Identification of mercury methylation product by tert-butyl compounds in aqueous solution under light irradiation

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ABSTRACT

The methylation of mercury (Hg) is of great concern as methylmercury (MeHg), the most toxic species, is produced. This study examined the possibilities of tert-butyl compounds (tert-butyl alcohol (TBA) and tert-butyl hydroperoxide (TBH)) and other alcohols serving as methyl donors for Hg photo-methylation under light irradiation. The yield of MeHg varied among the methyl donors, and it was also significantly influenced by salinity and pH. MeHg could be generated in the presence of TBH under visible light irradiation. The hydroxyl radical ($\cdot\text{OH}$) was found to promote MeHg production at low levels, but degrade MeHg in excess. The photo-production of MeHg was tentatively proposed via the complexation of Hg and methyl donors, the formation of an intermediate ($\text{O}(\text{Hg})(\text{CH}_3)_3$), and the intramolecular methyl transfer from methyl donors to Hg. This study implicates photoreactions between Hg and organic pollutants in understanding the fate and transformation of Hg in the aquatic environment.

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1. Introduction

Hg pollution is of great concern because mercuric compounds can accumulate along the food chain with high toxicity to animals and humans (Crespo-Lopez et al., 2005; van Vliet et al., 2008; Zhang et al., 2010). Mercury can be detected in various environmental compartments, such as the atmosphere, water, sediments, and soils (Hall et al., 2009; Kieber et al., 2008; Muir et al., 2009; Obrist et al., 2011). Mercury is released into the environment mainly in its inorganic forms. However, the methylation of inorganic Hg is ubiquitous in the environment (Jonsson et al., 2012; Parks et al., 2013), which consequently leads to a significant increase in Hg toxicity. Methylmercury is considered to be one of the most toxic Hg species present in the environment (Darbieu, 1993; Grandjean, 2007), thus posing a great public health risk (Diez, 2009).

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Many efforts have been made to elucidate how MeHg is produced in the environment via biotic and/or abiotic pathways (Celo et al., 2006; Jensen and Jernelov, 1969). Microorganisms, such as sulfate-reducing bacteria and iron-reducing bacteria (Bridou et al., 2011; Fleming et al., 2006), are the major microbial contributors to MeHg production in the environment. However, the abiotic methylation of Hg, which has been validated as an important pathway for MeHg production (Hammerschmidt et al., 2007), has not been studied thoroughly. Abiotic methylation of inorganic Hg by dissolved organic matter (DOM) under solar radiation is considered an important source of MeHg in lakes (Siciliano et al., 2005). Other methyl donors associated with Hg methylation in the environment, such as methylcobalamin, humic substances, methyltin compounds, and acetate, have also been reported (Cerrati et al., 1992; Chen et al., 2007a; Conaway et al., 2010; Weber et al., 1985).

Photoreactions play a key role in the transformation and biogeochemical cycling of elements in the environment (Guo et al., 2005; Hamilton et al., 2003; Moore, 2008). Elements (e.g., As, Se, and Sn) are photochemically transformed in the presence of low-molecular-weight organic compounds (LMWOCs) (Chen et al., 2012; Guo et al., 2003; McSheehy et al., 2005).

Photoreactions under solar or ultraviolet (UV) irradiation can contribute to both the production and degradation of MeHg in aquatic environments (Lehnherr and Louis, 2009; Li et al., 2010; Siciliano et al., 2005). In the presence of various LMWOCs, such as acetic acid, aldehydes, ketones, propionic acid, and ethanol, Hg photo-methylation was observed in aqueous solution under solar or UV irradiation (Yin et al., 2012). It is widely believed that the repertoire of methyl donors for Hg photo-methylation can be expanded continuously. Moreover, it is worth investigating the effects of other concurrent photoreactions on Hg methylation, for example, the photo-formation of reactive oxygen species (ROS).

Methyl tert-butyl ether (MTBE), in place of alkylated lead, has been used as a gasoline additive in the United States since the late 1970s. The level of MTBE in the environment is elevated due to accidental spill and leakage from underground tanks and transfer pipelines (Ayotte et al., 2008; Williams and Pierce, 2009). MTBE is highly hydrophilic; thus, it can readily dissolve in water and rapidly penetrate soils and aquifers. Consequently, MTBE and its major degradation product (tert-butyl alcohol, TBA) are often detected at the level of microgram per liter to milligram per liter in aquatic environments (Rosell et al., 2003; Schmidt et al., 2004). Furthermore, TBA, as a scavenger of $\cdot\text{OH}$, can produce methyl groups for methylating elements in the presence of $\cdot\text{OH}$ (Vonpiechowski et al., 1992). Therefore, TBA was selected as a methyl donor for inorganic Hg under UV irradiation.

The objectives of this study were to investigate the photo-methylation of Hg by TBA and tert-butyl hydroperoxide (TBH) in aqueous solution under the irradiation of UV or visible light, and to examine the influences of potential factors (salinity, pH, methyl donors, and hydroxide radical) on the photo-methylation of Hg. A tentative mechanism was proposed to elucidate the photo-generation of MeHg by tert-butyl compounds under UV irradiation.

2. Materials and methods

2.1. Chemicals

Monomethylmercury chloride and mercury chloride were purchased from Merck ($\geq 98\%$, Darmstadt, Germany). Stock solutions of monomethylmercury and inorganic mercury standards (1 mg mL^{-1} as Hg) were prepared by dissolving appropriate amounts of methylmercury chloride in methanol and mercury chloride in 10% (v/v) hydrochloric acid, respectively. Their working solutions were prepared daily by serial dilution in deionized water. Isopropyl alcohol (99.7%) was purchased from Beijing Chemical Reagent (Beijing, China). TBA (99%) and ethanol (100%) were obtained from Phentex Corp. (USA). TBH (70% aq.) was purchased from Alfa Aesar. All other chemicals were of analytical grade or higher. The mobile phase was prepared with deionized water obtained from a Barnstead ultrapure water system (Barnstead International, Dubuque, IA, USA).

2.2. Photo-methylation reactions of Hg under UV irradiation

The photo-methylation of Hg was conducted in a self-designed flow-through photoreactor equipped with a low-pressure Hg vapor UV lamp (254 nm, 11 W, Beijing Research Institute for Light and Electric Instruments, Beijing, China) wrapped with a 4.5-m polytetrafluoroethylene (PTFE) tubing (0.8 mm i.d. and 1.5 mm o.d., Kaisheng insulation material company, Shenzhen, China) (Yin et al., 2012). The reactor was enclosed in a sealed box for safety purposes. Photoreactions were conducted in a 10-mL aqueous solution containing inorganic Hg (500 ng mL^{-1}) and methyl donors (200 mM for TBA, isopropyl alcohol and ethanol; 20 mM for TBH).

The salinity and pH of the reaction solution were adjusted using sodium chloride (5.0 M) and sodium hydroxide (0.1 M), respectively. The reaction solution was passed through the reactor using a peristaltic pump (D100C, Huxi Instrumental Company, Shanghai, China). According to the flow rate, the reaction time was estimated to be approximately 6 min. The effluent from the reactor was analyzed directly using high-performance liquid chromatography hyphenated with atomic fluorescence spectrometry (HPLC-AFS) or inductively coupled plasma mass spectrometry (HPLC-ICPMS) techniques.

2.3. Photo-methylation reactions of Hg under visible light irradiation

The photo-methylation reactions of Hg under visible light irradiation were also carried out in glass tubes filled with 10 mL of aqueous solution containing inorganic Hg (100 ng mL^{-1}) and methyl donors (TBA (110 mM), ethanol (180 mM), and TBH (7.1 mM)). The pH and salinity of the reaction solutions were not adjusted ($\text{pH} = 7.1$). One group of reaction solutions were directly irradiated with natural sunlight in the laboratory, whereas the other group was placed in an incubator with a light intensity of $8000\text{ }\mu\text{mol m}^{-2}\text{ s}^{-1}$ ($390\text{--}700\text{ nm}$) at $25\text{ }^{\circ}\text{C}$ with a light/dark cycle of 14 h/10 h. After irradiation for 7 days, the reaction solutions were prepared using a MeHg extraction method reported in the literature (Yin et al., 2008), and these were subjected to HPLC-ICPMS analysis.

2.4. Instruments and analytical methods

Hg speciation analysis in the reaction solutions were carried out using the HPLC-AFS technique, as described in the literature (He et al., 2006). In brief, the HPLC system consisted of a quaternary pump (P680 HPLC Pump, Dionex, Sunnyvale, CA, USA), a Rheodyne model 7715i injector (Rheodyne, Cotati, CA, USA), and an Agilent Zorbax ODS column ($150 \times 4.6\text{ mm}$, $5\text{ }\mu\text{m}$). The mobile phase contained 5% (v/v) methanol (CH_3OH), 60 mM ammonia acetate (NH_4Ac), and 0.1% (v/v) 2-mercaptoethanol ($\text{pH} 6.8$). The flow rate of the mobile phase was 0.4 mL min^{-1} . A $20\text{-}\mu\text{L}$ aliquot of the reaction solution was injected. MeHg in the effluent from the HPLC system was decomposed into inorganic Hg by 0.5% $\text{K}_2\text{S}_2\text{O}_8$ in 10% (v/v) HCl under UV irradiation. After 0.5% KBH_4 was introduced into a 0.2% KOH solution, cold vapor of Hg was generated and thereafter detected by an AF-610A nondispersive atomic fluorescence spectrometer (Beijing Rayleigh Analytical Instrument Co., China).

An HPLC-ICPMS technique was used to further confirm the presence of MeHg in the reaction solutions. Herein, MeHg and inorganic Hg were separated on an Agilent Zorbax XDB column ($50 \times 2.1\text{ mm}$, $5\text{ }\mu\text{m}$). The mobile phase is similar to that used for HPLC-AFS. The effluent from the analytic column was directly introduced into a 7500ce ICPMS instrument (Agilent Technologies, Santa Clara, CA, USA). The ICPMS was operated at a radiofrequency (RF) power of 1500 W , a plasma gas flow rate of 15 L min^{-1} , an auxiliary gas flow rate of 0.22 L min^{-1} , a nebulizer gas flow rate of 0.82 L min^{-1} , and a dwell time of 100 ms . Mercury was monitored at $m/z 202$.

2.5. Electron paramagnetic resonance spectrometry

Following the photoreaction, the reaction solutions containing $1\text{ }\mu\text{g mL}^{-1}$ of HgCl_2 (as Hg), 1% NaCl (w/v), 0.1 M methyl donors, and 50 mM of the spin-trapping agent 5,5-dimethyl-1-pyrroline N-oxide (DMPO) were immediately analyzed using a Bruker E-500 electron paramagnetic resonance (EPR) spectrometer. The EPR spectrometer was operated at 9.774 GHz using a cavity equipped with a Bruker Aquax liquid sample cell. The typical

parameters of EPR were as follows: scanning range (100 G), field set (3480 G), time constant (40.96 ms), scanning time (83.89 s), modulation amplitude (1.0 G), modulation frequency (100 kHz), receiver gain (1.25×10^4), and microwave power (12.66 mW).

2.6. UV-visible spectrometry

A Hitachi U-3310 spectrophotometer was used to determine the absorbance spectrum of reaction solutions. Three solutions containing methyl donors (0.1 M), HgCl_2 (100 ng mL⁻¹), or the mixture of methyl donor and HgCl_2 were scanned. The scanning wavelength ranged from 190 to 700 nm. The sampling interval was 1.0 nm, and the slit width was set at 2 nm.

3. Results and discussion

3.1. Identification of MeHg

MeHg and inorganic Hg were separated well on an Agilent Zorbax ODS column, with the subsequent detection of Hg cold vapor using the AFS technique (He et al., 2006). Fig. 1 shows the typical HPLC–AFS chromatograms of Hg standards and the reaction solution (inorganic Hg and TBA). The retention times of MeHg and inorganic Hg were 17.1 and 20.3 min, respectively. The detection of MeHg in the reaction solution indicated that inorganic Hg can be transformed into MeHg, as well as other alcohols (e.g., isopropyl alcohol and ethanol), in the presence of TBA and TBH under UV irradiation. The HPLC–ICPMS technique was used to confirm the identity of the photo-methylation product of inorganic Hg under UV irradiation based on the mass-to-charge ratio of Hg. The result also showed that MeHg can be produced via the photo-methylation of inorganic Hg by TBA and TBH under UV irradiation.

3.2. The effects of different influencing factors

The pH and salinity are widely considered to be important factors influencing element methylation in aqueous solution (Chen et al., 2006, 2007a,b, 2012; Yin et al., 2012). Therefore, the influences of salinity and pH on the photo-methylation of inorganic Hg were also investigated in the present study, and the results are shown in Fig. 2. Both pH and salinity exhibited significant effects on the production of MeHg in aqueous solution under UV irradiation. At a constant salinity of 0.2 M, the concentration of MeHg decreased with increasing pH. The salinity used in this study ranged from 0 to 1.0 M, which covered all possible salinities

Fig. 1. HPLC–AFS chromatograms of Hg standards (100 ng mL⁻¹) and Hg species in reaction solution. The reaction solution was obtained from the reaction between inorganic Hg (500 ng mL⁻¹) and TBA (200 mM).

Fig. 2. Effects of pH (A) and salinity (B) on the photo-methylation of inorganic Hg by TBA in aqueous solution under UV irradiation.

observed in aquatic environments (e.g., about 0.5 M for the seawater). The concentration of MeHg was highest at a salinity of 0.5 M with a constant pH of 5.3. The equilibria between free Hg^{2+} and its complexes with some anions (e.g., OH^- and Cl^-) as the functions of pH and salinity exist in the aqueous solution. The complexation of Hg^{2+} with anions reduces the availability of Hg for methyl donors (Chen et al., 2007a; Gardfeldt et al., 2003; Yin et al., 2012). Consequently, the production of MeHg decreased under the conditions of high pH and excess Cl^- . However, the low level of Cl^- promoted the production of MeHg in the aqueous solution, which probably resulted from the formation of Cl_2^- facilitating the photolysis of LMWOCs under UV irradiation (Liu et al., 2009). Our results implied that the photo-methylation rate of inorganic Hg changed considerably among various hydrospheres due to great differences in their pH and salinity.

TBA can serve as a scavenger of the hydroxyl radical ($\cdot\text{OH}$) (Vonpiechowski et al., 1992), and thus it is degraded by $\cdot\text{OH}$ via an intermediate of the alkoxyl radical ($\cdot\text{OC}(\text{CH}_3)_3$) (Cederbaum et al., 1983a). The generation of hydroxyl radical ($\cdot\text{OH}$) could substantially affect the photo-methylation of inorganic Hg by TBA in the aqueous solution. Fig. 3 demonstrates that the addition of hydrogen peroxide (H_2O_2) initially increased the production of MeHg; thereafter, excess H_2O_2 over TBA drastically reduced MeHg production. The interaction between TBA and $\cdot\text{OH}$ can initially facilitate the formation of alkoxyl radical ($\cdot\text{OC}(\text{CH}_3)_3$), which is beneficial to MeHg production. This may imply that the methylation of Hg by LMWOCs can be promoted by a certain level of $\cdot\text{OH}$ even without UV irradiation, such as Fenton reactions,

Fig. 3. Effect of hydrogen peroxide on the photo-methylation of inorganic Hg by TBA in aqueous solution under UV irradiation.

iron-catalyzed oxidation of ascorbic acid, or an enzymatic system, for example, the coupled oxidation of xanthine by xanthine oxidase (Cederbaum et al., 1983b; Hwang et al., 2010; Li et al., 2012). However, as the molar ratio of H₂O₂ to TBA was higher than 0.5, the generation of excess $\cdot\text{OH}$ under UV irradiation caused the degradation of MeHg (Chen et al., 2003; Lehnher and Louis, 2009).

3.3. Yield of MeHg by various methyl donors

Several other small molecular organic compounds, including isopropyl alcohol, ethanol, and TBH, were also investigated as possible methyl donors under UV irradiation. The concentration and yield of MeHg are tabulated in Table 1. The yield of MeHg varied greatly for different methyl donors. The MeHg yield increased with the amount of methyl groups of the alcohols. Under the same reaction condition, TBA could produce over eight times more MeHg than isopropyl alcohol or ethanol could. In comparison with alcohols, the yield of MeHg was highest in the presence of TBH among all investigated organic compounds in this study, although the initial concentration of TBH was 10 times lower than other compounds.

Inorganic Hg was also photo-methylated by the methyl donors mentioned previously irradiation of visible light or sunlight. The result demonstrated that MeHg could only be detected in the presence of TBH under the irradiation of visible light or sunlight (Fig. 4), with significantly lower initial concentrations of both inorganic Hg (100 ng mL⁻¹) and TBH (7.1 mM) than under UV irradiation. MeHg accounted for approximately 0.05% of total Hg in the reaction solution.

Table 1
MeHg yield from photo-methylation of inorganic Hg by different methyl donors under UV irradiation^a.

Methyl donors (initial concentration)	Concentration of MeHg (ng mL ⁻¹)	Yield (%)
TBH (20 mmol L ⁻¹)	452	90.4
TBA (200 mmol L ⁻¹)	173	34.5
Isopropyl alcohol (200 mmol L ⁻¹)	21.2	4.3
Ethanol (200 mmol L ⁻¹)	17.6	3.5

^a Reaction conditions were as follows: a salinity of 0.2 mol L⁻¹, a pH of 5.3, and an initial concentration of inorganic Hg of 500 ng mL⁻¹.

Fig. 4. HPLC-ICPMS chromatogram of Hg species in reaction solution of inorganic Hg and TBH under visible light irradiation.

Fig. 5. UV-visible absorbance spectrum of TBA. The final concentrations of TBA and TBH were 0.1 M, and the concentration of HgCl₂ was 100 ng mL⁻¹ as Hg.

Fig. 6. EPR spectrum of methyl and hydroxyl radicals in the reaction solutions containing Hg and TBH or ethanol under UV irradiation. The experiments were conducted in solutions containing 1 $\mu\text{g mL}^{-1}$ (as Hg) of HgCl₂, 1% NaCl (w/v), 0.1 M methyl donors, and 50 mM of the spin-trapping agent 5,5-dimethyl-1-pyrroline N-oxide (DMPO). The control denotes the solution only containing Hg and DMPO.

3.4. Mechanism of photochemical methylation of Hg

The exact mechanism responsible for the photo-methylation of Hg by LMWOCs remains a matter of debate (Akagi et al., 1974; Hayashi et al., 1977). The formation of Hg^{2+} –LMWOC complexes is considered a key step preceding Hg photo-methylation in aqueous solution under UV irradiation (Akagi et al., 1974; Yin et al., 2012). The absorbance of TBA in the UV–visible spectrum was scanned using a Hitachi U-3310 spectrophotometer (Fig. 5A). The results demonstrated clear increase in the absorbance intensities of TBA and a shift of their light absorbance wavelength to the red region after the addition of Hg^{2+} , which supported the formation of complexes of Hg^{2+} and TBA. In fact, Hg^{2+} , as a strong Lewis acid, can complex with Lewis bases, for example, ketone and organic acid (Gardfeldt et al., 2003; King et al., 2002; Yin et al., 2012). Moreover, the low MeHg yield under irradiation of visible light or sunlight can be explained by the weak absorbance of methyl donors of visible light.

Methyl radical ($\cdot\text{CH}_3$) and $\cdot\text{OH}$ were also determined using the EPR technique, with DMPO as a trapping agent of free radicals. This experiment can further illustrate whether MeHg is generated

via a transfer of free methyl radicals from methyl donors to Hg. TBH and ethanol were selected as the model compounds for EPR analysis because of the maximal difference in their respective MeHg yields. Fig. 6 shows the EPR spectrum of methyl and hydroxyl radicals in the reaction solutions containing Hg and TBH or ethanol under UV irradiation. The results demonstrated that both TBH and ethanol could produce $\cdot\text{CH}_3$ and $\cdot\text{OH}$ in aqueous solution under UV irradiation. However, the difference in the concentration of $\cdot\text{CH}_3$ between TBH and ethanol was not consistently negligible as their respective MeHg yields varied greatly (Fig. 6). Therefore, the direct transfer of free methyl radical to Hg was not considered to be chiefly responsible for the photo-methylation of Hg by LMWOCs in aqueous solution under UV irradiation (Yin et al., 2012).

Fig. 7A shows a tentative mechanism for the photo-methylation of Hg^{2+} by TBA and TBH in aqueous solution under UV irradiation. The complexes of Hg^{2+} and TBA or TBH could form an intermediate ($\cdot\text{O}(\text{Hg})\text{C}(\text{CH}_3)_3$) in the aqueous solution under UV irradiation. MeHg was produced from ($\cdot\text{O}(\text{Hg})\text{C}(\text{CH}_3)_3$) via an intramolecular transfer of the methyl group. The formation of $\cdot\text{O}(\text{Hg})\text{C}(\text{CH}_3)_3$ was a key step in the photo-production of MeHg under UV irradiation.

Fig. 7. Schematic diagrams of proposed mechanism responsible for the photo-methylation of inorganic Hg by TBA and TBH under UV irradiation. (A) Photo-formation of MeHg; (B) the effect of $\cdot\text{OH}$ on the photo-formation of MeHg.

The bond energy of O–O in TBH is much lower than that of O–H in TBA. Consequently, the weaker bond energy of TBH facilitated the formation of $\cdot\text{O}(\text{Hg})\text{C}(\text{CH}_3)_3$, and in turn a higher yield, in comparison with TBA. Moreover, the low level of $\cdot\text{OH}$ could be produced by the photolysis of H_2O_2 under UV irradiation, which considerably promoted the generation of $\cdot\text{O}(\text{Hg})\text{C}(\text{CH}_3)_3$ and in turn the production of MeHg (Fig. 7B). Thus, the formation of $\cdot\text{OH}$ was also considered to be an important factor influencing the photo-methylation of elements.

4. Conclusion

MeHg can be produced in the presence of TBH under visible light irradiation. The photoreactions of inorganic Hg and LMWOCs potentially contributed to the production of MeHg in aquatic environments. Interestingly, a low level of $\cdot\text{OH}$ could promote the photo-methylation of Hg, via capture by organic methyl donors, whereas excess $\cdot\text{OH}$ could lead to the degradation of MeHg. Photoreactions between Hg and organic pollutants are important in understanding the fate and transformation of Hg in the environment.

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