

**AQUEOUS PHASE CHEMISTRY OF MERCURY**  
**IN THE ATMOSPHERE:**  
A KINETIC STUDY OF THE REACTION  
 $\text{Hg}^0 + \cdot\text{OH}$

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**Title:** Aqueous phase chemistry of mercury in the atmosphere:  
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## 1 SUMMARY

Mercury is a global pollutant that has been used by mankind for thousands of years. This has led to extensive discharges into the environment, contaminating air, lakes and soils. Bio-methylation of oxidized mercury species results in the highly toxic methyl-mercury thereby making mercury a threat to both humans and animals. The biogeochemical cycling of mercury between different natural compartments is governed by redox processes in both gas- and aqueous phase.

The understanding of these processes requires thorough knowledge of the involved redox reactions of mercury species. In this study, the oxidation rate of elemental mercury by hydroxyl radicals in aqueous phase has been re-determined, as the earlier reported values have shown differences. It was found that the rate constant for the reaction  $\text{Hg}^0 + \cdot\text{OH}$  was  $(2.9 \pm 0.6) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$  at pH 4.1 and  $(4.8 \pm 1.5) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$  at pH 7.2. A possible reason for the difference in the rate constant at the two pH-values may be a parallel reduction of  $\text{Hg(II)}$  to  $\text{Hg}^0$ .

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## 2 INTRODUCTION

The biological and environmental hazards of mercury have attracted the attention of scientists since the 1950's when the villagers of Minamata and Niigata, Japan were poisoned by methyl mercury. A chemical factory had been letting out large amounts of inorganic mercury upstream of the Minamata Bay. The inorganic mercury was later converted to methyl mercury by microorganisms and ingested by fish that was the main food source for people. In 1971-1972, over 400 people died in Iraq after having eaten homemade bread prepared from wheat seed treated with methylmercurial fungicide. Today many countries have banned the use of mercury, but since large quantities of mercury are still emitted from sources like coal combustion, mercury remains a serious problem.

### 2.1 Applications of mercury

Findings in Egyptian and Chinese tombs dating back to 1500 BC show that man has been using mercury for over 3000 years. In ancient times, the use was mainly as a dye for tattoos and wall painting in caves. Some people thought mercury could chase away evil spirits and the alchemists thought it had mystical properties and used it in their attempts to make gold out of base metals. The medical use of mercury and its compounds has been diverse. One example is the use of mercury as a treatment for syphilis that began in the 15:th century and did not end until 1928 [1], another the use of  $\text{HgCl}_2$  as an antiseptic. After the industrial revolution the use of mercury increased rapidly as its unique properties made it a valuable metal for use in industry, mining, manufacturing, dentistry and many other applications.

## 2.2 Properties of mercury

Mercury is a metal with three different states of oxidation, 0, +1 and +2. In the environment, it can be found in its elemental form (oxidation state 0) and as divalent and organic compounds.

### 1) Inorganic mercury

- a) Elemental mercury ( $\text{Hg}^0$ ) is a metal with unique physical and chemical properties. It shares the group II B of the periodic table with zinc and cadmium but unlike them, it is relatively inert. It is the only metal in the periodic table that is liquid at room temperature (m.p. – 38.87°C). It has such a high surface tension that it does not wet glass. The density is 13.55  $\text{kg dm}^{-3}$  at 20°C so that if one throws a rock or even a piece of lead in a pool of liquid mercury it would float. It is also resistant to corrosion and has a low electrical resistance.  $\text{Hg}^0$  readily forms alloys with most metals such as gold or silver, so called amalgamation.
- b) Monovalent ( $\text{Hg(I)}$ ) and divalent ( $\text{Hg(II)}$ ) mercury can form several different compounds with inorganic ligands. Important species in the environment are however entirely divalent such as  $\text{HgO}$  and  $\text{HgCl}_2$ .

### 2) Organic mercury

These are alkyl-, aryl and alkoxyalkyl- compounds of mercury. The major biogenically produced organic mercury species are dimethyl mercury ( $\text{Me}_2\text{Hg}$ ) and methyl mercury ( $\text{MeHg}^+$ ).

As can be seen in Table 1 there are large differences in physical and chemical properties for the different compounds. The main driving force of the biogeochemical cycling of mercury is the transformation between different species.

Table 1 Properties of some mercury compounds. (Adapted from [2])

| Property   | $\text{Hg}^0$ | $\text{HgCl}_2$              | $\text{HgO}$                  | $\text{CH}_3\text{HgCl}$ |
|--|---------------|------------------------------|-------------------------------|--------------------------|
| Melting point [°C]   | -39           | 277                          | Decomp. at 500°C              | 167 (sublim.)            |
| Boiling point [°C], 1 atm                                  | 357           | 303                          | -                             | -                        |
| Vapor pressure [Pa]  | 0.180 (20°C)  | $9.99 \times 10^{-3}$ (20°C) | $9.2 \times 10^{-12}$ (25°C)  | 1.76 (25°C)              |
| Henry's law constant<br>[Pa $\text{m}^3 \text{mol}^{-1}$ ] | 729 (20°C)    | $3.69 \times 10^{-5}$ (20°C) | $3.76 \times 10^{-11}$ (25°C) | 0.06<br>(15°C, pH=5.2)   |

### 2.2.1 Toxicity

The toxicity of mercury is highly dependent on specie. The absorption of metallic mercury in the gastro-intestinal tract is minimal making metallic mercury the least toxic of them all. Mercury vapor on the other hand is readily absorbed through the lungs into the blood. The blood then distributes it to different tissues where it in most cases is oxidized to Hg(II). Inhibition of the oxidation process can cause Hg<sup>0</sup> to remain in the body. As Hg<sup>0</sup> is highly fat-soluble, it can cross the placenta and the blood-brain barrier thereby entering the fetus or the brain where it accumulates. Hg<sup>0</sup>(g) can damage the lung tissue but the largest damages are on the central nervous system.

Generally Hg(II)-compounds are more soluble and cause more poisonings than does Hg(I)-compounds but the former can be absorbed in the gastro-intestinal tract as MeHg<sup>+</sup>[3,4]. The distribution and uptake in tissues of mercury ions is similar to that of mercury vapor but they do not pass the placenta or blood-brain barrier in any larger extent [3].

Of the organic compounds, methyl mercury is the most toxic. It is common in nature because of both extensive use and biomethylation by microorganisms that can transform all kinds of mercury species to MeHg in both soils and water. Acidified waters have shown a greater tendency for this biomethylation [3, 5, 6]. Methyl mercury is accumulated in the aquatic food chain. With man being the top predator, substantial amounts can be ingested when eating fish from contaminated lakes, as was the case in Minamata and Niigata. Absorption of organic mercury-compounds in the lungs, gastro-intestinal tract and through the skin is fast and the half-life in biological systems is long. It is also capable of passing the blood-brain barrier and the placenta, making it a potent neuro- and fetotoxin.

## 2.3 Sources, Emission & Atmospheric abundance

Mercury is emitted to the atmosphere from both natural and anthropogenic sources. Today approximately  $6 \times 10^9$  g of mercury is present in the troposphere [7].

### 2.3.1 Natural sources and emissions

One problem when classifying mercury emissions is the difficulty to distinguish between mercury originally emitted by anthropogenic sources and natural ones. True natural sources are geothermal activities, wind erosion and degassing from mercury mineralized soils and evasion from the Earth's crust [8]. Other sources that sometimes are viewed as natural are emissions from

oceanic and lake surfaces and re-emissions from soils although they are in most cases originally influenced by human activities.

Elemental mercury is very rare in nature and constitutes only about 0.5 ppm ( $\mu\text{g dm}^{-3}$ ) of the earth's crust, making it scarcer than uranium but more plentiful than gold and silver. Usually, mercury is extracted from cinnabar (HgS) which is the main mercury-containing mineral. Most of the world deposits are located around the Mediterranean, mainly in Almadén (Spain), Idria (Slovenia) and Monte Amiata (Italy) [2]. The fluxes of mercury from natural sources are currently being re-evaluated as new data show much higher values than the  $10\text{-}50 \text{ ng m}^{-2} \text{ h}^{-1}$  reported earlier. Ferrara et al [9] for example, have reported fluxes of  $1000\text{-}400000 \text{ ng m}^{-2} \text{ h}^{-1}$  over Almadén in Spain.

### 2.3.2 Anthropogenic sources and emissions

Estimates of the source strength of man-made emissions to the atmosphere vary between one and six thousand ton Hg per year [10]. Among the anthropogenic mercury sources, combustion of fossil fuels is the major source of mercury emissions to the atmosphere [8]. Emission from this source alone is  $700\text{-}3800 \text{ t yr}^{-1}$ . Other large sources are waste incineration, mining and smelting. (Table 2)

Table 2 Anthropogenic inputs to different environmental compartments. (Adapted from [10])

| Environmental compartment | Source category          | Emission ( $\text{t yr}^{-1}$ ) |
|---------------------------|--------------------------|---------------------------------|
| Air                       | Combustion of fuels      | 700- 3800                       |
|                           | Industrial manufacturing | 150-200                         |
|                           | Refuse incineration      | 200-2100                        |
| Water                     | Direct releases          | 1000-6700                       |
|                           | Dumping of sewage sludge | 1000-3000                       |
|                           | Atmospheric deposition   | 400-1800                        |
| Soil                      | Direct releases          | 1000-10700                      |
|                           | Atmospheric deposition   | 600-4300                        |

## 2.4 The biogeochemical cycling of mercury

In the atmosphere, mercury is present as vapor and as particulate-bound species. The dominant specie is elemental mercury, constituting more than 90% of the total mercury pool [11]. Typical background concentrations of  $\text{Hg}^0$  are  $1\text{-}3 \text{ ng m}^{-3}$  in the Southern Hemisphere and  $2\text{-}4 \text{ ng m}^{-3}$  in the Northern Hemisphere [12]. Recent measurements at Rörvik, Sweden have shown values between  $1\text{-}3 \text{ ng m}^{-3}$  [13].

The deposition rates of mercury from the atmosphere depend on its chemical and physical form.  $\text{Hg}^0$  has a residence time of 0.5 – 2 years [14], due to its low solubility in water and high vapor pressure. The  $\text{Hg(II)}$ -species on the other hand are generally more soluble and are easily scavenged into atmospheric droplets making them a target for wet deposition. Once back on the ground or in the ocean,  $\text{Hg(II)}$  can be reduced back to  $\text{Hg}^0$  or bio-methylated into organo-mercurial species. These redox processes govern the biogeochemical cycling of mercury. (Figure 1)

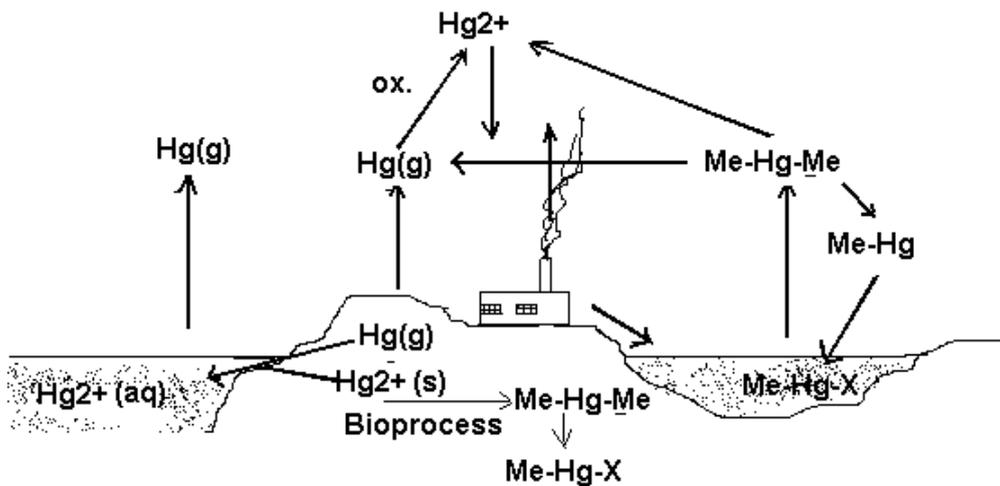


Figure 1 Biogeochemical cycling of mercury. (From [15])

## 2.5 Aqueous phase reactions of mercury

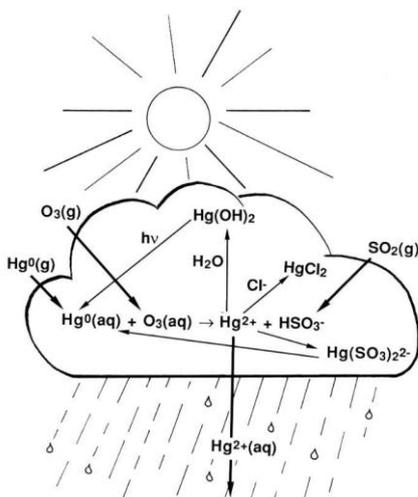


Table 2 Schematic picture of the heterogeneous chemistry influencing the wet deposition. (From [16])

The aqueous phase chemistry of mercury is associated with particle and droplet chemistry. Heterogeneous reactions may also occur at the surface of atmospheric particles. In **Error! Reference source not found.**, heterogeneous reactions occurring in clouds are depicted. Although the solubility of  $\text{Hg}^0$  is relatively low, its reactions in the aqueous phase are considered important, as many reactive species such as  $\bullet\text{OH}$  and  $\text{HO}_2\bullet$  are present in the aqueous phase in high concentrations.  $\text{Hg(II)}$ -species are generally more soluble than  $\text{Hg}^0$  and are therefore present at higher concentrations in the aqueous phase. To date many reactions of mercury in the aqueous phase have been investigated. In Table 3 rate constants for some redox reactions are listed.

Table 3 Rate constants for selected aqueous phase reactions of mercury

| Reaction   | Constant   | Reference |
|--|--|-----------|
| 1. $\text{Hg}^0_{(\text{aq})} + \bullet\text{OH}_{(\text{aq})} + 2\text{H}^+ \rightarrow \text{Hg}^{2+}_{(\text{aq})} + \text{products}$                       | $2.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (pH 3.9)                         | 17        |
|  | $4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$                                    | 18        |
| 2. $\text{Hg}^0_{(\text{aq})} + \text{O}_{3(\text{aq})} + 2\text{H}^+ \rightarrow \text{Hg}^{2+}_{(\text{aq})} + \text{H}_2\text{O} + \text{O}_{2(\text{aq})}$ | $4.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$                                  | 19        |
| 3. $\text{Hg}^0_{(\text{aq})} + \text{HOCl}_{(\text{aq})} + \text{H}^+ \rightarrow \text{Hg}^{2+}_{(\text{aq})} + \text{Cl}^- + \text{H}_2\text{O}$            | $2.09 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$                                 | 20        |
| 4. $\text{Hg}^0_{(\text{aq})} + \text{OCl}^-_{(\text{aq})} + \text{H}_2\text{O} \rightarrow \text{Hg}^{2+}_{(\text{aq})} + \text{Cl}^- + 2 \text{OH}^-$        | $1.99 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$                                 | 20        |
| 5. $\text{Hg(OH)}_2_{(\text{aq})} + h\nu \rightarrow \text{Hg}^0_{(\text{aq})} + \text{products}$  | $3 \times 10^{-7} \text{ s}^{-1}$ , midday 60°N                                  | 21        |
| 6. $\text{Hg(II)}_{(\text{aq})} + \text{HO}_2\bullet \rightarrow \text{Hg(I)} + \text{O}_2 + \text{H}^+$   | $1.7 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$                                  | 22        |
| 7. $\text{Hg(I)} + \text{HO}_2\bullet \rightarrow \text{Hg}^0 + \text{O}_{2(\text{aq})} + \text{H}^+$  | Fast   | 22        |
| 8. $\text{Hg}^{2+} + \text{SO}_3^{2-} \rightarrow \text{HgSO}_{3(\text{aq})}$  | $\log K_{\text{eq}} 12.7$ , $k=5.0 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1}$ | 23        |
| 9. $\text{HgSO}_3 + \text{SO}_3^{2-} \rightarrow [\text{Hg}(\text{SO}_3)_2]^{2-}$  | $\log K_{\text{eq}} 11.4$ , $k=1.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$    | 23        |
| 10. $\text{HgSO}_{3(\text{aq})} \rightarrow \text{Hg}^0_{(\text{aq})} + \text{S(VI)}$  | $\leq 0.6 \text{ s}^{-1}$  | 23        |
| 11. $[\text{Hg}(\text{SO}_3)_2]^{2-}_{(\text{aq})} \rightarrow \text{Hg}^0_{(\text{aq})} + \text{S(VI)}$   | $< 10^{-4} \text{ s}^{-1}$   | 23        |

The aim of this study is to re-determine the rate constant for the reaction  $\text{Hg}^0 + \bullet\text{OH}$  as previous investigations have shown two different results, both without confidence intervals. (See Table 3) Another goal is to develop and evaluate an instrumental set-up that can be used for future experiments of mercury in the aqueous phase.

### 3 EXPERIMENTAL

#### 3.1 Method

The determination of rate constants can be performed by either an absolute or a relative method.

##### 3.1.1 Absolute methods

In absolute methods, the rate of reaction between species A and X is determined by following the change in concentration of the different species over time.



This method requires that the time be measured alongside the change in concentration.

The disadvantage of this method, especially when dealing with radicals is that it can be difficult to isolate the reactants in situ in order to measure them. In addition, influences of secondary reactions might affect the results.

##### 3.1.2 Relative method

Relative rate experiments involves a second reaction with a known rate constant that compete with the studied reaction for one of the reactants [24]. In this study the two competing reactions were



The rate expressions for the reactions are

$$\frac{d[\text{Hg}^0]}{dt} = -k_1[\text{Hg}^0][\cdot\text{OH}] \quad (\text{Eq. 1})$$

and

$$\frac{d[\text{S(IV)}]}{dt} = -k_2[\text{S(IV)}][\cdot\text{OH}] \quad (\text{Eq. 2})$$

respectively, provided that no other reactions are involved that can remove any of the reactants.

Integrating the two rate expression with  $t_0=0$  and  $t_r=t$  gives

$$\ln \frac{[\text{Hg}^0]_t}{[\text{Hg}^0]_0} = -k_1[\cdot\text{OH}]t \quad (\text{Eq. 3})$$

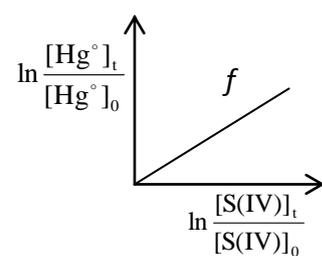
and

$$\ln \frac{[\text{S(IV)}]_t}{[\text{S(IV)}]_0} = -k_2[\cdot\text{OH}]t \quad (\text{Eq. 4})$$

A quotient between the two rate constants can be obtained by dividing the two rate expressions.

$$\ln \frac{[\text{Hg}^0]_t}{[\text{Hg}^0]_0} = \frac{k_1}{k_2} \times \ln \frac{[\text{S(IV)}]_t}{[\text{S(IV)}]_0} \quad (\text{Eq. 5})$$

A plot of the two expressions gives a curve with slope  $f$ .



As  $k_2$  is a known constant,  $k_1$  can be calculated.

$$k_1 = f \times k_2 \quad (\text{Eq. 6})$$

This way the unknown rate constant can be determined by measuring the change in concentration of  $\text{Hg}^0$  and  $\text{S(IV)}$  instead of the elusive OH-radical.

Another advantage of this method over the absolute method is that it is independent of time. Thereby there is one less parameter to measure. In addition, some property proportional to the concentration, e.g. conductivity, can be measured instead of the absolute concentrations of the reactants. The disadvantage is the possibility of built-in errors as the calculations are dependent on earlier measurements/estimates of rate constants.

## 3.2 Principles of analytical techniques

### 3.2.1 Atomic absorbance and fluorescence spectroscopy

The difference between atomic and molecular spectroscopic techniques is that free atoms cannot undergo rotational or vibrational transitions as most molecules can. Energy absorbed by atoms induce electronic transitions which give rise to sharp, well-defined lines, while molecular spectra in the UV/VIS region are characterized by broad absorption regions spanning over several wavelengths. In Atomic Absorption Spectroscopy (AAS), the amount of energy absorbed by the atoms during excitation is measured. Atomic Fluorescence Spectroscopy (AFS) on the other hand is based on the principle that the excited atoms emit light that can be detected while relaxing back to the ground state. As the fluorescent signal has virtually no background, it is possible to get a higher sensitivity in AFS than in AAS.

The excitation of the atoms is produced by irradiating them with light from a source that has a narrow wavelength interval matching the absorption maxima of the atoms in gas-phase. Usually an external heat source, e.g. a flame, is required to vaporize the sample before excitation. Mercury is volatile enough to allow the transfer to gas-phase to occur at room temperature, hence the expression Cold Vapor Atomic Fluorescence Spectroscopy (CVAFS).

CVAFS has become a frequently used technique for analyzing mercury in the environment. In the past years a number of relatively easy-to-use instruments for this purpose have been developed.

### 3.2.2 *Ion chromatography*

In ion chromatography, the stationary phase consists of a porous material onto which ionic groups are chemically bonded. The mobile phase is usually a buffered solution containing a counter ion with a charge opposite that of the stationary-phase groups. Competition between the sample ions and the mobile phase governs the separation of different ions. Ion exchangers can be either anion or cation exchangers depending on the type of ions to be analyzed.

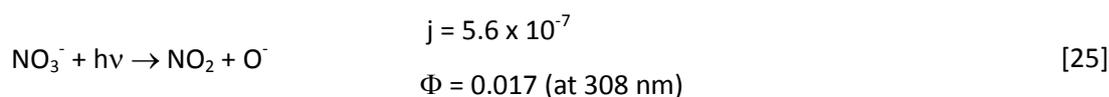
### 3.3 **Materials and instruments**

Chemicals used were potassium nitrate ( $\text{KNO}_3$ ) and nitric acid (65%  $\text{HNO}_3$ ) of p.a. grade from Merck Chemical company and sodium hydrogen sulfite ( $\text{NaHSO}_3$ ) of reagent grade from JT Baker. Ar-gas ( $\geq 99.9997\%$ ) and  $\text{N}_2$ -gas ( $\geq 99.996\%$ ) was from AGA Gas AB. The  $\text{N}_2$ -gas was cleaned from mercury by means of a gold trap.

### 3.4 **Source of OH-radicals**

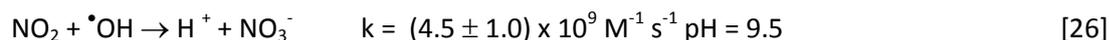
There are several ways to obtain OH-radicals in aqueous solutions. The photodecomposition of  $\text{H}_2\text{O}_2$  is perhaps the "cleanest" one of them as it produces two OH-radicals per  $\text{H}_2\text{O}_2$ -molecule and no byproducts. However,  $\text{H}_2\text{O}_2$  is a powerful oxidant that would react with the sulfite in the solution. Therefore the photodecomposition of  $\text{NO}_3^-$  has been chosen for this study.

The main pathway (~90%) for the photolysis of  $\text{NO}_3^-$  is



$\text{O}^-$  will then be hydrolyzed rapidly, yielding  $\cdot\text{OH}$  and  $\text{OH}^-$ .

The formed  $\text{NO}_2$  have several pathways to follow the fastest one being



### 3.5 Instrumental set-up

The experiments were performed using two different set-ups described in Figure 2 and Figure 3. In the first set-up (Figure 2), the aim was to achieve a mass-balance between  $\text{Hg}^0$  and  $\text{Hg(II)}$ . For this purpose, the CVAFS (Millenium Merlin, PSA Ltd.) was used to measure the increase in  $\text{Hg(II)}$  and the CVAAS the decrease in  $\text{Hg}^0$ . The sulfite concentration was measured on an ion chromatograph.

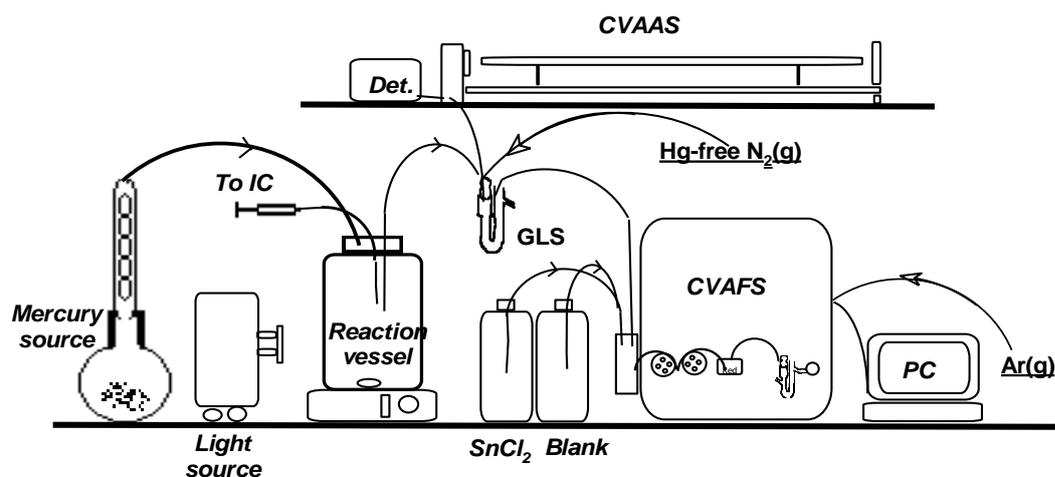


Figure 2. Instrumental set-up used in experiment 1 - 3.

Due to problems with the stability of the CVAAS the set-up was modified and somewhat simplified by excluding the CVAAS and the gas-liquid separator (GLS) (Figure 3). This made it possible to draw the sample directly from the reaction vessel thereby minimizing the time between sample outtake and analysis and the risk of losses to the surroundings. In this set-up, the CVAFS was used to measure the decrease in  $\text{Hg}^0$  instead of the  $\text{Hg(II)}$ -increase. The mass balance was measured by reducing one sample with  $\text{SnCl}_2$  to measure  $\text{Hg}_{\text{tot}}$  with the CVAFS.

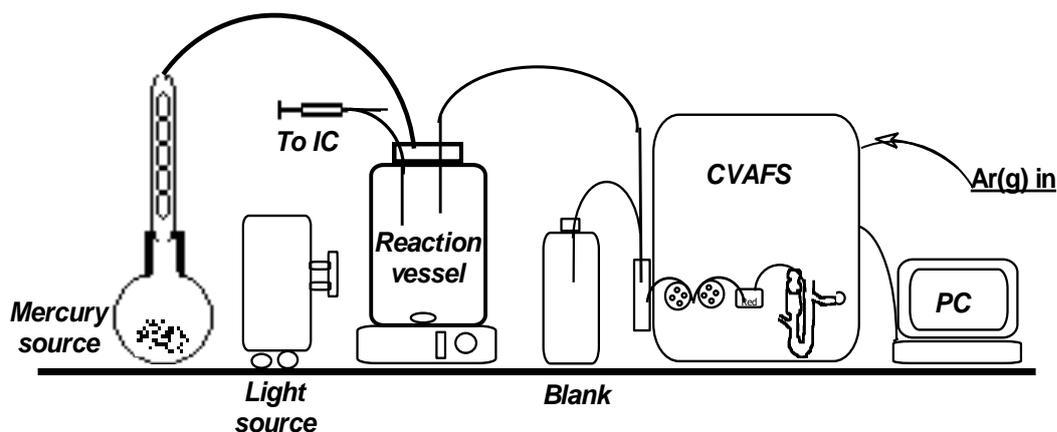


Figure 3. Instrumental set-up used in experiment 4 - 6.

In both set-ups the ion chromatography system (IC) was a Dionex equipped with an anion column, Ionpac AS4A-SC analytical column and 1.8 mM Na<sub>2</sub>CO<sub>3</sub> + 1.7 mM NaHCO<sub>3</sub> as eluent. The light source was a 450 W Xenon lamp (Oriel corp. model 66066) equipped with a wavelength filter (Oriel corp.) to ensure wavelengths above 300 nm.

### 3.6 Experimental procedure

A 2 l. Teflon container (FEP) was filled with double de-ionized water (Millipore Milli-Q) and saturated with Hg<sup>0</sup> by allowing air from the mercury source to bubble through the water for approximately three hours. Hg<sup>0</sup><sub>(aq)</sub>-concentrations obtained were in the range 0.1-0.2 μM, approximately 33-66% of the reported solubility of Hg<sup>0</sup> (0.3 μM at 298 K [27]). To the mercury solution, KNO<sub>3</sub> and a freshly prepared solution of NaHSO<sub>3</sub> were added, giving a concentration of 1 mM and 50 μM respectively. In experiment 1 - 3, the pH of the solution was 7.2 (± 0.1). In experiment 4 - 6 the pH was adjusted to 4.1 (± 0.1) by addition of HNO<sub>3</sub>, giving a total NO<sub>3</sub><sup>-</sup> concentration of 1.1 mM. The solution was stirred in all experiments with a magnetic stirrer. The choice of the different pH was made from the pH-intervals used for the rate determination of the reference reaction (see section 4.1, Table 5).

In experiment 1 - 3 a sample from the reaction vessel was pumped into the (GLS). In the GLS, the Hg<sup>0</sup> was removed from the solution into the CVAAS by allowing mercury-free argon gas to bubble through the sample for approx. one minute. After this time, the Hg(II)-concentration was analyzed on the CVAFS and a sample was extracted from the reaction vessel for sulfite analysis on the IC. In

experiment 4 - 6 the first step was eliminated and measurements of  $\text{Hg}^0$  and sulfite-concentration was performed concurrently. The temperature of the reaction vessel was  $22 \pm 0.5^\circ\text{C}$ .

Absorption of mercury to the walls of the vessel during the experiments or oxidation in the absence of light would influence the rate constant of the reaction. To exclude this possibility a dark control experiment was performed with the same experimental parameters as in the ordinary experiments but without the light source.

Since auto-oxidation of sulfite solutions with air can be a problem tests were performed to exclude this possibility. A solution of  $\text{HSO}_3^-$  with a concentration of 1 mM was made and analyzed on the IC for a period of 60 minutes. Between the analyses, the solution was kept in a closed volumetric flask in full light.

## 4 RESULT AND DISCUSSION

### 4.1 Determination of the rate constant

The slope  $f$  was calculated for each experiment using Equation 5 (Table 4, Appendices 2 -3)

Table 4 Calculated slope for experiment 1 – 6 and average slope at pH 4.1 and 7.2 respectively.

| Experiment | pH  | $f$             | Intercept        | $R^2$ | Average slope at different pH |
|------------|-----|-----------------|------------------|-------|-------------------------------|
| 1          | 7.2 | $1.29 \pm 0.39$ | $0.33 \pm 0.47$  | 0.955 | pH 7.2 = $1.3 \pm 0.4$        |
| 2          | 7.2 | $1.60 \pm 0.08$ | $0.02 \pm 0.47$  | 0.998 |                               |
| 3          | 7.2 | $1.07 \pm 0.11$ | $0.02 \pm 0.12$  | 0.990 |                               |
| 4          | 4.2 | $1.01 \pm 0.12$ | $-0.03 \pm 0.14$ | 0.983 | pH 4.1 = $1.1 \pm 0.2$        |
| 5          | 4.0 | $1.02 \pm 0.15$ | $-0.07 \pm 0.16$ | 0.972 |                               |
| 6          | 4.1 | $1.24 \pm 0.11$ | $-0.01 \pm 0.09$ | 0.991 |                               |

The oxidation of sulfite (S(IV)) by hydroxyl-radicals was chosen as reference reaction.



This choice was made since both sulfite and sulfate (S(VI)) are easily detected with ion chromatography and that the reaction have a rate constant close to the expected rate for the mercury reaction. Depending on pH the S(IV)-ion is present in solution as  $\text{H}_2\text{SO}_3$ ,  $\text{HSO}_3^-$  or  $\text{SO}_3^{2-}$ . (Figure 4)

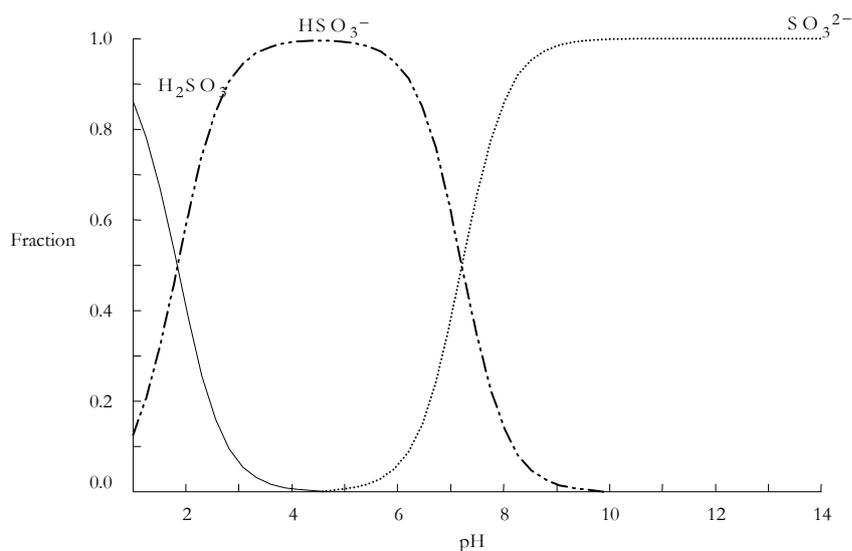


Figure 4 Fractions of sulfite species at different pH.

The rate constants for this reaction have been determined at both low pH ( $\leq 4.5$ ) with  $\text{HSO}_3^-$  being the dominant specie and at high pH ( $\geq 8.5$ ) with  $\text{SO}_3^{2-}$  as dominant specie. (Table 5) There are two different sets of rate constants available in the literature.

Table 5 Reported rate constants for the oxidation of sulfite by hydroxyl-radicals

| Reaction   | Rate constant   | pH   | Reference | Method<br>(see section 3.1) |
|--|---|------|-----------|-----------------------------|
| $\text{HSO}_3^- + \cdot\text{OH} \rightarrow \text{SO}_4^{2-}$   | $4.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$           | 4.4  | 28        | Relative                    |
|  | $(2.7 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ | 4.5  | 29        | Absolute                    |
| $\text{SO}_3^{2-} + \cdot\text{OH} \rightarrow \text{SO}_4^{2-}$ | $5.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$           | 11.2 | 28        | Relative                    |
|  | $(4.6 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ | 8.5  | 29        | Absolute                    |

In this study, the most recently reported values have been used [29]. Without re-determining the rate constants, it is difficult to conclude which one is more correct than the other.

As no rate constant has been determined at pH 7.2 this was calculated by assuming a linear relationship in rate constants at different pH. At pH 7.2 the distribution of  $\text{SO}_3^{2-}$  to  $\text{HSO}_3^-$  is approximately 50/50. The rate constant  $k_2$  in Equation 4 and 6 can then be calculated as

$$(2.7 \times 0.5 + 4.6 \times 0.5) = 3.65$$

The rate constant for the reaction between  $\text{Hg}^0$  and hydroxyl radicals was calculated to  $(2.9 \pm 0.6) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  at pH 4.1 and  $(4.8 \pm 1.5) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  at pH 7.2 using the average values in Table 4 and Equation 6. (see Appendix 1-3 for regression analysis and figures) As this reaction is not believed to be pH-dependent, there must be a reason for the difference in the two values.

## 4.2 Mercury's reaction with S(IV)-species

Aqueous phase chemistry of mercury is complex and includes several species. As can be seen in Table 3 and Figure 5, there are several possibilities of complex formation. Since sulfite has been chosen as reference in this study, reactions 8-11 in Table 3 may influence the observed rate of reaction between elemental mercury and hydroxyl radicals. The reduction of the  $\text{HgSO}_3$  and  $[\text{Hg}(\text{SO}_3)_2]^{2-}$ -complexes (reaction 10 & 11 in Table 3) during the experiments would cause the concentration of  $\text{Hg}^0$  to increase and thereby lower the measured rate of reaction. Because  $[\text{Hg}(\text{SO}_3)_2]^{2-}$  is more stable than the  $\text{HgSO}_3$ -complex (Figure 5), it may be possible to avoid this

problem to some extent by choosing a pH-interval, e.g. 9-10, where the formation of the former complex is favored. This is not a relevant pH-interval from an atmospheric point of view as the pH of most atmospheric waters is generally in the range 2-5. From a chemical point of view however this might make the experimental determination of the rate constant easier.

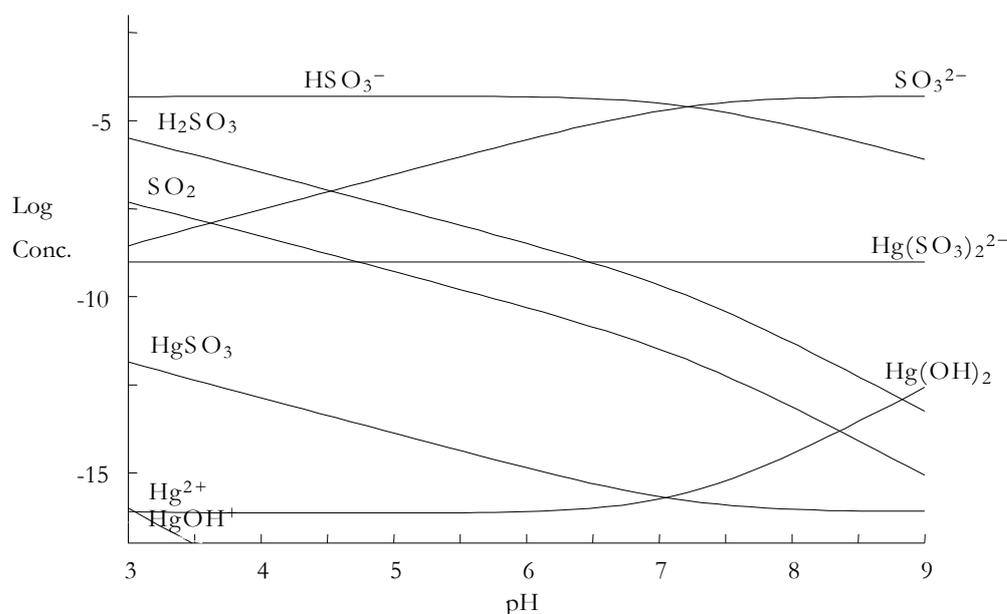


Figure 5 pH-dependence on complex formation with  $\text{OH}^-$  and  $\text{SO}_3^{2-}$  as ligands.  $[\text{Hg}^{2+}] = 1 \text{ nM}$  and  $[\text{S(IV)}] = 50 \mu\text{M}$ .

Further investigation of are required for a complete assessment of the impact on the rate of reaction for  $\text{Hg}^0 + \cdot\text{OH}$  by these reactions.

### 4.3 Auto-oxidation of sulfite & dark control-experiment

The auto-oxidation of S(IV) was investigated. Analysis of fresh solutions of bisulfite, pH 4.2, showed no change over a period of 45 minutes. As the experiments were completed within 35 minutes after addition of the  $\text{HSO}_3^-$ -solution to the reaction vessel, auto-oxidation of sulfite was not considered a problem.

As the reaction vessel was open to the mercury-source during the experiments, there was a risk that  $\text{Hg}^0$  was added to the solution. Mercury can also be adsorbed to the walls of the container, with losses of mercury other ways than through reactions as a consequent. The performed dark control experiment showed no change in initial and final mercury concentration and it was therefore concluded that no losses or additions of  $\text{Hg}^0$  was obtained this way.

#### 4.4 The photolysis of $\text{NO}_3^-$

The concentration of  $^{\bullet}\text{OH}$  in the solution was calculated by use of Equation 2 to  $3 \times 10^{-14}$  M. As there are more than one possible pathway for the photolysis of  $\text{NO}_3^-$  there is also a chance of additional products that might influence the rate of reaction. Modeling all possible pathways is a way to determine whether these reactions are significant or not. Unfortunately, there was not enough time to do this in this thesis.

#### 4.5 Conclusions

The rate constants obtained in this study show a higher rate of oxidation of  $\text{Hg}^0$  than the reported values by Lin & Pehkonen [17] and lower than the one reported by Pleijel [18]. The reduction of  $\text{HgS(IV)}$ -species should decrease the measured rate of reaction meaning that the constant at pH 4.1 achieved in this study should be considered as a minimum value. Further studies of this reaction with a different reference reaction can give a more correct picture of the rate of the oxidation of elemental mercury by hydroxyl-radicals. A possible pH-dependence should also be considered.

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