



PERGAMON

Atmospheric Environment 35 (2001) 3039–3047

**ATMOSPHERIC
ENVIRONMENT**

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Oxidation of atomic mercury by hydroxyl radicals and photoinduced decomposition of methylmercury in the aqueous phase

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Received 20 February 2000; received in revised form 10 October 2000; accepted 12 October 2000

Abstract

The rate constant for $\text{Hg}^0 + \cdot\text{OH}$, $k_{\text{Hg}^0 + \cdot\text{OH}} = (2.4 \pm 0.3) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, in the aqueous phase was determined using a relative rate technique with methyl mercury as reference compound. The $\cdot\text{OH}$ initiated mercury reaction proceeds via the molecular $\text{Hg}(\text{I})$ radical which is oxidised to $\text{Hg}(\text{II})$ by dissolved O_2 . The reaction can be of importance under certain atmospheric circumstances, such as when the aqueous phase capacity of forming OH radicals is significant and the gas phase concentration of ozone drops. The same end product, i.e. $\text{Hg}(\text{II})$ was observed from the photodegradation of methylmercury hydroxide. In this case, molecular $\text{Hg}(\text{I})$ radicals are again likely to be formed after photodegradation of the $\text{Hg}-\text{C}$ bond with subsequent oxidation. A lifetime of 230 h of methylmercury at outdoor conditions was estimated due to this reaction. The action of $\cdot\text{OH}$ on methylmercury species also involves breaking of organometallic bonds and formation of $\text{Hg}(\text{II})$. Speciation of these reaction products from methylmercury is important for the estimation of biogeochemical cycling of mercury. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Biogeochemical cycling; Flux; Photolysis; Redox reactions

1. Introduction

Mercury is present in the atmosphere mainly in its elemental form with a residence time of about 1 year (Lindqvist et al., 1991). Emissions of mercury can be both natural and anthropogenic, such as soil degassing, evasion from water surfaces and emissions from incinerators. Physical removal processes become important first after oxidation due to drastically increased water solubility. Even low concentrations of oxidised mercury are important for the biogeochemical cycling of the metal. In its oxidised form mercury is water soluble and will readily deposit through dry and wet processes. Once the mercury

is transferred into oxidised state, it can be methylated (Compeau and Bartha, 1985) and are thus available for bioaccumulation. The oxidation can take place in the gas phase, in the aqueous phase or heterogeneously on particle surfaces. Contrary to particles in the lower troposphere, stratospheric aerosols are reported to contain considerable amounts of mercury (Murphy et al., 1998). A plausible explanation is a faster formation of HgO in the gaseous phase reaction between Hg^0 and O_3 (Hall, 1995), which is more dominant in the stratosphere due to a higher O_3 concentration. In the troposphere, the sources of oxidised mercury are presumably more diverse. Identified pathways for the gas-phase oxidation of Hg^0 , besides that of O_3 , include the $\cdot\text{OH}$ (Sommar et al., 2001) and NO_3 radical (Sommar et al., 1997) and many closed-shell molecules such as Cl_2 , HCl , and H_2O_2 . Elemental mercury has been shown to be oxidised by O_3 in the aqueous phase (Iverfeldt and Lindqvist, 1986; Munthe,

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1992). In a recent study Lin and Pehkonen (1998), showed that HOCl/OCl⁻ could also oxidise Hg⁰.

Photochemical activity may largely effect the diurnal and seasonal variations of oxidised gaseous mercury in the troposphere (Lindberg and Stratton, 1998; Sommar et al., 1999). The ·OH radical is a daytime oxidant. It is photolytically produced and reacts with most trace constituents in the atmosphere. The concentration in water droplets is dependent on the OH concentration in the gas phase and direct production in the aqueous phase. In contrast to atomic mercury, methyl mercury species such as CH₃Hg⁺ and CH₃HgOH are readily degraded by ·OH but not by O₃ in the aqueous phase (Hoigné and Bader, 1978; Munthe, 1992). Dissolved methylmercury can also undergo photodecomposition, which in lakes is an important sink comparable to biotic demethylation processes (Sellers et al., 1996). It has not been known if the photodecomposition process produces Hg⁰. If it does, the amount calculated by Sellers and co-workers would in some studies be enough to influence the Hg⁰ flux to the atmosphere from lakes. Identification of photodegradation end products from methylmercury is thus necessary for a realistic estimation of the influence of methylmercury on Hg⁰ fluxes. Therefore, this study includes a product study of methylmercury photodegradation.

In the previous study of the Hg⁰ + ·OH reaction, Lin and Pehkonen (1997) employed a steady state approach to control the ·OH concentration by using an excess of benzene and oxidising a small fraction of Hg⁰ applied in a set-up similar to the one described here. The oxidation rate derived from the experiment (~ 2–3% h⁻¹) is of the same magnitude as the loss rates observed in our system during dark control experiments. Their experiments were performed in deaerated solutions and the oxidation of Hg⁰ to divalent inorganic mercury (Hg(II)) was only attributed to the reaction with ·OH. In order to exclude oxidative scavenging of monovalent inorganic mercury (Hg(I)) by oxygen, it is necessary to keep the O₂ concentration below that of ·OH, which is not easily achieved. The influence of photoreduction and the oxidation of the product phenol with the ·OH was not mentioned or discussed.

This further study of rate coefficient for the Hg⁰ + ·OH reaction was needed to supply a reaction mechanism and reliable data for atmospheric modelling within the integrated Mercury Over Europe (MOE) project. The rate constant for Hg⁰ + ·OH in the aqueous phase was determined by using a relative rate technique with methyl mercury (MeHg) as reference compound. The influence of photolysis of the reactants and products is crucial in the determination and consequently a product study has been carried out. Additionally, by comparing the coefficients obtained for photodecomposition of the hydroxides of methyl mercury and Hg(II) and a reference value for natural conditions for the latter, the life-

time of methylmercury due to photodegradation in natural waters was estimated.

2. Experimental

2.1. Material and equipment

The mercury species analysed in this study were elemental mercury, methylmercury and divalent inorganic fractions. In this context, inorganic mercury (Hg_{inorg}) is represented by atomic and divalent mercury. The atomic mercury was detected after being transferred into the gas phase. Discrimination between divalent inorganic and organic mercury was achieved by addition of stannous chloride (SnCl₂). Hg(II) species are readily reduced to Hg⁰ by SnCl₂, while methyl mercury is unaffected. The methyl mercury concentration was determined as inorganic mercury after oxidation of the Hg–C bond by bromine chloride solution and reduction of excess BrCl by NH₂OH·HCl. The methylmercury hydroxide stock solution contained ~ 10% inorganic mercury partly originating from the solid methylmercury chloride (Riedel de Haën). Hence, the actual methyl mercury concentration ([MeHg]) was calculated from the difference between the initial concentration of inorganic mercury and the final one obtained after the BrCl oxidation. Since the oxidation demands extended time, [MeHg] was monitored indirectly during the experiments using the following equation:

$$[\text{MeHg}]_t = [\text{MeHg}]_0 - [\text{Hg}_{\text{inorg}}]_t + [\text{Hg}_{\text{inorg}}]_0, \quad (1)$$

where subscripts 0 and *t* refer to the reaction time at zero and *t*. By measuring the inorganic mercury concentration [Hg_{inorg}]_{*t*} and using the known concentrations of initially added methyl mercury and Hg_{inorg}, [MeHg]_{*t*} can be calculated.

A schematic diagram of the experimental set-up is shown in Fig. 1. The reaction vessel was a 2 l FEP Teflon bottle capped with a silicon–rubber stopper with moulded-in silicon–rubber drop tubes used for extracting aliquots for analysis of Hg⁰ and Hg_{inorg}. In order to minimise losses of atomic mercury, the reactor was kept open to mercury saturated air through one of the tubes during the experiment. The stream for Hg⁰ analysis was carried to a gas–liquid separator by means of a time-controlled peristaltic pump. The elemental mercury was transferred to the gas phase in a flow of nitrogen. The carrier gas stream was stripped from moisture in a drying system (PermaPure Inc.) and subsequently analysed for Hg⁰. The mercury pulse obtained was monitored with a Zeeman-modulated atomic absorption spectrometer (Semtech 2000 Hg analyser, Semtech AB) and acquired on a personal computer with a integration time of 1 s. Hg_{inorg} was determined using an automated Hg analyser

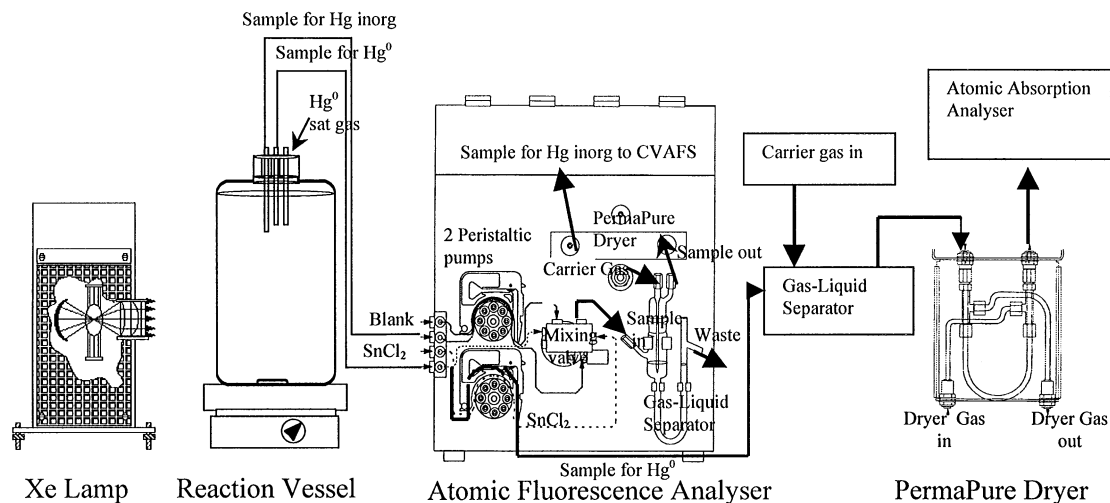


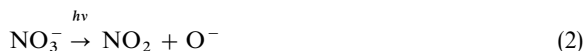
Fig. 1. Schematic diagram of the experimental set-up.

(Millennium Merlin, PSA Ltd.) for aqueous phase based on cold vapour atomic fluorescence spectrometry. The instrument has a broad working range that spans over 6 orders of magnitudes with a detection limit of < 1 ppt claimed by manufactures data sheet. In this study the instrument was operated in ppb range. Atomic and inorganic mercury in the sample were detected after liberating Hg^0 by purging it with argon gas preceded with or without mixing in the reducing agent SnCl_2 , respectively. The 2% SnCl_2 solution was purified from traces of mercury by purging with mercury free nitrogen overnight before use. The instrument was calibrated by adding 5–100 ppb solutions of HgCl_2 made up from a 1001 ppm $\text{Hg}(\text{NO}_3)_2$ stock solution. As diluted mercury solutions undergo losses during storage, all mercury working solutions were freshly prepared prior to each experiment. The light source used for photolysis experiments was a collimated 450 W Xenon lamp (Oriel Corp. Model 66066) fitted with a filter (Oriel Corp. 51225) blocking out radiation with $\lambda < 290$ nm.

2.2. Speciation in experimental solution

All chemicals used were of reagent grade and Millipore MQ-water was used throughout the study. In particular, methylmercury species are very toxic and should be handled with extreme care and safety precautions. In the relative rate experiments, solutions of atomic mercury were initially prepared by bubbling air saturated with mercury through purified water (Millipore MQ-water) stirred with a magnet. The gas was saturated when passing through a reflux distillation of mercury. The Hg^0 (aq) concentrations obtained by this method were in the range 15–30 ppb. Aliquots of CH_3HgCl added to the

reactor, yielding an initial concentration of 25 ± 1 ppb of methylmercury complexes. The pH of the solution was kept at 7.9 with a phosphate buffer in accordance with the determination of the $\text{MeHg} + \cdot\text{OH}$ reference reaction (Zepp et al., 1987). As can be seen in Fig. 2, the dominant methylmercury species are methylmercury hydroxide and methylmercury hydrogenphosphate. The solution was kept dark when dissolving ~ 70 mg NaNO_3 in the OH radical experiment. Nitrate molar concentrations were at least 2 order of magnitude higher than those of the mercury reactants but lower than 0.5 mM where deviation of linearity is reported to occur (Zepp et al., 1987). The solution was then exposed to artificial sunlight yielding photodecomposition of nitrate ions with the major (90%) pathway:



at the absorption maximum between 305 and 355 nm. The $\text{p}K_a$ of the OH radical is 11.9, so that at the pH used in these experiments encountered the O^- radical becomes rapidly protonated:



The temperature was $22 \pm 1^\circ\text{C}$ throughout the experiments. Additional experiments were made in order to determine the influence of photodecomposition of alkaline solutions of methyl mercury and $\text{Hg}(\text{II})$. By monitoring the concentration-time dependence of the mercury fractions analysed when radiating the species separately in MQ-water with added buffer, kinetics and product distribution can be obtained. Dark control experiments were performed in order to evaluate the decomposition of methylmercury from trace impurities. Similar runs

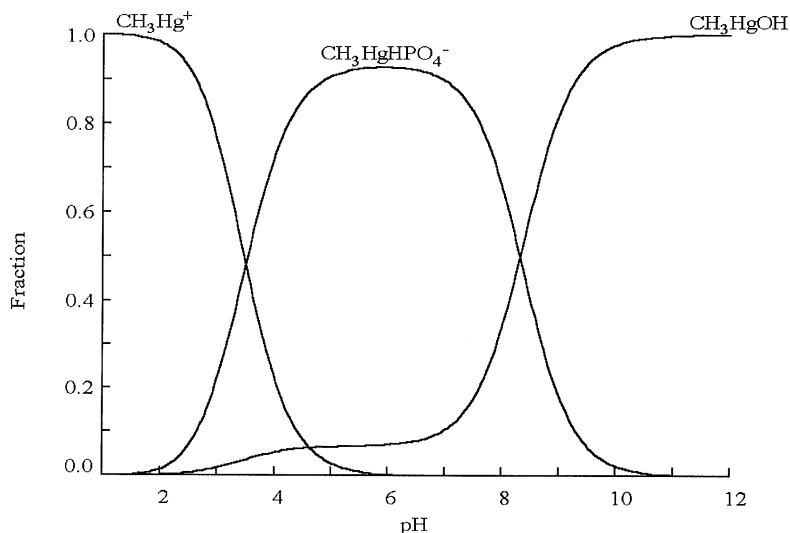


Fig. 2. Methyl mercury species as a function of pH.

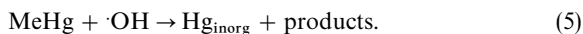
were performed with the inorganic mercury forms encountered as well. Evaporation losses of Hg^0 from the reactant solution were evaluated.

2.3. Relative rate kinetic technique

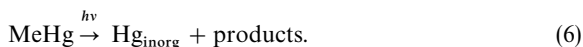
A convenient way to determine rate coefficients in a static system is to use competition between two species for the OH radicals. It is essential that the coefficient of the competing reference reaction is well known. To obtain reliable results, it is important if the investigated and the reference rate coefficients are of the same magnitude. It is also advantageous if the reference species can be accurately measured at a concentration level similar to that of Hg^0 present in the reactor. Moreover, by using another mercury species, MeHg, as the reference compound, it is convenient to use the same equipment and detection method. Zepp et al. (1987) determined the rate for the reaction between MeHg and $\cdot\text{OH}$ in phosphate buffer. Consequently the relative rate experiments were performed under the same conditions. The oxidation of Hg^0 by the OH radical is initiated by the reaction:



The oxidation step from Hg(I) to Hg(II) is fast (see reaction (11) and (12)). The reaction of MeHg with $\cdot\text{OH}$ radicals yields inorganic mercury forms (Zepp et al., 1987):



Additionally, methylmercury is photodegraded (Inoko, 1981):



The derived rate laws are as follows:

$$d[\text{Hg}^0]/dt = -k_7[\text{Hg}^0][\cdot\text{OH}] \quad (7)$$

and

$$d[\text{MeHg}]/dt = -k_8[\text{MeHg}][\cdot\text{OH}] - k_{8p}[\text{MeHg}], \quad (8)$$

where $k_8 = 1.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Zepp et al., 1987).

Integration of Eqs. (7) and (8) followed by elimination of $\int_0^t [\cdot\text{OH}] dt$ by dividing them yields:

$$\ln \frac{[\text{Hg}^0]_0}{[\text{Hg}^0]_t} = \frac{k_7}{k_8} \times \left(\ln \frac{[\text{MeHg}]_0}{[\text{MeHg}]_t} - k_{8p}t \right). \quad (9)$$

Using the relationship in (1) transforms (9) into

$$\begin{aligned} \frac{1}{t} \ln \frac{[\text{Hg}^0]_0}{[\text{Hg}^0]_t} &= \frac{k_7}{k_8} \times \frac{1}{t} \ln \frac{[\text{MeHg}]_0}{[\text{MeHg}]_0 - [\text{Hg}_{\text{inorg}}]_t + [\text{Hg}_{\text{inorg}}]_0} \\ &\quad - \frac{k_7}{k_8} \times k_{8p}. \end{aligned} \quad (10)$$

Where $[\text{Hg}_{\text{inorg}}] = [\text{Hg}^0] + [\text{Hg}^{2+}]$. The rate coefficient k_7 can thus be obtained from the slope of a plot of $\ln([\text{Hg}]_0/[\text{Hg}]_t)/t$ vs. $\ln([\text{MeHg}]_0/[\text{MeHg}]_t)/t$.

3. Results and discussion

3.1. Reactions for Hg^0 , Hg(I) and Hg(II)

A series of Hg/MeHg/ NO_3^- /buffer aqueous solutions were irradiated over a period of approximately 40 min.

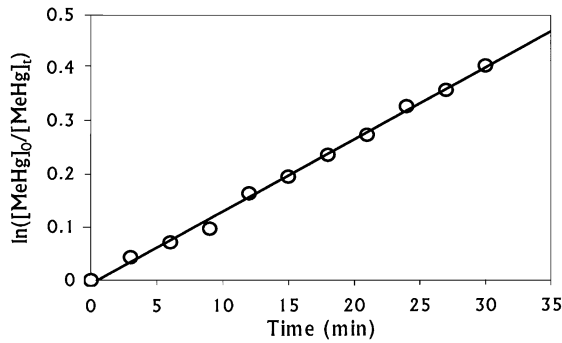


Fig. 3. Photodecomposition of methylmercury as a function of time.

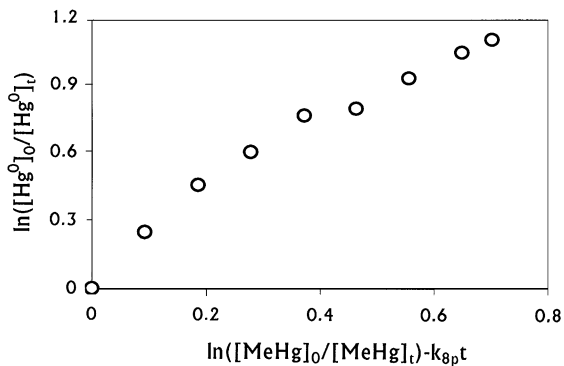
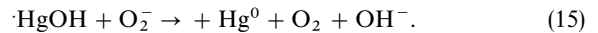
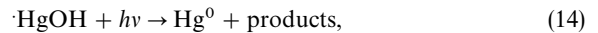
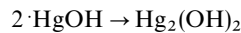
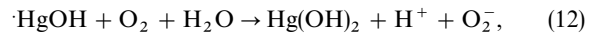
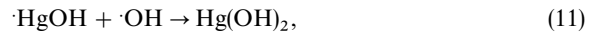


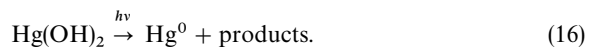
Fig. 4. Relative rate plot for determination of k_7 showing the time dependent nonlinearity behaviour due to Hg^0 replenishment.

All runs resulted in plots of $\ln([\text{Hg}^0]_0/[\text{Hg}^0]_t)/t$ vs. $\ln([\text{MeHg}]_0/[\text{MeHg}]_t)/t$ with the data confined to a narrow interval, resulting in large uncertainties of k_7 . In order to obtain a more accurate determination, the photodecomposition frequency of methylmercury was determined in separate experiments. A corresponding first-order plot is shown in Fig. 3. Irradiation of MeHg solutions yielded, independently if buffer was applied or not, a k_{8p} of $(2.2 \pm 0.2) \times 10^{-4} \text{ s}^{-1}$ (cf. *Photodecomposition of methylmercury*). By applying Eq. (9), k_7 may now be extracted from the slope of a plot of $\ln([\text{Hg}^0]_0/[\text{Hg}^0]_t)$ vs. $\ln([\text{MeHg}]_0/[\text{MeHg}]_t) - k_{8p}t$. The experimental data however gave plots that slightly deviates from linearity by a downward curvature. An example of such behaviour from an experiment is shown in Fig. 4. The curvature shows that elemental mercury is replenished at least one reaction opposed to the consumption caused by $\cdot\text{OH}$ and that the relative importance of this reaction increases with time. In order to identify possible pathways to explain this, it is essential to know the product species in the reactor. In the experiments, 60–80% of the

applied mercury species were consumed. Hg^0 reacts with $\cdot\text{OH}$ in reaction (4) forming a molecule radical $\cdot\text{HgOH}$ intermediate that is assumed to be the dominant Hg(I) species in the aqueous phase, at present conditions, since pK_a of Hg^+ is ~ 5 (Fujita et al., 1975). $\cdot\text{HgOH}$ may undergo oxidation by reaction (11) and (12) or dimerisation by (13) or reduction by (14) and (15):



The rate coefficient for reaction (11) is about one order of magnitude higher than that of reaction (12) ($k_{11} \sim 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, Nazhat and Asmus, 1973; $k_{12} \sim 10^9 \text{ M}^{-1} \text{ s}^{-1}$, Nazhat and Asmus, 1973; Pikaev et al., 1975), but since $[\text{O}_2] \gg [\cdot\text{OH}]$ in air saturated solutions, reaction (12) will completely dominate the oxidation of Hg(I) to Hg(II) species. The concentration of $\cdot\text{OH}$ radicals in our system was estimated from the rate of the reference reaction and found to be in the order of 100 fM. The rate coefficient for dimerisation (13) is $\sim 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Fujita et al., 1975). The modelling study by FACSIMILE described below shows that $\cdot\text{HgOH}$ is present in concentrations even lower than that of $\cdot\text{OH}$ due to efficient oxidative scavenging by oxygen. Therefore, the influence of dimerisation can be precluded in aerated solutions. The importance of reaction (14) was estimated relative to the likewise photoinduced reduction of $\text{Hg}(\text{OH})_2$ to Hg^0 occurring concurrently:



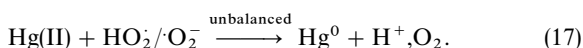
The frequency of reaction (16) was determined to be $0.6 \times 10^{-4} \text{ s}^{-1}$ in our system. k_{14} was estimated to be two or three magnitudes larger than k_{16} using extinction coefficients 1–10 and $\sim 2000 \text{ M}^{-1} \text{ cm}^{-1}$ from Xiao et al. (1994) and Fujita et al. (1975) for $\text{Hg}(\text{OH})_2$ and $\cdot\text{HgOH}$, respectively, provided that both species absorbing in the same actinic region. In order to quantify the importance of reaction (16) it is essential to determine the oxidation state of the inorganic mercury formed in reactions (5) and (6). At the present pH, rapid disproportion of $\text{Hg}_2(\text{OH})_2$, formed in reaction (13), to Hg^0 and $\text{Hg}(\text{II})$ occurs due to efficient complexation of Hg(II). But, as implied, the concentration of $\text{Hg}_2(\text{OH})_2$ is negligible and has no importance. The photodecomposition as well as the oxidation of methylmercury fractions by $\cdot\text{OH}$ was observed to, principally, only produce divalent mercury except small amounts of Hg^0 likely to originate from

Table 1

Possible reactions and lifetimes τ for $\cdot\text{HgOH}$ in the experimental system. In addition, τ_{O_2} and $\tau_{\text{O}_2^-}$ are also relevant for atmospheric water

Reaction	τ (s)
$\cdot\text{HgOH} + \cdot\text{OH} \rightarrow \text{Hg}(\text{OH})_2$	10^3
$\cdot\text{HgOH} + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Hg}(\text{OH})_2 + \cdot\text{O}_2^- + \text{H}^+$	4×10^{-6}
$2 \cdot\text{HgOH} \rightarrow \text{Hg}_2(\text{OH})_2$	$> 5 \times 10^3$
$\cdot\text{HgOH} + h\nu \rightarrow \text{Hg}^0 + \text{products}$	8.3–83
$\cdot\text{HgOH} + \cdot\text{O}_2^- \rightarrow \text{Hg}^0 + \text{O}_2 + \text{OH}^-$	1×10^{-2}

photoreduction of $\text{Hg}(\text{OH})_2$. The relative importance of $\text{Hg}(\text{OH})_2$ formed essentially by reactions (5), (6) and (12), as a source of Hg^0 increases with time. Consequently, the relative rate approach is invalidated by this secondary reaction resulting in unlinear plots. The superoxide radical anion, $\cdot\text{O}_2^-$ observed by Jungbluth et al. (1976) is formed in reaction (12) and counteracting the oxidation of mercury by reaction (15). The unbalanced reaction (17) may occur in several steps and the overall rate coefficient for the reaction at pH above and below $\text{p}K_a(\text{HO}_2) \sim 4.8$ was studied by Pehkonen and Lin (1998).



The corresponding reduction rate ($k_{17} = 1.7 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$) was not observed to significantly depend on pH and subsequently on $\text{Hg}(\text{II})$ speciation. In the same work, the reduction of mercury is assumed to proceed via the $\text{Hg}(\text{I})$ intermediate, which reacts with $\cdot\text{HO}_2/\cdot\text{O}_2^-$ very fast forming Hg^0 . Reduction via $\text{Hg}(\text{I})$ as an intermediate, i.e. reaction (15), is very unlikely because

this species would immediately react with oxygen, with subsequent oxidation to $\text{Hg}(\text{II})$ (Nazhat and Asmus, 1973; Pikaev et al., 1975) rather than react with HO_2 . Table 1 includes the lifetime $\tau = k_{\text{photolysis}}^{-1}; k^{-1}[\text{ox}]^{-1}; k^{-1}[\text{red}]^{-1}$ of $\cdot\text{HgOH}$ due to reactions (11)–(15). The lifetime for $\cdot\text{HgOH}$ due to reaction with $\cdot\text{O}_2^-$ at diffusion limited rate is incorporated. The calculation was based on the predicted maximum concentration of $\cdot\text{O}_2^-$ (10 nM) during an experiment in this work. This value is likewise representative for $\cdot\text{HO}_2$ in atmospheric water hence the lifetimes of $\cdot\text{HgOH}$ for both reactions (12) and (15) are comparable under atmospheric conditions.

It is evident that τ of $\cdot\text{HgOH}$ is entirely determined by the O_2 oxidation step (12) with an expected lifetime of a few μs in oxygen saturated solution. The lifetime due to reaction (14) is of order of minutes is adjacent to τ_{11} and τ_{13} . The $\cdot\text{HgOH}$ radical may also equilibrate with hydrogen phosphate ligands in the buffer solution. This is not considered to influence the oxidation of $\text{Hg}(\text{I})$ by O_2 since this reaction is so fast that even a minor fraction of $\cdot\text{HgOH}$ complex is enough to make this oxidation pathway being dominating.

The oxidation of $\cdot\text{HgOH}$ eventually yields inorganic divalent mercury. The speciation of $\text{Hg}(\text{II})$ as a function of pH under the experimental conditions is shown in Fig. 5. The corresponding diagram for methylmercury species is given in Fig. 2. The species considered in the equilibrium calculations are given in Table 2.

3.2. The rate of reaction between Hg^0 and the OH radical

The rate coefficient for reaction (4) was determined from three experiments, where the concentrations of methylmercury, atomic mercury and total inorganic mercury were followed and that of $\cdot\text{OH}$ was simulated from

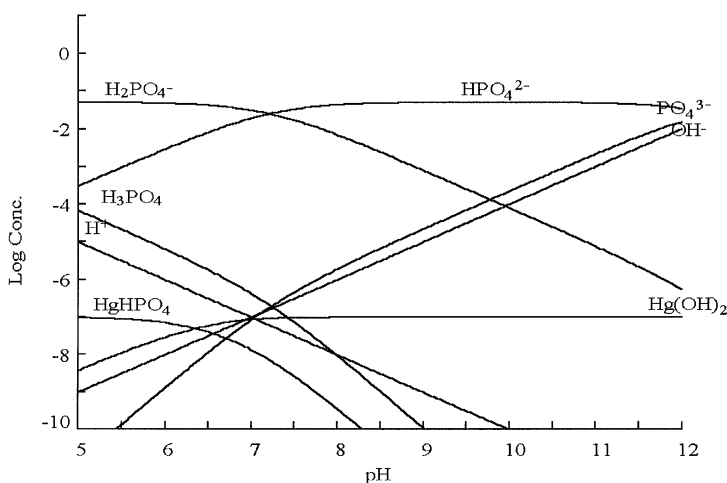


Fig. 5. Speciation of $\text{Hg}(\text{II})$ as a function of pH under experimental conditions.

Table 2
Species considered in equilibrium calculations

Equilibrium reaction	Log K	Reference
$\text{CH}_3\text{Hg}^+ + \text{HPO}_4^{2-} \rightarrow [\text{CH}_3\text{HgHPO}_4]^-$	5.0	Schwarzenbach and Schellenberg (1965)
$\text{CH}_3\text{Hg}^+ + \text{OH}^- \rightarrow \text{CH}_3\text{HgOH}$	9.4	Schwarzenbach and Schellenberg (1965)
$2\text{CH}_3\text{Hg}^+ + \text{OH}^- \rightarrow [(\text{CH}_3\text{Hg})_2\text{OH}]^+$	2.4	Libich and Robenstein (1973)
$\text{Hg}^{2+} + \text{OH}^- \rightarrow \text{HgOH}^+$	10.6	Dyrssen and Tyrell (1961)
$\text{Hg}^{2+} + 2\text{OH}^- \rightarrow \text{Hg}(\text{OH})_2$	21.9	Dyrssen and Tyrell (1961)
$\text{Hg}^{2+} + 3\text{OH}^- \rightarrow [\text{Hg}(\text{OH})_3]^-$	20.9	Garett and Hirschler (1938)
$2\text{Hg}^{2+} + \text{OH}^- \rightarrow [\text{Hg}_2\text{OH}]^+$	10.7	Ahlberg (1962)
$\text{Hg}^{2+} + \text{HPO}_4^{3-} \rightarrow [\text{HgHPO}_4]^-$	9.5	Quarfort-Dahlman (1975)
$3\text{Hg}^{2+} + \text{PO}_4^{3-} + 3\text{OH}^- \rightarrow (\text{HgOH})_3\text{PO}_4(\text{s})$	21.4	Quarfort-Dahlman (1975)
$\text{Hg}^{2+} + 2\text{OH}^- \rightarrow \text{Hg}(\text{OH})_2(\text{s})$	25.4	Dyrssen and Tyrell (1961)
$3\text{Hg}^{2+} + 2\text{PO}_4^{3-} \rightarrow \text{Hg}_3(\text{PO}_4)_2(\text{s})$	49.4	Quarfort and Dahlman (1975)
$\text{Hg}^{2+} + \text{HPO}_4^{2-} \rightarrow \text{HgHPO}_4(\text{s})$	13.1	Quarfort and Dahlman (1975)
$\text{Hg}^{2+} + \text{H}_2\text{O} \rightarrow \text{HgO}(\text{s}) + 2\text{H}^+$	-2.45	Hietanen and Högfeldt (1976)

the disappearance of the reference chemical. Least squares fitting of the required rate coefficient k_7 was made using the FACSIMILE software (Chance et al., 1987). The model consisted of reactions (5)–(7), (11)–(13) and (16). Analysis by FACSIMILE demonstrated generally a good fit between simulation and experiment. In Fig. 6 is shown the computed *best-fit* trace to the observations in one of the experiments. The resultant curve fitting including all experiments gave $k_7 = (2.4 \pm 0.3) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

Thus, our results tend to support a value of k_7 somewhat higher than that determined by Lin and Pehkonen (1997). In the same work, an assessment concerning the relative importance of oxidation of Hg^0 by $\cdot\text{OH}$ radicals compared to the oxidation by ozone, which was determined by Munthe (1992), was made. Lin and Pehkonen concluded that the reaction with $\cdot\text{OH}$ radicals is dominant only if the aqueous phase concentration of ozone is low (less than 50 pM, ~ 4 ppb in the gaseous phase), provided an $\cdot\text{OH}$ (aq) concentration of 10 pM. We assume that such scenario is rather unusual since the $\cdot\text{OH}$ radical concentration in atmospheric water is partly dependent on the gas phase concentration of ozone from which it can be produced in the gas and aqueous phase. However, direct formation of $\cdot\text{OH}$ radicals in the liquid phase can be of the same magnitude (Faust, 1994). Examples of such production are photoformation by absorbance of aqueous-phase nitrites (Arakaki et al., 1999) and nitrates (Zepp et al., 1987), and by the ferrioxalate/ H_2O_2 system (Hislop and Bolton, 1999). Furthermore, aqueous photo formation of superoxide radical $\cdot\text{O}_2^-$, will mediate the destruction of tropospheric ozone and can in cloudy environment be significant (Faust, 1994). Since several of the aqueous phase sources for $\cdot\text{OH}$ radicals are originally dependent on oxidation processes in the gas phase, and some will be able to produce ozone in the aqueous phase,

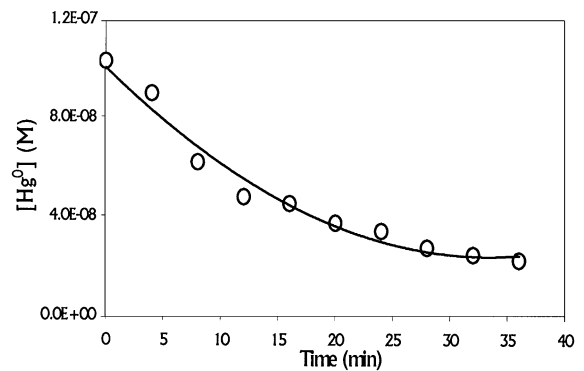


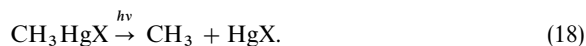
Fig. 6. Computed *best-fit* trace (line) to experimental observations (circles).

the oxidation of Hg with $\cdot\text{OH}$ radicals from different atmospheric sources is clearly a subject for modelling studies.

3.3. Photodegradation of methylmercury

The photodecomposition of methylmercury including kinetics and mechanisms was studied in separate experiments. Irradiation of MeHg solutions yielded independently if phosphate buffer was applied or not, a k_{8p} of $(2.2 \pm 0.2) \times 10^{-4} \text{ s}^{-1}$. Using the ratio $k_{8p}/k_{16} \sim 4$ obtained in this work and the value of $3 \times 10^{-7} \text{ s}^{-1}$ estimated for k_{15} at summer and 60°N by Xiao et al. (1994), a lifetime of 230 h of methylmercury at outdoor conditions can be estimated due to this reaction. This is according to a solution composition given by Fig. 2 or in MQ-water. Since the photo reactivity might very well be affected by the ligand bonded to the methylmercury entity (Baughman et al., 1973), it should be noticed that

the same result was obtained in MQ-water with and without phosphate buffer added. The result supports the unpublished data mentioned by Sellers et al. (1996), that several comparisons of photodegradation rates in different lakes show no differences in rates due to water chemistry. Inoko (1981) proposed the initial step of the methylmercury photolysis to be the cleavage of the Hg–C bond forming a Hg(I) molecule radical:



The HgX entity can undergo oxidation, dimerisation and reduction by reactions (12), (13), (14) and (15) respectively. At very high methylmercury concentrations, as in the experiments by Inoko (1981) ($\sim 5 \text{ g l}^{-1}$), the formation of mercurous compounds was reported which is compatible with reaction (13) as well as with the low solubility of Hg_2^{2+} salts. In more diluted solutions, similar to our conditions and in natural waters, oxidation of Hg(I) by dissolved oxygen to Hg(II) readily dominates (see previous section) which is in accordance with the results obtained in this work.

4. Conclusions

- The oxidation of Hg^0 initiated with $\cdot\text{OH}$ radicals in aqueous phase proceeds via the molecular Hg(I) radical $\cdot\text{HgOH}$. By comparing lifetimes for $\cdot\text{HgOH}$ due to different conceivable reactions, it is evident that the fate of $\cdot\text{HgOH}$ in presence of oxygen is oxidation to Hg(II).
- The reaction between Hg^0 and $\cdot\text{OH}$ can be of importance under certain atmospheric circumstances, such as when the aqueous phase capacity of forming $\cdot\text{OH}$ radicals is significant and the gas phase concentration of ozone drops.
- Hg(II) was also observed from the photodegradation of methylmercury hydroxide. In this case, Hg(I) radicals are again likely to be formed after photodegradation of the Hg–C bond with subsequent oxidation. The action of $\cdot\text{OH}$ on methylmercury also involve breaking of organometallic bond and formation of divalent mercury. Speciation of these reaction products from methylmercury is important for estimation of the influence of methylmercury on Hg^0 fluxes, and the assessment of biogeochemical cycling of mercury.

Acknowledgements

This research was a contribution to the Mercury Species over Europe (MOE) project being carried out in the specific RTD program sponsored by the European Commission under contract number ENV4-ET97-0595, and it is part of the European Land-Ocean Interaction Studies

(ELOISE) network (Ref. No. 208). It was also a contribution to the EUROTRAC 2 framework within the sub-project on mercury and persistent organic pollutants (MEPOP).

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