Gaseous Elemental Mercury in the Ambient Atmosphere: Review of the Application of Theoretical Calculations and Experimental Studies for Determination of Reaction Coefficients and Mechanisms with Halogens and Other Reactants

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Abstract

Understanding the kinetics and mechanisms associated with the atmospheric chemistry of mercury is of great importance to protecting the environment. This review will focus on theoretical calculations to advance understanding of gas phase oxidation of gaseous elemental mercury (GEM) by halogen species. Understanding the gas phase oxidation process between atmospheric mercury and halogen compounds is particularly important as all studies indicate that this interaction is the primary conversion mechanism in the troposphere leading to deposition of mercury. Theoretically predicting the thermochemistry of mercury containing species in the atmosphere is important because of the lack of experimental results. In this article a review of theoretical calculations of rate constants and reaction products is presented. Available laboratory data are listed and discussed as well in order to highlight the subjects where theoretical calculations in particular can be of value in the future.

1. INTRODUCTION

This review will focus on theoretical calculations to advance understanding of gas phase oxidation of gaseous elemental mercury (GEM) by halogen species. Computational and experimental studies to help parameterize models have been performed to make a more reliable description of the dynamics of mercury in the atmosphere so that the consequences of abatement strategies can be assessed. Quantum chemical calculations are the only way to viably investigate the mechanisms and advance what is observed in field and laboratory studies.

As the atmosphere plays a significant role as a medium for chemical and physical transformation, it is imperative to understand the fundamental of the kinetics and thermodynamics of the elementary and complex reactions that remove and generate GEM in the atmosphere. In Arctic and Antarctic regions after polar sunrise, field studies have demonstrated that GEM is rapidly oxidized to Hg(M) compounds, known operationally as reactive gaseous mercury (RGM), which is quickly deposited to the surface, a phenomenon known as Arctic Mercury Depletion Events (AMDEs). After deposition, RGM may be reduced back to GEM and reemitted to the atmosphere. The true constituents of RGM are not known and the composition is estimated based on observed correlation of GEM with a competing depletion of surface ozone concentration, in accordance with what is known about the depletion of ozone in the Arctic atmosphere (ozone depletion events, ODEs). Observations of AMDEs and ODEs in the polar boundary layer have provoked several theories on reactions of elemental mercury with various atmospheric oxidants. Atmospheric mercury has thus been theorized to be oxidized by photochemically initiated catalytic reactions involving halogen species, particularly Br and BrO, though other halogens species such as IO may play a role in the marine boundary layer, and the Antarctic as well. The reaction of GEM and BrO to produce HgO and Br was first thought to be the dominant reaction, but recent theoretical studies have decisively shown that this reaction is highly endothermic. However, this result is in conflict with experimental data on the energetics of the species existing in the vapour over heated HgO(s) [1]. The ox- idized mercury can further deposit on the Earth's surface and may bioaccumulate in the aquatic food chain, through complex, but not well understood mechanisms. A significant part of the deposited mercury is photo-reduced and re-emitted as GEM [2–7]. Recent field studies indicate that despite the efficient photoreduction, a net sea ice/snow interface may constitute a site for Hg accumulation [8]. Hence there is a net deposition of mercury is occurring in the Arctic, particularly in locations where bioaccumulation are expected [8]. Recent regional and global modeling studies have considered the oxidation as well as photoreduction and re-emission, and they report a net deposition of atmospheric mercury overall in the Arctic region [9,10] in accordance with previous field studies (cf. [11]). There have been several excellent review articles on mercury transformation in the atmosphere [12–16], particularly on its properties, sources, sinks, and fluxes. We review the current state of knowledge of the kinetics, product distribution, and thermo-chemical studies of elemental mercury with known atmospheric oxidants, in this case with halogen compounds. We focus on a comprehensive review of the experimental and theoretical kinetic evaluation of gaseous elemental mercury reactions with atmospheric halogen oxidants. We do not consider the body of re- search of mercury halogen interaction at higher than ambient temperatures, such as those found in industrial processes. We will outline major gaps and some future research directions.

Unlike the reactions of GEM in solution, experimental data on the gas-phase reactions of elemental mercury with some atmospheric oxidants are limited due to challenges including complexity of reactions, the low concentrations of species at atmospheric conditions, the low volatility of products, sensitivity to temperature and pressure, and the strong effects of water vapour and surface on kinetics. The possible effects and distribution of mercury isotope fractionation have not been analysed in any of the studies. The isotopes dilute the signal and mean that with current mass spectrometry techniques, ambient RGM compounds can not be identified. The possibility of theoretically predicting the thermochemistry of mercury-containing species of atmospheric interest is important and is complementary to laboratory and field studies.

Observations by Schroeder *et al.* [17] on concomitant rapid depletion of elemental mercury and ozone in the boundary layer indeed provoked several theoretical, laboratory and field studies on reactions of elemental mercury with various atmospheric oxidants see Table 4.1 and references therein.

2. KINETIC AND PRODUCT EXPERIMENTS

The rate of the atmospheric chemical transformation of elemental mercury with a given oxidant is dependent on two factors. The first factor is the reactivity of mercury towards a given oxidant at environmentally relevant conditions, such as temperature, pressure, oxygen concentration, and relative humidity. The second factor is the concentration (or mixing ratio) of the oxidant. The existing laboratory studies of mercury kinetic reactions have been obtained using steady state reaction

TABLE 4.1 Available rate constants for selected atmospheric reactions from the literature at room temperature (296 ± 2 K) or other temperatures (modified after Steffen *et al.* [16])[a]

Reaction 1	Rate constants (molecule $cm^{-3} s^{-1}$)	Reference	Comments
$Hg^0 + O_3$ → products	$(3 \pm 2) \times 10^{-20}$	Hall [18]	
	$(7.5 \pm 0.9) \times 10^{-19}$	Pal and Ariya [19]	Temperature dependence is evaluated
	$(6.4 \pm 2.3) \times 10^{-19}$	Sumner *et al.* [20]	– given reaction rate is extrapolated, – at zero relative humidity.
$Hg^0 + HO$	$(8.7 \pm 2.8) \times 10^{-14}$	Sommar *et al.* [21]	
→ products	$(1.6 \pm 0.2) \times 10^{-12}$	Miller *et al.* [22]	70 °C
	$(9.3 \pm 1.3) \times 10^{-14}$	Pal and Ariya [19]	Temperature dependence evaluated at 100 and 400 Torr He and air
	$<10^{-13}$	Bauer *et al.* [23]	
$Hg^0 + Cl$	$(1.0 \pm 0.2) \times 10^{-11}$	Ariya *et al.* [24]	
→ products	$(1.5) \times 10^{-11}$	Horne *et al.* [25]	383–443 K
	2.8×10^{-11}	Khalizov *et al.* [26]	Theo.—calc. at 298 K, 760 Torr
	7.6×10^{-13}	Goodsite *et al.* [27]	Theo.—calc. at 298 K, 760 Torr
		Donohoue *et al.* [28]	Second-order rate was calculated at 260 K and 760 Torr
$Hg^0 + Cl_2$ → products	$(2.7 \pm 0.2) \times 10^{-18}$	Ariya *et al.* [24]	
	$(2.5 \pm 0.9) \times 10^{-18}$	Sumner *et al.* [20]	
$Hg^0 + Br$ → products See also Holmes *et al.* [30] Table 1 for k_2, k_3 and k_4 constants	$(3.2 \pm 0.3) \times 10^{-12}$	Ariya *et al.* [24]	1 atm, 298 K
	10^{-13}	Grieg *et al.* [29]	383–443 K
	1.0×10^{-12}	Khalizov *et al.* [26]	Theo.—calc. at 298 K, 760 Torr
	1.1×10^{-12}	Goodsite *et al.* [27]	Theo.—calc. at 298 K, 760 Torr
	3.6×10^{-13}	Donohoue *et al.* [31]	243–298 K, 200–600 Torr
	0.8	Skov *et al.* [32]	Interpretation of field study assuming[a]
	1.2	Skov *et al.* [32]	−40 °C Interpretation of field study assuming [a] −10 °C
$Hg^0 + BrO$ →products	$1 \times 10^{-15} < k < 1 \times 10^{-13}$	Raofie and Ariya [33]	
	1×10^{-14}	Sumner *et al.* [20]	
$Hg^0 + Br_2$ → products	™$(9 \pm 2) \times 10^{-17}$	Ariya *et al.* [24]	No reaction was observed under experimental conditions employed.
	No reaction	Sumner *et al.* [20]	
	2.7×10^{-31} and 3.4×10^{-31}	Balabanov *et al.* [34]	Theo.—calc.
$Hg^0Br + Br$ →products	2.5×10^{-10}	Goodsite *et al.* [27]	Theo.—calc. at 298 K, 760 Torr
	$1.05 \pm 0.14 \times 10^{-10}$	Balabanov *et al.* [34]	Theo.—calc.
$Hg^0 + F_2$ →products	$(1.8 \pm 0.4) \times 10^{-15}$	Sumner *et al.* [20]	
$Hg^0 + NO_3$ →products	™4×10^{-15}	Sommar *et al.* [35]	
	™ 7×10^{-15}	Sumner *et al.* [20]	
$Hg^0 + H_2O_2$ →products	™8×10^{-19}	Tokos *et al.* [36]	
$Hg(CH_3)_2 + HO$ → products	$(1.97 \pm 0.23) \times 10^{-11}$	Niki *et al.* [37]	
$Hg(CH_3)_2 + Cl$ → products	$(2.75 \pm 0.3) \times 10^{-10}$	Niki *et al.* [38]	
$Hg(CH_3)_2 +$ NO_3→products	$(7.4 \pm 2.6) \times 10^{-14}$	Sommar *et al.* [39]	

[a] The difference in results at 10 and 40 °C is due to the temperature dependence of the competing reaction between ozone and Br.

chamber or fast flow tubes. A single study has been carried out on the analysis on field data. Both relative and absolute techniques were used in these studies (cf. [40]).

Both absolute and relative techniques have advantages as well as disadvantages. The disadvantage of the relative rate is that the calculated reaction rate constant is only as good as the original value of the reaction rate constant for the reference molecule used, and this is why most detailed relative rate studies include several reference molecules to overcome this challenge. Another disadvantage is the complexity of the reactants and enhanced potential for side reactions. This challenge can be overcome with careful experimental setup and additional targeted experiments to minimize and characterize the extent of undesired reactions. An advantage of a detailed relative study is that one can readily perform the experiments under simulated tropospheric conditions, and also that the reaction chambers can be coupled with several state-of-the-art instruments for simultaneous analysis, which allows detailed product analysis as well as kinetic determinations.

The advantage of the absolute method is clearly that there is no need for incorporation of errors due to the reference molecules. However, in many ab- solute studies, one can follow merely one or two reactants, and considering the complexity of mercury reactions, and the extent of secondary reactions, the calculated values may be affected. Another challenge is that absolute rate studies often are performed at lower pressure than tropospheric boundary layer pressure (740 Torr) and at concentrations orders of magnitude higher than tropospheric levels. Hence the data obtained under such conditions must be properly corrected for the ambient tropospheric situation, particularly in the case of complex mercury adduct reactions, and given the lack of detailed product analysis, and different carrier gases, this is not trivial. However, as shown in Pal and Ariya [19], both relative and absolute studies of the same reaction can yield the same values of rate constants within the experimental uncertainties, and thus increase the confidence in the overall result.

There are limited temperature dependence studies of reactions of elemental mercury with atmospheric oxidants (e.g., with O_3, HO, Br and Cl). Some reactions are expected to have slight temperature dependence and hence the data can be directly used for wide range of atmospheric temperature. However, some others can exhibit stronger temperature dependence. We hence require temperature dependence kinetic data that can reflect the general conditions in the troposphere. We thus recommend strongly to have the available data over a wide range of temperatures.

Mercury and halogen interaction has been experimentally studied under the conditions as summarized below.

Methyl iodide was shown to be non-reactive toward GEM under atmospheric conditions ($k < 1X10^{-21}$ cm^3 molecule^{-1} s^{-1}) [36].

Ultraviolet bands of the HgCl, HgBr and HgI molecules have been investigated [41–43]. The authors coupled their measurements with computer analysis to determine precise vibrational constants for the molecules. For HgI a vibrational analysis was proposed for the E–X system. Approximate rotational constants were also determined for the C state.

The first study of Hg^0 and chlorine atoms was published in 1968 [25] HgCl was measured by time resolved absorption spectroscopy in the temperature range 383–443 K significantly higher than ambient temperatures:

$$\mathrm{Hg} + \mathrm{Cl} \longrightarrow \mathrm{HgCl}. \tag{1}$$

The rate constant, k_1 for the reaction of mercury with chlorine atoms was then derived to be 5.0×10^{-11} cm^3 $molecule^{-1}$ s^{-1} in 720 Torr CF_3Cl and 1.5×10^{-11} cm^3 $molecule^{-1}$ s^{-1} in 10 Torr CF_3Cl+710 Torr Ar. The authors [25] mentioned that k_1 has an uncertainty of a factor of three because of the accumulation of experimental errors in evaluating the separate terms, and the rate constant can be considered to be more accurate than the order of magnitude when the results are transferred to atmospheric conditions.

Molecular chlorine was suggested to have a relatively modest reaction rate, 4×10^{-16} cm^3 $molecule^{-1}$ s^{-1} [13,44–47] though the reaction was found to be strongly surface catalysed [45,46], and the experimental value should be considered as an upper limit.

In 2002 extensive kinetic and product studies on the reactions of gaseous Hg^0 with molecular and atomic halogens (X/X_2 where X Cl, Br) were performed at atmospheric pressure (750 ±1 Torr) and room temperature (298 ±1 K) in air and N_2 [24]. Kinetics of the reactions with X/X_2 were studied using both relative and absolute techniques. Cold vapour atomic absorption spectroscopy (CVAAS) and gas chromatography with mass spectroscopic detection (GC-MS) were the analytical methods applied. The measured rate constants for the reactions of Hg^0 with Cl_2, Cl, Br_2, and Br were $(2.6\pm 0.2) \times 10^{-18}$, $(1.0\pm0.2) \times 10^{-11}$, $< (0.9 \pm0.2) \times10^{-16}$, and (3.2 ± 0.3) 10^{-12} cm^3 $molecule^{-1}$ s^{-1}, respectively. Thus Cl_2 and Br_2 are not important reactants in the troposphere for the Cl_2 and Br_2 concentrations reported in literature [24].

Chlorine and bromine atoms were generated using UV and visible photolysis of molecular chlorine and bromine, respectively, in addition to UV ($300 \leq \lambda \leq 400$ nm) photolysis of chloroacetyl chloride and dibromomethane. The reaction products were analyzed in the gas-phase, in suspended aerosols and on the wall of the reactor using MS, GC-MS and inductively coupled plasma massspectrometry (ICP-MS). The major products identified were $HgCl_2$ and $HgBr_2$ adsorbed on the wall. Suspended aerosols, collected on the micron filters, contributed to less than 0.5% of the reaction products under the experimental conditions.

Donohoue *et al.* [31] has reported two other kinetic data sets for Cl and Br reactions using a pulsed laser photolysis-pulsed laser induced fluorescence spectroscopy. These data sets are obtained using pseudo-first order conditions with respect to halogens or mercury and experiments were performed at a broad range of temperatures. The authors of these studies indicate an uncertainty estimation of ±50% in the rate coefficientsdue to the determination of absolute concentrations of chlorine and bromine atoms [31]. Sumner *et al.* [20] reinvestigated both reactions using a 17.3 m^3 environmental chambers equipped with fluorescent lamps and sun lamps to mimic environmental reactions, and evaluated the rate constants to be in the order of 10^{-12} cm^3 molecule^{-1} s^{-1} and 10^{-11} cm^3 molecule^{-1} s^{-1} for reactions of Br and Cl, respectively.

Reactions of mercury with Br-containing radicals, either Br or BrO were necessary to investigate once satellite 'BrO' total surface column measurements showed correlation with the geographical and temporal extension, where models predict AMDEs [32,48–51]. Experimental studies of XO reactions are very scarce. To our knowledge there is only one published laboratory kinetic study on the reaction of BrO with elemental mercury [33] during which, using the relative rate methods, the room temperature bimolecular rate constant for BrO + Hg^0 was estimated to lie within the range $10^{-15} < k < 10^{-13}$ cm^3 molecule^{-1} s^{-1}, and in the later product study this reaction was estimated to be $<5\times10^{-14}$ cm^3 molecule^{-1} s^{-1} (Raofie and Ariya, personal communication). The faster end of this range makes BrO a significant potential contributor to mercury depletion events in the Arctic, however the lower range renders this radical less effective than Br radicals using both lower and upper limit of existing experimental literature data. This is some- how in contradiction with theoretical calculations, see next section. A report was published on the first experimental product study of BrO-initiated oxidation of elemental mercury at atmospheric pressure of 740 Torr and T 296 2 K [52]. The authors used chemical ionization and electron impact mass spectrometry, gas chromatography coupled to a mass spectrometer, a MALDI-TOF mass spectrometer, a cold vapour atomic fluorescence spectrometer, and high-resolution transmission electron microscopy coupled to energy dispersive spectrometry. BrO radicals were formed using visible and UV photolysis of Br_2 and CH_2Br_2 in the presence of ozone. They analyzed the products in the gas phase, on suspended aerosols and on wall deposits, and identified HgBr, HgOBr or HgBrO, and HgO as reaction products. Experimentally, they were unable to distinguish between HgBrO and HgOBr. The existence of stable Hg$^+$ in form of HgBr, along with Hg^{2+} upon BrO-initiated oxidation of Hg^0, suggests that in field studies, it is fundamental to selectively quantify various mercury species in mercury aerosols and deposits both in oxidation state I and II. The majority of mercury containing products were identified as deposits, however, aerosols accounted for a substantial portion of products. Noticeably the authors pointed out that although the extent of heterogeneous reactions in their experiments were reduced significantly, the existence of these reactions should have not been totally neglected under their experimental conditions.

No definite conclusions on the potential primary or secondary reactions of BrO, can be made at this stage. Even considering one order of magnitude uncertainties in the existing kinetic data, Br reactions make it the likely radical to explain elemental mercury depletion in the Arctic. Two independent studies [10,32] support this conclusion. The existing kinetic results indicate that the direct BrO impact is less important than Br, but further studies are required to examine this conclusion. For example, A. Saiz-Lopez *et al.* [53] have unexpectedly, recently discovered via long path DOAS measurements, significant amounts of iodine oxide (IO) above the Antarctic ice, and that bromine persists there for several months, throughout the summer, thus giving rise to a greater oxidizing effect than formerly thought possible, given observations in the Arctic.

Interesting models have been developed on the importance of iodine chemistry and its potential impact on mercury depletion events [54,55]. Since there is no existing laboratory study on kinetics and products of I_2, I and IO with elemental mercury, we encourage additional studies in this domain to evaluate further the implication of iodine chemistry in the troposphere.

Significant concentrations of halogens are observed predominantly over the polar regions and over the marine boundary layer and not generally over the continents, with the exception of coastal regions, high halide source regions such as salt lakes, and some industrial regions where halogens are widely used [56].

3. THEORETICAL EVALUATION OF KINETIC DATA

The possibility of theoretically predicting the thermochemistry of mercury- containing species of atmospheric interest is of strong importance due to the relative lack of accurate experimental information at all temperatures relevant to ambient air, especially to temperatures different than room temperature. They also serve fundamentally to further comprehend the complex reaction mechanisms. Accurate *ab initio* studies for measurements such as heats of formation, reaction enthalpies, and activation energies are particularly challenging, particularly in light of the large nuclear charge (80) and large number of electrons intrinsic to mercury. There is a detailed review on *ab initio* thermochemical and kinetic studies on mercury reactions [15] and hence we discuss previous studies mainly in relation to experimental results. The existing theoretical kinetic data are also shown in Table 4.1. *Ab initio* calculations rely on careful choice of electron correlation method, treatment of relativistic effects, basis set truncation errors, etc., in order to obtain accurate kinetic data. The latter depends intimately on the under- lying potential energy surface. A rigorous calculation of the rate coefficient for a given reaction generally involves either quantum scattering or classical trajectory calculations, which in turn require a global or semi-global potential energy surface (PES). While these treatments are feasible for relatively small systems depending on the required accuracy of the underlying PES, most studies employ more ap- proximate treatments of the reaction dynamics, e.g., transition state theory (TST) or RRKM theory (Rice–Ramsberger–Kassel–Marcus theory).

For bimolecular reactions involving a barrier, transition state theory is often used. The basic tenet is that there exists a critical configuration lying between re- actants and products where all trajectories arising from reactants are assumed to irreversibly lead to products [57,58]. For reactions that proceed without a barrier, e.g., unimolecular dissociation or recombination reactions, RRKM theory is often employed. The use of RRKM involves two central approximations (cf. Steinfeld *et al.* and Gilbert and Smith [57,59] and references therein): (i) as with transition state theory, RRKM assumes the existence of a critical configuration between re- actants and products which is not recrossed and (ii) the energy of the excited reactant is distributed randomly throughout all the available molecular states. To satisfy the first approximation, it is generally very important to employ the variational version, which is equivalent to a microcanonical VTST calculation. So as above, one needs to calculate structures and vibrational frequencies along the re- action path. In order to satisfy the second criterion, the reactant must be a molecule large enough to provide efficient intramolecular vibrational energy redistribution. Hence, the use of RRKM for atom-atom recombination reactions should probably not be used as the main approach for theoretical kinetic evaluation. In these cases, quasiclassical trajectory calculations would seem to be the most reliable method. For reaction rate constant calculations for barrierless reactions using RRKM and VTST-like methods, the Variflex program [60] is a convenient choice for poly- atomic systems, since it also allows several options for the calculation of pressure effects on the rate constant (standard VTST yields only a high pressure limit rate constant).

Since 2003 several studies have contributed to the understanding of the reaction system of reactions (2a), (2b), (3a), (3b) and (4) [26,27,34,61,62,65]

$$\mathrm{Hg} + \mathrm{X} \longrightarrow \mathrm{HgX}, \tag{2a}$$

$$\mathrm{HgX} \longrightarrow \mathrm{Hg} + \mathrm{X}, \tag{2b}$$

$$\mathrm{HgX} + \mathrm{X} \longrightarrow \mathrm{HgX_2}, \tag{3a}$$

$$\mathrm{XHg} + \mathrm{X} \longrightarrow \mathrm{X} + \mathrm{HgX}, \tag{3b}$$

$$\mathrm{Hg} + \mathrm{XO} \longrightarrow \mathrm{HgO} + \mathrm{X}, \tag{4}$$

where X is either Cl, Br or I.

The contributions will be briefly sketched here following the chronological order of appearance in the literature. Shepler and Peterson [61] calculated the potential energy curves of HgO using multi reference configuration interaction (MRCI) as well as coupled cluster theory (CCSD(T)). Their result showed that the reaction Hg+BrO $\longrightarrow$HgO + Br is strongly endothermic. Notably they also found that HgO was stable with respect to Hg^0 by just 4 kcal mol^{-1}, suggesting that the previous experimental results from the nineteeneighties were erroneous [63,64].

Khalizov *et al.* [26] used DFT and *ab intio* calculations at B3LYP and QCISD level of theory to determine geometry optimisations and frequencies for various molecules, HgX and $\mathrm{HgX_2}$, where X = F, Cl or Br. Furthermore reaction enthalpies were calculated for the nine possible reactions (2a), (3a) and $\mathrm{Hg} + \mathrm{X_2} \longrightarrow \mathrm{HgX_2}$. The back reaction rate constants for the reactions (2b) were calculated in the high pressure limit using collision theory comparing to calculations using canonical VTST. These rate constants are tabulated in Table 4.1.

Tossell [62] calculated energetics for oxidation of GEM for various reactions in- cluding (2a), (3a) and (4), with X= Br and Cl. The methods and levels of theory included Hartree–Fock (HF), Moller–Plesset to the second order (MP2), quadratic CI (QCISD) and CCSD(T). Novel results included findings of the optical transitions of HgO, HgX and $\mathrm{HgX_2}$. These indicated that HgO as well as HgX would be unstable towards sunlight in the troposphere, whereas $\mathrm{HgX_2}$, would be quite stable for energies in the visible region.

Goodsite *et al.* [27] calculated optimised geometries and molecular parameters at B3LYP level of theory for HgX and HgXY where X = Br (and I and OH) and Y = Br, I, OH and $\mathrm{O_2}$. This was followed by RRKM theory to yield the reaction rate constants for reactions (2a) and (2b) for X= Br and I, and (3a) for X=Br. The reaction rates for X=Br are tabulated in Table 4.1.

Balabanov *et al.* [34] computed the potential energy surfaces for $HgBr_2$ using internally contracted MRCI. The potential surfaces were then used for quasi classical trajectory (QST) and VTST calculations to evaluate the rate constants for the seven reactions including (3a) and (3b), $Hg+Br_2 \longrightarrow HgBr_2$ and $HgBr_2 \longrightarrow$ products. The calculations yielded some very interesting results, i.e. they found the rates for the reactions $Hg + Br_2 \longrightarrow HgBr_2$ and $Hg + Br_2 \longrightarrow HgBr + Br$ to be as small as of $k = 2.7\times 10^{-31}\ cm^3\ mol^{-1}\ s^{-1}$ and k 3.4 $10^{-31}\ cm^3\ mol^{-1}\ s^{-1}$, respectively. They discuss the likeness of these reaction paths to the ones of the re- actions of Hg with BrO, and suggest that a more complex mechanism like the one introduced in the modeling work of Calvert and Lindberg [54,55] is considered for explaining the larger reaction rates found in experiments [24,33]:

$$HgBr + Br_2 \longrightarrow HgBr_2 + Br. \tag{5}$$

As can be seen in Table 4.1 they also found the reaction rate for reaction (3a) to be lower than Goodsite *et al.* [27], and explained this by the higher level of theory used in the Balabanov *et al.* [34] calculations.

Additionally we want to mention two investigations by Shepler *et al.* [65,66]. The first [65] is of the reactions Hg+IX for X =I, Br, Cl and O with respect to enthalpies; for the stable triatomics also heats of formation, bond lengths and harmonic vibrational frequencies, together with dissociation energies, equilibrium bond lengths, and harmonic vibrational frequencies for the diatomics involved. The calculations were carried out employing the CCSD(T) method. There are a wealth of results that are compared to experimental outcomes and that can be used in atmospheric modeling. We repeat here our call for laboratory studies on the reaction chemistry of mercury and the iodine compounds I_2, I and IO, as these are missing in this context.

The other study [66] is a very recent one on aqueous micro solvation of mercury halide species. The methods and level of theory employed were MP2 and DFT/B3LYP. The general trend was that oxidation of mercury halide species was seen to be favoured by the presence of water molecules. Notably the reactions (2a) and (3a)-like channel $HgX+Y \longrightarrow HgXY$ together with the reaction $Hg+XY \longrightarrow HgXY$ became more exothermic in the presence of water, whereas the abstraction channel HgX Y Hg XY became less exothermic.

To summarise the outcome of these papers with respect to the reaction sys- tem (2)–(4) Reaction (4) was investigated for X = Br [61,62,67] and X= I [65] to be endothermic and most probably without any importance in the atmosphere, in the absence of water, whereas reaction (2) is exothermic [26,27,34,62]. Khalizov concluded that Hg Br might be the dominant process for atmospheric mercury depletion episodes (AMDE) occurring during Arctic Spring. This conclusion is in line with previous laboratory kinetic studies of the same reaction system [24]. This conclusion is further supported by Goodsite *et al.* [27] that studied the temperature dependence of the reaction and showed that the HgBr intermediate is stabilised towards uni-molecular degradation at low temperatures which permits the addition of the Br reaction (3) and thus $HgBr_2$ is a possible candidate for the formation of the otherwise unknown RGM. Balabanov *et al.* [34] suggest a more complex reac- tion path (5), also including HgBr.

4. PERSPECTIVES

Despite the novel positive acquisitions of knowledge from experimental and theoretical studies of gas-phase elemental mercury chemistry there are still large gaps before a complete understanding of the fate of mercury in the atmosphere is obtained. It is essential to provide kinetic data and information about formed products. There are some limited studies on the kinetics of gas-phase elemental mercury oxidation on surfaces [68–70]. However, experimental studies on uptake or kinetics of heterogeneous reactions of mercury on various environmentally relevant surfaces such as ice, snow, and aerosols and biomaterials, are needed.

The present paper describes the most important progress that has been made within the understanding of the atmospheric chemistry of mercury within the ap- plication of theoretical calculations and experimental studies for determination of reaction coefficients and mechanisms with halogens and other reactants. There are still large uncertainties to cope with before a reliable description of dynamics and fate of mercury can be established. Theoretical calculations represent a very cost effective method to get the first information about rate constants, reaction products and as to what experimentalists should examine. Finally, theoretical calculations can document that we actually have a full understanding of the fundamental processes of atmospheric mercury. The study of IO [53] in the Antarctic opens the possibility that I and IO plays an important role in the oxidation of Hg^0. These reaction mechanisms should continue to be studied in the field and with theoretical methods. As most laboratory studies of the oxidation mercury in the atmosphere are carried out at room temperature it is very important that theoretical calculations state the temperature dependence of the various reaction steps and the thermally stability of the reaction intermediates and end products.

A particular challenge is the reaction between Hg^0 and ozone to form HgO and O_2. There are large discrepancies in the existing laboratory study and theoretical studies are difficult because the spin of reactants are different from those of the reaction intermediates, such as HgO_3, and the end product.

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