Identification of photochemical methylation products of tin(II) in aqueous solutions using headspace SPME coupled with GC-FPD or GC-MS

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Methylation is an important transformation process for elements in the environment. Herein, headspace solid phase micro-extraction (HP-SPME) coupled with gas chromatography–flame photometric detection (GC-FPD) or gas chromatography–mass spectrometry (GC-MS) techniques were employed to study the photochemical methylation of inorganic tin(II) by eight organic compounds (including acetone, pyruvic acid, acetic acid, propionic acid, dimethyl sulfoxide, *N,N*-dimethylformamide, *tert*-butyl alcohol and isopropyl alcohol) in aqueous solutions. The major products were identified as monomethyltin (MMT) and dimethyltin (DMT), as well as trimethyltin (TMT) as the minor product. The yields of methyltin products were closely related to the chemical structures of methyl donors, and the pH and salinity of the reaction solution. The concentrations of methyltin products peaked at a pH of 5.0 and a salinity of 0.5 M. The dominating product also changed from MMT to DMT with an increase in pH value. Notably, pyruvic acid can readily methylate tin(II) under irradiation by sunlight in view of its absorption of sunlight, demonstrating that photochemical methylation is a possible transformation pathway for tin(II) in the environment.

Introduction

The widespread use of organotin compounds as antifouling paints, pesticides, preservatives and stabilizers in agriculture and industry has resulted in serious pollution of the environment with tin.^{1–3} Toxicological studies have demonstrated that organotin compounds are neurotoxic, immunotoxic, and endocrine disruptors.^{3–8} Therefore, the fate of organotin compounds in the environment is of great concern. Organotin compounds can be degraded into their inorganic forms in the environment *via* abio- or bio-processes.^{9–13} However, inorganic tin can also be transformed into methyltin in the environment,^{14–16} which leads to a significant increase in its toxicity to animals and human beings.¹⁷

Recent developments in the speciation analysis of tin compounds have been greatly supportive of studies that are involved with their toxicities, metabolism, and environmental behavior. Separation techniques such as gas chromatography (GC) or high performance liquid chromatography (HPLC) have been successfully hyphenated with various detectors that included FPD,^{18–20} MS,^{21,22} or ICP-MS.^{23–26} Prior to tin speciation analysis, sample extraction and derivatization are often

necessary, especially for GC separation. Herein, sodium tetraethylborate has been recommended as a good ethylation derivative for liquid samples as it can be directly derivatized in aqueous solutions. The solid phase microextraction (SPME) technique is featured with solvent-free and low solvent consumption for sample preparation. The integration of tetraethylborate derivatization, SPME, and sensitive detectors (FPD or MS) could diversify the armoury for the speciation analysis of methyltin compounds,²⁷ which will be helpful in the understanding of the biogeochemical behavior of tin in the environment.

Inorganic tin(II) can be chemically methylated by some methyl donors that possibly exist in the environment, *e.g.* methylcobalamine and methyl iodide.^{28–31} Biological methylation also has a significant contribution to the methyltin compounds in the environment. Both estuary microorganisms and marsh grass exhibited the abilities to convert inorganic tin into methylated counterparts.^{32,33} Guard *et al.* also demonstrated that trimethyltin compounds can be further methylated in estuarine sediments.³⁴ Although previous studies have proved that methylation of inorganic tin can happen in the environment through either chemical or biological pathways, photochemical methylation of inorganic tin has been rarely reported. Previous studies have demonstrated the photochemical methylation of mercury and arsenic in aqueous solutions.^{35,36} With respect to tin, the photo-irradiation was only investigated for its influence on the reaction between inorganic tin(II) and ethanol.³⁷ However, the ubiquity and potential methyl donors for the photochemical methylation of inorganic tin remain to be explored.

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The objective of this study was to use the sophisticated HP-SPME–GC–FPD or –MS techniques to study the photochemical methylation of inorganic tin(II) in aqueous solutions. Firstly, the photochemical methylation was simulated between tin(II) and eight organic compounds with different chemical structures in aqueous solutions under ultraviolet (UV) irradiation. The influences of pH and salinity on the photochemical methylation of tin(II) by acetone were investigated as well. In addition, the absorption spectrogram was utilized to identify the compounds that can act as the photochemical methyl donors towards tin(II) under irradiation by sunlight.

Experimental section

Materials

All reagents were obtained commercially and used without further purification. The standards of trimethyltin chloride (98%), dimethyltin (97%) and monomethyltin (97%) were obtained from Aldrich Chem. Co. (USA). Sodium tetraethylborate (98%) was purchased from Strem Chemicals (USA). Stannous chloride (98%), propionic acid (99%) and *N,N*-dimethylformamide (analytical purity) was obtained from Beijing Yili Company of Chemical Reagents (China). Isopropyl alcohol (99.7%), acetic acid (99.5%) and acetone (99.5%) were purchased from Beijing Chemical Plant (China). Dimethyl sulfoxide (analytical purity) was obtained from Tianjin Fuchen Company of Chemical Reagents (China). Pyruvic acid was purchased from Sinopharm Chemical Reagent Company (China). *tert*-Butyl alcohol (99%) was obtained from PHENTEX CORP. (USA). De-ionized water (EASY pure LF, Barnstead Co., USA) was used throughout the experiments unless otherwise mentioned.

Instruments

A GC-9A gas chromatograph (Shimadzu, Japan) equipped with a capillary column (HP-1, 25 m $\times$ 0.32 mm i.d. $\times$ 0.17 μ m) was used for the separation of methyltin compounds. A laboratory-made flame photometric detector using quartz surface-induced luminescence (QSIL-FPD) was used for the detection of methyltin compounds. Its configuration, application, and evaluation have been previously reported.^{38,39} An Agilent 5793N GC–MS equipped with a capillary column (HP-5, 30 m $\times$ 0.25 mm i.d. $\times$ 0.25 μ m) was used to acquire the molecular structure information of the photochemical methylation products of tin(II). Detailed operation parameters for GC–QSIL–FPD and GC–MS have been described in previous literature.⁴⁰ Absorption spectrograms of methyl donors were obtained using an UV 3310 spectrophotometer (Hitachi, Japan).

Photochemical reaction

A reaction apparatus was designed to study the photochemical methylation of tin(II) in aqueous solution under UV irradiation. The photochemical reactor included a low-pressure Hg vapor UV lamp (254 nm, 11 W, Beijing Research Institute for Light and Electric Instrument, Beijing, China) wrapped by a 4.5 m length of PTFE tubing (0.8 mm i.d., 1.5 mm o.d., Kaisheng Insulation Material Company, Shenzhen, China). In general, photochemical reactions were performed in 10 mL of aqueous solution. Ten

μ L of tin(II) stock solution (0.2 M in 2 M HCl) was mixed with 100 μ L of the methyl donors, and the final concentration of tin(II) in the reaction solution was 0.2 mM. The salinity and pH of the reaction solution were adjusted using sodium hydroxide (0.1 M) and sodium chloride (5.0 M), respectively. In order to remove the dissolved oxygen, the reaction solution was placed in an ultrasonic bath, and simultaneously bubbled with nitrogen gas prior to the reaction. The reaction solution was driven through a photochemical reactor using a peristaltic pump (D100C, Huxi Instrumental Company, Shanghai, China). The reaction time was approximately 6 min, which was calculated according to the flow rate and length of PTFE tubing in the reactor. The formation of methyltin compounds in the reaction solution was detected using HP-SPME–GC–FPD or –MS. Moreover, the photochemical methylation of tin(II) by pyruvic acid was also performed under irradiation by sunlight. Ten μ L of tin(II) stock solution was mixed with 100 μ L of pyruvic acid in a conical flask. The pH of the solution was adjusted to 5.0, and the salinity to 0.1 M. The conical flask was sealed using parafilm, and was exposed to sunlight for four days at ambient temperature.

Speciation analysis of methyltin compounds

Methyltin products were directly derivatized with sodium tetraethylborate in the aqueous solution, and extracted from the headspace using SPME. The derivatization method was as follows. Three mL of 0.2 M acetic–acetate buffer (pH 4.0) and 17 mL of de-ionized water were added into a 50 mL glass vial wrapped with aluminium foil, and then was mixed with 50 μ L of reaction solution. Following the addition of 200 μ L of sodium tetraethylborate (1%, w/v), the vial was immediately sealed with a cap wrapped with aluminium foil. A commercially available PDMS coated fiber (100 μ m, Supelco, Bellefonte, PA, USA) was inserted into the headspace in the glass vial for the extraction of methyltin derivatives. The solution was stirred with a PTFE coated magnetic stirrer. The fiber was exposed in the headspace above the solution for 20 min, and thereafter inserted into the GC injector port for thermal desorption (1 min).

Results and discussion

Identification of methylation products

Eight organic compounds including acetone, pyruvic acid, acetic acid, propionic acid, dimethyl sulfoxide, *N,N*-dimethylformamide, *tert*-butyl alcohol, and isopropyl alcohol were investigated as possible methyl donors for the photochemical methylation of tin(II) in the aqueous solutions under UV irradiation. The reaction solutions containing methylation products of tin(II) were analyzed using HP-SPME–GC–FPD. Fig. 1 shows the chromatograms of methyltin standard substances and methylation products of tin(II). Based on a comparison of the retention times of the methylation products and those of the standard substances, the major products were determined as being MMT and DMT, and a low level of TMT was also sporadically produced under certain conditions, e.g., the methylation reaction of tin(II) and acetone in solutions of pH 4.9 and 8.9.

The GC–FPD technique cannot provide information on the molecular structure of methylation products. Therefore, the reaction solutions were further analyzed using HP-SPME–GC–MS in

Fig. 1 GC-FPD chromatograms of standard substances and the reaction products. 1, standard substances, 2, methylation products, TMT, DMT and MMT. The methyltin standards and reaction solutions were derivatized by sodium tetraethylborate. The derivatives were analyzed using GC-FPD.

order to reconfirm the photochemical methylation products of tin(II). The mass spectra of ethylation-derivatized methylation products are presented in Fig. 2. Characteristic fragment ions of ethylation derivatives of methylation products were as follows: m/z 193 (SnMeEt_2^+), 165 (SnMeEt^+), 135 (SnMe^+), and 121 (Sn^+) for MMT and m/z 179 (SnMe_2Et^+), 151 (SnMe_2^+), 135 (SnMe^+), and 121 (Sn^+) for DMT, which were highly identical to those obtained from their respective standards. Due to the low concentration of

Fig. 2 Mass spectra of ethylation derivatives of methyltin products. The identities of MMT and DMT were the same as those in Fig. 1. m/z indicates the ratio of mass to charge. Ethylation derivatives of methyltin products were analyzed using GC-MS.

TMT in the reaction solution, TMT products could not be detected by HP-SPME-GC-MS.

Table 1 shows the concentrations of methyltin products in the reaction solutions that resulted from the photochemical methylation reactions of tin(II) and different methyl donors under the same conditions (pH = 2.8 and salinity = 0.2 M). Methyl donors exhibited varying methylation reactivities towards tin(II) in aqueous solution under UV irradiation. According to their chemical structures, methyl donors can be categorized into four groups which consisted of $\text{CH}_3\text{-C=O}$ (acetone, pyruvic acid, acetic acid and propionic acid), $\text{CH}_3\text{-S=O}$ (dimethyl sulfoxide), $\text{CH}_3\text{-N}$ (*N,N*-dimethylformamide), and $\text{CH}_3\text{-C-OH}$ (*tert*-butyl alcohol and isopropyl alcohol). Their methylation reactivities were presented in descending order, pyruvic acid > dimethyl sulfoxide > acetone > *tert*-butyl alcohol and acetic acid > isopropyl alcohol > *N,N*-dimethylformamide > propionic acid. In general, the compounds were highly reactive when they contained the methyl group directly adjacent to a carbonyl or sulfide group. Pyruvic acid, which contains two carbonyl groups, had the highest reactivity among the investigated organic compounds.

Effects of pH value and salinity

Acetone, which has a typical carbonyl structure, was selected as the model compound to study the effects of pH and salinity on the photochemical methylation of tin(II) in aqueous solution under UV irradiation. Our results demonstrated that pH and salinity of reaction solutions had a great influence on the photochemical methylation of tin(II) (Fig. 3a and b). Total yield of methyltin compounds was highest at pH 5.0, and was low under both strongly acidic and basic conditions. In regard to each of the methyltin species, the yield of MMT was highest at pH 2.8, but the yields of DMT and TMT peaked at pH 5.0. The increase in the pH of reaction solutions also caused the conversion of the predominant product from MMT to DMT. The range of salinity in this study was from 0 to 1.0 M, which covered the salinity levels found in the aquatic environment (e.g. about 0.5 M for seawater). Both the yield of MMT and total yield of methyltin compounds peaked at a salinity of 0.5 M in the pH 2.8 solution, as shown in Fig. 3b. However, the yield of DMT was only slightly influenced by the salinity under the above conditions.

Table 1 Concentrations of methyltin products in the reaction solutions^{a,b}

	MMT	DMT	TMT	Total methyltin
Acetone	220.53	67.96	N.D.	288.49
Pyruvic acid	1256.35	23.49	N.D.	1279.84
Acetic acid	20.83	15.94	N.D.	36.77
Propionic acid	N.D.	N.D.	N.D.	N.D.
<i>tert</i> -Butyl alcohol	37.05	3.17	N.D.	40.22
Isopropyl alcohol	17.73	5.81	N.D.	23.53
<i>N,N</i> -Dimethylformamide	9.16	4.98	N.D.	14.14
Dimethyl sulfoxide	707.21	155.45	N.D.	862.66

^a Reaction conditions: salinity of 200 mM, pH 2.8, and 0.2 mM inorganic tin(II). ^b The unit is ng mL⁻¹.

Fig. 3 Influence of pH (a) and salinity (b) on the photochemical methylation of tin(II) by acetone in aqueous solution. In (a), the left Y axis shows the concentrations of MMT, DMT or total methyltin, and the right Y axis shows the concentration of TMT.

Analysis of absorption spectra

Fig. 4 shows the absorption spectrograms of methyl donors. The donors were scanned at wavelengths between 190 nm and 450 nm. The absorption spectrograms of methyl donors can not

Fig. 4 Absorption spectrograms of methyl donors. The donors were scanned at wavelengths between 190 nm and 450 nm.

only indicate their photochemical reactivities towards tin(II), but can also be helpful to judge under what conditions the organic compound can perform as a photochemical methyl donor in the methylation of tin(II). Under the same conditions, the donors with high absorbance can generally exhibit higher reactivities than those with low absorbance, except for dimethylformamide. For instance, pyruvic acid and dimethyl sulfoxide produced more methyltin compounds than the others because of their stronger absorption to UV light. Pyruvic acid is ubiquitous in the environment due to its wide application in agriculture, medicine, and cosmetics, as well as the important output of anaerobic metabolism of glucose known as glycolysis.^{41–43} Interestingly, the absorption spectrogram of pyruvic acid showed an absorption peak at 330 nm, which probably implied that pyruvic acid could be a potential methyl donor under irradiation by sunlight. The subsequent experiment indeed demonstrated that MMT can be detected in the solution containing tin(II) and pyruvic acid under irradiation by sunlight, and its yield reached 0.3% after exposure to sunlight for 4 days. This finding had an important environmental implication, which demonstrated that the photochemical methylation of tin(II) can probably occur in the environment under irradiation by sunlight although the present simulation was conducted in the lab.

Discussion

Organic methyl donors can be protonated in acidic solution.⁴⁴ Under UV irradiation, the protonated methyl donors can produce the carbonium methyl group in aqueous solution.⁴⁵ Subsequently, the carbonium methyl group can be transferred to tin(II) accompanying by the oxidation of tin(II) to MMT(IV). The reaction mechanism is shown in eqn (1)–(4) in Fig. 5.

The chemical structures of methyl donors had a strong influence on the formation of the carbonium methyl group in aqueous solution under light irradiation. Thus, the production of methyltin compounds varied among methyl donors. The carbonium

Fig. 5 Schematic showing photochemical methylation mechanisms of tin(II) under UV irradiation. $h\nu$ indicates UV irradiation.

methyl group was more easily produced from the methyl group directly connected to carbonyl or sulfoxide (double bond) compared with the others (single bond), *e.g.* alcohols. In the case of pyruvic acid, more than one carbonyl group in its structure facilitated the formation of a carbonium methyl group. As a result, pyruvic acid showed the highest ability to methylate tin(II) among the methyl donors in this study. A comparison of the bond properties of methyl donors gives more insight into the influence of chemical structure on the photochemical methylation of tin(II). Mean bond length and bond energy are 0.181 nm and 275 kJ mol⁻¹ for C–S bond, and 0.154 nm and 348 kJ mol⁻¹ for C–C bond.⁴⁶ Apparently, the lower bond energy of C–S bond eased the detachment of the carbonium methyl group from the methyl donor. As predicted, dimethyl sulfoxide showed higher photochemical reactivity than acetone under UV irradiation. Moreover, the methylation reactivity of alcohol compounds correlated positively with the number of methyl groups in the α -position. *tert*-Butyl alcohol (α -methyl, 3) exhibited higher reactivity than isopropyl alcohol (α -methyl, 2).

The pH of the solution exerts a significant influence on the photodegradation of organic compounds^{47–49} and the photo-methylation of mercury.³⁶ In the present study, the pH of the reaction solutions was highly associated with the major product from the photochemical methylation between tin(II) and acetone under UV irradiation (Fig. 4a). The strong acidity favored the formation of a carbonium methyl group from acetone under UV irradiation (eqn (1) in Fig. 5). Consequently, the methylation of tin(II) was completed mainly through an oxidative transfer of carbonium methyl, as a result of which MMT was the predominant methylation product. However, the predominant product changed from MMT to DMT as the pH of reaction solution increased. In aqueous solutions with a low acidity, acetone produced the free methyl radical under UV irradiation, as shown in eqn (5) and (6) in Fig. 5. Following the transfer of two free methyl radicals, most of the tin(II) was transformed into DMT. Moreover, the pH also affected the redox potential of tin(II) in aqueous solution. The redox potential of tin is low in solutions with high pH, which may facilitate the oxidative methylation of tin(II). Nevertheless, the combined effects of pH on the redox potential and the photochemical formation of free methyl groups led to the highest total yield of methyltin products at pH 5.0.

Conclusion

Headspace SPME coupled with GC-FPD or GC–MS techniques was helpful in identifying the photochemical methylation products of tin(II) in aqueous solutions, and demonstrated the plausibility of the photochemical methylation of tin(II). Photochemical methylation of tin(II) was closely associated with the chemical structures of methyl donors, and the salinity and pH value of the reaction system. Strikingly, pyruvic acid can methylate tin(II) under irradiation by sunlight, implying that the photochemical methylation of tin(II) is a possible pathway in the environment.

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