BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (5), 1341—1342 (1977)

ESR of F Center in $HgI_2 \cdot 2HgS$ Darkened with Sunlight

Kunio Takei, Hitoshi Hagiwara, and Hiroshi Tanaka*

Department of Industrial Chemistry, Faculty of Engineering, Miyazaki University, Miyazaki 880

**Minami Kyushu Coca Cola Bottling Co., Kumamoto 860*

(Received October 25, 1976)

Synopsis. When yellow powders of $HgI_2 \cdot 2HgS$ turn black in sunlight in a few seconds, the black powders show an ESR signal, whose intensity increases with the time of irradiation; its *g*-value is 2.0046±0.00028. The result of analysis shows that this signal is due to F centers, consisting of electrons captured by positive holes prepared at sites of S^{2-} ions in the crystal.

Twenty five years ago one of the authors[1)] observed by means of Gouy's method that initially diamagnetic yellow powders of $HgI_2 \cdot 2HgS$ become paramagnetic after a darkening with sunlight. A print-out of mercury atoms and evolution of SO_2 and I_2 from these crystals during irradiation with sunlight were confirmed by chemical analysis[2)] and the darkening process was considered to occur as follows. When electrons belonging to S^{2-} or I^- ions in the crystals absorb wavelengths shorter than 510 nm and are excited to upper states, these electrons leave behind neutral S or I atoms, which diffuse toward the crystal surface, resulting in the formation of gases of SO_2 or I_2. Some parts of the excited electrons neutralize Hg^{2+} ions in the crystal, resulting in the formation of Hg atoms, which diffuse toward the crystal surface and aggregate there to form colloidal mercury. Other excited electrons are captured by positive holes, which were created at the sites of S^{2-} or I^- ions in the crystals after neutral S or I atoms escaped thermally out of the crystals. These trapped electrons, *i. e.*, F center electrons exhibit a paramagnetic behavior.

In recent years the authors[3)] found by means of a radioactive tracer technique that when the yellow $HgI_2 \cdot 2Hg^{35}S$ or $Hg^{131}I_2 \cdot 2HgS$ is darkened in sunlight, gases of $^{35}SO_2$ or $^{131}I_2$ evolve and that the evolution velocity of the former gases is larger than that of the latter. It was found that the longer the time of irradiation, the larger the quantity of $^{35}SO_2$. This fact suggests that S^{2-} ions are more sensitive to sunlight than I^- ions and the paramagnetism of the darkened crystals is chiefly due to the F center electrons, consisting of positive holes and electrons belonging to S^{2-} ions. These trapped electrons must show an ESR signal, the details of which will be discussed in the present paper.

The ESR measurements were carried out at liquid nitrogen temperature by using a JEOL X-band spectrometer. Yellow powders of $HgI_2 \cdot 2HgS$ were made by the action of purified H_2S on a methanol solution of mercury(II) iodide, which was purified three times by sublimation. If crude powders of mercury(II) iodide were used as the material, the yellow powders showed an ESR signal in the dark. When the yellow powders prepared from the purified mercury(II) iodide, which gave no ESR signal, were darkened black as much as possible in sunlight with stirring by a glass rod for 1 or 2 h, an ESR signal appeared, as is shown in Fig. 1. The obtained signal is not sharp and the intensity is weak. This is due to the fact that the samples are powders, the particles of which are not completely darkened with sunlight. If the signal is due to a formation of a color center, the density of the color center of the darkened powders must be larger than 10^{16} cm^{-3}, because in general a color center can be recognized as an ESR line when the density reaches this value. The *g*-value of the observed signal, with a mean value from about 8 measurements for 8 different samples, was estimated to be 2.0046±0.00028. This signal intensity increased with the time of irradiation with sunlight. This relation is shown in Fig. 2. When the darkened samples were heated at 95 °C for 30 and 60 min, the

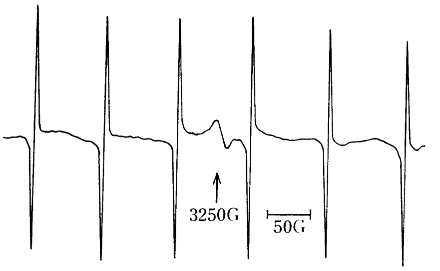

Fig. 1. ESR spectrum of $HgI_2 \cdot 2HgS$ irradiated by sunlight for 10 min.

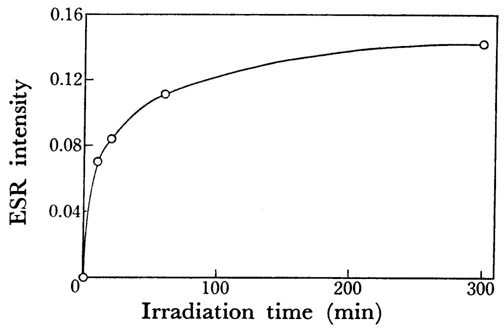

Fig. 2. ESR signal as a function of exposure time.

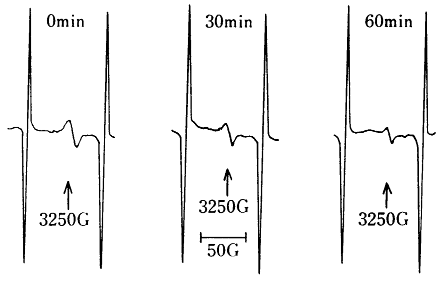

Fig. 3. ESR spectra of $(HgI_2 \cdot 2HgS)^*$ heated at 95 °C for some min.

intensity decreased with the time of heating and the sharpness increased, accompanied by a rapid recovery of the color. This relation is shown in Fig. 3. The *g*-value after thermal treatment, with a mean value of about 6 measurements for 6 different samples, was estimated to be 2.0026±0.00018.

The *g*-value obtained for the darkened $HgI_2 \cdot 2HgS$ is in agreement with the *g*-values of F centers presented by Alger$^{4)}$ for different inorganic powder substances, and with the *g*-values of F centers for alkali halides given by Holton and Blum,$^{5)}$ and with the *g*-value of the F center for MgO obtained by Wertz and his co-workers.$^{6)}$ The F center ESR line often has some nuclear isotropic effects. Wertz and Auzins,$^{6)}$ for example, found the F center ESR line for MgO with one or two ^{25}Mg ions around the negative ion vacancy, giving a six- or eleven-line hyperfine pattern centered upon the strong component. Similarly, Hausmann$^{7)}$ found the F center ESR line for ZnO with one ^{67}Zn ion around the negative ion vacancy, giving a hyperfine pattern centered upon the strong component. In our sample, however, no effects of the nuclear spin of ^{199}Hg or ^{201}Hg on the pattern were observed, because of the complexity of the crystal structure of the sample. In 1972, Fujiwara and Isobe$^{8)}$ showed that hot ions of the paramagnetic Hg(I) complex are formed by γ-irradiation of powders of $K_2[Hg(CN)_4]$ and that these ions are thermally very unstable at room temperature. All the spectra of the hot ions showed isotropic hyperfine splitting, which was recorded at K- or X-band frequency. The paramagnetism of the darkened $HgI_2 \cdot 2HgS$, however, is thermally very stable at room temperature and no isotropic hyperfine splitting appeared in spite of a sweep from 1000 to 10000 G. In 1966, Shields$^{9)}$ reported that a reduction of silver ions in a pyrex glass by γ-rays induces an ESR spectra of Ag^0 accompanied with an isotropic hyperfine splitting. In our sample, the Hg^0 or Hg atom has nuclear spin, but no unpaired electrons. These discussions show that the ESR line in our sample cannot be explained by the mechanism of formation of Hg(I) or Hg^0.

Moran and his co-workers$^{10)}$ reported that the bleaching of an F band produces a more rapid decrease in the density of magnetic centers than of the centers giving optical absorption in the F band; they suggested the presence of R, M, or N centers by a study of the temperature dependence of the relaxation time of F centers. Our complicated mercury complex exhibits a characteristic magnetic behavior, *i. e.*, a more rapid decrease in optical absorption centers than of the magnetic centers. This behavior is possible, because the results of thermal bleaching depend on the preparation methods of the F centers, as is reported by Alger.$^{11)}$ If the signal in our sample is related to the existence of Hg^+ ions, or S or I neutral atoms in the crystal, the intensity of the signal should decrease rapidly when heated at 95 °C, because these ions or atoms are thermaly mobile in the crystal at 95 °C. It is conculded that the signal is not due to Hg^+ ions or S or I neutral atoms, but due to F centers, which are located at a deep energy level. When heated at 95 °C, the centers release slowly a small part of the trapped electrons, most of which are still captured, resulting in a formation of a new center, as is shown in Fig. 3. This new center has 2.0026±0.00018 as its *g*-value. The released electrons will be again captured by neutral atoms of S or I in the crystals to form S^{2-} or I^- ions, which react with Hg^{2+} ions to form HgS(black) or HgI_2, the existence of which was already chemically confirmed by the one of the authors.$^{2)}$

The authors with to thank Dr. S. Fujiwara, Dr. L. Shields, and Dr. A. Hausmann for many helpful discussions and suggestions during this work.

References

1) K. Takei, *Bull. Chem. Soc. Jpn.*, **28**, 403 (1955).
2) K. Takei, *Nippon Kagaku Zasshi*, **77**, 965 (1956).
3) K. Takei and H. Hagiwara, *Radioisotopes*, **24**, 715 (1975).
4) R. S. Alger, "Denshi Supin Kyomei" (Translated edition of Electron Paramagnetic Resonance : Tecnhiques and Applications by T. Isobe, M. Iwamizu, T. Okabe, A. Hanyu, and M. Hirayama), Yoshioka Publ. Co., Tokyo (1973), p. 409.
5) W. C. Holton and H. Blum, *Phys. Rev.*, **125**, 89 (1962).
6) J. E. Wertz, P. Auzins, R. A. Weeks, and R. H. Silsbee, *Phys. Rev.*, **107**, 1535 (1957).
7) A. Hausmann, *Z. Phys.*, **237**, 86 (1970).
8) S. Fujiwara and J. Isobe, *Bull. Chem. Soc. Jpn.*, **45**, 2182 (1972).
9) L. Shields, *J. Chem. Phys.*, **45**, 2332 (1966).
10) P. R. Moran, S. H. Christensen, and R. H. Silsbee, *Phys. Rev.*, **124**, 442 (1961).
11) R. S. Alger, Ref. 4, p. 391.