Fundamentals of Mercury Oxidation in Flue Gas

Final Report

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ABSTRACT

The objective of this project was to understand the importance of and the contribution of gas-phase and solid-phase coal constituents in the mercury oxidation reactions. The project involved both experimental and modeling efforts. The team was comprised of the University of Utah, Reaction Engineering International, and the University of Connecticut. The objective was to determine the experimental parameters of importance in the homogeneous and heterogeneous oxidation reactions; validate models; and, improve existing models. Parameters studied include HCl, NO_x, and SO₂ concentrations, ash constituents, and temperature.

The results suggested that homogeneous mercury oxidation is below 10% which is not consistent with previous data of others and work which was completed early in this research program. Previous data showed oxidation above 10% and up to 100%. However, the previous data are suspect due to apparent oxidation occurring within the sampling system where hypochlorite ion forms in the KCl impinger, which in turn oxidized mercury. Initial tests with entrained iron oxide particles injected into a flame reactor suggest that iron present on fly ash particle surfaces can promote heterogeneous oxidation of mercury in the presence of HCl under entrained flow conditions.

Using the data generated above, with homogeneous reactions accounting for less than 10% of the oxidation, comparisons were made to pilot- and full-scale data. The results suggest that heterogeneous reactions, as with the case of iron oxide, and adsorption on solid carbon must be taking place in the full-scale system.

Modeling of mercury oxidation using parameters from the literature was conducted to further study the contribution of homogeneous pathways to Hg oxidation in coal combustion systems. Calculations from the literature used rate parameters developed in different studies, in some cases using transition state theory with a range of approaches and basis sets, and in other cases using empirical approaches. To address this, rate constants for the entire 8-step homogeneous Hg oxidation sequence were developed using an internally consistent transition state approach. These rate constants when combined with the appropriate sub-mechanisms produced lower estimates of the overall extent of homogeneous oxidation, further suggesting that heterogeneous pathways play an important role in Hg oxidation in coal-fired systems.

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INTRODUCTION

The objective of this project was to understand the importance and contribution of gas-phase and solid-phase constituents in the reactions of mercury oxidation. Included in the investigation were the effects of chlorine concentrations, NO_x concentration, SO₂ concentration, and reactions with ash constituents. It is well-known that a wet flue gas desulphurization system can remove most of the oxidized gaseous mercury in a coal-fired power plant. In addition, oxidized mercury is more likely to adsorb on fly ash, and, hence, be removed by the particulate control device, or be adsorbed by activated carbon. This removal uses existing equipment and requires no additives, making it a low-cost option. However, elemental mercury cannot be removed effectively using these methods. By understanding the important mechanisms in mercury oxidation, a greater fraction of the Hg could be captured using “back end” technology.

The project team included the University of Utah, Reaction Engineering International, and the University of Connecticut. The team collaborated on an experimental and modeling effort that involved determination of experimental parameters, validation of a mercury oxidation model, and improvement of rate constants used in homogeneous oxidation models.

Three tasks were completed:

Task 1.0 – Experimental Investigation of Mercury Chemistry

The University of Utah performed natural gas experiments in a mercury reactor. The experiments utilized “doped” constituents to investigate the importance of these constituents in the homogeneous mercury oxidation mechanism. Gas (HCl, NO_x, and SO₂) constituents were investigated. The University of Connecticut also performed a small set of experiments investigating the influence of heterogeneous chemistry on mercury oxidation. These were performed in a flame-based entrained flow reactor.

Task 2.0 – Model Validation

REI and UConn used existing versions of mercury oxidation models to predict the oxidation of mercury. These models were, in turn, improved as validation data obtained in Task 1.0 suggested that the existing mechanisms were not correct and over predicted the extent of mercury oxidation. UConn then developed an internally consistent set of rate constants for the accepted 8-step homogeneous Hg oxidation submodel using transition state theory.

Task 3.0 – Evaluation of Control Strategies

The effectiveness of mercury control strategies varies depending on the speciation of mercury in the flue gas. As a result of the experimental and model validation activities, the speciation of mercury in flue gas for a range of coal types and conditions was predicted. This information is useful for recommending modifications to existing control strategies or to suggest new control strategies.

EXPERIMENTAL METHODS

University of Utah - Mercury Reactor Furnace and Mercury Analyzer

The mercury reactor used in this study is shown in Figure 1. The reactor has been fitted with a natural gas, premixed burner. In these experiments all reactants are introduced through the burner and pass through the flame. The details of the quartz reactor are given in [1]. A 50-mm OD by 47-mm ID quartz reaction tube, 127 cm in length runs through the center of a high temperature Thermcraft heater. The section below the heater is temperature-controlled using heating tape and insulation. This control allows for investigation of different quench rates. The important aspect of this reactor is that the chlorine and mercury are introduced into the burner, allowing radical formation as would occur in a coal-fired plant. The burner is designed to operate at approximately 1,000 BTU/hr, producing 6 SLPM of combustion gas.

A sample of flue gas is withdrawn from the bottom of the reactor and enters the sample-conditioning system, designed by Southern Research Institute (SRI). In this system the sample gas is pulled in two streams directly from the last section of the quartz reaction tube into a set of conditioning impingers. One stream is bubbled through a solution of stannous chloride to reduce oxidized mercury species to elemental mercury. The stream then contacts a solution of sodium hydroxide to remove acid gases. This stream represents the total mercury concentration in the reactor. The second stream is first treated with a solution of potassium chloride to remove oxidized mercury species and then is also treated in a caustic solution for acid gas removal. This stream is representative of the elemental mercury concentration in the reactor. Oxidized mercury species are represented by the difference between total and elemental mercury concentrations. Water is removed from the sample gas by a chiller and then each stream is intermittently sent to the analyzer by a valve box connected to the analyzer. Analysis is performed using a Tekran 2537A mercury vapor analyzer. Studies were performed using this system; in certain experiments, $\text{Na}_2\text{S}_2\text{O}_3$ was added to the potassium chloride impinger. Studies by others [2, 3] and this group [4] have shown that a significant portion of the oxidation seen in many experiments is really a result of oxidation in the impingers. This is discussed further below. Figure 2 illustrates a simplified version of the sampling condition system. The PS Analytical Mercury Calibration Gas Generator, or “CavKit”, was used to generate the vapor mercury stream.

Two temperature profiles, illustrated in Figure 3, were studied. The quench rates are representative of power plant post-combustion conditions. The low temperature region represents flue gas temperatures at the air preheater inlet.

Figure 1. Schematic of Mercury Reactor at the University of Utah

Figure 2. Sampling condition system

Figure 3. Temperature profiles in the reactor.

University of Connecticut – Entrained Flow Reactor and Analysis

The experimental system of Mamani-Paco and Helble [5] and Sterling et al. [6] was used for conducting heterogeneous Hg oxidation experiments in the presence of iron oxide particles. A schematic diagram of the experimental system is shown in Figure 4. The system is described in detail in the above-mentioned references and only a brief description is presented here.

A multi-element micro-diffusion flat-flame burner was used to generate the simulated flue gas by burning CH_4 in O_2 and by using N_2 as diluent. A 16cm $L \times 17\text{cm } W \times 21\text{cm } H$ stainless steel mixing chamber internally coated with ceramic furnace cement was placed directly on top of the flat-flame burner. There were a total of six ports of 6.35 mm diameter each located on the mixing chamber, each designed for introduction of dopants into the burner-generated flue gas stream. The simulated flue gases exited the mixing chamber through an outlet approximately 13 cm in diameter which diverted flue gases from the vertically-upward fired burner into a circular cross section quartz reactor in the horizontal position. Ports 1 and 3 located at the rear of the mixing chamber were used for the introduction of HCl gas and Hg laden N_2 gas respectively. Port 5 located at the side of the mixing chamber was used to introduce Fe_2O_3 laden N_2 gas into the simulated flue gas stream.

The flue gases exiting the mixing chamber flowed into a quartz reactor, approximately 80 cm long and 12.7 cm in diameter. The quartz reactor was placed 5–8 cm inside the mixing chamber and the quartz reactor–mixing chamber junction was sealed with furnace cement. The reactor was mounted at an angle of 5–10 degrees below horizontal to prevent the accumulation of condensed water. Electrical resistance heating tapes and insulation tapes were wrapped around the reactor to provide additional heating and to reduce heat losses to the environment. There were three 36/28 ball and socket ports for sampling the reacting gas and these ports were located at approximately 20 cm from each other and from the ends of the reactor. Sample port 2 (SP2) was used for flue gas sampling throughout this work because it provided a post-combustion thermal history representative of coal-fired power plants. The length of the reactor till SP2 was approximately 35 cm.

To provide a uniform mercury concentration in the simulated flue gas, a mercury permeation tube manufactured by VICI™ Metronics was used. The mercury permeation tube was housed in a glass U-tube placed in a bath solution containing a water (80%) –antifreeze (20%) mixture, which was maintained at a fixed temperature of 95 °C. A Fischer Isotemp temperature controlled immersion heater and stirrer was used to maintain the bath temperature. The permeation tube had a manufacturer specified mercury vaporization rate of 3100 ng/min at 100°C. Nitrogen gas at a flow rate of 0.75 slpm was used as the carrier gas to introduce Hg from the U-tube into the simulated flue gas stream. N_2/Hg gas stream from the U-tube was connected to the mixing chamber port 2 using stainless steel tubing, which was maintained at 90°C using heating tapes.

A 300 ml perfluoroalkoxy polymer threaded fluid transfer vessel with an outside diameter of 95 mm was purchased from Savillex™ Corporation for entraining iron oxide particles and injecting them into the flue gas. The vessel consisted of a threaded closure at the top with two 6.35 mm diameter ports. The first port was connected to N_2 gas and the second port was connected to the

mixing chamber. Industrial nanoarc α -Fe₂O₃ powder purchased from AlfaAesar™ with a manufacturer specified size and surface area range between 20- 50 nm and 30-60 m²/g, respectively, was used. Average particle loading was calculated by dividing loss of weight of the Fe₂O₃ transfer vessel by the time duration of particle injection experiments. The initial amount of iron oxide placed in the transfer vessel was typically 20 g and the maximum amount entrained in any experiment did not exceed 5 g.

Flue gases were sampled from sample port 2 (SP2) of the quartz reactor using a quartz sampling probe. The sample probe was connected to a self regulating heating line (SRHL). The SRHL core was made of Teflon tubing with an outside diameter of 6.35 mm wrapped in a heating cable with a temperature controller that was used to maintain average surface temperature of the tubing at approximately 127°C to prevent condensation of mercury and/or moisture on the tube surface. From the SRHL, the sample gases flowed through a quartz fiber filter enclosed in a miniature temperature- controlled oven maintained at 150°C. From the filter assembly, the sample gas was transported by another SRHL to a cryotherm. The cryotherm consisted of glass impingers through which sample flue gas flowed on the inside while on the outside, cold water (less than 5°C) was circulated to condense moisture from flue gas. The condensate was continuously removed using a peristaltic pump connected to the bottom of the impingers. The particle- and moisture-free sample gas was then analyzed for its mercury concentration using a Semtech™ 2010 continuous Hg monitor. The Semtech Hg analyzer continuously recorded elemental mercury (Hg⁰_(g)) concentrations from the sample gas, which was regulated at a flow rate of 4 slpm. The Hg analyzer is a Zeeman modulated atomic absorption spectrometer that measures Hg⁰ concentration by measuring the atomic absorption of Hg⁰ at the resonance line of 253.7 nm. If mercury is oxidized in the experiments there is a decrease in the elemental Hg concentration measured by the analyzer, which corresponds to the level of oxidized mercury. The difference between initial mercury concentration and mercury concentration of the sample gas is taken as the concentration of oxidized mercury. The extent of mercury oxidation expressed as a percentage is:

$$\% \text{ Hg oxidation} = 100 \frac{C_{\text{Hg}^0}^{\text{Initial}} - C_{\text{Hg}^0}^{\text{Sample}}}{C_{\text{Hg}^0}^{\text{Initial}}}$$

where C_{Hg^0} is the concentration of Hg⁰.

The temperature profile in the reactor is shown in Figure 5.

Figure 4. Experimental system for entrained flow studies.

Figure 5. Temperature profile within the reactor.

EXPERIMENTAL RESULTS and DISCUSSION

Homogeneous Oxidation – University of Utah Results

The initial studies during this study focused on the homogeneous oxidation of mercury. The high temperature of the flame should result in most of the chlorine becoming HCl in the flame, though some Cl₂ will form via recombination of Cl radicals at low, post-flame temperatures. The published results from these experiments are shown in Figure 6 [1]. As seen in this figure, modeling was able to predict the data taken with a quench rate of 440 K/s in the absence of SO₂, but the apparent inhibition of oxidation by SO₂ that is shown was not predicted by modeling. This suggested that there might be errors in the measured extents of homogeneous oxidation and/or the kinetic model for gas-phase oxidation of mercury. In this work, we examined the possibility that Cl₂ in the flue gas might bias mercury speciation by oxidizing some of the elemental mercury in the KCl impinger, similar to the bias previously reported for the Ontario Hydro method [3] and discussed above. Small amounts of Cl₂ in the KCl impinger can oxidize mercury in aqueous solutions via the hypochlorite ion according to:

Sodium thiosulfate (Na₂S₂O₃) can prevent this mercury oxidation by reducing the hypochlorite ion before it can react with the elemental mercury. Several experiments were performed in which a small concentration of Cl₂ was added to the gas at the inlet to the KCl impinger to observe the effects of the hypochlorite ion in solution.

ChemKin 4 was used as a modeling platform along with a core kinetic mechanism developed by Niksa, Helble, and coworkers [7] with the chlorine chemistry of Roessler et al. [8, 9] to predict the concentrations of Cl₂ present in the flue gas as it enters the impingers, using the time-temperature history in the furnace as previously reported. In Roessler's model, the Cl₂ is formed from the recombination of chlorine radicals within the reactor. Predictions suggested a concentration of less than 10 ppmv Cl₂ at the end of the reactor for the equivalent HCl concentrations used in previous experimentation up to 500 ppmv. This concentration was much lower than those previously investigated for interference by hypochlorite ion.

Experiments were performed to determine if these low Cl₂ concentrations entering the KCl impinger could cause the strong mercury oxidation as had been observed in previous experimentation. A small flow of Cl₂ calibration gas (between 0.3 SLPM and 1.5 SLPM of 6000 ppmv Cl₂ in air) was injected into the reactor flue gas directly before entering the impingers. Injecting less than 10 ppm Cl₂ directly into the impingers with the reactor flue gas (440 K/s) yielded significant oxidation, as shown in Figure 7. The addition of 0.5 weight % Na₂S₂O₃ to the KCl impinger completely inhibited the oxidation. Increasing the Na₂S₂O₃ concentration in the KCl impinger also had no effect indicating 0.5 wt% was sufficient to eliminate all impinger oxidation.

Additional experiments demonstrated that Na₂S₂O₃ did not hinder the KCl solution's ability to capture oxidized mercury species. A HgCl₂ permeation tube was used to introduce only oxidized mercury into the KCl solution to show that all of the Hg²⁺ would be retained in solution with and

without $\text{Na}_2\text{S}_2\text{O}_3$ present. Adding sodium thiosulfate to the KCl impinger did not alter the capture of oxidized mercury. A HgCl_2 permeation tube experiment was repeated while introducing NO and SO_2 . These species did not affect the KCl / $\text{Na}_2\text{S}_2\text{O}_3$ solution's ability to capture oxidized mercury.

While there appears to be some homogeneous oxidation, it is clearly not at levels previously suggested [1]. These high levels are likely caused by a combination of oxidation via Cl_2 in the KCl impinger and oxidation in the gas phase. Sodium thiosulfate, when added to the KCl impinger prevents this oxidation without altering the ability of the impinger to capture and retain mercuric chloride.

This conclusion brought into question the validity of the model used by Fry et al. [1]. The apparent inhibition of oxidation by SO_2 seen in Figure 6 is also an effect of impinger chemistry as SO_2 behaves similarly to $\text{Na}_2\text{S}_2\text{O}_3$ in removing hypochlorite ion [2, 3]. The low oxidation values in the presence of SO_2 may in fact be closer to actual extents of homogenous oxidation. It was clear a new model was needed to predict these lower oxidation rates. This is discussed further below.

To determine the amount of homogeneous mercury oxidation occurring in the reactor, the previous experiments were repeated using a 10% KCl, 0.5% $\text{Na}_2\text{S}_2\text{O}_3$ impinger solution. Both the 440 K/s and 210 K/s quench rates were investigated. The measured homogeneous mercury oxidation levels ranged from 2 to 8% at reactor chlorine levels of 100 to 500 ppmv (as HCl). The results of these experiments using the 440 K/s quench rate are shown in Figure 8 along with the initial experimental data of Fry et al. [1] at the same quench rate. It can be seen that the previous experiments without $\text{Na}_2\text{S}_2\text{O}_3$ doping of the KCl impinger showed drastically higher extents of homogenous oxidation. The previous experiments conducted with SO_2 show low levels of Hg oxidation that are much closer to those observed here using the doped impinger solutions. SO_2 does not inhibit gas phase oxidation, but behaves similarly to $\text{Na}_2\text{S}_2\text{O}_3$ in preventing oxidation of Hg^0 in the impinger. At reactor chlorine concentrations above 400 ppmv (as HCl), 300 ppmv SO_2 is not sufficient to completely prevent impinger oxidation.

Figure 6. Initial experiments demonstrated significant homogeneous oxidation, dependent on chlorine concentration. SO_2 appeared to inhibit oxidation and this effect was not predicted by modeling.

Figure 7. Measured oxidation of Hg as a function of inlet Cl₂ concentration in flue gas, with and without the addition of 0.5% sodium thiosulfate to the KCl impinger. Measured oxidation of mercury as a function of inlet Cl₂ concentration in flue gas, with and without the addition of 0.5% sodium thiosulfate to the KCl impinger.

Figure 8. Measured Hg oxidation as a function of total chlorine, comparison of previous data with that collected using the modified conditioning system. Error bars are the average of multiple experiments.

Heterogeneous Oxidation – UConn Results

The effect of Fe_2O_3 particle injection on Hg oxidation under entrained flow conditions was examined by UConn investigators. Only a limited set of homogeneous Hg oxidation experiments were conducted with HCl as the chlorine species. These experiments were aimed at establishing baseline levels of Hg oxidation by gas phase species prior to evaluating the effect of particle injection. Four flue gas HCl concentrations of 200, 300, 400, and 555 ppmv were evaluated. A total of seven homogeneous Hg oxidation tests at different HCl concentrations were performed. At all four flue gas HCl concentrations, insignificant extents of Hg oxidation were observed. The extent of homogeneous Hg oxidation ranged between 3.5% (200 ppm HCl) and 5.5%, and this latter value was observed at a flue gas HCl concentration of 300 ppmv. At 400 and 555 ppmv HCl concentrations, the extent of Hg oxidation was 5.2 and 4.2%, respectively.

The results of homogeneous Hg oxidation experiments presented above are significantly different than those reported previously by Sterling et al. [6] for experiments conducted using the same experimental set-up but at a different location. Sterling reported that as flue gas HCl concentration was varied from 100 to 300 ppmv at an equivalence ratio of 0.90, the extent of homogeneous Hg oxidation increased from 8 to 43%. The only major difference between the two experiments is that the temperatures measured in this study were higher than those reported by Sterling et al. Specifically, the measured temperature at the HCl injection port in this study was 120°C greater than that reported by Sterling (1021 v. ~900°C). It is expected that at a higher temperature (as observed in this study), a greater fraction of HCl would dissociate to generate more Cl atoms thereby resulting in (relatively) greater Hg oxidation. It is also possible that in the Sterling experiments, the mixing chamber and quartz reactor surfaces were contributing to heterogeneous Hg oxidation and this contribution was lost at the higher temperature. The differences in these experimental results are therefore difficult to explain; however, the lower oxidation results are consistent with those from the University of Utah homogeneous experiments (discussed above).

After establishing the baseline levels of homogeneous Hg oxidation, particle injection studies were conducted to evaluate the effect of entrained Fe_2O_3 particles on Hg oxidation. Uniform particle loading was not achieved in these experiments and the results are therefore reported at the measured particle loading for the different experiments expressed as a surface-to-volume ratio of Fe_2O_3 surface area to flue gas volumetric flow rate.

Mercury (Hg^0) concentration measurements from the SEMTECH™ 2010 continuous Hg monitor for a typical particle injection experiment is presented in Figure 8. The experiments evaluated the effect of particle injection at a flue gas HCl concentration of 555 ppm on Hg oxidation. Fe_2O_3 particle loading was approximately 0.14 g/min over an approximately 9.7 min duration experiment. The particle surface-to-flue gas volume ratio for these experiments was 123.3 m^2/Nm^3 . This amount is several orders of magnitude greater than might be expected in a full-scale system.

Figure 9 shows that the initial flue gas Hg concentration was 52.2 $\mu\text{g}/\text{dry Nm}^3$ and this concentration dropped marginally to approximately 50 $\mu\text{g}/\text{dry Nm}^3$ in the presence of 555 ppm HCl thereby resulting in 4.2% Hg oxidation. From the point of Fe_2O_3 injection (~ 1120 s), the

concentration of Hg continuously decreases to a steady value representing 66% Hg oxidation. HCl at a flue gas concentration of 555 ppm was continuously supplied during the time of particle injection. When particle injection alone was turned off, the level of Hg oxidation did not appreciably decrease in any of the experiments. This was because a significant portion of the injected particles deposited on the sides of the mixing chamber and the quartz reactor thereby providing a continuous presence of high surface area material in the reaction environment. It was therefore necessary to clean the surfaces of mixing chamber and quartz reactor subsequent to each particle injection experiment. When HCl was turned off (~ 1760 s), the level of Hg oxidation decreased (35.7% v. 66%) but the flue gas Hg concentration did not reach the levels prior to Fe_2O_3 injection. This is also attributed to the presence of chlorinated sites on the deposited iron oxide on the surface of the mixing chamber and the quartz reactor. This behavior was observed in all particle injection experiments.

It is conceivable that an extended period of HCl addition would saturate the deposited iron oxide sites with chlorine and subsequently turning off the HCl may not result in a decrease in the extent of Hg oxidation. Limited experiments with only Fe_2O_3 (without HCl) resulted in negligible Hg oxidation implying that oxidizing species such as HCl are needed in addition to surfaces and an oxygen-rich environment for any Hg oxidation.

The results of the particle injection experiments are summarized in Figure 10. It must be noted that the heterogeneous experiments are single measurements only because, as mentioned before, the particle loading was not replicated in the different experiments. The figure shows the extent of Hg oxidation at different flue gas HCl concentrations and Fe_2O_3 loading. The Hg oxidation during particle injection experiments as shown in Figure 10 indicates the baseline Hg oxidation level (i.e. Hg oxidation in the presence of HCl gas alone) plus oxidation in the presence of both iron oxide and HCl.

Figure 10 indicates that the baseline homogeneous Hg oxidation was less than approximately 5% at all HCl concentrations examined. The extent of Hg oxidation correlated linearly with S/V ratio and HCl concentration at all experimental data points except at an S/V ratio of $92.5 \text{ m}^2 \text{ Fe}_2\text{O}_3/\text{m}^3$ flue gas at an HCl concentration of 300 ppm. The measured Hg oxidation at these latter conditions (18.1%) was significantly lower than the oxidation at 200 ppm HCl concentration at an S/V ratio of $26.4 \text{ m}^2/\text{m}^3$ (27%).

The extent of Hg oxidation at 400 ppm HCl concentration and $622 \text{ m}^2/\text{m}^3$ was significantly greater than at 555 ppm HCl concentration at $123.3 \text{ m}^2/\text{m}^3$ (88.4% v. 66%) indicating that with an increase in surface area, a lower level of HCl is required for achieving the same level of Hg oxidation. This was also observed in the results of Hg oxidation at S/V ratios of 26.4, 92.5 and $354.2 \text{ m}^2/\text{m}^3$ presented in Figure 18. The extent of Hg oxidation at the latter two S/V ratios increased by a factor of approximately two to three when the HCl concentration was increased from a range of 200 to 300 to a range of 300 to 400 ppm. In contrast, when the HCl concentration was increased from 200 to 555 ppm, the extent of Hg oxidation increased by a factor of 1.75 at the lowest S/V ratio of $26.4 \text{ m}^2/\text{m}^3$. Saturation in the extent of Hg oxidation with increase in S/V ratio was not observed for the particle loadings examined in this study.

Figure 9. Time-resolved Hg concentration measurement for Fe_2O_3 injection experiments.

Figure 10. Measured extent of Hg oxidation (%) as functions of particle surface area to flue gas volume and flue gas HCl concentration.

MODELING RESULTS

Preliminary Modeling and Full-Scale Predictions – REI

The gas-phase experimental data from the University of Utah was used to find kinetic parameters for a suggested mercury-chlorine reaction mechanism. All calculations were done with REKS (Reaction Engineering Kinetic Solver) which is a detailed chemical kinetic solver similar to ChemKin. The time-temperature profiles used in this study are shown in Figure 3. The two reactions being investigated are:

Reactions 1 and 2 were selected because they have been previously found to be the main reaction pathway for mercury oxidation by chlorine. A set of parameters found to fit the experimental data is shown in Table 1.

Table 1. Fitted parameters for Hg-Cl reactions.

Reaction	A (cm ³ /mol-s) ^a	E(cal/mol)
Hg+Cl+M=HgCl+M	2.19E14	-1200
HgCl+Cl ₂ =HgCl ₂ +Cl	2.47E10	-1000

The experimental data (previously shown in Figure 8) and the model predictions using the fitted parameters are shown in Figure 11. The model, using these two fitted rate constants, does a good job of predicting the data obtained at the high quench rate, but the model does not predict the low quench data well. The model suggests that there should be an effect of quench rate that was not observed in the data. However, the observed oxidation of Hg was small, with either quench rate. There may be more uncertainty in the experimental results than was quantified in the error bars.

From data on mercury speciation collected from full-scale coal-fired power plants, it has been shown that halogens in coal affect mercury speciation, as well as removal, in APCDs [10]. Many sets of full-scale validation data were assembled from published reports from work sponsored by DOE NETL and EPRI.; each data set contained boiler descriptions, fuel compositions, and Ontario Hydro Measurement (OHM) mercury speciation data. A subset of this database consisting of data from 19 boilers (Table 2) can be used to look at general trends in mercury speciation in coal-fired boilers.

From the full-scale data sets, it is apparent that a significant amount of mercury oxidation can take place in the boiler, from the flame to the outlet of the air preheater, as shown in Figure 12 in which the measured Hg speciation (as %Hg⁰) at the air heater outlet is displayed as a function of equivalent HCl in the flue gas (based on the coal chlorine content). Generally, there is more elemental mercury present in the flue gas when the concentration of HCl in the flue gas is lower; however, there are other confounding factors, such as the level of unburned carbon in the fly ash, which affect mercury speciation. Boilers with SCRs, which are known to oxidize mercury, are not included in the data in Figure 12.

Table 2. Description of full-scale Hg speciation data sets.

Boiler	Combustion system	Avg MW	Boiler	Combustion system	Avg MW
<i>Bituminous-fired boilers:</i>			<i>Subbituminous-fired boilers:</i>		
BP1	Tangential	238	HA	Wall	116
C4(U1)	Wall	459	HL	Wall	360
C5(U2)	Wall	1,315	S1	Cyclone	547
C6 (no SCR)	Wall	512	S9(U1)	Wall	617
C7 (no SCR)	Tangential	546	<i>Lignite-fired boilers:</i>		
S2	Wall	1,352	CC	Tangential	589
S5(U1)	Wall	660	MRY	Cyclone	448
Y1	Tangential	106	<i>Lignite/Subbituminous-fired boilers:</i>		
<i>Subbit./Bituminous-fired boilers:</i>			MO	Wall	840
S8(U2)	Wall	680	<i>Subbituminous-fired boilers with ACI:</i>		
<i>Bituminous-fired boilers with ACI:</i>			HL	Wall	360
BP	Tangential	245	PP	Wall	619

Thus, both full-scale power plant data and the laboratory data show that increasing chlorine in the flue gas resulted in increased mercury oxidation. The laboratory data represent only the result of homogeneous oxidation, whereas the full-scale data represent the influence of both homogeneous and heterogeneous data. In order to provide some insight into the relative effect of the two oxidation pathways in coal combustion systems, the full kinetic model was used to calculate homogeneous mercury oxidation in a pilot-scale coal combustor. Southern Research Institute (SoRI) has published data for mercury speciation in a 1 MW pilot scale coal-fired facility in which two bituminous coals were burned [11]. The SoRI testing was carried out with two different US bituminous coals, Galatia (high chlorine) and Blacksville (low chlorine). Table 3 gives the details of the two coals. Unburned carbon (UBC) in fly ash was varied by changing the furnace exit oxygen (FEO). Table 4 summarizes the test conditions.

Table 3. SoRI Coal Ultimate Analysis [11].

	Blacksville	Galatia
C	77.24%	72.94%
H	4.67%	4.58%
O	5.83%	7.80%
N	1.85%	1.68%
S	0.87%	1.31%
Ash	8.05%	6.59%
Moisture	1.49%	5.10%
Cl	0.084%	0.44%
Hg, $\mu\text{g/g}$	0.078	0.107

Table 4. Experimental Conditions for SoRI Tests [11].

	run 1	run 2	run 3	run 4	run 5
Quench Rate, F/s	922	938	1139	1157	899
Coal	Galatia	Blacksville	Blacksville	Blacksville	Blacksville
%UBC	0.34	0.57	0.35	7.32	7.71
%LOI	1.7	1.9	1.9	9.8	9.8
%FEO	5	5	5	2.5	2.5
%OFA	0	0	0	15	15
SR	1.33	1.33	1.33	1.14	1.14
Gas Composition*					
N ₂ , vol%	73.93%	74.43%	74.43%	74.07%	74.45%
CO ₂ , vol%	12.76%	12.82%	12.82%	14.87%	14.86%
H ₂ O, vol%	8.37%	7.81%	7.81%	8.59%	8.59%
O ₂ , vol%	4.86%	4.89%	4.89%	2.41%	2.41%
SO ₂ , ppm	858	541	541	631	631
NO, ppm	620	564	581	218	228
HCl, ppm	247.5	46.5	46.5	54.3	54.3
Hg, ppb	1.06	0.76	0.76	0.89	0.89

*Calculated from coal analysis and SR, except for measured NO.

The overall temperature profiles for these experiments at the pilot-scale facility are plotted in Figure 13. These profiles are based on those found in Appendix G of SoRI's Biennial Report [11]. In the experiments, the cooling rate in the heat exchanger was varied. This is the portion of the flue gas path that corresponds to the air preheater in a full-scale combustor. Sample locations are indicated in Figure 13. The first sample point was located at the end of the quench section. Temperatures at this point ranged from 351 to 550 °F. The second sample point was downstream from the quench section.

REKS calculations were carried out for experimental conditions corresponding to SoRI's runs 1 to 5. These calculations included a minor amount of bromine in the fuel (equivalent to less than 2 ppm HBr in the gas). At these levels of HBr, bromine is not the major oxidant for mercury, but might contribute to the overall oxidation of mercury in a minor way. The kinetics of mercury oxidation by bromine are the subject of another UCR program and will not be discussed here.

The profiles in the Biennial Report began at 1830 °F. A section (taken from SoRI's standard temperature profile) was added to the beginning of the profile to model upstream locations in the SoRI furnace in order to match the times with the temperatures reported by SoRI. It is important to note that although the times and temperatures of the profiles match the experimental results, the quench rates do not match those reported in the experimental conditions in Table 4. Low quench rates listed in Table 4 are about 900 °F/s, however, the temperature profiles for these cases have a quench rate of 630 °F/s. Likewise, the high quench rates in Table 4 are about 1150 °F/s, while the temperature profiles have quench rates of about 750 °F/s.

Figure 14 presents the SoRI experimental results on mercury speciation at the final sampling point. Decreasing the halogens in the coal caused an increase in the amount of elemental mercury at the final sampling point. There was less oxidation, and, therefore, more elemental

mercury in the flue gas for the lower chlorine Blacksville coal. At the lower quench rate, there was more mercury oxidation (or less elemental mercury at the sampling point). This was observed for both low and high levels of UBC in the fly ash. Increasing the UBC from about 0.4% to about 7% promoted Hg oxidation (less elemental mercury at the sample point). Thus, both the halogens in the coal and the amount of unburned carbon in ash affect mercury oxidation.

Comparison of the measured Hg speciation and the predicted speciation in Table 5 shows that the homogeneous model predicted about 1% oxidation for the higher chlorine Galatia coal (~250 ppm HCl in flue gas) and 0.3% oxidation for the lower chlorine Blacksville coal (~50 ppm HCl in flue gas). Based on the laboratory experimental results in Figure 11, little Hg oxidation would be expected to occur via the homogeneous pathways at these levels of HCl in the flue gas. A purely homogeneous model will not suffice to predict Hg oxidation in a coal combustion system with fly ash present. The observed effect of quench rate in the SoRI coal combustion data reaffirms the need for a kinetic model, but this kinetic model must include homogeneous and heterogeneous oxidation pathways.

Table 5. SoRI experimental results compared with homogeneous model predictions [11].

	Time, s	T, °F	Measured Hg(0) %	Calculated Hg(0) %
run 1	6.4	547	81	99.0
	8.18	325	54	98.9
run 2	6.7	535	66	99.8
	8.27	325	64	99.8
run 3	6.75	431	76	99.8
	8.4	318	74	99.8
run 4	6.98	351	83	99.7
	8.6	288	61	99.7
run 5	6.8	550	55	99.7
	8.3	328	42	99.6

Figure 11. Predicted Hg oxidation compared to measured Hg oxidation in UU laboratory experiments.

Figure 12. Mercury speciation at air preheater outlet from full-scale power plants, as a function of equivalent HCl concentration in flue gas.²

Figure 13. SoRI time-temperature history [11].

Figure 14. SoRI measured Hg speciation at final sampling point.

Development of Fundamental Rate Constants for Models – UConn

The long term goal (and a specific objective of this project) was to develop fundamentally-based rate constants using a theoretical framework. Development of an accurate homogeneous model that is based on a fundamental approach is important because even if purely homogeneous pathways contribute little to Hg oxidation, gas-solid interactions might generate Cl species and HgCl in the gas phase which might subsequently oxidize in the gas phase. Accurate rate constants for homogeneous Hg oxidation reactions would also enable the adjustment of surface reaction rates and identify additional gas-solid interaction reactions. It was, therefore, a focus of this work to determine rate constants for all eight Hg/Cl reactions described in the commonly employed homogeneous Hg oxidation model using theoretical methods derived from first principles and therefore that do not involve empirically adjusted parameters. Transition state theory was therefore used to develop the rate constants described in this section.

Transition state theory rate constants have been reported in the literature for several homogeneous Hg oxidation reactions of interest. These rate constants show significant deviation from each other and these differences are compared with the values calculated in this study later in this report. In addition, others have developed these constants based on available data. Table 6 illustrates some of the rate constants developed by Widmer et al. [12], Niksa et al. [7], Qiu et al. [13], and Wilcox et al. [14-16] for the eight main reactions for mercury chemistry.

Table 6. Development of Hg/Cl reaction rate constants in the different Hg oxidation models reported in literature.

Reactions	Widmer et al.	Niksa et al.	Qiu et al.	Wilcox et al.
R1 $\text{Hg} + \text{Cl} + \text{M} = \text{HgCl} + \text{M}$	emp.	emp.*	emp. (Niksa)	TST
R2 $\text{Hg} + \text{Cl}_2 = \text{HgCl} + \text{Cl}$	est.#	est.# (Widmer)	TST	TST
R3 $\text{Hg} + \text{HCl} = \text{HgCl} + \text{H}$	est.	est. (Widmer)	est. (Widmer)	TST
R4 $\text{Hg} + \text{HOCl} = \text{HgCl} + \text{OH}$	emp.	emp. (Widmer)	TST	TST
R5 $\text{HgCl} + \text{Cl} + \text{M} = \text{HgCl}_2 + \text{M}$	emp.	Collision limit	emp.	TST
R6 $\text{HgCl} + \text{Cl}_2 = \text{HgCl}_2 + \text{Cl}$	emp.	emp. (Widmer)	TST	-
R7 $\text{HgCl} + \text{HCl} = \text{HgCl}_2 + \text{H}$	emp.	TST (Sliger)	emp. (Widmer)	TST
R8 $\text{HgCl} + \text{HOCl} = \text{HgCl}_2 + \text{OH}$	emp.	emp. (Widmer)	emp. (Widmer)	-

est. - estimates based on analogous reactions of Pb

* emp. - empirical adjustments

Eyring[17] and Evans et al. [18] published the kinetic theory of rates for bimolecular reactions that is now referred to as conventional transition state theory (CTST). The mathematical form of the CTST reaction rate constant as a function of temperature is:

$$k(T) = L \frac{k_B T}{h} \times \frac{Q_{TS}}{Q_A Q_B} \times e^{-E_0 / k_B T} \quad \frac{cm^3}{mol \cdot s}$$

where L is statistical factor used to correct for molecular symmetry, h is Planck's constant, Q is the volumetric overall partition function (A , B : reactants; TS : transition state), and E_0 is the Activation energy.

In addition to bimolecular reactions, the 8-step Hg/Cl reaction mechanism includes three body collision reactions of the type $A + B (+M) = AB (+M)$, which are bimolecular in the forward direction but unimolecular in the reverse. According to Lindemann-Hinshelwood theory [19], the three body collisional recombination reaction is assumed to proceed by the following path:

where AB^* is the activated intermediate complex.

To determine TST rate constants for such reactions, two approaches can be used: (i) a conventional TST rate constant can be calculated for the bimolecular atom-atom recombination reaction with empirical fall-off parameters describing low pressure behavior, or (ii) a Rice-Ramsberger-Kassel-Marcus (RRKM [20]) rate constant can be calculated for the unimolecular dissociation with explicit consideration of pressure. At the high-pressure limit, the CTST and the RRKM rate constants are mathematically equivalent. Because utility coal combustion occurs at atmospheric pressure conditions, the RRKM method alone was used here to determine the TST rate constant for Hg/Cl reactions R1: $Hg + Cl + M = HgCl + M$ and R5: $HgCl + Cl + M = HgCl_2 + M$, as it is more reliable than the use of empirical fall-off parameters with a CTST rate constant to describe low pressure reactions.

The rate constants for the unimolecular collisional decomposition reactions (R1 and R5) were therefore calculated using the RRKM theory formulation [21] presented below:

$$k(T) = L \frac{Q_1^+}{h Q_1 Q_2} \frac{e^{-E_0 / k_B T}}{\int_{E^+=0}^{\infty} \frac{W(E^+) e^{-E^+ / k_B T}}{1 + k_a(E^*) / \beta_c Z_{LJ}[M]} \cdot dE^+}$$

where:

$$k_a = \frac{L Q_1^+ W(E^+)}{h Q_1 \rho(E^*)}$$

Q_1^+	Partition function for the rotation of reactant A ⁺
Q_1	Partition function for the rotation of reactant A
Q_2	Partition function for the active non-rotational modes of reactant A
$W(E^+)$	Sum of states
E^+	Total energy of a given transition state
E^*	Total non-fixed energy of the reactant
$P(E^*)$	Density of states
β_c	Collision efficiency
Z_{LJ}	Lennard-Jones collision frequency
$[M]$	Concentration of the bath gas

The superscripts ‘+’ and ‘*’ refer to the activated state and energized ground state species respectively. All the parameters in the RRKM formulation can be determined except the collision efficiency, which is an empirically fit parameter. Additional details are provided in the Krishnakumar thesis [22].

For all eight Hg/Cl reactions, the TST rate constants were determined only in one direction and the corresponding reverse rate constants were determined by using the equilibrium constant for the reaction.

To determine theoretical rate constants using transition state theory, an accurate description of the structure of the activated state complex and the associated properties such as energy are required. As these activated complexes and the associated properties are not experimentally observable, computational chemistry methods using quantum chemistry are used to determine the transition state for the reactions.

The electronic structure calculations based on quantum chemistry used for solving the Schrodinger wave equation (SWE) can be broadly classified into two classes: (i) semi-empirical and (ii) ab initio. Recently, a particular subset of semi-empirical methods employing calculations based on density functional theory (DFT) has gained prominence due to relatively low computational cost and high accuracy. Semi-empirical methods as the name suggests involve solving the SWE by using a set of available parameters for the system under investigation, typically the spectroscopic data. On the other hand, ab-initio methods, also called first principles methods, use only the laws of quantum chemistry along with physical constants such as Planck’s constant. Semi-empirical methods can provide accurate results for systems where reasonable parameter sets exist but therefore cannot be in general applied for all systems. In this project semi-empirical methods were not used with the exception of DFT, and otherwise only ab-initio methods were employed. *Gaussian 03W* software [23] was used to perform numerical computations seeking the solution of the Schrödinger’s wave equation through the various methods.

A total of six all-electron basis sets were examined for elements other than mercury (i.e. for Cl, O, and H). These were: 6-311++G(3df,3pd) [24], D95++(3df,3pd) [25], SHC[26], STO-3G* [27], MIDI! [28], and aug-cc-pVTZ [29]. Geometry optimization (i.e. energy minimization) calculations were performed for Cl₂, HCl and OH using the six basis sets mentioned above. Six calculation methods were used in conjunction with each of the six basis sets resulting in 36

individual calculations. The six methods used were: HF [29], MP2 [30], MP4 [31], B3LYP [32], QCISD [33], and QCISD(T) [34]. The SHC*, STO-3G* and MIDI! basis sets provided significantly higher energies than the other three basis sets, which were comparable to each other at the HF-SCF level of theory. These three basis sets were eliminated from further consideration based on the variation principle which stipulates that the wave function corresponding to the lowest HF-SCF expectation energy most closely approximates the exact electronic wave function. This criterion alone cannot be used for the selection of basis sets because the work in this study involves Hg/Cl atoms that have basis sets with pseudopotential. For such cases the variational principle is not applicable because the Hamiltonian itself is modified in basis sets with the inclusion of pseudopotential. Therefore, the calculated values of molecular geometry and vibrational frequency of Cl₂, HCl, and OH using the three remaining basis sets were compared with experimental values and with each other. The calculated values of bond length and vibration frequency for Cl₂, HCl and OH are presented in Tables 7, 8, and 9 respectively. The calculations are presented for combination of three basis sets: 6-311++G(3df,3pd), D95++(3df,3pd), and aug-cc-pVTZ with each of the six calculation methods mentioned above.

Table 7. Comparison of calculated values of equilibrium bond length (R_{eq}) and vibrational frequency (ω_e) of Cl₂ with experimental values. The boxed bold type represents the best agreement of the calculated values with the experimentally measured values.

Method	Basis Set	R_{eq} (Å)	error* (%)	ω_e (cm ⁻¹)	error* (%)
HF	6-311++G(3df,3pd)	1.9742	0.6	616.4	-10.1
	D95++(3df,3pd)	1.9739	0.7	620.4	-10.8
	aug-cc-pVTZ	1.9842	0.1	613.8	-9.7
MP2	6-311++G(3df,3pd)	1.9934	-0.3	565.0	-1.0
	D95++(3df,3pd)	1.9817	0.3	588.1	-5.1
	aug-cc-pVTZ	1.9986	-0.6	573.5	-2.5
MP4	6-311++G(3df,3pd)	2.0036	-0.8	549.2	1.9
	D95++(3df,3pd)	2.0002	-0.7	559.9	0.0
	aug-cc-pVTZ	2.0177	-1.5	545.3	2.6
B3LYP	6-311++G(3df,3pd)	2.0104	-1.2	540.6	3.4
	D95++(3df,3pd)	2.0104	-1.2	545.8	2.5
	aug-cc-pVTZ	2.024	-1.9	537.4	4.0
QCISD	6-311++G(3df,3pd)	1.9979	-0.5	561.5	-0.3
	D95++(3df,3pd)	1.9947	-0.4	571.8	-2.2
	aug-cc-pVTZ	2.0103	-1.2	559.3	0.1
QCISD(T)	6-311++G(3df,3pd)	2.0057	-0.9	545.2	2.6
	D95++(3df,3pd)	2.0026	-0.8	555.0	0.8
	aug-cc-pVTZ	2.0196	-1.6	541.7	3.2
Experimental		1.987		559.7	

*error (%) = (experimental–calculated)/experimental × 100

Table 8. Comparison of calculated values of equilibrium bond length (R_{eq}) and vibrational frequency (ω_e) of HCl with experimental values. The boxed bold type represents the best agreement of the calculated values with the experimentally measured values.

Method	Basis Set	R_{eq} (Å)	error* (%)	ω_e (cm ⁻¹)	error* (%)
HF	6-311++G(3df,3pd)	1.2647	0.8	3145.0	-5.2
	D95++(3df,3pd)	1.2662	0.7	3152.4	-5.4
	aug-cc-pVTZ	1.2674	0.6	3135.8	-4.8
MP2	6-311++G(3df,3pd)	1.2714	0.3	3061.1	-2.3
	D95++(3df,3pd)	1.2739	0.1	3063.2	-2.4
	aug-cc-pVTZ	1.2747	0.0	3044.2	-1.8
MP4	6-311++G(3df,3pd)	1.2755	-0.1	3013.1	-0.7
	D95++(3df,3pd)	1.2773	-0.2	3021.6	-1.0
	aug-cc-pVTZ	1.2783	-0.3	2999.8	-0.3
B3LYP	6-311++G(3df,3pd)	1.2808	-0.5	2943.9	1.6
	D95++(3df,3pd)	1.2825	-0.6	2948.7	1.4
	aug-cc-pVTZ	1.2837	-0.7	2935.3	1.9
QCISD	6-311++G(3df,3pd)	1.274	0.0	3025.3	-1.2
	D95++(3df,3pd)	1.2757	-0.1	3034.5	-1.5
	aug-cc-pVTZ	1.2768	-0.2	3012.6	-0.7
QCISD(T)	6-311++G(3df,3pd)	1.2762	-0.1	3002.7	-0.4
	D95++(3df,3pd)	1.278	-0.3	3011.0	-0.7
	aug-cc-pVTZ	1.279	-0.3	2989.9	0.0
Experimental		1.2746		2990.9	

*error (%) = (experimental–calculated)/experimental × 100

Table 9. Comparison of calculated values of equilibrium bond length (R_{eq}) and vibrational frequency (ω_e) of OH with experimental values. The boxed bold type represents the best agreement of the calculated values with the experimentally measured values.

Method	Basis Set	R_{eq} (Å)	error* (%)	ω_e (cm ⁻¹)	error* (%)
HF	6-311++G(3df,3pd)	0.9506	2.0	4044.1	-8.2
	D95++(3df,3pd)	0.9512	1.9	4041.6	-8.1
	aug-cc-pVTZ	0.9517	1.9	4031.8	-7.9
MP2	6-311++G(3df,3pd)	0.9664	0.3	3850.5	-3.0
	D95++(3df,3pd)	0.9623	0.8	3873.0	-3.6
	aug-cc-pVTZ	0.9694	0.0	3795.1	-1.5
MP4	6-311++G(3df,3pd)	0.9699	0.0	3787.0	-1.3
	D95++(3df,3pd)	0.9656	0.4	3821.4	-2.2
	aug-cc-pVTZ	0.9724	-0.3	3739.1	0.0
B3LYP	6-311++G(3df,3pd)	0.9742	-0.5	3714.2	0.6
	D95++(3df,3pd)	0.9743	-0.5	3727.5	0.3
	aug-cc-pVTZ	0.9753	-0.6	3695.1	1.1
QCISD	6-311++G(3df,3pd)	0.9683	0.1	3801.1	-1.7
	D95++(3df,3pd)	0.9652	0.5	3819.7	-2.2
	aug-cc-pVTZ	0.971	-0.1	3750.6	-0.3
QCISD(T)	6-311++G(3df,3pd)	0.9702	-0.1	3773.2	-0.9
	D95++(3df,3pd)	0.9665	0.3	3801.5	-1.7
	aug-cc-pVTZ	0.9732	-0.4	3719.5	0.5
Experimental		0.9697		3737.8	

*error (%) = (experimental–calculated)/experimental × 100

The comparisons in Tables 7-9 suggest that the three basis sets provided similar calculated values for molecular properties when using the same computational method.

As the emphasis here was to identify a suitable basis set to describe Cl, O and H species and not on comparing the accuracy of different methods and basis set combinations, it was concluded that the three selected basis sets provided similar results. D95++(3df,3pd) was preferred to the other two basis sets due to significant reduction in computational time especially relative to the aug-cc-pVTZ basis set. The D95++(3df,3pd) basis set was therefore used for describing Cl, O and H species for a majority of the work in this project. In limited cases where computational time was not a concern, the 6–311++G(3df,3pd) was also employed.

Several basis sets with pseudopotentials as-defined in the *Gaussian 03W* software were used for Hg: SDD[33], CEP-121G [34], LanL2DZ, LanL2MB [35, 36], MDF [37], and MHF. The LanL2MB basis set uses STO-3G basis functions for first row atoms whereas the LanL2DZ and

SDD basis sets use D95V basis functions. In the evaluation of Cl₂, OH and HCl molecules presented above, STO-3G was found to inadequately represent the molecular systems. In addition, the inclusion of polarization (3df,3pd) and diffuse functions (++) to the D95 basis set was essential to obtaining reasonably accurate values of calculated properties of the considered species.

Calculated molecular structure and reaction enthalpies were more accurate when Hg-specific and non-Hg-specific basis sets were used for the different elements. These results, presented in Table 10, were therefore used throughout this project.

Table 10. Comparison of calculated values of equilibrium bond length (R_{eq}), vibrational frequency (ω_e) of HgCl, and standard reaction enthalpy (ΔH°_{298}) of reaction R1 with the experimental values. D95++(3df,3pd) basis set was used for Cl. The boxed bold type represents the best agreement of the calculated values with the experimentally measured values.

Method	Basis Set for Hg	R_{eq} (Å)	error*	S.P.E. [#] (H)	ω_e (cm ⁻¹)	error*	ΔH°_{298} (kJ mol ⁻¹)	error*
HF	CEP-121G	2.4428	-0.9	-612.314	288.9	1.3	60.44	42.0
	LanL2MB	2.4568	-1.5	-500.878	287.6	1.7	64.29	38.3
	LanL2DZ	2.4483	-1.2	-500.884	290.4	0.7	79.57	23.7
	SDD	2.4349	-0.6	-612.013	283.9	3.0	55.52	46.7
MP2	CEP-121G	2.3991	0.9	-612.646	303.0	-3.5	102.18	2.0
	LanL2MB	2.4297	-0.4	-501.092	300.1	-2.6	164.45	-57.7
	LanL2DZ	2.4219	-0.1	-501.147	291.1	0.5	157.52	-51.1
	SDD	2.3887	1.3	-612.328	298.3	-1.9	128.14	-22.9
MP4	CEP-121G	2.4117	0.3	-612.678	292.8	-0.1	76.74	26.4
	LanL2MB	2.4415	-0.9	-501.12	287.6	1.7	41966.13	-40155.3
	LanL2DZ	2.438	-0.7	-501.183	279.8	4.4	122.45	-17.5
	SDD	2.4045	0.6	-612.363	285.5	2.4	102.23	1.9
B3LYP	CEP-121G	2.4951	-3.1	-613.99	244.4	16.5	85.51	18.0
	LanL2MB	2.5623	-5.9	-502.95	235.6	19.5	101.68	2.5
	LanL2DZ	2.5675	-6.1	-502.963	235.2	19.6	115.49	-10.8
	SDD	2.4909	-2.9	-613.74	234.0	20.0	83.80	19.6
QCISD	CEP-121G	2.4171	0.1	-612.667	290.3	0.8	67.36	35.4
	LanL2MB	2.4427	-0.9	-501.112	284.4	2.8	128.49	-23.3
	LanL2DZ	2.4422	-0.9	-501.172	277.4	5.2	113.42	-8.8
	SDD	2.4105	0.4	-612.351	282.9	3.3	92.81	11.0
QCISD(T)	CEP-121G	2.42	0.0	-612.679	288.0	1.6	75.16	27.9
	LanL2MB	2.4441	-1.0	-501.121	284.3	2.8	41858.91	-40052.4
	LanL2DZ	2.4467	-1.1	-501.185	274.9	6.1	122.58	-17.6
	SDD	2.4138	0.3	-612.364	280.6	4.1	101.01	3.1
Experimental		2.42		none	292.6		104.25	

*error (%) = (experimental–calculated)/experimental × 100; [#]S.P.E: Single point energy corrected for zero point and thermal energy in Hartrees (H). 1 H = 627.51 kcal mol⁻¹.

Based on these calculations, the basis sets LanL2DZ and LanL2MB were eliminated from further consideration because the calculated single point energies (S.P.E) for all the molecules were significantly higher than those calculated using other basis sets for all quantum computational methods. For the two remaining basis sets for Hg, the HgCl bond length was accurately predicted by all the method/basis set combinations with a relative error of less than 4%. The B3LYP method with the CEP-121G and SDD basis sets had the largest error and the other methods typically predicted the HgCl bond length within 1% relative error. The HgCl vibrational frequency was predicted with less than 4% relative error using all methods and basis set combinations except for the B3LYP method with either basis set. Three combinations: MP2/CEP-121G, MP4/SDD, and QCISD(T)/SDD provided calculated values within acceptable deviation of the measured values for all three parameters for which validation was performed. Preliminary calculations using the MP4 and QCISD(T) methods with the SDD basis set provided nearly identical transition structure properties and hence the rate constants calculated using these were also expected to provide identical results. To determine the transition state for reaction R1, two combinations of method and basis sets were therefore chosen: MP2/CEP-121G and QCISD(T)/SDD.

To determine the enthalpy of reactions R2–R4, the six methods considered herein were combined with the SDD and CEP-121G basis sets for Hg and the D95++(3df,3pd) basis set for Cl, O and H, resulting in 12 individual combinations. The computed standard reaction enthalpy for the three reactions was compared with the measured values (NIST). For reaction R2, the QCISD/CEP-121G combination resulted in excellent agreement with the measured reaction enthalpy (less than 0.2% relative error) and hence was selected to compute the transition state. Three methods with the SDD basis set provided reaction enthalpies for reaction R3 within a relative error of 3% and the best agreement was obtained using the QCISD(T) method. For reaction R4, B3LYP/CEP-121G, MP4/SDD and QCISD/SDD provided good comparisons with measured reaction enthalpy and the error for the QCISD(T)/SDD combination was the least (1.6% of the measured value). Based on these comparisons, the QCISD/CEP-121G, QCISD(T)/SDD, and QCISD(T)/SDD combinations were selected to determine the transition state for reactions R2, R3, and R4 respectively.

The second stage of Hg oxidation as presented in reactions R5–R8 involves both HgCl and HgCl₂ as oxidized mercury species. Geometry and vibration frequency comparisons cannot be performed for HgCl₂. This is because the reported values in the literature for the Hg-Cl bond length in HgCl₂ vary by more than 7% from 2.25 (CRC) to 2.43 Å. Hence, only the reaction enthalpy was used to select the method/basis set combination for the transition state calculations for reactions R5–R8. The selected method/basis set combinations for determination of the transition state for these reactions as well as for R1–R4 are summarized in Table 11.

Table 11. The method(s)/basis set(s) combination(s) selected for determination of the transition state for the 8 Hg/Cl reactions.

Hg/ Cl reactions		Selected method/basis set combinations
R1.	$\text{Hg} + \text{Cl} + \text{M} \rightarrow \text{HgCl} + \text{M}$	MP2/CEP-121G ^a QCISD(T)/SDD ^a
R2.	$\text{Hg} + \text{Cl}_2 \rightarrow \text{HgCl} + \text{Cl}$	QCISD/CEP-121G ^a
R3.	$\text{Hg} + \text{HCl} \rightarrow \text{HgCl} + \text{H}$	QCISD(T)/SDD ^a
R4.	$\text{Hg} + \text{HOCl} \rightarrow \text{HgCl} + \text{OH}$	QCISD(T)/SDD ^a
R5.	$\text{HgCl} + \text{Cl} + \text{M} \rightarrow \text{HgCl}_2 + \text{M}$	MP4/SDD ^a
R6.	$\text{HgCl} + \text{Cl}_2 \rightarrow \text{HgCl}_2 + \text{Cl}$	B3LYP/MDF60 ^b
R7.	$\text{HgCl} + \text{HCl} \rightarrow \text{HgCl}_2 + \text{H}$	B3LYP/MHF60 ^b
R8.	$\text{HgCl} + \text{HOCl} \rightarrow \text{HgCl}_2 + \text{OH}$	B3LYP/MDF60 ^b

^a basis set for H, O, and Cl was D95++(3df,3pd)

^b basis set for H, O, and Cl was 6-311++G(3df,3pd)

Reaction R1: $\text{Hg} + \text{Cl} + \text{M} = \text{HgCl} + \text{M}$

The method/basis set combinations of MP2/CEP-121G and QCISD(T)/SDD were used to determine the transition state for the reaction R1. As the reaction involves the dissociation of a diatomic molecule (HgCl), it is a ‘barrierless’ reaction. The RRKM rate constant was therefore variationally minimized. In the calculation of the RRKM rate constant, the bath gas was assumed to be nitrogen. Since experimental data for reaction R1 are not available, an approximate value for the collision deactivation efficiency of 0.1 was assumed.

The variational RRKM rate constant obtained using the MP2/CEP-121G combination in the temperature range 298–2000K (reproduced below) is recommended for reaction R1:

$$k_{\text{Hg}+\text{Cl}+\text{M}=\text{HgCl}+\text{M}}(T) = 1.92 \times 10^{13} T \exp(-1072/T) \quad (\text{cm}^6 \text{ mol}^{-2} \text{ s}^{-1})$$

Reaction R5: $\text{HgCl} + \text{Cl} + \text{M} = \text{HgCl}_2 + \text{M}$

The rate constant for reaction R5 was determined using the MP4/SDD combination. The calculated RRKM rate constant for reaction R5 for the temperature range of 298–2000 K is:

$$k_{\text{HgCl}+\text{Cl}+\text{M}=\text{HgCl}_2+\text{M}}(T) = 1.66 \times 10^{12} T \exp(605/T) \quad (\text{cm}^6 \text{ mol}^{-2} \text{ s}^{-1})$$

Reaction R2: $\text{Hg} + \text{Cl}_2 = \text{HgCl} + \text{Cl}$

The QCISD/CEP-121G combination was selected for the determination of the transition state and its properties for reaction R2. The potential energy surface for this reaction was constructed by fixing the bond angle Hg-Cl(1)-Cl(2) at 180° and varying the two atomic bond lengths corresponding to Hg-Cl(1) bond formation and Cl(1)-Cl(2) bond dissociation.

The calculated CTST rate constant for reaction R2 in the temperature range 298–2000 K is:

$$k_{\text{Hg}+\text{Cl}_2=\text{HgCl}+\text{Cl}}(T) = 4.52 \times 10^{13} \exp(-18113/T) \quad (\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1})$$

Reaction R3: $\text{Hg} + \text{HCl} = \text{HgCl} + \text{H}$

Reaction R3 is similar to reaction R2 and involves formation of an Hg–Cl bond with the simultaneous dissociation of an H–Cl bond. The QCISD(T)/SDD combination was used to determine the transition state for reaction R3. Similar to the procedure followed for reaction R2, two potential energy surfaces were constructed corresponding to the ground state reactant and product by assuming a linear approach of Hg to Cl–H. In contrast to reaction R2, the potential energy surfaces for reaction R3 did not show any evidence of surface crossing. The singlet surface showed a definite maximum in energy along the reaction coordinate and remained the lower energy surface for the ranges of bond separation considered (Hg–Cl: 2.2–4.0 Å, Cl–H: 1.0–3.0 Å).

The calculated CTST rate constant for reaction R3 for the temperature range of 298–2000 K is:

$$k_{\text{Hg}+\text{HCl}=\text{HgCl}+\text{H}}(T) = 2.76 \times 10^{15} \exp(-40148/T) \quad (\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1})$$

Reaction R4: $\text{Hg} + \text{HOCl} = \text{HgCl} + \text{OH}$

The QCISD(T)/SDD combination was selected to determine the transition state for reaction R4. As reaction R4 involves four atoms, it is difficult to visualize the progress of the reaction using a potential energy surface diagram because the molecular system is comprised of six internal coordinates: three bond lengths, two bond angles and one dihedral angle. Three internal coordinates can however be considered fixed: the O–H bond length at approximately 1 Å, the bond angle Hg–Cl–O=180° (assuming a linear approach), and consequently the dihedral angle=0°. Considering the difficulty in examining the potential energy surface, the possibility of surface crossing was not studied. In addition, a definite transition state was located on the potential energy surface implying that a maximum was observed along the reaction coordinate. Even if there were surface crossing, typically occurring at the longer bond separations, it was not likely to have any effect on the transition state and consequently on the rate constant. Several potential energy surfaces were constructed for a range of Hg–Cl (2.2–4.4 Å) and Cl–O (1.7–3.7 Å) bond lengths at different Cl–O–H bond angles. The Cl–O–H bond angle was independently varied from 103° to 180° corresponding to the starting reactant and a completely linear molecule, respectively. Of the many potential energy surfaces corresponding to the different Cl–O–H bond angles, the transition state corresponding to the lowest energy configuration was selected as the transition state for the reaction R4.

The rate constant computed using CTST for the temperature range of 298–2000K is:

$$k_{\text{Hg}+\text{HOCl}=\text{HgCl}+\text{OH}}(T) = 2.69 \times 10^{14} \exp(-16000/T) \quad (\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1})$$

Reaction R6: $\text{HgCl} + \text{Cl}_2 = \text{HgCl}_2 + \text{Cl}$

Reaction R6 involves formation of the Cl(1)Hg–Cl(2) bond with the simultaneous breaking of the Cl(2)–Cl(3) bond. There are three bond lengths, two bond angles and one dihedral angle involved in the molecular system. As HgCl₂ is a linear molecule, the transition state is likely to be a completely linear structure. In addition, the Cl(1)–Hg bond length shortens from approximately 2.5 to 2.2 Å during the formation of HgCl₂ from HgCl, implying that the variation in this bond

length lies within a narrow range. Several potential energy surfaces were constructed for a range of Hg-Cl(2) (2.2–3.2 Å) and Cl(2)-Cl(3) (2.0–3.0 Å) bond lengths at different values of the Cl(1)-Hg (2.2–2.5 Å) bond length. The different potential energy surfaces indicated that the reaction appeared to be ‘barrierless’ because there was a continuous decrease in energy in moving from the reactant structure to the product without a maximum. The VTST procedure was therefore used to determine the rate constant for reaction R6. The transition state corresponding to the lowest energy and the rate constant was variationally minimized along the selected reaction coordinate.

The calculated VTST rate constant for reaction R6 for the temperature range of 298–2000 K is:

$$k_{\text{HgCl}+\text{Cl}_2=\text{HgCl}_2+\text{Cl}}(T) = 5.18 \times 10^4 T^{2.4} \exp(1714/T) \quad (\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1})$$

Reaction R7: HgCl + HCl = HgCl₂ + H

Reaction R7 is similar to R6 with the Cl₂ molecule replaced by HCl. To generate the potential energy surface, a procedure similar to that used for R6 was employed by assuming a completely linear transition state Cl(1)-Hg-Cl(2)-H.

The CTST rate constant for reaction R7 for the temperature range 298–2000 K is:

$$k_{\text{HgCl}+\text{HCl}=\text{HgCl}_2+\text{H}}(T) = 2.49 \times 10^{13} \exp(-12564/T) \quad (\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1})$$

Reaction R8: HgCl + HOCl = HgCl₂ + OH

The molecular system constituting reaction R8 is Cl(1)-Hg-Cl(2)-O-H. This structure has several internal molecular coordinates, with four bond lengths, three bond angles and two dihedral angles. Simplifications were incorporated to visualize this system using a potential energy surface by treating Cl(1)-Hg-Cl(2) and Hg-Cl(2)-O as linear and thereby also fixing the dihedral angles. The measured O-H bond length in the reactant (HOCl) and the product (OH) is nearly identical at approximately 1 Å. For the energy calculations, the O-H bond length was therefore fixed at approximately 1 Å and the Cl(1)-Hg bond length was varied within a narrow range as was done previously for reactions R6 and R7. By taking these steps, the variables were reduced to two bond lengths and one bond angle. The potential energy surfaces were constructed for different Cl(2)-O-H bond angles between 100 and 180° by varying Hg-Cl(2) and Cl(2)-O bond lengths. The different potential energy surfaces suggested that the reaction is “barrierless” as there was no maximum along the reaction coordinate. The transition state corresponding to the lowest energy potential energy surface was chosen and the calculated rate constant was variationally minimized along the selected reaction coordinate.

The calculated VTST rate constant for R8 for the temperature range 298–2000 K is:

$$k_{\text{HgCl}+\text{HOCl}=\text{HgCl}_2+\text{OH}}(T) = 3.28 \times 10^5 T^{2.4} \exp(-148/T) \quad (\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1})$$

The rate constants for the 8 Hg/Cl reactions are presented in Figure 15 for the temperature range of 298–2000 K. The Hg/HgCl recombination reactions with Cl were observed to be the fastest mercury-chlorine reactions. The rate constants of mercury reactions with HOCl were faster or comparable to that with Cl₂. The reactions involving HCl (R3 and R7) were the slowest,

especially at lower temperatures, due to the high activation energy barrier associated with these reactions. The Hg/HCl interactions are therefore unlikely to contribute significantly to the formation of HgCl from Hg and HgCl₂ from HgCl despite the high concentrations of HCl relative to other chlorine species present in combustion flue gas. As expected, the conversion of Hg⁺ to Hg²⁺ is faster than the conversion of Hg⁰ to Hg⁺ suggesting that HgCl is a reactive intermediate under these conditions.

Theoretical rate constants calculated using TST for several of the reactions in the 8-step Hg/Cl reaction mechanism have been reported in the literature. Specifically, theoretical rate constants reported by the following authors were compared against the calculations presented herein: Sliger et al. [38] Li et al.[39], Qiu et al. {Qiu, 2003 #14}, Wilcox et al. [14-16], and Zheng et al. [37]. In all comparisons, it should be noted that all authors, with the exception of Wilcox, used uniform basis sets for Hg and Cl and it has been shown that such a basis set description might not suitably represent Cl and O atoms. Sliger, Li, Zheng, and Qiu calculated theoretical rate constant for reaction R7, reactions R3 and R4, reactions R3 and R4, and reactions R2, R4 and R6, respectively. Wilcox calculated rate constants for reactions R1–R5 and R7. No theoretical rate constants for reaction R8 were available in the literature.

R1: Hg + Cl + M = HgCl + M - Comparisons

The different rate constants for R1 are compared with the MP2/CEP-121G rate constant in Figure 16. The empirical rate constant of Widmer et al. [12] that was adjusted to match their experimental data is two to eleven orders of magnitude lower than the MP2/CEP-121G rate constant for the temperature range of 400 to 2000 K. The Niksa rate constant is two to three orders greater than the MP2/CEP-121G rate constant. The rate constant calculated here is therefore one to two orders of magnitude below the collision limit.

R5: HgCl + Cl + M = HgCl₂ + M

Wilcox et al. calculated the rate constant of reaction R5 using the RRKM method and the transition state was determined at the B3LYP level of theory. The rate constant calculated using the MP4/SDD combination in this study is one to eight orders of magnitude lower than that reported by Wilcox for the temperature range 298–2000 K. The forward activation energy of the rate constant reported by Wilcox for the reaction R5 was calculated to be approximately -247 kJ mol⁻¹ over 298–2000 K, which appears to be high for the three body radical recombination reaction which are ‘barrierless’. The Wilcox rate constant is one to five orders of magnitude greater than the MP4/SDD rate constant calculated in this study in the temperature range of 298 to 2000 K.

The empirical rate constants of Widmer et al. and Niksa et al. are one to three orders of magnitude greater than the MP4/SDD rate constant in this study over the temperature range of 298 to 2000 K, however, all three rate constants have similar temperature dependence unlike the high activation energy of the Wilcox rate constant.

R2: Hg + Cl₂ = HgCl + Cl

Qiu et al. and Wilcox et al. calculated theoretical rate constants for reaction R2. The rate constant for reaction R2 calculated by Qiu et al. (B3LYP/SDD) is one order of magnitude lower than the one calculated here (QCISD/CEP-121G) at temperatures greater than 1600 K and is one to seven

orders of magnitude greater at temperatures below 700 K. In contrast, the rate constant for reaction R2 calculated by Wilcox et al. is within one order of magnitude of that calculated here for the temperature range 900 to 2000 K whereas at temperatures lower than 900 K, the Wilcox rate constant is two to five orders of magnitude lower. The empirical rate constant of Widmer et al. is one (298 K) to two (2000K) orders of magnitude greater than the value calculated in this project. Figure 17 illustrates these results.

R3: $\text{Hg} + \text{HCl} = \text{HgCl} + \text{H}$

The calculated rate constants reported in the literature for reaction R3 show a wide range of variability. The rate constant calculated by Li et al. (MP2/SDD) is three (2000 K) to thirteen (298 K) orders of magnitude greater than the value calculated herein whereas the value calculated by Wilcox et al. (B3LYP/CEP-121G) is three (2000 K) to twelve (298 K) orders of magnitude lower. The rate constant calculated by Zheng et al. (MP2/SDD) is five orders of magnitude higher at 298 K and seven orders of magnitude lower at 2000 K than the value calculated here. All the rate constants, however, indicate a high activation energy barrier for the reaction R3. The empirical rate constant of Widmer et al. for the reaction R3 is within a factor of five of the rate constant calculated in this study using the QCISD(T)/SDD combination.

R4: $\text{Hg} + \text{HOCl} = \text{HgCl} + \text{OH}$

Li et al., Zheng et al., Wilcox et al., and Qiu et al. calculated theoretical rate constants for reaction R4. The rate constant for reaction R4 calculated by Qiu et al. is one (2000 K) to thirteen (298 K) orders of magnitude greater than the one calculated here. The rate constants calculated by Li et al. and Zheng et al. **Error! Bookmark not defined.** are two (2000 K) to eleven (298 K) orders of magnitude higher and that calculated by Wilcox et al. is one (2000 K) to four (298 K) orders of magnitude lower than the value calculated here. The MP2/SDD rate constants calculated by Qiu, Li and Zheng are comparable to each other and to the empirical rate constant of Widmer et al. whereas the value presented herein and that reported by Wilcox are comparable. This suggests that in addition to different quantum calculation methods, the use of separate basis sets for Hg and non-Hg elements significantly affects the rate constant calculations.

R6: $\text{HgCl} + \text{Cl}_2 = \text{HgCl}_2 + \text{Cl}$

The rate constant calculated using B3LYP/MDF60 combination for reaction R6 is two (2000 K) to four (298 K) orders of magnitude lower than that calculated by Qiu et al. (B3LYP/LanL2DZ). The Qiu et al. rate constant is comparable to the empirical rate constant of Widmer et al. The temperature dependence of the rate constant is similar to Qiu et al. and Widmer et al. rate constants whereas that reported by Li et al. (MP2/SDD) shows stronger temperature dependence resulting in several orders of magnitude difference in the rate constant. The different rate constants for R6 are compared with the B3LYP/MDF60 rate constant in Figure 18.

R7: $\text{HgCl} + \text{HCl} = \text{HgCl}_2 + \text{H}$

The rate constant calculated in this study (B3LYP/MHF60) is comparable to that calculated by Sliger et al. (B3LYP/LanL2DZ) for the entire temperature range but is two to six orders of magnitude greater than those reported by Wilcox et al. The difference between the rate constants is perhaps due to the use of different calculation methods as Sliger used the B3LYP method as used in this work whereas Wilcox used the QCISD method. The MP2/SDD rate constant of Li et al. is one to eight orders of magnitude higher than the value calculated here. Recall that other

than the study presented here, only Wilcox used different basis sets for mercury and non-mercury species. The empirical rate constant of Widmer et al. shows an identical temperature to that calculated here but the rate constant is two orders of magnitude greater. The empirical rate constant of Niksa et al. is within a factor of two to the Sliger rate constant and consequently is within an order of magnitude to the value calculated here.

R8: $\text{HgCl} + \text{HOCl} = \text{HgCl}_2 + \text{OH}$

There are no theoretical rate constants reported for reaction R8. The rate constant calculated using the B3LYP/MDF60 combination is within two orders of magnitude of the empirical rate constant of Widmer et al. at temperatures lower than 600 K and is within one order of magnitude in the temperature range 700–2000 K.

In using these or other rate constants, attention must also be paid to the C-H-N-O-S-Cl submodels and associated rate constants. One reaction of particular importance is that involving HONO. One significant difference between different sub-mechanisms is the value of the rate constant for the reaction $\text{NO} + \text{OH} + \text{M} = \text{HONO} + \text{M}$. Because three body recombination reactions of the type $\text{NO} + \text{OH} + \text{M}$ are pressure dependent ($[\text{M}]$), the reaction rate is of second order at high pressures whereas at low pressures, the reaction rate is of third order. In the literature, the Niksa mechanism used a high pressure rate constant with Troe fall-off parameters to describe the low pressure reaction rate whereas the Qiu mechanism used only the high pressure rate constant. As utility coal boilers are operated at near atmospheric pressure, the Niksa approach is more appropriate as it describes low pressure fall-off behavior describing a reaction of order three.

This is of significant consequence because when the low pressure rate constant is used to describe conditions representative of full-scale coal combustion, negligible extent of homogeneous Hg oxidation is generally predicted. The ratio of the low pressure to the high pressure rate constant varies between 7×10^4 and 2×10^3 over a temperature range of 298 to 2000 K respectively. This results in the rapid conversion of OH into HONO when the low pressure rate constant is used especially in modeling conditions that have high NO. Consequently, the amount of Cl in the system is very low because the primary pathway for releasing Cl atoms into the system, $\text{OH} + \text{HCl} = \text{H}_2\text{O} + \text{Cl}$, is inhibited due to a lack of OH radicals.

Figure 15. Transition state theory rate constants for the 8 homogeneous mercury oxidation reactions mediated by chlorine species.

Figure 16. Comparison of theoretical (Wilcox et al.) and empirical (Widmer et al., Niksa et al.) rate constants with the theoretical rate constant calculated in this study using the MP2/CEP-121G combination for the reaction R1 (black line)

Figure 17. Comparison of theoretical (Wilcox et al., and Qiu et al.) and empirical (Widmer et al) rate constants with the theoretical rate constant calculated using the QCISD/CEP-121G combination for the reaction R2.

Figure 18. Comparison of theoretical (Qiu et al., and Li et al.) and empirical (Widmer et al.) rate constants with the theoretical rate constant calculated using the B3LYP/MDF60 combination for the reaction R6.

CONCLUSIONS

Several important conclusions have been drawn from this study, as listed below:

1. Homogeneous oxidation mechanisms do not account for the levels of mercury oxidation that are observed in coal-fired systems. The experimental results here suggest that the levels of homogeneous oxidation with the chlorine concentrations found in a full-scale system are likely to be below 10%. Using the bench-scale data obtained in this project, the predicted oxidation in a full-scale system is only 1% under typical operating conditions. However, data taken from the plant showed 20-40% removal, suggesting other mechanisms are dominant in coal-fired, full-scale systems.
2. Heterogeneous oxidation appears to be important as suggested by the limited experimental data collected in an entrained flow reactor in the presence of Fe_2O_3 particles. The data showed that oxidation ranged from 20-80% depending upon the particle feed rate and the amount of HCl , with increasing oxidation as both parameters were increased. There was some evidence of wall effects, however, which suggest that particles attached to the wall continued to oxidize mercury even after the feed was shut off.
3. Quantum mechanical calculations of key rate constants yield consistent results using three different basis sets.
4. Predicted extents of homogeneous oxidation as a function of quench rate do not agree with the experimental data. The differences may be due to uncertainties in the experimental data or to the fact that the kinetic parameters for other species such as elemental and molecular chlorine are not accurately predicting their concentrations. In any event, the homogeneous oxidation appears to make a small contribution to the total oxidation and accurate predictions require consideration of heterogeneous effects.
5. The aqueous chemistry of the sample conditioning system is critical to the accurate measurement of elemental and oxidized mercury concentrations. It is particularly important that halogen species are reduced in potassium chloride containing solutions so that they cannot oxidize elemental mercury in the impinger. This was accomplished by adding sodium thiosulfate to the potassium chloride solution.

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