Study of Reversible Photo-Chemical Reactions. IV. Phototropy of $HgX_2 \cdot 2HgS$ *and* HgXCNS

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In the previous paper[1] the mechanism of phototropy of $HgI_2 \cdot 2HgS$ was reported. Now the author prepared mercuric complex salts, $HgX_2 \cdot 2HgS$ and HgXCNS and studied their phototropic phenomena. From the measurement of magnetic susceptibilities and X-ray diffraction of these powders, it was ascertained that the mechanism of their phototropy is identical with that of $HgI_2 \cdot 2HgS$. The reflectance spectra, darkening velocity, reverse reaction rate, activation energy in reverse reaction, decomposition temperature, discoloring temperature and specific weight were measured. The difference in the phototropy characteristics from the difference in halogen of complex salts will also be discussed.

Materials

The materials $HgI_2 \cdot 2HgS$, $HgBr_2 \cdot 2HgS$ and $HgCl_2 \cdot 2HgS$ were prepared by the action of

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[1] Kunio Takei, This Bulletin, 28, 403 (1955).

hydrogen sulfide on the methyl alcoholic solution of mercuric iodide, mercuric bromide and mercuric chloride, respectively. When the mixture of mercuric halide and mercuric sulfide (black) in powder in a mole ratio of 1.1: 2 was heated at 170°C for one hour in an electric furnace, the same complex salts as those of hydrogen method were also produced. When the mixture of mercuric halide and rhodanide in powder in the mole ratio of 1: 1 was put in a porcelain crucible and heated at 160°C, stirring with a glass-rod and quickly cooled, an orange yellow powder, was produced from the mixture of mercuric iodide and rhodanide yellow white powder from mercuric bromide and rhodanide yellow-white powder from mercuric chloride and rhodanide. Impurity was removed by washing the powders with methyl alcohol. From chemical analysis of them, it was recognized that they were HgICNS (orange yellow), HgBrCNS (white yellow) and HgClCNS (white yellow), respectively. The materials obtained have phototropic characteristis. No large single crystal other than $HgI_2 \cdot 2HgS$ could be obtained.

Experimental Results

(1) **Reflectance Spectra.**—The reflectance spectra of the above powders determined with a Shimazu Reflectance Spectrometer was shown in Fig. 1.

(2) **Physical and Phototropic Properties.**—The data of the physical and phototropic properties were shown in Table I.

(1) **Magnetic Susceptibility.**—For instance, the value of magnetic susceptibility, χ_0, for the yellow powder $HgI_2 \cdot 2HgS$, was -0.18×10^{-6} and changed to χ_1, i.e. $+0.030 \times 10^{-6}$, under action of daylight. After this darkened powder was heated at 90°C (discoloring temp.) for about ten minutes the susceptibility of this powder, χ_2, was measured. When the darkened powder was kept in the dark at room temp. for 3 days, the value χ_3 reversed to the original value, χ_0. The words in the parenthesis in every column show the days during which the darkened powder was kept in the dark. χ_i for darkened HgXCNS was paramagnetic, but it did not reverse to the original value when kept in the dark.

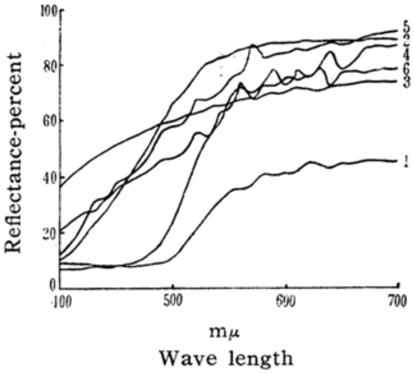

Fig. 1. Diffuse reflectance spectra:
(1) $HgI_2 \cdot 2HgS$, (2) $HgBr_2 \cdot 2HgS$,
(3) $HgCl_2 \cdot 2HgS$, (4) HgICNS,
(5) HgBrCNS, (6) HgClCNS.

(2) **X-ray Diffraction Powder Pattern.**—The patterns of every powder which was not yet illuminated in sunlight were identical with that of the darkened powder. No new lines were found in the patterns of the darkened powder.

(3) **Darkening Velocity.**—The darkening velocity constants at +5°C obtained by the method of an earlier report²⁾ were larger in the following order: $HgI_2 \cdot 2HgS > HgBr_2 \cdot 2HgS > HgCl_2 \cdot 2HgS$ and HgICNS>HgBrCNS>HgClCNS. The order was identical with that of Rao's value³⁾: the darkening time of $HgI_2 \cdot 2HgS < 1$ min., $HgBr_2 \cdot 2HgS$ 3 min., $HgCl_2 \cdot 2HgS$ 10 min. and HgICNS 1 min., HgBrCNS 2 min., HgClCNS 20 min.

(4) **Activation Energy in Reverse Reaction.**

TABLE I

PHYSICAL AND PHOTOTROPIC PROPERTIES

Substance		$HgI_2 \cdot 2HgS$	$HgBr_2 \cdot 2HgS$	$HgCl_2 \cdot 2HgS$	HgICNS	HgBrCNS	HgClCNS
Magnetic suscep. $\times 10^{-6}$ C.G.S. Unit.	χ_0	−0.18	−0.19	−0.22	−0.22	−0.23	−0.24
	χ_1	+0.030	−0.15	−0.15	+0.0020	+0.0034	−0.16
	χ_2	+0.012	−0.15	−0.15	+0.0020	+0.0034	−0.16
	χ_3	−0.18 (3 days)	−0.19 (3 days)	−0.22 (1 month)	+0.0010 (3 days)	+0.0010 (13 days)	−0.16 (16 days)
Darkening velocity at 5°C per sec.		0.00234	0.000690	0.000184	0.00131	0.000253	0.00006
Activation energy in reverse reaction, kcal./mol.		12.8	17.4	19.9	17.6	23.8	——
Decomposition temp., °C		185	200 332	200 347	213	288	290
Discoloring temp., °C		90	197	225	136	202	260
Specific weight		6.75 ±0.02	6.85 ±0.01	6.63 ±0.02	5.06 ±0.02	5.73 ±0.01	6.26 ±0.02
Çolor		orange yellow	pale yellow	white	orange yellow	white yellow	white yellow

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2) Kunio Takei, *J. Chem. Soc. Japan*, 73, 294 (1952) (in Japanese).

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

—The velocity constants in reverse reaction were measured at various temperatures by the method of 2nd report[2]. The activation energy in reverse reaction was calculated from temperature coefficient of logarithm of the velocity constants. The magnitudes obtained were in the following order: I<Br<Cl. The extent of darkening of HgClCNS in sunlight was very small, so that the activation energy for HgClCNS could not be calculated.

(5) **Decomposition Temperature.**—The decomposition temperature of the complex salts found by the method of thermal balance were in the following order in height: I<Br<Cl. For $HgBr_2 \cdot 2HgS$ and $HgCl_2 \cdot 2HgS$, there were first and second decomposition temperatures.

(6) **Discoloring Temperature.**—The blackened powder by daylight recovers instantly the original color on being heated. The bleaching temperature increases in the following order: I<Br<Cl.

(7) **Specific Weight.**—The mercuric complex salts were not wet in water. However, they were wet in a dilute solution of surface active agent. As an agent sodium-dodecylbenzene-sulfonate was used. When the above solution was used as a standered solution, sp. wt. of complex salts were determined at 30°C.

Discussion

From the results that the powder patterns before darkening are identical with those after darkening, it is confirmed that the degree of decomposition of mercuric complex salts ($HgX_2 \cdot 2HgS$ and HgXCNS) is below 20 mole % as in the case of $HgI_2 \cdot 2HgS$. The value χ_1 for darkened powder of $HgX_2 \cdot 2HgS$ was reversed to the original value in the dark after some days. However, χ_1 for darkened HgXCNS did not reverse to the original value. This is explained as follows, Under the action of light, HgXCNS decomposes into its components. Simultaneously a positive hole remains in the crystal when an electron belonging to the molecule is raised to the conduction band. The positive hole diffuses to the outside of the crystal and escapes as gas in the atmosphere. In the case of HgXCNS most of the positive holes may escape in the atmosphere. However, in the case of $HgX_2 \cdot 2HgS$, most of the positive holes may remain in the crystal, for χ_1 of $HgX_2 \cdot 2HgS$ reverses to the original value, χ_0. An interstitial mercury is deposited as colloidal metal on the crystal surface. Comparing the values of activation energy with that of decomposition and discoloring temp., it is understood that the complex salts are more stable to heat in the following order: I<Br<Cl. From the difference in discoloring temp. due to the difference in halogen, it was found that the colloidal mercury deposit has still an interaction with the original molecule. The darkening velocity decreases in the following order: I<Br<Cl. The decrease of sensitivity to light in the above order may be not only due to the decrease of the quantity of interstitial mercuric ion in the same order, but also due to the increase of activation energy of diffusion of interstitial mercuric ion to the crystal surface.

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