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THERMAL DECOMPOSITION OF MAGNESIUM MONOPEROXY-PHTHALATE HEXAHYDRATE

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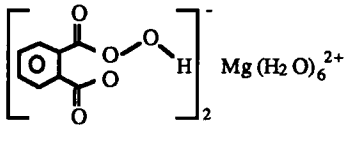
Abstract. Loss of the peroxy oxygen from the title compound yields magnesium hydrogen phthalate. Below ~80°C the process is accompanied by loss of water of hydration and of crystallinity. For the product, four polymorphic forms have been observed containing between 2 and 8 molecules of water per cation.

INTRODUCTION

The mode of molecular packing has been shown to influence greatly photoreactivity in the solid state.[1] X-ray diffractometry has been an invaluable tool in these studies especially in systems which on complete conversion, yield single crystals good enough for structure solution. In the solid state, the mechanism and rate of thermal reactions are also known to be influenced by structural factors.[2]

An aim of this investigation has been to study the structural changes which accompany thermal decomposition of magnesium monoperoxy-phthalate hexahydrate (MMPP) in the solid state. One interest in this compound is the relatively high thermal stability observed in the solid when compared to that shown in solution.



MMPP

EXPERIMENTAL

Samples of MMPP were provided by Interox Chemicals Ltd. The amount of peroxy oxygen was determined by titration of the iodine liberated from potassium iodide solution against sodium thiosulphate. A Gallenkamp vacuum oven was used for heating. Intensity measurements were made using an Enraf Nonius CAD-4 diffractometer (Mo radiation). A Stanton Redcroft TG-770 instrument was used for thermogravimetric analysis (TGA) with the sample temperature being raised at the rate of 3°/minute under a stream of dry N_2 gas. X-ray diffraction patterns were obtained using a Philips PW1710 powder diffractometer.

RESULTS AND DISCUSSION

I. Decomposition of magnesium monoperoxyphthalate hexahydrate

When MMPP is heated in a dry inert atmosphere, TGA shows two weight losses below 300°C; the first at about 60°C (30%) and the second close to 140°C (15%). In addition, powder X-ray diffraction (XRD) shows loss of crystallinity after several hours of heating at ~60 - 80°C. The patterns for MMPP and the product (**B**) are shown in Figures 1A & B respectively. This change is retarded by water vapour. For example, heating 0.5 g of MMPP i) for the same length of time at the same temperature in a gas stream saturated with water vapour, or ii) in a closed container for 20 hours at 75°C, did not result in significant changes in the XRD pattern or loss of oxygen.

The first loss in weight, and of crystallinity, may be attributed to expulsion of water of hydration and the peroxy oxygen (water content of MMPP is about 22% by weight). The product is amorphous magnesium hydrogen phthalate as shown by ^{13}C and proton solution NMR, infrared and microanalysis. Above 140 °C further decomposition and loss of some of the organic component occurs.

Visual observation of a crystal of MMPP shows a phase boundary moving from the surface towards the centre at about 70°C. The process may therefore be described as topochemical dissociation[3] as opposed to the intracrystalline process where

decomposition centres are distributed within the whole volume of the crystal.

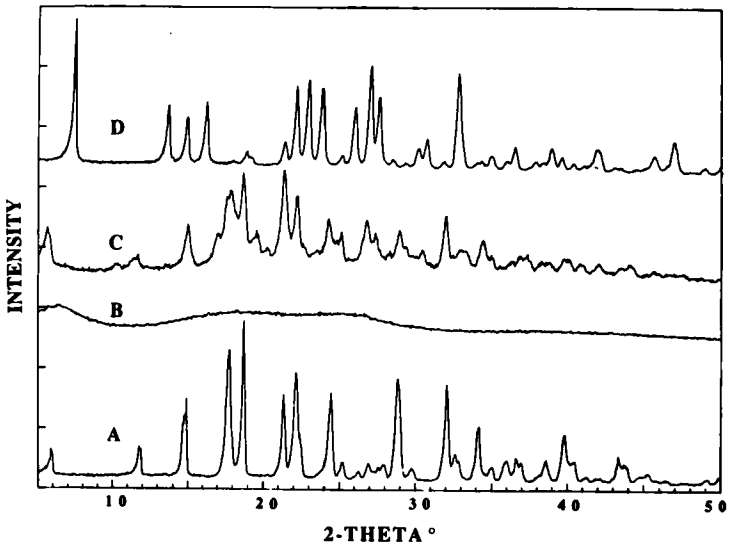


FIGURE 1. XRD patterns for: A) MMPP, B) decomposition product below ~80°C, C) **B** on exposure to water vapour at 20°C, D) **B** on exposure to water vapour above ~50°C.

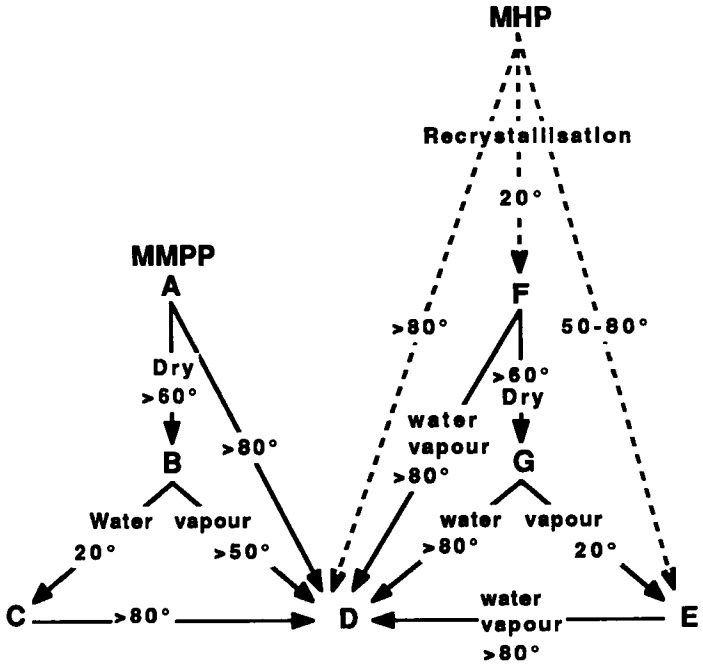
When a 0.5 g sample of MMPP is heated at 85°C in a closed container, close to 100% decomposition results after about one hour yielding a crystalline form of magnesium hydrogen phthalate. The reaction is vigorous and the product is foam-like in appearance suggesting that "melting" occurs during decomposition at this temperature. Pure MMPP melts at 96°C.

The generation of an amorphous intermediate below ~80°C and a liquid-like intermediate at higher temperatures suggests that disorder may be a prerequisite to the loss of the peroxy oxygen in MMPP. The decomposition of m-nitroperoxybenzoic (m. p. 92°C) and p-peroxytoluic (m. p. 97.5°C) acids is reported to proceed at 66.5°C and 84°C respectively without going through a liquid-like intermediate.[4] At higher temperatures, however, the process is

accompanied by melting (below the melting point of the parent material). During decomposition, the crystals of p-nitroperoxybenzoic acid undergo sublimation.[5]

Since the loss of water of hydration at lower temperatures appears to be important, it is possible that the rate of decomposition could be influenced by changing the crystal morphology of MMPP. For example, it has been reported that the rate of dehydration of magnesium heptahydrate[6] and potash alum[7] depends on crystal habit.

The scheme below summarises the observations made during the study. Temperatures are in °C.



MHP	-	Solution of magnesium hydrogen phthalate in water
MMPP (A)	-	$Mg(H_2O)_6(O_2CC_6H_4CO_3H)_2$
B & G	-	$Mg(O_2CC_6H_4CO_2H)_2$
D	-	$Mg(H_2O)_2(O_2CC_6H_4CO_2H)_2$
E (& C?)	-	$Mg(H_2O)_6(O_2CC_6H_4CO_2H)_2$
F	-	$Mg(H_2O)_6(O_2CC_6H_4CO_2H)_2(H_2O)_2$

II. Polymorphs of magnesium hydrogen phthalate

The amorphous product **B** yields highly crystalline phases, **C** and **D**, when exposed to moisture at 20 and ~50°C respectively (Figures 1C & D). The XRD pattern of **C** is fairly similar to that of MMPP but the material contains no peroxy oxygen. Heating **C** above 80°C yields **D** which is also obtained by recrystallisation of magnesium hydrogen phthalate (MHP) from water above 80°C. Recrystallisation of MHP between ~50 and 80°C yields another crystalline form, **E** (Figure 2E), while **F** is obtained at room temperature (Figure 2F).

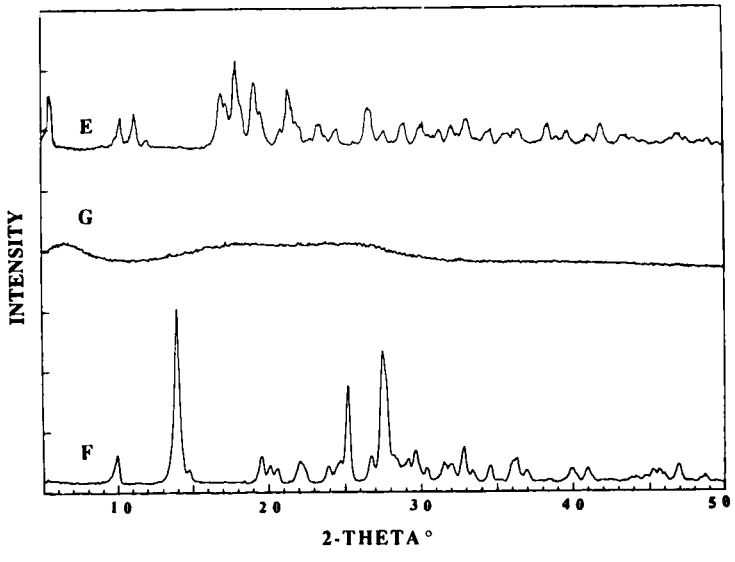


FIGURE 2. XRD patterns for: F) hexa-aqua magnesium hydrogen phthalate dihydrate, G) product of its dehydration, E) **G** on exposure to water vapour at 20°C.

E may also be obtained by dehydrating **F** at 70°C to give amorphous **G** (Figure 2G) and then exposing it to water vapour below 80°C. The molecular orientation in **B** and **G** is however not entirely random as shown by the generation of different crystalline forms on exposure to moisture at 20°C - **C** and **E** respectively.

The crystal structure of MMPP has been reported.[8] Those of **D**[9], **E**[10] and **F**[10] were determined during this study. Table I summarises some crystallographic data obtained at 20°C for **D**, **E** and **F** and crystal packing is shown in Figures 3-5.

TABLE I Crystallographic data for three forms of magnesium hydrogen phthalate.

	D	E	F
a	12.916(1)	6.565(1)	7.042(1)
b	5.092(1)	30.840(4)	9.286(2)
c	12.956(2)	10.055(1)	9.549(2)
α	90	90	84.31(1)
β	113.98(1)	89.22(1)	109.34(1)
γ	90	90	108.99(1)
Sp. Gp.	$P2_1/c$	$P2_1/c$	$P\bar{1}$
Z	2	4	1

Note: a,b,c in Å units; α,β,γ in degrees

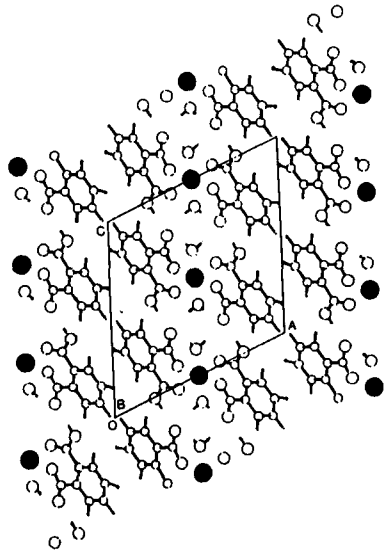


FIGURE 3. Packing in the crystal of magnesium hydrogen phthalate dihydrate (**D**) viewed along the *b* axis.

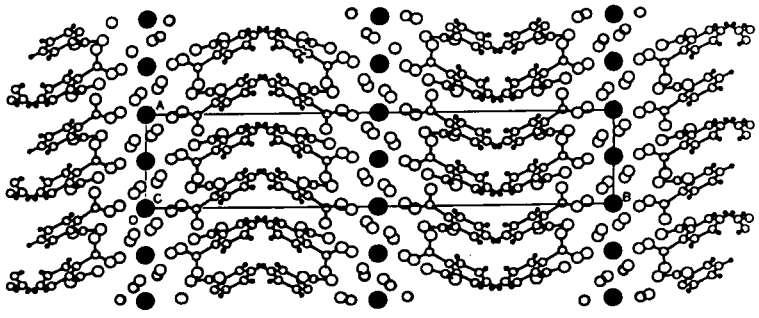


FIGURE 4. Packing in the crystal of hexa-aquamagnesium hydrogen phthalate (**E**) viewed along the *c* axis.

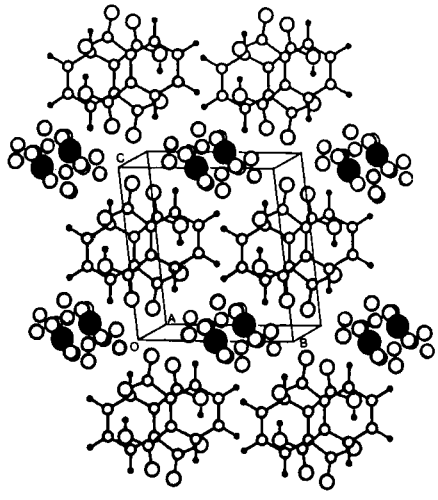


FIGURE 5. Packing in the crystal of hexa-aquamagnesium hydrogen phthalate dihydrate (**F**) viewed perpendicular to the benzene ring.

A feature common to all these structures is the octahedral arrangement of O atoms around the Mg^{2+} ion at a distance of about 2 Å. The number of water molecules per Mg^{2+} ranges from 2 (for **D**) to

8 (for **F**). In **D** the other four O atoms are provided by the anion. Evidence from TGA and microanalysis suggests that **C** is a hexahydrate. The structure requires powder data analysis which is currently under way.

Concluding remarks

We have demonstrated with these preliminary results that the crystal chemistry associated with peroxyacid salts and the decomposition products is quite complex. An understanding of the structural changes taking place will be of general interest in organic solid state chemistry.

Acknowledgement

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