Study of Reversible Photo-Chemical Reactions. III. Mechanism of the Phototropy of Mercuric Complex Salts (II). Absorption Spectrum and Microscopic Observation of Single Crystals of $HgI_2 \cdot 2HgS$

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It is desirable to obtain a single crystal as large as possible for the study of the physical properties of $HgI_2 \cdot 2HgS$. The author made a comparably large single crystal by the vapor phase reaction of mercuric iodide and sulfide. In this paper the results of microscopic and absorption-spectroscopic observations of this single crystal will be reported.

Materials

About 30 g. of a mixture of mercuric iodide and sulfide in powder form in 1.1:2 mole ratio was put in a glass test tube (1 cm. wide and 80 cm. long) buried in an electric furnace. Mercuric iodide, m.p. 250°C, b.p. 350°C; mercuric sulfide sublimes at 455°C. The furnace was slowly heated. Solid phase reaction takes place at 170°C between mercuric iodide and mercuric sulfide, forming $HgI_2 \cdot 2HgS$ which dissociates at 185°C into its components. At 250°C the iodide melts and at 330°C its vapor adheres to the upper cool part of the tube. At 480–500°C the sulfide sublimes and begins to react with the iodide in the vapor phase, and yellow crystals adhere to the wall. After keeping the furnace at 510–520°C for 30 min., the test tube was taken out and kept in the dark. Inside the tube it was observed there were red crystals of mercuric iodide at 50–60 cm. from the bottom, yellow crystals 10 cm. lower than this, black crystals of mercuric sulfide at the bottom. By analysis the yellow crystals of plate-form thus obtained were found to contain 64.8%Hg and 6.5%S (Calcd. for $HgI_2 \cdot 2HgS$: Hg, 65.4%; S, 6.9%). As they show the characteristic phototropy it is certain that they are $HgI_2 \cdot 2HgS$. The dimension of the largest single crystal obtained was $600 \times 500 \times 40 \mu^3$.

Experiments and Results

To study the spectral absorption characteristics of this single crystal in the visible region, a Beckman Spectrophotometer was employed. A sheet of black paper with 17 pinholes (0.3 mm. in diameter), each hole being covered with a single crystal, was mounted. On the neighboring absorption cell frame a black paper sheet with equal number of pinholes, but not carrying crystals, was mounted. All the measurements were carried out at room temperature. The absorption curve obtained (Fig. 1-1) shows an apparent absorption edge at 510 mμ, and small absorption maxima at 430, 470, 560, 630, 650, 700 and 770 mμ. Fig. 1-1 shows

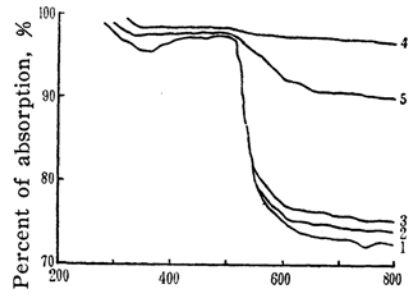
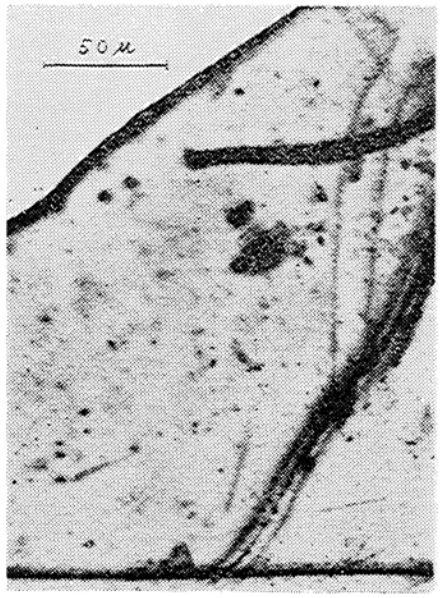


Fig. 1. Absorption spectra of single crystal, $HgI_2 \cdot 2HgS$.

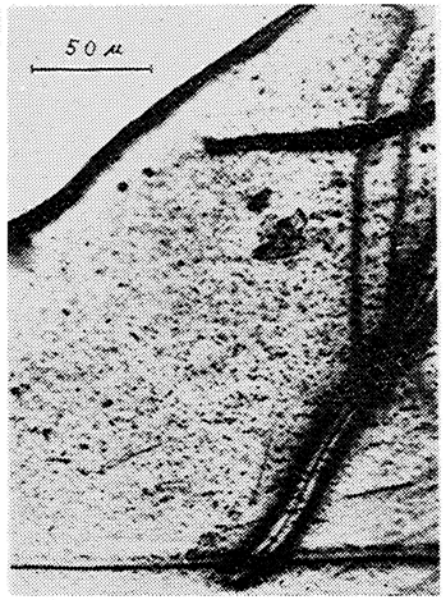
also that the percentage absorption of wavelength shorter than λ 340 mμ becomes gradually larger than that of λ 350 mμ. In the course of the measurement the yellow crystals turned slightly black by the light from the tungsten lamp source and the percentage absorption slowly increased if we kept the position of the prism unchanged, for instance at 470 mμ for five min. With this in mind, we first measured the region between 510 and 800 mμ speedily, leaving the other region for separate experiments. In Fig. 1-2 is shown the absorption curve which was obtained after the crystals were irradiated by λ 470 mμ light by keeping the prism position constant for twenty five minutes. It is almost identical with the curve 1, except for the increased absorption of the wavelength region longer than 560 mμ. Curve 3 shows the same effect after two hr. irradiation. Curve 4 is for the sample blackened by daylight. It has no selective absorption in visible part. The crystals darkened in this experiment became yellow again if left in the dark at ordinary temp. for 2 months, after which they gave the curve 5, having the limit at 510 mμ. It shows an over-all decrease of absorption compared with curve 4, but an increase as compared with curve 1.

Microscopic Observations

Micro- photograms of the darkening process of a $HgI_2 \cdot 2HgS$ single crystal were obtained in the following way. When a single crystal of a size $450 \times 250 \times 10\ \mu^3$ was exposed to a 60W tungsten lamp at 20 cm. distance, a few small black spots were produced on the surface of the crystal (photo. No. 1). After eighteen hr. the exposure crack increased, and the whole crystal turned darkish in appearance (phote. No. 2). If warmed at 90°C for twenty minutes the blackened crystal was bleached to yellow. But, under a microscope some small black spots were observed to remain still on its surface (photo. No. 3), and the bleaching was not complete. These spots did not disappear completely after several hr's warming at 90°C. This observation could be reproduced with several other specimens of $HgI_2 \cdot 2HgS$ single crystals, but the number of the spots produced by light differed with different specimens.



Photograph No. 1-Single crystal which was illuminated by tungsten lamp for 2 hrs.



Photograph No. 2-Single crystal which was illuminated by tungsten lamp for 18 hr.

Photograph No. 3-Single crystal which was warmed at 90°C for 20 mins.

To identify the black spots in photo. No. 2 the following experiment was performed. A few drops of conc. nitric acid were added to a darkened single crystal which was placed in a dish. Then it was observed by a microscope that most of the black spots in the darkened single crystal wer dissolved in the acid and some black spots were not dissolved. Simultaneously the existence of mercuric ion in the acid was recognized by violet color reaction of diphenylcarbazone. Mercury and its iodide dissolve easily in conc. nitric acid but mercuric sulfide does not dissolve. So, the soluble black spots seem to be mercury. We can assume the black spots in photo. No. 2 to be colloidal mercury. The evidence for the fact that the black spots in photo. No. 3 are mercuric sulfide was given by the following experiment. A quantity of the yellow powder of $HgI_2 \cdot 2HgS$ was placed in a glass mortar covered by a glass dish, darkened by daylight, and warmed at 90°C for ten minutes. These operations were repeated 20 times. Then some gray and red powders adhered to the cover glass. The former powder was found to be the mercury by violet color reaction of diphenylearbazone and the latter to be mercuric iodide, by the iodine-starch reaction. By the analysis of the powder left in the glassmortar thus obtained 7.6%S (mean of 3 values) was found (Calcd. for $HgI_2 \cdot 2HgS$: S, 6.9%). The above result shows that, by warming the black powder, mercury and its iodide sublime and sulfide remains in the

powder. This phenomenon will also take place in a darkened single crystal. Therefore it is concluded that the black spots in photo. No. 3 are mercuric sulfide. On the othr hand, these spots did not dissolve in conc. nitric acid. This suggests that the spots are mercuric sulfide.

Discussion

The strong absorption in the wavelength region shorter than 510 mμ and the sharp absorption edge at 510 mμ (Fig. 1–1) are the origin of the yellow color of the crystal. The minor absorption maxima at 560, 630, 650, 700 and 770 mμ are considered to be of no great importance. That the black $HgI_2 \cdot 2HgS$ has no selective absorption is shown by curve 4 in Fig. 1. Now, the question in point is the relation between the mechanism of the phototropy and light absorption. If the phototropy in this case be explained by electron excitation in the molecule, it must be due to the absorption of light of wavelengths shorter than λ 300 mμ, rather than λ 430 mμ or λ 470 mμ, which have insufficient energies for the excitation. The existence of strong absorption of wavelengths shorter than 300 mμ is easily anticipated from Fig. 1.

On the other hand, it is considered from microscopic observation that the number of black spots produced on the crystal surface by illumination by a 60W tungsten lamp is small. This is due to the weakness of intensity of ultra-violet ray in the tungsten lamp. When a crystal is irradiated by daylight of very strong intensity of ultraviolet ray, many black spots are produced in a few seconds. It is clear from photo No. 1 and 2 that the darkening is due to the increase of the number of black spots on the crystal surface. These black spots are colloidal mercury. Curve 4 corresponds to the absorption curve of a single crystal whose surface is covered wholly by colloidal mercury. Colloidal mercury can vaporize rapidly by being heated. At room temp., however, its vaporization velocity is slow. Therefore we can point out that the percentage absorption for curve 5 decreases slightly as compared with that for curve 4 on account of slow vaporization of colloidal mercury.

Conclusion

(1) Absorption spectra of yellow single crystal $HgI_2 \cdot 2HgS$ show an apparent absorption edge at 510 mμ, and small absorption maxima at 430 and 470 mμ.

(2) By the exposing a single crystal to daylight, colloidal mercury are produced on the crystal surface as black spots. By heating the black powder, mercury and mercuric iodide vaporize into the atmosphere and sulfide remains on the crystal surface.

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