Effects of Quench Rate, NO, and Quartz Surface Area on Gas Phase Oxidation of Mercury by Bromine

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Abstract

Oxidized mercury species may be formed in combustion systems through gas-phase reactions between elemental mercury and halogens, such as chorine or bromine. Injection of bromine compounds or brominated sorbents have been shown to affect mercury speciation and removal in coal-fired power plants. This study examines how bromine species affect mercury oxidation in the gas-phase. Experiments were conducted in a bench-scale, laminar, methane fired (300 W), quartz-lined reactor in which gas composition (Br₂, NOₓ), quench rate, and quartz surface area were varied. Speciated mercury was measured using a wet conditioning system and continuous emissions monitor (CEM). Oxidation levels ranged from 13% to 80% with a quench rate of 450 K/s and bromine concentrations ranging from 3.5 to 41 ppmv equivalent HBr. A lower quench rate (220 K/s) increased oxidation by about one third. Most of the experiments were conducted with 30 ppm NO (dry). Mercury oxidation was unaffected by the presence of 500 ppmv NO. The surface area was increased by inserting a bundle of thin-walled quartz tubes. The insert decreases the reactor residence time by about 5 %. Tripling the interior, quartz surface area of the reactor from 1000 cm² to 3000 cm² did not appreciably affect the extent of oxidation. The experimental results were compared to detailed kinetic modeling predictions.

Introduction

The recent U.S. EPA Clean Air Mercury Rule (CAMR) (1) has put limits on mercury emissions from U.S. coal-fired utilities. The related Clean Air Interstate Rule or CAIR (2) specifies reductions in NOₓ and SO₂ emissions, which are projected to result in a 40% reduction in mercury emissions in the utility sector by 2010, the start of Phase I of the CAMR. The CAIR mercury reduction is assumed to result from existing technologies, primarily as a co-benefit of reducing other pollutants such as NOₓ, and SO₂, and will affect 28 eastern states and the District of Columbia. A similar plan has been introduced in Canada, with emissions caps in 2010 that vary from province to province, and the possibility of more stringent reductions by 2018 (3). Mercury-specific technology will be required in the U.S. to achieve more stringent reductions in mercury emissions mandated by 2018 under the Clean Air Mercury Rule. CAIR and CAMR are currently in the midst of legal battles, and have been vacated by the DC circuit court. As of December, 2007, nineteen states had passed their own
mercury regulations, some incorporating parts of CAMR (4). The timing and extent of federal mercury regulations are in question, but states are going ahead with their own regulations.

In the last several years, demonstrations of a number of different mercury control technologies have been performed in the US on commercial coal-fired power plants in anticipation of the control of mercury emissions from electricity generating plants, as promulgated by CAMR. Activated carbon injection is one technology that is considered close to commercial application. Wet flue gas desulphurization (FGD) scrubbers are also effective for removing mercury if there is sufficient oxidized mercury in the flue gas at the FGD inlet. The ability to oxidize elemental mercury or to make activated carbon more effective at removing mercury from coal-fired power plants could substantially lower the cost of compliance; thus, a better understanding of the role of flue gas composition, boiler conditions, and homogeneous oxidation processes in combustion gases is of great importance.

Mercury exists in the elemental form (Hg\textsuperscript{0}) in the high temperature regions of the coal-fired boiler. As the flue gas cools, complex reactions transform the elemental mercury into gaseous oxidized forms (Hg\textsuperscript{2+}) (5) and particulate bound mercury (Hg\textsubscript{p}). The amount of Hg\textsuperscript{0} which is converted to Hg\textsuperscript{2+} and Hg\textsubscript{p} depends on several factors including the quench rate, the flue-gas composition, and the amount and properties of fly ash.

Mercury speciation and capture is affected by halogens. Full-scale demonstrations have shown that bromine is effective for mitigating mercury emissions. Vosteen et al. (6) have patented one method for introducing bromine species into the combustion system, involving the addition of bromine containing compounds to the furnace or flue-gas. This method has been licensed in the U.S. by ALSTOM under the name KNX\textsuperscript{TM} additive. The addition of bromine compounds has been shown to increase oxidation and mercury capture at numerous power plants firing various coal types (7-12). The addition of bromine compounds to the flue gas of boilers in which activated carbon is injected has been shown to increase oxidation and enhance the activated carbon mercury capture (8-10), (12), (13). Various brominated sorbents have also been shown to be effective for decreasing mercury emissions (8-10), (13-17).

We have performed a study of homogeneous mercury oxidation in a methane fired furnace. Mercury and bromine (Br\textsubscript{2}) were added through the flame. When bromine is injected through the flame, Br, Br\textsubscript{2}, and HBr should all be present at various temperatures in the reactor. Impingers were used to speciate and condition the flue gas upstream of a mercury continuous emission monitor (CEM). A KCl impinger, similar to the Ontario Hydro method, was treated with Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} and used to remove oxidized mercury in order to allow the CEM to quantify elemental mercury in the flue-gas.

Mercury-bromine reactions have not been studied under combustion conditions using time-temperature profiles representative of a power plant. Laboratory studies have focused on specific individual reactions, not overall speciation, and most experiments have been performed at atmospheric conditions. Ariya et al. (18) and Donohoue et al. (19) studied the reaction between Hg and Br under atmospheric conditions in Pyrex flasks using photolysis. The reaction rate found by Donohoue et al. was nine times slower than that determined by Ariya et al. There is obvious discrepancy in the calculated homogeneous rates even when performing similar experiments. Liu et al. (20) studied the reaction between Hg and Br\textsubscript{2} under flue gas conditions in Pyrex flasks. Arrhenius Law constants were found for temperatures
between 298 K and 365 K. Although the gaseous mixture contained flue gas constituents, the higher temperatures seen by flue gas in a power plant could not be obtained due to the melting point of the halocarbon wax used to coat the Pyrex flasks and prevent wall reactions. In this paper, we report experimental data that were collected using actual flue gas and temperature profiles which cover the wide range of temperatures seen in power plants.

**Experimental**

The reactor used in this study was developed to study gas-phase mercury oxidation and is described in detail in Fry et al. (21). The reactor is a 47 mm-ID quartz glass tube, 132 cm in length. Five separately controlled temperature regions allow the time-temperature profile of the reactor to be manipulated to create various quench rates. The quench rates used in these experiments are representative of industrial conditions and allow adequate time at temperatures necessary for mercury oxidation reactions. The temperature profiles used are shown in Figure 1. The low temperature region (around 350°C) represents flue gas temperatures through air pollution control devices.

![Figure 1: Time-temperature profiles used in this study](image)

A radical pool representative of real combustion systems was created in the reactor by introducing all species through the flame of a 300 W methane-fired burner. A PS Analytical Mercury Calibration Gas Generator or “CavKit” was the source of elemental mercury. The reactor gas was analyzed for mercury, O2, and NO. For mercury analysis, two sample streams were taken from the outlet of the reactor and introduced into a wet-chemical conditioning system. Mercury speciation was accomplished by passing one stream through impinger solutions containing KCl/Na2S2O3 (to remove oxidized mercury while preventing oxidation of
elemental mercury in solution) and NaOH, and the other stream through impingers containing SnCl₂ (to convert all mercury to the elemental form) and NaOH. A Tekran 2537A mercury analyzer coupled with an intermittent 4-port sampler was used to measure the elemental mercury concentration of each stream. At the start of each experiment, a mass balance on mercury was closed through the reactor with a flame, before any oxidant was introduced.

Bromine was introduced using a 3000 ppm Br₂ in air calibration gas. The flow of bromine was controlled by a stainless steel micro-needle valve. A Gilian Gilibrator automated bubble flow column was used to measure the flowrate before and after introducing bromine into the reactor. Bromine concentration was then calculated by mass balance.

The effect of NO was also investigated. Pure NO was used as the source for these experiments. The flows in the reactor were adjusted to maintain a constant 6 standard liters per minute through the reactor and 1.5% O₂ in the dry exhaust gas. The NO concentration was continuously measured after the conditioning system.

For some experiments with bromine, the quartz reactor surface area was increased. The reactor normally has 1000 cm² of surface area. This value was increased to 3000 cm² by inserting a bundle of thin walled quartz tubes. The bundle was made of seven tubes arranged in a hexagonal configuration. Each tube was 60 cm in length, 14 mm-OD, and 12 mm-ID. The tube bundle decreased the residence time in the reactor by only 5%.

Results and Discussion

Baseline oxidation experiments with bromine were performed with a high quench rate (450 K/s). The concentrations of O₂ and NO were 1.5% (dry) and 30 ppm (dry) respectively. Bromine concentrations ranged from 6.7 to 41.4 ppmv equivalent HBr (wet). Results from these experiments are shown in Figure 2. Oxidation ranged from 18% to 78%. Increasing the bromine concentration significantly increased mercury oxidation in the reactor. Error ranged from 2.2-6.3% based on the oxidation through the reactor during the initial mass balance with no bromine.

Several operating conditions were changed individually to see the effect they had on homogeneous mercury oxidation by bromine. First, the lower quench rate (220 K/s) was applied, keeping all other operating conditions the same. These results are compared to the high quench results in Figure 2. Decreasing the quench rate increased the extent of oxidation by about one third for similar bromine concentrations. The effect of quench rate may be due to bromine radical chemistry. HBr, Br₂, and Br are present in the system at various ratios depending on temperature (22). Second, at the high quench rate, 500 NO (dry) was added. The NO concentration in the flue gas was continuously monitored, after a slip stream was removed for mercury analysis. The increased NO concentration had no discernable impact on oxidation, as shown in Figure 3. This is in contrast to modeling predictions presented by Senior et al. (23) and Niksa et al., (24) which predicted decreased oxidation with increased NO concentration. It is unclear why these modeling predictions do not match the experimental data. Perhaps the detailed kinetics involving NO₂ and bromine species used in the modeling are incorrect. Lastly, the quartz surface area in the reactor was increased from 1000 cm² to 3000 cm². The increased surface area, again at 30 ppm NO, slightly increased oxidation, as shown in Figure 4. This surface area effect needs to be investigated further to ensure
accurate extents of oxidation are being reported. Varying the surface area further will yield a correlation which may be extrapolated to zero surface area. This will isolate the gas-phase reactions from any possible surface area reactions.

![Figure 2: Comparison of homogeneous mercury oxidation by bromine at high and low quench rates (The lines are drawn to indicate trends and are not based on model predictions, error ranges from 2.2-6.3%)](image)

Figure 2: Comparison of homogeneous mercury oxidation by bromine at high and low quench rates (The lines are drawn to indicate trends and are not based on model predictions, error ranges from 2.2-6.3%)
Figure 3: Effect of NO concentration on homogeneous mercury oxidation by bromine

Figure 4: Effect of increased surface area on homogeneous mercury oxidation by bromine
Kinetic Modeling

The Hg-Br experiments were modeled using the Reaction Engineering Kinetics Solver (REKS). This program is similar to ChemKin. The model includes sub-mechanisms for hydrocarbon, mercury, bromine, SO₂, and NOₓ chemistry. The bromine mechanism was put together using NIST Halon chemistry. The kinetic parameters for a simple, global Hg-Br mechanism were found by fitting the experimental data. The reactions used and the corresponding pre-exponential factors and activation energies are shown in Table 1. The model predictions are compared to the experimental data in Figure 5. Reactions 1 and 2 were selected because they have been previously found to be the main reaction pathway for mercury oxidation by chlorine. Reaction 3 was added later after the dependence on quench rate could not be matched using reactions 1 and 2 only. While the shape and general effect of quench rate (lower quench rate gives larger oxidation) are predicted, the magnitude of the effect of quench rate is under-predicted. The separation between the two quench rates needs to be larger to predict the experimental data correctly. Because a more global mechanism is being used and multiple parameters are being changed, several parameter combinations will results in an appropriate fitting of the experimental data. The effect of quench rate is most likely caused by differences in bromine radical chemistry at different temperatures.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>A</th>
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<tbody>
<tr>
<td>1) Hg + Br + M = HgBr + M</td>
<td>1.0E16 cm⁶/mol⁶-sec</td>
<td>0 cal/mol</td>
</tr>
<tr>
<td>2) HgBr + Br₂ = HgBr₂ + Br</td>
<td>2.0E16 cm³/mol-sec</td>
<td>1000 cal/mol</td>
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<tr>
<td>3) HgBr + HBr = HgBr₂ + H</td>
<td>2.7E14 cm⁹/mol-sec</td>
<td>1000 cal/mol</td>
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Figure 5: Comparison of model predictions and experimental data
Conclusions

In summary, bench-scale experiments were performed in a laminar, methane fired (300 W), quartz-lined reactor in which gas composition (Br₂, NOₓ), quench rate, and quartz surface area were varied. Baseline oxidation with bromine using a quench rate of 450 K/s and 30 ppm NO (dry) showed oxidation of Hg⁰ varied from 18% to 78% with bromine concentrations ranging from 6.7 to 41.4 ppmv (equivalent HBr wet). Lowering the quench rate to 220 K/s increased oxidation by approximately one third. Increasing the NO concentration to 500 ppm had negligible impact on oxidation. Tripling the quartz surface area slightly increased oxidation. These results indicate that a large fraction of elemental mercury in the gas phase is oxidized homogeneously by bromine species. A simple Hg-Br reaction mechanism was developed which approximates the experimental data.

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References


