

FORMATION AND SOURCES II

THE IMPORTANCE OF CHLORINE SOURCES DURING 1 SECOND *DE NOVO* FORMATION OF PCDD AND PCDF IN AN ENTRAINED-FLOW REACTOR

Evalena Wikström^{1#}, Abderrahmane Touati², Marnie Telfer^{1#}, and Brian Gullett¹

¹U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, MD-65, Research Triangle Park, NC 27711, USA.

²ARCADIS Geraghty & Miller, Inc., P.O. Box 13109, Research Triangle Park, NC 27709, USA.

[#]Joint program with Oak Ridge Institute for Science and Education postdoctoral program

Introduction

The role and importance of chlorine in the formation of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) during combustion has been discussed frequently for several years. Some investigations report a correlation between fuel chlorine input and the emissions of PCDDs/Fs, while other investigations do not. The discrepancy between the studies suggests that parameters other than the chlorine content, such as type of chlorine and combustion efficiency, may also affect the formation of PCDDs/Fs. These parameters are linked in that gas-phase fractions of hydrogen chloride (HCl), molecular chlorine (Cl₂), and chlorine radicals (Cl•) in the flue gas depend upon the combustion conditions and temperature of the process. HCl is typically the most predominant form of chlorine (>85%), while the amount of Cl₂ varies between 5 and 20 % of the total chlorine. A considerably smaller fraction, less than a few percent, of the total chlorine is present as Cl•, which corresponds to low ppm levels in the flue gas¹. The amount of Cl• depends strongly on the temperature of the flue gas since the recombination into Cl₂ readily occurs¹. Thus the quench rate and the residence time of the flue gas in the convector (cooling zone 450-250 °C) of an incinerator can be very important parameters effecting chlorine speciation and, hence, formation of polychlorinated aromatic compounds². Chlorination reactions of aromatics and chloroaromatics have been shown to be very important for heterogeneous³ and homogenous formations of chlorinated aromatics⁴⁻⁶. Studies of heterogeneous formation with chemically solid-phase chlorine (*e.g.*, CuCl₂) reveal that this inorganic chlorine source can be active in the chlorination reaction in three ways: as a catalyst in the Deacon reaction (*i.e.*, conversion of HCl to Cl₂), as a direct chlorine source by transferring chlorine in the ash to the macro carbon structure, and as a direct source of gas-phase Cl₂⁷⁻⁹. This study focuses on the role and importance of HCl, Cl₂, and Cl• in the gas phase and the Cl in the ash solid phase bonded in the ash for chlorination during 1 second *de novo* formation of PCDDs/Fs.

Methods and Materials

Experiments were conducted in an entrained-flow reactor (EFR), consisting of two (one horizontal and one vertical) concentric tube quartz reactors connected in series. The experiments were performed at 1000 °C in the horizontal reactor and a quenched temperature profile (650-240 °C) in the vertical reactor to simulate post-combustion conditions. A constant flow of 12 L/min was employed in all

FORMATION AND SOURCES II

experiments giving rise to a residence time of 0.6 s in the horizontal and an additional 1.0 s in the vertical reactor. Nitrogen (N_2), air, and a chlorination agent (HCl or Cl_2) are pre heated in the outer annulus of the horizontal reactor before entering the inner quartz tube that is connected to the vertical reactor through a quartz cap. A partially fluidized bed ash feeder is connected to the quartz cap. The fly ash particles ($<105 \mu m$) were fed into the reactor by a carrier gas (90 mL/min of N_2) through a vibrating feeder line. Two fly ashes were employed in these experiments: as-received (AR) collected from the electrostatic precipitator of a grate-fired municipal solid waste incinerator, and an extracted (EX) fly ash. The EX fly ash was prepared by extracting AR fly ash with toluene for 48 h and then heating to 500 °C in a N_2 atmosphere for 24 h. This procedure minimized organic compounds (such as PCDDs/Fs) on the fly ash. All chemical and physical properties, such as chlorine and metal content of the two ashes, were shown to be very similar except that the initial content of PCDDs/Fs in the AR ash was 740 ng/g (mono- to octa-CDDs/Fs) and virtually zero in EX ash. In addition the total amount of carbon in EX was reduced from 1.30% (in AR) to 0.52%.

To study the importance of the chlorination agent for the *de novo* formation of PCDDs/Fs, 23 experiments were performed in both a N_2 and an air environment with no gas-phase chlorine, HCl , or Cl_2 added to the horizontal reactor. The sampling and analyses of the mono- to octa-PCDDs/Fs in the flue gas were conducted according to a slightly modified version of U.S. EPA Method 0023a¹⁰. To evaluate the results of the experimental work, the theoretical concentrations of HCl , Cl_2 , and $Cl\bullet$ in the EFR were calculated using REKINET, a program based on CHEMKIN-II¹¹ to solve homogeneous gas-phase kinetics. A chlorocombustion mechanism, originally compiled by Ho *et al.*¹² and refined and verified by Procaccini¹³, was employed in the simulations.

Results and Discussion

Figure 1 presents the total PCDD/F levels formed during 13 test conditions. The first eight bars display four experimental conditions performed in pairs using two different ashes AR (white bars) and EX (gray bars). No significant differences in PCDD/F yields and profiles between the two ashes at each condition can be observed. The results reveal that the two fly ashes are equally active for *de novo* synthesis of PCDDs/Fs, implying that the initial differences in PCDD/F levels (740 ng/g in AR and 0 ng/g in EX) in the ash have no effect on the formation rate. As a consequence, discussion of subsequent experiments will consider AR and EX ash to be equally reactive. The amount of solid-phase chlorine in both the ashes is 6.3%, significantly higher than the amount of chlorine required to form the levels of PCDDs/Fs observed in these experiments. The four experiments without any gas-phase chlorine added into the gas (#1,2 and #3,4 see Figure 1) reveal that the chlorine present in the ash forms between 50 and 550 ng PCDDs/Fs per dscm, supporting theories that chlorine bound in the ash either can be transferred to the macromolecular carbon structure or act as a source of Cl_2 ^{7,9}, even for these short time (1s) *de novo* reactions.

Further experiments with 200 ppm of Cl_2 added at 1000 °C in N_2 (#5,6) or air (#7,8) exhibit a significant increase in yields, from about 200 to 2000 ng PCDDs/Fs per dscm. At gas temperatures higher than 500 °C, Cl_2 partly thermally dissociates into $Cl\bullet$. CHEMKIN-II/REKINET simulations show that the $Cl\bullet$ levels in the quenched vertical reactor of the EFR vary from 115 to 1 ppm when 200 ppm of Cl_2 is added (Figure 2a). The variation in $Cl\bullet$ and Cl_2 levels in the vertical reactor at different

FORMATION AND SOURCES II

experimental conditions is displayed in Figures 2a and 2b, respectively. These experiments (#5-8) quite clearly imply that additional gas-phase chlorine, $\text{Cl}_2/\text{Cl}\bullet$, significantly affects the *de novo* formation rate of PCDDs/Fs. Additional experiments in air environment with only 5 ppm of Cl_2 (resulting in 5-2 ppm of $\text{Cl}\bullet$) added to the gas-phase (Figure 1, #9) display PCDD/F levels (140 ng/dscm) in the same range as when no gas-phase chlorine is added. These shows that 5 ppm of gas-phase chlorine is too low for an increase in PCDD/F formation. Two possible explanations can be suggested: that other faster chlorine competing reactions occur, and/or that the gas-phase chlorination reactions are limited by the probability of the chlorine to contact and react with the ash particle. The effect of HCl as a chlorinating agent is studied in two experimental conditions, one in air (#10) and one in inert N_2 (#11). To maintain the same amount of chlorine as in the high Cl_2 experiments, 400 ppm of HCl is added. CHEMKIN-II/REKINET simulations reveal that, unlike Cl_2 , dissociation of HCl to hydrogen radicals and $\text{Cl}\bullet$ did not occur in inert N_2 at 1000 °C (Figure 2a), due to a stronger bond between H and Cl (103 kcal/mole) than Cl and Cl (58 kcal/mole). However, in the presence of oxygen, CHEMKIN-II simulations revealed that approximately 10 ppm of Cl_2 and between 14 and 1 ppm of $\text{Cl}\bullet$ should be present in the gas due to reactions between HCl, O_2 , and O radicals (see Figures 2a and 2b). Nevertheless, the major chlorine compound is still HCl. The experiment with only HCl present as a chlorination agent in the flue gas shows convincingly that HCl alone is not active as a gas-phase chlorine source for PCDDs/Fs formation (see Figure 1 #11). However, when HCl is added into an air environment (#10) *i.e.*, with low levels of Cl_2 and $\text{Cl}\bullet$ present in the flue gas, slightly higher yields of PCDDs/Fs are formed (500 ng/dscm) although still within the same range as when only air is present in the gas phase (#3,4).

To elucidate the role of the two chlorinating agents, Cl_2 and $\text{Cl}\bullet$, experiments are performed at a temperature below that required for dissociation of Cl_2 . A temperature of 500 °C in the horizontal reactor and a quenched temperature profile from 500 to 240 °C in the vertical reactor is employed to prevent formation of $\text{Cl}\bullet$ (Experiment #12 in Figure 1). All other experimental conditions are the same: *i.e.*, 200 ppm of Cl_2 is added in N_2 . The experimental conditions of the second additional experiment (#13, Figure 1) are the same as the first (#12) except that the temperature in the horizontal reactor is maintained at 1000 °C to allow dissociation of Cl_2 to $\text{Cl}\bullet$. The yields of PCDDs/Fs formed at these two experimental conditions are similar. The fact that the experiment with only Cl_2 present results in equal level of PCDDs/Fs as when both $\text{Cl}_2/\text{Cl}\bullet$ are present shows that Cl_2 alone is sufficient to be the chlorine source in fast *de novo* synthesis of PCDDs/Fs. The more reactive species, $\text{Cl}\bullet$, was not solely responsible for *de novo* chlorination. Because the amount of Cl_2 in the flue gas from a combustion process is significantly higher than the amount of $\text{Cl}\bullet$ and since the chlorination reactions appear to be limited by concentration, this result implies that Cl_2 is the major chlorination agent that controls chlorination during fast heterogeneous *de novo* formation of PCDDs/Fs.

Acknowledgment

This research was performed at the U.S. EPA and supported in part by appointments of Evalena Wikström and Marnie Telfer to the Postdoctoral Research Program at the National Risk Management Research Laboratory, administrated by the Oak Ridge Institute for Science and Education (ORISE) through interagency agreement BW89938167 between the U.S. Department of Energy and the U.S. Environmental Protection Agency.

FORMATION AND SOURCES II

References

1. Procaccini C., Bozzelli J. W., Longwell J. P., Smith K. A., and Sarofim A. F. (2000) *Environ.Sci.Technol.*, *34*, 4565.
2. Fängmark I. E., van Bavel B., Marklund S., Strömberg B., Berge N., and Rappe C. (1993) *Environ.Sci.Technol.*, *27*, 1602.
3. Wikström E. and Marklund S. (1999) *Environ.Sci.Technol.*, *34*, 604.
4. Gullett B. K., Sarofim A. F., Smith K. A., and Procaccini C. (2000) *Trans IChem*, *78*, 47.
5. Young C. M. and Voorhees K. J. (1990) *Organohalogen Compd.*, *3*, 203.
6. Sommeling P. M., Mulder P., and Louw R. (1994) *Chemosphere*, *29*, 2015.
7. Bruce K. R., Beach L. O., and Gullett B. K. (1991) *Waste Manage.*, *11*, 97.
8. Addink R., Espourteille F., and Altwicker E. R. (1998) *Environ.Sci.Technol.*, *32*, 3356.
9. Stieglitz L. (1998) *Environ.Eng.Sci.*, *15*, 5.
10. U.S.EPA (1996) *SW-856 (NTIS PB88-239223)*, office of solid waste, Washington, DC, USA.
11. Kee R. J., Rupley F. M., and Miller J. A. (1989) Sandia National Laboratories, Albuquerque, NM, USA,
12. Ho W. P., Yu Q., and Bozzelli J. W. (1992) *Combust.Sci.Technol.*, *85*, 23.
13. Procaccini, C., Thesis: The chemistry of chlorine in combustion systems and the gas-phase formation of chlorinated and oxygenated pollutants. *Massachusetts Institute of Technology, Cambridge, MA, USA, 1999.*

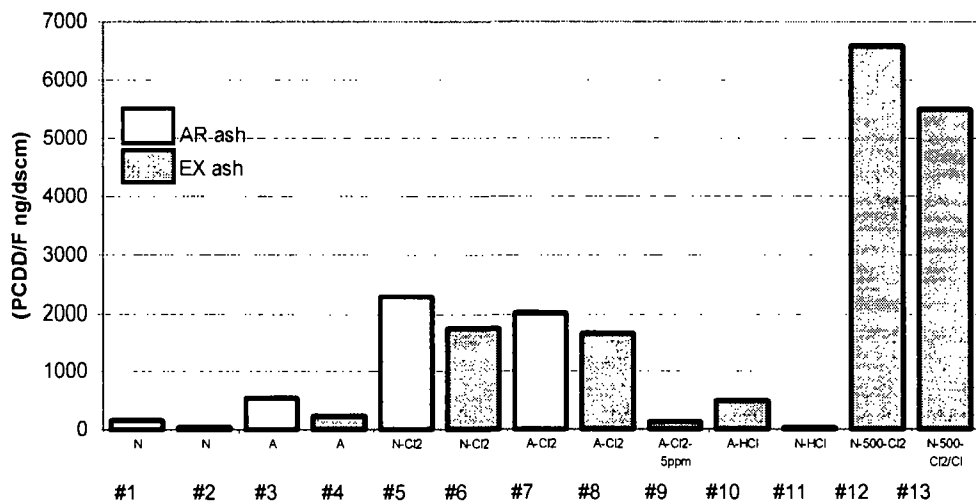
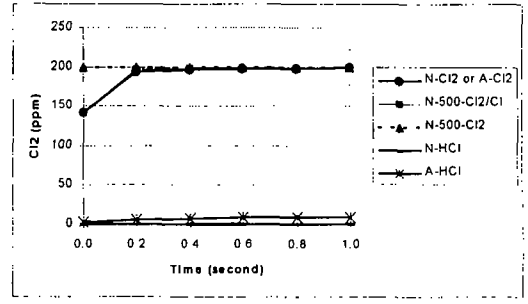
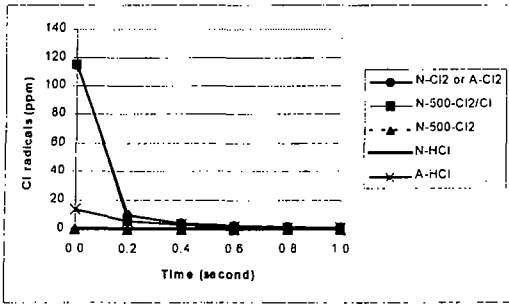


Figure 1. PCDD/F formation at 13 experimental conditions, N (in N₂), A (in Air), AR ash (white bars), EX ash (gray bars), Cl₂ (with Cl₂ added), HCl (with HCl added).

FORMATION AND SOURCES II



2b

Figures 2a and 2b Results from CHEMKIN-II/REKINET simulations of Cl radical and Cl₂ levels in the vertical reactor of the EFR at six experimental conditions. Cl₂ or HCl added into air or N₂ environment. Cl₂ added into N₂ at 500 °C in the horizontal reactor and the top of the vertical reactor (N-500-Cl2) and at 1000 °C (default temperature) in the horizontal reactor, and 500 °C in the top of the vertical (N-500-Cl2/C1).