

DIOXIN PREVENTION & REDUCTION

EXPERIMENTAL INVESTIGATIONS OF HOMOGENEOUS GAS-PHASE SO₂ AND Cl₂ REACTIONS FOR PCDD/F SUPPRESSION

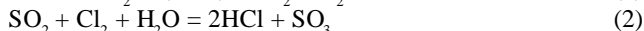
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Introduction

Emissions of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are significantly lower from coal combustion boilers compared to those from municipal solid waste (MSW) incinerators, despite coal's having apparently equally sufficient ingredients for PCDD/F formation, namely: fuelborne chlorine (Cl), metal catalysts, and the potential for trace aromatic emissions. Cofiring high sulfur (S) coal with MSW has demonstrated significant suppression of PCDDs/Fs compared to normal waste firing^{1,2}. The high S to Cl ratio (S/Cl) in coal and cofired MSW/coal combustion has been deduced as a major reason for the drastically reduced PCDD/F emissions compared to those from MSW combustion³. The proposed mechanisms of S inhibition can potentially be as diverse as the proposed mechanisms of PCDD/F formation (e.g., high/low temperature formation; homogeneous gas-phase/surface *de novo*) where the predominant mechanism(s) are yet to be ascertained. One possible suppression mechanism⁴ is that sulfur dioxide (SO₂), in the presence of water (H₂O), depletes available molecular chlorine (Cl₂) formed from the Deacon reaction (1), by undergoing oxidation to sulfur trioxide (SO₃) and converting Cl₂ to hydrogen chloride (HCl) :



Reaction (2), which is postulated to occur at around 400 °C⁴, reduces the active Cl₂ and suppresses further chlorination and PCDD/F formation reactions. Alternatively, catalytic poisoning (e.g., formation of copper sulfate, CuSO₄) has also been argued to inhibit the Deacon reaction and, hence, the availability of Cl₂⁵. Reaction (2) has been considered the main mechanism responsible for reduction of chlorophenols formed in PCDD/F precursor formation reactions by Xie et al.⁶ and used to explain HCl and SO₂ interactions in fluidized-bed studies by Liu et al.⁷ Very few experiments on direct Cl₂ and SO₂ reactions, on the other hand, have been performed. One set of experiments⁵ demonstrated reaction (2) at 400 °C and observed that this mechanism contributed more significantly to the decreased availability of Cl₂ than the catalyst poisoning. More recently, chemical kinetic modeling has been conducted⁸ to investigate S and Cl interactions over a broader range of temperatures and reactor residence times. A S/Cl/hydrogen(H)/oxygen(O) kinetic reaction mechanism was developed⁸ to simulate the rapid decrease of SO₂ upon injection of 1,2-dichlorobenzene (1,2-diClBz) into the combustion mixture of a North American Package Boiler (NAPB) fed with #2 fuel oil (0.03 wt % S) and copper (II) naphthenate (CuNA). A number of elementary steps from previously validated S/H/O and Cl/H/O mechanisms were combined to describe global reaction (2). CHEMKIN⁹ plug flow simulations (SENKIN¹⁰) of the NAPB system showed that the conversion of SO₂ to SO₃ could occur via the following reaction: SO₂ + HO₂ =

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$\text{SO}_3 + \text{OH}$ which was activated only at temperatures greater than 665 °C. Unlike Raghunathan and Gullett's⁵ experiments, no significant conversion of reactants was observed at 400 °C.

The current work examines experimentally direct interactions of Cl_2 and SO_2 aimed to validate the S/Cl/H/O mechanism⁸ and understand the effect of SO_2 on Cl_2 availability. Experimental results of direct interactions of 600 ppm of Cl_2 and 1000 ppm of SO_2 in the presence of 10 % O_2 and 3 % H_2O over the temperature range of 600 to 950 °C will be presented and discussed.

Experimental

The homogeneous gas-phase reaction between SO_2 and Cl_2 , reaction (2), was investigated in a quartz flow reactor (19 mm ID, 1 m long) located inside two Watlow preheaters in series with a Lindberg furnace. Water (H_2O , 0.23 g/min, 3 %), was delivered to the reactor as a liquid by a small water pump and carried through the preheaters via a stream of nitrogen (N_2 , 10.3 L/min, STP). The preheater temperatures were set to the desired reaction temperature to preheat the bulk N_2 flow and ensure vaporization of the water. Flowrates of 0.14 L/min of Cl_2 (from 5 % Cl_2 /argon), 0.11 L/min of SO_2 (from 10.2 % SO_2/N_2), and 1.14 L/min of O_2 (from 100 % O_2) were fed into side ports of the reactor, between the preheaters and the Lindberg furnace, to produce 600 ppm of Cl_2 , 1000 ppm of SO_2 , and 10 % O_2 (dry basis) in the final reactor mixture. The total flow of 12 L/min resulted in a residence time of 0.50 to 0.42 s for isothermal run temperatures between 600 and 950 °C, respectively. Reactions of 600 ppm Cl_2 in the absence of SO_2 and 1000 ppm SO_2 in the absence of Cl_2 , both with 10 % O_2 and 3 % H_2O , were also investigated over the 600 – 950 °C temperature range as baseline experiments for Cl_2 and SO_2 behavior. The exit gas stream was split in two and transported to a series of gas analyzers via two separate heated lines, both operating at a temperature greater than 120 °C to prevent condensation of water. A PermaPure dryer (77 °C) upstream of an Air Instruments and Measurements (AIM) non-dispersive infrared (NDIR) analyzer and in series with a Novatech oxygen analyzer, removed water before analysis of SO_2 , HCl, and O_2 . An AIM hot/wet ultraviolet (UV) analyzer operating at 250 °C was located downstream of the second heated line to monitor Cl_2 and SO_2 concentrations. The exhaust of the NDIR and O_2 analyzer was directed to a third analyzer, a Perkin-Elmer MCS-1000 hot/wet Multicomponent IR Continuous Emissions Monitor (CEM), to measure SO_2 and HCl as well as to confirm the AIM NDIR and UV readings.

Results and Discussion

Figure 1 compares the NDIR analyzer results for the 600 ppm Cl_2 (no SO_2) and for the 1000 ppm SO_2 (no Cl_2) baseline experiments with the SO_2/Cl_2 reaction. The CEM results came within 10-15 % and 4-6 % of the 750-950 °C NDIR analyzer results, for the HCl and SO_2 readings, respectively. Discrepancies between the NDIR analyzer and CEM for HCl were greater (30-76 %) at the lower temperatures (600-700 °C), most likely because lower concentrations do not saturate the sample lines with HCl as rapidly as the higher concentrations. In addition, concentrations at the lower end of the calibration range for the CEM are likely to deviate due to the execution of a single-point calibration procedure using a gas at a concentration of 75 % of the calibration range, rather than a multipoint calibration where linearity could be confirmed.

Agreement between the measured UV readings for SO_2 and the NDIR analysis was also very good (<6.1 %, 750-950 °C and <16.4 %, 650-700 °C, respectively). Calculated Cl_2 values from NDIR HCl readings were within 20 % of Cl_2 UV measurements for all temperatures except 800 and 850 °C (50-60 %). A very good comparison between trends for baseline and SO_2/Cl_2 reactions, for all compounds, was observed. The two experiments involving Cl_2 show that for temperatures above 650 °C, Cl_2 steadily transforms to HCl. When 1000 ppm of SO_2 is present, the conversion of Cl_2 to HCl is much greater and

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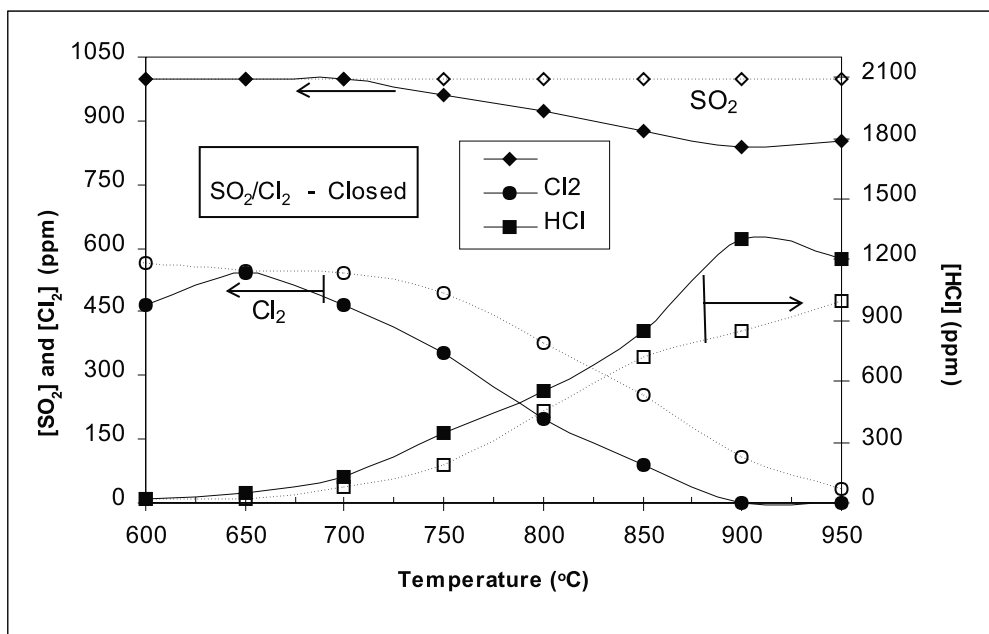


Figure 1. Concentrations of Cl_2 , SO_2 , and HCl with temperature for the baseline reactions (open symbols) of 600 ppm Cl_2 (no SO_2) and 1000 ppm SO_2 (no Cl_2), both with 10 % O_2 and 3 % H_2O , and the reaction with 600 ppm Cl_2 , 1000 ppm SO_2 , 10 % O_2 , and 3 % H_2O (closed symbols). Measurements from UV analyzer for Cl_2 and NDIR analyzer for HCl and SO_2 .

achieves complete conversion by 950 °C. For the baseline experiment without SO_2 , conversion to HCl occurs only to 83 %. Additionally, oxidation of SO_2 is facilitated only in the presence of Cl_2 : the baseline reaction (no Cl_2) reveals negligible conversion of SO_2 , while the reaction with 1000 ppm SO_2 /600 ppm Cl_2 shows that by 950 °C 15 % of SO_2 is converted. It is evident from these results that, for temperatures between 650 and 950 °C, SO_2 and Cl_2 influence each other: the presence of Cl_2 appears to facilitate SO_2 oxidation and the presence of SO_2 increases the rate at which Cl_2 converts to HCl .

Figure 1 also shows, however, that for the 1000 ppm SO_2 /600 ppm Cl_2 experiment, little or no conversion of Cl_2 to HCl is likely to occur at temperatures less than 600 °C. Raghunathan and Gullett⁵ observed 24 % conversion of 500 ppm Cl_2 in the presence of 1000 ppm SO_2 , 10 % O_2 , and 3 % H_2O at 400 °C, over a 10 s residence time. These experiments employed much greater residence times (10 s) than could be accommodated in the current experimental setup due to minimum flow requirements in the UV and NDIR analyzers. This may be a reason for the reaction observed at 400 °C; furthermore, as a consequence of these longer residence times, wall effects may also contribute to significant conversion at 400 °C. If Cl_2 is necessary at temperatures to form PCDD/Fs around 400 °C, then it does not appear from the results in Figure 1 that the presence of SO_2 could affect the availability of Cl_2 and hence PCDD/F formation via gas-phase mechanism reaction (2). It is possible that the observed gas-phase interactions of Cl_2 and SO_2 between 650 and 900 °C may influence high-temperature gas-phase PCDD/F formation from precursor compounds; e.g., chlorinated benzenes (CIBz) and chlorinated phenols (ClPh). Results from earlier modeling work¹¹ had downplayed the significance of this mechanism. The model, however, employed estimated rate constants and, after adaptation to

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subsequent experimental work^{12,13}, Huang and Buekens¹⁴ concluded that the model had significantly underestimated PCDD yields. More recent modeling investigations¹⁵ have demonstrated potential for high-temperature PCDD/F formation with good agreement with experimental data. Other work¹⁶ has demonstrated the inhibition of SO₂ on chlorinated benzenes during cocombustion of Cl-containing polymer (Saran plastic wrap) with high-S coals. Such evidence enriches the significance of the current findings and also encourages future investigations of the suppression of SO₂ on high-temperature gas-phase formation pathways.

Acknowledgments

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