REDUCTION OF INHERENT MERCURY EMISSIONS IN PC COMBUSTION

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Abstract

Mercury emission compliance presents one of the major potential challenges raised by the 1990 Clean Air Act Amendments. Simple ways of controlling emissions have not been identified. The variability in the field data suggest that inherent mercury emissions may be reduced if the source of this inherent capture can be identified and controlled. The key mechanisms appear to involve the oxidation of mercury to Hg^{++} , generally producing the more reactive HgCl_2 , followed by its capture by certain components of the fly ash or char, or in the air pollution control equipment. This research focuses on identifying the rate-limiting steps associated with the oxidation step.

Work in this reporting period focused on the refinement of the rate constants used in the kinetic mechanism for mercury oxidation. The possible reactions leading to mercury oxidation are reviewed. Rate constants for these reactions are discussed, using both literature sources and detailed estimates. The resulting mechanism represents the best present picture of the overall chlorine homogeneous oxidation chemistry. Application of this mechanism to the data will be explored in the subsequent reporting period.

Work conducted under the present grant has been the subject of two meeting papers presented during the reporting period (Sliger *et al.*, 1998a,b).

Introduction

The possible imposition of mercury emission regulations presents a serious challenge to the coal-fired utility industry and to the waste incineration industry. Field studies show that coal fired plants emit anywhere from 5% to 95% of the mercury contained in their coal. The reasons for this variability are poorly understood, but appear to involve the oxidation state of the mercury, the properties of the mineral matter associated with the coal, and the type of existing air pollution control equipment installed on the furnace. In particular, oxidized mercury (almost exclusively as HgCl_2) is known to show higher retention in the furnace and air pollution control equipment, a property attributed to its water solubility and its higher reactivity relative to elemental mercury. Thus, oxidation is a critical step that tends to reduce stack emissions. The factors that govern the oxidation of mercury in furnaces are, however, not known. The identification of the mechanisms that are active in promoting oxidation is the first step in devising means of controlling the oxidation and capture process.

The literature clearly shows that homogeneous oxidation pathways exist (Hall *et al.*, 1991; Widmer *et al.*, 1998). In addition, heterogeneous processes are also considered to be important contributors in some regimes, either via promoting direct oxidation or by

catalytically generating reactants for homogeneous oxidation (Senior *et al.*, 1997). In any case, an *accurate homogeneous oxidation mechanism* is needed as a component in any overall model of the fate of mercury in practical combustion. The work reported here focuses on this goal.

Mercury Oxidation Chemistry

Mercury is of sufficiently high volatility that it is presumed to completely vaporize in the flame irrespective of its original form. At flame temperatures, equilibrium indicates mercury will exist in the elemental state. As temperatures fall, the favored equilibrium product shifts to HgCl_2 , with cross-over temperatures ranging from 530 to 740°C, depending on the background HCl concentration. Thus, mercury oxidation would appear to be a low-temperature process.

In fuel-lean flames, the predominant form of chlorine is as HCl, so the examination of HCl as an oxidant has been an important component in oxidation studies. The global reaction of $\text{Hg}+\text{HCl}$ has been studied in flow reactor experiments (Hall *et al.*, 1991; Widmer *et al.*, 1998). The results show that mercury oxidation increases with temperature, at least to 900°C. This is in apparent contradiction to the equilibrium results, which indicate that at these temperatures elemental mercury is the exclusive form. To understand these results, we need to examine the elementary reactions involved.

Due to the high energy barrier of the $\text{Hg}+\text{HCl}$ reaction (Hranisavljevic and Fontijn, 1997), the direct elementary oxidation of mercury by HCl will not occur under the present conditions. This suggests that the oxidation occurs via an intermediate derived from HCl. The temperature dependence of the oxidation suggests a reactive intermediate whose concentration is promoted by high temperatures. This does not support Cl_2 , whose concentration increases with lower temperatures. One likely candidate is atomic chlorine.

The fast oxidation of mercury at room temperature via:

has been reported in the literature with $k_1=1.95\pm1.05\times10^{13} \text{ cm}^3/\text{mole}\cdot\text{s}$ (Horne *et al.*, 1968). The subsequent oxidation of HgCl to HgCl_2 could occur via several paths, including:

Although an abstraction path must be considered for the latter reaction:

Due to the high concentration of HCl in the system, Reaction 2 has been considered in some detail by our group in collaboration with Dr. Nick Marinov of the Lawrence Livermore National Laboratory.

The geometries of the reactants and transition state for the $\text{HgCl}_2+\text{H} \rightarrow \text{HgCl}+\text{HCl}$ (k_{2b}) reaction were determined using the B3LYP hybrid density functional theory (Becke, 1988; Lee *et al.*, 1988; Becke, 1993), with a standard double-zeta basis set, LANL2DZ,

1. HgCl_2

2. TS1

Figure 1. Optimized geometries of HgCl_2 and the $\text{H}\cdots\text{Cl}\cdots\text{Hg}-\text{Cl}$ transition state involved in the $\text{HgCl}_2 + \text{H}$ reaction at the B3LYP/LANL2DZ level of theory. Bond lengths and bond angles are in units of angstrom and degree.

associated with the relativistic effective core potential (ECP) for mercury (Wadt and Hay, 1985), and the nonrelativistic ECP for chlorine. The optimized geometries of the reactants and transition state for this reaction are shown in Figure 1. The relative energy, zero-point vibrational energy correction, rotational constants, and frequencies obtained at the B3LYP/LANL2DZ level of theory using Gaussian98 (Frisch *et al.*, 1998) are shown in Table 1. We have assumed that the reaction of HgCl_2 with H-atom occurs by direct chlorine abstraction, produces $\text{HgCl} + \text{HCl}$ without involving a long-lived complex, and has two equivalent reaction pathways leading to products. The transition state was determined to be nearly linear and is shown as TS1 in Figure 1. The critical energy barrier for this reaction lies slightly downhill from the HgCl_2 and H reactants by approximately -0.19 kcal/mol. Conventional transition-state theory was employed to calculate the rate constant for the $\text{HgCl}_2 + \text{H} \rightarrow \text{HgCl} + \text{HCl}$ reaction. The calculation was based on the critical energy computed using the B3LYP hybrid density functional method. According to the general TST, rate constant k at temperature T for a bimolecular reaction can be expressed as (Connors, 1990; Steinfeld *et al.*, 1999):

Table 1
Relative Energies, Zero-Point Energy Correction, Rotational Constants,
and Frequencies of Reactants and Transition State

Species	Relative Energy (in Hartrees)	Zero-Point Energy Correction (in Hartrees)	Rotational Constants (cm ⁻¹)	Frequencies ^(a) (cm ⁻¹)
H···Cl···Hg-Cl	-73.2150355	0.001986	22200.26 0.03782 0.03782	61,90, 103,283, 335,247i ^(b)
Cl-Hg-Cl	-72.7158256	0.000521	0.0 0.03782 0.03782	66,66 288,345
H	-0.4989111	—	—	—

(a) Frequencies are not scaled

(b) Denotes the imaginary frequency

$$k(T) = L^\ddagger k_B T / h \exp(-\Delta G^\ddagger(T) / k_B T)$$

The $L^\ddagger$ is the statistical factor which accounts for the number of equivalent reaction pathways; h is the Planck's constant; k_B is Boltzmann constant; and $\Delta G^\ddagger(T)$ is the standard-state free energy of activation change at temperature, T , going from the initial state to the transition state. A least squares analysis of the calculated rate constants leads to the following rate expression

$$k_{2b} = 6.406\text{E}+09 \text{ T}^{1.02} \text{ Exp}(+195\text{K} / T) \text{ cm}^3/\text{mole-sec}$$

valid over the 900-2000 K temperature range. The rate constant for the reverse reaction may be obtained through the principal of detailed balancing. The $\text{HgCl}_2 + \text{H} \leftrightarrow \text{HgCl} + \text{HCl}$ equilibrium constant was calculated as $K_{\text{eq}} = 1.381\text{E}+06 \text{ T}^{-1.48} \text{ Exp}(9811/T)$ from the JANAF Tables (Chase *et al.*, 1985). The $\text{HgCl} + \text{HCl} \rightarrow \text{HgCl}_2 + \text{H}$ rate expression was determined from $K_{\text{eq}} = k_{2b} / k_{2f}$ and the following result was obtained

$$k_{2f} = 4.638\text{E}+03 \text{ T}^{2.5} \text{ Exp}(-9811\text{K} / T) \text{ cm}^3/\text{mole-sec}$$

for the 900-2000K temperature range.

This reaction is thus very slow under the present conditions, and as will be seen presently, does not significantly contribute to oxidation. Reaction 4 is exothermic and is expected to proceed at near the collisional limit since no energy barrier is present for addition. Reaction 5 is also exothermic (33 kcal/mol), and at high temperature conditions this abstraction reaction may compete with Reaction 4 for chlorine atoms. Reaction 2 suffers from the absence of Cl_2 under high temperatures. Thus, two relatively fast reactions involving Cl have the potential to oxidize mercury at any temperature. If so, the key to predicting

homogeneous mercury oxidation is to predict chlorine atom behavior. (Note, however, that all the potential reactions should be included in calculations.)

A mechanism was assembled using the $\text{H}_2/\text{O}_2/\text{CO}/\text{CO}_2$ reaction set from Warnatz *et al.* (1996) along with the reactions involving Cl , Cl_2 , HCl , ClO , HOCl , from the NIST data base (NIST, 1999). In addition, Reactions 1- 5 involving mercury were included. The present experimental system is modeled as a plug-flow reactor at the measured temperature. The calculation is initialized at the chlorine injection point with the assumption the species arriving from the flame are equilibrated at the injection temperature. The HCl is assumed to be rapidly dispersed into the post-flame gases. Note that since the HCl enters without preheating, the calculations are started with all chlorine as HCl (*i.e.*, no initial disassociation). Due to the potential for continued reaction within the sampling system during the cooling of the gases, the probe is treated as an extension of the plug-flow reactor. The probe temperature profile is calculated from heat transfer based on a constant wall temperature equal to that of the cooling medium. This results in a temperature profile that varies linearly from 922 to 868°C over 1.4 s in the furnace, followed by a quench to room temperature at ~5400 K/s in the probe.

The results of the use of this kinetic mechanism and reactor model will be discussed in the following semi-annual progress report.

Conclusions

All of the likely reactions involving the oxidation of mercury by chlorine species have been examined. The results suggest that only those reactions involving chlorine atom ($\text{Hg} + \text{Cl} \rightarrow \text{HgCl}$ and $\text{HgCl} + \text{Cl} \rightarrow \text{HgCl}_2$) are sufficiently fast to account for significant oxidation under the present conditions. Other reactions suffer from either the existence of a high energy barrier or the lack of significant concentrations of reactant species. Since both the chlorine atom reactions appear to have isothermal rate constants that are near the collisional limit, the key to predicting mercury oxidation appears to depend strongly on predicting chlorine atom behavior.

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