JOURNAL OF
Materials
CHEMISTRY

Chemistry of sulfate chloride perhydrates

Part 2.[†]—Reperhydration by H_2O_2

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The perhydrate, $4Na_2SO_4 \cdot NaCl \cdot 2H_2O_2$, has been heated in order to fully desorb the H_2O_2. The resulting powder [an intimate mixture of Na_2SO_4(III) and NaCl] was exposed to the vapour above a solution of H_2O_2. Two mechanisms are observed for the regeneration of the perhydrate: at high concentrations of H_2O_2 (>0.60 g cm^{-3}), direct reaction between the powder and the gaseous H_2O_2 occurs; at concentrations <0.60 g cm^{-3}, the powder becomes wet and the Na_2SO_4 phase (III) transforms into phase (V). Regeneration into the perhydrate then proceeds by crystallisation of the perhydrate from the slurry of Na_2SO_4(V) and NaCl. The two mechanisms occur together at intermediate concentrations of H_2O_2.

Perhydrates are important components of powder laundry detergents and can be regarded as a convenient solid form of H_2O_2. Of particular interest is the stable perhydrate, $4Na_2SO_4 \cdot NaCl \cdot 2H_2O_2$ (SSCP), developed for use with neutral detergents.[1] The H_2O_2 is *included* within channels defined by sulfate oxygens in the *ab* plane.[2] In Part 1,[3] we reported that when SSCP is heated, the H_2O_2 is released intact, leaving a very intimate mixture, denoted SSCPD, of Na_2SO_4(III) and NaCl. It is at first surprising that Na_2SO_4(III) is formed since phase V is regarded as the stable form of Na_2SO_4.[4] We believe that the reason for its formation is due to the existence of an epitaxial relationship between the Na_2SO_4(III) and NaCl.

Adams *et al.* showed[5] that the decomposition of $K_2C_2O_4 \cdot H_2O_2$ and $Na_2C_2O_4 \cdot H_2O_2$ under humid conditions could be retarded by low pressures of H_2O_2, implying that eqn. (1) is reversible.

$$MX \cdot H_2O_2(s) \leftrightarrow MX_{(s)} + H_2O_{2(g)} \tag{1}$$

We were therefore interested to find out whether a perhydrate may be regenerated once all of the H_2O_2 had been desorbed. We have termed this regeneration *reperhydration*, akin to rehydration to form a hydrate. We have previously communicated that reperhydration of SSCP is indeed possible.[6] In this paper, we report in detail on the kinetics and mechanisms of reperhydration using a range of concentrations of H_2O_2 up to 0.85 g cm^{-3}.

Experimental

Using laboratory grade reagents, a solution of 0.42 g (7.2×10^{-3} mol) NaCl in 8 g of 0.30 g cm^{-3} 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 of 0.30 g cm^{-3} H_2O_2. The resulting solution was allowed to evaporate in air and yielded well formed crystals of SSCP. These were ground and then heated to fully desorb the H_2O_2 (grinding did not affect the structure or H_2O_2 content). The resultant powder was then placed in contact with the vapour above a 0.30 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 for 0.10, 0.20, 0.38, 0.50, 0.55, 0.60 and 0.85 g cm^{-3} concentrations. In the same way, the effect of pure H_2O vapour (*i.e.* 0 g cm^{-3} H_2O_2) was also examined, using H_2SO_4 solutions of different known relative humidities.[7] The extent of reperhydration was followed by powder X-ray diffraction (PXRD), thermogravimetry (TG) and titrimetric available oxygen content (AVOX).[3] Optical microscopy of samples before and after reperhydration was also performed. Evidence for first order kinetic behaviour can be obtained using a form of the Avrami–Eroveef equation[8]

$$-\ln(1-\alpha) = kt \tag{2}$$

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.

Results

The influence upon SSCPD of the vapour above H_2O_2 solutions up to 0.85 g cm^{-3} concentration is discussed below. The observations suggest reperhydration can occur *via* two different mechanisms. The first occurs using >0.60 g cm^{-3} H_2O_2 whilst the second happens when <0.50 g cm^{-3} H_2O_2 is used. A combination of both mechanisms occurs for concentrations 0.50–0.60 g cm^{-3} H_2O_2.

(i) 0.60–0.85 g cm^{-3} H_2O_2

Fig. 1 shows PXRDs of SSCPD exposed to 0.60 g cm^{-3} H_2O_2 for different periods of time up to 6 days. Reperhydration appears to be close to the reverse of deperhydration:[3,6] there is a decrease in reflection intensity over time of Na_2SO_4(III) and NaCl phases and a corresponding increase in intensity of

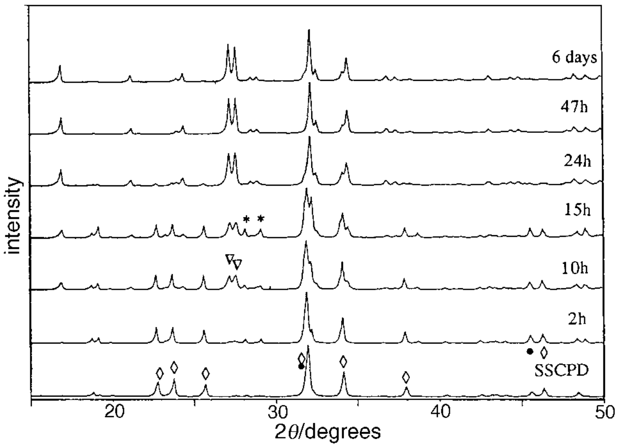


Fig. 1 PXRD patterns showing reperhydration of SSCPD using a 0.60 g cm^{-3} H_2O_2 solution (▽, SSCP; ◇, Na_2SO_4(III); *, Na_2SO_4(V); ●, NaCl. For clarity, only representative reflections are labelled)

[†] Part 1: ref. 3.

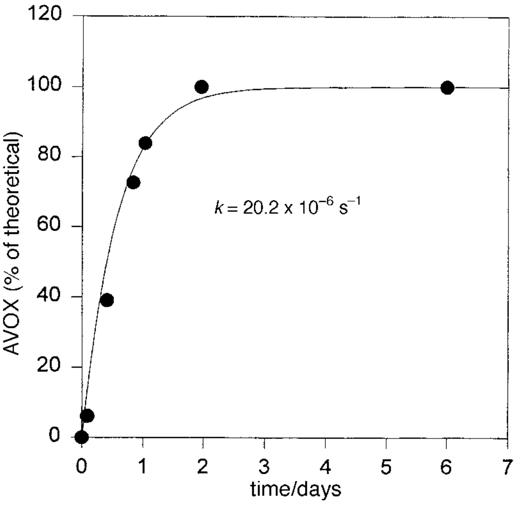


Fig. 2 Reperhydration of SSCPD using a 0.60 g cm^{-3} H_2O_2 solution as shown by AVOX. The curve is obtained from eqn. (2)

reflections due to regenerated SSCP. A fourth phase, Na_2SO_4(V), is discernible after 15 h and is present in much lower concentrations in the preceding two samples (2 and 10 h). However Na_2SO_4(III), NaCl and SSCP phases generally dominate the patterns.

The corresponding AVOX (as a percentage of that theoretically expected for a pure sample of SSCP) of the sample *vs.* time of exposure to the vapour above 0.60 g cm^{-3} H_2O_2 solution is plotted in Fig. 2. There is apparently very little induction period, but rather, a rapid rise in oxygen content levelling off at 100% after 48 h. In other words after 48 h there are 2 mol of H_2O_2 per mol of sample. Regeneration into $4Na_2SO_4 \cdot NaCl \cdot 2H_2O_2$ is therefore complete and the sample contains just one phase, SSCP. There is reasonable correlation of the points to eqn. (2) ($R^2 = 0.984$), giving a first order rate constant of $20.2 \times 10^{-6}\ s^{-1}$.

Moving to the highest concentration of H_2O_2 available to us, 0.85 g cm^{-3}, results in almost identical behaviour. PXRD shows that only Na_2SO_4(III), NaCl and regenerated SSCP phases are present throughout the reperhydration.[9] No Na_2SO_4(V) is observed and reperhydration occurs directly from Na_2SO_4(III) and NaCl. As at 0.60 g cm^{-3} concentration, completion of the reaction has also occurred by 48 h (Table 1). Furthermore, the rate constant obtained from the AVOX values, $20.7 \times 10^{-6}\ s^{-1}$, is very similar to that obtained using a concentration of 0.60 g cm^{-3} H_2O_2 (Table 1).

The powder remained visibly dry throughout the experiment and did not adhere to the Petri dish. Fig. 3 shows optical micrographs of crystals of SSCP which have been heated in order to desorb all H_2O_2 and the same crystals after 4 days reperhydration at 0.85 g cm^{-3} H_2O_2. Although the shape of the SSCPD particles is less well defined after reperhydration, there is little evidence of condensate around the powder. Thermal analysis also confirms that the powder remains dry. Fig. 4(a) reveals that the loss of H_2O_2 from SSCPD exposed to 0.60 g cm^{-3} H_2O_2 for 10 h occurs between 150 and 200 °C (comparable to that from pure SSCP). More importantly, a mass loss at lower temperatures which would be indicative of water loss, is not observed.

Before

After

Fig. 3 Optical micrographs of crystals of SSCPD before and after reperhydration using a 0.85 g cm^{-3} H_2O_2 solution for 4 days

(ii) $<$0.50 g cm^{-3} H_2O_2

At concentrations of H_2O_2 $<$0.50 g cm^{-3}, the powder becomes visibly damp and adheres to the Petri dish. Indeed after 6 days the powder is better described as a slurry. Fig. 5 shows the optical micrographs of crystals of SSCPD before and after it has been exposed to 0.30 g cm^{-3} H_2O_2 for 4 days. Considerable condensation of liquid has formed on and around the crystals. Further evidence for the powder becoming wet is afforded by the TG of SSCPD exposed to 0.30 g cm^{-3} H_2O_2 for 10 h [Fig. 4(b)]. There is a significant mass loss of physisorbed

Table 1 Summary of experimental details of reperhydration of SSCPD

H_2O_2 solution/ g cm^{-3}	equivalent %RH above solution	mol fraction of H_2O_2 in vapour above solution	AVOX after 6 days[a] (% of theoretical)	first order rate constant $10^{-6}\ s^{-1}$	correlation of points (R^2)
0.10	94	0.002	10	—	—
0.20	88	0.004	30	—	—
0.30	80	0.008	65	9.4	0.999
0.38	74	0.011	87	10.0	0.985
0.50	62	0.020	96	10.5	0.983
0.55	58	0.025	98	18.2	0.983
0.60	54	0.033	100	20.2	0.984
0.85	36	0.079	100	20.7	0.934

[a] An equilibrium value was always obtained after 6 days.

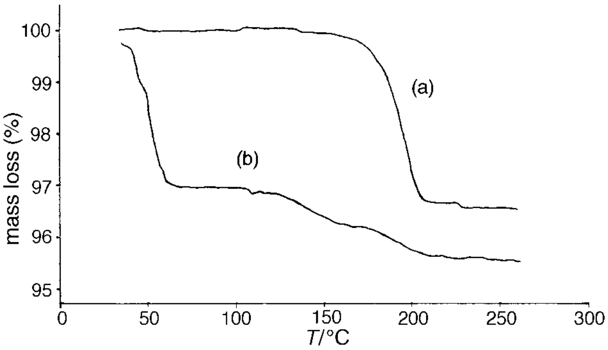


Fig. 4 TG traces of SSCPD exposed to (a) 0.60 g cm^{-3} and (b) 0.30 g cm^{-3} H_2O_2 solutions for 10 h

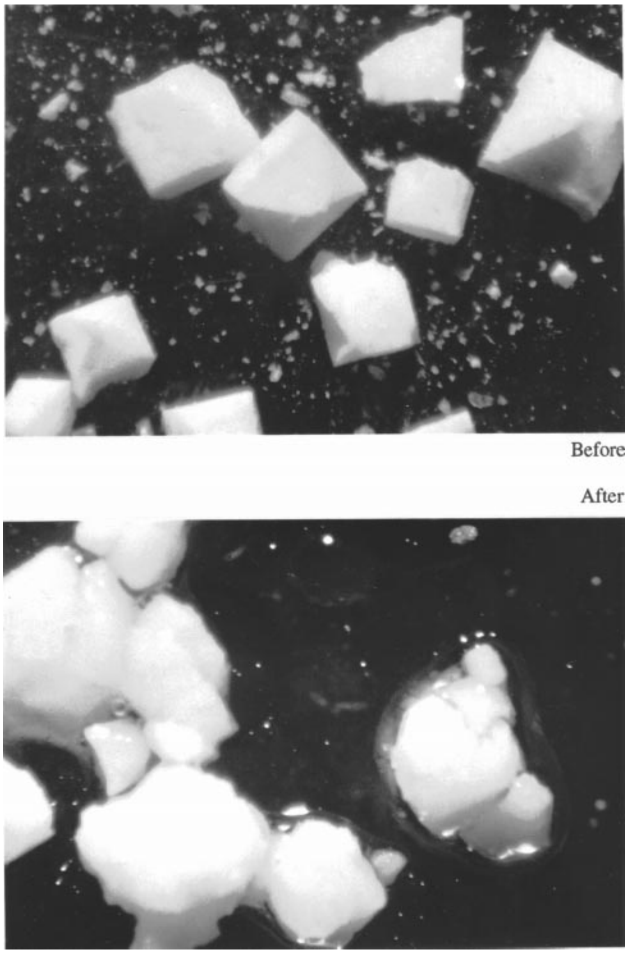


Fig. 5 Optical micrographs of crystals of SSCPD before and after reperhydration using a 0.30 g cm^{-3} H_2O_2 solution for 4 days

H_2O occurring at 50 °C. The second mass loss (120–165 °C) corresponds to either physisorbed H_2O_2 or to bound H_2O associated with hydrate formation. The third mass loss (165–210 °C) is identified with tightly bound H_2O_2, *i.e.* H_2O_2 held within the channels of SSCP, since its magnitude of *ca.* 0.6% of the total mass would give an expected AVOX (as % of the theoretical) of this sample of $0.6/9.8 = 6.1\%$ (*cf.* 5.6% measured).

The powder X-ray diffraction patterns of successive exposures of SSCPD to 0.30 g cm^{-3} H_2O_2 are shown in Fig. 6. A powder pattern of pure Na_2SO_4(V) is also included in the figure. All of the reflections in the PXRDs can be assigned as either Na_2SO_4(III), Na_2SO_4(V), NaCl or SSCP. Within 2 h, the powder has changed from being a mixture of Na_2SO_4(III) and NaCl to a mixture of Na_2SO_4(V) and NaCl. Although there is little evidence for SSCP in the PXRD before 15 h, AVOX measurements show that there is some active oxygen present even after 2 h.

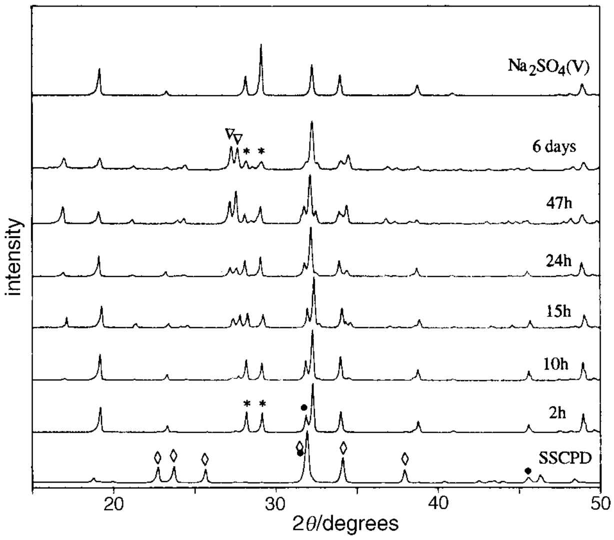


Fig. 6 PXRD patterns showing reperhydration of SSCPD using a 0.30 g cm^{-3} H_2O_2 solution. The PXRD pattern of Na_2SO_4(V) is also included (key as in Fig. 1).

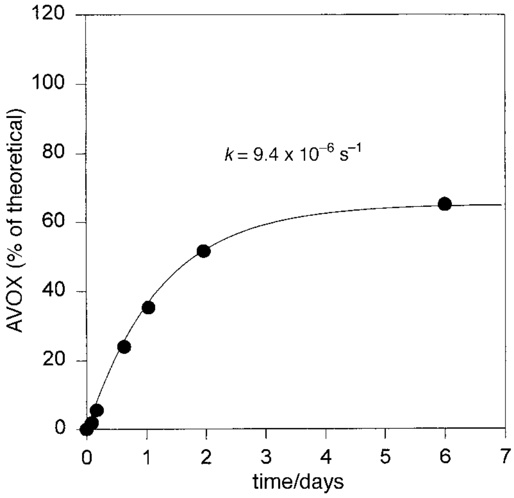


Fig. 7 Reperhydration of SSCPD using a 0.30 g cm^{-3} H_2O_2 solution as shown by AVOX. The curve is obtained from eqn. (2).

Despite SSCP reflections dominating the PXRD pattern after 6 days, reflections due to Na_2SO_4(V) and NaCl still remain and complete regeneration of the solid has not occurred. Fig. 7 shows the rise in AVOX of the samples during reperhydration. There is no induction period and the available oxygen content rises to 65% (of the theoretical value expected for pure SSCP) over 6 days. Further reaction is unlikely to occur beyond 65% regeneration, as shown by the levelling off of the AVOX in the figure. The AVOX values fit well to the model curve, obtained using eqn. (2), and a first order rate constant of $9.4 \times 10^{-6}\ s^{-1}$ (Fig. 7). This rate constant is half that observed for solutions $\geqslant 0.60$ g cm^{-3} H_2O_2.

Using a slightly higher H_2O_2 concentration of 0.38 g cm^{-3}, behaviour remains the same in the PXRD: within 2 h all Na_2SO_4(III) has transformed to Na_2SO_4(V) and subsequent growth of the SSCP phase proceeds from Na_2SO_4(V) and NaCl phases.[9] The rate constant of reperhydration, $10.0 \times 10^{-6}\ s^{-1}$, is also in very close agreement with that obtained at 0.30 g cm^{-3} H_2O_2 concentration (Table 1). The final equilibrium AVOX is 87%, significantly higher than that measured for 0.30 g cm^{-3} H_2O_2 (65%).

Fig. 8 shows the influence upon SSCPD of solutions of

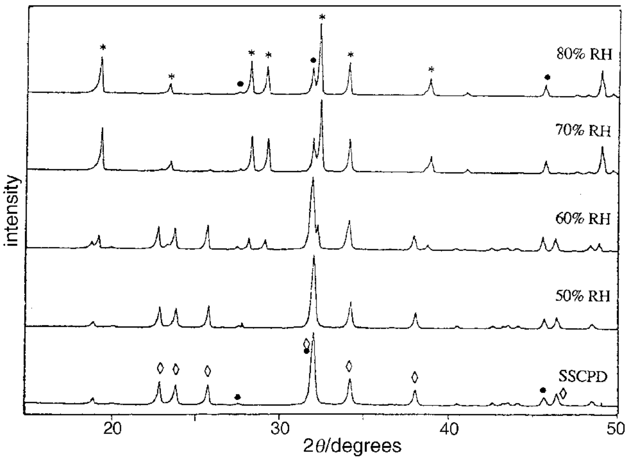


Fig. 8 PXRD patterns of SSCPD exposed to H_2SO_4 solutions of different relative humidities (key as in Fig. 1)

H_2SO_4 having different relative humidities (% RH) at 25 °C. Each pattern was measured after 2 h exposure to the vapour above the H_2SO_4 solution. It is clear that SSCPD is stable for 2 h at humidities $\leqslant$50% RH but that partial (III→V) phase transformation of Na_2SO_4 occurs after 2 h at 60% RH. Exposure of SSCPD to the vapour above solutions of $\geqslant$70% RH results in complete phase transformation.

(iii) 0.50–0.60 g cm^{-3} H_2O_2

The transition between the two mechanisms occurs in the range 0.50–0.60 g cm^{-3} H_2O_2. Fig. 9 and 10 show reperhydration of SSCPD using 0.55 g cm^{-3} H_2O_2 over 6 days as monitored by PXRD and AVOX respectively. After 2 h there are four phases very clearly visible in the PXRD: Na_2SO_4(III), Na_2SO_4(V), NaCl and regenerated SSCP. After 10 h, the Na_2SO_4(III) phase is much less prominent but still visible and regeneration of the product, SSCP, is clearly underway. There is good first order obedience of the values obtained by AVOX to eqn. (2), giving a rate constant of 18.2×10^{-6} s^{-1}. This value approaches that observed for $\geqslant$0.60 g cm^{-3} solutions.

Reperhydration using 0.50 g cm^{-3} H_2O_2 shows similar behaviour to more dilute solutions, with Na_2SO_4(V) and NaCl forming within 2 h. However, unlike behaviour shown by more dilute solutions, the Na_2SO_4(III) phase persists throughout the reaction as monitored by PXRD.[9] The trend towards complete reperhydration at higher concentrations is seen to continue at 0.50 g cm^{-3} H_2O_2 as seen by an AVOX value after 6 days of 95.8% (Table 1). Good first order kinetics are displayed giving a rate constant of 10.5×10^{-6} s^{-1}, in agreement with those obtained at 0.30 and 0.38 g cm^{-3} (Table 1).

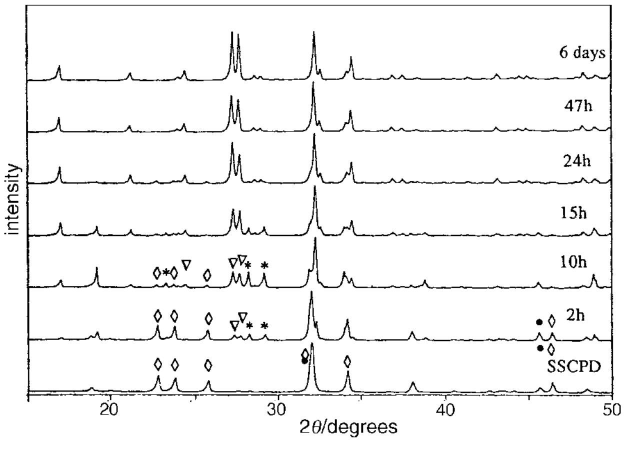


Fig. 9 PXRD patterns showing reperhydration of SSCPD using a 0.55 g cm^{-3} H_2O_2 solution (key as in Fig. 1)

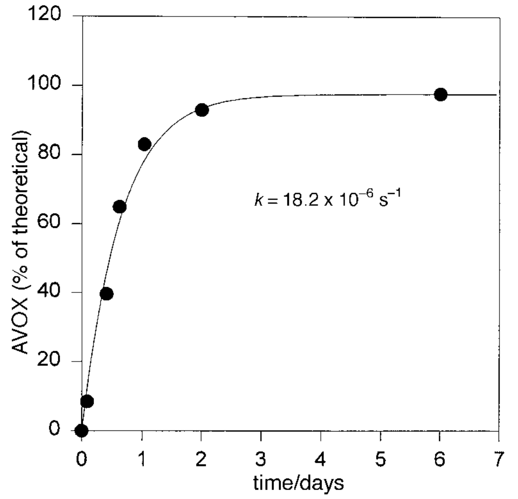


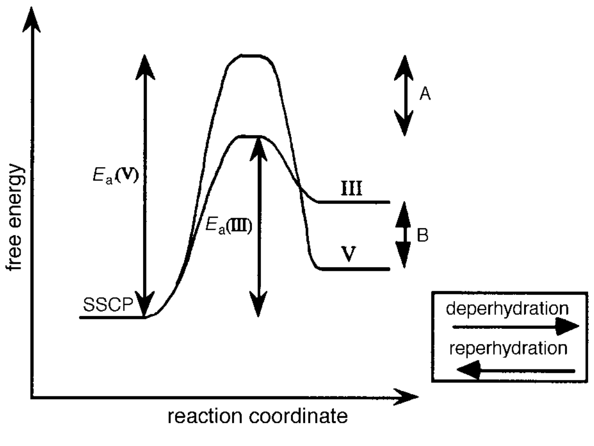
Fig. 10 Reperhydration of SSCPD using a 0.55 g cm^{-3} H_2O_2 solution as shown by AVOX. The curve is obtained from eqn. (2).

Discussion

That SSCP can be regenerated after thermal treatment is understandable for a number of reasons. Firstly, the Na_2SO_4(III) and NaCl components remain intimately mixed because the crystal morphology remains intact upon heating (Fig. 3). The retention of close proximity between the Na_2SO_4 and NaCl components results in the ability of SSCPD to act as a template for the reaction. In other words some 'memory' of the original (*i.e.* SSCP) structure is able to be preserved. Secondly, during the regeneration of SSCP, strong hydrogen bonds are formed,[2] which also act to drive the reaction.

Brodale and Giauque have shown that Na_2SO_4(V) has a lower free energy (and hence a higher stability[10]) than Na_2SO_4(III) at temperatures up to 244 °C.[4] That SSCP deperhydrates to Na_2SO_4(III) rather than Na_2SO_4(V), suggests that the activation energy of deperhydration is lower if Na_2SO_4(III) rather than Na_2SO_4(V) is formed. Using these two pieces of information a free energy diagram is constructed in Scheme 1. The position of SSCP has been arbitrarily chosen in relation to Na_2SO_4(V).

It is clear from Scheme 1 that for Na_2SO_4(V) to react during reperhydration it must either obtain additional energy (A + B) or proceed *via* a dissolution stage whereby preferential crystallisation of either Na_2SO_4(III) or SSCP can occur. This therefore implies that the formation of SSCP is favoured from Na_2SO_4(III) rather than Na_2SO_4(V). Indeed, the rate constant



Scheme 1 Free energy diagram for SSCP, Na_2SO_4(V) and Na_2SO_4(III)

for formation of SSCP directly from Na_2SO_4(III) (observed using solutions $\geqslant 0.60$ g cm^{-3}) is higher than that from Na_2SO_4(V) (observed using lower concentrations).

The degree of formation of SSCP is dependent on the concentration of H_2O_2 (Table 1). Incomplete conversion to SSCP occurs when low concentrations of H_2O_2 are used and is accompanied by the SSCP powder becoming wet. Galwey and Hood showed that H_2O_2 decomposes in solutions of Na_2CO_3 and that $Na_2CO_3 \cdot 1.5H_2O_2$ itself decomposes in saturated salt solutions.[11] Rapid decomposition of SSCP is known to occur at humidities $>70\%$ RH (equivalent[12] to a $\leqslant 0.40$ g cm^{-3} H_2O_2 solution).[9] It therefore seems probable that as the powder becomes wet, the rate of decomposition of H_2O_2 or SSCP within the slurry increases. If either rate approaches the rate of formation of SSCP, regeneration will slow down and stop, thus resulting in incomplete conversion. Since the powder becomes less wet at higher concentrations, due to the decreasing vapour pressure of the H_2O_2 solution, the percentage conversion is higher.

In all of the PXRDs the reflections can be assigned as either Na_2SO_4(III), Na_2SO_4(V), NaCl or SSCP, thus indicating that a single or mixed salt hydrate is not formed during reperhydration. Indeed, since NaCl depresses the temperature of transition between anhydrous and hydrated Na_2SO_4 from 32.4 to 18 °C,[13] it seems unlikely either $Na_2SO_4 \cdot 7H_2O$ or $Na_2SO_4 \cdot 10H_2O$ would form, given the experimental conditions employed here. The TG mass loss at 120–150 °C in Fig. 4(b) is therefore attributed to physisorbed H_2O_2 and not H_2O from a hydrate intermediate.

There are two types of behaviour observed in the reperhydration of SSCPD, suggesting two different mechanisms. These will be denoted M1 for H_2O_2 solutions <0.50 g cm^{-3} and M2 for solutions $\geqslant 0.60$ g cm^{-3}. Evidence for the different behaviour stems from the first order rate of increase of available oxygen content, the persistence of the Na_2SO_4(III) phase and the lack of Na_2SO_4(V) phase formation in the PXRD patterns, together with the observed dryness of the powder. The mechanisms will be discussed separately, M1 first.

It is well known that water causes phase transformation of phase III of Na_2SO_4 into phase V.[14] PXRD shows here that the III→V transformation proceeds rapidly under the experimental conditions of reperhydration using H_2O_2 solutions <0.50 g cm^{-3}. Table 1 also shows that since water has a far higher vapour pressure than H_2O_2, the vapour composition is dominated by water at all but very high concentrations. It is therefore understandable that within 2 h the PXRD patterns of reperhydration show complete conversion of the Na_2SO_4(III) in SSCPD to Na_2SO_4(V), when using 0.30 and 0.38 g cm^{-3} H_2O_2 solutions. That the powders become wet over the course of the experiment, suggests water is not only acting as a catalyst for the transformation but also condensing onto the powder forming a slurry. Again this is understandable since Na_2SO_4 is well known for being hygroscopic.

Phase transformation into Na_2SO_4(V) and NaCl is therefore likely to occur far faster at low H_2O_2 concentrations than is the reaction of H_2O_2 to form the perhydrate. Indeed any product formed from the direct reaction between the gaseous H_2O_2 and the solid may soon dissolve into the slurry. Most of the reaction to form SSCP, however, occurs after the powder becomes wet. The rate constant observed for reperhydration using <0.50 g cm^{-3} solutions (*ca.* 10×10^{-6} s^{-1}) therefore corresponds to the rate of crystallisation of SSCP from the slurry. This rate is too slow for complete conversion to SSCP to occur before factors such as the decomposition of H_2O_2 or SSCP become important.

PXRD patterns show that phase transformation into Na_2SO_4(V) and NaCl does not occur at 0.85 g cm^{-3} H_2O_2 and occurs only slightly at 0.60 g cm^{-3} H_2O_2. Rather, the Na_2SO_4(III) and NaCl phases persist for over a day by which time reperhydration is almost complete. This is somewhat remarkable since at 0.60 g cm^{-3} of the solution the mol fraction of H_2O in the vapour is still 0.93 (Table 1). Despite an apparently large amount of water present, the III→V phase transformation is resisted. Shumb *et al.*[12] point out that H_2O_2 solutions >60 mass% are hygroscopic and are likely to absorb water vapour from the atmosphere. Therefore, under laboratory conditions, there is a net reduction in water vapour above the solution. Since Na_2SO_4(III) is essentially stable for a few days at typical laboratory humidity (*ca.* 50% RH), it certainly will be stable in the presence of a hygroscopic solution of H_2O_2 (*e.g.* a 0.85 g cm^{-3} solution of H_2O_2 at 25 °C corresponds to a humidity of 36% RH). This is shown by the PXRD patterns in Fig. 8 in which the III→V phase transformation occurs after 2 h, only at relative humidities of $\geqslant 60\%$.

The evidence presented here suggests that reperhydration using solutions of $H_2O_2 \geqslant 0.60$ g cm^{-3} proceeds *via* direct reaction of the solid [Na_2SO_4(III) and NaCl] with the gaseous H_2O_2, in the absence of any discernible liquid intermediate. A direct solid–gas reaction mechanism is supported by observations by Sakaguchi *et al.* that Na_2SO_4 has an affinity to sorb O_2 gas.[15] It is probable that Na_2SO_4 has an affinity towards H_2O_2, especially if the influence of H_2O can be minimised *i.e.* by the use of hygroscopic H_2O_2 solutions.

Reperhydration using solutions <0.50 g cm^{-3} always give rate constants of *ca.* 10×10^{-6} s^{-1} whilst for solutions $\geqslant 0.60$ g cm^{-3} H_2O_2, $k \approx 20 \times 10^{-6}$ s^{-1}. The consistency of k within each category gives credence to these values and hence to two mechanisms. Intermediate rate constants are obtained for the narrow range 0.50–0.60 g cm^{-3} H_2O_2. This range could be even narrower since reperhydration at 0.55 g cm^{-3} gives a rate constant very close to 20×10^{-6} s^{-1} suggesting an upper limit nearer *ca.* 0.58 g cm^{-3} H_2O_2. The stability of Na_2SO_4(III), as monitored by PXRD, also testifies that the range in which both mechanisms are active is narrow. The vapour pressure curve for the H_2O_2–H_2O system[16] is shown in Fig. 11. The point of inflection of the curve given by the minimum of the first differential, occurs at 0.545 g cm^{-3} H_2O_2. This value correlates exceptionally well with the middle of the transition between the mechanisms if 0.50 and 0.57 g cm^{-3} are taken as the transition extremes. It is also in good agreement with the PXRD patterns in Fig. 8, since 60% RH (the humidity at which phase transformation is starting to occur after 2 h) corresponds to a H_2O_2 solution slightly above 0.50 g cm^{-3}. We propose therefore that a direct reaction between the solid SSCPD and H_2O_2 vapour only occurs when the H_2O_2 solution has a concentration >0.545 g cm^{-3} and hence a relative humidity of $<59\%$. These observations are in accord with

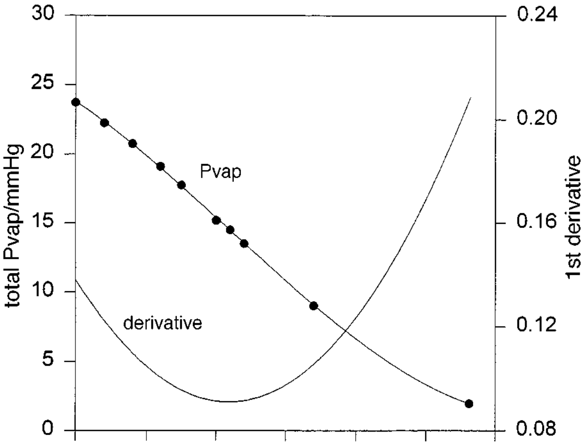


Fig. 11 Total vapour pressure curve for the H_2O_2–H_2O system and the derivative of the curve showing point of inflection at 0.545 g cm^{-3} H_2O_2

those made by Adams and co-workers who associated a critical dependence of perhydrate stability upon relative humidity with the formation on the surface of the solid, of a film of saturated solution.[5,17]

Conclusions

Although the channel structure of SSCP does not remain intact upon desorption of H_2O_2, the resulting product, SSCPD, is able to regenerate SSCP when exposed to low pressures of H_2O_2 (in the form of the vapour above H_2O_2 solutions). The fraction of SSCP formed and the mechanism by which it is formed, has been shown to be dependent on the total vapour pressure of the H_2O_2 solution used. Very concentrated H_2O_2 solutions are hygroscopic and therefore decrease the humidity of the atmosphere whilst more dilute solutions increase the humidity. The concentration of the H_2O_2 solution therefore determines whether the Na_2SO_4, which is itself hygroscopic, becomes wet and in particular whether phase transformation of any Na_2SO_4(III) into Na_2SO_4(V) occurs.

If the powder becomes wet, Na_2SO_4 (III→V) phase transformation occurs and reperhydration proceeds *via* crystallisation from a Na_2SO_4(V)/NaCl slurry. In this case SSCP formation is incomplete because a saturated salt solution is formed which is known to promote decomposition of H_2O_2 and perhydrates. The rate constant obtained for reperhydration using solutions <0.50 g cm^{-3} H_2O_2 corresponds to the crystallisation of SSCP from the slurry of Na_2SO_4(V), NaCl and H_2O/H_2O_2. From considerations of the free energies of Na_2SO_4(V) and Na_2SO_4(III), using observations from Part 1,[3] it is shown that reperhydration of SSCPD from Na_2SO_4(V) is energetically less favourable than from Na_2SO_4(III). This manifests itself in a lower first order rate constant (10×10^{-6} s^{-1}).

The hygroscopic nature of very concentrated solutions prevents the water catalysed phase transformation of Na_2SO_4 (III→V). Since H_2O is being removed from the atmosphere, the sample remains essentially dry, therefore allowing the direct reaction of H_2O_2 with the solid. This mechanism is active as long as there is insufficient water vapour pressure to cause the (III→V) transformation within the sample. This has been achieved here by using very concentrated H_2O_2 solutions.

The financial assistance of EPSRC and Solvay Interox Ltd. (CASE award to S. D. C.) is appreciated.

References

1 Kao Soap Co. Ltd. and Nippon Peroxide Co. Ltd., *Ger. Pat.* 2 530 539, 1975.
2 J. M. Adams, V. Ramdas and A. W. Hewat, *Acta Crystallogr., Sect. B*, 1981, **37**, 915.
3 S. D. Cosgrove and W. Jones, *J. Mater. Chem.*, preceding paper.
4 G. E. Brodale and W. F. Giauque, *J. Phys. Chem.*, 1972, **76**, 737.
5 J. M. Adams, L. A. Ashe and C. J. Adams, *Inorg. Chim. Acta*, 1980, **44**, L195.
6 S. D. Cosgrove and W. Jones, *J. Chem. Soc., Chem Commun.*, 1994, 2255.
7 M. E. Solomon, *Bull. Entomol. Research*, 1951, **42**, 543.
8 A. K. Galwey, *Chemistry of Solids*, Chapman and Hall, London, 1967, p. 180.
9 S. D. Cosgrove, PhD Thesis, University of Cambridge, 1996.
10 M. J. Buerger, in *Phase Transformations in Solids*, ed. R. Smoluchowski, J. E Mayer and W. A. Weyl, Wiley, New York, 1951, p. 199.
11 A. K. Galwey and W. J. Hood, *J. Chem. Soc., Faraday Trans.*, 1982, **78**, 2815.
12 W. C. Shumb, C. N. Satterfield and R. L. Wentworth, *Hydrogen Peroxide*, Reinhold, New York, 1955, pp. 221–231.
13 H. G. Wiedemann, W. Smykatz-Kloss and W. Eysel, *Therm. Analysis, 2 Proc. 6th ICTA Bayreuth*, Birkhäuser Verlag, Basel, 1980, p. 347.
14 M. Sakaguchi, M. Ohta and S. Miyazaki, *J. Electrochem. Soc.*, 1984, **131**, 1942.
15 M. Sakaguchi, M. Ohta and Y. Takashima, *Rare Earths*, 1983, **2**, 24.
16 G. Scatchard, G. M. Kavanagh and L. B. Ticknor, *J. Am. Chem. Soc.*, 1952, **74**, 3715.
17 C. J. Adams, J. M. Adams, R. G. Pritchard and V. Ramdas, *J. Inorg. Nucl. Chem.*, 1979, **41**, 937.

Paper 7/06385G; *Received* 1st *September*, 1997