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Chemistry of sulfate chloride perhydrates

Part 3.†—The properties of $4Na_2SO_4{\cdot}NH_4Cl{\cdot}2H_2O_2$

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The perhydrate $4Na_2SO_4{\cdot}NH_4Cl{\cdot}2H_2O_2$ (SSACP) crystallises in a channel like structure similar to that of $4Na_2SO_4{\cdot}NaCl{\cdot}2H_2O_2$ (SSCP). Thermal desorption of the H_2O_2 from SSACP at temperatures <200 °C results in the formation of Na_2SO_4(III), $(NH_4)_2SO_4$ and NaCl. SSACP can be regenerated from the deperhydrated powder by exposure to the vapour above a H_2O_2 solution. Although NH_4Cl is not initially formed on heating SSACP, heating further to 300 °C results in an exchange reaction between the NaCl and $(NH_4)_2SO_4$, and NH_4Cl is desorbed from the sample. As expected, regeneration of the resulting powder [Na_2SO_4(III)] into SSACP does not occur when the powder is exposed to the vapour above a H_2O_2 solution.

Introduction

Interest in inclusion compounds continues to grow. Guests include a wide variety of small and large molecules. Very few inclusion compounds are however known for H_2O_2. Urea hydrogen peroxide has uses as an oxidant[1] and possesses a channel like structure.[2] We are aware of only one other inclusion compound known to contain H_2O_2, the channel complex $4Na_2SO_4{\cdot}NaCl{\cdot}2H_2O_2$ (SSCP).[3] In SSCP, the H_2O_2 molecules are disordered and lie within channels defined by the sulfate oxygens. In Part 1, we showed that desorption of H_2O_2 from the channels of SSCP results in an intimate mixture of Na_2SO_4(III) and NaCl.[4] The formation of Na_2SO_4(III) rather than the expected phase (V) is thought to be due to an epitaxial relationship between SSCP, Na_2SO_4(III) and NaCl. Furthermore, we showed in Part 2 that when this mixture is exposed to the vapour above H_2O_2 solutions, the perhydrate $4Na_2SO_4{\cdot}NaCl{\cdot}2H_2O_2$ can be regenerated.[5] At high concentrations of H_2O_2 ($\geqslant 0.60$ g cm^{-3}), the reaction between the powder and the gaseous H_2O_2 is direct. At concentrations <0.50 g cm^{-3}, regeneration proceeds *via* a liquid intermediate.

Just as there exists a family of oxalate perhydrates,[6] it is possible to form chemically analogous compounds to SSCP. One such analogue is $4Na_2SO_4{\cdot}KCl{\cdot}2H_2O_2$ (SSKCP) which has been patented as an ingredient in the formulation of a hair dye.[7] Analogues may also be made from NH_4Cl and from LiCl, and powder X-ray diffraction indicates that each of these analogues is isostructural with SSCP.[8] In this article, we describe in detail the deperhydration and reperhydration[5] of SSACP ($4Na_2SO_4{\cdot}NH_4Cl{\cdot}2H_2O_2$).

When SSCP is heated to desorb all of the H_2O_2, the two possible products are Na_2SO_4 and NaCl. The number of possible products of deperhydration, however, clearly increases when analogues of SSCP are considered. There are four possible products of the thermal decomposition of SSACP: Na_2SO_4, $(NH_4)_2SO_4$, NaCl and NH_4Cl. Polymorphism further increases the number of possibilities. Na_2SO_4 has five polymorphic forms (see ref. 4). Ammonium chloride is dimorphic, the phase transition occurring at 183 °C [eqn. (1)]. The crystal structure of phase II is CsCl type whilst that of phase I is NaCl type.[9]

$$NH_4Cl\text{: II} \xrightarrow{183\,^{\circ}C} \text{I} \xrightarrow{200\text{–}300\,^{\circ}C} \text{sublimation} \qquad (1)$$

There is only one polymorphic form of $(NH_4)_2SO_4$ stable above -50 °C.[10,11]

Experimental

Synthesis of SSACP

Using laboratory grade reagents, a solution of 0.39 g (7.2×10^{-3} mol) NH_4Cl in 8 g 0.30 g cm^{-3} (30%w/v) H_2O_2 was added dropwise to a solution of 4.09 g (28.8×10^{-3} mol) of Na_2SO_4 in 20 g 0.30 g cm^{-3} H_2O_2. The resulting solution was left to crystallise in air to yield crystals of SSACP.

Deperhydration of SSACP

Crystals of SSACP were ground (grinding did not affect the structure or H_2O_2 content) and the powder dispersed in Petri dishes. These samples were placed in a preheated isothermal oven and removed periodically and immediately refrigerated at 0 °C in order to prevent further decomposition. The extent of isothermal deperhydration was analysed at ambient temperature as soon as possible by powder X-ray diffraction (PXRD), thermogravimetry (TG) using a heating rate of 10 °C min^{-1} and a N_2 flow of 25 cm^3 min^{-1}, and titrimetric available oxygen content (AVOX).[4] The fully deperhydrated powder obtained when all H_2O_2 has been desorbed at temperatures <200 °C is termed SSACPD.

Evidence for obedience to a particular kinetic law can be obtained from α/t *vs.* t plots[12] using eqn. (2):

$$\alpha = \frac{A_0 - A}{A_0} \qquad (2)$$

where A_0 is the initial AVOX value and A is the AVOX at time t.

Reperhydration of SSACPD

Ground samples of SSACP were heated at 144 °C to remove all the H_2O_2. The resultant powder was then placed in contact with the vapour above a 0.60 g cm^{-3} solution of H_2O_2 and the whole covered with a large crystallising dish for up to 6 days. This was repeated using 0.30 g cm^{-3} H_2O_2. The extent of reperhydration was followed by PXRD and AVOX. The Avrami–Erofeev equation [eqn. (3)] was used to confirm first order kinetic behaviour of reperhydration (as observed for SSCP[5])

$$-\ln(1-\alpha) = kt \qquad (3)$$

where α is the extent of reperhydration and k is the first order rate constant. Since we can extrapolate to A_∞ (the final AVOX after equilibrium has been reached) α can be obtained from the ratio of A to A_∞, where A is the AVOX at time t.

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†Part 2: ref. 4.

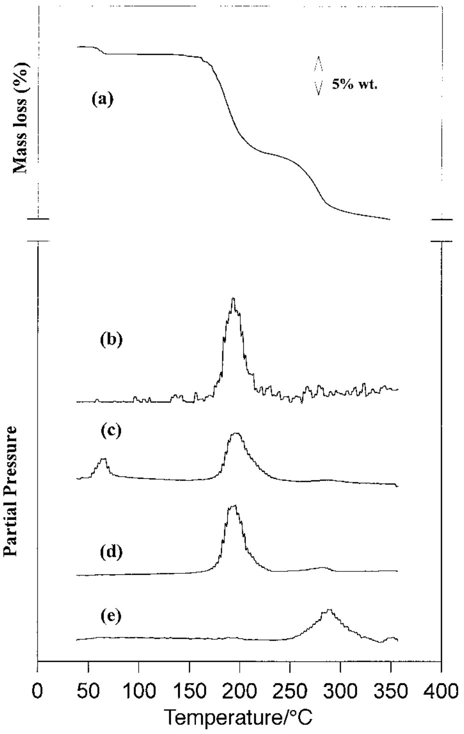

Fig. 1 TG–MS traces of SSACP: (a) TG curve; MS scanning (b) *m/z* 34 (H_2O_2); (c) *m/z* 18 (H_2O); (d) *m/z* 32 (O_2); (e) *m/z* 15 (NH)

Results

Characterisation of the products of thermal deperhydration of SSACP

Fig. 1(a) shows the TG of SSACP. Fig. 1(b), (c), (d) and (e) indicate the mass signal as a function of temperature for *m/z* 34 (H_2O_2), *m/z* 18 (H_2O), *m/z* 32 (O_2) and *m/z* 15 (NH), respectively. There are three mass losses observed in the TG curve of SSACP. The first, at 60 °C, is shown to be 1% by mass of physisorbed H_2O by the MS peak at *m/z* 18. The second mass loss of 10%, between 150 and 200 °C, corresponds to the loss of 2 H_2O_2 per formula unit. Peaks which are coincident with this mass loss are observed in the MS for *m/z* 34, 18 and 32. The onset of the third mass loss overlaps the final stages of H_2O_2 release and corresponds to a mass loss of 7.4% *i.e.* sublimation of NH_4Cl. The broad NH peak (using *m/z* 15) in the MS trace mirrors the assignment in the TG curve.

SSACP heated at 126 °C for 3 days results in desorption of all H_2O_2 as indicated by a zero AVOX (product is denoted SSACPD). This temperature provided convenient time intervals for studying the isothermal deperhydration (see below). Fig. 2 compares the PXRD patterns obtained for SSACPD and SSACPD heated further to 300 °C for 3 h, compared to those of possible decomposition products. Reflections due to Na_2SO_4(III) and $(NH_4)_2SO_4$ are readily recognisable in the pattern of SSACPD. The doublet of reflections in the pattern at 45.6 and 46.2° is due to NaCl and Na_2SO_4(III) respectively. There is little evidence for the presence of any NH_4Cl in SSACPD. Upon heating SSACPD to 300 °C for 3 h, reflections in the PXRD pattern due to $(NH_4)_2SO_4$ and NaCl disappear and the pattern resembles that of Na_2SO_4(III).

Isothermal decomposition of SSACP at 88 and 126 °C

Fig. 3 shows the PXRD patterns of samples of SSACP heated at 126 °C for between 100 and 4200 min. There is a gradual increase in intensity of reflections due to the product phases [$(NH_4)_2SO_4$, Na_2SO_4(III) and NaCl] and a corresponding decrease in intensity of SSACP reflections. The emergence of reflections due to the product phases [*e.g.* those of Na_2SO_4(III) at 22.6, 23.6 and 25.6°] occurs much faster for SSACP than for SSCP,[13] indicating lower thermal stability. This rapid onset of the reaction in SSACP is mirrored by a sharp fall in the available oxygen content within 100 min of heating. Subsequent desorption of the H_2O_2 becomes increasingly more difficult and after 3300 minutes there is still some residual AVOX (2% of the theoretical maximum). Fig. 4 shows the α/t *vs.* t plot, obtained from AVOX values, of samples of SSACP heated at 126 °C. The plot does not clearly fit any of the Avrami–Erofeev [$-\ln(1-\alpha)=kt^n$], power law ($\alpha=kt^n$) or contracting solid [*e.g.* $1-(1-\alpha)^{1/2}=kt$] models.[12]

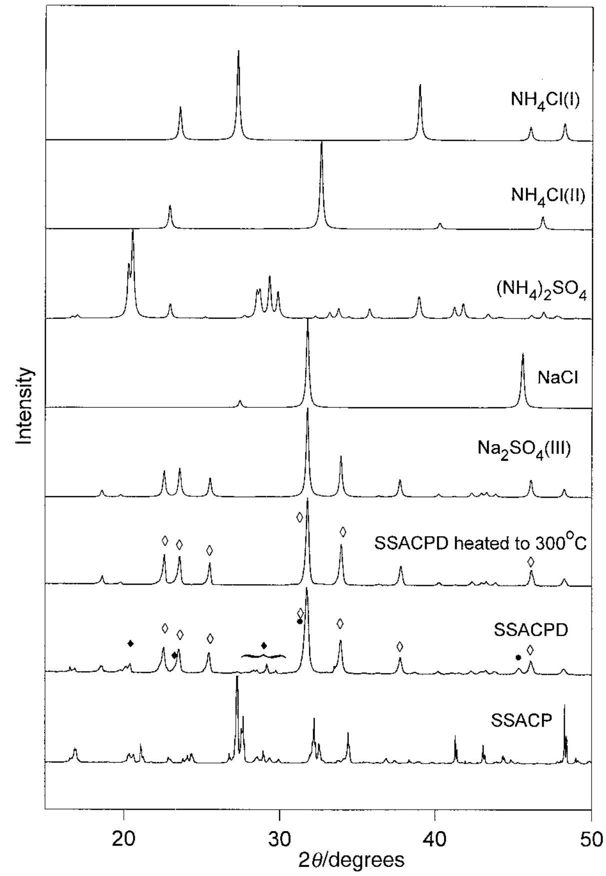

Fig. 2 Experimental PXRD patterns of SSACP, SSACPD and SSACPD heated at 300 °C for 3 h, compared to patterns of SSACP, Na_2SO_4(III), $(NH_4)_2SO_4$, NaCl and NH_4Cl. Reflections due to $(NH_4)_2SO_4$, NaCl vanish on heating to 300 °C [key: (◇) Na_2SO_4(III), (●) NaCl, (◆) $(NH_4)_2SO_4$; for clarity, only representative reflections are labelled].

TG of samples partially deperhydrated at 126 °C shows two mass losses (Fig. 5). The first (150–200 °C) decreases in magnitude with time and is attributed to H_2O_2. There is little change in the magnitude of the second TG mass loss (> 200 °C) in any of the samples. This mass loss is due to the sublimation of NH_4Cl (*cf.* Fig. 1). Any physisorbed water, initially present in the SSACP, has been released during deperhydration.

Deperhydration of SSACP was also performed at 88 °C. As expected the loss of AVOX occurs less dramatically at 88 °C than at 126 °C, with some residual oxygen content after 100 days. PXRD patterns of the partially heated samples show similar trends to those in Fig. 3. TG of samples of SSACP partially deperhydrated at 88 °C exhibit three distinct mass losses, namely 150–180, 180–210 and 210–300 °C (Fig. 6). The magnitudes of both of the two outer mass losses are less than those expected from the AVOX value (*i.e.* H_2O_2 content) and initial NH_4Cl content. This suggests that the central mass loss (180–210 °C) corresponds to the simultaneous loss of H_2O_2 and NH_4Cl.

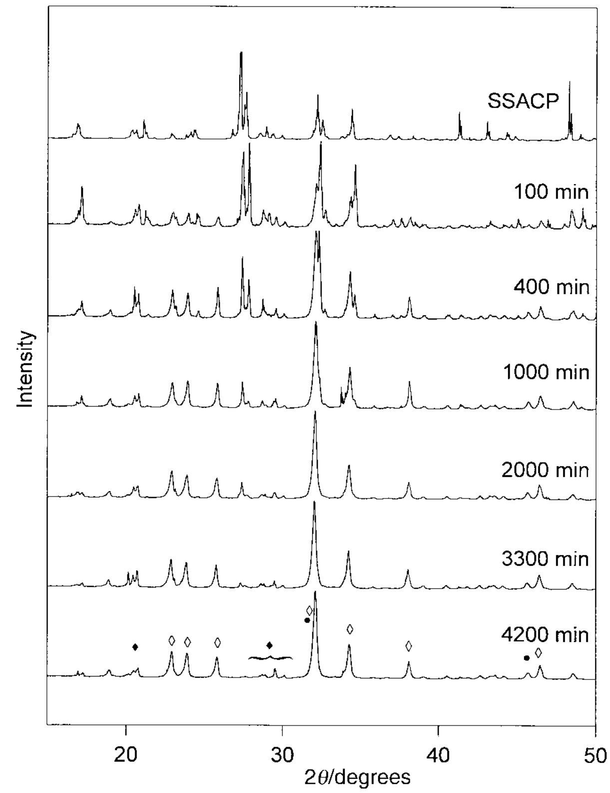

Fig. 3 PXRD patterns of samples of SSACP after heating at 126 °C. [Key: (◇) Na_2SO_4(III), (●) NaCl, (◆) $(NH_4)_2SO_4$; for clarity, only representative reflections are labelled]

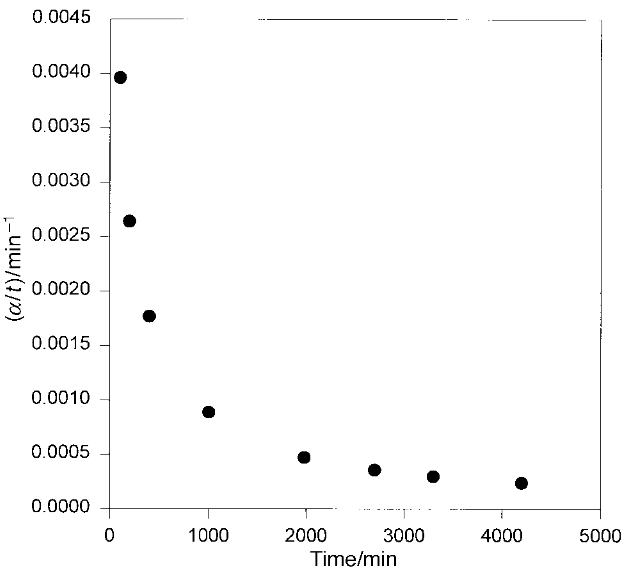

Fig. 4 α/t *vs.* t plot of samples of SSACP after heating at 126 °C

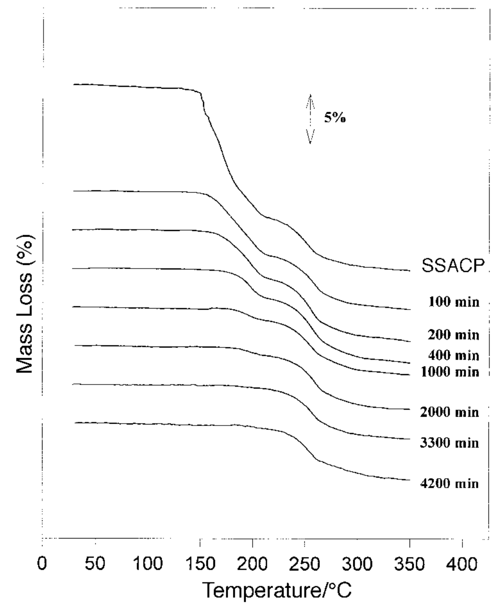

Fig. 5 TG traces of samples of SSACP after heating at 126 °C

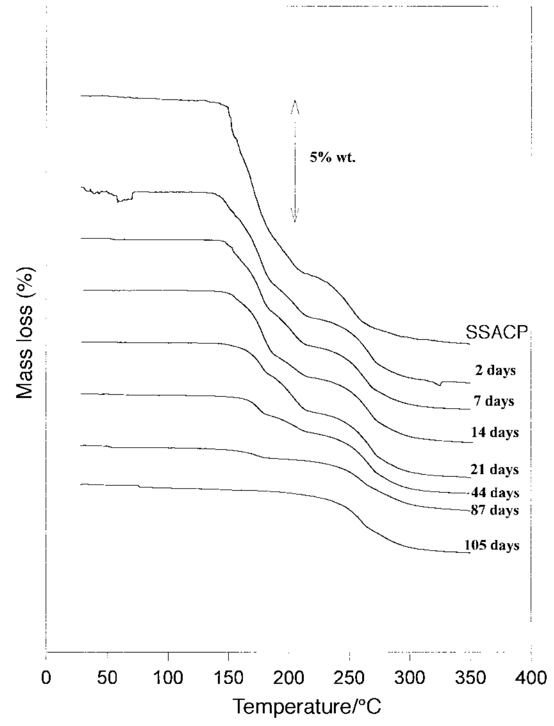

Fig. 6 TG traces of samples of SSACP after heating at 88 °C

Reperhydration of SSACPD

(i) 0.60 g cm^{-3} H_2O_2. PXRD patterns of samples of SSACPD exposed to the vapour above a 0.60 g cm^{-3} H_2O_2 solution are shown in Fig. 7. All of the phases which constitute SSACPD are clearly still present after 2 h. These include Na_2SO_4(III) (three characteristic reflections 22.6, 23.6 and 25.6°) and $(NH_4)_2SO_4$ (characteristic reflections 18–21°). In addition, new reflections present after 2 h include 27.1 and 27.6° (due to SSACP), and 28.1 and 29.0° [due to Na_2SO_4(V)]. By 10 h the most intense reflections are due to SSACP and Na_2SO_4(V). After 6 days the pattern is dominated by reflections due to SSACP although some weak reflections due to either Na_2SO_4(V) or $(NH_4)_2SO_4$ are still present. Conversion into SSACP as monitored by PXRD is, therefore, not complete after 6 days using 0.60 g cm^{-3} H_2O_2. Furthermore, after 6 days the available oxygen content has not reached the theoretical maximum but rather has dipped to 81.9% from a value of 90.2% after 48 h (Fig. 8). The initial rate of increase of AVOX shows good first order behaviour [eqn. (3)], with a first order rate constant of 13.9×10^{-6} s^{-1} (model curve).

(ii) 0.30 g cm^{-3} H_2O_2. Reperhydration of SSACPD using a dilute H_2O_2 solution (0.30 g cm^{-3}) leads to rapid Na_2SO_4 (III→V) phase transformation within 2 h (Fig. 9). Although some (III→V) transformation occurs after 2 h when concentrated H_2O_2 solutions are used, the transformation is not only more complete under the atmosphere of dilute concentrations, there is also no evidence of any $(NH_4)_2SO_4$ in the 18–21°

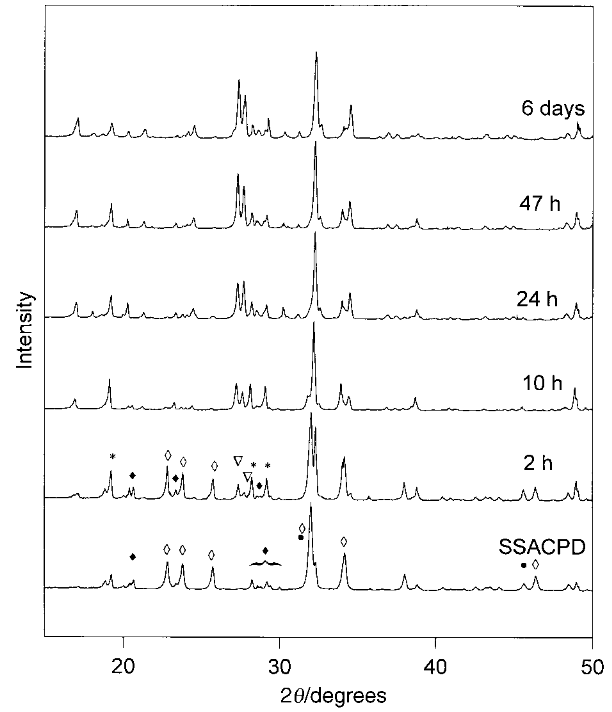

Fig. 7 PXRD patterns showing reperhydration of SSACPD using a 0.60 g cm^{-3} H_2O_2 solution [key: (▽) SSACP, (◇) Na_2SO_4(III), (*) Na_2SO_4(V), (●) NaCl, (◆) $(NH_4)_2SO_4$; for clarity, only representative reflections are labelled]

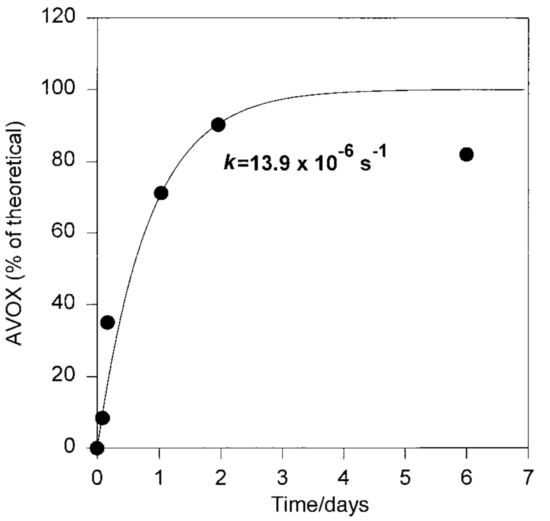

Fig. 8 Reperhydration of SSACPD using a 0.60 g cm^{-3} H_2O_2 solution as shown by AVOX; the curve is obtained from eqn. (3)

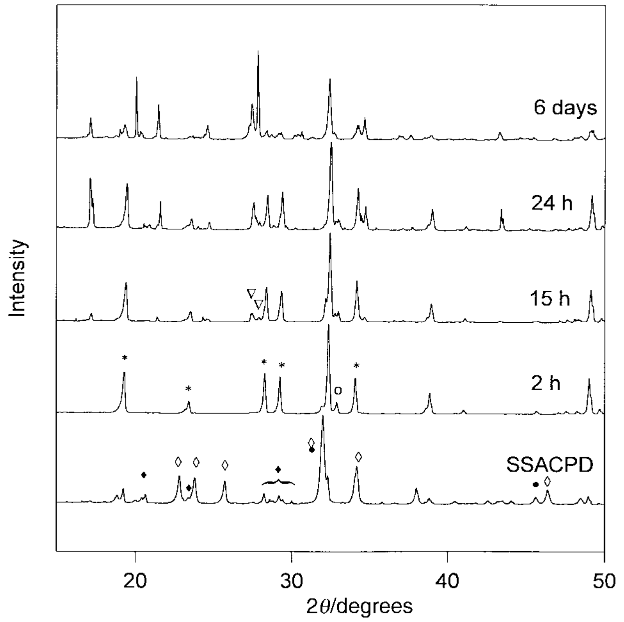

Fig. 9 PXRD patterns showing reperhydration of SSACPD using a 0.30 g cm^{-3} H_2O_2 solution [key: (▽) SSACP, (◇) Na_2SO_4(III), (*) Na_2SO_4(V), (●) NaCl, (◆) $(NH_4)_2SO_4$, (○) NH_4Cl(II); for clarity, only representative reflections are labelled]

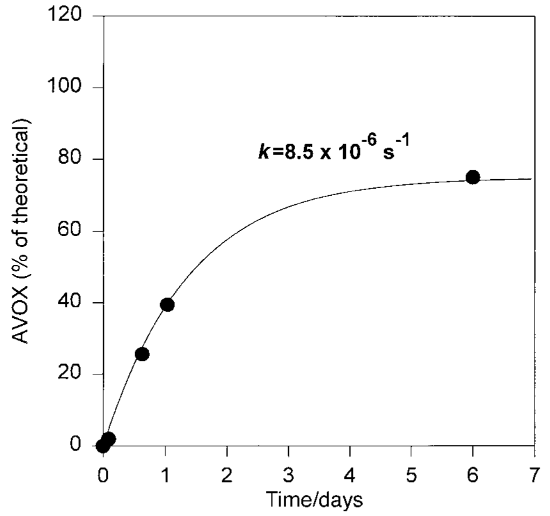

Fig. 10 Reperhydration of SSACPD using a 0.30 g cm^{-3} H_2O_2 solution as shown by AVOX; the curve is obtained from eqn. (3)

region of the pattern. After 2 h, a reflection at 32.8° appears in the pattern, which is indicative of NH_4Cl(II). This reflection is not present in SSACPD.

Conversion of SSACPD into SSACP is incomplete after 6 days using the atmosphere above 0.30 g cm^{-3} H_2O_2, as shown by PXRD and quantified by AVOX as being 75.0% (Fig. 10). Fitting the change in AVOX to first order behaviour results in a rate constant of 8.5×10^{-6} s^{-1}. This is significantly lower than the rate constant obtained for reperhydration at 0.60 g cm^{-3} H_2O_2 (*cf.* 13.9×10^{-6} s^{-1}).

Discussion

Thermal studies on SSACP

Deperhydration of SSACP at 88, 126 and 144 °C proceeds to give Na_2SO_4(III), $(NH_4)_2SO_4$ and NaCl as shown by PXRD. There is no evidence for the formation of NH_4Cl. SSACP may therefore be said to deperhydrate <144 °C according to eqn. (4).

$$4Na_2SO_4{\cdot}NH_4Cl{\cdot}2H_2O_2 \xrightarrow{<144\,^{\circ}C} Na_2SO_4(III) + (NH_4)_2SO_4 + NaCl \qquad (4)$$

From the molecular formula, one would expect four times as much NaCl to be formed than NH_4Cl. However, that no NH_4Cl is observed suggests preferential formation of NaCl. In Part 2[5] we showed that NaCl is epitaxially related to Na_2SO_4(III) and SSCP. NaCl is also epitaxially related to the isostructural SSACP,[8] *i.e.* an interface of sufficiently similar surface area and shape can be formed between the NaCl and SSACP crystals to generate enhanced rate of growth of one crystallite on the other. Thus as SSACP deperhydrates, NaCl crystallites are able to preferentially form either on the SSACP or on any Na_2SO_4(III) which has been formed. The enhanced rate of formation of NaCl, and hence removal of Cl^- ions, therefore prohibits formation of NH_4Cl.

When SSACPD is further heated to 300 °C, reflections in the PXRD pattern due to $(NH_4)_2SO_4$ disappear. In addition, reflections due to NaCl also vanish. The resulting powder pattern resembles that of pure Na_2SO_4(III). That NaCl is not present in the pattern implies that the product salts are either reacting to form NH_4Cl [eqn. (5)], or that the salts are so intimately mixed that the cations are able to migrate between them. We note that the energy for this process to occur must be less than that necessary to decompose $(NH_4)_2SO_4$.

$$(NH_4)_2SO_4 + NaCl \xrightarrow{210\text{–}300\,^\circ C} Na_2SO_4(III) + NH_4Cl \quad (5)$$

$$NH_4Cl \rightarrow \text{sublimation} \quad (6)$$

TG of samples heated at 126 °C exhibit slightly different traces to those heated at 88 °C. When the sample is deperhydrated at 126 °C, two distinct mass losses occur in the subsequent TG (Fig. 5). The first (150–200 °C) decreases in magnitude with time and is attributed to H_2O_2. The second mass loss of 4.9% (>210 °C) is attributed to NH_4Cl (Fig. 1). Since NH_4Cl is not present in the partially deperhydrated sample, it must originate from $(NH_4)_2SO_4$ formed during the TG [eqn. (5)]. That the magnitude of this mass loss remains constant indicates that this reaction [eqn. (5)] and the subsequent sublimation of the NH_4Cl [eqn. (6)] do not occur during the isothermal deperhydration at 126 °C.

For samples of SSACP which have been partially deperhydrated at 88 °C, an additional distinct mass loss is observed in the TG (180–210 °C) and is attributed to simultaneous loss of H_2O_2 and NH_4Cl. That this additional mass loss is so distinct from that above 210 °C suggests the NH_4Cl is released in two stages. The first is aided by the release of H_2O_2 and so occurs at a lower temperature than would usually be expected for sublimation of NH_4Cl. The second and most significant loss of NH_4Cl takes place above 210 °C.

The initial rapid rate of deperhydration of SSACP at 126 °C subsequently diminishes as displayed by the α/t *vs.* t plot (Fig. 4). The α/t *vs.* t plot of the deperhydration of SSCP at 126 °C possesses a more constant gradient but is similar in shape.[8] This suggests that SSCP and SSACP deperhydrate at 126 °C according to similar kinetic laws (probably based on contracting solid) but with different rate constants. At 88 °C, however, the α/t *vs.* t plots of SSACP and SSCP are similar only in the initial stages up to *ca.* 10 days.[4]

Reperhydration of SSACPD

The rate and extent of reperhydration depends on whether the Na_2SO_4(III) in the deperhydrated mixture transforms to Na_2SO_4(V).[5] Regeneration is most complete and occurs fastest if the transformation is prevented. The presence of a foreign material may affect Na_2SO_4 (III→V) phase transformation.[14] The transformation will be accelerated if the foreign material is isostructural with Na_2SO_4(V) and/or more hygroscopic than Na_2SO_4. On the other hand, the transformation will be suppressed if the foreign material is isostructural with Na_2SO_4(III).

Reperhydration of SSACPD results in significant Na_2SO_4 (III→V) phase transformation even when using concentrated solutions of H_2O_2 ($0.60\ \mathrm{g\ cm^{-3}}$). This is in contrast to the reperhydration of SSCP for which significant phase transformation is not observed at $0.60\ \mathrm{g\ cm^{-3}}$ H_2O_2.[5] $(NH_4)_2SO_4$ is neither isostructural with Na_2SO_4(III) nor with Na_2SO_4(V) and might, therefore, be expected not to influence the Na_2SO_4 (III→V) transformation. $(NH_4)_2SO_4$ is, however, significantly more hygroscopic than Na_2SO_4[15] and is able to enhance the transformation by promoting the sorption of water vapour onto the powder.[14] Thus for SSACPD, the Na_2SO_4 (III→V) transformation occurs at a lower humidity and hence a higher concentration of H_2O_2.

The available oxygen content of the reperhydrated SSACP decreases after *ca.* 2 days. This suggests that after two days decomposition of SSACP is more significant than its formation and that SSACP is less stable than SSCP to relative humidity.

Reperhydration of SSACPD using $0.30\ \mathrm{g\ cm^{-3}}$ H_2O_2 shows very similar behaviour to SSCPD. Rapid and complete (III→V) phase transformation of Na_2SO_4 occurs within 2 h. During this phase transformation NH_4Cl(II) is formed by the reaction or ion migration between $(NH_4)_2SO_4$ and NaCl. The capacity for NaCl and $(NH_4)_2SO_4$ to exchange is also displayed when SSACPD is heated at 300 °C. Within the first 2 h of reperhydration, therefore, the reaction proceeds according to eqn. (7). Regeneration of SSACP then proceeds from Na_2SO_4(V) and NH_4Cl [eqn. (8)].

$$\begin{aligned} Na_2SO_4(III) + (NH_4)_2SO_4 + NaCl &\longrightarrow Na_2SO_4(V) \\ &\quad + NH_4Cl(II) \end{aligned} \quad (7)$$

$$Na_2SO_4(V) + NH_4Cl(II) \xrightarrow{H_2O_2} 4Na_2SO_4{\cdot}NH_4Cl{\cdot}2H_2O_2 \quad (8)$$

The rate constants obtained from the AVOX values (13.9 and $8.5 \times 10^{-6}\ \mathrm{s^{-1}}$) are lower than those obtained for reperhydration of SSCP using the same concentrations of H_2O_2.

Conclusions

SSACP ($4Na_2SO_4{\cdot}NH_4Cl{\cdot}2H_2O_2$) possesses lower thermal stability relative to its NaCl analogue, SSCP. Regeneration of SSACPD shows some dependence on the concentration of H_2O_2. An exchange reaction between $(NH_4)_2SO_4$ and NaCl is observed at high temperature deperhydration, and during reperhydration using low concentrations of H_2O_2.

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