EXPERIMENTAL STUDY OF MERCURY HOMOGENEOUS REACTION CHEMISTRY UNDER POST-FLAME CONDITIONS

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Introduction

In the United States, coal combustion remains the primary anthropogenic source of mercury air pollution (1). Calculations have shown that gas phase oxidized mercury is thermodynamically favored at stack conditions, but recent studies suggest that conversion is kinetically limited (2-5). Efforts to reduce mercury emissions require knowledge of mercury speciation at stack conditions, since the oxidation state directly affects mercury capture efficiencies. Oxidized forms such as $HgCl_2$, for example, are water-soluble and easily captured by wet scrubbers, whereas elemental mercury is insoluble and therefore difficult to remove.

Several recent studies have focused on developing an elementary kinetic mechanism for homogeneous Hg oxidation to predict Hg conversion in coal combustion systems. Sliger et al. (5) proposed a four step mechanism that incorporated a global reaction with Cl_2. Widmer et al. subsequently presented an 8 step mechanism that included chlorinated species such as HOCl (6). Edwards et al. (3) expanded the Cl chemistry, Niksa and coworkers incorporated NOx chemistry and recalculated several rate constants (4), and Qiu and co-workers further refined the rate constants and expanded the Cl chemistry (7). In each of these efforts, Cl atoms were identified as a key component in the oxidation pathway.

While the models have provided considerable insight into possible reaction pathways, detailed experimental studies of mercury oxidation in the presence of important coal combustion product gases such as SO_2 and NO in systems with the relevant radical pool are lacking. For example, Hall et al. (8) examined Hg oxidation by HCl in a heated quartz tube using bottled gas mixtures consisting of 10% O_2 in N_2. Sliger et al. (5) used the product gases from a natural gas flame in a high quench rate system to examine Hg oxidation by HCl. Neither SO_2 nor NO were considered in this study. Similarly, Mamani-Paco and Helble (9) examined Hg oxidation by both HCl and Cl_2 in the post-flame gases produced by a methane flat flame burner. Insights into reaction pathways were gained from these studies, but there is no information provided on the importance of SO_2 and NO. Ghorishi et al. (10) conducted bench scale isothermal experiments to investigate the effects of SO_2 and H_2O and temperature on mercury oxidation in simulated flue gas mixtures, and found that no Hg oxidation by HCl occurred at temperatures below 250°C. At higher temperatures oxidation did occur, but inhibition was reported at 754°C with the addition of SO_2. As part of an investigation that studied the effects of flue gas constituents on speciation methods, Laudal et al. (11) also examined the effects of SO_2 and NO. Results indicated that both SO_2 and NO could inhibit Hg oxidation by Cl_2.

While these studies provide insight into inhibitory effects associated with SO_2 and NO, the relevant studies were either performed without SO_2 and NO, or with bottled gas mixtures that do not reproduce the radical pool associated with a flame environment. This study was undertaken to address these questions.

Experimental

Homogeneous oxidation of mercury was examined in a flame-fired bench-scale system shown schematically in Figure 1. Combustion gases were generated by oxidation of metered methane-oxygen-nitrogen mixtures fed to a Research Technologies Inc. multi-element micro-diffusion flat flame burner. For these experiments, the equivalence ratio was adjusted to vary the temperature profile and the flue gas composition downstream of the flame. All experiments were conducted under either stoichiometric or fuel lean combustion conditions. A rectangular insulated stainless steel mixing chamber (0.21 m tall, 0.16 m in length and 0.17 m wide) was placed on top of the diffusion burner for gas mixing. At the back of the mixing chamber, three 6.35 mm ports were used for the injection of the mercury laden vapor stream, any chlorine containing species, and other contaminant gases (SO_2 and NO in nitrogen). Mercury vapors were generated from a mercury permeation device using nitrogen as the carrier gas. The permeation device was held in a constant temperature heating bath throughout the course of each experiment. The mercury-containing flue gas mixture then exited the mixing chamber through an outlet 0.13 m in diameter.

Gases exiting the mixing chamber flowed into a quartz reactor 80 cm long and 12.7 cm in diameter. The reactor- chamber junction was sealed with castable cement before the start of each experiment. To prevent the accumulation of condensed water as the simulated flue gases were cooled the reactor was mounted at 10 degrees to the horizontal. Heating tapes and insulation were wrapped around the reactor to provide additional heating and to reduce heat losses to the environment. Four ball and socket ports were located along the length of the reactor for sampling the reacting gas mixture.

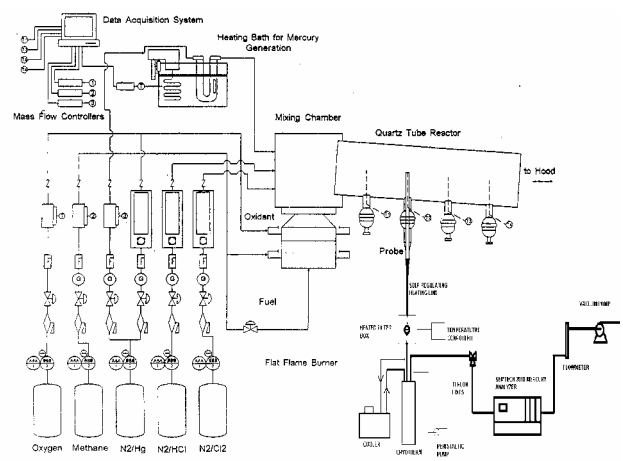

Figure 1: Schematic diagram of the mercury homogeneous oxidation experimental apparatus, modified from (9).

Quartz probes were used to collect flue gas samples from the center of the reactor. To measure the temperature at the sample ports, a thin-wire K-type thermocouple was inserted in a quartz capillary at the center of each probe.

Flue gases were sampled by a quartz probe connected to a self regulating heating line (SRHL). The SRHL core was made of Teflon^{TM} tubing wrapped in a heating cable with a temperature controller used to maintain a tubing surface temperature of 150°C. Gas flows leaving the SRHL entered a glass fiber filter enclosed in a miniature heated filter box used to separate any particles from the gas stream. Reaction gases then entered a series of three glass impingers enclosed in a container through which water at a temperature of less than 5°C was recirculated to keep the surfaces of the impingers cold.

Gases exiting the impingers were fed to a Semtech cold vapor atomic absorption spectroscopy-based continuous Hg analyzer for analysis of Hg concentrations. Differences between oxidized and elemental mercury were determined by cycling the oxidizer (HCl or Cl_2) on and off in 30 or 60 second intervals during the course of an experiment.

The range of conditions considered in this study is presented in Table 1. In all cases, samples were extracted from sampling port 2 at a system temperature of approximately 350°C.

Table.1: Experimental test matrix used for evaluating Hg homogeneous oxidation. All concentrations in ppm.

#	Cl_2	HCl	NO	SO_2
1	250	0	0	0
	500	0	0	0
2	250	0	100/300	0
	500	0	100/300	0
3	250	0	0	100/400
	500	0	0	100/400
4	150	0	0	0
	250	0	0	0
5	0	100/300	0	0
6	0	100/300	100/300	0
7	0	100/300	0	100/400
8	0	300	0	0

Results and Discussion

Experiments were conducted with varying concentrations of NO, SO_2, HCl, Cl_2, and O_2 as described above and in Table 1. Typical results for an experiment involving NO and HCl addition are shown in Figure 2, and for an experiment involving SO_2 and Cl_2 in Figure 3. Error bars in each figure represent the standard deviation about the mean for a series of repeat experiments, with N ranging from 3 to 5. Addition of NO (beyond any thermal NO) is seen to have a slight inhibitory effect on Hg oxidation by HCl at HCl concentrations of 300 ppm. In contrast, SO_2 is seen to have

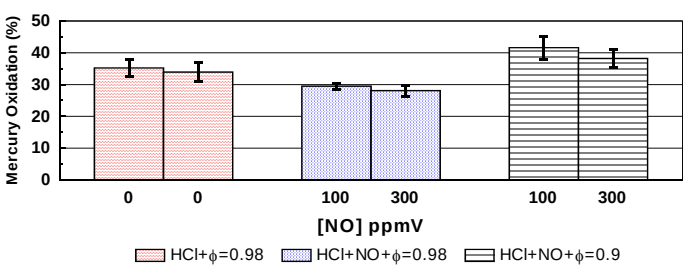

Figure 2 Hg oxidation in the presence of NO and 300 ppm HCl.

a large inhibitory effect on oxidation by Cl_2. Not shown are results from experiments with HCl and SO_2; here, very little effect was observed. In the presence of 100 ppm HCl at a flame equivalence ratio of 1, 6% of the Hg present was oxidized to $HgCl_2$. In the presence of 100 ppm SO_2, oxidation remained unchanged at 6%. Increasing the SO_2 concentration to 400 ppm resulted in a statistically insignificant change in Hg oxidation to 7%.

As implied by the data in Figures 2 and 3, increasing oxygen levels also contribute to an increase in Hg oxidation. Results from a series of experiments at two different flame stoichiometries in the presence of varying levels of HCl are shown in Figure 4. Differences at low HCl concentrations are minimal but become apparent as HCl concentrations increase above 200 ppm.

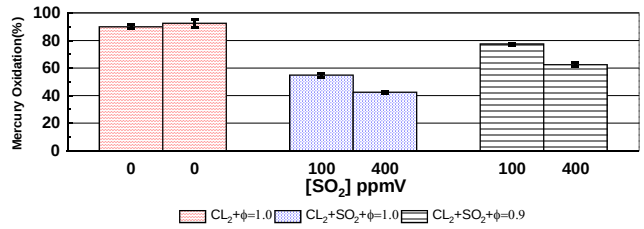

Figure 3 Hg oxidation in the presence of SO_2 and 500 ppm Cl_2.

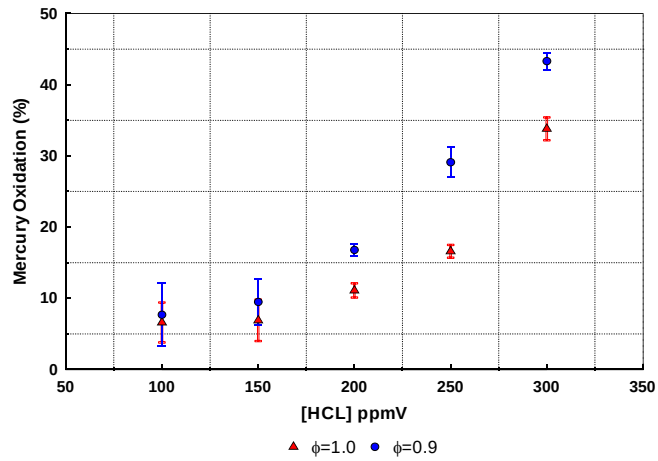

Figure 4 Hg oxidation as a function of equivalence ratio ϕ and [HCl]

Acknowledgement

This project was supported by US EPA STAR grant number R-82817001-1

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