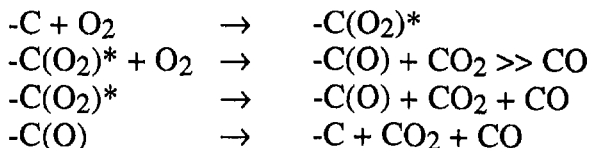


Formation of Dioxins: Competing Rates Between Chemically Similar Precursors and De Novo Reactions

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At the Dioxin 91-Conference we reported on an apparent relationship between native carbon (i.e., unextractable) gasification rates in fly ash - as measured by CO + CO₂ formation- and maximum PCDD/F-yields at 300°C.¹ This suggests a ranking scale of fly ashes. Although these results might imply that CO participates in PCDD/F-formation, it has not been possible to prove incorporation of labelled carbon¹³ into PCDD/F when the reactions were carried out in the presence of labelled CO. This finding is actually consistent with the suggested mechanism² for carbon gasification by oxygen



where -C(O₂)* represents a metastable surface complex.

A result reported earlier³ has been confirmed, however, namely the incorporation of carbon from an added ¹³C-activated carbon into the PCDD/F skeleton. Amorphous ¹³C was activated in air at 450°C; this was added to a fly ash sample (furnished by Prof. C. Rappe) so that the final sample contained 4.25% by weight ¹³C carbon and 7.4% native carbon. Exposure to a 10% O₂/90% N₂-flow at 325°C gave (after 30 min) the following results: 9% of all chlorobenzene and 18% of all PCDD/F has complete ¹³C-labelled aromatic rings.

The experiments suggested that site activation and competition might be important factors in controlling PCDD/F-rates and yields. The logical precursors to use were chlorobenzenes and chlorophenols.

Initial studies were conducted with 1,2-dichlorobenzene. Two reasons for this choice: where measurements have been reported from incinerators, it is one

of the more abundant chlorobenzenes; and, some of our spouted bed combustion studies of chlorinated hydrocarbons have been conducted with this compound.⁴ When 1,2-dichlorobenzene in air was passed over fly ash that was active in deNovo synthesis, the PCDD/F congener pattern was altered and some conversion of the reactant occurred. This suggested that 1,2-dichlorobenzene was participating in the PCDD/F reaction mechanism, but without using isotopically labelled 1,2-dichlorobenzene we could not prove incorporation of the reactant into the observed PCDD/F. ¹³C-labelled 1,4-dichlorobenzene (labelled 1,2-dichlorobenzene was quoted at a price 40 times greater than 1,4-dichlorobenzene, hence the switch) was then used in identical experiments as above. GC/MS analysis showed that no ¹³C-carbon from the labelled precursor was incorporated into PCDD/F. However, the congener pattern was altered and the yield reduced, suggesting that there was some interference with the active carbon sites participating in deNovo reactions due, perhaps, to gas phase precursor adsorption.

Experiments with chlorophenols had previously been reported by Dickson,⁵ without, however, accounting for deNovo formation. We also felt that shorter reaction times (2-15 minutes) and lower gas phase concentrations would be more relevant. Experiments were run with three different chlorophenols: 2,4,5-, 2,4,6-, and 2,3,4,6-. A five minute de Novo experiment (i.e., no gas phase precursor) was used to establish a baseline yield for a given fly ash (data are reported for an Ontario fly ash, supplied by Prof. F. Karasek).

The results obtained for a five minute reaction time are reported in Table 1. The distinctly different PCDD/F-congener patterns from the chlorophenols permitted quantitative distinction between gas phase precursor and deNovo reactions. For short times the PCDD/PCDF-ratio with this particular fly ash is >1. Yields of both deNovo PCDD and PCDF decrease in the presence of the phenols. The tetrachlorophenol appears to be considerably more reactive in PCDD-formation; none of the phenols formed PCDF.

Unlike the results reported by Ross, et al.⁶ (an initial high rate of PCDD-formation followed by a steep decline and a subsequent slow increase in the rate) a linear increase in PCDD-yield was observed with time (Figure 1).

The results reported in Table 2 suggest that the gas precursor PCDD-yields may be sensitive to both the precursor concentration and the quantity of fly ash, i.e., a gas phase precursor/active site ratio. In cases where 0.1 g fly ash was used, it was mixed with 0.9 g glass beads (which were shown to be inert in a separate experiment). Note that a gas phase precursor limitation is indicated by the results with 1 g of fly ash, but not with 0.1 g, i.e., the PCDD-yield appears independent of the phenol concentration, but depends on the ratio.

A possible mechanistic scheme incorporating this ratio and mass transfer limitations and its applicability to incinerators will be outlined.

References

- 1 Milligan, MS and Altwicker, ER. Low temperature carbon vaporization from MSW-fly ash - implications to deNovo synthesis of PCDD/F. Paper presented at Dioxin 91, 1991, Sept. 23-27, Research Triangle Park, NC, USA.
- 2 Lear, AE, Brown, TC, and Haynes, BS. Formation of metastable oxide complexes during the oxidation of carbons at low temperatures. 23rd Symp. (Int.) on Combustion, 1990:1191-1197.
- 3 Altwicker, ER, Schonberg, JS, Konduri, RKNV, and Milligan, MS. Polychlorinated dioxin/furan formation in incinerators. *Haz. Waste Haz. Materials* 1990;7:73-87.
- 4 Altwicker, ER, Schonberg, JS, and Konduri, RKNV. Formation of polychlorodibenzo-p-dioxins and polychlorodibenzofurans during heterogeneous combustion. In: Clement, R and Kagel, R, eds. *Emissions from Combustion Processes: Origin, Measurement, Control*. Lewis Publisher, 1990:Chapter 2, 25-56.
- 5 Dickson, LC, Ph.D. thesis, Dept. of Chemistry, University of Waterloo, 1987.
- 6 Ross, BJ, Naikwadi, KP, and Karasek, FW. Kinetic study of PCDD formation from a model chlorinated precursor by catalytic activity of MSW incinerator fly ash. In: Dioxin 90, Volume 3, 1990:147-150.

Table 1
Competition Experiments Between Chlorophenols, Pg, and de Novo Reactions

Compound	No Gas-Phase Precursor De Novo	2,4,6-T ₃ CP = 47 ng/ml		2,4,5-T ₃ CP = 43 ng/ml		2,3,4,6-T ₄ CP = 35 ng/ml	
		Pg	de Novo	Pg	de Novo	Pg	de Novo
T ₄ CDD	13 ¹	43	4	3	10	0	14
P ₅	16	0	20	20	7	0	15
H ₆	18	8	5	38	8	266	~0
H ₇	19	0	3	6	15	115	~0
O ₈	8	0	1	0	3	4	9
PCDD	70	51	33	67	43	385	38
T ₄ CDF	15	0	16	0	16	0	16
P ₅	13	0	6	0	6	0	12
H ₆	13	0	6	0	6	0	11
H ₇	11	0	3	0	3	0	6
O ₈	2	0	1	0	1	0	1
PCDF	54	0	32	0	32	0	46

¹ng g⁻¹ fly ash, 5 min., T = 300°C, Ontario 1 Fly Ash, 10% O₂/90% N₂ at 80 ml/min.

Table 2
PCDD/F Yields From 2,3,4,6-T₄CP/Fly Ash

Compound	2,3,4-T ₄ CP = 371 ng/ml Fly Ash,		2,3,4,6-T ₄ CP = 35 ng/ml Fly Ash,	
	0.10 g	1.00 g	0.10 g	1.00 g
PCDD	2000 ¹	2300	2500	400
PCDF	200	20	200	~0

¹ ng g⁻¹ fly ash
Five minutes, T = 300°C
10% O₂/90% N₂ at 80 ml/min

Fig. 1 PCDD Yield from T₄CP at 300°C
2,3,4,8-T₄CP = 371 ng/ml

