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Aqueous photoreduction of oxidized mercury species in presence of selected alkanethiols

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Abstract

Mercury is a global environmental contaminant with severe toxicity impact. The chemical processes resulting in the transformation of oxidized mercury species (Hg^{2+}) to elemental mercury (Hg^0), greatly affects the fate and transport of mercury in the natural environment. We hereby provide the first study on the photo- chemistry of Hg^{2+} with selected alkanethiols (R-SH) as model compounds to represent thiols and thiol-type binding sites on humic substances in natural waters because of the common sulfhydryl functional group (–SH). Kinetic studies were performed using cold vapor atomic fluorescence spectroscopy (CVAFS), the formation of Hg^{2+}-thiol complexes ($Hg(SR)_2$) were confirmed by UV–visible spectrometry and Atmospheric Pressure Chemical Ionization-Mass Spectrometry (APCI-MS), and the reaction products were analyzed using Electron Impact-Mass Spectrometry (EI-MS) and Solid Phase Microextraction coupled with Gas Chromatography–Mass Spectrometry (SPME/GC–MS). Our results indicated that the photoreduction of Hg^{2+} by selected alkanethiols may be mediated by Hg^{2+}-thiol complexes to produce Hg^0. Under our experimental conditions, the apparent first order rate constants obtained for 1-propanethiol, 1-butanethiol, and 1-pentanethiol were $(2.0 \pm 0.2) \times 10^{-7}$ s^{-1}, $(1.4 \pm 0.1) \times 10^{-7}$ s^{-1}, $(8.3 \pm 0.5) \times 10^{-8}$ s^{-1}, respectively. The effects of ionic strength, dissolved oxygen or chloride ion on reaction rates were found to be minimal under our experimental conditions. The identified products of the reaction between oxidized mercury species with selected alkanethiols (C_3–C_5) were Hg^0 and disulfides (RS-SR). The potential environmental implications are herein discussed.

1. Introduction

Mercury is highly toxic environmental pollutant and due to its global importance and its cycling amongst different planetary eco- systems, it is a focus of many studies (Xiao et al., 1991; Nriagu, 1993; Gårdfeldt et al., 2003). Redox chemical processes of mercury controls its chemical speciation, bioavailability, toxicity and mobility in the environment (Borch et al., 2010). The photoreduction of Hg^{2+} to Hg^0 has two major environmental significances. One is to boost the amount of elemental mercury and thus, may lengthen the perceived lifetime of Hg^0 in the atmosphere (O'Driscoll et al., 2006). The other is to reduce the mercury burden in aquatic environment and may decrease the methylmercury production and bioaccumulation in fish (Gårdfeldt et al., 2001).

Photoreduction of Hg^{2+} has been observed in various natural water systems, albeit its mechanism is still poorly understood (Si and Ariya, 2008). The typical Hg^0 evasion rates observed in natural waters were in the range of 3–20 ng h^{-1} m^{-2} (Xiao et al., 1991; Rolfhus and Fitzgerald, 2004). The photochemical reduction observed in natural water samples were reported to be pseudo-first order with the rate constants of 0.2–1.0 h^{-1} (Poulain et al., 2004; O'Driscoll et al., 2006; Qureshi et al., 2010). To date, the reduction pathways identified in aqueous phase include the reduction of Hg^{2+} by sulfite (Munthe et al., 1991; van Loon et al., 2000), the photoreduction of mercuric hydroxide (Xiao et al., 1994a,b), and the photoreduction of Hg^{2+} by dicarboxylic acids (Gårdfeldt and Jons- son, 2003; Si and Ariya, 2008)and humic substances (Allard and Arsenie, 1991). Current atmospheric and aquatic models require the discovery of new reduction pathways to balance the oxidation of mercury in natural environment (Seigneur et al., 2006).

Nanomolar to micromolar levels of thiols have been reported in various surface water systems (Tang et al., 2000; Al-Farawati and van den Berg, 2001). Studies have shown that thiols can not only act as strong complexants (Krezel and Bal, 1999), but also undergo redox reactions with some trace metals (Jameson et al., 1988; Krezel et al., 2003). Relativistic quantum calculations on the $Hg(SH)_2(H_2O)_4$ molecule suggested that direct photoreduction of $Hg(SH)_2(aq)$ by sunlight is feasible (Stromberg et al., 1991). It has been implied that photoreduction of Hg-sulfide species in sea water, yielding Hg^0, could be an important source of mercury in the atmosphere (Dyrssen, 1988).

Recent experimental evidence has indicated the strong interactions between mercury and dissolved organic matter (DOM), most likely through covalent bonding at thiol-type functional groups in organic matter (Ravichandran et al., 1998). Xiao et al. has indicated that the photolysis rate of divalent mercury in aqueous solution containing humic substances is likely dependent on the binding sites of Hg^{2+} on DOM (Xiao et al., 1995). Factors reported to affect the photoreduction rate of Hg^{2+} by humic substances, include pH (Matthiessen, 1996; Matthiessen, 1998), the concentration of chloride ions (Allard and Arsenie, 1991), and dissolved oxygen (Allard and Arsenie, 1991; Pehkonen and Lin, 1998; Beucher et al., 2002; Ababneh et al., 2006).

Photolysis of mercury dibenzyl mercaptide at ppm levels in benzene solution using a mercury arc lamp resulted in 77% formation of Hg^0 and 23% formation of HgS(s) (Kern, 1953). Thermal decomposition of mercuric alkylthiolates resulted in the formation of elemental mercury and dialkyl disulfides (Hoffmann and Steinf-att, 1999).Despite the strong complexation reaction of Hg^{2+} with thiols, no study on the photochemical reaction between oxidized mercury species and thiols has been reported in the literature at environmental conditions. Because of the common sulfhydryl functional group (–SH), alkanethiols (R-SH) were used as a model to represent thiols and thiol-type binding sites on large DOM molecules such as humic substances in natural aquatic systems (Lin and Pehkonen, 1999). We hereby provided the first study on the photoreduction of Hg^{2+} by an extended set of alkanethiols (C_3–C_5) in the aqueous phase at near environmental conditions. The purposes of our study were: (i) to investigate if Hg^{2+} could be photoreduced in presence of alkanethiols and to study the effects of ionic strength, dissolved oxygen and chloride ion on the reaction rates under our experimental conditions; (ii) to identify the products formed for the photoreduction reaction.

2. Experimental

Stock solution of mercuric ion were prepared by dissolving mercuric nitrate solids in concentrated HNO_3 followed by dilution with water to produce stock solutions containing 1000 ppm (1 ppm = $3.1\times10^{-6\ \mathrm{mol\ L}^{-1}}$) Hg^{2+} in 1% HNO_3 solution. To prevent the absorption losses of Hg^{2+} onto the container walls, all mercury working solutions were prepared daily by diluting the Hg^{2+} stock solution to the desired concentration for use. The alkanethiol solutions were freshly prepared by diluting R-SH with oxygen-free water in order to avoid the possibility of oxidation in air. The reaction system containing the mixture of mercuric ion and alkanethiol solutions, were purged with UHP Argon gas via Teflon tubing for at least 20 min to remove dissolved oxygen, except for the kinetic studies under saturated-O_2 conditions. The experiments were carried out in the Pyrex vessels equipped with Teflon-coated magnetic stirrers to assure homogeneous mixing. The irradiation of the reaction mixtures were conducted using either UV ($290 \leq \lambda \leq 400$ nm) or visible ($400 \leq \lambda \leq 700$ nm) lamps in the photolysis box. The average radiant intensity used in our experiments was 22.5 W m^{-2}. To evaluate the dark reactions, the dark control experiments were performed by keeping the reaction mixtures in the photolysis box with all the lamps turned off. Constant temperature ($T = 296 \pm 2$ K) were maintained by using a constant velocity fan in the photolysis chamber.

2.1.Formation of *Hg^{2+}-thiol complexes*

2.1.1. UV–visible (UV–vis) spectroscopy

UV–vis spectra were acquired with a Varian Cary-50-Bio spectrophotometer at 1 nm resolution and the scan rate of 12 scans min^{-1}. A quartz cell with the path length of 1.000 cm was used for measurements. UV–vis spectra were taken for the reaction mixtures containing 10–60 μM mercuric chloride and 0–180 μM alkanethiols at pH 7, $T = 296$ K. The control spectra were recorded for the solutions containing mercuric chloride alone and alkanethiols alone to ensure the absorbance data reflecting Hg-thiol complexes.

2.1.2. Atmospheric pressure chemical ionization-mass spectrometry (APCI-MS)

The reaction mixture containing 0.3 mM mercuric nitrate and 10 mM 1-propanethiol were analyzed using APCI-MS after filtering with a 0.22 μm filter to remove any undissolved solids. Detailed operating parameters can be found in Supplementary material.

2.2. Kinetic studies

Kinetic data were obtained by monitoring the production of elemental mercury (Hg^0) using a cold vapor atomic fluorescent spectrometer (CVAFS) (Tekran 2600). The Hg^0 quantification was done by irradiating a freshly prepared reaction mixture in closed gas- tight containers at a specific time interval followed by purging the produced Hg^0 into a gold trap. The sample collection time was 180 s. The experimental setup was shown in Fig. S1. Experiments were conducted with typical initial concentrations of 0.25–16 ppb (1 ppb = 3.1×10^{-9} mol L^{-1}) for $Hg(NO_3)_2$ and 1–25 μmol L^{-1} for alkanethiols. The effects of various parameters (light, chloride ions, dissolved oxygen and ionic strength) on the reaction rates were investigated. The dependence of rate constants on light intensity was investigated by varying the average radiant intensity from 5.5 to 22.5 W m^{-2}. The effect of chloride ions on the reaction rates were evaluated by adding up to 5 mM sodium chloride into the reaction systems before purging with the Ar gas. The ionic strengths of the solutions were varied up to 0.1 M by adding various amounts of potassium nitrate into the reaction mixtures. Our QA/QC protocols included analysis of blanks, laboratory control samples (LCS), matrix spikes (MS) and matrix spikes duplicates (MSD).

2.3. Product analysis

The reaction products formed after UV exposure of the mixture of 60 μM Hg^{2+} and 120 μM alkanthiols were collected into separate gas-tight vials and analyzed using Electron Impact-Mass spectrometry and solid-phase microextraction coupled with gas chromatography–mass spectrometry (SPME/GC–MS). Electron impact (70 eV) mass spectra were recorded on a Kratos MS25RFA instrument. This method had been previously described to study the redox chemistry of mercury in our laboratory (Raofie and Ariya, 2004). For the product analysis using SPME/GC–MS, the reaction products was extracted with SPME (75 μm Carboxen/Polydimethylsiloxane (CAR/PDMS) fibre; Supelco, Bellefonte, PA, USA) at 296 K for 30 min. A Hewlett–Packard gas chromatograph equipped with single-quadrupole mass spectrometric detection (GC–MS, HP GC 6890 and MSD 5973, Agilent Technologies, Mississauga, ON, Canada), was used to identify the retention times and mass spectra of the extracted reaction products at both scan and SIM modes. Detailed operating parameters can be found in Supplementary material.

2.4. Chemicals and materials

Mercuric Nitrate (98+%), nitric acid (Trace metal grade), and the ACS-grade sodium chloride and potassium nitrate were supplied by Fisher Scientific. 1-propanethiol (99+%), 1-butanethiol (99+%) and 1-pentanethiol (98+%) from Aldrich Chemical Company were used as received and stored under Ar-saturated atmosphere. Milli- pore MQ-water (18.2 MX cm) was used throughout the experiment. The ultra high purity (UHP) argon (certified oxygen content <5 ppmv) was obtained from BOC Canada.

3. Results and discussion

3.1. Formation of $Hg(SR)_2$ complexe

UV–visible spectra recorded immediately after mixing Hg^{2+} with alkanethiol solutions were identical as those kept in the dark for up to 24 h at room temperature (e.g. Fig. S2). The UV–visible spectrophotometric studies of complex ions in the reaction systems using the mole ratio and continuous variation methods, suggested the formation of a *c.a.* 1:2 complex, i.e. $Hg(SR)_2$ complexes where R-represents an alkyl group herein and after. Significant absorption was observed at the wavelength higher than 290 nm (sunlight limit), which implied Hg-thiol complexes formed from the reaction of Hg^{2+} with R-SH could absorb photons from sur- face-reached tropospheric sunlight. The formation of Hg^{2+}-thiol complexes was also confirmed by APCI-MS. As shown in the sample APCI-MS spectrum (Fig. S3), the observed isotopic ratio of 31.0, 52.5, 74.0, 50.0, 100, 11.5, and 28.5, matched *m*/*z* ratios of 349, 350, 351, 352, 353, 354, and 355, illustrating the presence of $Hg(SC_3H_7)_2$. It should be noted that NH_3 was used as a reagent gas in the ion source. Hence, $(M + 1)^+$ ions, as opposed to M^+ ions, were observed.

The generation of elemental mercury (Hg^0) as a function of irradiation time in the reaction system containing Hg^{2+} and 1-butane- thiol was shown in Fig. S4. As previously reported (Si and Ariya, 2008), trivial Hg^0 concentration changes were detected in the blanks under our experimental conditions. The photoreduction rate upon visible irradiation (400 6 k 6 700 nm) was slightly above the rate of the dark control system, yet, was significantly slower than that under UV lights (290 6 k 6 400 nm). Similar trends were also found for 1-propanethiol and 1-pentanethiol. These results suggested that divalent mercury may be photo-chemically reduced in the presence of either of three alkanethiols (RSHs) by sunlight and that UV lights may be responsible for the reduction of Hg^{2+} by RSHs. Combining with our APCI-MS and UV–vis spectrometric data, we propose that the photoreduction reaction may occur via $Hg(SR)_2$ complexes, formed as a simple or complex reaction resulting to a net Eq. (1) shown below.

$$Hg^{2+}2R-SH\ \rightarrow Hg(SR)_2+2H^+\#(1)$$

Both direct and indirect photochemical processes may be in- volved in the reaction of Hg^{2+} with selected alkanethiols.

3.2.Kinetic results

The kinetics of the reaction was followed by monitoring the production of Hg^0 as a function of irradiation time using CVAFS. By plotting the observed concentration changes in logarithmic for- mat ($\ln([Hg^{2+}]_0/[Hg^{2+}]_t)$ vs. reaction time), we obtained straight lines for all three alkanethiols studied (Fig. 1), indicating the reaction was (pseudo-) first-order with respect to Hg^{2+}. Here we assumed that all the Hg^{2+} losses are due to the reduction of Hg^{2+} to Hg^0 by the RSHs (Xiao and Munthe, 1994a,b) and therefore the remaining Hg^{2+} is the difference between the initial Hg and measured Hg^0. This assumption was supported by our product analysis. Under pseudo-first-order conditions where [RSH] are present in large excess, the rate constant is independent of $[Hg(SR)_2]$ and free [RSH]. The rate constant is invariant with ionic strength in the range 10^{-3}–0.1 M (Fig. 2a), indicating that the photo-reaction of Hg^{2+} with RSHs may be mediated by a neutral complex whose reaction involves little or no charge formation in the transition state. As shown in Fig. 2b, the rate constants were insensitive to the presence or absence of $[O_2(aq)]$.

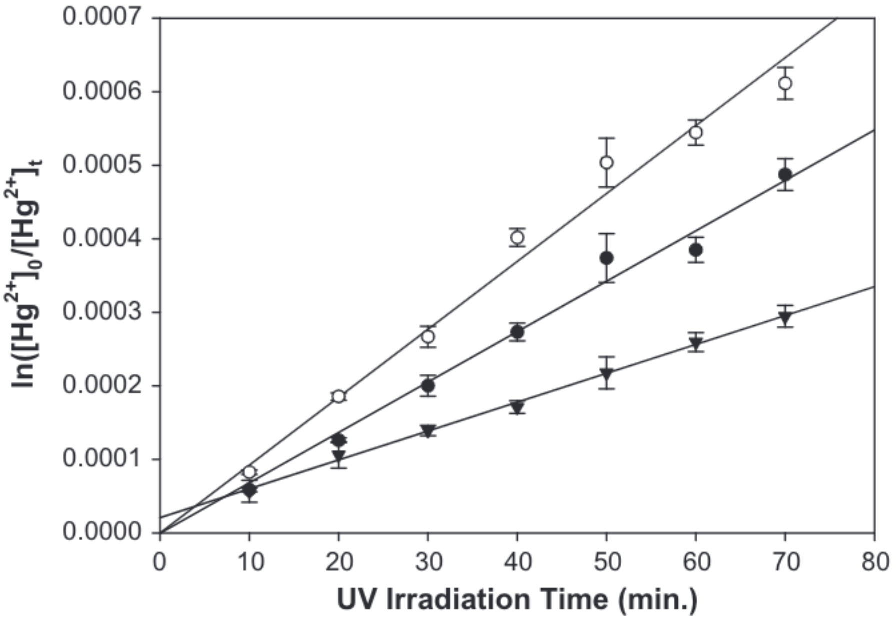

Fig. 1. The photoreduction of Hg^{2+} to Hg^0 in presence of various alkanethiols, where ●, ○, and ▼ represents 1-propanethiol, 1-butanethiol and 1-pentanethiol, respectively. Error bars are two standard deviations ($\pm 2\sigma$).

We incubated our samples for up to 72 h and there was little effect of thiol oxidation on photoreduction rates. Thus the rate law is apparently first-order and not pseudo-first-order. The measured rate constants were collected in Table 1. The rate law at pH 7.0 is therefore

$$\frac{d[Hg^0]}{dt} = -\frac{d[Hg(SR)_2]}{dt} = k' \cdot [Hg(SR)_2]\#(2)$$

The rate constants were a function of the light intensity used under our experimental conditions (Table S1). Using the radiant intensity and rate constant values, we found that quantum yield of our reactions were very small ($<10^{-6}$) under our experimental conditions. All the reported data are blank-corrected and the relative percent difference of the LCS, MS and MSD results are within 15%.

The similarities in kinetic behaviors of the studied reactions indicated that Hg^{2+} was likely nreduced by the intermediates with similar chemical structures. Table 1 shows that under the similar experimental conditions, as the carbon chain of alkanethiols get longer, the apparent rate constants become smaller. The variation of the apparent rate constants implied that the reduction of Hg^{2+} by alkanethiols is mediated by the intermediates with different re- dox potentials. Applying these trends to natural DOM using structure–activity relationships, we speculate that the photoreduction rates may be gradually lowered when longer linear alkyl chains are attached to sulfhydryl functional groups on DOM. However, due to the complexity of aquatic environment, more studies are needed to further evaluate this hypothesis.

Fig. 2c showed the photoreduction of Hg^{2+} when chloride ion were added into the Ar-saturated reaction mixtures of Hg^{2+} and 1-propanethiol. The addition of $Cl^{—}$ had little effect on the production of Hg^0 in reaction systems. Similar findings were obtained for 1-butanethiol and 1-pentanethiol. It is generally believed that chloride ion may affect the complexation step of the photoreduction reaction of Hg^{2+} with organics (Pehkonen and Lin, 1998; Si and Ariya, 2008). The complexation reactions between Hg^{2+} and $Cl^{—}$ could be expressed as Eq. (3) (Lin and Pehkonen, 1997).

$$[Hg^{2+}]\cdot[Cl^{-}]^{n}=K_{eq}\left[HgCl_{n}^{(2-n)}\right]\#(3)$$

where n = 1–4 and $\log(K_{eq})$ = 7.30, 14.0, 15.0, 15.6, respectively (Lin and Pehkonen, 1999). However, the equilibrium constants of the complexation reaction between Hg^{2+} and RSHs are in the magnitude of 10^{43} (Ravichandran, 2004), which is much larger than those of $HgCl_n^{(2-n)}$ (n = 1–4) complexes. Even when $[Cl^{—}]$ is much higher than [RSH], the concentration of the photoactive species, i.e. $Hg(SR)_2$, in the reaction systems remains unaffected. This is why the variation of the reaction rate is insignificant with the presence of chloride ion under our experimental conditions. The calculations for the Hg species relevant to natural $Cl^{—}$

concentrations (0.5 M for seawaters) were performed and Hg-thiol compounds were the major Hg species in aqueous phase.

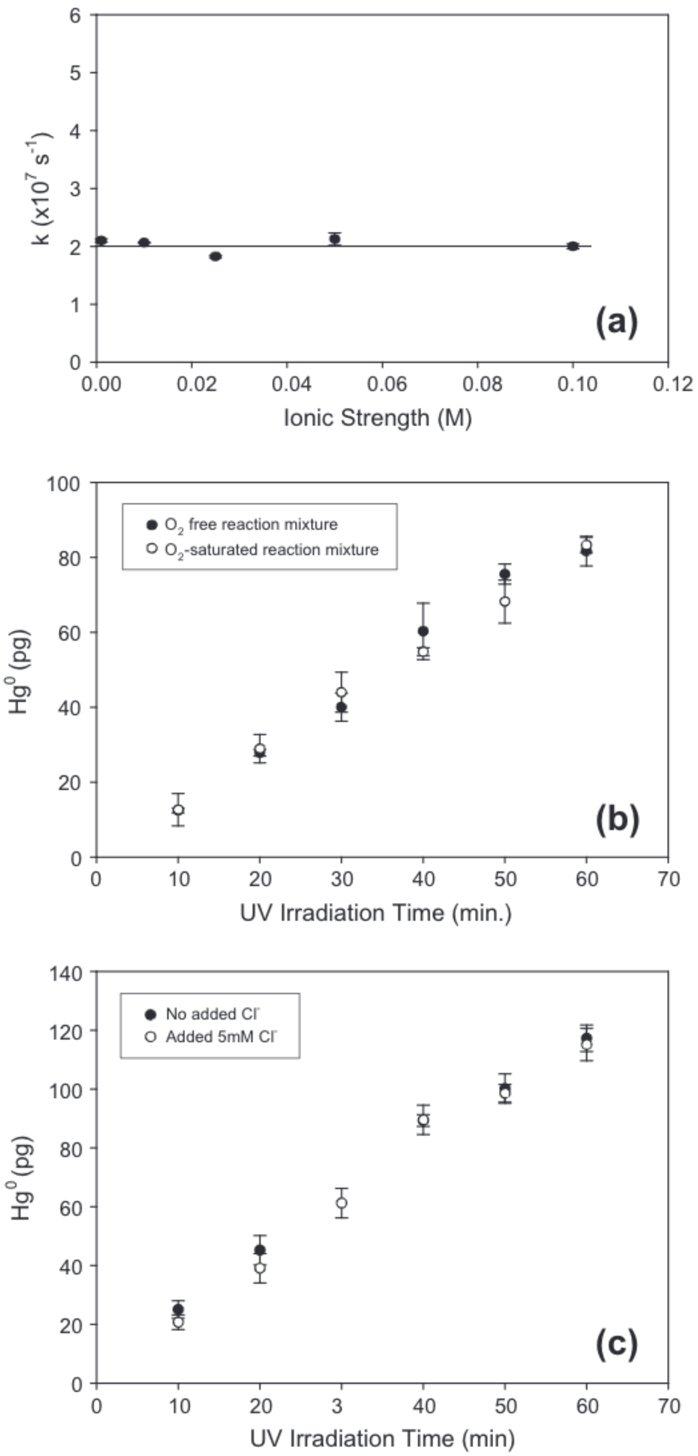

Fig. 2. Effect of (a) ionic strength; (b) dissolved oxygen; and (c) chloride ion on the photoreduction of Hg^{2+} by 1-propanethiol. Error bars are $\pm 2\sigma$.

Table 1
Rate constants of the photoreduction of oxidized mercury species by different alkanethiols ($T = 296 \pm 2$ K).

Alkanethiol (R-SH)	Reaction rate constant, k^a (s^{-1})
1-propanethiol	$(2.0 \pm 0.2) \times 10^{-7}$
1-butanethiol	$(1.4 \pm 0.1) \times 10^{-7}$
1-pentanethiol	$(8.3 \pm 0.5) \times 10^{-8}$

[a] Errors are calculated to be $\pm t\sigma/\sqrt{n}$ (95% C.I.), where $n = 6$, and t is the t-test value for $(n - 1)$ degrees of freedom.

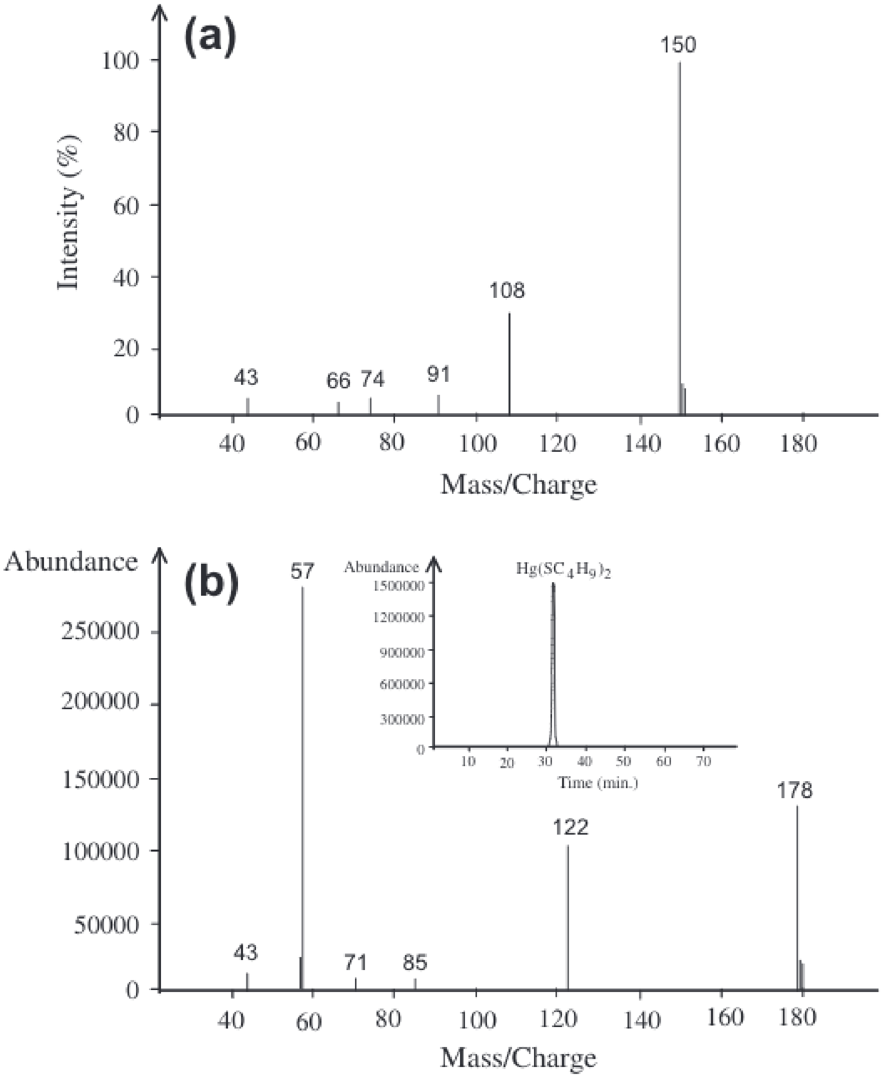

Fig. 3. Mass spectra of products formed in the reaction of Hg^{2+} with 1-propanethiol, detected by (a) EI-MS and (b) SPME-GC/MS.

3.3. Products

The reaction products were identified using a direct MS instrument equipped with an electron impact with probe temperature elevated to 430 K. Fig. 3a represents mass spectra of the products detected after photolysis of the reaction mixture of Hg^{2+} and 1-propanethiol. The observed isotopic ratios matched *m*/*z* ratios of 150, 151 and 152, illustrating the presence of dipropyl disulfide. Disulfides were also identified as reaction products using another complementary technique, SPME/GC–MS. This technique has been widely applied to determine volatile organic sulfur compounds in both liquid and solid samples (Hori, 2007; Ras et al., 2008) with very low detection limit. As illustrated in the sample GC–MS spectrum (Fig. 3b), the compound peaking at retention time of 31.8 min was identified as dibutyl disulfide by comparison of GC retention time and mass spectra to those of the standard chemicals. Table S2 gives the retention times and the fragment ions chosen to identify the products. Quantitative data using SIM mode indicated that there was a net generation of disulfides after photolysis of the reaction mixtures. The identified products of the reaction mixture after UV irradiation were dipropyl, dibutyl and dipentyl disulfides, for 1-propanethiol, 1-butanethiol and 1-pentanethiol, respectively, un- der our experimental conditions.

Combining the observation of Hg^0 using CVAFS with the results obtained using various mass spectrometry, the identified products of the photoreduction of Hg^{2+} by alkanethiols in our current studies were elemental mercury and disulfides (Eq. (4)).

$$Hg^{2+} + 2RS^{-} \leftrightarrow Hg(SR_2) \xrightarrow{\text{hv}} Hg^0 + RS - SR \tag{4}$$

Studies have shown that exposure of aqueous organomercuric solutions to sunlight resulted in either the formation of HgS(s) (Baughman et al., 1973) or Hg^0 (Si and Ariya, 2008). Quantum calculations of Hg-sulfide complexes indicated the necessity to perform an experimental study of their photolytical behaviour to answer the question (Stromberg et al., 1991). In our study, if the photolysis of $Hg(SR)_2$ complexes caused the formation of HgS(s) to occur, one expects a complex reaction system, yet the simplified reaction equa- tion should be as

$$Hg^{2+} + \ 2RS^{-} \leftrightarrow Hg(SR_2) \rightarrow Hg^0 + R - S - R \tag{5}$$

In our product analysis experiments where the initial concentrations of the reactants were at micromolar levels and the irradiation time were up to 15 d, we did not observe R–S–R as the reaction products indicating that reaction (5) is minimal when aqueous mixture of Hg^{2+} and RSHs were exposed to sunlight, or the generation of R–S–R could not be observed using our experimental analytical techniques; despite the fact that the detection limits of volatile organic sulfur compounds by SPME-GC/MS were reported to be at nanomolar levels (Fedrizzi et al. 2007; Ras et al., 2008).

4. Conclusions

An extensive kinetic and product study of the reactions between Hg^{2+} and selected alkanethiols was performed at near environmental conditions using complementary experimental techniques. These reactions were found to be photo-sensitive and exhibited apparent first-order behaviour which was independent of ionic strength or the presence of dissolved oxygen. Elemental mercury and dialkyl disulfides are observed as products under our experimental conditions. Our results suggested that Hg^{2+} could be reduced to Hg^0 upon the photolysis of $Hg(SR)_2$ complexes. Further studies are required to evaluate the reactivity variability for different environmental systems. With the values of the obtained rate constants in the present work under given experimental conditions, the half-lives of $Hg(SR)_2$ complexes during midday are approximately 40, 57, 97 days for Hg(SC$_3$H$_7$)$_2$, Hg(SC$_4$H$_9$)$_2$ and Hg(SC$_5$H$_{11}$)$_2$, respectively. Such a long half-life means that the direct photoreduction pathway is too slow to be significant in the selected atmospheric aqueous systems. Assuming Hg(SR)^2 is the dominant species at the lake surface and using the similar estimation previously made for Hg(OH)$_2$ complex (Xiao et al., 1994a,b), the Hg^0 emission rate was estimated to be ~ 2–4 ng h^{-1} m^{-2}. Comparing with the field measurements (3–20 ng h^{-1} m^{-2}), we may suggest that the photoreduction of Hg(SR)$_2$ could be important in terms of Hg air/water exchange for surface waters. The little effect of Cl$^-$ on the photoreduction indicated that the production of Hg^0 could happen even in Cl$^-$-rich environments, such as marine systems (Ababneh et al., 2006). More studies are desired to further clarify the potential role of the photolysis of Hg-sulfur-containing organic systems in natural aquatic systems.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2011.04.061.

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