Formation and Aging of Precipitates. XII. Studies on Types of Crystal Growth of Barium Sulfate by Dissolution in Water*

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Barium sulfate is one of the sparingly soluble salts and it gradually dissolves in water. The investigation of dissolution of barium sulfate in EDTA solution was reported[1], but hitherto no morphological study has been made. The author previously reported the investigation of growth process of barium sulfate precipitate[2]. The precipitate was purified by the diffusion washing, that is, a drop containing the precipitate was placed on a Formvar film floating on the surface of distilled water for about ten minutes and the soluble matter was made to diffuse through the film into the water below. About ten minutes were suitable for the washing process while, under too long time of washing, the precipitate tended to dissolve in water. The present investigation is intended to study the type of crystal growth of barium sulfate by the dissolution of the crystal under the diffusion washing for a long period.

Sample.—Two kinds of barium sulfate precipitates were used in the dissolution by diffusion washing. One was the oval particles prepared by the method described in the previous paper[3], and the other was the thin rectangular particles prepared by direct mixing of dilute reagents[4].

Experimental.—A drop of the suspension containing the precipitate mentioned above was placed on a thin Formvar film floating on the surface of distilled water. The drop was left for several hours or one day to let ions diffuse from the drop into the water below. The film was then scooped up with a specimen grid for electron microscopy. Both the fresh and the aged precipitates were examined.

Experimental Results and Consideration

Oval Crystal. — The freshly prepared oval particles as shown in Fig. 1a changed to those as shown in Figs. 1b and c after they were treated with water for three hours. The radial arrangement of small particles are observed in each oval particles. It seems that the oval particles, subjected to dissolution, have been formed by the repetition of dendritic growth, the rate of which is rapid and slow alternately, and that the weakly oriented parts around the particles dissolve in water easily while the comparatively stable parts are not easily soluble, thus the radially arranged particles can be observed. Several hours after, the oval particles dissolved in water and changed in appearance as shown in Figs. 2a and c. The particle shown in Fig. 2a has still the original orientation of crystal structure and the orientation of crystal shown in Fig. 2c was disordered, as was proved by electron diffraction pattern shown in Figs. 2b and d.

Oval particles which were aged for about one day in the mother liquid changed in appearance as shown in Figs. 3a and b. In the aging process, the crystal structure of particles, especially that of the surface of particles, seems to become perfect gradually. Thus in the case of an aged particle, the inner part

* The eleventh paper of this series, This Bulletin, **32**, 387 (1959).

1) K. Mukai and K. Goto, *Japan Analyst (Bunseki Kagaku)*, **6**, 732 (1957).

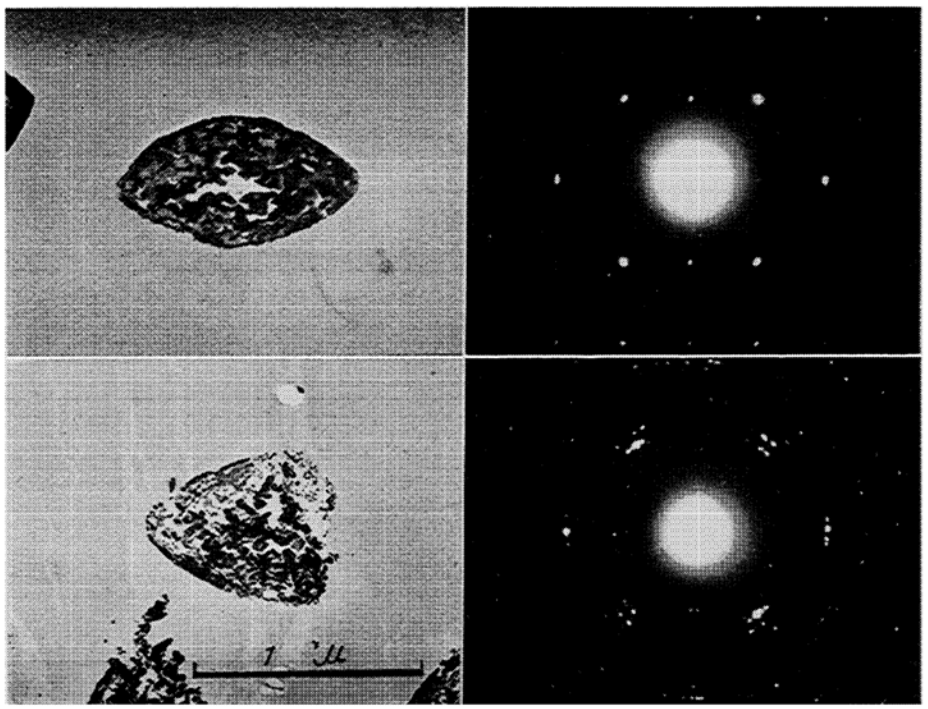
2) K. Takiyama, This Bulletin, **31**, 950 (1958).

3) K. Takiyama. ibid., **32**, 387 (1959).

4) K. Takiyama, ibid., **27**, 121 (1954); **32**, 68 (1959).

a b e ×30,000

Fig. 1. Dissolution of freshly prepared barium sulfate particles in water.
a: original particles; b, c: after treatment for three hours

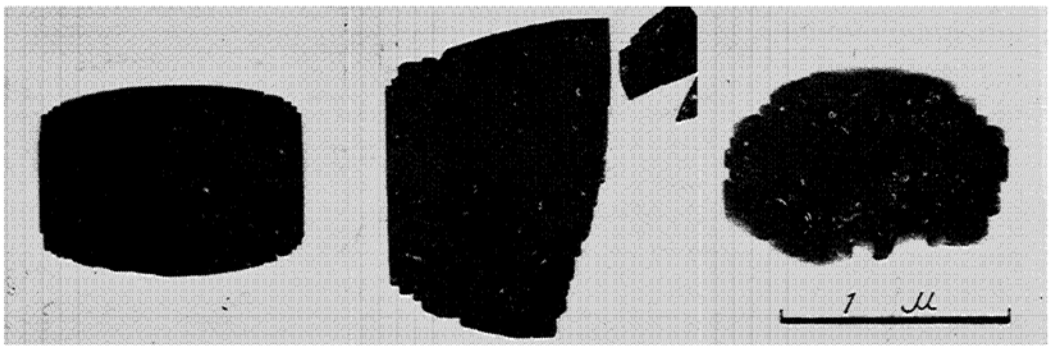


×30,000

Fig. 2. Dissolution of freshly prepared barium sulfate particles by treatment with water for six hours.

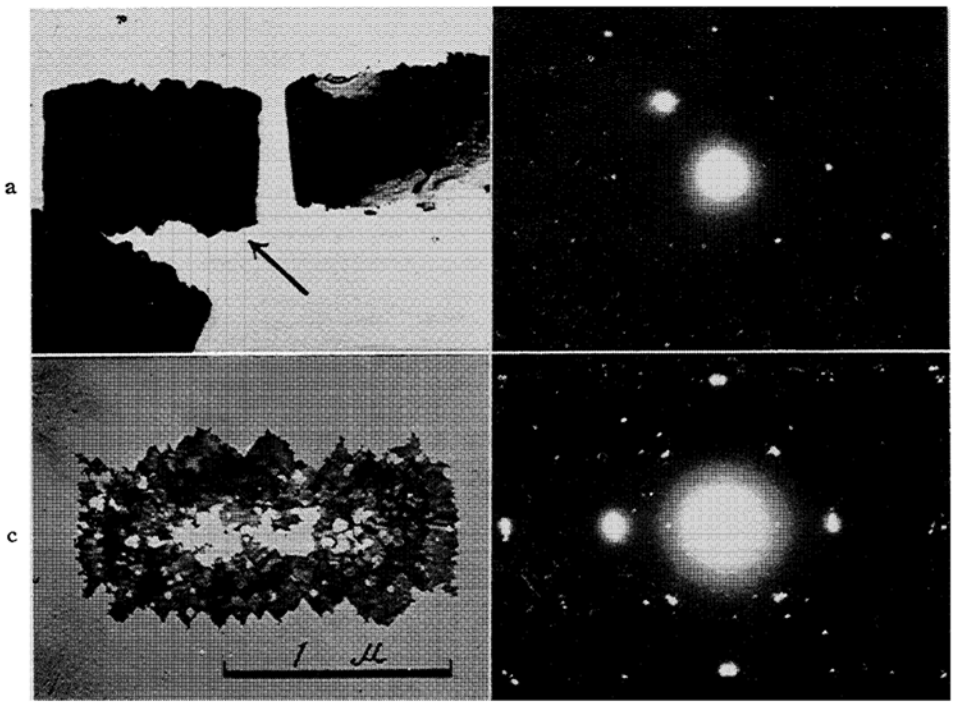
a b ×30,000

Fig. 3. Dissolution of aged barium sulfate particles in water.
a: after treatment for three hours; b: after treatment for six hours



a b c ×30,000

Fig. 4. Dissolution of freshly prepared barium sulfate particles by treatment with water for three hours.



×30,000

Fig. 5. Dissolution of aged barium sulfate particles in water.
a, b: after treatment for six hours
c, d: after treatment for one day

of particle dissolved faster than the surface part which remained undissolved as shown in Fig. 3b.

Rectangular Thin Crystal.—Freshly prepared rectangular particles dissolved from the corner of particles as shown in Fig. 4. The corner of the slightly dissolved particles has many steps as shown in Figs. 4b and c. The rectangular particles are the perfect single crystal as described in the previous paper[4] and their growth seems to agree with the perfect crystal growth theory proposed by Kossel and Stranski[5]. Thus the particles seem to have grown stepwise and to have many steps which are large in some parts. Then weak parts at the surface of particles dissolved quickly and many of these large steps appeared around the particles.

The aged rectangular perfect crystals dissolved in water and gave the figure as shown in Fig. 5. The particles began to dissolve from the side of crystals, that is, from (0 1 0) plane (Fig. 5a), and the inner parts dissolved faster than the surface parts of particles (Fig. 5c). The surface of aged particles seems to become stable by complete orientation of crystal structure during digestion in mother liquid as in the case of oval particles. The particle shown in Fig. 5a (arrow) has a perfect single crystal structure (Fig. 5b) and the single crystal structure of the particle shown in Fig. 5c has begun to decompose (Fig. 5d) as examined by electron diffraction method. The crystal structure of the surface part remained almost perfect even after one day's treatment with water.

5) I. M. Stranski, *Z. phys. Chem.*, **136**, 259 (1928).

Summary

The oval and rectangular crystals of barium sulfate precipitates seem to grow through the dendritic and perfect crystal growth processes, respectively. These particles dissolve in the process of diffusion washing. The oval particles dissolved slightly show the dendrite structure in them, and the rectangular particles dissolved slightly show the large steps around the particles. Thus these particles proved to have grown through dendritic and perfect crystal growth processes, respectively. The surface of the aged particles of both oval and rectangular crystals become stable by digestion in mother liquid; hereby the dissolution rate of inner parts of particles is faster than that of surface parts of them.

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