Reduction of Oxidized Mercury Species by Dicarboxylic Acids (C₂−C₄): Kinetic and Product Studies

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Abstract

Mercury is an environmental contaminant of global concern. The reduction of oxidized mercury species (HgII) by organic acids to elemental mercury (Hg⁰) is significant for understanding the cycling of mercury between the atmosphere and aqueous systems. This study focused on the reduction of HgII by small, semivolatile dicarboxylic acids (C₂−C₄). The reaction kinetics was studied using cold vapor atomic fluorescence spectroscopy (CVAFS), and the products of the reaction were analyzed using matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) and nuclear magnetic resonance (NMR) spectrometry. The effects of light, dissolved oxygen and chloride ion on reaction rates were also investigated. The highest reaction rates were observed in systems free of both oxygen and chloride ion with the second-order apparent rate constants of 1.2 × 10⁴, 4.9 × 10³, and 2.8 × 10³ (L·mol⁻¹·s⁻¹) for oxalic, malonic, and succinic acids at pH 3.0 and T = 296 ± 2 K, respectively. The photoreduction of HgII was mediated by the complexes formed between HgII and dicarboxylic acids, and the identified products were Hg⁰, hydroxycarboxylic acids and monocarboxylic acids. Our results also indicated that the presence of chloride ion significantly reduced the reduction rate by competing with the complexation of HgII with dicarboxylic acids, while dissolved oxygen retarded the production of Hg⁰ by involving in the reoxidation of reduced Hg species to HgII. Based on our experimental results, a tentative mechanism is proposed and the potential environmental implications are discussed.

Introduction

Mercury is one of the most toxic global pollutants in the environment (1-3). Mercury speciation determines its physical–chemical properties and consequently, dramatically affects the fate, transport and potential toxicity of mercury to the ecosystems (4). The reactions causing the changes of the chemical forms of mercury are thus of great importance.

In the atmosphere, elemental mercury (Hg⁰) has long been assumed to have a lifetime of about 0.5–2 years, and thus subject to long-range transportation (5, 6). However, recent studies in the marine boundary layer and the polar regions indicate this assumed lifetime may be shorter due to the existence of reactive halogen species such as Br, and the lack of consideration for efficient reduction pathways (7, 8). In contrast to Hg⁰, divalent mercury (HgII) has a relatively short atmospheric lifetime, and can complex with a variety of ligands available in atmospheric aerosols and clouds such as OH⁻, Cl⁻, SO₃²⁻, and dissolved organic carbon (DOC) (9). Dicarboxylic acids (DCA) are a major identified class of components in atmospheric waters, which readily complex with HgII (10). Mercuric oxalate can be the dominant aqueous-phase species of HgII when the chloride concentration is low (11). It has been suggested that HgII is reduced by hydroperoxyl radicals (HO₂) produced by the photolysis of oxalate with the second-order rate constant of 1.7 × 10⁴ (M⁻¹·s⁻¹) (12), which is commonly used in current atmospheric mercury models. Yet, both recent computer simulations (13) and pulse radiolysis experiments (14) indicated the need to re-evaluate the reduction of HgII in presence of oxalate in atmospheric droplets.
Photoreduction of Hg\textsuperscript{II} has also been observed in seawater (15, 16) and freshwater (17-20) systems, of which the mechanisms are still poorly understood. Photoreduction of Hg\textsuperscript{II} to Hg\textsuperscript{0} affects the global distribution of mercury (19) and competes for methylation processes of mercury in aquatic environment (21). Estimates suggest that the abiotic reduction of Hg\textsuperscript{II}, principally by DOC, could account for 10−70% of DGM released from a contaminant stream (22). Therefore, the reaction between Hg\textsuperscript{II} and DOC may play an important role in the transformations of mercury in the environment. Since carboxylic groups are one of the major binding sites on DOC to trace metals, knowledge on the reduction of Hg\textsuperscript{II} by relatively small DCA molecules may provide insights on complex reaction mechanisms between Hg\textsuperscript{II} and large DOC molecules such as humic substances in natural aquatic systems (9). It has been demonstrated that the reduction of Hg\textsuperscript{II} by humic substances in presence of light is pH-dependent (23, 24) and variable with the concentration of chloride ions (22). Dissolved oxygen has been reported to affect the reduction of Hg\textsuperscript{II} by organic acids (4, 12, 21, 22). One product study has shown that in the presence of UV light, Hg\textsuperscript{II} reacts with oxalate to form elemental mercury and carbon dioxide (25). However, the kinetic data for the reactions between Hg\textsuperscript{II} and DCA are desirable; and no detailed product study, other than Hg\textsuperscript{0} and CO\textsubscript{2}, has been performed. The objectives of this study were (i) to investigate the kinetics of the photoreduction of Hg\textsuperscript{II} using an extended set of three dicarboxylic acids, i.e. oxalic, malonic and succinic acid, at near environmental conditions; (ii) to report for the first time the detailed product analysis for the reaction between Hg\textsuperscript{II} and dicarboxylic acids and (iii) to provide a tentative mechanism for the reaction. The environmental implications of our results were herein discussed.

Experimental Section

A 1000 ppm (1 ppm = 3.1 × 10\textsuperscript{-6} mol/L) mercuric nitrate stock solution was made by dissolving mercuric nitrate solids into a 1% HNO\textsubscript{3} solution. As diluted mercury solutions undergo losses during storage due to the absorption of metal ions onto the container walls, all mercury working solutions were freshly prepared for each experiment by diluting 1000 ppm Hg(NO\textsubscript{3})\textsubscript{2} stock solution. The DCA working solutions were obtained through dilutions from the 1000 ppm stock solutions which were made up by dissolving each DCA. The reaction system was the mixture of mercuric nitrate and dicarboxylic acid solutions. A 80 mL Pyrex reaction vessel with gas-tight caps was used for all experiments. To ensure the homogeneity of the mixture, the reaction vessel was equipped with a Teflon-coated magnetic stirrer. All the experiments were carried out with an initial pH of 3.0 which consistently falls in the range of most atmospheric waters (i.e., pH 2−5) (11). The irradiation sources were either UV (290 ≤ λ ≤ 400 nm) or visible (400 ≤ λ ≤ 700 nm) lamps.

Kinetic Experiments

The production of elemental mercury (Hg\textsuperscript{0}) was monitored using a cold vapor atomic fluorescent spectrometer (CVAFS) (Tekran 2600). The blank was the solution containing only mercuric nitrate. The dark control experiments were performed in a completely closed wooden box with all the lamps turned off to evaluate dark reactions. The effects of various parameters (light, chloride ions, and dissolved oxygen) on the reaction rates were investigated. All reaction mixtures were first purged with UHP Argon gas via Teflon tubing for at least 20 min to remove oxygen in reaction systems. In case of chloride ions, various amounts of Cl\textsuperscript{-} were added before purging with the Ar gas, while in case of the aerobic conditions, oxygen was introduced by air-bubbling after purging of the pure Ar gas.

Product Identification

The reaction products formed before and after UV exposure, were collected into separate gastight vials. The solution used for product analysis by matrix-assisted laser desorption ionization time of flight mass spectrometer (MALDI-TOF-MS) was the mixture of (3.1 ± 0.1) × 10\textsuperscript{-6} mol/L Hg(NO\textsubscript{3})\textsubscript{2} and (6.2 ± 0.2) × 10\textsuperscript{-6} mol/L DCA. We also aged the samples in dark to monitor any alterations in observed products. The analysis was performed using Krotos Kompakt MALDI-TOF-MS in reflectron mode. The matrix and cationization agent used were dithranol and lithium bromide, respectively. Since the matrix has resonance absorption at laser energy (λ = 377 nm), its absorption of the laser energy results in rapid heating of the matrix and consequently, provides expulsion and soft ionization of the sample molecules without fragmentation (26). When using solution NMR, \textsuperscript{13}C-DCA was used as the starting reactant instead of DCA to increase the signal. The mixture of (3.1 ± 0.1) × 10\textsuperscript{-6} mol/L Hg(NO\textsubscript{3})\textsubscript{2} and (6.2 ± 0.2) × 10\textsuperscript{-3} mol/L DCA was used for NMR analysis. 1000 μL of the collected products was mixed with 1000 μL D\textsubscript{6}-dimethyl sulfoxide (DMSO) in a vial. Then, the solution mixture was filtered through a 0.22 μm filter using a liquid-tight syringe to remove any undissolved solids, and 600 μL of the filtrate was collected into a 5 mm NMR tube from Wilmad Company for analysis. Hence, the obtained results do not include solid products larger than aerodynamic diameter of 0.22 μm.

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Routine $^{13}$C NMR spectra were acquired with a 300 MHz Varian NMR spectrometer. A total of 128 scans were collected for $^{13}$C nucleus.

**Chemicals and Materials**

Mercuric Nitrate (98+%), sodium chloride (reagent grade), and nitric acid (trace metal grade) were supplied by Fisher Scientific. All the dicarboxylic acids ($\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, $\text{C}_3\text{H}_4\text{O}_4$ and $\text{C}_4\text{H}_6\text{O}_4$) (99%) were obtained from Aldrich Chemical Co.. The ultra high purity (UHP) argon (certified oxygen content < 5 ppmv) was obtained from BOC Canada. Millipore MQ-water with a resistance of 18.2 MΩ·cm was used throughout the experiment.

**Results and Discussion**

The generation of elemental mercury (Hg$^0$) as a function of irradiation time in the reaction system containing Hg$^{II}$ and oxalic acid was shown in Figure 1. Trivial Hg$^0$ concentration changes were detected in either the blank or dark control systems under our experimental conditions. However, the production of elemental Hg$^0$ in the reaction system was significantly above the blank values (Figure 1(a)). The photoreduction rate upon visible irradiation (400 $\leq$ λ $\leq$ 700 nm) was slightly above the rate of the dark control system, yet, was significantly slower than that under UV lights (290 $\leq$ λ $\leq$ 400 nm) (Figure 1(b)). Similar trends were also found for malonic acid and succinic acid. These results suggested that divalent mercury can be photochemically reduced in the presence of either of three dicarboxylic acids under study and that UV lights may be responsible for the reduction of Hg$^{II}$ by DCAs. Our results were consistent with the studies performed by Gärdfeldt and Jonsson (14), where it was proposed that the reduction of Hg$^{II}$ could be induced by the weak absorption of Hg(C$_2$O$_4$) complex at the wavelength of $\sim$305 nm. We also monitored the generation of Hg$^0$ in reaction mixtures exposed to UV light for 15 min. followed by aging in the dark for up to 12 h. (Figure 1(c)). The amount of Hg$^0$ produced after aging is similar to that without aging, indicating that the backoxidation of reduced Hg species to Hg$^{II}$ is minimal in Ar-saturated solutions.
FIGURE 1. (a) The generation of Hg\(^2\) in blanks (○) and in reaction systems (●) containing Hg\(^0\) and oxalic acid; (b) Formation of Hg\(^2\) vs time in reaction systems exposed to UV (●) or visible (○) lights, and in dark control (▲) systems containing Hg\(^0\) and oxalic acid; (c) The generation of Hg\(^0\) in reaction systems (6.2 ± 0.3) \times 10^{-11} \text{ M} Hg\(^0\) and (7.5 ± 0.9) \times 10^{-5} \text{ M} oxalic acid) irradiated with UV light for 15 min, followed by aging in the dark for 1, 3 and 12 h; (d) The reduction of (6.2 ± 0.3) \times 10^{-11} \text{ M} Hg\(^0\) to Hg\(^0\) in presence of various concentrations of oxalic acid, where ●, ○, and ▲ represents (7.5 ± 0.3) \times 10^{-4} \text{ M}, (5.8 ± 0.2) \times 10^{-5} \text{ M} and (7.5 ± 0.5) \times 10^{-2} \text{ M} oxalic acid, respectively.
Figure 1(d) showed the production of Hg⁰ as a function of irradiation time at different concentrations of oxalic acid at a fixed Hg²⁺ concentration, for Ar-saturated reaction systems. The DCA concentration was in excess relative to Hg²⁺ so that the changes of DCA concentrations remained insignificant. [Hg²⁺]₀ is the initial Hg²⁺ concentration, and [Hg²⁺], is the concentration of Hg²⁺ at reaction time, i.e., [Hg²⁺]₀ is calculated by assuming all the Hg²⁺ losses are due to the reduction of Hg²⁺ to Hg⁰ by the DCAs (27). This assumption was supported within our experimental uncertainties by a series of experiments including the reactants alone, aging in the dark, and aging after photolysis. By plotting the observed concentration changes in logarithmic format (ln([Hg²⁺]₀/[Hg²⁺]₀) vs reaction time), we obtained straight lines for all three dicarboxylic acids studied, indicating the reaction was (pseudo-) first-order with respect to Hg²⁺. The initial DCA concentration was varied while it was still much larger than the Hg²⁺ concentration. It was found that the slopes of the straight lines (k’) were proportional to the concentration of DCA, i.e., k’ = k·[DCA]. Thus, the reduction of Hg²⁺ by DCAs was assumed to have apparent second-order behavior:

\[
d[\text{Hg}^0]/dt = -d[\text{Hg}^{2+}]/dt = k’[\text{Hg}^{2+}] = k[DCA][\text{Hg}^{2+}] \tag{1}
\]

where \(k\) is the apparent reaction rate coefficient, \(t\) is reaction time; and [DCA], [Hg⁰] and [Hg²⁺] represent dicarboxylic acid, Hg⁰, and Hg²⁺ concentrations, respectively. The measured apparent rate constants of the reductions of Hg²⁺ by DCAs are summarized in Table 1. We opt to report the total uncertainty which is the combined uncertainty from hardware used for preparation of solutions, regression uncertainty, instrumental uncertainty, and operator uncertainty. However, to demonstrate the variability of individual experiments, standard deviations were used for all depicted figures. The similarities in kinetic behaviors of the studied reactions indicated that Hg²⁺ was likely reduced by the intermediates possessing similar chemical backbone structure. Table 1 shows that under the similar experimental conditions, oxalic acid was the most effective electron donors of these three dicarboxylic acids, while succinic acid reduces the mercuric ion at the slowest rate among these three studied acids. The variation of the apparent rate constants implies that the reduction of Hg²⁺ by DCAs is mediated by the intermediates with different reactivity potentials.

**Table 1. Apparent Rate Constants of the Photo-Reduction of Hg²⁺ by Different Dicarboxylic Acids in Absence of Cl⁻ and O₂ (\(T = 296 \pm 2K, \text{pH }3.0\))**

<table>
<thead>
<tr>
<th>dicarboxylic acid (DCA)</th>
<th>reaction rate constant, (k) (L·mol⁻¹·s⁻¹)</th>
<th>total uncertainty (L·mol⁻¹·s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>oxalic acid</td>
<td>1.2 × 10⁴</td>
<td>0.2 × 10⁴</td>
</tr>
<tr>
<td>malonic acid</td>
<td>4.9 × 10³</td>
<td>0.8 × 10³</td>
</tr>
<tr>
<td>succinic acid</td>
<td>2.8 × 10³</td>
<td>0.5 × 10³</td>
</tr>
</tbody>
</table>

Table 2 summarized the compounds present in the reaction mixtures before and after UV irradiation, determined by MALDI-TOF-MS. To our knowledge, this is the first time that organic products of the reduction of Hg²⁺ by DCAs have been reported in the literature. A typical spectrum was shown in Figure 2. The identified complexes formed immediately after mixing Hg(NO₃)₂ and DCAs were Hg(OOC)₂, Hg(OOCC₂H₂), and Hg(OOC)₂(CH₂)₂, for oxalic, malonic, and succinic acids, respectively. The presence of Hg(OOC)₂ (chemical shifts, δ = 167.7 ppm) and Hg(OOCC₂H₂) (δ = 43.2 ppm) (Figure S1 of the Supporting Information) complexes in reaction systems before irradiation was also confirmed by solution NMR for oxalic and malonic acids, respectively. A generalized complexation equation for the observed processes can be described as follows:

\[
\text{Hg}^{2+} + R(\text{COO})_2^2⁻ \leftrightarrow \text{Hg}(\text{OOCC})_2R \tag{2}
\]

where \(R\) represents no moiety, the moiety of CH₂, and (CH₂)₂, for oxalic, malonic, and succinic acids, respectively; and \(R\) represents the same moieties hereafter. Hg(OOCH)₂ was observed upon UV photolysis of the mixture of Hg(NO₃)₂ and oxalic acid. In case of malonic acid, the organic compounds determined by MALDI-TOF-MS were Hg(OOCC₂H₂), Hg(OOCC₂H₂), and Hg(OOCC₂H₂). For the reaction between Hg²⁺ and succinic acid, Hg(OOCC₂H₂), Hg(OOCC₂H₂), and Hg(OOCC₂H₂), were observed after UV irradiation. No stable Hg⁰ compounds were detected by MALDI-TOF-MS under our experimental conditions. Combining the observation of Hg⁰ using CVAFS with the results obtained using MALDI-TOF-MS, the identified products of the photoreduction of Hg²⁺ by dicarboxylic acids in our current studies were elemental mercury, hydroxycarboxylic acids, and monocarboxylic acids.
Effect of Chloride Ion

Figure 3(a) showed the photoreduction of Hg$^{II}$ when different concentrations of chloride ion were added into the Ar-saturated reaction mixtures of Hg$^{II}$ and malonic acid. The addition of Cl$^{-}$ significantly slowed down the production of Hg$^{0}$ at all concentrations under study, but the extent varied with the concentration of chloride ion. Similar retarding effects of Cl$^{-}$ were also observed for malonic acid and succinic acid. The retarding effect of Cl$^{-}$ on the reduction of Hg$^{II}$ by DCAs could be caused by the complexation reactions between Hg$^{II}$ and Cl$^{-}$ (Equation 3) \((11)\).

$$\text{Hg}^{2+}\cdot[n\text{Cl}^{-}] = K_{eq}\left[\text{HgCl}_{n}^{2(n-n)}\right]$$ \hspace{1cm} (3)

where \(n = 1-4\) and \(\log(K_{eq}) = 7.30, 14.0, 15.0, 15.6\), respectively \((9)\). When Cl$^{-}$ concentrations were high, the mercury was expected to present mainly as HgCl$_{4}^{2-}$. While when [Cl$^{-}$] was low, the major mercury form in the solutions could be the mixture of HgCl$_{n}^{2-n}$ \((n = 1-4)\). This is why the retarding effect of Cl$^{-}$ becomes more significant when the
chloride-ion concentrations got higher. The formation of any HgCl_{n}^{2-n} (n = 1−4) complex would decrease the formation of the Hg(OOC)_{2}R complex in the reaction systems and thus, the decrease of the reaction rate.

Effect of Dissolved Oxygen

Depicted in Figure 3(b), oxygen inhibited the generation of Hg^{0} at various concentrations. It could be seen that as more oxygen was introduced into the reaction system, the production of Hg^{0} became less. The retarding effects of O_{2} on the photoreduction of Hg^{II} were observed for all three dicarboxylic acids under study. This may be due to the fact that dissolved oxygen could be involved in the reformation of Hg^{II}.

Reaction Mechanism

In analogous to the photoredox processes of Fe^{III}-polycarboxylate compounds (28), Hg^{II} may be reduced by organic radicals formed as the consequence of the photolysis of Hg(OOC)_{2}R complexes.
Acetic acid, one of the products for the reaction between Hg$^{II}$ and malonic acid (Table 2), could be produced from the recombination of acetic acid radical followed by hydrolysis at acidic conditions (29).

Another product determined by MALDI-TOF-MS, HORCO$_2^-$ (Table 2), can be produced from both the reaction of Hg$^{II}$ with dicarboxylic radical anions and the recombination of RCO$_2^-$ radical anion.

It is also possible that the reduction of Hg$^{II}$ by DCA$s$ occurs through the intramolecular 2-electron transfer via the formed Hg-organic complexes as suggested by Gårdfeldt and Jonsson (14).

In the presence of oxygen, dissolved O$_2$ could react with highly reducing R(CO$_2^-$) as shown in eqs 9–11. In case of oxalic acid, hydroxyl radical could be potentially formed as products (eqs 9 and 10), while for malonic and succinic acid, organic hydroperoxyl radical may be produced (eq 11).

In solutions containing Hg$^{II}$ and oxalic acid, since the fate of O$_2^·$ is expected to form H$_2$O$_2$ eventually (eq 12), Hg$^0$ produced in the reaction systems can be reoxidized by H$_2$O$_2$ (eq 13) (30).

In reaction systems of Hg$^{II}$-malonic acid and Hg$^{II}$-succinic acid, one of the products determined by MALDI-TOF-MS is HR$_2$COO$^-$ (Table 2). Previous studies have shown that the peracids can oxidize elemental mercury at the trace level to Hg$^{II}$ (31). Therefore, HR$_2$COO$^-$ may be formed via reactions of Hg$^0$ with radicals such as $^·$O$_2$CROO (eq 14). Further studies are needed to elucidate further information on the mechanism of this oxidization step of Hg$^0$ to Hg$^{II}$.

Since the reaction of Hg$^I$ species with oxygen, forming Hg$^{II}$, has high rate constants (32, 33), it is possible that in aerated conditions, oxygen will oxidize Hg$^I$ to Hg$^{II}$. The experimental reaction system was modeled using the ACUCHEM program (34). The calculated product concentrations were very sensitive to the value of the Hg-DCA
complex photolysis rate which was assumed using structure-reactivity relationship and was varied over the range of 3 orders of magnitude ($10^{-3}$ to $10^{-6}$ s$^{-1}$). It was found that regardless of the value used for the photolysis of Hg–DCA complex, the major reduction of Hg$^{II}$ occurred through the intramolecular 2-electron transfer via the formed Hg–DCA complexes, yet, reactions 5 and 6 contributed to the reduction of Hg$^{II}$ to Hg$^{0}$ as well. Further photolysis rate calculations on Hg–organic complexes are required to provide detailed information on reaction mechanism.

In summary, an extensive kinetic and product study of the reactions between Hg$^{II}$ and dicarboxylic acids were performed at near environmental conditions using complementary experimental techniques. These reactions were found to be photosensitive and exhibit the overall apparent second-order behavior when both chloride ion and dissolved oxygen were absent in reaction systems. Observed products suggest that Hg$^{II}$ could be reduced by R(CO$_2$)$_2$• radical or through the intramolecular 2-electron transfer upon the photolysis of Hg–DCA complexes (Figure 4). The photoreduction of Hg$^{II}$ by DCAs was inhibited by the presence of either Cl$^-$ or O$_2$. Hinting to the fact that chloride ion reduced the generation of Hg$^{0}$ by forming stable complexes with Hg$^{II}$, it thus resulted in less Hg$^{0}$ available for the complexation with DCA and therefore, less formation of Hg$^{0}$. The presence of dissolved oxygen causes the back oxidation of reduced Hg species to Hg$^{II}$ and therefore, the decrease of the net production of Hg$^{0}$ in reaction systems. The formation of Hg$^{0}$ as the result of the reaction of Hg$^{II}$ with DCAs, may enhance elemental mercury in gas phase and elongate the perceived lifetime of Hg$^{0}$ in the atmosphere. The reduction of Hg$^{II}$ by DCAs in aqueous phase reduces the mercury burden in the water and may decrease the methylmercury production and bioaccumulation in fish (35). The retarding effects of oxygen or chloride ion on the photoreduction of Hg$^{0}$ indicate that the Hg$^{0}$ production will be less significant for O$_2$- or Cl$^-$-rich environments, such as marine systems (21).

**FIGURE 4.** Schematic diagram of the simplified proposed mechanism for the reaction between Hg$^{II}$ and DCA. Bolded compounds were identified in the current study.

Supporting Information

The presence of Hg(OOC)$_2$R complex in the reaction systems determined by $^{13}$C NMR spectroscopy is displayed in Figure S1. This material is available free of charge via the Internet at [http://pubs.acs.org](http://pubs.acs.org).

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Literature Cited