4478 *J. Phys. Chem. A* **2003,** *107,* 4478−4482

Is Bimolecular Reduction of Hg(II) Complexes Possible in Aqueous Systems of Environmental Importance

Katarina Gårdfeldt*

Department of Chemistry, Inorganic Chemistry, Göteborg University, SE-412 96 Göteborg, Sweden

Mats Jonsson

Department of Chemistry, Nuclear Chemistry, Royal Institute of Technology, SE-100 44 Stockholm, Sweden

Received: November 22, 2002; In Final Form: February 27, 2003

One-electron reduction potentials for Hg(II) complexes were calculated from experimental data obtained from pulse radiolysis experiments in order to investigate the importance of some reducing agents in the environment, i.e., $HO_2^\bullet$ and/or $O_2^{\bullet-}$. Knowledge on such potentials is valuable to foresee reduction pathways for mercury species in different environmental surroundings. The behavior of an aqueous system containing different proportions of $Hg^{2+}/H_2C_2O_4/Cl^-$ in the presence of actinic light was also investigated. The one-electron reduction potentials for the Hg(II) species during the experimental conditions in this study were found to be below −0.45 V. Consequently, Hg(II) should not be reduced by $HO_2^\bullet$ or $O_2^{\bullet-}$ under ambient conditions. Hence, the proposed aqueous phase reduction of Hg(II) species by $O_2^{\bullet-}/HO_2^\bullet$ should not be included in models describing the atmospheric transport and transformation of mercury. Results from the photolytical experiments show that reduction of Hg(II) may occur via photo fragmentation of an organic ligand, such as oxalate, bound to the metal.

Introduction

Mercury is an environmental contaminant, and its toxicity is one of the most severe known. It is released to the atmosphere from combustion processes, mainly from fossil fuel combustion, but also from natural sources such as volcanic activities. In the atmosphere mercury is transported and transformed into a variety of mercury species with different properties. In its elemental state (Hg^0) the metal has a natural atmospheric lifetime of approximately 1 year, while in its oxidized form, i.e., Hg(II), the natural lifetime is much shorter. The low surface resistance of Hg(II) compounds makes them easily deposited either as dry or wet deposition.[1]

The most dangerous forms of mercury are organic mercury species of which monomethylmercury (CH_3Hg^+) and dimethylmercury (CH_3HgCH_3) are the most frequently detected. These species may be formed by microorganisms in lake sediments after atmospheric deposition of Hg(II).[2] In addition, abiotic formation of CH_3Hg^+ with relevancy for rainwater has been suggested and recently studied in terms of a kinetic investigation.[3,4] Moreover, monomethylmercury is bioaccumulated in plankton and so enters the fish food chain. Strategies to reduce anthropogenic mercury emissions have not been successful enough to bring down the methylmercury content in fish to acceptable levels. Fish in thousands of lakes in Sweden and Finland are contaminated. Also, biota in the Mediterranean, Norway, Faroe Islands, and the Arctic is contaminated with mercury. Long-range transport of mercury in the atmosphere explains why mercury is found in remote areas.

Processes that contribute to make mercury more or less volatile in the environment are important to study because they may influence the atmospheric lifetime of the compound. In this meaning chemical reduction of Hg(II) in the aqueous phase may influence the pool of elemental mercury in aqueous atmospheric and terrestrial compartments and the physical processes regulating its flux to the gaseous phase.

In the gaseous phase, in this context ambient air, several oxidation reactions for Hg^0 are known, for example, with ozone and hydroxyl radicals.[5,6] In the aqueous phase, in this context natural waters such as hydrometeors, terrestrial water, and seawater, reactions with these oxidants also occur,[7−9] but in contrast to the gaseous phase, some reduction reactions for Hg(II) are also identified. The speciation of Hg(II) in natural waters is dependent on pH and available ligands, such as sulfite and chloride. Fractions of organic ligands, as for example oxalate and acetate, and more complex molecules, like humic matter, may also be important for mercury speciation. Knowledge of reduction of oxidized mercury in the aqueous phase is of importance to foresee reduction pathways for the various mercury species in different environmental surroundings. Moreover, these reactions may have implications for evasion of mercury from sea and lake surfaces and atmospheric water. Additionally, knowledge of these reactions is very important for all modeling work trying to estimate the ultimate fate of mercury in the environment. Among these reactions, the reduction of Hg(II) through sulfite complexes[10,11] and by humic matter[12] and in the presence of humic or dissolved organic matter and actinic radiation[13,14] has been studied.

Laboratory studies show that mercury hydroxide, $Hg(OH)_2$, can be photoreduced and form Hg^0, while the halide complex is found to be more stable.[15,16] Horvath and Vogler found that Hg(II) in chloride complexes was under certain circumstances reduced to Hg(I), but in the presence of oxygen this species is rapidly oxidized back to Hg(II).[16] However, the mechanism for

---

* Corresponding author: Fax +46 31 7722853; e-mail katarina.gardfeldt@inoc.gu.se.

10.1021/jp0275342 CCC: $25.00

the observed reduction of $Hg(OH)_2$ in aerated solutions is still unknown.

Reduction of Hg(II) by hydroperoxyl radicals ($HO_2^•$) has been proposed in the literature.[17] In that study Hg^0 was observed as a reaction product in UV-irradiated ($\lambda > 290$ nm) aqueous solution containing $Hg^{2+}/C_2O_4^{2-}$. The production of Hg^0 was explained by two consecutive one-electron reductions performed by $HO_2^•/O_2^{•-}$ (pK_a 4.8) produced from the photolysis of $C_2O_4^{2-}$ in an aerated solution. No pH dependence on the reduction rate of Hg(II) was found, which is surprising considering that the $O_2^{•-}$ radical is a more potent reductant than the $HO_2^•$ radical. Moreover, the fate of the redox intermediate monomeric monovalent mercury (Hg(I)) under environmental conditions has been evaluated by comparing its lifetime due to different conceivable reactions.[9] Radical Hg(I) species display high rate constants for reactions with abundant dissolved oxygen[18,19] and are thereby withdrawn from further $1e^-$ reduction to the volatile elemental state. Hence, the fact that Hg(I) actually is reoxidized by oxygen is contradicting the suggested mechanism. Since the proposed reaction 1 is frequently used in mercury chemistry models,[20,21] we consider it of high importance to investigate whether Hg(II) in fact can be reduced by $HO_2^•/O_2^{•-}$.

The aim of this study is to determine the reduction potential for some Hg(II)/Hg(I) couples in order to assess the thermodynamics of possible reduction pathways for Hg(II) in the environment.

In addition, we try to distinguish between two possible reduction pathways for Hg(II) in irradiated solutions containing $HO_2^•$ and oxalic acid: (I) reduction via two consecutive intermolecular one-electron transfers (reaction 1), involving Hg(I) as a reaction intermediate, or (II) direct photolysis of the Hg(II) complex (two-electron donation by the organic ligand(s) bound to Hg(II)) (reaction 2).

$$\mathrm{Hg(II)} \xrightarrow{HO_2^•/O_2^{•-}} \mathrm{Hg(I)} \xrightarrow{HO_2^•/O_2^{•-}} \mathrm{Hg}^0 \qquad (1)$$

$$[\mathrm{Hg(C_2O_4)}_n]^{(2-2n)+} \xrightarrow{h\nu} \mathrm{Hg}^0 + 2\mathrm{CO_2} + (n-1)\mathrm{C_2O_4}^{2-} \qquad (2)$$

The reduction potentials for the Hg(II)/Hg(I) couple in some different experimental solutions were determined using pulse radiolysis. The direct reaction between some Hg(II) species and $O_2^{•-}$ was studied under aerated conditions using steady-state γ-radiolysis. The photochemical behavior of some divalent mercury species in aqueous solutions, that is, $Hg(C_2O_4)$ and $HgCl_2$, was also investigated.

Experimental Section

Determination of Reduction Potentials Using Pulse Radiolysis. Formation of monomeric Hg(I) in pulse radiolytic experiments has been observed.[18,22,23] Radiolysis of water results in the formation of $OH^•$, e_{aq}^-, $H^•$, H_2O_2, H_2, and H_3O^+, with $OH^•$ and e_{aq}^- being the major radical species with primary radiation chemical yields of 0.28 μmol/J each above pH 3.[24] Ar-saturated solutions were used throughout in order minimize the concentration of dissolved oxygen. Millipore Milli-Q filtered water was used throughout.

The pulse radiolysis equipment consists of a linear accelerator delivering 3 MeV electrons and a computerized optical detection system.[25] The pulses were of 5−10 ns duration, delivering doses of 3−6 Gy. For dosimetry a N_2O-saturated 10^{-2} M KSCN solution was used.[26] The $G\epsilon$ value of $(SCN)_2^{•-}$ was taken to be 4.78×10^{-4} m^2/J at 500 nm.

Experimental solutions for determination of the reduction potentials for Hg(II)/Hg(I) were prepared for three different Hg(II) species: HgC_2O_4, $HgCl_2$, and $Hg(OH)_2$. As diluted mercury solutions undergo losses during storage, all mercury working solutions were freshly prepared prior to each experiment. The solutions were made up from reagent grade $C_2H_2O_4 \cdot 2H_2O$, KCl, a commercially available 1001 ppm $Hg(NO_3)_2$ standard, and Millipore MQ water.

Phosphate buffer (K_2HPO_4 and KH_2PO_4) was added to the solutions to achieve pH ∼ 6. However, no phosphate buffer was added to the solution containing $Hg(OH)_2$ to avoid formation of $HgPO_4^-$.

Primary reduction of the Hg(II) complexes was achieved by the solvated electron, e_{aq}^-, and the 2-hydroxyl-2-propyl radical produced in the reaction of $OH^•$ with 2-propanol (5%). To determine one-electron reduction potentials of the Hg(II) complexes, the redox equilibrium between the Hg(II)/Hg(I) redox couple and a reference redox couple with known reduction potential was studied (reaction 3).

$$\mathrm{Hg(I)} + \mathrm{MV}^{2+} \leftrightarrow \mathrm{Hg(II)} + \mathrm{MV}^{•+} \qquad (3)$$

The reference redox couple used in this work was methylviologen ($MV^{2+}/MV^{•+}$) having a one-electron reduction potential of −0.45 V vs NHE. The starting concentration of Hg(II) was varied between 1.0×10^{-4} and 2.0×10^{-3} M while the concentration of MV^{2+} was kept constant at 5×10^{-4} M. The changes in the optical absorption of $MV^{•+}$ were monitored at 625 nm.

The equilibrium constant for reaction 3 can be derived from the rate constants of the electron-transfer reaction and the back-reaction and/or the equilibrium concentrations of the two redox couples.[27]

The one-electron reduction potential of interest is then calculated from the equilibrium constant and the one-electron reduction potential of the redox reference couple using Nernst's equation ($\Delta E° = 0.0591 \log K$).

γ-Radiolysis. The proposed reactions between $O_2^{•-}$ and some Hg(II) species were studied in order to test whether Hg(II) could in fact be reduced by $O_2^{•-}$ under aerated conditions. Solutions of 10^{-4} M $Hg(OH)_2$ and $Hg(C_2O_4)$ were prepared as described above. The $Hg(C_2O_4)$ solution contained oxalic acid to a concentration of 0.05 M. The pH of the experimental solutions was adjusted to 12 and 5.3, respectively, with 0.1 M NaOH in order to achieve desirable complexation. Both solutions contained 5% 2-propanol in order to scavenge hydroxyl radicals. $O_2^{•-}$ was produced upon reduction of O_2 by e_{aq}^- or the 2-hydroxyl-2-propyl radical.

As a reference, γ-radiolysis experiments were also performed under strong reducing conditions. In these experiments the experimental solution was first dearated by purging with Ar gas.

The production of Hg^0 was determined using an automated Hg analyzer (Millenium Merlin, PSA Ltd.) for aqueous phase based on vapor atomic fluorescence spectrometry (CVAFS). The working principle of the instrument is transference of Hg^0 from the aqueous phase to a stream of argon by a gas−liquid separator. This experimental setup has been described in detail elsewhere.[9] The instrument has a broad working range that spans over 6 orders of magnitude with a detection limit of <1 ppt claimed by manufacturer's data sheet. In this study the instrument was operating in the range 0−20 ppb. The instrument is normally calibrated by routine by analysis of $HgCl_2$ solutions of various concentrations which are automatically mixed with a reducing agent, i.e., $SnCl_2$ in the interior of the analyzer. To avoid unexpected reduction of Hg(II) during our experiments by residuals of the reducing agent, the analyzer was run without

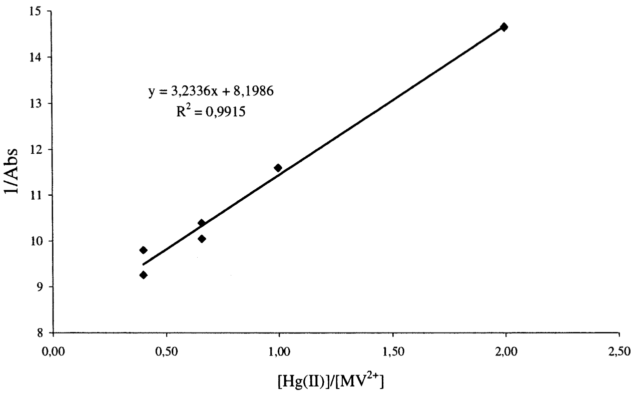

Figure 1. Data from pulse radiolysis experiments. The inverse of the $MV^{\bullet+}$ absorbance at equilibrium is plotted against the concentration ratio between Hg(II) and MV^{2+}.

TABLE 1: One-Electron Reduction Potentials

substance	$E^0(M^n/M^{n-1})$, V vs NHE	K^a	reference
$HgCl_2$	-0.47^b	2.5	this work
HgC_2O_4	<-0.55	>40	this work
O_2	-0.155 (standard state 1 MO_2)		27

[a] Equilibrium constant between the redox couple (M^{2+}/M^+) and the reference redox couple (methylviologen). [b] At [Cl] = 0.05 M. Assuming 100% of Hg(I) is complexed as $HgClHgCl_2/HgCl$, $Cl^-E^0 = -0.55$ V.

calibration and the production of Hg^0 was recorded as the relative peak height area of the CVAFS signal.

Photochemistry of Hg(II). Aqueous solutions containing different proportions of $Hg^{2+}/H_2C_2O_4/Cl^-$ were investigated in the presence of actinic light. Two experimental solutions with 10^{-5} M Hg(II) were prepared from a 1001 ppm $Hg(NO_3)_2$ standard solution. To the first solution oxalic acid ($C_2H_2O_4\cdot 2H_2O$) was added to a concentration of 10^{-3} M. The second solution also contained oxalic acid (10^{-3} M), but KCl was also added to a concentration of 10^{-2} M. All chemicals used were of reagent grade, and Millipore MQ water was used throughout the study. The experiments were carried out at pH 3. The reaction vessels were 2 L FEP Teflon or Pyrex bottles transparent to actinic light. The light source used for the photolysis experiments was a collimated 450 W xenon lamp (Oriel Corp. model 66066) fitted with a filter (Oriel Corp. model 51225) blocking out radiation with $\lambda < 290$ nm.

Production of Hg^0 was measured as described above.

Results and Discussion

Determination of Reduction Potentials Using Pulse Radiolysis. The redox equilibrium between the Hg(II) complexes and methylviologen could only be quantitatively determined for $HgCl_2$. For the oxalate complex we could determine an upper limit for the one-electron reduction potential, and in the case of $Hg(OH)_2$ we were limited by the rather low solubility. In Figure 1 we have plotted the inverse of the $MV^{\bullet+}$ absorbance at equilibrium against the concentration ratio between Hg(II) and MV^{2+}.

The equilibrium constant is calculated from the ratio between the slope and the intercept. In Table 1 the operationally defined reduction potentials and the redox equilibrium data according to reaction 3 obtained in this work are given along with redox data for O_2.

It should be noted that speciation of the monovalent mercury species was not performed in this study. However, in a pulse radiolysis study by Nazhat and Asmus, HgCl was detected as the product formed upon reduction of $HgCl_2$ in aqueous solution.[18] It is therefore reasonable to assume the same reaction to occur also under our experimental conditions (reaction 4).

$$HgCl_2 + e^- \rightarrow HgCl + Cl^- \tag{4}$$

As can be seen in Table 1, the one-electron reduction potential of $HgCl_2$ is slightly lower than that of the reference redox couple. The one-electron reduction potential of HgC_2O_4 was found to be even lower than that of $HgCl_2$. Hence, it would be more difficult to reduce the oxalate complex.

For practical reasons the one-electron reduction potential for uncomplexed Hg^{2+} is difficult to measure in aqueous solution. However, the one-electron reduction potentials and solvation data for Ag^{2+} and Cu^{2+} can provide some additional information. The differences in free energy of solvation between M^{2+} and M^+ are virtually identical for Ag and Cu.[33] It is therefore reasonable to assume that Hg would display the same difference in solvation energy (since the ionic radii for M^{2+} and M^+ for Hg are in the same range as for Ag and Cu).[34] Consequently, the relative one-electron reduction potentials of these divalent metal ions should mainly be governed by the relative gas-phase ionization potentials of the corresponding monovalent metal ions (i.e., the second ionization potential of the element). From this assumption we can estimate the one-electron reduction potential for Hg^{2+} to be lower than -2.0 V vs NHE (E^0 for one-electron reduction of Ag^{2+} and Cu^{2+} are 2.0 and 0.153 V, respectively).[33] While the solvation energy for Hg^{2+} is on the order of -2.7×10^3 kJ mol^{-1},[33] the solvation energy for $HgCl_2$ is only -30 kJ mol^{-1},[33] and the strong stabilization of the doubly charged Hg^{2+} due to solvation can, as expected, not be seen for the neutral Cl complex. This partly explains why the reduction potential of the Cl complex is as high as -0.47 V vs NHE compared to that estimated for free Hg^{2+}.

Implication for Reduction of Hg(II) by $HO_2/O_2^{\bullet-}$ in Natural Waters. Using the data in Table 1, we can also obtain the thermodynamics of the proposed reduction of Hg(II) complexes by $O_2^{\bullet-}$ in air-saturated aqueous solution ($Hg(II) + O_2^{\bullet-} \rightarrow Hg(I) + O_2$) i.e., reaction 1. For the $HgCl_2$ complex, ΔE for the reaction is -0.32 V, which corresponds to $\Delta G° = 31$ kJ mol^{-1} and $K = 5 \times 10^{-6}$, where K is the operational equilibrium constant at $[Cl^-] = 0.05$ M. Consequently, the proposed reaction is clearly not thermodynamically favorable. Given the rate constant for oxidation of Hg(I) species by O_2 (ca. 10^9 M^{-1} s^{-1}) by refs 18 and 19 and the equilibrium constant calculated above, we calculate the rate constant for reduction of Hg(II) by $O_2^{\bullet-}$ to ca. 5×10^3 M^{-1} s^{-1} under our operating conditions. Furthermore, under normal (environmental) conditions where the concentration of O_2 is several orders of magnitude higher [assuming a concentration of $[HO_2\ ] = 10^{-8}$ M and $[O_2] = 8.3$ mg/L $= 2{,}5{*}10^{-4}$ M, which corresponds to oxygen-saturated water (relevant for atmospheric waters)] than that of $O_2^{\bullet-}$, the suggested two-step reduction of Hg(II) by $O_2^{\bullet-}/HO_2^{\bullet}$ according to reaction 1 should be of minor significance. At lower pH where $O_2^{\bullet-}$ is protonated the reaction would be even less favorable since $HO_2^{\bullet}$ is a weaker reductant than $O_2^{\bullet-}$.

However, one-electron reduction of $HgCl_2$ in aqueous solutions has experimentally been found to be a dissociative electron-transfer process.[18] Therefore, the proposed reduction of the Cl complex above should be written according to

$$HgCl_2 + O_2^{\bullet-} \rightarrow HgCl + Cl^- + O_2 \tag{5}$$

Moreover, it should be noted that Jungbluth et al. investigated the mechanism for the reaction between molecular oxygen and several intermediate HgX compounds (X = Cl, Br, I, SCN,

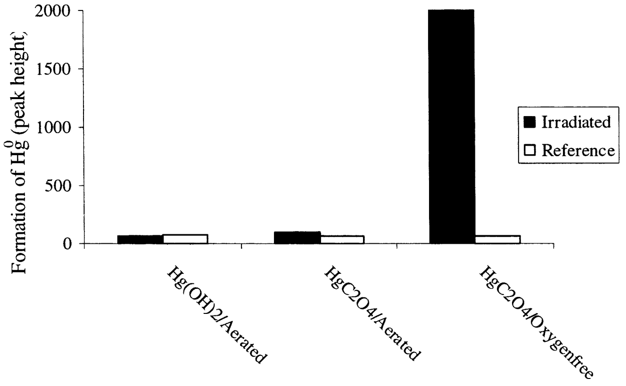

Figure 2. Experimental data from γ-radiolysis showing that Hg(II) is not reduced by $O_2^{\bullet-}$ under aerated conditions. Under strong reducing conditions, however, a remarkably high production of Hg^0 was found from two consecutive one-electron reduction steps.

CN).[22] They found that HgCN reacts with oxygen by electron transfer to form $Hg(CN)_2$ and $O_2^{\bullet-}$ while all the other Hg(I) complexes appear to form a peroxyl radical upon reaction with oxygen. The redox properties of these peroxyl radicals ($^{\bullet}$OOHgX) were found to be very similar to that of $O_2^{\bullet-}$.

This complicates the situation somewhat, and reaction 5 must be further modified to

$$HgCl + O_2 + Cl^- \leftrightarrow {}^{\bullet}OOHgCl + Cl^- \leftrightarrow HgCl_2 + O_2^{\bullet-} \quad (6)$$

As the lifetime of the proposed intermediate peroxyl radical is unknown, we cannot calculate the two individual equilibrium constants. Still, the relative concentrations of O_2 and $O_2^{\bullet-}$ in systems of environmental importance are factors strongly in favor of the oxidized form of mercury.

These results suggest that the experimental study by Pehkonen and Lin should be reevaluated.[17] Furthermore, the proposed aqueous phase reduction of Hg(II) species by $O_2^{\bullet-}/HO_2^{\bullet}$ should not be included in models describing the atmospheric transport and transformation of mercury.[21]

γ-Radiolysis. To further discriminate between the two proposed mechanisms, i.e., reaction 1 or reaction 2, γ-radiolysis experiments were employed, producing alternative precursors for one-electron transfers. In the study by Pehkonen and Lin, the $HO_2^{\bullet}/O_2^{\bullet-}$ were produced from oxalate and dissolved O_2 in the presence of simulated actinic radiation.[17] In such an experimental setup the production of Hg^0 from direct photolysis of $Hg(C_2O_4)$ cannot be excluded. By the γ-radiolysis technique used in this study $O_2^{\bullet-}$ was produced during dark conditions, and hence the possible photoreduction of $Hg(C_2O_4)$ to Hg^0 could be ruled out. To avoid reaction between hydroxyl radicals and chloride producing oxidants for Hg^0, the experimental solutions were in these experiments free from chloride as ligands for Hg(II). Our experiments show that Hg(II) is not reduced by $O_2^{\bullet-}$ under aerated conditions (Figure 2). This result is well in agreement with the thermodynamics of the proposed reaction. However, under strong reducing conditions, i.e., when the O_2 concentration was minimized by purging with argon prior to irradiation and the residuals of O_2 were scavenged by e^-, a remarkably high production of Hg^0 was found (Figure 2). In these experiments, e_{aq}^- and $(HO)(CH_3)_2C^{\bullet}$ were the main reductants present, and the solution was free from oxidants. Hence, it is possible to produce Hg^0 from Hg(II) species by two consecutive one-electron reduction steps when using strong reductants in the absence of oxidants.

Photochemistry of Hg(II). The speciation of Hg(II) in the experimental solutions is shown in Figure 3a,b.[29] In an experimental solution containing $Hg(C_2O_4)$ as the dominating species (Figure 3a), a relatively high production of Hg^0 was found where approximately 0.5% of the $Hg(C_2O_4)$ was reduced to Hg^0 in 30 min. In contrast, in an experimental solution containing oxalic acid but where chloride ions dominated the mercury complexation (Figure 3b), the reduction was remarkably inhibited. This trend is opposite to what would be expected from the thermochemical data on one-electron reduction of the Hg(II) complexes. If the reduction was caused by a bimolecular reduction according to reaction 1, the chloride complex should be somewhat easier to reduce than the oxalate complex. The formation of Hg^0 vs time under UV irradiation is shown in Figure 4.

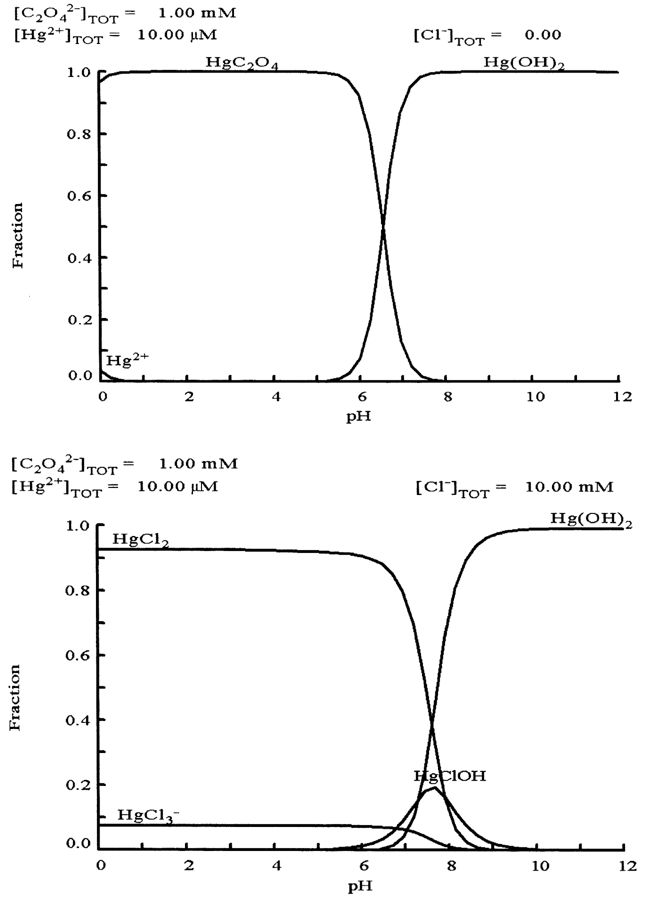

Figure 3. Speciation of Hg(II) in experimental solutions used in the photochemical experiments containing $Hg(C_2O_4)$ (a, top) and $Hg(Cl)_2$ (b, bottom) as the dominating species at pH 3.

These results imply that Hg(II) is reduced to Hg^0 by direct photolysis of mercuric oxalate complexes according to reaction 2. Nevertheless, uncertainties in the evaluation of the reduction experiments persist due to dichotomous data present in the literature on the chemical complexation in $Hg^{2+}/C_2O_4^{2-}/Cl^-$ aqueous solutions.[30,31] It has been known for a long time that a mixture of Hg(II) and oxalate in the presence of light at $\lambda <$ 260 nm reacts to form reduced mercury species and carbon dioxide.[32] The reduction at this wavelength can be explained by the absorption maxima found at ~200 nm. At our experimental conditions only photons in the actinic region are available. The mercury oxalate absorption in this region is not that well-defined as for shorter wavelengths. However, a weak absorption by $Hg(C_2O_4)$ occurs also at higher wavelengths as is shown in Figure 5, and this may explain the reduction of Hg(II) according to reaction 2. More studies are needed in order

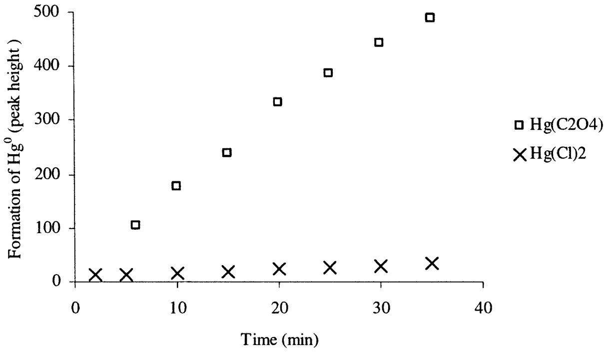

Figure 4. Formation of Hg^0 vs time under UV irradiation. As is demonstrated by the figure, Hg^0 is formed in a solution containing $Hg(C_2O_4)$ as the dominating Hg species. In a solution containing $HC_2O_4^-$ but where $Hg(Cl)_2$ was the dominating mercury species, the reduction of Hg(II) was remarkably inhibited.

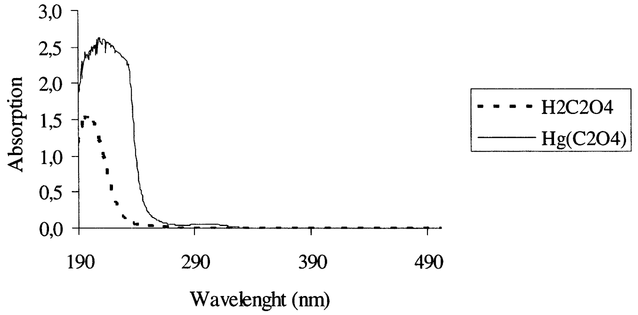

Figure 5. Absorption spectra of solutions containing oxalic acid and $Hg(C_2O_4)$.

to determine the quantum yield of the reduction of $Hg(C_2O_4)$ at various wavelengths.

Conclusions

The reduction potentials for some Hg(II) species were studied and found to be lower than the corresponding potential for oxygen. Consequently, reduction of Hg(II) to Hg^0 by $O_2^{\bullet -}/HO_2^{\bullet}$ radicals should be of minor importance.

These results suggest that an experimental study previous presented in the literature should be reevaluated.[17] Furthermore, the proposed aqueous phase reduction of Hg(II) species by $O_2^{\bullet -}/HO_2^{\bullet}$ should not be included in models describing the atmospheric transport and transformation of mercury.[21]

In all aqueous systems containing dissolved oxygen this species is a stronger oxidant than Hg(II). Consequently, Hg^0 cannot be formed through consecutive one-electron reductions during such conditions. However, formation of Hg^0 can occur for example via fragmentation of an organic ligand bound to Hg(II) under actinic radiation. Further experiments are needed in order to asses the importance of these processes under ambient conditions.

References and Notes

(1) Sommar, J. Ph.D. Thesis, Department of Inorganic Chemistry, University of Göteborg, Sweden, 2001.

(2) Compeau, G. C.; Bartha, R. *Appl. Environ. Microbiol.* **1985**, *50*, 498−502.

(3) Prestbo, E.; Bloom, N. *Water, Air, Soil Pollut.* **1995**, *80*, 145−158.

(4) Gårdfeldt, K.; Munthe, J.; Strömberg, D.; Lindqvist, O. Accepted for publication in *Sci. Total Environ.*, in press.

(5) Hall, B. *Water, Air Soil Pollut.* **1995**, *80*, 301−315.

(6) Sommar, J.; Gårdfeldt, K.; Feng, X.; Strömberg, D. *Atmos. Environ.* **2001**, *35*, 3049−3054.

(7) Munthe, J. *Atmos. Environ.* **1992**, *26A*, 1461−1468.

(8) Lin, C.-J.; Pehkonen, S. O. *Atmos. Environ.* **1997**, *31*, 4125−4137.

(9) Gårdfeldt, K.; Sommar, J.; Strömberg, D.; Feng, X. *Atmos. Environ.* **2001**, *35*, 3039−3047.

(10) Munthe, J.; Xiao, Z.; Lindqvist, O. *Water, Air, Soil Pollut.* **1991**, *56*, 621−630.

(11) van Loon, L.; Mader, E.; Scott, S. L. *J. Phys. Chem. A* **2000**, *104*, 1621−1626.

(12) Allard, B.; Arsenie, I. *Water, Air, Soil Pollut.* **1991**, *56*, 457−464.

(13) Xiao, Z. F.; Strömberg, D.; Lindqvist, O. *Water, Air, Soil Pollut.* **1995**, *80*, 789−798.

(14) Costa, M.; Liss, P. S. *Marine Chem.* **1999**, *68*, 87−95.

(15) Xiao, Z. F.; Munthe, J.; Strömberg, D.; Lindqvist, O. In *Mercury Pollution—Integration and Synthesis*; Watras, C., Huchabee, J., Eds.; Lewis Publisher: Boca Raton, FL, 1994; Section VI, Chapter 6, pp 581−594.

(16) Horvath, O.; Vogler, A. *Inorg. Chem.* **1993**, *32*, 5485−5489.

(17) Pehkonen, S. O.; Lin, C.-J. *J. Air Waste Manage. Assoc.* **1998**, *48*, 144−150.

(18) Nazhat, N. B.; Asmus, K.-D. *J. Phys. Chem.* **1973**, *77*, 614−620.

(19) Pikaev, K. R.; Sibirskaya, G. K.; Spitsyn, V. I. *Dokl. Akad. Nauk SSSR* **1975**, *224*, 638−641.

(20) Lin, C.-J.; Pehkonen, S. O. *Atmos. Environ.* **1998**, *32*, 2543−2558.

(21) Ryaboshapko, A.; Bullock, R.; Ebinghaus, R.; Ilyin, I.; Lohman, K.; Munthe, J.; Petersen, G.; Seigneur, C.; Wängberg, I. *Atmos. Environ.* **2002**, *36*, 3881−3898.

(22) Jungbluth, H.; Beyrich, J.; Asmus, K.-D. *J. Phys. Chem.* **1976**, *80*, 1049−1053.

(23) Fujita, S.-I.; Horii, H.; Mori, T.; Taniguchi, S. *J. Phys. Chem.* **1975**, *79*, 960−964.

(24) Spinks, J. W. T.; Woods, R. J. *Introduction to Radiation Chemistry*; Wiley: New York, 1990.

(25) Eriksen, T. E.; Lind, J.; Reitberger, T. *Chem. Scr.* **1976**, *10*, 5.

(26) Fielden, E. M. In *The Study of Fast Processes and Transient Species by Pulse Radiolysis*; Baxendale, J. H., Busi, F., Eds.; Reidel: Dordrecht, 1982; NATO Advanced Study Institutes Series, pp 49−62.

(27) Wardman, P. *J. Phys. Chem. Ref. Data* **1989**, *18*, 1637.

(28) Nazhat, N. B.; Asmus, K.-D. *J. Phys. Chem.* **1973**, *77*, 614−620.

(29) Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum Cop.: New York, 1977.

(30) Zajdler, A. M.; Czakis-Sulikowska, D. M. *Rocz. Chem.* **1975**, *49*, 487−495.

(31) Zajdler, A. M.; Czakis-Sulikowska, D. M. *Rocz. Chem.* **1968**, *42*, 1827−1835.

(32) De Waal, D. J. A.; Van den Berg, J. A. *Tydskr. Natuurwetensk.* **1969**, *9*, 1−9.

(33) *Standard Potentials in Aqueous Solution*; Bard, A. J., Parsons, R., Jordan, J., Eds.; Marcel Dekker: New York, 1985.

(34) *CRC Handbook of Chemistry and Physics*, 78th ed.; CRC Press: Boca Raton, FL, 1997.