

## Calcium Phosphate Crystallization. III. Overall Growth Kinetics of Tetracalcium Monohydrogen Phosphate

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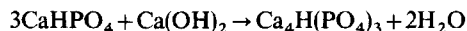
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The growth kinetics of OCP crystals (OCP =  $\text{Ca}_4\text{H}(\text{PO}_4)_3 \cdot 2.5\text{H}_2\text{O}$ ) in brushite ( $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ) suspensions has been investigated by pH-static titration with calcium hydroxide solution. At high supersaturation growth takes place mainly by surface nucleation, whereas at lower supersaturation the growth rate is proportional to  $(\beta - 1) \ln \beta$ , where  $\beta$  is the ratio between the ionic product and the solubility product of OCP, which indicates a spiral growth mechanism. On the basis of the values of the kinetic parameters for spiral growth, including the activation energy, and the edge free energy determined from the rate of surface nucleation, it is shown that the spiral growth follows a BCF surface diffusion mechanism with the rate of incorporation of growth units as the rate-determining step.

In the first paper in this series<sup>1</sup> a study of the kinetics of crystallization of tetracalcium monohydrogen phosphate [ $\text{Ca}_4\text{H}(\text{PO}_4)_3 \cdot 2.5\text{H}_2\text{O}$ , "octacalcium phosphate", in the following abbreviated OCP] in suspensions of brushite ( $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ) under conditions of freely varying pH was reported. The initial supersaturation was very high ( $6.4 < \ln \beta < 10.8$ , where  $\beta$  is the saturation ratio defined as the ionic product of the substance divided by its solubility product) and it was found that the time lag of crystallization does not follow the classical (Becker-Döring-Volmer) scheme of surface nucleation, but is proportional to  $[\text{PO}_4^{3-}]^{-2}$ , i.e. nucleation is a second-order process for an ionic species occurring in very low concentration (of the order of  $10^{-8}$  M). The method suffers from two disadvantages, however: (1) the course of the reaction is very difficult to analyze since the degree of supersaturation is not constant, and (2) we cannot separate the individual contributions from nuclea-

tion and from crystal growth to the overall rate of precipitation. It would be desirable to determine the growth kinetics of OCP by measurements on single crystals, but these are very difficult to obtain in good quality, as the substance normally crystallizes in spherulites, and furthermore, the growth rate would be expected to be so low that it could be measured only with difficulty and at very high supersaturation. Instead the overall growth rate of a well-defined, though unknown, number of crystals has been measured; the total surface area may eventually be determined by an adsorption method.

When growth of OCP crystals takes place in a brushite suspension under vigorous agitation it may be assumed that the rate of dissolution of brushite is so much faster than the rate of growth of the OCP crystals that the solution is constantly saturated with respect to brushite. Even if heterogeneous nucleation on the brushite crystals should take place simultaneously with growth of the added OCP seeds, there should be no risk of blocking the surface of the brushite crystals, as shown in previous investigations.<sup>1</sup> We are then dealing with equilibrium in a 2-phase, 3-component system if no foreign component is added, whence, according to the phase rule, there are 3 degrees of freedom. Temperature and pressure are constant, and pH is kept constant by pH-static titration with calcium hydroxide solution. As  $\text{Ca}(\text{OH})_2$  is one of the components, the system is invariant, and if the amount of OCP is allowed to increase by only a small fraction, *in casu* about 10 %, we should expect an essentially constant rate of precipitation during an experiment. The overall reaction is, omitting water of crystallization



from which it is seen that apart from the effect of volume increase of the solution, the number of mol of  $\text{Ca}(\text{OH})_2$  added is equal to the number of mol of  $\text{Ca}_4\text{H}(\text{PO}_4)_3$  formed.

The precision of the results reported here is limited by a number of factors. Firstly, there is the amount of substance available for a single series of experiments: The OCP is prepared by hydrolysis of brushite in dilute phosphoric acid, and by this method only a few grams at a time are obtained, permitting not more than about 20 experiments. The product obtained is not sufficiently reproducible with respect to size, defect concentration, and surface properties of the individual crystals to permit pooling of results for different preparations. Another source of uncertainty is the variation in pH which takes place at each addition of  $\text{Ca}(\text{OH})_2$  as a result of "nonvanishing" mixing time. This variation, though probably not exceeding 0.05 pH units, leads to an uncertainty in  $\beta$  which may amount to as much as 20%. The results, however, seem to indicate that the uncertainty is substantially lower, but it was preferred not to carry out series of experiments with pH increments of less than 0.1 between successive experiments.

## EXPERIMENTAL

**Apparatus.** The pH-static titrations were carried out with Radiometer equipment comprising an SBR 2 syringe burette recorder, an ABU 11 auto-burette unit equipped with a 2.5 cm<sup>2</sup> syringe burette, and either a TTT 1 titrator or a TTT 60 titrator in conjunction with a PHM 64 digital pH-meter. Standard phthalate buffer (pH 4) and standard equimolar phosphate buffer were used for pH calibration.

The temperature of the thermostatted titration vessel was constant within 0.05 K or less.

**Materials.** Water of adequate purity was obtained by passing ordinary demineralized water first through an activated carbon filter, then through a Silex-1 mixed-bed ion-exchange column. The outflow was monitored with a conductivity meter which indicated a resistivity well above 10<sup>5</sup> ohm m; the resistivity of pure water is 1.8 × 10<sup>5</sup> ohm m.

Brushite was prepared as described by Tovborg Jensen and Rathlev.<sup>3</sup> The product was sieved, and the fraction passing the 90 μm sieve was used.

OCP was prepared by addition of 16 g brushite (in one case 32 g) to 4 dm<sup>3</sup> 10<sup>-4</sup> or 2 × 10<sup>-4</sup> M phosphoric acid at 37 °C under constant stirring.

The solution was renewed twice when pH had fallen below 6. At the third run pH stabilized near 6, indicating complete hydrolysis, and calculations showed that the Ca/P molar ratio of the solid phase should now be equal to 1.33. The crystals were filtered off, washed with ethanol, and dried at ambient temperature. The use of dilute phosphoric acid for the hydrolysis ensures a product free from apatite, and X-ray powder diffractometry showed only reflections due to OCP; in any case, the presence of minute amounts of brushite would be of no consequence. Individual crystals of OCP thus obtained were typically 0.01 mm long.

Saturated calcium hydroxide solution used for pH-static titrations was standardized by titration against standardized dilute hydrochloric acid. The calcium hydroxide concentration was about 0.02 M.

**Determination of the solubility product of OCP.** To 25 cm<sup>3</sup> 10<sup>-4</sup> M H<sub>3</sub>PO<sub>4</sub> in a thermostatted vessel were added 0.25 g brushite and 0.25 g OCP. After 3 days of vigorous agitation pH became constant within <0.01. The solubility product of OCP was then calculated from this equilibrium pH value and the known solubility product of brushite<sup>4</sup> ( $pK_{sp} = 6.59$ ).

**Determination of growth rate of OCP.** To 25 cm<sup>3</sup> phosphoric acid of suitable concentration in a thermostatted vessel was added 0.25 g brushite. The suspension was stirred so rapidly that no solid rested on the bottom, and pH was adjusted to the desired value by dropwise addition of 0.01 M H<sub>3</sub>PO<sub>4</sub>. When, after a few minutes, equilibrium had been attained, 0.25 g OCP was added and the pH-stat recording was started immediately. After each experiment the vessel, electrodes, stirrer and delivery tube from the burette were rinsed carefully, first with dilute hydrochloric acid to remove all crystal seeds and then with water.

## RESULTS

For the sake of consistency, Bjerrum's and Unmack's values<sup>5</sup> for the dissociation constants of phosphoric acid were used together with Bjerrum's values<sup>4</sup> of the solubility products in all the calculations. Activity coefficients were calculated from the Debye-Hückel formula using Kielland's values for the ionic radii.<sup>2</sup>

Bjerrum used the definition (1) of the solubility product of OCP. The measurement of solubility

$$K_{sp} = a(\text{Ca}^{2+})^4 a(\text{HPO}_4^{2-})^3 / a(\text{H}^+)^2 \quad (1)$$

at 25 °C yielded pH = 5.879 for the three-phase equilibrium. This leads to

$$pK_{sp} = 10.84$$

for OCP at 25 °C with the above definition of  $K_{sp}$ .

Values of the equilibrium constants at other temperatures than those at which they have been measured were calculated from the van't Hoff equation, assuming  $\Delta H^\theta$  constant.

Kinetic experiments were carried out at pH values ranging from 5.7 to 7.5, corresponding to  $7 < \beta < 10^4$ .

The recorded growth curves were perfectly straight lines at high supersaturation, but showed a steadily decreasing slope at low supersaturation. For this reason the initial slope was chosen as representative of the growth rate. All results have been calculated as mol  $\text{Ca(OH)}_2$  per mol OCP per second.

Fig. 1 shows the results at 37 °C for two different preparations of OCP, one using  $10^{-4}$  M  $\text{H}_3\text{PO}_4$ , the other using  $2 \times 10^{-4}$  M  $\text{H}_3\text{PO}_4$  yielding larger crystals. Fig. 2 shows the results obtained at four different temperatures using OCP from a third preparation.

DISCUSSION

We see from Fig. 1 that as the level of supersaturation becomes high, there is a tendency for growth rate to level off or even decrease, at least for the larger crystals. This behaviour sets in at some-

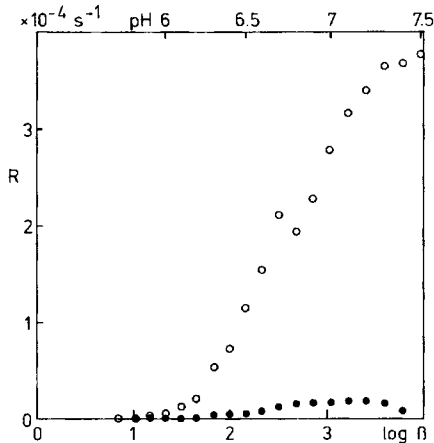


Fig. 1. Growth rate of OCP at 37 °C as a function of supersaturation for two different preparations. Open circles: preparation I, fine crystals. Filled circles: preparation II, coarse crystals.

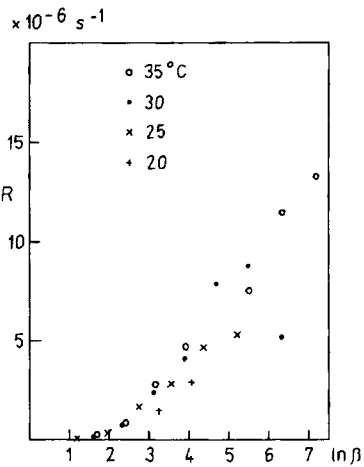


Fig. 2. Growth rate as a function of supersaturation at four different temperatures.

what lower supersaturation levels as temperature decreases (Fig. 2).

The shape of the curves of  $R$  against  $\ln \beta$  at lower supersaturations suggests a surface-nucleation mechanism. Assuming a "polynuclear" mechanism and square nuclei,  $R$  is given by<sup>6,7</sup> eqn. (2), where  $\lambda$

$$R = f\{c_i\} \exp(-4\lambda^2\bar{s}/3k^2T^2 \ln \beta) \tag{2}$$

is the edge free energy,  $\bar{s}$  is the surface area of one formula unit, and  $f\{c_i\}$  is a function of the concentrations of the different ionic species present. Several expressions for this function are to be found in the literature, but only rather simple systems have been considered, and the approximations used are often valid only for relatively low supersaturations.

At very high supersaturation the exponential tends to 1, and the growth rate then becomes limited by the supply of growth units, *i.e.* calcium and phosphate ions. All phosphate species will probably contribute, because the deprotonation is so fast that it can hardly be rate-determining. We thus postulate that the rate-determining step in the absence of a nucleation barrier is the bimolecular reaction between a calcium and a phosphate ion, which leads to the expression (2a) for  $R$ , where  $[P]$

$$R = k_2[\text{Ca}^{2+}][P] \exp(-4\lambda^2\bar{s}/3k^2T^2 \ln \beta) \tag{2a}$$

is the total phosphate concentration in solution. Eqn. (2a) predicts a decrease in growth rate at very high supersaturation due to the decreasing solubility

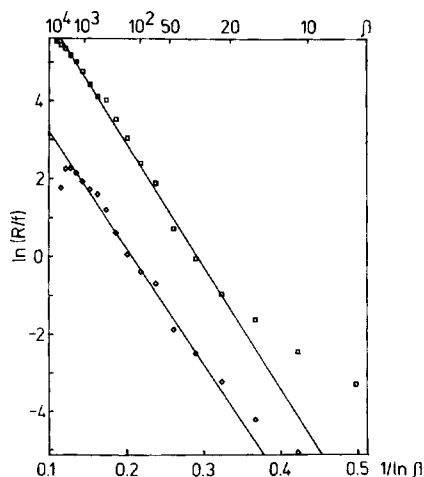


Fig. 3. Test of surface nucleation for preparations I (upper curve) and II (lower curve).  $f = [\text{Ca}^{2+}][\text{P}]$ .

of brushite with increasing pH, in good agreement with experiment. If our hypothesis is valid, a plot of  $\ln(R/[\text{Ca}^{2+}][\text{P}])$  against  $1/\ln \beta$  should yield a straight line with slope  $-4\lambda^2\bar{s}/3k^2T^2$ . Fig. 3 shows the result.

Since two parallel lines are obtained for  $\ln \beta > 3$ , the hypothesis is confirmed. The following parameters are found by linear regression:

$$\begin{aligned} \text{Upper curve: } \lambda\sqrt{\bar{s}} &= 12.6 \pm 0.1 \text{ kJ/mol} \\ k_2 &= 10\,000 \pm 2000 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1} \\ \text{Lower curve: } \lambda\sqrt{\bar{s}} &= 12.2 \pm 0.2 \text{ kJ/mol} \\ k_2 &= 500 \pm 100 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1} \\ \text{Mean value: } \lambda\sqrt{\bar{s}} &= 12.5 \pm 0.1 \text{ kJ/mol} \end{aligned}$$

Putting  $\sqrt{\bar{s}} = 6.79 \times 10^{-10}$  m, the cubic root of the molar volume of OCP calculated from unit cell parameters,<sup>8</sup> we find

$$\lambda = 3.06 \times 10^{-11} \text{ J/m}$$

This is the order of magnitude to be expected for an ionic crystal in aqueous solution. The number of formula units in the critical nucleus is given by eqn. (3), which in the actual range,  $3 < \ln \beta < 9$ ,

$$N^* = 4\lambda^2\bar{s}/(kT \ln \beta)^2 \quad (3)$$

yields values between 1 and 10.

However, the growth rate does not tend to zero with decreasing supersaturation as fast as it should if surface nucleation were the only mechanism, so

we must try a BCF mechanism<sup>9,10</sup> as well. The general expression for the surface-diffusion mechanism is eqn. (4), where  $D_s$  is the surface-diffusion

$$R = 2 \frac{D_s \alpha C_o n_{s0} \Omega}{x_s y_o} (\beta - 1) \tanh(y_o/2x_s) \quad (4)$$

coefficient,  $n_{s0}$  is the equilibrium surface concentration of growth units,  $\Omega$  is the volume of a growth unit in the crystal,  $x_s$  is the mean distance travelled by a growth unit on the surface,  $y_o$  is the distance between steps in the growth spiral, and  $\alpha$  and  $C_o$  are special correction factors.  $\alpha$  is related to the rate of incorporation of growth units into the step and is given by eqn. (5), where  $\tau_k$  is the time constant for

$$\alpha = \left[ 1 + \frac{D_s C_o \tau_k}{x_s a} \tanh(y_o/2x_s) \right]^{-1} \quad (5)$$

incorporation of growth units, and  $a (= \sqrt{\bar{s}})$  is the distance between growth units in the crystal. If  $\tau_k$  is large, we have  $\alpha \ll 1$  and, from (4) and (5), eqn. (6),

$$R = 2 \frac{n_{s0} \Omega a}{\tau_k y_o} (\beta - 1) \quad (6)$$

which is known as the secondary law due to  $\alpha \ll 1$ .  $C_o$  is related to the roughness of the steps and is in general a complicated function of  $x_o$ , the distance between kinks, and  $x_s$ . If the step is rough, so that  $x_o \ll x_s$ , then  $C_o = 1$ , but if the step is smooth, the situation depends on how much diffusion along the step contributes to the transport of growth units along the kinks. If  $x_s \sim a$ , we have<sup>9</sup> eqn. (7) with  $b$

$$C_o = \{1 + 2b \tanh(y_o/2x_s) [\ln(4bx_s/a[1 + (1 + b^2)^{\frac{1}{2}}]) + (2x_s/y_o) \arctan b]\}^{-1} \quad (7)$$

defined in eqn. (8).

$$b = x_o/2\pi x_s \quad (8)$$

Eqn. (7) is interesting only if  $C_o \ll 1$  which yields, when inserted into (4) ( $C_o$  cancels out if  $\alpha$  is not  $\approx 1$ ) eqn. (9).

$$R = 2\pi \frac{D_s n_{s0} \Omega}{x_o y_o} (\beta - 1) \{ \ln(4bx_s/a[1 + (1 + b^2)^{\frac{1}{2}}]) + (2x_s/y_o) \arctan b \}^{-1} \quad (9)$$

If  $b \gg 1$  the first term in braces may be simplified to  $\ln(4x_s/a)$ , and if  $x_s \ll y_o$ , the second term may be neglected, and we then obtain eqn. (10), whereas

$$R = 2\pi \frac{D_s n_{s0} \Omega}{x_o y_o \ln(4x_s/a)} (\beta - 1) \quad (10)$$

$x_s \gg y_o$  yields eqn. (11).

$$R = \pi \frac{D_s n_{so} \Omega}{x_s x_o \arctan(x_o/2\pi x_s)} (\beta - 1) \tag{11}$$

In (11)  $x_o \gg x_s$  yields  $\arctan(x_o/2\pi x_s) \approx \frac{\pi}{2}$  whence

$$R = 2 \frac{D_s n_{so} \Omega}{x_o x_s} (\beta - 1) \tag{12}$$

whereas  $x_o \ll x_s$  yields  $\arctan(x_o/2\pi x_s) \approx x_o/2\pi x_s$  and

$$R = 2\pi^2 \frac{D_s n_{so} \Omega}{x_o^2} (\beta - 1) \tag{13}$$

Let us now return to (4) with  $\alpha = C_o = 1$ . There are two cases to consider:  $x_s \ll y_o$ , which leads to  $\tanh(y_o/2x_s) \approx 1$ , and  $x_s \gg y_o$ , which leads to  $\tanh(y_o/2x_s) \approx y_o/2x_s$ . The former yields eqn. (14), the so-called

$$R = 2 \frac{D_s n_{so} \Omega}{x_s y_o} (\beta - 1) \tag{14}$$

primary law, and the latter yields eqn. (15).

$$R = \frac{D_s n_{so} \Omega}{x_s^2} (\beta - 1) \tag{15}$$

All the above expressions are based on the assumption of surface diffusion. If this is unimportant, we must consider volume diffusion<sup>9</sup> or direct integration.<sup>10</sup> The former mechanism yields eqn.

$$R = \frac{DN_o \Omega a}{x_o y_o} (\beta(x_o) - 1) \tag{16}$$

(16), where  $D$  is the volume-diffusion coefficient, and  $N_o$  is the volume concentration of growth units at equilibrium.  $\beta(x_o)$ , the saturation ratio at the distance  $x_o$  from a kink, is given by eqn. (17),

$$\frac{\beta(x_o) - 1}{\beta - 1} = \left[ 1 + \frac{2\pi a(\delta - y_o)}{x_o y_o} + \frac{2a}{x_o} \ln \frac{y_o}{x_o} \right]^{-1} \tag{17}$$

where  $\delta$  is the thickness of the diffusion layer. The direct-integration mechanism yields eqn. (18), where

$$R = \frac{l^2 N_o \Omega}{\tau'_k y_o} (\beta - 1) \tag{18}$$

$\tau'_k$  is the time constant for the incorporation of growth units, and  $l$  has been designated<sup>10</sup> as the mean free path of growth units in solution; however, it should rather be considered a molecular jump distance.<sup>14</sup>

Since  $y_o = 19r^{*11,12}$ , where  $r^*$ , the radius of the critical nucleus, is given by the two-dimensional Gibbs-Kelvin equation, eqn. (19), the equations

$$kT \ln \beta = 2\lambda \bar{s} / r^* \tag{19}$$

(6, 10, 14, 16, 18) yield an expression of the

$$R = b(\beta - 1) \ln \beta \tag{20}$$

form (20) whereas (11–13, 15) and in some cases (16) yield eqn. (21).

$$R = b(\beta - 1) \tag{21}$$

Figs. 4 and 5 show that (20) accounts well for the growth rate at low supersaturations, but (21) does not. We thus have the following possibilities: (1) a primary law with  $x_s \ll y_o$  [eqn. (14)], (2) a secondary law with slow integration [eqn. (6)], (3) a secondary law with widely spaced kinks [eqn. (10)], (4) one of the cases of volume diffusion [eqn. (16)], and (5) direct integration [eqn. (18)].

An important parameter to be considered when choosing a mechanism is the overall activation energy  $E_a$ , eqn. (22).

$$E_a = -R \frac{\partial \ln b}{\partial (1/T)} \tag{22}$$

If we plot the results given in Fig. 2 as a function of  $(\beta - 1) \ln \beta$ , we find  $b$  for the different temperatures, and an Arrhenius plot then yields

$$E_a = 33 \pm 3 \text{ kJ/mol}$$

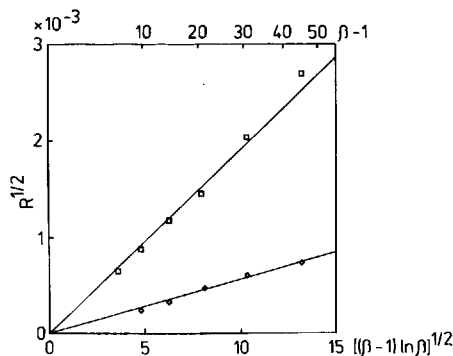


Fig. 4. Test of spiral growth for preparations I (upper curve) and II (lower curve).

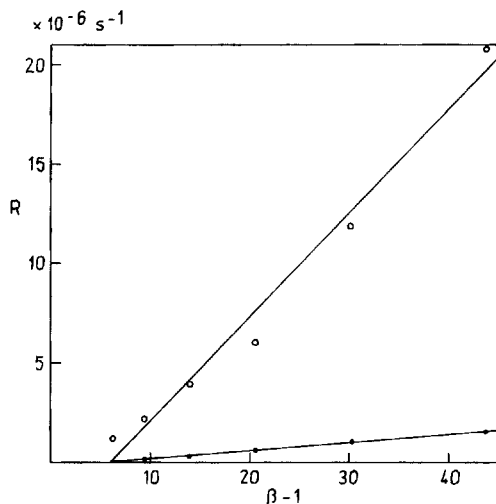


Fig. 5. Test of a linear growth law. The regression lines are drawn in order to show the deviation from linearity more clearly.

Before drawing any conclusions on the basis of this value, we should make clear what is meant by a growth unit in the present case, as the surface or volume concentration of growth units enters into all the expressions to be considered. This question is trivial for non-electrolytes or for congruent solutions of electrolytes, but not for incongruent solutions. Since no really satisfactory discussion of this problem appears to be found in literature, we shall use an *ad hoc* definition based on the following considerations:

It is desirable to define the growth unit in such a way that the formalism developed for simple systems of one solvent and one solute may be applied. This is possible in the present case because, apart from temperature and pressure, the system has only one degree of freedom; as a matter of fact, the system behaves as if we were dealing with the crystallization of calcium hydroxide from solution. The ionic product of OCP, defined in accordance with (1), is given by eqn. (23), where  $K_B$  is the solubility

$$Q = \frac{a(\text{Ca}^{2+})^4 a(\text{HPO}_4^{2-})^3}{(K_B^3/K_W^2) a(\text{Ca}^{2+}) a(\text{OH}^-)^2} = \quad (23)$$

product of brushite, and  $K_W$  is the dissociation constant of water. With the values of the constants inserted, we find at saturation with respect to OCP at 37 °C

$$a(\text{Ca}^{2+}) a(\text{OH}^-)^2 = 3.29 \times 10^{-20}$$

which is, of course, much lower than the actual solubility product of calcium hydroxide.

The standard enthalpy of solution  $\Delta H_d^\theta$  of calcium hydroxide in our system may now be calculated from the temperature coefficients of the constants  $K_{sp}$  for OCP,  $K_B$ , and  $K_W$ . We find

$$\begin{aligned} K_{sp}(\text{OCP}): \Delta H_d^\theta &= -186 \text{ kJ/mol} \\ K_B &: \Delta H_d^\theta = -4.5 \text{ kJ/mol} \\ K_W &: \Delta H_d^\theta = 56 \text{ kJ/mol} \end{aligned}$$

which yields

$$\Delta H_d^\theta = -60.5 \text{ kJ/mol}$$

for calcium hydroxide in our system. This quantity contributes to the overall activation energy calculated from (16) and (18). The total contribution from all the other temperature-dependent factors would then amount to  $33 - (-60.5) = 93.5$  kJ/mol.

In (16), the temperature-dependent factors are  $N_o$ ,  $D$ ,  $x_o$ , and  $y_o$ . The activation energy for volume diffusion may be calculated from the variation of the equivalent conductivity of calcium hydroxide with temperature.<sup>13</sup> We find

$$E_{a,\text{diff}} = 11.0 \text{ kJ/mol}$$

In order to calculate the temperature dependence of  $x_o$  and  $y_o$ , we make use of a set of equations derived by Burton, Cabrera, and Frank.<sup>9</sup> The edge free energy is given by eqn. (24), where  $\phi_1$  is the

$$\lambda a = \phi_1/2 - kT \ln q \quad (24)$$

nearest-neighbour interaction energy, and  $q$  is the partition function per interstice, given by eqn. (25).

$$q = \coth(\phi_1/4kT) \quad (25)$$

The (total) edge energy per interstice is given by

$$U_\lambda = \frac{1}{2} \phi_1 (1 + s) \quad (26)$$

eqn. (26), where  $s$  is the roughness, given by eqn. (27).

$$s = 1/\sinh(\phi_1/2kT) \quad (27)$$

If  $s \ll 1$ , then  $x_o$  is approximately equal to  $a/s$ .

These equations are strictly valid only for a crystal-vapour system where second-nearest neigh-

bour interaction is negligible. For a crystal-solution system  $\phi_1$  is somewhat ambiguous; however, if we define it from eqns. (24) and (25), we may consider it as a characteristic parameter of the system and use it in calculating  $U_\lambda$  and  $s$  from (26) and (27). The values thus obtained should then be at least approximately correct.

We find accordingly

$$\begin{aligned} \phi_1 &= 25.1 \text{ kJ/mol} \\ s &= 0.0155 \\ U_\lambda &= 12.7 \text{ kJ/mol} \end{aligned}$$

As  $s \ll 1$ , we have

$$x_o = a/s = 65a = 438 \text{ \AA}$$

This ensures  $\beta(x_o) = \beta$  according to (17). We further have

$$\frac{\partial \ln x_o}{\partial (1/T)} = \frac{\phi_1}{2k} \coth\left(\frac{\phi_1}{2kT}\right) \quad (28)$$

which yields the contribution

$$E_{a,rough} = 12.5 \text{ kJ/mol}$$

Finally, as

$$y_o = \frac{38 \lambda \bar{s}}{kT \ln \beta} \quad (29)$$

we obtain a contribution to  $E_a$  from eqn. (30), where

$$\frac{\partial \ln y_o}{\partial (1/T)} = \frac{\partial \ln (\lambda/T)}{\partial (1/T)} = \frac{TU_\lambda}{\lambda a} \quad (30)$$

we have made use of the Gibbs-Helmholtz equation. The corresponding contribution to  $E_a$  is

$$E_{a,spiral} = 2.63 \text{ kJ/mol}$$

The resultant activation energy is

$$E_a = \Delta H_d^\theta + E_{a,diff} + E_{a,rough} + E_{a,spiral} = -34 \text{ kJ/mol}$$

This is far below the experimental value, whence we must exclude the BCF volume-diffusion mechanism.

In the expression (18) for the direct-integration mechanism we may probably neglect the temperature-dependence of  $l$ , and there are then three

factors to consider:  $N_o$ ,  $\tau_k$ , and  $y_o$ . The expression for the activation energy becomes eqn. (31), where

$$E_a = \Delta H_d^\theta + E_{a,k} + E_{a,spiral} \quad (31)$$

$E_{a,k}$  is the activation energy for the integration process. We cannot calculate this quantity theoretically, but insertion of the other values yields

$$E_{a,k} = 91 \text{ kJ/mol}$$

All that can be said for the moment is that this value is acceptable.

In all the expressions for a surface-diffusion mechanism we find the factor  $n_{so}$ , the temperature dependence of which is given for a dilute adlayer by<sup>14</sup> eqn. (32), where  $\Gamma_1^\circ$  is the interface excess of

$$\frac{\partial \ln n_{so}}{\partial (1/T)} = - \frac{\Gamma_1^\circ a_2^* \Delta H_{1des}^\circ + \Delta H_{ks}^*}{k} \quad (32)$$

water,  $a_2^*$  is the partial molar area of adsorbed growth units,  $\Delta H_{1des}^\circ$  is the desorption enthalpy of water, and  $\Delta H_{ks}^*$  is the enthalpy increment for transfer of growth units from crystal to adlayer (kink  $\rightarrow$  surface).  $\Delta H_{1des}^\circ$  and  $\Delta H_{ks}^*$  are very difficult to calculate for an aqueous electrolyte system, whence we shall not try to exclude any of the remaining possibilities by considering the activation energy.

We may easily show, by considering the conditions for the primary law, that this mechanism is not possible. The conditions are (1)  $x_s \ll y_o$  and (2)  $C_o \simeq 1$ , which is equivalent to  $x_s \gg x_o$ . We have already calculated  $x_o$ . Using (29) we obtain

$$y_o = \frac{184 a}{\ln \beta}$$

We found that  $R$  is proportional to  $(\beta - 1) \ln \beta$  up to  $\ln \beta = 3.5$ , which corresponds to  $y_o = 53a$ . Comparison of this value with the value of  $x_o = 65a$  shows that the two conditions cannot be met simultaneously.

We are thus left with three possible mechanisms: (1) the secondary law due to  $\alpha \ll 1$ , (2) the secondary law due to  $C_o \ll 1$ , and (3) the direct integration, and we cannot proceed any further without knowing at least the order of magnitude of the absolute growth rate, which means that we must know the specific surface of the substance. The straightforward way of determining this quantity is by nitrogen adsorption, using the BET isotherm. Unfortunately,

it was impossible to degas the sample sufficiently without losing some of the water of crystallization, and this certainly has some effect on the surface area. However, this result is probably not too far from the true value.

It was found that 4 g of OCP from preparation III (used for activation energy determinations) adsorbed 16.3 cm<sup>3</sup> N<sub>2</sub> at STP. This corresponds to an area of 8750 m<sup>2</sup>/mol; the mean linear dimensions of the crystals should then be equal to 0.13 μm, which agrees fairly well with microscopic observations. We may then calculate the absolute value of *b* in eqn. (20); the result at 37 °C is

$$b = 9.47 \times 10^{-16} \text{ m/s}$$

We have the following expressions for *b*:

(1)  $\alpha \ll 1$ :

$$b = \frac{n_{so} \Omega a k T}{19 \lambda \bar{s} \tau_k} \quad (33)$$

(2)  $C_o \ll 1$ :

$$b = \frac{D_s n_{so} \Omega k T}{19 \lambda \bar{s} x_o \ln(4x_s/a)} \quad (34)$$

(3) direct integration:

$$b = \frac{l^2 N_o \Omega k T}{38 \lambda \bar{s} \tau'_k} \quad (35)$$

We start with case (2):  $C_o \ll 1$  means  $x_s \ll x_o$  and hence  $\ln(4x_s/a)$  must lie between 1 and 5; let us take  $\ln(4x_s/a) = 3$ . Insertion of the known values leads to

$$D_s n_{so} = 0.0249 \text{ s}^{-1}$$

The minimum value of  $n_{so}$  is found if we assume that the concentration in the adlayer is the same as in solution. Assuming further that the effective thickness of the adlayer is equal to *a*, which is also a lower bound, we find, with a volume concentration of growth units equal to  $4 \times 10^{-4}$  M:

$$n_{so} \geq 1.7 \times 10^{14} \text{ m}^{-2}$$

which yields

$$D_s \leq 1.5 \times 10^{-16} \text{ m}^2 \text{ s}^{-1}$$

As the volume-diffusion coefficient, calculated from conductivity data,<sup>13</sup> is about  $8 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  for Ca(OH)<sub>2</sub> at 37 °C, it is evident that the product  $D_s n_{so}$  is too low for surface diffusion to contribute significantly to the transport of growth units to the kinks, whence the secondary law due to  $C_o \ll 1$  must be excluded.

In case 3 we assume  $l \simeq a$  and find, with  $N_o = 4 \times 10^{-4} \text{ M} = 2.4 \times 10^{23} \text{ m}^{-3}$

$$\tau'_k = 0.3 \text{ s}$$

According to the Arrhenius equation we have

$$1/\tau'_k = A \exp(-E_{a,k}/kT) \quad (36)$$

which, with the value of  $E_{a,k}$  previously found, yields

$$A = 7 \times 10^{15} \text{ s}^{-1}$$

In order to see whether this value is possible, we make use of collision theory which, although derived for a solid-gas interface, should yield reasonable results also for the solid-solution interface.<sup>15</sup> The collision frequency of growth units is

$$Z = N_o \sqrt{kT/2\pi m} \quad (37)$$

where *m* is the mass of a growth unit. The number of growth units arriving at a growth site per unit time is *A*, whence

$$A = Z \bar{s} \quad (38)$$

Insertion of the known values yields

$$A = 8 \times 10^6 \text{ s}^{-1}$$

Comparison of the two values of *A* shows that the direct-integration mechanism is not possible; growth must be assisted by surface diffusion, and the only possibility remaining is the secondary law due to  $\alpha \ll 1$ .

We now have

$$n_{so}/\tau_k = 2.79 \times 10^{14} \text{ m}^{-2} \text{ s}^{-1}$$

and as  $n_{so} \geq 1.7 \times 10^{14}$  as above, we find

$$\tau_k \geq 0.6 \text{ s}$$



which is a plausible value. The condition  $\alpha \ll 1$ , with  $\alpha$  given by (5), leads to

$$\frac{D_s C_o \tau_k}{x_s a} \tanh\left(\frac{y_o}{2x_s}\right) \gg 1$$

There are two subcases to consider: (1a)  $x_s \ll y_o$ , which also means  $x_s \ll x_o$  and hence

$$\tanh(y_o/2x_s) \simeq 1$$

as well as, from (7)

$$C_o \simeq \frac{\pi x_s}{x_o \ln(4x_s/a)} \ll 1$$

and (1b)  $x_s \gg y_o$ , which means  $x_s \gg x_o$  and hence

$$\tanh(y_o/2x_s) \simeq y_o/2x_s$$

as well as

$$C_o \simeq 1$$

1a yields

$$\frac{\pi D_s \tau_k}{a x_o \ln(4x_s/a)} \gg 1$$

or, with  $\ln(4x_s/a) \simeq 3$  as above

$$D_s \tau_k \gg 2.8 \times 10^{-17} \text{ m}^2$$

An upper bound for  $\tau_k$  is found by taking  $n_{so} = n_o$ , the total number of adsorption sites on the surface. We have  $n_o = \bar{s}^{-1} = 2.18 \times 10^{18} \text{ m}^{-2}$  and find, with the above value of  $n_{so}/\tau_k$

$$\tau_k \leq 8 \times 10^3 \text{ s}$$

and thus

$$D_s \gg 3.6 \times 10^{-21} \text{ m}^2 \text{ s}^{-1}$$

There should be no difficulty in fulfilling this condition. On the other hand, 1b yields

$$\frac{\tau_k y_o}{2 \tau_{des} a} \gg 1$$

with the substitution  $x_s^2 = D_s \tau_{des} \tau_k$  being the time constant for desorption of growth units. We then find

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$$\tau_k/\tau_{des} \gg 0.0109 \ln \beta$$

or, as  $\ln \beta$  may be at least 3.5

$$\tau_k/\tau_{des} \gg 0.04$$

With the same upper bound for  $\tau_k$  as above, we have

$$\tau_{des} \ll 2 \times 10^5 \text{ s}$$

which is also easily fulfilled.

From transition-state theory we have<sup>10</sup>

$$\tau_k = (h/kT) \exp(\Delta G_k^\ddagger/kT) \quad (39)$$

With the limits we have found for  $\tau_k$ , this yields

$$75 < \Delta G_k^\ddagger < 100 \text{ kJ/mol}$$

We cannot know much about the activation entropy for incorporation; if the adsorbed growth units were unhydrated, we should expect a negative  $\Delta S_k^\ddagger$ , but the adsorbed calcium ions are probably highly hydrated, and the dehydration prior to incorporation leads to an entropy increase. If we assume  $\Delta S_k^\ddagger = 0$ , we have  $75 < \Delta H_k^\ddagger < 100 \text{ kJ/mol}$ .

Calculating  $E_a$  from (6) in the same manner as we did for the other mechanisms yields eqn. (40),

$$E_a = \Gamma_1^\circ a_2^* \Delta H_{1des}^\circ + \Delta H_{ks}^* + E_{a,spiral} + E_{a,k} \quad (40)$$

and we find with  $E_{a,k} = \Delta H_k^\ddagger$

$$-60 < \Gamma_1^\circ a_2^* \Delta H_{1des}^\circ + \Delta H_{ks}^* < -45 \text{ kJ/mol}$$

which means that the enthalpy increment for transfer of growth units from the kink to the surface plus the enthalpy increment for desorption of the amount of water occupying the same area as a growth unit is somewhat less negative than the enthalpy of solution, which is to be expected.  $\Delta H_{ks}^*$  is probably the dominating term and comprises the enthalpy of hydration of calcium ions in the adlayer; we may expect it to be approximately equal to  $-\Delta H_k^\ddagger$ , which requires a small, positive value of  $\Delta H_{1des}^\circ$  and a moderately negative value of  $\Delta S_k^\ddagger$ . This appears reasonable.

Finally we should verify that the kinetic constants of the upper and the lower parts of the curve of  $R$  versus  $\beta$  agree with each other. At low supersaturation, crystals from preparation I consume calcium

hydroxide 2.2 times as fast as do crystals from preparation III. We therefore assume that the specific area of I is 2.2 times as large as that of III, or 19000 m<sup>2</sup>/mol, and we may now recalculate the rate constant  $k_2$  for surface nucleation into absolute growth rate; the result is

$$k_2 = 0.526 \text{ mol m}^{-2} \text{ s}^{-1} \text{ M}^{-2}$$

Under the given conditions,  $\beta$  is an increasing function of pH, and for increasing supersaturation, the right-hand side of (2a) tends to eqn. (41).

$$R_{\max} = k_2 [\text{Ca}^{2+}] [\text{HPO}_4^{2-}] \quad (41)$$

From the solubility product of brushite we find

$$R_{\max} = 3.68 \times 10^{-11} \text{ m/s}$$

The growth rate resulting from the polynuclear mechanism is<sup>6,7</sup>

$$R = d \left( \frac{\pi}{3} J n_0 v^2 \right)^{1/3} \quad (42)$$

where  $d$  is the thickness of a crystal layer ( $=a$ ),  $J$  is the rate of nucleation at a site, and  $v$  is the rate of advancement of a step; the nuclei are assumed to be circular. Inserting known parameters yields for the limiting rate of nucleation

$$J_{\max} v_{\max}^2 = 7.01 \times 10^{-23} \text{ m}^2 \text{ s}^{-3}$$

where  $v_{\max}$  is the limiting rate of advancement of a step. The number of growth units being incorporated per unit length of step and per unit time is given by<sup>10</sup>

$$J_{\text{step}} = 2 \frac{a n_{\text{so}}}{\tau_k} (1 - \alpha) (\beta - 1) \quad (43)$$

In the present case we have  $\alpha \ll 1$ , and the limiting value of  $J_{\text{step}}$  is found by substituting  $n_0$  for  $n_{\text{so}}$  ( $\beta - 1$ ), taking into account the non-ideality of a concentrated adlayer.<sup>16</sup> Further, the rate of advancement of a step is related to  $J_{\text{step}}$  by

$$v = J_{\text{step}} \bar{s} \quad (44)$$

whence, as  $n_0 = \bar{s}^{-1}$

$$v_{\max} = 2a/\tau_k \quad (45)$$

which yields, with the limits of  $\tau_k$  found above,

$$1.7 \times 10^{-13} < v < 2.3 \times 10^{-9} \text{ m/s}$$

and then

$$1.38 \times 10^{-5} < J_{\max} < 2400 \text{ s}^{-1}$$

$J_{\max}$  is presumably approximately equal to  $1/\tau_k$ ; we should then have

$$\tau_k = 30 \text{ s}$$

and

$$J_{\max} = 0.03 \text{ s}^{-1}$$

As both  $\tau_k$  and  $J_{\max}$  are found within the permitted limits, we have now seen that the kinetic constants of spiral growth and of surface nucleation agree well with each other

## CONCLUSION

The analysis of the crystal growth kinetics of OCP has been performed along the same lines as those followed previously for paraffin crystals.<sup>17</sup> An aqueous electrolyte system is, however, less suited for detailed theoretical calculations than nonpolar crystals in a nonpolar solvent. In spite of this, it has been possible to demonstrate that at low supersaturation growth takes place according to a surface-diffusion (BCF) mechanism in which the rate-determining step is the incorporation of growth units into the kinks. It is reasonable to assume that the adsorbed calcium ions are highly hydrated, though probably less so than in solution, and that the dehydration which must take place prior to incorporation into the growth site is a slow process in comparison with surface diffusion. This assumption is borne out by numerous examples of the rule that anhydrous salts crystallize much more slowly than their hydrated counterparts.<sup>18</sup>

Two observations have not been discussed: the decrease of growth rate with time at low supersaturation, and the sudden transition from spiral growth to surface nucleation at a certain supersaturation, as compared to the mixed kinetics of hexatriacontane in light petroleum.<sup>17</sup> Both are probably morphological phenomena like habit change during growth and cooperation of growth spirals. A growth pyramid which is not a spiral may

even originate from repetitive nucleation at the same point,<sup>19</sup> i.e. without the intervention of a screw dislocation, and such a pyramid may eventually disappear. These hypotheses are, however, very difficult, if not impossible, to test experimentally.

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