Studies on the Monodisperse Aerosols. III. The Formation of Sulfur Aerosols

By Susumu KITANI

(Received July 22, 1957)

The formation of monodisperse aerosols of various substances has been frequently investigated with relation to the colloid chemical studies on aerosols. Since the studies of La Mer-Sinclair using their aerosol generator[1,2], the preparation of uniform aerosols has become easy to perform and it has been possible to extend the method to any kind of aerosol.

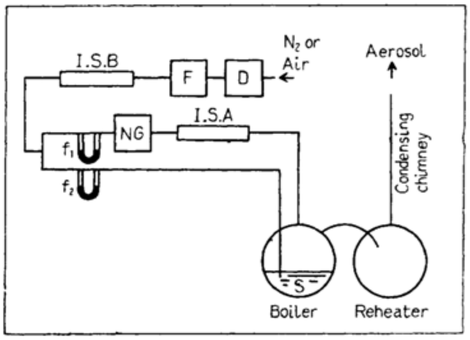
Ford and La Mer[3] measured the vapor pressure of a supercooled liquid sulfur droplet which was prepared by the La Mer-Sinclair generator with the nuclei of sodium chloride. Kerker and others[4] announced that a sulfur aerosol could be nucleated with sulfuric acid vapor to produce smaller particles, while large particles of sulfur aerosols were prepared by self-nucleation. As a rule, monodisperse aerosols are obtained only when proper nuclei are given homogeneously to a supersaturated vapor. Sinclair[2] mentioned that, in the formation of monodisperse aerosols by the La Mer-Sinclair generator, the condensation nuclei are formed in the ionizer by a high-voltage electric spark, and that the nuclei may be ionized molecules of air and its related compounds.

It was found in this experiment that monodispersed aerosols were obtained by introduction of the nuclei produced by the flaming spark of silver electrodes. We attempted to investigate what nuclei are effective in the formation of sulfur aerosol by the condensation method.

1) D. Sinclair and V. K. La Mer, *Chem. Rev.*, **44**, 245 (1949).
2) Atomic Energy Commission, "Handbook on Aerosols", Washington, D. C., (1950), p. 77.
3) G. P. Ford and V. K. La Mer, *J. Am. Chem. Soc.*, **72**, 1959 (1950).
4) M. Kerker and others, *J. Colloid Sci.*, **10**, 413 (1950).

Experimental

The apparatus used for the formation of sulfur aerosols is shown schematically in Fig. 1. The sulfur aerosols have been prepared by using a modified La Mer-Sinclair aerosol generator and ion separators A and B. The modification consists in separating the ionizer from the boiler. The



D: Drier
F: Glasswool filter
I. S. A., I. S. B.: Ion separator
NG: Nuclei generator
f_1, f_2: Flow-meter
S: Sulfur

Fig. 1. The apparatus for the formation of sulfur aerosols.

ionizer is called "nuclei generator" in this paper. It consists of a glass tube, 35 mm. in diameter and 90 mm. in length, fitted with the electrodes, made of silver wires (0.5 mm. in diameter) and fixed 6 mm. apart. An electric current of 10 mA. was applied at 11 kV. of A.C. in nitrogen or air. The ion separator A was placed between the boiler and the nuclei generator in order to remove the charged substances resulting from the electric spark; another ion separator B was used to exclude air ions and charged particles of dust. The separators A and B consist of rectangular pipe, 20 cm. in length, made of aluminum plates, 1 cm. in width and 20 cm. in length, set parallel and 1 cm. apart from each other, and other parallel plates are made of bakelite of the same size as the aluminum electrodes and serve as the electric insulator.

The boiler and the reheater were heated electrically and kept at a given temperature by thermoregulators: the former was operated at from 120° to 140°C, and the latter at from 130° to 150°C. In most runs of experiment, the latter was maintained higher by 10°C than the former.

The air, purified by passing through concentrated sulfuric acid, glasswool and the ion separator B, was passed through both of two branches at the rate of 0.25 l./min. into the boiler; one branch served to bubble through liquid sulfur and the other to send condensation nuclei through the ion separator A.

The distribution of particle size was measured by the "Owl"[1,2] and an ultramicroscope. The average radius $\bar{r}$ was calculated by application of the Stokes-Cunningham's equation from the terminal velocity of particles in the cell of the ultramicroscope[5]. The standard deviation σ was evaluated by

$$\sigma=\left\{\frac{\sum_i N_i(r_i-\bar{r})^2}{\sum_i N_i}\right\}^{1/2} \tag{1}$$

where N_i is the number of particles of radius r_i. The fractions of charged particles were also measured from the direction of electrophoresis of particles in the cell of the ultramicroscope. Sulfur, used in this experiment, was purified by recrystallization from carbon disulfide solution.

Results

The condensing chimney of La Mer-Sinclair generator consists of a double tube and, for comparison, the chimney of a single tube was also used in the present work. In both cases, the monodisperse aerosols in the state of supercooled liquid were formed only when the nuclei were given by the flaming spark of silver electrodes. In the case of the absence of nuclei, polydisperse aerosols were produced in the condensing chimney of a single tube but we could hardly get the aerosols in the chimney of the double tube. When the single tube was used, the aerosols might be produced by self-nucleation owing to a rapid cooling.

It is found in Fig. 2 that the higher the temperature of the boiler, the larger the average radius $\bar{r}$. The higher order Tyndall spectra on sulfur aerosols were

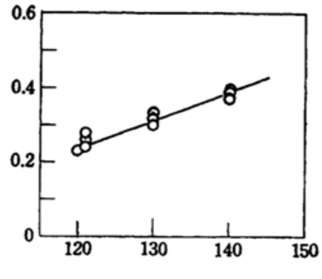


Fig. 2. Dependence of the average radius, $\bar{r}$, as a function of boiler temperature.

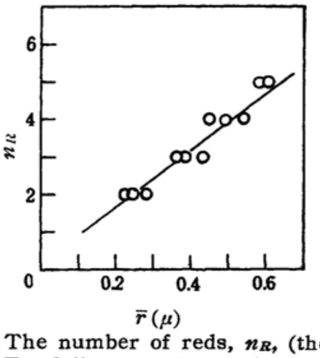
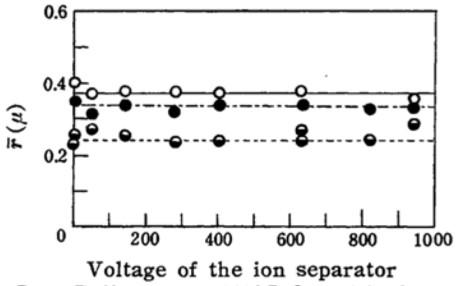


Fig. 3. The number of reds, n_R, (the higher order Tyndall spectra) vs. the particle of average radius, $\bar{r}$.

observed by the "Owl". The number of red bands, n_R, is plotted against $\bar{r}$ in Fig. 3. The $\bar{r}$, σ and the fractions of charged particles obtained using the condensing chimney of a single tube and of a double one were plotted as the function of voltage of the ion separator A as shown in Figs. 4, 5 and 6.



---◒---: Boiler temp. 120°C & reheater temp. 130°C.
---●---: Boiler temp. 130°C & reheater temp. 140°C.
} with the condensing chimney of double tube.

—○—: Boiler temp. 140°C & reheater temp. 150°C. } with the condensing chimney of single tube.

Fig. 4. Dependence of the average radius, $\bar{r}$, as a function of the voltage of the ion separator A.

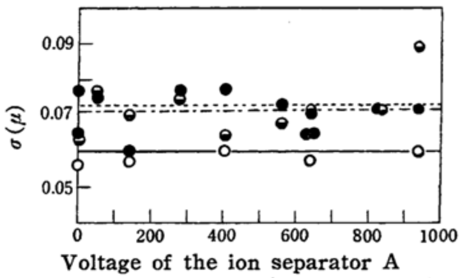


Fig. 5. Dependence of the standard deviation, $\sigma(\mu)$, as a function of the voltage of the ion separator A. (notations are the same as Fig. 4.)

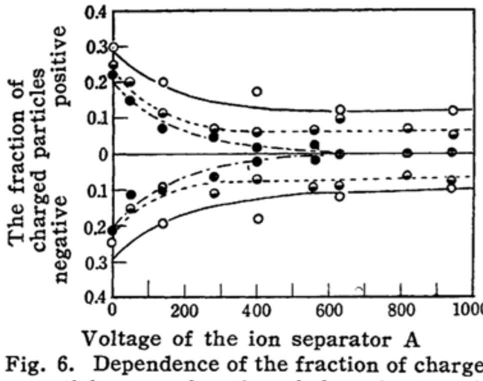


Fig. 6. Dependence of the fraction of charged particles as a function of the voltage of the ion separator A. (notations are the same as Fig. 4.)

It appears that $\bar{r}$ and σ remained almost constant while the fractions of charged particles decreased monotonously with the increase in the voltage of the ion separator A. It was noted that these tendencies were similar in all the other cases.

Discussion

The liquid sulfur aerosols were formed by means of the La Mer-Sinclair generator using the flaming spark of silver electrodes. It seems that silver is vaporized at high temperature in the process of eletric discharge. Particles of silver vapor can coalesce with each other both by condensation and by coagulation to yield minute particles. It appears in this work that the effective nuclei are such silver particles as described below.

If a particle of radius r, having an electric charge of n units, moves in air with velocity v in a uniform electric field E, it holds that

$$nEe=6\pi r\eta v(1+Al/r)^{-1} \qquad (2)$$

where η is the viscosity coefficient of air, A the Cunningham's constant and l the mean free path of air molecules. It is calculated from the flow rate of air that the charged particle moving towards the electrode of opposite sign, with a velocity greater than 0.21 cm., is excluded while it passes through the ion separator. Assuming that

$n=1$, $e=4.8\times10^{-10}$ e. s. u., $\eta=1.8\times10^{-4}$ c. g. s. u., $Al=1.0\times10^{-5}$ cm.
and $Al\gg r$, the relation between E' (the electric field expressed in terms of practical units) and the radius r of the particle to be excluded becomes

$$E'=4.5\times10^{13}\,r^2, \qquad (3)$$

which will be applicable in the range of gas molecules[6]. The equation (3) is plotted in Fig. 7.

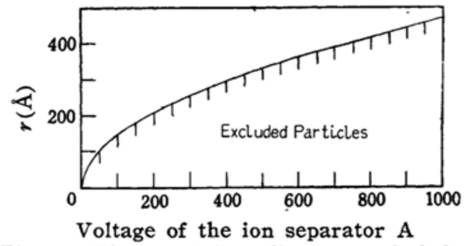
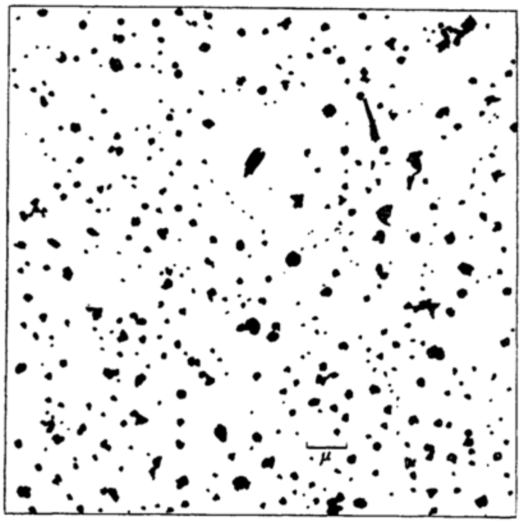


Fig. 7. The particle radius, r, excluded vs. the voltage of the ion separator.

5) R. Whytlaw-Gray and H. S. Patterson, "Smoke", London, (1932), p. 94.
6) J. W. Thomas, *J. Colloid Sci.*, **10**, 25 (1955).

It is seen from equation (3) that ordinary air ions were easily removed under the condition of 0.1 V./cm. through the ion separator A owing to their large mobility. If these air ions were effective nuclei as presumed by Sinclair, both values of $\bar{r}$ and σ of aerosols would be remarkably altered by excluding them. But it is difficult to find such an effect in this experiment (cf. Figs. 4 & 5).

Silver was detected by spectrographic analysis of the flaming spark in the nuclei generator. The silver particles resulting from the electrodes at high temperature were detected in the electron microscopic photograph. Although the particles found in the photograph are large, the nuclei, working in the process of the aerosol formation may be minute; the former particles might have grown by coagulation.



Photograph. Electron micrograph of the silver particles produced from the electrodes in nuclei generator (discharging 2.5 min. and standing 17 hours in nitrogen).

The oxygen compounds such as ozone and nitrogen dioxide which come out from discharge were detected easily. Ozone was detected in the gas passed through the nuclei generator by the iodine-starch reaction, and nitrogen dioxide was collected in a dry ice-alcohol cold trap from the above gas and detected by the change in color coming from the variation of the temperature. However, it is supposed that such substances do not act as the nuclei in the process of the aerosol formation, because the sulfur aerosols were formed equally in both nitrogen and air.

It is permissible from the above arguments to conclude that the minute silver particles are the effective nuclei in the process of aerosol formation, while neither ionized gaseous molecules nor the oxygen compounds such as ozone and nitrogen dioxide act as the nuclei.

The author expresses his thanks to Professor I. Sano and Mr. Y. Fujitani for their helpful suggestion during this work.

Department of Chemistry
Faculty of Science
Nagoya University
Chikusa, Nagoya