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# PHOTOCHEMICAL METHYLATION OF INORGANIC MERCURY IN THE PRESENCE OF MERCURIC SULFIDE

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Photosensitized methylation of mercuric acetate in aqueous acetic acid solutions in the presence of mercuric sulfide has been studied. Mercuric sulfide solubilizes rapidly in the dark coupled with the reduction of inorganic mercury, and the resulting sulfur atoms photo-polymerize under irradiation with a black-light-lamp to give a milky white suspension, photo-sulfur, which acts as an efficient photosensitizer for the production of methylmercury.

It has been well recognized that methylmercury in natural environments is produced from inorganic mercury by the action of certain microorganisms[1,2] and of a tuna[3] or ox[4] liver. The important role of methylcobalamin for the methylation in the above systems has been pointed out based on intensive studies[5-7] of the methylation of inorganic mercury with methylcobalamin. On the other hand, mercuric sulfide has long been considered to be the most stable form of mercurials in aquatic environments on account of its extremely low solubility in water and unreactivity against mineral acids. Yamada et al.[8] have reported that no methylmercury is produced from pure mercuric sulfide either by the chemical reaction with methylcobalamin or by the action of a microbial system having a high methylating activity. However, Fagerström et al.[9] have observed a slight production of methylmercury from mercuric sulfide incubated with aquarium sediments, indicating that the sediments may be capable of solubilizing mercuric sulfide which is available for the biological methylation. Yamada et al.[8] have also observed the conversion of mercuric sulfide into a weak acid-soluble compound by the action of iron-oxidizing bacteria in the presence of ferrous sulfate.

Recently, the authors have reported the photochemical methylation of inorganic mercury in aqueous acetic acid solutions under irradiation with sunlight or the light of a blacklight-lamp,[10,11] where the photochemical methylation is found to be enhanced in the presence of colored solids such as mercuric oxide,[12] basic mercuric sulfate,[13] and solid sulfur.[13] The investigation on the photosensitized methylation of inorganic mercury by solids in aqueous solutions is of deep significance in connection with the origin of methylmercury distributed widely in aquatic environments.[14] We have recently found a more markedly photo-enhanced methylation of inorganic mercury by mercuric sulfide, and a rapid and complete dissolution of a black mercuric sulfide by the action of mercuric ions in water. The latter finding is very important because mercuric sulfide may easily be solubilized in the presence of other metal ions having redox potentials as high as that of mercuric ions ( $E_0$=0.906V )15); in fact a black mercuric sulfide is solubilized in the presence of ferric ions ( $E_0$= 0.771V )15) as has been revealed by the radioactive tracer method. It has also been found that the mercurial solubilized is methylated under photo-irradiation. Therefore, when mercuric sulfide, though it is quite stable under anaerobic conditions, is once brought into an aerobic environment, mercuric ions may be released ready for methylation by biological or chemical reactions. Such a possibility should not be overlooked because similar conditions quoted above may easily be attained in our aquatic environments. In this letter, the results of studies on the photosensitized methylation of inorganic mercury in the presence of mercuric sulfide as well as on the solubilization of mercuric sulfide by metal ions are described.

A red mercuric sulfide was obtained from Wako Pure Chemical Industries, Inc., and a black mercuric sulfide was prepared by bubbling hydrogen sulfide into an aqueous mercuric chloride solution acidified with hydrochloric acid and heating for 15 min at 90°C. The thus obtained black mercuric sulfide was washed with dilute hydrochloric acid, distilled water, and finally with ethanol, and then dried in vacuo. A radioactive mercuric sulfide(black) was prepared using 203-mercuric chloride in the same manner as is described above. The other chemicals used were of analytical reagent grade. A blacklight-lamp( Toshiba FL-20BL; 20 W, nominal emission region 310 - 410 nm ) was used as a light source.

The red or black mercuric sulfide( 10 mg ) was suspended by vigorous stirring with a magnetic stirrer in 100 ml of an aqueous solution containing 1 mmole of mercuric acetate and 3 mmole of acetic acid in a quartz vessel with a stoppered serum-cap. Powdered quartz( 100 mg ) was further added into the suspension in order to prevent the adhesion of the suspended solids on the wall of the vessel during the reaction. The aqueous suspension was immediately irradiated with the light of a blacklight-lamp at a distance of 15 cm under gentle stirring at 20°C. An aliquot of the irradiated reaction mixture was acidified with hydrochloric acid, extracted with benzene, and then methylmercury produced was analyzed by the conventional gas chromatography.

No production of methylmercury was observed without irradiation, but a pronounced photochemical methylation of inorganic mercury occurred in both aqueous suspensions of the red and black mercuric sulfides under irradiation. The yield of methylmercury produced was about 280 μmole in the red mercuric sulfide system and about 360 μmole in the black mercuric sulfide system after irradiation for 48 hr. These values in the red and black mercuric sulfide systems were about $5\times10^3$ and $6\times10^3$ times, respectively, larger than that in an aqueous solution without any mercuric sulfides. The rate of the photochemical production of methylmercury, however differed significantly between the two reaction systems as is shown in Fig. 1. In the black mercuric sulfide system, the amount of methylmercury photo-produced increased at a remarkably high rate and almost linearly with irradiation time, and reached about 215 μmole in 10 hr, although this reaction had initially a short induction period. On the other hand, the photochemical methylation in the red mercuric sulfide system initiated autocatalytically after a long induction period of about 10 hr followed then by a steady rise, and the amount of methylmercury reached about 205 μmole in 28 hr. The black mercuric sulfide suspension turned milky white within about 2.5 hr, and a similar color change was observed after 12 hr in the red mercuric sulfide system, indicating that the decomposition of mercuric sulfide in both systems occurred. The milky white suspension in both systems turned gradually to a yellow-tinged one on prolonged irradiation; for example, after about 24 hr in the system of the black mercuric sulfide.

Irradiation of the aqueous mercuric sulfide suspension containing only acetic acid caused neither the decomposition of the mercuric sulfide nor the production of methylmercury. This observation indicates that the decomposition of the mercuric sulfide occurs in the presence of mercuric ions and the resulting milky white precipitate acts as an efficient photosensitizer.

The solubilization of the black mercuric sulfide in the presence of mercuric ions was investigated by the radioactive tracer method using 203-mercury. An aqueous suspension containing 1 mmole of mercuric acetate, 3 mmole of acetic acid, and 10 mg ( 0.04 mmole ) of 203-mercuric sulfide in a 100 ml solution was irradiated with a blacklight-lamp under stirring at 20°C. The same aqueous suspension was stirred in the dark as a control experiment. After various intervals an aliquot of the sus-

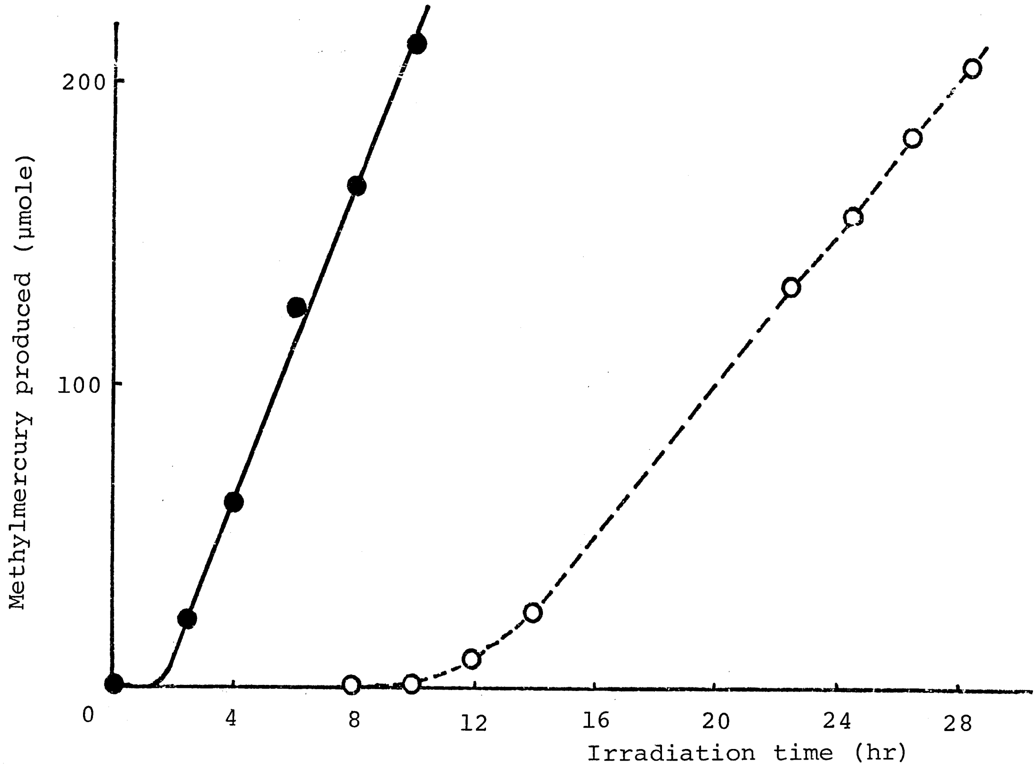


Fig. 1. Photosensitized methylation in the presence of mercuric sulfide.
Reaction conditions: 1 mmole $Hg(CO_2CH_3)_2$ + 3 mmole $CH_3COOH$ + 0.04 mmole HgS in 100 ml $H_2O$, irradiated with blacklight-lamp at 20°C.

—●— HgS (black), ----○---- HgS (red)

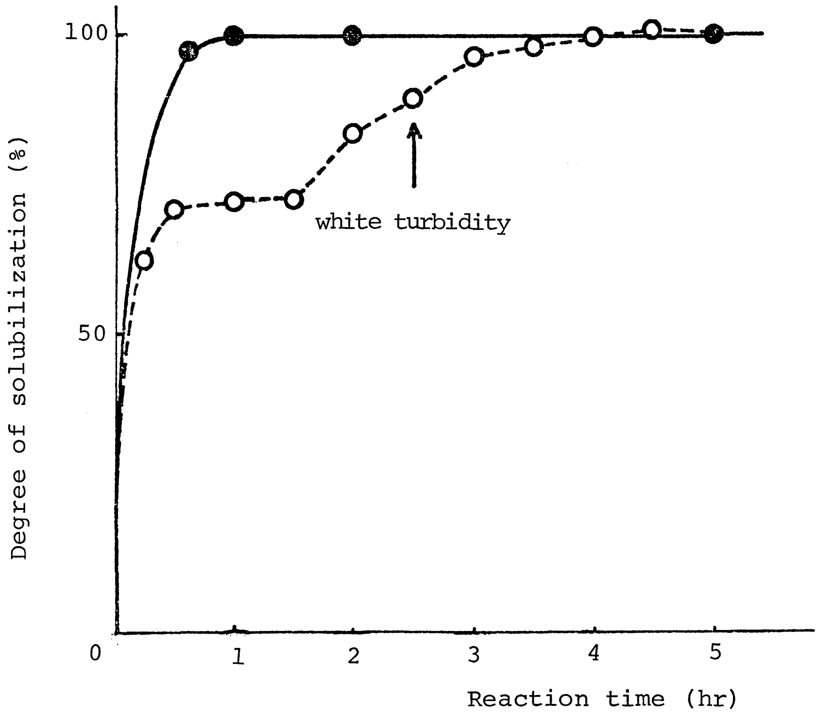


Fig. 2. Solubilization of mercuric sulfide (black) in the presence of mercuric ions.

Reaction conditions: 1 mmole $Hg(CO_2CH_3)_2$ + 3 mmole $CH_3COOH$ + 0.04 mmole $^{203}HgS$ in 100 ml $H_2O$, at 20°C.

—●— without irradiation, ---○--- with irradiation

pension was filtered and the radioactivity for 203-mercury in the filtrate was measured. The results of such measurements are shown in Fig. 2. It is seen from the figure that the solubilization is essentially complete in a short time with or without irradiation. In the dark, especially, a rapid solubilization of mercuric sulfide was observed and the aqueous suspension turned into an almost clear solution within about 1 hr. In the irradiated system a similar result was also obtained at an initial stage, but the solubilization was suppressed to some extent by irradiation after that time as is shown in Fig. 2. When chloride ions were added to the reaction mixtures, a white precipitate of mercurous chloride was produced. After the precipitate was removed from the mixtures, the radioactivities in the filtrates were measured similarly. As a result, the radioactivities were not affected appreciably by the elimination of mercurous ions, indicating that the mercuric sulfide is solubilized in a form of mercuric ions along with the simultaneous reduction of the mercuric ions in the solution into mercurous ions. Similar but slower solubilizations of the mercuric sulfide were also observed with other metal ions, for example, $Hg^+$ ( $E_O$=0.792V ) and $Fe^{3+}$( $E_O$=0.771V ). It is reasonable that the rates of solubilization by metal ions are dependent on their redox potentials.

Spectroscopic studies of the irradiated systems showed that sulfur was also liberated as the milky white precipitate from the mercuric sulfide under irradiation, since the optical absorption of the n-hexane layer extracted from the irradiated sample agreed well with that of the n-hexane solution of sulfur. Therefore, it appears that the sulfur atoms from the mercuric sulfide photo-polymerize to the milky white precipitate, photo-sulfur, and an apparent photosensitized methylation occurs after the generation of photo-sulfur; that is, after the induction periods such as are shown in Fig. 1.

In a previous report,[13)] the authors have shown that the photo-oxidation of solid sulfur in aqueous acetic acid solutions of mercuric acetate couples with the reduction of mercuric ions, and the resulting sulfate ions react immediately with mercuric ions to produce basic mercuric sulfate, a yellow precipitate, which acts as an additional photosensitizer for the methylation. Similarly in the case of solid sulfur, mercurous ions and sulfate ions were confirmed to be produced also in the present systems. Therefore, it is considered that the decomposition of the mercuric sulfides in both reaction systems occur preferencially to liberate photo-sulfur under irradiation, and that the photo-sulfur produced acts as an efficient photosensitizer for the production of methylmercury. Furthermore, the photo-sulfur seems to be photo-oxidized into sulfate ions which accumulate as basic mercuric sulfate in the reaction systems on prolonged irradiation, as in the case of the photosensitization by solid sulfur.

A large difference in the photosensitization reactivities between the red and the black mercuric sulfide systems is considered to depend on the difference in the solubilization rate of the mercuric sulfides due to the difference in surface reactivities of the solids. In fact, the surface area of the black mercuric sulfide ( 20 $m^2/g$; measured by the BET method[16)] using nitrogen at 77K ) is twenty times larger than that of the red one, and the former is well known as an unstable form ( meta cinnabar ) of mercuric sulfide.

Gas chromatographic analyses demonstrated that the gases evolved from the irradiated reaction mixture consisted of a large amount of carbon dioxide and traces of methane and ethane. When the air atmosphere in the reaction vessel was replaced by nitrogen, the amount of methylmercury produced increased appreciably; that is, the photosensitized methylation is partly inhibited by oxygen.

In previous papers,[12,13)] we assumed an energy transfer mechanism for the primary step of photosensitized methylation by a solid such as mercuric oxide or solid sulfur, where the photon energy is transferred from the solid to a mercuric acetate molecule as is illustrated in the following:

$$\text{Solid-}(CH_3CO_2{}^-Hg^{2+}X^-) \xrightarrow{h\nu} \text{Solid}^{*}\text{-}(CH_3CO_2{}^-Hg^{2+}X^-) \longrightarrow$$

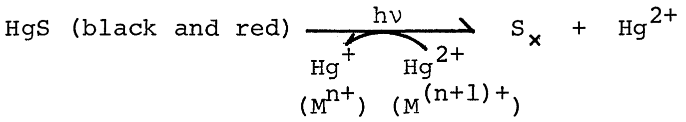
$$\text{Solid-}(CH_3CO_2{}^-Hg^{2+}X^-)^{*} \longrightarrow \text{Solid-}(CH_3\overset{\curvearrowright}{CO_2{}^-\ Hg}{}^{2+}X^-) \longrightarrow$$

$$\text{Solid-}(CH_3 \vdots CO_2 \vdots Hg^{+}X^-) \longrightarrow \text{Solid} + CH_3HgX + CO_2$$

where X denotes an acetate ion or a coordinated anion, and the asterisk an excited state.

As for the reaction mechanism of the photosensitized methylation in the present systems, we propose the following scheme on the basis of the present results;

i) Production of photo-sulfur:

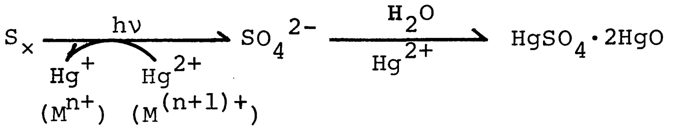


$$\text{HgS (black and red)} \xrightarrow[\underset{(M^{n+})\ \ (M^{(n+1)+})}{Hg^{+}\ \ Hg^{2+}}]{h\nu} S_x + Hg^{2+}$$

ii) Photosensitization by photo-sulfur:

$$Hg(CO_2CH_3)_2 \xrightarrow[S_x]{h\nu} CH_3Hg(CO_2CH_3) + CO_2$$

iii) Production of basic mercuric sulfate:



$$S_x \xrightarrow[\underset{(M^{n+})\ \ (M^{(n+1)+})}{Hg^{+}\ \ Hg^{2+}}]{h\nu} SO_4{}^{2-} \xrightarrow[Hg^{2+}]{H_2O} HgSO_4 \cdot 2HgO$$

iv) Photosensitization by basic mercuric sulfate:

$$Hg(CO_2CH_3)_2 \xrightarrow[HgSO_4 \cdot 2HgO]{h\nu} CH_3Hg(CO_2CH_3) + CO_2$$

Further work is now in progress to elucidate more detailed mechanisms of the photosensitized methylation in the present systems, and the possibility of analogous photosensitized reactions in real aquatic environments where the concentration of mercury is lower.

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