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THE CHEMICAL AND CRYSTAL CHANGES ACCOMPANYING THE THERMAL DECOMPOSITION OF HEXA-AQUOMAGNESIUM MONOPEROXYPHTHALATE

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Abstract: The crystal chemistry associated with the thermal decomposition of hexa-aquomagnesium monoperoxyphthalate is described. Decomposition in an open atmosphere, monitored using powder X-ray diffraction, differential scanning calorimetry, thermogravimetric analysis and infra-red spectroscopy, proceeds, with accompanying water and oxygen evolution, through an amorphous intermediate phase. Upon exposure of the amorphous intermediate to moisture at room temperature a crystalline product is generated which produces a powder X-ray diffraction pattern very similar to that of the peroxy phthalate. Infra-red spectroscopy suggests that decomposition of the persalt may proceed via phthalic anhydride. In a closed environment decomposition occurs only after melting of the peroxyphthalate. The requirement for loss of crystallinity to allow oxygen evolution to take place is discussed.

Keywords: Peroxy acid salt, Decomposition, X-Ray diffraction, Infrared spectroscopy, Differential scanning calorimetry

INTRODUCTION

As part of a general study of the influence of crystal structure on reactivity,[1,2,3] we have investigated the solid state properties of peroxy acid salts. In particular, we hope to explore the exact influences which molecular substitution as well as the nature of the charge-balancing cation have on the stability of such salts.

The particular peracid salt discussed in this paper, hexa-aquomagnesium monoperoxyphthalate, designated A, is known to have potential application as a bleaching agent.[4] The structure of A consists of monoperoxyphthalate

anions, magnesium cations and water molecules[5,6]. Each cation is co-ordinated to six water molecules. Despite the importance of understanding the factors which control stability of such salts in the development of new types of bleaching agents no detailed study of the decomposition process has been reported.

EXPERIMENTAL.

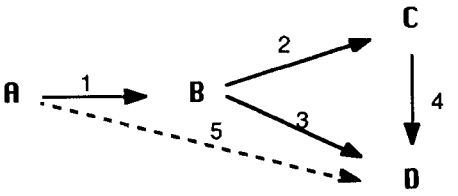
A was prepared following the previously reported method.[6] Phthalic anhydride (122.0 g, 0.82 moles) and magnesium oxide (16.5 g, 0.41 moles) were mixed, then added over 30 minutes to a mixture of 50% w/w hydrogen peroxide (56.0 g, 0.82 moles) and 300 cm^3 of deionized water. The mixture was kept below 20°C throughout. The reaction was continued for 90 minutes before the solution was cooled to 10°C and filtered. The white crystals were washed with ethylacetate followed by dichloromethane and dried in air.

Samples were heated either in open or sealed containers. For 'open' heating the sample was spread on a petri dish so as to give a maximum exposed surface area. For 'sealed' heating, the sample was placed in a test tube which was typically about a third full and loosely sealed. Heating in both cases was in air. Calcined samples were exposed to moisture by placing them on a petri dish next to a 50 cm^{-3} beaker containing water. The petri dish and beaker were then covered with a 500 cm^{-3} beaker and left to stand for various lengths of time. There was no direct contact between the sample and liquid water.

The effect of water vapour on the decomposition process was investigated by heating samples in a glass U-tube which was heated using a water bath. Nitrogen, argon and oxygen gases were passed over the material either dry or moistened (by first bubbling through water at room temperature).

Thermogravimetric analysis (TGA) was performed using a Perkin Elmer TGA7 instrument - starting weight usually less than 10 mg. The differential scanning calorimeter (DSC) employed was a Perkin Elmer DSC7. Both instruments were linked to a 3700 data station and a TAC7/3 instrument controller. The heating rate was 10°/minute under nitrogen gas. Infra-red spectra were recorded at room temperature on a Nicolet model 10MX spectrometer. Sample discs were prepared by grinding ~1 mg of sample with ~800 mg of potassium chloride and pressing at 10 tons/cm^2 under a rotary pump vacuum for ~1 minute. Typically, 32 scans at 2 cm^{-1} resolution were made. A Philips PW1710 diffractometer was used to obtain powder X-ray diffraction data. About 0.5 grams of sample were ground and placed on a glass holder. The data were collected at room temperature using the θ-2θ technique and Cu Ka radiation (λ = 1.5418 Å) at a scan rate of 2°/minute in 2θ. Available oxygen contents for the peroxy compound were determined by dissolving approximately 0.2g of sample in a mixture of 50 cm^3 of sulphuric acid (100 cm^3 of d1.84 acid in 900 cm^3 of water) before adding 10 cm^3 of potassium iodide solution (50 g in 500 cm^3). The mixture was kept in the dark for five minutes before the liberated iodine was titrated against 0.1 molar sodium thiosulphate solution, adding starch indicator near the endpoint. The AVOX for the sample of A used was found to be 58.3 g/Kg, compared with a theoretical value of 64.6 g/Kg.

RESULTS



A	-	$Mg(H_2O)_6(O_2CC_6H_4CO_3H)_2$
B*	-	$Mg(O_2CC_6H_4CO_2H)_2$
C	-	$Mg(H_2O)_6(O_2CC_6H_4CO_2H)_2$
D	-	$Mg(H_2O)_2(O_2CC_6H_4CO_2H)_2$

(* B contains some phthalic anhydride(see text).)

SCHEME 1 Relationship between the various phases (A-D) and the processes involved (1-5). The assumed formulae are based on data described in the test.

Scheme 1 shows the steps and phases we have found to be associated with the decomposition of A. The numbers refer to the various processes which have been followed - see below. The formulae which are given are based on the various results which we have obtained and present below. They are given at this stage for ease of discussion. Analytical data to support the formulae are given in Table 1.

Table 1 Microanalysis results (% Obtained/Expected).

	C	H
A	39.6/38.8	4.5/4.4
B*	50.3/54.2	3.4/2.8
C	44.4/41.6	4.9/4.8
D	48.4/49.3	3.7/3.6

* The phthalic anhydride in B (see text) was not taken into account in the calculation of the expected amounts.

Process 1 - The Conversion of A to B

Figure 1 shows the TGA trace obtained when A is heated at 10°C per minute in a stream of dry nitrogen. The gradual loss in weight above 140°C is attributed to sublimation of the organic component of the product of decomposition. Of particular interest is the two-step weight loss below this temperature. The first loss occurs between ~75 and 130°C and involves about 25% decrease in weight. This is followed by a sharp loss of about 6% at approximately 130°C. The magnitude of the first loss suggests that it is associated with the removal of six water molecules (theoretical value of 21.8%) while the second one is attributed to the loss of peroxy-oxygen (theoretical value 6.5%).

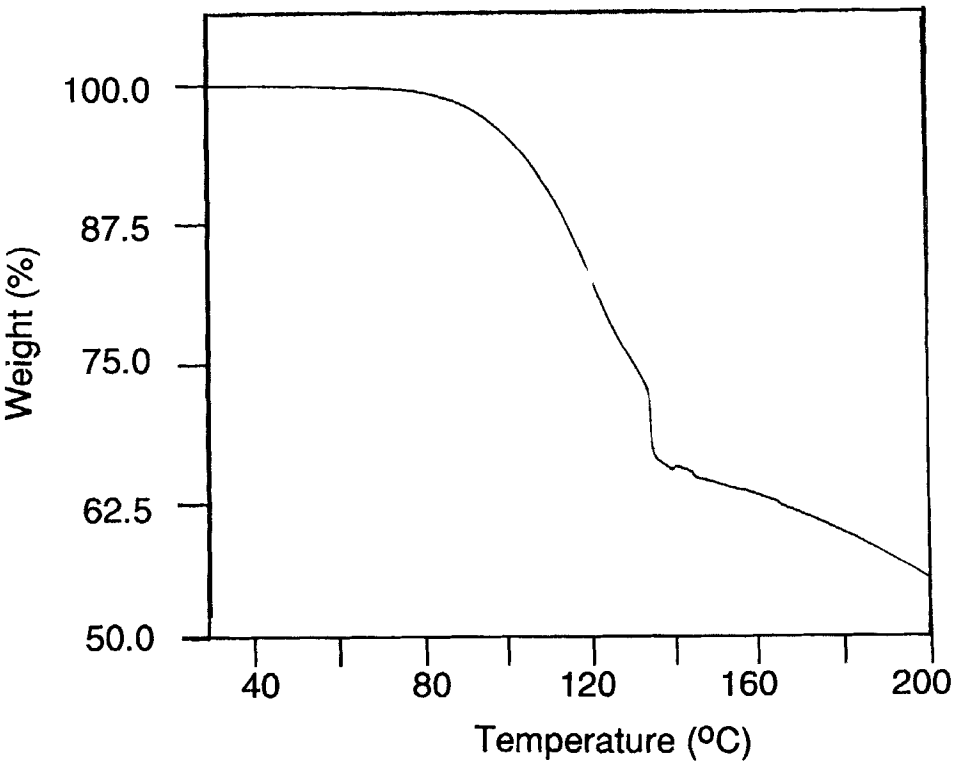


FIGURE 1 TGA trace for MMPP (A) obtained at a heating rate of 10 °C/min.

DSC (Figure 2(a)) of an unsealed sample of A reveals two broad features - an endothermic peak (~400 J/g) between ~60 and 105°C and an exothermic one (~-265 J/g) between 105 and 155°C. The endothermic peak is attributed to the loss of the six water molecules around the magnesium cation whilst the exothermic one is believed to result from the decomposition of the peracid to acid - in agreement with the conclusions from the TGA measurements. TGA and DSC results, therefore, imply that dehydration occurs before the loss of oxygen. This important point is discussed further under Process 2. Figure 2(b) shows the trace, for comparision, with a sealed pan.

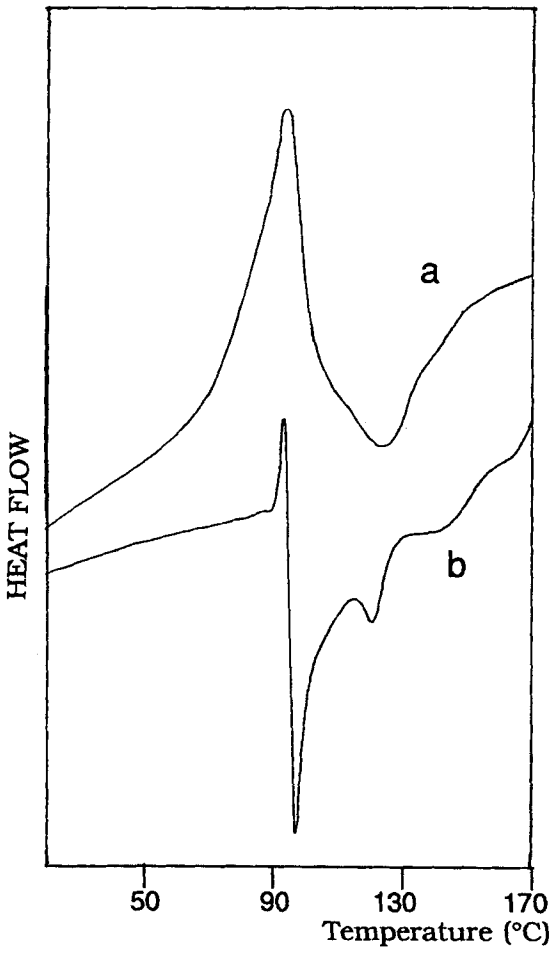


FIGURE 2 DSC traces for decomposition of A in (a) open and (b) sealed containers.

Structural changes accompanying decomposition were studied using powder X-ray diffraction. Figure 3(a) shows the powder pattern for A. (Simulation of the powder pattern using the DBW 3.2 program for Rietveld analysis[7] confirmed that the pattern corresponds to the reported crystal structure). When A is heated in the open or under flowing nitrogen for several hours at ~60 - 80°C, the pattern shown in Figure 3(b) is obtained. This semi-amorphous phase is designated B in Scheme 1.

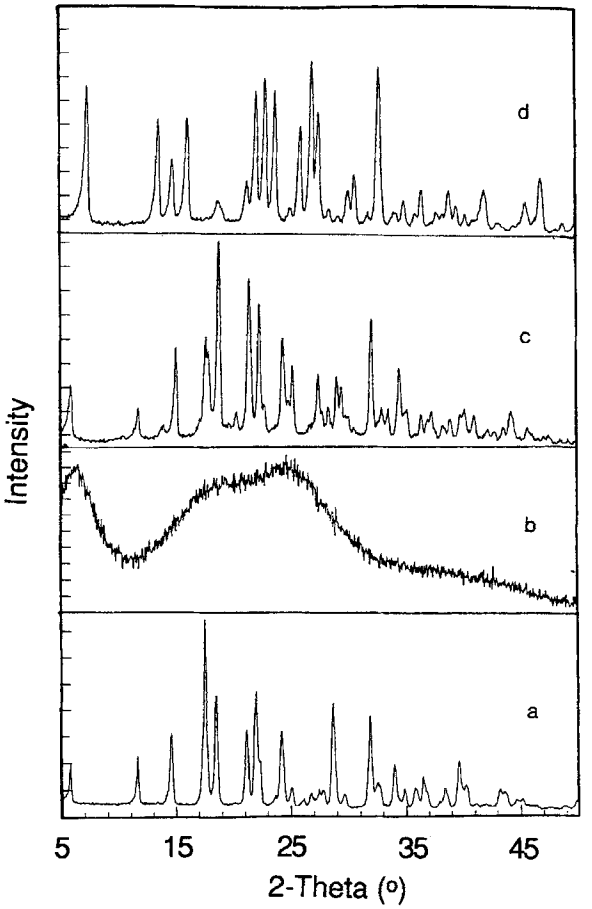


FIGURE 3 PXRD patterns for (a) A, (b) materials obtained on decomposition without melting , i.e. B, and product of rehydration (c) at room temperature and (b) above 80 °C.

To investigate how this loss of crystallinity is a result of the elimination of water or oxygen or both, further experiments were undertaken. The following results were obtained.

a) A was kept at 60°C for 5 hours in a U-tube under a stream of dry gas. The product which resulted had an AVOX value of 46.3g/Kg (lower than the original value of 58.3 g/Kg) and an X-ray pattern similar to that seen in Figure 3(b).

b) On similar treatment to that in (a) but under moist gas, crystallinity was retained, with no significant change in the X-ray powder pattern or AVOX.

c) Heating A at 75°C for 20 hours in a sealed tube did not result in any changes in the powder pattern. In addition, no change in AVOX was observed.

d) Each product from the above experiments loses all AVOX when heated at 75°C in the open.

From (a) and (b), it is clear that the loss of oxygen is linked to the loss of crystallinity. In addition, (b) and (c) suggest that it is dehydration which leads to loss of crystallinity. This is in agreement with the TGA and DSC results in that dehydration precedes loss of oxygen.

Infra-red spectroscopy (IR) was used to investigate the relation between the loss of the water of hydration and of the peroxy oxygen. The carbonyl (C=O) and peroxide (O-O) stretch absorptions, which occur at 1744 and 898 cm^{-1} respectively,[5,6] were used to monitor the process. These are numbered 1 and 7 respectively in Figure 4(a). The bands in the 1600-1700 cm^{-1} region are possibly due to OH deformation.

When A is heated at 70°C (accompanied by dehydration and complete loss of the peroxy oxygen) the product (B) shows a carbonyl band at 1690 cm^{-1} (Figure 4(b), peak 5). In addition, absorptions at 1774, 1789 and 1851 cm^{-1} (Figure 4(b), peaks 2,3 & 4) due to a small amount of phthalic anhydride are also observed. The significance of the phthalic anhydride is discussed later.

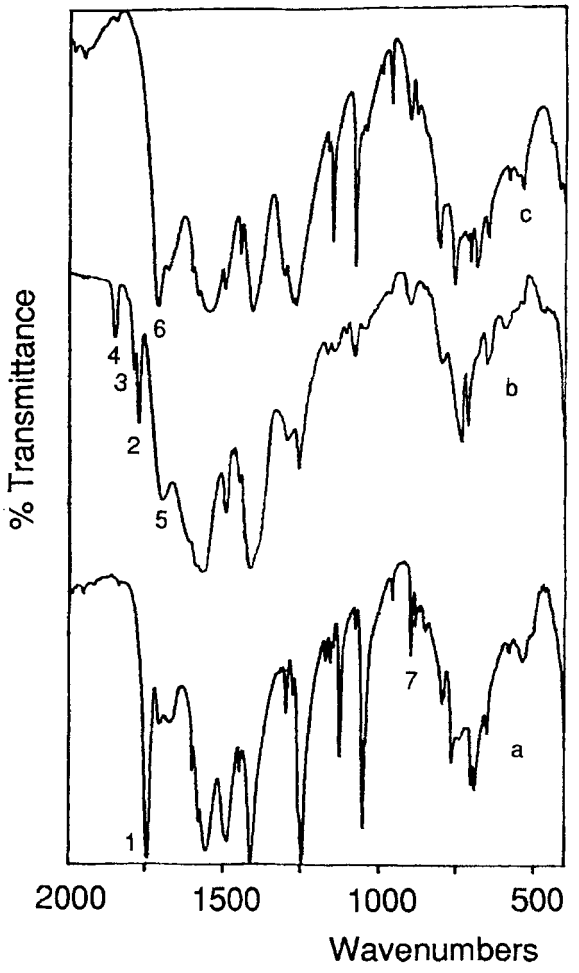


FIGURE 4 IR spectra for (a) A, (b) product of decomposition without melting and (c) material following rehydration at room temperature i.e. C.

A was also partially decomposed and analysed. On heating two samples, one at 50°C and another at 60°C, in a U-tube under a stream of dry argon for 5 hours, the spectra in Figure 5(b) and (c) were obtained. Powder X-ray diffractometry indicated that the product obtained at 60°C was semi-amorphous. For both products, the intensity of the absorption at 1744 cm^{-1} decreased whilst new ones due to phthalic anhydride appeared at 1774, 1789 and 1851 cm^{-1} (Figure 5(b) and (c), peaks 2,3 & 4). These changes are more pronounced for the one heated to the higher temperature (60°C).

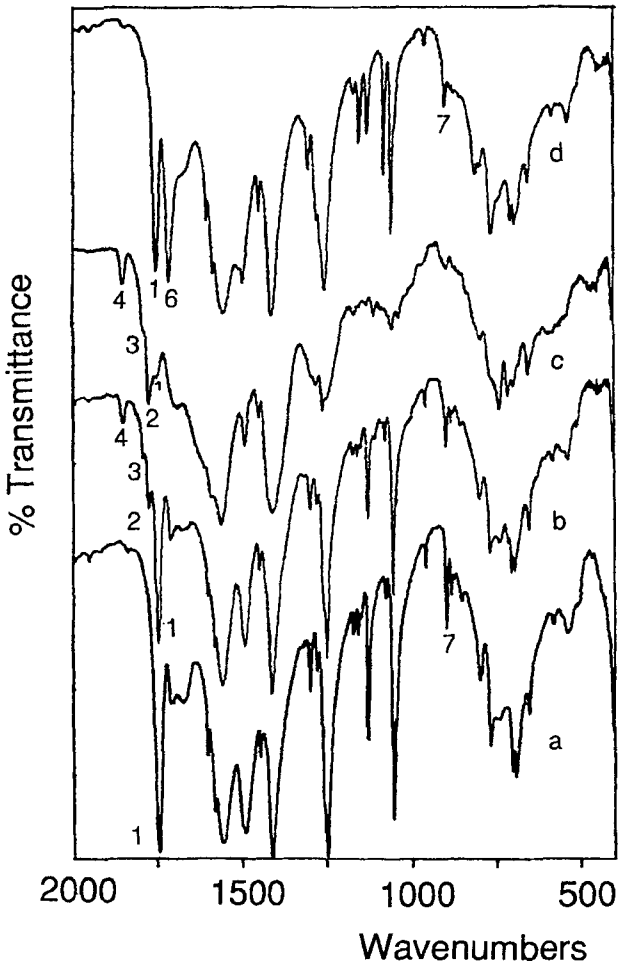


FIGURE 5 IR spectra for (a) A, product after 12 hr heating at (b) 50 and (c) 60 ^{o}C and (d) product of rehydration of the sample heated at 60 ^{o}C

Process 2 - Conversion of B to C

When B is exposed to moisture at room temperature, crystallinity is restored yielding product C - see Figure 3(c). The only apparent requirement for this rehydration process is the presence of moisture. The process is observed in air as well as in moist nitrogen and moist argon. The powder diffraction pattern for C is fairly similar to that of A even though the former contains no peroxy oxygen. This similarity has been discussed elsewhere.[3]

Powder X-ray diffraction further indicates that heating an unsealed sample of C yielded an amorphous product, which could also be rehydrated. The structure of the main product of this second rehydration was identical to that of C. (The product was contaminated by a second phase, the structure of which has been established and is described elsewhere[8]). Process 2 is, therefore, reversible.

On hydration of B to C by exposure to water vapour the IR absorptions due to phthalic anhydride (mentioned under Process 1) disappear. The other absorptions sharpen, as the groups concerned occupy clearly defined crystallographic positions. The carbonyl (C=O) absorption shifted to 1710 cm^{-1} (Figure 4(c), peak 6).

On hydration of the product of partial decomposition of A (mentioned under Process 1), increased absorption due to peroxycarboxylic carbonyl and peroxide stretches (Figure 5(d), peaks 1 & 7) occur at 1749 and 898 cm^{-1} respectively. In addition, an acid carbonyl stretch absorption at 1710 cm^{-1} is observed (Figure 5(d), peak 6). The shift of the carbonyl absorption from 1744 (for A) to 1749 cm^{-1} suggests some change in the surrounding environment. This may well to due to the formation of a solid solution of the peroxyacid and the acid forms of the salt.

Process 3 - Conversion of B to D

Exposure of B to moisture at high temperatures (above ~50°C) results in a crystalline product - designated D. Figure 3(d) shows the powder X-ray diffraction pattern obtained for this additional phase.

Process 4 - Conversion of C to D

D may also be obtained by heating C above 80°C in a sealed container or in the presence of moisture.

Process 5 - Conversion of A to D

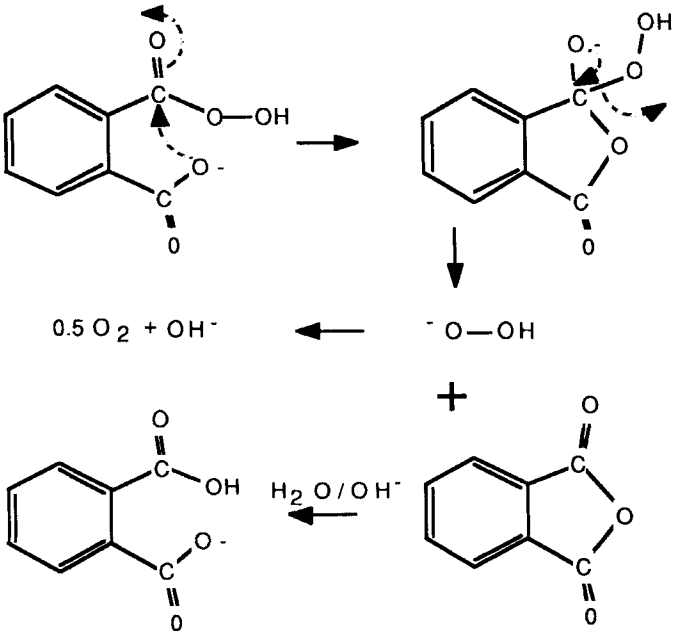
When a sealed sample of A is heated above ~80°C melting is observed, followed by gas (oxygen) evolution. The product is foam-like in appearance because crystallisation occurs during gas evolution. Analysis reveals that it is similar to product D. DSC indicates an endothermic process (~25 J/g) between 90 and 95°C followed by an exothermic one (~-600 J/g) between 95 and 160°C (Figure 2(b)). The DSC results are in agreement with the visual

observations - melting being the exothermic process and decomposition and recrystallisation the exothermic ones. For a sealed sample decomposition is preceded by melting.

CONCLUSIONS

For both methods of heating of A (i.e. in an open atmosphere or sealed, processes 1 and 5 respectively) endothermic steps precede oxygen loss. Thus, an 'open' sample undergoes dehydration before decomposition whilst the sealed sample first melts. DSC (Figure 2) shows that changes commence at higher temperatures for sealed samples than for open ones (90 and ~60°C respectively, at 10°/min heating rate). This difference in reaction pathway is because for the sealed sample the water of hydration cannot escape readily. As a result the material remains crystalline and, therefore, stable until it melts. It is concluded that disruption of crystalline order is a prerequisite to the loss of the peroxy oxygen, indicating an extreme case of molecular loosening.[9]

Infra-red spectroscopy reveals that phthalic anhydride is formed during decomposition of A. This was observed at temperatures as low as 50°C, but was not observed during the dehydration of hexa-aquomagnesium hydrogen phthalate dihydrate[3,10] at 60°C. It is likely, therefore, that phthalic anhydride is a reaction intermediate between the peracid and acid. Its planar conformation would not readily allow for its formation within the ordered structure of A and could partly account for the need for loss of crystallinity during decomposition. A possible mechanism of the decomposition which is in agreement with the above results is shown in Scheme 2.



SCHEME 2 Decomposition pathway for the decomposition of hexa-aquomagnesium monoperoxyphthalate (A)

This study has shown that hexa-aquomagnesium monoperoxyphthalate (A) can decompose in two ways, with the route of the decomposition and the nature of the products depending upon the experimental conditions. At low temperatures (below 80°C) and in an open atmosphere, a semi-amorphous phase containing phthalic anhydride is obtained. This phase can be rehydrated and crystallinity restored. In a sealed environment and at higher temperatures, A first melts and then decomposes to give a crystalline product.

Loss of crystallinity of A is therefore common to both decomposition routes and appears to be a requirement for effective oxygen loss.

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