

***de Novo* Reactions to Form PCDD/F and the Role of Chlorobenzenes**

E.R. Altwicker

Department of Chemical Engineering, Rensselaer Polytechnic Institute
Troy, NY 12180-3590

M.S. Milligan

Department of Chemistry, State University of New York at Fredonia
Fredonia, NY 14063

S. Marklund and C. Rappe

Institute of Environmental Chemistry, University of Umea
S-90187 Umea, SWEDEN

INTRODUCTION

Investigations to clarify the routes to polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) in incinerators have focused on the so-called *de Novo* reaction, formation from unextractable carbon held in the fly ash matrix, and gas phase precursors. Of these chlorophenols (CP) and chlorobenzenes (CB) have been shown to be capable of forming both PCDD and PCDF under a variety of conditions.

In their extensive studies of the *de Novo* reaction, Stieglitz and coworkers¹⁻³) showed that CBs were formed in yields comparable (or greater than) to PCDD/F; CBs were typically found in the downstream trap, indicating formation reaction on fly ash followed by desorption. Such observations gave no information on the possible participation of CBs in PCDD/F-formation under *de Novo* conditions. However, there was reason to believe that CBs could compete with *de Novo* formation, though perhaps not with CPs. Ross, et al.⁴) had shown that the yield of PCDD from pentachlorophenol (PCP) was much greater than from tetrachlorobenzene (T₄CB); the PCP/T₄CB ratio was 300 (in N₂) and 52 (in O₂), respectively.

From laboratory combustion studies and incinerator measurements it is clear that CBs are present and can act as precursors to PCDD/F. Therefore, we chose to study three commonly observed CBs, 1,2-dichlorobenzene, 1,4-dichlorobenzene, and 1,2,4,5-tetrachlorobenzene and their influence and participation in reactions over fly ash under *de Novo* type conditions. The 1,4-DCB was used in carbon 13 labelled form; the choice of the labelled compound was dictated by cost; ¹³C-labelled 1,2,-dichlorobenzene was several times more expensive than the 1,4-isomer. This fact was not established until after a number of experiments had been performed with unlabelled 1,2-DCB. The objective for including labelled precursor was to check on its incorporation into the PCDD/F molecules, analogous to the type of mechanistic probing originally reported by Karasek and Dickson⁵).

SOU/FRM

EXPERIMENTAL AND ANALYTICAL

The experimental apparatus and sample cleanup has been described elsewhere⁶). Reactions were conducted at 300°C and 10% O₂ for 5-60 mins. Analyses were conducted both at Rensselaer (LRGC/MS) and Umea (HRGC/MS).

RESULTS AND DISCUSSION

The major effect observed when CBs were present in the inlet gas stream at high concentrations, O (10⁴-10⁵ µg/m³), i.e., 100-1000 times larger than reported for municipal solid waste incinerators, was a decrease in the yield of PCDD/F congeners. This is shown in Table 1, as the % decline (or increase) for the individual congener classes relative to the *de Novo* result for this fly ash. In most instances, the reductions are quite substantial, which suggests that CBs interfere with *de Novo* reactions. Most of the CB introduced was recovered in the downstream cold trap of the reactor system.

The substantial declines in most cases were more than offset by increases in the H₆CDD-OCDD levels when 1,2,4,5-T₄CB was used, leading to an overall increase in PCDD-amounts of 73%, while PCDF declined by 92%. Since the major non PCDD/F-product in this reaction is a tetrachlorophenol, and since it has been shown elsewhere⁷) that 2,3,4,6-tetrachlorophenol reacts rapidly over fly ash to form predominantly PCDD, it is reasonable to presume that the increase in higher chlorinated PCDD can be accounted for by the hydroxylation of the tetrachlorobenzenes followed by a condensation reaction. However, chlorination must also occur, leading to pentachlorophenol which can condense to form OCDD.

Table 2 summarizes the average (from at least two runs) PCDD/PCDF ratios. There is a greater suppression of PCDD-formation in the presence of dichlorobenzenes, whereas the large increase in the ratio in the presence of 1,2,4,5-T₄CB is attributable to the added formation of H₆CDD-OCDD as well as the reduction in the PCDF-yield. Although in the presence of 3% water in the inlet gas stream an increase in that ratio is observed also, it is interesting to note that it is only about one half of the increase observed when water is absent. This suggests that added water is not needed to support the hydroxylation reaction.

Elsewhere, extensive studies with 2,3,4,6-tetrachlorophenol as a precursor to PCDD over fly ash have been reported⁷). This reaction was tested in the presence pentachlorobenzene, under the assumption that the latter might be hydroxylated and subsequently undergo condensation to PCDD. Instead, most of the pentachlorobenzene was recovered in the downstream trap and the yield of PCDD - vs. that in the absence of pentachlorobenzene - decreased by about 70% (from 771 ng to 220 ng), pointing to inhibition rather than participation in synthesis.

Observed PCDD/PCDF-ratios in incinerators - and also typically less than one (the fly ash used here is one of the few exceptions) in the *de Novo* reaction - are in sharp contrast to the influence of CBs reported here. The results may be due to poisoning of sites when CB-gas phase concentrations are high. In the experiments with ¹³C-labelled-DCB other CBs, just as expected in the *de Novo* reaction, were obtained. However, none of them were labelled which must mean that site deactivation and synthesis of CBs are separate processes. Our findings also suggest that *de Novo* results in the presence of gas phase precursors which may undergo adsorption and perhaps reaction cannot be interpreted in an unambiguous way.

Table 1

% Decline or Increase (+) in PCDD/F-Congeners Over Fly Ash
In the Presence of Chlorobenzenes

	<u>+1,2=DCB</u> %	<u>+¹³C-1,4-DCB</u> %	<u>+1,2,4,5-T₄CB</u> %, w/o H ₂ O
T ₄ CDD	41	40	88
P ₅ CDD	38	65	82
H ₆ CDD	2	94	+ 50
H ₇ CDD	13	90	+ 418
OCDD	36	100	+ 104
ΣPCDD	22	83	+ 73
T ₄ CDF	68	86	88
P ₅ CDF	57	87	93
H ₆ CDF	56	95	90
H ₇ CDF	38	100	93
OCDF	17	100	100
ΣPCDF	53	93	92

Table 2

Average PCDD/PCDF-Ratios from the *de Novo* Reaction
and in the Presence of Chlorobenzenes

<i>de Novo</i>	1.9
<i>de Novo</i> + 1,2-DCB	3.0
<i>de Novo</i> + ¹³ C-1,4-DCB	3.2
<i>de Novo</i> + 1,2,4,5-T ₄ CB (w/o H ₂ O)	39.3
<i>de Novo</i> + 1,2,4,5-T ₄ CB (w H ₂ O)	20.0

The fly ash used in all these studies was an Ontario fly ash characterized by a PCDD/PCDF > 1.

SOU/FRM

It should also be pointed out that in the experiments with dichlorobenzenes, DBD, DBF, and the mono-trichloro-PCDD/F were not analyzed. Such compounds might have been formed in these reactions.

Partial support of this work by the New York State Solid Waste Combustion Institute and the U.S. Environmental Protection Agency is gratefully acknowledged.

REFERENCES

1. L. Stieglitz, G. Zwick, J. Beck, H. Bautz and W. Roth, Carbonaceous particles in fly ash - a source for the *de novo* synthesis of organochloro compounds, *Chemosphere*, 19, (1989) 283-290.
2. L. Stieglitz, H. Vogg, G. Zwick, J. Beck and H. Bautz, On formation conditions of organohalogen compounds from particulate carbon in fly ash, *Chemosphere*, 23 (1991) 1255-1264.
3. G. Schwarz and L. Stieglitz, Formation of organohalogen compounds in fly ash by metal-catalyzed oxidation of residual carbon, *Chemosphere*, 25 (1992) 277-282.
4. B.J. Ross, K.P. Naikwadi and F.W. Karasek, Effect of temperature, carrier gas, and precursor structure on PCDD and PCDF formed from precursors by catalytic activity of MSW incinerator fly ash, *Chemosphere*, 19 (1989) 277-282.
5. F.W. Karasek and L.C. Dickson, Model studies of PCDD-formation during refuse incineration, *Science*, 237 (1987) 754-756.
6. M.S. Milligan and E. Altwicker, The relationship between the *de novo* synthesis of polychlorinated dibenzo-p-dioxins and dibenzofurans and low temperature carbon gasification in fly ash, *Environ. Sci. Technol.* 27 (1993) 1595-1601.
7. E.R. Altwicker and M.S. Milligan, Dioxin formation from tetrachlorophenol under breakthrough conditions, *Organohalogen Compounds*, 11 (1993) 269-273. Dioxin 93, Vienna, Austria, Short papers.