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THE PYROLYSIS OF METAL ACETATES*

PART I. SOME GROUP II ACETATES

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ABSTRACT

The thermal decomposition of a selection of group II metal acetates has been examined in atmospheres of nitrogen and of oxygen, using DTA, TG and X-ray diffraction techniques, illustrating the variety of solid phases appearing during the decomposition process. X-ray amorphous intermediates were detected in the dehydration of hydrated magnesium and cadmium acetates, the anhydrous acetate at least partially melting prior to decomposition. Under oxygen the pyrolytic decomposition proceeded generally with fewer intermediate stages than observed under non-oxidative conditions, with the major exothermal decomposition process occurring at somewhat lower temperatures.

Combining these results with earlier data on strontium and zinc acetates, at 500°C the decomposition products were the corresponding oxides, except in the case of barium and strontium acetates where the carbonates were produced. The sensitivity of the thermal decomposition processes to sample configuration and to the effect of possible product accumulation appears to underlie much of the controversy regarding these processes which exists in the literature.

INTRODUCTION

The majority of studies on the pyrolysis of metal acetates have been oriented towards determination of the form in which the organic residue is volatilized. Where intermediate solid phases were examined, considerable controversy exists as to their nature. Continuing the study of acetate, decompositions begun in relation to the pyrosynthesis of strontium zincate[1], the present series of papers attempts to clarify some of the stages in the thermal decomposition of a number of the more common metal acetates.

EXPERIMENTAL

Starting materials were sieved to −200 mesh and used without further purification. Barium and magnesium acetates were Fisher Certified Reagent Grade, cadmium acetate was Matheson, Coleman, and Bell Reagent Grade. In each case the manufacturers' lot analysis was accepted.

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Differential thermograms were obtained using the R. L. Stone Model KA-W DTA equipment with the SH-11BR2-NIW flat-pan type of sample holder on which 1-2 mg of sample were fully exposed to ambient atmospheres flowing at 15 $cm^3 \cdot min^{-1}$ and atmospheric pressure. High purity oxygen and nitrogen were used. Samples were heated or cooled at $5°C \cdot min^{-1}$ and the reference material was 100–200 mesh aluminum oxide previously calcined at 1200°C. Sensitivity is indicated on the individual thermograms with changes denoted by broken vertical lines.

In addition to triplicate experiments up to the maximum temperature (usually 400–500°C) a number of other runs were made to intermediate temperatures. Reversibility of thermal effects was checked by heating and cooling through the regions of interest, but no reversible phase transitions were detected in the systems studied up to the particular maximum temperatures. Samples were removed from the DTA apparatus at various temperatures and immediately examined by Debye–Scherrer powder patterns obtained at room temperature using Cu(Ni) or Fe(Mn) radiation. Cases where the diffraction pattern could not be identified from the ASTM Index[2], or other literature sources, are indicated on the figures by a question mark (?).

Simultaneous DTA–TG experiments were carried out on 40-mg samples heated in a 0.1-cm^3 crucible at $8°C \cdot min^{-1}$ under a nitrogen flow of $5 \, l \cdot h^{-1}$ on a Mettler Vacuum Thermoanalyzer equipped with an HF-2A sample head[3]. Visual observations during heating were also made using conventional Kofler micro hot-stage techniques.

RESULTS

Barium acetate

The thermal decomposition of anhydrous barium acetate has been reported to yield barium carbonate[4–9] with the evolution of acetone[4,7,10]. Formation of barium oxide is prohibited thermodynamically[7] at the decomposition temperature of the acetate, which has been reported variously from 240 to 480°C. The decomposition mechanism has been suggested to involve the growth of planar nuclei within the barium acetate[7] involving an activation energy of approximately 40 $kcal \cdot mole^{-1}$ over the temperature range 457–474°C. The high temperature required for rapid reaction has been cited as support for a chain mechanism initiated by free methyl radicals, although such a mechanism has been disputed for related alkaline earth acetates[6]. Unfortunately at these temperatures, which are relatively high for decompositions involving organic residues, it is difficult to resolve whether catalytic effects within the different experimental approaches have contributed to the observed discrepancies in activation energy, upon which much of the argument is based.

The differential thermogram of barium acetate (Fig. 1) under nitrogen showed four principal exothermal processes in the range 449–477°C. The resolution of these exotherms, their reproducibility, and the absence of conditions favourable to secondary catalysis and decomposition (*i.e.* small samples, minimum exposure to the sample holder surface, inert atmosphere) suggest a stepwise decomposition. The decomposition was complete by 487 ±5°C and the product at 500°C was the hexagonal form of barium carbonate. Under oxygen, only two exothermal processes were resolved and the decomposition was completed over a smaller temperature interval, *viz.* 443–456°C. While it was difficult to quench the DTA sample from a temperature

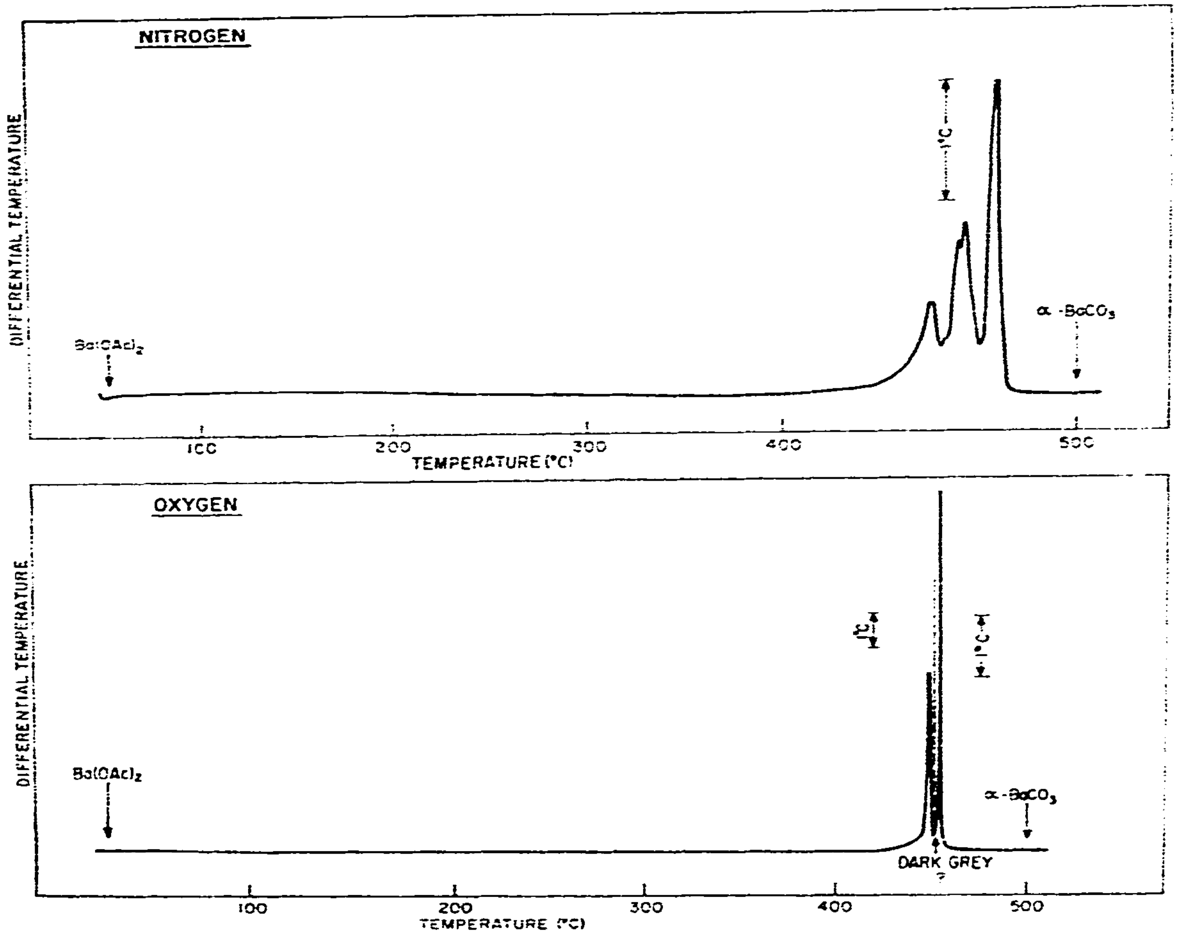

Fig. 1. Differential thermograms of $Ba(OAc)_2$ in nitrogen and oxygen.

exactly between these two closely occurring exotherms, a dark gray crystalline intermediate was found following the first exothermal process. Its diffraction pattern indicated a mixture of the original acetate and carbonate. The final product was hexagonal $BaCO_3$. In oxygen, a stepwise decomposition mechanism was also indicated, however the thermogravimetry of considerably larger samples having limited exposure to the ambient atmosphere (air) did not resolve any such steps[10,11].

The simultaneous DTA–TG of barium acetate in nitrogen under more confined conditions exhibited a single *endothermal* process accompanying the expected loss in weight (Fig. 2). Similar observations on other acetate systems suggest that any conditions which can impede the escape of the organic residue can also drastically alter the thermal characteristics of the decomposition. For the process

$$Ba(OAc)_2(s) \rightarrow \alpha\text{-}BaCO_3(s) + CH_3COCH_3(v)$$

$\Delta H_{298^\circ C} = -12.1$ kcal (refs. 12, 13), so that the well-exposed sample would be expected to decompose exothermally, whereas the more confined sample in which a variety of complex organic degradations can occur could exhibit endothermal decomposition under non-oxidative conditions. The single-stage weight loss observed by simultaneous DTA–TG then reflects primarily the evolution of final volatile products from the decomposing mass.

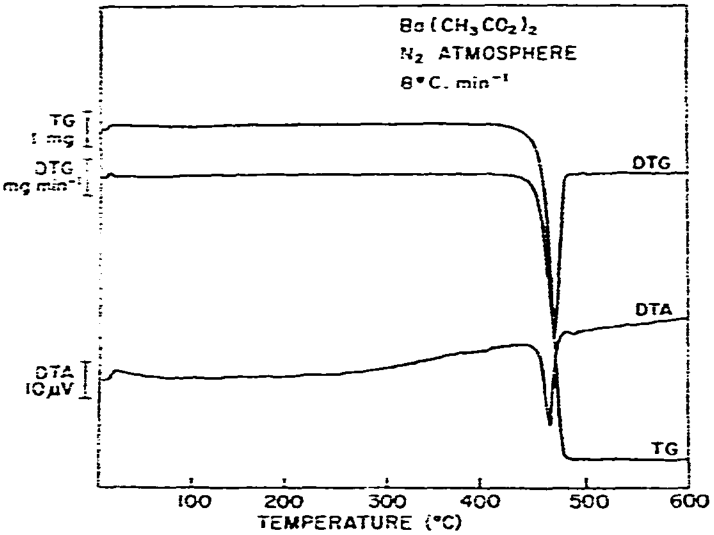

Fig. 2. Simultaneous DTA–TG–DTG of $Ba(OAc)_2$ in nitrogen.

Thus, while the final residue of α-$BaCO_3$ is obtained independently of the atmosphere or sample confinement, the intermediate degradation process clearly depends upon the latter circumstances.

Cadmium acetate dihydrate

This material has been stated to lose both moles of water below 150–190°C (refs. 10, 14–16) while others have reported the loss of 0.5 mole H_2O below 100°C followed by the remaining 1.5 moles at 150°C (ref. 6). Isolation of the sesquihydrate has also been reported[17].

Yakerson and co-workers[7,18] suggest that when anhydrous cadmium acetate is decomposed at a reasonable rate an amorphous form of $CdCO_3$ is produced which readily decomposes to CdO and CO_2. Only under conditions where the rate of decomposition of cadmium acetate is slow might evidence for $CdCO_3$ be obtained. This would account for the reported lack of evidence for the carbonate from several workers[14–16,19]. The decomposition mechanism has been suggested to be similar to that for barium acetate[7] with the exception that the carbonate is metastable and decomposes directly to the oxide.

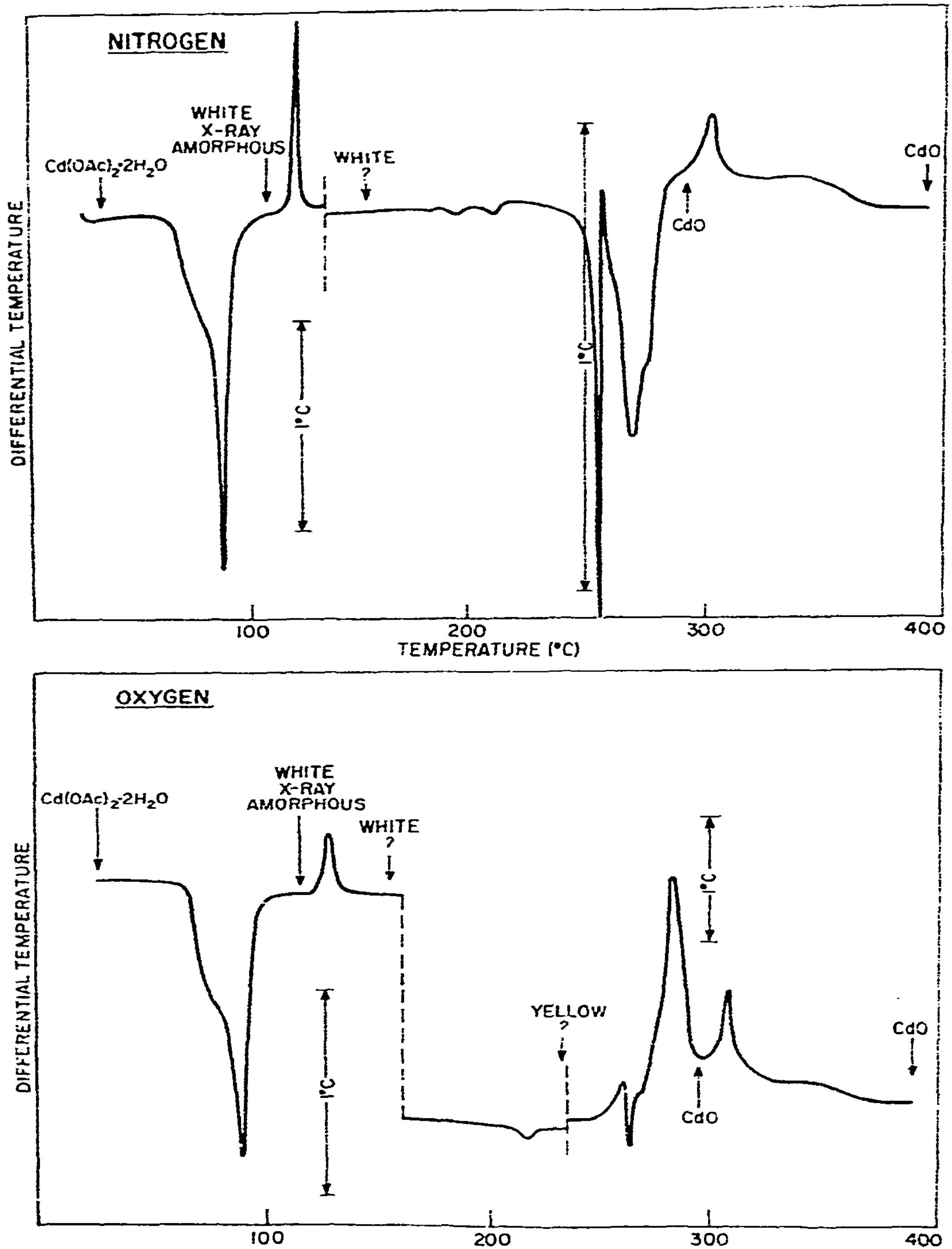

Fig. 3. Differential thermograms of $Cd(OAc)_2 \cdot 2H_2O$ in nitrogen and oxygen.

The present DTA study (Fig. 3) showed a two-stage loss of water, under both nitrogen and oxygen, the relative magnitudes of the overlapping endotherms being roughly consistent with losses of 0.5 and 1.5 moles of water. That these endotherms were not resolved indicates that product water vapour could not accumulate to a sufficient extent to permit separation on the basis of dissociation pressure[15]. In both cases a white, X-ray amorphous dehydration product was obtained which crystallized at 122–125°C as the anhydrous cadmium acetate. While the formation of X-ray amorphous dehydration products is well known for many salt hydrates[20], normally these metastable species occur under conditions of vacuum dehydration in the presence of small pressures of water vapour. However, if their formation is dependent upon the rate of removal of liberated water from the dehydration site by vacuum, then it is possible that the combination of small exposed samples and flowing dry gases approximate these conditions even at atmospheric pressure.

Minor endothermal activity was detected about 200–225°C resulting in a colour change (white to yellow) and a somewhat more complex X-ray diffraction pattern. Similar activity has been noted by others[15,16], marking the visual appearance of a second solid phase, however corresponding structural data have not been published.

Above 250°C, the thermal behaviour of the sample was atmosphere dependent. Under nitrogen there was clear evidence for melting at 257°C, both from DTA and visual observation of individual crystals, contradicting the reports of Yakerson[7,18]. Decomposition was also observed to take place from the melt, and the thermogram showed overlapping endothermal processes following fusion. The second solid phase was not observed to melt but decomposed directly at about 275°C. Semenko[19] considers that cadmium oxyacetate may form, although he was unable to isolate this material. The analogous decomposition of zinc acetate[1,19] has also been shown to produce the oxyacetate as a secondary process, and the suggestion of a similar partial production of cadmium oxyacetate[16] during the pyrolysis of cadmium acetate is supported by the present work. In oxygen, endothermal melting was followed directly by exothermal decomposition so that any endothermal oxyacetate formation is masked by the more exothermal pyrolysis of the organic residue.

At 300°C, under both oxygen and nitrogen, the product was cadmium oxide. A final exothermal process varied considerably in peak area from run to run, suggesting a disorder → order type of process. With the limitations of Debye–Scherrer powder patterns, only relatively small differences could be observed in diffraction patterns of CdO before and after this event.

Thermodynamically[12,13] the overall decomposition process is endothermal:

$$\mathrm{Cd(OAc)_2(s)} \rightarrow \mathrm{CdO(s)} + \mathrm{CO_2(g)} + \mathrm{CH_3COCH_3(v)} \quad \Delta H_{298^\circ\mathrm{C}} = +40\ \mathrm{kcal.}$$

In nitrogen decomposition from the melt is mainly endothermal indicating the majority of volatile products escape before secondary degradation can be detected by the ΔT thermocouple. In oxygen, however, decomposition from the melt is followed by immediate pyrolysis of the evolved organic on contact with the atmosphere with consequent marked exothermal activity.

Magnesium acetate tetrahydrate

Loss of water has been reported for this salt between 100 and 200 °C, producing the anhydrous acetate which subsequently decomposes to MgO at 330 °C (ref. 9). The intermediate formation of a mixed oxide–acetate salt, similar to that suggested in the decomposition of cadmium acetate, has been postulated but without supporting evidence[21]. While Yakerson *et al.*[18] found no evidence for the melting of magnesium acetate, Späth[22] has reported a melting point of 232 °C. These same authors[18] argue that magnesium carbonate is the decomposition product of anhydrous magnesium acetate, and that magnesium oxide results only from the secondary decomposition of the carbonate possibly through a hydroxy carbonate if water vapour is present[23].

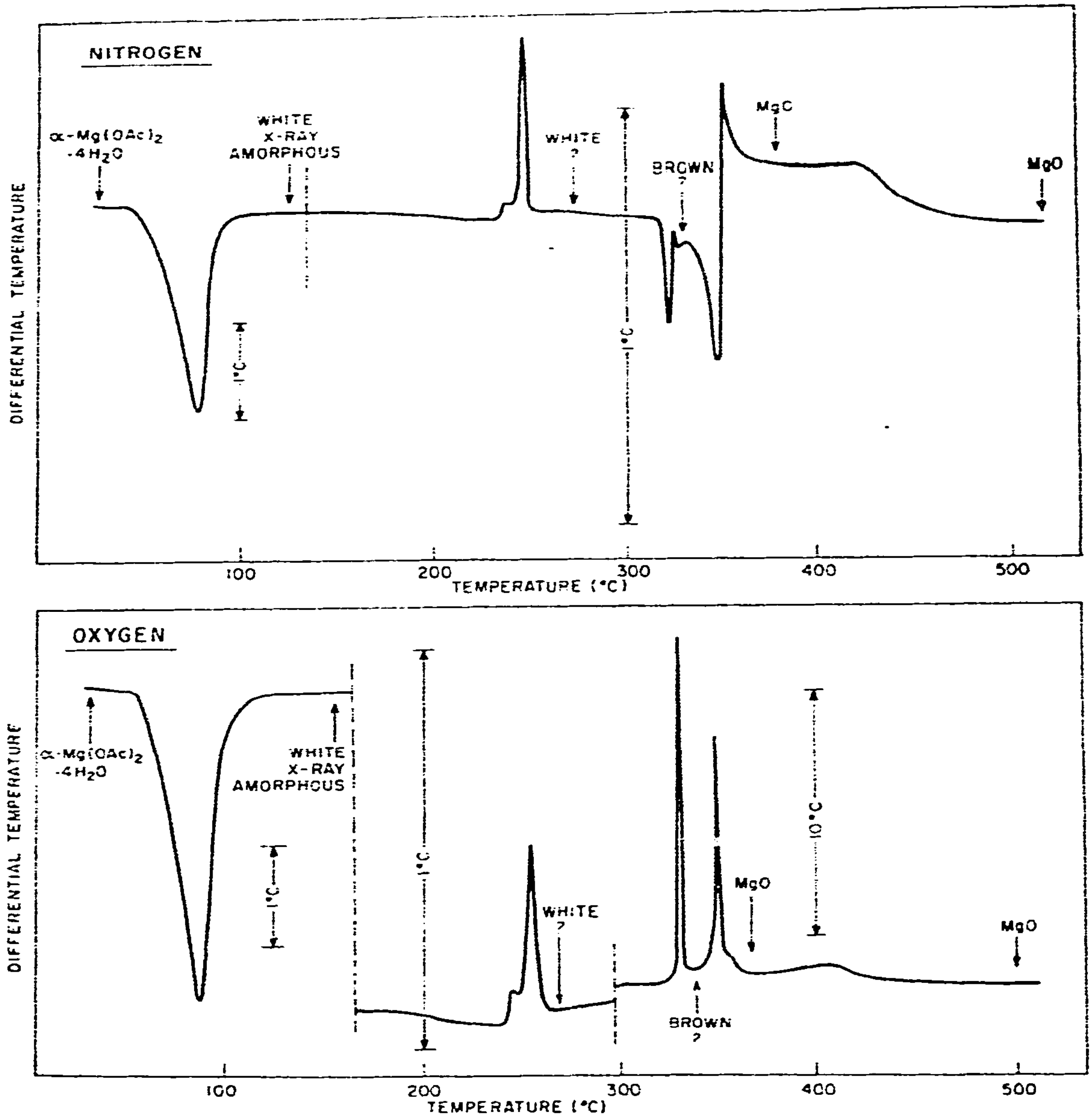

Fig. 4. Differential thermograms of $Mg(OAc)_2 \cdot 4H_2O$ in nitrogen and oxygen.

The thermal stability of anhydrous magnesium acetate has also been suggested to depend upon the initial crystal structure, orthorhombic and triclinic modifications having been reported to decompose at different procedural decomposition temperatures[24]. Two monoclinic forms also exist[2] and present studies were carried out on the α-modification of this form.

The evolution of the organic residue as acetone has been confirmed by a number of workers[4,7,18].

Present studies (Fig. 4) showed that below 300 °C the decomposition of magnesium acetate tetrahydrate was independent of whether or not nitrogen or oxygen was the ambient atmosphere. A single-stage loss of water was observed, producing an X-ray amorphous material stable to 230 °C. The subsequent exothermal process was judged to be recrystallization, since no accompanying weight change was found (Fig. 5). The X-ray pattern of the sample at 275 °C (Fig. 4) was clearly crystalline but did not correspond with either patterns reported for the orthorhombic or triclinic forms of anhydrous magnesium acetate[24]. No pattern was available for the anhydrous material in the monoclinic modification, or for the double salt $4Mg(OAc)_2 \cdot Mg(OH)_2$ claimed by Bernard and Busnot[25].

Under conditions of more restricted atmosphere exchange[3] (Fig. 5) it was possible to resolve three steps in the dehydration process prior to the recrystallization exotherm, indicating the presence of three intermediate hydrates having different dissociation pressures.

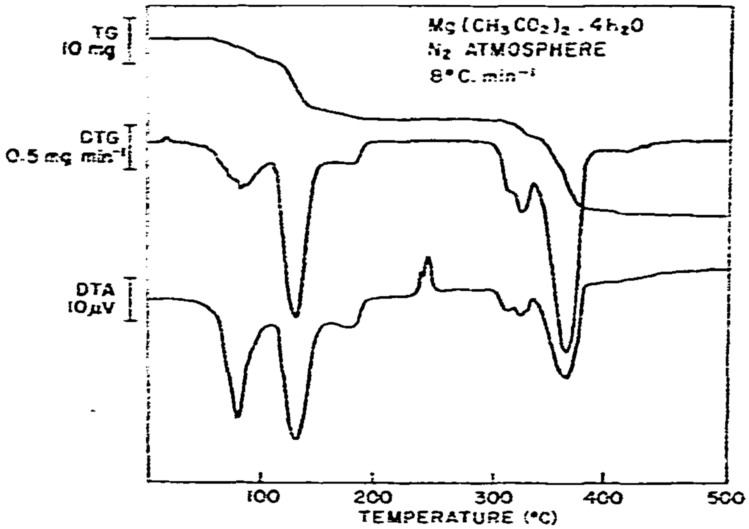

Fig. 5. Simultaneous DTA–TG–DTG of $Mg(OAc)_2 \cdot 4H_2O$ in nitrogen.

Above 300 °C the thermal decomposition of magnesium acetate was atmosphere dependent (Fig. 4). In nitrogen, endothermal decomposition at 321 °C produced a brown crystalline residue which subsequently decomposed at 351 °C, in an overlapping endothermal and exothermal sequence, to produce magnesium oxide by 380 °C. A limited amount of melting was observed visually at 324 °C, accompanied by expansion of the mass, and the general pattern is indicative of intermediate compound formation in the initial decomposition stages. Some vague exothermal activity above 400 °C did not alter the composition of the residue or the definition of the diffraction lines. When the sample was more confined (Fig. 5) at least three endothermal stages were observed in the decomposition pattern shown by DTA and DTG.

In oxygen, endothermal melting was overshadowed by the violently exothermal decomposition in two well-defined steps having peak temperatures at 335 and 351 °C. Between these steps (at 340 °C) a brown crystalline intermediate was obtained, which could not be characterized from available diffraction patterns, while magnesium oxide was the only solid phase remaining at 370 °C. As under nitrogen, vague exothermal activity was observed in the vicinity of 400 °C which did not alter the composition of the final residue within the limits detectable by Debye–Scherrer powder patterns.

The two-stage decomposition of magnesium acetate has also been observed with larger samples heated in static air[11]. As in the case of cadmium acetate an intermediate mixed acetate–oxide salt has been proposed[21], which is consistent with present observations of a distinct crystalline intermediate. Contrary to the suggestions of Yakerson[6,16] no evidence for the formation of magnesium carbonate could be obtained during or immediately following the decomposition processes, either under nitrogen or under oxygen. Concurrent and independent work on this same system[25] confirms this conclusion.

For the overall process:

$$Mg(OAc)_2(s) \rightarrow MgO(s) + CO_2(g) + CH_3COCH_3(v)$$

$\Delta H_{298\,°C}$ was estimated to be +34 kcal (refs. 12, 13). Decomposition under nitrogen involves at least two distinct stages, the first of which includes a partial melting of the magnesium acetate, and which are separated by a crystalline intermediate. As with cadmium acetate, pyrolysis of the initial decomposition product which accompanies melting in an oxygen atmosphere causes a strong exothermal response masking out the lesser endothermal activity.

COMMENT

Decomposition of those group II metal acetates studied up to 500 °C confirmed that carbonates were produced in the cases of barium and strontium[1], and oxides in the cases of magnesium and cadmium and zinc[1]. These latter materials also appeared to decompose, at least partially, from the molten state, involving formation of crystalline intermediates, possibly of the mixed acetate–oxide or oxyacetate type. No evidence was found in the diffraction patterns of these intermediates to support carbonate formation.

Comparison of the present work with other accounts in the literature demonstrates the particular sensitivity of these thermal decomposition processes to ambient atmosphere. Even under conditions where relatively small samples are contained in crucible-type holders placed in well-controlled atmospheres, there appears to be sufficient accumulation of volatilized organic products within the decomposing mass to alter the thermal character of the decomposition process from exothermal to endothermal. Such sensitivity to atmosphere may well have contributed to discrepancies found in the literature, complicated further by secondary decomposition of the evolved organic residues under conditions where these are not removed promptly from a sample area.

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