A kinetic study of the gas-phase reaction between the hydroxyl radical and atomic mercury

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Abstract

The atom is the dominating species of mercury in the atmosphere. Its oxidation processes are of great interest since it is mainly oxidised mercury that undergoes deposition and thereby spreads into the ecosystems and becomes bioaccumulated. The kinetics of the gas-phase reaction between atomic mercury and hydroxyl radical has been determined at room temperature and atmospheric pressure of air by relative rate technique. OH radicals were produced by photolysis employing methyl nitrite. By using cyclohexane as the reference compound, the rate coefficient obtained was $k(\mathrm{Hg}^0 + {}^{\cdot}\mathrm{OH}) = (8.7 \pm 2.8) \times 10^{-14}$ cm^3 s^{-1} leading to natural lifetimes of mercury at global mean conditions of 4–7 month due to this reaction. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Unlike most metals, whose transport is restricted to erosion and leaching processes, the semi-volatility of many mercury species adds to the complexity of its biogeochemical cycle. In this aspect, mercury has more in common with certain persistent organic pollutants than with other metals. The atmosphere is an important media not only for transport but also for chemical transformation of mercury (Schroeder and Munthe, 1998). Only the volatile mercury species Hg^0 and $(\mathrm{CH}_3)_2\mathrm{Hg}$ have little tendency to be scavenged by physical removal processes and are therefore candidates for a long tropospheric lifetime.

Recently, we have shown that night-time chemical gas phase degradation of dimethyl mercury by NO$_3$ radicals is quite efficient besides day-time processes and the corresponding turn-over time is short (Sommar et al., 1997). The ultimate fate of atmospheric mercury represented by its major constituent elemental gaseous mercury is physical removal usually preceded by oxidation. The presence of gas-to-particle phase conversion in ambient air preceded by gas-phase oxidation of Hg^0 has been inferred using correlations between mercury fractions in air and precipitation with co-sampled lead isotopes (^{210}Pb for Lamborg et al., 2000; ^{206}Pb/^{204}Pb for Chiaradia and Cupelin, 2000). Shia et al. (1999) suggest that the oxidation of Hg^0 occurs largely in the gas-phase, since the aqueous phase reactions are slower on a unit-volume-of-air basis because of the low solubility of Hg^0. To date, most studies of gaseous oxidation of Hg^0 have involved closed-shell molecules, which act as slow oxidants, such as O$_3$ (P'yankov, 1949; Hall, 1995), H$_2$O$_2$ (Tokos et al., 1998), Cl$_2$ (Shia et al., 1999) and HCl (Seigneur et al., 1994) or upper-limit estimates of faster radical-mercury reactions (Sommar et al., 1997). Explicit kinetic data on gaseous radical-mercury reactions as we are aware of is limited to that involving chlorine atoms (Horne et al., 1968). The only important gaseous reaction globally identified so far is that between Hg^0 and O$_3$ with an expected lifetime of $\mathrm{Hg}^0 (\tau = k_1^{-1}[\mathrm{O}_3]^{-1})$ of 1.4 yr at an ozone concentration of 30 ppb. This is in the range of current estimates of the

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residence time of Hg^0 in the atmosphere, classifying mercury as a global pollutant (Lindqvist and Rodhe, 1985; Mason et al., 1994; Slemr, 1996; Bergan et al., 1999; Shia et al., 1999).

Some atmospheric phenomena related to mercury have been attributed to its gas-phase oxidation. For example, the enrichment of mercury in stratospheric aerosols (Murphy et al., 1998), depletion events of gaseous mercury in arctic boundary layer during the polar spring sunrise and subsequent enhanced concentration in the particulate phase (Lu et al., 1997; Schroeder et al., 1998; Boudries and Bottenheim, 2000) with O_3 and BrO molecules acting as oxidants, respectively. Moreover, it is not until recently that time resolved data on the diurnal and seasonal behaviour of gaseous oxidised mercury in ambient air has become available (Lindberg and Stratton, 1998; Sommar et al., 1999). This fraction has been found to be higher at early afternoon and during summer and typically anti-correlates with relative humidity. Photochemical activity may thus be predicted with some certainty as a source. In a companion paper (Gårdfeldt et al., 2001), the reaction of OH radicals with atomic mercury in the aqueous phase was described and found to be important under atmospheric conditions. The OH radical is the most important reactive species in the troposphere and a key player for initiating oxidation of trace compounds in the atmosphere, such as dimethyl mercury (Niki et al., 1983). The aim of this study was to investigate the reactivity of $\cdot$OH towards Hg^0 in the gas phase.

2. Experimental

The room temperature (295 ± 2 K) rate coefficient for the reaction between mercury and hydroxyl radicals was determined by relative rate experiments. The kinetic investigations were performed in 100 l Tedlar-film bags equipped with valve for filling and removing samples for analysis (SKC Inc.). The fitting is a combined shut-off valve with hose and injection port with Teflon-lined septum. The bags were modified with two opposing quartz windows inserted in the Teflon material to allow direct in situ determination of mercury atom concentration. The Hg^0 was monitored by exciting the $6(^3P_1) - 6(^1S_0)$ transition at 253.7 nm with radiation from a Hg-lamp. Excited state mercury, $Hg(^3P_1)$ and $Hg(^3P_0)$ obtained were effectively relaxed by the presence of the bulk gas molecules (Zhang et al., 1987). The probe beam had an analytical pathlength of approximately 11 cm. Zeeman modulation was used in order to discriminate influences from other absorbing species. An example of an otherwise interfering species is methyl nitrite, which was introduced in large excess to mercury and consumed simultaneously. The detector situated at the opposite side of the bag from the lamp and the windows were

conveniently mounted in an optical bench to achieve an optimised and stable signal. A few litres of nitrogen nearly saturated with mercury vapour were mixed into the bag by passing a stream through a flask containing mercury. Final dilution was made in order to obtain concentrations within the instrument's working range 2.4×10^{12} atoms cm^{-3} (Semtech AB, Semtech 2000 Hg analyser). The organic reference compound cyclohexane was brought into the reactor by injecting pure liquid into a steam of nitrogen with microliter syringes. Gases other than mercury were introduced after being measured in a gas handling system. The system made of glass included two bulbs of well-known volume connected by valves to a gas supply and the reaction chamber as well as to a pressure head and a rotary vane vacuum pump (Edwards RV3). Pressure was monitored using a capacitance barometer (Edwards Model 600 Barocel). The bulbs were wrapped in aluminium foil to prevent photodecomposition of the stored compound. Dry compressed synthetic air was used as diluting gas and measured with a mass-flow meter. Once the gas mixture was prepared the bag was thoroughly shaken and left to stand in the dark with the mercury analytical system blocked until reproducible reactant concentrations were obtained.

Adjacent to the bag, directed perpendicular to the Hg-lamp beam was a collimated 450 W Xenon arc light source (Oriel Inc. Model 66066). The radiation obtained was filtered (Oriel Inc. Filter 59458) from $\lambda < 320$ nm. The photolysis of methyl nitrite was used as the OH radical source:

$$CH_3ONO + h\nu \rightarrow CH_3O + NO, \qquad (1)$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2, \qquad (2)$$

$$HO_2 + NO \rightarrow OH + NO_2. \qquad (3)$$

Starting concentrations of the reactants were as follows: Hg^0, $(0.5-2.2) \times 10^{12}$ atoms cm^{-3}; C_6H_{12}, $(4.0-5.2) \times 10^{14}$ molecules cm^{-3}; CH_3ONO, $(0.9-3.0) \times 10^{15}$ molecules cm^{-3}; NO, $(2.6-8.2) \times 10^{14}$ molecules cm^{-3}. Synthetic air was used as batch gas. The reason for the addition of nitric oxide other than that chemically produced in the reactor was to promote formation of OH radicals and to reduce ozone concentrations via the reaction $O_3 + NO \rightarrow O_2 + NO_2$.

The relative consumption of the organic reference compound was followed by GC-FID (Finnigan 9001). Samples were taken by a gas-tight syringe equipped with an appropriate needle from the centre of the reactor close to where the mercury concentration was monitored. The GC column was a 0.25 mm ID $\times$ 60 m DB-5 capillary column (J & W Scientific) kept at 420 K. The gas mixtures described above were photolysed for periods of one half to three-quarters of an hour. Samples were taken from the bag every fifth minute

and injected into the GC-FID. After completion of each experiment, the reaction chamber was evacuated and filled with purified nitrogen gas several times. Measurements of a nitrogen-filled bag revealed no cross contamination between runs. Chemicals used in the bag were elemental mercury (> 99%), cyclohexane (> 99.5%), nitrogen (> 99.9%), nitric oxide (5000 ppm in Ar) and oxygen (> 99.9%) as stated from commercial sources and were not further purified before use. Methyl nitrite synthesised at our lab according to Hartung and Crossley (1939) was freshly distilled ahead of admission to the reactor. The quality was confirmed by long-path FT-IR measurements.

3. Results and discussion

Provided that both mercury and the reference compound are lost solely by reactions with ˙OH and not consumed or replenished from the products, the following rate laws apply to the decay of mercury and the reference:

$$-\mathrm{d}[\mathrm{Hg}^0]/\mathrm{d}t = k_4[\mathrm{Hg}][\mathrm{˙OH}] \tag{4}$$

$$-\mathrm{d}[\mathrm{cyclohexane}]/\mathrm{d}t = k_5[\mathrm{cyclohexane}][\mathrm{˙OH}] \tag{5}$$

Integration of Eqs. (4) and (5) followed by elimination of $\int_0^t [\mathrm{˙OH}]\,\mathrm{d}t$ and their division yields:

$$\ln\left(\frac{[\mathrm{Hg}^0]_0}{[\mathrm{Hg}^0]_t}\right) = \frac{k_4}{k_5} \times \ln\left(\frac{[\mathrm{cyclohexane}]_0}{[\mathrm{cyclohexane}]_t}\right) \tag{6}$$

Preliminary experiments were performed in order to determine if wall losses or dark reactions of the reactants occurred. Neither mercury nor the organic compound showed any critical wall losses. Based on the precision of cyclohexane measurements (RSD 4%), they were not significant for cyclohexane. The bag used in the experiments gave losses of mercury with a frequency, k_w estimated to $1.3 \pm 0.3\%$ h^{-1}. A slow, but not negligible decrease in mercury concentration was recorded when a $\mathrm{Hg}^0/\mathrm{CH_3ONO}/\mathrm{NO}/\mathrm{air}$ mixture was kept dark with the mercury analysing system on. This was attributed to photolysis caused by the Hg-lamp. During similar experiments with the lamp switched off, where mercury concentration was determined externally after preconcentration by double amalgamation on gold followed by thermal desorption and cold vapour atomic fluorescence detection (Brooks Rand Inc, CVAFS-2 Mercury Analyser), the loss of mercury was below the experimental error (RSD 3%). Dark reaction with cyclohexane was too slow to interfere on the time-scale of an experiment. Since $\mathrm{NO_2}$ is known to react slowly with mercury (Hall et al., 1995), the maximum $\mathrm{NO_2}$ concentration during an experiment was estimated. The rate of the $\mathrm{Hg} + \mathrm{NO_2}$ reaction calculated accordingly was suggested not to influence the result.
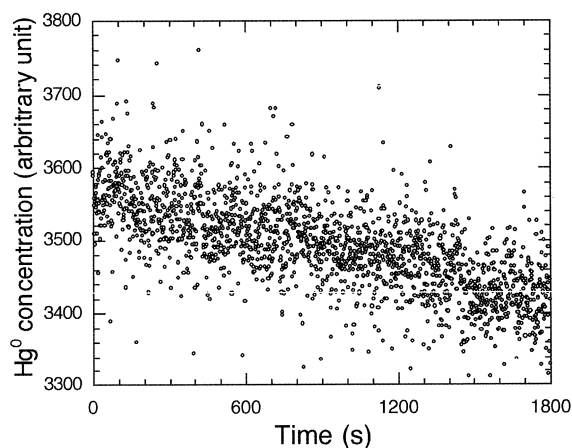

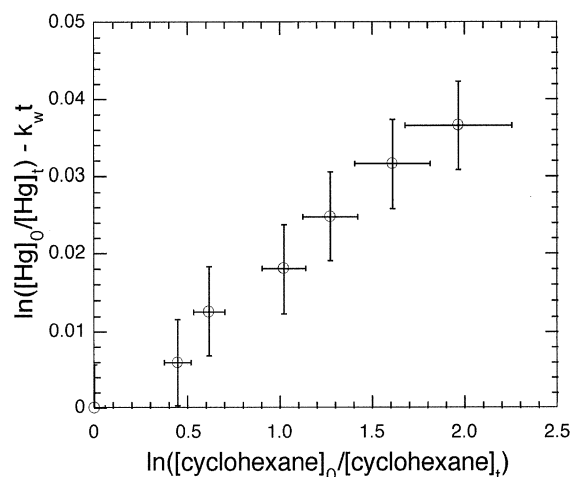Fig. 1. Typical decay of Hg^0 during a relative rate experiment.

Fig. 2. Plot of $\ln([\mathrm{Hg}^0]_0/[\mathrm{Hg}^0]_t) - k_w t$ vs. $\ln([\mathrm{cyclohexane}]_0/[\mathrm{cyclohexane}]_t)$ obtained from a relative rate experiment.

In Fig. 1, the decay in gas phase mercury concentration during a relative rate experiment is shown. The integration time was 1 s. The consumption of mercury during the experiments was in the range 3–5% and showed reasonable linearity with time. By using linear regression, predicted mercury concentrations were calculated to match the intervals where a cyclohexane sample was taken. These interpolated values, corrected for losses to walls during the reaction were plotted versus the corresponding values of the reference compound in the form of Eq. (6). A typical example with representative errors is given in Fig. 2. Table 1 shows a summary of the relative rate experiments performed in this study. Regression analysis was performed by ranking $\ln([\mathrm{cyclohexane}]_0/[\mathrm{cyclohexane}])$ as the dependent variable and weighting by $1/\sigma^2$ of the

Table 1
Summary of relative rates observed in this study when plotting
$\ln([Hg^0]_0/[Hg^0]_t) - k_w t$ vs. $\ln([cyclohexane]_0/[cyclohexane]_t)$

Experiment #	Intercept	Slope
1	-0.001 ± 0.003	0.012 ± 0.002
2	-0.001 ± 0.004	0.014 ± 0.004
3	0.001 ± 0.005	0.011 ± 0.002
4	-0.001 ± 0.002	0.009 ± 0.002

errors obtained from injecting start concentrations from the reaction chamber. The straight lines and intercepts passing through the origin within the uncertainties indicate that the relative rate assumption is valid. The given error limits include the 95% confidence interval obtained from the weighted least squares fitting. The average and standard deviation for all runs were 0.012 ± 0.003 relative to $k \, (\cdot OH + cyclohexane) = (7.21 \pm 1.44) \times 10^{-12} \, cm^3 \, molecule^{-1} \, s^{-1}$ recommended by Atkinson (1997) from absolute and relative determinations (Sommerlade et al., 1993; Saunders et al., 1994; Donahue et al., 1996). The absolute value k_1 obtained is $(8.7 \pm 2.8) \times 10^{-14} \, cm^3 \, molecule^{-1} \, s^{-1}$. No investigations have been made concerning the possible influence from heterogeneous reactions of adsorbed reactants that may occur on the walls of the reaction chamber. Indeed, several studies of gas-phase mercury reactions report the encounter of gas to solid processes (i.e. Hall, 1992; Skare and Johansson, 1992; Hall, 1995; Sommar et al., 1997; Zhao and Rochelle, 1999). However, according to what Hall (1995) reported for the $Hg^0 + O_3$ reaction our relatively low surface-to-volume ratio ($\sim 0.1 \, cm^{-1}$) and use of perfluorinated material might make heterogeneous processes to be of minor importance. The literature material does not provide any contrasting data, since as far as we are aware of, this is the first determination of the gas-phase reaction of OH radicals with mercury.

From a thermodynamic point of view, the reaction between mercury and hydroxyl radicals is slightly exothermal $\sim 6 \, kJ \, mol^{-1}$, based on an estimate of ΔG^0_{298} for $\cdot HgOH$ made by Strömberg (1990). The most likely fate of the HgOH molecule radical in ambient air is scavenging by oxygen given by Eq. (8) as is the case in aerated aqueous phase under environmental conditions (Gårdfeldt et al., 2001). The perquisite for formation of HgO is not due to an exothermal reaction (8) but due to the low ratio $p(HO_2^\cdot)/p(O_2)$ present in the ambient air. Reaction (8) is in fact endothermal with $\sim 30 \, kJ \, mol^{-1}$ estimated with mercury data again from Strömberg (1990).

$$Hg + \cdot OH \rightarrow \cdot HgOH \tag{7}$$

$$\cdot HgOH + O_2 \rightarrow HgO + HO_2^\cdot. \tag{8}$$
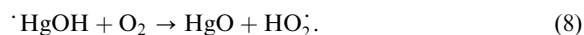
3.1. Atmospheric implications

The relative importance of the $Hg^0 + \cdot OH$ reaction for the atmospheric gas-phase oxidation of Hg^0 is ambiguous since reactions between Hg^0 and key atmospheric oxidants such as $O_3, \cdot NO_3$ and $\cdot Cl$, have not been thoroughly investigated. The lifetime of different chemical oxidation routes may fall in the same order of magnitude, making the actual atmospheric conditions crucial. The presence of the latter three species is relying on the light intensity. The OH radical and Cl atom exist mainly during day-time while $\cdot NO_3$ is destroyed by actinic light. Crucial constraints on the atmospheric lifetime of a spatially well dispersed species such as Hg^0 can be provided by long-term monitoring preferably in global networks, since the lifetime is inversely related to concentration variability (Junge, 1974). The current scarcity of such data on mercury makes it difficult to forecast such a parameter with high significance. Slemr (1996) suggested the variation of mercury in the continental background air to be controlled by sinks rather than sources. Indeed, measurements of total gaseous mercury (TGM) performed within the mercury species over Europe (MOE) project during 1998–1999 frequently showed higher concentrations at the Atlantic in-flow boundary than over continental Europe (Wängberg et al., 2001). Long-term background measurements of TGM at Mount Wank, Germany and at Mace Head, Ireland showed a seasonally modulated pattern (Slemr and Scheel, 1998; Ebinghaus et al., 2000). TGM is entirely dominated and readily approximated by atomic mercury. Simulation of the spatial and temporal behaviour of Hg^0 indicates that OH radicals rather than O_3 may well be responsible for a dominant part of the removal of Hg^0 from the troposphere (Bergan and Rodhe, 2001). The principal loss process of many saturated hydrocarbons is normally oxidation initiated by the OH radical. The seasonal cycles observed for these species at the background sites of middle and higher latitudes are predominantly due to modulation of the $\cdot OH$ concentration (Bottenheim and Shepherd, 1995). Comparing the mercury amplification with those of some hydrocarbons, put in between that of methane and ethane with a predicted atmospheric lifetime of 6–10 months. Using a global mean estimate of the $\cdot OH$ concentration (Krol et al., 1998), the natural lifetime ($\tau = k_1^{-1}[\cdot OH]^{-1}$) for atomic mercury with respect to reaction with $\cdot OH$ (4–7 months) falls within this range, taking the rate coefficient determined in this study.

Most reliable TGM measurements have been performed during periods of perturbation of the dynamic steady state of atmospheric Hg^0 (Iverfeldt et al., 1995; Slemr and Scheel, 1998). These perturbations include a complex source distribution of different mercury species including recycling of anthropogenically mobilised mercury and multiple simultaneous removal

processes which influence atmospheric atomic mercury. Moreover, in the aqueous phase, a reversible redox balance is present (Munthe, 1992; Pehkonen and Lin, 1998; Van Loon et al., 2000), making it a possible source of atomic mercury. In 3 D global simulations by Shia et al. (1999) and Bergan et al. (1999), the lifetime of Hg^0 was predicted to be 1.2 yr and in the range 0.5–1.5 yr, respectively when gas-phase oxidation was considered. The corresponding lifetime in the former model was extended to 1.7 yr when including water-phase chemistry balancing the $Hg^0(g) + O_3(g)$ reaction.

The mercury-containing product in this study was assumed to be HgO according to reaction (8). This species has been identified as a product from the $Hg^0 + O_3$ gas-phase reaction (P'yankov, 1949). The ability for molecular HgO to condense on existing particles is considerable and associated with low vapour pressure at ambient temperature (Strömberg, 1990). The linkage of Hg^0 oxidation by the oxygenated species BrO and O_3 to the growth of particulate mercury concentration (Lu et al., 1997; Murphy et al., 1998), likewise argues that HgO exhibits this property. While time resolved measurements of particulate mercury are currently not available to our knowledge, the diurnal patterns of divalent gaseous mercury are characterised by a peak occurring in the early afternoon, which can be explained in terms of chemical production and air stagnation. Compounds with similar surface resistance as well as diurnal and seasonal cycles are often produced proto-chemically during the day and/or scavenged during the night-time under the influence of a stable nocturnal boundary layer. In order to assess the importance of sinks and sources and whether the source is more consistent (O_3) or light modulated ($\cdot OH$) in character, process oriented modelling (e.g. Pleijel and Munthe, 1995) of the behaviour of oxidised gaseous mercury in ambient air is required.

Acknowledgements

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