Dehydration of Calcium Hydrogen Phosphate Dihydrate

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The dehydration of $CaHPO_4,2H_2O$ has been studied isothermally between 409 and 537 K and over a range of partial pressures of water vapour between 1·3 cN m^{-2} and 6·0 kN m^{-2} at a total pressure of 1 atm. The rate of dehydration is controlled by diffusion of water, and below 478 K the activation energy is 190 kJ mol^{-1} and this value is not affected by the partial pressure of water vapour. However, above 478 K the activation energy drops markedly and is then affected by partial pressure of water vapour. Some evidence has been obtained for the formation of a monohydrate as an intermediate and, while this is not conclusive, this postulate helps to clarify the results of previous work.

THE dehydration of $CaHPO_4,2H_2O$ has been studied by several groups of workers over many years.[1-7] All agree that the primary anhydrous product is $CaHPO_4$ which dehydrates at higher temperatures to produce pyrophosphate. The course of the initial dehydration is extremely complicated, however, and greatly dependent on the amount of water vapour present near the sample. At low vapour pressures the dehydration proceeds in a number of stages while at high partial pressures, generally unspecified, the reaction is smooth and proceeds in a single step. Suggestions made to account for the complicated, low-pressure dehydration include the formation of (*a*) amorphous material,[4] (*b*) lower hydrates of uncertain composition,[1,2,4] (*c*) mixed crystals of dihydrate and anhydrous material,[7] and (*d*) an intermediate of formula $Ca_2(HPO_4)_2,3H_2O$.[8]

EXPERIMENTAL

The $CaHPO_4,2H_2O$ used throughout was G.P.R. grade (99% $CaHPO_4,2H_2O$) material. *X*-Ray powder diffraction gave a pattern in excellent agreement with that published[9] in the A.S.T.M. index. All reaction products were also checked by *X*-ray diffraction. Dehydration at 573 K gave a weight loss of 20·83% (Calc. for $CaHPO_4,2H_2O - 2H_2O$, 20·91%) and ignition at 973 K gave an additional weight loss of 5·10% (Calc. for $2CaHPO_4,2H_2O - 3H_2O$, 20·91 + 5·23%). A bulk sample was stored over silica gel until required.

The isothermal dehydrations were carried out as previously described,[10] with a recording electrobalance (25 mg f.s.d., sensitivity 1×10^{-4} mg) and 100 mg ± 10% of powdered sample. Boiling solvents were used to maintain constant temperatures and constant partial pressures of water vapour were maintained by passing nitrogen through water or salt solutions, or over drying agents, and then over the sample. Some thermogravimetric runs were carried out with a Du Pont 950A thermobalance. Nitrogen was passed over 50 mg samples after being saturated with water vapour at partial pressures of 6·1 hN m^{-2}, 2·3 kN m^{-2}, and 3·2 kN m^{-2}. Heating rates of 0·17 and 0·034 K s^{-1} were used.

RESULTS AND DISCUSSION

Products.—At 452 K and above, the dehydration product was always the anhydrous phosphate $CaHPO_4$, as indicated by weight losses and by *X*-ray diffraction.

At 433 K and below, and at all vapour pressures used, it was found that a maximum of half the water content was lost, corresponding to the formation of a monohydrate $CaHPO_4,H_2O$. Samples were heated for up to 46 h without losing more than one mole of water. One sample which had been heated at 428 K and a partial pressure of 5·55 kN m^{-2} for 25 h, and which had lost 10·4% weight (Calc. for $CaHPO_4,2H_2O - H_2O$ = 10·46%) was ground in a small mortar, reweighed, and reheated under the same conditions for a further 48 h. No further loss in weight was observed tending to suggest that the sample was homogeneous, in contrast to the work of Dugleux and de Sallier Dupin[7] who suggested the formation of heterogeneous mixed crystals of dihydrate and $CaHPO_4$, which lost weight after grinding.

Another sample heated at 433 K and 1·54 kN m^{-2} of water vapour for 24 h lost 10·41% of its original weight. The vapour pressure was reduced to 0·61 kN m^{-2} for 24 h and no further loss in weight was detected. The partial pressure of water vapour was then raised to 7·7 kN m^{-2} and no rehydration occurred during 24 h.

A sample of the 'monohydrate' prepared at 428 K and 5·55 kN m^{-2} was used to determine the *X*-ray diffraction pattern; this was very little different from the original dihydrate except that some relative intensities had changed. The diffraction pattern is in good agreement with that given by Duff,[8] and agrees with the results of Rabatin *et al.*[4]

Some of the lower-temperature runs appeared to produce a compound with a lower proportion of water, approximating to 5% loss. This is very close to the loss of 0·5 mole of water described by Duff.[8] This possibility was rejected, however, because a further slow loss in weight occurred, and the initial loss of *ca.* 5% could not be correlated with temperature or vapour pressure, unlike the formation of the monohydrate. The upper temperature limit for the intermediate of 433 K found in this study agrees closely with that found by Duff[8] who suggests a temperature of 438 K for the dehydration to $CaHPO_4$.

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[1] A. Boullé, *Compt. rend.*, 1948, **226**, 1617.

[2] S. I. Vol'fkovich and V. V. Urosov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1951, **4**, 341.

[3] A. Boullé and M. Dupont, *Compt. rend.*, 1955, **240**, 860; *ibid.*, **241**, 42.

[4] J. G. Rabatin, R. H. Gale, and A. E. Newkirk, *J. Phys. Chem.*, 1960, **64**, 491.

[5] R. E. Mesner and R. R. Irani, *J. Chem. and Eng. Data*, 1963, **8**, 530.

[6] J. Fraissard and A. de Sallier Dupin, *Compt. rend.*, 1965, **261**, 5040.

[7] P. Dugleux and A. de Sallier Dupin, *Bull. Soc. chim. France*, 1967, 144, 973, 978.

[8] E. J. Duff, *J. Appl. Chem. Biotechnol.*, 1971, **21**, 233.

[9] A. S. T. M. Index, card nos. 9-77, 9-80.

[10] M. C. Ball and L. S. Norwood, *J. Chem. Soc.* (*A*), 1969, 1633.

Thermogravimetric Results.—These runs apparently produced different results from those derived from isothermal runs, and could only be interpreted as indicating an intermediate of formula $CaHPO_4,1{\cdot}5H_2O$, *i.e.*, one having lost one quarter of the water content. This loss was not affected by water vapour pressure or by heating rate, except that increased heating rate raised the recorded temperature of decomposition somewhat. The obvious explanation is that the very slow rate of dehydration of the 'monohydrate' allowed the formation of $CaHPO_4$ to overlap with the first stage, giving an intermediate with apparently *ca.* $1{\cdot}5H_2O$.

Kinetics and Mechanisms.—The results for all runs carried out (49 in all) were tested by comparison of the experimental reduced-time plots, based on the time for 50% reaction (α against $t/t_{0\cdot5}$), with those for various model systems based on nucleation-, phase-boundary-, or diffusion-control[11] of the dehydration reaction. In all cases a correction was applied to the starting time to allow for the heating-up time of the sample. All the curves were decelatory and indicated some type of diffusion control, although the formal geometry of the diffusion process appeared to change with temperature. Variation in partial pressure of water vapour appeared to have little effect at low temperatures. Figure 1 shows comparisons of experimental and theoretical reduced-time curves for the higher-temperature runs, and Table 1 gives details of the effect of temperature on the mechanism.

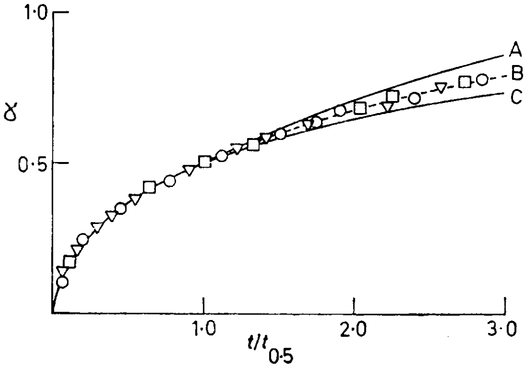

FIGURE 1 Experimental and theoretical reduced-time plots, for high-temperature runs: A, one-dimensional diffusion; B, two-dimensional diffusion; and C, three-dimensional diffusion; (○), 537 K at 3·2 kN m^{-2}; (□), 489 K at $0{\cdot}13 \times 10^{-4}$ kN m^{-2}; and (▽), 477 K at 6·1 kN m^{-2}

The poorest fit between experimental and theoretical plots was for those described as 'three-dimensional' in Table 1. These low-temperature runs consistently indicated the type of behaviour shown in Figure 2, where the early part of the reaction (up to $\alpha = 0{\cdot}5$) was faster than expected for any of the models considered and the latter part ($\alpha > 0{\cdot}5$) was slower than expected. This type of behaviour was noted for the runs at 452 K where the product was anhydrous $CaHPO_4$, as well as for the lower-temperature runs where the monohydrate is postulated, although of course the α values refer to different reactions. The rapid approach to $\alpha = 0{\cdot}5$ for the monohydrate reaction is obviously the reason for the postulate of $Ca_2(HPO_4)_2,3H_2O$ as intermediate by Duff.[8]

The most likely reason for this behaviour is a non-uniform distribution in particle size. The effects of the latter on diffusion-controlled reactions have been discussed by Gallagher[12] who showed that a logarithmic normal distribution in particle size causes the initial rates of reaction to be higher than that for a uniform distribution. The rate for the latter part of the reaction would be slower than expected, exactly as observed in the present work. Optical examination of the dihydrate (starting material) showed the crystals to be very small plates (face diameter 5—15 μm) but also that considerable 'stacking' of these plates occurred, making the decision as to a real particle size for the material extremely difficult. It is clear, however, that the particle-size distribution is not uniform; attempts to measure this by sedimentation were abandoned after it became obvious that the necessary handling of the samples gave non-reproducible results.

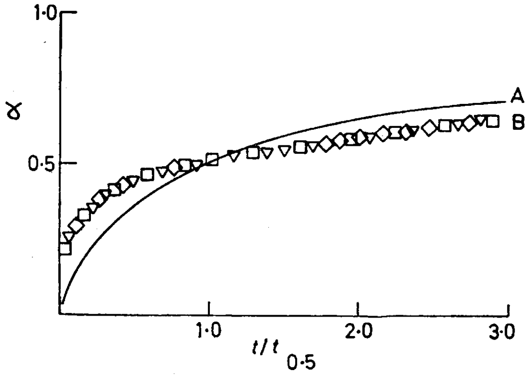

FIGURE 2 Experimental and theoretical reduced-time plots, for low-temperature runs: A, three-dimensional diffusion plot; B, experimental curve; (□), 433 K at $0{\cdot}13 \times 10^{-4}$ kN m^{-2}; (◇), 428 K at 1·46 kN m^{-2}; and (▽), 409 K at 5·6 kN m^{-2}

TABLE 1

Products and reaction mechanisms in the dehydration of $CaHPO_4,2H_2O$

T/K	Product	Mechanism[a]
537	$CaHPO_4$	B
489	$CaHPO_4$	B
477	$CaHPO_4$	B
468	$CaHPO_4$	A
452	$CaHPO_4$	C
433	'Monohydrate'	C
428	'Monohydrate'	C
409	'Monohydrate'	C

[a] Best-fit diffusion mechanism: A, one-dimensional diffusion following $\alpha^2 = kt$; B, two-dimensional diffusion following $(1 - \alpha)\ln(1 - \alpha) + \alpha = kt$; and C, three-dimensional diffusion following $[1 - (1 - \alpha)^{\frac{1}{3}}]^2 = kt$ (see Discussion section)

The problems associated with the particle-size distribution also make the choice of a precise reaction mechanism difficult. The low-temperature runs assigned

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[11] J. H. Sharp, G. W. Brindley, and B. N. N. Achar, *J. Amer. Ceram. Soc.*, 1966, **49**, 379.

[12] K. J. Gallagher, 'Reactivity of Solids,' ed. G. M. Schwab, Elsevier, Amsterdam, 1966, p. 192.

to Jander's equation in Table 1 did not fit this equation particularly well, as has been mentioned. Of all the model equations considered, Jander's lies lowest in the plot of α against $t/t_{0\cdot5}$ for a given value of $t/t_{0\cdot5} > 1\cdot0$, and therefore lies closest to the experimental data. The derivation of this equation assumes diffusion in a sphere and also that the specific volumes of reactant and product are equal. Although Carter has improved this equation by allowing for a difference in specific volumes, it is not possible to decide between these two for the present results in the absence of an accurate particle-size distribution. Since this 'spherical diffusion' is simply an assumption of three equal diffusion coefficients at right angles in a theoretical particle, it is not possible to reject it on the grounds of the external morphology of the starting material. Even in a plate-like crystal it is possible to have three approximately equal diffusion coefficients.

Equally a similarity in specific volumes of reactant and product cannot be immediately ruled out because of the close similarity between the diffraction patterns of di- and mono-hydrate. This does not prove similar specific volumes, but equally it makes it difficult to prove a difference.

The high-temperature mechanisms involved in the formation of the anhydrous material change rather markedly with temperature, but give much closer agreement with the models. These changes with temperature can be qualitatively explained if it is assumed that the three-dimensional case (452 K) is not truly isotropic but consists of three diffusion coefficients having different activation energies, but which are approximately equal at 452 K. As the temperature rises, these diffusion coefficients D change to give the observed diffusion geometries as follows: at 452 K, $D_x \simeq D_y \simeq D_z$, spherical diffusion; at 468 K, $D_x > D_y \simeq D_z$, one-dimensional; and at 477 K, $D_x \simeq D_y > D_z$ two-dimensional diffusion, where $E_x > E_y > E_z$.

TABLE 2

Arrhenius parameters

Temp. range/K	Water vapour pressure range/kN m^{-2}	E_a/ kJ mol^{-1}	log A/s^{-1}
409—433	$0\cdot13 \times 10^{-4} - 5\cdot6$	188	21·0
452—477	$0\cdot13 \times 10^{-4} - 5\cdot6$	192	19·8
477—537	$0\cdot13 \times 10^{-4}$	54	4·4
477—537	0·61	71	5·8
477—537	1·46	63	5·1
477—537	3·2	50	4·0
477—537	5·6	21	1·3

Arrhenius Parameters.—Variation of the water vapour pressure had little effect on reaction rate except at the highest temperatures studied. The effect is shown in Figure 3 which is an Arrhenius plot from which the activation energies and frequency factors given in Table 2 were derived. Not all the experimental points are included in Figure 3 for the sake of clarity, but the clustering of points at particular temperatures indicates a very small effect of water vapour.

The absence of a partial pressure effect on these activation energies is unexpected for a diffusion-controlled reaction. It is possible that the crystals are under a high internal pressure of water vapour, so that a constant diffusion gradient exists over a wide range of temperature. An alternative explanation is that an adsorbed film of water modifies the diffusion gradient at lower temperatures. It is difficult to see why the breakdown of either constraint should be as sudden as is observed.

The activation energies calculated for the formation of monohydrate or $CaHPO_4$ are the same, and the frequency factors are similar, which obviously suggests a close similarity between the two diffusion processes. This reinforces the similarity observed between the dihydrate and monohydrate X-ray powder patterns.

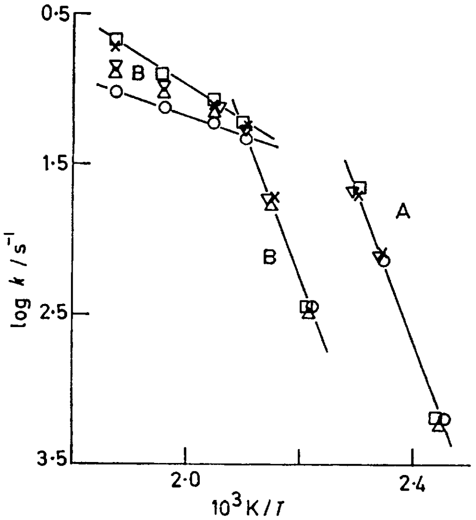

FIGURE 3 Arrhenius plot; A, for monohydrate formation; B, for formation of anhydrous material; (▽), $0\cdot13 \times 10^{-4}$; (□), 0·61; (×), 1·46; (△), 3·2; and (○), 5·6 kN m^{-2}

The frequency factors are high, relative to the value log $A = 13\cdot0$ for a gaseous molecule,[13] which suggests that the transition state has a large number of degrees of freedom. An alternative explanation is that the reaction is a bulk process rather than a surface one.

The sudden drop in activation energy at higher temperatures is unexpected, but similar behaviour has been noted[14] in the dehydration of $CaSO_4,\frac{1}{2}H_2O$, where a phase change occurred in the temperature range used. A similar explanation is possible here, for although no pyrophosphate was detected in the reaction products from the isothermal runs, the transformation occurred in a sample heated at 513 K for one week. The transformation of pyrophosphate has been detected[1] as low as 498 K and i.r. studies[15] indicate a breakdown of the HPO_4^{2-} groups at temperatures as low as 428 K. The apparent sensitivity of reaction rate to structural changes has been remarked on.[16]

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[13] H. F. Cordes, *J. Phys. Chem.*, 1968, **72**, 2185.

[14] M. C. Ball and L. S. Norwood, *J. Chem. Soc.* (*A*), 1970, 1476.

[15] V. V. Pechkovskii, L. N. Shchegrov, A. S. Shul'man, R. Ya. Melinkova, and M. D. Mochalina, *Russ. J. Inorg. Chem.*, 1968, **13**, 1217.

[16] A. K. Galwey, 'Chemistry of Solids,' Science Paperbacks SP42, London, 1967, p. 173.

The frequency factors for this stage of the dehydration are extremely low, indicating an activated complex with very few degrees of freedom, although it is difficult to know how much the phase transformation affects the values calculated.

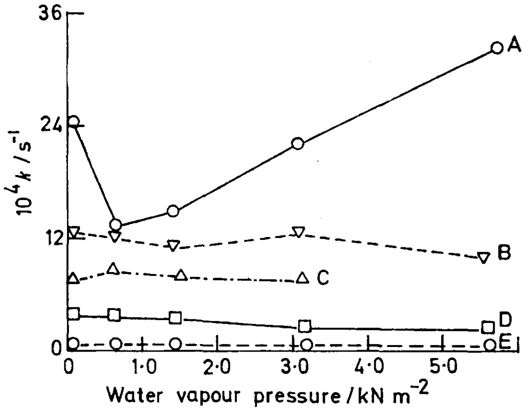

FIGURE 4 Effect of the partial pressure of water vapour on the reaction rate: A, 537; B, 489; C, 477; D, 468; and E, 452 K

Effect of Water Vapour on the Reaction Rate.—Figure 4 shows the effect of varying water vapour pressure on reaction rate at different temperatures. Only at the highest temperatures is there any indication[17] of a 'Smith–Topley effect,' *i.e.*, a minimum in the graph of rate against pressure. This effect is usually taken[18] to indicate the formation of an amorphous or poorly crystalline intermediate which requires some threshold pressure of water vapour to crystallise into the normal reaction product. The absence of such an effect from the temperature region where the monohydrate is postulated suggests that the compound is real and not due to the formation of an amorphous layer of product which sufficiently modifies the kinetics that a 'monohydrate' appears to be formed fortuitously.

The formation of a monohydrate is also suggested by the n.m.r. results of Fraissard and de Sallier Dupin[6] which indicate the presence of two types of water molecule in the layer structure of the dihydrate, one of which was relatively free and the other tightly bound in the lattice. This has been recently confirmed by neutron diffraction.[19]

[1/1866 *Received*, 12*th October*, 1971]

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[17] B. Topley and M. L. Smith, *J. Chem. Soc.*, 1935, 321.

[18] R. C. Wheeler and G. B. Frost, *Canad. J. Chem.*, 1955, **33**, 546.

[19] N. A. Curry and D. W. Jones, *J. Chem. Soc.* (*A*), 1971, 3725.