

KINETIC STUDY OF PCDD FORMATION FROM A MODEL CHLORINATED  
PRECURSOR BY CATALYTIC ACTIVITY OF MSW INCINERATOR FLY ASH

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ABSTRACT

Municipal solid waste (MSW) incinerator fly ash has previously been implicated in the formation of PCDD and PCDF during MSW incineration. Whether these compounds are derived from structurally similar chlorinated precursors or from *de novo* synthesis from elemental carbon is currently the topic of considerable debate. The time window in which the temperature is favourable (near 300°C) for formation of PCDD/F in incinerators is much shorter than that required for maximum yields from *de novo* synthesis. In a series of laboratory experiments fly ash catalysed synthesis of PCDD from a model chlorinated precursor is demonstrated to reach maximum yield in less than five minutes, demonstrating better kinetic agreement with incinerator models. As the reaction time increases a greater proportion of lower chlorinated isomers is observed.

KEYWORDS

Polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans, mechanism, fly ash, incineration

INTRODUCTION

It has been established that formation of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) in municipal solid waste (MSW) incinerators occurs with the participation of fly ash produced during combustion (Karasek and Dickson, 1987). However, the nature of the catalyst is not fully understood and there is considerable debate over the degree to which the starting materials resemble the product PCDD/Fs (Choudry *et al.*, 1983). One hypothesis suggests that the most important sources of PCDD/Fs in MSW incinerators are structurally similar chlorinated aromatic precursors such as chlorinated phenols and benzenes, chlorinated diphenylethers, and PCBs, all of which have been found on the fly ash surface (Junk and Ford, 1980) and many of which have been shown experimentally to form PCDD/Fs when reacted over fly ash (Dickson and Karasek, 1987, Ross, *et al.*, 1989). A second hypothesis argues that PCDD/Fs in MSW incinerators arise from elemental carbon on the ash via *de novo* synthesis (Stieglitz *et al.*, 1987).

While *de novo* synthesis of PCDD/F from elemental carbon has been shown to occur on a Mg-Al-silicate matrix with a copper catalyst (artificial fly ash), it has not been clearly demonstrated on a true fly ash matrix. Furthermore, this model requires a reaction time of 2-4 hours to achieve maximum yields (Stieglitz *et al.*, 1989). The residence time of a fly ash particle in the post-combustion zone where PCDD/F synthesis is accepted to take place has been estimated at a few seconds or less, although one could expect somewhat longer residence times if the particle adhered to the duct wall or while it resided on the surface of an electrostatic precipitator (Altwicker *et al.*, 1990, Shaub and Tsang, 1983).

The experiment described below investigates the kinetics of the precursor hypothesis using <sup>14</sup>C-pentachlorophenol

as a model compound

## EXPERIMENTAL

### Reaction of Precursor

Fly ash for the experiments described below was obtained from an incinerator in the United States. The fly ash was ground and sieved to < 150 micrometers particle size, then Soxhlet extracted continuously for 48 hours with benzene to clean the fly ash of organic materials. The clean fly ash was heated to 550 °C at least eight hours (overnight) under an air flow of 20 mL/min

A solution of 200 µg of <sup>14</sup>C-Pentachlorophenol (MSD Isotopes) was deposited dropwise on glass beads and the solvent allowed to evaporate. The glass beads were located just above a column (20 cm X 1 cm i.d.) packed with about 4 cm of fly ash (approx. 1.5 g). The column was placed vertically in a preheated oven (Thermcraft) and the reaction was carried out for the appointed time period at 300 °C under a 3-5 mL/min flow of purified air. Products volatilized during the reaction were collected in a cooled (0 °C) impinger of toluene located downstream outside of the oven. The carrier gas was then passed through a Florisil trap prior to exhaust

### Work-up and Analysis

Following a reaction the oven was rapidly cooled, the air flow stopped, and the apparatus disassembled. The fly ash column was eluted with 200 mL of toluene (BDH) and this was combined with the impinger contents and rinses. The total volume of the combined products was then reduced to 100 µL first by heated evaporation under vacuum (rotary evaporator), then by evaporation to the final volume under a gentle stream of high purity nitrogen. The products were analyzed for PCDD and PCDF using a DB-5 (30 m X 0.25 mm i.d., J & W Scientific) by GC/MS (HP 5890 GC/MSD System) with electron impact ionization in the selected ion monitoring mode. Ions monitored corresponded to the two most abundant ions in the molecular ion cluster as well as the M-COCl ion for dioxins and furans. <sup>14</sup>C-PCP molecular ions were also monitored.

## RESULTS AND DISCUSSION

Reaction times studied ranged from 5 to 120 minutes and at each reaction time the experiment was performed in triplicate. Chrysene-D<sub>12</sub> was used as a recovery spike for all experiments. All recoveries of this spike were greater than 85%.

The variation of PCDD yield with time is shown in Figure 1. As indicated by the figure, the reaction proceeds rapidly, and it can be seen that by the time the first measurement is taken (5 minutes), the maximum yield may have already been reached and decomposition started to compete with formation. Throughout the remainder of the measurement period the total PCDD measured is decreasing, slowly leveling off with time, and it is expected that the PCDD measured will fall below the detection limit after several hours.

The reaction of pentachlorophenol to form other products, shown in figure 2, is also very fast, with less than 5% of the starting material detected after the first five minutes. This is further evidence that dioxin synthesis from precursors may be possible within the short time period in which a fly ash particle is in the optimum temperature region of an incinerator. It is, however, uncertain from this data at what time the maximum yield of PCDD occurs. Equipment modifications will be necessary to achieve reproducibility at reaction times of less than five minutes.

Table 1 shows the percentage each isomer group represents of the total PCDD (on average) formed at each reaction time examined. There is clearly a shift to lower chlorinated isomers with time. This effect, however, is not especially pronounced until the later stages of the degradation. After 15 minutes, roughly the same time as the PCP has almost

completely disappeared (Figure 2), the proportion of higher chlorinated isomers drops dramatically. This suggests that PCDD formation and destruction occur concurrently until the PCP supply has been exhausted. That the joining of the two pentachlorophenol molecules occurs prior to dechlorination (rather than dechlorination followed by reaction between the two) is evident from these results.

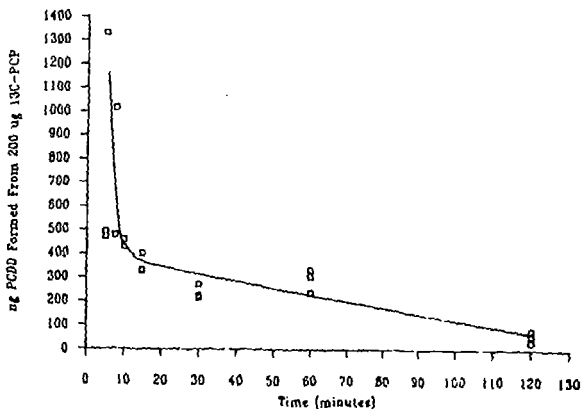


Figure 1: Total PCDD formed from 200 µg PCP as a function of heating time (300°C).

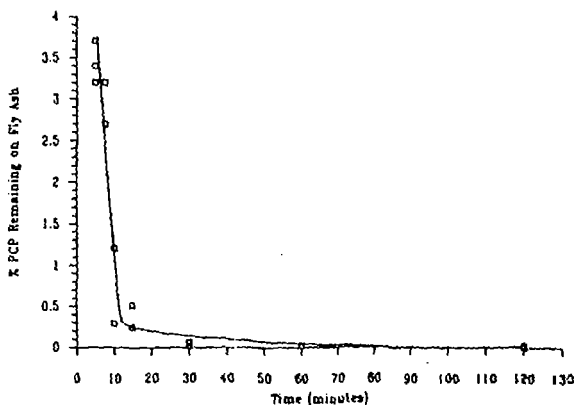


Figure 2: Pentachlorophenol remaining on fly ash after reaction to form PCDD and other products (300°C)

TABLE 1: PERCENTAGE OF TOTAL PCDD FOR EACH ISOMER GROUP

PCDD	REACTION TIME (minutes)					
	5	10	15	30	60	120
TCDD	<0.1	<0.1	<0.1	0.9	<0.1	5.3
PCDD	0.4	1.3	0.7	7.7	1.4	19.3
H6CDD	5.4	10.1	10.5	27.2	12.9	33.3
H7CDD	26.5	29.3	28.8	32.3	33.9	24.6
OCDD	67.7	59.3	60.0	31.9	51.7	17.5

#### CONCLUSIONS

The above results demonstrate that precursor synthesis can occur on a time scale consistent with that proposed for MSW incinerators. Thus these results support the theory that the dioxins and furans found in incinerator fly ash are derived from chlorinated precursors of chemical similarity rather than by *de novo* synthesis from elemental carbon. Further study of the early stages of PCDD formation from chlorinated precursors is essential, as this will lead to a better understanding of the mechanism of formation.

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