**Kinetics of precipitation of calcium oxalates and phosphates from solutions supersaturated with both solid phases**

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**Introduction**

The urine of patients with disorders of calcium metabolism is frequently supersaturated with calcium oxalates and phosphates (6), a state that increases the tendency of such patients to form renal stones. Such stones, containing both calcium oxalates and phosphates, are commonly observed (1). Several studies on crystal growth of calcium oxalates upon seed crystals of calcium phosphates and vice versa have been reported (3,5), but no kinetic study on the spontaneous precipitation of both solid phases from supersaturated solutions has so far been published. Recent observations made under conditions of metastable equilibrium (2) suggest that phosphate ions retard crystal growth and delay equilibration of the calcium oxalate phases. In this paper, the kinetics of precipitation of calcium oxalate trihydrate (COT) and calcium hydrogenphosphate dihydrate, (DCPD) from unseeded solutions supersaturated to both solid phases are described. Attention is given to the mutual interaction of the solid phases and to the influence of excess phosphate ions on the kinetics of COT crystal growth.

**Materials and Methods**

**Experimental**

Samples were prepared by simultaneous mixing of solutions of known concentrations of oxalic and/or phosphoric acid, adjusted with sodium hydroxide to pH 5.1–5.2, with equal volumes of a calcium chloride solution, equimolar with respect to the phosphate solution. Sodium chloride was added to both solutions to make up the ionic strength after mixing to I = 0.26 mol dm⁻³. All solutions were thermostatted at 298 K and those used for particle size analysis were purified by filtering through 0.22 μm millipore filters. The kinetic experiments were carried out in double-walled vessels at 298 ± 0.1 K and the suspensions stirred continuously by magnetic means or ”mixed” (e.g. magnetically until the appearance of the first precipitate, afterwards by stirring paddle (9)). In one set of experiments (Fig. 1) the pH was monitored continuously as a function of time. The appearance of the first precipitate (COT) was detected visually (change in turbidity) and verified by optical microscopy. Subsequent precipitation of DCPD was detected by the change in solution pH. In a parallel
set of experiments (Figs. 2, 3) the kinetics of precipitation of calcium oxalate was followed by particle size analysis (Coulter counter Mo TA 2). The composition of the precipitates formed was ascertained by optical microscopy, TG analysis and X-ray powder patterns.

**Treatment of data**

The precipitation kinetics of COT was interpreted according to the general rate equation (ref. [7]):

\[
\frac{d \alpha}{dt} \alpha^{-2/3} = KN_t^{1/3} S^P
\]  

where \( \alpha \) is the degree of the reaction calculated from Coulter counter output data (e.g. \( \alpha = \frac{V_t}{V_{\text{max}}} \) where \( V_t \) is the total and \( V_{\text{max}} \) the maximum attainable volume of the precipitate), \( N_t \) is the number of particles, \( K \) is a constant and \( p \) is the order of the reaction. The supersaturation, \( S \), has been defined as \( 1 - \alpha \). For dominant crystal growth, Eq. (1) reduces to the crystal growth equation:

\[
\frac{d \alpha}{dt} \alpha^{-2/3} = K_\alpha (1 - \alpha)^P
\]  

and the parameters \( K_\alpha \) and \( p \) may be obtained as the intercept and slope of the straight line defined by the logarithmic form of Eq. (2). The parameter \( p \) was used as a criterion for the intensity of the influence of phosphate ions on the rate of crystal growth of calcium oxalate.

**Results and Discussion**

In the following kinetic experiments, the calcium and phosphate concentrations were equimolar and the phosphate and oxalate concentrations were as in urine (e.g. \( c(Ca) = c(PO_4) = 2.6 - 2.8 \times 10^{-2} \text{ mol dm}^{-3}, c(C_2O_4) = 1.5 \times 10^{-4} \text{ mol dm}^{-3} \)). The initial supersaturations with respect to DCPD and COT (the only solid phases precipitating under the given experimental conditions) were also similar to those in urine (6), e.g. \( S_0(\text{DCPD}) = 2.62 - 3.57 \) and \( S_0(\text{COT}) = 6.86 \).

In all kinetic experiments, COT precipitated first with an induction period of 10-12 min. Figure 1 shows that this precipitate significantly reduced the induction time of DCPD which, in systems without oxalate, was \( t_i \approx 3 \text{ h} \), while in the presence of COT it varied between 75 and 150 min (4). The latter induction times, however, were still long enough to study the influence of the phosphate ions present in solution on the kinetics of precipitation of COT. In Figs. 2 and 3 these results are compared with those obtained for the respective control systems prepared without phosphate ions. It is quite obvious (Fig. 2) that in the presence of phosphate (curve 2) the calcium oxalate precipitate appears later and is less abundant than in the controls (curve 1).

Quantitative interpretation of the results is possible according to Eqs. (1) and (2). Equation (1) shows that the precipitation rate depends on the supersaturation, \( S \), and on the number of particles, \( N_t \). A logarithmic plot of Eq. (1) (Fig. 3) can be resolved into parts showing nucleation (part A, increasing rate because of increasing