Study of Reversible Photo-Chemical Reactions. III. Mechanism of the Phototropy of Mercuric Complex Salts (I). Changes of the Physical Properties in the Reversible Color Change Reaction of $HgI_2 \cdot 2HgS$

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S. V. Raghava Rao¹⁾ reported that $HgI_2 \cdot 2HgS$ rapidly turns black in sunlight owing to the formation of mercuric iodide and sulfide, which returns to the initial compound after a few days when left in the dark, and instantly when heated. However, according to the present author's earlier report²⁾ it appears more probable that mercuric complex salt is not decomposed by the action of light. Recently Lawrence Schow and George R. Pond³⁾ referred to a mechanism of phototropy of $HgI_2 \cdot 2HgS$ in a study of X-ray and optical absorption of Ag_2S-HgI_2 system. Mean-while we have investigated magnetic susceptibilities, X-ray diffraction patterns, possibility of phosphorescence or luminescence, as well as the effects of admixture of impurity and CO_2 or O_2 on it and related compounds. From the results obtained it was found that the degree of decomposition of $HgI_2 \cdot 2HgS$ in sunlight is small and a change of electronic structure of the crystal occurs. The sample studied was the yellow powder of $HgI_2 \cdot 2HgS$ prepared by the hydrogen sulfide method; however in the case of the study of the impurity effect, powder prepared in an electric furnace was used.

Experiments and Discussion of Results

1. Magnetic Susceptibility.—In a previous paper²⁾ the magnetic behaviour of $HgI_2 \cdot 2HgS$ was briefly reported. The Gouy method was employed for the measurement of magnetic susceptibility. About 1.5 g. of the sample ($HgI_2 \cdot 2HgS$, yellow powder) was packed as tightly as possible into a cylin-

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1) S. V. Raghava Rao and H. E. Watson, *J. Phys. Chem.*, 32, 1354 (1938).

2) Kunio Takei, *J. Chem. Soc. Japan*, 73, 202 (1952) (in Japanese).

3) Lawrence Schow and George R. Pond, *J. Phys. Chem.*, 58, 240 (1954).

drical glass tube 6 mm. wide and 130 mm. long. A Weiss type electromagnet (pole diameter 20 mm.: gap 15 mm.) was employed, which gave 9000 gausses field when excited with 10 amp. current. The accuracy of measurement was estimated to be about 3%. First the susceptibility of the yellow powder, χ_0, was measured, then the powder was placed on a watch glass, turned uniformly black by exposure to daylight, and the susceptibility of this darkened powder, χ_1, was measured. When this darkened powder was heated at 90°C for about 10 min., the color of the powder returned to the original, and the susceptibility of this powder, χ_2, was measured. When the darkened powder was kept continually in the dark at room temperature for two days, the susceptibility, χ_3, was measured. The susceptibility of mercuric iodide, sulfide, and silver bromide, which were treated similarly by daylight were measured. The results are shown in Table I.

TABLE I

MAGNETIC SUSCEPTIBILITY ($\times 10^6$ C.G.S.)

Substance	χ_0	χ_1	χ_2	χ_3
$HgI_2 \cdot 2HgS$ (yellow)	−0.18	+0.14, −0.044, +0.0060, −0.056	−0.059	−0.18
HgI_2 (red)	−0.26	+0.0067	−0.0623	−0.015*
HgS (black)	−0.23	−0.23	−0.23	−0.23*
AgBr (yellow)	−0.33	+0.00060	−0.00060	−0.13*

From the above table it is evident that the initially diamagnetic yellow powder becomes paramagnetic after the blackening by sunlight. The extent of blackening was different according to the intensity of light, the time of exposure, and the degree of stirring; accordingly χ was not reproducible, but it was ascertained that the darkening causes a few paramagnetic characteristics. Mercuric iodide and sulfide are both diamagnetic, so that if the phototropy of $HgI_2 \cdot 2HgS$ were due to the decomposition into iodide and sulfide, the black powder must be diamagnetic with a negative value of χ on account of the additive law of magnetic susceptibility. The observed paramagnetism shows that the phototropic behaviour of this substance is not due to the decomposition but is due very probably to the change of the electronic structure of $HgI_2 \cdot 2HgS$. χ_2 was nearly equal to χ_1. χ_3 returned to the original value, -0.18×10^{-6}. On the other hand, when mercuric iodide and silver bromide were darkened by exposure to light, χ_1 became paramagnetic and χ_2 was nearly equal to χ_1, but χ_3 did not return to the original value even after a month. The mechanism of photodecomposition of silver bromide is well known. Comparing the above magnetic properties of $HgI_2 \cdot 2HgS$ with that of mercuric iodide and silver bromide, the magnetic behaviour of $HgI_2 \cdot 2HgS$ is explained as follows. Irradiation of $HgI_2 \cdot 2HgS$ by light elevates the electrons of I^- or S^{--} ion to the conduction band and leave positive holes in the crystal. Electrons move freely until captured by the centers. The observed paramagnetism is due to the existence of the spin of the trapped unpaired electrons. On heating the powder at 90°C, the trapped electrons return to the ground-states by enhanced thermal agitation and cannot recombine with positive holes, because most of the positive holes escape out of the crystal by heating. Therefore χ_2 is nearly equal to χ_1. However, when the darkened powder was kept in the dark, most of the holes remain in the crystal and the electrons released from the trapping centers react with these holes, so that χ_3 will return to yellow value.

2. Study of X-ray Diffraction of $HgI_2 \cdot 2HgS$ Powder.—The commonly employed Debye-Scherrer diffraction method was used. Copper K_α radiation filtered through a nickel plate was employed. The exposure length was 5—6 hr., at a potential of 30 kV and with a tube current of 20 m amp. Fig. 1 shows the powder diffraction pattern of $HgI_2 \cdot 2HgS$ (yellow), $HgI_2 \cdot 2HgS$ (black), 0.8[$HgI_2 \cdot 2HgS$(yellow)]+0.2[HgI_2+2HgS], 0.7[$HgI_2 \cdot$2HgS(yellow)]+0.3[HgI_2+2HgS], and 0.6[$HgI_2 \cdot 2HgS$ (yellow)]+0.4[HgI_2+2HgS] in comparison with those of mercuric iodide and sulfide. If the complex salt decomposes into mercuric iodide and sulfide in sunlight, the pattern of the darkened powder may consist of the degenerated lines of $HgI_2 \cdot$2HgS (yellow) and mercuric iodide and sulfide. However, in the pattern of the mixtures containing 20%, 30% and 40% of [HgI_2+2HgS], respectively, the intensity of the lines of 3.54, 3.37 and 1.78Å became very much stronger than that of the yellow powder. The line of 3.54 Å is due

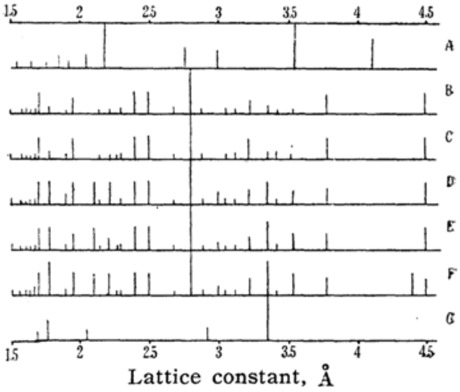

Fig. 1. X-ray diffraction pattern of powder:
(A) HgI_2, (B) $HgI_2 \cdot 2HgS$ (yellow),
(C) $HgI_2 \cdot 2HgS$ (black),
(D) 0.8[$HgI_2 \cdot 2HgS$ (yellow)]+0.2[HgI_2+2HgS],
(E) 0.7[$HgI_2 \cdot 2HgS$ (yellow)]+0.3[HgI_2+2HgS],
(F) 0.6[$HgI_2 \cdot 2HgS$ (yellow)]+0.4[HgI_2+2HgS],
(G) HgS (black).

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* This value is for the darkened sample which was kept continually in the dark for a month.

to that of mercuric iodide and the lines of 3.37 and 1.78Å are due to that of mercuric sulfide. New lines of 3.00 and 2.10Å also are found in them. The former line is attributable to mercuric iodide. Therefore, even though the darkened powder contained mercuric iodide and sulfide, the lines of iodide and sulfide may not appear in the pattern of the darkened powder, if the powder contains [HgI_2+2HgS] less than 20% mole. From the fact that the black powder pattern of $HgI_2 \cdot 2HgS$ is identical with that of the yellow powder, it is evident that darkening does not change the crystal structure. Even if the change occurs, the degree may be below 20%.

3. Fluorescence, Phosphorescence.—From the measurements of magnetic susceptibility and X-ray diffraction it is considered that the yellow substance, specifically an electron belonging to its molecule is raised to an excited state by exposure to light; this substance returns slowly to the ground state while it is kept in the dark, presumably accompanied by emission of radiation. However, direct confirmation of fluorescence or phosphorescence could not be obtained by the eye nor by photographic observation.

4. Impurity Effects.—About 10 g. of a mixture of red mercuric iodide and black sulfide powder with 1.1: 2 mole ratio was heated in a porcelain crucible with lid, and placed in an electric furnace. The temperature of the furnace was kept at 170°C for one hour. After cooling slowly a yellow powder was obtained. Mercuric iodide melts at 250°C. and boils at 350°C, while mercuric sulfide could not have been fused, and at 170°C the vapor pressure of mercuric iodide is small. The yellow powder thus obtained was washed with methyl alcohol to remove unreacted mercuric iodide, and was dried under 80°C. The resulting substance was found to show the phototropy characteristic of the yellow $HgI_2 \cdot 2HgS$ completely prepared by the hydrogen sulfide method. Also the χ -value and X-ray pattern are entirely identical with those of the latter. On analysis it was found to 64.8% Hg and 6.4% S, while the values calculated as were $HgI_2 \cdot 2HgS$ are 65.4%Hg and 6.4%S respectively. The velocity of darkening of the above synthesized powder under the action of light was measured by the method previously reported[4]. It is also identical with that of $HgI_2 \cdot 2HgS$ obtained by the hydrogen sulfide method. To test the effects of impurity, a variously-determined amount of selenium was added to the 1.1: 2 mole mixture of mercuric iodide and mercuric sulfide, and the mixture was heated at 170°C for an hour. The darkening velocity of the product is shown in Fig. 2. With the sample containing 0.65–1.1% Se, the velocity is larger than with the pure $HgI_2 \cdot 2HgS$ or with the samples containing Se in any other percentage. From the above experiments it is evident that the photosensitivity increases by the addition of certain small amounts of foreign substances.

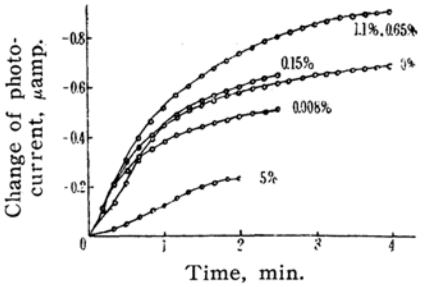

Fig. 2. Change of photo-current of mixed powder with time.

5. Effects of Carbon Dioxide and Oxygen.—No change of the darkening velocity of the yellow powder was observed either in carbon dioxide or oxygen atmosphere (760 mmHg) or in air. It was also the same in vacuum.

Summary and Conclusion

From magnetic and X-ray experiments it is suggested that an electron belonging to the yellow $HgI_2 \cdot 2HgS$ is excited to an activated state by the action of light, without accompanying change in crystal structure. Even though a change of crystal structure may occur, it would be a degree below 20 mole %, the pattern of darkened form having almost the same form as the yellow one. As the oxygen has no influence at all on the darkening velocity, the darkening itself is not due to the oxidation-reduction process of mercuric ion. It is also sensitive to the existence of impurity. This suggests that the phototropy concerned has a structure sensitive factor. When the blackened powder is kept in the dark for two days at room temperature the color does not completely return to yellow, but the magnetic susceptibility becomes nearly equal to the value of the yellow form. Therefore the activated state seems to have a very long life at room temperature.

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[4] Kunio Takei, *J. Chem. Soc. Japan*, 73, 204 (1952) (in Japanese).