# *Formation and Aging of Precipitates. XI*. An Electron Micro-Diffraction Study on Nucleation of Barium Sulfate Precipitate from Homogeneous Solution*

By Kazuyoshi TAKIYAMA

(Received October 6, 1958)

In the course of precipitate formation, the nucleation process is the idea generally accepted. The nucleation involves a process of formation of embryo, which is an unstable intermediate, and a process of the nucleus formation. When the precipitate is formed with direct mixing of ions, the growth of the nuclei formed in small numbers plays a predominant part in the region of the lower concentration, and the nucleation plays a predominant part in the higher concentration region[1,2]. When the precipitate is formed from a homogeneous solution, the nucleation occurs when a certain degree of supersaturation is attained[3]. During the

* The tenth paper of this series, This Bulletin, 32, 68 (1959).

1) K. Takiyama, ibid., **31**, 950 (1958).
2) K. Takiyama, ibid., **32**, 68 (1959).
3) V. K. LaMer and R. H. Dinegar, *J. Am. Chem. Soc.*, **73**, 380 (1951).

precipitation process the crystal property of particles seems to appear after nucleation.

An attempt has been made in the present investigation to employ the electron micro-diffraction method with a view to observe the nucleation process during the formation of barium sulfate precipitate according to LaMer and Dinegar's method[3].

## Experimental

**Procedure.**—Fifty ml. of 0.02 M ammonium persulfate solution was added to a 200 ml. beaker containing 50 ml. of 0.02 M barium nitrate solution. Barium sulfate formed from the sulfate in persulfate was filtered with a glass filter. Ten ml. of 0.1 M sodium thiosulfate solution was then added to the clear filtrate and the reaction solution thoroughly mixed was kept in a thermostat at 25°C. The precipitate, when examined with a beam of white light, exhibited Tyndal beam 7 minutes after the addition of thiosulfate.

The reaction mixture was poured into a spray bottle which was kept in the thermostat, and was sprayed on tiny Formvar films floating on the surface of distilled water 5, 6, 7, 8, 9 and 10 minutes after the addition of thiosulfate. A few minutes were allowed for diffusion of soluble salts from the drop of reaction mixture into the water below. The films were scooped with specimen grids for observation with an electron microscope.

**Calculation of Size of Crystalline Nucleus.**—From the Thomson's equation[4] on nucleation in the supersaturated vapor, the size of nucleus formed in the supersaturated sparingly soluble salt solution is expressed by the following equation,

$$r=\frac{2M\sigma}{i\boldsymbol{R}T\rho\ln S/S_{\infty}} \qquad (1)$$

where $r$ is the radius of spherical nucleus, $M$ the molecular weight, $\sigma$ and $\rho$ are the surface tension and the density of the crystal, $\boldsymbol{R}$ is the gas constant, $T$ the absolute temperature, $S$ the supersaturation concentration, $S_{\infty}$ the solubility of the salt and $i$ the van't Hoff factor. According to LaMer and Dinegar[3], the value of the supersaturation ratio, $\sqrt{K_{SS}^{\circ}/K_{SP}^{\circ}}$ ($K_{SS}^{\circ}$ and $K_{SP}^{\circ}$ are the activity products of both supersaturated and saturated solutions), is a constant and is 22 on an average at 25°C. The value of $r$ is calculated in the present case, as 100 Å from the equation 1, when this limiting value, 22, is substituted for $S/S_{\infty}$. On the other hand, the condition of concentration of reacting ions at the time that the precipitate begins to appear in the case of homogeneous solution method, seems to correspond to the limiting supersaturation concentration at which the precipitate appears without an induction period in the case of direct mixing method. This limiting supersaturation concentration is about 0.002 M[1]. The size of nucleus, $r$, is calculated as 60 Å according to the equation 1, when this value of 0.002 is substituted for $S$. It seems that the size of crystalline nucleus formed under the experimental condition mentioned above is in the range of 100 to 200 Å in diameter.

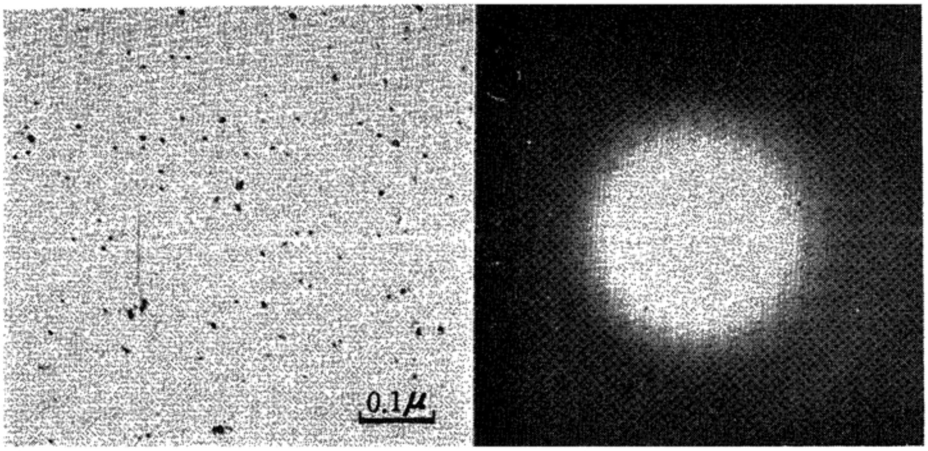
## Results

The image of particles began to be observed with the electron microscope after 6 minutes and the particles grew gradually as the time passed. An electron micrograph and an electron diffraction pattern obtained from the six minutes' specimen are shown in Figs. 1 a and b. The diameter of particles shown in Fig. 1 a measures 30 to 80 Å and the particles looked like unstable embryos formed by aggregation of monomers. As the crystal structure of these particles is not perfect, the diffraction pattern is composed of a few broad rings. The particles in the seven minutes' specimen are nearly spherical and measure 100 to 200 Å in diameter as shown in Fig. 2 a. The size of these particles coincides with that obtained by the calculation from equation 1. The electron diffraction pattern obtained from these particles is composed of indistinct coarse rings as shown in Fig. 2 b. But the rings indicate that the crystal structure of particles is more perfect than that of particles shown in Fig. 1 a. The size of particles in the eight minutes' specimen is 300 to 400 Å in diameter as shown in Fig. 3 a. The electron diffraction pattern is composed of distinct coarse Debye-Scherrer rings as shown in Fig. 3 b. The crystal structure of particles seems to have been completed in this stage. The particles in the ten minutes' specimen are spindle-shaped and the length of the long axis is about 1000 Å as shown in Fig. 4 a. The electron diffraction pattern obtained from one of the particles arrow is N-pattern as shown in Fig. 4 b. Each particle is obviously a single crystal, and the long axis proves to be $b$-axis from the analysis of the pattern shown in Fig. 4 b. The shape of the particle grown completely is oval. The oval particle of barium sulfate seems to be formed through dendritic growth in every direction from a crystal nucleus and the particle has a single crystal structure. The growth along $b$-axis seems to be more or less marked.

The particles of barium sulfate began

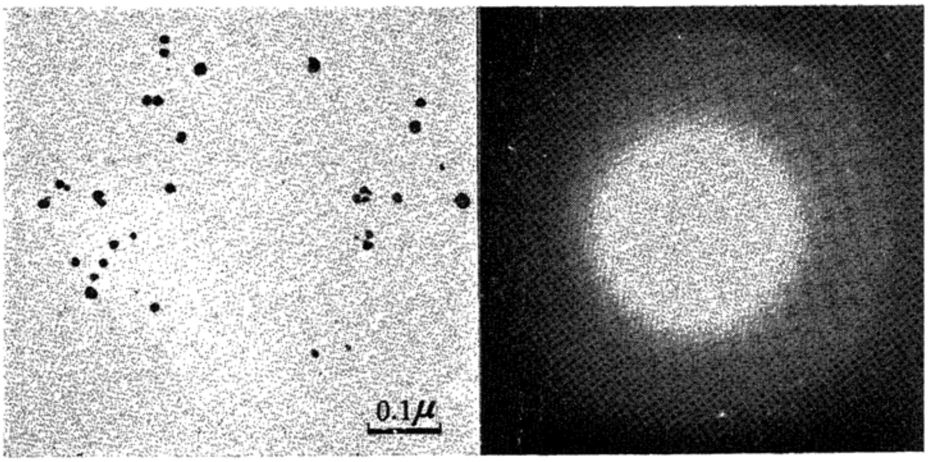
4) W. Thomson, *Phil. Mag.*, **42**, 448 (1871).

Electron micrographs and diffraction patterns of barium sulfate presipitates.




a (×100,000) b

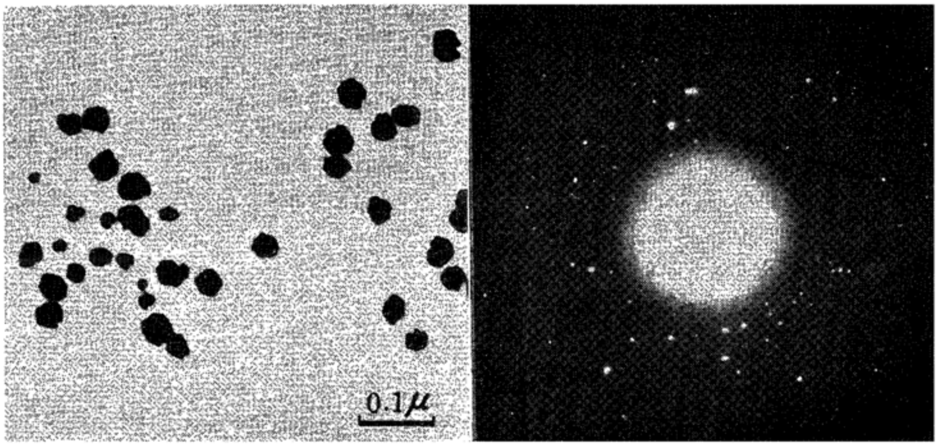
Fig. 1. Embryos of barium sulfate precipitate sampled after 6 minutes.




a (×100,000) b

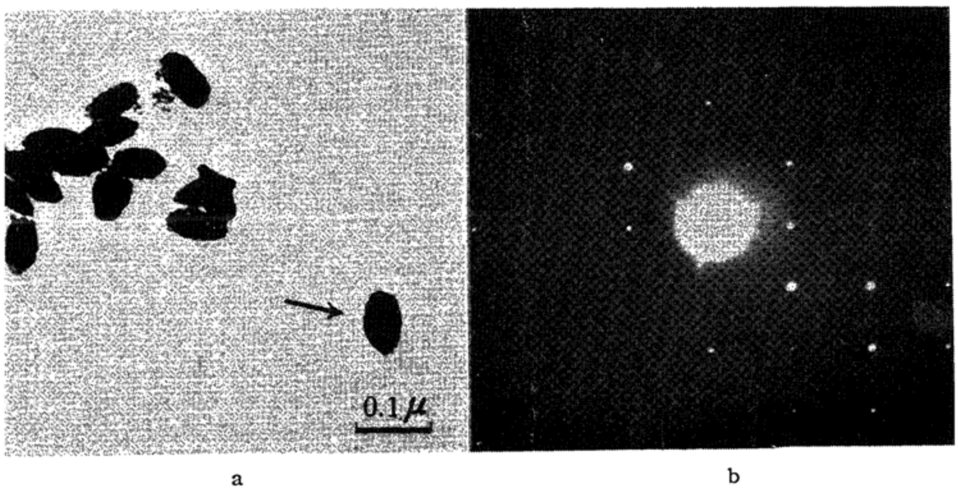
Fig. 2. Crystal nuclei of barium sulfate precipitate sampled after 7 minutes.

Electron micrographs and diffraction patterns of barium sulfate presipitates.




a (×100, 000) b

Fig. 3. Crystals of barium sulfate precipitate sampled after 8 minutes.




a (×100, 000) b

Fig. 4 Single crystals of barium sulfate precipitate sampled after 10 minutes.

to appear after 6 minutes and grew up continuously into large crystals. During the precipitation process, the existence of the nucleus with a certain size can be logically proved from the standpoint of thermodynamics[3,4], but in fact only the continuous growth of a particle is observed by electron microscopy and the particle appears to form a distinct crystal structure when it has attained the size as large as that of the nucleus calculated thermodynamically.


### Summary

The nucleation process of the precipitation of barium sulfate from the homogeneous solution of persulfate-thiosulfate system was observed by the electron micro-diffraction method. The particles grew continuously, but the distinct crystal structure began to appear in the particles having the length of 100 to 200 Å in diameter, corresponding to the nucleus calculated thermodynamically.


The author gratefully acknowledges the guidance of Professor Eiji Suito of Kyoto University. He also wishes to express his hearty thanks particularly to Professor Masayoshi Ishibashi of Kyoto University for his continuous advice and encouragement.

*Institute for Chemical Research*
*Kyoto University*
*Takatsuki, Osaka*