Effects of Sulfur Dioxide and Nitric Oxide on Mercury Oxidation and Reduction Under Homogeneous Conditions

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ABSTRACT

This paper is particularly related to elemental mercury (Hg\(^0\)) oxidation and divalent mercury (Hg\(^{2+}\)) reduction under simulated flue gas conditions in the presence of nitric oxide (NO) and sulfur dioxide (SO\(^2\)). As a powerful oxidant and chlorinating reagent, Cl\(^2\) has the potential for Hg oxidation. However, the detailed mechanism for the interactions, especially among chlorine (Cl)-containing species, SO\(^2\), NO, as well as H\(_2\)O, remains ambiguous. Research described in this paper therefore focused on the impacts of SO\(^2\) and NO on Hg\(^0\) oxidation and Hg\(^{2+}\) reduction with the intent of unraveling unrecognized interactions among Cl species, SO\(^2\), and NO most importantly in the presence of H\(_2\)O. The experimental results demonstrated that SO\(^2\) and NO had pronounced inhibitory effects on Hg\(^0\) oxidation at high temperatures when H\(_2\)O was also present in the gas blend. Such a demonstration was further confirmed by the reduction of Hg\(^{2+}\) back into its elemental form. Data revealed that SO\(^2\) and NO were capable of promoting homogeneous reduction of Hg\(^{2+}\) to Hg\(^0\) with H\(_2\)O being present. However, the above inhibition or promotion disappeared under homogeneous conditions when H\(_2\)O was removed from the gas blend.

INTRODUCTION

Of the hazardous and toxic pollutants identified under Title III of the 1990 Clean Air Act Amendments, mercury (Hg) is a leading concern because of its environmental and health impacts. According to the Mercury Study Report to Congress, coal-fired utility boilers are concluded as the primary source of anthropogenic emissions in the United States, contributing ~48 t or ~30% of all U.S. Hg emissions. In March 2005, U.S. Environmental Protection Agency (EPA) promulgated the first-ever Clean Air Mercury Rule, through which EPA plans to reduce Hg emissions in two phases. In the first phase, due by 2010, emissions of Hg will be reduced by taking advantage of “cobenefit” reduction while reducing SO\(^2\) and nitrogen oxides (NO\(^x\)) under Clean Air Interstate Rule. The second phase will reduce Hg emissions to 15 t by 2018, an overall reduction of nearly 70%.

Development of Hg control technologies has been ongoing over the past years. However, although progress has been made, based on the data to date, there is currently no single best control technology that can be broadly applied. Capture of Hg in wet scrubbers, the same devices that capture sulfur dioxide (SO\(^2\)), shows promise. However, none of the wet scrubbers can effectively capture and remove elemental mercury (Hg\(^0\)). Therefore, if the Hg control target is to be met by taking advantage of cobenefit reduction with scrubbers currently used for SO\(^2\) removal, effective methods to transform Hg\(^0\) to water-soluble divalent mercury (Hg\(^{2+}\)) must be developed.

In recent years, research efforts have been and continue to shed light on various aspects of Hg oxidation, especially with chlorine-containing species, under conditions relevant to those encountered in coal-fired utility boilers. Through these efforts, the Hg\(^0\) oxidation chemistry with chlorine (Cl)-containing species was progressively elucidated. Hg leaves the high-temperature combustion zone as elemental Hg, part of which transforms into oxidized form during the postcombustion zone as flue gas cools. One-step global reaction mechanisms have been proposed to model this observed depletion of Hg\(^0\) in the presence of chlorine...
and hydrogen chloride (HCl). Although such mechanisms can give plausible qualitative results, the global mechanisms, nevertheless, provide little insight into the details of the conversion process and, hence, are not instrumental for the examination of other flue gas effects, such as SO\(_2\) and NO\(_x\).

The pivotal parameters that were identified to affect the Hg\(^0\) conversion through this mechanism were Cl and Cl\(_2\) concentrations in flue gas, the flue gas quench rate, and the rate at which Cl recombines into Cl\(_2\).

This finding was one of the evidence for NO in inhibiting Hg\(^0\) oxidation. It is apparent that both Niksa et al.\(^{19}\) and Qiu et al.\(^{20}\) supported such an idea, because Hg\(^0\) oxidation was inhibited by the elimination of OH radicals. However, with respect to the specific inhibitory pathways, in particular, how the role of OH was involved, the indication by Niksa et al.\(^{19}\) was somewhat vague. Although the explanation by Qiu et al.\(^{20}\) was capable of characterizing the inhibitory role of SO\(^2\) through arguing for the importance of HOCl, they cannot interpret the simulations of Niksa et al.\(^{19}\) where Cl\(_2\) was thought to be the dominant species in oxidizing HgCl into HgCl\(_2\). In addition, because HOCl was formed through Cl reacting with OH, Qiu et al.\(^{20}\) cannot account for such an instance as the elimination of OH by SO\(^2\), which will, instead, result in more Cl radicals or Cl\(_2\) to directly react with HgCl. Thus, in this paper, the specific objective is to advance these initial efforts such that the inhibitory roles of NO and SO\(^2\) can be theoretically elucidated by depicting the inhibitory roles of NO and SO\(^2\) under homogeneous reactions when Cl\(_2\) is the primary Cl-containing species.

**EXPERIMENTAL WORK**

A bench-scale system (Figure 1) was constructed to investigate the inhibitory effects of NO and SO\(^2\) in this research. This system mainly consisted of a quartz reactor, a temperature-controlled furnace, a chemical conversion unit, and an Hg\(^0\) online analytical instrument. The quartz reactor, horizontally sitting in a temperature-controlled furnace, consisted of two sections with one responsible for preheating gas and the other functioning as the reaction chamber where Hg\(^0\) oxidation subsequently occurred. When HgCl\(_2\) reduction was investigated, both sections functioned as reaction chambers. The preheating section was 120 cm in length to ensure that reactant gases are sufficiently preheated before being sent to the reaction chamber. Testing demonstrated that the inlet of the reaction chamber could be heated to 750 C (the setting temperature for the furnace is indicated by the thermocouple in Figure 1). The 65-cm-long reaction section (2.2 cm in diameter) provided the reaction zone where a series of oxidation tests were performed. The temperature profile in the reaction chamber was measured by sliding a thermocouple into various locations and was found not to be uniformly distributed, but followed a declining pattern as shown in Figure 2. Reactant gases, such as Cl\(_2\), NO, and SO\(^2\), from cylinders were added into the simulated gas blend to obtain the desired testing conditions. Gas-phase Hg\(^0\) and Hg\(^+\) were obtained by passing a portion of dry N\(_2\) through permeation devices that contain either Hg\(^0\) permeation tubes or HgCl\(_2\) crystals at elevated temperatures. Moisture vapor was generated by pumping a measured flow of deionized water into a diffusion chamber where water was heated to 200 C. For these tests, the rate was controlled to establish 8% H\(_2\)O in the simulated gas stream. To rapidly quench the reaction when gas leaves from the reaction tube, a 10-cm-long double-cooling condenser was added at the exit of the reactor, which was able to lower the gas temperature quickly down to 280 C.

**RESULTS AND DISCUSSION**
Effects of SO$^{\text{sub 2}}$ and NO on Mercury Oxidation

The first set of data was obtained to evaluate the effect of SO$^{\text{sub 2}}$ on Hg$^{0}$ oxidation at an elevated temperature. The first four tests were in effect a 2$^{\text{sup 2}}$ factorial design to identify the interaction effects of SO$^{\text{sub 2}}$ and H2O. During testing, the temperature at the reaction chamber inlet was maintained at 750 C, which is indicated by the thermocouple in Figure 1, with the temperature profile along the reaction chamber presented in Figure 2. At the initial stage, ~12 g/m$^{\text{sup 3}}$ Hg$^{0}$ and 13 ppmv Cl$^{\text{sub 2}}$ were simultaneously added into the gas blend at a total flow rate of 14 L/min. Under this simulated condition, ~7 g/m$^{\text{sup 3}}$ gas-phase Hg$^{0}$ was detected at the outlet of the reactor. The residence time in this reactor chamber was ~0.31 sec. The calculated Reynolds numbers at 600 and 700 C were 414 and 378, respectively. Subsequently, SO$^{\text{sub 2}}$ (2000 ppmv) was added to the gas blend. As displayed in Figure 3, there was little change to the Hg$^{0}$ concentration within 60 min, indicating that dry SO$^{\text{sub 2}}$, in essence, had no significant effect on Hg$^{0}$ oxidation with Cl$^{\text{sub 2}}$ as the primary Cl-containing species. Then, SO$^{\text{sub 2}}$ was removed from the gas blend, and 8% H2O was instead added. In comparison with the baseline data, the result also revealed that Hg$^{0}$ oxidation was unaffected by the presence of moisture. This was consistent with the findings of Widmer et al.4 and Hall et al.,9 where nearly identical extents of Hg$^{0}$ oxidation were identified with and without moisture for temperatures >800 C when 300 ppmv HCl was present. However, when 2000 ppmv SO$^{\text{sub 2}}$ was readied into the gas blend along with the 8% H2O, strong inhibition on Hg$^{0}$ oxidation was observed according to the striking increase of gas-phase Hg$^{0}$ concentration at the outlet of reactor. The calculated Hg$^{0}$ oxidation lowered to ~5%. A subsequent decrease of SO$^{\text{sub 2}}$ from 2000 to 1000 ppmv in the gas blend was capable of increasing the extent of Hg$^{0}$ oxidation to slightly more than 10%, still suggesting that SO$^{\text{sub 2}}$, in conjunction with H2O, had a salient effect on Hg$^{0}$ oxidation when the primary Cl-containing reagent was Cl$^{\text{sub 2}}$.

Figure 4. The effect of NO on Hg$^{0}$ oxidation.

The NO chemistry on Hg$^{0}$ oxidation was also examined in this effort by following the same procedure as mentioned above with the replacement of SO$^{\text{sub 2}}$ by NO. As illustrated in Figure 4, when 600 ppmv NO and 13 ppmv Cl$^{\text{sub 2}}$ was added to the gas blend, it showed insignificant decline of Hg$^{0}$ oxidation as compared with the baseline result. The subsequent replacement of NO by 8% H2O in gas blend basically confirmed that H2O had a minor effect on Hg$^{0}$ oxidation with temperatures >800 C when 300 ppmv HCl was present. However, when 2000 ppmv NO$^{\text{sub 2}}$ was added into the gas blend along with the 8% H2O, strong inhibition on Hg$^{0}$ oxidation was observed according to the striking increase of gas-phase Hg$^{0}$ concentration at the outlet of reactor. The calculated Hg$^{0}$ oxidation lowered to ~5%. A subsequent decrease of NO$^{\text{sub 2}}$ from 2000 to 1000 ppmv in the gas blend was capable of increasing the extent of Hg$^{0}$ oxidation to slightly more than 10%, still suggesting that NO$^{\text{sub 2}}$, in conjunction with H2O, had a salient effect on Hg$^{0}$ oxidation when the primary Cl-containing reagent was Cl$^{\text{sub 2}}$.

Figure 5. The effect of increasing Cl$^{\text{sub 2}}$ concentration Hg$^{0}$ oxidation.

These two sets of tests basically identified the adverse effects of SO$^{\text{sub 2}}$ and NO on Hg$^{0}$ oxidation in the presence of 8% of H2O. However, as the Cl$^{\text{sub 2}}$ concentration was increased, as seen in Figure 5, more Hg$^{0}$ was oxidized into its oxidized form. Cl$^{\text{sub 2}}$ of 100 ppmv in the gas with 8% H2O and 2000 ppmv SO$^{\text{sub 2}}$ had oxidation rates of >25%. These results first suggested that the adverse effects of SO$^{\text{sub 2}}$ and NO on Hg$^{0}$ oxidation can be alleviated by enhancing Cl-containing species concentration. It also implies that the inhibitory roles of SO$^{\text{sub 2}}$ and NO in Hg$^{0}$ oxidation are to reduce the effective concentration of Cl-containing species, Cl and Cl$^{\text{sub 2}}$.

Figure 6. The effect of SO$^{\text{sub 2}}$ on HgCl$^{\text{sub 2}}$ reduction.

Effects of SO$^{\text{sub 2}}$ and NO on Mercury Reduction

Examination of the impacts of SO$^{\text{sub 2}}$ and NO on Hg$^{0}$ reduction was subsequently carried out with Hg$^{0}$ being replaced by Hg$^{2+}$. The specific goal was to determine how SO$^{\text{sub 2}}$ and NO affect the backward reaction of Hg$^{0}$ + Cl$^{\text{sub 2}}$ [Lef-right arrow] HgCl$^{\text{sub 2}}$. The reaction temperatures in the 160-cm-long preheating section were assumed to be as low as 200 C at the inlet and as high as 750 C (as
indicated by the thermocouple in Figure 1) at the outlet of preheating section. The temperature profile in the 60-
cm-long reaction section was presented in Figure 2. A 14-L/min gas blend containing ~12 g/m^sup 3^ HgCl^sub 2^ (balanced with N^sub 2^) was first sent through the reaction system. At steady state, ~6.5 g/m^sup 3^ Hg^sup 0^ at the outlet of the quartz reactor was constantly detected, which accounted for ~44% of Hg^sup 2+^ thermal decomposition. Subsequently, the individual effects of SO^sub 2^ and NO on Hg^sup 2+^ reduction were evaluated in sequence. In the SO^sub 2^ case (Figure 6), the Hg^sup 2+^ reduction, similar to the Hg^sup 0^ oxidation, was minimally affected by the addition SO^sub 2^ in the absence of H2O. NO exhibited some inhibitory effects on Hg^sup 2+^ reduction without H2O (Figure 7). The measurement indicated slightly less than 35% of Hg^sup 2+^ being decomposed (or reduced) when 600 ppmv NO was introduced into the gas blend. Duplicated tests under various conditions, such as slower flow rate and lower NO concentration, confirmed this result as reproducible.

Figure 7. The effect of NO on HgCl^sub 2^ reduction.

Before proceeding to verify the effects of SO^sub 2^ and NO on Hg^sup 2+^ reduction, particularly in the presence of H2O, a second baseline of Hg^sup 2+^ reduction was established by adding only 8% H2O into the gas blend, which showed that H2O basically had no effect on Hg^sup 2+^ reduction, much resembling the occurrence during Hg^sup 0^ oxidation testing. The subsequent addition of either SO^sub 2^ or NO individually showed that Hg^sup 2+^ reduction was greatly enhanced from ~41% of baseline to 80% and 70%, respectively. Consequently, the participation of H2O is of importance for SO^sub 2^ and NO to result in Hg^sup 2+^ reduction.

These aforementioned tests were performed at relatively high temperatures and measured with the Sir Galahad. The Cl and Cl^sub 2^ generated through the thermal decomposition of HgCl^sub 2^ were essentially high. Tests performed at relatively low temperature settings (400-600 C) were also used to further determine the effects of SO^sub 2^ and NO, in combination with H2O, on Hg^sup 2+^ reduction. Less Cl and Cl^sub 2^ were generated from the thermal decomposition of Hg^sup 2+^ at these lower temperatures. In this array of tests, gas blend totaling 3.5 L/min was sent through the reactor. The concentration of Hg^sup 2+^, determined by the Semtech 2000, was ~50 g/m^sup 3^, and the temperature along the reactor, although not uniformly distributed, was assumed to be as high as the setting temperature of the furnace and as low as 200 C at the inlet of reactor. For each temperature test, Hg^sup 2+^ alone was first introduced into the reactor to identify its own thermal decomposition. Subsequently, 8% H2O was added into the gas blend to establish a second baseline data to compare the effects of SO^sub 2^ and NO. After that, individual SO^sub 2^ (2000 ppmv) and NO (600 ppmv) were, in turn, brought into the gas blend. Interesting observations are apparent based on the data presented in Figure 8. First, the reduction of Hg^sup 2+^ across the reactor, in the presence of SO^sub 2^, NO, and H2O, was shown as a function of temperature. Second, consistent with foregoing results, SO^sub 2^ and NO showed significant effects on Hg^sup 2+^ reduction in comparison with the baseline data, but the effects declined with decreasing temperature. Because less Cl and Cl^sub 2^ were generated at the lower temperatures, it was, therefore, conjectured that the promotional roles of SO^sub 2^ and NO on Hg^sup 2+^ reduction, in effect, depended on reaction temperature and the yield rate of Cl and Cl^sub 2^ in the gas.

Figure 8. The effects of SO^sub 2^ and NO on HgCl^sub 2^ reduction at various setting temperatures (indicated by the thermocouple) of furnace. (black triangle up)) HgCl + 8% H2O + 2000 ppm SO^sub 2^; (diamonds)) HgCl^sub 2^; (D) HgCl^sub 2^ + 8% H2O + 600 ppm NO; (C) HgCl^sub 2^ + 8% H2O.

Mechanism Discussion

However, in Figures 3 and 6, the data apparently indicated that Hg oxidation and reduction were little changed by SO^sub 2^ without the participation of H2O. It is, therefore, speculated that the formed SO^sub 2^Cl and SO^sub 2^Cl^sub 2^ are capable of decomposing back to Cl and Cl^sub 2^ or have nearly an equal oxidizing property as Cl and Cl^sub 2^, respectively. Although individual H2O and SO^sub 2^ had negligible effects on Hg oxidation and reduction, the conjugation of H2O and SO^sub 2^ revealed pronounced impacts, which was highly consistent with that of reported.

It was noticed that both Niksa et al.19 and Qiu et al.20 addressed the concept that the OH radicals were eliminated when either SO^sub 2^ or NO was added into the gas blend. One might wonder why the elimination
of OH radicals has such a pronounced effect on Hg\(^{0}\) oxidation and Hg\(^{2+}\) reduction. As reflected in eqs 17 and 19, the formation of HOSO\(^{2-}\) and HONO implicitly confirms the consumption of OH radicals and implies that in effect the OH radicals resulted from H\(_2\)O in this study. Thus, when detailed elementary reactions for eqs 16-19 are specified, eqs 16-19 are still able to include the roles of NO and SO\(^{2-}\) in consuming OH radicals. In sharp contrast to the arguments by Qiu et al.20 where the key role of HOCl in Hg\(^{0}\) oxidation was emphasized, eqs 16-19 otherwise support the key roles of Cl and Cl\(^{2-}\) in oxidizing Hg\(^{0}\), which agreed well with the conclusion of Niksa et al.19 In particular, our results showed that SO\(^{2-}\) and NO, in the absence of H\(_2\)O, had a negligible inhibitory impact on Hg\(^{0}\) oxidation, which apparently did not support the key role of HOCl in this study, although HOCl is capable of oxidizing Hg\(^{0}\) as well. Therefore, the emphasis of OH consumption might lead researchers to focus more on the role of HOCl instead of Cl and Cl\(^{2-}\). Instead, eqs 16-19 allow us to concentrate on the concentrations and generation rate of atomic and molecular chlorine that are vital to Hg\(^{0}\) oxidation and Hg\(^{2+}\) reduction by hiding the consumption of OH. It should be specially noted that the formed HCl in eqs 16-19 had little oxidizing capability without the assistance of oxidizing reagents, such as O\(_2\)/O.15 In comparison with Cl\(^{2-}\), Laudal et al.23 found that the addition of Cl\(^{2-}\) (10 ppmv) decreased the amount of flue gas Hg\(^{0}\) by 31%, whereas the addition of HCl (50 ppm) only resulted in a decrease of 1%. In the verification test by the authors for the oxidation capability of HCl, the addition of 75 ppmv HCl in the presence of 6% O\(_2\) only caused an Hg\(^{0}\) decrease ~5%.

CONCLUSIONS

The primary objective of this study was to identify the inhibitory effects of SO\(^{2-}\) and NO in the simulated flue gas under homogeneous conditions. Although it was well recognized that the Cl atom recycle process plays a prominent role in Hg\(^{0}\) oxidation, data and mechanisms currently available do not yet elaborate the inhibition process of SO\(^{2-}\) and NO on Hg\(^{0}\) oxidation. The testing conducted here showed that neither SO\(^{2-}\) nor NO individually can substantially inhibit Hg\(^{0}\) oxidation and promote HgCl\(^{2-}\) reduction. However, in the presence of H\(_2\)O, SO\(^{2-}\) and NO exhibited pronounced differences. This difference can be characterized by the mechanism in which SO\(^{2-}\) and NO can largely scavenge atomic and molecular chlorine with the assistance of H\(_2\)O. The scavenging of available atomic and molecular chlorine led less Hg\(^{0}\) to be oxidized and, accordingly, more Hg\(^{2+}\) to be reduced. At low temperatures, the effects of SO\(^{2-}\) and NO on Hg\(^{0}\) oxidation were greatly reduced, indicating that such effects are temperature dependent and can be alleviated by lowering temperature.

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DISCLAIMER

This paper has not been subjected to EPA's required peer and policy review and, therefore, does not necessarily reflect the views of EPA, and no official endorsement should be inferred.

IMPLICATIONS

Coal-fired utility boilers are the primary stationary sources of anthropogenic Hg emissions, accounting for ~48 t or 30% of total U.S. emissions annually. In developing Hg emission control technology, if Hg control is to be met by taking advantage of "cobenefit" multipollutant control technologies, such as wet scrubbers, effective methods to transform Hg\(^{0}\) to water-soluble Hg\(^{2+}\) must be developed. One of the proposed ways is to add Cl-containing reagents. However, the fundamental data as to how the flue gas constituents, such as SO\(^{2-}\) and NO, affect Hg\(^{0}\) oxidations are yet not adequate. This research, therefore, was intended to develop a mechanism to elucidate and interpret the interactions among SO\(^{2-}\), NO, and Cl-containing species.
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