Kinetic and mass-spectrometric studies of atmospherically relevant

mercury-bromine chemistry

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Abstract

Bromine radicals are thought to play an important role in the chemistry of atmospheric elemental mercury, however uncertainties remain concerning the rate and the mechanism of the reaction. The products of the atmospheric reaction are thought to be mercury halides of the form HgBrX, where X = Cl, Br, I.

This thesis describes the early stages of development of a methodology for the detection of atmospheric mercury halides by Atmospheric Pressure Chemical Ionisation Mass Spectrometry (APCI-MS). It also reports the results of laboratory experiments aimed at identifying the product(s) and determining the rate coefficient of the reaction at near atmospheric conditions. The kinetics were studied using the relative rate method with 1-butene as the reference molecule and the value of the $k_{Hg+Br}/k_{1-C_4H_8+Br}$ ratio was mapped for a wide variety of experimental conditions.

The experiments confirm the lack of oxygen dependence of the mercury reaction. A rate coefficient of $(3.1 \pm 1.9) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ was obtained, which is in agreement with the most recent peer-reviewed study. Using solid-phase micro-extraction (SPME) in the gas phase, HgBr₂ was confirmed as one of the end products of the mercury reaction under our laboratory conditions, and two products of the 1-butene reaction (1-bromo-2-butanone and 1-bromo-2-butanol) were also identified for the first time.

Résumé

Les radicaux de brome jouent potentiellement un rôle important dans la chimie atmosphérique du mercure élémentaire, mais la vitesse ainsi que le mécanisme de la réaction demeurent incertains. Dans l'atmosphère, les produits de la réactions sont probablement des halogénures de mercure de la forme HgBrX (X = Cl, Br, I).

Ce mémoire décrit les premiers stades de développement d'une méthode pour la détection des halogénures de mercure dans l'air par ionisation chimique à pression atmosphérique et spectrométrie de masse (APCI-MS). Les résultats d'expériences de laboratoire visant l'identification du ou des produits de la réaction ainsi que la détermination de sa constante de vitesse sous des conditions quasi-atmosphériques sont aussi présentés. La méthode des vitesses relatives a été utilisé pour étudier la cinétique de la réaction. Le 1-butène était la molécule de référence. Le ratio des constantes de vitesse, $k_{Hg+Br}/k_{1-C_4H_8+Br}$, a été déterminé sous des conditions variées.

Les résultats confirment que la vitesse de réaction ne dépend pas sur la pression partielle d'oxygène dans le système. Une constante de vitesse de $(3.1 \pm 1.9) \times 10^{-13}$ cm³ molécule⁻¹ s⁻¹ a été obtenue. Ce résultat est comparable à ceux publiés par d'autres groupes récemment. La micro-extraction sur phase solide a permis de confirmer que HgBr₂ est l'un des produits finaux de la réaction sous nos conditions expérimentales. Deux produits de la réaction entre les radicaux de brome et le 1-butène, le 1-bromobutan-2-one et le 1-bromobutan-2-ol, ont aussi été identifiés pour la première fois.

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1 Introduction

Mercury is an element with a rich history. It was known to the ancients, was important to the alchemists, was used in medicine and featured in scientific discovery. Its unique properties made it a global commodity, with applications in industry, agriculture, electrical devices and measuring equipment. The recent realization that mercury can cycle through the environment and contaminate even remote pristine ecosystems has led to regulations to limit and control its usage and to intensified scientific research in a bid to understand its geochemical cycle. It is now recognized that mercury can undergo long-range atmospheric transport and that, following chemical and or physical transformations, it can enter remote ecosystems. This is exemplified by atmospheric mercury depletions events (MDEs). Atmospheric bromine radicals are thought to initiate these events, but uncertainty remains concerning the rate and the mechanism of the reaction. Research is needed to refine the kinetic parameters and to identify the product(s) of the reaction. This thesis reports on progress made towards these objectives.

1.1 Background

1.1.1 Mercury – The Element

Mercury is a naturally occurring element. As such, it is indestructible and cannot be broken down into other entities. It can, however, react to form a variety of mercury-containing species. Its atomic number is 80 and it belongs to Group 12 of the periodic table, along with zinc and cadmium. Its atomic weight is 200.59 g/mol. It has seven stable isotopes (¹⁹⁶Hg, ¹⁹⁸Hg, ¹⁹⁹Hg, ²⁰⁰Hg, ²⁰¹Hg, ²⁰²Hg, ²⁰⁴Hg), the most naturally abundant of which is ²⁰²Hg at 29.86%. Its electronic configuration is [*Xe*] $4f^{14} 5d^{10} 6s^2$. It can be found in three different oxidation states (0, +1

and +2). Its most easily recognizable form, however, is its elemental, or metallic form. Elemental mercury, Hg^0 , has low melting and boiling points, a high density and surface tension, and low viscosity. These properties combine to give elemental mercury its characteristic appearance: it is a beautiful, silvery-white liquid that forms very mobile round droplets. It is from this appearance that mercury gets its common name, quicksilver (from the Latin *argentum vivum*, or live silver) and its chemical symbol, Hg (from the Greek *hydrargyros*, or watery silver).

1.1.2 Mercury throughout History

This section provides an overview of mercury through the ages, in six parts: Mercury and the Ancients, Alchemy, Mercury in Medicine, Mercury in Scientific Discovery, Mercury as a Commodity and Modern Stance: Mercury as a Global Pollutant. A timeline of some the important facts is shown in Figure 1.

1.1.2.1 Mercury and the Ancients

Mercury is one of the elements mankind has known about for the longest, although the exact time of its discovery is unknown. It is widely reported as having been 'known to the ancient Chinese and Hindus and found in Egyptian tombs dating from circa 1500 B.C.' [*Hammond*, 2009-2010], although there is little actual documented evidence supporting these statements. The story about flasks of metallic mercury being found at Kurna, in a tomb dating from 1500 B.C., probably originated from an anonymous paper published in *Pharmazeutische Zeitung* in 1890. The story was then propagated, with some variations, through the archaeological literature by several authors [*Goldwater*, 1972], even though the actual flasks have never been found. As for the ancient Chinese and Hindus, it seems true that they knew of cinnabar (HgS), the red ore from which mercury is extracted, very early on. Actual dates are hard to come by, but cinnabar was used



Figure 1: A brief history of mercury

as a decorative pigment and as an ink by the Chinese at least as early as the Shang-Yin dynasty (1751-1112 B.C.) [*Goldwater*, 1972]. This knowledge does not seem to have been restricted to Asia. A cinnabar mine in Konia, Cyprus, was dated

to 1500 B.C. [Goldwater, 1972] and cinnabar was also found in burial grounds dating from 3000 B.C. in Osorno, Spain [Martin-Gil et al., 1995].

As for elemental mercury itself, it does not appear in the record until the 4^{th} century B.C. It is mentioned by the Greek philosopher Theophrastus of Eresus (c. 372-288 B.C.) in a short treatise on rocks and minerals. More specifically, the treatise mentions that hydrargyros can be obtained from cinnabar by rubbing it with vinegar in a copper vessel, and that cinnabar itself originates from Spain [*Stillman*, 1924]. Later on, Marcus Vitruvius Pollio (c. 70 – c. 25 B.C.), a Roman architect, described the use of quicksilver to attract the gold scattered amongst the ashes obtained from burning worn-out gold-adorned clothes [*Stillman*, 1924]. A century later, the Roman encyclopaedist, Gaius Plinius Cecilius Secundus (23-79 A.D.), known as 'Pliny the Elder', describes the use of quicksilver in the gilding of metals, but notes that the method is expensive. The method described by Pliny remained in use and virtually unchanged until the 1840s [*Oddy*, 1981].

The Egyptians also had knowledge of mercury and used it as part of a tin alloy intended to give the appearance of silver [*Stillman*, 1924]. Two very technical papyri dating from the 2nd or 3rd century A.D. have been found, describing the processes, amongst others, for making fake gold and silver from lesser metals. They are known as the Leyden papyrus and the Stockholm papyrus, and were part of a collection of Egyptian papyri written in Greek. They are thought to have been entombed with the mummy of an early chemist, thus surviving the decree by Diocletian in 290 A.D. that all documents pertaining to the making of gold and silver from lesser metals be destroyed [*Stillman*, 1924]. The documents are unusual in that they mostly lack the mysticism usually associated with these kinds of documents. It is also interesting to note that the papyri do not contain any signs of self-deception or belief that the gold made is genuine. In fact, several recipes are accompanied by claims that the product will 'answer the usual tests for genuine products' and that it should 'deceive even the artisans' [*Stillman*, 1924].

1.1.2.2 Alchemy

Whereas the mysticism of the Egyptians might have been a way of keeping their metallurgic secrets from laypeople [*Stillman*, 1924], the mysticism of the alchemists seemed to be rooted in a deep belief in the transmutability of matter. The idea might have been inspired by Plato and Aristotle, who believed that nature was made of four transmutable elements. The alchemists also believed in the influence of astrological bodies. Mercury got its name from the alchemists, who associated it with the planet Mercury, possibly because of its very mobile nature (the planet, Mercury, having the fastest orbit around the Sun). They also adhered to the concept that all metals (gold, silver, lead, copper, tin, iron) were composed of mercury and sulphur. The different metals were thought to be the result of shorter or longer 'incubations' of mercury and sulphur within the Earth's crust. This led to the famous alchemical belief that base metals could be transmuted into gold under the right conditions [*Stillman*, 1924].

The first famous Chinese alchemist, Ge Hong (Ko Hung, 283 - 343 A.D.), believed in physical immortality and thought it could be achieved by drinking 'immortal' (i.e. neither destroyed nor altered by fire) substances like gold or mercury [*Knapp*, 2003]. This kind of belief might have paved the way for the use of mercury in medicine, since it associated mercury with a long life.

1.1.2.3 Mercury in Medicine

It is difficult to trace the origins of the use of mercury in medicine, since there is much confusion in the early literature. The confusion stems as much from linguistic considerations and muddled chronology as from the lack of identification by chemical analysis.

Both Pliny and Pedanius Dioscorides (c. 40- c. 90 A.D.), his Greek contemporary, knew of the poisonous nature of mercury [*Stillman*, 1924] and refer to the masks worn by the workers exposed to cinnabar and mercury vapours [*Gold*- *water*, 1972]. Knowledge of the potential adverse health effects of mercury is not so surprising considering that Vitruvius wrote of the toxicity of lead in the 1st century B.C. [*Stillman*, 1924].

Both authors also reported on the common confusion arising from the different terminology used by Greek and Roman authors. The Romans called HgS *minium*, whereas the Greeks called it cinnabar. The confusion arose from the fact that the Romans used dragon's blood (a red gum obtained from certain varieties of palm), which they called *cinnabaris*, in medicines. Pliny expresses the problem thus: *The Greeks* [...] give to minium the name of cinnabar, and hence the error caused by the two meanings of the same word, this being properly the name given to [dragon's blood]. Indeed this last is the only colour which in painting gives a proper representation of blood. This cinnabar, too, is extremely useful as an ingredient in antidotes and various medicaments. But, by Hercules, our physicians, because minium also has the name of cinnabaris, use it as a substitute for the other and so employ a poison.' [Stillman, 1924]. Some of the confusion might also have arisen from the fact that both substances, dragon's blood and cinnabar (HgS), were used as paint pigments at the time.

So it seems that the Greeks and the Romans did not voluntarily use mercury as a medicine. It is unclear whether the Egyptians did, since the names they used for mercury and cinnabar are not known [*Goldwater*, 1972]. As mentioned in the previous section, the Chinese of the same time period might have ingested mercury as a way to prolong life.

The introduction of mercury into western medicines is thought to have come from Muslim physicians, who possibly gained their knowledge about the benefits of mercury from Eastern physicians, since there were Indian physicians in Baghdad during the reign of Haroun-al-Rashid (786-809 A.D.) [*Goldwater*, 1972]. Examples of mercury use in western medicine include the following:

- Mercury inhalations or fumigations for the treatment of syphilis were popular from the first decade of the 16th century and were still being used at least as late as 1928 [*Goldwater*, 1972].
- In the 19th century, elemental mercury was ingested in large quantities by patients suffering from intestinal blockage [*Newton Friend*, 1961].
- Mercury(II) chloride (HgCl₂) was used in external/topical ointments to treat wounds and parasite infections as early as the 12th century [*Goldwater*, 1972]. A 1% solution can be used as an antiseptic [*Calvert*, 2002].
- Some organomercury compounds, including merbromin, and nitromersol were sold as over-the-counter antiseptic solutions to treat cuts and scratches. They are still available in most countries, although their sale has been prohibited in the USA [*Calvert*, 2002].
- Thimerosal, an organomercury compound, is currently used as a preservative in vaccines.

The effectiveness of the above treatments, especially in the case of syphilis, is dubious. This has been expressed by [Goldwater, 1972] in the following way: 'Mercury clearly deserves an honored place in the annals of medical history, particularly in syphilology. It was the first drug to be used for the purpose of killing pathogenic microorganisms in the human body, antedating the sulfonamides and antibiotics by more than 400 years. ... No other drug has such a long and distinguished, if at times stormy, record. Whether or not this reputation was deserved is uncertain.'

1.1.2.4 Mercury in Scientific Discovery

Mercury's unusual physical properties have been put to use by the scientific community. The barometer, the thermometer and the diffusion pump are three common laboratory items that were developed using mercury's high density, uniform thermal expansion and low boiling point, respectively [*Calvert*, 2002]. Other instances of mercury being involved in scientific discovery are numerous – a few are described below.

One of the earliest descriptions of the distillation process is that of cinnabar (HgS) to obtain elemental mercury. [Stillman, 1924], translating from Dioscorides' Materia Medica, describes it as follows: 'From [...] cinnabar, it is obtained by heating in an iron dish placed in an earthen vessel which is provided with a domed cover that is luted on with clay. The quicksilver collects in drops on the domed cover.' More recently, mercury is credited with being part of the experiments of van Helmont (1579-1644) in showing the indestructibility of matter (showing that dissolved metals could be recovered in their original quantity) and those of Robert Boyle (1627-1691), which led to his formulation of Boyle's law (1662) [Goldwater, 1972]. Boyle's Law states that for a given mass, at a constant temperature, the pressure multiplied by the volume is a constant (PV = c) and is effectively one half of the ideal gas law. Mercury also played a part in the discovery of oxygen, since Joseph Priestley (1733-1804), Carl Wilhelm Scheele (1742-1786), Pierre Bayen (1725-1798) and Antoine Laurent Lavoisier (1745-1794) all used mercury oxide in their experiments [Goldwater, 1972]. It is interesting to note that Lavoisier was the first to have recognized mercury as being an element. Until then, it had retained its alchemical meaning, i.e. it was thought to be the 'essence' in metals that made them white and shiny [Calvert, 2002]. In 1828, Friederich Wohler (1800-1882), used mercury in his synthesis of urea, making mercury a part of the first ever laboratory synthesis of an organic compound. Finally, mercury was also used in the experiments that validated Einstein's 1905 formula for the diffusion of colloidal particles [*Goldwater*, 1972].

1.1.2.5 Mercury as a Commodity

Mercury has been mined since at least 1500 B.C. and has been used as a decorative pigment and in metallurgy since ancient times. Its unique properties and multiple uses paved the way to mercury becoming a global commodity in the industrial era. The main sectors of industry that use mercury are [*Maxson*, 2005]:

- mercury oxide and other batteries
- chlor-alkali production
- small-scale/artisanal gold mining
- dental amalgams
- thermometers
- other measurement and control equipment
- neon, compact fluorescent, HID and other energy-efficient lamps
- electrical switches, contacts and relays
- industrial processes requiring catalysts
- laboratory and educational uses
- pharmaceutical processes, products and preservatives
- cosmetics
- paints and pesticides/agricultural chemicals
- cultural uses and traditional medicine



Figure 2: Global mercury consumption in tonnes (2003). Redrawn from [Maxson, 2005]

The global demand for mercury has steadily decreased since the 1960s, declining from over 9000 tonnes to less than 4000 tonnes. The main drivers of this reduction were increased awareness of mercury's toxicity and tougher regulations in Europe and North America, with these two regions now consuming less than 10% of the total each. Demand in Asia and South America remains high, especially in regions where artisanal gold mining activities are important¹, and also as a result of a general shift of mercury product manufacturing operations from the developed to the developing world [Maxson, 2005]. Figure 2 shows how global mercury consumption in 2003 was divided between different sectors.

New regulations are being adopted regularly. One such regulation in the US is the Mercury Export Ban Act of 2008, which prohibits export or transfer of

¹ Artisanal gold mining is generally illegal and the data concerning mercury consumption in this sector is uncertain.

governmental mercury stockpiles except for the purpose of permanent storage in the US. The ban will extend to private companies from January 1st, 2013. Although there are provisions in these regulations that allow for certain exceptions to be made, the fact that these laws are implemented is indicative of the present mindset towards mercury.

This phasing-out of elemental mercury as a commodity is being enforced in a bid to reduce mercury pollution by minimizing potential local sources of contamination. As mercury-containing species go, elemental mercury is relatively mildly toxic, but pathways exist in the environment that allow the transformation of relatively harmless forms of mercury into highly toxic ones.

1.1.2.6 Modern stance – Mercury as a global pollutant

Mercury is now widely regarded as a highly toxic pollutant of global importance. This stems from episodes of acute human poisoning, such as the Minamata Bay Disaster in Japan (1956), and from the realisation that mercury can cycle through the environment to the extent that even remote pristine environments show signs of contamination.

Organomercury compounds, especially methylmercury species (MeHg), were found to be responsible for the catastrophic effects of acute mercury exposure on human populations [*Harada*, 1995]. This is due to MeHg being a potent neurotoxin that has the ability to cross the blood/brain and blood/placenta barriers. MeHg concentrations above recommended levels for safe consumption were measured in fish from remote Swedish lakes in the 1970s. In most cases, there were no direct sources of MeHg for these ecosystems, and contamination was attributed to the deposition of airborne mercury-containing species [*Brosset*, 1982]. Recently, a direct link between deposition of atmospheric mercury-containing species and MeHg concentrations in freshwater fish (bass) in the USA has been suggested [*Hammerschmidt and Fitzgerald*, 2006].

1.2 Atmospheric chemistry of mercury

Mercury in the atmosphere is thought to be mainly gaseous elemental mercury (GEM, Hg⁰). Its ubiquitous presence around the globe, even in remote air, and an inter-hemispheric difference in background concentration, indicate a tropospheric lifetime of ~1 year [*Slemr et al.*, 1985]. Its sources are natural (oceans and other surface waters, rocks, top soils, vegetation, volcanoes and other geothermal activities, biomass burning) and anthropogenic (coal-fired plants, smelters, waste incinerators, artisanal small-scale gold mining, cement production). Revolatization of previously deposited mercury (originating from either natural or anthropogenic sources) is included in the natural sources of atmospheric mercury. These are now thought to be much greater than direct anthropogenic sources (5207 tonnes *versus* 2909 tonnes) [*Pirrone et al.*, 2009].

Since Hg⁰ is quite volatile, relatively inert and only slightly water soluble, it is generally understood that other, more soluble and less volatile mercury species, are responsible for removal – through wet and dry deposition processes- of mercury from the troposphere [*Brosset*, 1981; *Lindqvist and Rodhe*, 1985].

The actual chemical identity of these more 'reactive' mercury species (dubbed Reactive Gaseous Mercury, or RGM), however, remains unknown to this day. This gap in our understanding arises both from analytical limitations and from uncertainties in field data and laboratory-derived rates for the various atmospheric mercury cycling processes. Table 1 lists some physical and chemical properties of selected mercury compounds that might be of importance in the atmospheric cycling of mercury.

	Hg^{0}	$HgCl_2$	HgBr ₂	Hg_2Br_2	HgO	$Hg(CH_3)_2$
Molecular mass	200.59	271.52	360.41	560.99	216.59	230.66
Physical state (ambient conditions)	Silver-coloured liquid	White crystalline solid	White crystalline solid	White crystalline solid	Red or yellow crystalline solid	Colourless liquid
Melting point (°C)	-38.72	276	236			-43
Boiling point (°C)	356.73	304	322	345 (sublimates)	500 (decomposes)	93-94
Vapour pressure ^a at 25°C	2.4 x10 ⁻⁶ atm	1.55 x 10 ⁻⁷ atm	1.45 x 10 ⁻⁷ atm	5.5 x 10 ⁻⁹ atm (extrapolated to 25°C)	2.5 x 10 ⁻¹¹ atm (extrapolated to 25°C)	6.6 x 10 ⁻² atm
Solubility in water ^b at 25°C	3 x 10 ⁻⁷ M	0.27 M $K_{sp} = 2.7 \text{ x } 10^{-15}$	$1.70 \ge 10^{-2} M$ $K_{sp} = 6.2 \ge 10^{-20}$	$K_{sp} = 6.4 \text{ x } 10^{-23}$	$K_{sp} = 3.6 \times 10^{-26}$	4 x 10 ⁻³ M at 21°C
Henry's Law constant, $k_{\rm H}{}^{\rm c}$	0.32 434 / atm	2.9 x 10 ⁻⁸				0.31
Density (kg/m ³)	13579.04	5600	6030	7307	11140	2961
Ionization Energy (kJ/mol)	1007.1	1098	1018.9			878
$\Delta H (kJ/mol)$	0	-224.3	-169.45	-206.9	-90.79	-162.2
$\Delta G (kJ/mol)$	0	-178.6	-153.1	-181.08		
Hg oxidation state	0	2	2	1	2	2

Table 1: Selected physical and chemical properties of mercury compounds*

* modified from [Ariya and Peterson, 2005]

^a taken from [Oppermann et al., 1989]: Hg₂Br₂; [Taylor and Hulett, 1913]: HgO; [Blayney et al., 1997]: Hg(CH₃)₂

^b taken from [*Clever et al.*, 1985], except value for Hg(CH₃)₂(taken from [*National Research Council (U.S.)*, 2000])

c taken from [Lindqvist and Rodhe, 1985], except values for Hg⁰ (taken from[Andersson et al., 2008])

1.2.1 Analytical methods for the determination of atmospheric mercury

1.2.1.1 Current methods

Mercury concentrations in the atmosphere are very low. Typical background concentrations are in the 1 - 2 ng/m³ range. This is equivalent to 0.12-0.24 ppt (parts per 10¹²) at atmospheric pressure and temperature (1 atm, 298 K)². Hg⁰ is the main tropospheric species and other mercury-containing compounds are expected to be present at much lower concentrations (in the low pg/m³ or ppq (parts per 10¹⁵) range). This poses a significant analytical challenge, since no instrument has a high enough sensitivity towards individual mercury-containing species, with the exception of Hg⁰, to allow for direct analysis, and mercury species therefore have to be pre-concentrated on various types of traps. All mercury species, except Hg⁰, are therefore commonly measured as operationally defined fractions instead of being directly identified and quantified as distinct chemical species.

1.2.1.1.1 Active sampling methods

Gaseous Elemental Mercury (GEM)

Typically, Hg⁰ is actively sampled (using a pump) at a known flow rate (typically 1.0-1.5 L/minute) and pre-concentrated through amalgamation on gold traps (quartz tube filled with gold particles or gold-coated quartz beads or containing a gold wire). It is then thermally released (500°C) from the traps and introduced to a Hg-free carrier gas (typically, argon) to be detected by cold vapour atomic fluorescence or absorbance spectroscopy (CVAFS or CVAAS). Commercial units (e.g. Tekran 2537A) have a resolution of 5 minutes and detection limits

² A table of conversion for units of concentration, pressure and temperature is available in Appendix A.

< 0.1 ng/m³. Known difficulties linked to this methodology are passivation of the gold traps through adsorption of other atmospheric species [*Landis et al.*, 2002] and possible simultaneous sampling of gaseous oxidized mercury species. Another issue might arise from the ability of gold to act as a catalyst for the oxidation of GEM by chlorine (Cl₂) [*Schofield*, 2008; *Zhao et al.*, 2006]. It is reasonable to assume that a similar reaction could occur in the presence of bromine (Br₂).

Adding a soda lime trap in line with the instrument inlet prevents passivation [*Landis et al.*, 2002], whereas different configurations, such as adding a filter or a KCl denuder (for the trapping of oxidized mercury, see next subsection) in line with the inlet of the instrument allow for the selective monitoring of GEM [*Steffen et al.*, 2002]. The various filters and traps placed in line with the instrument might also successfully scavenge any potentially interfering halogen species.

Reactive gaseous mercury (RGM) / Gaseous Oxidized Mercury (GOM)

Reactive gaseous mercury used to be defined as the fraction of atmospheric mercury that could be reduced by stannic chloride (SnCl₂) [*Brosset and Iverfeldt*, 1989]. It is now generally defined as the fraction that is trapped on a KClcoated, annular quartz denuder. These denuders are made of two coaxial quartz tubes and the airflow is directed through the annular space. An impactor removes coarse particulates (>2.5µm) from the air stream ahead of the denuder. Typical sampling flow rates are 10 L/minute. The denuder is kept at 50°C to avoid water condensation. After a sampling time of ~1 to several hours, the denuder is typically heated to 500°C (although temperatures up to 900°C are sometimes used) for several minutes to desorb and decompose the trapped species and the resulting Hg⁰ is quantified as described in the previous subsection. The methodology described above is available commercially (Tekran 1130) and detection limits as low as ~0.5 pg Hg⁰/m³ have been reported [*Landis et al.*, 2002]. Issues with this type of analysis include low reproducibility [*Aspmo et al.*, 2005] and interference by ozone [*Lyman et al.*, 2010]. It should also be noted that since the chemical identity of the species trapped is unknown, it is currently impossible to calibrate the denuders [*Aspmo et al.*, 2005]. Tests carried out with HgCl₂ and HgBr₂ demonstrated high trapping efficiencies [*Landis et al.*, 2002; *Lyman et al.*, 2010; *Xiao et al.*, 1997] and KCl denuders are thought to trap gaseous divalent mercury species, a.k.a RGM, also referred to as gaseous oxidized mercury (GOM).

Typical concentrations measured with this method range from a few pg Hg^{0}/m^{3} in background air to several hundred pg Hg^{0}/m^{3} near sources or under specific meteorological conditions.

Particulate-bound mercury $(Hg_{(p)})$

Particulate-bound mercury, $Hg_{(p)}$, is defined as the fraction of atmospheric mercury that is trapped when air is sampled through a glass fibre or quartz filter with pore size < 2.5 µm. Analysis is performed by microwave-aided acid extraction or by thermal desorption and decomposition of the trapped species at temperatures c. 800-900°C followed by detection of the resulting Hg⁰ by CVAFS. A commercially available unit (Tekran 1135) is often used in conjunction with the other units and most recent field studies report GEM, GOM and Hg_(p) fractions. The particulate filter is usually placed after the KCl denuder in order to avoid artefact due to absorption of GOM onto the filter [*Lynam and Keeler*, 2002]. As with GOM, the chemical composition of Hg_(p) is unknown and calibration is thus currently impossible.

Typical concentrations measured through the various methods range from a few pg Hg^0 / m^3 in background air to several hundred pg Hg^0 / m^3 near sources or under specific meteorological conditions.

1.2.1.1.2 Passive sampling methods

The methods described above are available commercially as the Tekran 1130/1135/2537A. The instrument provides automated and reasonably high-resolution (typically 1 h) measurements [*Lyman et al.*, 2009]. However, this type of system is expensive and its operation is labour-intensive. Moreover, the need for electrical power and Hg-free carrier gas make its use in remote areas difficult if not impossible. There have been calls for the development of passive sampling methodologies as a low-cost, easy-to-operate alternative for remote areas [*Gustin and Jaffe*, 2010]. Two recently developed passive sampling methodologies [*Lyman et al.*, 2009] and [*Skov et al.*, 2007] are included in Table 2, which is intended as a summary of currently used analytical techniques.

Every atmospheric mercury fraction, be it GEM, GOM or $Hg_{(p)}$, is reported as Hg^0 . This is mainly due to the fact that methods for atomic mercury detection are highly sensitive and adapted to the low concentrations found in the environment. The disadvantage is that no chemical identification of the species making up the GOM and $Hg_{(p)}$ fractions is currently available. Chemical identification is important since different mercury species have different physical and chemical properties (see Table 1) that are bound to influence the rate at which they are scavenged and deposited out of the atmosphere. Different species are also expected to have varying methylation propensities [*Ullrich et al.*, 2001]. This is important since methylated mercury-containing species are more bio-available and can accumulate in biota.

Species Detected	Type of sampling	Description of Methodology	Detection Limit, Sampling time	Comments	References
Hg ⁰	Active (~1-1.5L/min)	 amalgamation of GEM onto a gold trap (pre- concentration step) thermal desorption of the amalgamated Hg detection and quantification of Hg⁰ by Cold Vapour Atomic Fluorescence Spectroscopy or Cold Vapour Atomic Absorbance Spectroscopy 	<0.1 – 0.2 ng/m ³ , 5 min	 potential passivation of the gold trap by other atmospheric species possible reactions of the adsorbed Hg⁰ with other atmospheric species Other mercury species, especially divalent inorganic mercury (e.g. HgCl₂, HgBr₂) can also be trapped by gold 	[Aspmo et al., 2005; Ebinghaus et al., 2002; Landis et al., 2002; Munthe et al., 2001]
Hg ⁰ + RGM (GOM)	Passive	 1- Trapping of mercury onto a gold tube placed inside a porous (<2.5µm) HDPE tube 2- desorption and decomposition of RGM species at 500°C 3- detection and quantification of Hg⁰ as outlined above 	0.14 – 0.05 ng/m ³ , 1 – 3 days	 no electrical power needed uptake rate is dependent on wind speed not tested for RGM sampling not tested in the field 	[<i>Skov et al.</i> , 2007]
RGM (GOM)	Active (sampling: 10L/min; analysis: 1-1.5L/min)	1- trapping of RGM onto KCl- coated annular denuder (made of two coaxial tubes wherein airflow is directed through the annular space). An impactor removes coarse particulates (>2.5µm) from air stream ahead of the denuder 2- desorption and	6.2 pg/m ³ for 1 hr 0.5 pg/m ³ for 12 hours 2 - 25 pg/m ³ , 1200L	 denuder has to be kept at 50°C during sampling to avoid water condensation does not allow chemical identification of RGM species ozone might reduce trapping efficiency can have poor reproducibility as the identity of GOM species is 	[Aspmo et al., 2005; Landis et al., 2002; Lyman et al., 2010]

Table 2: Summary of current analytical methodologies for the determination of atmospheric mercury species

Species Detected	Type of sampling	Description of Methodology	Detection Limit, Sampling time	Comments	References
		decomposition of RGM species at 500°C 3- detection and quantification of Hg ⁰ as outlined above		unknown, it is currently not possible to calibrate denuders - Typical resolution is 3 hours	
	Passive	 Trapping of RGM onto an activated polysulphone cation- exchange membrane. Acrylic plates act as the diffusion barrier. The sampler is housed in a polycarbonate container and positioned so that the sampling membrane is facing downwards. digestion of the membrane in 100 mL of 1% HCl solution and 6 mL of 0.2 M BrCl solution 3- analysis of Hg⁰ as outlined above 	~5 pg/m ³ , 2 weeks	 detection limit is dependent on wind speed reproducibility is comparable to that of commercially available active sampling systems (~30%) no electrical power needed 	[<i>Lyman et al.</i> , 2009]
$\mathrm{Hg}_{(p)}$	Active (sampling: 10L/min; analysis: 1-1.5L/min)	 sampling by pulling air through a glass fibre or quartz filter thermal desorption and pyrolysis (800-900°C) of the adsorbed species OR microwave-aided acid extraction analysis of Hg⁰ as outlined above 	4 - 7 pg/m ³ , 1200L (at 1-1.5L/min)	 usually sampled in tandem with RGM susceptible to artefact when GOM is > 15 ng/m³, but placing the filter downstream of a KCl denuder minimizes the problem filter is kept at 50°Cin commercial unit does not allow chemical identification of Hg_(p) species 	[Aspmo et al., 2005; Landis et al., 2002; Lynam and Keeler, 2002]

1.2.1.2 Potential methods

To help unravel the complexities of the atmospheric mercury cycle, it is of primordial importance to identify the species that make up the GOM and $Hg_{(p)}$ fractions [Brosset and Iverfeldt, 1989]. Preliminary work on two potential analytical tools for the identification of GOM will be presented in this thesis. One methodology uses atmospheric pressure chemical ionization mass spectrometry (APCI-MS) and the other solid-phase micro-extraction coupled with mass spectrometry (SPME-MS).

1.2.1.2.1 Atmospheric Pressure Chemical Ionization Mass Spectrometry (APCI-MS)

Atmospheric Pressure Chemical Ionization Mass Spectrometry (AP-CI-MS) is often coupled to High Pressure Liquid Chromatography (HPLC) and indeed commercial LC-APCI/ESI-MS units are available. However, APCI-MS was originally designed to sample ambient air, and it remains possible to modify commercial units to perform air analysis. In such cases, the mass spectrometer samples air directly into its inlet at atmospheric pressure. Trace contaminants in the sampled air stream are ionized by a corona discharge at atmospheric pressure. Ionized molecules are then accelerated by a potential difference into the vacuum of the mass spectrometer [Spicer et al., 1994]. APCI-MS offers two modes of ionization – positive and negative – and most instruments allow for rapid switching from one mode to the other. This allows for the identification of a wide range of airborne chemical species. APCI-MS has been used in airborne measurements of a variety of chemical species with detection limits ranging from 0.2 - 500 ppt [Chapman et al., 1995; Spicer and Kenny, 1996; Spicer et al., 1994] and in the surface monitoring of halogen species in the marine boundary layer. The reported detection limits are 2 ppt for Cl₂ and BrCl and 0.2 ppt for Br₂ in negative ionization mode [Foster et al., 2001; Spicer et al., 1998; Spicer et al., 2002b].

Because of its great sensitivity to halogen species, APCI-MS might be suitable for detection of gaseous mercury halides such as HgBr₂ and HgCl₂. The concentration of these species in background air, if they are indeed constituents of GOM, would be in the ppq (parts per 10¹⁵) range, and a trapping method would need to be used in line with the instrument in order to pre-concentrate the sample. This trapping (and subsequent desorption) would need to be achieved without changing the chemical speciation of the sample.

1.2.1.2.2 Solid-Phase Micro-Extraction (SPME)

Another methodology that has been successfully applied to measuring environmentally relevant chemical species is Solid-Phase Micro-Extraction (SPME). SPME is a sampling/pre-concentration method that is usually coupled with gasphase chromatography with flame ionization (GC-FID) or mass spectrometry (GC-MS) detection. It has been used to isolate a variety of mercury species, including organomercury compounds, labile Hg²⁺ and inorganic mercury salts from a variety of environmental matrices, including seawater, river water, soil, sediment and biota (fish, crab, prawn, bivalves) [*Kaur et al.*, 2006, and references therein; *Mishra et al.*, 2005]. For a review of the analysis protocols currently in use for mercury compounds, see [*Diez and Bayona*, 2008].

SPME can also be used to sample chemical species directly from ambient air. Several types of compounds have been successfully quantified in air, including volatile organic compounds (VOCs), semi-volatile organic compounds SVOCs [*Augusto et al.*, 2001; *Khaled and Pawliszyn*, 2000; *Koziel et al.*, 2000; *Koziel et al.*, 1999] and pesticides [*Wang et al.*, 2009]. To our knowledge, SPME has never been used for the detection of mercury species in ambient air, probably because typical detection limits are in the ppt – low ppb range, and too high to be suited for direct atmospheric sampling of GOM. SPME, however, could enable *in situ* monitoring of oxidation reaction products in laboratory-based experiments, since concentrations used in a laboratory setting are generally several orders of magnitude higher than those found in the environment.

1.2.2 Pathways for the chemical formation of gaseous oxidized mercury (GOM)

Another way to gain insight into the composition of GOM is to study its possible tropospheric formation pathways. This can be done by monitoring meteorological parameters (wind speed, solar radiation, relative humidity, temperature, etc.) and the concentrations of common atmospheric oxidants and testing whether they correlate with measured GEM, GOM and $Hg_{(p)}$ concentrations. An additional approach is to study potentially relevant reactions and mechanisms in a laboratory setting and to evaluate their importance using extensive modelling of the troposphere [Ariya et al., 2004; Bullock et al., 2009; Dastoor et al., 2008; Skov et al., 2004].

1.2.2.1 Chemical transformation of GEM: insights from field data

There is an ever growing body of evidence supporting the fast oxidation of mercury in the atmosphere. Sharp decreases in GEM concentrations, accompanied with increased concentrations of GOM species, were discovered to occur in the troposphere at Alert (Canadian Arctic) in 1995 [*Schroeder et al.*, 1998]. Since then, the phenomenon has been shown to occur throughout the Arctic [*Berg et al.*, 2003; *Lindberg et al.*, 2001; *Poissant and Pilote*, 2003; *Skov et al.*, 2004; *Sprovieri et al.*, 2003; *Steffen et al.*, 2005] and in Antarctica [*Ebinghaus et al.*, 2002; *Temme et al.*, 2003]. These occurrences have been given the name of mercury depletion events (MDEs) and were thought to be an essentially polar phenomenon until recently, when MDEs were observed near the Dead Sea in Israel [*Peleg et al.*, 2007]. Other evidence of atmospheric transformations include the

observation of relatively fast increases in the concentration of particulate-bound mercury species associated with decreases in background Hg⁰ concentrations at a continental site [*Poissant et al.*, 2005]and GOM formation in the marine boundary layer [*Laurier et al.*, 2003].

In MDEs, GEM concentrations are usually strongly correlated with tropospheric ozone concentrations and associated with increased BrO concentrations [*Lindberg et al.*, 2002; *Peleg et al.*, 2007; *Schroeder and Munthe*, 1998]. Tropospheric ozone also undergoes periods of depletion (ODEs) in the polar springtime and the mechanism for this phenomenon is thought to be based mainly on bromine chemistry [*Jones et al.*, 2009, and references therein]. It has been proposed that a similar mechanism – based on halogen chemistry – might be responsible for MDEs [*Ariya et al.*, 2002; *Ariya et al.*, 2004; *Lindberg et al.*, 2002; *Lu et al.*, 2001; *Sprovieri et al.*, 2005; *Steffen et al.*, 2005]. This hypothesis is supported by observations that GOM has a strong diurnal profile, indicating photochemical production of the species responsible for GEM oxidation [Hynes et al., 2009; Lindberg et al., 2002].

1.2.2.2 Chemical transformation of GEM: insights from laboratory-based experiments

Several experimental studies of the reaction between GEM and various atmospherically-relevant oxidant species can be found in the recent peer-reviewed literature. Table 3 is a compilation of the known rate coefficients. Only those coefficients that were determined at or near atmospheric conditions were included. The potential importance of a given oxidant species in the atmospheric mercury cycle depends not only on the rate coefficient of its reaction with GEM, but also on its ambient concentration (mixing ratio in the atmosphere).

Reaction	Type of determination	Gas Bath, Pressure	Temperature	Rate coefficient	Reference
			(K)	$R = J K^{-1} mol^{-1}$; $T = Kelvin$	
$Hg^0 + O_2 \rightarrow products$	Absolute	Air, 1 atm	293	$< 1 \times 10^{-23}$	[B. Hall et al., 1995a]
Hg0 + OH \rightarrow products	Relative to cyclohexane	Air, 1atm	295 ± 2	$(8.7 \pm 2.8) \ge 10-14$	[Sommar et al., 2001]
	Absolute (PLP-PLIF)	Air, 1atm	~295	$< 1.2 \text{ x } 10^{-13}$	[<i>Bauer et al.</i> , 2003]
	Relative to ethane	N ₂ , air, 1 atm	282 - 353	$3.55 \text{ x } 10^{-14} \text{ e}^{-(2440 \pm 130)/\text{RT}}$	[Pal and Ariya, 2004a]
	Rel. to ethane, cyclopropane		298	$(9.3 \pm 1.3) \ge 10^{-14}$	
	RRKM/B3LYP	N ₂ , 1atm	180 - 400	$3.2 \times 10^{-13} \times (T/298)^{-3.06}$	[Goodsite et al., 2004]
$Hg^0 + O_3 \rightarrow products$	Abs. Extrapolated to $S/V = 0$	$N_2 (2 - 10\% O_2), 1 atm$	293	$(3 \pm 2) \ge 10^{-20}$	[B. Hall, 1995]
	Abs. Extrapolated to $S/V = 0$, $[O_3] = 0$	N ₂ , 1atm	283 - 353	8.43 x 10 ⁻¹⁷ $e^{-(11700 \pm 270)/RT}$	[Pal and Ariya, 2004b]
			298	$(7.5 \pm 0.9) \ge 10^{-19}$	
	Absolute	Air, 1 atm	~298	$(6.4 \pm 2.3) \ge 10^{-19}$	[Sumner et al., 2005]
	Absolute	N ₂ , 1atm	296 ± 2	$(6.2 \pm 1.1) \ge 10^{-19}$	[Snider et al., 2008]
	QCIS(T)/MP2; TST Theory	N/A	298	1.2 x 10 ⁻⁴⁰	[<i>Xu et al.</i> , 2008]
$Hg^0 + F \cdot \rightarrow products$	Ab initio	Air, 1 atm	Range?	9.2 x 10^{-13} e ^{1720/RT} 1 86 x 10^{-12}	[Khalizov et al., 2003]
$Hg^0 + F_2 \rightarrow products$	Absolute	Air, 1 atm	~298	$(1.8 \pm 0.4) \ge 10^{-15}$	[Sumner et al., 2005]
$Hg^0 + Cl \rightarrow products$	Absolute (Fitted equation)	Ar, 0.93 atm	383 - 443	$(1.5) \ge 10^{-11}$ [†]	[Horne et al., 1968]
		CF ₃ Cl, 0.93 atm	383 - 443	$(5) \times 10^{-11}$ [†]	
	Rel. to 1,3-dichloropropane	N ₂ , 1atm	298	$(1.0 \pm 0.2) \ge 10^{-11}$	[<i>Ariya et al.</i> , 2002]
	Ab initio	Air, 1 atm	Range?	$1.38 \ge 10^{-12} e^{1729/RT}$	[Khalizov et al., 2003]
			298	2.81 x 10 ⁻¹¹	
	Absolute (PLP-PLIF)	N_2 , 0.26 – 0.79 atm	243 - 293	$(2.2 \pm 0.5) \ge 10^{-32} e^{[(680 \pm 400)(1/T-1/298)]} *$	[Donohoue et al., 2005]
		N ₂ , 1atm	298	5.4 x 10 ⁻¹³ **	
		He, 0.26 – 0.79 atm	293	$(9.37 \pm 0.95) \ge 10^{-33} $ *	

Table 3: Compilation of Known Rate Coefficients for Gas-Phase Reactions of Mercury at Near-Atmospheric Conditions

Reaction	Type of determination	Gas Bath, Pressure	Temperature (K)	Rate coefficient (cm ³ molecule ⁻¹ s ⁻¹) $R = J K^{-1} mol^{-1}$; T = Kelvin	Reference
$Hg^0 + Cl_2 \rightarrow products$	Absolute	Humid air	273	\leq 0.4 (13% R.H.) - 2.5 (80% R.H.) x 10 ⁻¹⁵	[Schroeder et al., 1991], with data from [Menke and Wallis, 1980]
	Absolute	Air or N ₂ , 1 atm	298	$(2.6 \pm 0.2) \ge 10^{-18}$	[Ariya et al., 2002]
	Absolute	Air, 1 atm	~298	$(2.5 \pm 0.9) \ge 10^{-18}$	[Sumner et al., 2005]
$Hg^0 + Br \rightarrow products$	Absolute (Fitted equation)	CF ₃ Br, 0.26 atm	393 - 448	(2.8) x 10 ⁻¹³ [†]	[Greig et al., 1970]
	Relative to 1-butene	Air, 1 atm	298	$(3.2 \pm 0.3) \ge 10^{-12}$	[Ariya et al., 2002]
	Relative to DMS			3.0×10^{-13}	[Spicer et al., 2002a]
	Relative to propene			9.7×10^{-13}	
	Ab initio	Air, 1 atm	Range? 298	$\frac{1.01 \times 10^{-12} e^{1738/RT}}{2.07 \times 10^{-12}}$	[Khalizov et al., 2003]
	RRKM/B3LYP	N_2 , 1 atm	180 - 400	$1.1 \times 10^{-12} \times (T/298)^{-2.37}$	[Goodsite et al., 2004]
	Absolute (PLP-PLIF)	N_2 , 0.26 – 0.79 atm N_2 , 1atm	243 – 293 298	$(1.46 \pm 0.34) \times 10^{-32} (T/298)^{(-1.86 \pm 1.49)} * (3.6 \pm 0.8) \times 10^{-13} **$	[Donohoue et al., 2005]
	CCSD(T)	He, 0.26 – 0.79 atm Ar, 1 atm	293 200 – 400 298	$(4.2 \pm 0.2) \times 10^{-33} *$ $4.07 \times 10^{-32} e^{[112(1/T-1/298)]} *$ 9.8×10^{-13}	[Shepler et al., 2007]
$Hg^0 + Br_2 \rightarrow products$	Absolute	Air or N ₂ . 1 atm	298	$< (9 \pm 2) \ge 10^{-17}$	[<i>Ariva et al.</i> , 2002]
0 - 1	Absolute	Air, 1 atm	~298	No reaction detected	[Sumner et al., 2005]
	icMRCI+Q/CBS+SO, µVT	N/Å	298	2.74 x 10 ⁻³¹	[Balabanov et al., 2005]
$Hg^0 + BrO \rightarrow products$	Relative to DMS, butane,	N ₂ , 1atm	298 ± 1	$10^{-15} \le k \le 10^{-13}$	[Raofie and Ariya, 2003]
	Relative to DMS			$3 - 6.4 \ge 10^{-14}$	[Spicer et al., 2002a]
$Hg^0 + I \cdot \rightarrow products$	RRKM/B3LYP	N ₂ , 1 atm	180 - 400	4.0 x 10 ⁻¹³ (T/298) ^{-2.38}	[Goodsite et al., 2004]
$Hg^0 + I_2 \rightarrow products$	Absolute	Air, 1 atm	296 ± 2	$\leq 1.27 \text{ x } 10^{-19}$	[Raofie et al., 2008]

Reaction	Type of determination	Gas Bath, Pressure	Temperature (K)	Rate coefficient (cm ³ molecule ⁻¹ s ⁻¹) $R = J K^{-1} mol^{-1}$; $T = Kelvin$	Reference
$Hg^0 + NO_2 \rightarrow products$	Absolute	N ₂ , 1 atm	293	$(2.8 \pm 0.5) \ge 10^{-35} $	[B. Hall et al., 1995b]
$Hg^0 + NO_3 \rightarrow products$	Abs. Extrapolated to $S/V = 0$	N_2 , (5 – 10) x 10 ⁻³ atm	294 ± 2	$ \leq 4 \ge 10^{-15} \\ \leq 7 \ge 10^{-15} $	[Sommar et al., 1997] [Sumner et al., 2005]
$Hg^0 + H_2O_2 \rightarrow products$	Absolute	N_2	293	$\leq 8 \ge 10^{-19}$	[Tokos et al., 1998]

† Reported error is a factor of 3
‡ Second order with respect to [NO₂]
* Units are cm⁶ molec⁻² s⁻²

** Extrapolated to 'atmospheric' conditions (1 atm, 298K), overall error on the coefficient was reported as ± 50%. PLP-PLIF stands for Pulsed Laser Photolysis – Pulsed Laser Induced Fluorescence

Table 3 reveals that the rate coefficient determined for the same reaction sometimes spans several orders of magnitude. This is the case for the reaction of elemental mercury with ozone (O_3) and the reaction with molecular bromine (Br_2) and is illustrated in Figure 3.



Figure 3: Illustration of the uncertainty in the available rate coefficients of selected gas-phase oxidation reactions of GEM

In both cases, the theoretical rate determinations yield values that are several orders of magnitude lower than those determined experimentally. This is due to the thermodynamics of the reactions being unfavourable [Ariya et al., 2009; Balabanov et al., 2005; Hynes et al., 2009]. Heterogeneous processes are thought to enable the reactions under experimental conditions and indeed, all the experimental studies for both reactions report enhancement rates of reaction at higher surface-to-volume (S/V) ratios.

In the case of the reaction of GEM with hydroxyl radicals (OH \cdot), the theoretical determination yields a rate coefficient that is slightly higher than the experi-
mentally-derived ones. The theory explored the formation of HgOH, a weaklybound species, as the reaction product. The lifetime of HgOH under atmospheric conditions is expected to be ~0.3 milliseconds and the overall reaction is not expected to proceed at an appreciable rate. Only one experimental study examined the products of the reaction, and they identified HgO as the main product [Pal and Ariya, 2004a]. The thermodynamics of HgO formation from Hg⁰ and OH· are unfavourable and the reaction is thus suspected to proceed through a heterogeneous mechanism [Ariya et al., 2009; Hynes et al., 2009, and references therein].

The reaction between Hg^0 and bromine radicals is different in that, although the various rate constant determinations yield values for the coefficient that are scattered over an order of magnitude, the thermodynamics of the homogeneous gas-phase reaction are favourable. Very high-level calculations [Shepler et al., 2007] have yielded a rate coefficient that is in the middle of the range of experimentally-derived rate coefficients. The lifetime of the HgBr intermediate is thought to be on the order of seconds under atmospheric conditions, and this, coupled to the relatively high rate coefficient of the reaction, makes the recombination of Hg^0 with Br a candidate for the initiation of MDEs.

1.2.2.3 The homogeneous gas-phase reaction of elemental mercury and bromine radicals $Hg^0 + Br \leftrightarrow HgBr$

Both field data and laboratory experiments indicate that the homogeneous gas-phase reaction of elemental mercury with bromine radicals could play an important role in the atmospheric cycling of mercury. Figure 4 illustrates the mercury cycle as it is thought to occur in the Arctic



Figure 4: A schematic diagram illustrating the mercury cycle in the Arctic. Adapted from [Macdonald et al., 2005]

The extent of GEM depletion would probably depend on the fate of the HgBr intermediate, but few kinetic data exist for the reactions of HgBr with common atmospheric species. Some experimental rate coefficients were obtained from studies into the feasibility of mercury halide lasers [Erlandson and Cool, 1983; Schilowitz and Wiesenfeld, 1982], but these were determined at very low pressures and high temperatures. The only rate coefficients determined at near atmospheric conditions were derived from theoretical calculations [Balabanov et al., 2005; Goodsite et al., 2004; Shepler et al., 2007].

Reaction	Type of determination	Gas Bath, Pressure	Temperature (K)	Rate coefficient (cm ³ molecule ⁻¹ s ⁻¹) $R = J K^{-1} mol^{-1}$; $T = Kelvin$	Reference
$HgBr \rightarrow Hg + Br$	RRKM/B3LYP	N ₂ , 1 atm	180 - 400	$1.2 \text{ x } 10^{10} \text{ e}^{(-8357/\text{T})} \text{ s}^{-1}$	[Goodsite et al., 2004]
$HgBr + Ar \rightarrow Hg + Br \cdot + Ar$	CCSD(T)	Ar, 1 atm	200 - 400	$1.95 \ge 10^{-20} e^{[-7670(1/T - 1/298)]}$	[Shepler et al., 2007]
$HgBr + HgBr \rightarrow Hg + HgBr_2$	Absolute	HgBr ₂ , $< 1.3 \text{ x } 10^{-5} \text{ atm}$	435	$\leq 5 \ge 10^{-16}$	[Schilowitz and Wiesenfeld, 1982]
$\mathrm{HgBr} + \mathrm{HgBr} \to \mathrm{Hg_2Br_2}$	Absolute (fitted equation)	CF ₃ Br, 0.26 atm	393 - 448	2.1 x 10-11	[Greig et al., 1970]
$HgBr + Br \cdot \to HgBr_2$	MRCI/Quasi-CT	N/A	298	$3.0 \ge 10^{-11}$	[Balabanov et al., 2005]
	Estimation	CF ₃ Br, 0.26 atm	397	6.6 x 10 ⁻¹⁴	[Greig et al., 1970]
HgBr + Br, OH·, I· → $HgBr_2$, HgBrOH, HgBrI	RRKM/B3LYP	N ₂ , 1 atm	180 - 400	2.5 x 10 ⁻¹⁰ (T/298) ^{-0.57}	[Goodsite et al., 2004]
$HgBr + Br \cdot \to Hg + Br_2$	MRCI/Quasi-CT	N/A	298	3.9 x 10 ⁻¹¹	[Balabanov et al., 2005]
$HgBr + Br \cdot \to HgBr + Br \cdot$	MRCI/Quasi-CT	N/A	298	4.0 x 10 ⁻¹¹	[Balabanov et al., 2005]
$HgBr + Br_2 \rightarrow HgBr2 + Br \cdot$	Absolute (fitted equation)	He, 0.66 atm	415	$(7.7 \pm 0.6) \ge 10^{-11}$	[Erlandson and Cool, 1983]

Table 4: Compilation of known rate coefficients for gas-phase reactions of HgBr

The only experimental study to have examined the products of the reaction reported HgBr₂ as the main product under their experimental conditions [*Ariya et al.*, 2002], but [*Greig et al.*, 1970] observed the dimerization of HgBr and assumed formation of Hg₂Br₂ in their analysis. Table 4 lists the available rate coefficients for the various possible gas-phase reactions of HgBr.

1.3 Objectives

Considering that field and laboratory studies both point to the reaction between GEM and bromine radicals as having potential atmospheric significance, the objectives of this work were to:

- Participate in the development of an analytical methodology based on atmospheric pressure chemical ionization mass spectrometry (APCI-MS) for the gas-phase trapping and identification of mercury halide (HgBr₂, HgCl₂) species in ambient air
- Test whether solid-phase micro-extraction coupled with mass spectrometry detection (SPME-MS) can be applied to *in situ* monitoring of the product(s) of the gas-phase reaction between Hg⁰ and Br·
- Expand the kinetic analysis performed by [*Ariya et al.*, 2002] by studying the reaction under a wider range of experimental conditions

The overall longer term aim of these investigations is to reduce uncertainty with regards to the importance of the bromine reaction in the atmospheric cycling of mercury by identifying whether mercury halide species are a significant part of GOM and by unravelling the mechanism of the reaction.

2 Methodology

2.1 Method development for the determination of mercury halides in ambient air through atmospheric chemical ionization mass spectrometry (APCI-MS) analysis

The instrument is a Quattro LC (Micromass UK Ltd), a bench-top triple quadrupole mass spectrometer designed for routine LC-MS-MS operation. It can be coupled with a high pressure liquid chromatography (HPLC) unit, to an infusion pump or to a syringe pump.

Ionisation takes place in the source at atmospheric pressure. These ions are sampled through a series of orifices into the first quadrupole where they are filtered according to their mass to charge ratio (m/z). The mass separated ions then pass into the hexapole collision cell where they either undergo collision induced decomposition (CID) or pass unhindered to the second quadrupole. The fragment ions are then mass analysed by the second quadrupole. Finally the transmitted ions are detected by a conversion dynode, phosphor and photomultiplier detection system. The output signal is amplified, digitised and presented to the data system. The instrument is operated through the MassLink NT Data System software. It can be operated in positive ($[M+H]^+$) or negative ($[M-H]^-$) ionization mode.

Two different atmospheric ionization probes are available for the instrument: an electrospray (ESI) probe and an atmospheric pressure chemical ionization (APCI) probe. In ESI, the vaporization of the liquid sample creates the ions, so analysis of gas samples is not feasible. In APCI, however, the sample is ionized by a corona discharge and so the sample can be a liquid or a gas. Figure 5 shows a schematic of the instrument fitted with the APCI probe.



Figure 5: Schematic representation of the Quattro LC when in APCI mode

After testing whether APCI-MS could detect mercury halide species, we modified the APCI probe of the Quattro LC to accommodate gas-phase analysis and gold solid phase micro-extraction (Au-SPME) fibre desorption. All the method development presented in this section (2.1) was done in collaboration with Dr. Daniel Deeds, and with the help of Alain Tessier from the Centre for Biological Applications of Mass Spectrometry (CBAMS) at Concordia University, where the instrument is located.

2.1.1 Preliminary tests

Saturated solutions of HgO, HgCl₂ and HgBr₂ in methanol were prepared and fed to the unmodified instrument using a syringe pump in order to test whether oxidized mercury species could be detected using APCI-MS.

2.1.2 Gold solid-phase micro-extraction (Au-SPME)

The original APCI probe (shown in Figure 6) was modified so that a custom-designed Au-SPME fibre could be inserted and desorbed using the heater of the original inlet. The end of the fibre would be positioned inside the heater and the sorbed analytes released by exposing the fibre to a temperature of ~400°C. The nebuliser gas intake was moved so that the nebuliser gas could act as a carrier gas (0.5 - 3.0 L/minute) for the analytes.



Figure 6: Original APCI probe of the Quattro LC (before the modifications)

2.1.2.1 Modification of the original APCI probe for SPME desorption

So that it could accommodate a SPME fibre, the inlet was modified: the filter and adapter nut, as well as the fused silica capillary, were removed and a new stainless-steel block was machined to fit inside the cylindrical part of the probe. The aim was to provide an unobstructed passage (1/16in. diameter) for the fibre between the sample introduction end (represented by the letter A on Figure 6) and the heater (letter B).

The new stainless-steel block was identical to the old one, except that it had a larger borehole through its centre and did not have a nebuliser gas intake. The filter and adapter nut were replaced by a Swagelok Ultra-Torr vacuum adapter (¼ in.) and soldered to the block. The 'finger tight nut and ferrule' were replaced by a ¼ in. stainless-steel T-junction with one end fitted with a Swagelok Ultra-Torr vacuum adapter. This second adapter was used to hold a septum in place. The Au-SPME fibres were inserted through this septum, ensuring that the system remained closed. The perpendicular arm of the T-junction was used to introduce the nebuliser gas, so it could act as both the carrier gas and the ionisation gas. Figure 7 summarizes the modifications. The probe could also be operated without the stainless-steel T-junction. In this case, the nebuliser gas line could be introduced directly into the 1/4in. Ultra-Torr fitting.



Figure 7: Modified APCI probe. See text for details.

2.1.2.2 Sampling device - Au-SPME

2.1.2.2.1 Fibre Design

The distance between the first Ultra-Torr adapter and the heater inside the probe was ~25 cm so oversized SPME fibres were built. Old commercially-available fibre assemblies from which both the fibre and other metal tube had been removed were fitted with a length of stainless-steel wire placed inside a 25 cm long stainless-steel tube. The wire was a few centimetres longer than the tube so that the wire tip could be exposed using the spring assembly.

2.1.2.2.2 Gold-coating protocol

Cleaning: The tip of the stainless-steel wire (~ 1.5 cm) was cleaned by dipping it in a 1:4 H₂O₂:H₂SO₄ solution until bubbling on the surface of the wire stopped. The tip was then rinsed with Milli-Q water (18.2 Ω) and dried under a stream of nitrogen gas. *Silanisation*: The tip of the wire was then silanised using a solution of 3-aminopropyltrimethoxysilane (APTMS, 0.3% in ethanol) in 1:3 H₂O:EtOH. The solution was prepared and left to stand for 8 minutes. The wire tip was then immersed for 1 minute. The wire was then dried under nitrogen gas and cured in air at 100°C for 1 hour. *Coating*: The fibre was allowed to cool and the tip was then immersed in a suspension of gold particles in water. The suspension was stirred at a constant rate (150 rpm) to avoid settling of the particles to the bottom. The tip was checked every 15 minutes until a uniform coating of gold particles was obtained. The tip was then allowed to dry in air.

2.1.2.2.3 Sampling protocol

The gold-coated fibres were then conditioned through heating inside a tubular furnace held at 500°C for a minimum of an hour. Nitrogen was flowed over the fibres to displace released contaminants. Blanks were performed by introducing a clean fibre into the modified probe and desorbing it. Sampling tests were performed by exposing the Au-SPME fibre to the atmosphere of a flask containing nitrogen saturated with HgBr₂ vapour for up to 24 hours.

2.2 Homogeneous gas-phase reaction of elemental mercury and bromine radicals: product and kinetic studies

2.2.1 General considerations

The same protocol was followed to perform experiments whether they were intended for product determination or for kinetic study. The sections describing the experimental set-up and the preparation of the reaction mixtures should therefore be considered to apply to both types of experiments.

2.2.1.1 Experimental set-up

For health and safety reasons, all experiments that required UV irradiation were performed in a ventilated wooden box. This prevented exposure of laboratory workers to the UV light and at the same time avoided build-up of ozone inside the box. Figure 8 shows a typical experimental set-up.





The experiments were conducted in spherical Pyrex vessels of varying volumes (3.3 or 5.5 L). The inside wall of the reaction vessel was treated with a 5% solution of dimethyldichlorosilane (DMDCS) in toluene in order to minimize surface adsorption of the reactants. The vessels were equipped with a sampling port, consisting of a screw glass connection covered by a 15 mm laminated silicone rubber septum (Hamilton Co.) held in place by an open-ended screw cap (Schott, GL-18). A Teflon stoppered connection allowed transfer of gaseous reagents to the flask. A 5 cm quartz window inserted in a Teflon bushing served as

the irradiation window. A Teflon-coated magnetic stirrer placed inside the reaction vessel was used to help reagent mixing.

The temperature of all the experiments performed in the 3.3L Pyrex reaction vessel was 298 ± 1 K, since the flask had an outer layer through which thermostated water could be circulated (Neslab RTE 111). Experiments performed in the 5.5L flasks, however, were not thermostated, and the temperature for these experiments is estimated at (295 ± 3) K.

2.2.1.1.2 UV light irradiation

A 100W mercury arc lamp (Oriel, #6281) was used for the *in situ* production of bromine radicals through photolysis of dibromomethane (CH_2Br_2). In some experiments, a mercury line filter (254 ± 11 nm, Newport) was used to block most of the lamp's output, as shown in Figure 8.

High-pressure mercury arc lamps, unlike low-pressure mercury lamps, do not emit well-defined, narrow atomic lines, but a continuum punctuated by stronger emission lines (Figure 9). This is due to the high pressure inside the bulb causing collisions between the atoms and, thus, broadening of the emission lines. Another characteristic of the spectrum is the self-absorption of the atomic emission line at 253.7nm. This means that the lamp's output, when filtered with a 254 nm line filter, allows for the photolysis of CH₂Br₂ at wavelengths ~250 nm without causing excitation of the mercury atoms in the reaction mixture. This is important since excited mercury potentially has a different reactivity towards bromine radicals. This self-absorption phenomenon cannot be observed in the spectra shown in Figure 9 since the spectrometer (USB 4000 UV-VIS Miniature Fibre Optic Spectrometer, Ocean Optics) used to record them did not have high enough resolution (~1.5 nm). In a typical experiment, the reaction mixture was irradiated for several discrete periods of 5 to 60 seconds. The lamp was turned on and given time to warm up. Once the voltage had stabilized (5-10 minutes), the reaction mixture would be irradiated for a pre-determined length of time and the lamp turned off at the end of the period. This procedure was repeated on average 5 times for each reaction mixture.



Figure 9: 100W Hg arc lamp output

Left: Comparison between unfiltered (dashed line) and filtered (254nm line filter) light; *Right*: Filtered light with optical fibre repositioned to maximize sensitivity to UV light

High-pressure mercury arc lamps have a finite lifetime and their emission spectrum changes in intensity as the bulb ages; consequently, several different bulbs of various ages were used in the course of these investigations.

2.2.1.2 Preparation of the reactant mixtures

Reaction mixtures were made of dilute mixtures of CH₂Br₂ and of the reactants prepared in nitrogen gas or in synthetic air. Prior to an experiment, the reaction vessel would be washed with dilute nitric acid, scrubbed with a nylon brush in soapy water, washed with milli-Q water (Millipore, 18.2 M Ω) and rinsed with HPLC-grade ethanol. The vessel was then dried at 120°C for at least 1 hour. To prepare reaction mixtures, the reaction vessel was evacuated to a pressure < 7 x 10⁻⁵ atmosphere with a two-stage pump (Savant VP 190) and flushed with nitrogen 2-3 times. Dilute CH₂Br₂ vapour was introduced *via* vacuum line, followed by mercury vapour. Synthetic air and/or pure oxygen were then introduced until the desired partial pressure of oxygen was reached (0 – 0.4 atm). The total pressure in the reaction vessel was brought up to its final value of 1 atmosphere by admitting UHP nitrogen. All experiments were performed at atmospheric pressure, 1.0 ± 0.1 atmosphere.

Other reactants were typically added through the sampling port with a gastight syringe (Hamilton, 250 μ L). The reaction mixture was then allowed to stand in the dark for two hours to ensure thorough mixing and, when the temperature was regulated, to allow the mixture to reach thermal equilibrium. Typical concentrations were 0.5 – 1 ppm for elemental mercury (1 ppm is 2.5 x 10¹³ molecules cm⁻³ at 1 atm and 298 K), 2 ppm for 1-butene and 10 – 500 ppm for dibromomethane. The composition of the reaction mixtures was reproducible, with the initial concentrations (measured as integrated peak areas from chromatograms) generally being within ±10% of the average value, as shown in Figure 10. As these values were obtained on different days, the uncertainty includes any variation in GC-MS response over time.



Figure 10: Reproducibility of the composition of the reaction mixtures

Left: [1-butene]₀ = 2 ppm (•) and $[Hg0]_0 = 1$ ppm (\circ) in 16 separate experiments.

Right: $[CH2Br2]_0 = 100$, 300 and 500 ppm (11 distinct experiments). In every case, the upper dashed line represent the average initial concentration plus 10% and the lower dashed line indicate the average initial concentration minus 10%. The error bars on the individual data points are, in general, <±5% and represent the standard deviation associated with 3 or more replicate chromatograms.

2.2.2 Detection of reaction products using solid-phase micro-extraction (SPME)

2.2.2.1 Solid-phase micro-extraction coupled with electron impact mass spectrometry (SPME-GC-EI-MS)

A solid phase micro-extraction fibre with a 65 µm polydimethylsiloxane /di-vinylbenzene coating (PDMS/DVB, Supelco) was selected for two reasons: it is recommended for volatile molecules with molecular weights ranging from 50 to 300 g/mol and preliminary experiments conducted in our laboratory showed that the PDMS/DVB coating was suited for analysis of mercury and mercury halides.

2.2.2.1.1 Preliminary tests – detection of mercury bromide

In order to assess whether the proposed solid-phase micro-extraction – gas chromatography – electron impact mass spectrometry (SPME-GC-EI-MS) scheme could work, its different parts were tested individually before full scale trials were undertaken.

Electron impact (EI) mass spectra of HgBr₂ and Hg₂Br₂

Electron impact (EI) mass spectra were obtained for HgBr₂ and for Hg₂Br₂, since they are both potential products of the reaction. Solid crystals of HgBr₂ and Hg₂Br₂ were packed into capillary tubes and introduced directly into the probe of an electron impact (EI) mass spectrometer (Kratos MS 25RFA). The probe temperature was kept at 523K and a full scan (m/z = 30 - 430 for HgBr₂ and m/z = 30 - 600 for Hg₂Br₂) was obtained for each compound.

Extraction tests for HgBr₂ and Hg₂Br₂

Some preliminary tests were performed in which the SPME fibre was used to sample the atmosphere of a sealed flask containing solid crystals of either Hg-Br₂ or Hg₂Br₂. Sampling times varied from 15 seconds to 60 minutes. Tests were also performed at higher temperatures. The temperature of the flask containing the crystals could be raised above room temperature by placing it in a heating jacket controlled by a programmable variable transformer. The total pressure in the flask was maintained at atmospheric pressure (~1 atm). Analysis was performed as described in the next section.

2.2.2.1.2 Chemical analysis: Product determination experiments

Operating conditions for the GC-EI-MS: product(s) determinations

Chemical analysis was performed by gas chromatography (HP-6890) coupled with electron impact ionization mass spectrometry (EI-MS) detection (HP-5973). Resolution of the analyte peaks was achieved on a 30m x 0.25mm i.d. x 1.0 μ m cross-linked phenyl-methyl-siloxane column (HP5-MS) operated at a constant flow of helium (1.5 mL/min). The inlet was kept at a temperature of 250°C and fitted with a narrow borehole inlet liner and a pre-pierced septum, as recommended for SPME desorption. Early tests were performed with the column at 200°C and the mass spectrometer operating in selected ion monitoring (SIM) mode (m/z = 56, 174, 198, 199, 200, 201, 202, 277, 278, 279, 280, 281, 282, 283, 356, 357, 358, 359, 360, 361, 362, 363, 364) however the conditions were later modified to a temperature programme (100°C for 1.5 min, ramp to 200°C at 25°C per minute, hold for 2 minutes or more) with the mass spectrometer scanning all m/z between 50 and 575. This new temperature programme gave better resolved chromatograms. SIM mode was given up mainly because of the possibility that other products would be missed if only specific m/z values were monitored.

SPME extraction conditions

The fibre was conditioned as per the manufacturer's instructions (30 minutes at 250°C) at the beginning of each experiment and blanked between each run. These blanks were obtained by analysing the clean (desorbed) fibre as if it were loaded with sample. The sample extraction time was generally 15 minutes, but some extractions lasted as long as 60 minutes. Desorption times (the time the fibre was left inside the GC inlet for analysis) varied from 3 to 6 minutes. Once the desorption time was over, the fibre was retracted and removed from the inlet. A fibre blank measurement was obtained in between each desorption runs to ensure that no memory effect would bias the results.

Calibration of SPME fibre for quantitative HgBr₂ analysis

Sampling HgBr₂ from a saturated headspace as described above did not result in reproducible peaks areas. This reproducibility issue was also observed for syringe injections of saturated Hg⁰ vapour. It is hypothesised that condensation occurs on the surfaces of the syringe/fibre and causes unexpected variations in peak areas. In the case of Hg⁰, the problem is easily resolved by diluting the saturated vapour using the vacuum line. Several dilution attempts were made, but it proved impossible to transfer HgBr₂ vapour from one flask to another, HgBr₂ seemingly being scavenged by the vacuum line. Several configurations meant to minimize contact with glass and Teflon surfaces were attempted, without success. This prevented the preparation of dilute HgBr₂ standards for the external calibration of the methodology (SPME-GC-EI-MS). Varying the temperature of the 'stock' flask would effectively change the concentration of HgBr₂ in the headspace since the saturated vapour pressure is temperature dependent, but this would still require sampling from a saturated headspace and would lead to a low reproducibility. In the end, no calibration curve was obtained for HgBr₂. This means that all the results presented herein are qualitative and that the detection limit for the methodology is as yet unknown.

2.2.3 Kinetics studies

The apparent rate coefficient of the $Hg^0 + Br$ reaction was determined by measuring the loss in concentration of Hg^0 relative to the loss in concentration of a reference molecule, in this case 1-butene.

2.2.3.1 Methodology – the relative rate method

In the relative rate method, two reactions – the reaction of interest and another, ideally well-characterized reaction, are monitored simultaneously. The rate constant of the reaction of interest is then determined relative to the rate constant of the well-characterized reaction:

$$R_1 + X \xrightarrow{k_1} P_1 \tag{1}$$

$$R_2 + X \xrightarrow{k_2} P_2 \tag{2}$$

where (1) is the reaction of interest and (2) is the reference reaction. The kinetic analysis generally assumes that reactions (1) and (2) are the only loss pathways for the reactants and that the reactants are not regenerated:

$$-\frac{d[R_1]}{dt} = k_1[R_1][X]$$
(3)

$$-\frac{d[R_2]}{dt} = k_2[R_2][X]$$
(4)

If both reactions are of the same order with respect to X, the following integrated relative rate equation can be derived:

$$\ln \frac{[R_2]_0}{[R_2]} = \frac{k_1}{k_2} \ln \frac{[R_1]_0}{[R_1]}$$
(5)

A linear relationship should exist between $\ln \frac{[R_1]_0}{[R_1]}$ and $\ln \frac{[R_2]_0}{[R_2]}$ and plotting one *versus* the other should yield a straight line of slope $\frac{k_1}{k_2}$ and passing through the origin, from which the value of k_1 can be obtained (since k_2 is known).

2.2.3.2 Chemical Analysis: Kinetic experiments

2.2.3.2.1 Operating conditions for the GC-EI-MS: Kinetic experiments

Chemical analysis of reaction mixture aliquots was performed on the same gas chromatograph, electron impact mass spectrometer (GC-EI-MS) as described above. Resolution of the analyte peaks was achieved on a 30m x 0.25mm i.d. X 1.0 µm cross-linked phenyl-methyl-siloxane column (HP5-MS) operated at a constant flow of helium (1.5 mL/min). The inlet temperature was lowered to 120°C. The inlet liner in this case had a wide borehole and contained some silanized glass wool. The septum was also switched to one adequate for syringe injections (not pre-pierced). Temperature programming (55°C for 1.5 min, ramp to 70°C at 20°C per minute, hold for 2 to 3 minutes) achieved good analyte separation in a reasonably short length of time and permitted integration of the analyte peak areas under isothermal conditions.

The MS source was operated at 230°C and the MS quadupole was kept at 150°C. The mass spectrometer was operated in single ion monitoring (SIM) mode, with mercury ions with mass to charge ratios, or m/z, of 198, 199, 200, 201 and 202. Similarly, the concentrations of 1-butene and dibromomethane were monitored using ions with m/z ratios of 56 and 174, respectively.

2.2.3.2.2 Sampling procedure

Aliquots (200 μ l) were withdrawn from the reaction mixture using a gastight syringe (250 μ L, Hamilton Co.) and injected directly into the injection port of the GC-MS. The volume withdrawn was small enough that several aliquots could be obtained without affecting the pressure within the reaction vessel. The concentration of the reactants was measured at the start of the experiment and after each irradiation period. For this purpose, three replicate gas chromatograms were obtained. Peak areas integrated from replicate chromatograms had a standard deviation of 5% or less.

2.2.3.3 Preliminary tests

2.2.3.3.1 Linearity of the mass spectrometer response

The response of the mass spectrometer (MS) was linear over the range of concentrations used in the experiments (Figure 11).



Figure 11: Linearity of the mass spectrometer response

Left: Hg(0) •; 1-butene \circ ; *Right*: Dibromomethane In both graphs, the errors bars are smaller than the size of the data point symbols.

2.2.3.3.2 Detection limits

The detection limits for the two reactants were determined empirically instead of statistically, because the statistical method (i.e. the detection limit is equal to the standard deviation of the blank multiplied by 3) tends to underestimate detection limits [*Armbruster et al.*, 1994]. Smaller and smaller concentrations of the reactants were injected until identification of the compound was no longer possible (the peak area was smaller than 300 counts or so). The detection limits obtained were ~ 20 ppb for Hg⁰ and ~ 300 ppb for 1-butene.

2.2.3.3.3 Blank experiments

Blank experiments were performed in order to verify that no dark reaction occurred between mercury and the reference molecule, and between either of the reactants and the bromine source. This involved preparing a reaction mixture and keeping it in the dark and monitoring the concentration levels after the equilibration time and again at the end of the usual experimental time (~4 hours). Other blank experiments were performed in order to verify that the photolysis light did not deplete the reactants (i.e. break down the reference molecule and/or photo-excite the mercury atoms). In this case, a reaction mixture was prepared in which the bromine source (dibromomethane) was omitted. The reaction mixture was then irradiated for at least as long as it would have been in a typical kinetic experiment (~300 seconds). In all cases it was found that no dark reaction occurred in the kin-



Figure 12: Blank experiments performed in a gas bath containing 0.4 atmosphere of oxygen

Left: Results from the blank experiment testing for dark reactions; *Right*: Results from the experiment testing for photolysis reactions in the absence of dibromomethane. In both cases, the concentrations of the reactants after the tests were not significantly different (at the 95% confidence level) from the initial concentrations.

etic system and that the photolysis light only affected the bromine source, and not the reactants, as required. The results for these blank experiments, performed in a bath gas containing 0.4 atm of O₂, are shown in Figure 12.

2.2.3.4 Initial slope experiments

Experiments were conducted in which the starting concentrations were 1 ppm (1 ppm = 2.46 x 10¹³ molecules cm⁻³ at 1 atmosphere and 298K) for elemental mercury, 2 ppm for 1-butene and from 10 to 500 ppm for dibromomethane. The partial pressure of oxygen was also systematically varied (0.03 to 0.4 atm). The reactions were monitored until the ratio $[Hg]/[Hg]_0$ reached 0.9 (i.e. 10% of the mercury had reacted). Values for -d[Hg]/dt and $-d[1-C_4H_8]/dt$ were obtained from the 'concentration' *versus* 'irradiation time' plots by weighted linear regression (see Error Analysis in the next section). These experiments were intended to give initial slopes that could be used as a diagnostic tool to detect dependence on oxygen and/or CH₂Br₂. The data obtained in the initial slope experiments was also used to obtain values for the $k_{Hg+Br}/k_{1-C_4H_8+Br}$ ratio (using the relative rate equation). An example of data processing can be found in Appendix B.

2.2.3.5 Error analysis

Irradiation time measurements

The irradiation times were clocked using a hand-held stopwatch. Each irradiation period therefore had an uncertainty of

$$\delta_{t,i} = \sqrt{(\delta_{start})^2 + (\delta_{stop})^2} = \pm 0.42 \, seconds$$
,

assuming a reaction time of 0.3 seconds. Accordingly, the uncertainty on the total irradiation time grew with each additional irradiation period, in the following pattern:

1 st irradiation period	$\delta_t = \sqrt{(0.3 s)^2 + (0.3 s)^2}$	$=\pm 0.42 \text{ s}$
2 nd irradiation period	$\delta_t = \sqrt{(0.42 s)^2 + (0.42 s)^2}$	$=\pm 0.59 \text{ s}$
3 rd irradiation period	$\delta_t = \sqrt{(0.59 s)^2 + (0.42 s)^2}$	$=\pm 0.72 \text{ s}$
etc.		

Concentration measurements

As mentioned above, the concentration of the reactants and the bromine radical precursor was measured at the start of the experiment and after each irradiation period. For this purpose, a minimum of three replicate gas chromatograms were obtained. Peak areas integrated from these replicate chromatograms had a standard deviation of 5% or less.

Initial slope determinations

Values for -d[Hg]/dt and $-d[1-C_4H_8]/dt$ were obtained from 'concentration' *versus* 'irradiation time' plots. The uncertainty in both variables as determined above was taken into account and a linear regression weighted in both x and y was used to find the best fit. Few, if any, curve fitting software offer this option, so the algorithm devised by [*Irvin and Quickenden*, 1983] was used for this purpose. The algorithm is presented in Appendix C. The regression parameters were then used to calculate the uncertainties for the obtained -d[Hg]/dtand $-d[1-C_4H_8]/dt$ values.

Determination of $k_{Hg+Br} / k_{1-C_4H_8+Br}$

Uncertainties for $\ln ([1-C_4H_8]_0/[1-C_4H_8])$ and $\ln ([Hg]_0/[Hg])$ were calculated from the above according to the rules for the propagation of random errors. Values for $\ln ([Hg]_0/[Hg])$ were then plotted against $\ln ([1-C_4H_8]_0/[1-C_4H_8])$ and a linear regression weighted in both x and y was used to find the best value for the $k_{Hg+Br}/k_{1-C_4H_8+Br}$ ratio. The regression parameters were used to derive the uncertainty on the obtained $k_{Hg+Br}/k_{1-C_4H_8+Br}$ ratio.

2.3 Materials & Supplies

Chemicals

1-butene (\geq 99%), dibromomethane (99%), mercury (99.9995%), mercury (I) bromide (\geq 99.9%), mercury (II) bromide (99.998%), and the gold powder (<10 μ m, \geq 99.99%) were purchased from Sigma Aldrich. Dimethyldichlorosilane (5% in toluene) was purchased from Supelco, concentrated nitric acid from Anachemia and sulphuric acid and hydrogen peroxide (30%) from Fisher. Mercury was further purified by regularly evacuating the gas-tight flask it was stored in to < 6 x 10⁻⁵ atmosphere for 30 minutes.

Gases

Extra dry air, extra dry oxygen (2.6) and UHP nitrogen (99.999 %) were purchased from MEGS Gases Ltd.

3 Results and Discussion

3.1 General considerations

The seven natural isotopes of mercury (¹⁹⁶Hg, ¹⁹⁸Hg, ¹⁹⁹Hg, ²⁰⁰Hg, ²⁰¹Hg, ²⁰²Hg, ²⁰²Hg, ²⁰⁴Hg) give it a very recognizable mass spectrum. It follows that mercury-containing species are easily recognized as such since they exhibit a similar pattern. In the case of bromomercury species the isotopic pattern is further complicated by the presence of both ⁷⁹Br and ⁸¹Br. The calculated isotopic patterns (MassLink NT Data System) for HgBr₂ and Hg₂Br₂ are shown in Figure 13.



Figure 13: Calculated isotopic pattern for HgBr₂ (top) and Hg₂Br₂ (bottom)

3.2 Method development for the determination of mercury halides in ambient air through atmospheric chemical ionization mass spectrometry (APCI-MS) analysis

All the results presented in this section (3.2) were obtained from work done in collaboration with Dr. Daniel Deeds, a current post-graduate researcher in our group. His focus was on mercury oxide (HgO) and mercury chloride (HgCl₂) whilst mine was on mercury bromide (HgBr₂). The expertise of Alain Tessier, from CBAMS at Concordia University, is also acknowledged.

3.2.1 Preliminary tests



Figure 14: Mass spectrum for HgBr₂ solution in methanol

The inset is a magnified view of the greyed portion of the mass spectrum and shows that the parent ions are preserved to a certain extent.

Saturated solutions of oxidized mercury species (HgO, HgCl₂, HgBr₂) in methanol were fed to the unmodified Quattro LC operated with the APCI probe. The tests showed that HgBr₂ could be detected in negative chemical ionisation mode. Figure 14 shows a typical mass spectrum for the HgBr₂ solution. The inset shows a magnified view of the m/z values associated with HgBr₂. The isotopic pattern shows similar features to the calculated one shown in Figure 13a. The presence of other mercury species besides HgBr₂ is due to ion reactions taking place in the corona discharge.

3.2.2 Gold solid-phase micro-extraction (Au-SPME) results

Custom-built gold solid-phase micro-extraction fibres were built and used to sample from a sealed flask containing HgBr₂ crystals. Gold was chosen because of its well-known ability to trap mercury and because tests performed in our laboratory showed that gold could also trap mercury halide species [*Deeds et al.*, 2009]. This phenomenon has been noted by other researchers as well [*Brosset and Iverfeldt*, 1989].

After being exposed to $HgBr_2$ vapour for up to a few hours, the fibre was inserted into the modified APCI probe (shown in Figure 7) and kept at 50°C for a few minutes and then desorbed at a temperature of 400°C. Figure 15 shows a typical desorption curve. The temperature gradient of the heater is superimposed. The temperature change achieved by the heating element is almost instantaneous.

Although mercury bromide could successfully be introduced to the instrument using the Au-SPME fibres, there were a number of concerns regarding reproducibility and memory effects. The gold-particle coating was very fragile and needed retouching frequently. This meant that the surface could not be assumed to be the same from analysis to analysis. By far the biggest problem, however, was the strong memory effect observed for HgBr₂, and it led to the eventual rejection of the Au-SPME fibres as trappings devices.



Figure 15: Au-SPME desorption curve (total ion current) with temperature gradient shown

Indeed, once a fibre had been exposed to the HgBr₂ standard, it was nearly impossible to get it completely clean again. The first desorption run would yield a peak as seen in Figure 15. Letting the fibre cool for a few minutes and reheating it to 400°C would either yield a small peak or nothing at all. Letting the fibre rest unused for longer (hours to days) before desorbing it again, however, would lead to more HgBr₂ being released upon heating at 400°C. A persistent blank was even observed on a fibre that had had its coating retouched and had been conditioned!

This seems to indicate that HgBr₂ penetrates deeply inside the gold particles, in a manner that is reminiscent of amalgamation. The fact that the fibres had to be heated to a temperature above the boiling point of HgBr₂ in order to release it also points to an interaction that is stronger than simple physisorption. Gold is not generally thought to amalgamate oxidised mercury species, however its ability to quantitatively retain dimethylmercury (CH₃HgCH₃) has been noted in the past [Braman and Johnson, 1974]. Some mercury halides, for example HgCl₂, can amalgamate with metals such as aluminium.

3.2.3 Reducing unfavourable ions reactions in the APCI source - isobutane as chemical ionisation gas



Figure 16: Mass spectrum for HgBr₂ introduced by Au-SPME with nitrogen as the ionisation gas.

Ions reactions also occurred when the sample was introduced by Au-SPME (Figure 16). The species formed include HgBr₂O, HgBr₂Cl and HgBr₃. The chlorine (in HgBr₂Cl) was probably present in the APCI source before the introduction of the sample. It is likely that it originated from a previous analysis involving HgCl₂, since it proved difficult to completely purge the chamber between runs. In fact, it was necessary to dismantle the probe and to rinse it with dilute nitric acid in order to completely clean the system.



Figure 17: Mass spectrum obtained for HgBr₂ using a mix of isobutane and nitrogen as ionisation gas

Since the presence of ions reactions inside the source would preclude the definitive chemical identification of any mercury-containing species found in the atmosphere, the ionisation gas was varied. The aim was to find conditions under which the HgBr₂ parent ions would be preserved, either as [M]⁻, or as a distinct-ive adduct, [M + fragment]⁻. The nitrogen gas was passed over HgBr₂ crystals and mixed with another potential ionisation gas before being introduced directly into the probe via the ¹/₄ in. Ultra-Torr fitting (the stainless-steel T-junction was removed, see Figure 7). Argon (Ar), helium (He), hydrogen (H₂), nitrogen dioxide

(NO₂), acetylene (C₂H₂), acetone and benzene were all tried with limited success. Isobutane (i-C₄H₁₀), however, yielded a relatively simple mass spectrum dominated by [M+26]⁻, as shown in Figure 17. It was determined that all further experiments would therefore be performed using a mix of isobutane and nitrogen as ionisation gas. These experiments will not be presented here since the author was not fully involved with the work – including the design and building of a custom-built inlet for the instrument (see Appendix D for details) and its characterisation. Instrumental detection limits of ~20 pg were obtained for both mercury chloride and mercury bromide using this inlet and work is ongoing to further reduce instrumental detection limits by another order of magnitude.

Although Au-SPME did not prove very convenient for the trapping of mercury bromide, APCI-MS showed promise as a detection technique. Indeed, although some fragmentation of the parent molecule does occur, as evidenced by the presence of bromine ions in the mass spectra obtained (not shown on the spectra included herein), the parent ions can be preserved as [M+26]⁻, making unambiguous chemical identification possible. Also, we observed that ionisation by APCI is too soft (not energetic enough) to ionize elemental mercury. This is important since elemental mercury is present in the remote atmosphere in concentrations that are up to a 1000 times larger than the concentration of GOM (ng/m³ vs pg/m³), and if trapped alongside it, could dominate the mass spectrum in a way that would make the mercury halide species hardly detectable.

APCI-MS, once coupled with a suitable trapping technique, could potentially be a highly selective analytical method for the detection of atmospheric mercury halide species. The concentration of mercury halide species in the atmosphere is unknown, but if they indeed make up a significant fraction of GOM, sampling times on the order of hours would be sufficient (assuming a sampling rate of 10L/minute and mercury halide concentrations in the very low pg m⁻³) to get a detectable signal using adapted APCI-MS.

3.3 Homogeneous gas-phase reaction of elemental mercury with bromine radicals: product and kinetic studies

This section covers work done towards achieving the second and third objectives listed in section 1.3, namely testing whether solid-phase micro-extraction coupled with mass spectrometry detection (SPME-MS) can be applied to *in situ* monitoring of the product(s) of the gas-phase reaction between elemental mercury (Hg⁰) and bromine radicals (Br·) and expand the kinetic analysis performed by [*Ariya et al.*, 2002] by studying the reaction under a wider range of experimental conditions.

3.3.1 Product studies

3.3.1.1 Solid-phase micro-extraction coupled with electron impact mass spectrometry (SPME-GC-EI-MS)

3.3.1.1.1 Results of preliminary tests – detection of mercury bromide Electron impact (EI) mass spectra of HgBr₂ and Hg₂Br₂

In order to determine whether HgBr₂ and Hg₂Br₂ could effectively be distinguished by electron impact mass spectrometry, EI-MS chromatograms were obtained from solid crystals packed into a capillary tube and introduced directly into the probe of an electron impact (EI) mass spectrometer (Kratos MS 25RFA). The chromatograms obtained were almost identical to each other (Figure 18). The parent ions are completely absent from the Hg₂Br₂ chromatogram, and the ions associated with HgBr (m/z = 275, 277, 278, 279, 280, 281, 282, 283, 285) are not more prominent than in the HgBr₂ spectrum. The ions associated with mercury, however, are present in a slightly higher proportion, indicating that Hg₂Br₂ breaks down to Hg and HgBr₂ inside the mass spectrometer. The lack of parent ions in the mass spectrum obtained for Hg_2Br_2 makes it nearly impossible to distinguish one species from the other using EI-MS.



Figure 18: Electron impact mass spectrum for (a) HgBr₂ and (b) Hg₂Br₂

*Extraction tests for HgBr*₂ and Hg₂Br₂

The saturated vapour pressure of HgBr₂ at 298 K is 1.45×10^{-7} atm or 3.7×10^{12} molecules cm⁻³. This is equivalent to 0.15 ppm at 298 K and 1 atmosphere and represents from 15 to 30% of the initial concentration of elemental mercury in the reaction mixtures (0.5 – 1 ppm). However, the saturated vapour pressure of Hg₂Br₂ (0.5 ppb) represents only about 0.05 to 0.1 % of the initial concentration of mercury in the reaction flask . This means that, at room temperature, the only product likely to be present in the gas phase in concentrations easily detectable by GC-MS is HgBr₂. This hypothesis was tested by exposing a PDMS/DVB SPME fibre to the atmosphere of flasks containing saturated vapour of HgBr₂ and Hg₂Br₂. Even after extraction times as long as 60 minutes, no Hg₂Br₂ was detected at room temperature (295 ± 3 K) whereas an appreciable signal was obtained for HgBr₂ in as little as 15 seconds.

This test was repeated at 323 K and 353 K. No signal was obtained for Hg_2Br_2 for 5 and 15 minute extractions at 323 K but a peak was obtained at 353 K. Unsurprisingly, the mass spectra are almost identical, but the fact that the chromatograms obtained are also identical (i.e. same retention time of 5.83 ± 0.01 minutes) indicates that Hg_2Br_2 breaks down to $HgBr_2$ at some point along the analysis. [Oppermann et al., 1989] showed that this phenomenon occurs at temperatures as low as 473 K. Figure 19 shows the chromatogram obtained for $HgBr_2$ at room temperature and that obtained for Hg_2Br_2 at 353 K along with the mass spectra obtained for the 5.83 ± 0.01 minutes peaks. In a bid to prevent Hg_2Br_2 from breaking apart before it reached the mass spectrometer (i.e. to allow separation of $HgBr_2$ and Hg_2Br_2 on the column), the temperature of the GC inlet was lowered from 250 to 120°C (523 to 393 K), but this did not alter the resulting chromatogram significantly, i.e. it did not prevent the break-up of Hg_2Br_2 . Since separation of both species on the column was not possible, sampling at 353 K was ruled out

and it was decided that gas-phase product analysis would take place at room temperature in order to selectively analyse for HgBr₂.



Figure 19:Extraction tests for HgBr₂ and Hg₂Br₂

Left. Top: Chromatogram for HgBr₂ sampled at room temperature; Bottom: Mass spectrum of the peak at 5.83 ± 0.01 minutes from the chromatogram of HgBr₂ sampled at room temperature

Right: Top: Chromatogram for Hg₂Br₂ sampled at 353K; Bottom: Mass spectrum of the peak at 5.83 ± 0.01 minutes from the chromatogram of Hg₂Br₂ sampled at 353K
3.3.1.1.2 In situ detection of reaction products by SPME-GC-EI-MS

SIM mode

In situ sampling tests were performed on three 5.5L flasks: a blank mixture, i.e. an unreacted mixture of 0.5 ppm mercury, 2 ppm 1-butene and 25 ppm of dibromomethane in 1 atm of UHP nitrogen; a partially reacted mixture (irradiated until 40% of the Hg⁰ had reacted) and a fully reacted mixture (irradiated until >95% of the Hg⁰ had reacted). Figure 20 shows the chromatogram obtained in each case. The extraction time was 15 minutes and analysis was done in SIM mode using the early version of the GC-MS method. HgBr₂ was only detected in the last chromatogram (21c: >95%). The mass spectrum obtained is shown at the bottom of Figure 20.

There are many potential reasons why HgBr₂ is not observed earlier on in the reaction. It might be that it is not formed until later on in the reaction under our experimental conditions. [*Khalizov et al.*, 2008] reported HgBr as the only product of the reaction when the concentration of bromine atoms was much lower than the concentration of elemental mercury. They studied the reaction in a fastflow turbulent reactor coupled to a ion-drift chemical ionisation mass spectrometer (ID-CIMS) at room temperature and in the pressure range 0.13-0.4 atmosphere. Another reason might be that HgBr₂ is produced, but in quantities that are below the detection limit for the SPME-GC-EI-MS methodology used in the experiments. It is also possible that most of the HgBr₂ produced is deposited to the wall, since HgBr₂ is known to be very 'sticky'. This seems likely considering that [*Ariya et al.*, 2002], using a very similar experimental set-up and examining the products in a fully reacted flask, found >80% of the products deposited to the wall and only 6 to 15 % in the gas phase.



Figure 20: SIM mode product experiment results

a) unreacted flask; b) 40% Hg⁰ reacted; c) >95% Hg⁰ reacted. HgBr₂ only detected in c). MS shown at bottom. The insets are magnified views of the 2.1 - 2.5 minute sections of the chromatograms where the HgBr₂ peak is expected under the operating conditions.

They identified the gas-phase product as HgBr₂. Their methodology involved heating the reaction flask to 353 K before condensing the contents into a small tube immersed in liquid nitrogen. Half of the tube would then be introduced directly into the probe of a mass spectrometer (Kratos MS25RFA) and heated stepwise to 700 K. They observed fragments between 300 and 500 K, which they identified as HgBr₂. They interpreted the lack of additional signal when the temperature was raised between 500 and 700 K as demonstrating the absence of Hg₂Br₂. Hg₂Br₂, they argued, would decompose into HgBr at high temperatures. The results presented above, however, indicate that the methodology used by [Ariya et al., 2002] could not in fact distinguish between HgBr₂ and Hg₂Br₂. The electron impact mass spectra for both species are virtually identical since Hg₂Br₂ breaks down to Hg + HgBr₂ and not to HgBr. Also, the flask was heated to 353 K, a temperature at which both HgBr₂ and Hg₂Br₂ are volatile enough to be transferred to the sample tube.

[Ariya et al., 2002] also identified the wall product as HgBr₂. In this case, the inside wall of the reaction flask was washed with small amounts of hot toluene. Ultrasound was used to hastens dissolution of the mercury products. The washings were then combined and derivatized using the method described by [Snell et al., 1998] and analysed by GC-MS. [Ariya et al., 2002] described the method as being specific for Hg(II) compounds, and used their results as supporting evidence for the formation of HgBr₂. [Snell et al., 1998] in fact reported that Hg(I) compounds could also be derivatized by their method, especially if the sample is exposed to ultrasound before derivatization. It therefore seems that the methodology used by [Ariya et al., 2002] to identify the wall product(s) cannot distinguish without doubt between HgBr₂ and Hg₂Br₂.

Finally, [Ariya et al., 2002] checked whether aerosol formation was an important process in their reaction system. The methodology involved evacuating the flask through a Teflon filter, treating the filter with a mixture of nitric acid (HNO₃) and hydrogen peroxide (H_2O_2), and analysing the mixture using ICP-MS. Filters with pores measuring 0.5µm or 1µm were used and collected between 0 and 0.5% of the initial mercury loading in the flask, indicating that formation of large aerosols was not a dominant process in their reaction system.

It should be noted that the methodology used in the work presented in this thesis cannot give any indication as to whether Hg₂Br₂ is one of the products of the reaction or not, but it can, and did, identify HgBr₂ unequivocally.

Scan mode

Further tests were done on a mixture of 1.0 ppm mercury, 2 ppm 1-butene and 500 ppm of dibromomethane in 1 atm of air. The flask was irradiated for 5 seconds five times and sampled for products after each irradiation period. The extent of reaction for mercury was $\leq 10\%$. The SPME extraction time was 15 minutes and analysis was done in scan mode (m/z = 50-575) using the later version of the GC-MS method. The aim was to try to detect any mercury product formed in the early stages of the reaction. Figure 21 shows the chromatograms obtained after 0, 10 and 20s irradiation. The insets are magnified views of regions where products are appearing/should appear. The insets on the left (2.8 to 3.1 minutes) show the appearance of products from the 1-butene + Br reaction and those on the right (5.8 to 6.1 minutes) show the lack of appearance of HgBr₂, the retention time of which is ~5.95 minutes under the new operating conditions. No product whatsoever of the mercury + Br \cdot reaction could be detected. Once again, there are several potential reasons why no mercury products are detected early on in the reaction. It might be that the detection limit of the methodology is too high or that the products formed adhere to the wall of the reaction vessel, despite the deactivation of the wall through treatment with DMDCS. There is also the possibility that the fibre used was not appropriate: HgBr, a potential early product, is polar and the PDMS/DVB coating is not suitable for such molecules.



Figure 21: Scan mode product experiment results

a) 0s (unreacted); b) 10s; c) 20s. No mercury products detected. Insets show magnified views of where products appeared/should have appeared. The HgBr₂ peak was expected in the 5.95-6min section under the operating conditions. The two MS at the bottom identify the 1-butene products as 1-bromo-2-butanone (2.02 min) and 1-bromo-2-butanol (2.99min).

The peak at 2.92 minutes was identified through its mass spectrum as 1bromo-2-butanone (CH₃CH₂CH(O)CH₂Br) and that at 2.99 minutes as 1-bromo2butanol (CH₃CH₂CH(OH)CH₂Br). To the best of our knoledge, products of the 1butene + Br · reaction had never been identified before. The mechanism for the reaction between 1-butene and bromine radicals is well understood and is known to be the same as that of smaller alkenes, such as ethene. This mechanism will be discussed in detail with the kinetic results. The products of the ethene + Br · reaction in air have been identified by at least two different groups as bromoacetaldehyde (BrCH₂CHO), 2-bromoethanol (BrCH₂CH₂OH) and bromoacetic acid (BrCH₂CH(O)OH) [*Barnes et al.*, 1989; *Yarwood et al.*, 1992]. The products can then react further to form smaller products such as CO, CO₂, HBr, HOBr and BrCHO. The products identified here are thus amongst those expected. By analogy with the ethene reaction, smaller products such as CO, CO₂, HBr, HOBr and BrCHO are also expected to be produced in our reaction system.

3.3.2 Kinetic results

3.3.2.1 Determination of the rate coefficient for the gas-phase reaction between elemental mercury and bromine radicals

Values for the $k_{Hg+Br} / k_{1-C_4H_8+Br}$ ratio at different initial concentrations of dibromomethane and at varying partial pressures of oxygen were derived from the data obtained in the initial slope experiments using the relative rate equation. These values were plotted against the initial concentration of dibromomethane and against the partial pressure of oxygen. Figure 22 illustrates how the $k_{Hg+Br}/k_{1-C_4H_8+Br}$ ratio seems to depend on both variables.



Figure 22: Plot of $k_{Hg+Br}/k_{1-butene+Br}$ at different partial pressures of oxygen and concentrations of dibromomethane

Legend: \bigvee 0.03 atm O₂; • 0.065 atm O₂; \circ 0.13 atm O₂; \square 0.2 atm O₂; \blacktriangle 0.4 atm O₂ The curved lines (\bigvee 0.03 atm O₂; \square 0.2 atm O₂; \bigstar 0.4 atm O₂) are there to facilitate the visual interpretation of the graph. The straight lines (for • 0.065 atm O₂; \circ 0.13 atm O₂) are regression lines.

That the $k_{Hg+Br}/k_{1-C_4H_8+Br}$ ratio varies with the partial pressure of oxygen in the reaction mixture is not surprising since the rate of the reaction of 1-butene with bromine radicals is known to depend on the partial pressure of oxygen in the kinetic system.

There has only been one published study on the reaction [*Barnes et al.*, 1989], but it showed that the mechanism of the oxidation of 1-butene by bromine

radicals is the same as that of other alkenes such as propene and ethene. The mechanism of the ethene reaction was also studied by [*Anthony and Roscoe*, 2004], and their results also point towards a mechanism in which 1-butene adds a bromine atom to form an adduct, $Br-C_4H_8$, that can then decompose back to the reactants or react with oxygen to form products:

$$1 - C_4 H_8 + Br + M \underset{k_{-6}}{\overset{k_6}{\leftrightarrow}} Br - C_4 H_8 + M \tag{6}$$

$$Br - C_4 H_8 + O_2 \xrightarrow{k_7} products \tag{7}$$

In the case of 1-butene, the products include 1-bromo-2-butanone (CH₃CH₂CH(O)CH₂Br) and 1-bromo2-butanol (CH₃CH₂CH(OH)CH₂Br), as identified by SPME-GC-EI-MS in this work.

Assuming steady-state for the adduct, $Br-C_4H_8$, the following expression can be derived for the apparent rate constant of the reaction:

$$\frac{1}{k_{1-butene+Br}} = \frac{k_{-6}}{k_6 k_7 [O_2]} + \frac{1}{k_6 [M]}$$
(8)

Accordingly, a plot of $1/k_{1-butene+Br}$ versus $1/[O_2]$ should show good linearity. Plotting $k_{Hg+Br}/k_{1-C_4H_8+Br}$ against the inverse of the partial pressure of oxygen, P_{O_2} , for various concentration of dibromomethane, however, does not yield linear plots, as can be seen in Figure 23.



Figure 23: $k_{Hg+Br}/k_{1-C_4H_8+Br}$ ratios plotted against the inverse of the partial pressure of oxygen for different concentrations of dibromomethane

The fact that the relationship is not obeyed reveals either that $k_{Hg + Br}$ also has an oxygen dependence of some sort; or that CH_2Br_2 , or one of its photolytic fragments, interfere with either, or both, reactions.

To test for possible oxygen dependence of the mercury reaction, the initial slopes, -d[Hg]/dt and $-d[1-C_4H_8]/dt$ were plotted against the initial concentration of CH₂Br₂ for various partial pressures of oxygen. The top panels of Figure 24 show that -d[Hg]/dt varies with increasing [CH₂Br₂]₀ in a similar pattern whether the system contains 0.03 atm or 0.4 atm O₂, whereas

 $-d[1-C_4H_8]/dt$ increases much more sharply with increasing $[CH_2Br_2]_0$ at 0.4 atm O₂ than at 0.03 atm O₂.

Plotting -d[Hg]/dt and $-d[1-C_4H_8]/dt$ against the partial pressure of oxygen in the system, P₀₂, for 500 ppm [CH₂Br₂]₀ confirms the oxygen dependence of the 1-butene reaction and shows that the rate of the mercury reaction is unchanged by oxygen (Figure 24, bottom panel).



Figure 24: Testing for potential oxygen dependence

Top: \blacksquare 0.03 atm O₂; \blacktriangle 0.2 atm O₂; \square 0.4 atm O₂ Bottom: $\bullet -d[1-C_4H_8]/dt$; $\circ -d[Hg]/dt$ So there remains the possibility that CH_2Br_2 interferes with either, or both, reactions. This is harder to test for since CH_2Br_2 is the bromine radical precursor and increasing its concentration should lead to increases in both -d[Hg]/dt and $-d[1-C_4H_8]/dt$, as observed in the two top panels of Figure 24.

The photolysis process can be written as:

$$CH_2Br_2 \xrightarrow{hv \simeq 250 \text{nm}} products$$
 (9)

where the products are bromine radicals (Br·), of course, but also others such as CH_2Br , $CHBr_2$ and CH_2 , all of which are known to react quickly with O_2 [Baulch et al., 1994; Bayes et al., 2005; Eskola et al., 2006; McGivern et al., 2004; Orlando et al., 1996]. The possible reactions are summarized in Figure 25.

$$CH_{2}Br_{2} \xrightarrow{hv} \{ \begin{array}{c} CH_{2}Br + Br \\ CHBr_{2} \end{array} \} \xrightarrow{O_{2}} \{ \begin{array}{c} CH_{2}BrO_{2} \rightarrow CH_{2}BrO \rightarrow HCHO \\ CHBr_{2}O_{2} \end{array} \} \xrightarrow{O_{2}} \{ \begin{array}{c} CHBr_{2}O_{2} \rightarrow CHBrO + Br \rightarrow HCO + Br \\ CH_{2} + 2Br \end{array} \} \xrightarrow{O_{2}} \{ \begin{array}{c} CHBr_{2}O_{2} \rightarrow CHBrO + Br \rightarrow HCO + Br \\ CH_{2}O_{2} \rightarrow CO + H_{2}O \end{array} \}$$

Figure 25: Reaction pathways for the photolytic fragments of CH₂Br₂

This should imply that the photolysis of dibromomethane, and therefore the bromine radical production, should be more efficient at higher partial pressures of oxygen, because the reformation of CH_2Br_2 by recombination of the formed radicals should be less likely. This, however, is not what was observed in this study. If the production of bromine were favoured at higher partial pressures of oxygen, -d[Hg]/dt would increase as P_{o_2} increased for a given concentration of dibromomethane, due to the resulting increase in $[Br \cdot]$. This increase would be expected to be less pronounced than that of $-d[1-C_4H_8]/dt$, since the 1-butene reaction would benefit from the direct increase in oxygen, as well as the increase in $[Br \cdot]$. The bottom panel of Figure 24, however, shows no increase in -d[Hg]/dt. If anything, there might even be a slight decrease in -d[Hg]/dt as the oxygen concentration is increased.

This seems to indicate that production of bromine is hindered at higher oxygen concentrations. Plotting $-d[CH_2Br_2]/dt$ against $[CH_2Br_2]_0$ confirms this suspicion. As the left panel of Figure 26 shows, at 0.03 atm, $-d[CH_2Br_2]/dt$ increases with $[CH_2Br_2]_0$ as expected from:

The same behaviour is not observed at 0.4 torr. Indeed, $-d[CH_2Br_2]/dt$ at 500 ppm $[CH_2Br_2]_0$ is lower than $-d[CH_2Br_2]/dt$ at 300 ppm $[CH_2Br_2]_0$. The right side of Figure 27 shows how $-d[CH_2Br_2]/dt$ for 500 ppm $[CH_2Br_2]_0$ actually decreases with increasing Po₂.



Figure 26: Decrease in photolysis efficiency as P_{O_2} is increased

Left: \bullet 0.03 atm O₂; \diamond 0.2 atm O₂; \Box 0.4 atm O₂ Right: \bullet $-d[CH_2Br_2]/dt$ at various oxygen partial pressures and 500 ppm CH₂Br₂ As mentioned above, this behaviour goes against what is expected from CH_2Br_2 photolysis. Dibromomethane (50 ppm) was therefore irradiated on its own, in air and in UHP N₂. As depicted in Figure 27, the same behaviour was observed, i.e. the photolysis seemed to be hindered at the higher concentration of oxygen. This at least excludes interference with the reactants as the cause of this unexpected phenomenon.



Figure 27: Photolysis of dibromomethane in the absence of 1-butene and elemental mercury

Although the photolytic fragments of dibromomethane have been the subject of several studies, the photolysis of dibromomethane itself has not been so thoroughly investigated, since most studies into the fragments did not use photolysis of dibromomethane as their radical source. At least one study, however, used CH_2Br_2 to produce CH_2Br radicals. [*Eskola et al.*, 2006] studied the reaction between CH_2Br and oxygen at varying oxygen concentrations, but CH_2Br_2 was not monitored.

It seems therefore that the photolysis of dibromomethane, and therefore, the production of bromine radicals, is a complex process involving oxygen. This, coupled to the dependence of the 1-butene reaction on oxygen, probably contribute to the lack of linearity observed in the $k_{Hg+Br}/k_{1-C_4H_8+Br}$ versus P₀₂ plots shown in Figure 23. It is, however, impossible to rule out possible interactions between dibromomethane and one of the reactants (or both).

Using a different bromine radical precursor could act as a diagnostic test. An obvious choice would be molecular bromine (Br₂). It is a clean source of bromine radicals, i.e. its photolysis produces only bromine radicals, and no organic fragments. It can also be conveniently photolysed using visible light. It has, however, been reported to heterogeneously react with elemental mercury, even under dark conditions [*Ariya et al.*, 2002; *Donohoue et al.*, 2006]. This was also observed in tests performed in this study (Appendix E).

Going back to the results presented in Figure 22, it is difficult to determine which values of $k_{Hg+Br}/k_{1-C_4H_8+Br}$ are the least influenced by external factors and would yield the most reliable k_{Hg+Br} values. Two data series, 0.065 atm O₂ and 0.13 atm O₂, show a dependence on $[CH_2Br_2]_0$ that is linear enough that a value for $k_{Hg+Br}/k_{1-C_4H_8+Br}$ at 0 ppm $[CH_2Br_2]_0$ can be extrapolated by weighted linear regression. This process yields a value for $k_{Hg+Br}/k_{1-C_4H_8+Br}$ of 0.192 ± 0.011 at 0.065 atm O₂ and 0.82 ± 0.14 at 0.13 atm O₂.

Using the values for $k_{1-butene + Br}$ reported by [*Barnes et al.*, 1989] for these partial pressures of oxygen yield $k_{Hg+Br} = (3.9 \pm 0.2) \times 10^{-13}$ and $(2.3 \pm 0.4) \times 10^{-13}$

cm³ molecule⁻¹ s⁻¹, respectively. Since the mercury reaction does not depend on the partial pressure of oxygen in the system, and since any influence from CH_2Br_2 is removed by the regression process, the rate coefficient, k_{Hg+Br} , is expected to be the same at both partial pressures. The fact that they are different probably reflects errors in the experimental work, as well as in the data treatment.

Experimental errors that have not been taken into account in error analysis so far are the <10% variation in the initial concentrations of mercury and 1butene. As these are not correlated, they can be added quadratically to yield an additional error of <15% on the $k_{Hg+Br}/k_{1-C_4H_8+Br}$ ratios. Also, the reproducibility of replicate determinations of $k_{Hg+Br}/k_{1-C_4H_8+Br}$ should be into account. The maximum observed standard deviation for replicate measurements was 15%. Adding these two gives an additional \pm 30% uncertainty to the determined values of k_{Hg+Br} , yielding (3.9 \pm 1.4) x 10⁻¹³ and (2.3 \pm 1.3) x 10⁻¹³ cm³ molecule⁻¹ s⁻¹. These values are not significantly different at the 95% confidence level. Combining them together gives $k_{Hg+Br} = (3.1 \pm 1.9) \times 10^{-13} \text{ cm}^3$ molecule⁻¹ s⁻¹. The largest uncertainty with respect to the data treatment is the last linear regression, since there is no mechanistic evidence supporting a linear relationship. Passing a straight line through the points is simply a convenient way of obtaining a value for the intercept. The error associated with this cannot be quantified at this time.

The rate coefficient obtained in this study agrees quite well with the most recent, and also the most direct, kinetic study to date, that of [*Donohoue et al.*, 2006]. They reported a rate coefficient of $(3.6 \pm 0.8) \times 10^{-13} \text{ cm}^3$ molecule⁻¹ s⁻¹ at 1 atmosphere and 298 K, however the overall uncertainty on the coefficient was reported to be \pm 50%.

4 Conclusions

Atmospheric Pressure Chemical Ionisation Mass Spectrometry (AP-CI-MS) has been identified as a potentially highly selective analytical method for the detection of atmospheric mercury halide species. The current instrumental detection limit, using a custom-built inlet, is ~20 pg for both HgCl₂ and HgBr₂, two mercury-containing compounds that are thought to make up a significant fraction of gaseous oxidized mercury (GOM). Work is in progress to lower this detection limit further. Once combined with a suitable trapping technique, modified APCI-MS could yield atmospheric measurements for mercury halide species with a resolution of a few hours or better. This would be an important contribution towards the chemical identification of the mercury species thought to drive mercury deposition to remote and sensitive ecosystems.

Tests with Solid-Phase Micro-Extraction coupled to Gas Chromatography Electron Impact Mass Spectrometry (SPME-GC-EI-MS) confirmed the findings by [*Ariya et al.*, 2002] HgBr₂ is one of the end products of the recombination of mercury atoms with bromine radicals under the experimental conditions used. The tests also allowed the identification of two products of the oxidation of 1-butene by bromine radicals. The products identified, 1-bromo-2-butanone and 1-bromo2-butanol, support the proposed mechanism for the reaction.

Finally, in the kinetic experiments, the value of the $k_{Hg+Br}/k_{1-C_4H_8+Br}$ ratio was mapped for a wide variety of experimental conditions. The concentration of the bromine radical precursor, dibromomethane (CH₂Br₂), was varied from 10 to 500 ppm and the partial pressure of oxygen was varied from 0.03 to 0.4 atmosphere. The experiments confirm the lack of oxygen dependence of the reaction of elemental mercury with bromine radicals, and yield a new value for the rate coefficient of the reaction (3.1 ± 1.9 cm³ molecule⁻¹ s⁻¹), using 1-butene as the reference, that is in agreement with the most recent peer-reviewed study.

5 Future work

The recent acquisition of a Liquid Chromatograph - Atmospheric Pressure Ionisation Mass Spectrometer (LC-APIMS, Agilent 6100) by our research group opens up a few possibilities that should be explored as a continuation of the work presented herein. For example, the instrument could be used without modification to study the products of the reaction between elemental mercury and bromine radicals that are absorbed on the wall of the reaction vessel. A suitable solvent might be methanol, since both mercurous bromide (Hg₂Br₂) and mercury bromide (Hg-Br₂) are soluble in it and the low boiling point of methanol would allow analysis at low temperatures.

Also, the instrument could easily be adapted for the detection of gaseous species, such as mercury halides. The development work started at CBAMS at Concordia on a methodology for the detection of atmospheric mercury halides could then be continued using our own facilities. Also, the design of the Atmospheric Pressure Chemical Ionisation probe is such that commercially-sold Solid-Phase Micro-Extraction fibres could potentially be desorbed within the heater without extensive modifications. This would offer an alternative detection method for the products of the reaction between elemental mercury and bromine radicals. It could also be possible to couple the APCI-MS unit to a flow system, providing an alternative to the static set-up used in this work.

Other areas of investigation could include the effect of oxygen on the photolysis of dibromomethane, possibly using Solid-Phase Micro-Extraction with onfibre derivatization to monitor one of the products, formaldehyde (HCHO). It would also be beneficial to use a calibration gas generator to produce a gas flow containing a constant concentration of, for example, HgBr₂, in order to test and calibrate various commercially-available SPME fibre coatings.

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Appendix A: Table of unit conversion

Table A: Unit conversion

Concentration

	molecule/cm ³	Ра
1 ng Hg/m ³	$3 \ge 10^6$	
1 ppq (parts per 10 ¹⁵)	2.46 x 10 ⁴	
1 ppt (parts per 10 ¹²)	2.46 x 10 ⁷	
1 ppm (parts per 10 ⁶)	2.46 x 10 ¹³	
Pressure		
1 atmosphere	2.46 x 10 ¹⁹	101325 Pa
Temperature		
	Κ	
0°C	273	

	Time (s)		Peak	Peak areas			Time (s)		Peal	areas	
		1-but	ene Hg⁰	CH	Br			1-bute	ene Hg⁰	CH	H_2Br_2
		0	4270	16858	581436			80	3652	16279	537068
			4187	16615	560479				3611	15890	524601
			3977	16453	544815				3726	16158	532426
			4022	16318	564962	Average			3663	16109	531365
Average			4114	16561	562923	Std. Dev.			58	199	6301
Std. Dev.			138	232	15064	RSD (%)			1.6	1.2	1.2
RSD (%)			3.3	1.4	2.7						
								100	3630	15965	523515
		20	3857	16162	549666				3460	15725	530734
			3837	16089	558268				3494	15470	528017
			3845	16180	563856	Average			3528	15720	527422
Average			3846	16144	557263	Std. Dev.			90	248	3646
Std. Dev.			10	48	7148	RSD (%)			2.5	1.6	0.7
RSD (%)			0.3	0.3	1.3						
								120	3246	15096	500674
		40	3823	16362	560649				3385	15368	517952
			3796	16074	550497				3403	14994	509272
			3834	16185	550410	Average			3345	15153	509299
Average			3818	16207	553852	Std. Dev.			86	193	8639
Std. Dev.			20	145	5887	RSD (%)			2.6	1.3	1.7
RSD (%)			0.5	0.9	1.1						
		60	3864	16384	545433						
			3722	16052	542918						
			3653	16035	538210						
			3601	15728	526739						
			3538	15754	533874						
			3762	16227	537024						
Average			3690	16030	537366						
Std. Dev.			117	258	6661						

Appendix B: Example of data processing

Table B1: Raw data for June 17th, 2010. $[Hg^0]_0 = 1$ ppm, [1-butene $]_0 = 2$ ppm $[CH_2Br_2]_0 = 100$ ppm, $P_{O_2} = 0.065$ atmosphere

Time (s)	$\sigma_{_{time}}(s)$	Ave. 1-butene	$\sigma_{_{1\text{-butene}}}$	Ave. Hg ^o	$\sigma_{_{Hg^0}}$	Ave. CH_2Br_2	$\sigma_{_{CH2Br2}}$
0	0	4114	138	16561	232	562923	15064
20	0.42	3846	10	16144	48	557263	7148
40	0.59	3818	20	16207	145	553852	5887
60	0.72	3690	117	16030	258	537366	6661
80	0.83	3663	58	16109	199	531365	6301
100	0.93	3528	90	15720	248	527422	3646
120	1.02	3345	86	15153	193	509299	8639

Table B2: Collated data for June 17th, 2010

Table B3: Normalized data for June 17th, 2010

Time (s)	$\sigma_{_{time}}(s)$		1-butene/1-butene ₀	$\sigma_{_{1\text{-butene/1-butene0}}}$	Hgº/Hg° ₀	$\sigma_{_{Hg^{0/}Hg^{0_0}}}$	CH_2Br_2/CH_2Br_{20}	σ _{CH2Br2/CH2Br20}
	0	0	1	0.03	1	0.01	1	0.03
	20	0.42	0.93	0	0.97	0	0.99	0.01
	40	0.59	0.93	0	0.98	0.01	0.98	0.01
	60	0.72	0.9	0.03	0.97	0.02	0.95	0.01
	80	0.83	0.89	0.01	0.97	0.01	0.94	0.01
	100	0.93	0.86	0.02	0.95	0.01	0.94	0.01
	120	1.02	0.81	0.02	0.91	0.01	0.9	0.02

Table B4: Data for determination of $k_{Hg+Br}/k_{1-butene+Br}$

In (1-butene ₀ /1butene)	$\sigma_{_{In(1-butene)}}$	In (Hg ⁰ ₀ /Hg ⁰)	$\sigma_{_{In(Hg)}}$
0	0.03	0	0.01
0.07	0	0.03	0
0.07	0.01	0.02	0.01
0.11	0.03	0.03	0.02
0.12	0.02	0.03	0.01
0.15	0.03	0.05	0.02
0.21	0.03	0.09	0.01







• 1-butene; \circ Hg⁰

Appendix C: Algorithm for linear regression (errors in both x and y)

Variable	Symbol	Equation
Weights	W_i	$1/(\sigma_{y_i}^2 + b_2 \sigma_{x_i}^2)$
Intercept	а	$\sum x_{x_i}^2 W_i * \sum y_i W_i - \sum x_i W_i * \sum x_i y_i W_i$
		$\Sigma W_i * \Sigma x_i^2 W_i - (\Sigma x_i W_i)^2$
Slope	b	$\Sigma W_i * \Sigma x_i y_i W_i - \Sigma x_i W_i * \Sigma y_i W_i$
		$\Sigma W_i * \Sigma x_i^2 W_i - (\Sigma x_i W_i)^2$
Error in intercept	σ_a^2	$\sum x_i^2 W_i * \sum d_i^2 W_i$
		$\overline{(n-2)(\Sigma W_i * \Sigma x_i^2 W_i - (\Sigma x_i W_i)^2)}$
		where $d_i = b * x_i - a$
Error in slope	σ_b^2	$\sum W_i * \sum d_i^2 W_i$
		$(n-2)(\Sigma W_i * \Sigma x_i^2 W_i - (\Sigma x_i W_i)^2)$
Covariance	cov(a,b)	$-\Sigma x_i W_i * \Sigma d_i^2 W_i$
		$\overline{(n-2)(\Sigma W_i * \Sigma x_i^2 W_i - (\Sigma x_i W_i)^2)}$
Correlation coefficient	r	$\Sigma W_i * \Sigma x_i y_i W_i - \Sigma x_i W_i * \Sigma y_i W_i$
		$\overline{(\Sigma W_i * \Sigma x_i^2 W_i - (\Sigma x_i W_i)^2)^{1/2} * (\Sigma W_i * \Sigma y_i^2 W_i - (\Sigma y_i W_i)^2)^{1/2}}$

* $\sum_{i=1}^{n}$ in which *n* is the number of data points, is abbreviated by Σ



Figure C1: Flow chart for the linear least squares programme
The line of best fit is usually found by minimizing the weighted sum of the squares, s, of the deviation of the measured points from the fitted line. The quantity, s, is given by:

$$s = \frac{(y_i - a - b * x_i)^2}{\sigma_{y_i}^2 + b^2 \sigma_{x_i}^2}$$
(C)

and is minimized with respect to the intercept (*a*) and the slope (*b*), of the least squares line. The exact solution to this problem requires a complicated numerical approach when σ_{x_i} is non-zero. In the algorithm presented by [*Irvin and Quickenden*, 1983], *b* is kept constant in the denominator and s is then minimized with respect to *a* and *b* in the numerator. The resulting new estimate of *b* is inserted into the denominator and the process reiterated until convergence is obtained. No more then 2 iterations were needed to obtain convergence in this work.

The approximate solution obtained through this algorithm converges to yeild a slope and an intercept that lie within a few percent of the exact solution. The standard errors in the slope and in the intercept may to too large by up to 40% in certain cases. See [*Irvin and Quickenden*, 1983] and references therein for details.





Figure B1: Quattro LC, stripped from its probe, glass chamber and cover

In a bid to increase sensitivity, the probe, as well as the glass chamber and its cover, were removed from the instrument and replaced by a smaller chamber made of Teflon in which ¹/₄ in. Teflon tubing could be introduced directly. Figure B1 shows the instrument stripped from it probe, glass chamber and cover.

The new inlet was comprised from a small Teflon chamber designed to enclose the space between the corona discharge pin, the sample cone and the sample introduction tube as tightly as possible (Figure B2).

Sample cone



Figure B2: The new chamber should enclose the space between the sample cone, the corona discharge pin and the sample introduction tube as closely as possible.

The resulting chamber had a volume of only 9mL. It was designed so that it would fit smugly around the sample cone and would not need extra support. The tip of the corona discharge pin could be introduced through a hole pierced in one of its sides. The chamber had a cover made of Teflon and another made of silanized glass. Both had a hole ($\frac{1}{4}$ in.) in the centre to allow sample introduction. The Teflon cover was held to the main body of the chamber by screws, however the glass cover, when used, had to be held by tape, as shown in the pictures shown in Figure B3. In between uses, the chamber would be soaked in a solution of 10% HNO₃ in water and then rinsed with Milli-Q water (18.2 Ω). The chamber was then dried gently using non-abrasive paper towels (Kimwipes).

Determination of instrumental detection limit

The ionisation gas was flowed over $HgBr_2$ crystals before being introduced to the 9mL chamber. The flow rate could be varied from 0.5 to 3 L/min. The concentration in the gas stream could be calculated from the flow rate and the rate of volatilisation of $HgBr_2$ from the solid phase:

$$C_{HgBr_2}(g/L) = \frac{Rate of volatilisation_{HgBr_2}(g/min)}{Flow rate (L/min)}$$
(B)

which was measured by periodically weighing a dish containing $HgBr_2$ crystals and opened to the atmosphere.



Figure B3: 9 mL Teflon chamber, shown with silanized glass cover (photographic credit: Dr. Daniel Deeds)

Appendix E: Results from tests using Br₂ as the bromine radical precursor



Figure E: Elemental mercury (Hg⁰) and molecular bromine (Br₂) react in the dark

Figure E shows how elemental mercury (Hg^0) and molecular bromine (Br_2) react in the dark. The point at 0 second corresponds to the initial concentration of elemental mercury (prior to the addition of molecular bromine). The other points correspond to the concentration of elemental mercury after the indicated time has elapsed since the addition of molecular bromine. Initial concentrations were 1 ppm for elemental mercury and 0.1 ppm for molecular bromine.