Environmental Health Perspectives
Vol. 79, pp. 273–282, 1989

Thermally Induced Formation of Polychlorinated Dibenzofurans from Aroclor 1254-Contaminated Mineral Oil

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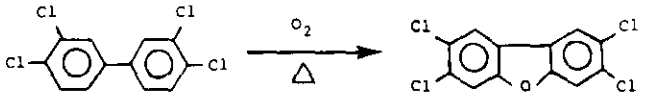
Numerous laboratory simulations and real-world events have demonstrated the thermal conversion of neat or high concentration of PCBs into the much more toxic PCDFs. Since millions of mineral oil transformers currently in service contain PCB concentrations in the 50 to 5000 ppm range, the thermal behavior of dilute PCB solutions is of practical and regulatory significance. In this work, neat Aroclor 1254 and 5000 ppm Aroclor 1254 in mineral oil were subjected to pyrolysis and combustion under a range of experimental conditions to define parameters resulting in maximal PCDF yields. The dependence of PCDF yield on Aroclor 1254 concentrations was then investigated in the 5000 to 50 ppm range. Combustion experiments demonstrated that PCDF yields expressed as micrograms PCDF/gram PCB were independent of concentration range, confirming that the process is kinetically first order in PCB. Much lower yields of PCDF were observed in the open tube pyrolysis experiments, as compared to combustion experiments and to earlier and concurrent sealed tube experiments. Slightly improved yields were observed in the pyrolysis experiments at lower concentrations, suggesting the existence of a PCB or PCDF destruction process of higher than first order kinetics. In all cases, yields expressed as micrograms PCDF/gram mixture were sharply and monotonically lower as concentrations decreased between neat or 5000 ppm Aroclor 1254 and 50 ppm Aroclor 1254.

Introduction

There is now ample evidence to demonstrate that polychlorinated biphenyl (PCB) samples subjected to high temperatures can form elevated concentrations of the more toxic polychlorinated dibenzofurans (PCDFs) (Eq. 1). For example, Miyata and Kashimoto (*1*) heated Kanechlor-400 for varying time periods (2–20 days); PCDF concentrations, as compared to initial amounts of PCDFs present, increased in samples held at 360°C. Morita et al. (*2*) heated PCBs in air or



oxygen for 1 week or more; PCDFs were formed at temperatures over 270°C, reaching maximum levels at about 300°C, and declining at 330°C, suggesting that some PCDF decomposition might be occurring at the higher temperatures. Pyrolysis of Aroclor 1254 and 1260 at temperatures up to 700°C for a few seconds produced substantial (up to a few percent) yields of PCDFs (*3*). Qualitatively similar results were obtained elsewhere in 1985 (*4*). Pyrolysis of individual chlorinated biphenyl congeners has resulted in the identification of four basic mechanisms of PCDF formation produced substantial (up to a few percent) yields of PCDFs (*3*). Qualitatively similar results were obtained elsewhere in 1985 (*4*). Pyrolysis of individual chlorinated biphenyl congeners has resulted in the identification of four basic mechanisms of PCDF formation (*5*). Numerous examples of real-world incidents in which PCBs formed PCDFs under thermal stress can also be cited. For example, in the Yusho incident, PCB contained in a heat exchange device formed elevated PCDF concentrations (*6,7*). In a series of electrical equipment fires involving capacitors or transformers,

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elevated PCDF concentrations as compared to initial concentrations have been noted (*8*).

These real-world events and laboratory simulations have a common feature. The fluid subjected to thermal stress was invariably highly concentrated (either neat PCB or ca 2:1 PCB to chlorinated benzenes) (*9*). However, the behavior of solutions containing low concentrations (less than 5000 ppm) of PCB is also of some practical interest. For example, an estimated 2,000,000 mineral oil transformers have, over the years, inadvertently become contaminated with PCBs at 50 ppm or higher, and 200,000 such transformers have become contaminated above 500 ppm (*10*). Furthermore, one method of removing transformers containing synthetic dielectric materials (askarel) from service is retrofilling. In this process, the askarel fluid is, as completely as possible, drained from the transformer and replaced with an alternative dielectric fluid. However, current technology leaves sufficient PCB in the transformer to cause the transformer to be legally classified as "PCB containing" (> 500 ppm) or "PCB contaminated" (> 50 ppm). Thus, after a suitable equilibration period (typically months), the dilution process must be repeated until an acceptable PCB concentration is attained. Obviously, the retrofilling process produces substantial volumes of waste fluid containing low PCB concentrations and a transformer filled with the retrofilling fluid but also containing measurable PCBs. The facility with which these dilute PCB solutions might form PCDFs was virtually unknown when the current project was initiated. It is obvious that PCDF formation in dilute PCB solution could be a significant factor in evaluating the hazards associated with operation of contaminated mineral oil and retrofilled transformers, in the viability of the retrofilling process, and in the process of governmental regulation. Thus, a laboratory program was initiated to assess the ability of various dilute (50–5000 ppm) PCB-containing fluids to form PCDFs under thermal stress.

The two distinct sets of experimental conditions used in this study will be referred to as "pyrolysis" and "combustion." Some confusion exists over the definitions of these terms. Combustion here denotes a chemical process that produces light and heat; pyrolysis indicates an irreversible chemical decomposition caused by heat. These definitions are consistent with those used by the American Society for Testing and Materials (*11*) and in standard texts (*12*).

Within the broad outlines of these definitions, numerous heating regimens and apparatus designs are possible. The conditions used here were chosen to be somewhat relevant to real-world scenarios. Thus, pyrolyses were performed at atmospheric pressure, and with 15-min heating times, which are plausible situations for real-world incidents and conditions very different from the few seconds contact time and sealed tube most commonly employed (*3,13–15*). Combustion experiments were performed in a flow system in the presence of a flame, for similar reasons.

Experimental

Pyrolysis

Pyrolyses were conducted in vertically mounted pyrex glass tubes (50 × 0.4 cm ID) sealed at their lower end. The polychlorinated biphenyl congener (or Aroclor 1254) to be pyrolyzed was introduced to the bottom of the pyrolysis tube as a 50,000 or 5000 μg/mL solution in benzene using a 50-cm long, 27-gauge needle attached to a 1 mL syringe. The tube was then placed in a warm water bath and the solvent removed under reduced pressure. After dryness had been attained, the tube was removed from the water bath and sufficient diluent (mineral oil) was similarly added to produce a final volume of 100 μL. In order to avoid the escape of potentially toxic products, the topmost 5 cm of the tube was chilled in dry ice, and a charcoal trap was attached to the tube's end for the duration of the pyrolysis.

The heating device used in these experiments was based on a thermostatically controlled Mini-Melt Furnace (Model #F-25810, Thermolyne Corp., Dubuque, IA). The graphite crucible supplied with the furnace was replaced with a stainless-steel block, 11 cm × 4 cm. Holes (8 cm × 0.6 cm ID) were drilled into the block to accommodate the glass tubes used in the pyrolysis. A thermocouple was inserted into one of the holes and connected to a digital pyrometer (Model #8350, Cole Parmer Instrument Co., Chicago, IL) to permit accurate temperature measurement (Fig. 1).

In a typical experiment, the furnace was adjusted to equilibrate at the temperature of interest; the range of temperatures investigated in this project was 450 to 750°C, although most work was performed between 500 and 650°C. After thermal equilibrium had been reached, the sealed end of the glass tube (already charged with the material to be pyrolyzed) was inserted into the stainless-steel block. In most experiments, contact times of 15 min were used. Typically, the liquid refluxed up the inner walls of the tube. The tube's length and its large unheated volume kept the reflux level well below the open end in all experiments. No visible material was trapped in the chilled region, and excellent mass balance was generally observed.

After the glass tube had cooled to room temperature, about 150 μL of benzene was added to the pyrolysis tube and refluxed gently for 2 min. The benzene extract was then transferred to an appropriate container and the process repeated 3 to 4 times. The volume of the combined extracts was then adjusted and the mixture subjected to analysis.

Pyrolysates derived from biphenyl or chlorinated biphenyls either neat or in mineral oil were generally purified by column chromatography on acidic alumina and analyzed for specific expected dibenzofuran products using either capillary column gas chromatography/flame ionisation detector (GC/FID) or gas chromatography/electron capture detector (GC/ECD). Certain pyrolysates required more exten-

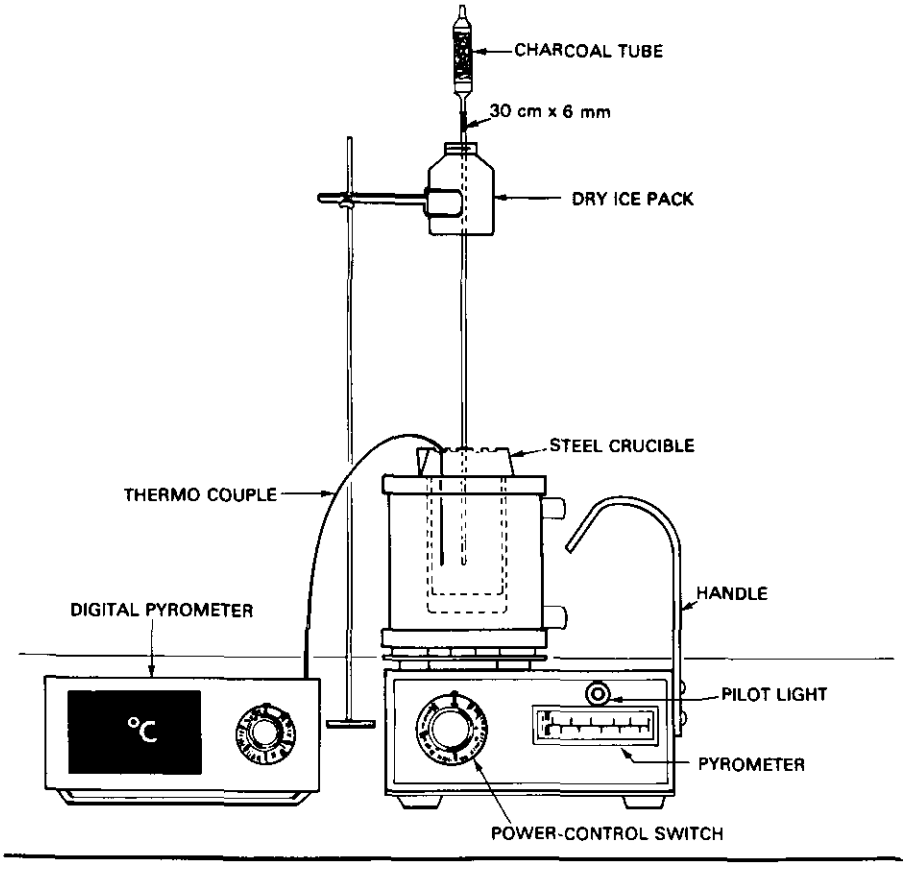

FIGURE 1. Pyrolysis apparatus.

sive clean-up. Thus, analysis of octachlorodibenzofuran formation from pyrolysis of decachlorobiphenyl in mineral oil required multilayer silica gel chromatography, followed by acidic alumina chromatography, then activated carbon chromatography, and, finally, neutral alumina chromatography (A. S. Narang, unpublished data).

Pyrolysis of Aroclor 1254 mixtures produced product mixtures of such complexity that GC analysis was clearly impractical. These samples were spiked with ^{13}C-labeled 2,3,7,8-TCDF and TCDD; 1,2,3,7,8-PeCDF and PeCDD; 1,2,3,4,7,8-HxCDF; 1,2,3,6,7,8-HxCDD; 1,2,3,4,6,7,8-HpCDD; and OCDD to permit quantitation by the internal standard technique. The samples were then purified by preliminary column chromatography on silica, followed by a semi-automated clean-up procedure involving acidic alumina, activated carbon, and neutral alumina column chromatography. This methodology is described in detail elsewhere (*16*).

Combustion

The combustion apparatus designed for this study (Fig. 2) consists of four parts: (a) blast burner; (b) combustion chamber; (c) sample introduction unit; (d) sample collection unit.

(a) The blast burner in which combustion gases are premixed was purchased from A. H. Thomas Company. It was fitted with an aluminum casing (~3.9 cm ID). (b) The combustion chamber was made of quartz tubing (115 × 2.5 cm). To one end was attached a ball joint (28/15); the other end was widened (~3.8 cm) so that the outside casing of the burner could slide over it. A side tube, approximately 12 × 1.3 cm, was attached to the combustion chamber 4 cm from the burner end. Through this tube the sample was introduced so that it fell almost into the center of the flame.

(c) The sample introduction unit consists of a 10-mL syringe to which a modified needle (16 gauge) approximately 95 cm long is attached. It was placed in a motor-driven syringe drive (Harvard Compact Infusion Pump Model 975) that is capable of maintaining constant flow of sample at low volume. The needle was pushed through a septum attached to one leg of a Tee and then through an 11-gauge tube (~23 cm) attached to the other leg of the Tee. The needle along with 11 gauge tubing was pushed through a septum attached to the side tube of the combustion chamber. The position of the needle was adjusted so that its end was near the flame. The third leg of the Tee was used as an inlet for introducing any make up gas.

(d) The sample collection unit consists of an impinger (trap) and an adsorbent tube fitted with ball joints. One end of the impinger was connected to the end of the combustion chamber, to the other end was

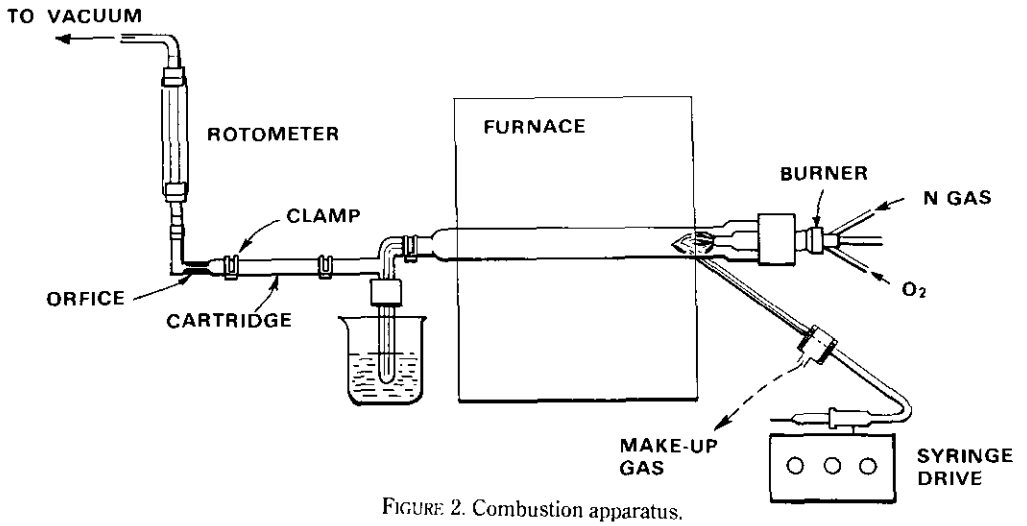

FIGURE 2. Combustion apparatus.

attached an adsorbent tube, which in turn was attached to a vacuum line. The size of the orifice was determined by the flow through the combustion chamber.

A Lindberg Furnace (Model 58331) was used to vary the temperature of the combustion chamber. The experimental conditions that were varied included sample matrix, oxygen concentration, combustion chamber temperature, and residence time. The oxygen concentration was evaluated at three levels: > 20% excess; 2 to 8% excess; and 80% of the required amount. The residence times evaluated were: high, 12.0 sec; medium, 6.0 sec; low, 3.0 sec.

At the start of each run, the combustion chamber was placed in the furnace, and the unit was equilibrated at the required temperature for 30 min. After igniting the flame, the blast burner was then slipped onto the chamber. It was allowed to burn for a few minutes with the collection end open to the atmosphere. The collection unit fitted with the appropriate orifice and the rotameter was attached to the combustion tube and the vacuum pump started. The sample introduction unit was attached at the inlet tube. All connections were made using slip-on clamps. The syringe drive was started and the solution was allowed to fall into the flame at the rate of 70 to 100 μL/min. After the required amount of material was combusted, the collection unit was separated first followed by the sampling unit and then the burner was extinguished.

Two extraction procedures were evaluated: (a) method 1: The XAD-2 cartridge was removed from the unit and the resin was poured into a Soxhlet along with the glass wool plugs. The tube itself was washed with benzene (~20 mL). The wash benzene along with more solvent (total volume ~100 mL) was used to extract the resin overnight. After the extraction was completed, the condenser from the Soxhlet unit was removed and the volume of the solvent was reduced to 10 mL; water in the trap was extracted with 3 × 25 mL of 50:50 hexane:ether. The organic layer was dried over anhydrous sodium sulfate and transferred to a Kuderna-Danish (K-D) apparatus. It was combined with the benzene extract of the resin, and the volume was brought down initially to 5 mL over a steam bath and then to 1.0 mL under a stream of nitrogen.

(b) Method 2: The XAD-2 cartridge was eluted with 1:1 mixture of ether:hexane (100 mL). The eluate was combined with the water trap extract (as done in method 1). The combined extracts were initially concentrated to 5 mL using a K-D apparatus over a steam bath and then to 1 mL under a stream of nitrogen.

Crude extracts were purified by column chromatography on alumina. A glass column (30 cm × 1 cm) was packed with dry acidic alumina (12 g) topped with anhydrous sodium sulfate (3 g). The extract (~1 mL) in benzene was transferred onto the column using disposable pipettes and the container was washed with 3 to 5 mL of hexane and the wash also transferred onto the column. The column is then eluted with different solvents and the following six fractions are collected: Fr 1, 100 mL with 1% CH_2Cl_2 in hexane; Fr 2, 100 mL with 2% CH_2Cl_2 in hexane; Fr 3, 50 mL with 10% CH_2Cl_2 in hexane; Fr 4, 75 mL with 50% CH_2Cl_2 in hexane; Fr 5, 100 mL with 100% CH_2Cl_2; and Fr 6, 25 mL with 50% CH_2Cl_2 in methanol.

The first two fractions were combined and concentrated to 10 mL using a K-D apparatus over a steam bath. This was analyzed by GC for the uncombusted starting material and other compounds of interest. Fractions 4 and 5 were combined and concentrated first using K-D apparatus over a steam bath to 5 mL and then under a stream of nitrogen to 0.1 mL. An appropriate amount of the internal standard was added and the concentrate transferred into a 1 mL vial fitted with a septum. It was then analyzed by GC/MSD for PCDDs and PCDFs.

A Hewlett-Packard integrated system consisting of 5890 GC, 5970 mass selective detector (MSD) and a 5997OA work station was used for the analysis of PCDDs and PCDFs. The GC was equipped with a Grob type splitless injector. It was attached to the MSD using

a direct capillary interface. A fused silica column (60 m × 0.25 mm) coated with DB-5 (J and W Scientific, Rancho Cadora, CA) was used for the separation of various PCDDs and PCDFs. General operating conditions for the gas chromatograph were carrier gas (He) at a head pressure of 30 pounds/square inch, interface temperature 240°C; small injector temperature 215°C. The oven was programmed in stages; from 70°C to 230°C at a rate of 7°C/min with a hold of 2 min at initial temperature and 5 min at 230°C; it was further programmed to 250°C at a rate of 3°C/min and held at this temperature for 5 min; finally it was programmed to 295°C at a rate of 4°C/min and held at final temperature for 30 min. The MSD was operated at a fixed voltage of 70 E.V. and in the single ion monitoring mode. At any time, 3 to 5 ions, characteristic of various groups of PCDDs and PCDFs, were monitored. The data were collected on the HP5997OA work station. Quantitation was accomplished using 2,2′,4,6,6,′-pentachlorobiphenyl as an internal standard with response factors measured from one isomer of each PCDD and PCDF chlorination group.

Establishing Collection Parameters

A solution of biphenyl (5–40 mg/mL) in tetrachloroethylene (TCE) was combusted and products collected by using various traps connected in a series as follows: cold trap containing hexane followed by a Florisil cartridge and then a Porapak N cartridge; Florisil cartridge connected to a Porapak N cartridge followed by a cold trap containing hexane; empty cold trap connected to a Florisil cartridge and then a Porapak N cartridge; two silica gel cartridges followed by a hexane trap; two XAD-2 cartridges followed by a cold trap containing hexane, ice-cold trap followed by two XAD-2 cartridges.

XAD-2 cartridge of the collection system was spiked with 10 μg each of biphenyl and dibenzofuran and 0.1 μg each of decachlorobiphenyl and octachlorodibenzofuran. Mineral oil (3 mL) was combusted and the gases passed through the collection system. After completion of the combustion, the trap and the cartridge were worked up by the established procedure.

A Tee with one end sealed with a septum was attached between the orifice and the vacuum inlet. The amount of natural gas used was kept constant while the amount of oxygen, make-up gases like nitrogen or air, was varied to achieve different levels of oxygen and the flows required to attain different residence times. The burner was ignited and mineral oil containing 5000 μg/mL of biphenyl were dropped onto the flame at a rate of 70 to 100 mL/min. A gas tight syringe was used to withdraw the sample (20–100 μL) through the septum and then injected onto the gas chromatograph.

Results

Combustion experiments were first performed to select the combination of traps and adsorbents to be used in subsequent experiments. Trapping efficiency was measured using biphenyl in TCE. Both biphenyl and dibenzofuran are relatively innocuous compounds (and thus are safely worked with), and are more volatile (and thus less readily trapped) than more chlorinated analogs. TCE was used as a solvent to provide a source of HCl; the latter might conceivably influence the stability of the combustion products or trapping materials. The typical sample collection train studied consisted of two traps (empty, or containing water or hexane) and two cartridges (packed with Florisil, Porapak, silica gel, or XAD-2) arranged in various sequences. As Table 1 demonstrates, the first three trapping devices in every case sufficed to capture 100% of the biphenyl and dibenzofuran. Thus practical considerations were used to decide on the standard collection system. The fine particles formed under certain sets of combustion experiments, as well as the substantial water formed in the combustion process, tended to clog up Florisil, Porapak, and silica gel cartridges. This led to increased back-pressure on the flame, resulting in eventual flame blow-off. This problem was generally less severe with XAD-2 cartridges.

Another interesting feature apparent in the data of Table 1 is the drastically decreased trapping efficiency of silica gel and Florisil cartridges when connected directly to the exhaust end of the combustion chamber. Although the trapping efficiency of XAD-2 was less influenced by high gas temperatures, decomposition was observed at the high gas flows characteristic of 3-sec residence times. As Table 1 indicates, no breakthrough into the second cartridge was observed even when flow volumes of as much as 240 L were used. Thus, the standard gas sampling train used in these studies consisted of a water-filled gas trap followed by a XAD-2 cartridge.

A second set of preliminary experiments was performed to verify that analytes trapped on XAD-2 were successfully desorbed from the agent by the extraction technique used and were successfully recovered through the alumina column clean-up procedure. Soxhlet extraction of XAD-2 with benzene or elution with 1:1 ether:hexane gave 98 to 110% recovery of biphenyl, decachlorobiphenyl, dibenzofuran, and octachlorodibenzofuran. Recoveries of 95 to 100% were observed for these compounds after the alumina column clean-up.

Additional experiments were performed to verify the stability of typical biphenyl and dibenzofuran congeners in the collection apparatus in the presence of hot combustion gases. As Table 2 demonstrates, individual congeners spiked onto XAD-2 or into a water trap and exposed to 30–50 L of gas resulting from the combustion of mineral oil, silicone oil, or TCE were nevertheless well recovered, demonstrating the stability of these materials and their retention in the sampling device despite exposure to hot combustion gases.

Preliminary experiments were also performed to establish operating parameters for the combustion

Table 1. Distribution of biphenyl (BP) and dibenzofuran (DBF) formed from combustion of tetrachloroethylene/biphenyl mixtures at 400°–600°C among various sequentially arranged collection devices.

BP concentration in mixture	Flow, L	Device #1	Device #2	Device #3	Device #4
10,000 μg/mL		Hexane trap	Hexane trap	Florisil cartridge	Florisil cartridge
	28	2% BP, 2% DBF	97% BP, 91% DBF	1% BP, 7% DBF	<1% BP, <1% DBF
10,000 μg/mL		Empty trap	Empty trap	Florisil cartridge	Florisil cartridge
	28	<1% BP, <1% DBF	55% BP, 59% DBF	45% BP, 39% DBF	<1% BP, <1% DBF
10,000 μg/mL		Empty trap	Empty trap	Porapak Cartridge	Florisil Cartridge
	56	<1% BP, <1% DBF	22% BP, 51% DBF	78% BP, 49% DBF	<1% BP, >1% DBF
10,000 μg/mL		Hexane trap	Hexane trap	Porapak Cartridge	Florisil Cartridge
	28	<1% BP, <1% DBF	61% BP, 23% DBF	39% BP, 77% DBF	<1% BP, <1% DBF
10,000 μg/mL		Empty trap	Empty trap	Florisil cartridge	Porapak cartridge
	28	<1% BP, <1% DBF	59% BP, 61% DBF	41% BP, 39% DBF	<1% BP, <1% DBF
10,000 μg/mL		Hexane trap	Hexane trap	Florisil cartridge	Porapak cartridge
	56	<1% BP, <1% DBF	98% BP, 90% DBF	2% BP, 8% DBF	<1% BP, <1% DBF
10,000 μg/mL		Hexane trap	Hexane trap	Florisil cartridge	Porapak cartridge
	28	<1% BP, <1% DBF	100% BP, 100% DBF	<1% BP, <1% DBF	<1% BP, <1% DBF
40,000 μg/mL		Hexane trap	Hexane trap	Florisil cartridge	Porapak cartridge
	56	1% BP, 50% DBF	<1% BP, 50% DBF	99% BP, <1% DBF	<1% BP, <1% DBF
		<1% BP, 45% DBF	<1% BP, 43% DBF	100% BP, <14% DBF	<1% BP, <1% DBF
5,000 μg/mL	56	<1% BP, <1% DBF	100% BP, 100% DBF	<1% BP, <1% DBF	<1% BP, <1% DBF
	45	<1% BP, <1% DBF	54% BP, 59% DBF	46% BP, 41% DBF	<1% BP, <1% DBF
	56	<1% BP, <1% DBF	94% BP, 94% DBF	6% BP, 6% DBF	<1% BP, <1% DBF
5,000 μg/mL		Florisil cartridge	Porapak cartridge	Hexane trap	Hexane trap
	28	10% BP, 63% DBF	64% BP, 8% DBF	1% BP, 36% DBF	<1% BP, <1% DBF
	34	46% BP, <1% DBF	51% BP, 5% DBF	1% BP, 96% DBF	<1% BP, <1% DBF
5,000 μg/mL		Silica cartridge	Silica cartridge	Hexane trap	Hexane trap
	15	5% BP, <1% DBF	1%BP, <1% DBF	95% BP, 100% DBF	<1% BP, <1% DBF
	13	24% BP, 35% DBF	2% BP, 8% DBF	73% BP, 54% DBF	<1% BP, <1% DBF
40,000 μg/mL		XAD-2 cartridge	XAD-2 cartridge	Empty trap	Empty trap
	13	100% BP, 100% DBF	<1% BP, <1% DBF	<1% BP, <1% DBF	<1% BP, <1% DBF
5,000 μg/mL		Water trap	XAD-2 cartridge	XAD-2 cartridge	Empty trap
	240	1% BP, 1% DBF	>98% BP, >98% DBF	<1% BP, <1% DBF	<1% BP, <1% DBF

Table 2. Effect of exposure to combustion gas on recoveries of spiked biphenyls and dibenzofurans.[a]

Collection device spiked	Dielectric fluid	Wall temperature, °C	Combustion gas volume, L	Biphenyl recovery, %	Decachloro-biphenyl recovery, %	Dibenzofuran recovery, %	Octachloro-dibenzofuran recovery, %
XAD-2 cartridge[b]	Mineral oil	550	45	98 ± 2	100 ± 7	98 ± 2	97 ± 2
Water trap[c]	Silicone oil	550	30	93 ± 4	91 ± 2	90 ± 6	76 ± 3
Water trap[d]	Tetrachloroethylene	540	50	92	—[e]	82	—[e]

[a]Isolated by Soxhlet Extraction with ether/hexane (method 2 in "Experimental").
[b]Spiked with 10 μg each of biphenyl and dibenzofuran and 0.1 μg of decachlorobiphenyl and octachlorodibenzofuran.
[c]Spiked with 5 μg each of biphenyl and dibenzofuran and 0.1 μg of decachlorobiphenyl and octachlorodibenzofuran.
[d]Spiked with 50 μg of biphenyl and dibenzofuran.
[e]Analysis precluded by interferences.

apparatus that influence the concentration of unreacted oxygen in the exhaust gases. While the rate of flow of the natural gas fuel was maintained at 0.3 L/min and the wall temperature at 550°C, the composition to the dielectric fluid, the flow rate of oxygen into the system, and the flow rate of nitrogen and air make-up gas were varied (Table 3). For example, while combusting 5000 ppm biphenyl in mineral oil, the oxygen input was varied from 1 to 6 L/min, resulting in the percent residual oxygen increasing from 5 to 71%. In another sequence of experiments, 5000 ppm biphenyl in silicone oil was combusted with constant oxygen flow but with sufficient change in make-up gas flow to vary residence times from 12 to 3 sec; these changes had little effect on residual oxygen content. Similarly, the residual oxygen present when 5000 ppm biphenyl in TCE was burned was essentially identical to the results of the corresponding experiment with 5000 ppm biphenyl in mineral oil.

Once an understanding of the influence of various operating parameters on residual oxygen concentration had been gained, experiments were performed to select "optimal" residual oxygen content for producing maximum yields of PCDFs. Thus, 5000 ppm solutions of Aroclor 1254 in mineral oil with low (2–8%) and high (> 20%) residual oxygen. As Table 3 indicates, markedly higher yields were observed at 2 to

Table 3. Influence of residual oxygen concentration on yields of TCDF from combustion of 5000 μg/mL Aroclor 1254 solutions in mineral oil.

Dielectric fluid	Residence time, sec	Wall temperature, °C	Residual O_2, %	% TCDF recovered
Mineral oil	6	450	2-8	0.08
	6	450	>20	0.000006
	3	550	2-8	0.44
	2-3	550	>20	0.007
	12	550	< 1	ND[a]
	12	550	2-8	0.5

[a]TCDFs not detected. However, indications of substantial concentrations of chlorinated biphenylenes were observed.

8% residual oxygen versus > 20% residual oxygen in all cases studied. A single experiment was performed with very low residual oxygen (< 1%), and PCDF formation was not observed. The substantial soot formation observed under these conditions precluded their use in routine studies. Thus, all further runs were performed with 2 to 8% excess oxygen.

The next phase of the project involved systematic studies of the combustion of Aroclor 1254 in mineral oil at concentrations ranging from 5000 to 50 ppm. The first sets of experiments were designed to select the conditions that produced maximum yields of PCDFs. Sample introduction rates were maintained at 70 μL/min (arbitrarily chosen) and excess oxygen in the 2 to 8% range (selected based on the single congener experiments already discussed). The principal adjustable variables then were wall temperature (450–650°C) and residence time (3–12 sec). As the data in Table 4 demonstrate, optimal yields were obtained at 3-sec residence times; the design of the combustion apparatus precludes study of shorter residence times. Yields of tetra and pentachlorodibenzofurans were marginally better at 550°C than at 650°C wall temperature; conversely, superior yields of trichlorodibenzofurans were observed at 650°C (Table 4). Hexa, hepta, and octachlorodibenzofurans were not quantifiable under any conditions studied here. Thus, 550°C wall temperature and 3-sec residence time were selected as reasonable conditions to study the dependence of PCDF formation on PCB concentration. The yields of PCDF from the combustion of 500 and 50 ppm Aroclor 1254 solutions in mineral oil are also contained in Table 4. Combustion of mineral oil alone did not yield detectable amounts of PCDFs.

Aroclor 1254 was pyrolyzed neat, at 5000 μg/mL and 50 μg/mL in mineral oil at 500°C, 550°C and 600°C, for 15 min in an open tube. The resulting mixtures were subjected to multicolumn clean-up followed by GC/MS analysis. These experiments permitted the following observations: (a) Although yields were not sharply temperature dependent, formation of Cl_4-Cl_6 dibenzofuran maximized at 550°C; (b) Yields from the 50 μg/mL solution were insufficient for accurate measurement; (c) Putative duplicate pyrolyses gave differences in yield well in excess of those attributable to the analysis and presumably reflect the influence of subtle, uncontrolled variables (e.g., shape of tube, presence or absence of trace amounts of catalytic impurities or catalytically active surfaces). These observations necessitated several changes in the experimental protocol. First, an intermediate concentration of PCB (i.e., 500 μg/mL) was studied, so that PCDF yields would be measurable at least two dilutions. Second, in order to improve the precision of the measurements, a single set of conditions based on apparent maximum conversion of PCBs to PCDFs was selected for the concentration dependence studies, and six runs were performed. The six runs were combined randomly into a pair of samples, with the expectation that run to run variations would be averaged out. Additionally, these

Table 4. Yields of polychlorinated dibenzofuran from the combustion of Aroclor 1254/mineral oil solutions.[a]

Aroclor 1254 concentration μg/mL	Wall temperature, °C	Residence time, sec	PCB destruction, %	μg PCDF/g of Aroclor 1254			
				Cl_3	Cl_4	Cl_5	Cl_6-Cl_8
5000	450	12	98-99	180 ± 50	20 ± 4	+	
	450	6	98	6700 ± 700	800 ± 100	170 ± 30	ND
	450	3	88 ± 3	3800 ± 200	1400 ± 200	360 ± 70	ND
	550	12	ND	700	100	+	ND
	550[b]	6	ND	4200 ± 400	500 ± 0	80 ± 4	ND
	550	3	85 ± 3	18000 ± 3000	4400 ± 900	1300 ± 200	ND
	650	12	99	900 ± 200	70 ± 10	4 ± 2	ND
	650	6	96 ± 2	7400 ± 1000	700 ± 100	20 ± 6	ND
	650	3	86 ± 3	30000 ± 3000	3900 ± 400	500 ± 100	ND
500	550[c]	3	95 ± 3	10000 ± 1000	2600 ± 300	600 ± 60	ND
50	550[c]	3	89 ± 1	7400 ± 1800	2200 ± 200	400 ± 40	ND
0[d]	550	3	–	–	–	–	–

[a]Numbers are average of 4 combustion experiments. Error limits represent one SD. Sample introduction at 70 μL/min, excess oxygen 2-8%. ND, not determined; +, present, but insufficient amount for quantitation; –, not detected.
[b]Average of 2 runs.
[c]Average of 3 runs.
[d]Mineral oil without added PCB. ND = not determined; (+) present, but insufficient amount for quantitation; (–) not detected.

larger samples permit lower detection limits, thus offering the possibility of generating useful data from the 50 ppm experiments and these results are presented in Tables 5 and 6. Much better run-to-run precision was observed here.

Discussion

The data generated in this study can be evaluated from two perspectives. First, the yields of PCDF can be discussed on the basis of microgram or nanogram PCDF per gram of mixture pyrolyzed or combusted. It is hypothetically possible that dilution might so drastically improve the efficiency of conversion that a 5000 μg/mL solution could produce an amount of PCDF comparable to that observed from a 1,000,000 μg/mL solution. In fact, as demonstrated in the previous section, and as illustrated in Figure 3, yields of pyrolytically generated PCDF expressed on a mass PCDF/mass of mixture basis are at least two orders of magnitude lower in the 5000 μg/mL solutions. On the same basis, yields are in every case lower still in the 500 μg/mL solutions and continue to decline in the 50 μg/mL solutions. Since the apparatus used in combustion experiments was incapable of combusting neat 1,000,000 μg/mL solutions, comparisons of yields on a mass PCDF/mass of mixture basis for these experiments must be confined to the 5000 to 50 μg/mL concentration range. Further, not all mixture produced significant PCDF/PCDD on combustion

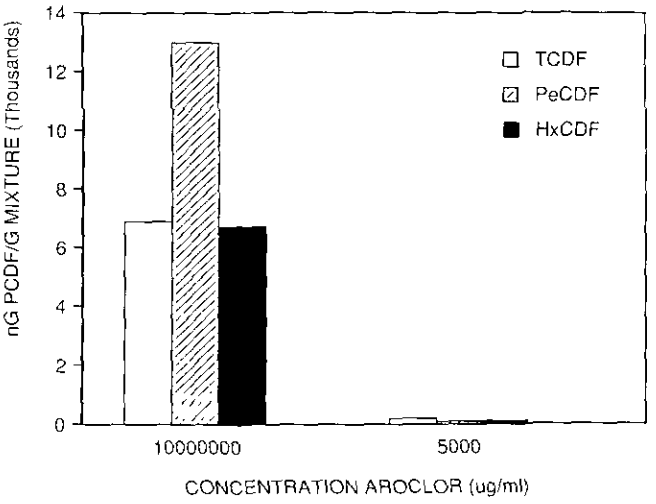

FIGURE 3. Pyrolysis of Aroclor 1254 in mineral oil. Comparison of yields (ng PCDF/g mixture) from neat Aroclor 1254 and 5000 ppm Aroclor 1254 in mineral oil.

Table 5. Polychlorinated dibenzofuran formed per gram of mixture pyrolyzed: Aroclor 1254 neat and in mineral oil.[a]

Concentration of Aroclor 1254, ppm	Temperature, °C	PCDF formed, ng			
		Total TCDF	Total PeCDF	Total HxCDF	Total HPCDF
1,000,000[b]	550	8,200	16,000	8,000	
	550	5,500	16,000	5,100	
5,000[c]	550	45	160	160	24
	550	35	170	200	14
500[c]	550	1.6	17	17	
	550	3.1	18	18	
50[c]	550		3.1	3.5	
	550		3.4		

[a]Open-tube pyrolysis, 15-min contact time.
[b]Data are produced from single runs.
[c]Each sample represents a composite of three separate pyrolysis which were combined prior to analysis to minimize run to run variations.

Table 6. Polychlorinated dibenzofuran formed per gram of Aroclor 1254 pyrolyzed: Aroclor 1254 neat and in mineral oil.[a]

Concentration of Aroclor 1254, ppm	Temperature, °C	TCDFs	PeCDFs	HxCDFs
1,000,000[b]	550	8,200	16,000	8,000
	550	5,500	10,000	5,100
5,000[c]	550	9,000	33,000	32,000
	550	6,000	34,000	41,000
500[c]	550		34,000	34,000
	550	6,200	36,000	36,000
50[c]	550		62,000	70,000
	550		68,000	

[a]Open-tube pyrolysis, 15-min contact time.
[b]Data are produced from single runs.

even at 5000 μg/mL. However, as Figure 4 demonstrates, whenever PCDF/PCDD formation was measurable at 5000 μg/mL, yields expressed on a mass PCDF/mass of mixture basis declined sharply at lower concentrations. These sharp decreases have important practical implications for persons assessing the hazards associated with thermal events involving electrical equipment containing dilute solutions of PCBs.

An alternative way to discuss these results is to consider yields of PCDD or PCDF per gram of PCB pyrolyzed or combusted. This approach, although perhaps of less practical interest, can offer potential insight into the mechanistic details of the conversion process. From this perspective, a variety of distinct behaviors are encountered with the various chlorinated compounds and mixtures. Pyrolysis of PCB in mineral oil in the 5000 to 50 μg/mL range produces PCDF yields that are remarkably similar to those observed from neat PCBs (Fig. 5). Both mixtures exhibit somewhat better yields at the lowest concentrations studied than at 5000 μg/mL. This result demands that a process exists in these solvents that is kinetically second order in PCBs and results in destruction of the starting PCB, the intermediate or the PCDF product. This process might be formulated as reaction between solvent and PCB to generate an intermediate, perhaps a phenoxy radical, that in turn couples with another PCB derived molecule to produce high molecular weight by-products. Phenoxy radicals are the proposed reactive species since they should be comparatively long-lived and are, in fact, known to undergo intermolecular coupling (*17*).

Yields of PCDF (again expressed as microgram PCDF/gram chlorinated compound combusted) from combustion of 5000 μg/mL solutions of Aroclor 1254 in mineral oil were adequate to allow determination of yield at 500 and 50 ppm at 3 sec retention time and 550° wall temperature (Fig. 6). In general, these yields appeared to vary by less than a factor of two as

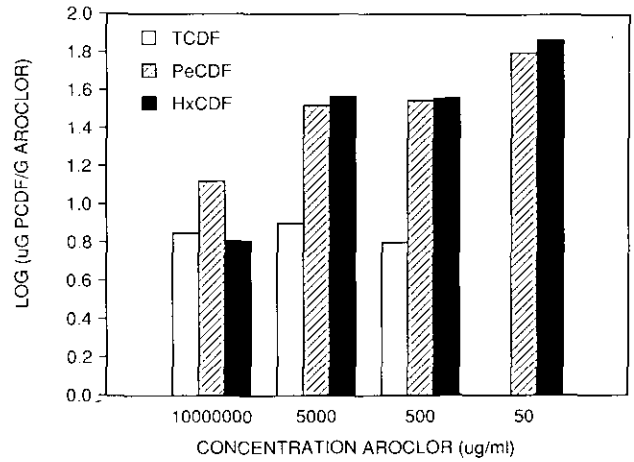

FIGURE 5. Pyrolysis of Aroclor 1254 in mineral oil. Comparison of yields (log [μg PCDF/g Aroclor]) from neat Aroclor 1254, 5000, 500, and 50 ppm Aroclor 1254 in mineral oil.

concentration varied 100-fold. In view of the facts that some reproducibility problems were encountered during combustion experiments and that low concentration runs produced yields near limits of detection, little significance can be ascribed to the modest variation in yield observed. Thus, there is no convincing evidence to demonstrate that yield is concentration dependent for combustion of PCBs in mineral oil at 5000 to 50 ppm.

Conclusions

It is clear from this work that no small set of laboratory experiments could reasonably model the range of real-world thermal events that might befall a transformer or capacitor. These experiments confirm that the relative PCDF/PCDD forming potential of the Aroclor 1254/mineral oil combinations varies markedly between the two sets of experimental conditions studied.

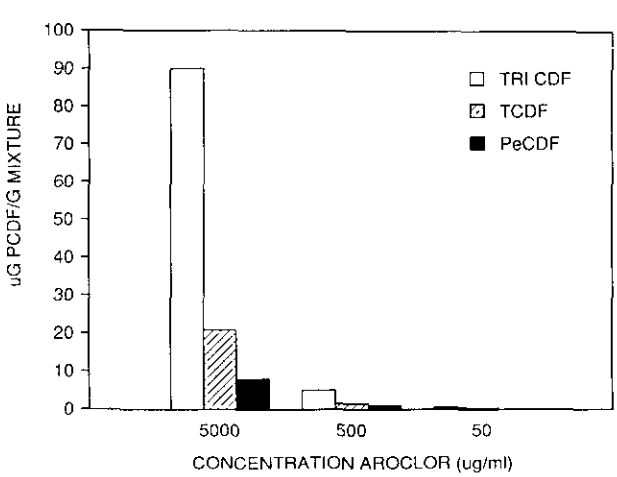

FIGURE 4. Combustion of Aroclor 1254 in mineral oil. Comparison of yields (μg PCDF/g mixture) from 5000, 500, and 50 ppm Aroclor 1254 in mineral oil.

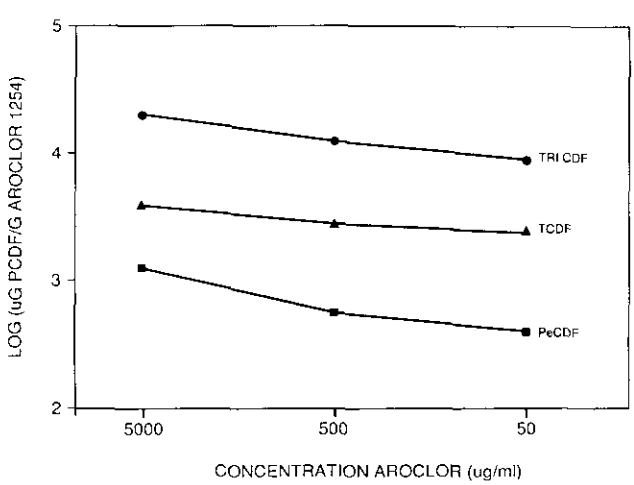

FIGURE 6. Combustion of Aroclor 1254 in mineral oil. Comparison of yields (log[μg PCDF/g Aroclor]) from 5000, 500, and 50 ppm Aroclor 1254 in mineral oil.

It is notable that, even under the optimal conditions studied here, pyrolytic PCDF yields from neat Aroclor 1254 remained low compared to those noted in earlier work in a sealed tube apparatus (*3*). In part this can be attributed to the higher pressure of oxygen in the sealed tube, since attack of oxygen on the biphenyl is likely to be the rate limiting step in PCDF formation. Additionally, the ability of the mineral oil/Aroclor mixture to boil in the open tube, and thus minimize its exposure to very high temperatures may be a major factor.

Yields of PCDF formed by combustion were two to three orders of magnitude higher than those formed by pyrolysis when optimal conditions are compared. In the 5000 to 50 μg/mL range, PCDF yields, expressed as microgram PCDF/gram mixture dropped drastically for all pyrolytic and combustive conditions studied, a result of considerable practical consequences for those assessing the hazard posed by PCB contaminated equipment. PCDF yields, expressed as microgram PCDF/gram PCB, were essentially unchanged over the 5000 to 50 μg/mL range in the combustion experiments, a result that demonstrates the absence of significant PCDF formation or destruction processes that are bimolecular in PCB or PCDF. In contrast, in the condensed phase pyrolysis experiments, PCDF yields, expressed as microgram PCDF/gram PCB, trend upward as concentrations are decreased in the 5000 to 50 ppm range. Currently, we are studying the combustion and pyrolysis of Aroclor 1254 in other solvents to determine the generality and the origins of the effects described here.

The authors acknowledge support of this work by the Electric Power Research Institute (Pyrolysis and Combustion of Aroclor 1254 Contaminated Dielectric Fluids), EPRI No. RP20284.

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