

Atmospheric reactions of gaseous mercury with ozone and hydroxyl radical: Kinetics and product studies

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Abstract.

The dominant form of mercury in the atmosphere is Hg^0 . The oxidation processes are of great importance since oxidized mercury undergoes deposition and can become subject to bio-accumulation. Experimental data on the gaseous reactions of elemental mercury are very limited with compare to the reactions of Hg^0 in solutions. We herein carried out kinetic and product studies on the reactions of gaseous Hg^0 with O_3 and hydroxyl radical (HO) under near atmospheric pressure (750 ± 1 Torr) and room temperature (298 ± 1 K) in air and N_2 . O_3 was produced in a silent discharge generator (OL 100/SB). Hydroxyl radicals were produced from the photolysis of isopropyl nitrite in the presence of NO. Kinetics of the reactions with O_3 /HO was studied using absolute and relative techniques by gas chromatography with mass spectroscopic detection (GC-MS). The gas phase reaction between elemental Hg^0 with O_3 , has been studied in different surface- to-volume (sly) ratios, and evidence for heterogeneous reactions was observed. Existence of mercuric oxide, HgO by the reaction of atomic Hg^0 with O_3 has been determined in the gas phase from the suspended aerosols using high temperature mass spectrometry.

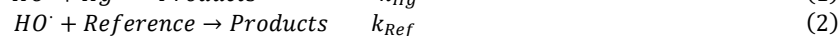
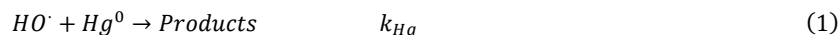
1. INTRODUCTION

One of the most toxic elements, Hg is released into the lower atmosphere from a variety of natural and anthropogenic sources [1]. Rapid depletion of Hg^0 has been observed from the atmospheric boundary during spring in the high-Arctic region [2], Arctic [3], sub-Arctic [4] and is associated with surface snow and ice [5]. The concentration of atmospheric Hg^0 which is mainly in the elemental mercury in the range of 1 to 4 ngm⁻³ [6] and play a important role in the atmospheric chemistry of the heavy metal. The average lifetime of elemental Hg^0 is estimated to be from 0.5 to 2 years [7]. Due to some atmospheric oxidants, elemental mercury is transferred into the oxidized state, e.g., as in its methylated form, thereby spreads into the ecosystem and becomes subject to bio-accumulation [8]. The evidence for oxidation of elemental mercury by O_3 in the aqueous phase due to high O_3 concentration in the stratosphere has been suggested [9, 10]. It is important to evaluate the direct impact of O_3 -initiated oxidation reaction of mercury on human health and the chemistry of the global atmosphere. The major daytime oxidant is HO radical, the most important reactive species in the troposphere and a key player for initiating oxidation of trace compounds in the atmosphere [11]. The studies of gaseous reactions of elemental mercury with HO radicals are very limited in contrast to the reactions of Hg^0 in solution. An attempt has therefore been made to study the chemistry of mercury with HO and ozone in connection with mercury depletion events observed in several locations in the high-Arctic, -Antarctic, and sub-Arctic. Our present study has been carried out for understanding the kinetics and product of gas phase reactions of Hg with O_3 and HO under near atmospheric condition using absolute and relative rate techniques by gas chromatography with mass spectroscopic detection.

2. EXPERIMENTAL

The kinetic investigations of the reactions of gaseous Hg^0 with O_3 and hydroxyl radical (HO) were performed under near atmospheric pressure (750 ± 1 Torr) and room temperature (298 ± 1 K) in air and N_2 using absolute and relative techniques by gas chromatography with mass spectroscopic detection (GC-MS). Mercury and reference concentrations were monitored by MS (quadrupole MSD HP5973) after a separation on gas chromatograph equipped with 0.25 mm ID x 30 m crossed linked phenyl-methyl-siloxane column using SIM mode.

The absolute reaction rate of the reaction of mercury with O_3 were studied under pseudo-first-order conditions with respect to Hg^0 . To perform kinetic studies of the reaction of Hg^0 with HO, we used relative rate technique:



The ratio of the rate constants k_{Hg}/k_{Ref} was determined from the following equation:

$$\ln \left\{ \frac{[Hg]_0}{[Hg]_t} \right\} = \frac{k_{Hg}}{k_{Ref}} \ln \left\{ \frac{[Ref]_0}{[Ref]_t} \right\} \quad (3)$$

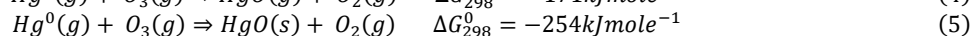
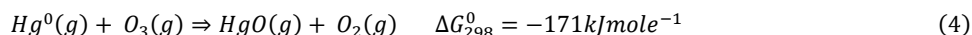
where $[Hg]_0$ and $[Ref]_0$ are the initial concentrations, and $[Hg]_t$ and $[Ref]_t$ are the concentration at time t. A plot of $\ln \left\{ \frac{[Hg]_0}{[Hg]_t} \right\}$ vs $\ln \left\{ \frac{[Ref]_0}{[Ref]_t} \right\}$ should give a straight line with a zero intercept, if

the extend of secondary reactions are negligible.

Experiments were carried out in double-walled 2- and 3- L Pyrex flasks. Temperature was regulated to $\pm 1^\circ\text{C}$ by circulating water through the outer jacket, using a circulator (Neslab RTE 111). In order to avoid wall losses, the flask inside was treated by Halocarbon Wax (SUPELCO) as described by in our group's publication previously [12]. A vacuum system was used to prepare the gaseous reactants. O_3 was produced in a silent discharge generator (OL 100/SB). An ultraviolet-visible spectrophotometer (UV-VIS, Varian Cary-50 Bio) was used to monitor the ozone concentration. HO radicals were produced by photolysis ($300 < \lambda < 400 \text{ nm}$) employing isopropyl nitrite in presence of NO which enhances the formation of HO radical and reduces the ozone formation. Synthetic air was used as batch gas. Isopropyl nitrite was prepared by the action of nitrous acid and isopropyl alcohol at 0°C . Purity was checked with GC-MS and stored at 0°C in the dark.

3. RESULTS AND DISCUSSION

It has been mentioned in the literature that the reaction of mercury with O_3 can be catalyzed by surfaces [6]. To minimize this effect, the reaction cell was coated with halocarbon wax for kinetic experiments. The reaction of Hg with O_3 may precede [6] either according to equations (4) or (5), where reaction (4) is simple bimolecular gas phase reaction and reaction (5) has a complex nature.



The large negative Gibbs free energy indicates the near complete conversion of Hg^0 to HgO. Existence of mercuric oxide, HgO has been determined in the gas phase from the suspended aerosols, and on the wall of the reaction chambers using high temperature mass spectrometry according to the method. Products were collected by a flow of gas from a reaction chamber through a 1.1 mm ID x 10 cm length Pyrex liquid N_2 cooled trap. Condensed products were evaporated at step-wise elevated temperature from the tube to a chemical ionization ion source using direct probe technique. An example of a pseudo-first-order plot, depicted in Figure 1, of the reaction of Hg^0 with O_3 suggested that both a gas phase reaction and a heterogeneous gas-solid reaction occurring simultaneously and there is a significant increase in the

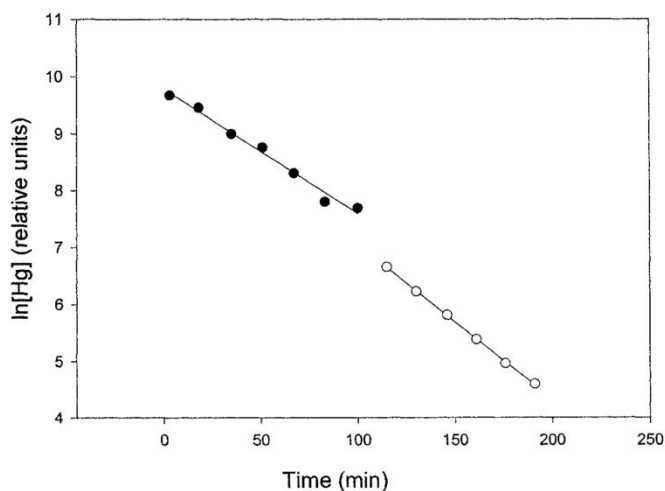


Figure 1. Typical pseudo-first-order plot for the reaction of Hg^0 with O_3 at 298 K. Wall treated with halocarbon wax.

rate constant with increasing s/v ratio.

HO- initiated reactions of Hg^0 were studied by relative rate technique using cyclohexane and n-butane as the Reference molecule. The mechanism of the HO-initiated reaction of Hg^0 has been suggested [13] that there is a initial formation of HgOH, which is slightly exothermic $\sim 6 \text{ kJ mole}^{-1}$. HgOH finally scavenged by O_2 in an ambient air according to the equation (7).



Good linearity of relative rate plots was obtained for both references of cyclohexane and n-butane. Both ozone and HO initiated reactions seem to be kinetically too slow to account for ozone depletion observed in the poles during the sunrise.

Acknowledgements

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