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PHOTOCHEMICAL TRANSFORMATION OF MERCURIC SULFIDE INTO METHYLMERCURY IN AQUEOUS SOLUTIONS

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Photochemical solubilization and methylation of mercuric sulfide have been studied in aqueous acetic acid solutions. Mercuric sulfide was solubilized gradually and almost completely after three weeks by irradiation with the light of a blacklight lamp. The measurements of methylmercury photo-produced in the aqueous system demonstrated that the rate of the production of methylmercury was in good agreement with that of the photo-solubilization of mercuric sulfide.

Mercury has a great affinity for sulfide sulfur and mercuric sulfide has long been believed to be the most stable form among mercuric compounds in aquatic environments, because of its extremely low solubility in water or even in mineral acids. It is generally accepted that inorganic mercury in the environment is converted into methylmercury by the action of certain microbial systems involving methylcobalamin, but Yamada and Tonomura1) have recently reported no production of methylmercury from *pure mercuric sulfide* either by the chemical reaction with methylcobalamin or by the action of microbial systems having a high methylating activity.

On the contrary, Fagerström and Jernelöv2) have observed a slight production of methylmercury from mercuric sulfide incubated with aquarium sediments, suggesting the possibility of solubilization of mercuric sulfide in the sediments. As for such a conversion of mercuric sulfide, Yamada and Tonomura1) have shown evidence that mercuric sulfide is transformed into some mercurials being soluble in weak acids by the action of iron-oxidizing bacteria in the presence of ferrous sulfate. The authors3) have also reported the solubilization of mercuric sulfide in water by the action of metal ions having high oxidation potentials, such as mercuric, mercurous, and ferric ions.

On the other hand, mercuric sulfide, as well as the other mercurials has been well known to be labile to light, so the possibility that mercuric sulfide is converted photochemically into mercurials which are available for methylation in the environment can not be excluded.

Recently, we have studied the photochemical transformation of inorganic mercury into methylmercury in an aqueous acetic acid solution under irradiation with sunlight[4,5] and found a markedly photosensitized methylation of inorganic mercury in the presence of colored inorganic solids such as mercuric oxide,[6] solid sulfur,[7] and mercuric sulfide.[3]

This communication concerns with the photo-production of methylmercury from mercuric sulfide in the presence of acetic acid, as well as the photo-solubilization of mercuric sulfide in aqueous solutions.

Radioactive mercuric sulfide, black powder, was prepared by bubbling hydrogen sulfide into an aqueous solution of 203-mercuric chloride acidified with hydrochloric acid and heated in a boiling water bath for 15 minutes. The 203-mercuric sulfide thus obtained was washed with dilute hydrochloric acid, distilled water, finally with ethanol, and then dried under reduced pressure. The other chemicals used were of reagent grade. A 20W blacklight lamp(Toshiba FL-20BL, nominal emission region 310 - 420 nm) was used as a light source.

Each 10 mg of 203-mercuric sulfide was added to 100 ml of distilled water in a 100 ml quartz vessel. To this aqueous suspension 100 mg of powdered quartz was further added in order to prevent the adhesion of suspended solids on the wall of the vessel during the photoreaction. The aqueous suspension was stirred gently with or without 5 mmole of acetic acid by the use of a magnetic stirrer under irradiation with the light of a blacklight lamp at a distance of 15 cm at 20°C. Non-irradiated sample was used as a control. The solubilization of mercuric sulfide was estimated by measuring the radioactivity of 203-mercury released in the liquid phase; at predetermined time intervals an aliquot from each sample was centrifuged at 3000 rpm for 10 minutes and the radioactivity in the supernatant was measured with a well-type scintillation counter. Another aliquot from each sample was acidified with hydrochloric acid, extracted with benzene, and the benzene layer was used for determination of methylmercury by means of ECD gas chromatography.

Neither the solubilization of mercuric sulfide nor the production of methylmercury was observed in the dark. While, mercuric sulfide was found to be solubilized due to the photo-decomposition and to be methylated in the presence of acetic acid when irradiated for a long time.[8] These results are summarized in Fig. 1. The rate of the photo-solubilization of mercuric sulfide in the aqueous suspension containing acetic acid was considerably large compared with that in the aqueous suspension without acetic acid. In the suspension with acetic acid, the yield of mercury solubilized increased gradually with the irradiation time and mercuric sulfide was almost completely solubilized after photo-irradiation for about 3 weeks. On the other hand, the photo-conversion of mercuric sulfide into methylmercury occurred simultaneously as is shown in Fig. 1. It can be seen from the figure that the rate of the photo-production of methylmercury is in good agreement with that of the photo-solubilization of mercuric sulfide; that is, the mercury photo-solubilized is present almost entirely as methylmercury. Black mercuric sulfide in the aqueous suspension turned gradually into a yellow-tinged one under photo-irradiation. This color change indicates that sulfur atoms liberated from mercuric sulfide photo-polymerize to produce "photo-sulfur", similarly in the case of the photosensitized methylation of inorganic mercury in the presence of mercuric sulfide as was reported previously.[3,†]

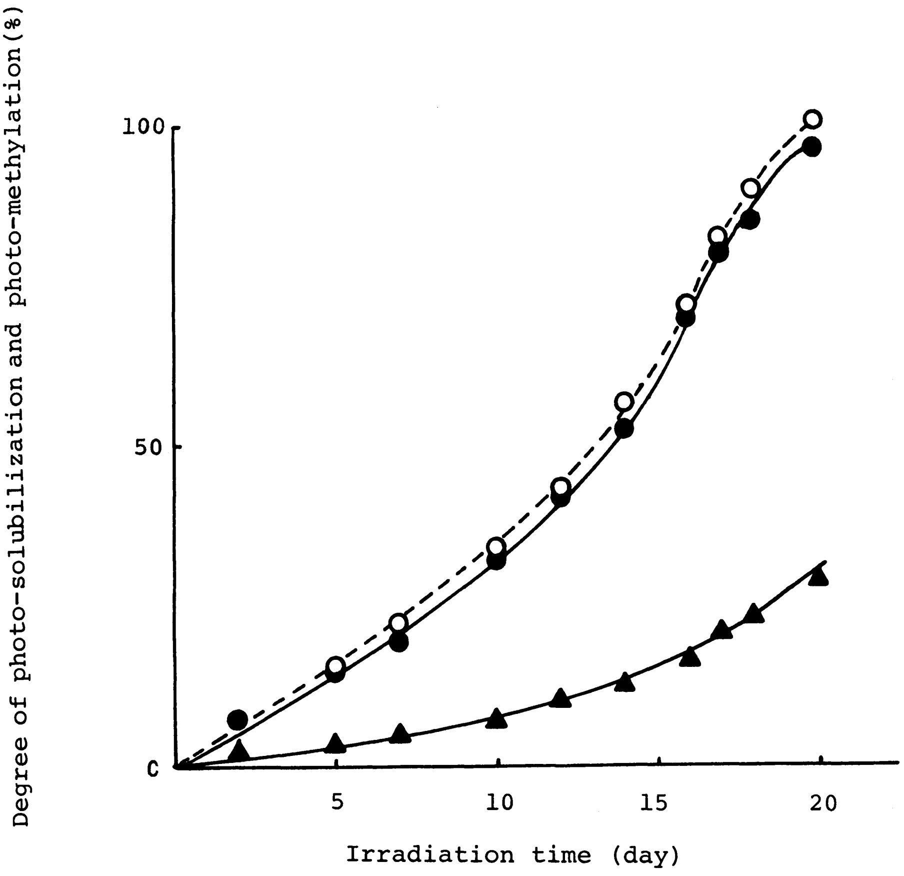

Fig. 1. Photo-solubilization and photo-methylation of mercuric sulfide in the presence of acetic acid.

—▲— Photo-solubilization in water
—●— Photo-solubilization in water with acetic acid
---○--- Production of methylmercury

In order to investigate the effect of oxygen on both the photo-solubilization and photo-methylation of mercuric sulfide, air in the reaction vessel was replaced by oxygen or nitrogen. Under an oxygen atmosphere, the yield of mercury solubilized was about 3.5 times as high as that under a nitrogen atmosphere after irradiation for 5 days. While, the mercury photo-solubilized under a nitrogen atmosphere was occurred completely in the form of methylmercury, but about 70 percent of mercury solubilized was present as methylated form under an oxygen atmosphere. These facts demonstrate that the presence of oxygen enhances the photo-solubilization mentioned above but inhibits the methylation of mercury to some extent.3)

Separate experiments, using an electrode of mercuric sulfide evaporated on a platinum plate to investigate the photoelectrochemical characteristics of the sulfide in a potassium chloride solution, revealed that the photocurrent due to photo-holes was observed only on anodic polarization (excitation wavelength $\lambda \geq 520$ nm); that is, mercuric sulfide acts as an n-type semiconductor.[9]

Although further study is necessary to elucidate detailed reaction mechanisms, the following scheme can tentatively be proposed at the present stage;

(a) Formation of charge carriers by photo-irradiation:

$$\mathrm{HgS} \xrightarrow{h\nu} \text{hole} + \text{electron}$$

(b) Solubilization of mercuric sulfide by hole trapping:

$$\mathrm{HgS} + 2\ \text{holes} \longrightarrow \mathrm{Hg}^{++} + \mathrm{S}$$

(c) Photo-polymerization of sulfur atoms:

$$\mathrm{S} \xrightarrow{h\nu} \mathrm{S}_x$$

(d) Photosensitized methylation by "photo-sulfur":

$$\mathrm{Hg(OCOCH_3)_2} \xrightarrow[\mathrm{S}_x]{h\nu} \mathrm{CH_3HgOCOCH_3} + \mathrm{CO_2}$$

It is considered that oxygen serves as an acceptor for electrons at step (a) and accelerates the decomposition of mercuric sulfide preventing the recombination between the charge carriers of opposite sign.

From the experimental results obtained in the present study, it may be suggested that mercuric ions are released ready for the methylation in the presence of methyl donors such as acetate ions under irradiation with sunlight, when sediments contaminated with mercurials are brought into aerobic conditions. Such a possibility should not be overlooked because aerobic conditions may easily be attained in our environments, especially in dredging works.

References and Notes:

1) M. Yamada and K. Tonomura, J. Ferment. Technol., 50, 901 (1972).

2) T. Fagerström and A. Jernelöv, Water Research, 5, 121 (1971).

3) H. Akagi, Y. Fujita, and E. Takabatake, Chem. Lett., 1975, 171.

†) Absorption spectrum of the n-hexane extract from the irradiated sample agreed well with that of the n-hexane solution of sulfur.

4) H. Akagi and Y. Sakagami, J. Hyg. Chem. (Japan) , 18, 358 (1972).

5) H. Akagi, Y. Fujita, and E. Takabatake, J. Chem. Soc. Japan, 1974, 1180.

6) H. Akagi and E. Takabatake, Chemosphere, 2, 131 (1973).

7) H. Akagi, E. Takabatake, and Y. Fujita, Chem. Lett., 1974, 761.

8) The production of methylmercury from mercuric sulfide could not be observed under photo-irradiation within about 30 hours as was reported previously.[3]

9) See, for example, H. Gerischer, in " Physical Chemistry: An Advanced Treatise," Vol. IX A , pp. 463 - 542, ed. by Eyring et al., Academic Press, New York (1970). Details will soon be reported elsewhere.

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