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Production of methyltin compounds related to possible conditions in the environment

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The methylation of heavy-metal compounds (e.g. mercury, lead, tin) in the environment has great significance owing to the much higher toxicity of their methyl derivatives in comparison with inorganic metal species.

In this paper abiological methylation of inorganic tin is described. Ethanol, acetic acid and propionic acid abiologically methylated inorganic tin, and the highest yield of methyltin was observed in the reaction between inorganic tin(II) and ethanol. Furthermore, environmental factors for the methylation, such as pH, temperature, added ethanol, concentration of sodium chloride and photoirradiation, were investigated in this reaction. Methyltin production increased at low pH, and decreased at higher concentrations of sodium chloride. Photoirradiation accelerated the reaction rate, and a shorter wavelength showed a higher rate. Inorganic tin(II) was converted rapidly into monomethyltin, and gradually transformed into dimethyltin and trimethyltin with the course time.

Keywords: Methyltin, environment, abiological methylation, methanol, ethanol, acetic acid, propionic acid, humic acid, fulvic acid, hexamethyldisiloxane

INTRODUCTION

Organotin compounds have given rise to marine pollution in recent years.[1–3] Tributyltin compounds, especially, are widely used as antifouling paints on ships, boats and fishing nets. The applications of organotin compounds are not only as biocides for their biological activity, but also as heat stabilizers for PVC and catalysts for production of urethanes or for esterification, etc.[1] Since organotin compounds, particularly tributyltin compounds, show high toxicity for aquatic organisms, environmental monitoring for organotin compounds has been carried out in many countries.[4,5]

These organotin compounds might also be converted to other tin species, biologically or abiologically in the environment. The environmental degradation of organotin compounds has already been reviewed e.g. by Blunden and Chapman.[6] For instance, tributyltin compounds in aqueous solution are decomposed under UV irradiation,[7] and furthermore, the persistence of tributyltin compounds in freshwater ecosystems is controlled by microbial degradation.[8] This suggests that organotin compounds are degraded, and perhaps turn into less toxic inorganic tin species, in the environment.

On the other hand, methyltin compounds, which are rarely used in industry, have been found in marine sediments[9–11] and natural waters,[12–14] so there might be a possibility of formation of methyltin species in the environment.

Methylation of inorganic tin in the environment has occurred biologically or abiologically. Guard *et al.*[15] demonstrated the conversion of $(CH_3)_3SnOH$ to $(CH_3)_4Sn$ in biologically active sediment, and Hallas *et al.*[16] showed that inorganic tin ($SnCl_4$) was transformed into dimethyltin and trimethyltin compounds by microorganisms isolated from the sediment in Chesapeake Bay. As to chemical methylation for tin compounds, the production of methyltins from CH_3I and inorganic tins has been reported,[17,18] and Fanchang and Wood[19] found that inorganic tin ($SnCl_2$) was converted into CH_3SnCl_3 by methylcobalamin in acidic solution under aerobic conditions.

Methyltin compounds have a higher toxicity for mammals in comparison with other organotin compounds,[20,21] in particular, trimethyltin chlor-

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ide shows toxicity (4–5 mg kg^{-1} in rats) for the central nervous system made evident by, for example, necrosis of neurons.[22,23] Therefore it is important that these processes, and the environmental factors related to the methylation of tin compounds, are made clear. Moreover, it is significant to investigate whether inorganic tin species (with a lower toxicity) will be methylated by the action of chemical substances distributed widely in the environment.

In this paper methanol, ethanol, acetic acid, propionic acid, hexamethyldisiloxane, humic acid and fulvic acid (which have been already known as methyl donors for inorganic mercury(II)[24]) were studied as to whether they would act as methyl donors for inorganic tin ($SnCl_2$ or $SnCl_4$) in aqueous solution. Environmental factors such as pH, temperature, time course, photo-irradiation, etc., with regard to the production of methyltins were also investigated in the reaction of inorganic tin and ethanol.

MATERIAL AND METHODS

Chemicals

$SnCl_4.xH_2O$ (97% as $5H_2O$) and $SnCl_2.2H_2O$ were obtained from Hayashi Pure Chemical Industries. CH_3OH (Koso Chemical Co.), C_2H_5OH (Hayashi Pure Chemical Industries), CH_3COOH (Koso Chemical Co.), C_2H_5COOH (Kishida Chemical Co.) and $(CH_3)_3SiOSi(CH_3)_3$ (Kishida Chemical Co.) were purchased from the company indicated. Humic acid and fulvic acid were prepared from leaf moulds collected at Kiyomi, Gifu, Japan, by a literature method:[25] 0.1 g of this humic acid is equivalent to 9.6 mg of $KMnO_4$ consumption, and 0.1 g of the fulvic acid is equivalent to 11.9 mg of $KMnO_4$ consumption. A 4% solution of $NaBH_4$ (Kishida Chemical Co.) was freshly prepared with distilled water. Benzene (Hayashi Pure Chemical Co.) used in extracting was of pesticide residue analysis grade. Bu_4Sn (Merck), benzene solution (5 μg cm^{-3} as Sn), was prepared as internal standard.

No methyltin species was detected in the reagent blanks. As standard methyltin compounds, CH_3SnCl_3 (Aldrich), $(CH_3)_2SnCl_2$ (Kantoh Chemical Co.) and $(CH_3)_3SnCl$ (Kantoh Chemical Co.) were used.

Analytical procedure for methyltins

Analysis of reaction solutions

We slightly modified the Matthias method[26] to determine methyltin species in the reaction solutions.

Sample (50 cm^3) was adjusted to pH 2.5, using HCl or NaCH (0.1 or 1.0 M), and 10 cm^3 of benzene and 4 cm^3 of aqueous 4% (w/v) $NaBH_4$ were added to this solution, and the solution was shaken for 10 min in a 100-cm^3 separating funnel. The benzene layer was dried out with anhydrous Na_2SO_4, then 1 cm^3 of Bu_4Sn/benzene solution (5 μg cm^{-3} as Sn) as internal standard (Bu_4Sn retention time was 17.7 min) was added to 4 cm^3 of dehydrated benzene layer. The benzene solution was subjected to gas chromatography with a flame photometric detector (GC–FPD) for quantitative analysis.

GC–FPD conditions were as follows. Instrument, Hitachi 163 with FPD (detection wavelength 585–610 nm); glass column, 3 mm i.d. × 3 m; column packing 10% SP2100 + 3% SP2401 on Supelcoport 80–100 mesh; carrier gas, N_2, 1.2 kg cm^{-2}; gas supporting the flame, H_2 (1.5 kg cm^{-2}), O_2 (0.4 kg cm^{-2}), added N_2 (0.25 kg cm^{-2}); column temperature, programmed at 50°C for 7 min and then heated to 230°C at 20°C min^{-1}; detector temperature, 280°C; injection temperature, 280°C.

A calibration curve of $MeSnH_3$ in solution was prepared in the range 0.5–250 μg Sn per 50 cm^3 using GC–FID the ethanol and benzene retention times overlapped at 5 min. Retention time of Sn_2H_6 with GC–FID (similar conditions to GC–FPD) was 3.7 min, so there was no interference with these solvents.

Analysis of the gas phase

After reaction 1 cm^3 of the head-space gas was collected with a gas-tight syringe and analysed with GC–FPD for the detection of volatile tin compounds produced. Benzene solutions of $(CH_3)_4Sn$, containing 0.1 and 1.0 μg Sn cm^{-3}, were previously prepared for the determination. GC–FPD conditions were as above.

Identification of methyltins produced

The reaction products were identified by their retention times on GC–FPD, and were also confirmed by their mass spectra using a gas chromatography–mass spectrometer (GC–MS).

GC–MS conditions were as follows. Instrument, JEOL JMS-D300; glass column, 2 mm i.d. × 3 m; column packing, 10% SP2100 + 3% SP2401 on Supelcoport 80–100 mesh; carrier gas, He (0.8 kg cm^{-2}); injection temperature, 280°C; column temperature, 60°C; ionization voltage, 20 eV; ionization current, 100 μA; scan limit, 40–600.

Reaction conditions

Reaction between inorganic tin and reactant chemicals in darkness

Each 10 mmol of chemical (0.1 g in the case of humic acid or fulvic acid) was added to 50 cm^3 of an aqueous solution containing 1.0 mmol of $SnCl_2$ or $SnCl_4$. The solution was not buffered.

The reaction mixture was put into a 100-cm^3 Erlenmeyer flask and sealed tightly with a silicone rubber cap. In the dark the reaction solution was stirred with a magnetic stirrer for 6 h at room temperature.

Reaction between inorganic tin and reactant chemicals under photoirradiation

The added amount of each chemical substance was 10 mmol (for humic acid or fulvic acid 0.1 g was used), and 50 cm^3 of aqueous solution containing 1.0 mmol of inorganic tin was used in this reaction. The reaction was carried out both in a 100-ml beaker, which was open to the air, and in a 100-ml flask sealed with a silicone rubber cap. The reaction mixture was stirred under irradiation with a UV lamp (Ultra Violet Co., wavelength 200–280 nm) at a distance of 8 cm for 1 h. In the case of the reaction in a 100-ml beaker, the irradiating lamp was above the beaker; and with a quartz flask, the lamp was irradiated from the side of the flask.

All of the reactions were carried out in duplicate.

RESULTS AND DISCUSSIONS

Reaction between inorganic tin and reactant chemicals in darkness

In the dark, only ethanol could methylate inorganic tin ($SnCl_2$ or $SnCl_4$) to methyltins.

Figure 1 shows the reconstructed ion chromatogram of a benzene extract of the reaction between C_2H_5OH and $SnCl_2$. Peaks 2, 3 and 4 were identified as CH_3SnH_3, $(CH_3)_2SnH_2$ and $(CH_3)_3SnH$ by their respective retention times and mass spectra (Fig. 2). Peaks 1 and 5 were considered to be SnH_4 and Sn_2H_6 by their mass spectra, and these came from unreacted inorganic tin.

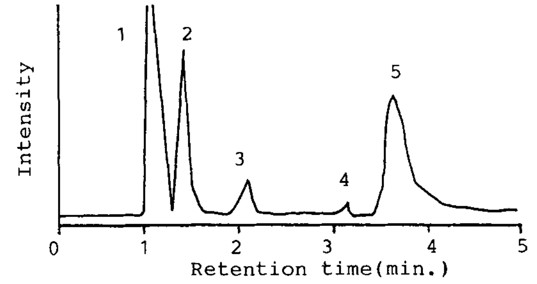

Figure 1 Reconstructed ion chromatogram of reaction products from ethanol and inorganic tin(II). Peak 1 = SnH_4, peak 2 = CH_3SnH_3, peak 3 = $(CH_3)_2$ SnH_2, peak 4 = $(CH_3)_3SnH$, peak 5 = Sn_2H_6.

The yield of total methyltins for added inorganic tin in the reaction between divalent tin and ethanol was 0.31% and between tetravalent tin and ethanol the yield was 0.029%.

Reaction between inorganic tin and reactant chemicals under photoirradiation

When the reaction was carried out in the tightly sealed quartz flask, only ethanol showed an ability for the methylation of inorganic tin. Ethanol and divalent tin yielded methyltins (0.18% yield on added inorganic tin), and ethanol and tetravalent tin produced a 0.046% yield.

In the case of the reaction in a 100-ml beaker, which was left open during reaction, ethanol and divalent tin formed methyltins (0.18% yield on added inorganic tin), ethanol and tetravalent tin yielded 0.018%, acetic acid and divalent tin produced 0.025%, and in the reaction between propionic acid and tetravalent tin the yield was very small (0.001%).

It was considered that the difference in the amounts of methyltins produced between the beaker and the quartz flask might be caused by differences in the irradiated area and the photointensity.

In this way, photoirradiation was an important factor for the production of methyltins. Acetic acid, propionic acid and ethanol found in the aquatic environment may be possible sources for the formation of methyltins in shallows and surface layers of water in the environment.

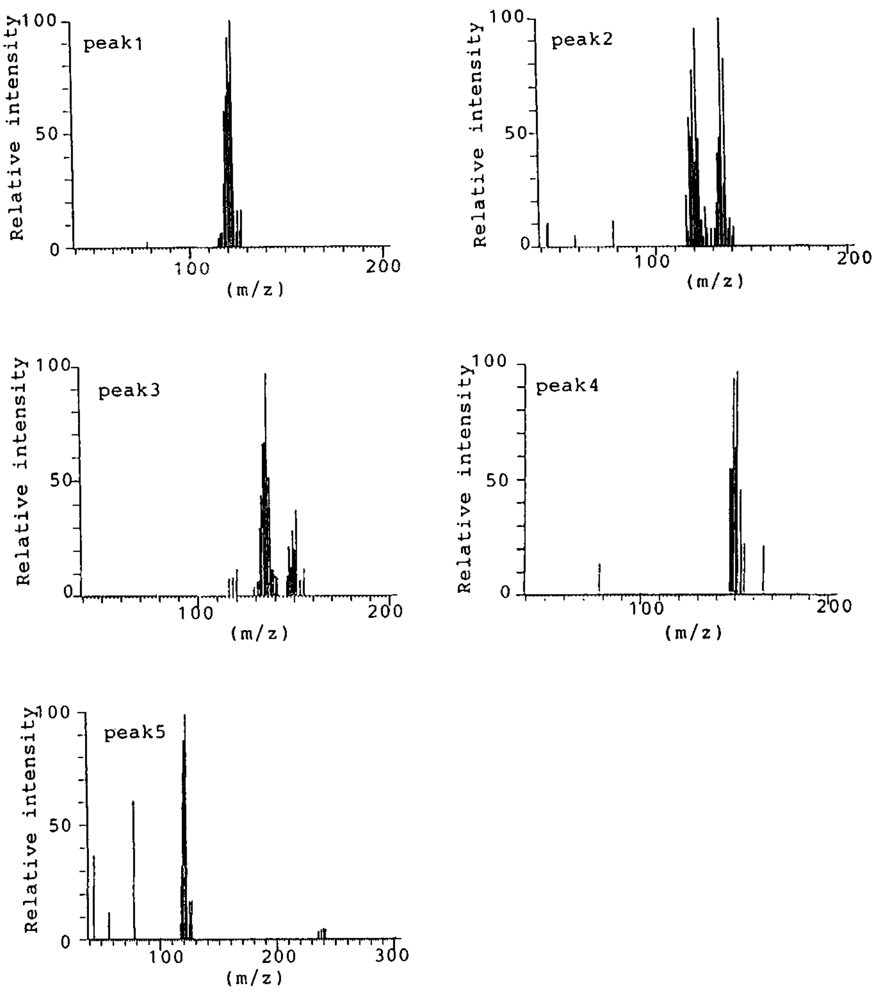

Figure 2 Mass spectra of reaction products.

From the results, a combination of ethanol and divalent tin yielded the highest amounts of methyltins both in the dark and in the case of UV irradiation.

Since the valence of the tin atom in the organotin compounds is four, it seems therefore that the production of methyltins from inorganic tin(II) would occur through oxidative processes concerned with CH_3^+ or $\cdot CH_3$.

In the reaction relating to humic acid or fulvic acid, methyltins were note detected in the reaction mixture. However, this does not mean that methyltins were not formed. The negative result might be caused by the adsorption of inorganic or organic tin compounds to them. If the concentration of inorganic tin was reduced by adsorption, methyltin formation might decrease. If the produced methyltins were in small yields and were also adsorbed on the acids, they might not be detected. Donard and Weber[27] investigated the behaviour of methyltins in simulated estuarine conditions, and reported that fulvic acid showed an adsorption of methyltins.

Condition of methyltin formation in the reaction between divalent tin and ethanol

Effect of pH

C_2H_5OH (10 mmol) and $SnCl_2$ (1 mmol) were used in this reaction. The reaction solution was adjusted to various pH values (1, 2, 2.5, 3, 4, 6, 8 and 11). Then the reaction solution was put into a 50-ml vial sealed with a rubber cap and kept at 22°C in the dark for 48 h. The effect of pH on the production of methyltins is shown in Fig. 3.

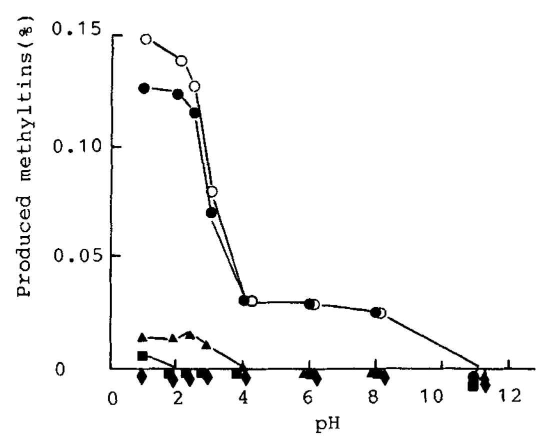

Figure 3 Effect of pH on the production of methyltins: ●, Ch_3Sn^{3+}; ▲, $(CH_3)_2Sn^{2+}$; ■, $(CH_3)_3Sn^+$; ◆, $(CH_3)_4Sn$; ○, total methyltins.

Approximattely 0.03% of inorganic tin was transformed into CH_3Sn^{3+} between pH 4 and pH 8, which is as observed in the real aquatic environment. The lower the pH of the reaction solution, the higher was the amount of methyltin that was produced. The methyltin species produced were mainly CH_3Sn^{3+}, and no $(CH_3)_4Sn$ was detected. These results suggested that more inorganic tin hydroxide occurs at higher pH and the hydroxide would be inactive.

Effect of temperature

The reactions were carried out at pH 2.5 in the dark for 48 h without stirring, and temperature was varied. Results are shown in Fig. 4. The amounts of methyltins produced slightly decreased at 70°C; volatilization of ethanol from the reaction solution may be a reason for this. At a low temperature (8°C) the amount of methyltins produced was observed to be a little more than that at higher temperature. The formation at low temperature is very significant for the environment.

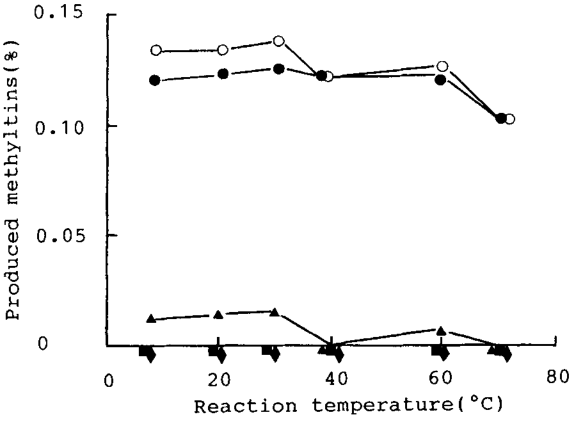

Figure 4 Effect of temperature on the production of methyltins. ●, CH_3Sn^{3+}; ▲, $(CH_3)_2Sn^{2+}$; ■, $(CH_3)_3Sn^+$; ◆, $(CH_3)_4Sn$; ○, total methyltins.

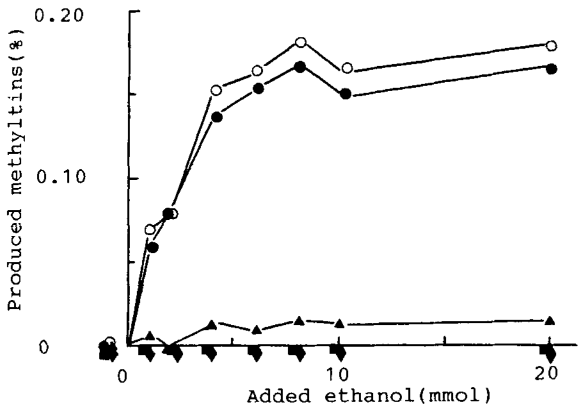

Figure 5 Effect of the amount of ethanol on the production of methyltins. ●, CH_3Sn^{3+}; ▲, $(CH_3)_2Sn^{2+}$; ■, $(CH_3)_3Sn^+$; ◆, $(CH_3)_4Sn$; ○, total methyltins.

Effect of the amount of ethanol

The amount of ethanol added was varied, being 1, 2, 4, 8, 10 and 20 mmol for 1 mmol of $SnCl_2$. Each mixture was kept at pH 2.5 in the dark for 120 h without stirring. The result is shown in Fig. 5. The methyltins produced increased to about 4 mmol of ethanol (i.e. a four-fold amount compared with added inorganic tin), but when the amount of ethanol increased more than this the production of methyltins did not increase and was almost constant.

Effect of the concentration of sodium chloride

The concentration of sodium chloride was varied; concentrations of 0, 5, 10, 20 and 30 g dm^{-3}, were used and the reaction was carried out at 22°C in the dark for 6 h with stirring both for pH 2.5 and pH 7.8. As shown in Fig. 6, the yielded methyltin decreased with increasing concentration of sodium chloride in the reaction both at pH 2.5 and pH 7.8. At a concentration of 20 g dm^{-3}, which is the level seen in real seawater, the yields became about 50% of that without sodium chloride. Methylation of inorganic tin would therefore occur more easily in freshwater than the seawater.

Effect of reaction time

Each reaction solution was adjusted to pH 2.5, and was kept at 22°C in the dark. The reaction

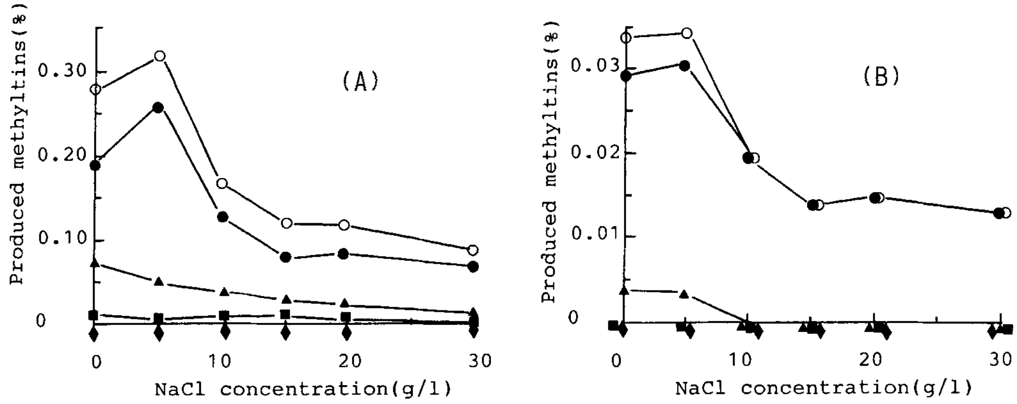

Figure 6 Effect of concentration of sodium chloride on the production of methyltins. ●, CH_3Sn^{3+}; ▲, $(CH_3)_2Sn^{2+}$; ■, $(CH_3)_3Sn^+$; ◆, $(CH_3)_4Sn$; ○, total methyltins. (A) Reaction at pH 2.5; (B) reaction at pH 7.8.

was carried out from 6 h to 10 days. Results are shown in Fig. 7. In the period between 2 days and 10 days, toal methyltins produced were approximately constant, 0.15%. On the other hand, monomethyltin increased for first 5 days, but decreased after 5 days. Further, dimethyltin was produced after 1 day, and trimethyltin was yielded after 5 days. From these results, production of methyltins from inorganic tin would proceed as shown in Eqn [1].

$$Sn^{2+} \xrightarrow{(i)} CH_3Sn^{3+} \xrightarrow{(ii)} (CH_3)_2Sn^{2+} \xrightarrow{(iii)} (CH_3)_3Sn^{+} \quad [1]$$

The process of stage (i) was comparatively fast and the reaction of stage (ii) or (iii) was much slower than the reaction of (i).

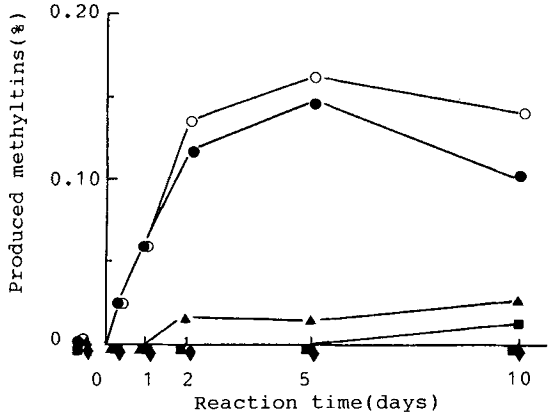

Figure 7 Time course of methyltins produced from the reaction without stirring. ●, CH_3Sn^{3+}; ▲, $(CH_3)_2Sn^{2+}$; ■, $(CH_3)_3Sn^+$; ◆, $(CH_3)_4Sn$; ○, total methyltins.

Effect of stirring

The reaction solution was stirred with a magnetic stirrer from 1 to 144 h. The time course of methyltins production is shown in Fig. 8. Maximum yield of total methyltins was observed after 24 h, and it was 0.30% of added inorganic tin. Compared with the reaction without stirring (Fig. 7), the time elapsed to the maximum amount of methyltins produced was shorter, and the yield was 97% higher at the maximum amount.

Effect of irradiation

A UV lamp or the black-light lamp (National Co.; wavelength 300–420 nm) was used in the experiment. Each lamp was set up at a distance of 8 cm from the side of the flask. The reaction was carried out from 10 to 240 min.

On irradiating with the UV lamp, the total methyltins produced reached the maximum

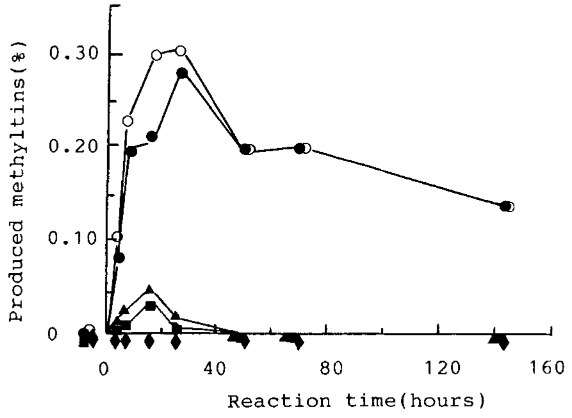

Figure 8 Time course of methyltins produced from the reaction with stirring. ●, CH_3Sn^{3+}; ▲, $(CH_3)_2Sn^{2+}$; ■, $(CH_3)_3Sn^+$; ◆, $(CH_3)_4Sn$; ○, total methyltins.

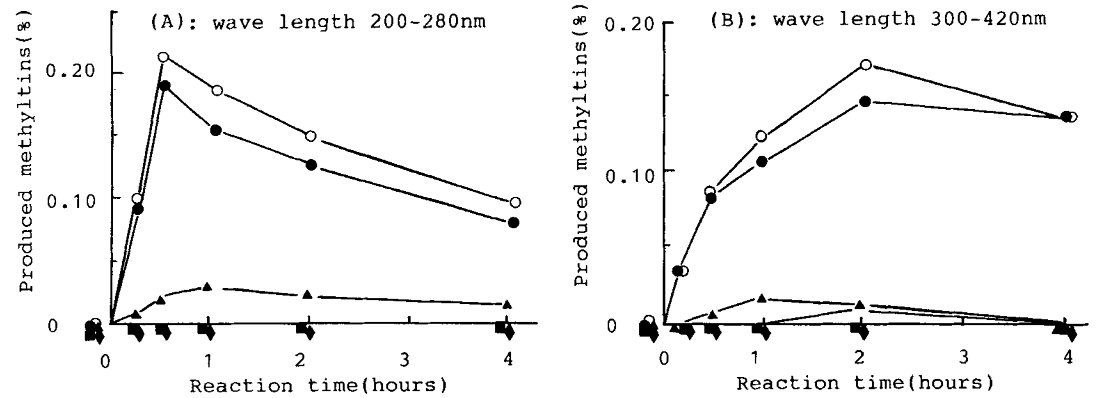

Figure 9 Effect of photoirradiation on the production of methyltins. ●, CH_3Sn^{3+}; ▲, $(CH_3)_2Sn^{2+}$; ■, $(CH_3)_3Sn^+$; ◆, $(CH_3)_4Sn$; ○, total methyltins. (A) Irradiated with UV lamp; (B) irradiated with black-light lamp.

amount after 30 min, and subsequently decreased as shown in Fig. 9. In the case of the black-light lamp it took 2 h to reach the highest value. As shown in Fig. 8, the amount of methyltins produced by photoirradiation was slightly less than in the dark. However, the reaction rate was accelerated compared with that in the dark. This tendency was observed particularly in the irradiation with shorter wavelength. This may be explained by a radical reaction mechanism with $\cdot CH_3$ or Sn(III).

CONCLUSIONS

From the results, there might be a possibility of chemical methylation for added inorganic tin under environmental conditions. The chemical substances which reacted as methyl donors were ethanol, acetic acid and propionic acid, and the production ratio of methyltins from inoirganic tin was in the range 0.001–0.3%.

Although the yields of methyltins were small, compounds such as ethanol, acetic acid and propionic acid exist widely as decomposition products of various organisms in the environment, and they have a great significance as one of the sources for the production of methyltins in the environment. It is important to make the environmental conditions for this process clear, since the methyl–metal compounds generally have much greater toxicity than inorganic metal derivatives. It is considered that methyltins in the environment would be in equilibrium between production and decomposition, and the amount of methyltins produced depends upon the concentration of the tin compounds and the occurrence of substances as methyl donors, and upon environmental factors, such as light, pH, temperature and salinity.

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