FATE OF PCB'S
IN ROLLINS ENVIRONMENTAL
SERVICES PLANT FIRE

MAY 1978

CONTRACT NO. 68-02-2165

TRW®
DEFENSE AND SPACE SYSTEMS GROUP

EP 600/2

FATE OF PCB'S
IN ROLLINS ENVIRONMENTAL
SERVICES PLANT FIRE

MAY 1978

CONTRACT NO. 68-02-2165

TRW.
DEFENSE AND SPACE SYSTEMS GROUP

FATE OF PCB'S IN ROLLINS ENVIRONMENTAL SERVICES PLANT FIRE

May 1978

Contract No. 68-02-2165
Task 54
EPA Project Officer: F. E. Briden

Prepared for
Industrial and Environmental Research Laboratory
Office of Research and Development
U. S. Environmental Protection Agency

Prepared by
M. K. O'Rell

Approved by: _____

R. F. Maddalone
Program Manager

TABLE OF CONTENTS

1. Executive Summary

This study indicates that under certain conditions that may have existed at the Rollins Environmental Services fire polychlorinated biphenyl compounds could conceivably serve as precursors for the formation of other environmentally undesirable compounds. The most probable class of compounds formed are dibenzofurans. Favorable reaction pathways to these compounds to these compounds exist under oxygen deficient combustion conditions and low temperature. Conversely, it seems improbable that di-benzo-p-dioxins are formed under similar conditions. If dibenzo-p-dioxins were to be formed, they would most probably come from the di-benzofurans that are initially generated from the PCB's. Formation of poly-cyclic aromatic hydrocarbons (PAH) is possible via pyrolysis of PCB's in oxygen deficient conditions that could have existed in the Rollins fire.

2. Introduction

This study was conducted for the Industrial and Environmental Research Laboratory of the Environmental Protection Agency, Research Triangle Park, North Carolina, as Task 54 on Contract No. 68-02-2165. Dr. Ronald Venezia was the EPA Task Officer. The study was performed in the Applied Chemistry Department of the Chemistry and Chemical Engineering Laboratory, Applied Technology Division, TRW Defense and Space Systems Group, Redondo Beach, California. Dr. Ray Maddalone, Head, Environmental and Process Chemistry Section, was Program Manager and Mr. Michael O'Rell was the Task Manager.

The objective of this study was to investigate the fate of polychlorinated biphenyl compounds (PCB's) that were stored in a tank farm at a chemical disposal site when a catastrophic fire struck the facility in December 1977. The PCB's were selected for study because they are not only toxic and environmentally long lived, but they may also serve as precursors for the formation of new compounds which are even more toxic. This study attempts to define what new products may have been formed under the conditions that existed at the time of the accident.

Two compounds of particular concern that may have been formed are the polychlorinated dibenzofurans and the polychlorinated dibenzo-p-dioxins. Both of these compounds are highly toxic when partially chlorinated. Dioxins have been shown to have pronounced fetotoxic and some teratogenic effects even in
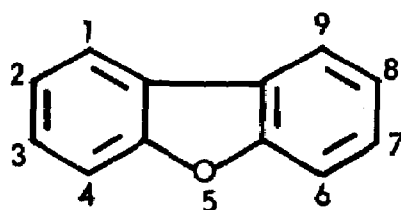
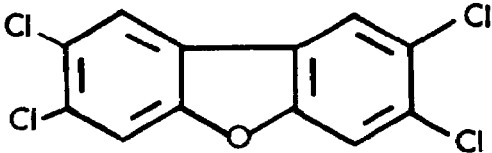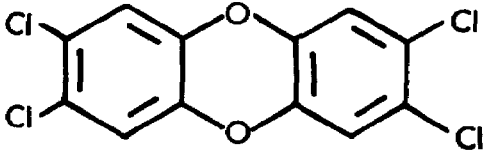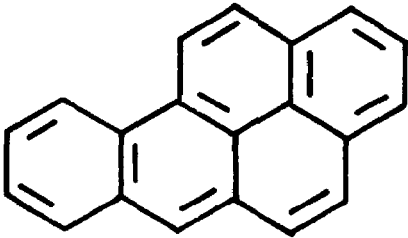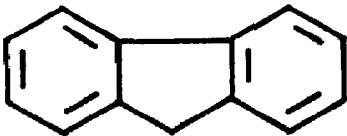**DIBENZOFURAN**   **DIBENZO-P-DIOXIN**

2
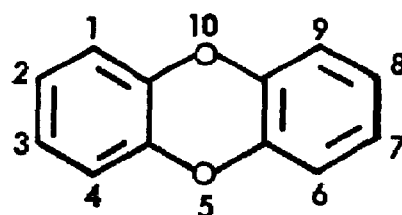
the absence of any noticeable acute toxicity (Reference 1). The toxicity
of 2,3,7,8-tetrachlorodibenzofuran is similar to that reported for 2,3,7,8-
tetrachlorodibenzo-p-dioxin (TCDD) (Reference 2) The toxicities of these
two compounds are given in Table I.

The formation of polycyclic aromatic hydrocarbons (PAH's) from PCB's
also is a concern because they are known carcinogens (see Table I). PAH
formation is favorable under pyrolysis (no oxidizing species present) and
oxygen deficient conditions which were expected to have existed as a result
of the fire.

The study was divided into three major elements of activity. The first
activity was dedicated to the definition of the probable conditions to which
the PCB's were exposed. The second activity addressed the question of what
new products could be formed given the conditions that were defined in the
first activity. The approach employed to define the new products was to
allow the PCB's to react with the simple radical species likely to exist in
combustion processes. Particular emphasis was placed on the formation of
dibenzofurans and dibenzo-p-dioxins. Part of this activity was also directed
to a definition of how the PCB's and reaction products may have been dispersed
in the environment during the accident. The last activity summarized results
of commercial scale incineration of PCB materials for comparison to the results
of this study.

Using this methodology it was concluded that formation of chlorinated
dibenzofurans from PCB's was highly probable during this accident. Conversely,
it was very unlikely that dibenzo-p-dioxins were formed. Conditions were
favorable for the formation of fluorenes and PAH's.

3

Table I. Toxicities of Selected Compounds

Compound	Structure	Toxicity
2,3,7,8-Tetrachloro Dibenzofuran		5µg/kg/day chicks died within 8-15 days (Reference 2)
2,3,7,8-Tetrachloro dibenzo-p-dioxin		0.6µg/kg dose killed 50% of guinea pigs (Reference 1)
Benzo(a)Pyrene		2µg/kg induces a carcinogenic response LD_{50}(subcutaneous,rat) 50 mg/kg (Reference 3)
Fluorene		No evidence that fluorene alone is carcinogenic

3. Background

This section presents the details of the accident that occurred at the Rollins disposal site and some aspects of the chemistry of polychlorinated biphenyls that will provide a basis for the discussions in Section 3.

3.1 Description of the Accident

In December 1977, a series of explosions and fire occurred at a chemical waste disposal site at Bridgeport, New Jersey, operated by Rollins Environmental Services. The fire was in the tank farm which contained a variety of organic compounds listed in Table II. Figures 1 and 2 present two pictures of the disposal site after the fire which were furnished by M. Polito, Environmental Protection Agency, Region II, Edison New Jersey. Of particular interest in this study are the two tanks containing PCB's. One tank contained 4300 gallons of a mixture of PCB's and aromatics (composition of aromatics and ratio of PCB's to aromatics unknown) and the second tank contained 11,000 gallons of a mixture of water and PCB's.

No detailed report of the accident exists at this time and it is impossible to model with any degree of certainty the conditions to which PCB's were exposed as a result of this accident. However, it is safe to assume that all possible conditions conceivable during an uncontrolled fire existed during this accident. For these conditions, temperatures may have ranged from those associated with a "cool flame" (lower temperature limit of 275-300°C) up to those expected in more idealized combustion processes (>1500°C). It is also expected that conditions existed in which combustion occurred in "oxygen rich" and in "oxygen deficient" environments. The oxygen deficient conditions would

5

Table II. Contents of Tank Farm at Rollins Site[+]

Tank No.	Contents	Quantity, Gallons
1	Waste Solvent, benzene sulfonic acid, cresylic acid, toluene, waste nonene	16,800
2	Trichloroethane, methylene chloride, nitrobenzene, phenol, methyl carbitol, methyl cellosolve, isopropyl alcohol, methyl alcohol, chlorobenzene, nonenes, water	15,400
3	Sludge residue	NA
4	PCB, Aromatics	4,300
5	Acetone, toluene, alcohol solvent with fatty acids	900
6	Sludge (Constituents unknown)	5,800
7	Nitrobenzene, phenol, methyl carbitol, methyl cellosolve, isopropyl alcohol, methanol, chlorobenzene, oils, kerosene, ethyl acetate, ethyl alcohol waste solvent	5,000
12	Otto fuel[*], allyl chloride, nitrochloro-benzene solvents	15,000
13	Hexane, paint solvents, 5% ethylene/propylene polymer, Otto fuel, aniline, ethanol	4,200
20	Methanol, water and BEB (composition unknown)	15,000
21	DMT (dimethyl terephthalate)	13,000

6

Table II. Contents of Tank Farm at Rollins Site (Cont'd)

Tank No.	Contents	Quantity, (total) Gallons
22	PCB and water	11,000
23	Unknown	1,100
24	Nitrobenzene, phenol, methyl carbitol, methyl cellosolve, isopropyl alcohol, methanol, chlorobenzene, waste nonene, bromoethylbenzene	Unknown
25	Waste fluorocarbon, fluorinated solvents, trichloroethylene, methylene chloride	11,500

* Otto fuel - propylene glycol dinitrate 76%, Di-n-butylsebatate 22%, nitrodiphenyl amine 2%.

+ Information supplied by M. Polito, EPA Region II, Edison, N. J.

Figure 1. Rollins Environmental Services Plant

Figure 2. Rollins Environmental Services and Surroundings

lead to partially combusted and pyrolysis products rather than complete
combustion products (i.e., CO_2, H_2O, HCl).

3.2 Structure of PCB's

PCB's are prepared by the chlorination of biphenyl. The chlorination
process produces a mixture of biphenyl compounds containing a varying number
of chlorines and the degree of chlorination (chlorine content) is dictated by
the end use of the product. It is also apparent upon examination of the

biphenyl ring structure (see below) that a number of different isomers is possible for each degree of chlorination. For example, monochlorobiphenyl has three different isomers. The chlorine may be located at the 2,3 or 4 position (positions 5 and 6 are identical to positions 2 and 3 for monosubstituted biphenyl).
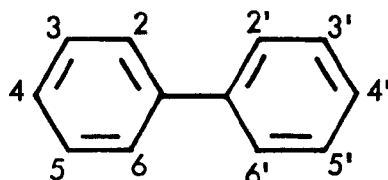
BIPHENYL

The number and position of chlorines on the rings is important because it determines the structure of the products that are formed from PCB's. An extensive analytical study of PCB's was conducted by Sissons and Welti (Reference 4) in which they separated and identified the major constituents of various commercial PCB's marketed under the trade name Aroclor.® Many different PCB mixtures have been sold in the United States and one representative of this family is Aroclor® 1254. Aroclor® 1254 contains 54% by weight chlorine and is therefore representative of a biphenyl compound containing five chlorines. Other significant chlorinated species also present in 1254 are tetra and hexachlorobiphenyls.

In a study conducted by TRW on destroying PCB's by incineration (Reference 5) the composition of a PCB containing an average of 3 chlorines (42% by weight chlorine) was determined. The major constituents as shown in Table III are dichlorobiphenyl, trichlorobiphenyl, and tetrachlorobiphenyl. Lesser amounts of monochlorobiphenyl and pentachlorobiphenyl also were detected. These results confirm those of Sissons and Wilte. They observed

9

that the major constituents in a particular PCB mixture are the compound representative of the degree of chlorination (e.g., pentachloro for 54% w/w chlorine) and compounds containing one more and one less chlorine atoms (i.e., tetrachloro and hexachloro).

Table III. Composition of PCB Containing 42% (w/w) Chlorine[+]

Compound	Estimated Concentration, (percent w/w)
Biphenyl	0.2
Monochlorobiphenyl	2
Dichlorobiphenyl	18
Trichlorobiphenyl	41
Tetrachlorobiphenyl	37
Pentachlorobiphenyl	2

+ Data from Reference 5

The major constituents of Aroclor® 1254 as determined by Sissons and Welti are shown in Table IV. Based on this work it was concluded that the most abundant chlorine substitution occurs at 2,5; 3,4; 2,3,4; 2,3,6; 2,4,5 and 2,3,4,5. Rarely does substitution occur at 2,4,6, and infrequently at 3; 3,5 and 2,3. For hexasubstituted biphenyls, the distribution is similar to that observed for Aroclor® 1254, although 2,3,5, 2,3,4,6 and 2,3,5,6 are in greater evidence.

10

Table IV. Major PCB Constituents in Aroclor® 1254[+]

Number of Chlorines	NMR Determined Structure[‡]
4	2,5-2',5'
4	2,3-2',5'
4	2,5-3',4'
5	2,5-2',3',6'
5	2,3-2',3',6'
5	2,5-2',4',5'
5	2,4-2',4',5'
5	2,3-2',4',5'
5	2,5-2',3',4'
5	3,4-2',3',6'
5	3,4-2',4',5'
6	2,3,6-2',4',5'
6	2,4,5-2',4',5'
6	2,3,4-2',4',5'

+Data from Reference 4

‡Nuclear magnetic resonance spectroscopy

3.3 Stereochemistry of Chlorinated Biphenyls

Another major consideration in determining the potential products that could be formed from PCB's is the stereochemistry of the PCB's. The presence of the chlorine atoms in the 2 and 2' positions have a strong influence on the spatial relationship of the two phenyl rings to each other. Biphenyl prefers to be a planar molecule to permit maximum orbital overlap and consequently, maximized stabilization energy through electron delocalization. (The stabilization energy of biphenyl is 83 kcal/mole). However, addition of substituents

11

in the ortho positions (2,2',6,6' in numbering of biphenyl) causes the two phenyl rings to rotate in relationship to each other resulting in an interplanar angle between the rings that varies from 60° to 90°, depending on the substituent. In particular, in 2,2'-dichlorobiphenyl, the angle is estimated to be between 62° and 74° and based on dipole moment studies, the rings are so inclined in their equilibrium positions as to place the chlorine atoms on the same side of the rings (Reference 6). This configuration has been attributed to attractive London forces between the chlorine atoms. As will be discussed in Section 3, this preferred configuration makes it possible to remove two chlorines from the PCB during the formation of a new product. If the chlorines were located on opposite sides of the rings, then only one chlorine atom might be eliminated during product formation.

3.4 Photochemistry of PCB's

The results of studies conducted on the photochemistry of PCB's give additional insight into the certain preferred reactions that PCB's undergo. It has been shown that all PCB compounds containing ortho (2-position) chlorines yield products arising from the loss of these positional isomers in preference to other isomer positions (i.e., 3 and 4 positions). The reason given for preferential reaction of the ortho substituents is steric hindrance. Crowded conditions created by ortho substituents results in a greater interplanar angle (twisting) (see Section 3.3) with a subsequent decrease in its double bond character. Products obtained in greatest yields arise from the loss of ortho (2 position) chlorines thereby relieving bond strain. For example, in solvents containing reactive hydrocarbons the radical formed by cleavage of the carbon-chlorines bond at the 2 position abstracts hydrogen from the solvent and results in dechlorination (Reference 7). Chlorines in the meta

12

positions (3 and 5 positions) are cleaved in the absence of ortho chlorines. Chlorines in the para position (4 position) were not cleaved after 20 hours of irradiation.

4. Chemical Fate of PCB's

Presented in this section are discussions concerning the potential
formation of new chemical compounds from PCB's as a result of the conditions
that were likely to exist during the fire and explosions. Particular emphasis
was placed on the formation of dibenzofurans and dibenzo-p-dioxins, two
extremely toxic classes of compounds. Other compounds considered in this study
included fluorene and polycyclic aromatic hydrocarbons (PAH's).

To maintain the scope of this study within the allocated technical
effort, formation of new products from PCB's was limited to the following
reaction pathways:

1) Reaction of PCB's with the species that are expected to exist
   during combustion (e.g., $OH^\bullet$, $O^\bullet$, $H^\bullet$, $CH_3^\bullet$) and

2) Pyrolysis of PCB's.

No considerations were given to potential reactions which may have occurred
between the PCB's and other compounds that were present in the tank farm,
because of the limited scope of this study.

The discussions in Section 3 cited evidence that the normal isomer dis-
tribution of polychlorinated biphenyl compounds is such that there is a high
concentration of the diortho chloro isomer (2,2'-isomer). For convenience,
a general structure for PCB's will be used as shown below in which the 2,2'-isomer
is shown. It will also be recalled that Aroclor® 1254 is representative of PCB's
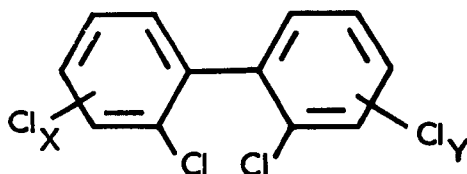
GENERALIZED PCB STRUCTURE

14

having 5 chlorine groups. Therefore, in the general structure given above X + Y is equal to 3. The location of the three chlorines is not given in the general structure but the preferred isomer distribution for a penta-chlorobiphenyl was given in Section 3.

Presented below are the results of an evaluation of the products that may have formed as a result of the accident.

4.1 Formation of Dibenzofurans

A number of similar pathways exist for the formation of dibenzofuran from PCB's. The difference between the routes is dependent on the selection of the attacking group.

4.1.1 Dibenzofuran via Hydroperoxide Intermediate.

This route to bibenzofurans requires fairly mild conditions which may have existed in cool flames. However, more vigorous combustion processes are thought to have been prevalent in the fire. In the absence of highly reactive radical species (very unlikely in combustion processes) it would be expected that the first step is cleavage of a carbon chlorine bond because it is the weakest bond present. The C-Cl bond energy is 81 kcal/mole, considerably lower than the bond energies measured for the C-H and the C-C (between the phenyl rings) bonds which are 103 kcal/mole and 100 kcal/mole, respectively. The radical formed has a number of reaction pathways available to it. It can recombine with the chlorine radical to reform the original compound or it may abstract a hydrogen radical which results in dechlorination. Alternatively, the radical may react with a second identical radical to form a dimer. However, the expected reaction is that of combination of the radical with oxygen to give a radical with the general structure ROO• as shown in Figure 3. This free radical may be fairly stable or it may be merely a collision complex which breaks down
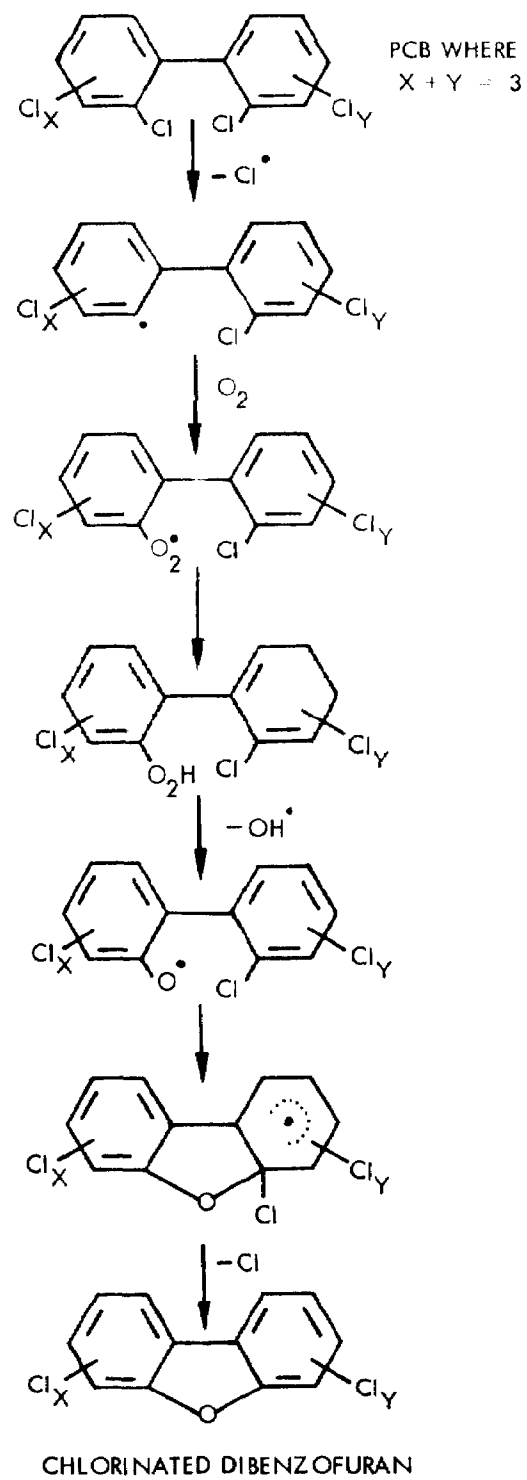
15

Figure 3. Hydroperoxide Route to Chlorinated Dibenzofuran

16

within the period of a single molecular vibration (picoseconds). As reported
by Fish (Reference 8), it is believed that at temperatures of about 300 to 400°C
$RO_2^{\bullet}$ radicals are quite stable but at temperatures in excess of 450°C the
complex breaks up more rapidly. The next step, assuming the radical
remains intact, is abstraction of a hydrogen from the surrounding environ-
ment to produce a hydroperoxide. Cleavage of the O-O bond then occurs, a
common decomposition process of hydroperoxides. Recalling that there is
another chlorine in the same vicinity on the second ring, and if rotation
of the phenyl rings is slow relative to the $O^{\bullet}$ insertion reaction, it
is expected that the oxygen adds to the second ring forming the basic
dibenzofuran ring structure. Subsequent loss of chlorine gives the chlori-
nated dibenzofuran as shown in Figure 3.

4.1.2 Formation of Dibenzofuran via $OH^{\bullet}$ Attack

There are more likely routes to the chlorinated dibenzofurans which are
expected to predominate in combustion processes. It was mentioned at the
beginning of this section that some of the reactive species present in com-
bustion environments are $O^{\bullet}$ and $OH^{\bullet}$. Consider the formation of dibenzo-
furan from PCB and $OH^{\bullet}$. The $OH^{\bullet}$ species adds to an electropositive carbon on
the biphenyl ring (carbons in the 2 and 2' positions are electropositive because
of the chlorine substitution). The resultant structure is shown in Figure 4.
The presence of the hydrogen provides an easy route for elimination of HCl and
results in the same intermediate species proposed in the hydroperoxide route
to dibenzofurans. The remainder of the reaction pathway is the same as for
the hydroperoxide route.

4.1.3 Formation of Dibenzofuran via Oxygen Radical Attack

Similar arguments can be made for the formation of the dibenzofuran ring
system from PCB's and $O^{\bullet}$. The oxygen radical is also a common species during
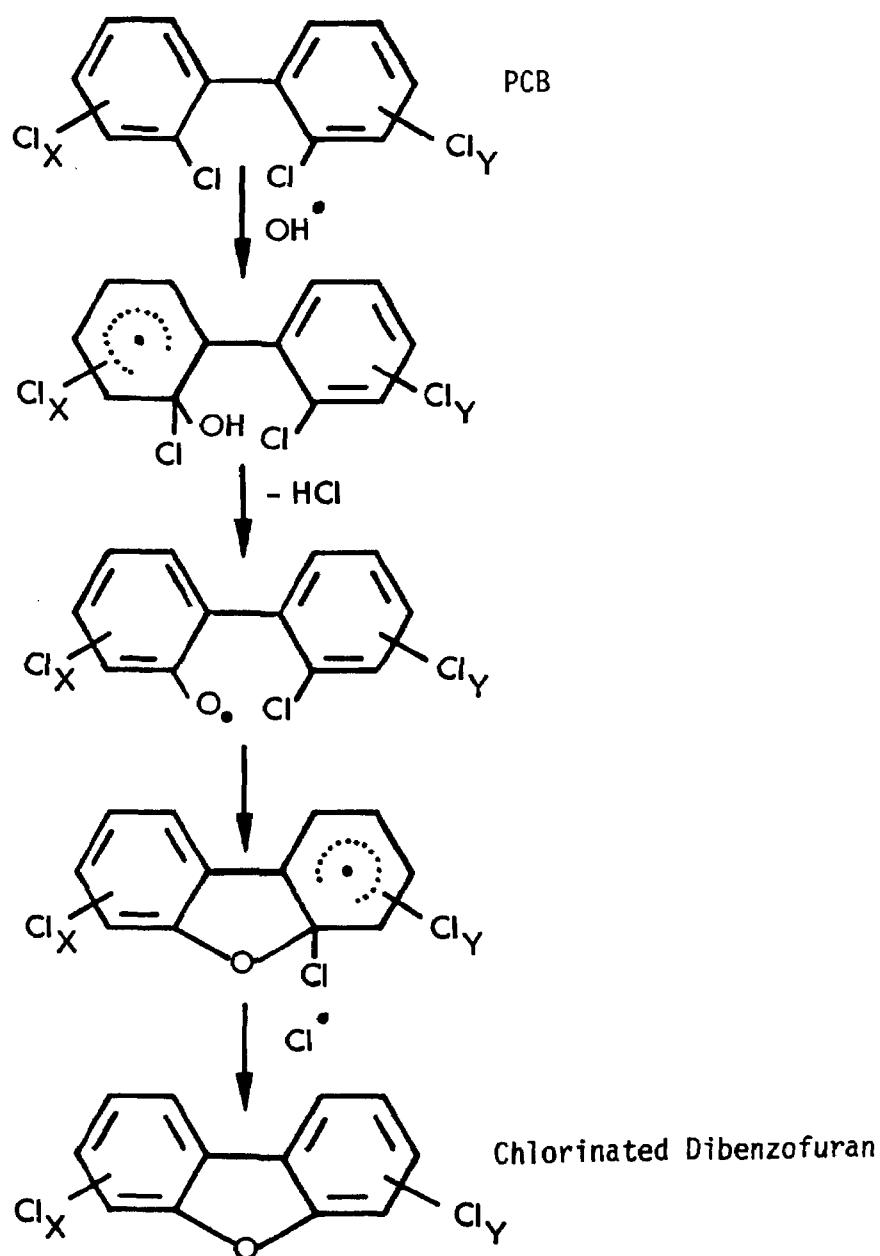
17

Figure 4. Route to Chlorinated Dibenzofurans Via OH• Attack

18

combustion processes. In this case the oxygen radical adds to the electro-positive carbon in the same fashion as does •OH. Elimination of Cl• gives the same intermediate that has been proposed for the two previous mechanisms. The reaction pathway then proceeds as has been outlined in the last two cases to give a dibenzofuran ring system. The reaction pathway is shown in Figure 5.

It would appear based on these discussions that dibenzofuran compounds are formed under certain combustion conditions. However, it must be assumed that residence times are extremely short and only permit the oxygen insertion reaction sequence to occur. Longer residence times permit additional reactions to occur and result in destruction of the dibenzofuran system, or at a minimum, removal of a number of the remaining chlorine atoms. (See Section 6 on Commercial Scale Incineration of PCB's).

4.2 Dibenzo-p-dioxin Formation from PCB's

A second group of compounds that is of interest in this study is composed of the dioxins. A direct route for dioxin formation from PCB's is not evident because the sequence requires the formation of two carbon-oxygen bonds and cleavage of the carbon-carbon bond between the rings as shown below.

PCB

DIBENZO-P-DIOXIN
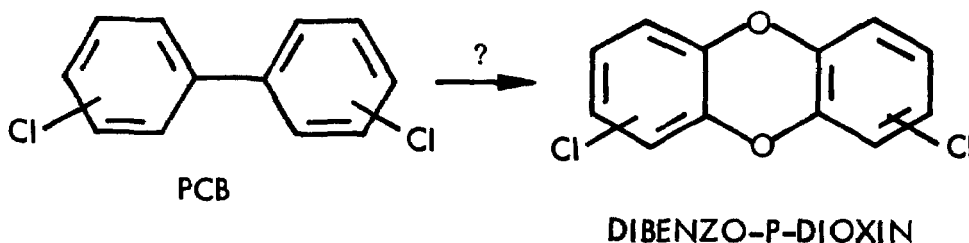
One potential route to dioxin from PCB's starts with the cleavage of the C-C bond joining the phenyl rings. This would be a very energetic reaction because the bond energy of the C-C bond is 100 kcal/mole. The favored
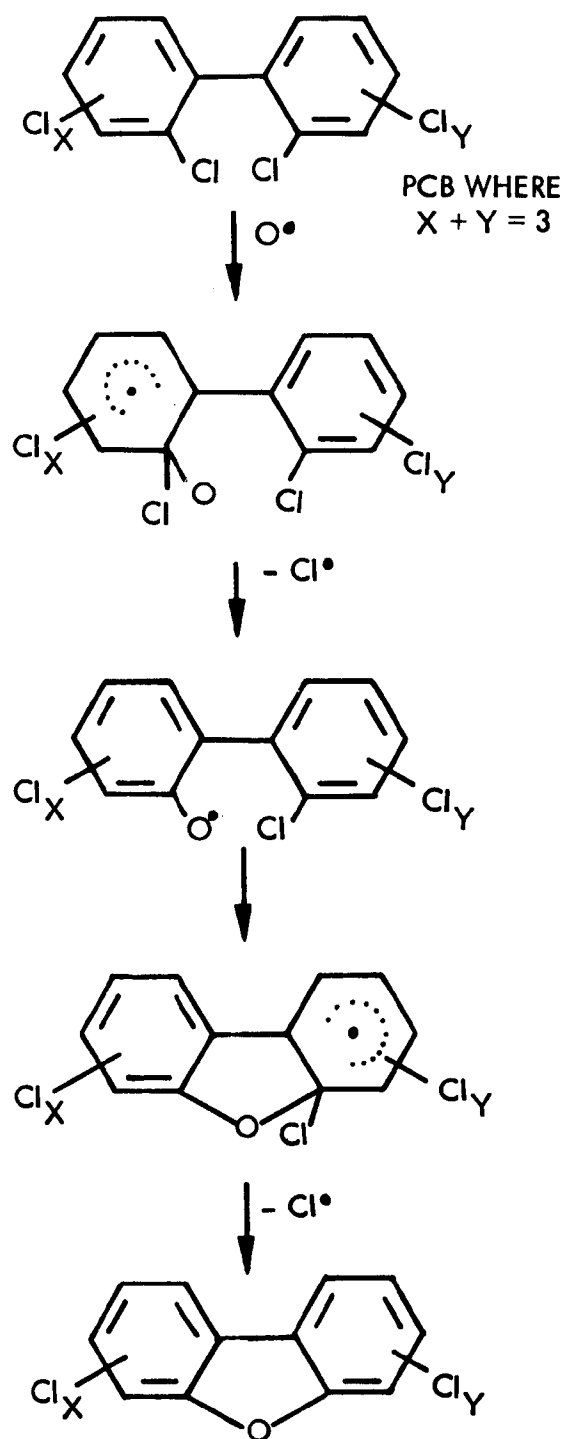
Figure 5. Route to Chlorinated Dibenzofurans Via O° Attack

reaction site is at the carbon-chlorine bond as was discussed in Section 4.1.1 because the bond energy is 81 kcal/mole. Should cleavage of the C-C bond occur in any case, the two phenyl radicals would quickly separate in relationship to each other and recombination after reaction with oxygen (or an oxygen containing radical) is highly unlikely. This sequence is shown below. One potential product from the cleavage of the C-C bond is a chlorinated
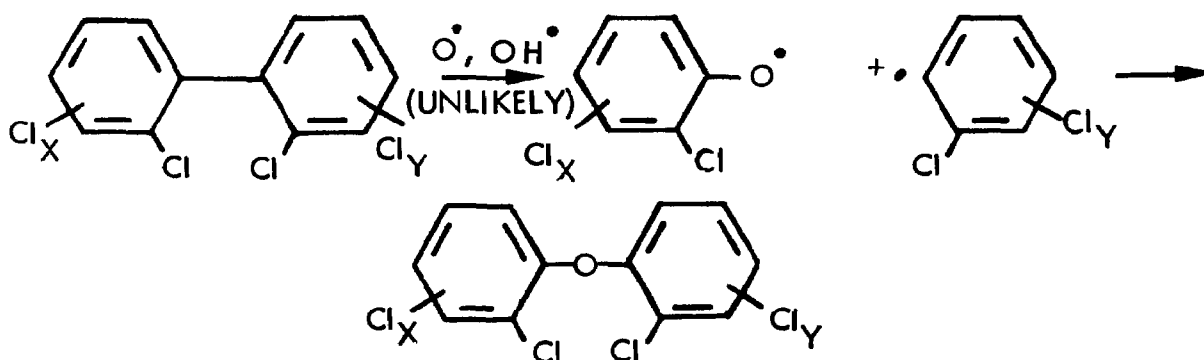
phenol which could subsequently react with a second chlorinated phenol to form a dioxin via the normal condensation route. However, it is also very unlikely that this sequence of reactions takes place in a combustion environment. Abstraction of chlorine remains the thermodynamically favored reaction.
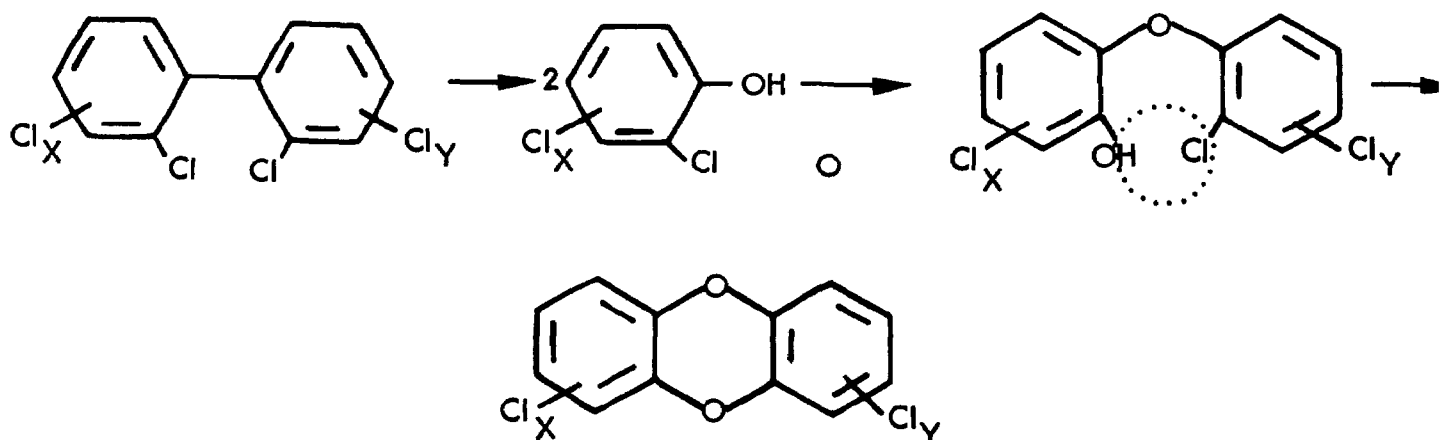
A more probable route to dioxin is the transformation of the dibenzofuran into dioxin via an oxygen insertion reaction. It was shown in the previous sections that the formation of dibenzofuran can occur in a number of ways and represents an intermediate for dioxin formation. As shown below, cleavage of the C-C bond with oxygen radical ultimately results in a dibenzo-p-dioxin. For this illustration, a hydroxyl radical has been used as an example.
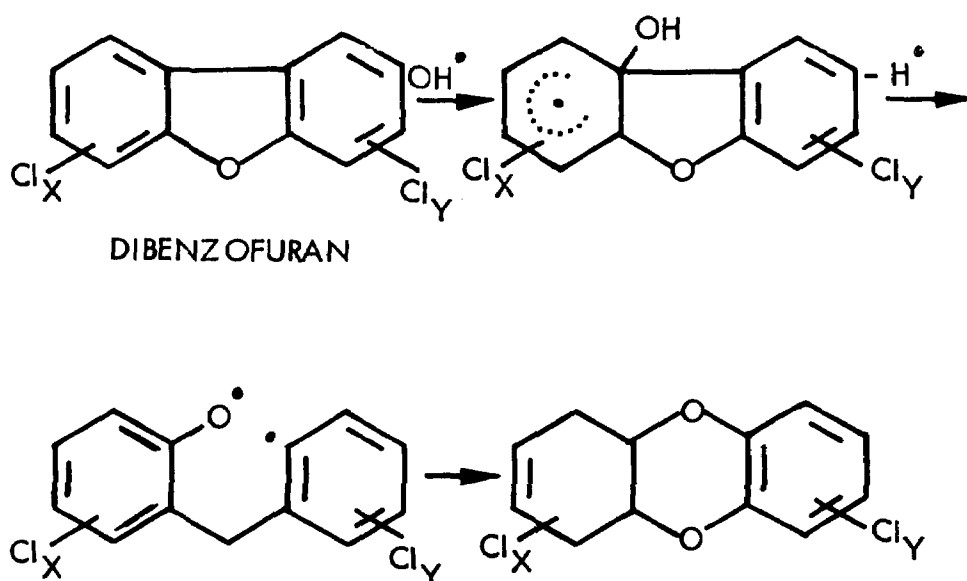
DIBENZOFURAN

This route requires that dibenzofurans first be formed from PCB's in order to obtain dioxins. The relative concentrations of dibenzo-p-dioxin to dibenzofuran is dependent upon the rate of the second oxygen insertion. A slow rate for the second oxygen insertion would result in a low concentration of dioxins relative to dibenzofuran. Conversely, a fast second reaction results in a higher concentration of dioxin relative to dibenzofuran. However, since the second reaction is more energetic than the first, the concentration of dioxin from this reaction sequence is expected to be very low or nonexistant.

Based on these two proposed pathways it appears unlikely that significant amounts of dioxins are formed.

22

4.3 Formation of Fluorene

Other radical species present in a combustion environment are the hydrocarbon fragments generated by decomposition of the fuel molecules. These species include $\cdot CH_3$, $\cdot CH_2$ and the like. It is also possible that these species add to the PCB's and result in another new compound. In this case, a fluorene ring structure (see below) would result. A possible route to the fluorenes is presented in Figure 6.

FLUORENE
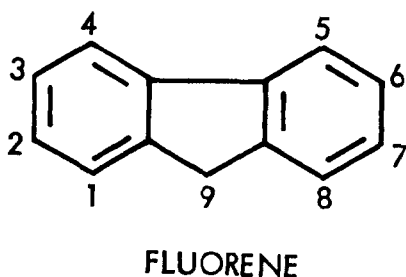
In this pathway the carbon radical again adds to an electropositive carbon atom. The radical formed then splits out a chlorine radical and in the process it abstracts a hydrogen radical from the methyl group resulting in HCl and a hydrocarbon radical. The $CH_2\cdot$ radical then adds to the second ring forming the fluorene ring system in an analogous fashion to the dibenzofuran formation. Elimination of a chlorine radical results in the final chlorinated fluorene compound. The other hydrocarbon radicals are also expected to result in similar compounds.

4.4 Formation of Polycyclic Aromatic Hydrocarbons.

The formation of polycyclic aromatic hydrocarbons is also a concern because they are known carcinogens. These compounds are expected to be formed by pyrolysis of PCB's. (Pyrolysis refers to thermal degradation in the absence
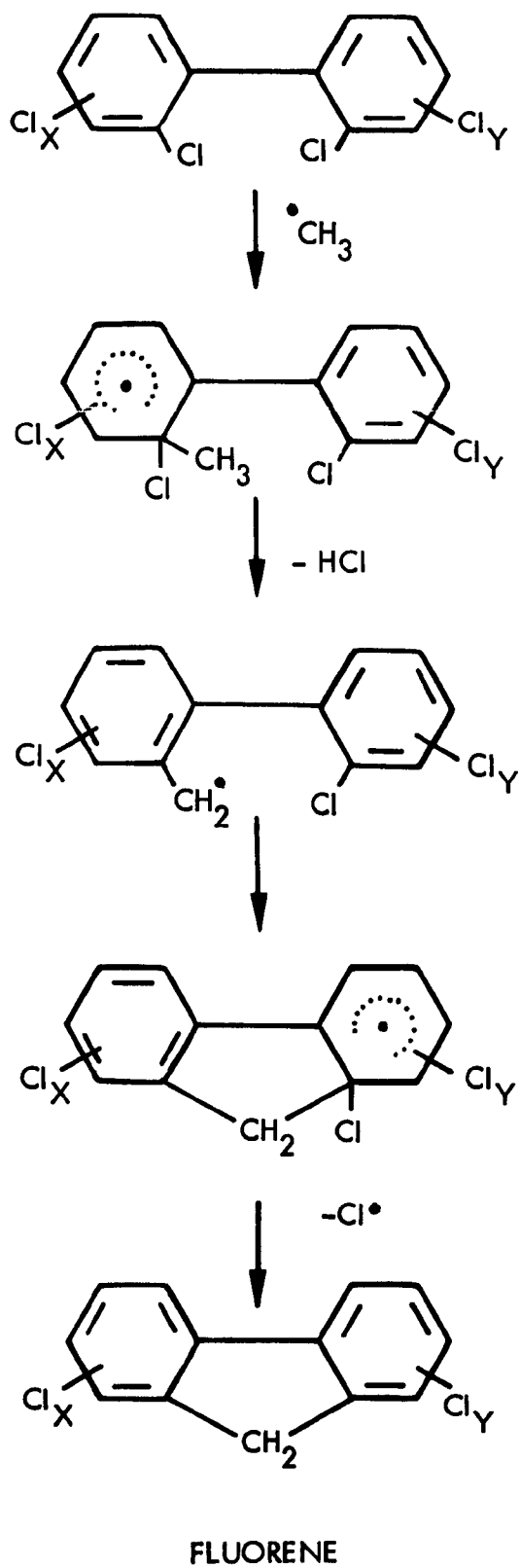
23

Figure 6. Route to Fluorene Via •CH₃ Attack

24

or near absence of oxidizing species). Presented in this study are the results obtained on a previous TRW study (Reference 9) on the thermal degradation of chlorinated hydrocarbon species in which the TRW Chemical Analysis Program was applied to determine not only the equilibrium product distribution from pyrolysis, but also the secondary thermodynamically feasible reaction products. The pyrolysis cases examined assumed the complete absence of oxidizing species and covered the temperature range 399° to 1093°C for three cases:

Case 1: No restriction placed on and solid carbon is allowed to be formed.

Case 2: Solid carbon is not allowed to be formed.

Case 3: Both solid carbon and polynuclear aromatic hydrocarbons are not allowed to be formed.

The reason for examining all three cases was to identify pyrolysis products that were less thermodynamically favored but more likely to be formed from the kinetic standpoint.

The PCB's are somewhat different in structure from the chlorinated hydrocarbon wastes that were used for these calculations. However, the results are informative and show support for PAH formation. The results for Case 1, Case 2 and Case 3 are shown in Tables V, VI and VII, respectively. Of particular interest to this study is Case 2 wherein PAH's are formed. The major equilibrium products are CH_4, C_2H_2, C_2H_4, C_6H_6, pyrene, benzo(a) pyrene, benzo(e)pyrene, H_2 and HCl. These PAH's are reasonably stable at high temperatures and may survive the fire and escape into the environment.

It was also intended to use the TRW Chemical Analysis Program to predict formation of dibenzofuran and dibenzo-p-dioxin from PCB's. This was not feasible because the model requires accurate data describing the thermo-chemical behavior of potential products and these were not available for these two compounds. The data required are the enthalpy and entropy as a function of temperature.

25

Table V. Equilibrium Product Distribution from the Pyrolysis of Military
Standard Pesticide Formulations - Case 1:   Solid Carbon
Allowed to be Formed

Major Equilibrium Products:

CH_4, H_2, HCl, and graphite; and CO, CO_2, and

H_2O for formulations containing oxygen.

Minor Equilibrium Products:

C_2H_4 (<2 ppm)

C_2H_2 (<2 ppm)

C_2H_6 (<9 ppm)

H   (<4 ppm)

Table VI. Equilibrium Product Distribution from the Pyrolysis of Military
Standard Pesticide Formulations - Case 2:   Solid Carbon Not
Allowed to be Formed

Major Equilibrium Products:

CH_4, C_2H_2, C_2H_4, C_6H_6, pyrene, benzo(a)pyrene
benzo(e)pyrene, H_2, and HCl; and

CO, CO_2, and H_2O for formulations containing oxygen

Minor Equilibrium Products (<500 ppm):

CH_3 (<12 ppm)
C_2H_6 (<136 ppm)
Propyne (<28 ppm)
Allene (<10 ppm)
Propylene (<16 ppm)
1,3 - butadiene (<2 ppm)
Toluene (<11 ppm)
Styrene (<2 ppm)
Naphthalene (<189 ppm)
Fluoranthene (<393 ppm)
Acenaphthalene (<14 ppm)
Anthracene (<4 ppm)
Phenanthrene (<45 ppm)
Perylene (<426 ppm)
Triphenylene (<11 ppm)
Chrysene (<20 ppm)
Coronene (<13 ppm)
H (<3 ppm)
Methyl chloride (<28 ppm)
Monochlorobenzene (<2 ppm)

26

Table VII. Equilibrium Product Distribution from the Pyrolysis of
Military Standard Pesticide Formulations - Case 3: Solid
Carbon and PAHs Not Allowed to be Formed

Major Equilibrium Products:

CH_4, C_2H_2, C_2H_4, C_6H_6, toluene, styrene, H_2, HCl, and monochlorobenzene; and

CO and CO_2 for formulations containing oxygen

Minor Equilibrium Products (<100 ppm):

CH_3 (<21 ppm)
C_2H_6 (<184 ppm)
Allene (<126 ppm)
Propyne (<369 ppm)
Propylene (<136 ppm)
1,2 - butadiene (<2 ppm)
1,3 - butadiene (<33 ppm)
Ethylbenzene (<142 ppm)
o - xylene (<424 ppm)
m - xylene (<918 ppm)
p - xylene (<413 ppm)
Propenylbenzene-cis (<12 ppm)
Propenylbenzene-trans (<14 ppm)
o - methylstyrene (<15 ppm)
m - methylstyrene (<39 ppm)
p - methylstyrene (<21 ppm)
Cyclopentadiene (<22 ppm)
H (<3 ppm)
Methyl chloride (<39 ppm)
H_2O for formulations containing oxygen (<48 ppm)

5. Dispersion of PCB's and Decomposition Products

An additional consideration in this study is the ultimate fate of the PCB's (unreacted) and of the chemical compounds formed from the PCB's as a result of the accident. Basically, it is expected that the high degree of chlorination of the PCB's and chlorinated decomposition products would cause them to volatilize and move with the smoke rather than burn. As a result, some of these materials may have been widely dispersed over a large surrounding area in the smoke plume. The PAH's are relatively stable and are also expected to be dispersed via the same pathway.

Very little information exists on the physicochemical properties of the chlorinated products that may have been formed. All compounds are listed as insoluble in water although concentrations in some cases may be in the ppm range. A brief summary of other physical properties are given below.

Aroclor® 1254 has a boiling point (bp) range of 365-390°C and a specific gravity of ~1.5. Chrysene, a 4-ring PAH, possesses a melting point (mp) of 256°C and a bp of 448°C. Benzopyrene melts at 177°C and boils at 500°C and fluorene boils at 295°C. 3-Chlorodibenzofuran has a mp of 101°C. Dioxins melt at 300-350°C and are reported to be stable up to 800°C.

Based on these limited data, it is expected that the chlorinated substances (high density) would settle to the bottom of bodies of water and enter the soil. Of course a finite concentration (although small) of these materials would exist in water. The depth of penetration of the substances into the soil is dependent upon soil compositions.

An additional consideration in the fate of these materials is their stability (or lack thereof) to photochemical decomposition. The PAH's are unstable under solar radiation. For example, benzo(a)pyrene has a chemical half-life of less than 1 day with solar radiation and several days without solar radiation (Reference 10). The dioxins and dibenzofurans also are photochemically unstable with half-lives of days to weeks (References 11 and 12). More recent evidence (Reference 7) shows that even PCB's undergo some dechlorination in photochemical experiments but the half-lives have not been measured. These data suggest that the products formed will not persist in the environment for long periods of time (except the PCB's).

6. Commercial Scale Incineration of PCB's

In previous work (Reference 5) incineration tests with PCB's were conducted at a disposal facility operated by Rollins Environmental Services, Inc., in Deer Park, Texas. The incineration system consisted of a rotary kiln and a liquid injection afterburner. Number 2 oil was utilized as auxiliary fuel in the destruction of the waste. The kiln flame temperature was 1250°C and afterburner temperature was 1330°C. The calculated residence time was 3.2 seconds.

Samples of the combustion products were taken from the hot duct leading from the afterburner. No PCB's were found and destruction efficiency for total organic was calculated to 99.98%. (Destruction efficiency for total organics compares the input rate of combined waste and auxiliary fuel to the emitted rate of all organic material found in the combustion samples). Thus, long residence times (3 seconds) at temperatures in excess of 1250°C result in complete destruction of PCB's. Conversely, the conditions required for formation of dibenzofurans and fluorenes are very short residence times and lower temperatures (the lower minimum temperature is expected to be 350-400°C in order to initiate the radical reactions).

7. References

1. Report on 2,4,5-T, a report of the Panel on Herbicides of the President's Science Advisory Committee, USGPO, Washington, D.C., 1971.

2. Goldstein, J.A., McKinney, J.D., Lucier, G.W., Moore, J.A., Hickman, P., and Bergman, H. Pharmacologist 16, 239 (Abstract No. 278) (1974).

3. Cleland, J.G., and Kingsbury G.L. Multimedia Environmental Goals for Environmental Assessment Volume II. MEG Charts and Background Information. EPA-600/7-77-1366 U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1977.

4. Sissons, D. and Welti, D. Structural Identification of Polychlorinated Biphenyls. J. Chromat., 60: 15-32, 1971.

5. Ackerman, D.G., Clausen, J.F., Johnson, R.J., Tobias, R.F., and Zee, C.A. Destroying Chemical Wastes in Commercial Scale Incinerators. Published under EPA Contract No. 68-01-2966, June 1977.

6. Weissberger, A., Sängewald, R., and Hampson, G.C. Trans. Faraday Soc., 30, 1 (1934); Hampson, G.C., and Weissberger, A. J. Am. Chem. Soc., 58, 2111 (1936).

7. Ruzo, L.O., Zbik, M.J., and Schuetz, R.D. J. Am. Chem. Soc., 96 (12) 3809 (1974).

8. Fish, A. Angew. Chem. Internat. Edit., 7(1) 45 (1968).

9. Shih, C.C., Tobias, R.F., Clausen, J.F., and Johnson, R.J. Thermal Degradation of Military Standard Pesticide Formulations. Published under Army contract DADA 17-73-C-3132, December 1974.

10. Chemical Industry Institute of Toxicology. First Priority Chemicals. Chemical Industry Institute of Toxicology; Annual Report. Research Triangle Park, NC (1976).

11. Crosby, D.G. and Wong, A.S. Science, 195, 1337 (1977).

12. Safe, S. and Hatzinger, O. Nature (London) 232, 641 (1971).