EXPERIMENTAL

In this study two DTA units were used: (i) Du Pont 500 thermal analysis unit, and (ii) the Netzsch DTA unit 404. Crucibles of the same shape and size were used but of differing materials. Also on the Netzsch an experiment was undertaken in which clean pieces of platinum were placed unto the sample and standard material to prove whether the anomalies were due to

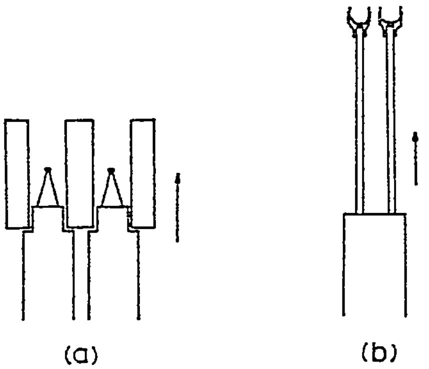


Fig. 1. Schematic diagram of DTA cells with arrows indicating the normal direction of gas flow. (a) Netzsch standard cell (nickel block, wells approximately 8 mm diameter). (b) Du Pont high temperature cell (cups approximately 5 mm diameter).

the geometry or the container material.

Figure 1 (a, b) shows the instrument heads in a schematic representation. Runs were made under four conditions, namely vacuum, dry nitrogen, dry air and dry oxygen. In all cases the vacuum and nitrogen gave the same type of peaks and also the air and oxygen gave the same type of peaks. From this it can be concluded that the presence or absence of oxygen can be responsible for differences in results between air and nitrogen. It is generally accepted that the oxidation of carbon monoxide at the surface of the sample in the presence of oxygen is responsible for the differences [2]. In the decomposition of oxalates it is generalised that decarboxylation in the presence of oxygen is exothermic while in nitrogen it is endothermic. In this study the use of different equipment and sample holders enabled the specific case of the thermal decomposition of magnesium oxalate to be studied with respect to the gaseous environment of the sample.

RESULTS

The results obtained in the Netzsch using a nickel block are recorded in Fig. 2, and it is seen that the decarboxylation peak is endothermic both in

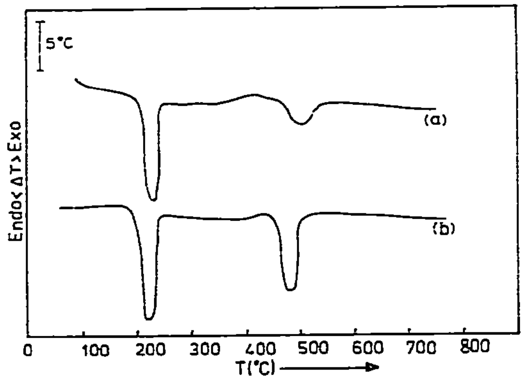
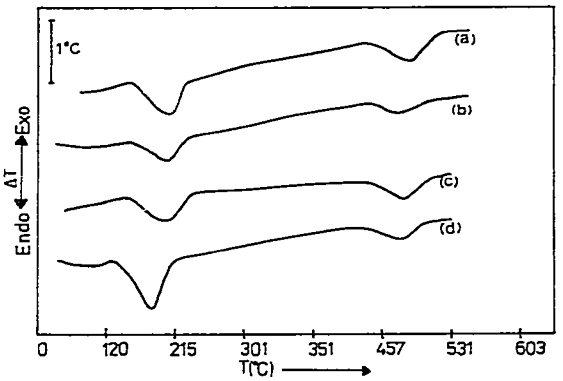


Fig. 2. DTA traces for magnesium oxalate dihydrate using the Netzsch standard cell. (a) In flowing air; (b) in flowing nitrogen.



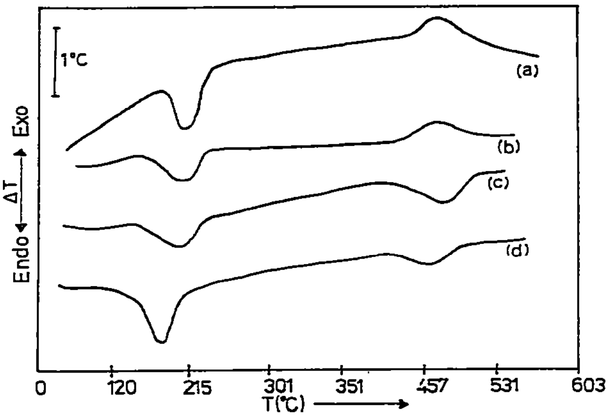


Fig. 3. DTA traces for magnesium oxalate dihydrate using the Du Pont high temperature cell with porcelain sample cups. (a) In flowing oxygen; (b) in flowing air; (c) in vacuum; (d) in flowing nitrogen.

Fig. 4. DTA traces for magnesium oxalate dihydrate using the Du Pont high temperature cell with platinum sample cups. (a) In flowing oxygen; (b) in flowing air; (c) in vacuum; (d) in flowing nitrogen.

the presence and absence of oxygen. The results obtained on the Du Pont using a porcelain crucible are given in Fig. 3 and using a platinum crucible are given in Fig. 4.

In the presence of platinum the decarboxylation peak in oxygen and air on Du Pont DTA units is exothermic whilst in nitrogen and vacuum it is endothermic. Using a DTA head made of a nickel block or of porcelain the decarboxylation peaks in oxygen, air, nitrogen and vacuum are all endothermic.

The results of a run in which a clean piece of platinum was inserted into each side of the nickel block is shown in Fig. 5, the decarboxylation peak being compared to a similar run in a nickel block. The results are all repro-

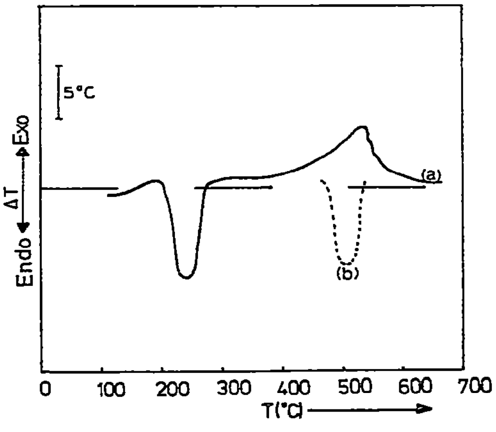


Fig. 5. DTA traces for magnesium oxalate dihydrate using the Netzsch standard cell, using a nickel block sample holder with a piece of platinum inserted in the reference and sample. (a) Result with platinum added; (b) expected result without platinum.

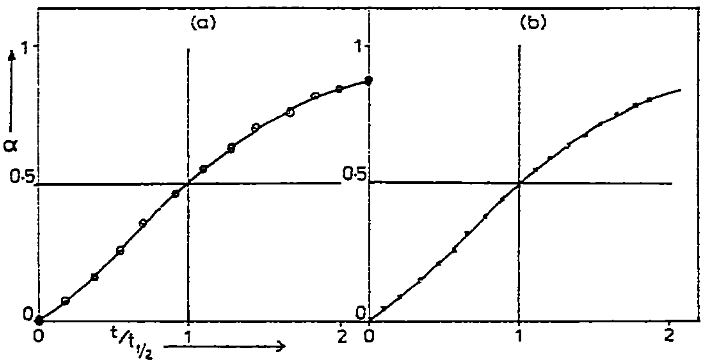


Fig. 6. Reduced-time plots (Sharp et al. [4]) for isothermal decarboxylation of magnesium oxalate. (a) In a porelain container; (b) in a platinum container. Abscissa: reduced time $t/t_{1/2}$. Ordinate: Fraction decomposed α.

ducible and work has been done on various samples of magnesium oxalate dihydrate, prepared by different methods, and all preparations gave the same results.

A Stanton 750 thermobalance was modified to allow the use of the same sample cups as the Du Pont 500 thermal analyser. Isothermal runs were carried out to compare kinetic results between the porcelain and the platinum crucibles. It was found, by comparing reduced time plots [4], that the kinetics were the same for both types of crucible (Fig. 6). The reaction proceeds at a faster rate for the platinum crucible run, this is due to the efficient removal of carbon monoxide from the reaction sphere ($2CO + O_2 \rightarrow 2CO_2$).

DISCUSSION

The results show that in the case of magnesium oxalate the decarboxylation peak in the DTA trace is dependent on the crucible material. Several other samples have been tried but this seems to be an exception. Barium oxalate, lead oxalate and sodium oxalate all behave in an identical manner in both porcelain and platinum containers.

This effect may be attributed to the catalyst activity of the decomposition product. Magnesium oxide which is the final product is an insulator and is a poor catalyst for the oxidation of carbon monoxide. Most efficient oxides are those with *p*-type conduction and next best are those with *n*-type [5].

The activity is also dependent on the temperature. Generally, the lower the temperature of decarboxylation and the lower the activity of product, the higher the likelihood of producing a similar result to that seen in the case of magnesium oxalate decarboxylation reported in this study.

CONCLUSION

This work shows the need to state all conditions when using DTA. In the case of magnesium oxalate a DTA trace using a platinum sample holder in air will result in an exothermic decarboxylation. Another DTA trace again in air but using an inert sample holder would result in an endothermic decarboxylation. The reaction is

$$MgC_2O_4 \rightarrow MgO + CO_2$$

but in the case where platinum or other active sample holders are used, and in the presence of oxygen

$$CO + \frac{1}{2}O_2 \rightarrow CO_2$$

If either oxygen is absent or the holder is inactive then this latter reaction does not take place. The catalyst process is exothermic and the net result is an exothermic peak on the DTA trace.

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