



## 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 ( $\cdot\text{O}(\text{Hg})\text{C}(\text{CH}_3)_3$ ), 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).

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).

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Photoreactions under solar or ultraviolet (UV) irradiation can contribute to both the production and degradation of MeHg in aquatic environments (Lehnerr 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 ( $1\text{ mg mL}^{-1}$  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 ( $500\text{ ng mL}^{-1}$ ) 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 ( $100\text{ ng mL}^{-1}$ ) 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 (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  $8000\text{ }\mu\text{mol m}^{-2}\text{ s}^{-1}$  (390–700 nm) at 25 °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 ( $\text{CH}_3\text{OH}$ ), 60 mM ammonia acetate ( $\text{NH}_4\text{Ac}$ ), and 0.1% (v/v) 2-mercaptoethanol (pH 6.8). The flow rate of the mobile phase was  $0.4\text{ mL min}^{-1}$ . A 20- $\mu\text{L}$  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%  $\text{KBH}_4$  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  $15\text{ L min}^{-1}$ , an auxiliary gas flow rate of  $0.22\text{ L min}^{-1}$ , a nebulizer gas flow rate of  $0.82\text{ L min}^{-1}$ , 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  $\text{HgCl}_2$  (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

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