FORMATION OF MONO AND POLYCHLORINATED DIBENZO-P-DIOXINS AND FURANS IN OXIDATION OF 4-CHLOROBIPHENYL

Song Hou[1*], John C. Mackie[1,2], Eric M. Kennedy[1], Bogdan Z. Dlugogorski[1†]

[1]Priority Research Centre for Energy, Faculty of Engineering and Built Environment, The University of Newcastle, Callaghan, New South Wales 2308, Australia; [2]Also at School of Chemistry, The University of Sydney, New South Wales 2006, Australia

[†]Corresponding author: Phone: +61 2 4985-4433; Email: Bogdan.Dlugogorski@newcastle.edu.au

Introduction

Polychlorinated biphenyls (PCB) have been widely applied in industrial processes since the 1930s until the late 1970s. They were first discovered as environmental pollutants in 1966 and prohibited in the early 1980s[1]. It has been reported that about 640 thousand tonnes of PCB were produced alone in the U.S. between 1929 and 1977. Approximately 25 % was used either in transformers, which functioned submerged in solutions of PCB and polychlorobenzene (PCBz), or in capacitors operated with PCB[2]. Even in recent years, PCB continue to be detected in water, sediments, soil, as well as tissue of animal species in every part of the world[3]. Thermal decomposition of PCB is the most widely deployed method to destroy PCB, and a number of earlier studies reported that polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F) form during the PCB combustion, fires of electrical equipment and waste incineration of PCB[4,5]. Due to the environmental toxicity and bioaccumulative nature of PCDD/F, a study on the formation and distribution of PCDD/F in PCB combustion should be helpful to estimate the risk of PCB disposal to the environment, especially in uncontrolled combustion, such as fires. For this study, we selected 4-chlorobiphenyl (4-CB) which has a simple structure that allows us to focus on elucidating the mechanism of its oxidation. To this end, we have carried out a series of laboratory-scale experiments to study the formation of PCDD/F under conditions similar of PCB fires. We also determined the formation of species regarded as precursors for the formation of PCDD/F.

Materials and methods

All experiments were performed on a bench-scale apparatus. The detailed design has been published elsewhere[6]. In brief, our system consisted of a reactant vaporiser, an alumina reactor, and a sample collecting system. The vaporiser, made of polytetrafluoroethylene (PTFE), was installed in an oven maintained at 75 °C to generate 4-CB at a rate of approximately 0.05 mg/min. The 4-CB vapour was diluted in nitrogen flow and mixed with a controlled amount of oxygen to result in the fuel equivalence ratio of 0.07. We constructed an alumina-tube (99.5%) reactor to perform all experiments, focussing on determining the effect of the impurities in alumina on observed emissions of PCDD/F.

Two alumina rods (4 mm o.d.) were inserted from both ends of the alumina tube, with the space between the ends of the rods delimiting the volume of the reactor. Approaching the reactor, the gases flowed in the annular space between the outside diameter of one of the rods and the tube. This arrangement forced the 4-CB vapour to reach the reaction zone rapidly. Adjusting the inserted length of the rods permitted to maintain the same residence time (5 s) at different temperatures. A XAD-2 resin cartridge (200 mg) was installed after the reactor tube to trap all PCDD/F products formed in the experiments.

The experiments lasted for 6 h to accrue enough PCDD/F in the XAD-2 cartridge for the analysis. The United States Environmental Protection Agency (USEPA) Standard Method 1613 was modified to include the determination of mono to trichlorinated congeners. The XAD-2 resin was Soxhlet extracted in hot mode in toluene for 12 hours. The extract and sample from washing the alumina reactor tube were cleaned up to remove their matrix by using glass chromatography columns loaded with basic and acidic silica gel, followed by further cleaning columns containing basic and acidic alumina. The solutions were concentrated prior to HRGC-ion trap

(IT) MS/MS analysis. The sample (1μL) was introduced into an injector (280 °C) operated in a splitless mode. A VF-5ms capillary column (60 m length, 0.25 mm i.d., 0.25 μm film thickness) was installed to achieve the chromatography separation with helium as the carrier gas with its flow rate maintained at 1 mL/min. The oven temperature program started from 80 °C (held for 1 min), and then imposed a temperature rise to 235 °C (held for 10 min) at 10 °C/min, subsequent increase to 275 °C (held for 9 min) at 5 °C/min and then to 310 °C (held for 6 min) at 10 °C/min. The temperature of the transfer line, ion trap, and manifold were set up at 270 °C, 200 °C and 80 °C, respectively. The detection limits of GC-(IT)MS/MS for PCDD/F corresponded to between 0.3 and 3.0 pg/μL (except 6.0 pg/μL for octachlorinated dibenzofuran).

Results and discussion

Figure 1 presents the formation of the main PCDD/F homologue groups (MCDF, MCDD, DCDF and TriCDF) as a function of temperature during oxidation of 4-CB. MCDF and DCDF constitute the two principal homologue groups. We have observed the formation of all of the four MCDF congeners, with the dominant 3-MCDF, followed by 2-MCDF, 1-MCDF and 4-MCDF. Figure 2 illustrates the distribution of the MCDF congeners. 1-MCDD was the only MCDD congener formed, identified initially at 450 °C in the exhaust gases from the reactor. Note that a small amount of 1-MCDD listed in Table 1 for 300 °C might originate from impurities present in the Soxhlet extraction system. Figure 3 presents the identification of MCDF isomers and 1-MCDD. We injected authentic standards for 2-MCDF, 4-MCDF and 1-MCDD, and the elution order of the other two MCDF congeners was confirmed from figures available in literature[7].

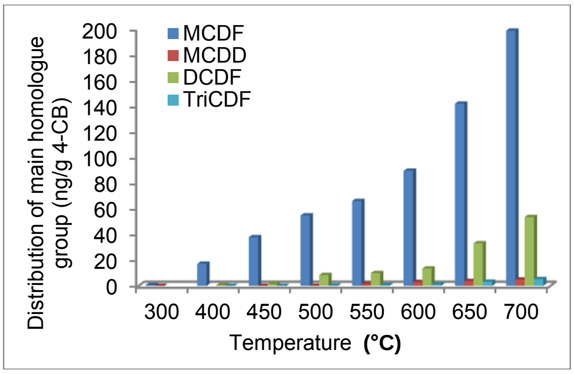

Figure 1. Yields of main homologue group

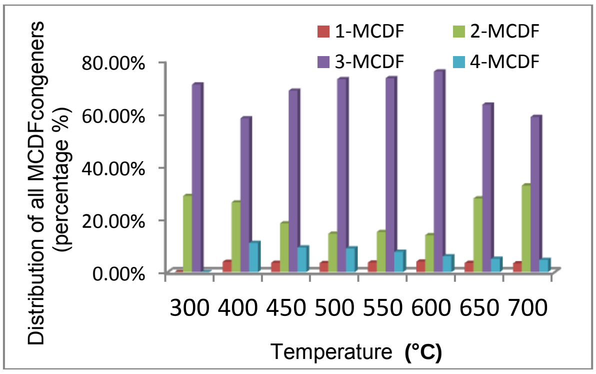

Figure 2. Distribution of MCDF congeners

Table 1. The distribution of MCDF congeners at different temperature

T (ºC)	300	400	450	500	550	600	650	700
Congeners	Yield (ng/g 4-CB)							
1-MCDF	n.d.	0.640	1.38	1.89	2.41	3.59	4.98	6.64
2-MCDF	0.168	4.32	7.22	8.02	10.1	12.6	39.8	65.5
3-MCDF	0.042	9.50	26.8	40.1	48.6	68.2	90.1	117
4-MCDF	n.d.	1.81	3.65	4.94	5.10	5.39	7.21	9.25
1-MCDD	0.010	n.d.	0.040	0.120	1.51	3.08	3.89	5.000

n.d. – not detected or below the limit of detection

The oxidation of 4-CB leads preferentially to the formation of PCDF rather than PCDD, with the ratio of PCDD/PCDF varying from 0.001 to 0.031. The yields of each of the tetra to octachlorinated homologue groups amounted to less than 0.1 pg/g of 4-CB. We detected more congeners at higher temperature, especially at 650 and 700 °C, identifying species belonging to all PCDD/F homologue groups. The yields of PCDD/F increase significantly with rising temperature. At low temperatures, only mono-tri CDD/F were observed, with the toxic congeners (2,3,7,8-TCDF, 1,2,3,7,8-PCDF and 2,3,4,7,8-PCDF) first identified at 550 °C. In particular, the yields of the toxic PCDD increased significantly at higher temperatures. All of the 17 toxic congeners were produced in the experiments conducted at 650 and 700°C; 2,3,7,8-TCDF represented the highest contributor to the TEQ. Table 2 illustrates the yields of the 17 toxic dioxin congeners as function of temperature. The labelled standards added into the XAD-2 resin yielded good recoveries; 44.2 – 112%, compared with a range of 25-164% allowed by the EPA Method 1613.

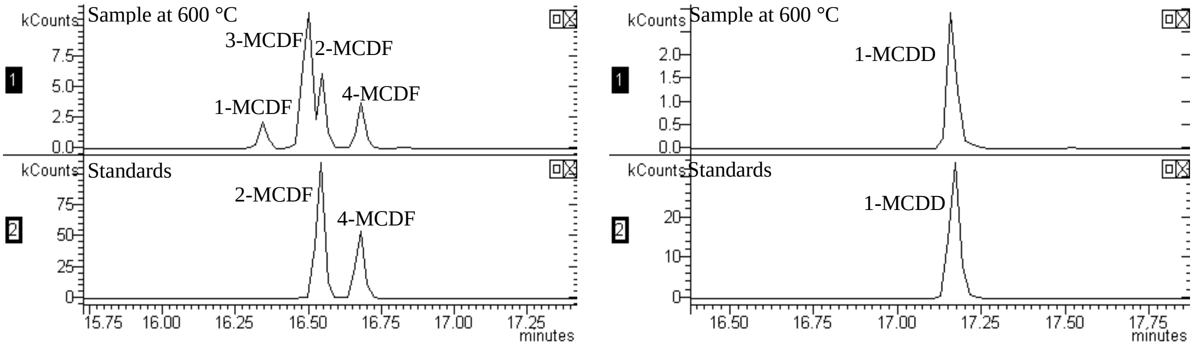

Figure 3. The identification of congeners in MCDF and MCDD homologue group

Table 2. Emission factor and TEQ of the 17 toxic congeners at different temperature

Temperature (°C)	550		600		650	
Congener	Emission factor (pg/g of 4-CB)	TEQ-WHO$_{2005}$ pg/g 4-CB	Emission factor (pg/g of 4-CB)	TEQ-WHO$_{2005}$ pg/g 4-CB	Emission factor (pg/g of 4-CB)	TEQ-WHO$_{2005}$ pg/g 4-CB
2,3,7,8-TCDD	n.d.	n.d.	n.d.	n.d.	0.300	0.300
2,3,7,8-TCDF	18.0	1.80	25.0	2.50	182	18.2
1,2,3,7,8-PCDD	n.d.	n.d.	n.d.	n.d.	1.10	1.10
1,2,3,7,8-PCDF	8.00	0.240	10.0	0.300	12.0	0.400
2,3,4,7,8-PCDF	3.20	0.960	36.0	12.0	66.6	20.0
1,2,3,4,7,8-HxCDD	n.d.	n.d.	n.d.	n.d.	5.00	0.500
1,2,3,6,7,8-HxCDD	n.d.	n.d.	n.d.	n.d.	7.00	0.700
1,2,3,7,8,9-HxCDD	n.d.	n.d.	n.d.	n.d.	10.0	1.00
1,2,3,4,7,8-HxCDF	n.d.	n.d.	34.0	3.40	38.0	3.80
1,2,3,6,7,8-HxCDF	n.d.	n.d.	14.0	1.40	27.0	2.70
1,2,3,7,8,9-HxCDF	n.d.	n.d.	95.0	9.50	30.0	3.00
2,3,4,6,7,8-HxCDF	n.d.	n.d.	22.0	2.20	160	16.0
1,2,3,4,6,7,8-HpCDD	n.d.	n.d.	n.d.	n.d.	50.0	0.500
1,2,3,4,6,7,8-HpCDF	n.d.	n.d.	80.0	0.800	80.0	0.800
1,2,3,4,7,8,9-HpCDF	n.d.	n.d.	10.0	0.100	10.0	0.100
OctaCDD	n.d.	n.d.	n.d.	n.d.	10.0	0.003
OctaCDF	n.d.	n.d.	100	0.100	14.0	0.004
Total	29.2	3.00	426	32.3	603	69.1

n.d. – not detected or below the limit of detection

As we aimed to gain improved understanding of the formation mechanism of PCDD/F, we also investigated the production of PCDD/F precursors, namely polychlorobenzenes (PCBz) and polychlorophenols (PCP).

Monochlorobenzene (MCBz) and 2,4-dichlorophenol (2,4-DCP) are the main precursor species identified in the exhaust gases leaving the reactor. Other important PCDD/F precursors detected included dichlorobenzenes (DCBz) and 2-chlorobiphenyl (2-CP). Figure 4 presents the total yields of PCBz and PCP as a function of temperature. By performing additional experiments using a reactor made of ultra pure quartz[8], we concluded that two types of surface reactions are induced by alumina surfaces; (i) chlorination and dechlorination reactions that lead to the formation of PCBz and PCP at temperatures as low as 400 °C, and (ii) reactions forming singlet oxygen ($^1O_2$ or $^1\Delta_g$ O_2) that oxidises 4-CB directly to 3-MCDF commencing at 300 °C. Clearly, reactions (i) are predicated on surface breakage of the biphenyl bond. We observed no PCBz and PCP forming below 600 °C in the ultra pure quartz reactor, leading us to propose that chlorination and dechlorination reaction occur only on the alumina surfaces. In access of 600 °C, significant amounts of benzene, chlorobenzene, phenol and monchlorophenols formed in the quartz reactor, by gas phase dissociation of 4-CB, as expected. Both reactors showed similar yields of MCDF as illustrated in Table 3. These observations suggest that both reactors facilitate the formation of $^1O_2$. Finally, by comparing no formation of 1-MCDD in the quartz reactor and minor production of this species in the alumina reactor (Table 3), we suggest that alumina surfaces also facilitate condensation of the chlorophenoxy moieties.

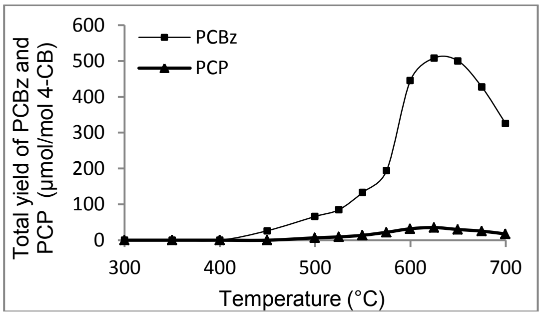

Figure 4. Total yield of PCBz and PCP

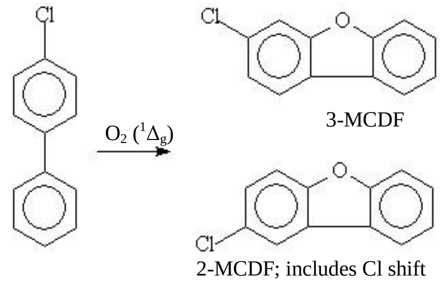

Figure 5. Formation of MCDF ($^1O_2$ pathway)

Table 3. Yield of MCDD/F congeners in both reactors at 450 °C[8]

MCDD/F congeners	Yield for the quartz reactor (ng/g 4-CB)	Yield for the alumina reactor (ng/g 4-CB)
1-MCDF	0.030	1.38
2-MCDF	0.570	7.22
3-MCDF	28.4	26.8
4-MCDF	0.040	3.65
1-MCDD	0.000	0.040

Acknowledgements

This study has been funded by the Australian Research Council. SH thanks the University of Newcastle, Australia, for a research scholarship. We thank Dr Mohammednoor Altarawneh for many stimulating discussions.

References:

1. El-Shahawi M, Hamza A, Bashammakh A, Al-Saggaf W. (2010) *Talanta* 80: 1587-97
2. Hutzinger O, Choudhry G, Chittim B, Johnston L. (1985) *Environ Health Perspect.* 60: 3-9
3. Korytar P, Leonards P, de Boer J, Brinkman U. (2002) *Chemosphere* 68:203-218
4. Tsuji M, Nakano T, Okuno T. (1987) *Chemosphere* 16:1889-94
5. Erickson M, Swanson S, Flora J, Hinshaw G. (1989) *Environ Sci Technol.* 23:462-470
6. Hou S, Wojtalewicz D, Mackie J, Kennedy E, Dlugogorski B. (2011) *Aust Combust Symp*. Newcastle, 1-4
7. Summoogum S, Wojtalewicz D, Mackie J, Kennedy E, Dlugogorski B. (2011) *Fire Saf Scie.* 10:239-253
8. Hou S, Mackie J, Kennedy E, Dlugogorski B. (2012) 9th *Asia-Oceania Symp Fire Scie Technol.* (submitted)