

Unusual Growth of Calcium Oxalate Crystals in Water Medium[†]

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Received February 27, 1975

Calcium oxalate particles which were firstly precipitated from homogeneous solution by means of the hydrolysis of dimethyl oxalate at 50°C dissolved partially during the reaction and then grew again to the perfect crystals. During the reaction pH of the solution decreased from 9 to 1.25, and it seems that the unusual growth of calcium oxalate crystals depended upon the change of concentrations of oxalate and hydrogen oxalate ions produced from oxalic acid at various pH's.

I. INTRODUCTION

The precipitation in solution is generally performed by the direct mixing of reagent solutions or by the PFHS (precipitation from homogeneous solution¹⁾) method. Generally, at the first stage of precipitation the crystalline nuclei which are considered as the original particles of the precipitate appear and they grow continuously to large particles by the deposition of components of the precipitate. Such a process is the primary growth of the precipitated particles and is followed by the secondary growth process which contains the coagulation, the recrystallization, the transformation, the perfection, *etc.*²⁾ But an unusual growth of particles was found in the case of the precipitation of calcium oxalate produced by the PFHS method by means of the hydrolysis of dimethyl oxalate.³⁾ That is, the crystals formed at first dissolved partially and grew again to perfect crystals. In this paper such an abnormal growth of calcium oxalate crystals will be described.

II. EXPERIMENTAL

100 ml of 0.010 M solution of calcium chloride, 500 ml of the buffer solution (a solution containing each 50 g of sodium citrate and sodium borate in 2,000 ml) and 400 ml of water were taken into a three-necked flask with a reflux condenser and a stirrer and the solution was kept at 50°C followed by adding 25 g of dimethyl oxalate. After various time intervals a portion of the solution was filtered and the concentration of calcium in each filtrate was measured by flame analysis. The precipitated particles were analyzed by the electron microscopy and the X-ray diffraction techniques.

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† The investigation was supported in part by a grant of the Japanese Ministry of Education (1973, General Study, Section D).

Unusual Growth of Calcium Oxalate Crystals

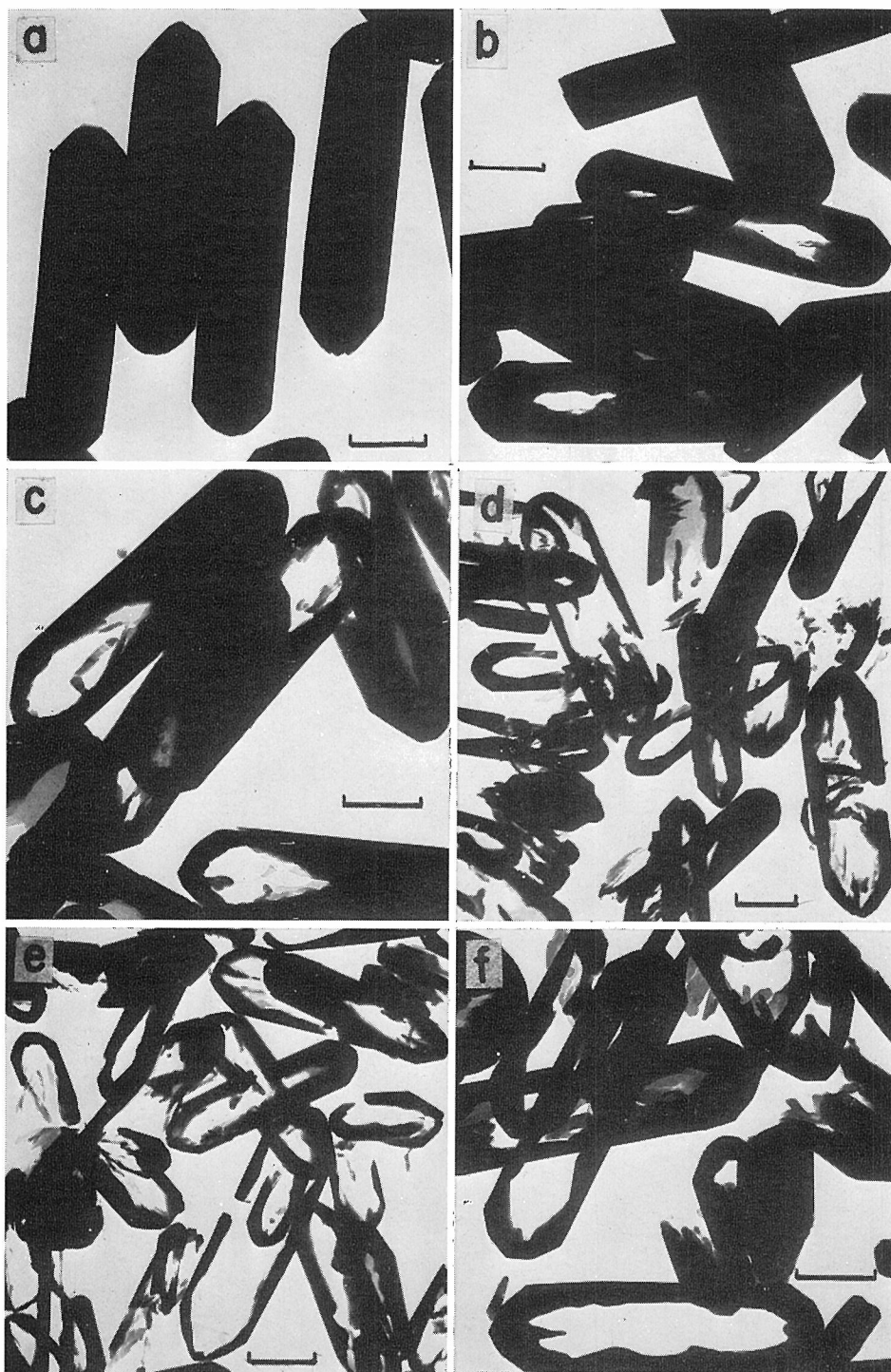


Fig. 1. a~f

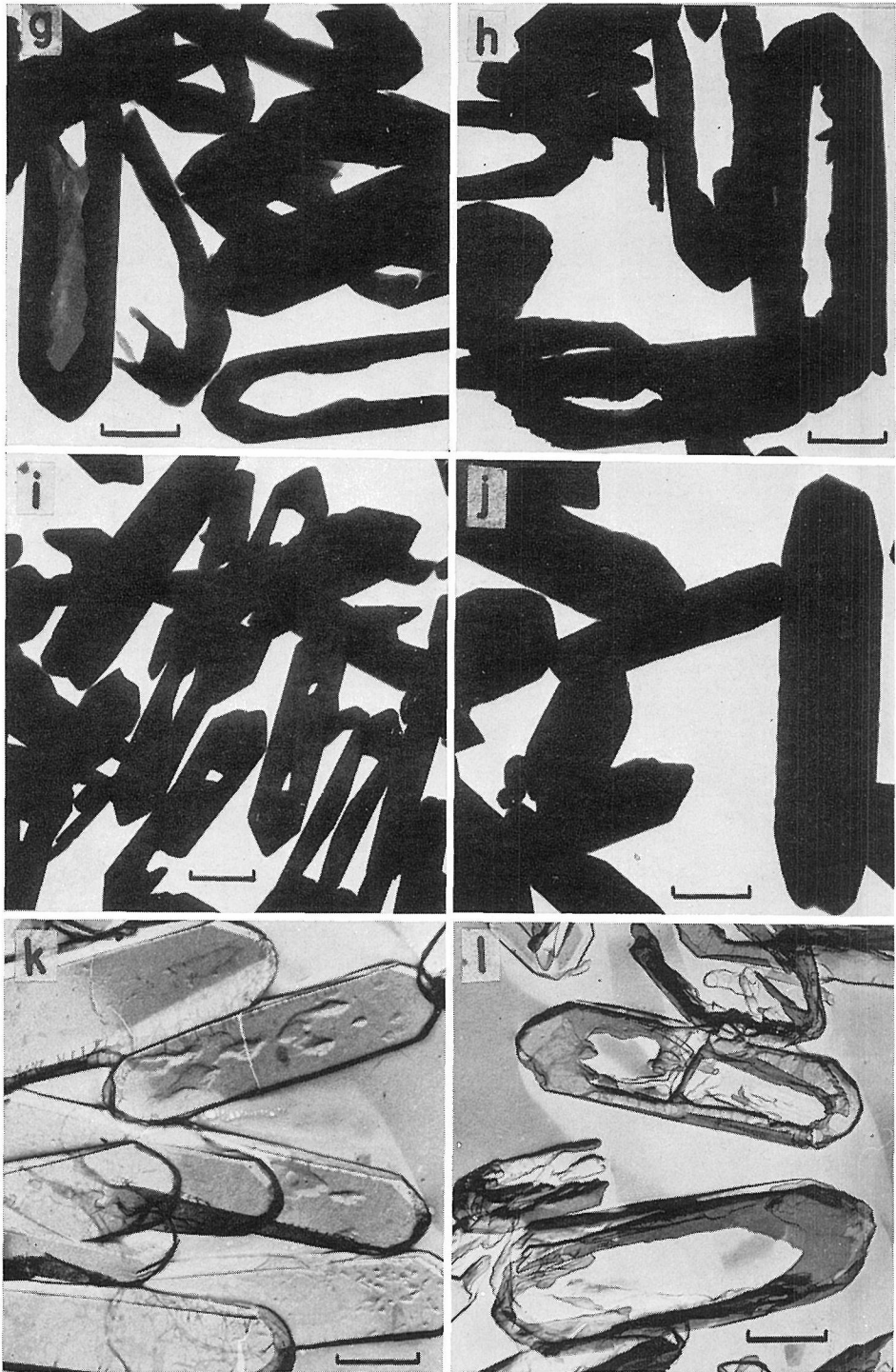


Fig. 1. g~l

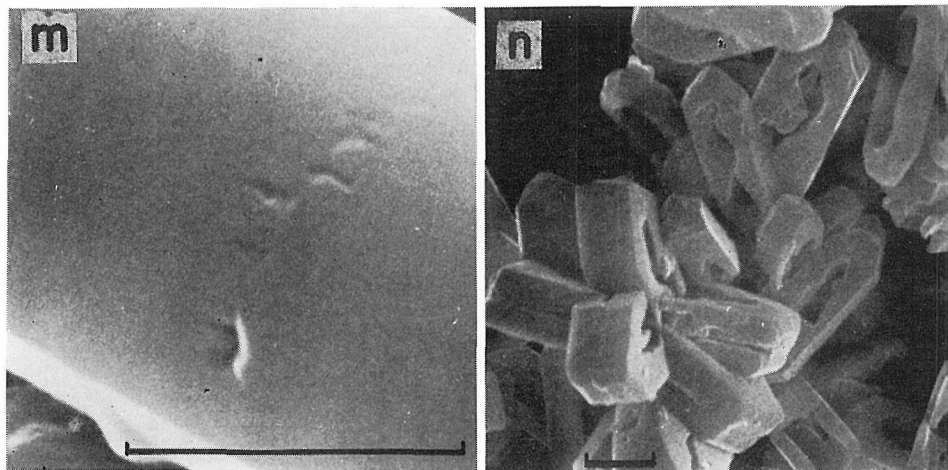


Fig. 1. m~n

Fig. 1. Electron micrographs of calcium oxalate crystals after various reaction times
 a: 10 min, b: 20 min, c: 30 min, d: 60 min, e: 90 min, f: 120 min,
 g: 180 min, h: 240 min, i: 360 min, j: 480 min, k: 15 min (carbon replica),
 l: 60 min (carbon replica), m: 15 min (scanning microscopy),
 n: 60 min (scanning microscopy)

III. EXPERIMENTAL RESULTS

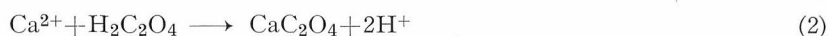
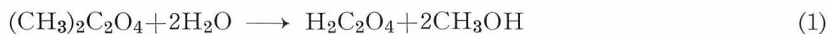
III.1 Morphology of Crystals

Electron micrographs of calcium oxalate produced after various reaction times are shown in Fig. 1 a to n. Calcium oxalate grew to perfect crystals after 10 to 20 minutes (Fig. 1 a), but they began to dissolve after that (Fig. 1 b, c). After 60 to 90 minutes only edges of the particles remained (Fig. 1 d, e), but after 120 minutes the holes in the crystals began to be filled up by the deposition of crystal components (Fig. 1 f, g, h, i). Then after 480 minutes the crystals grew up again completely (Fig. 1 j). The beginning of dissolution of crystals was shown by the carbon replica and the scanning microscopy techniques (Fig. 1 k, m). The remained edges of particles undissolved after 60 minutes are also shown (Fig. 1 l, n).

The crystal structure of calcium oxalate was not changed in spite of the remarkable change of morphology.

III.2 Rate of Precipitation

The hydrolysis of dimethyl oxalate and the formation of calcium oxalate are expressed as follows:



The rate of precipitation of calcium oxalate and the change of pH of the solution are shown in Fig. 2. Calcium oxalate precipitated almost completely after 20 minutes from the beginning of reaction, but the proportion of precipitate began to decrease after that

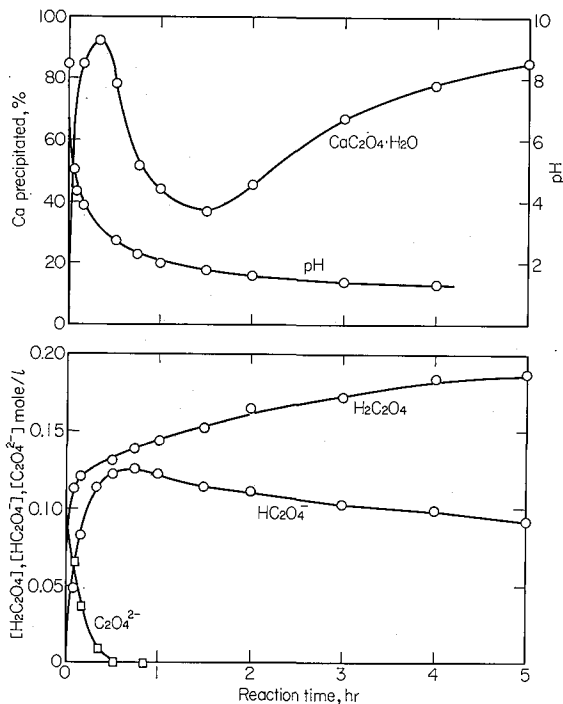


Fig. 2. Change of quantities of calcium oxalate precipitate, pH, oxalic acid, oxalate ion and hydrogen oxalate ion during the precipitation of calcium oxalate from homogeneous solution.

and it reached to a minimum value of about 35% after 90 minutes. However, it increased gradually as the reaction proceeded after that. The change of the proportion of calcium oxalate precipitate related with the change of morphology of crystals shown in Fig. 1.

The change of the concentration of oxalic acid obtained by the determination of remained dimethyl oxalate by the extraction with ethyl ether is also shown in Fig. 2.

IV. DISCUSSION

As the hydrolysis of dimethyl oxalate progressed, the concentration of oxalic acid increased (Fig. 2) and pH of the solution decreased as shown in Fig. 2, because the buffer solution did not act well. It was considered that the decrease of pH of the solution was the primary cause of the abnormal growth of calcium oxalate crystals. The concentration of oxalate ion calculated from that of oxalic acid according to Eq. (3) decreased as shown in Fig. 2, but even after 4 hours enough oxalate ions were present to precipitate

$$[\text{C}_2\text{O}_4^{2-}] = a_2[\text{H}_2\text{C}_2\text{O}_4] \quad (3)$$

$$a_2 = \frac{K_1 K_2}{[\text{H}^+]^2 + [\text{H}^+]K_1 + K_1 K_2}$$

calcium oxalate. The concentration of hydrogen oxalate ion calculated from that of oxalic acid according to Eq. (4) was changed as shown in Fig. 2. That is, it increased

Unusual Growth of Calcium Oxalate Crystals

$$[\text{HC}_2\text{O}_4^-] = \alpha_1[\text{H}_2\text{C}_2\text{O}_4] \quad (4)$$
$$\alpha_1 = \frac{[\text{H}^+]\text{K}_1}{[\text{H}^+]^2 + [\text{H}^+]\text{K}_1 + \text{K}_1\text{K}_2}$$

from the beginning of the reaction and reached to the maximum value after 45 minutes. Around the maximum concentration of hydrogen oxalate ion calcium oxalate precipitate began to dissolve as shown in Fig. 2. After about 90 minutes from the beginning of the reaction calcium oxalate crystals which were dissolved partially were again growing gradually with decreasing the concentration of hydrogen oxalate ion. It seems that the abnormal growth of calcium oxalate crystals mentioned above was related to the change of concentration of hydrogen oxalate and calcium hydrogen oxalate seems to be a soluble compound.

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