

## Fly Ash Mediated Oxychlorination of 2,3-Dimethyl-1-butene; Formation of PolyChlorinated Dibenzo-p-Dioxins and -DibenzoFurans.

de Graaf E.J.<sup>A</sup>, van Bavel B.<sup>B</sup>, Rappe C.<sup>B</sup> and Louw R.<sup>A</sup>

<sup>A</sup> Center for Chemistry and the Environment, Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands.

<sup>B</sup> Institute of Environmental Chemistry, University of Umeå, S-901 87 Umeå, Sweden.

### Abstract

During fly ash catalyzed oxychlorination of 2,3-dimethyl-1-butene(I) at temperatures between 350 and 550 °C, CO and CO<sub>2</sub> are major products, together with the isomeric 2,3-dimethyl-2-butene(II), dimethylbutadiene(III) and chlorinated derivatives of I-III. Besides these products polychlorinated dibenzofurans (PCDFs) and -dioxins (PCDDs) are detected. Analytical data on PCDFs and PCDDs stemming from the butene at 450, 500 and 550 °C are presented.

### Introduction

Fly ash, present in the post-furnace zone of a municipal waste incinerator (MSWI), greatly enhances the production of PCDDs and PCDFs<sup>1-5</sup>. In laboratory studies<sup>3</sup>, structurally related (chlorinated) aromatics, including phenols, benzenes, biphenyls and diphenylethers have been shown to form PCDDs and/or PCDFs with fly ash as a catalyst. When passed over a fixed bed of MSWI fly-ash together with air containing water vapour and HCl, phenols are by far the most reactive; they are easily (poly)chlorinated at 350°C, and condensed to give PCDDs with negligible proportions of PCDFs<sup>3</sup>. Polychlorinated benzenes (PCBzs) and monobenzofurans (PCBFs) are also formed. With increasing temperature catalytic combustion to mainly CO<sub>2</sub> becomes the major reaction<sup>3</sup>.

The analogous fly-ash mediated oxychlorination of ethylene sets in at ca 250°C and primarily produces 1,2-dichloroethane and vinyl chloride. Above 350°C numerous other (poly)chlorinated compounds are formed, including ethanes, ethylenes, methanes, some propenes, and around 500°C, traces of PCBzs<sup>3</sup>.

Using propene as the substrate, smooth oxychlorination to 1,2-dichloropropane and a variety of chlorinated propenes occurs at 350°C, again with catalytic combustion as a parallel reaction<sup>4</sup>. With T→500°C propene conversion neared completion, the effluent then containing amongst others polychlorinated propenes, hexachlorobutadiene, hexachlorocyclopentadiene, PCBzs, PCBFs and PCDD/Fs, albeit much less than PCBFs.

In order to obtain more insight into the behaviour of nonaromatic organic substrates in general, we have now used 2,3-dimethyl-1-butene (I) as the substrate. Apart from studying oxychlorination and catalytic combustion, special attention has been paid to qualification and quantification of the PCDDs and PCDFs.

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## Experimental

The flow reactor set-up is described in more detail elsewhere<sup>3</sup>. Reactions were conducted in a tubular quartz reactor (L 47 cm, ID 7 mm). The MSWI fly ash bed<sup>3</sup> (3.4 g, length 8.5 cm) was pretreated at 550 °C in a stream of air for 24 h. to remove all organic compounds and particulate organic carbon. Void residence times were around 2.8 s. Oxygen (Air Products 99.995%) and nitrogen (99.995%) were used as such. Flows were regulated and metered using calibrated flow controllers. Gaseous 2,3-dimethyl-1-butene(I) (98% purity) was introduced in the reactor by purging a metered nitrogen flow through a glass impinger filled with liquid 2,3-dimethyl-1-butene(I) and kept at 1 °C. Using a plastic motorized 50 ml syringe, hydrogen chloride (12.8% in water) was introduced and vaporized before entering the reactor. The effluent flow was maintained at 130 °C by heating tape to prevent condensation of less volatile compounds. The products first passed a cold trap at 0 °C and then a trap cooled by liquid nitrogen. Analysis of reaction gas mixtures was performed by collection of 0.50 ml samples of exit gas - gathered frequently (5 times) following wet HCl scrubbing - via a gas-tight syringe. Volatiles were analyzed by GC using a Carboplot (L 10 m, ID 0.53 mm) wide bore column equipped with a methanizer and a flame ionization detector. Absolute amounts were based on peak surface areas relative to those of calibration gas mixtures. After collecting the oxychlorination products in diethylether, the water and organic phases were separated. The organic phase was analyzed using GC-FID with a CP-Sil-5-CB capillary column (50 m). Absolute amounts were based on peak surface areas relative to that of the internal standard. For PCDD and PCDF analysis clean-up<sup>6</sup> involved chromatography over silica, basic alumina and Carbopack c/celite. GC/MSD analyses were performed using a RT-2330 capillary column. Absolute amounts were based on peak surface areas relative to that of the corresponding internal <sup>13</sup>C standard.

## Results and Discussion

The oxychlorination reaction of 2,3-dimethyl-1-butene(I) in contact with fly ash was followed over a temperature range of 352-550 °C (Table). At 352 °C part of the substrate had undergone double bond isomerisation to 2,3-dimethyl-2-butene(II) or was oxidised to 2,3-dimethyl-1,3-butadiene(III). Furthermore, chlorinated derivatives including 2,3-dimethyl-1-chloro-1-butene and chlorinated 2,3-dimethyl-1,3-butadienes were formed. At 450 °C the 2,3-dimethyl-1-butene(I) conversion was 96% and PCDDs and PCDFs were detected. In a separate blank experiment, without I, no PCDD and PCDF products could be found, substantiating that the PCDDs and PCDFs stem from I. Above 550 °C not only I is fully converted, but at this temperature also quantitative destruction occurs of H<sub>7</sub>CDF, O<sub>8</sub>CDF and O<sub>8</sub>CDD.

Total yields of tetra- and higher chlorinated dibenzofurans have been measured for runs at 450, 500 and 550 °C (see Figure 1); analogous data on dibenzodioxins are depicted in Figure 2. Due to the absence of the <sup>13</sup>C standard, H<sub>7</sub>CDDs could not be quantified.

In Figure 1 it can be seen that the optimum yield of PCDFs during oxychlorination of I lies at ca 450 °C for H<sub>7</sub>CDF and O<sub>8</sub>CDF, at 500 °C for T<sub>4</sub>CDF and P<sub>5</sub>CDF and at 550 °C for H<sub>6</sub>CDF. Figure 2 shows that the yield of PCDDs reaches its maximum at 450 °C for O<sub>8</sub>CDD and at 500 °C for T<sub>4</sub>CDD, P<sub>5</sub>CDD and H<sub>6</sub>CDD.

Figures 1 and 2 have the same Y-scale. Hence, formation of PCDFs is more prominent than that of PCDDs. In general T<sub>4</sub>CDF/T<sub>4</sub>CDD (14/1), P<sub>5</sub>CDF/P<sub>5</sub>CDD (3/1), H<sub>6</sub>CDF/H<sub>6</sub>CDD (5/1) and O<sub>8</sub>CDF/O<sub>8</sub>CDD (1/1). Overall, the PCDF/PCDD ratio is around 4-5. Quantitation at 500 °C leads to 6 µMol PCDF per Mol 2,3-dimethyl-1-butene(I) (inflow).

Conclusions

The PCDF/PCDD ratio of 4-5 for fly-ash mediated conversion of 2,3-dimethyl-1-butene(I) is in sharp contrast with the results<sup>3</sup> obtained with (chloro)phenol, which leads to essentially only PCDD. Therefore, in MSW combustion, phenols do not appear to be the only important precursors of PCDD/F. Several authors<sup>1</sup> have advanced carbonaceous particles admixed with the fly-ash as a source of PCDD/F, but others<sup>2</sup> reject this proposal. Our results point at the operation of a nonaromatic - or perhaps better: not yet aromatic - oxygen and chlorine containing species, which can condense with an aromatic - phenolic - entity to result in a PCDF congener.

TABLE 1: Experimental data on the MSW fly ash mediated conversion of 2,3-dimethyl-1-butene(I).

EXPERIMENT (no.)	1	2	3	4
Fly ash (g)	3.4	3.4	3.4	3.4
Temperature ( C)	352	450	500	550
Residence time (s)	2.77	2.94	2.91	2.73
INFLOWS (mMol/h)				
2,3-Dimethyl-1-butene	3.54	4.46	3.42	3.38
Water	156	154	154	154
Hydrogen chloride	8.5	10.5	10.5	10.5
Oxygen	20.6	22.6	21.7	21.7
Nitrogen	100.6	43.9	33.2	33.2
CONVERSION (%)	66.3	96.4	98.7	100.0
PRODUCTS[1]				
CO	0.37	6.2	15.1	16.1
CO2	0.30	18.4	21.3	21.8
CH4	0.01	0.12	1.6	4.2
C2's[2]	ND	0.14	1.0	2.2
Sum II,III	16	5	1	0.1
Sum I-Cl's[3]	2	2	3	0.1

[1]: in Mol% on substrate inflow

[2]: C<sub>2</sub>H<sub>2</sub> + C<sub>2</sub>H<sub>4</sub>(major) + trace of C<sub>2</sub>H<sub>6</sub>

[3]: sum of mono- and dichlorobutenes and -butadienes, as identified by GC-MS

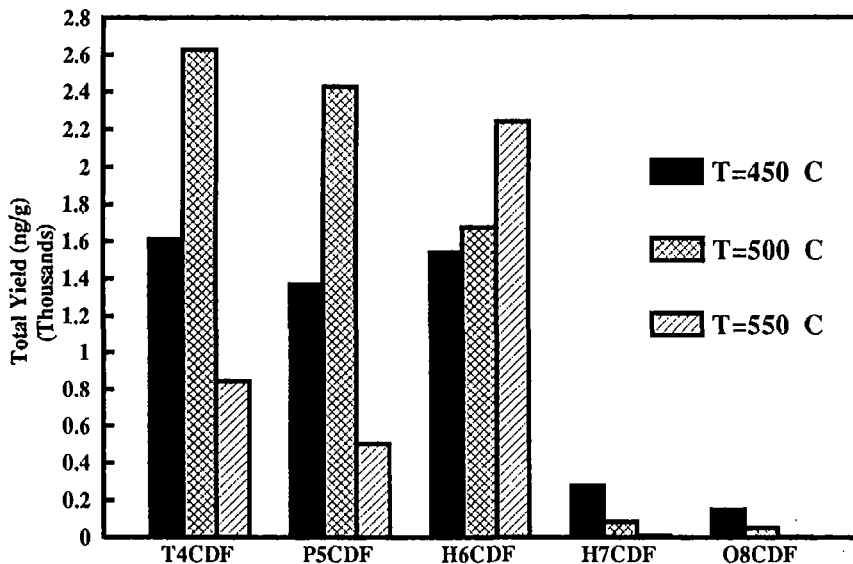
ND : Not detected (detection limit GC-FID ca. 0.25  $\mu$ Mol/h)

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## Figure 1: PCDF analysis



## Figure 2: PCDD analysis

