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**Ionization-Induced Regioselective Dechlorination Reactions of
Polychlorinated Biphenyls**

by
Robert Thompson O'Brien

A thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfilment of
the requirements for the degree of

Doctor of Philosophy

Department of Chemistry
Carleton University
Ottawa, Ontario
November 13, 1997

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the Faculty of Graduate Studies and Research
acceptance of the thesis,

**"Ionization-Induced Regioselective Dechlorination Reactions of
Polychlorinated Biphenyls"**

submitted by
Robert Thompson O'Brien, B.Sc.

In partial fulfilment of the requirements
for the degree of Doctor of Philosophy

Chair, Department of Chemistry

Thesis Supervisor

External Examiner

Carleton University
January 15, 1998

Abstract : The regioselective nature of five PCB dechlorination reactions were probed: (1) the electron impact induced loss of a single chlorine forming a fragment cation ($[M-Cl]^+$), (2) the electron impact induced loss of two chlorines forming a fragment cation ($[M-2Cl]^+$), (3) the electron capture induced loss of a single chlorine forming a fragment anion ($[M-Cl]^-$), (4) the electron capture induced loss of a single chlorine and addition of hydrogen forming an anion ($[M+H-Cl]^-$), and (5) the electron capture induced loss of a single chlorine and addition of an oxygen forming an anion ($[M+O-Cl]^-$). Semi-empirical calculations were also performed and critically reviewed. Selected calculated values were used to augment experimental measurements. The $[M-Cl]^+$ fragment generated from PCB congeners containing one ortho-chlorine on each aromatic ring was found to have a chloronium ion structure which contained a hypervalent chlorine at the apex of a 5-membered ring fusing the phenyl rings. This structure was the result of a concerted bond-breaking and bond-formation mechanism. The $[M-2Cl]^+$ fragment formed as two chlorines were lost from two of four active sites. This loss occurred after randomization of the chlorines localized on each aromatic ring. The $[M-Cl]^-$ fragment retained chlorines originally at the 3,4,5- or the 3',4'- positions. This fragment formed as a result of two consecutive electron capture events with $[M-Cl]^\bullet$ being the intermediate between the molecular ion and $[M-Cl]^-$. Experiments were performed to classify the $[M+H-Cl]^-$ ion as the result of either a wall-modified radical reaction or a gas-phase radical reaction. Most congeners formed $[M+H-Cl]^-$ via the gas-phase radical reaction. Four congeners, each of which contained a fully chlorinated aromatic ring, formed $[M+H-Cl]^-$ from a gas-phase radical reaction at a pressure of 0.50 torr, but from a wall-modified-radical reaction at a pressure of 0.25 torr. Regioselectivity was also evident in the formation of the $[M+O-Cl]^-$ fragment ion, particularly in those congeners that contained one fully chlorinated aromatic ring and only one chlorine on the other aromatic ring. In these, the single chlorine was selectively retained, supporting the speculation that $[M+O-Cl]^-$ formed in a reaction between molecular oxygen and the appropriate molecular anion which had its negative charge localized on the fully chlorinated aromatic ring.

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*"There is a crack in everything,
that's how the light gets in.."*

from "Anthem", Leonard Cohen, 1992

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Chapter 1 : Introduction

1.1 Introduction

Polychlorinated biphenyls (PCBs) are a class of anthropogenic chemicals that have become widely distributed throughout the global ecosystem ¹⁻⁴. These compounds have valuable industrial properties, such as chemical stability, thermal stability, and high dielectric strength ^{3,5}. Originally they were perceived to be relatively nontoxic, and thus numerous applications were developed, including use as dielectric fluids, paint additives, wood preservatives, plasticisers, etc ^{3,5}. However, as the wide distribution of these compounds began to become evident ⁶, concerns were raised about their long term toxicity ^{5,7}.

Subsequent studies indicated that certain PCB congeners could be potential carcinogens ^{8,9}. Although these concerns have led to the restriction and control of PCBs in many countries ^{3,10}, the carcinogenic potential of PCBs is still being investigated and debated ^{3,11,12}. While some sources indicate that there is sufficient evidence to warrant PCBs being listed as confirmed carcinogens ¹³, the evidence for this classification is based only on animal studies. It has also been argued that the liver tumours associated with PCB administration are non-aggressive and may not be life-shortening ³. The relationship between PCBs and cancer in humans is presently an area of active research. For example, a 1996 compilation of ongoing epidemiology studies by the International Agency for Research on Cancer (IARC) listed 12 separate ongoing projects that are examining the link between PCB exposure and various forms of cancer ¹⁴. In addition to carcinogenic properties,

PCBs have been linked to numerous other biological effects, including endocrine disruption effects ¹⁵ and developmental delays in children ¹⁶. For a more complete examination of the toxicological and biological effects of PCBs, the reader is referred to a number of recent critical reviews ^{3,11,12,17}.

Although many aspects of the biological action of PCBs are still being investigated, there is a general consensus that many of the biological effects of PCBs are congener specific ¹⁷. Thus the ability to differentiate between individual congeners, both in their presence and concentration as well as in their chemical properties, is of prime importance if the toxicity of these compounds is to be understood.

The particular aspect of PCB chemistry that will be examined in this thesis will be the dechlorination reactions induced by ionization. Dechlorinations are prevalent in PCB chemistry. For example, it has been demonstrated that animal metabolism can induce dechlorinations ¹⁸⁻²⁰. In addition, dechlorinations have been demonstrated to be important degradation routes for PCBs in sediments ²¹⁻²⁴. The ionization of PCBs in a mass spectrometer leads to the production of series of dechlorinated ions. This occurs for both PCB cations produced by electron impact^{5,25} or chemical ionization ^{26,27} as well as PCB anions produced by electron capture ²⁸.

It has been observed that degradation of PCBs in sediments transforms the initial mixture to a less chlorinated mixture of PCBs that has reduced biological effects ²⁹. This dechlorination has been attributed to the action of anaerobic

bacteria²¹, which are believed to transfer an electron to the PCB as an initiation of this degradation. These reactions have also been demonstrated to be both congener dependent and regioselective^{23,24}. This information has been taken by some investigators to indicate the involvement of a structure-dependent binding site²¹ that facilitates regioselective dechlorinations for specific congeners.

Dechlorination of PCBs as observed in mass spectrometry will be discussed in detail below.

1.2 Chemical Structure and Nomenclature

A schematic representation of the PCB structure is presented in Figure 1. The numbering convention is indicated. In standard terminology, the 2 and 6 chlorines are referred to as ortho chlorines (this name reflects the chlorines' relative position to the biphenyl linkage) the 3 and 5 as meta chlorines, and the 4 as a para chlorine. The carbon at the biphenyl linkage is numbered 1 and is referred to as the ipso carbon. In the IUPAC convention for naming a PCB the lowest numbers possible are used to indicate the chlorination sites. Primed notations are given to higher numbers; for example, a PCB that has one ortho chlorine on one ring and one meta chlorine on the other is referred to as 2,3'- dichlorobiphenyl, not 3,2'- , or 3,6'- , or 6,3'-. A shorthand convention has been developed to simplify the naming of PCB congeners. In this convention PCB congeners are sequentially numbered from 1 to 209, beginning with number 1 for 2-monochlorobiphenyl and ending with number 209 for decachlorobiphenyl. The prefix BZ is commonly used in reference

Figure 1 - PCB Labelling Scheme

to the authors (Ballschmiter and Zell³⁰) who originated this numbering scheme. In Ballschmiter and Zell's³⁰ original paper, congeners BZ 199, BZ 200, and BZ 201 were apparently misnumbered; that is to say, using the numbering convention rules devised by the authors, these congeners should have been numbered differently. As a result, the official IUPAC numbering system is slightly different from the original BZ numbering system. The specific differences are: IUPAC 199 = BZ 201, IUPAC 200 = BZ 199, and IUPAC 201 = BZ 200. This thesis will use the original BZ notation since none of the "mislabelled" congeners will be discussed, and the BZ notation is still dominant in the literature. A convenient table relating the BZ number to PCB structure is presented in Appendix I. It should also be noted that PCBs of different levels of chlorination are technically not isomers, but rather only members of the same class of compounds. Therefore, the term congener is used to describe a member of the PCB class of compounds.

Amongst the 209 different structural congeners, 78 have chiral centers and thus could possibly have optical activity³¹. Within this sub-set, 19 congeners have 3 or 4 ortho chlorines and each has a rotation barrier of such magnitude that the two enantiomers are not interchangeable under ambient conditions^{31,32}. Techniques have been developed using chiral stationary phases that permit the separation of these enantiomers by means of both gas chromatography (GC)³³⁻³⁷ and high-performance liquid chromatography (HPLC)³⁸. Using these techniques, it has been demonstrated that there is an enantioselective bias measurable in environmental samples (sediment³⁶, human milk³⁹ and shark liver⁴⁰) that is not

present in PCB technical mixtures ³⁶. Therefore, it may also become important to be able to distinguish between optical isomers.

1.3 PCB Production and Chlorination

PCBs were prepared industrially

"...by chlorination of biphenyl with anhydrous chlorine and iron filings or ferric chloride as catalyst. The crude product is generally purified to remove color, traces of hydrogen chloride, and catalyst which is usually achieved by treatment with alkali and distillation." ⁴¹

The chemistry of the chlorination of biphenyl is similar to the chlorination of any unsubstituted aromatic compound, and this has been reviewed in a number of texts ⁴²⁻⁴⁵. The steps involved are outlined in a series of equations presented below. The symbol "Ar" represents an aromatic ring.

It is believed that a Lewis acid, FeCl_3 , is generated in situ by the action of molecular chlorine on the iron powder (Equation 1). This Lewis acid then acts to break the molecular chlorine bond and converts the halogen to an electrophilic reagent (Equation 2). As an electrophile, the chlorine cation is believed to first interact with the π electrons of the aromatic species to form a weak complex (Equation 3). The electrophile then attacks one of the ring carbons and forms a σ complex (Equation 4). The carbon at the centre of this new σ complex is forced to change from the aromatic sp^2 hybridization into sp^3 hybridization in order to accommodate both the electrophilic chlorine and the original substituent (H in Equation 4). The σ complex is considered to be the transition state of the rate-determining step. The reaction progresses when the bond to the original substituent is broken and the carbon returns to the energetically more favourable sp^2 hybridization (Equation 5). To account for the reversibility of the reaction, the original substituent, a proton, is believed to first form a weak π complex before departing. The departure of the proton is believed to be facilitated by reaction with the Lewis base, FeCl_4^- , formed in Equation 2. This reaction with the Lewis base leads to the regeneration of the Lewis acid catalyst, FeCl_3 (see Equation 6).

There has, however, been some debate as to the validity of the previously discussed mechanism. It has been suggested that the formation of Cl^+ is energetically unlikely⁴⁵, and that it is more likely that either a (Lewis acid)-(molecular chlorine) complex is the active electrophile or that molecular chlorine forms a π complex with the aromatic reagent; it is this complex that is attacked by

the Lewis acid (FeCl_3) to form the σ complex and the corresponding Lewis base (FeCl_4^-). In either of these cases, the formation of the σ complex is still considered the rate-determining step. The assumption that the σ complex resembles the transition state structure in the rate determining step facilitates a quantitative description of both the kinetics and structure reactivity concepts.

It has been reported in many cases that the rate law for the chlorination of benzene can be described by Equation 7 ⁴⁵ (E = the electrophile) ;

$$\frac{d [\text{C}_6\text{H}_5\text{Cl}]}{dt} = k [\text{C}_6\text{H}_6][\text{Cl}_2][E] \quad (7)$$

The rate law presented in Equation 7 supports the involvement of the Lewis acid, molecular chlorine and aromatic reagent in the formation of the transition state σ complex. If a number of ArCl isomers is possible, the observed distribution of these isomers may provide some insight into the relative stabilities of the appropriate σ complexes (all isomers originate from a common aromatic species). The traditional argument that a chlorine substituent is an ortho/para director suggests that the presence of an additional chlorine ortho or para to the σ complex stabilizes this state. In biphenyl, the directing effects are complicated by the interaction between the phenyl units, which is a function of the angle between the aromatic rings. This angle between the phenyl units is influenced by the number and nature of the ortho substituents.

Lepine et al. ⁴⁶ recognized that when a pure PCB congener is chlorinated,

the new chlorine simply replaces an aromatic hydrogen and does not alter the original chlorination pattern. Therefore, if a pure PCB congener is chlorinated with isotopically enriched chlorine, the new PCB isomer produced will contain the original chlorine pattern plus isotopically enriched chlorine(s) at new position(s). If the new PCB product is unambiguously identified, then the location of the label or labels will also be defined. The reader will find this aspect of PCB chemistry exploited in the dechlorination studies of this thesis work.

1.4 Mass Spectrometry of PCBs

1.4.1 Analytical Chemistry

A comprehensive review of the analytical chemistry of PCBs has been presented in a monograph by Erickson ⁴⁷. In that review, the importance of mass spectrometry (MS) for detection was emphasized. The same idea was also stated in a more recent review which focused primarily on the role of MS in the analytical chemistry of PCBs ¹⁰. In general, MS is often used as a means of detection after high-resolution gas chromatographic (HRGC) separation of a "cleaned" extract from a given sample matrix.

The lipophilic nature of PCBs enhances their partitioning from a given sample matrix (i.e., soil, sediment, animal tissue, blood, etc.) into an extracting organic solvent (i.e., hexane, methylene chloride, supercritical CO₂, etc.). Once extracted, PCBs can then be separated from the lipid and other biogenic material that are co-extracted by means of a treatment with a strong acid or base, which

degrades lipids and oil but not inert compounds such as PCBs ^a. Adsorption column chromatography ^b is then applied to further fractionate the extract such that PCBs are isolated from their co-extractants. This isolation of an analyte from other co-extractants that may interfere in an analysis is often referred to as a clean-up procedure ⁴⁷.

Once the PCB fraction is cleaned up, the eluting solvent is selectively removed by evaporation. This permits significant sample pre-concentration prior to HRGC/MS analysis.

Although there have been substantial advances in HRGC, it is still not possible to separate all 209 PCB congeners on a single HRGC column ⁴⁸. That is to say, some congeners co-elute and as a result it is desirable to introduce some degree of specificity or discrimination of the congeners at the detection stage. The degree to which MS can provide this discrimination will be discussed below.

1.4.2 Electron Impact Ionization of PCBs - Literature Review

1.4.2.1 General PCB Studies

There has been a number of investigations of the electron impact (EI) induced mass spectra of PCBs ^{46, 49-59}. The EI mass spectra typically consists of a dominant parent ion and a series of dechlorinated fragment ions. In most cases,

^a Other methods such as gel permeation chromatography can also be used

^b

This term refers to the separation of analytes by using liquid-solid adsorption. Common adsorbents include Florisil, silica gel, alumina, and carbon. (Ref. 47)

the $[M-2Cl]^+$ ion is the second most abundant ion⁵. The majority of previous investigations have examined the fragmentation of the metastable^c parent ion with the objective of obtaining analytically or theoretically important information^{50-52, 55, 57-59}. Even though metastable ion analysis is not addressed experimentally in this thesis, these studies did provide some insight into dechlorination mechanisms and thus will be reviewed here. In general, the main questions addressed in these metastable ion studies were: A) are the chlorines scrambled prior to dechlorination; B) can analytically discriminating information be obtained for some isomers; and C) what is the mechanism of dechlorination?

The issue of chlorine scrambling was addressed in all^{50-53, 55, 57-59} of the metastable ion investigations reviewed in this thesis. The metastable ion decompositions can provide insight into possible scrambling using two distinct approaches: A) monitoring the kinetic energy release (KER) or B) monitoring the relative abundances of metastable fragments. The term KER will be discussed again in Section 1.5 of this chapter after a few fundamental thermochemical quantities are introduced. In brief, KER is an indication of the excess energy of the ion above the thermochemical minimum for the fragmentation that is partitioned into the translational energy of the fragment ions. If different isomers rearrange to a common structure prior to fragmentation, then the KER values for the isomers will be very similar. Thus, chlorine scrambling is one plausible explanation if a number

c

Metastable ions are those ions stable enough to be accelerated from a MS source but then fragment prior to reaching the detector.

of isomers have very similar or identical KER values for a common reaction pathway. On the other hand, different KERs imply that chlorine atom rearrangement to a common fragmenting structure is unlikely. Likewise, metastable ion (MI) MS is indicative of both the energetics and structure(s) of the metastable ion. Identical MI mass spectra from metastable ions originating from different isomers would suggest chlorine scrambling. The relative abundances of the product ions from metastable decompositions can be measured using an experimental technique called a B/E linked scan⁶⁰. In this type of experiment, fragment ions with a fixed velocity are permitted to pass through the instrument. This ensures that all the observed ions originate from metastable ions of a particular m/z value. Unfortunately, in a B/E linked scan, information on the kinetic energy release is lost and only the relative abundances of the fragment (product) ions can be monitored. The advantage associated with this loss of energy information is a significant increase in the mass resolution. In a mass-analysed ion kinetic energy spectrum (MIKE spectrum) or an ion kinetic energy spectrum (IKE spectrum) the resolution is sometimes so poor that distinctions between different fragment ions with similar masses (± 1 amu) cannot be made⁶⁰. In the earliest papers complete or partial chlorine randomization after electron impact ionization was proposed^{55, 57-59}. This proposal was based on examining IKE information from the metastable decomposition of $[M]^+\bullet$. In these studies, however, it was not possible to fully distinguish between the $[M]^+\bullet \Rightarrow [M-Cl]^+$ and the $[M]^+\bullet \Rightarrow [M-HCl]^+\bullet$ reaction channels⁵¹. The distinction between these two channels can

be made with a B/E examination ⁵¹. Using this method, it was noted that some isomers do in fact have significant $[M]^+ \Rightarrow [M-HCl]^+$ decompositions, although isomers with at least one ortho chlorine on each ring (the 2,2'-subset) produce less significant $[M]^+ \Rightarrow [M-HCl]^+$ decompositions ⁵¹.

In general, this 2,2'-subset was observed to exhibit unique IKE results. This raised the possibility that this type of analysis could be used to distinguish between some PCB isomers. This is important because A) HRGC cannot separate all congeners⁴⁸; and B) the EI mass spectra of many PCB isomers are indistinguishable ^{47, 10, 5}. This being said, the 2,2'-subset can be distinguished from other congeners based on the relative abundance of the $[M-Cl]^+$ ion to the $[M]^+$ ion in their EI mass spectra. This relative abundance is greater in this subset^{10, 49, 53, 54} than it is for other congeners. This distinction was first pointed out by Levy and Oswald ⁵³, who proposed the formation of a novel reaction intermediate, a "5-membered chloronium ion", with a Cl bridging the phenyl units, to explain the increased $[M-Cl]^+$ intensity⁵³. It is interesting to note that more recent work by Lepine et al. ⁴⁶ indicated the exclusive loss of an ortho chlorine from PCB congeners with 2 ortho chlorines on opposite rings. This is what is expected in the model presented in Levy and Oswald's paper ⁵³.

In another approach to correlate structural information to the observed MS results, Shushan et al. ⁵¹ correlated the steric interactions of the ortho chlorine and the potential for delocalization over both rings by monitoring the "A-band" (or k-band) UV absorption ($\lambda_{max} = 230-250$ nm). The excited state produced by this

absorption was hypothesized to be planar and hence sensitive to ortho substituent effects. A correlation between the "A-band" UV absorption and the ratio of the metastable peak heights, $[M-2Cl]^+ \bullet / [M-Cl]^+ \bullet$, was proposed by these authors. However, many of the "A-band" UV absorption values were not available and the data for the less chlorinated isomers had to be statistically corrected to "...reflect the increased probability that a more chlorinated species will lose a chlorine".

The model of Levy and Oswald⁵³ and the correlations of Shushan et al.⁵¹ can be compared by examining selected data extracted from the paper of Shushan et al.⁵¹ In particular, data for the 2,2'- sub-set as well as the related 2,6- sub-set. These data are presented in Tables 1 and 2. The barrier to obtaining a co-planar configuration is similar for each of these sub-sets (Cl - H repulsion) and, as such, the "A-band" absorptions are similar. However, in the model of Levy & Oswald⁵³ the 2,2' substituted species would form a chloronium ion intermediate whereas the 2,6 substituted species could not. There are significant distinctions in both the KER values (from MIKE spectra) and relative peak heights (from B/E linked scans) between the 2,2' and 2,6 congeners, as would be predicted from the model of Levy & Oswald⁵³.

Hass et al.⁵² also described structural correlations with kinetic energy release data from metastable ion dechlorinations. Their values for kinetic energy release for selected PCB isomers are presented in Table 3. Some of the isomers examined by Hass et al.⁵² were also examined by Shushan et al.⁵¹, and these are indicated in Table 3 as well. The apparent discrepancy between these two sets of

Table 1* - "A-band" Maximum Absorption Wavelengths for PCB Congeners with 2 or more Ortho-Chlorines.

Compound	λ_{max} (a-band)	K.E.R (meV)[M]⁺ => [M-Cl]⁺
2,2'	<235 shoulder on main band	34±2 (26 => Hass et al. ⁵²)
2,6	<238 shoulder on main band	63±2
2,4,6	<240 shoulder on main band	69±3
2,2',5	<235 shoulder on main band	36±3
2,2',6,6'	nr not resolved from main band	55±3 (30 => Hass et al. ⁵²)
2,2',5,6'	nr not resolved from main band	45±4
2,2',5,5'	nr not resolved from main band	51±4
2,2',4,4'	<236 shoulder on main band	63±4
2,2',4,5'	nr not resolved from main band	not reported
2,2',3,5'	nr not resolved from main band	50±3
2,2',3,3'	nr not resolved from main band	38±3

* λ_{max} (A-band) values from Shushan et al.⁵¹, K.E.R values from Boyd & Shushan⁵⁰

Table 2 - Metastable Peak Heights (B/E linked scans)
Ion Intensity Normalized to 10⁵**

Compound	λ_{max}	[M-Cl]⁺	[M-HCl]⁺	[M-2Cl]⁺	[M-2Cl]⁺/[M-Cl]⁺
2,2'	<235	1280	41	30	0.02
2,6	<238	385	75	85	0.22
2,4,6	<240	275	55	115	0.43
2,2',5	<235	1685	33	47	0.03
2,2',6,6'	nr	650	nr	41	0.06
2,2',5,6'	nr	1395	nr	26	0.02
2,2',5,5'	nr	1445	nr	28	0.02
2,2',4,4'	<236	995	nr	47	0.05
2,2',4,5'	nr	1240	nr	26	0.02
2,2',3,5'	nr	1425	6	28	0.02
2,2',3,3'	nr	1580	7	31	0.02

**values from Shushan et al.⁵¹

Table 3*: Kinetic Energy Release (meV) - from Metastable Molecular Ion Decomposition

<u>Compounds</u>	<u>[M]⁺ => [M-Cl]⁺</u>	<u>[M-Cl]⁺ => [M-2Cl]⁺•</u>	<u>[M]⁺ => [M-2Cl]⁺•</u>
2	31	NA	NA
2,2'	26 (34 Boyd et al. ⁵⁰)	20	24
2,2',6,6'	30	21	35
3,	36	NA	NA
3,3'	53 (62 Boyd et al. ⁵⁰)	nr	21
3,3',5,5'	76 (50 Boyd et al. ⁵⁰)	nr	26
4	36	NA	NA
4,4'	38 (50 Boyd et al. ⁵⁰)	nr	21
2,3,4,5,6	50	31	31
2,2',3,4,5,6	34	30	62
2,3,3',4,5,6	45	33	33
2,3,4,4',5,6	55	33	31
2,2',3,3',5,5',6,6'	40	36	30
2,2',4,4',6,6'	45	29	33
3,3',4,4',5,5'	88	nr	36
2,2',3,3',4,4',5,5',6,6'	46	32	40
2,2',3,3',4,4'	29	21	nr
3,3',4,4'	100 (54 Boyd et al. ⁵⁰)	nr	27
2,2',4,4',5,5'	34	23	nr

*values from Hass et al. ⁵² unless otherwise noted

values was addressed⁵⁰, but could not be fully accounted for.

In their study, Hass et al.⁵² reported a correlation between the magnitude of the kinetic energy release and the vibrational frequency that corresponded "... to (the) C-Cl bond stretching combined with the breathing of the ring " (this is found in the vicinity of 1075 cm^{-1} - labelled ν_6). Because of the complexity of IR spectra for molecules the size of PCBs (the number of vibrational modes = $3N-6 = 60$ modes; where N = the number of atoms = 22), only those isomers with one type of chlorine substituent were correlated. The authors indicated that if the ν_6 vibration resembles the reaction coordinate, then the activated complex states will be determined by ν_6 .

The following conclusions were made in the paper by Hass et al.⁵²: A) the loss of $\text{Cl}\cdot$ is not the result of a simple cleavage; and B) "...the loss of two chlorines from $[\text{M}]^+\cdot$ is a process which does not compete with the loss of one chlorine atom, and is probably from a different structure."

Rosenstock et al.⁶¹, addressed the relationship between vibration frequency and the dechlorination reaction coordinate in chlorobenzene. Of the thirty normal vibration modes of chlorobenzene, six were found to involve the force constants of the carbon-chlorine bond. The mode that became the reaction coordinate for the dechlorination reaction had a characteristic frequency of 702 cm^{-1} . The other five chlorine-sensitive modes had frequencies of 1085 cm^{-1} , 467 cm^{-1} , 416 cm^{-1} , 297 cm^{-1} and 196 cm^{-1} . In an investigation of the IR spectra of PCBs, Nyquist et al.⁶² correlated the IR spectra of selected PCBs to chlorinated benzenes. The

frequencies of comparable modes were observed to have similar frequencies in the chlorobenzenes and in the biphenyls. For example, the band observed at 703 cm^{-1} in chlorobenzene ($\equiv 702\text{ cm}^{-1}$ mode discussed by Rosenstock et al.⁶¹) corresponded to a band at 719 cm^{-1} in BZ 116. Because of this, the suggestion by Hass et al.⁵² that vibrational frequency in the vicinity of 1075 cm^{-1} for PCBs resembles the dechlorination reaction coordinate is, at the very least, questionable.

In addition to the metastable ion studies already discussed, two recent studies are applicable to the present investigation^{46,49}. In one of these, EI mass spectra were collected for all 209 PCB congeners and structural correlations were investigated⁴⁹. The intensities of the $[M-Cl]^+$ ions relative to other fragment ions in the mass spectra were correlated with the structures of the congeners. For congeners with the same number of ortho chlorines, a correlation was observed between the number of adjacent ortho-meta chlorines and the relative intensity of $[M-Cl]^+$. The data supporting this correlation is presented in Table 4. This correlation was explained by the suggestion that a chloronium ion is formed on the dechlorinated ring which stabilized the $[M-Cl]^+$ (see Figure 2).

1.4.2.2 Literature Basis for Present Thesis Investigation

The experiments in this thesis are derived from a series of investigations by Lepine et al.^{46, 63}. In these studies, a series of ^{35}Cl -labelled PCB isomers was produced and regioselective dechlorinations examined. In short, a selected series of pure PCB isomers was chlorinated non-selectively with isotopically enriched

Table 4* - Relative Intensities of [M-Cl]⁺ for Selected PCB Congeners Correlated to Number of Ortho-Chlorines and Number of Adjacent-Ortho-Chlorines

PCB Isomer	Relative	# Adjacent	
	% [M-Cl] ⁺	# Ortho-Cl	Ortho-Meta-Cl's
3,3',4,4',5,5'	0.17	0	0
2,3',4,4',5,5'	0.55	1	0
2,3,3',4,4',5	0.46	1	1
2,3,3',4,5,5'	0.50	1	1
2,3,3',4',5,5'	0.61	1	1
2,3,3',4,4',5'	0.70	1	1
2,3,3',4,4',6	0.61	2 (2,6- set)	1
2,3,4,4',5,6	0.74	2 (2,6- set)	2
2,3,3',4',5,6	0.87	2 (2,6- set)	2
2,3,3',4,5,6	0.99	2 (2,6- set)	2
2,3',4,4',5',6	1.07	2 (2,6- set)	0
2,3,3',4,5',6	1.26	2 (2,6- set)	1
2,3,3',4',5',6	1.35	2 (2,6- set)	1
2,3,3',5,5',6	1.71	2 (2,6- set)	2
2,2',4,4',5,5'	5.90	2 (2,2'- set)	0
2,2',3,4,4',5'	11.47	2 (2,2'- set)	1
2,2',3,4,4',5	12.59	2 (2,2'- set)	1
2,2',3,4',5,5'	15.58	2 (2,2'- set)	1
2,2',3,4,5,5'	18.09	2 (2,2'- set)	1
2,2',3,3',4,4'	22.61	2 (2,2'- set)	2
2,2',3,3',4,5	28.93	2 (2,2'- set)	2
2,2',3,3',4,5'	29.02	2 (2,2'- set)	2
2,2',3,3',5,5'	37.03	2 (2,2'- set)	2
2,2',4,4',5,6'	10.18	3	0
2,2',3,4,4',6	14.99	3	1
2,2',3,4',5',6	16.78	3	1
2,2',3,4,5',6	18.93	3	1
2,2',3,4,4',6'	19.72	3	1
2,2',3,4',5,6	21.74	3	1
2,2',3,4,5,6'	22.06	3	1
2,2',3,4',5,6	22.96	3	2
2,2',3,5,5',6	24.69	3	2
2,2',3,4,5,6	26.42	3	2
2,2',3,3',4,6'	28.20	3	2
2,2',3,3',4,6	29.33	3	2
2,2',3,3',5,6'	29.99	3	2
2,2',3,3',5,6	38.43	3	3
2,2',4,4',6,6'	1.48	4	0
2,2',3,4',6,6'	2.10	4	1
2,2',3,4,6,6'	2.55	4	1
2,2',3,3',6,6'	2.87	4	2
2,2',3,5',6,6'	3.04	4	2

* % [M-Cl]⁺ Values from Bolgar et al. (reference 49). Selected Congeners and Listed Order also Reflects Presentation by Bolgar et al.

Figure 2 - Formation of Chloronium Ion as per Bolgar et al.⁴⁹

chlorine to produce a mixture of labelled products that could be separated and identified using HRGC (via their retention times) prior to MS analysis. In the work of Lepine et al.⁴⁶, four tetrachlorobiphenyls 2,2',4,4'- (BZ 47), 2,2',5,5'- (BZ 52), 2,2',6,6'- (BZ 54), and 3,3',4,4'- (BZ 77) were chlorinated with ³⁵Cl to produce 17 reported labelled products⁴⁶.

In order to quantify the loss of the label from these 17 products, Lepine et al.⁴⁶ monitored 3 peaks from each of the chlorine isotope clusters^d for the ions $[M-Cl]^+$, $[M-2Cl]^+$, and $[M-3Cl]^+$. Abundance ratios of the observed peaks were compared to theoretically generated abundance tables to determine the quantity of ³⁵Cl remaining in the molecules. Ions of the type $[M-HCl]^+$, $[M-H-2Cl]^+$, $[M-2(HCl)]^+$, $[M-H-3Cl]^+$, etc., were not monitored, even though other investigators have observed the presence of some of these ion types for some congeners^{5,25,59}. Furthermore, hydrogen involvement with the loss of 3 chlorines was evident in the spectra of BZ 96 and BZ 136 presented in the paper by Lepine et al.⁴⁶.

Three of the isomers prepared by Lepine et al.⁴⁶ have two ortho chlorines in the 2,2' positions. In this case, the $[M-Cl]^+$ ion dominates the $[M-HCl]^+$ ion and any potential errors associated with neglecting the $[M-HCl]^+$ ion involvement are minimal. For two of these congeners, **2,2'**,3,4,4',5' hexachlorobiphenyl (BZ 138) and **2,2'**,4,4',5,5' hexachlorobiphenyl (BZ 153) {where **bold** indicates a label position}, there was found to be almost an exclusive loss of a labelled ortho chlorine

^d

The concept of chlorine isotope clusters is reviewed in section 2.4 of the following chapter in this thesis.

in the formation of $[M-Cl]^+$. The other congener, 2,2',3,3',5,5' hexachlorobiphenyl (BZ 128), also has one ortho chlorine on each ring; however, in this case the labels were located at the meta position, and there was almost an exclusive retention of the labelled meta chlorine in the formation of $[M-Cl]^+$.

1.4.3 Electron Capture Ionization of PCBs - Literature Review

1.4.3.1 Electron Capture Ionization Background Information

Electron capture negative ion mass spectrometry (ECNI/MS) is a well established analytical technique⁶⁴⁻⁶⁶. It has been demonstrated that ECNI/MS is a sensitive analytical technique capable of providing femtogram ($fg \equiv 1 \times 10^{-15}$ gram) detection⁶⁷. However, significant reproducibility problems have also been associated with ECNI/MS^{69, 70}. These will be discussed in more detail below. Some of these reproducibility problems have been demonstrated to be associated with variations in instrument parameters and moderator gas purity^{67, 69}. Therefore, it is essential to understand the function of and interaction between different experimental parameters.

In a typical ECNI/MS analysis, energetic electrons emitted from a hot filament are allowed to collide with the molecules of a moderator gas, commonly methane, held at a pressure of ~ 0.1 to 1 torr. These collisions and ionization of the moderator gas molecules produce a plasma rich in electrons. The energies of a fraction of these electrons are low enough that they are considered thermalised⁶⁴⁻⁶⁶. Molecules of high electron affinities can capture these thermalised electrons to

form anions that can then be ejected from the source and mass analysed. Since only molecules with high electron affinities that form stable anions will be detected, this technique is relatively selective^{67, 71,72}. Many molecules that have environmental or biological significance can form, or can be chemically converted to molecules which are able to form, stable anions^{64,65,71}. For molecules that have high electron affinities, electron capture occurs in virtually every collision. Therefore, ECNI/MS is both a selective and sensitive technique for many analytically significant compounds.

The ECNI/MS spectra of numerous PCB congeners have been reported by various researchers^{28, 63, 68,71-72}. In general, there is a number of dechlorination ions commonly reported, although different groups reported significant differences in the relative intensities and observed ion types⁷⁰. A crude distinction can be made between the highly chlorinated (>5 chlorines) and the less highly chlorinated (<5 chlorines) congeners. The more highly chlorinated congeners have spectra dominated by the parent ion, $[M]^+$, and dechlorination fragments of the form $[M+nH-nCl]^+$, $[M-Cl]^+$, and $[M+O-Cl]^+$ are observed. The ions, $[M+nH-nCl]^+$ and $[M+O-Cl]^+$, are not products of simple electron capture reactions, but those of multi-step reactions of which one is electron capture. The source of the hydrogen observed in the $[M+nH-nCl]^+$ ion is the methane moderator gas⁶³, while, the oxygen in $[M+O-Cl]^+$ originates from trace impurities of oxygen in the moderator gas⁶⁶. The possible reaction channels that produce these ion types will be discussed further below. The less highly chlorinated congeners can have spectra dominated by the fragment ion

$[Cl]^-$, although $[M-H]^-$, $[M]^\bullet$, $[M+nH-nCl]^\bullet$, $[M-Cl]^-$, $[M-HCl]^\bullet$, and $[M+O-Cl]^-$ are also observed and can become dominant for some congeners under some experimental conditions ²⁸. In this analysis, discussion will be limited to the dechlorinated ions: $[M+nH-nCl]^\bullet$, $[M-Cl]^-$, and $[M+O-Cl]^-$.

The $[M+H-Cl]^\bullet$ reaction channel in PCBs has been postulated to involve a wall-induced reaction prior to electron capture ⁷². This hypothesis was based on an analysis of the generalized ionization dynamics occurring within an ECNI source ⁷³. The proposed mechanism for the formation of $[M+H-Cl]^\bullet$ ions for polyhalogenated unsaturated hydrocarbons is ⁷³

The relative abundance of the $[M+H-Cl]^\bullet$ reaction channel has been reported to increase with decreasing pressure ⁷². This enhancement with decreasing pressure has been explained by an increase of diffusion to the source walls ⁷⁴. In the work of Lepine et al. ⁶³, the formation of the $[M+H-Cl]^\bullet$ was attributed to a gas-phase radical reaction based, in part, on the observed relatively rapid turnover between the $[M+H-Cl]^\bullet$ and $[M+D-Cl]^\bullet$ reaction channels after the introduction of deuterated methane gas. In addition, Lepine et al. ⁶³ observed a selective loss of ortho chlorine, which was taken to imply a gas-phase radical reaction mechanism.

The formation of $[M-Cl]^-$ can result from either Equation 9, or a combination of Equations 10 and 11.

The $[M+O-Cl]^-$ ion is generally regarded to form as a result of the following mechanism^{66,75} :

In the case of PCBs, however, this mechanism has been disputed⁷⁶. Instead, the following mechanism was proposed :

The proposal of this mechanism was based, in part, on the apparent random loss of chlorine in the formation of $[M+O-Cl]^-$ ⁷⁶.

A comprehensive analysis of the relationship between instrument parameters and observed ion intensity has been developed by Sears et al.⁷³. The predicted ion intensities were sensitive to a number of instrumental parameters including source volume, volumetric flow rate through the ion source, diffusion of neutral species to source walls, and electron concentration. The effects of variations in temperature, pressure, and other parameters commonly reported with ECNI spectra were also indicated. A change in a commonly reported parameter, such as

pressure, can affect a number of factors such as volumetric flow rate, diffusion, etc., which are also dependent on unreported parameters such as the magnitudes of leaks in the source and source volume.

The problem of the reproducibility of ECNI/MS spectra between laboratories and instruments ^{69,70} will now be addressed. This problem has been demonstrated in an interlaboratory comparison study ⁷⁰ in which a set of twelve compounds were examined by six different laboratories using various instrument types. Two PCB congeners were included in the set examined, specifically, 2,2',3,3' tetrachlorobiphenyl and 2,2',4,4',6,6' hexachlorobiphenyl. The relative abundance values for different ion types reported for these two PCBs are summarized in Table 5.

If the variations between the reported spectral characteristics of the two PCB congeners are examined, four key variations are observed: A) the relative abundances of $[M+O-Cl]^-$, B) the relative abundances of Cl^- , C) the relative abundances of $[M-H]^-$, and D) the abundances of $[M+H-Cl]^\bullet$ relative to $[M-Cl]^-$.

The abundance of the $[M+O-Cl]^-$ can be controlled by using high purity moderator gas and eliminating gas line leaks ⁶⁷, and thus this is simply a technical quality control issue.

The deviation in the relative proportion of Cl^- has subsequently been explained to result from a mass discrimination by the ion optics of some quadrupole instruments ⁷⁷. Therefore, this is also not a chemistry issue.

In the case of the $[M-H]^-$ reaction channel, there is, at present, no explanation

Table 5 : Comparison of PCB ECNI Mass Spectra Between Laboratories*

2,2',3,3' Tetrachlorobiphenyl

Location **	IU	FSU	UU	OSU	MSU	EPA
Instrument ***	HP 5985	Finn 4500	Finn 4500	Finn 4500	VG 7070	MS 80
[M]-	83.0%	nr****	3.0%	3.0%	nr****	nr****
[M-H]-	3.0%	1.0%	3.0%	0.6%	nr****	nr****
[M+H-Cl]-	5.0%	nr****	1.0%	1.0%	nr****	nr****
[M-Cl]-	nr****	nr****	1.0%	0.4%	nr****	nr****
[M-2Cl]-	6.0%	nr****	3.0%	4.0%	nr****	nr****
[Cl]-	15.0%	100.0%	100.0%	100.0%	100.0%	nr****

2,2',4,4',5,5' Hexachlorobiphenyl

Location **	IU	FSU	UU	OSU	MSU	EPA
Instrument ***	HP 5985	Finn 4500	Finn 4500	Finn 4500	VG 7070	MS 80
[M]-	53.0%	36.0%	53.0%	52.0%	51.0%	50.0%
[M+O-Cl]-	1.0%	34.0%	2.0%	0.8%	0.2%	8.0%
[M+H-Cl]-	14.0%	3.0%	2.0%	16.0%	8.0%	nr****
[M-Cl]-	nr****	2.0%	2.0%	2.0%	1.0%	nr****
[M+2H-2Cl]-	3.0%	0.7%	1.0%	8.0%	3.0%	nr****
[Cl]-	nr****	100.0%	100.0%	64.0%	100.0%	12.0%

* Stemmler et al., Anal. Chem., 60, 781-787. (1988)

** IU - Indiana Univ ; FSU - Florida State Univ ; UU - University of Utah ; OSU - Oregon State Univ

** EPA - US EPA ; MSU - Montana State Univ

*** HP 5985 & Finn 4500 - Quadrupole instruments ; MS 80 & VG 7070 - Sector Instruments

**** nr => not reported

for the spectral variation. In this thesis work dechlorination mechanisms are the primary interest; therefore this anomaly will not be discussed.

The difference in the abundance of $[M+H-Cl]^+$ relative to $[M-Cl]^+$ is important to this investigation. It has been noted that the relative abundance of the $[M+H-Cl]^+$ reaction channel increases with decreasing pressure⁷². This parameter was not held constant during the interlaboratory comparison study⁷³, and thus could be a source of variation. The same pressure was reported for the HP 5985 operated at Indiana University and the Finnigan 4500 operated at Oregon State University. In this case there was a difference between the reported $[M-Cl]^+$ abundance; however, in one case, this ion was not detected, and therefore this difference could simply be related to detection limits.

Although the preceding discussion highlighting the reproducibility problems in ECNI/MS appears somewhat discouraging, it should be noted that, in the particular interlaboratory comparison study⁷⁰ cited, many experimental parameters were not controlled. Therefore, that investigation could be considered an example of a worst case scenario in terms of control of the ECNI/MS experiment. In a more recent study⁶⁷, it was demonstrated that tight control of experimental parameters in ECNI/MS enabled the quantification of trace levels of PCBs with high accuracy and precision.

1.4.3.2 Electron Capture Ionization - PCB Mass Spectral Distinctions

A couple of recent studies^{63,68} have addressed the spectral differences

between individual congeners with the objective of providing theoretical insight. In one of these studies ⁶⁸, molecular parameters, such as twist angle and lowest unoccupied molecular orbital (LUMO) energy, were correlated to the degree of fragmentation. Unfortunately, significant $[M-H]^+$ ions were reported in this study that were not reported by other investigators ^{28, 63, 70-72}; thus, the conclusions reached may not be universal. In the other study, ³⁵Cl-labelled PCB congeners were examined ⁶³ to investigate the presence of regioselective dechlorinations.

Lepine et al. ⁶³ observed the $[M+H-Cl]^+$ fragment ion and concluded that A) the $[M+H-Cl]^+$ reaction appeared to be a gas phase, radical-induced reaction; B) label loss at the ortho position was noted to be much more significant than loss at any other position (explained by radical stabilization in the ipso position as the ortho position adopts an sp^3 configuration); and C) para chlorine loss was only important when there were two adjacent meta chlorines present.

1.5 Ion Thermochemistry of PCB Dechlorinations

An understanding of the ion thermochemistry of PCB dechlorinations provides a framework to evaluate experimental findings as well as to predict possible regioselective discriminations. Some of the terminology required to discuss pertinent thermochemical issues will be introduced here. An analysis of the application of these terms will be presented in Chapter 5, where molecular modelling and calculations of specific parameters are presented.

The energetics of a given reaction pathway will be gauged by the enthalpies

of formation of the appropriate radicals, cations, and anions. Since the competing reaction pathways have the same reagent (parent molecule) and the products are very similar, the entropy changes will be considered to be constant, and as such will not be considered. These thermochemical values can be related to observed spectral ion intensity via the application of quasi-equilibrium theory (QET) ⁷⁸ concepts which will be discussed in Chapter 5. Selected thermochemical terms for cations are schematically depicted in Figure 3 (adapted, in part, from references 79 and 80). The enthalpies of formation ($\Delta_f H^\circ$) indicate the relative positions of the molecules, radicals, and cations on the potential energy diagram represented in Figure 3. In the case of the neutral molecule, the homolytic bond dissociation reaction is represented by the lower potential energy curve in Figure 3. The enthalpy of the reaction ($\Delta_r H^\circ$) is calculated by the difference in enthalpies of formation of the fragment products and the reagent parent molecule. This $\Delta_r H^\circ$ is equivalent to the bond dissociation energy (BDE) of the particular bond broken to form the fragments. In other words, for the reaction,

$$\Delta_r H^\circ = \Delta_f H^\circ(R\bullet) + \Delta_f H^\circ(Cl\bullet) - \Delta_f H^\circ(RCI) = BDE(R-Cl) \quad (15)$$

The activation energy for this reaction is represented symbolically in Figure 3 by ϵ_0^n and it is equal to the C-Cl bond strength.

The energy required to make the transition from the ground state of the neutral to the ground state of the cation is called the adiabatic ionization potential

Figure 3 : Cation Thermochemical Terms*

* Individual Terms are Defined in Accompanying Text (Section 1.5)

(IP RCl (ad)). This can be estimated in two ways : 1) by determining the enthalpy change of the following reaction ^{81, e} :

$$IP\ RCl\ (ad) = \Delta_f H^\circ = \Delta_f H^\circ(RCl^{\cdot+}) + \Delta_f H^\circ(e^-) - \Delta_f H^\circ(RCl) \quad (17)$$

or 2) by applying Koopman's theory ⁸² , which equates ionization energy to the negative of the highest occupied molecular orbital (HOMO) energy.

The vertical ionization potential (IP RCl (vert)) presented in Figure 3 represents the most probable ionization achieved experimentally. In this process, the cation is initially formed with the ground state geometry of the neutral, and is in a vibrationally excited state ⁸⁰.

In the case of cations, the mass spectrometer provides a means of experimentally determining some of the energies discussed. This is accomplished by monitoring the energy required to produce either molecular ions or fragment ions. The magnitude of this appearance potential is indicated in Figure 3 for the production of the dechlorinated fragment and is indicated by the symbol (AP). The minimum theoretical energy required to observe the fragment R⁺ is referred to as the adiabatic appearance potential (AP(ad)). In practice the experimentally determined appearance energy (AP(exp)) is often larger than the AP(ad). The excess energy above the AP(ad) required to produce the observed fragment R⁺ is

e

In this discussion the ion convention ⁸¹ will be adapted in which the $\Delta_f H^\circ$ of e⁻ is considered to be 0 at all temperatures.

called the non-fixed energy (ϵ^+)⁸³. This is the energy required in the transition state to achieve a dissociation rate observable on the time-scale of the mass spectrometer used; it is also referred to as the kinetic shift and corresponds to the excess energy above the minimum activation energy required to induce a detectable quantity of fragment ions to form within the residence time of the molecular ion in the source (typically on the order of 10^{-6} seconds)⁸³. As a result, some energy higher than the AP(ad) minimum is often required to obtain a detectable signal⁷⁹. The magnitude of the non-fixed energy is a function of both instrument parameters and molecular characteristics. Since these cannot be completely distinguished, the non-fixed energy adds an uncertainty to the measurement of appearance potentials.

The fragment ion (R^+) formed in Figure 3, will have an excess energy equivalent to the sum of the non-fixed energy plus the reverse activation energy (ie., $\epsilon^+ + \epsilon_o^{rc}$). A proportion of these excess energies will be partitioned into the translational energy (T) of the fragment ion and the chlorine radical ($Cl\bullet$)⁷⁹. If the kinetic energy profile of the fragment ion beam is monitored using an appropriate sector instrument, then the magnitude of this translational energy can be measured. Typically, the monitoring of this kinetic energy released (KER) is accomplished using an ion kinetic energy (IKE) or a mass analysed ion kinetic energy (MIKE) experiment. The information obtained from this type of analysis can provide some insight into the nature of the potential energy surface in the region of the transition state.

In the case of anions, analogous processes exist. For halogenated molecules, the electron capture ionization reaction is exothermic. That is to say the electron affinity (EA - defined below) is positive. A schematic of the hypothetical potential energy curves is presented in Figure 4. The electron affinity (EA (RCI)) is defined as the difference in enthalpy between the ground state of the neutral and the ground state of the anion. In other words, it is the negative of the enthalpy change for the following reaction^{81, 84, 85} :

$$EA (RCI) = -\Delta_r H^\circ = \Delta_r H^\circ(RCI) - \Delta_r H^\circ(RCI \bullet) \quad (19)$$

The vertical detachment energy⁸⁶ (VDE) is the energy corresponding to a vertical transition from the anion to the molecule.

A complicating factor in the examination of fragmentation patterns for electron capture generated anions is the possibility of dissociative electron attachment (DEA)^{64, 86}. DEA occurs when a repulsive anionic state is formed that instantly dissociates to a radical and anion^{86, 87}. DEA can arise from the initial formation of a repulsive negative-ion resonance state (NIRS - see Figure 4)⁸⁶. A resonance state is a discrete, weakly bound transient interaction between a molecule and electron⁸⁷. It has been suggested that "A most significant mode of electron capture by molecules is via negative-ion resonant states (NIRSs)"⁸⁸. This suggests that NIRSs can convert to more stable anion states, lead to electron detachment, or induce fragmentation⁸⁶.

Figure 4 : Anion Thermochemical Terms*

* Individual Terms are Defined in Accompanying Text (Section 1.5)

1.6 Issues Addressed in This Thesis

As discussed earlier, environmental dechlorinations exhibit congener specificity and regioselectivity^{23,24}. It would be valuable to know to what extent this specificity can be attributed to biological action and to what extent to the intrinsic chemistry of PCBs. Therefore, the objective of this thesis is to examine the intrinsic nature of PCB dechlorinations by measuring regioselective bias associated with selected dechlorination reactions.

Molecules are ionized in a mass spectrometer under vacuum (1×10^{-7} torr - EI) or near vacuum (0.1 to 1.0 torr - ECNI) conditions. Within the mass spectrometer, dechlorination reactions occur in an isolated environment and are free from contributions of complex reagents or solvents. Thus, insight into the intrinsic chemistry of PCBs is possible. Furthermore, dechlorinations are prominent in the mass spectra of PCBs implying that mass spectrometry is a legitimate experimental means to probe a number of PCB dechlorinations.

Regioselective dechlorinations can be effectively monitored in a mass spectrometer using PCBs that have been labelled with isotopically enriched chlorine^{46, 63}. In this thesis we capitalized on available synthetic methods to produce a relatively large number (~60) of isotopically (^{37}Cl) enriched PCB congeners. These isotopically labelled PCB congeners were separated using high-resolution gas chromatographic techniques and then analysed in a mass spectrometer to reveal the regioselective nature of five different dechlorination reactions ($[\text{M}-\text{Cl}]^+$ induced by EI, $[\text{M}-2\text{Cl}]^+$ induced by EI, $[\text{M}-\text{Cl}]^+$ induced by ECNI,

$[M+H-Cl]^+$ induced by ECNI, and $[M+O-Cl]^+$ induced by ECNI). This experimental information was then further augmented by molecular modelling calculations, which were also performed in this study.

Observed regioselective biases associated with these dechlorination reactions will provide valuable clues to reaction mechanisms as well as indicate the intrinsic chemistry of these processes.

1.7 Chapter Summary

This chapter began with a brief sketch of the PCB properties which make this class of chemicals a significant environmental concern. After this, the chemistry of PCBs, including the production and chlorination of these molecules, was reviewed. The chlorination of PCBs provided a means to synthesize sets of PCBs labelled with isotopically enriched chlorine-37. Dechlorination experiments were carried out and monitored with a mass spectrometer. Therefore, the mass spectrometry of PCBs was reviewed. Ion thermochemistry will be used to describe and explain the results we collected, and thus related terminology and concepts were also reviewed in this chapter. Finally, the objective of this research and the experimental means to attain it were briefly outlined.

Chapter 2 : Experimental Description and Calculations

2.1 Introduction

The research undertaken for this thesis can be divided into three stages: 1) ^{37}Cl -labelled PCB congeners were synthesised and identified; 2) individual labelled congeners were ionized and the dechlorinated fragments monitored by mass spectrometry; and 3) the mass spectral information was mathematically manipulated to reveal the tendency of the label to be selectively removed relative to other chlorines. The organization of this chapter will reflect these stages.

2.2 Synthesis and Identification of Isotopically Labelled PCB Congeners

2.2.1 Synthesis of Isotopically Labelled PCB Congeners

Ten pure PCB congeners were isotopically labelled with ^{37}Cl . They all contained three or more chlorines on one ring, and none on the other. A schematic representation of the congeners used as starting materials and a few of the typical products are presented in Figure 5^f. Pure PCB congeners (solid) were purchased from Ultra Scientific (North Kingston, RI) and were used without further purification. Stock solutions of these congeners were prepared in hexane (99.99 % - Caledon). Initial concentrations were approximately 2000 ppm and were accurately determined by weighing each component. Each solution was vortexed and allowed to sit for a minimum of 6 hours to ensure complete dissolution. To prepare the

^f

PCB congeners represented throughout the thesis by: unlabelled chlorines = filled circles, labelled chlorines = unfilled circles, and hydrogens are implicit.

Figure 5 : ^{37}Cl Isotope Labelling Experiments

Other PCB Congeners Labelled :

Synthesis based on work of Lepine et al., Org. Mass Spectrom. 27, 1311-1316, 1992

Note : $\bigcirc$ = ^{37}Cl Label ; $\bullet$ = Naturally Occuring ^{37}Cl & ^{35}Cl

reagent mixture, an appropriate quantity of the stock solution (calculated to make a final solution of 2.5 mM of PCB congener in 0.7 ml of hexane) was added to a pre-cleaned 1.5 ml Pyrex vial containing a weighed quantity of iron powder (~4 mg - Aldrich Chemical Company, Inc., Milwaukee). 0.7 millilitre of hexane was then added to make a final solution mass of approximately 0.45 g. The reaction vial was then sealed with a Teflon-lined screw cap. The chlorination reaction was initiated by bubbling of $^{37}\text{Cl}_2$ gas into the reaction vial.

Anhydrous $^{37}\text{Cl}_2$ gas was prepared by the method initially reported by Brown et al.⁸⁹. Approximately 60 mg of commercially available Na ^{37}Cl (Isotec Inc., Maimisburg) was dissolved in approximately 4 ml of 1.5 M H_2SO_4 and then combined with approximately 810 mg $\text{K}_2\text{S}_2\text{O}_8$ (Aldrich Chemical Company, Inc., Milwaukee). This solution was stirred with a small magnetic bar and heated in a water bath. When this mixture was heated to between 65°C and 80°C, $^{37}\text{Cl}_2$ gas was generated. The $^{37}\text{Cl}_2$ gas was transferred⁹ by entraining it in a stream of nitrogen gas, which was bubbled slowly through the solution for a minimum of 20 minutes. The generation of the $^{37}\text{Cl}_2$ gas from the Na^{37}Cl solution was monitored visually by the degree of effervescence in the solution. Generation of $^{37}\text{Cl}_2$ gas was typically complete within 15 minutes at a temperature of approximately 75°C. Traces of water were removed from the gas stream mixture by sequential passage through a concentrated sulfuric acid solution⁸⁹.

⁹

Note : the use of inert (Teflon) tubing is recommended since Cl_2 gas is relatively corrosive.

This gas stream was then bubbled into the reaction vial containing the PCB solution and iron powder mixture that was described above. In order to condense the $^{37}\text{Cl}_2$ gas from the N_2 gas stream, the reaction vial was cooled to -76°C in a bath of dry ice in acetone. A schematic representation of the apparatus used to generate and transfer the $^{37}\text{Cl}_2$ gas is presented in Figure 6.

After all the $^{37}\text{Cl}_2$ gas was transferred, the reaction vial containing the PCB solution, $^{37}\text{Cl}_2$, and iron powder was removed from the dry ice / acetone bath, sealed tightly, and then allowed to react in the dark at room temperature for approximately 24 hours. To terminate the reaction, approximately 0.5 ml of 1 M NaOH was added to the reaction vial, shaken, and then the hexane phase was removed. If any traces of colour were evident in the hexane phase, the NaOH extraction was repeated. The clear hexane solution was then ready for HRGC/MS analysis.

2.2.2 High Resolution GC/MS Identification of Isotopically Labelled PCB Congeners

Individual hexane solutions containing the ^{37}Cl -labelled PCB congeners were characterized by HRGC/MS using a Varian Saturn GC/MS system (described in Section 2.3.2.1). The HRGC separation was accomplished with a 30 m x 0.25 mm ID, DB-5MS column with a film thickness of 0.10 μm (Chromatographic Specialties Inc., Order # J122-5531) ^h. The carrier gas was Ultra-High Purity (UHP) grade

^h

VG ZAB (see later description) experiments used a Varian Vista GC system with a column of 0.25 μm film thickness.

Figure 6 : Chlorine Transfer Apparatus

A - $^{37}\text{Cl}_2$ -Generating Solution

B - Concentrated Sulphuric Acid

C - Dry ice / Acetone Bath (-76°C)

D - Reaction Vial (PCB, Iron, & $^{37}\text{Cl}_2$)

E - Flow Monitor

helium (Liquid Carbonic Inc.). Congener identification was based on a comparison of measured retention times with those of pure PCB standards. This identification was further supported by comparison of the appropriate mass spectra. Two types of PCB standards were used : commercially available certified reference materials of PCB mixtures (CLB-1-A, CLB-1-B, CLB-1-C, & CLB-1-C : available from National Research Council, Marine Analytical Chemistry Standards Program, 1411 Oxford Street, Halifax, N.S. B3H 3Z1) and solutions prepared from neat PCB standards (AccuStandard, New Haven, CT or Ultra Scientific, North Kingston, RI). The compositions of these mixtures are presented in Table 6.

Standards and labelled mixtures were analysed in a series of sequential runs. In a typical analysis, sets of four standards and one labelled mixture were run with solvent blanks interspersed to minimize memory effects. Labelled mixtures were run at least in duplicate. Results of these analyses will be detailed in the following Chapter.

2.3 Mass Spectrometry : Experimental Parameters

2.3.1 Introduction

The experimental basis of this investigation is the monitoring of selected dechlorinated fragments induced by the ionization of individual labelled congeners within the ion source of a mass spectrometer. Two different ionization techniques were investigated: electron impact to produce cations, and electron capture to produce anions. The electron impact studies were undertaken using both a VG

Table 6a : Standard Compositions

Mix ID	BZ #	Conc. (/ppm) **
CLB1-A	18	11.8
	54	16.6
	31	6.6
	49	7.6
	44	5.9
	40	4.9
	121	3.1
	86	2.9
	87	3.8
	77	5.5
	153	2.1
	159	1.2
	156	1.5
	OCN	NQ*
	209	1.7

Mix ID	BZ #	Conc. (/ppm) **
CLB1-B	15	91.9
	52	15.2
	103	10.8
	60	3.9
	154	6.2
	143	5.7
	105	4.0
	182	3.8
	128	4.9
	202	3.6
	173	2.3
	208	2.4
	207	3.8
	205	3.2
	OCN	NQ*
	209	2.8

Mix ID	BZ #	Conc. (/ppm) **
CLB1-C	15	138.1
	114	6.3
	153	7.3
	137	7.4
	129	8.3
	183	6.6
	185	3.5
	171	5.2
	201	7.0
	191	5.0
	199	4.8
	203	5.1
	189	4.7
	OCN	NQ*
	206	6.7
	209	5.1

Mix ID	BZ #	Conc. (/ppm) **
CLB1-D	15	76.7
	101	8.9
	151	5.0
	118	3.9
	153	3.3
	141	2.8
	138	4.2
	187	3.2
	180	2.8
	170	3.0
	199	3.6
	196	3.3
	195	2.6
	194	2.4
	OCN	NQ*
	209	2.7

* NQ - Not quantified, not in commercial mixture

** Conc. (/ppm) => concentration in ppm

Table 6b : Standard Compositions

Mix ID	BZ #	Conc. (/ppm) **
Amix	24	31.0
	64	15.5
	102	15.6
	109	15.9
	85	16.7
	142	18.2
Mix ID	BZ #	Conc. (/ppm) **
Bmix	23	28.5
	96	15.1
	93	16.2
	83	21.0
	120	15.6
	131	16.5
Mix ID	BZ #	Conc. (/ppm) **
C Mix	45	13.6
	57	14.0
	88	14.8
	152	20.5
	82	16.4
	122	20.8
Mix ID	BZ #	Conc. (/ppm) **
D mix	69	16.0
	100	18.6
	91	17.3
	97	15.4
	144	16.6
	161	16.4
Mix ID	BZ #	Conc. (/ppm) **
E Mix	43	16.8
	67	20.7
	55	14.6
	125	15.6
	124	15.5
	127	17.1
Mix ID	BZ #	Conc. (/ppm) **
F mix	75	14.8
	63	21.0
	92	14.3
	145	18.4
	147	16.5
	158	15.2

Mix ID	BZ #	Conc. (/ppm) **
G mix	48	13.9
	94	17.6
	84	21.2
	81	17.3
	108	15.3
	185	14.9
Mix ID	BZ #	Conc. (/ppm) **
H mix	62	18.6
	74	18.6
	89	16.1
	117	15.3
	107	17.7
	181	16.4
Mix ID	BZ #	Conc. (/ppm) **
I mix	59	18.1
	76	20.4
	90	14.0
	87	17.9
	123	16.0
	173	13.9
Mix ID	BZ #	Conc. (/ppm) **
J mix	41	17.2
	98	16.1
	113	14.2
	111	16.4
	134	15.4
	192	21.1
Mix ID	BZ #	Conc. (/ppm) **
K mix	65	67.8
	95	36.5
	110	22.2
	139	30.3
	105	23.5
	166	10.3
Mix ID	BZ #	Conc. (/ppm) **
L mix	61	23.3
	101	48.9
	115	22.5
	118	24.9
	114	9.4
	160	9.2

** Conc. (/ppm) => concentration in ppm

ZAB mass spectrometer and a Varian Saturn Ion Trap mass spectrometer. The electron capture studies were performed on only the VG ZAB mass spectrometer. In all cases, individual congeners present in the chlorinated mixtures were separated using a gas chromatograph coupled directly to the specific mass spectrometer. A summary of the experiments performed and the respective mass spectrometer's instrument parameters are presented in Table 7. Particular instrument parameters are defined and described in Section 2.3.2 and Section 2.3.3.

2.3.2 Mass Spectrometric Experiments : EI/MS Parameters

As mentioned above, the two instruments used to undertake the EI investigations were A) a Varian Saturn Ion Trap GC/MS and B) a Varian Vista GC coupled to a VG ZAB mass spectrometer.

2.3.2.1 Varian Saturn Ion Trap GC/MS

In the ion trap, which has also been referred to as a three-dimensional quadrupole^{90,91}, ions are generated and mass-separated within the same volume. Ions are trapped in stable orbits induced by applied rf voltage fields^{60,90,91}. These orbits are a function of the ion's m/z ratio and the rf field. The rf field can be altered in such a way as to destabilize the orbits of specific m/z ratio ions. These ions with destabilized orbits are ejected from the trap and can be detected to produce a characteristic mass spectrum. The ion trap mass spectrometer functions optimally

Table 7 : Experiment Summaries *

Instrument	Units	Experiment types							
		VG ZAB	Ion Trap	VG ZAB	VG ZAB	VG ZAB	VG ZAB	VG ZAB	VG ZAB
Mode	NA	EI	EI	ECNI	ECNI	ECNI	ECNI	ECNI	ECNI
Pressure	torr	1 x 10e-7	1 x 10e-3	0.25	0.25	0.25	0.50	0.50	0.50
Temperature	C	250	250	140	140	140	140	140	140
Electron Energy	eV	70	70	150	150	150	150	150	150
Repeller Voltage	V	4	4	0	0	0	0	0	0
	uA	200	NA	NA	NA	NA	NA	NA	NA
Emission Current	uA	NA	50	1000	1000	1000	1000	1000	1000
Ionization Time	usec	NA	100	NA	NA	NA	NA	NA	NA
Probe Hole	NA	Open	NA	Closed	Open	Closed	Closed	Open	Open

* Parameters defined in Sections 2.3.2 and 2.3.3

with a helium background pressure of approximately 10^{-3} torr (note: 1 torr = 133.3 Pa)^{60,90,91}. The historic development, present status, and related theory of the ion trap have been reviewed by March⁹⁰, and comprehensively detailed in the seminal text of March and Hughes⁹¹.

For the Varian ion trap, the important experimental parameters available to the operator are the electron energy, ionization time, emission current, and source temperature. The electron energy was set to 70 eV. The two parameters, ionization time and emission current, together control the number of electrons allowed into the ionization volume. In the ion trap, the number of ions that can be held within stable orbits is limited by space charge effects; thus, the number of ions formed must be restricted. This is accomplished by pulsing the electron flux entering the source using an electric gate while the number of electrons generated is controlled by the emission current. In this investigation the emission current was set at 50 μ A. The time period during which electrons are permitted to enter the ion trap is the ionization time, which was set to 100 μ sec. The ion trap was operated with a source temperature of 250°C.

2.3.2.2 Varian GC / VG ZAB MS

The VG ZAB is a sector instrument of reverse (BE) geometry. The letters BE indicate the presence of both a magnetic (B) and an electric (E) sector, in that sequence. The terms "magnetic" and "electric" indicate the fields experienced by the ions as they pass through the instrument. In the VG ZAB, ions are generated

in the source, and accelerated from it to the magnetic and the electric sector. Ions exiting the source are accelerated to high velocities by passing through a potential difference, typically 8000 V, which is established by “floating” the source above ground. In the EI studies, the source was set at a voltage of +8000 V relative to the rest of the instrument. Monoenergetic ions of different m/z values have different trajectories within the magnetic sector, which constitutes the basis of mass separation.

In the case of the VG ZAB, the instrument parameters typically controlled are the electron energy, trap current, repeller potential, and source temperature. The electron energy was set at 70 eV. The trap current is the current that flows between the filament and a metal plate on the opposite side of the source; in other words, it is proportional to the flux of electrons that transverse the ZAB source. This value is monitored and a feedback loop maintains the emission of electrons at a pre-selected value. In these experiments, the trap current was set to 200 μA . The repeller potential in the ZAB is used to “push” the ions toward the ion exit plate, where they exit the source. In EI work of this investigation, this was set slightly positive to +4 V. The source temperature was set to 250°C.

2.3.2.3 Comparison of EI/MS on VG ZAB and Varian Saturn Ion Trap

Electron impact is relatively insensitive to small differences in experimental parameters as long as the electron energy is greater than ~30 eV. Therefore, the EI ionization in the VG ZAB and the Varian Saturn ion trap should be comparable.

The higher background pressure in the ion trap ($\sim 10^{-3}$ torr relative to $\sim 10^{-7}$ torr in VG ZAB) introduces the possibility of collisional stabilization which is not present in the sector instrument at the source pressures studied. In addition, the time period between the initial ionization and ion detection could be different between these two instrument types. However, the similarity of the observed spectra between these instruments suggests that these effects did not have a significant impact on the nature of the EI-induced dechlorinations being examined.

2.3.3 Mass Spectrometric Experiments : ECNI/MS Parameters

2.3.3.1 Instrument Parameters for the VG ZAB MS

All ECNI/MS experiments were performed on the VG ZAB described above. To switch operation from EI to ECNI, a number of operational changes were made. Since the VG ZAB was designed to enable a rapid conversion between these experiment types, these changes are trivial. However, because the changes alter both the electronic and mechanical characteristics of the source, pertinent consequences will be discussed here.

For the examination of negative ions, the source voltage must be set negative relative to the rest of the instrument, and, therefore, was set to -6000 V. The remaining electronic changes were made automatically by selecting CI control. For CI, the important experimental parameters available to the operator are the emission current, electron energy, ion repeller potential, and source temperature. The emission current setting regulates a feed-back loop which controls the flux of

electrons from the filament to the CI source. The emission current was set to 1 mA for our experiments. In chemical ionization, the electron energy is typically set at a much higher value (150 eV - 300 eV) than in EI. In these investigations an electron energy of 150 eV was used. The ion repeller potential was set to 0V for these studies. The ECNI experiments were performed with as low a source temperature as possible. For the VG ZAB, this temperature was approximately 140°C. The filament was a constant heat source, and as such raised the source temperature from ambient until a steady state was reached, effectively eliminating lower temperature operation.

In ECNI, the source pressure is typically set to a fraction of one torr. Therefore, a few mechanical modifications were needed to facilitate this. The holes or leaks present in the source were minimized. This was accomplished by using a narrow ion exit slit and by plugging all open holes in the source, notably, the probe inlet hole. This enabled the source to be pressurized to approximately 0.5 torr while the region immediately outside the source was still held at a much lower pressure (approximately 10^{-5} torr). Operationally, this lower pressure outside the source was required so that the source could be floated at -6 kV without producing electrical discharges. To create the elevated pressure inside the source, methane was leaked into it through a 0.18 mm ID fused silica capillary tube (~1m long).

Last but not least, another pertinent parameter is the ventilation rate (volumetric flow rate per source volume : F/V). However, this parameter is not normally reported, or manipulated. According to the kinetic model of ECNI

developed by Sears et al.⁷³, a variation in the ventilation rate was calculated to have a significant effect on predicted spectra. Ventilation rate is considered independent of pressure⁷³, although it is dependent on the magnitude of source leaks and the temperature. The opening or closing of the probe inlet hole (~1.2 mm ID) provides a means of drastically changing the source leaks, and thus, provides a convenient method of obtaining different ventilation rates on the VG ZAB.

2.3.3.2 Instrument Modifications of VG ZAB MS for ECNI Operation

As will be demonstrated in a later chapter, the source pressure was a key parameter that affected a number of chemically important characteristics. Because of this, control and measurement of the source pressure were essential. When this investigation was initiated, the VG ZAB was not equipped with any monitoring equipment that could provide an accurate indication of the source pressure. Subsequently, two pressure monitoring techniques were designed and implemented.

In the first approach, a modified probe inlet connection was used to couple a Pirani gauge to the source at the probe inlet. This method had been utilized by others to obtain an indication of source pressure⁷³. The modified probe inlet connection was a stainless steel tube of the same outer diameter as the original connector and fitted with a conical ceramic fitting at one end and a standard vacuum gauge connection at the other. An indication of the source pressure was

obtained when this device was pressed tightly against the MS source (connected through the probe interface). This method had a number of drawbacks. The pressure could only be measured when the high voltages were off, and more importantly, the device had to be removed and substituted with a similar “dummy” plug when the source was in operation. Furthermore, the accuracy of this type of pressure measurement hinges on the assumption that the fit between the pressure measuring connection and the plug are identical. To overcome part of this problem, a second sensor was designed, constructed, and mounted directly onto the source.

To construct the second sensor, the working sensor was removed from a thermocouple gauge and sealed into a connector machined to fit snugly into an unused source inlet hole. The electrical connections to this sensor were made using available, unused electrical feed-throughs. In the case of this prototype, the normal operating source temperature was higher than the calibrated range of the gauge; therefore, recalibration using the external Pirani gauge was required. With this sensor, the probe plug was not required to have the same fit as the probe connection. In fact, pressure measurements could be, and were, made with the probe hole completely open. As with the Pirani gauge, pressure measurements could only be made when the high voltage was not applied, but, for this pressure sensor, only the electrical connections needed to be disconnected. In these investigations, data sets were collected at two different pressures, 0.25 ± 0.05 torr and 0.50 ± 0.05 torr (see Table 7).

2.4 Calculations

Data reduction was required to convert the mass spectral data into a useful indication of the proportion of label loss. This calculation involved a mathematical comparison of the different isotope patterns obtained when the labelled congener loses either a labelled or an unlabelled chlorine. Therefore, prior to describing the details of this mathematical comparison, the manner in which the possible isotope patterns were calculated is presented. Once the proportion of label loss is known, the significance of this finding can be discussed in a chemical context. To facilitate this comparison, reference will be made to statistically expected losses, and to chemical parameters such as bond length, bond angle, and enthalpies. The manner in which these values were calculated is also presented (in Section 2.4.5).

2.4.1 Chlorine Isotopic Patterns

2.4.1.1 Naturally Occurring Chlorine

The natural abundances of the chlorine isotopes, ^{35}Cl and ^{37}Cl , are 75.8% and 24.2 %, respectively. Therefore, a molecule containing one chlorine will have two chemically identical forms with different masses. One of these forms (R^{35}Cl) will have a mass that is 2 atomic mass units (amu) lower than the other (R^{37}Cl). In a mass spectrometer, each of these different masses can be detected. The relative intensities of the R^{35}Cl form will be approximately three times the relative intensities of the R^{37}Cl form, which reflects the natural abundance ratio of 75.8% to 24.2 %. Similarly, if a molecule has more than one chlorine, it will have a series of different masses, each representing a different combination of ^{35}Cl and ^{37}Cl . In a mass

spectrometer, these different masses will produce a characteristic mass isotopic distribution pattern. This pattern (or cluster) is significantly distinctive to be used to indicate both the presence and the number of chlorines in a given molecule⁹². The appearance of these isotopic patterns can be simulated mathematically⁹² by means of expanding a binominal expression of the form $(a+b)^n$, where a is the natural abundance of the lower mass isotope, b is the fractional natural abundance of the higher mass isotope, and n is the number of atoms present in the molecule. For example, consider the expected distributions for a hypothetical compound containing three chlorines:

Example 1 : Binominal expansion of $(0.7577 + 0.2423)^3$ to simulate the mass isotopic distribution pattern for a compound with 3 chlorines.

$^{35}\text{Cl}_3$	$= 105 \text{ amu} = a^3$	$= (0.7577)^3$	$= 0.4350 = 43.50 \%$
$^{35}\text{Cl}_2^{37}\text{Cl}$	$= 107 \text{ amu} = 3a^2b$	$= 3(0.7577)^2(0.2423)$	$= 0.4173 = 41.73 \%$
$^{35}\text{Cl}^{37}\text{Cl}_2$	$= 109 \text{ amu} = 3ab^2$	$= 3(0.7577)(0.2423)^2$	$= 0.1335 = 13.55 \%$
$^{37}\text{Cl}_3$	$= 111 \text{ amu} = b^3$	$= (0.2423)^3$	$= 0.0142 = 1.42 \%$

Notice that the sum of all the ion intensity fractions in Example 1 is unity (1). In reality, the ion masses shown in Example 1 are offset by the mass of the remaining part of the molecule. In the case of a trichlorobiphenyl ($\text{C}_{12}\text{H}_7\text{Cl}_3$) this shift would be 151 atomic mass units (amu) for ^{12}C and ^1H . Therefore, the $^{12}\text{C}_{12}^{1}\text{H}_7^{35}\text{Cl}_3$ ion would have a mass of 256 amu.

The natural isotopic distribution of carbon ($^{12}\text{C} = 98.9 \%$, $^{13}\text{C} = 1.1 \%$) will induce yet a further distribution of the molecular mass. The isotope distribution pattern induced by two different elements each having two isotopes, can be

simulated by expanding the expression $(a+b)^n(c+d)^m$. In this expression a , b , and n represent the same quantities as in Example 1, while c , d , and m are the analogous values for carbon, the second element. Furthermore, the presence of even more elements with two isotopes can be accommodated by adding additional similar terms (i.e., of the form $(a+b)^n$).

A portion of a typical mass spectrum for a trichlorobiphenyl is presented in Figure 7. The ion at a mass-to-charge ratio (m/z) of 256 is the most abundant ion in the spectrum, and the intensities of all the other ions are scaled relative to this. A comparison of the observed relative abundances of the molecular ion, $[M]^+\bullet$, to corresponding values calculated using the binomial expansion method are presented in Figure 8. The correlation between the calculated and observed relative abundance values is evident from the graph presented in Figure 8. This correlation was quantified using a regression analysis, and these results are also presented in Figure 8. The fit between the calculated and observed relative abundances is good. The small differences observed between the two sets were due to the presence of noise in the experimentally measured relative abundances.

In addition to the molecular ion cluster present in Figure 7, there is an additional significant ion cluster with the most intense ion being at m/z 186. This cluster corresponds to the fragment ion produced by the loss of two chlorines from the molecular ion. This ion type will be referred to by the symbol $[M-2Cl]^+\bullet$. Since the molecular ion has three chlorines, the $[M-2Cl]^+\bullet$ fragment ion contains only one chlorine. This is evident since the ion at m/z 186 is approximately three times as

Figure 7 : Typical $C_{12}H_7Cl_3$ Spectra (BZ 24)

m/z 256 = $^{12}C_{12}H_7^{35}Cl_3$ = 100%

m/z 258 = $^{12}C_{12}H_7^{35}Cl_2^{37}Cl$ = 95%

m/z 260 = $^{12}C_{12}H_7^{35}Cl^{37}Cl_2$ = 30%

m/z 262 = $^{12}C_{12}H_7^{37}Cl_3$ = 3%

Figure 8 : Comparison of Calculated to Measured Ion Intensities

Mass	Calculated 37Cl & 35Cl Intensities		Calculated 37Cl, 35Cl, 13C & 12C Intensities		Figure 7 : Molecular Ion Measured Intensities	
	Normalized	% Base	Normalized	% Base	% Base	Normalized
256	43.5%	100.0%	38.1%	100.0%	100.0%	39.3%
257			5.1%	13.5%	12.3%	4.8%
258	41.7%	95.9%	36.8%	96.8%	92.7%	36.4%
259			4.9%	12.9%	11.5%	4.5%
260	13.4%	30.7%	12.0%	31.5%	30.6%	12.0%
261			1.6%	4.2%	4.2%	1.7%
262	1.4%	3.3%	1.3%	3.5%	3.0%	1.2%
263			0.2%	0.5%	0.2%	0.1%

intense as the ion at m/z 188, reflecting the relationship between the natural abundance of ^{35}Cl (~76%) and that of ^{37}Cl (~24%).

In Figure 9 three EI mass spectra (labelled A, B, and C) for the congeners BZ 62 (a Cl_4 congener - spectrum 9a), BZ 116 (a Cl_5 congener - spectrum 9b), and BZ 142 (a Cl_6 congener - spectrum 9c) are presented. In the molecular structures presented, chlorines are indicated with black circles and hydrogen presence is implicit. In each case, $[\text{M}]^+\bullet$ is the most intense ion cluster, and exhibits a characteristic chlorine isotope pattern representative of the particular chlorination level. A closer examination of the spectrum of BZ 142 reveals the presence of both a $[\text{M}-\text{Cl}]^+\bullet$ and a $[\text{M}-2\text{Cl}]^+\bullet$ ion cluster. Note that the isotope pattern of the $[\text{M}-\text{Cl}]^+\bullet$ cluster from BZ 142 closely resembles that of the $[\text{M}]^+\bullet$ of BZ 116 with the exception that it begins at a m/z value one unit lower. Similarly, the isotope pattern of the $[\text{M}-2\text{Cl}]^+\bullet$ cluster from BZ 142 closely resembles that of the $[\text{M}]^+\bullet$ of BZ 62 with the exception that the former cluster begins 2 m/z units lower.

2.4.1.2 Chlorine Isotopic Patterns with an Isotopically Enriched ^{37}Cl

In general, the addition of an isotopically enriched element can, for the purposes of simulating isotope distribution patterns, be considered to be analogous to adding a new element with its own distinct isotope pattern. In the limit of 100% enrichment of the desired isotope, the expression associated with this additional term would be $(1+0)^n$, and would not alter the isotope distribution pattern induced by the other elements of the compound. To demonstrate the effect of adding an

Figure 9 - Selected Mass Spectra

isotopically enriched ($^{37}\text{Cl} > 95\%$ enrichment) chlorine label to a PCB congener, consider the three spectra presented in Figure 10.

The congener whose spectrum is shown in 10c is the ^{37}Cl -labelled analog of the PCB congener whose spectrum is shown in 10b. Notice that the relative intensities of the ions present in spectrum 10c (i.e., $[\text{M}]^+$, $[\text{M}-\text{Cl}]^+$, & $[\text{M}-2\text{Cl}]^+$) are similar to those in spectrum 10b. However, the isotope distribution patterns are different. The $[\text{M}]^+$ cluster in spectrum 10c resembles the $[\text{M}]^+$ cluster in spectrum 10a, although the mass-to-charge values of the $[\text{M}]^+$ in spectrum 10c are higher by 36 units than those of the $[\text{M}]^+$ in spectrum 10a (i.e., +37 - 1 units). The $[\text{M}-\text{Cl}]^+$ cluster in spectrum 10c does not resemble any of the ion clusters in spectrum 10a or spectrum 10b. Instead, the $[\text{M}-\text{Cl}]^+$ cluster in spectrum 10c has a unique isotope distribution pattern. This unique pattern arises from the additive overlap of the different patterns of the cluster produced from either the loss of a labelled chlorine (i.e., $[\text{M}-^{37}\text{Cl}]^+$), or the loss of an unlabelled chlorine (i.e., $[\text{M}-^{\text{unlabelled}}\text{Cl}]^+$). The differentiation of the isotope distribution pattern produced from $[\text{M}-^{37}\text{Cl}]^+$ and that produced from $[\text{M}-^{\text{unlabelled}}\text{Cl}]^+$ is of paramount importance in this thesis.

In the case of the labelled BZ 142 depicted in spectrum 10c, the $[\text{M}-^{37}\text{Cl}]^+$ isotopic pattern is identical to a Cl_5 pattern except that it begins at m/z 323 rather than m/z 324. The $[\text{M}-^{\text{unlabelled}}\text{Cl}]^+$ isotopic pattern is identical to a Cl_4 pattern, except that it begins at m/z 325 rather than m/z 326 (i.e., as a Cl_4 species plus one label would). If the fraction of label lost is known, then the resulting composite pattern could be simulated after adding the appropriate scaling factors. In other words,

Figure 10 - Selected Mass Spectra

$$(Composite\ Pattern)_{mass} = X (Cl_5\ Pattern)_{mass} + Y (Cl_4\ Pattern)_{mass} \quad (20)$$

where X and Y are the contributions (scaling factors) of the patterns. If additional overlapping patterns were present, Equation 20 could simply be expanded to include the appropriate terms. As a result, a set of simultaneous equations, each corresponding to a given ion within the cluster, can be written and solved for X and Y using multiple regression analysis.

2.4.3 Deconvolution of Overlapping Chlorine Isotopic Patterns

In this investigation, the following procedure was used to deconvolute overlapping isotope patterns and determine the fraction of label lost. The intensities of all the ions in an observed cluster were normalized and then compared with the normalized calculated isotope distribution patterns for all possible ion types that could have contributed. For example, in the case of the loss of a single chlorine induced by electron impact ionization, the possible ion types were $[M-Cl]^+$, $[M-^{37}Cl]^+$, $[M-HCl]^+$, and $[M-H^{37}Cl]^+$. The contributions of each of these ions was solved using the method of least squares (multiple regression analysis). Specifically, we utilized the algorithms available in the spreadsheet program, Quattro Pro 5.0. The quality of the match between the calculated and observed isotope distribution pattern was monitored via the coefficient of correlation (R^2) value⁹³ provided by the calculation.

**2.4.3.1 Deconvoluting Overlapping Chlorine Isotopic Patterns:
Specific EI Application**

In our work, the first two dechlorination clusters in the EI spectra of labelled congeners were deconvoluted to determine the partition between available reaction channels and thus the fraction of label loss. In particular, these were the clusters that were previously referred to as $[M-Cl]^+$ and $[M-2Cl]^+$ in spectrum 10c. To avoid confusion, these will now be referred to as the first and second dechlorination clusters, respectively. As indicated above, there were four possible ions ($[M-Cl]^+$, $[M-^{37}Cl]^+$, $[M-HCl]^+$, and $[M-H^{37}Cl]^+$) that could contribute to the first dechlorination cluster. An example of a typical calculation set-up and results is presented in Figure 11. In this example, the data, possible chlorination patterns, and regression results are presented for the first dechlorination cluster in spectrum 10c. Multiple regression analysis shows that the measured isotope cluster is best represented by 39% $[M-^{37}Cl]^+$, 59% $[M-Cl]^+$, 5% $[M-H^{37}Cl]^+$, and -2% $[M-HCl]^+$. Notice that the R^2 value and standard error of Y estimate presented in Figure 11, 0.9982 and 0.005 respectively, are similar to values presented in Figure 8, 0.9992 and 0.005 respectively, for unlabelled BZ 24.

For the second dechlorination cluster, the number of possible ions increased significantly because of the possible loss of one or two hydrogens with the chlorines. Considering this, all the possible ions are $[M-Cl_2]^+$, $[M-Cl^{37}Cl]^+$, $[M-^{37}Cl_2]^+$, $[M-HCl_2]^+$, $[M-HCl^{37}Cl]^+$, $[M-H^{37}Cl_2]^+$, $[M-H_2Cl_2]^+$, $[M-H_2Cl^{37}Cl]^+$, and $[M-H_2^{37}Cl_2]^+$. We found that the solutions obtained using multiple regression analysis

Figure 11 : Sample Calculation**BZ 142 <704-706>****704_116A****EI ZAB**

Observed		Normalized	Calculated Mass / Isotopic Patterns				Calculated
Mass	%base	Measured	[M-37Cl]+	[M-Cl]+	[M-H37Cl]+	[M-HCl]+	
322	0.0%	0.00	0.00	0.00	0.22	0.00	-0.00
323	5.7%	0.08	0.22	0.00	0.03	0.00	0.09
324	1.2%	0.02	0.03	0.00	0.35	0.29	0.02
325	22.8%	0.32	0.35	0.29	0.05	0.04	0.31
326	4.0%	0.06	0.05	0.04	0.23	0.37	0.06
327	22.4%	0.31	0.23	0.37	0.03	0.05	0.31
328	3.9%	0.05	0.03	0.05	0.07	0.18	0.05
329	9.2%	0.13	0.07	0.18	0.01	0.02	0.14
330	1.3%	0.02	0.01	0.02	0.01	0.04	0.02
331	1.5%	0.02	0.01	0.04	0.00	0.01	0.03
332	0.0%	0.00	0.00	0.01	0.00	0.00	0.00
333	0.0%	0.00	0.00	0.00	0.00	0.00	0.00
334	0.0%	0.00	0.00	0.00	0.00	0.00	0.00
335	0.0%	0.00	0.00	0.00	0.00	0.00	0.00
Sum							1.02

Regression Output:

Constant 0
 Standard Error of Y Estimate 0.005345
 R Squared 0.99816
 Number of Observations 14
 Degrees of Freedom 10

X Coefficient (s)

Standard Error of X Coefficient

[M-37Cl]+	[M-Cl]+	[M-H37Cl]+	[M-HCl]+
39%	59%	-2%	5%
2%	2%	2%	2%

Determined % Label Lost from [M-X]+ 40%**Measured vs Calculated
Isotope Patterns**

were less reliable when there was more than one ion distribution pattern with a common starting mass. For example, the $[M-Cl^{37}Cl]^+$ ion's isotope distribution pattern begins at m/z 72 unitsⁱ below the parent ion's first m/z , as does the $[M-H_2Cl_2]^+$ ion's isotope distribution pattern. This made deconvolution of these ions difficult. Fortunately, the $[M-H_2Cl_2]^+$ ion was not typically observed in the unlabelled spectrum, thus justifying our ignoring of $[M-H_2Cl_2]^+$, $[M-H_2Cl^{37}Cl]^+$, and $[M-H_2^{37}Cl_2]^+$. This being said, the decision to exclude certain ions was only exercised provided the following conditions were met: 1) the ions could be ruled out by an examination of the mass spectrum of the corresponding unlabelled congener **and** 2) their m/z values began at the same mass as an ion type that could not be ruled out. Therefore, during the examination of the second dechlorination cluster in congeners containing one label, all of the following ions were considered $[M-Cl_2]^+$, $[M-Cl^{37}Cl]^+$, $[M-HCl_2]^+$, $[M-HCl^{37}Cl]^+$, and $[M-H_2Cl^{37}Cl]^+$. The only ion not considered was $[M-H_2Cl_2]^+$. In the case of congeners containing two labels, the following ions were analysed for $[M-Cl_2]^+$, $[M-Cl^{37}Cl]^+$, $[M-^{37}Cl_2]^+$, $[M-HCl_2]^+$, $[M-HCl^{37}Cl]^+$, $[M-H^{37}Cl_2]^+$, and $[M-H_2^{37}Cl_2]^+$. The only ions not considered were $[M-H_2Cl_2]^+$ and $[M-H_2Cl^{37}Cl]^+$.

**2.4.3.2 Deconvolution of Overlapping Chlorine Isotopic Patterns:
Specific ECNI Application**

The deconvolution of the dechlorination clusters observed in ECNI mass

ⁱ i.e., for a single labelled Cl_6 congener (see spectrum C in Figure 10) the first m/z value is $360 - 72 \text{ units} = m/z \text{ } 288$

spectra was completely analogous to the process described for EI. The only distinction was in the nature of the ions observed. In ECNI, hydrogen gain associated with dechlorination was not uncommon and thus ions of the type $[M+H-Cl]^+$ are possible. Thus, for the first dechlorination cluster in ECNI, the possible ion types were $[M-Cl]^+$, $[M-^{37}Cl]^+$, $[M-HCl]^+$, $[M-H^{37}Cl]^+$, $[M+H-Cl]^+$, and $[M+H-^{37}Cl]^+$. For this set, only the possibility of the $[M-HCl]^+$ ion was not considered.

In the case of the second and third dechlorination clusters in ECNI, the number of ion types needed to be taken into account began to approach the number of ions in the isotope patterns observed. This made results of the multiple regression analysis unreliable. Because of this, only the first dechlorination cluster was analysed for ECNI data.

2.4.4 Probability of Label Loss

Once the fraction of label loss had been determined, this value was analysed within a chemical context. One of the simplest yet most valuable comparisons is that between what was actually lost and what would be expected to be lost, had this loss been random. In the case of the loss of a single label, the probability of random loss is simply the number of labels divided by the total number of chlorines. In the case of the loss of two labels, a determination of the probability is less obvious. However, it can be modelled after the probability of extracting two items from a set containing two different item types. For instance, if we have a set of four items (○●●●), one of which is white and three of which are

black, the probability of randomly selecting 2 black items (●●) is $(3/4) \times (2/3) = (6/12)$ or 50%. Similarly the probability of randomly selecting 2 white items (○○) is $(1/4) \times (0/3) = 0/12$ or 0% while the probability of selecting one white and one black (○●) is $(1/4) \times (3/3) + (3/4) \times (1/3) = (6/12)$ or 50%. A similar type of analysis for a series of sets related to the labelled species examined in this thesis is presented in Figure 12.

To continue the analogy between this simple model and our dechlorination calculation, consider the following: In our calculation, we would be able to determine the partition between different remaining types after the removal of the two items. In context to the set of 4 items discussed above, two residue types are possible. One is the result of the random loss of two black items (●●), leaving a residue of one black and one white (○●). This occurs 50% of the time. The other residue results from the random loss of one white and one black (○●), leaving a residue of two black (●●), which also occurs 50% of the time. As mentioned above, a multiple regression method was used to determine the observed partition between these residues. A probability larger or smaller than 50% would indicate non-random loss.

Alternatively, it is also possible to measure how close the experimental removal of two items is to a random removal by counting all the individual white and black items remaining in each of the two residue types. If this ratio of the remaining white and black items is compared with the ratio corresponding to a random loss, an indication of how close the extraction method is to random can be

Figure 12 : Probabilities of Random Loss of Two Items from Selected Sets

Set	2 White ○○	White & Black ●○	2 Black ●●	Fraction Label Lost
●●●○	0%	50%	50%	0.250
●●●●○	0%	40%	60%	0.200
●●●●●○	0%	33%	67%	0.167
●●●●○○	10%	60%	30%	0.400
●●●●●○○	7%	53%	40%	0.333
●●●●●○○○	5%	48%	48%	0.286
●●○	0%	67%	33%	0.333
●●○○	17%	66%	17%	0.500

$$\text{Fraction Label Lost} = \frac{2 \times P(\text{○○}) + P(\text{●○○})}{2 \times P(\text{○○}) + 2 \times P(\text{●○○}) + 2 \times P(\text{●●○})}$$

Where $P(\text{○○})$, $P(\text{●○○})$, and $P(\text{●●○})$ are the probabilities of losing the indicated items.

made. This, in effect, was the method used by Lepine et al.⁴⁶ In the case of chlorine labels, this approach is complicated significantly because the unlabelled chlorines contain both ^{35}Cl and ^{37}Cl . The distinction between this calculation method and the multiple regression method becomes most significant when there are two or more white items (i.e., two or more labels). Using the individual item-counting method, it is impossible to distinguish between the loss of two white (○○) items and the loss of one white plus one black (○●) item. In the context of the loss of labelled chlorines, the distinction between the loss of two labelled chlorines and the loss of one labelled chlorine plus one unlabelled chlorine may contain chemically important information.

There is some merit in expressing the magnitude of label loss as one number. A single value indicating the fraction of label loss can be calculated from the results of the multiple regression analysis. An equation relating the fraction of label loss to the percentage of each fragment is presented in Figure 12 along with the statistical probabilities of losing labels from different types of limited sets.

2.4.5 Calculation of Thermochemical and Molecular Properties

The linking of an observed regioselective dechlorination to a specific molecular property facilitates the development of a predictive model. The molecular properties most likely to be indicative of favoured dechlorination pathways include bond lengths and angles, enthalpies, and molecular orbital characteristics. For PCBs, reliable measured values for these properties are not readily available;

however, computational methods are available that permit the estimation of these types of values.

Specifically, calculations were performed using Hyperchem, a commercially available quantum mechanical program⁹⁴. This program provides a simple graphic user interface for setting up calculations that can be performed at a number of different levels of theory. For our application, a semi-empirical quantum mechanical method, AM1 (Austin Method 1)⁹⁵, was selected. A quantum mechanical method is a technique to obtain approximate solutions for the quantum mechanical equations that define a specific molecule or ion. The phrase “semi-empirical” suggests that some of the calculation parameters were chosen (by the creators of the method) in such a manner that results obtained correlate with experimentally determined values. AM1 has been proven to provide reasonably accurate results with low to modest cost of time and computer resources^{95,96}.

The first step in performing any calculation on Hyperchem is the drawing of a representative structure of the specific molecule to be examined. The graphic user interface provides a convenient way of creating and setting approximate bond lengths and bond angles. An initial approximate structure is then optimized using available algorithms which alter the relative atomic distances, monitor energy deviations, and ultimately determine geometries corresponding to minimum energies. In this investigation, neutral PCB congeners were optimized using the Polak-Ribiere conjugate gradient algorithm with the termination energy gradient set to 0.001 kcal/mol. The bond lengths and angles and thermochemical properties

obtained in this manner matched well with literature values^j. There is no guarantee that the optimum geometry thus determined is the lowest energy structure of the molecule; in other words, that the optimum geometry determined is the global minimum. Instead, this geometry may be a minimum only for a small range of localized movements, in which case it is a local minimum. This issue is significant when thermochemical calculations are subsequently performed since the results obtained are necessarily structure dependent. This problem was minimized by performing the optimization on a number of starting geometries and by comparing the optimized geometric parameters and thermochemical properties with available literature values.

Once an appropriate geometry was obtained, the energetics of this structure was evaluated via its enthalpy of formation ($\Delta_f H^{298}$). This was determined by performing a single point calculation with the semi-empirical / AM1 option selected. The ground state energy of the cation was considered to be greater than the ground state energy of the neutral by an amount equal to the energy of the highest occupied molecular orbital (HOMO), which, in turn, was considered to be equivalent to the ionization energy of the neutral.

In addition to the HOMO energy, other molecular orbital characteristics can provide insight into the chemistry of PCBs. Of particular relevance to this investigation is the calculation of bond order, a parameter which has been used to express the relative bond strengths in a molecule⁹⁷. The bond order is an

^j Specific examples are presented in Chapter 5.

indication of the bond multiplicity between two atoms in a molecule; for example, a single bond such as the one in H_2 has a bond order of 1, whereas, a double bond such as the $C=C$ bond in ethylene (C_2H_4) has a bond order of 2. In other molecules, the bond order does not necessarily have an integer value; for example, the calculated bond order for the $C=O$ bond in glycine (H_2N-CH_2-COOH) is 1.86⁹⁸.

The bond order is calculated from the density matrices, which can be obtained from Hyperchem by setting up an appropriate log file. The density matrix contains the net coefficients for each atomic orbital in a molecule. The bond order between atoms A and B is simply the sum of the squares of the electron densities of the orbitals of atoms A and B in the density matrix.

Chapter 3 : Identification of ^{37}Cl -Labelled Products

3.1 Introduction

The chlorination of the ten pure PCB congeners described in Section 2.2, produced a series of labelled congener mixtures. These were analysed by the techniques outlined in Section 2.3. In this Chapter, the results obtained from this analysis are presented. The individual mixtures will be discussed in groups sorted by the number of chlorines present in the pure PCB starting material. In all, 59 labelled congeners containing one or two labels were identified. Of these, 48 could be unambiguously identified based on their retention times; identification of the remaining 11 congeners, however, required additional information. In most cases, an examination of the mass spectra and a consideration of the probability of formation based on chemical arguments allowed us to make a reliable identification. The time that we will spend on discussing these 11 congeners should not overshadow the fact that identification was unambiguous for the vast majority of products.

3.2 Analysis of Individual Mixtures

3.2.1 Pentachlorobiphenyl Starting Material : BZ 116 Mixture

In the case of the pentachlorobiphenyl starting material, BZ 116 (2,3,4,5,6-pentachlorobiphenyl), one of the two phenyl rings is fully chlorinated and thus additional chlorine(s) could only be added to the originally unchlorinated phenyl ring. A representative chromatogram obtained from the mixture of products arising

from the chlorination of BZ 116 is presented in Figure 13. The peaks in Figure 13 were identified, based on the retention time table included in the same figure. This retention time table contains five columns. The first identifies the BZ number of a particular product and the second shows the retention times calculated from published data on a liquid phase of very similar material ⁹⁹. The third displays the relevant standard mixtures which contained the particular congeners (for standard mixture compositions, see Table 6 in Chapter 2). The fourth shows the measured retention times of the particular standards, and the fifth is the retention times of the components of the BZ 116 mixture that were identified. The format of this retention-time table will be repeated for similar tables of the other mixtures discussed. The observed retention times were reproducible within approximately 5 seconds (0.08 minutes); the error for the calculated retention times (second column in table) is dependent on the quality of the fit but was usually no worse than approximately 7 seconds (0.12 minutes).

The identity of the labelled products produced from BZ 116 indicates that only certain sites of this reagent were chlorinated; these were 2'- (to produce BZ 142), 3'- (BZ 160), 4'- (BZ 166), 2',3'- (BZ 173), 2',5'- (BZ 185), and 3',4'- (BZ 190). The presence of all three products containing one label (i.e., at positions 2'-ortho, 3'-meta, and 4' -para) in approximately equal proportions implies that these products were created (and consumed) without significant biases or directing effects. This suggests that the penta-chlorinated ring did not have a significant directing effect on the next chlorination event. The three products containing two

Figure 13 : Sample Chromatogram and Retention Time Table for BZ 116

BZ #	Predicted	Standard	Measured	Sample
	RT* (/min) +/- 0.15		RT* (/min) +/- 0.1	
116	21.33	SM**	21.35	21.33
142	23.56	A	23.55	23.58
160	25.28	L	25.28	25.33
166	25.82	K	25.81	25.89
173	27.64	I	27.64	27.66
181	27.06	H	27.06	
185	26.69	G	26.68	26.69
186	25.34			
190	29.47			29.56
192	28.00	J	28.03	

* RT - Retention Time in Minutes

** SM - Starting Material

*** = Mixture identification - see Table 6

labels contained these labels in positions that were orientated ortho and para to each other. This was expected since chlorine is known as an ortho / para directing substituent ⁴³⁻⁴⁵.

3.2.2 Tetrachlorobiphenyl Starting Materials : The BZ 61, BZ 62 and BZ 65 Mixtures

In the case of the three tetrachlorinated biphenyls chlorinated, BZ 61 (2,3,4,5-), BZ 62 (2,3,4,6), and BZ 65 (2,3,5,6), the number of possible products increased because it was possible (albeit not probable) to add a chlorine to the more highly chlorinated ring. The chromatograms of these mixtures were similar and they were also comparable to the chromatogram of the BZ 116 product mixture. For example, compare Figure 14, which depicts a typical chromatogram for the BZ 62 mixture, with Figure 13 which depicts that for the BZ 116 mixture. The topic of structure / retention time relationships implied by this comparison will be addressed in Section 3.4. Figure 14 also contains a retention time table for the BZ 62 mixture. Four products were unambiguously identified: BZ 88, BZ 109, BZ 144 and BZ 158. These identified products have their structural equivalents identified in the BZ 116 mixture. The two other peaks observed each had two possible identities. One of these peaks could be either BZ 115 (+4'-) ^k or BZ 116 (+5-); the other either BZ 131 (+2',3'-) or BZ 142 (+5,2'-). In both cases, one of the possibilities would involve addition of a label to the more highly chlorinated ring. If label addition occurred on only the originally unchlorinated phenyl ring, then all the products present in the BZ

^k (+4'-) notation indicates the location of labelled chlorine.

Figure 14 : Sample Chromatogram and Retention Time Table for BZ 62

BZ #	Predicted	Standard	Measured	Sample	
	RT* (/min) +/- 0.15		RT* (/min) +/- 0.1		
62	16.62	H	16.64	16.68	
88	19.17	C	19.19	19.19	
109	20.85	A	20.89	20.90	
115	21.35	L	21.41	21.38	**a
116	21.22	PMB	21.35		
131	23.52	B	23.53	23.53	**b
139	23.05	K	22.91		
144	22.59	D	22.61	22.60	
145	21.28	F	21.31		
142	23.50	A	23.55		
158	25.35	F	25.38	25.36	
161	23.88	D	23.88		
160	25.24	L	25.28		
166	25.80	K	25.81		

* RT - Retention Time in Minutes ** see text

*** = Mixture identification - see Table 6

62 mixture would mirror those present in the BZ 116 mixture.

The retention time tables for the BZ 61 and BZ 65 mixtures are presented in Table 8 and Table 9, respectively. In the case of BZ 61, the appropriate retention time differences were large enough to permit unambiguous identification of all products. No addition to the more highly chlorinated ring was observed. Again, all the observed products had structural equivalents observed in the BZ 116 mixture. In the BZ 65 mixture, two products could have had two possible identifications. As in the case of the BZ 62 mixture, if no chlorination occurred on the tetrachlorinated ring, then an analogous set of products to the BZ 116 and BZ 61 mixtures were obtained.

The similarity in product types for the tetrachlorinated and pentachlorinated starting materials suggested that further chlorination of the tetrachlorinated ring in BZ 61, BZ 62 or BZ 65 was unlikely using our method outlined in Section 2.2. Therefore, as a first approximation, it will be assumed that this was the case. However, the specific labelled products that could possibly be assigned other structures (or as mixtures) will be indicated (flagged) by lettered superscripts throughout this thesis. For example, the BZ 115 peak in the BZ 62 mixture will be flagged by the reference letter a; the BZ 131 peak in the same mixture will be flagged by the letter b; the BZ 117 peak in the BZ 65 mixture will be flagged by the letter c; and the BZ 163 peak in the same mixture will be flagged by the letter d.

Table 8 : BZ 61 Mix - Retention Times Table.

	Predicted		Measured	Sample
	RT* (/min)	Standard	RT* (/min)	RT* (/min)
BZ #	+/- 0.15	Mix ***	+/- 0.1	+/- 0.1
61	10.39	L	10.34	10.43
86	11.94	CLB-A	11.88	11.89
106	13.21			13.23
114	13.55	L	13.56	13.63
116	12.00	PMB		
129	15.17	CLB-C	15.19	15.14
137	14.74	CLB-C	14.66	
141	14.43	CLB-D	14.46	14.44
143	13.46	CLB-B	13.39	
142	13.59	A		
156	16.73	CLB-A	16.89	16.83
159	15.56	CLB-A	15.66	
160	14.91	L	14.89	
166	15.35	K		

Table 9 : BZ 65 Mix - Retention Times Table.

	Predicted		Measured	Sample
	RT* (/min)	Standard	RT* (/min)	RT* (/min)
BZ #	+/- 0.15	Mix ***	+/- 0.1	+/- 0.1
65	19.01	K	19.00	18.98
93	21.49	B	21.44	21.46
112	23.27	112S		23.24
117	23.80	H	23.78	23.81 **c
116	23.74	PMB	23.75	
134	25.89	J	25.85	25.81
147	25.28	F	25.21	
151	24.93	CLB-D	24.90	24.88
152	23.51	C	23.48	
142	26.06	A	26.00	
163	27.83			27.73 **d
165	26.29			
160	27.83	L		
166	28.40	K	28.36	

* RT - Retention Time in Minutes ** see text

*** = Mixture identification - see Table 6

3.2.3 Trichlorobiphenyl Starting Materials : The BZ 21, BZ 23, BZ 24, BZ 29, BZ 30, and BZ 38 Mixtures

Chlorination of the trichlorobiphenyl congeners: BZ 21 (2,3,4-), BZ 23(2,3,5-), BZ 24 (2,3,6-), BZ 29 (2,4,5-), BZ 30 (2,4,6-), and BZ 38 (3,4,5-), was not restricted to the unchlorinated ring. Furthermore, the trichlorinated ring appeared to play the role of a directing group. Reactivity of the trichlorobiphenyl congeners appeared greater as more multiple chlorinations were observed (ie., the addition of two and three chlorines). This resulted in a complex product mixture which increased the possibility of co-elution or poorly separated products. Fortunately, the HRGC separation technique employed permitted the separation of many, though not all, of these products. As an indication of this, consider Figure 15 which depicts a typical chromatogram and retention time table for the BZ 23 mixture. In this mixture, eight products each containing one or two labels have been identified, and seven of these were unambiguously identified based on retention times alone. The identity of the remaining product in this mixture was deduced, and details of this will be presented in Section 3.2.3.2 below.

Each of the trichlorobiphenyl mixtures will be discussed individually. Note that only products containing one and two labelled chlorines were investigated.

3.2.3.1 Analysis of the BZ 21 (2,3,4-) Mixture

In the BZ 21 mixture five peaks were identified: BZ 41 (+2'-) , BZ 60 (+4'-), BZ 87 (+2',5' -), BZ 82 (+2',3' -), and BZ 105 (+3',4'-). A retention time table listing

Figure 15 : Sample Chromatogram and Retention Times Table for BZ 23

BZ #	Predicted	Standard	Measured	Sample
	RT* (/min) +/- 0.15		RT* (/min) +/- 0.1	RT* (/min) +/- 0.1
23	13.71	B	13.69	
43	16.31	E	16.29	16.28
57	18.11	C	18.13	
63	18.54	F	18.58	18.56
61	18.67	L	18.71	
65	16.57	K	16.63	
83	20.90	B	20.91	20.89
90	20.21	I	20.21	
92	19.98	F	19.98	19.98
94	18.67	G	18.66	
86	21.14	CLB-A	21.16	
93	19.17	B	19.03	19.01
107	22.80	H	22.84	22.81
111	21.39	J	21.39	
106	22.97			
112	20.76	112S		
114	23.44	L	23.48	23.46
117	21.28	H	21.33	21.31 ***f
116	21.22	<SM>	21.35	

* RT - Retention Time in Minutes ** see text

*** = Mixture identification - see Table 6

all possible products ^l for the BZ 21 mixture is presented in Table 10. Only one of the observed peaks could not be unambiguously identified based solely on retention time. This peak was listed as BZ 87 (+2',5' -) and it was flagged by the reference letter e. Based only on retention time, this peak could also have been identified as BZ 116, BZ 115, or BZ 85, but the EI mass spectrum of this peak showed a significant [M-Cl]⁺ fragment. Since the mass spectra of BZ 116 and BZ 115 do not, these congeners can be ruled out. In the case of the other two possibilities, BZ 85 (+2',4') and BZ 87 (+2',5'), ortho/para directing arguments suggest the formation of BZ 87 (+2',5'). That is, the first labelled chlorine added would be expected to facilitate addition of the next labelled chlorine ortho- or para- to itself. In the case of BZ 85 (+2',4'), the second chlorine would be added meta to the first. The peak in question had a small satellite peak that also had significant [M-Cl]⁺ intensity. From the expected elution order and arguments just presented, this satellite was determined to be BZ 85, and the main peak BZ 87.

3.2.3.2 Analysis of the BZ 23 (2,3,5-) Mixture

Eight products were identified in the BZ 23 mixture: BZ 43 (+2'-), BZ 63(+4'-), BZ 93 (+6,2'), BZ 92 (+2',5' -), BZ 83 (+2',3'-), BZ 117 (+6,4'-), and BZ 107 (+3',4'-). A retention time table and sample chromatogram has been presented in Figure 15. Based on retention times, there was only one peak whose assignment was ambiguous. This peak was listed as BZ 117 (+6,4'-) and was flagged by the

^l with one or two additional chlorine(s)

Table 10 : BZ 21 Mix - Retention Times Table.

	Predicted		Measured	Sample
	RT* (/min)	Standard	RT* (/min)	RT* (/min)
BZ #	+/- 0.15	Mix ***	+/- 0.1	+/- 0.1
21	14.87	PMB	14.94	
41	17.59	J	17.59	17.63
55	19.41	E	19.44	
60	19.77	CLB-B	19.84	19.86
61	18.67	L	18.71	
62	16.62	H	16.64	
82	22.24	C	22.28	22.31
85	21.52	A	21.56	
87	21.36	I	21.38	21.45 ^{**e}
89	20.10	H	20.13	
86	21.14	CLB-A	21.16	
88	19.17	C	19.19	
105	24.14	K	24.16	24.21
108	22.79	G	22.79	
106	22.97			
109	20.85	A	20.89	
114	23.44	L	23.48	
115	21.35	L	21.41	
116	21.22	PMB	21.35	

* RT - Retention Time in Minutes ** see text

*** = Mixture identification - see Table 6

reference letter f. Based only on retention time, this peak could also have been BZ 116, BZ 111, or BZ 86. The EI mass spectrum of this peak did not, however, show significant $[\text{M}-\text{Cl}]^+$ intensity. The EI mass spectrum of BZ 86 did and this congener was ruled out. Furthermore, in order for this product to be BZ 116, two chlorines must have been added to the more highly chlorinated ring. The addition of the first of these chlorines would produce either BZ 61 or BZ 65, neither of which was observed. Furthermore, it has already been suggested that the formation of BZ 116 from either BZ 61 or BZ 65 was unlikely (see previous discussion on tetrachlorobiphenyl chlorinations). Therefore, by elimination, the product was either BZ 117 (+6,4'-) or BZ 111 (+3',5'). The addition of the two labels meta to each other was deemed less likely. Furthermore, there were other products in the BZ 23 mixture that were related to BZ 117, specifically BZ 114 (+4,4'-) and BZ 93 (+6, 2'-). As a result, this product was identified as BZ 117.

3.2.3.3 Analysis of the BZ 24 (2,3,6-) Mixture

In the BZ 24 mixture six peaks were unambiguously identified based on their retention times. These are BZ 45 (+2'-), BZ 59 (+3'-), BZ 64 (+4'), BZ 95 (+2',5'-), BZ 84 (+2',3'-), and BZ 110 (+3',4'-). A retention time table listing all possible products for the BZ 24 mixture is presented in Table 11

3.2.3.4 Analysis of the BZ 29 (2,4,5-) Mixture

In the BZ 29 mixture five peaks were identified: BZ 48 (+2'-) , BZ 74 (+4'-),

Table 11 : BZ 24 Mix - Retention Times Table.

	Predicted		Measured	Sample
	RT* (/min)	Standard	RT* (/min)	RT* (/min)
BZ #	+/- 0.15	Mix ***	+/- 0.1	+/- 0.1
24	12.87	A	12.84	
45	15.50			15.49
59	17.18			17.16
64	17.62	A	17.65	17.66
62	16.62	H	16.64	
65	16.57	K	16.63	
84	19.99	G	20.01	20.01
91	19.37	D	19.38	
95	19.10	K	19.11	19.14
96	17.80	B	17.8	
86	21.14	CLB-A	21.16	
93	19.17	B	19.03	
110	21.80	K	21.83	21.83
113	20.36	J	20.36	
106	22.97			
112	20.76	112S		
114	23.44	L	23.48	
117	21.28	H	21.33	
116	21.22	PMB	21.35	

Table 12 : BZ 29 Mix - Retention Times Table.

	Predicted		Measured	Sample
	RT* (/min)	Standard	RT* (/min)	RT* (/min)
BZ #	+/- 0.15	Mix ***	+/- 0.1	+/- 0.1
29	13.87	PMB	13.95	
48	16.51	G	16.49	16.51
67	18.30	E	18.34	
74	18.71	H	18.76	18.76 **g
61	18.67	L	18.71	
62	16.62	H	16.64	
97	21.12	D	21.14	21.14 **h
99	20.42			
101	20.22	L	20.26	20.26
102	18.99	A	18.99	
86	21.14	CLB-A	21.16	
88	19.17	C	19.19	
118	23.01	L	23.06	23.06
120	21.62	B	21.63	
106	22.97			
109	20.85	A	20.89	
114	23.44	L	23.48	
115	21.35	L	21.41	
116	21.22	PMB	21.35	

* RT - Retention Time in Minutes

** see text

*** = Mixture identification - see Table 6

BZ 101 (+2',5'-), BZ 97 (+2',3'-), and BZ 118 (+3',4'-). A retention time table listing all possible products for the BZ 29 mixture is presented in Table 12. Two of these products require further discussion. These are the peaks listed as BZ 74 (flagged by letter g) and BZ 97 (flagged by letter h). In the first case, the peak in question could have been BZ 74 (+4') or BZ 61 (+3) based on the listed retention times. But in order for this peak to be BZ 61, chlorine would have had to be added to the trichlorinated ring between two chlorines. This is less likely than the addition to the 4' position. In the second case, the peak in question was either BZ 97 (+2', 3'-) or BZ 86 (+2',3'-). Ortho/para directing arguments, and a similarity to the tetrachlorobiphenyl product mixtures, supported our tentative assignment of BZ 97.

3.2.3.5 *Analysis of the BZ 30 (2,4,6-) Mixture*

In the BZ 30 mixture seven peaks were identified: BZ 75 (+4'-), BZ 103 (+2',5'-), BZ 98 (+2',3' -), BZ 88 (+3,2' -), BZ 119 (+3',4'-), BZ 109 (+3,3' -), and BZ 115 (+3,4'-). A retention time table listing all possible products for the BZ 30 mixture is presented in Table 13. This mixture contained 4 flagged products, the peaks listed as BZ 75 (flagged by letter l), BZ 88 (flagged by letter j), BZ 119 and BZ 109 (both flagged by letter k), and BZ 115 (flagged by letter l). The product labelled BZ 75 could also have been BZ 62 and thus this identification is tenuous. The product labelled BZ 88 could also have been identified as BZ 121; however, the EI mass spectrum associated with the product peak showed significant $[\text{M}-\text{Cl}]^+$. Significant $[\text{M}-\text{Cl}]^+$ intensity is characteristic of BZ 88 not BZ 121, which confirmed

Table 13 : BZ 30 Mix - Retention Times Table.

	Predicted		Measured	Sample	
	RT* (/min)	Standard	RT* (/min)	RT* (/min)	
BZ #	+/- 0.15	Mix ***	+/- 0.1	+/- 0.1	
30	14.14				
50	16.87				
69	18.49	D	18.45		
75	18.92	F	18.96	18.98	**i
62	19.06	H			
98	21.42	J		21.43	
100	20.76	D	20.78	20.79	
103	20.54	CLB-B		20.58	
104	19.29				
88	21.65	C	21.63	21.69	**j
119	23.21			23.24	**k
121	21.75	CLB-A	21.66		
109	23.36	A	23.33	23.36	**k
115	23.87	L		23.99	**l
116	23.74	PMB			

Table 14 : BZ 38 Mix - Retention Times Table.

	Predicted		Measured	Sample	
	RT* (/min)	Standard	RT* (/min)	RT* (/min)	
BZ #	+/- 0.15	Mix ***	+/- 0.1	+/- 0.1	
38	9.06				
76	10.54	I	10.46	10.54	
78	11.77				
81	12.04	G	12.11	12.16	
61	10.39	L	10.31		
122	13.65	C	13.66	13.74	
123	13.16				
124	12.99	E	13.01	13.09	**m
125	12.02	E	11.89		
86	11.94	CLB-A	11.88	11.94	**n
126	15.20				
127	14.13	E	14.21		
106	13.21			13.21	**m
114	13.55	L	13.56		
116	12.00	PMB			

* RT - Retention Time in Minutes ** see text

*** = Mixture identification - see Table 6

the BZ 88 identification. The products labelled BZ 119 and BZ 109 were identified based on their relative retention order. The presence of two peaks implies both congeners were present, and these likely followed the indicated elution order. The product labelled BZ 115 could also have been BZ 116; however, the addition of two chlorines to the tri-chlorinated ring is unlikely (see discussion on flag f in section 3.2.3.1). Hence, this peak was identified as BZ 115.

3.2.3.6 Analysis of the BZ 38 (3,4,5-) Mixture

In the BZ 38 mixture six peaks were identified: BZ 76 (+2'-), BZ 81 (+4'-), BZ 86 (+2,2'), BZ 124 (+2',5' -), BZ 106 (+2,3' -), and BZ 122 (+3',4'-). A retention time table listing all possible products for the BZ 38 mixture is presented in Table 14. Two of the identified congeners are flagged: BZ 124 (flagged by letter m) and BZ 86 (flagged by letter n). The peak that was identified as BZ 124 could also have been BZ 123 or BZ 106, but ortho/para directing arguments favoured the formation of BZ 124 (+2',5') over BZ 123 (+2',4'). This peak was followed closely by a smaller peak which was identified as BZ 106. The peak identified as BZ 86 could also have been BZ 125; however, the EI mass spectrum associated with this peak showed significant $[\text{M}-\text{Cl}]^+$ intensity, which confirmed the BZ 86 identification.

3.4 Structure-Retention Time Relationships

The similarity of the chromatographic "fingerprints" for the tetrachlorobiphenyl and pentachlorobiphenyl mixtures resulted from the presence

of analogous product types. These sets of analogous products are related by the positions chlorinated with ^{37}Cl (i.e., at positions 2'-, 3'-, 4'-, 2',3'-, 2',5'-, and 3',4'-). The relationship between structure and retention time is evident from an analysis of the published relative retention times⁹⁹ of these compounds. To demonstrate this, the published relative retention times^{m,99} (RRTs) were used to calculate the expected differences in RRT (dRRT) between the individual starting congeners and each of the six similar product types observed. This information is presented in Table 15. The first column in this table different chlorination pattern on the less highly chlorinated ring. The second column indicates (a) the chlorination pattern (in the second row) of the PCB reagent and (b) the BZ numbers of the PCB products whose additional chlorines are in positions identified in the first column. The third column, beginning with the heading "RRT," indicates the relative retention time of the appropriate PCB starting material (in the second row) as well as the difference in RRT between this starting material and the PCB products identified in the second column. The remaining columns are equivalents of columns 2 and 3 with different PCB reagents. In the bottom right-hand corner of Table 15 is a listing of average differences in RRT's and appropriate standard deviations for additional chlorination.

Notice that the changes in RRTs were very similar for additional chlorination of different PCB reagents. For example, consider the effect of adding a chlorine to the 3'- position in the set of ten PCB reagents. This caused an average increase

^m relative to octachloronaphthalene (OCN)

Table 15 : Comparison of Literature * RRT's for Selected Chlorination Types

	Initial	RRT	Initial	RRT	Initial	RRT	Initial	RRT	Initial	RRT	Initial	RRT
	2,3,4 -	0.4135	2,3,5	0.377	2,3,6	0.3508	2,4,5	0.382	2,4,6	0.3165	3,4,5	0.4593
	BZ #	RRT (ini)	BZ #	RRT (ini)	BZ #	RRT (ini)	BZ #	RRT (ini)	BZ #	RRT (ini)	BZ #	RRT (ini)
start	21	0.000	23	0.000	24	0.000	29	0.000	30	0.000	38	0.000
2'-	41	0.086	43	0.082	45	0.083	48	0.083	50	0.084	76	0.081
3'-	55	0.143	57	0.138	59	0.135	67	0.139	69	0.135	78	0.143
4'-	60	0.154	63	0.152	64	0.149	74	0.152	75	0.148	81	0.156
2',3'	82	0.232	83	0.226	84	0.224	97	0.228	98	0.225	122	0.228
2',5'-	87	0.204	92	0.197	95	0.196	101	0.200	103	0.198	124	0.199
3',4'-	105	0.291	107	0.286	110	0.281	118	0.287	119	0.280	126	0.292

Initial	RRT	Initial	RRT	Initial	RRT	Initial	RRT	
2,3,4,5	0.5331	2,3,4,6	0.4685	2,3,5,6	0.4671	2,3,4,5,6	0.6132	
BZ #	RRT (ini)	BZ #	RRT (ini)	BZ #	RRT (ini)	BZ #	RRT (ini)	
start	61	0.000	62	0.000	65	0.000	116	0.000
2'-	86	0.077	88	0.080	93	0.077	142	0.072
3'-	106	0.135	109	0.133	112	0.132	160	0.126
4'-	114	0.150	115	0.149	117	0.148	166	0.144
2',3'	129	0.217	131	0.217	134	0.212	173	0.202
2',5'-	141	0.187	144	0.188	151	0.183	185	0.172
3',4'-	156	0.277	158	0.274	163	0.273	190	0.261

Average Values

	Ave RRT	STD
start	NA	NA
2'-	0.080	0.004
3'-	0.136	0.005
4'-	0.150	0.003
2',3'	0.221	0.009
2',5'-	0.192	0.009
3',4'-	0.280	0.009

* Mullen et al., Environ. Sci. Technol., 18, 486-476 (1980)

in RRT of 0.136 with a standard deviation of 0.005. As a graphical demonstration of this, the similarity of the relative retention times among the chlorination products of BZ 116 and BZ 65 is self-evident (Figure 16).

3.5 Summary of ^{37}Cl -Labelled Products Identified

In this investigation, 48 ^{37}Cl -labelled products were unambiguously identified by means of retention time. The identities of an additional nine products were deduced based on EI mass spectra as well as chemical arguments. Two other products were each identified as having two possible structures, one of which was more likely. In all, 59 labelled congeners, each containing one or two labels were produced and identified. These products are sorted by their starting materials and are presented in Figure 17.

Chromatograms of BZ 116 ³⁷Cl Mix and BZ 65 ³⁷Cl Mix

93

Figure 16a

Figure 16b

Figure 17a : List of Labelled Product Mixtures

Initial Congener	³⁷ Cl Labelled Products
BZ 21	BZ 41	BZ 60	*e BZ 87	BZ 82	BZ 105
BZ 23	BZ 43	BZ 63	BZ 93	BZ 83	*f BZ 117
BZ 24	BZ 45	BZ 59	BZ 64	BZ 95	BZ 84
BZ 29	BZ 48	*g BZ 74	BZ 101	*h BZ 97	BZ 118
BZ 30	*i BZ 75	BZ 103	BZ 98	*j BZ 88	*k BZ 119
BZ 38	BZ 76	BZ 81	*n BZ 86	*m BZ 124	*m BZ 106
					BZ 122

Figure 17b : List of Labelled Product Mixtures

Initial Congener	³⁷ Cl Labelled Products				
BZ 61
BZ 62
BZ 65
BZ 116

* see accompanying text for identification explanation

CHAPTER 4 : EI and ECNI Dechlorinations - ^{37}Cl Label Loss Results

4.1 Introduction

In this chapter, we describe our experimental findings on the regioselective nature of EI and ECNI induced dechlorinations. The principal results presented relate only to the proportion of a particular reaction channel associated with the loss of a specific chlorine or chlorines - in other words, the percentage of label lost (or retained) relative to other chlorines. These data do not indicate the intensity of a given ion type (e.g. $[\text{M}-\text{Cl}]^+$) relative to other ion types observed in the particular mass spectrum (e.g., $[\text{M}]^+$ or $[\text{M}-2\text{Cl}]^+$) unless the two ion types have overlapping isotopic patterns (i.e., $[\text{M}+\text{H}-\text{Cl}]^+$ and $[\text{M}-\text{Cl}]^+$). As described in Chapter 2, all results were extracted from mass spectra collected after HRGC separation of ^{37}Cl -labelled mixtures.

The EI mass spectra were collected on both a Varian Saturn ion trap and a VG ZAB mass spectrometer (see Table 7 of Chapter 2 for instrument parameters). Results for the loss of one or two chlorines after EI ionization of the isotopically labelled PCB congeners identified in Chapter 3 are presented in Section 4.2 below.

The ECNI mass spectra were collected on a VG ZAB mass spectrometer. Spectra were obtained with the variation of two instrument parameters: source pressure and ventilation rate. (See Table 7 of Chapter 2 for details concerning instrument parameters.) Investigations were limited to reactions involving the loss of one chlorine. From this, data relating to three distinct reaction channel types were obtained. These reaction channels were classified by the ion fragment

produced, specifically the $[M+H-X]^+$, $[M+O-X]^+$, and $[M-X]^+$ reaction channels (where X refers to either labelled or unlabelled chlorine). As demonstrated in Figure 18, the $[M+H-X]^+$ ion is distributed over a similar m/z ratio range as the $[M-X]^+$ ion, and hence information on both these fragments is obtained simultaneously. Information on the regioselective loss of chlorine in the formation of each of the three fragment ions $[M+H-X]^+$, $[M+O-X]^+$, and $[M-X]^+$ will be discussed below.

As mentioned above, all mass spectra were those of labelled products resolved chromatographically. Typically, five to seven full scan mass spectraⁿ were recorded per GC peak. Three to five of the most intense of these mass spectra were then averaged to yield a representative spectrum. Next, the percentages of label loss from relevant reaction channels were calculated as described in Section 2.4.3. This produced the results for an individual measurement. Two to four GC runs were typically performed on each mixture for each of the experiment types listed in Table 7, with some of these repeats occurring months apart. The precision of a particular measurement is a function of the signal-to-noise ratio in the representative spectrum, and as such, was dependent on the quantity of product present, the relative intensity of the particular ion cluster within the spectrum and the noise. The multiple regression analysis performed provided a measurement, via the R² value, of the quality of the fit between the simulated and observed ion pattern. Only fits with an R² value greater than 0.990 were considered reliable enough for further analyses. Even with this

ⁿ Ion trap, 50 m/z to 550 m/z ; VG ZAB, typically 200 m/z to 520 m/z

Figure 18 : Sections of Mass Spectra from BZ 142, BZ 160 and BZ 166 with the m/z Range for the Molecular Ion $[M]^-$, and the Three Fragment Ions : $[M+O-X]^-$, $[M+H-X]^{\pm}$, and $[M-X]^-$ - Indicated.

screening process, some relatively large variation in the measured percentage of label lost was observed. This variation was experiment dependent, and as such will be addressed in the appropriate sections that follow.

4.2 Electron Impact Mass Spectra of Isotopically Labelled PCBs

4.2.1 Percentage of Label Lost in the Formation of $[\text{M-X}]^+$

In the EI mass spectrum, those ions that correspond to the fragment which had lost one chlorine will be referred to here as the first dechlorination cluster. The relative abundances of these first-dechlorination-cluster ions to other ions in the mass spectrum is congener dependent. It has already been noted that this relative abundance is greater^o in congeners that have either three ortho chlorines or two ortho chlorines with at least one of these present on each aromatic ring. For the purpose of this discussion, these congener types will be referred to as adjacent-ortho (AO) congeners. The higher intensity of the $[\text{M-X}]^+$ ions in the AO congeners means that the signal-to-noise ratio of this cluster is higher, and thus subsequent calculations are more reliable. In this investigation, 59 ^{37}Cl -labelled products were produced and identified. Of these, 30 congeners have the AO characteristic. Our observations were that only a few of the congeners that did not have the AO characteristic, had a sufficiently intense first dechlorination cluster to enable reliable determination of label loss for $[\text{M-X}]^+$. In contrast, 27 of the 30 AO congeners

^o

~10 % to 40 % of the most abundant ion in AO congeners, as compared to ~0% to 20 % of the most abundant ion in non-AO congeners.

produced reliable results (R^2 value greater than 0.990). A previous investigation⁵⁴ implied that unique reaction channels could be operative for the AO congeners. Therefore, this set of 27 AO congeners will be addressed exclusively.

There are four possible ion types corresponding to the loss of one chlorine^p, $[M-Cl]^+$, $[M-^{37}Cl]^+$, $[M-HCl]^+$, and $[M-H^{37}Cl]^+$. These ion types were deconvoluted from one another using the multiple regression analysis technique discussed in Section 2.4.3.1. In the AO congeners examined, the contributions from the $[M-HCl]^+$ and the $[M-H^{37}Cl]^+$ ions were either minor or not detected. The normalized percentages of ^{37}Cl -label lost in the $[M-X]^+$ reaction channel for the 27 AO congeners are presented in Table 16. This table is divided into nine columns. The first column identifies the starting material for a particular labelled congener. The second identifies the labelled product congener. The third column lists the average percent label loss of all the reliable values ($R^2 > 0.990$) for a particular congener. This average is taken from all reliable measurements irregardless of which instrument (VG ZAB or Varian Saturn ion trap) was used. The fourth column lists the standard deviation of the means. The next two columns list the reliable measurements obtained using the VG ZAB, while the last three columns list those using the Varian Saturn ion trap.

Of the experiments performed in this thesis work, the determination of label loss in forming the $[M-X]^+$ ion via EI ionization was considered the most

^p

Note : "Cl" indicates loss of unlabelled chlorine ; " ^{37}Cl " indicates loss of labelled chlorine

Table 16 : Percent Label Lost in Forming the [M-X]⁺ Fragment Ion

MIXTURE	BZ#	% Label	Standard	% Label		% Label		
		Average	Deviation	ZAB**	Measurements	Saturn***	Measurements	
21	41	47%	0.5	47%		46%		
21	82	58%	1.5	56%		59%		
21	87 *e	62%	3.0	65%		59%		
23	43	32%	0.0	32%		32%		
23	83	47%	4.1	46%	52%	42%		
23	92	50%	2.2	53%	49%	48%		
23	93	70%	1.7	69%	72%	68%		
24	45	46%	0.5	46%	46%	45%		
24	84	58%	0.0	58%		58%		
24	95	63%	3.7	67%	64%	58%		
29	48	45%	2.0	47%		43%		
29	97 *h	57%	4.0	55%	63%	54%		
29	101	59%	2.5	61%		56%		
30	88 *i	53%	0.5			53%	52%	
30	103	74%	3.0			77%	71%	
38	86 *m	99%	1.3	100%	100%	100%	97%	98%
61	86	36%	2.1	39%	36%	33%	36%	34%
61	129	52%	0.0	52%		52%		
61	141	53%	0.0			53%		
62	88	48%	0.8	49%		47%	48%	
62	131 *b	68%	0.5	68%		67%		
62	144	69%	2.1	71%		69%	66%	
65	93	35%	2.8	39%	35%	35%	31%	
65	134 *d	51%	0.0	51%				
65	151	56%	0.0	56%		56%		
116	142	34%	4.1	40%		32%	29%	36%
116	185	54%	0.0			54%		

* See Chapter 3 for Identification

** Data collected on VG ZAB MS - see Table 7 for experimental details

*** Data collected on Varian Saturn ion Trap MS - see Table 7 for experimental details

reproducible. Therefore, the maximum standard deviation of 4.1 observed for both labelled congeners BZ 83 and BZ 142 was adopted as a benchmark against which the precision of other label loss determinations were judged.

4.2.2 Percentage of Label Lost in the Formation of $[M-2X]^+\bullet$

In the EI mass spectrum of PCBs, the abundance of the ion cluster corresponding to the loss of two chlorines (the second dechlorination cluster) is relatively constant and intense. The abundance of the most intense peak in this second dechlorination cluster is typically around 40% to 70% of that of the molecular ion ($[M]^+\bullet$) base peak. The acquisition of high signal-to-noise data increases the reliability of the subsequent multiple regression analysis. As a result, reliable label-loss values were obtained for the second dechlorination reaction channels in all 59 labelled congeners produced.

Because very little contribution from any reaction channels involving hydrogen was observed, results from only the $[M-2X]^+\bullet$ reaction channel will be reported. For this reaction channel, there are three possible types of losses $[M-2(^{37}\text{Cl})]^+\bullet$, $[M-^{37}\text{ClCl}]^+\bullet$, and $[M-2(\text{Cl})]^+\bullet$. These possible losses are represented in Table 17 as $M-2(^{37}\text{Cl})\equiv[M-2(^{37}\text{Cl})]^+\bullet$, $M-\text{Cl}^{37}\text{Cl}\equiv[M-^{37}\text{ClCl}]^+\bullet$, and $M-2\text{Cl}\equiv[M-2(\text{Cl})]^+\bullet$. Table 17 is divided into ten columns. The first column lists the starting materials from which particular labelled congeners were produced, and the second identifies the particular labelled congeners. The third and fourth columns list the average $[M-2(^{37}\text{Cl})]^+\bullet$ percent contributions and the corresponding $\pm$ values for a

Table 17a : Percent Label Lost in Forming [M-2X]⁺

MIX	BZ #	M-2(37Cl)	+/- *	M-Cl37Cl	+/- *	M-2Cl	+/- *	N***	Fraction****
21	41	0%	NA**	68%	2.3	32%	2.3	2	0.34
21	60	0%	NA**	59%	1.6	41%	1.6	2	0.30
21	82	14%	4.3	67%	8.0	18%	3.8	3	0.48
21	87*e	17%	2.5	62%	5.5	21%	4.1	3	0.48
21	105	13%	4.8	62%	6.6	24%	2.6	3	0.45
23	43	0%	NA**	67%	2.3	33%	2.3	2	0.34
23	63	0%	NA**	61%	2.3	39%	2.3	2	0.31
23	83	15%	0.4	61%	2.0	23%	2.2	3	0.46
23	92	15%	2.7	61%	4.0	24%	2.3	4	0.45
23	93	21%	2.4	61%	5.6	18%	4.6	6	0.52
23	107	15%	1.0	59%	2.7	26%	1.8	3	0.45
23	114	15%	1.2	62%	3.2	23%	2.0	3	0.46
23	117*f	19%	3.4	63%	3.8	17%	1.3	4	0.51
24	45	0%	NA**	66%	1.7	34%	1.7	3	0.33
24	59	0%	NA**	61%	3.5	39%	3.5	2	0.30
24	64	0%	NA**	60%	4.5	40%	4.5	3	0.30
24	84	15%	3.2	64%	4.4	21%	1.4	5	0.47
24	110	12%	3.7	63%	5.4	25%	3.6	4	0.44
29	48	0%	NA**	67%	0.5	33%	0.5	2	0.34
29	74*g	0%	NA**	64%	4.0	36%	4.0	3	0.32
29	97*h	16%	4.6	66%	5.8	18%	1.7	4	0.49
29	101	16%	1.2	64%	3.2	20%	4.0	3	0.48
29	118	15%	1.8	61%	3.9	24%	2.8	4	0.45
30	75*i	0%	NA**	59%	1.7	41%	1.7	3	0.30
30	88*j	14%	1.8	63%	0.1	23%	1.9	2	0.45
30	103	19%	1.4	67%	3.3	14%	2.4	3	0.52
30	109*k	5%	5.7	74%	8.6	21%	2.9	3	0.42
30	115*l	12%	0.9	64%	1.7	24%	2.6	2	0.44
30	119*k	17%	1.5	62%	1.3	21%	1.6	3	0.48
38	76	0%	NA**	68%	2.8	32%	2.8	3	0.34
38	81	0%	NA**	66%	NA**	34%	NA**	1	0.33
38	86*m	32%	2.4	60%	2.5	8%	2.0	5	0.62
38	106*n	16%	1.3	66%	4.6	18%	3.4	2	0.49
38	122	23%	1.7	61%	4.7	16%	4.2	4	0.54
38	124*n	19%	0.8	62%	1.8	20%	2.1	4	0.49

* 95% Confidence Limit Level

** Confidence Limit Not Determined

*** N = Number of Measurements

****Fraction calculated from formula in Figure 11

Table 17b : Percent Label Lost in Forming [M-2X]⁺

MIX	BZ #	M-2(37Cl)	+/- *	M-Cl37Cl	+/- *	M-2Cl	+/- *	N***	Fraction****
61	86	0%	NA**	62%	4.1	38%	4.1	5	0.31
61	106	0%	NA**	57%	3.1	43%	3.1	5	0.29
61	114	0%	NA**	58%	2.1	42%	2.1	5	0.29
61	129	15%	1.1	61%	1.3	24%	0.2	2	0.46
61	141	13%	3.7	68%	8.2	19%	5.0	4	0.47
61	156	11%	6.2	64%	8.3	25%	2.2	4	0.43
62	88	0%	NA**	63%	6.5	37%	6.5	3	0.32
62	109	0%	NA**	55%	5.3	45%	5.3	4	0.27
62	115*a	0%	NA**	58%	4.4	42%	4.4	4	0.29
62	131*b	18%	1.4	60%	0.7	22%	0.7	2	0.48
62	144	16%	2.4	64%	4.0	20%	2.2	5	0.48
62	158	10%	0.5	66%	1.3	25%	1.8	2	0.43
65	93	0%	NA*	60%	3.8	40%	3.8	4	0.30
65	112	0%	NA**	53%	5.1	47%	5.1	4	0.26
65	117*c	0%	NA**	52%	4.9	48%	4.9	4	0.26
65	134*d	10%	7.3	68%	10.1	22%	3.1	3	0.44
65	151	15%	3.2	64%	5.3	22%	2.1	2	0.47
65	163	8%	3.6	64%	4.6	28%	0.9	2	0.40
116	142	0%	NA**	58%	5.3	42%	5.3	4	0.29
116	160	0%	NA**	53%	1.9	47%	1.9	4	0.27
116	166	0%	NA**	50%	4.0	50%	4.0	4	0.25
116	173	15%	NA**	56%	NA**	29%	NA**	1	0.43
116	185	12%	2.4	63%	6.6	25%	4.2	3	0.43
116	190	7%	6.8	64%	16.8	29%	9.9	2	0.39

* 95% Confidence Limit Level

** Confidence Limit Not Determined

*** N = Number of Measurements

****Fraction calculated from formula in Figure 11

95% confidence limit, based on the standard deviation and the number of values averaged. The fifth and sixth columns list the average $[\text{M}-\text{Cl}^{37}\text{Cl}]^+ \bullet$ percent contributions and corresponding 95% confidence intervals while the seventh and eighth columns list the average $[\text{M}-2\text{Cl}]^+ \bullet$ percent contributions and corresponding 95% confidence intervals. The ninth column lists the number of values averaged to produce the reported values. The tenth column lists the fraction of label lost based on the values in the third, fifth, and seventh columns as per the equation presented in Figure 12. Again, the average was taken from all reliable measurements regardless of which instrument (VG ZAB or Varian Saturn ion trap) they were collected on.

4.3 Electron Capture Mass Spectra of Isotopically Labelled PCBs

In the ECNI mass spectrum of PCBs, three different ion types are formed by the loss of one chlorine. These ions are $[\text{M}-\text{X}]^-$, $[\text{M}+\text{H}-\text{X}]^- \bullet$, and $[\text{M}+\text{O}-\text{X}]^-$. The fraction of label lost in the formation of each of these fragment ions was determined using the method outlined in Section 2.4.3.2.

4.3.1 Percentage of Label Lost in the Formation of $[\text{M}-\text{X}]^-$ and $[\text{M}+\text{H}-\text{X}]^- \bullet$

The information pertaining to the loss of labelled chlorine for either the $[\text{M}-\text{X}]^-$ or $[\text{M}+\text{H}-\text{X}]^- \bullet$ ions can be subdivided into two components: A) the percentage of label loss and B) the dependency of this value on pressure and ventilation rate. If the percentage loss does not change significantly with either pressure or ventilation rate, an evaluation of the data is simplified. At first glance it appeared

that many values did not change significantly. To quantify this observation, all the reliable values, as judged by an R^2 value greater than 0.990, were averaged together irregardless of the pressure or ventilation rate at which they were obtained. The standard deviation for each of these averaged values was then also determined and used to gauge the significance of the change. Using this approach, data which was affected significantly by changes in either pressure or ventilation rate could be identified by a relatively high standard deviation value. Since the maximum standard deviation observed for the $[M-Cl]^+$ reaction channel in EI/MS was 4.1, a measurement associated with the loss of a single chlorine in ECNI/MS was considered to have a high standard deviation only if this value was greater than 5.

The average values for percent label loss for both the $[M-Cl]^+$ and $[M+H-Cl]^+$ channels are presented in Table 18. Each page of Table 18 is divided vertically into two halves (sets). Each set describes the results for one series of labelled congeners produced from one starting material. Each set is divided into two columns, the first showing the structure of the particular labelled products, and the second containing two bar graphs per labelled congener. The top bar graph is labelled " $M+H-^{37}Cl$ ", while the bottom bar graph is labelled " $M-^{37}Cl$ ". These indicate the percent loss of ^{37}Cl -labelled chlorine. In each bar graph, a black band is used to visually indicate the percentage of label loss in the particular reaction channel. In addition, a number is placed to the immediate right of the bar graph indicating the percent label loss in the particular channel. To the right of the titles above the bar

Table 18a - Percent Label Lost in Forming $[M+H-X]^+$ and $[M-X]^+$

BZ 21 Set		BZ 23 Set
BZ 41	$M+H-^{37}Cl$ (0#0) ND** $M-^{37}Cl$ (0#0) ND**	BZ 43	$M+H-^{37}Cl$ (0#0) ND** $M-^{37}Cl$ (0#0) ND**
BZ 60	$M+H-^{37}Cl$ (7#3) 95 $M-^{37}Cl$ (1#3) 26	BZ 63	$M+H-^{37}Cl$ (32#2) 84 $M-^{37}Cl$ (15#2) 27
BZ 87 *e	$M+H-^{37}Cl$ (2#3) 54 $M-^{37}Cl$ (1#3) 28	BZ 93	$M+H-^{37}Cl$ (0#0) ND** $M-^{37}Cl$ (0#0) ND**
BZ 82	$M+H-^{37}Cl$ (0#1) 55 $M-^{37}Cl$ (0#1) 45	BZ 92	$M+H-^{37}Cl$ (5#5) 39 $M-^{37}Cl$ (5#5) 64
BZ 105	$M+H-^{37}Cl$ (2#3) 15 $M-^{37}Cl$ (2#3) 11	BZ 83	$M+H-^{37}Cl$ (0#1) 58 $M-^{37}Cl$ (0#1) 46
		BZ 117 *f	$M+H-^{37}Cl$ (15#5) 74 $M-^{37}Cl$ (3#5) 53
BZ 114	$M+H-^{37}Cl$ (5#4) 22 $M-^{37}Cl$ (2#4) 32	BZ 107	$M+H-^{37}Cl$ (2#4) 14 $M-^{37}Cl$ (2#4) 13

Legend : $M+H-^{37}Cl$ (10#3) 20 $M-^{37}Cl$ (10#3) 8

(Standard deviation#number averaged)

% Label loss =

* see Chapter 3 for Identification

** ND = Not Detected

Table 18b - Percent Label Lost in Forming $[M+H-X]^+$ and $[M-X]^+$

BZ 24 Set		BZ 29 Set
BZ 45	$M+H-^{37}\text{Cl}$ (0#0) ND** $M-^{37}\text{Cl}$ (0#0) ND**	BZ 48	$M+H-^{37}\text{Cl}$ (0#0) ND** $M-^{37}\text{Cl}$ (0#0) ND**
BZ 59	$M+H-^{37}\text{Cl}$ (0#0) ND** $M-^{37}\text{Cl}$ (0#0) ND**	BZ 74	$M+H-^{37}\text{Cl}$ (2#5) 98 $M-^{37}\text{Cl}$ (3#5) 74
BZ 64	$M+H-^{37}\text{Cl}$ (2#3) 99 $M-^{37}\text{Cl}$ (2#3) 58	BZ 101	$M+H-^{37}\text{Cl}$ (18#5) 53 $M-^{37}\text{Cl}$ (3#5) 79
BZ 95	$M+H-^{37}\text{Cl}$ (8#5) 66 $M-^{37}\text{Cl}$ (5#5) 4	BZ 97	$M+H-^{37}\text{Cl}$ (10#2) 85 $M-^{37}\text{Cl}$ (1#2) 73
BZ 84	$M+H-^{37}\text{Cl}$ (0#0) ND** $M-^{37}\text{Cl}$ (0#0) ND**	BZ 118	$M+H-^{37}\text{Cl}$ (5#3) 13 $M-^{37}\text{Cl}$ (4#3) 16
BZ 110	$M+H-^{37}\text{Cl}$ (0#1) 46 $M-^{37}\text{Cl}$ (0#1) 20		

Legend : $M+H-^{37}\text{Cl}$ (10#3) 20 $M-^{37}\text{Cl}$ (10#3) 8

(Standard deviation#number averaged)

% Label loss $\equiv$

* see Chapter 3 for Identification

** ND = Not Detected

Table 18c - Percent Label Lost in Forming $[M+H-X]^+$ and $[M-X]^+$

BZ 30 Set		BZ 38 Set
BZ 75 *i	$M+H-^{37}Cl$ (0#2) 100 $M-^{37}Cl$ (1#3) 14	BZ 76	$M+H-^{37}Cl$ (0#1) 98 $M-^{37}Cl$ (0#1) 62
BZ 103	$M+H-^{37}Cl$ (9#4) 66 $M-^{37}Cl$ (3#4) 74	BZ 81	$M+H-^{37}Cl$ (0#1) 100 $M-^{37}Cl$ (0#1) 58
BZ 98	$M+H-^{37}Cl$ (0#0) ND** $M-^{37}Cl$ (0#0) ND**	BZ 86 *m	$M+H-^{37}Cl$ (1#5) 100 $M-^{37}Cl$ (1#5) 58
BZ 88 *j	$M+H-^{37}Cl$ (10#3) 89 $M-^{37}Cl$ (5#3) 24	BZ 124 *n	$M+H-^{37}Cl$ (4#4) 93 $M-^{37}Cl$ (4#4) 77
BZ 119 *k	$M+H-^{37}Cl$ (0#0) ND** $M-^{37}Cl$ (0#0) ND**	BZ 106 *n	$M+H-^{37}Cl$ (1#2) 93 $M-^{37}Cl$ (3#2) 87
BZ 109 *k	$M+H-^{37}Cl$ (23#2) 78 $M-^{37}Cl$ (2#2) 31	BZ 122	$M+H-^{37}Cl$ (2#4) 99 $M-^{37}Cl$ (5#4) 73
BZ 115 *l	$M+H-^{37}Cl$ (12#4) 51 $M-^{37}Cl$ (6#4) 54		

Legend : $M+H-^{37}Cl$ (10#3) (Standard deviation#number averaged)
20
 $M-^{37}Cl$ (10#3)
8
 % Label loss =
 * see Chapter 3 for Identification
 ** ND = Not Detected

Table 18d - Percent Label Lost in Forming $[M+H-X]^+$ and $[M-X]^+$

BZ 61 Set		BZ 62 Set
BZ 86	M+H- ³⁷ Cl (14#8) 85 M- ³⁷ Cl (3#8) 24	BZ 88	M+H- ³⁷ Cl (12#4) 90 M- ³⁷ Cl (2#4) 2
BZ 106	M+H- ³⁷ Cl (3#8) 13 M- ³⁷ Cl (6#8) 25	BZ 109	M+H- ³⁷ Cl (19#6) 64 M- ³⁷ Cl (5#6) 20
BZ 114	M+H- ³⁷ Cl (3#8) 16 M- ³⁷ Cl (5#8) 16	BZ 115	^a M+H- ³⁷ Cl (13#6) 67 M- ³⁷ Cl (1#6) 13
BZ 141	M+H- ³⁷ Cl (7#3) 34 M- ³⁷ Cl (5#3) 30	BZ 144	M+H- ³⁷ Cl (16#5) 70 M- ³⁷ Cl (5#6) 30
BZ 129	M+H- ³⁷ Cl (0#0) ND** M- ³⁷ Cl (0#0) ND**	BZ 131	^b M+H- ³⁷ Cl (0#0) ND** M- ³⁷ Cl (0#0) ND**
BZ 156	M+H- ³⁷ Cl (0#0) ND** M- ³⁷ Cl (0#0) ND**	BZ 158	M+H- ³⁷ Cl (5#4) 20 M- ³⁷ Cl (4#4) 12

Legend :

(Standard deviation#number averaged)

% Label loss =

* see Chapter 3 for Identification

** ND = Not Detected

Table 18e - Percent Label Lost in Forming $[M+H-X]^+$ and $[M-X]^+$

BZ 65 Set		BZ 116 Set
BZ 93	M+H- ³⁷ Cl (19#4) 63 M- ³⁷ Cl (8#4) 9	BZ 142	M+H- ³⁷ Cl (27#13) 83 M- ³⁷ Cl (1#13) 3
BZ 112	M+H- ³⁷ Cl (29#5) 45 M- ³⁷ Cl (6#5) 45	BZ 160	M+H- ³⁷ Cl (6#13) 20 M- ³⁷ Cl (2#13) 6
BZ 117	^{*c} M+H- ³⁷ Cl (24#7) 60 M- ³⁷ Cl (5#7) 21	BZ 166	M+H- ³⁷ Cl (12#14) 25 M- ³⁷ Cl (2#14) 5
BZ 151	M+H- ³⁷ Cl (3#3) 55 M- ³⁷ Cl (5#3) 43	BZ 185	M+H- ³⁷ Cl (8#13) 58 M- ³⁷ Cl (3#13) 12
BZ 134	^{*d} M+H- ³⁷ Cl (0#0) ND** M- ³⁷ Cl (0#0) ND**	BZ 173	M+H- ³⁷ Cl (5#3) 76 M- ³⁷ Cl (2#3) 12
BZ 163	M+H- ³⁷ Cl (0#1) 17 M- ³⁷ Cl (0#1) 10	BZ 190	M+H- ³⁷ Cl (5#6) 28 M- ³⁷ Cl (3#6) 11

Legend : M+H-³⁷Cl (10#3)
20
M-³⁷Cl (10#3)
8

(Standard deviation#number averaged)
% Label loss =
* see Chapter 3 for Identification
** ND = Not Detected

graphs, i.e., " $M+H-^{37}Cl$ " and " $M-^{37}Cl$ ", the corresponding standard deviation and number of data points averaged to obtain the particular percent label loss are indicated. These numbers are in parenthesis and are reported in the form of "standard deviation # number averaged".

As an example, consider BZ 60 listed on the first page of Table 18. For this congener, 95% percent of the signal from the $[M+H-X]^+$ ion type involved the loss of a ^{37}Cl label. This was determined from the average of three measurements and these measurements had a standard deviation of 7. For the same labelled congener, 26% percent of the signal from the $[M-X]^+$ ion type involved the loss of a ^{37}Cl label. This was determined from the average of 3 measurements and these measurements had a standard deviation of 1.

For some congeners listed in Table 18, no reliable values (i.e., R^2 value > 0.990) for a particular congener or reaction channel were obtained. These are indicated with the symbol ND.

4.3.2 Partition Between the $[M-X]^+$ and $[M+H-X]^+$ Channels

Since the isotopic patterns of $[M-X]^+$ and $[M+H-X]^+$ overlap, we obtained a reliable indication of the relative abundance of these ions with each percent label loss determination. The data describing this partition between the $[M-X]^+$ and $[M+H-X]^+$ channels are presented in Table 19. This partition is presented as the percentage of $[M+H-X]^+$ which was calculated by Equation 21.

Table 19a - Variation in the Partition to the $[M+H-X]^+$ Reaction Channel With Changes in Pressure and Ventilation Rate. 113

BZ 21 Set		BZ 23 Set
BZ 41		BZ 43

BZ 60		BZ 63

BZ 87		BZ 93

BZ 82		BZ 92

BZ 105		BZ 83

BZ 117

BZ 114		BZ 107

Legend :

$[M+H-Cl]^+$ - fraction % $[M+H-Cl]^+$
0.25 torr, 320 cm³/s 0.50 torr, 320 cm³/s
0.25 torr, 530 cm³/s 0.50 torr, 530 cm³/s

ND - Not detected in sufficient quantities. * see Chapter 3 for identification

Table 19b - Variation in the Partition to the $[M+H-X]^+$ Reaction Channel With Changes in Pressure and Ventilation Rate. ¹¹⁴

BZ 24 Set		BZ 29 Set
BZ 45		BZ 48

BZ 59		BZ 74

BZ 64		BZ 101

BZ 95		BZ 97

BZ 84		BZ 118

BZ 110

Legend :

$[M+H-Cl]^+$ - fraction % $[M+H-Cl]^+$
0.25 torr, 320 cm³/s 0.50 torr, 320 cm³/s
0.25 torr, 530 cm³/s 0.50 torr, 530 cm³/s

ND - Not detected in sufficient quantities. * see Chapter 3 for identification

Table 19c - Variation in the Partition to the $[M+H-X]^+$ Reaction Channel With Changes in Pressure and Ventilation Rate. ¹¹⁵

BZ 30 Set		BZ 38 Set	
*i BZ 75		 BZ 76	
 BZ 103		 BZ 81	
 BZ 98		*m BZ 86	
*j BZ 88		 BZ 124	*n
*k BZ 119		 BZ 106	*n
*k BZ 109		 BZ 122	
 BZ 115			

Legend :

[M+H-Cl]⁺ fraction % [M+H-Cl]⁺
 0.25 torr, 320 cm³/s 0.50 torr, 320 cm³/s
 0.25 torr, 530 cm³/s 0.50 torr, 530 cm³/s

ND - Not detected in sufficient quantities. * see Chapter 3 for Identification

Table 19d - Variation in the Partition to the $[M+H-X]^+$ Reaction Channel With Changes in Pressure and Ventilation Rate. ¹¹⁶

BZ 61 Set		BZ 62 Set
BZ 86	ND 15 13 4	BZ 88	ND 18 15 2
BZ 106	81 66 54 41	BZ 109	23 17 10 6
BZ 114	62 48 44 24	*a BZ 115	15 10 8 2
BZ 141	ND 38 26 16	BZ 144	18 10 9 0
BZ 129	ND ND ND ND	*b BZ 131	ND ND ND ND
BZ 156	ND ND ND ND	BZ 158	55 43 36 ND

Legend :

$[M+H-Cl]^+$ - fraction % $[M+H-Cl]^+$ -
0.25 torr, 320 cm³/s 0.50 torr, 320 cm³/s
0.25 torr, 530 cm³/s 0.50 torr, 530 cm³/s

ND - Not detected in sufficient quantities. * see Chapter 3 for Identification

Table 19e - Variation in the Partition to the $[M+H-X]^+$ Reaction Channel With Changes in Pressure and Ventilation Rate. ¹¹⁷

BZ 65 Set		BZ 116 Set
BZ 93		BZ 142

BZ 112		BZ 160

BZ 117 ^{*c}		BZ 166

BZ 151		BZ 185

BZ 134 ^{*d}		BZ 173

BZ 163		BZ 190

Legend :

$[M+H-Cl]^+$ - fraction % $[M+H-Cl]^+$ -
0.25 torr, 320 cm³/s 0.50 torr, 320 cm³/s
0.25 torr, 530 cm³/s 0.50 torr, 530 cm³/s

ND - Not detected in sufficient quantities. * see Chapter 3 for Identification

$$\%[M+H-X]^{\bullet} = \frac{f([M+H-X]^{\bullet})}{(f([M+H-X]^{\bullet}) + f([M-X]^{\bullet}))} \times 100 \quad (21)$$

where $f([M+H-X]^{\bullet})$ is the sum of the relative abundances for the loss of label and loss of non-labelled chlorine in the formation of the $[M+H-X]^{\bullet}$ fragment, and $f([M-X]^{\bullet})$ is the analogous summation in the formation of the $[M-X]^{\bullet}$ fragment. The percent of $[M+H-X]^{\bullet}$ determined with Equation 21 is reported in Table 19 for each pressure / ventilation setting.

Table 19 is organized in much the same manner as Table 18, the major exception being in the second column, which contained two bar graphs in Table 18, but contains four bar graphs in Table 19. The top two bar graphs have a grey background and indicate results obtained with the source pressure at 0.25 torr. The bottom two bar graphs have a white background and indicate results obtained with the source pressure at 0.50 torr. One of the grey background bars and one of the white background bars contain diagonal stripes; this indicates results collected with the probe hole open. The bars that do not have diagonal stripes indicate results collected with the probe hole closed. The ventilation rate through the source can be calculated. Details of this calculation will be described in Chapter 7. They will show ventilation rates of 320 cm³/s with the probe hole closed and 530 cm³/s with the probe hole open.

Similar to Table 18, the percent of $[M+H-X]^{\bullet}$ is indicated on each bar graph with a black bar as well as a number immediately to the right of each bar. Again,

in some cases no reliable values were obtained and these are indicated with the symbol ND.

4.3.3 Percentage of Label Lost in the Formation of $[\text{M}+\text{O}-\text{X}]^-$

In some instances ions of the type $[\text{M}+\text{O}-\text{X}]^-$ were observed. This only occurred if the moderator gas contained a trace quantity of oxygen. In the present investigation, actions were taken to limit the quantity of trace oxygen present. As a result, fewer spectra were collected with sufficiently intense $[\text{M}+\text{O}-\text{X}]^-$ ions to reliably determine the percent label loss in this reaction channel. However, information on $[\text{M}+\text{O}-\text{X}]^-$ formation for 30 of the labelled congeners was obtained during the course of this study. The reliable percent-label lost values (again invoking the $R^2 > 0.990$ criteria) are presented in Table 20. In this table, each measured value and it's corresponding pressure and ventilation rate information are indicated. The last column shows the percent-label-lost values expected for random dechlorination.

Table 20a : Percent Label Lost in Forming [M+O-X]- Fragment

0.50 torr Measurements			Random
Mix	Product	Low Flow *	
BZ 21	87	39%	40%
BZ 21	105	19%	40%
0.25 torr Measurements			
High Flow *	Low Flow *		
39%	35%		
24%	ND**		
ND**	34%		
0.25 torr Measurements			Random
Low Flow *			40%
17%			
0.25 torr Measurements			Random
High Flow *	Low Flow *		40%
ND**	19%		40%
15%	14%		
0.25 torr Measurements			Random
High Flow *			40%
ND**			40%
19%			
0.25 torr Measurements			Random
High Flow *	Low Flow *		40%
70%	68%		40%
87%	84%		40%
51%	49%		

* Low Flow = 320 cm3 s-1 : High Flow = 530 cm3 s-1

** ND - Signal Below Reliable Measurement

Table 20b : Percent Label Lost in Forming [M+O-X]- Fragment

0.50 torr Measurements			
Mix	Product	Low Flow *	Low Flow *
BZ 61	106	17%	33%
BZ 61	114	22%	31%
BZ 61	141	20% ND**	ND**

0.50 torr Measurements

Mix	Product	Low Flow *	Low Flow *
BZ 62	109	20% ND**	
BZ 62	115	20%	18%
BZ 62	144	24% ND**	
BZ 62	158	20% ND**	

0.50 torr Measurements

Mix	Product	Low Flow *	Low Flow *
BZ 65	112	13%	15%
BZ 65	117	ND**	17%
BZ 65	151	ND**	19%
BZ 65	163	ND**	20%

0.50 torr Measurements

Mix	Product	Low Flow *	Low Flow *
BZ 116	142	5% ND**	8%
BZ 116	160	6%	8%
BZ 116	166	6%	10%
BZ 116	185	10% ND**	ND**
BZ 116	173	ND**	ND**
BZ 116	190	ND**	ND**

0.25 torr Measurements

	High Flow *	High Flow *	Low Flow *
	12%	14%	7%
	13%	14%	7%
	19% ND**	ND**	

Random
20%
20%
33%

0.25 torr Measurements

	High Flow *	High Flow *	Low Flow *
	10%	9%	7%
	10%	4%	8%
	14% ND**	ND**	
	15% ND**	ND**	

Random
20%
20%
33%
33%

0.25 torr Measurements

	High Flow *	Low Flow *
	10%	6%
	10%	7%
	ND**	ND**
	17% ND**	

Random
20%
20%
33%
33%

0.25 torr Measurements

	High Flow *	High Flow *	High Flow	Low Flow *	Low Flow	Random
	4%	6% ND**		2%	4%	17%
	7%	4%	5%	5%	6%	17%
	3%	4%	5%	3%	5%	17%
	13%	11%	10%	10%	12%	29%
	ND**	11% ND**		ND**	8%	29%
	11%	11%	11%	ND**	9%	29%

* Low Flow = 320 cm3 s-1 : High Flow = 530 cm3 s-1

** ND - Signal Below Reliable Measurement

Chapter 5 : Molecular Modelling of PCBs

5.1 Introduction

In order to explain the results presented in the previous chapter, some appreciation of the thermochemical properties of PCBs and their ions is required. This chapter will address the determination and application of selected PCB molecular properties using Hyperchem 4.5. In Section 5.2, the validation of the calculation method by a comparison of calculations with published data for chlorobenzenes is described. After this validation, the calculated molecular properties of selected PCBs are presented. In Section 5.3, some of these molecular properties will then be related through quasi-equilibrium theory (QET) to the fragmentation pathways observed.

5.2 Molecular Properties Calculated using Hyperchem

The Hyperchem program has already been introduced briefly in Chapter 2. This program was used to calculate the thermochemical properties of the PCB congeners and their fragments. The accuracy of these calculations is dependent on the class of molecules being examined^{95,100}. To obtain a “ball-park” estimate of the magnitude of error for the AM1-semi-empirical calculations performed on PCBs, a comparison of the calculated and experimental or critically evaluated enthalpies of formation for chlorinated benzenes was carried out. Chlorinated benzenes have been studied extensively, and as a result, a number of critically evaluated

thermochemical quantities are available ⁸¹. While, for the most part, chlorinated benzenes and PCBs can be considered to be in the same class of compounds, PCBs are unique in that the interaction between the two aromatic rings is a function of the angle between the two aromatic rings, in other words, the degree of coplanarity.

This thesis work also included an investigation of the energetic and geometric effects of rotation about the biphenyl linkage. Previous research had indicated that the barrier to formation of a planar structure was related to the number of ortho chlorines ¹⁰¹, and this energy barrier was subsequently correlated to the toxicity of PCBs ¹⁰². In addition, EI mass spectral characteristics have also been linked to the tendency toward coplanarity ⁵⁰. This property will be addressed in Section 5.2.3.

In order to explain some of the ortho-chlorine effects observed in the EI mass spectra of PCBs, Levy and Oswald ⁵³ have proposed the formation of a chloronium ion bridging the two phenyl units. The stability of such a chloronium ion was examined here, and the results are presented in 5.2.4. It has been proposed that bond strength and subsequent regioselective bond breaking can be predicted from an analysis of relative bond orders ⁹⁷. This issue will be addressed in Section 5.2.5.

5.2.1 Validation of Hyperchem Calculations using Chlorobenzenes

In this work, the critically evaluated thermochemical data published in the monograph by Lias et al. ⁸¹ were taken to be “accepted” values. In that

monograph, enthalpies of formation for both the neutral and cations of all 12 possible chlorinated benzene congeners and those of benzene are available. In this thesis, this set of 13 compounds was then used to evaluate the calculation accuracy for neutral and cationic chlorinated aromatic species. In the case of the chlorobenzene anions critically assessed values are not available, but electron affinities for the set of chlorobenzenes and a number of PCBs have been calculated based on experimental reduction potentials ¹⁰³. These were used as the “best available values” to assess anion calculations.

5.2.1.1 Validation of Hyperchem Calculations for Neutral Chlorobenzenes

The enthalpies of formation (ΔH_f^{298}) calculated with Hyperchem 4.5 and the corresponding accepted enthalpies of the ground state neutral for the set of chlorobenzenes are presented in Table 21. A plot of these calculated versus accepted values is presented in Figure 19. All the calculated values presented in Table 21 are greater than their corresponding accepted values. This difference cannot be corrected by a simple subtraction since the magnitude of the deviation changes among congeners. In fact, there is an apparent direct relationship between the number of chlorines present and the magnitude of the deviation from the accepted values. That is to say, as the number of chlorines increases, so does the magnitude of the deviation. This is a concern since all the PCBs investigated in this work have at least four chlorines and may have as many as seven chlorines.

This being said, for some congeners the relative order of the calculated

Table 21 : Enthalpies of Formation Calculated with Hyperchem 4.5 Compared to Accepted Enthalpies of Formation for Neutral Chlorobenzenes (kcal mol⁻¹)**

Compound	Calculated * Enthalpies (Ec)	Accepted ** Enthalpies (Ea)	Difference (Ec-Ea)
Benzene	22	19.8	2.1
Chlorobenzene	15	13	1.6
1,2 Dichlorobenzene	9	7.9	1.2
1,3 Dichlorobenzene	8	6.7	1.3
1,4 Dichlorobenzene	8	5.9	1.9
1,2,3 Trichlorobenzene	4	-1.9	5.9
1,2,4 Trichlorobenzene	3	1.9	0.9
1,3,5 Trichlorobenzene	2	0	2.0
1,2,3,4 Tetrachlorobenzene	1	-6.1	6.9
1,2,3,5 Tetrachlorobenzene	-2	-8.3	6.5
1,2,4,5 Tetrachlorobenzene	-2	-7.8	5.7
Pentachlorobenzene	-5	-9.6	4.5
Hexachlorobenzene	-8	-10.7	2.7
Average Absolute Deviation			3.3
Maximum Absolute Deviation			6.9

Figure 19 : Calculated vs Accepted Enthalpies of Formation From Table 21

* Calculated Using Hyperchem 4.5

** Lias et al., J. Phys. Chem. Ref. Data 17, suppl. 1 (1988)

enthalpies of formation at a given level of chlorination reflects that of the measured enthalpies of formation⁸¹. For example, in the case of the three tetrachlorobenzenes: 1,2,3,4-, 1,2,3,5-, and 1,2,4,5-, the first congener in this list is calculated to have an enthalpy of formation 3 kcal/mol lower than the other two, which are calculated to have the same enthalpy of formation. The accepted values approximately reflect this (-6.1 relative to -8.3 and -7.8 kcal/mol, respectively). However, this degree of agreement is not reflected in other congeners; for instance, 1,2,3-trichlorobenzene is the most stable of the trichlorobenzenes although it is calculated to be the least stable. Because of this, a correction factor that accounts for a particular chlorination level would produce misleading results. Extrapolating these difficulties to PCBs, we, therefore, sought no corrections for the enthalpies of formation of PCBs.

To provide some indication of the magnitude of the expected deviation, the average absolute deviation was used. This type of error estimate is commonly used to indicate global accuracies for molecular calculations^{95,100,104}. For the set of neutral chlorinated benzenes examined, the average absolute deviation was 3.3 kcal/mol and the maximum absolute deviation was 6.9 kcal/mol.

5.2.1.2 Validation of Hyperchem Calculations for Cationic Chlorobenzenes

Three methods could be used to estimate the enthalpies of formation of the cations. Two of these used the enthalpy of formation of the cation calculated by Hyperchem. In one of these, the geometry of the cation was set to be identical to

the optimized geometry of the neutral. In the other, the geometry of the cation was optimized prior to the enthalpy of formation calculation. The third method used the ionization energy of the neutral, as indicated by the negative of the highest occupied molecular orbital (HOMO) eigenvalue (ϵ), as the difference between the enthalpies of formation of the cation and neutral. The results of these three approaches and their comparisons with the accepted data are shown in Tables 22 to 24 and Figures 20 to 22 respectively. Based on the average absolute deviations, the most accurate of these three methods is the one where the cation geometry was optimized. This method produced an average absolute deviation of 4.5 kcal/mole while the corresponding values for the neutral geometry enthalpy calculation and the ionization potential method were 8.3 and 18.5 respectively. The average absolute deviation of 4.5 for the enthalpies of formation calculation using the optimized cationic geometries compared very well with similar determinations¹⁰⁰ for a wide range of halogenated compounds where the average absolute error for AM1 relative to experimental values was found to be 5.3 kcal/mol.

It may be of interest to note that the graphs associated with the neutral geometry enthalpy calculation and the ionization potential method both clearly show that the calculated values are offset. If the offsets of these two methods are corrected for (by subtracting the average absolute deviation from the calculated enthalpy) then the error with these two methods improves significantly. It is important to note, however, that more highly chlorinated congeners are still offset more than the less highly chlorinated congeners. With this offset correction, the

Table 22 : Enthalpies of Formation Calculated with Hyperchem 4.5 for Cationic Chlorobenzenes with Geometries Corresponding to the Optimized Neutral Geometry Compared to Accepted Cation Enthalpies of Formation (kcal mol⁻¹)**

Compound	Calculated * Enthalpies (Ec)	Accepted ** Enthalpies (Ea)	Difference (Ec-Ea)
Benzene	238	233.2	5.2
Chlorobenzene	226	222	4.2
1,2 Dichlorobenzene	221	217.3	3.4
1,3 Dichlorobenzene	217	216.8	0.3
1,4 Dichlorobenzene	219	210.9	7.7
1,2,3 Trichlorobenzene	220	209.8	10.1
1,2,4 Trichlorobenzene	215	210	4.9
1,3,5 Trichlorobenzene	219	215	4.5
1,2,3,4 Tetrachlorobenzene	213	199.1	14.4
1,2,3,5 Tetrachlorobenzene	213	199	13.9
1,2,4,5 Tetrachlorobenzene	210	197.4	12.8
Pentachlorobenzene	209	195.7	13.6
Hexachlorobenzene	209	196.4	12.3
Average Absolute Deviation			8.2
Maximum Absolute Deviation			14.4

Figure 20 : Calculated vs Accepted Enthalpies of Formation from Table 22

* Calculated Using Hyperchem 4.5

** Lias et al., J. Phys. Chem. Ref. Data 17, suppl. 1 (1988)

Table 23 : Enthalpies of Formation Calculated with Hyperchem 4.5 for Cationic Chlorobenzenes with Geometries Corresponding to the Optimized Cation Geometry Compared to Accepted Cation Enthalpies of Formation (kcal mol⁻¹)**

Compound	Calculated * Enthalpies (Ec)	Accepted ** Enthalpies (Ea)	Difference (Ec-Ea)
Benzene	231	233.2	-2.2
Chlorobenzene	222	222	-0.4
1,2 Dichlorobenzene	216	217.3	-0.9
1,3 Dichlorobenzene	217	216.8	0.3
1,4 Dichlorobenzene	214	210.9	2.7
1,2,3 Trichlorobenzene	216	209.8	6.1
1,2,4 Trichlorobenzene	210	210	0.3
1,3,5 Trichlorobenzene	215	215	0.2
1,2,3,4 Tetrachlorobenzene	209	199.1	9.8
1,2,3,5 Tetrachlorobenzene	208	199	9.2
1,2,4,5 Tetrachlorobenzene	206	197.4	8.5
Pentachlorobenzene	206	195.7	10.0
Hexachlorobenzene	205	196.4	8.3
Average Absolute Deviation			4.5
Maximum Absolute Deviation			10.0

Figure 21 : Calculated vs Accepted Enthalpies of Formation From Table 23

* Calculated Using Hyperchem 4.5

** Lias et al., J. Phys. Chem. Ref. Data 17, suppl. 1 (1988)

Table 24 : Enthalpies of Formation Calculated with Hyperchem 4.5 from the IP and Neutral Enthalpy for Chlorobenzenes Compared to Accepted Cation Enthalpies of Formation (kcal mol⁻¹)**

Compound	Calculated *	Calculated *	Calculated *	Accepted ***	Deviation
	HOMO (/eV) = -IP	Neutral Enthalpies (Hn)	Cation ** Enthalpies (Hc)		
Benzene	-9.65	22	244	233.2	11.2
Chlorobenzene	-9.56	15	235	222	13.1
1,2 Dichlorobenzene	-9.60	9	230	217.3	13.1
1,3 Dichlorobenzene	-9.68	8	231	216.8	14.5
1,4 Dichlorobenzene	-9.52	8	227	210.9	16.4
1,2,3 Trichlorobenzene	-9.78	4	230	209.8	19.7
1,2,4 Trichlorobenzene	-9.62	3	225	210	14.6
1,3,5 Trichlorobenzene	-9.92	2	231	215	15.8
1,2,3,4 Tetrachlorobenzene	-9.73	1	225	199.1	26.1
1,2,3,5 Tetrachlorobenzene	-9.76	-2	223	199	24.3
1,2,4,5 Tetrachlorobenzene	-9.65	-2	220	197.4	23.0
Pentachlorobenzene	-9.78	-5	220	195.7	24.7
Hexachlorobenzene	-9.91	-8	221	196.4	24.1
Average Absolute Deviation					18.5
Maximum Absolute Deviation					26.1

Figure 22 : Calculated vs Accepted Enthalpies of Formation from Table 24

* Calculated Using Hyperchem 4.5

** Determined by : $H_c = IP \cdot 23.06 + H_n$; IP = -Homo eV

*** Lias et al., J. Phys. Chem. Ref. Data 17, suppl. 1 (1988)

neutral geometry enthalpy calculation method becomes almost as good as the optimized geometry enthalpy calculation method. The calculation of the enthalpy of formation of the cation with the neutral molecule's geometry can be considered to be equivalent to the determination of the cationic state which would result from a vertical (i.e., Franck-Condon) excitation⁸¹. This type of transition occurs without any change in the relative positions of the nuclei and thus is simulated by a determination of the enthalpy with the cation in the most stable neutral geometry. The enthalpies of formation of PCB cations in this thesis work were calculated with neutral PCB geometries.

An interesting observation can be made by correlating the magnitude of error in the calculated cation enthalpies with the structure of the chlorinated benzenes. There appear to be two distinct clusters of errors: the lower chlorinated benzenes seem to be offset by a constant amount and the higher chlorinated benzenes offset by a different higher amount. Of the three trichlorobenzenes, one (1,2,3-) has an offset similar to that of the higher chlorinated benzenes, while the other two (1,2,4- and 1,3,5-) have an offset similar to that of the lower chlorinated benzenes. This is interesting for two reasons. First, it is commonly believed that the error associated with a semiempirical method should have the "... same magnitude for all isomeric (same number of substituents but different positions) and homologous (different number of substituents) compounds of a given substance class"¹⁰⁵. Secondly, this error may imply that there is some property of the higher chlorinated benzenes and 1,2,3-trichlorobenzene that is not taken into account in the AM1 level

calculation but nevertheless stabilizes the cations of these molecules.

5.2.1.3 Validation of Hyperchem Calculations for Anionic Chlorobenzenes

Because a complete set of evaluated enthalpies of formation for the chlorobenzene anions was not available, electron affinity values were used instead. Electron affinity is a measure of the difference in the enthalpies of formation of the anion and ground state neutral as described by Equation 19 presented in the Introduction of this thesis. A series of “absolute” electron affinity values determined from experimental reduction potentials has been reported for all the chlorinated benzenes ¹⁰³. These electron affinity values were used as “accepted values” here for comparison with electron affinities calculated for the appropriate enthalpies of formation determined with Hyperchem. The electron affinities for the chlorobenzenes that were determined from the enthalpies of formation calculated with Hyperchem 4.5 did not agree well with the literature values. In fact, the correlation between the two sets as measured by a linear regression analysis yielded a correlation coefficient (R^2) of only 0.125. As a result of this unsatisfactory result, another method of calculating electron affinities was pursued.

The EA of a molecule has been correlated to the eigenvalue (ϵ) of the lowest unoccupied molecular orbital (LUMO) of the molecule by the relationship presented in Equation 22 ^{84,106}.

$$EA = -\xi(\epsilon_{LUMO}) - \delta \quad (22)$$

Here ξ represents a scaling constant and δ is a constant which represents the "... reorganization energy correction term to account for the charge density readjustment when an electron is added to a molecule." ¹⁰⁶ Since a set of EA values is available ¹⁰³ for all the chlorinated benzenes, and we could calculate LUMO eigenvalues with Hyperchem, the linear relationship between the calculated LUMO eigenvalues and the literature EA values was used to determine the ξ and δ values for the chlorinated benzenes via a linear regression analysis. For the chlorinated benzenes, the scaling constant (ξ) was determined to be 0.882, and the reorganization energy correction term (δ) was calculated as 0.05 eV. The R^2 value for the fit was 0.9635, and the determined standard error of the estimate of EAs from the calculated LUMO eigenvalues was 0.07 eV. The calculation table and corresponding plot for the chlorinated benzenes are presented in Table 25 and Figure 23.

If a sufficient number of the EAs and LUMOs were known for a given class of molecules, such as the chlorinated benzenes or PCBs, then the unknown EAs could be estimated from the calculated LUMO eigenvalues once the scaling constant (ξ) and the reorganization energy correction term (δ) were determined. The standard error of the estimate from the same linear regression analysis could then be used to indicate the confidence limits of the estimate. This approach was applied to the determination of the electron affinities of all the PCB congeners (see the following section).

Table 25 : Correlation Between Literature Electron Affinities (EAs) and LUMO Eigenvalues Determined by a Linear Regression Analysis

Compound	Calculated * LUMO (/eV)	Literature** EA (/eV)	Modelled *** EA (/eV)	Deviation (Literature - Modelled)
Chlorobenzene	0.16	-0.14	-0.18	0.04
1,2 Dichlorobenzene	-0.14	0.08	0.08	0.00
1,3 Dichlorobenzene	-0.16	0.10	0.09	0.01
1,4 Dichlorobenzene	-0.22	0.10	0.14	-0.04
1,2,3 Trichlorobenzene	-0.36	0.34	0.27	0.07
1,2,4 Trichlorobenzene	-0.47	0.30	0.37	-0.07
1,3,5 Trichlorobenzene	-0.40	0.32	0.31	0.01
1,2,3,4 Tetrachlorobenzene	-0.65	0.54	0.53	0.01
1,2,3,5 Tetrachlorobenzene	-0.68	0.51	0.56	-0.05
1,2,4,5 Tetrachlorobenzene	-0.73	0.49	0.60	-0.11
Pentachlorobenzene	-0.88	0.73	0.73	0.00
Hexachlorobenzene	-1.04	0.98	0.87	0.11
Standard Error of Estimate				0.06
Average Absolute Deviation				0.04
Maximum Absolute Deviation				0.11

Figure 23 : Hyperchem Calculated LUMOs vs Electron Affinities (EAs)

* Calculated Using Hyperchem 4.5

** Wiley et al., J. Electroanal. Chem., 307, 169-182. (1991)

*** Modelled from Linear Regression fit : EA = -0.8820*(LUMO) - 0.048

***R² for Regression = 0.9635

5.2.2 Thermochemical Values for Selected PCBs and PCB Fragments

5.2.2.1 Enthalpies of Formation for Selected PCBs and Corresponding Molecular Ions

The enthalpies of formation of all the labelled congeners synthesized for this thesis work as well as those of the starting congeners are presented in Table 26. Enthalpies are reported for the neutral, cation, and anion states. All these values were calculated using the optimized geometry of the neutral. The reader is reminded that the calculated values for these molecular ions are likely higher than the actual values.

The electron affinities of PCBs were calculated from the LUMO eigenvalues using the method described in the previous section. In short, LUMO eigenvalues calculated with Hyperchem 4.5 were correlated to the published PCB electron affinities¹⁰³ using a linear regression analysis which yielded a scaling constant (ξ) of 0.655 and a reorganization energy correction term (δ) of 0.08 eV. From this an “error of estimate” of 0.069 eV was determined. Another research group also calculated the LUMO eigenvalues of PCBs using the AM1 semi-empirical method⁶⁸. Using their eigenvalues, a scaling constant (ξ) of 0.6655, a reorganization energy correction term (δ) of 0.07 eV, and an error of estimate of 0.069 were determined. The LUMO eigenvalues and EA data used to determine these correlations are presented in Table 27, and a corresponding graph is presented in Figure 24. The similarity between these two correlations from different LUMO eigenvalues implies that either set of eigenvalues could be used to calculate PCB electron affinities. In the publication of Greaves et al.⁶⁸, LUMO eigenvalues were reported for only 49

Table 26a : Enthalpies of Formation for Selected PCB Molecular Ions as Determined by Hyperchem 4.5

BZ #	Structure	Enthalpy of Formation (kcal mole ⁻¹)		
		Neutral	Cation	Anion
BZ 21	2,3,4	32	235	28
BZ 23	2,3,5	31	236	35
BZ 24	2,3,6	32	241	45
BZ 29	2,4,5	31	233	26
BZ 30	2,4,6	31	241	27
BZ 38	3,4,5	29	230	34
BZ 41	2,2',3,4	27	236	22
BZ 43	2,2',3,5	25	236	21
BZ 45	2,2',3,6	27	234	40
BZ 48	2,2',4,5	25	232	21
BZ 59	2,3,3',6	26	235	36
BZ 60	2,3,4,4'	25	229	19
BZ 61	2,3,4,5	27	234	19
BZ 62	2,3,4,6	28	237	29
BZ 63	2,3,4',5	24	229	17
BZ 64	2,3,4',6	25	235	36
BZ 65	2,3,5,6	28	236	28
BZ 74	2,4,4',5	24	228	17
BZ 75	2,4,4',6	24	232	26
BZ 76	2',3,4,5	25	231	30
BZ 81	3,4,4',5	23	224	22
BZ 82	2,2',3,3',4	21	232	15
BZ 83	2,2',3,3',5	20	237	24
BZ 84	2,2',3,3',6	22	231	33
BZ 86	2,2',3,4,5	22	233	21
BZ 87	2,2',3,4,5'	20	229	14
BZ 88	2,2',3,4,6	22	233	13
BZ 92	2,2',3,5,5'	19	229	21
BZ 93	2,2',3,5,6	22	230	23
BZ 95	2,2',3,5',6	22	230	32
BZ 97	2,2',3',4,5	20	235	14
BZ 98	2,2',3',4,6	21	230	23
BZ 101	2,2',4,5,5'	19	228	-13
BZ 103	2,2',4,5',6	19	227	21
BZ 105	2,3,3',4,4'	20	226	11
BZ 106	2,3,3',4,5	21	229	18
BZ 107	2,3,3',4',5	19	227	19
BZ 109	2,3,3',4,6	21	232	10
BZ 110	2,3,3',4',6	20	231	29
BZ 112	2,3,3',5,6	21	231	20

Table 26b : Enthalpies of Formation for Selected PCB Molecular Ions as Determined by Hyperchem 4.5

BZ #	Structure	Enthalpy of Formation (kcal mole ⁻¹)		
		Neutral	Cation	Anion
BZ 114	2,3,4,4',5	29	239	10
BZ 115	2,3,4,4',6	21	230	10
BZ 116	2,3,4,5,6	25	236	12
BZ 117	2,3,4',5,6	21	230	20
BZ 118	2,3',4,4',5	18	225	10
BZ 119	2,3',4,4',6	19	227	19
BZ 122	2',3,3',4,5	20	229	14
BZ 124	2',3,4,5,5'	19	227	19
BZ 129	2,2',3,3',4,5	17	229	7
BZ 131	2,2',3,3',4,6	17	228	7
BZ 134	2,2',3,3',5,6	17	226	16
BZ 141	2,2',3,4,5,5'	15	226	13
BZ 142	2,2',3,4,5,6	19	231	6
BZ 144	2,2',3,4,5',6	16	225	5
BZ 151	2,2',3,5,5',6	25	240	15
BZ 156	2,3,3',4,4',5	15	224	11
BZ 158	2,3,3',4,4',6	16	225	3
BZ 160	2,3,3',4,5,6	18	230	4
BZ 163	2,3,3',4',5,6	18	228	13
BZ 166	2,3,4,4',5,6	17	228	12
BZ 173	2,2',3,3',4,5,6	14	226	0
BZ 185	2,2',3,4,5,5',6	13	223	-2
BZ 190	2,3,3',4,4',5,6	13	224	4

Table 27 : Correlation Between LUMO Eigenvalues and Electron Affinities for Selected PCB Congeners as Determined by a Linear Regression Analysis.

BZ #	Structure	Literature *	Calculated **	Accepted***	Modelled EAs ****	
		LUMO (/eV)	LUMO (/eV)	EA (/ eV)	Literature EA / eV	Calculated EA / eV
1	2	-0.0428	-0.0582	0.20	0.10	0.12
2	3	-0.2633	-0.2703	0.19	0.24	0.25
3	4	-0.3164	-0.3196	0.24	0.28	0.29
4	2,2'	-0.1151	-0.0234	0.17	0.15	0.09
5	2,3	-0.2934	-0.2916	0.34	0.26	0.27
7	2,4	-0.3922	-0.3923	0.32	0.33	0.33
8	2,4'	-0.3615	-0.3559	0.26	0.31	0.31
9	2,5	-0.3698	-0.3677	0.36	0.32	0.32
11	3,3'	-0.4553	-0.4585	0.27	0.37	0.38
12	3,4	-0.5095	-0.5133	0.43	0.41	0.41
14	3,5	-0.4594	-0.4673	0.40	0.37	0.38
15	4,4'	-0.5449	-0.5479	0.30	0.43	0.44
23	2,3,5	-0.5273	-0.5266	0.52	0.42	0.42
24	2,3,6	-0.4263	-0.4239	0.36	0.35	0.36
29	2,4,5	-0.6131	-0.6087	0.46	0.48	0.48
30	2,4,6	-0.4575	-0.4529	0.33	0.37	0.37
38	3,4,5	-0.6743	-0.6839	0.60	0.52	0.53
52	2,2',5,5'	-0.5066	-0.4705	0.40	0.41	0.39
54	2,2',6,6'	-0.2098	-0.2128	0.18	0.21	0.22
61	2,3,4,5	-0.7508	-0.7452	0.62	0.57	0.57
62	2,3,4,6	-0.6448	-0.6434	0.52	0.50	0.50
65	2,3,5,6	-0.6608	-0.6563	0.51	0.51	0.51
77	3,3',4,4'	-0.8440	-0.8465	0.54	0.63	0.63
80	3,3',5,5'	-0.8042	-0.8057	0.58	0.60	0.61
101	2,2',4,5,5'	-0.6742	-0.6608	0.53	0.52	0.51
116	2,3,4,5,6	-0.8094	-0.8090	0.73	0.61	0.61
153	2,2',4,4',5,5'	-0.8570	-0.8177	0.54	0.64	0.61
155	2,2',4,4',6,6'	-0.6129	-0.6152	0.39	0.48	0.48
209	Deca-	-1.0952	-1.1030	0.89	0.80	0.80
-(Scaling Constant)					-0.6655	-0.6552
-(Reorganization Energy)					0.0691	0.0778
Error of Estimate					0.0687	0.0689

*Greaves et al., J. Am. Soc. Mass Spectrom. 5, 44-52 (1994)

** Calculated Using Hyperchem 4.5

*** Wiley et al., J. Electroanal. Chem., 307, 169-182. (1991)

**** Modelled from Linear Regression fit : $EA = -(\text{Scaling Constant}) * (\text{LUMO}) - (\text{Reorganization Energy})$

Figure 24 : Correlation Between EA and Hyperchem Calculated LUMO Eigenvalues

of 209 PCBs; however, Dr. Greaves, in a private correspondence, provided the calculated values for all 209 PCBs. As a result, it was possible to calculate the electron affinities of all 209 PCB congeners using this complete set of Dr. Greaves, and this information is presented in Appendix II.

5.2.2.2 Dechlorination Reaction Enthalpies and Enthalpies of Selected PCB Fragments

As discussed earlier, the bond dissociation energy (BDE) is defined as the enthalpy of the homolytic bond breaking reaction, Equation 23.

$$\text{BDE} = \Delta H_{\text{rx}} = \Delta H_f^{298}([\text{M-Cl}]^{\bullet}) + \Delta H_f^{298}(\text{Cl}^{\bullet}) - \Delta H_f^{298}(\text{MCl}) \quad (24)$$

In the case of chlorobenzene, the BDE for the carbon-chlorine bond is 95 kcal/mol, as determined using the appropriate literature enthalpies of formation tabulated by Lias et al.⁸¹

Under EI conditions, dechlorination can take place via the following two reactions (Equation 25 and 26).

In the EI investigation, we have focussed on molecular fragments of the type $[\text{M-Cl}]^{+}$ and $[\text{M-2Cl}]^{+\bullet}$ and thus examined only reactions of the type described in Equation 25. Equation 26 is energetically unlikely relative to Equation 25. Again, using

chlorobenzene as an example and applying the appropriate literature enthalpies of formation (from Lias et al.⁸¹) the enthalpies of reaction for Equations 25 and 26 are 76 kcal/mol and 185 kcal/mol, respectively.

In order to evaluate the regioselective loss of chlorine from a polychlorinated molecule, it is necessary to compare the relative enthalpies of reaction for Equation 25 corresponding to the loss of each chlorine. In such an analysis, a common molecular ion, $[M]^+\bullet$, and a common product, $Cl\bullet$, are involved in each case. Therefore, the comparison between relative enthalpies of reaction for the loss of different chlorines can be made by comparing only the relative enthalpies of formation for the appropriate fragment ions.

As an example, consider the fragmentation of BZ 86 (2,2',3,4,5-). In this case, the enthalpy of formation (ΔH_f^{298}) for the molecular cation, $[M]^+\bullet$, equals 225 kcal/mol, the enthalpy of formation for the chlorine radical, $Cl\bullet$, equals 29 kcal/mol, and the enthalpy of formation of the dechlorination fragment, $[M-Cl]^+$, is dependent on which of the chlorines is removed. If the remaining electrons in the ionic fragment ($[M-Cl]^+$) are paired after the removal of the chlorine, the ion is in a singlet state; if two of the electrons are unpaired then the ion is in a triplet state. The corresponding ΔH_f^{298} for the singlet state and triplet state of the particular fragments and the ΔH_{rx} that results are presented in Table 28.

For electron capture (EC) induced dechlorinations, carbon-chlorine bond cleavage again produces two sets of products (Equation 27 and 28). There is a significant possibility that many of the radical fragments of the type $[M-Cl]\bullet$ have

Table 28 : Enthalpies of Formation of [M-Cl]+ Fragments and the Corresponding Enthalpy of Reaction for Dechlorinations from 2,2',3,4,5 Pentachlorobiphenyl - BZ 86

Cl loss	Singlet Fragment		Triplet Fragment	
	Enthalpy of Formation (/kcal mole-1)	Enthalpy of Reaction * (/kcal mole-1)	Enthalpy of Formation (/kcal mole-1)	Enthalpy of Reaction * (/kcal mole-1)
2' O	292	96	299	103
2 O	304	108	293	97
3 M	325	129	296	100
4 P	326	130	296	100
5 M	298	102	295	99

* Calculated from ;

$$dH_{rx} = dH_f (\text{Fragment}) + dH_f (\text{Cl radical}) - dH_f (\text{Molecular ion})$$

Where ;

$$dH_f (\text{Cl radical}) = 29 \text{ kcal/mole and } dH_f (\text{Molecular ion}) = 225 \text{ kcal/mol}$$

positive electron affinities. Therefore, electron capture by the fragment, $[M-Cl]^\bullet$, must also be considered as a source of the $[M-Cl]^-$ measured in this investigation (Equation 29). Assuming the electron affinity of $[M-Cl]^\bullet$ is of the same order of magnitude as analogous PCBs containing the same number of chlorines (i.e., ~0.4 eV for tetrachlorobiphenyls and ~0.6 eV for hexachlorobiphenyls), it can be estimated that the enthalpy of formation of $[M-Cl]^\bullet$ and $[M-Cl]^-$ are within ~14 kcal/mol (i.e., 0.6 eV $\times$ 23 kcal mole⁻¹eV⁻¹ = 13.8 kcal/mol) of each other. On the other hand, the enthalpy of formation of Cl^- ($\Delta H_f^{298} = -54$ kcal/mol⁸¹) is much lower than the enthalpy of formation of $Cl^\bullet$ ($\Delta H_f^{298} = 29$ kcal/mol⁸¹). As a result, the reaction described in Equation 27 is expected to require significantly less energy (~70 kcal/mol) than the reaction described in Equation 28. Therefore, the reaction sequence of Equation 27 followed by Equation 29 is the more probable source of the observed $[M-Cl]^-$ ions.

It has been suggested that only molecules with positive electron affinities can be detected under normal ECNI/MS operating conditions^{66,106}. According to the electron affinities calculated here (see Appendix II), all PCBs meet this criterion. A positive electron affinity means that the electron capture process is exothermic, and thus the anion is formed initially with an excess energy equivalent to the electron affinity plus the kinetic energy of the captured electron. This excess energy

can be dissipated by inelastic collisions with the moderator gas, electron dissociation, or fragmentations such as those described in Equations 27 and 28.

If the anion signal observed is the result of two consecutive electron capture steps, then it is reasonable to expect that each of the steps (electron capture to form $[M]^{\bullet-}$ and the formation of $[M-Cl]^{\bullet-}$ by the reaction of Equation 29) has a positive electron affinity. This would require that the fragment radical formed in Equation 27 to have a higher enthalpy of formation than the corresponding anion for the same fragment. In order to facilitate this analysis, the enthalpy of formation for every species: radical, cation (singlet), cation (triplet), anion (singlet) and anion (triplet), and for the loss of each possible chlorine, has been determined for all of the congeners studied. This information is presented in Appendix III. It should be noted that the enthalpies of formation for anions may be unreliable (see Section 5.2.1). However, in the absence of reliable electron affinity values for the radical fragments, a more accurate determination cannot be made at this time.

5.2.3 Effects of Variation in the Biphenyl Dihedral Angle

5.2.3.1 Energetics of Rotation about the Biphenyl Linkage

In order to analyse the effects that a variation in the biphenyl dihedral angle have on a congener's energy, a series of six congeners: BZ 77 (3,3',4,4'-tetrachlorobiphenyl), BZ 106 (2,3,3',4,5- pentachlorobiphenyl), BZ 86 (2,2',3,4,5- pentachlorobiphenyl), BZ 88 (2,2',3,4,6- pentachlorobiphenyl), BZ 93 (2,2',3,5,6- pentachlorobiphenyl), and BZ 142 (2,2',3,4,5,6- hexachlorobiphenyl) were

examined. Specifically, the variation in enthalpy of formation was used to monitor the relative stability of specific orientations. Some technical issues arose when determining the enthalpy associated with a given dihedral angle. Notably, how to take into account geometric changes that could be induced by a dihedral angle change. The simplest approach was to fix the geometry of all the atoms in the molecule at bond lengths and angles corresponding to the most stable geometry before altering the dihedral angle. This approach over-estimated the magnitude of rotation barriers and provided no insight into possible geometric changes in the molecule. A more informative approach was to restrict which geometric changes could occur and optimize only these specific changes. In a recent article,¹⁰⁷ this method was employed by permitting variations only in the phenyl-phenyl bond length. In our investigation, we found that PCB isomers with no ortho chlorine (such as BZ 77) do maintain a reasonably constant geometry as they rotate. However, this was not found to be the case for other congeners which contained ortho-chlorines (see Section 5.2.3.2).

The best approach, and the one applied here, was to optimize the geometry of all aspects of the molecular system, with the exception of the biphenyl dihedral angle which was restrained by introducing a significantly high force constant so that it became effectively locked. However, even with this approach, difficulties arose. For example, in congeners with one or more ortho chlorines on each ring, we had difficulty using the geometric optimization algorithm to determine an energy minimum for planar biphenyl dihedral angles (planar angles = 0° and 180°). In fact,

for some of the species analysed, no solution was obtained for the planar geometry using an AM1 approach. To circumvent this problem, a molecular mechanics (MM+) approach was used to determine optimized geometries at each selected dihedral angle. After these geometries were obtained, the semiempirical AM1 method was used to calculate the enthalpy of formation associated with these geometries. The dihedral angle was varied from 0° to 360° in steps of 45°. An angle of 0° was defined to be the configuration with the 2 and 2' substituents on the same side of the molecule. It should be noted that in stepping the dihedral angle in this manner it was unlikely that the specific optimum, or most stable, dihedral angle would be selected for calculation. Instead, the most stable orientation was determined when the geometry of the entire molecule was optimized. The stepped variation in the dihedral angle provided only a crude estimate of the rotation barrier. This calculation was performed on the ground state neutral and cation of each of the six congeners. A comparison of the results from different charge states of the same congener provided some indication of the effect of ionization on the rotation barriers. The results for the neutral and cationic species of the six congeners examined are presented graphically in Figures 25 to 30.

The rotation barriers calculated here compare very well to similar previous calculations. For example, the barrier to assuming a planar orientation in BZ 77 was estimated by Tang et al.¹⁰² to be 2.2 kcal/mol, compared to our estimate of 2 kcal/mol. This is also in line with other experimental estimations; for example, in a temperature dependent NMR experiment the barrier of rotation was estimated to be

Figure 25 : Variation in Enthalpy of Formation with Biphenyl Dihedral Angle Changes for the Cationic and Neutral States of BZ 77

Figure 26 : Variation in Enthalpy of Formation with Biphenyl Dihedral Angle Changes for the Cationic and Neutral States of BZ 106

Figure 27 : Variation in Enthalpy of Formation with Biphenyl Dihedral Angle Changes for the Cationic and Neutral States of BZ 86

Figure 28 : Variation in Enthalpy of Formation with Biphenyl Dihedral Angle Changes for the Cationic and Neutral States of BZ 88

Figure 29 : Variation in Enthalpy of Formation with Biphenyl Dihedral Angle Changes for the Cationic and Neutral States of BZ 93

Figure 30 : Variation in Enthalpy of Formation with Biphenyl Dihedral Angle Changes for the Cationic and Neutral States of BZ 142

1-4 kcal/mol for non-ortho substituted PCBs ¹⁰⁸. This same NMR study also estimated that the rotation barrier for AO congeners was approximately 9 kcal/mol or less.

Figure 25 shows the calculation results obtained for BZ 77, a congener without ortho chlorine. Two types of rotational barriers are evident for the neutral molecule: one forming a planar structure, the other an orthogonal structure. In both cases, the magnitudes of the barriers are quite small, approximately 2 kcal/mol for the planar and approximately 1 kcal/mol for the orthogonal structure. The planar barrier arises as a result of the steric repulsion between the ortho substituents. Thus, even when both ortho substituents are hydrogens, some repulsion occurs. The orthogonal barrier results from a lack of resonance stabilization between the two aromatic systems. At an angle of 90°, no resonance stabilization can occur. Any deviation from 90° permits a finite overlap between the aromatic systems, resulting in a stabilization effect. Thus, the dihedral angle is an optimization of these repulsive and resonance effects. When the geometry of the entire BZ 77 molecule was optimized, the dihedral angle was 41°. This is very close to the angle expected (45°) if the repulsion and stabilization effect are of the same magnitude. In addition, this angle is very similar to that determined for other non-ortho-substituted biphenyls where the average angle was assessed to be $44.3^\circ \pm 0.4^\circ$ based on a combination of calculational and experimental values ¹⁰⁹.

The ionization of BZ 77 causes a drastic increase (from ~1 kcal/mol to ~18 kcal/mol) in the magnitude of the orthogonal barrier, while simultaneously

eliminating the planar barrier - in other words, the optimal configuration of the cation is nearly planar. This increased importance of resonance stabilization with the formation of the cation is expected. Since a delocalized charge is more stable than a localized charge, a distribution of charge over the two phenyl rings (via resonance stabilization) is more favourable than localization on one ring.

Figure 26 presents the calculation results for BZ 106 (2,3,3',4,5-). This congener has one ortho chlorine and a different number of chlorines on each ring. The barrier to formation of the orthogonal configuration (~ 1 kcal/mol) is similar to that in BZ 77; however, in BZ 106 the barrier to formation of the planar configuration increases significantly to ~ 11 kcal/mole. This is because the planar structure is destabilized by the repulsion between the ortho chlorine (2-) and the ortho hydrogen (2'-). When a cation is formed, the orthogonal barrier increases by approximately an order of magnitude from ~ 1 kcal/mol to ~ 12 kcal/mol, while the barrier to forming the planar configuration decreases to approximately 7 kcal/mol.

Figure 27 shows the calculation results for BZ 86 (2,2',3,4,5-). This congener has one ortho chlorine on each ring (an AO congener) as well as a different number of chlorines on each ring. The barrier to formation of the planar configuration is significant at ~ 23 kcal/mole. In fact, the repulsion between the ortho chlorines destabilizes the structure at 45° , so that the most stable configuration is near the orthogonal configuration. On formation of the cation, a barrier of ~ 9 kcal/mole to the formation of the orthogonal configuration develops, while a significant barrier to a planar configuration is maintained (~ 18 kcal/mole).

This results in an optimum structure for the cation around 45°.

All the other congeners studied, BZ 88 (2,2',3,4,6-), BZ 93 (2,2',3,5,6-), and BZ 142 (2,2',3,4,5,6-), have two ortho chlorines on one phenyl ring and one ortho chlorine on the second phenyl ring (ie., AO congeners). The observed rotational barrier plots are very similar in these congeners. The neutral species have a barrier to planarity of ~32 kcal/mol, and the orthogonal configuration is the most stable configurations found. When the cation is formed, a small barrier to the orthogonal configuration develops (~2 kcal/mol). In the planar configuration, however, the barrier decreases only slightly to ~25 kcal/mol. The most stable configuration of those cations calculated is near 45°.

5.2.3.2 Structural Effects of Rotation about the Biphenyl Linkage

A geometric optimization at each selected biphenyl dihedral angle produced useful geometric information in addition to the enthalpy of formation. The resulting geometric parameters for three configurations of each of the six congeners examined are presented in Table 29. Specifically, the three conformations are the optimized ground state structures of the neutrals, the structures of the neutrals with the dihedral angles of the ground state cations, and the optimized ground state structures of the cations.

The optimized ground state structure of the neutral was determined at the AM1 level of theory. A previous investigation¹⁰⁰ determined the average absolute error from AM1 level calculation from a large set (>60) of halogenated compounds

Table 29a - Selected Structure Parameters for BZ 77, BZ 106, BZ 86, BZ 88, BZ 93 and BZ 142

Set =>	BZ 77 (3,3',4,4'-)				BZ 106 (2,3,3',4,5-)				BZ 86 (2,2',3,4,5-)			
	Optimum*	Neutral**	Cation***		Optimum*	Neutral**	Cation***		Optimum*	Neutral**	Cation***	
Torsion Angle (C2-C1-C1'-C2') ****	41	0	0		63	45	45		92	45	45	
Torsion Angle(X2-C2-C1-C6)	-180	-180	-180		-179	-177	-174		180	-172	-168	
Torsion Angle (X6-C6-C1-C2)	-180	-180	-180		180	-180	179		-180	-180	178	
Torsion Angle (X2'-C2'-C1'-C6')	-180	-180	-180		-180	-178	-176		-180	-173	-169	
Torsion Angle (X6'-C6'-C1'-C2')	-180	-180	-180		180	-180	180		-180	-180	178	
Angle (X2-C2-C1)	120	121	120		120	121	120		120	121	120	
Angle (X6-C6-C1)	120	121	121		119	119	119		119	119	119	
Angle (X2'-C2'-C1')	120	121	120		120	120	120		121	122	121	
Angle (X6'-C6'-C1')	120	121	121		120	120	120		119	119	119	
Bond Length (C1 - C1') / Angstrom	1.46	1.46	1.43		1.47	1.47	1.43		1.47	1.47	1.43	
Bond Length (C2 - X2) / Angstrom	1.10	1.10	1.10		1.70	1.70	1.68		1.69	1.70	1.68	
Bond Length (C6 - X6) / Angstrom	1.10	1.10	1.10		1.10	1.10	1.11		1.10	1.10	1.11	
Bond Length (C2' - X2') / Angstrom	1.10	1.10	1.10		1.10	1.10	1.10		1.70	1.70	1.68	
Bond Length (C6' - X6') / Angstrom	1.10	1.10	1.10		1.10	1.10	1.10		1.10	1.10	1.10

* Optimum structure determined with full optimization of molecule

** Structure of neutral molecule as determined with molecular mechanics with (C2-C1-C1'-C2') torsion angle fixed at indicated angle

*** Structure of cation as determined with molecular mechanics with (C2-C1-C1'-C2') torsion angle fixed at indicated angle

**** All angles in degrees

***** Torsion Angle (C2-C1-C1'-C2') = Biphenyl Dihedral Angle

Table 29b - Selected Structure Parameters for BZ 77, BZ 106, BZ 86, BZ 88, BZ 93 and BZ 142

Set =>	BZ 88 (2,2',3,4,6 -)				BZ 93 (2,2',3,5,6 -)				BZ 142 (2,2',3,4,5,6 -)			
	Optimum*	Neutral**	Cation***		Optimum*	Neutral**	Cation***		Optimum*	Neutral**	Cation***	
Torsion Angle (C2-C1-C1'-C2') ****	90	45	45		90	45	45		90	45	45	
Torsion Angle(X2-C2-C1-C6)	-180	-174	-171		-180	-174	-170		-180	-174	-171	
Torsion Angle (X6-C6-C1-C2)	180	-177	-177		180	-176	-176		180	-176	-176	
Torsion Angle (X2'-C2'-C1'-C6')	180	-175	-170		-180	-175	-170		-180	-175	-170	
Torsion Angle (X6'-C6'-C1'-C2')	-180	-178	-178		180	-177	-178		180	-178	-178	
Angle (X2-C2-C1)	120	120	120		120	121	120		120	121	120	
Angle (X6-C6-C1)	121	122	121		120	121	121		120	121	120	
Angle (X2'-C2'-C1')	121	122	121		121	122	121		121	122	121	
Angle (X6'-C6'-C1')	119	119	119		119	119	119		119	119	119	
Bond Length (C1 - C1') / Angstrom	1.47	1.47	1.43		1.47	1.47	1.43		1.47	1.47	1.44	
Bond Length (C2 - X2) / Angstrom	1.70	1.70	1.69		1.69	1.70	1.68		1.69	1.70	1.69	
Bond Length (C6 - X6) / Angstrom	1.70	1.70	1.68		1.69	1.70	1.68		1.69	1.70	1.69	
Bond Length (C2' - X2') / Angstrom	1.70	1.70	1.68		1.70	1.70	1.68		1.70	1.70	1.68	
Bond Length (C6' - X6') / Angstrom	1.10	1.10	1.10		1.10	1.10	1.11		1.10	1.10	1.10

* Optimum structure determined with full optimization of molecule

** Structure of neutral molecule as determined with molecular mechanics with (C2-C1-C1'-C2') torsion angle fixed at indicated angle

*** Structure of cation as determined with molecular mechanics with (C2-C1-C1'-C2') torsion angle fixed at indicated angle

**** All angles in degrees

***** Torsion Angle (C2-C1-C1'-C2') = Biphenyl Dihedral Angle

to be 0.05 Å for bond length and 2° for bond angles. We assumed a similar magnitude of error in this investigation. The other two configurations were each determined using molecular mechanics (MM+) level optimizations. The magnitude of error associated with this level of calculation is expected to be greater than that of AM1. The optimized ground state structure of the cation was taken to be equivalent to the lowest energy configuration indicated in the corresponding graph presented in Figures 25 to 30.

In all the congeners listed, there appeared to be a shortening of the biphenyl linkage on the formation of the cation (from 1.47 Å to 1.43 Å), although this deviation was within the magnitude of error expected from an AM1-level calculation. The most significant deviation observed was a distortion of the ortho chlorines out of the aromatic plane on the formation of the ground state cation configuration. The magnitude of this distortion was approximately 10° in the AO congeners and 5° in BZ 106, which has only one ortho chlorine. This distortion was observed in all four AO congeners examined.

5.2.4 Possible Chloronium Ion Formation from Selected Dechlorination Fragments of Selected Congeners.

The stability of a chloronium ion as an energetically feasible configuration of specific dechlorinated fragments was investigated in the following manner. The three AO congeners, BZ 86, BZ 88, and BZ 93, were each geometrically optimized as ground state neutrals. One ortho chlorine was then deleted from a congener, the molecule was assigned a positive charge, and the geometry was re-optimized. If

the congener contained more than one ortho chlorine, an analogous process was performed beginning with the ground state neutral molecule and then followed by the removal of a different ortho chlorine. This process is demonstrated graphically in Figure 31, which presents results from BZ 86. As this figure indicates, all starting fragments rearranged to a common geometry, the chloronium ion. That is to say, one ortho chlorine became situated in the aromatic plane equidistant (1.78 ± 0.05 Å) from the two ortho carbons to which it was bound. All the optimizations performed for this investigation were performed at the AM1 level of theory. Analogous results were obtained for BZ 88 and BZ 93. The enthalpy of formation of the chloronium ion from these congeners was ~250 kcal/mole. This is significantly lower (~40-50 kcal/mole) than the enthalpy of formation calculated from the corresponding fragment with the geometry of the ground state molecule (see Appendix III). The magnitude of this chloronium ion stabilization may be somewhat exaggerated by the presence of a calculation offset similar to that observed for the cations of the chlorinated benzenes discussed in Section 5.2.2.

It has been reported that biphenyl-based chloronium structures similar to the one presented in Figure 31 have been prepared in solution ^{110,111}. The chemistry of these and related halonium ions have been reviewed and discussed by Olah ¹¹². However, no indication of the relative stabilities of these molecules was given. A set of rigorous *ab initio* calculations (HF/6-31G(d,p), MP2/6-311G(d,p), and MP4(SDTQ)/6-311(2df,p)) on the stability of the chloronium ion with the structure $\text{H}_2\text{C}-\text{CH}_2\text{Cl}^+$ relative to other conformations with the same C-H bonding arrangement

Figure 31 : Optimized Structure of $[M-Cl]^+$ Ion Formed from BZ 86

indicated that the chloronium conformation was the most stable by approximately 12 to 27 kcal/mol^{113,114}. The C-Cl bond lengths were indicated to be 1.84 Å¹¹³. These findings are compatible with the AM1-level calculation performed on the AO-PCB congeners described above. Thus, it is probable that the chloronium ion conformation is indeed the most stable cation structure for AO congeners.

5.2.5 Bond Orders of Selected PCBs

As was indicated in the introductory chapter, Heming and Jianfen⁹⁷ have correlated bond order to activation energy, and have developed “the principle of the smallest bond order” to indicate the weakest bond in the molecule. However, in the case of PCBs, there is very little deviation of bond orders between different chlorine-carbon bonds in the molecule. For example, for the set of congeners BZ 77, BZ 86, BZ 88, BZ 93, BZ 106, and BZ 142 the bond orders for different chlorine-carbon bonds range only from 0.999 to 1.02. Therefore, it is unlikely that this parameter can be a useful discrimination indicator between individual chlorine-carbon bonds. In fact, the C-H bonds are indicated to be the weakest bonds in the molecule but are not normally broken in EI or ECNI.

5.3 QET and Regioselective Loss of Chlorine in PCBs

According to the quasi-equilibrium theory (QET), the observed intensities in a mass spectrum may be related to the thermochemical properties of the analyte

and its fragments. The energy deposited in the ionization step is distributed uniformly among the available rotational or vibrational modes of the molecule. It is assumed that the time required for fragmentation of a polyatomic ion (such as a PCB cation) is long in comparison with vibrational periods. Furthermore, the rate of fragmentation is assumed to be much slower than that of the redistribution of the excitation energy over all internal modes of the ion. The fragmentation products are, therefore, results of a series of competing and consecutive reactions. In this way, the rate constant (k) of fragmentation can be estimated using the following relationship⁷⁸ :

$$k(E) = \frac{\sigma}{h} \left(\frac{W^\ddagger(E-\epsilon_o)}{\rho(E)} \right) \quad (30)$$

In this equation, E is the energy deposited (internal energy), ϵ_o is the activation energy or critical energy of fragmentation (as introduced in Figure 3 of Chapter 1), h is Planck's constant, $W^\ddagger(E-\epsilon_o)$ is the number of vibrational and rotational states of the activated complex having an energy in the range from E to $E-\epsilon_o$, $\rho(E)$ is the density of states of the reactant ion, and σ is a symmetry factor to account for identical reactions. Equation 30 can be reduced to a more workable form by assuming, among other things, that excited electronic states are not involved, and oscillations are harmonic^{79,80,83}. This leads to the following equation :

$$k = \nu \left(\frac{E - \epsilon_o}{E} \right)^{s-1} \quad (31)$$

where ν is the frequency factor and accounts for the ratio of the product of the vibrational frequencies of the activated complex to that of the dissociating ion. The term s refers to the effective number⁹ of vibrational degrees of freedom. In the present investigation in which similar bond dissociations are investigated, the terms s and ν will be considered to be effectively equal for dechlorinations occurring from the same reactant. Likewise, E will also be the same. Therefore, the only variable in comparing a set of similar bond dissociations in the same molecule is ϵ_0 . In Figure 3 of Chapter 1, and in the accompanying discussion, the activation energy for the bond cleavage in the cationic state was indicated by the symbol ϵ_0^c rather than ϵ_0 ; therefore, this symbol will also be used here. The term ϵ_0^c is related to enthalpy changes since the magnitude of ϵ_0^c must be at least as large as the difference in the enthalpies of formation between the products and reactants described in Equation 25 (see also Figure 3). As discussed in Section 5.2.2.2, the relative difference in this enthalpy change with the loss of different chlorines from the same polychlorinated molecule is indicated by the relative difference in the corresponding enthalpies of formation for the appropriate dechlorinated fragments. These enthalpies of formation are presented in Appendix III.

The rate constant of fragment production, $k(E)$, defines the quantity of fragments produced within the specific time scale appropriate to the mass spectrometer being used. Some fraction of the fragments produced will be lost by

⁹

The number of vibrational degrees of freedom for a non-linear molecule can be determined from: $s = 3N - 6$, where N is the total number of atoms.

subsequent reactions or via venting. Nevertheless, a representative sample of ionic fragments in their appropriate relative abundances will be extracted from the source and mass analysed. All things being equal, the relative abundance of a given ion reflects the relative concentration of that ion present in the source. If two different m/z fragment ions originate from the same reactant, then the relative rate of fragment production is related to the relative ion abundance. This is described in the following equation :

$$\frac{\text{Ion Abundance } [M-A]^+}{\text{Ion Abundance } [M-B]^+} \propto \frac{(1 - e^{-k_a t})}{(1 - e^{-k_b t})} \quad (32)$$

Here t is the total time of ion formation, k_a is the rate constant of fragment production for fragment $[M-A]^+$, and k_b is the rate constant of fragment production for fragment $[M-B]^+$.

QET is applicable to both cations and anions; however, the assumption of unimolecular dissociation is more likely to be valid in EI, where pressure is relatively low, than in ECNI, where pressure is relatively high. It is possible that the $[M]^{\bullet+}$ decomposition described in Equations 27 and 28 may be described by QET, although it is also possible that repulsive negative-ion resonance states (NIRS) and repulsive anion states are involved. These types of states may lead to fragmentation rates which are faster than redistribution of excitation energy over all internal modes of the ion such that QET does not apply (see Section 1.5).

5.4 Chapter Summary

In this chapter, the calculations of a number of molecular properties are discussed and critically evaluated. Quasi-equilibrium theory was introduced as the link between the calculated thermochemical values and the resulting mass spectra. The calculated thermochemical data were presented to complement those experimental results presented in the preceding chapter and to facilitate the discussion of the experimental findings in the following two chapters.

Chapter 6 : Electron Impact Induced Dechlorinations

6.1 Introduction

This chapter will discuss the regioselective nature of EI induced dechlorinations. Experimental results were presented in Section 4.2. This chapter is organized much like Section 4.2, where the regioselective losses in the formation of the $[M-X]^+$ and $[M-2X]^+$ fragments were discussed separately and sequentially.

6.2 Regioselective Loss of Chlorine in the Formation of the $[M-X]^+$ Fragment from Labelled AO Congeners

In Section 4.2.1, the sub-set of labelled congeners with at least one ortho-chlorine on each phenyl ring (the AO congeners) was the only set examined for the investigation of regioselective bias in the formation of the $[M-X]^+$ fragment. Therefore, any conclusions that result from this discussion are, at best, applicable only to the AO sub-set. At worst, conclusions are applicable only to the specific 27 AO congeners monitored. The data presented in Table 16 suggested that the results obtained on the Varian Saturn were slightly different from the results obtained on the VG ZAB. However, there were too few measurements for this observation to be made with high confidence. Therefore, only the average percent label lost will be addressed.

From Table 16, a few important conclusions can be drawn. Specifically, there appeared to be an exclusive loss of ortho-chlorine in the formation of $[M-X]^+$. The tendency of the ortho-chlorine to be lost from the less chlorinated ring was correlated to specific structural properties. This correlation implied a very specific

dechlorination mechanism. The supporting evidence for these statements will be developed in the following paragraphs.

The exclusive loss of ortho-chlorine can be demonstrated most effectively with the labelled AO congeners that have been synthesized from two different starting materials. There were three such congeners: BZ 86 (2,2',3,4,5-) prepared from both BZ 38 and BZ 61; BZ 88 (2,2',3,4,6-) prepared from both BZ 30 and BZ 62; and BZ 93 (2,3',3,5,6-) prepared from both BZ 23 and BZ 65. The structure of these six labelled congeners and the fraction of label lost in forming $[M-X]^+$ after electron impact ionization are presented in Table 30. The results from BZ 86 clearly indicated an exclusive loss of ortho-chlorine. In the case of BZ 88, the fraction of label lost from the product that contained two labels compared to the product that contains one label was similar. This implies that the label was not lost from the meta position. In the BZ 93 product that contained only one, this label was present on the less chlorinated ring and was lost 35% of the time. In the BZ 93 product that contained two labels, the labels were lost 70% of the time. Because of the symmetry in the more highly chlorinated ring of BZ 93, it can be concluded that each ortho-chlorine was lost one third of the time, indicating exclusive ortho-chlorine loss.

The exclusive loss of ortho-chlorine can be explained if the activation energy for the dechlorination reaction leading to loss of ortho-chlorine was less than the activation energy for other dechlorination reactions. The activation energy for a given fragmentation must be at least as great as the difference in enthalpies of

Table 30 : Selected Average Percent-Label-Lost Values for the Formation of the $[M-X]^+$ Fragment

Note : error on measurements < 5 (in percent units)

formation between the molecular ion and the particular fragments. The stability of the chloronium ion (see Section 5.2.4) implies that this fragment is more stable than other possible fragments, which is consistent with the exclusive loss of ortho-chlorine. Therefore, our observation of exclusive loss of ortho-chlorine is in accordance with the structure of the $[M-X]^+$ ion resembling a chloronium ion.

From the few results presented in Table 30, it is notable that BZ 86 and BZ 93 had a similar tendency (36% verses 35%, respectively) to lose an ortho-chlorine from the less chlorinated ring, while BZ 88 had quite a different tendency (48%). To further investigate this difference, all the AO congeners containing one label were examined (see Table 31). Of the set presented here, all the congeners with one meta-chlorine on the more chlorinated ring had a similar tendency to lose the labelled ortho-chlorine on the less chlorinated ring. This set of four congeners had an average label loss of 47% with a standard deviation of only 1.1. Similarly, all the congeners with two meta-chlorine on the more chlorinated ring lost the labelled chlorine an average of 34% with a standard deviation of only 1.5. The small standard deviation in each of these sets coupled with the large difference (13% units) between the average values, clearly indicated that these two sets are different.

Several aspects of this correlation are interesting. First, the total number of chlorines in the congener is unrelated to the percentage of label lost. This is exactly the opposite of what would be expected if the chlorine were lost randomly. Second, the total number of ortho-chlorines on the more chlorinated ring also did

Table 31 : Selected Average Percent-Label-Lost Values for the Formation of the $[M-X]^+$ Fragment

Structure	% ^{37}Cl lost	Structure	% ^{37}Cl lost
BZ 41	47%
BZ 45	46%
BZ 48	45%
BZ 88	48%	BZ 88	53%
BZ 43	32%
BZ 86	36%	BZ 86	99%
BZ 93	35%	BZ 93	70%
BZ 142	34%		

Note : error on measurements < 5 (in percent units)

not have any influence on the tendency to lose the ortho-label on the same ring. This was also unexpected.

The relationship between the loss of an ortho-chlorine and the number of meta-chlorines present can be understood by examining the relationship between the reactive ortho-chlorines and the moderating meta-chlorines. A chlorine bound to an aromatic ring has a maximum resonance effect at positions ortho or para from its position in the aromatic ring. In the case of a chlorine meta- to the biphenyl linkage (position 3- or 5-), the resonance effect induced by this chlorine would occur at positions 2- and 6- (as well as at position 4-) relative to the biphenyl linkage. It is reasonable that the presence of two chlorines in meta-positions (relative to the biphenyl linkage; i.e., positions 3-, and 5-) would have a greater resonance effect than the presence of one meta-chlorine. Greater resonance stabilization facilitates, among other things, cation formation at the ortho-carbon.

The correlation between ortho-chlorine lability and the number of meta-chlorines suggests a particular reaction mechanism. Specifically, the formation of a chloronium-ion structure from a concerted chlorine-to-carbon bond breaking and a hypervalent chlorine-to-carbon bond formation. As previously indicated, a chloronium ion was the most stable dechlorinated fragment structure determined by our calculation methods (see also Appendix III). The stability of the chloronium-ion structure was used to explain the exclusive loss of ortho-chlorine. However, the preferred loss of ortho-chlorine from the more highly chlorinated ring indicates the presence of an activation energy barrier greater than the difference in enthalpy of

formation between the molecular ion and the chloronium ion. In other words, a reverse activation energy barrier must be present. Furthermore, this reverse activation energy barrier must be lower for the loss of an ortho-chlorine from an aromatic ring containing two meta-chlorines than it is for an ortho-chlorine from an aromatic ring containing no meta chlorine. To demonstrate this, a rough schematic of the energy barrier to the formation of $[M-Cl]^+$ from the molecular ion of BZ 86 is presented in Figure 32.

Further evidence supporting the above mechanism comes from an inspection of the mass spectra of two polybrominated biphenyls (PBBs). Specifically, these two PBBs are the isomers 3,3',5,5'- tetrabromobiphenyl and 2,2',5,5'- tetrabromobiphenyl. These spectra are presented in Figures 33 and 34, respectively. Since the steric repulsion between ortho-bromines is expected to be much greater than the steric repulsion between ortho-chlorines, it is reasonable to assume that the bending of the ortho-carbon-bromine bond out of the aromatic plane would be more pronounced than that of the ortho-carbon-chlorine bond. We have hypothesized a concerted bond-formation-bond-breaking transition state leading to the $[M-Cl]^+$ chloronium ion. Based on this, it is reasonable that an analogous, yet lower energy, transition state would lead to the formation of the $[M-Br]^+$ bromonium ion. If this is true, then the relative intensity of the $[M-Br]^+$ bromonium ion in the mass spectrum of 2,2',5,5'- tetrabromobiphenyl would be expected to be greater than the relative intensity of the $[M-Cl]^+$ chloronium ion in the mass spectrum of analogous PCBs under similar experimental conditions. In AO-

Figure 32 - Dechlorination Reaction of BZ 86

Figure 33 - 3,3',5,5' - Tetrabromobiphenyl, EI Spectrum

Figure 34 - 2,2',5,5' - Tetrabromobiphenyl, EI Spectrum

PCBs, the intensity of the $[M-Cl]^+$ ion was ~30 % of the base peak, while in 2,2',5,5'-tetrabromobiphenyl the $[M-Br]^+$ ion was the most intense ion in the spectrum (i.e., ~100% abundance). The spectrum of 3,3',5,5'-tetrabromobiphenyl, which does not contain ortho-bromine, is presented for comparison. No appreciable $[M-Br]^+$ ions are observed^r in this spectrum.

The chloronium model proposed here is distinct from models proposed by other researchers. At the same time, it is consistent with the findings of a number of these researchers. For example, Hass et al.⁵² indicated that the loss of $Cl\bullet$ is not the result of a simple cleavage. This is consistent with our model. When Levy and Oswald⁵³ suggested the formation of a chloronium ion, it was introduced as a reaction intermediate rather than an end product. This again, is distinct from, yet consistent with, our model. In the work of Lepine et al.⁴⁶, the AO congeners examined formed $[M-Cl]^+$ fragments with a loss of chlorine that was consistent with an exclusive loss of an ortho-chlorine, as would be predicted from our model. On the other hand, the formation of a chloronium ion centred on one aromatic ring (proposed by Bolgar et al.⁴⁹ - see Figure 2) is very different from the formation of a chloronium ion bridging the two aromatic rings (our proposal - see Figure 31). The model of Bolgar et al.⁴⁹ implies that the presence of a meta chlorine "cis" to the departing ortho-chlorine should have a different effect than a meta chlorine "trans"

^r The $[M-Br]^+$ ion from a Tetrabromobiphenyl is observed in the range from m/z 387 to m/z 394.

to the departing ortho-chlorine. This was not observed in our study. However, the model proposed by Bolgar et al.⁴⁹ was designed to explain the intensity of the $[M-Cl]^+$ fragment relative to the molecular ion. This variation was not considered in our model. Furthermore, our model is specific to the AO congeners, and because of the nature of our model, other mechanisms must be responsible for the observed $[M-Cl]^+$ fragments in non-AO congeners. Thus, the model of Bolgar et al.⁴⁹ may explain the formation of the $[M-Cl]^+$ fragments in those congeners; however, we have not investigated that issue here. In summary, our model is consistent with many of the results presented by other researchers who investigated $[M-Cl]^+$ reaction mechanisms.

6.3 Regioselective Loss of Chlorine in the Formation of $[M-2X]^+$

The experimentally measured percent of label lost in the formation of $[M-2X]^+$ was described in Section 4.2.2 and presented in Table 17. In order to explain these results, selected values from Table 17 are presented in Table 32 and Table 33. In Table 32, the structure and percent-label-lost values for 12 congeners containing only one label are presented. This table is divided into four quadrants, each of which contains labelled congeners produced from a different initial congener. One of the sets was from a trichlorobiphenyl starting material, two were from tetrachlorobiphenyl starting materials, and the other was from the pentachlorobiphenyl starting material. In Table 32, the measured relative percent of the three ion types ; $[M-2(^{37}Cl)]^+$, $[M-Cl^{37}Cl]^+$ and $[M-2Cl]^+$ are presented,

Table 32 : Percent Label Lost in Forming [M-2X]⁺ From Selected Congeners Which Contain Only One Label

Structure	Fraction				Structure	Fraction			
	M-2(³⁷ Cl) (Random)	M-Cl(³⁷ Cl) (Random)	M-2Cl (Random)	Label Lost (Random)		M-2(³⁷ Cl) (Random)	M-Cl(³⁷ Cl) (Random)	M-2Cl (Random)	Label Lost (Random)
BZ 45	0% (0%)	66% (50%)	34% (50%)	0.33 (0.25)	BZ 93	0% (0%)	60% (40%)	40% (60%)	0.30 (0.20)
BZ 59	0% (0%)	61% (50%)	39% (50%)	0.30 (0.25)	BZ 112	0% (0%)	53% (40%)	47% (60%)	0.27 (0.20)
BZ 64	0% (0%)	60% (50%)	40% (50%)	0.30 (0.25)	BZ 117	0% (0%)	52% (40%)	48% (60%)	0.26 (0.20)
BZ 86	0% (0%)	62% (40%)	38% (60%)	0.31 (0.20)	BZ 142	0% (0%)	52% (33%)	48% (67%)	0.26 (0.17)
BZ 106	0% (0%)	57% (40%)	43% (60%)	0.29 (0.20)	BZ 160	0% (0%)	53% (33%)	47% (67%)	0.29 (0.17)
BZ 114	0% (0%)	58% (40%)	42% (60%)	0.29 (0.20)	BZ 166	0% (0%)	50% (33%)	50% (67%)	0.25 (0.17)

Table 33 : Percent Label Lost in Forming [M-2X]⁺ From Selected Congeners Which Contain Two Labels

Structure	Fraction				Structure	Fraction			
	M-2(³⁷ Cl) (Random)	M-Cl(³⁷ Cl) (Random)	M-2Cl (Random)	Label Lost (Random)		M-2(³⁷ Cl) (Random)	M-Cl(³⁷ Cl) (Random)	M-2Cl (Random)	Label Lost (Random)
BZ 87	17% (10%)	62% (60%)	21% (30%)	0.48 (0.40)	BZ 151	15% (7%)	64% (53%)	22% (40%)	0.47 (0.33)
BZ 82	14% (10%)	67% (60%)	18% (30%)	0.48 (0.40)	BZ 134	10% (7%)	68% (53%)	22% (40%)	0.44 (0.33)
BZ 105	13% (10%)	62% (60%)	24% (30%)	0.45 (0.40)	BZ 163	8% (7%)	64% (53%)	28% (40%)	0.40 (0.33)
BZ 141	13% (7%)	68% (53%)	19% (40%)	0.47 (0.33)	BZ 185	12% (5%)	63% (48%)	25% (48%)	0.43 (0.29)
BZ 129	15% (7%)	61% (53%)	24% (40%)	0.46 (0.33)	BZ 173	15% (5%)	56% (48%)	29% (48%)	0.43 (0.29)
BZ 156	11% (7%)	64% (53%)	25% (40%)	0.43 (0.33)	BZ 190	7% (5%)	64% (48%)	29% (48%)	0.39 (0.29)

along with the corresponding values for the random loss of chlorines (*presented in italics and contained in brackets*). The random loss values were extracted from Figure 12 (Chapter 2). The corresponding fraction-of-label-lost values for both the measured and random losses are also presented. In Table 33, an analogous set of data is presented for selected doubly labelled congeners. Table 33 is also divided into four quadrants and the data is presented in the same manner as in Table 32.

The fraction-of-label-lost values (see Tables 32 and 33) decreased as the total number of chlorines in the molecule increased. This property is emphasized in Figure 35, where the fraction-of-label-lost values for all those congeners investigated (see Table 17) are plotted against the total number of chlorines. A decrease in the fraction-of-label-lost values was expected for the case of a random loss of label, and this is also demonstrated in Figure 35. The difference between the fraction-of-label-lost values observed and those expected for a random loss of label increased with the total number of chlorines in the molecule. At the same time, the observed fraction-of-label-lost values were always higher than the corresponding random loss values. These observations were consistent with an interpretation involving multiple reaction mechanisms leading to the formation of $[M-2Cl]^+\bullet$; at least one of these mechanisms involved a specific loss of chlorines, whereas others involved a random loss of chlorines.

For the most part, the location of the ortho-, meta-, or para- labels to the biphenyl linkage did not seem to have a significant influence on the fraction-of-

Figure 35 : Relationship Between Fraction of Label Lost and Total Number of Chlorines in the Labelled Congeners Studied

label-lost value. However, the determination of structural-reactivity relationship for $[M-2X]^+$ ion formation was complicated by the presence of both random and non-random chlorine loss. For congeners with the same total number of chlorines, any contribution from random processes are constant. Therefore, an analysis of a significant number of labelled congeners at the same level of chlorination provided a means to investigate possible label-position effects. To help visualize these, all the pentachlorobiphenyls presented in Table 17 were sorted by the chlorination pattern on the less-highly-chlorinated ring and then plotted. This plot is presented in Figure 36. The average fraction-of-label-lost value and the standard deviation for each of the chlorination pattern sub-sets are presented in Table 34. The average fraction-of-label-lost value for all the labelled congeners with one label was 0.29 with a standard deviation of 0.02. The labelled congeners with two labels had an average fraction-of-label-lost value of 0.48 with a standard deviation of 0.04. The low standard deviation in each of these cases indicated that the tendency to lose a label was unrelated to the position of the label. Even so, a subtle yet likely real ortho-position bias was observed.

The similarity of the observed fraction-of-label-lost values required a more detailed analysis. The fraction-of-label-lost value expected for a random loss of label is simply the number of labels divided by the total number of chlorines (including labels). This relationship can be restated to indicate the total number of active chlorines involved in a particular loss. This relationship is presented in Equation 33.

Figure 36 : Relationship Between Fraction of Label Lost and Location of Label in the Less Highly Chlorinated Ring

^ Pentachlorobiphenyls x Random

Table 34 : Average and Standard Deviation of Sub-sets in Figure 36

Label Position in Less Highly Chlorinated Ring	Average	Standard Deviation	Total Number of Labels	Number Active Chlorines
Ortho (2'-)	0.32	0.02	1	3.1
Meta (3'-)	0.28	0.01	1	3.6
Para (4'-)	0.29	0.02	1	3.4
Ortho (2'-)	0.53	0.07	2	3.8
Meta (3'-)	0.46	0.04	2	4.4
Para (4'-)	0.47	0.03	2	4.3
Ortho-Meta-Cis (2',3'-)	0.47	0.03	2	4.2
Ortho-Meta-Trans (2',5'-)	0.48	0.02	2	4.2
Meta-Para (3',4'-)	0.43	0.03	2	4.6
All With One Label	0.29	0.02	1	3.4
All With Two Labels	0.48	0.04	2	4.2

$$N_{Total\ active\ Cl} = \frac{1}{(Fraction\ Label\ Lost)} \times (N_{Labels}) \quad (33)$$

The average fraction-of-label-lost value for all the labelled pentachlorobiphenyl congeners containing one label was 0.29. This value indicates 3.4 active chlorines. In the case of the pentachlorobiphenyls with two labels, the average fraction-of-label-lost value was 0.48, indicating 4.2 active chlorines.

In the set of labelled congeners investigated in this thesis, all the congeners containing one label possessed a common structural property. The label was contained on the less highly chlorinated aromatic ring with no other chlorines. The number of chlorines on the more highly chlorinated ring varied between three, four, and five chlorines. Even though the total number of chlorines varied, the total number of active chlorines remained at approximately three. The sub-set of labelled congeners which contained two labelled chlorines also contained these chlorines on an aromatic ring with no other chlorines. In these cases, approximately four active chlorines were indicated.

This raises some interesting questions. Why did the number of active chlorines remain constant within a sub-set and why did the number of active chlorines change between the two sub-sets ? The information required to answer these questions will be developed below.

As was the case in the $[M-X]^+$ loss, the congeners which were produced from two different starting materials provided additional insights (see Table 35 where the results of the percent label loss values for all the congeners containing two labels

Table 35 : Percent Label Lost in Forming [M-2X]⁺ from Selected Congeners Which Contain One Label on each Aromatic Ring

Structure	Fraction				Structure	Fraction			
	M-2(³⁷ Cl) (Random)	M-Cl(³⁷ Cl) (Random)	M-2Cl (Random)	Label Lost (Random)		M-2(³⁷ Cl) (Random)	M-Cl(³⁷ Cl) (Random)	M-2Cl (Random)	Label Lost (Random)
BZ 86	32% (10%)	60% (60%)	8% (30%)	0.62 (0.40)	BZ 109	5% (10%)	74% (60%)	21% (30%)	0.42 (0.40)
	3.2 Active Chlorines					4.7 Active Chlorines
BZ 88	14% (10%)	63% (60%)	23% (30%)	0.45 (0.40)	BZ 114	15% (10%)	62% (60%)	23% (30%)	0.46 (0.40)
	4.4 Active Chlorines					4.4 Active Chlorines
BZ 93	15% (10%)	61% (60%)	24% (30%)	0.52 (0.40)	BZ 115	12% (10%)	64% (60%)	24% (30%)	0.44 (0.40)
	3.9 Active Chlorines					4.5 Active Chlorines
BZ 106	16% (10%)	66% (60%)	18% (30%)	0.49 (0.40)	BZ 117	19% (10%)	63% (60%)	17% (30%)	0.51 (0.40)
	4.1 Active Chlorines					3.9 Active Chlorines			

that were also produced from two sources are presented). In all these congeners, one of the two labels was contained on the less highly chlorinated ring, and the other on the more highly chlorinated ring. Furthermore, the label on the less highly chlorinated ring was in the same position as the label in the corresponding congener which contained only one label. Therefore, the difference between the fraction-of-label-lost value for a congener containing one label and the value for the analogous congener containing two labels provided information on the tendency to lose specific chlorines from the more highly chlorinated ring. For the three congeners in the sub-set containing a single label at the ortho-position on the less highly chlorinated ring, the fraction-of-label-lost values for this chlorine were approximately 0.32 (see Table 34). For the remaining five congeners in the sub-set containing labels in the meta- or para-positions, the corresponding values were approximately 0.28 (see Table 34). Therefore, in all cases the four chlorines on the more highly chlorinated ring were lost approximately 70% of the time (a fraction lost value of 0.70). Under these conditions, a random loss of any of these four chlorines would then be indicated by approximately a fraction lost value of 0.18.

Three congeners, BZ 88, BZ 109, and BZ 115 (see Table 17 and Table 35) contain a meta-chlorine label on the more highly chlorinated aromatic ring. The fraction-of-label-lost value for this meta-chlorine was 0.13, 0.15 and 0.15 respectively. Similarly, BZ 114, containing a para-chlorine label on the more highly chlorinated aromatic ring, had a fraction of label lost value for this labelled para-

chlorine of 0.17 ^s. Thus, both the meta- and para-chlorines on the more highly chlorinated aromatic ring were lost slightly less than expected for a random loss of chlorine. Three of the four congeners which contained an ortho-chlorine label on the more highly chlorinated aromatic ring also had a similar tendency to lose that label. Specifically, the fraction-of-label-lost values from the ortho-chlorine label on the more chlorinated aromatic ring were 0.22 for BZ 93, 0.20 for BZ 106, and 0.25 for BZ 117. Thus, the ortho-chlorines on the more highly chlorinated ring were lost slightly more than expected for a random loss of chlorine.

The other congener, BZ 86 (see Table 17 and Table 35), which contained an ortho-chlorine label on the more highly chlorinated aromatic ring, also contained an ortho-chlorine label on the less highly chlorinated aromatic ring. In this congener, both ortho-chlorines have an identical (0.31) fraction-of-label-lost values. The fraction-of-label-lost value for the congener containing two ortho-chlorine labels was 0.62, which indicated 3.2 active chlorines. The observed percentage of [M-2(³⁷Cl)]⁺• was 32%, [M-Cl³⁷Cl]⁺• was 60%, and [M-2Cl]⁺• was 8% (see Table 35). These values are not too different from to the probabilities of selecting two balls from a set containing one black ball and two white balls (●○○), which would have the corresponding values of 33% for the combination of two white balls (○○), 66% for the combination of one white and one black (●○), and 0% for the combination

s

e.g., The fraction-of-label lost value for BZ 114 with one label was 0.29 (see Table 32), the value for BZ 114 with two labels was 0.46 (see Table 35); therefore, the fraction of chlorine loss from position 4- is 0.17, while 4'- is 0.29.

of two black balls (●●) (see Figure 12).

The location of labelled chlorines adjacent to each other, as in positions 2',3'- or 3',4'-, did not lead to an increase in the relative abundance of the $[M-2(^{37}\text{Cl})]^+\bullet$ fragment ion (see Table 17 and 33) when compared to the location of labels across the aromatic ring as in positions 2',5'- (see Table 17 and 33). In fact, the location of labels in positions 3',4'- led to a lower fraction of label lost, and lower loss of two labels together, than did other combinations of two labels. As an extreme example, BZ 114 (2,3,4,4',5-) containing labels at positions 4- and 4'- (para positions on opposite aromatic rings) lost the two labels together 15% of the time (see Table 35), whereas BZ 156 (2,3,3',4,4',5-) containing adjacent labels at positions 3'- and 4'- lost the two labels together only 11% of the time (see Table 33).

These observations are consistent with a model where some degree of chlorine scrambling occurs on each aromatic ring prior to dechlorination from specific sites. The active sites where dechlorination takes place are hypothesized to be the ortho positions. Furthermore, for congeners that contain only a single chlorine on the less highly chlorinated ring, it would appear that there are only three as opposed to four active sites. It should also be noted the congeners that contained one labelled chlorine alone on the less highly chlorinated aromatic ring had a significant loss of two unlabelled chlorines, indicating that chlorines could be lost from the more highly chlorinated ring alone. The previously mentioned bias favouring ortho-chlorine loss suggests that the ortho-sites may be the dechlorination sites. In this hypothesis, chlorines that are not initially located in the

ortho-position migrate to this position for dechlorination. The efficiency of this migration may depend on which position the chlorine is migrating from as well as the structure of the congener, which manifests as different fraction-of-label-lost values depending on the label positions.

In order to further understand why the ortho positions would be preferred dechlorination sites, the possibility of structural rearrangement induced by dechlorination was investigated by examining the energetics of ion structures with the formula $[C_{12}H_8]^+\bullet$. Four isomers with this formula are listed in the data base of Lias et al⁸¹. The structures of these isomers and their corresponding enthalpies of formation are presented in Figure 37. The acenaphthylene structure is the most stable isomer listed; however, very significant structural rearrangement would be required to form this ion from biphenyl. This is also true for the other two naphthalene derivatives. The biphenylene structure is a more likely rearrangement product ion from biphenyl, and its formation would explain the activity of the ortho sites. Biphenylene can be synthesized by the induced dehalogenation of 2,2'-diiodobiphenyl or 2,2'-dibromobiphenyl¹¹⁵. In addition, chlorinated biphenylenes have been identified in soot after the burning of PCBs^{3,116}. The possibility of chlorinated biphenylenes as pyrolysis products of PCBs is relevant; it has been suggested that the EI process "has considerable similarity to the fragmentation process associated with the thermal decomposition of organic molecules."¹¹⁷. Additional support comes from a CID study performed on a number of disubstituted biphenyls¹¹⁸. In that study, an intense ion at m/z 152 was identified in the mass

Figure 37 : Structures* of $C_{12}H_8^+$ Ions and $C_{12}H_8$ Neutrals

Biphenylene

$\Delta_f H^\circ$, gas = 104 kcal/mol

$\Delta_f H^\circ$, ion = 279 kcal/mol

Acenaphthylene

$\Delta_f H^\circ$, gas = 62 kcal/mol

$\Delta_f H^\circ$, ion = 252 kcal/mol

Naphthalene, 1-ethynyl-

$\Delta_f H^\circ$, gas = 93 kcal/mol

$\Delta_f H^\circ$, ion = 278 kcal/mol

Naphthalene, 2-ethynyl-

$\Delta_f H^\circ$, gas = 93 kcal/mol

$\Delta_f H^\circ$, ion = 280 kcal/mol

* As per, Lias et al., J. Phys. Chem. Ref. Data, Vol. 17, Suppl. 1 (1988)

spectra of a number of the disubstituted biphenyls. The CID spectrum of this ion was identical for many of these biphenyl derivatives and it was proposed that this common ion was the biphenylene radical cation. Unfortunately, from the experiments performed in this thesis work, the formation of a biphenylene ion can only be hypothesized.

To reiterate our data suggest that partial chlorine scrambling is localized within each phenyl ring. The two active sites on each aromatic ring are interpreted as the ortho sites. Loss of adjacent chlorines on the same aromatic ring does not appear to be favoured.

6.4 Conclusion

Information is presented in this chapter concerning the dechlorination mechanisms that are induced by electron impact ionization. It is demonstrated that the AO congeners lose exclusively an ortho-chlorine to form the $[M-X]^+$ fragment. In this sub-set of PCB congeners there are at least two ortho-chlorines which could be lost. The presence of two additional meta-chlorines on the same aromatic ring increased the probability that this ortho-chlorine would be lost. It is hypothesized that the presence of meta-chlorines stabilized the transition state and lowered the activation energy relative to the aromatic ring without meta-chlorines. The $[M-X]^+$ ion is proposed to have a chloronium ion structure whose formation involves concerted bond breaking and forming. Data for the $[M-2X]^+$ ion are consistent with a hypothesis that the ion has a biphenylene structure. For congeners that have at

least two chlorines on each phenyl ring, it appears that there are four active sites, the ortho positions, where dechlorination can occur. This loss occurs only after partial chlorine scrambling, localized to each ring.

Chapter 7 : Electron-Capture-Induced Dechlorinations

7.1 Introduction

This chapter will discuss the regioselective nature of electron-capture-induced dechlorinations based on experimental results presented in Section 4.3. The chapter is divided into three major parts: Section 7.2 discusses the percent-label-lost in the formation of the fragment ion $[M-X]^+$; Section 7.3 presents an analogous discussion on the formation of the fragment ion $[M+H-X]^+$, along with the method used to classify this reaction as either wall-modified or gas-phase radical; Section 7.4 examines the percent-label-lost in the formation of the fragment ion $[M+O-X]^+$.

7.2 Regioselective Loss of Chlorine in the Formation of $[M-X]^+$

ECNI data were collected under a set of experimental conditions defined in Table 7. The experimental results were processed to yield percent-label-lost values and corresponding standard deviations shown in Table 18 (see Chapter 4 for details)

Since the experiments were conducted under several conditions, reliable data were selected in the following manner. If the standard deviation for a particular averaged percent-label-lost value was small, it was then assumed that variation in the experimental parameters did not affect the tendency of the label to be lost. In order to gauge what value of standard deviation could be considered small, the standard deviations observed for the $[M-X]^+$ fragments formed in the EI

experiments were used as benchmarks. The spectra collected from EI/MS experiments are generally considered to be reproducible even with slight changes in experimental parameters. This is demonstrated by the widespread use of EI/MS spectral libraries. In contrast, the spectra obtained from ECNI/MS have been demonstrated to vary between instruments and with relatively minor experimental parameter variations⁷⁰. Standard deviations observed for the EI [M-X]⁺ fragments were presented in Table 16. Four of the average values presented in Table 16 had standard deviations of approximately 4. As before, a standard deviation value of 5 was used as the “cut-off” value to determine variation in ECNI percent-label-lost averages.

In Table 18, only 5 of the 48 congeners with reliable data have standard deviations greater than 5 (and 3 of these 5 values have standard deviations of only 6). This reproducibility in the percent-label-lost values for 43 different congeners provided a sufficiently large set to permit the observation of specific structure-dechlorination relationships.

In order to describe the structure-dechlorination relationships that were observed in this investigation, PCBs are classified in the following manner. Each of the two phenyl rings is considered to be a substituent of the other. The labelled congeners with the same chlorination pattern in the more highly chlorinated phenyl ring are grouped together. For discussion purposes, the more highly chlorinated phenyl ring will be referred to as ring “A” and the less highly chlorinated phenyl ring as ring “B”

There are ten sets defined in Table 18. This represents a significant range of ring "A" properties; in fact, all the arrangements of three, four or five chlorines on ring "A" are represented. To determine any common influence of ring "A", the percent-label-lost values were initially used to indicate one of three classifications: 1) loss of label equivalent to a random loss, 2) loss of label greater than a random loss, or 3) loss of label smaller than a random loss. For the purpose of this classification, each measured percent-label-lost value was considered to have a $\pm$ range of two times the reported standard deviation.

Consistent structure-dechlorination relationships were observed for those sets of structures having chlorines at positions 3,4, and 5 on ring "A". For instance, all the congeners with the 3,4,5- pattern on ring "A" (BZ 38 set) had loss-of-label values which were greater than a random loss. All the congeners with the 2,3,4,5- pattern on ring "A" (BZ 61 set) had loss of label which were equivalent to a random loss. All the congeners with the 2,3,4,5,6- pattern on ring "A" (BZ 116 set) had loss of label which were smaller than a random loss. None of the other sets of ring "A" patterns had loss of label values which could be classified as being self-consistent.

In order to further investigate the influence of one aromatic ring on another, the congeners and values presented in Table 18 were sorted by the chlorine pattern on ring "B". The nature of the specific labelled products enabled an analysis of six sets of ring "B" chlorination patterns: ortho-position (2'-), meta-position (3'-), para-position (4'-), ortho-meta-cis-position (2',3'-), ortho-meta-trans-position (2',5'-), and meta-para-position (3',4'-). Of these six sets, only the members of the 3',4'- pattern

set had self-consistent loss-of-label values. These values were classified as smaller than a random loss. To demonstrate this trend, all the congeners that had the 3',4'- pattern set are presented in the right-hand column of Table 36. In this set of seven labelled congeners, the average loss-of-label value was 13% with a standard deviation of 3 (in % units). For comparison, all the congeners with the 2',3'- pattern set are presented in the left-hand column of Table 36. In this set, the percent-label- lost values ranged from 3% to 73%. It is worth noting that the 3,4- configuration is also common to the three ring "A" sets whose component congeners had similar loss-of-label values within a set.

Let us now examine the 2,3,4,5- chlorination pattern on ring "A" (BZ 61 set) in some detail. The members of the set are also produced from a different congener and thus provided additional information on the loss of selected chlorine from ring "A". These are BZ 86, also produced from BZ 38; BZ 106, also from BZ 38; and BZ 114, also from BZ 23. In each of these cases, the product from one starting material contained one label and the product for the other starting material two labels. All those labelled congeners with two labels contained one of their labels at the same position as the corresponding congener with one label. Therefore, to determine the loss from each labelled position, the percent-label-lost value determined for the congener with one label was subtracted from the corresponding value for the congener with two labels.

For BZ 86 (2,2',3,4,5-), position 2- on ring "A" was lost 34% of the time. For BZ 106 (2,3,3',4,5-), position 2- on ring "A" was lost 62% of the time. Both these

Table 36 : Percent-Label-Lost Values for the [M-X]- Fragment from Congeners with Labels in Positions 2',3'- and 3',4'-

Ortho-Meta-cis-Labelled (2',3'-)		Meta-Para-Labelled (3',4'-)
BZ 82	45 % (Random= 40%)	BZ 105	11 % (Random= 40%)
BZ 83	46 % (Random= 40%)	BZ 107	13 % (Random= 40%)
BZ 84	3 % (Random= 40%)	BZ 110	20 % (Random= 40%)
BZ 97	73 % (Random= 40%)	BZ 118	16 % (Random= 40%)
BZ 122	73 % (Random= 40%)	BZ 158	12 % (Random= 33%)
BZ 173	12 % (Random= 29%)	BZ 163	10 % (Random= 33%)
		BZ 190	11 % (Random= 29%)

losses were greater than the 20% that would have been expected if the loss had been purely random. Therefore, these indicate a directed loss of ortho-chlorine on ring "A".

For BZ 114 (2,3,4,4',5-), position 4- on ring "A" was lost 16% of the time. This was smaller than a random loss of label and was equal to the observed loss of label from position 4'- (ring "B"). It was possible that the ortho-position (2-) in BZ 114 had a similarly high tendency to be lost as the ortho-position in BZ 86 and BZ 106.

Each of the four subsets, 2,3,4,5,6- ring "A"; 2,3,4,5- ring "A"; 3,4,5- ring "A"; and 3',4'- ring "B", appeared to retain a specific chlorination pattern in the formation of $[M-X]^-$. In the 2,3,4,5- ring "A" set and the 3,4,5- ring "A" set, the retention of the 3,4,5- chlorination pattern on ring "A" was evident. Furthermore, the 3',4'- ring "B" set also demonstrated retention of the 3',4'- chlorination pattern. The loss of chlorine in the 2,3,4,5,6- ring "A" set occurred predominately from ring "A", and it could be possible that the 3,4,5- chlorination pattern on ring "A" was also retained.

In addition to indicating that certain chlorination patterns were selectively retained in the formation of $[M-X]^-$, the experiment also determined that the percent-label-lost in forming $[M-X]^-$ was independent of both pressure and ventilation rate. This was interpreted as an indication that $[M-X]^-$ could form from $[M]^- \bullet$ via a unimolecular decomposition. Even though QET is applicable to unimolecular decompositions, this would not be the case if the rate of fragmentation was faster than that of redistribution of excitation energy (Section 5.3). As was discussed in Section 1.5 and Section 5.3, it is possible that the negative-ion resonance state

(NIRS) formed by the initial electron capture was either a repulsive state that would lead to immediate fragmentation or a state that facilitated electron transition to a repulsive-anion state that would in turn lead to immediate fragmentation. In these cases, QET would not apply. Nevertheless, if the fragmentation leading to $[M-X]^-$ were to occur under the constraints of QET, an observed regioselective loss could indicate that a relatively stable fragment was formed or that the activation barrier to the favoured fragmentation was somewhat lower than that to unfavoured fragmentations (Equation 32 within Section 5.3).

The accuracy of Hyperchem 4.5 for calculating anion enthalpies was insufficient to permit calculation of reliable values (Section 5.2.1.3). In the neutral molecule, each of the different chlorine-carbon bonds (ie., ortho-chlorine to ortho-carbon, meta-chlorine to meta-carbon, etc.) were indicated to have almost identical bond-strengths (Section 5.2.5). It is possible that the different chlorine-carbon bonds in PCB molecular anions also have almost identical bond-strengths. If this is the case, then some specific, stable, structural conformation could possibly form. Alternately, repulsive-NIRS or repulsive-anion state(s) could be responsible for the observed regioselective dechlorinations. However, these could also not be confirmed by calculation.

Another explanation for the observed regioselective dechlorination bias in the formation $[M-X]^-$ is a possible discrimination in the anion formation from the radical fragment $[M-X]^\bullet$. As discussed in Section 5.2.2.2, it is probable that $[M-X]^-$ forms as a result of a two-electron-capture process (see Equations 27 and 29). The

rate of $[M-X]^-$ formation from $[M-X]^\bullet$ is dependent on the electron capture rate constant for this radical. Furthermore, in order for $[M-X]^-$ to be detected, it must have a sufficiently long lifetime, in the context of the time required to be extracted from the MS source, to travel through the instrument, and to be detected. It is possible that the radical fragments formed (i.e., $[M-X]^\bullet$) from the loss of different chlorines could have significantly different electron capture rate constants, and/or anion lifetimes. Significant differences in either or both of these properties could lead to a discrimination in the formation of $[M-X]^-$ from specific $[M-X]^\bullet$ structures. A bias would be evident even if the original loss of chlorine occurred completely randomly.

It is difficult to measure or predict either electron capture rate constants or anion lifetimes for reactive species such as those radical fragments (e.g. $[M-X]^\bullet$), investigated here. However, electron affinities can be estimated. The electron affinities of all the neutral PCB congeners containing an unchlorinated ring are listed in Table 37. The difference in electron affinities are small and the relatively large uncertainties make definitive comparisons impossible. However, the 3,4- and 3,4,5- chlorination patterns have among the largest electron affinities in their respective chlorination levels. It is possible that the electron capture rate constants or anion lifetimes of those radical fragments containing the 3,4- or 3,4,5- chlorination pattern can also be distinguished from those of other fragments without these chlorination patterns. This could facilitate the selective production of $[M-X]^-$ from these radicals and thus lead to the observed regioselective bias.

Table 37 : Calculated* Electron Affinities of Selected PCB Congeners with an Unchlorinated Aromatic Ring

Congener (BZ#)	Number of Chlorines	Chlorination Pattern	EA (/eV) +/- 0.1
1	1	2 -	0.1
2	1	3 -	0.2
3	1	4 -	0.3
5	2	2,3 -	0.3
7	2	2,4 -	0.3
9	2	2,5 -	0.3
10	2	2,6 -	0.2
12	2	3,4 -	0.4
14	2	3,5 -	0.4
21	3	2,3,4 -	0.4
23	3	2,3,5 -	0.4
24	3	2,3,6 -	0.4
29	3	2,4,5 -	0.5
30	3	2,4,6 -	0.4
38	3	3,4,5 -	0.5
61	4	2,3,4,5, -	0.6
62	4	2,3,4,6 -	0.5
65	4	2,3,5,6 -	0.5
116	5	2,3,4,5,6 -	0.6

* See Section 5.2.2.1 and Appendix II

The apparent preferred retention of the 3,4-, 3,4,5- and 3',4'- chlorination pattern on the formation of the $[M-X]^-$ fragment ion is quite intriguing because the three most toxic PCB's, BZ 77 (3,3',4,4'-), BZ 126 (3,3',4,4',5-), and BZ 169 (3,3',4,4',5,5'-), the so called "coplanar" congeners, all have combinations of these two chlorination patterns on both phenyl rings.

7.3 Electron-Capture-Induced Formation of $[M+H-X]^\bullet$

7.3.1 Distinguishing Between $[M+H-X]^\bullet$ Formed From a Wall-Modified Reaction and $[M+H-X]^\bullet$ Formed From a Gas-Phase-Radical Reaction

7.3.1.1 Derivation of Equations using ECNI Kinetic Model of Sears et al. ⁷³

In the kinetic model of ECNI developed by Sears et al. ⁷³, a set of simultaneous equations was derived to allow calculations of the steady-state concentrations of neutrals as well as ionic species from the original reagent concentrations and appropriate reaction rate constants. From these equations, the steady-state concentrations of ionic species were calculated for different experimental conditions and different rate constants, and compared with the relative abundances of ions in mass spectra. The appropriate production and elimination rates for a given ion type were dependent on the mechanisms of ion formation and destruction. These could also be influenced by instrumental parameters. Many of the critical reaction variables, such as the concentration of thermalised electrons and the diffusion coefficients of relevant species in the reactive plasma, were estimated to a sufficient level of accuracy that mechanistic details could be differentiated ⁷³.

Information was presented in Chapter 4 on the regioselective nature of three types of single dechlorinations in ECNI. One of these ion types, $[M+H-X]^{\bullet+}$, has been proposed by some researchers to originate from a wall-modified reaction⁷². Other investigators, however, argued that the $[M+H-X]^{\bullet+}$ ion of PCBs must be the result of a gas-phase-radical reaction⁶³. In the kinetic model of Sears et al.⁷³, both the wall-modified reaction and the gas-phase-radical reaction were considered. According to this kinetic model, these reactions responded differently to the experimental parameters selected in these investigations.

The $[M-X]^{\bullet-}$ reaction channel was not specifically addressed in the kinetic model described by Sears et al.⁷³. Instead, they modelled the $[M]^{\bullet-}$ ion. From the discussion presented in Section 7.2, it is reasonable to assume that the fraction of $[M]^{\bullet-}$ population partitioned into the $[M-X]^{\bullet-}$ channel was linked to the fraction of the $[M]^{\bullet-}$ signal by a constant factor C_x . In other words, some fraction of the $[M]^{\bullet-}$ population has sufficient energy to fragment and produce the $[M-X]^{\bullet-}$ signal. The equation below restates this in the notation of Sears et al.⁷³:

$$f_{[M-X]^{\bullet-}} = C_x f_{[M]^{\bullet-}} \quad (34)$$

Here $f_{[M-X]^{\bullet-}}$ is the fraction of the total analyte concentration as $[M-X]^{\bullet-}$ and $f_{[M]^{\bullet-}}$ is the fraction of the total analyte concentration as $[M]^{\bullet-}$. The term C_x is a proportionality constant introduced here to express the fraction of $[M]^{\bullet-}$ that fragments to form $[M-X]^{\bullet-}$.

In our investigation, we measured the relative abundance of $[M+H-X]^{\bullet+}$ and

$[M-X]^-$ simultaneously. It is convenient to express the relative amounts of these two ions as a ratio ($[M+H-X]^\bullet$ to $[M-X]^-$). If the appropriate algebraic equations presented by Sears et al.⁷³ are maintained, some of the terms cancel out and result in simplified equations. The appropriate simplified equations for the two cases, A) gas-phase-radical reaction (Equation 35) and B) wall-based reaction (Equation 36), are presented below :

$$\frac{f_{[M+H-X]^\bullet}}{f_{[M-X]^-}} = \frac{k_{emr} k_r [R]}{C_x k_{em}} \times \frac{1}{k_{emr} [e] + \frac{F}{V}} \quad (35)$$

$$\frac{f_{[M+H-X]^\bullet}}{f_{[M-X]^-}} = \frac{k_{ew} b \frac{D_n}{\Lambda^2}}{C_x k_{em}} \times \frac{1}{k_{ew} [e] + \frac{F}{V}} \quad (36)$$

where

k_{emr} = rate constant ($\text{cm}^3 \text{particles}^{-1} \text{s}^{-1}$) for reaction of thermal electrons with the gas-phase-radical modified PCBs

k_r = rate constant ($\text{cm}^3 \text{particles}^{-1} \text{s}^{-1}$) for gas-phase reaction of reagent radicals with neutral PCBs

k_{em} = rate constant ($\text{cm}^3 \text{particles}^{-1} \text{s}^{-1}$) for reaction of thermal electrons with neutral PCBs

k_{ew} = rate constant ($\text{cm}^3 \text{particles}^{-1} \text{s}^{-1}$) for reaction of thermal electrons with the wall-modified PCBs

$[R]$ = total reagent free radical concentrations (radicals cm^{-3})

$[e]$ = electron concentration (electrons cm^{-3})

b = efficiency (0 to 1) of conversion of neutral PCB to wall-modified species by a collision with the source wall (set to 0.1)

D_n = diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$) of neutral species

Λ = characteristic diffusion length (0.13 cm) of ion source

C_x = fraction of $[M]^\bullet$ (0 to 1) that fragments to $[M-X]^-$ (set to 0.1)

F = volumetric flow rate ($\text{cm}^3 \text{s}^{-1}$) of buffer gas (methane) through ion source

V = volume (1 cm^3) of ion source

It is assumed that rate constants (and radical recombination coefficients, etc) did not change within the range of source pressure examined. Thus, the variations that were applied to the pressure and volumetric flow rate could affect only six variables in the two equations above: C_x , b , F , D_n , $[R]$ and $[e]$. The values C_x and b are unknown and were assumed to be constants. For calculation purposes, they were arbitrarily set at 0.1. In our experiments, the value F (volumetric flow rate) was one of the parameters that we varied. The value D_n is inversely proportional to the pressure, which we also varied. The value of $[R]$ and $[e]$ are dependent in a complex manner on both F and D_n (and thus pressure).

The ventilation rate (volumetric flow rate per source volume, F/V) is considered independent of pressure⁷³, although it is dependent on the magnitude of source leaks and the temperature. The volumetric flow rate can be estimated using simple kinetic theory of gases if the magnitude of the holes in the source is known. In short, the pressure, temperature, and molecular weight of the gas define the collision frequency (Z_w), the number of collisions per unit wall surface area per unit time. This wall collision rate (Z_w) can be calculated from the equation presented below¹¹⁹. If the area (A_0) of the leaks (or holes) in the source is known, then the rate of collision with these holes can be determined (see Equation 37). This, of course, will be equivalent to the number of molecules leaving the source per unit time. This value can then be converted to a ventilation rate if an ideal gas is assumed (see Equation 38).

$$Z_w A_0 = \frac{\rho A_0}{(2\pi m k T)^{1/2}} \quad (37)$$

$$F = \frac{\frac{Z_w A_0}{N_a} RT}{\rho} \quad (38)$$

where

ρ = pressure, A_0 = hole area, m = molecular mass (CH_4 - 16 amu),

T = temperature (423 K), k = Boltzmann constant (1.38×10^{-23} J/K),

R = gas constant (8.314 J/(K mol)) , N_a = Avogadro's constant (6.022×10^{23} molecules / mole)

This calculation indicates a ventilation rate of $318 \text{ cm}^3 \text{ s}^{-1}$ for normal operation of the VG ZAB source used in these studies. If an opening the size of the probe inlet hole ($\sim 1.2 \text{ mm ID}$) is included, a ventilation rate of $529 \text{ cm}^3 \text{ s}^{-1}$ is obtained. Therefore, opening or closing the probe inlet hole provides a convenient method of obtaining different ventilation rates.

An interesting aspect of the ventilation rate is that, by varying the leaks in the system, identical temperature and pressure conditions can be obtained with different ventilation rates. Since it is likely that different types of MS sources will have different magnitudes of leaks, similar pressure and temperature conditions may not produce the same results on different instruments.

The diffusion rate is also inversely proportional to pressure. The diffusion coefficient for neutrals (molecular weight > 100 amu) in an ECNI source with methane as a moderator gas can be estimated from the following simplified equation ^{73,t}:

t

This equation as well as Equation 40 and 41 were greatly simplified by assuming such things as constant average molecular diameter ⁷³

$$D_n \text{ (cm}^2\text{sec}^{-1}\text{)} = 0.063 \left(\frac{T}{273}\right)^{\frac{3}{2}} \left(\frac{760}{P}\right) \quad (39)$$

The diffusion of ions is restricted by the natural tendencies toward charge neutrality. If cations or anions move to the wall at a faster rate than their counter ions, then a small potential develops between them. This potential acts to accelerate the movement of the slower ions while decelerating the movement of the faster ions. As a result, the rates of diffusion of both cations and anions (including electrons) become the same. This phenomenon is called ambipolar diffusion. The ambipolar diffusion rate (D_a) under ECNI conditions with CH_4 as a moderator gas can be estimated from the following ⁷³:

$$D_a \text{ (cm}^2\text{sec}^{-1}\text{)} = 0.11 \left(\frac{T}{273}\right)^2 \left(\frac{760}{P}\right) \quad (40)$$

The rate of total radical production (S_r) was estimated by Sears et al.⁷³, as follows :

$$S_r \left(\frac{\text{radicals}}{\text{sec}}\right) = 5 \times 10^{11} (I \times E) \quad (41)$$

In this equation, I (μA) is the intensity of the high energy electron beam entering the source and E (eV) is its energy. The electron energy (E) used in these studies was 150 eV. Sears et al.⁷³ measured the emission and trap currents with an evacuated

source and from this estimated that only 5% of the emission current actually entered the source. From this it was estimated that when 1 mA emission currents were used (as they were in these studies), the term "I" in the above equation would be equal to 50 μ A. This total rate of radical production was related to the steady state concentration of radicals by ⁷³

$$[R] = \frac{-\left(\frac{F}{V}\right) + \sqrt{\left(\frac{F}{V}\right)^2 + \frac{4R_r S_r}{V}}}{2R_r} \quad (42)$$

In the equation above F is the volumetric flow rate, V is the source volume (1 cm³), S_r is the total production rate of radicals (see Equation 41), and R_r is the radical-radical recombination coefficient. In our calculations, we followed the approach of Sears et al.⁷³ by using the rate of recombination of methyl radicals, R_r = 4 x 10⁻¹¹ cm³ s⁻¹, to approximate the rate of recombination of all reagent radicals.

Since the ionizing reagent in ECNI is low energy electrons, the steady state concentration of electrons [e] in the source is an important parameter. Generally in ECNI, low energy electrons are generated by the interaction of high energy electrons with a moderator gas at pressures ^u of 0.1 to 1.0 torr. Methane is the moderator gas most often used and this was also selected for our experiments. The high energy electrons used in ECNI, are generated in the same manner as in EI,

^u

Some authors⁶⁶ refer to this as high pressure (in context of other MS applications)

that is, by emission from a hot filament. These energetic electrons collide with the moderator gas molecules to induce ionization to produce a cation and a secondary electron for each collision. This is represented symbolically in Equation 43 :

Where Y is the energy expended in creating an ion-pair. It has been estimated ⁷³ that the creation of one cation-electron pair requires the expenditure of approximately 35 eV, which is relatively independent of the primary electron energy. In other words, the term Y in Equation 43 is 35 eV. It is the secondary electrons produced in this manner that become the steady state concentration of electrons which are the ECNI ionizing reagent. A single high energy electron can create a number of ion pairs, and thus, secondary electrons. The rate of secondary electron production, S_e , can be estimated by the equation ⁷³ ;

$$S_e \left(\frac{\text{pairs}}{\text{sec}} \right) = 1.7 \times 10^{11} (I \times E) \quad (44)$$

I (uA) is the intensity of the high energy electron beam and E (eV) is its energy. The values of I and E used earlier result in a rate of secondary electron formation (S_e) of 1×10^{15} ion pairs s^{-1} . In the absence of electron-capture analytes, secondary electrons are lost by either recombination with positive ions or diffusion to the source wall ^{66,73}. Based on this, the lifetime of an electron under typical ECNI conditions has been estimated to be 30 us ⁶⁶. Therefore, the steady state

concentration of ion pairs in our source was about $4 \times 10^{10} \text{ cm}^{-3}$ (for the $\sim 1 \text{ cm}^3$ source volume).

Another important property of electrons in an ECNI source is their energy distribution. It has been estimated that only a fraction ($\sim 60\%$) of the total electron population in an ECNI source is thermalised ⁶⁶. In addition, it has been suggested that the fraction of total electron population thermalised is instrument dependent ⁷⁰. For many molecules, electron capture reactions can occur with electron energies up to 15 eV ^{72, 86}. Therefore, some of the non-thermalised electrons can be captured. Because of conservation of energy, the anion initially formed by electron capture has an excess energy above its ground state equal to the molecular electron affinity plus the kinetic energy of the captured electron. In order for a stable anion to be formed, some of this excess energy must be dissipated. To a certain extent, this can be accomplished by collisions with the moderator gas. However, the higher the energy of the captured electrons, the more likely it will be that electron detachment or dissociative electron capture occurs. The latter reaction leads to fragmentation. The electron energy distribution will be affected most prominently by the nature of the moderator gas and source pressure.

At this point, all the variables required to solve the Equations 35 and 36 have been defined. The effects that changes in pressure and ventilation rate can have on the $[\text{M}+\text{H-X}]^\bullet$ to $[\text{M-X}]^-$ ratio can now be calculated. The results of these calculations are presented in Figures 38 and 39. Equation 35, which treats the $[\text{M}+\text{H-X}]^\bullet$ fragment as the product of a gas-phase-radical reaction, was used to

Figure 38 : Calculated Variation in [M+H-X]⁻ to [M-X]⁻ Ratio with Changes in Pressure and Ventillation Rate for [M+H-X]⁻ Formed from a Gas-Phase-Radical Reaction

Pressure	Ventillation (cm ³ /sec)	% [M+H-X] ⁻	[M+H-X] ⁻ /[M-X] ⁻ Ratio
0.25	318	49%	0.95
0.25	529	39%	0.65
0.50	318	39%	0.64
0.50	529	31%	0.44

Figure 39 : Calculated Variation in [M+H-X]- to [M-X]- Ratio with Changes in Pressure and Ventilation Rate for [M+H-X]- Formed from a Wall-Modified Reaction

Pressure	Ventilation (cm ³ /sec)	% [M+H-X]-	[M+H-X]-/[M-X]- Ratio
0.25	318	86%	6.22
0.25	529	85%	5.89
0.50	318	68%	2.10
0.50	529	67%	2.02

generate Figure 38. Whereas Equation 36, which treats the $[M+H-X]^{\bullet}$ fragment as the product of a wall-mediated reaction, was used to generate Figure 39. For calculation purposes, all the electron capture rate constants (k_{emr} , k_{em} , and k_{ew}) were assumed to be identical and equal to $3 \times 10^{-7} \text{ cm}^3 \text{ particles}^{-1} \text{ s}^{-1}$, while the rate constant for gas-phase reaction of reagent radicals with neutral PCBs (k_r) was set to $1 \times 10^{-10} \text{ cm}^3 \text{ particles}^{-1} \text{ s}^{-1}$. These choices mimicked those selected by Sears et al.⁷³.

An analysis of the results from Equation 35 (Figure 38) demonstrates that the magnitude of change in the $[M+H-X]^{\bullet}$ to $[M-X]^{\bullet}$ ratio induced by altering the volumetric flow rate is of comparable magnitude to a change in the pressure. If at 0.50 torr the volumetric flow rate is reduced from $\sim 530 \text{ cm}^3 \text{ s}^{-1}$ to $\sim 320 \text{ cm}^3 \text{ s}^{-1}$, the effect is almost the same as reducing the pressure from 0.50 torr to 0.25 torr at a constant volumetric flow rate of $\sim 530 \text{ cm}^3 \text{ s}^{-1}$. At the lower pressure a change in the flow rate has a slightly greater effect (i.e., steeper slope) than at higher pressure.

In the case of the wall-based reaction described by Equation 36 (Figure 39), the lower pressure plot is offset significantly from the plot at higher pressure. In addition, the slopes appear flatter than those in Figure 38; however, the lower pressure plot is still slightly steeper than the higher pressure plot.

As Figures 38 and 39 indicate, the ratio of $[M+H-X]^{\bullet}$ to $[M-X]^{\bullet}$ exhibits different characteristics depending on whether the $[M+H-X]^{\bullet}$ is produced from a wall-based or a gas-phase based reaction. It is therefore possible to determine experimentally whether the $[M+H-X]^{\bullet}$ ion of a particular congener was formed from

a gas-phase-radical or a surface-modified reaction.

7.3.1.2 Experimental Observation of Variation in $[M+H-X]^{\bullet}$ to $[M-X]^{\bullet}$ Ratio and the Classification of $[M+H-X]^{\bullet}$ as a Wall-Modified or Gas-Phase-Radical Reaction

To differentiate between a wall-modified reaction and a gas-phase-radical reaction, measurements were made at each of four pressure/ventilation values. Only 16 congeners provided reliable results at all four settings. The corresponding plots generated for six of these congeners are presented in Figures 40 to 42.

In Figures 40 and 41 the $[M+H-X]^{\bullet}$ to $[M-X]^{\bullet}$ ratios and corresponding plots for congeners BZ 87, BZ 95, BZ 117 and BZ 124 are presented. These plots resemble the simulated "gas-phase-radical reaction" plot in Figure 38 very closely. This implies that the kinetic model and estimation methods of Sears et al.⁷³ is valid for PCBs, and also that these four congeners likely form the $[M+H-X]^{\bullet}$ fragment via a gas-phase-radical mechanism.

The plots for BZ 166 and BZ 185 are presented in Figure 42. The plots of the experimental results do not resemble either of the simulated plots shown in Figure 38 or 39. Rather, it appears that the experimental plots are a hybrid of both simulated plots. At the lower pressure (0.25 torr), the magnitude of change resembles that predicted for a wall-modified reaction, whereas at higher pressure (0.50 torr) a gas-phase-radical reaction is indicated. If formation of $[M+H-X]^{\bullet}$ were to exhibit a mixed mechanism it would appear reasonable that the wall-modified reaction would be favoured at a lower pressure. This is because the higher

**Figure 40 : Measured Variation in [M+H-X]- to [M-X]- Ratio
with Changes in Pressure and Ventilation Rate**

BZ 87		BZ 87		BZ 95		BZ 95	
Pressure (torr)	(F/V) (/sec-1)	% [M+H-X]-	[M+H-X]- to [M-X]-	% [M+H-X]-	[M+H-X]-	% [M+H-X]-	[M+H-X]- to [M-X]-
0.25	318	46%	0.85	36%		0.56	
0.25	529	26%	0.35	17%		0.20	
0.5	318	30%	0.43	24%		0.32	
0.5	529	10%	0.11	7%		0.08	

BZ 87 : [M+H-X]- to [M-X]- Ratio vs Ventilation Rate

BZ 95 : [M+H-X]- to [M-X]- Ratio vs Ventilation Rate

Figure 41 : Measured Variation in [M+H-X]- to [M-X]- Ratio with Changes in Pressure and Ventilation Rate

BZ 117		BZ 117	
Pressure (torr)	(F/V) (/sec-1)	% [M+H-X]-	[M+H-X]- to [M-X]-
0.25	318	17%	0.20
0.25	529	12%	0.14
0.5	318	9%	0.10
0.5	529	5%	0.05

BZ 124		BZ 124	
% [M+H-X]-	[M+H-X]- to [M-X]-	% [M+H-X]-	[M+H-X]- to [M-X]-
65%	1.86		
53%	1.13		
49%	0.96		
25%	0.33		

BZ 117 : [M+H-X]- to [M-X]- Ratio vs Ventilation Rate

BZ 124 : [M+H-X]- to [M-X]- Ratio vs Ventilation Rate

Figure 42 : Measured Variation in [M+H-X]⁺ to [M-X]⁺ Ratio with Changes in Pressure and Ventilation Rate

BZ 166		BZ 166		BZ 185		BZ 185	
Pressure (torr)	(F/V) (/sec-1)	% [M+H-X] ⁺ to [M-X] ⁺	% [M+H-X] ⁺ to [M-X] ⁺	% [M+H-X] ⁺ to [M-X] ⁺	% [M+H-X] ⁺ to [M-X] ⁺	% [M+H-X] ⁺ to [M-X] ⁺	% [M+H-X] ⁺ to [M-X] ⁺
0.25	318	29%	0.41	40%	0.67		
0.25	529	28%	0.39	38%	0.61		
0.5	318	22%	0.28	26%	0.35		
0.5	529	16%	0.19	20%	0.25		

BZ 166 : [M+H-X]⁺ to [M-X]⁺ Ratio vs Ventilation Rate

BZ 185 : [M+H-X]⁺ to [M-X]⁺ Ratio vs Ventilation Rate

diffusion rate at a lower pressure implies a higher collision frequency with the source walls.

Of the 16 congeners examined in this manner, in only four cases the formation of $[M+H-X]^{\bullet}$ could **not** be classified as purely gas-phase-radical. In these four cases, hybrid plots were obtained. Interestingly, all four of these congeners had a fully chlorinated ring "A", whereas none of the congeners which were classified as purely gas-phase-radical types had this property. Three of the four congeners exhibiting a mixed mechanism contained six chlorines, while the other contained seven chlorines. Of the twelve congeners that were classified as having purely gas-phase-radical reactions, ten contained five chlorines, one contained four chlorines and one contained six chlorines.

The fact that the four congeners exhibiting a mixed mechanism were some of the more highly chlorinated ones of the set of sixteen was felt not to be the sole reason for the hybrid effect. This point was important because, assuming a physical adsorption, the higher molecular weight compounds could be argued to have a greater tendency to "stick" to the source walls. If a common structural property is related to the tendency to react via a wall-moderated reaction, this implies, among other possibilities, that a specific substrate-like interaction may occur.

7.3.2 Regioselective Loss of Chlorine in the Formation of $[M+H-X]^{\bullet}$

In Table 18, the average values of the percent label loss for the $[M+H-X]^{\bullet}$

channel are presented along with those for the $[M-X]^+$ channel. In contrast to the $[M-X]^+$ channel, a very high percentage (~50%) of the average values for the $[M+H-X]^+$ channel had standard deviations greater than 5; in fact, a significant number of these had standard deviations greater than 10. This indicated that percent-label-lost values for the formation of the $[M+H-X]^+$ fragment varied significantly with experimental variations. However, a detailed analysis revealed that this variation was not correlated to either the pressure or volumetric flow rate. We speculate that the percent-label-lost values from the $[M+H-X]^+$ reaction channel were sensitive to some parameter that was either not controlled or monitored in these measurements. The most likely parameters were the temperature and electron energy distribution. Despite this uncertainty, 19 congeners whose percent-label-lost values did not vary significantly (standard deviation ≤ 5), were used to develop structure-reactivity relationships. These are presented in Table 38.

The data in Table 38 show the percent-label-lost for different congeners producing the $[M+H-X]^+$ fragment ranged from 13% to 100%. Ten congeners (all the congeners in the first column of Table 38) had percent-label-lost values which were significantly greater than what was expected from a random loss of chlorine. All ten of these congeners contained at least one labelled chlorine in either a para- or ortho-position. Seven congeners (BZ 114 produced from BZ 23 as well as from BZ 61, BZ 158, BZ 105, BZ 106, BZ 107, and BZ 118) had percent-label-lost values which were significantly smaller than what was expected from a random loss of chlorine. Four (BZ 158, BZ 105, BZ 107, and BZ 118) of these seven congeners

Table 38 : Selected Percent-Label-Loss Values for the Formation of the $[M+H-X]^+$ Fragment

Structure	% Label Lost	Structure	% Label Lost
BZ 75	100 % (Random = 25 %)	BZ 92	39 % (Random = 40 %)
BZ 86	100 % (Random = 40 %)	BZ 190	28 % (Random = 29 %)
BZ 64	99 % (Random = 25 %)	BZ 114	22 % (Random = 40 %)
BZ 122	99 % (Random = 40 %)	BZ 158	20 % (Random = 33 %)
BZ 74	98 % (Random = 25 %)	BZ 114	16 % (Random = 20 %)
BZ 106	93 % (Random = 40 %)	BZ 105	15 % (Random = 40 %)
BZ 124	93 % (Random = 40 %)	BZ 107	14 % (Random = 40 %)
BZ 173	76 % (Random = 29 %)	BZ 106	13 % (Random = 20 %)
BZ 151	55 % (Random = 33 %)	BZ 118	13 % (Random = 40 %)
BZ 87	54 % (Random = 40 %)		

had a common structural characteristic, labels located in the 3',4'- positions, indicating that labels in these positions were selectively retained in the formation of the $[M+H-X]^+$ fragment.

Two forms of labelled BZ 114 (2,3,4,4',5-) are presented in Table 38. The para-chlorine (4'-) on the less highly chlorinated ring of BZ 114 was lost 16% of the time, while the para-chlorine (4-) on the more highly chlorinated ring was lost only 6% of the time. Thus in the case of BZ 114, para-chlorines were selectively retained in the formation of the $[M+H-X]^+$ fragment.

Two forms of labelled BZ 106 (2,3,3',4,5-) are also presented in Table 38. This congener has the same chlorination pattern on the more highly chlorinated ring as BZ 114, and thus may be considered related. In BZ 106, the meta-chlorine (3'-) on the less highly chlorinated ring was lost 13% of the time, while the ortho-chlorine (2-) on the more highly chlorinated ring was lost 80% of the time. Therefore, the 3,4,5- chlorination pattern was retained in the formation of $[M+H-X]^+$ 93% of the time. It is possible that in BZ 114, the ortho-chlorine on the more highly chlorinated ring is also selectively lost. There are no examples presented in Table 38 where a selective loss of meta-chlorine is indicated.

Eight (BZ 86, BZ 122, BZ 106 produced from BZ 38, BZ 106 produced from BZ 61, BZ 124, BZ 173, BZ 190, and BZ 114) of the seventeen different congeners presented in Table 38 contain chlorines at positions 3,4 and 5 in the more highly chlorinated ring. The exclusive retention of the 3,4,5- chlorination pattern in the $[M+H-X]^+$ fragment was clearly demonstrated in six of these congeners (BZ 86, BZ

122, BZ 106 produced from BZ 38, BZ 106 produced from BZ 61, BZ 124, and BZ 173). In BZ 114, the exclusive retention of the 3,4,5- chlorination pattern was inferred from a comparison with BZ 106 produced from BZ 38 (left column of Table 38). Therefore, a similar preferred retention of both the 3,4,5- and 3',4'- chlorination patterns was implied in both the formation of the $[M+H-X]^{\bullet}$ and the $[M-X]^{\bullet}$ fragment ions.

Section 7.3.1.2 indicated that the observed variation of the $[M+H-X]^{\bullet}$ to $[M-X]^{\bullet}$ ratio was, for the most part, consistent with $[M+H-X]^{\bullet}$ originating from a gas-phase radical reaction. The identity of the specific gas phase radical responsible was not determined from this experimental data, nor was the possible distinction between radical reacting with the molecular anion ($[M]^{\bullet}$) or neutral molecule (M). It is also possible that a radical reacts with the dechlorinated fragment radical ($[M-X]^{\bullet}$), or even the dechlorinated fragment anion ($[M-X]^{\bullet}$), to form $[M+H-X]^{\bullet}$. However, in many cases, the percent label lost in forming the $[M+H-X]^{\bullet}$ fragment ion is significantly greater than the corresponding value for forming the $[M-X]^{\bullet}$ fragment ion. This suggests that the $[M+H-X]^{\bullet}$ fragment ion is not formed from the $[M-X]^{\bullet}$ fragment ion. This is further supported by the observation that the percent-label-lost values observed for many of the $[M-X]^{\bullet}$ fragment ions had low standard deviations, whereas many of the percent-label-lost values for the $[M+H-X]^{\bullet}$ fragment ions had high standard deviations. This information leads to the conclusion that the majority of PCB congeners form $[M+H-X]^{\bullet}$ fragment ions from a gas-phase radical reaction with either the molecular anion, $[M]^{\bullet}$, or neutral

molecule, M. The known inertness of neutral molecular PCBs leads this author to speculate that the most likely reagent is the molecular anion, $[M]^{-\bullet}$.

The variation in the ratio of $[M+H-X]^{-\bullet}$ to $[M-X]^{-\bullet}$ also implies that, for at least four of the congeners examined, a wall-modified reaction could be responsible for the formation of $[M+H-X]^{-\bullet}$ under some conditions, whereas a gas-phase-radical reaction could be responsible under other conditions. Even so, no significant variation in the regioselective nature of the chlorine loss associated with the formation of $[M+H-X]^{-\bullet}$ was observed as the reaction type changed from a gas-phase-radical to a wall-modified reaction. For example, when we examined BZ 160 at 0.50 torr, a gas-phase-radical reaction was implicated and the average percent-label-lost value was 21% with a standard deviation of 4. The same congener reacted via a wall-modified reaction at 0.25 torr and the average percent-label-lost value was 16% with a standard deviation of 6. Both of these values were within a reasonable range of the percent-label-lost value expected for the random loss of chlorine from a hexachlorobiphenyl containing one label (17%). One possible explanation for this behaviour is that both the gas-phase-radical reaction and the wall-modified reaction involve the same population of fragment radicals ($[M-X]^{-\bullet}$) which already contain the observed regioselective-dechlorination bias. However, this hypothesis cannot be proven from our results.

7.4 Regioselective Loss of Chlorine in the Formation of $[M+O-X]^{-\bullet}$

In Table 20 of Chapter 4, the percent-label-lost values for the formation of

selected $[M+O-X]^-$ fragments were presented. These values were sorted by the pressure and ventilation rate conditions under which they were collected. Of the 30 labelled congeners reported, only one third could be argued to have exhibited a random loss of chlorine at 0.50 torr (using a $\pm$ value of 8). When the source pressure was at 0.25 torr, only three congeners had percent-label-lost values that were within the same range as those corresponding to a random loss of chlorine. In a previous investigation by Lepine et al.⁷⁶ a random loss of chlorine was indicated in the formation of the $[M+O-X]^-$ fragment from PCBs. In that study, the source pressure was stated to be 0.3 torr, although it was not indicated how this pressure was measured. The source temperature was 150°C, and a mixture of 20% oxygen in methane was used as the moderator gas. The study indicated that a random loss of chlorine occurred in the formation $[M+O-X]^-$ from PCBs. This random loss was accredited to the indiscriminating reaction of superoxide ($O_2^{\bullet-}$) with neutral PCB (see Equation 45 below). This explanation contradicted earlier finding of Knighton et al.⁷⁵ for other chlorinated aromatics, which were demonstrated to react by an attack of molecular oxygen (O_2) on the molecular anion ($[M]^-$) (see Equation 46 below). The results presented in this thesis are consistent with the displacement of chlorine by oxygen as described in Equation 46.

Even though oxygen has a positive electron affinity (EA = 0.44 eV), $O_2^{\bullet-}$ is

highly reactive and unstable. In the publication by Knighton et al.⁷⁵, $O_2^{\bullet-}$ was not observed in the mass spectra of p-chloronitrobenzene (EA = 1.2 eV⁸¹) even when the concentration of O_2 was 477 times greater than the concentration of p-chloronitrobenzene (4.77 mTorr relative to 0.010 mTorr). Lepine et al.⁷⁶ stated that the high concentration of O_2 used in their study (20%) increased the probability of $O_2^{\bullet-}$ formation. However, no spectral evidence of the $O_2^{\bullet-}$ ion was reported. Lepine et al.⁷⁶ also stated that a charge exchange reaction, such as the one represented by Equation 47, may not favour the electron transfer to neutral PCB from $O_2^{\bullet-}$ because the electron affinities of the PCB congeners examined were estimated to be similar in magnitude to that of O_2 .

The electron affinity estimate of selected PCBs made by Lepine et al.⁷⁶ was inaccurate. They used the electron affinity values for hexachlorobiphenyl (EA= 1.0 eV) and for pentachlorobenzene (EA = 0.7 eV) reported by Knighton et al.⁷⁵ to indicate the approximate magnitude of the decrease in electron affinity with a decrease in the number of chlorines on an aromatic ring. From this, Lepine et al.⁷⁶ suggested that the EAs of the PCB congeners that they examined, would likely not be much higher than the EA of oxygen.

In this thesis, electron affinities of all 209 PCBs were estimated. This calculation was discussed in Section 5.2.1.2, and the electron affinities are presented in Appendix II. The error associated with this calculation was estimated

to be 0.1 eV. The accuracy of these electron affinity values are likely better than the estimate of Lepine et al.⁷⁶. From these values, all but one of the 22 congeners examined by Lepine et al.⁷⁶ had electron affinities greater than the electron affinity of oxygen (EA=0.44 eV). Therefore, the suggestion that Equation 47 would not sufficiently decrease the concentration of superoxide ($O_2^{\bullet-}$) is incorrect. For our ECNI investigation, only trace amount of oxygen were present. Under these conditions the reduction of superoxide, $O_2^{\bullet-}$, concentration due to Equation 47 would be significant.

The observation that the regioselective dechlorination bias associated with the formation of $[M+O-X]^-$ varies with pressure means that any general classification of this reaction must be carefully qualified. A few congeners presented in Table 20 have percent-label-lost values that were relatively independent of experimental parameters. For example, all the labelled congeners containing a fully chlorinated aromatic ring had a common tendency to lose a chlorine from this fully chlorinated ring in the formation of $[M+O-X]^-$. It could be hypothesized that the negative charge in the molecular anion of those congeners that had a fully chlorinated aromatic ring was centred on this fully chlorinated ring. The near exclusive loss of a chlorine from this fully chlorinated aromatic ring would then imply that molecular oxygen preferably attacks and dechlorinates the charge bearing aromatic ring. In this case, our observations would reflect both the reaction mechanism as well as the nature of the molecular anion. However, for a proper analysis of the chemistry of $[M+O-X]^-$ formation, additional measurements with quantified oxygen (O_2) and superoxide

($\text{O}_2^{\bullet-}$) concentrations are required.

7.5 Conclusion

This chapter discusses the data presented in Chapter 4 pertaining to the electron capture induced dechlorinations of selected labelled PCBs. Monitoring the tendency of specific, labelled PCBs to lose or retain their ^{37}Cl -labels in the formation of $[\text{M-X}]^-$ or $[\text{M+H-X}]^\bullet$ demonstrated that the 3,4- and 3,4,5- chlorination patterns were selectively retained. The loss or retention of the ^{37}Cl - label in the formation of the $[\text{M-X}]^-$ anion was, for the most part, unrelated to experimental parameters. However, this was not true for the $[\text{M+H-X}]^\bullet$ anion. Many of the labelled congeners behaved as if the $[\text{M+H-X}]^\bullet$ anion was formed as a result of a gas-phase-radical reaction. A few of the congeners containing a fully chlorinated ring behaved as if the $[\text{M+H-X}]^\bullet$ anion was formed as a result of a wall-modified-radical reaction at a moderator gas pressure of 0.25 torr. However, even these congeners appeared to form the $[\text{M+H-X}]^\bullet$ anion as a result of a gas-phase-radical reaction at a higher moderator gas pressure of 0.50 torr. In addition to this, it was demonstrated that, for some congeners, the $[\text{M+O-X}]^-$ anion was formed with a regioselective loss of chlorine.

Chapter 8 : Conclusion

8.1 Introduction

This thesis describes an investigation of the regioselective nature of specific PCB dechlorinations. Five different reaction types were examined: (1) the $[M-X]^+$ formation induced by electron impact, (2) $[M-2X]^+\bullet$ formation induced by electron impact, (3) $[M-X]^-$ formation induced by electron capture, (4) $[M+H-X]^- \bullet$ formation induced by electron capture, and (5) $[M+O-X]^-$ formation induced by electron capture. The results of these investigations are summarised below.

8.2 Summary of Findings

Energetic PCB cations produced by electron impact ionization dechlorinate to yield a $[M-X]^+$ fragment ion, a $[M-2X]^+\bullet$ fragment ion, and other fragment ions. From the results presented in this investigation, it was determined that both the $[M-X]^+$ and $[M-2X]^+\bullet$ fragments had very specific structures. The $[M-X]^+$ fragment ion generated from PCB congeners containing at least one ortho-chlorine on each aromatic ring was determined to be a chloronium ion. Furthermore, it was postulated that this structure formed as a result of a concerted mechanism. In this mechanism the presence of two meta-chlorines on the same aromatic ring significantly increased the probability of the loss of an ortho-chlorine. This was attributed to a stabilization of the transition state leading to the expulsion of the ortho-chlorine on the same aromatic ring as the two meta-chlorines.

The $[M-2X]^+\bullet$ fragment was suggested to have a biphenylene structure. This

structure is consistent with the observation that the two chlorines were lost from two of four active sites, and that this loss occurred only after randomization of the chlorines localized to each aromatic ring. Of the probable rearrangement structures, the biphenylene structure was energetically favoured. In addition, its formation would involve the expulsion of the substituents present in two of the four ortho-sites, consistent with the observed results.

The PCB anions produced by electron capture dechlorinate to produce a series of fragment ions, three of which were studied: $[M-X]^-$, $[M+H-X]^\bullet$, and $[M+O-X]^-$. In all of these cases, examples were observed which demonstrated significant regioselective biases in the formation of the fragment anions.

In the formation of $[M-X]^-$, the results showed a tendency to retain the 3,4,5-chlorination pattern on the more highly chlorinated phenyl ring as well as the 3',4'-pattern on the less highly chlorinated ring. Furthermore, the $[M-X]^-$ fragment appeared to be a product of two consecutive electron capture events; the first one resulted in the formation of $[M-X]^\bullet$, which subsequently captured a second electron to yield $[M-X]^-$.

In the case of $[M+H-X]^\bullet$, the majority of the congeners examined formed the fragment ion via a gas-phase-radical reaction. The remaining congeners, which could not be classified to fragment via a purely gas-phase-radical reaction, all contained a fully chlorinated aromatic ring. This subset of congeners formed the $[M+H-X]^\bullet$ fragment anion from a gas-phase-radical reaction at a pressure of 0.50

torr; however, at a pressure of 0.25 torr, the fragmentation appeared to proceed via a wall-modified-radical reaction. For the majority of congeners, it appeared that the $[M+H-X]^{\bullet}$ fragment anion formed as a result of a gas-phase-radical reaction between the molecular anion ($[M]^{\bullet-}$) and some, as yet undetermined, radical species.

For $[M+O-X]^{\bullet}$, the single chlorine on the less highly chlorinated ring was selectively retained in the formation of this fragment ion. It was speculated that $[M+O-X]^{\bullet}$ was formed as a result of a reaction between molecular oxygen and the molecular anion, whose negative charge is centred on the more highly chlorinated phenyl ring.

8.3 Implications for Future Studies

The electron impact results suggested the formation of specific structures for both the $[M-X]^+$ and $[M-2X]^{\bullet+}$ fragments. In the case of the $[M-X]^+$ ion, speculations were also made regarding the energetics of the transition states leading to the formation of this ion. It would be interesting to investigate the KER for this reaction pathway to determine if the suggestion of a chloronium structure can be substantiated. For the $[M-2X]^{\bullet+}$ fragment, it was hypothesized that it has a biphenylene structure; if this is correct, the MIKE spectrum of the $[M-2X]^{\bullet+}$ from any dichlorobiphenyl should be identical to the MIKE spectrum of the molecular ion of biphenylene. If this is confirmed experimentally, then it would be quite valuable to

determine if there is any resemblance or correlation between the types of fragments formed by electron impact and the products obtained from the pyrolysis of PCBs.

Previous research indicated that the regioselective nature of electron capture- induced dechlorinations of chlorinated dioxins is dependent on the energy of the captured electron ¹¹⁵. Furthermore, a tuneable monochromatic electron source has been developed that permits the interaction of analyte molecules with low energy electrons of definable and variable energies ¹⁰⁷. An investigation of the energy dependence of the regioselective dechlorination of the PCB congeners presented in this thesis would be informative.

Future work may compare gas-phase electron-capture-induced dechlorinations to similar dechlorinations induced in solution by electrochemical methods as well as those occurring in the environment. A comprehensive understanding of these processes and their interrelationship would facilitate the use of MS data to interpret environmental processes and could provide insight into the mechanisms of relevant biological transformations.

Appendix I : PCB Isomer Table

Ring A		BZ #	
No Cl		0	BZ #
2		1	4
3		2	6
4		3	8
		5	16
2,3		7	17
2,4		9	18
2,5		10	19
2,6		12	33
3,4		14	34
3,5		21	41
2,3,4		23	43
2,3,5		24	45
2,3,6		29	48
2,4,5		30	50
2,4,6		38	76
3,4,5		61	86
2,3,4,5		62	88
2,3,4,6		65	93
2,3,5,6		116	142
2,3,4,5,6		No Cl	2
Ring B =		3	4
		5	6
		7	8
		9	10
		11	12
		13	14
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Appendix II - Modelled* Electron Affinities For PCBs

BZ #	STRUCTURE	LUMO *	EA (eV)	BZ #	STRUCTURE	LUMO **	EA (eV)
1	2	-0.0428	0.1	36	33'5	-0.6256	0.5
2	3	-0.2633	0.2	37	344'	-0.7090	0.5
3	4	-0.3164	0.3	38	345	-0.6743	0.5
4	22'	-0.1151	0.1	39	34'5	-0.6690	0.5
5	23	-0.2934	0.3	40	22'33'	-0.4254	0.4
6	23'	-0.3122	0.3	41	22'34	-0.4906	0.4
7	24	-0.3922	0.3	42	22'34'	-0.4877	0.4
8	24'	-0.3615	0.3	43	22'35	-0.4652	0.4
9	25	-0.3698	0.3	44	22'35'	-0.4407	0.4
10	26	-0.1400	0.2	45	22'36	-0.4226	0.4
11	33'	-0.4553	0.4	46	22'36'	-0.2562	0.2
12	34	-0.5095	0.4	47	22'44'	-0.5542	0.4
13	34'	-0.5052	0.4	48	22'45	-0.5579	0.4
14	35	-0.4594	0.4	49	22'45'	-0.4985	0.4
15	44'	-0.5449	0.4	50	22'46	-0.4690	0.4
16	22'3	-0.2578	0.2	51	22'46'	-0.3113	0.3
17	22'4	-0.3844	0.3	52	22'55'	-0.5066	0.4
18	22'5	-0.3286	0.3	53	22'56	-0.2829	0.3
19	22'6	-0.1466	0.2	54	22'66'	-0.2098	0.2
20	233'	-0.4598	0.4	55	233'4	-0.6908	0.5
21	234	-0.5548	0.4	56	233'4'	-0.6265	0.5
22	234'	-0.5114	0.4	57	233'5	-0.6707	0.5
23	235	-0.5273	0.4	58	233'5'	-0.6218	0.5
24	236	-0.4263	0.4	59	233'6	-0.5270	0.4
25	23'4	-0.4923	0.4	60	2344'	-0.7286	0.6
26	23'5	-0.5118	0.4	61	2345	-0.7508	0.6
27	23'6	-0.2932	0.3	62	2346	-0.6448	0.5
28	244'	-0.5931	0.5	63	234'5	-0.6938	0.5
29	245	-0.6131	0.5	64	234'6	-0.5222	0.4
30	246	-0.4575	0.4	65	2356	-0.6608	0.5
31	24'5	-0.5553	0.4	66	23'44'	-0.7217	0.5
32	24'6	-0.2638	0.2	67	23'45	-0.7456	0.6
33	2'34	-0.4836	0.4	68	23'45'	-0.7165	0.5
34	2'35	-0.4515	0.4	69	23'46	-0.6100	0.5
35	33'4	-0.6737	0.5	70	23'4'5	-0.6972	0.5

* Estimated via Equation

EA = -0.6655 (LUMO) + 0.06907 ; all EA values +/- 0.1 eV

** LUMO eigenvalues from AM1 Level Calculation by Graves et al., (ref. 68)

Appendix II - Modelled* Electron Affinities For PCBs

BZ #	STRUCTURE	LUMO *	EA (eV)	BZ #	STRUCTURE	LUMO **	EA (eV)
71	23'4'6	-0.4125	0.3	106	233'45	-0.8715	0.6
72	23'55'	-0.6656	0.5	107	233'4'5	-0.7991	0.6
73	23'5'6	-0.4518	0.4	108	233'45'	-0.8348	0.6
74	244'5	-0.7674	0.6	109	233'46	-0.7472	0.6
75	244'6	-0.5812	0.5	110	233'4'6	-0.6491	0.5
76	2'345	-0.6541	0.5	111	233'55'	-0.8049	0.6
77	33'44'	-0.8440	0.6	112	233'56	-0.7491	0.6
78	33'45	-0.8266	0.6	113	233'5'6	-0.6135	0.5
79	33'45'	-0.8314	0.6	114	2344'5	-0.9006	0.7
80	33'55'	-0.8042	0.6	115	2344'6	-0.7636	0.6
81	344'5	-0.8655	0.6	116	23456	-0.8094	0.6
82	22'33'4	-0.6532	0.5	117	234'56	-0.7504	0.6
83	22'33'5	-0.5823	0.5	118	23'44'5	-0.8913	0.7
84	22'33'6	-0.5119	0.4	119	23'44'6	-0.7311	0.6
85	22'344'	-0.6443	0.5	120	23'455'	-0.8794	0.7
86	22'345	-0.6694	0.5	121	23'45'6	-0.6724	0.5
87	22'345'	-0.6629	0.5	122	2'33'45	-0.7635	0.6
88	22'346	-0.6610	0.5	123	2'344'5	-0.8268	0.6
89	22'346'	-0.4589	0.4	124	2'3455'	-0.8071	0.6
90	22'34'5	-0.6010	0.5	125	2'3456'	-0.5764	0.5
91	22'34'6	-0.5215	0.4	126	33'44'5	-1.0013	0.7
92	22'355'	-0.6071	0.5	127	33'455'	-0.9669	0.7
93	22'356	-0.6561	0.5	128	22'33'44'	-0.8033	0.6
94	22'356'	-0.5063	0.4	129	22'33'45	-0.7990	0.6
95	22'35'6	-0.5165	0.4	130	22'33'45'	-0.7447	0.6
96	22'366'	-0.4304	0.4	131	22'33'46	-0.7523	0.6
97	22'3'45	-0.6743	0.5	132	22'33'46'	-0.6109	0.5
98	22'3'46	-0.5691	0.4	133	22'33'55'	-0.7627	0.6
99	22'44'5	-0.7628	0.6	134	22'33'56	-0.7362	0.6
100	22'44'6	-0.5809	0.5	135	22'33'56'	-0.5980	0.5
101	22'455'	-0.6742	0.5	136	22'33'66'	-0.5270	0.4
102	22'456'	-0.5330	0.4	137	22'344'5	-0.7997	0.6
103	22'45'6	-0.5642	0.4	138	22'344'5'	-0.7881	0.6
104	22'466'	-0.4849	0.4	139	22'344'6	-0.7627	0.6
105	233'44'	-0.8561	0.6	140	22'344'6'	-0.6963	0.5

* Estimated via Equation

$$EA = -0.6655 (LUMO) + 0.06907 ; \text{ all EA values } \pm 0.1 \text{ eV}$$

** LUMO eigenvalues from AM1 Level Calculation by Graves et al., (ref. 68)

Appendix II - Modelled* Electron Affinities For PCBs

BZ #	STRUCTURE	LUMO *	EA (/eV)	BZ #	STRUCTURE	LUMO **	EA (/eV)
141	22'3455'	-0.8219	0.6	176	22'33'466'	-0.7807	0.6
142	22'3456	-0.8165	0.6	177	22'33'4'56	-0.8094	0.6
143	22'3456'	-0.7020	0.5	178	22'33'55'6	-0.8116	0.6
144	22'345'6	-0.7699	0.6	179	22'33'566'	-0.7260	0.6
145	22'3466'	-0.6808	0.5	180	22'344'55'	-0.9473	0.7
146	22'34'55'	-0.7478	0.6	181	22'344'56	-0.9114	0.7
147	22'34'56	-0.7497	0.6	182	22'344'56'	-0.8354	0.6
148	22'34'56'	-0.6648	0.5	183	22'344'5'6	-0.8548	0.6
149	22'34'5'6	-0.5994	0.5	184	22'344'66'	-0.7735	0.6
150	22'34'66'	-0.5726	0.5	185	22'3455'6	-0.9106	0.7
151	22'355'6	-0.7454	0.6	186	22'34566'	-0.8313	0.6
152	22'3566'	-0.6516	0.5	187	22'34'55'6	-0.8136	0.6
153	22'44'55'	-0.8570	0.6	188	22'34'566'	-0.7355	0.6
154	22'44'56'	-0.6937	0.5	189	233'44'55'	-1.1330	0.8
155	22'44'66'	-0.6129	0.5	190	233'44'56	-0.9825	0.7
156	233'44'5	-1.0112	0.7	191	233'44'5'6	-0.9905	0.7
157	233'44'5'	-0.9959	0.7	192	233'455'6	-0.9873	0.7
158	233'44'6	-0.8804	0.7	193	233'4'55'6	-0.8880	0.7
159	233'455'	-1.0037	0.7	194	22'33'44'55'	-1.0600	0.8
160	233'456	-0.9198	0.7	195	22'33'44'56	-0.9811	0.7
161	233'45'6	-0.8533	0.6	196	22'33'44'5'6	-0.9302	0.7
162	233'4'55'	-0.9648	0.7	197	22'33'44'66'	-0.8669	0.6
163	233'4'56	-0.8229	0.6	198	22'33'455'6	-0.9930	0.7
164	233'4'5'6	-0.7723	0.6	199	22'33'4'55'6	-0.8699	0.6
165	233'55'6	-0.8258	0.6	200	22'33'4566'	-0.9161	0.7
166	2344'56	-0.9079	0.7	201	22'33'45'66'	-0.8508	0.6
167	23'44'55'	-1.0216	0.7	202	22'33'55'66'	-0.7969	0.6
168	23'44'5'6	-0.7755	0.6	203	22'344'55'6	-0.9888	0.7
169	33'44'55'	-1.1189	0.8	204	22'344'566'	-0.9387	0.7
170	22'33'44'5	-0.9287	0.7	205	233'44'55'6	-1.0491	0.8
171	22'33'44'6	-0.8389	0.6	206	22'33'44'55'6	-1.0560	0.8
172	22'33'455'	-0.9225	0.7	207	22'33'44'566'	-0.9922	0.7
173	22'33'456	-0.9099	0.7	208	22'33'455'66'	-0.9952	0.7
174	22'33'456'	-0.7903	0.6	209	22'33'44'55'66'	-1.0952	0.8
175	22'33'45'6	-0.8512	0.6				

* Estimated via Equation

EA = -0.6655 (LUMO) + 0.06907 ; all EA values +/- 0.1 eV

** LUMO eigenvalues from AM1 Level Calculation by Graves et al., (ref. 68)

Appendix III - Relative Enthalpies of Formation of Dechlorinated Fragments as Calculated by Hyperchem 4.5 (kcal mol⁻¹)

BZ #	Chlorine Lost	Radical	Singlet	Triplet	Singlet	Triplet
			Cation	Cation	Anion	Anion
BZ 21	2 O	91	300	296	53	95
	3 M	93	330	302	53	95
	4 P	93	330	297	55	67
BZ 41	2 O	90	299	296	48	62
	3 M	88	324	301	48	69
	4 P	88	325	300	50	67
	2' O	87	297	300	58	84
BZ 60	2 O	85	294	290	43	55
	3 M	86	291	296	44	58
	4 P	86	325	291	46	56
	4' P	86	297	292	58	82
BZ 87	2 O	80	293	289	38	77
	3 M	81	321	292	39	55
	4 P	81	320	291	41	53
	2' O	81	309	293	44	76
	5' M	82	292	293	48	76
BZ 82	2 O	81	295	295	39	54
	3 M	83	322	296	40	58
	4 P	82	321	296	42	55
	2' O	82	294	292	43	77
	3' M	85	317	296	47	77
BZ 105	2 O	79	318	288	36	48
	3 M	81	322	292	37	54
	4 P	81	321	289	39	50
	3' M	81	326	292	45	73
	4' P	81	318	291	45	75

Appendix III - Relative Enthalpies of Formation of Dechlorinated Fragments as Calculated by Hyperchem 4.5 (kcal mol⁻¹)

BZ #	Chlorine Lost	Radical	Singlet Cation	Triplet Cation	Singlet Anion	Triplet Anion
BZ 23	2 O	91	326	297	52	102
	3 M	91	297	302	53	89
	5 M	92	324	302	56	68
BZ 43	2 O	88	320	296	47	97
	3 M	86	298	297	48	84
	5 M	87	320	297	51	68
	2' O	87	294	301	57	82
BZ 63	2 O	84	294	290	42	93
	3 M	84	307	295	44	86
	5 M	85	302	295	47	86
	4' P	85	311	293	80	79
BZ 93	2 O	82	297	294	38	81
	3 M	83	298	294	40	82
	5 M	83	298	294	40	82
	6 O	82	293	294	38	81
	2' O	83	309	291	53	83
BZ 92	2 O	80	317	289	38	89
	3 M	80	294	293	39	78
	5 M	80	316	290	42	80
	2' O	80	299	293	44	82
	5' M	80	298	292	47	75
BZ 83	2 O	81	311	301	39	91
	3 M	81	295	294	41	57
	5 M	81	317	294	44	80
	2' O	81	310	296	43	75
	3' O	81	317	295	46	76
BZ 117	2 O	81	297	295	34	77
	3 M	81	298	295	36	78
	5 M	82	298	295	36	78
	6 O	81	297	295	34	77
	4' P	83	309	293	49	81
BZ 107	2 O	78	318	287	35	87
	3 M	79	291	290	37	53
	5 M	80	288	291	40	77
	3' M	80	316	291	44	73
	4' P	80	297	291	44	72
BZ 114	2 O	89	302	297	36	76
	3 M	88	299	303	37	52
	5 M	88	299	303	40	70
	4 P	88	335	298	37	50
	4' P	91	306	300	73	50

Appendix III - Relative Enthalpies of Formation of Dechlorinated Fragments as Calculated by Hyperchem 4.5 (kcal mol⁻¹)

BZ #	Chlorine Lost	Radical	Singlet	Triplet	Singlet	Triplet
			Cation	Cation	Anion	Anion
BZ 24	2 O	93	303	304	54	96
	3 M	93	302	304	57	106
	6 O	92	305	300	56	96
BZ 45	2 O	87	323	299	47	90
	3 M	88	305	298	51	100
	6 O	87	302	298	50	90
	2' O	88	312	296	60	84
BZ 59	2 O	86	299	299	44	87
	3 M	87	306	299	47	96
	6 O	86	301	294	47	60
	3' M	87	301	297	62	82
BZ 64	2 O	86	299	299	44	86
	3 M	86	324	299	47	96
	6 O	85	306	293	46	60
	4' P	89	305	297	82	59
BZ 95	2 O	82	296	295	40	83
	3 M	83	302	295	43	92
	6 O	82	298	295	43	56
	2' O	82	298	292	46	94
	5' M	83	316	295	49	77
BZ 110	2 O	80	292	295	36	79
	3 M	81	302	295	40	89
	6 O	80	297	288	39	80
	3' M	81	295	292	47	82
	4' P	81	299	293	73	90

Appendix III - Relative Enthalpies of Formation of Dechlorinated Fragments as Calculated by Hyperchem 4.5 (kcal mol⁻¹)

BZ #	Chlorine Lost	Radical	Singlet	Triplet	Singlet	Triplet
			Cation	Cation	Anion	Anion
BZ 29	2 O	90	300	294	54	93
	4 P	92	320	296	53	65
	5 M	92	297	298	54	94
BZ 48	2 O	86	300	295	49	60
	4 P	87	324	296	48	90
	5 M	87	322	296	49	68
	2' O	86	311	292	56	82
BZ 74	2 O	83	293	288	44	53
	4 P	85	325	291	44	54
	5 M	84	324	293	45	57
	4' P	84	310	290	55	80
BZ 101	2 O	79	295	288	39	76
	4 P	80	320	292	39	51
	5 M	80	296	290	40	54
	2' O	79	299	292	43	74
	5' M	80	313	292	46	74
BZ 97	2 O	80	296	292	41	53
	4 P	81	321	293	41	56
	5 M	81	319	293	42	57
	2' O	81	304	296	43	49
	3' M	81	316	295	46	75
BZ 118	2 O	78	290	285	36	45
	4 P	79	320	287	37	46
	5 M	79	313	298	38	52
	3' M	79	287	299	43	71
	4' P	81	290	287	43	73

Appendix III - Relative Enthalpies of Formation of Dechlorinated Fragments as Calculated by Hyperchem 4.5 (kcal mol⁻¹)

BZ #	Chlorine Lost	Radical	Singlet	Triplet	Singlet	Triplet
			Cation	Cation	Anion	Anion
BZ 30	2 O	91	303	300	54	88
	4 P	93	303	311	56	146
	6 O	91	304	300	54	88
BZ 75	2 O	85	298	292	44	79
	4 P	86	302	306	46	120
	6 O	84	298	292	44	79
	4' P	86	311	296	60	80
BZ 103	2 O	79	295	288	38	78
	4 P	80	297	301	41	117
	6 O	79	295	288	38	78
	2' O	80	300	292	46	74
	5' M	80	312	291	49	74
BZ 98	2 O	81	296	291	40	80
	4 P	82	298	302	43	81
	6 O	81	296	291	40	54
	2' O	81	309	295	74	75
	3' M	82	315	294	48	75
BZ 88	2 O	82	295	292	37	81
	4 P	83	297	296	39	122
	6 O	82	339	292	40	112
	3 M	83	300	294	38	91
	2' O	83	309	298	74	75
BZ 119	2 O	79	293	287	36	78
	4 P	80	299	289	39	112
	6 O	79	293	287	36	108
	3' P	80	314	291	46	72
	4' P	81	298	292	46	73
BZ 109	2 O	82	295	297	33	78
	4 P	82	297	297	36	60
	6 O	81	338	292	36	49
	3 M	82	315	297	35	77
	3' M	83	309	296	55	72
BZ 115	2 O	80	294	290	33	49
	4 P	82	297	296	35	49
	6 O	81	299	290	36	49
	3 M	82	325	299	35	87
	4' P	82	312	294	55	73

Appendix III - Relative Enthalpies of Formation of Dechlorinated Fragments as Calculated by Hyperchem 4.5 (kcal mol⁻¹)

BZ #	Chlorine Lost	Radical	Singlet	Triplet	Singlet	Triplet
			Cation	Cation	Anion	Anion
BZ 38	3 M	90	294	296	52	64
	4 P	91	301	294	50	84
	5 M	90	293	296	52	65
BZ 76	3 M	86	321	296	48	65
	4 P	87	327	295	46	58
	5 M	85	294	296	47	64
	2' O	85	295	292	53	88
BZ 81	3 M	83	287	291	43	82
	4 P	84	326	288	41	50
	5 M	83	287	291	43	56
	4' P	84	293	287	53	85
BZ 86	3 M	82	325	296	37	62
	4 P	83	326	296	37	91
	5 M	82	298	295	40	62
	6 O	82	304	293	38	88
	2' O	82	292	299	51	74
BZ 124	3 M	79	290	292	39	76
	4 P	80	322	290	37	47
	5 M	79	290	292	39	76
	2' O	79	314	288	41	73
	5' M	80	314	291	44	75
BZ 106	3 M	81	295	296	34	49
	4 P	81	326	292	34	47
	5 M	81	292	293	36	64
	2 O	80	295	290	34	82
	3' O	82	309	294	53	73
BZ 122	3 M	81	318	293	41	75
	4 P	81	323	293	39	50
	5 M	81	293	293	40	55
	2' O	80	317	290	40	74
	3' M	81	291	293	43	83

Appendix III - Relative Enthalpies of Formation of Dechlorinated Fragments as Calculated by Hyperchem 4.5 (kcal mol⁻¹)

BZ #	Chlorine Lost	Radical	Singlet	Triplet	Singlet	Triplet
			Cation	Cation	Anion	Anion
BZ 61	2 O	87	298	293	43	94
	3 M	87	295	300	42	59
	4 P	90	318	295	43	56
	5 M	88	295	297	45	58
BZ 86	3 M	82	325	296	37	62
	4 P	83	326	296	37	91
	5 M	82	298	295	40	62
	6 O	82	304	293	38	88
	2' O	82	292	299	51	74
BZ 106	3 M	81	295	296	34	49
	4 P	81	326	292	34	47
	5 M	81	292	293	36	64
	2 O	80	295	290	34	82
	3' O	82	309	294	53	73
BZ 114	2 O	89	302	297	36	76
	3 M	88	299	303	37	52
	5 M	88	299	303	40	70
	4 P	88	335	298	37	50
	4' P	91	306	300	73	50
BZ 141	2 O	75	293	286	29	72
	3 M	76	311	288	29	48
	4 P	76	322	288	29	83
	5 M	76	295	288	31	49
	2' O	76	306	291	38	66
	5' M	76	297	290	42	68
BZ 129	2 O	77	294	289	30	81
	3 M	77	321	293	30	51
	4 P	78	290	293	30	85
	5 M	77	295	290	33	53
	2' O	78	309	294	37	68
	3' M	78	309	293	41	69
BZ 156	2 O	75	290	284	26	69
	3 M	75	286	288	26	41
	4 P	76	323	286	26	72
	5 M	76	286	290	29	40
	3' M	77	287	288	39	66
	4' P	71	313	286	27	59

			Singlet	Triplet	Singlet	Triplet
BZ #	Chlorine Lost	Radical	Cation	Cation	Anion	Anion
BZ 62	2 O	87	345	302	43	86
	3 M	89	305	302	44	98
	4 P	88	302	301	45	121
	6 O	88	301	301	46	82
BZ 88	2 O	82	295	292	37	81
	4 P	83	297	296	39	122
	6 O	82	339	292	40	112
	3 M	83	300	294	38	91
	2' O	83	309	298	74	75
BZ 109	2 O	82	295	297	33	78
	4 P	82	297	297	36	60
	6 O	81	338	292	36	49
	3 M	82	315	297	35	77
	3' M	83	309	296	55	72
BZ 115	2 O	80	294	290	33	49
	4 P	82	297	296	35	49
	6 O	81	299	290	36	49
	3 M	82	325	299	35	87
	4' P	82	312	294	55	73
BZ 144	2 O	75	290	285	28	44
	3 M	77	320	287	30	81
	4 P	76	292	292	30	50
	6 O	76	332	285	31	44
	2' O	76	305	289	40	67
	5' M	76	310	289	44	67
BZ 131	2 O	77	291	293	29	46
	3 M	78	323	294	31	85
	4 P	78	293	293	32	93
	6 O	80	335	288	32	46
	2' O	78	295	292	67	68
	3' M	78	294	291	43	68
BZ 158	2 O	78	319	293	26	49
	3 M	77	322	294	28	80
	4 P	77	321	293	29	57
	6 O	75	316	296	29	49
	3' M	77	312	290	41	65
	4' P	77	314	290	41	66

Appendix III - Relative Enthalpies of Formation of Dechlorinate Fragments as Calculated by Hyperchem 4.5 (kcal mol⁻¹)

BZ #	Chlorine Lost	Radical	Singlet	Triplet	Singlet	Triplet
			Cation	Cation	Anion	Anion
BZ 65	2 O	88	302	300	44	86
	3 M	88	300	300	46	88
	5 M	89	300	300	46	88
	6 O	88	302	300	44	86
BZ 93	2 O	82	297	294	38	81
	3 M	83	298	294	40	82
	5 M	83	298	294	40	82
	6 O	82	293	294	38	81
	2' O	83	309	291	53	83
BZ 112	2 O	81	297	295	35	87
	3 M	83	298	295	37	78
	5 M	82	298	295	37	79
	6 O	81	335	295	34	87
	3' M	83	298	292	55	82
BZ 117	2 O	81	297	295	34	77
	3 M	81	298	295	36	78
	5 M	82	298	295	36	78
	6 O	81	297	295	34	77
	4' P	83	309	293	49	81
BZ 151	2 O	84	306	299	34	81
	3 M	86	307	303	36	77
	5 M	85	307	303	36	80
	6 O	84	298	298	34	81
	2' O	85	309	301	47	75
	5' M	86	322	301	50	76
BZ 134	2 O	77	294	291	30	83
	3 M	78	294	290	33	77
	5 M	78	294	290	33	54
	6 O	77	331	291	30	83
	2' O	77	308	297	40	76
	3' M	78	308	291	43	81
BZ 163	2 O	77	295	287	28	71
	3 M	80	287	289	30	50
	5 M	77	295	289	30	42
	6 O	77	288	287	28	80
	3' M	78	293	290	42	74
	4' P	79	299	292	42	75

Appendix III - Relative Enthalpies of Formation of Dechlorinate Fragments as Calculated by Hyperchem 4.5 (kcal mol⁻¹)

BZ #	Chlorine Lost	Radical	Singlet	Triplet	Singlet	Triplet
			Cation	Cation	Anion	Anion
BZ 116	2 O	136	299	301	36	119
	3 M	85	300	302	36	80
	4 P	141	299	302	35	125
	5 M	85	300	299	36	80
	6 O	142	342	301	36	79
BZ 142	2 O	124	294	290	30	74
	3 M	79	295	293	30	74
	4 P	135	293	296	29	82
	5 M	80	295	293	30	86
	6 O	125	332	290	29	105
	2' O	80	300	296	68	68
BZ 160	2 O	77	332	294	26	113
	3 M	78	295	291	27	78
	4 P	134	294	297	26	41
	5 M	78	295	297	27	79
	6 O	137	294	289	26	76
	3' M	79	309	293	51	65
BZ 166	2 O	77	330	288	26	102
	3 M	81	295	298	26	79
	4 P	134	293	297	26	40
	5 M	78	295	294	26	79
	6 O	84	294	288	26	102
	4' P	79	307	293	45	66
BZ 185	2 O	76	326	283	21	97
	3 M	75	290	284	21	73
	4 P	129	288	292	21	128
	5 M	73	290	284	21	74
	6 O	72	326	283	21	70
	2' O	73	295	287	36	60
	5' M	74	294	287	36	60
BZ 173	2 O	119	328	286	22	38
	3 M	74	291	290	23	76
	4 P	130	289	293	22	73
	5 M	74	293	290	23	76
	6 O	123	328	328	22	38
	2' O	75	292	290	35	61
	3' M	75	293	289	38	61
BZ 190	2 O	74	291	290	19	64
	3 M	73	292	290	20	45
	4 P	129	290	293	19	33
	5 M	73	292	290	20	72
	6 O	72	327	283	19	64
	3' M	74	291	288	37	58
	4' P	74	293	288	59	59

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IMAGE EVALUATION TEST TARGET (QA-3)

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