FORMATION OF TOXIC SPECIES IN THE OXIDATION OF CHLORINATED AND MIXED HALOGENATED BIPHENYLS

Hou S[1], Dlugogorski BZ[2*], Mackie JC[1], Kennedy EM[1], Altarawneh M[2]
[1]School of Engineering, The University of Newcastle, Callaghan NSW 2308, Australia; [2]School of Engineering and Information Technology, Murdoch University, Murdoch, WA 6150, Australia

Introduction

This study provides an assessment of the toxic pollutants formed during the thermal decomposition of polychlorinated and mixed halogenated (i.e., simultaneously chlorinated and brominated) biphenyls (PXB; X = Cl/Br). In particular, we have investigated the oxidation of 4-chlorobiphenyl (4-CB), 4,4'-dichlorobiphenyl (4,4'-DCB) and 4-bromo-4'-chlorobiphenyl (4,4'-BCB), at temperatures lower than those leading to complete conversion of PXB to HBr, HCl, H_2O and CO_2. Previous studies reported that partial oxidation of polychlorinated biphenyls, which found applications in transformer oil and capacitors, formed polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/F) [1-3]. However, these investigations reported limited measurements of volatile organic compounds (VOCs) and failed to separate the effects of surface and gas-phase pathways operating in the oxidation of PCBs. For example, Buser investigated the pyrolysis of mixtures of PCBs in air (residence time 20 s), finding the total yield of PCDFs of up to 2 % over a relatively low temperature range (300 – 400 ºC) [4]. In another study, Lemieux et al. performed long experiments of up to one week, pyrolysing PCB mixtures and reporting the formation of tetra-octaCDD/Fs at temperatures as low as 400 °C [5]. In our previous study on the oxidation of 4-CB in an alumina reactor (under residence time 5 s), we also observed the formation of toxic species (chlorobenzenes, chlorophenols, PCDD/Fs, etc) commencing from 350 ºC [6,7]. These low temperatures indicate the presence of surface reactions in the formation of PCDD/Fs, as the gas-phase synthesis of these species takes place in the window of between 550 °C and 700 °C. Previous studies neglected to differentiate between homogeneous and heterogeneous pathways. From this perspective, the present contribution aims to report VOC species, including important precursors of PCDD/F and PXDD/F (polyhalogenated dibenzo-*p*-dioxins and polyhalogenated dibenzofurans), appearing in the oxidation of PXBs under well-defined gas-phase conditions.

Materials and methods

A laboratory-scale apparatus consisted of a laminar-flow quartz reactor equipped with a sampling system for intercepting the volatile and condensable products. To remove the surface effects of transition metals present in the high-purity quartz, and to eliminate the conversion of triplet to singlet oxygen on quartz surfaces, we coated the quartz with boric acid [8,9]. Between experiments, we purged the reactor tube with dry nitrogen to avoid exposing the B_2O_3-coated surfaces to moisture. Baking the reactor tube at 800 °C for 2 h, before each experiment, removed condensed contamination from the preceding run. A XAD-2 cartridge served to trap the volatile organic compounds (VOCs) and PCDD/Fs.

We injected the samples (1 μL; split ratio 1:10) into the HRGC-QMS, equipped with the VF-5ms column (30 m length, 0.25 mm i.d., 0.25 μm film thickness) for the VOC analysis. Helium was used as the carrier gas, flowing at a constant flow rate of 1.0 mL/min through the column. The temperature program started at 35 °C, held for 5 min, and then increased with a temperature ramp of 10 °C/min up to 245 °C, and finally held for 10 min. The temperature of the injector, the ion source and the transfer line corresponded to 260, 250 and 250 °C, respectively. The MS source operated at 70 eV of the ionisation electron-impact voltage. We identified the eluted peaks by comparing their mass spectra with those from the NIST library, and with the available genuine standards. We detected no presence of VOC products, at signal/noise > 3, from washing the unexposed XAD-2 resin (blank).

The PCDD/F analysis followed the United States Environmental Protection Agency (USEPA) Standard Method 1613 [10], with minor modifications to quantitate mono- to trichlorinated congeners. That is, besides adding the 17 $^{13}C_{12}$ labelled toxic congeners, as mentioned in the EPA Method 1613, we also included 2,3-D[$^{13}C_{12}$]CDF to ascertain the recovery of mono-triCDD/Fs. The reactor and PTFE connection tube were washed with the *n*-hexane and collected together as one sample. We transferred the XAD-2 resin to a clean thimble and extracted it in the Soxhlet apparatus for 12 h in hot toluene (70-80 mL in the solvent cup). Before commencing the extraction process, we added the EPA-1613 labelled standards at the bottom of the thimble, and placed cotton

skeins on the top of the thimble to stop the resin and solvent spilling out. After extraction, we added the samples to the clean-up columns (silica gel columns and followed by the alumina columns). The samples were then concentrated to about 20 µl for injection. We employed the ITMS operated in tandem (in time) MS mode (electron voltage: 70 eV) to detect PCDD/F products. Samples for PCDD/Fs analysis (1 µL) were introduced into an injector (280 °C) operated in a splitless mode. Chromatographic separation was achieved with a VF-5ms capillary column (60 m length, 0.25 mm i.d., 0.25 µm film thickness) with helium as the carrier gas (1 mL/min). The oven temperature program commenced at 80 °C (held for one min), and then rose to 235 °C (held for 10 min) at 10 °C/min, with 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. We maintained the transfer line, ion trap, and manifold temperatures at 270, 200 and 80 °C, respectively.

To analyse PXDD/F products from the oxidation of 4,4'-BCB, we applied the Agilent GC-QTOF MS with a VF-5ms capillary column (60 m length; 0.25 mm i.d.; 0.25 µm film thickness). We maintained the transfer line, the injector and the source temperature at 250, 260 and 230 °C, respectively. The temperature program of the GC commenced from 45 °C, held for 5 min, followed by a temperature ramp of 10 °C/min up to 265 °C, then maintained for 10 min. We used 4 GHz mode and maintained emission current at 2.8 µA to increase the resolution for detecting trace amounts of PXDD/F. To determine the elemental composition of the unknown species, for which have had no genuine standards, we applied the mass calculator module in the QTOF software in conjuction with the isotopic analysis of molecular ion to determine the elemental composition and then analysed the fragmentation pattern to determine the chemical structure of these species.

Results and discussion

The thermal decomposition of 4-CB produces a number of volatile pollutants, including chlorophenols (4-chlorophenol detected under SIM mode) and chlorobenzenes, which function as important precursors for the formation of PCDD/Fs. Other VOCs included (chloro)benzaldehydes, 6-chlorobenzofuran, (chloro)ethynylbenzenes, naphthalene, (chloro)naphthalenols and dibenzofuran. Figure 1 illustrated the main VOC species formed in the oxidation of 4-CB, for the experiment conducted at 650 ºC. The results of the thermal decomposition of 4-CB also indicate the formation of mono-diCDD/Fs, at temperature in excess of 600 ºC, with 3-monochlorodibenzofuran (3-MCDF) being the most abundant CDD/Fs formed.
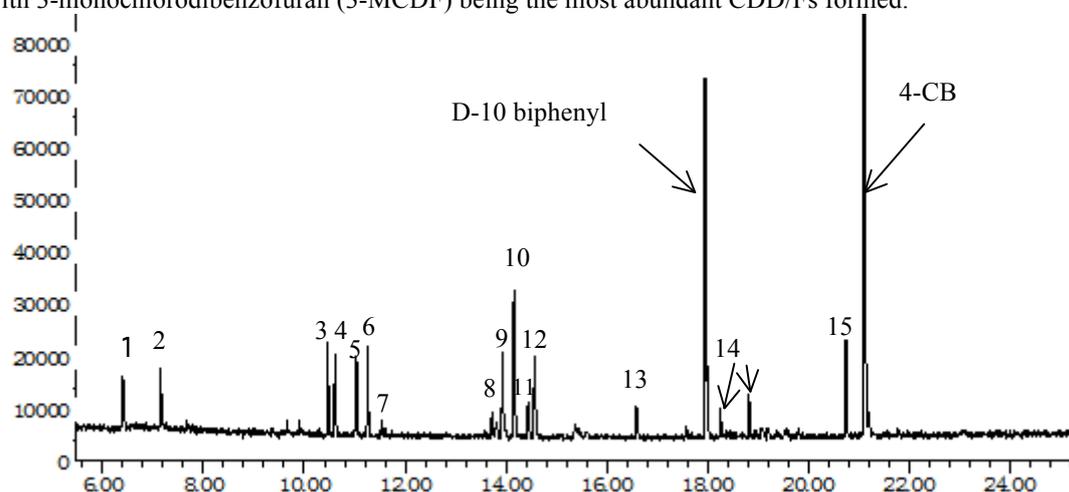

Figure 1. An example GC trace for the oxidation of 4-CB: experiment conducted at 650 ºC (1: monochlorobenzene; 2: 1-ethynylbenzene; 3: benzofuran; 4: 1-chloro-4-ethynylbenzene; 5. Benzaldehyde; 6: 2-chlorostyrene; 7: 6-chlorobenzofuran; 8: phenol; 9: naphthalene; 10: 3-chlorobenzaldehyde; 11: 4-chlorobenzaldehyde; 12: 1-naphthalenal; 13: 1,2-naphthalenedione; 14: 3-chloro-1-naphthalenol and its isomers; 15: dibenzofuran)

To gain further insights into the formation of VOC and to elucidate their reaction mechanisms, we investigated the decomposition of 4,4'-DCB. Benzene, monochlorobenzene, phenol and 4-chlorophenol (4-CP) functioned as the PCDD/F precursors, with monochlorobenzene as the dominant species. Especially, we confirmed the formation of benzene when we decreased the initial temperature of the GC oven to 35 ºC, to avoid the coelution

of the benzene peak with the solvent (*n*-hexane). We identified 2-chloronaphthalene as the main VOC product with a smaller amount of naphthalene, and even smaller abundance of 1-chloronaphthalene. Most of products were confirmed by the NIST database, with important species identified by injecting the genuine standards (benzene, monochlorobenzene, phenol, benzofuran, (chloro)benzaldehydes, 4-chlorophenol, (chloro)naphthalenes and dibenzofuran). The formation of PCDD/Fs included only MCDF, MCDD, DCDF and a minor quantity of DCDD detected at temperatures above 650 ºC. Figure 2 illustrated the main VOC species detected in the experiments.
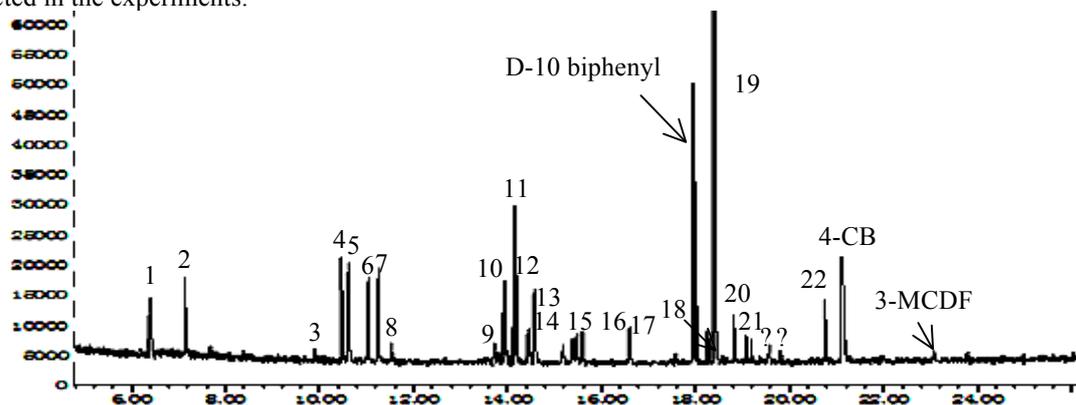

Figure 2. An example GC trace for the VOC products from the oxidation of 4,4'-DCB: experiment conducted at 685 ºC (1: monochlorobenzene; 2: 1-ethynylbenzene; 3: phenol; 4: benzofuran; 5: 1-chloro4-ethynyl-benzene; 6: 1-propynylbenzene; 7: benzaldehyde; 8: 1-chloro-4-ethynylbenzene; 9: 4-chlorophenol; 10: 6-chlorobenzofuran; 11: naphthalene; 12: 4-chlorobenzaldehyde; 13: 1-naphthalenol; 14, 15, 16: chloropropynylbenzenes; 17: 1,2-naphthalenedione; 18: 1-chloronaphthalene; 19: 2-chloronaphthalene; 20, 21: chloronaphthalenols; 22: dibenzofuran; ?: unidentified species)

We also studied the thermal decomposition of PXB with 4,4'-BCB as a probe molecule to gain insights into the effect of combined sources of chlorine and bromine on formation of mixed halogenated pollutants. We observed similar products as formed in the oxidation of 4-CB and 4,4'-DCB, such as benzene, monochlorobenzene, chloronaphthalenes, chlorobenzofurans, chloroethynylbenzenes, chloronaphthalenols and dibenzofuran. In addition, we also detected monobromobenzene, bromonaphthalenes, 6-bromobenzofuran (only one isomer), one isomer of bromoethynylbenzene, one isomer of mixed halogenated benzene and one isomer of mixed halogenated phenol (via GC-QTOF MS). We found a significant amount of 3-MCDF and one DCDF congener at temperature above 600 ºC. We confirmed one congener of monobromomonochlorodibenzofuran congener by using the mass calculator module and the isotopic distribution of the molecular ion.

Scheme 1 illustrates the formation pathways for important VOCs in the oxidation of 4,4'-DCB. Similar pathways operate in the formation of VOCs in partial oxidation of 4-CB and 4,4'-BCB. A triplet oxygen molecule substitutes the chlorine atom in the 4,4'-DCB molecule in a single-step process. This reaction results in the fission of the C-Cl bond and the subsequent formation of a 4-peroxychlorobiphenyl adduct. Barrierless fission of the peroxy O-O bond results the formation of the I adduct. Unimolecular decomposition of this adduct follows a three-step mechanism that features ring contraction/CO elimination pathways to form two-ring structure denoted as IV. Addition of triplet oxygen molecule to the IV moiety is thermodynamically neutral and results in the formation of the peroxy adduct of V. Fission of the O-O peroxy bond expels oxygen radical and forms the VI intermediate. 1,2-Hydrogen transfer into the C-C bridge stabilises the VI structure into the VII. A ring-opening reaction induces the appearance of the VIII. A CO molecule departs the VIII moiety and affords the generation of the IX intermediate. We regard the X intermediate as the direct source for 2-chloronaphthalene via a ring close reaction from IX. Elimination of the out-of-plane H atom from the X moiety produces the major experimentally detected product of 2-chloronaphthalene. Addition of a triplet oxygen to the same moiety (X) results in the formation of 3-chloronaphthalenol. The XI intermediate arising from the IX structure via elimination of a C_2H_2 acts as a direct intermediate for the formation of 1-chloro-4-ethynylbenzene. The addition of a triplet oxygen to species IX generates a precursor for 1-chloro-4-(1-propynyl)benzene. 4-

chlorobenzaldehyde and 6-chlorobenzofuran arise from two different reaction pathways with the same first step of adding the triplet oxygen to the XI radical.
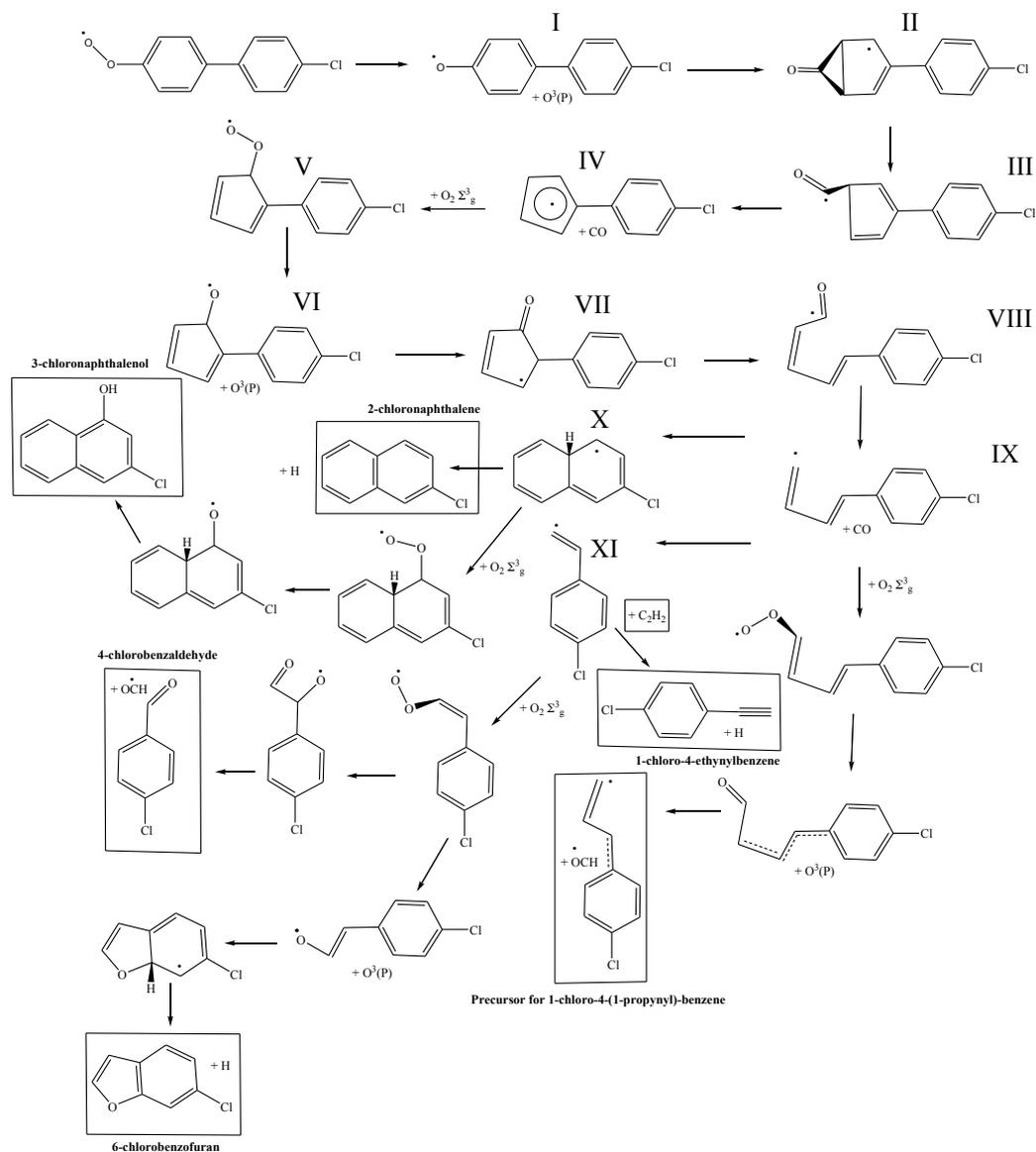
Scheme 1. Gas-phase pathways for the main VOC species in the oxidation of 4-CB, 4,4'-DCB and 4,4'-BCB

References
1. Hutzinger O, Choudhry G, Chittim B, Johnston L. (1985) *Environmental Health Perspectives* 60: 3-9
2. Korytar P, Leonards P, de Boer J, Brinkman U. (2002) *Chemosphere* 68: 203-218
3. Erickson M, Swanson S, Flora J, Hinshaw G. (1989) *Environmental Science Technology* 23: 462-470
4. Buser H. (1979) *Chemosphere* 3: 157-174
5. Lemieux M, Lee W, Ryan V, Lutes C. (2001) *Waste Management* 21: 419-425
6. Hou S, Mackie JC, Kennedy EM, Dlugogorski BZ. (2012) *Organohalogen Compounds* 74: 612-615
7. Hou S, Mackie JC, Kennedy EM, Dlugogorski BZ. (2013) *Procedia Engineering* 62: 350-358
8. Zhou C, Sendt K, Haynes B. (2013) *Proceedings of the Combustion Institute* 34: 625-632
9. Egerton A, Warren D. (1951) *Proceedings of the Royal Society A* 20: 465-476
10. US Environmental Protection Agency, *USEPA Method 1613*