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PHOTOCHEMICAL METHYLATION OF INORGANIC MERCURY IN THE PRESENCE OF SOLID SULFUR

Hirokatsu AKAGI and Eigo TAKABATAKE
The Institute of Public Health, Minato-ku, Tokyo 108
and
Yuzaburo FUJITA
Faculty of Pharmaceutical Sciences, The University of Tokyo,
Bunkyo-ku, Tokyo 113

The photosensitized methylation of inorganic mercury in the presence of solid sulfur was investigated in an aqueous acetic acid solution of mercuric acetate. It was found that the photooxidation of sulfur into sulfate ions coupled with the reduction of mercuric ions and the resulting sulfate ions reacted with mercuric acetate to produce basic mercuric sulfate, a yellow precipitate, which acted as an effective photosensitizer for the methylation.

In the course of studies on the photochemical transformation of inorganic mercury to alkylmercury in aquatic environments,[1,2,3] we have found that a yellow precipitate of mercuric oxide formed by the spontaneous hydrolysis of mercuric acetate acts as an effective photosensitizer in producing methylmercury under irradiation with the light of a blacklight lamp.[4] This communication deals with another example of heterogeneous photosensitized methylation of inorganic mercury in the presence of solid sulfur.

The chemicals used were of reagent grade. Sulfur (Koso Chemical Co., Ltd.) recrystallized from carbon disulfide was ground to powder and suspended in 100 ml of an aqueous solution containing 1 mmole of mercuric acetate and 3 mmoles of acetic acid in a quartz vessel with a stoppered serum cap by stirring with a magnetic stirrer. This suspension was then irradiated by a blacklight lamp (Toshiba FL-20BL)[*] placed at a distance of 15 cm at 20°C under gentle stirring. After the filteration of the reaction mixture, the filtrate was acidified with hydrochloric acid and then methylmercuric chloride was extracted with benzene and analyzed by a gas chromatograph equipped with an electron capture detector as was described in a previous paper.[2]

As shown in Fig. 1, the yield of methylmercury in 48 hours was approximately proportional to the amount of sulfur added up to about 30 mg, and then gradually decreased with another amount of sulfur probably owing to the light scattering. The yield of methylmercury in the reaction mixture containing 30 mg of sulfur was about 260 times as much as that without sulfur.

Similarly in the case of mercuric oxide, mercurous compound was also formed along with methylmercury in the case of sulfur, since the addition of hydrochloric acid to the irradiated reaction mixture produced mercurous chloride, a white precipitate which turned black by ammonium hydroxide. After mercurous chloride had been centrifuged out, the supernatant fluid gave white turbidity of barium sulfate on addition of barium chloride.

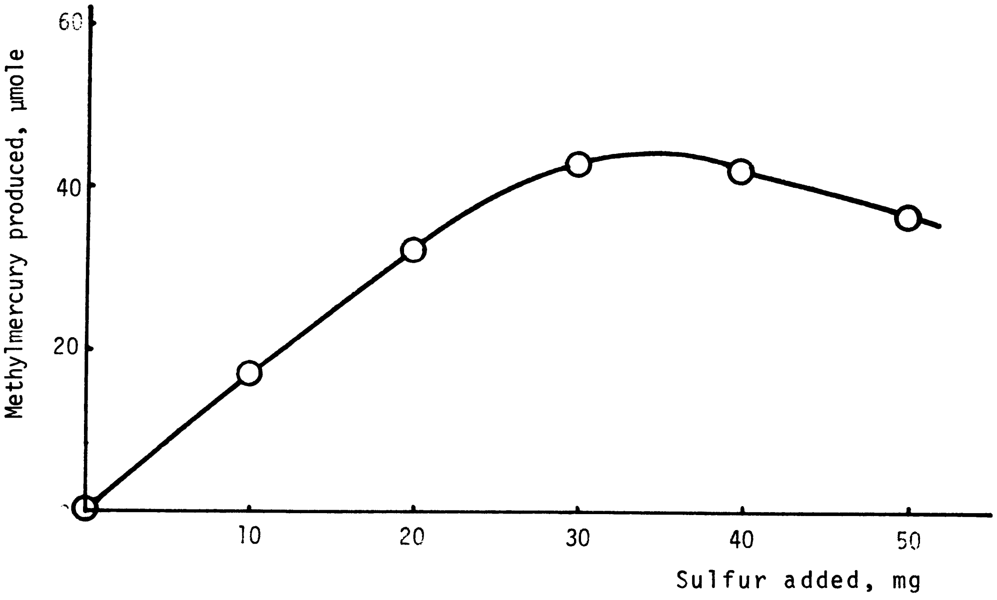


Fig. 1. Relationship between the photochemical production of methylmercury and the amount of sulfur added.

Aqueous acetic acid solutions of mercuric acetate containing various amounts of sulfur were irradiated with the light of a blacklight lamp for 48 hours at 20°C.

Fig. 2 shows the production of methylmercury and sulfate ions in the irradiated reaction mixture. Methylmercury increased autocatalytically with the irradiation time. The amount of sulfate ions in the filtrate increased linearly up to 72 hours and then reached to a constant value. However, when hydrochloric acid was added directly to the reaction mixture irradiated for 168 hours an additional amount of sulfate ions, 68 μmoles, was found in the filtrate. This fact suggests that a greater part of sulfate ions photoproduced in the reaction mixture occurred in water-insoluble compounds and was dissolved out by the addition of hydrochloric acid.

It is well known that mercuric sulfate is hydrolyzed immediately in water and changes to basic mercuric sulfate, $HgSO_4 \cdot 2HgO$, a yellow precipitate. Basic mercuric sulfate formed from 1 mmole of mercuric sulfate in 100 ml of water scarecely dissolved on addition of 5 mmoles of acetic acid but a pronounced photochemical methylation was observed in this aqueous suspension. A similar enhancement of the photochemical methylation was also observed on addition of sodium sulfate to an aqueous acetic acid solution of mercuric acetate. When more than 10 μmoles of sulfate ions was added to the solution, a yellow precipitate appeared immediately and its amount increased as the amount of sulfate ions increased. The rate of the production of methylmercury was remarkably higher in the aqueous suspension than in the control solution without sulfate ions. These findings indicate that sulfate ions react with mercuric acetate to produce mercuric sulfate which is spontaneously hydrolyzed into basic mercuric sulfate in an aqueous solution, and that the resulting yellow precipitate acts as an efficient heterogeneous photosensitizer for the photochemical methylation of inorganic mercury.

Fig. 3 shows the reflection spectra of sulfur, basic mercuric sulfate, and mercuric oxide together with the emission spectrum of a blacklight lamp. The effective emission region of a blacklight lamp is in the absorption region of these substances.

At an initial stage of the irradiation, sulfur is considered to act as a photosensitizer (step 1') and to change simultaneously to sulfate ions (step 1). An additional photosensitizer,

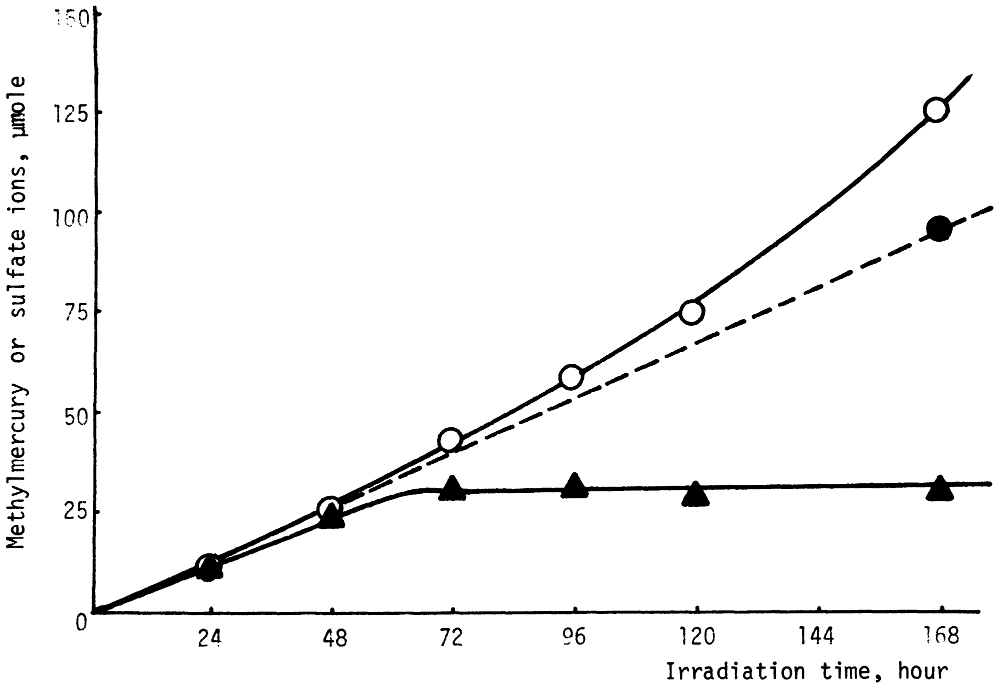


Fig. 2. Photochemical production of methylmercury and sulfate ions from the aqueous solution of mercuric acetate in the presence of sulfur.

Reaction system : 1 mmole $Hg(OCOCH_3)_2$ + 5 mmoles CH_3COOH + 30 mg sulfur in 100 ml H_2O.

—○— : methylmercury produced

—▲— : sulfate ions dissolved in the reaction mixture

---●--- : total sulfate ions produced

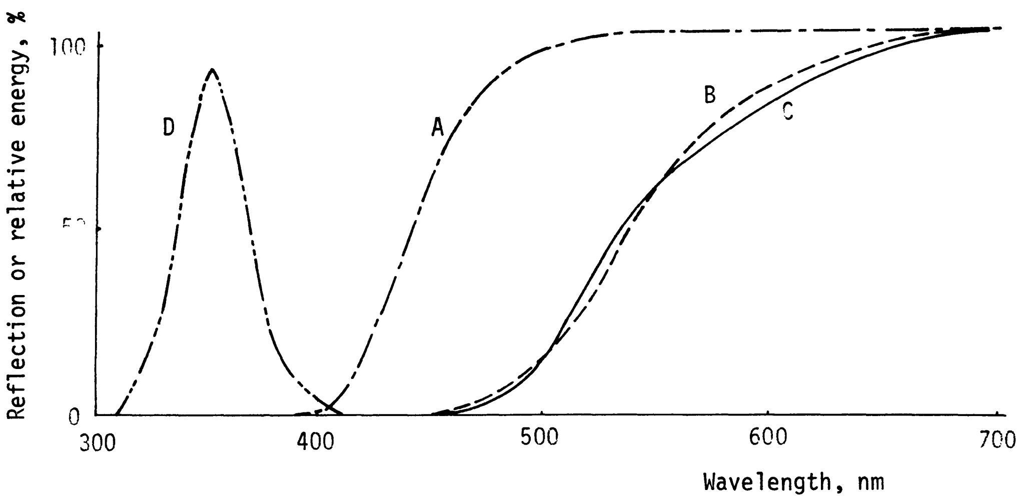


Fig. 3. Reflection spectra of sulfur, basic mercuric sulfate and mercuric oxide.

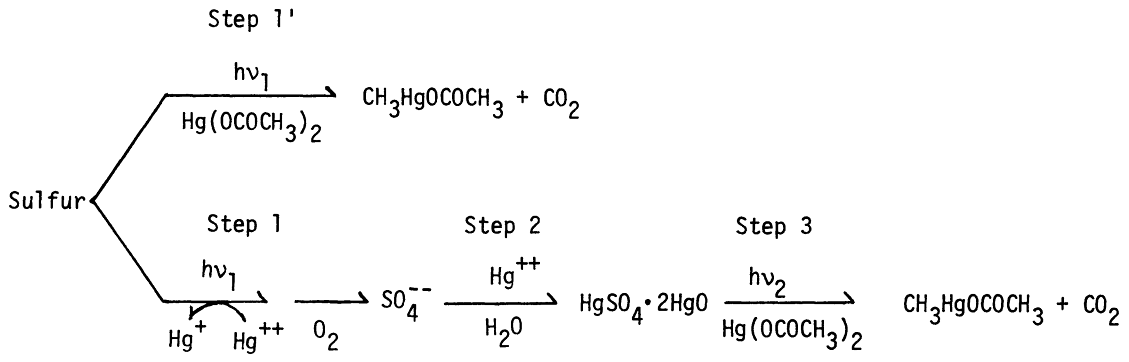
A : sulfur

B : mercuric oxide

C : basic mercuric sulfate

D : emission spectrum of a blacklight lamp basic mercuric sulfate, is gradually accumulated in the reaction mixture(step 2) and stimulates the rate of photochemical methylation autocatalytically(step 3).

Vollath[5)] reported that the thermal reaction of mercuric acetate with sulfur in glacial acetic acid at 135°C produced mainly mercurous acetate and sulfate ions and also mercurated acetic acid or a related compound on prolonged heating, whereas, in contrast with our results, the production of methylmercury was not involved. However, in both thermal and photochemical reaction systems, it seems that the reduction of mercuric ions and the oxidation of sulfur occur simultaneously. The fact that no sulfate ions was identified, when an aqueous suspension of sulfur containing only acetic acid was irradiated even for a long time, suggests the photochemical production of sulfate ions coupled with the reduction of mercuric ions. Carbon dioxide and traces of methane and ethane were identified as gaseous reaction products in our heterogeneous photosensitized reaction systems. Furthermore, we observed an appreciable increase in the yield of methylmercury under nitrogen atmophere, suggesting that the photosensitized methylation (step 1' and/or step 3) was partly inhibited by oxygen. Therefore, the following reaction scheme is reasonably proposed:



Step 1 : photosensitized SO_4^{--} formation coupled with Hg^{++} reduction.
Step 1': photosensitized methylation through energy transfer.
Step 2 : spontaneous hydrolysis of $HgSO_4$.
Step 3 : secondary heterogeneous photosensitized methylation.

Further investigations on the detailed mechanism of the present photosensitized methylation and on the possibility of this reaction in the real environments are now in progress.

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*) Nominant emission wavelength region : 300 - 400 nm, see reference 2).

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