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Electron Capture Induced Regioselective Dechlorinations of PCBs.

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Abstract

A series of ten pure PCB congeners were unselectively chlorinated with isotopically enriched (>95%) chlorine-37 to produce ten sets of labelled PCB congeners. The labelled congeners in each of these sets were identified by GC/MS analysis. A collection of the ECNI mass spectra of these labelled congeners provided information on the regioselective nature of dechlorinations induced by electron capture. Information was obtained for the [M-Cl]-, [M+H-Cl]-, and [M+O-Cl]- fragment ions although only information on the [M-Cl]- fragment was addressed in this report. Regioselective dechlorinations were observed, and these were dependent on the isomeric arrangement of the chlorines present. A structure-reactivity model was developed to explain the observed dechlorinations. In essence, the specific arrangement of chlorines on one aromatic ring directed dechlorination to specific sites. The 3,4- and 3,4,5- arrangement of chlorines were found to be retained in the fragment ion and to have significant directing effects.

Introduction

The regioselective nature of PCB dechlorinations in the absence of substrate or solvation effects has not been established. The near vacuum conditions in an electron capture negative ion mass spectrometer (ECNI/MS) source (~0.5 torr) provides an almost ideal "environment" to investigate the intrinsic chemistry of PCB induced by electron capture. With the exception of the molecular ion, [M]^{-•}, almost all fragment ions observed in the ECNI mass spectra of PCBs are the result of some form of dechlorination. Typical fragment ions that are observed in the ECNI mass spectra of PCBs have the form [M-nCl]-, [M+nH-nCl]^{-•}, and [M+O-Cl]^{-•}. Each of these ions can be monitored to examine the regioselective nature of processes leading to their formation. However, it is likely that the [M-Cl]- ion forms soon after [M]^{-•} formation and thus is the most representative of the intrinsic chemistry of the dechlorination process of [M]^{-•}.

The natural abundance of chlorine (³⁵Cl-76% ; ³⁷Cl -24%) induces a distinct abundance-m/z pattern that is characteristic of the number of chlorines contained in an ion¹. The addition of an isotopically pure ³⁷Cl to an ion containing multiple natural abundance chlorines does not alter the relative abundance values. Therefore, the loss or retention of a ³⁷Cl label in the formation of a dechlorinated fragment from a molecule containing both natural abundance chlorines and isotopically enriched ³⁷Cl can be unambiguously determined.

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Experimental Methods

Mixtures of labelled PCB congeners were produced by unselective chlorination of a pure PCB starting material (AccuStandard) with isotopically enriched (>95%) chlorine-37 (Isotec, Inc.,). An analogous method has been described previously². In this investigation, all the PCB congeners containing three, four, or five chlorines on one aromatic ring and no chlorine on the other aromatic ring were labelled (BZ 21, BZ 23, BZ 24, BZ 29, BZ 30, BZ 38, BZ 61, BZ 62, BZ 65 and BZ 116). This labelling produced mixtures of labelled congeners that could be separated and unambiguously identified. Identification of labelled products was confirmed by a comparison of GC retention time and electron impact (EI) mass spectra with unlabelled standards (AccuStandard, Ultra Scientific, and CLB mixtures from NRC's Marine Analytical Chemistry Standards Program)

The ECNI mass spectra were obtained using a VG ZAB mass spectrometer with UHP methane (Matheson) as the moderator gas. The source pressure was varied between 0.25 torr and 0.50 torr as measured by a Pirani Gauge. The source ventilation rate was varied between 320 cm³sec⁻¹ and 530 cm³sec⁻¹ by opening and closing the source probe inlet hole and readjusting the pressure. The source temperature was approximately 140°C. Mass spectra were collected by scanning from m/z 200 to m/z 550. The mass spectrum of each labelled congener was obtained as it eluted from a GC capillary column. Approximately five to eight scans were collected during each GC peak. Three to six of the most intense of these scans were averaged to obtain a representative mass spectrum.

The percentage of the ³⁷Cl label lost in the formation of [M-X]- (where X = ³⁷Cl or natural abundance chlorine) was determined by comparing, via multiple regression analysis, the observed abundance-m/z pattern with those expected from either a loss of ³⁷Cl, a loss of natural abundance chlorine, a loss of ³⁷Cl with the addition of hydrogen (i.e., [M+H-X]-), and a loss of natural abundance chlorine with the addition of hydrogen. The expected abundance-m/z patterns were calculated by the method of binomial expansion as described in the monograph of McLafferty and Turecek¹. The multiple regression analysis was performed using the regression function available in the Quattro Pro 5.0 spreadsheet program. The error associated with each calculation varied with the signal to noise levels in the appropriate m/z range of the fragment ions. In order to increase the confidence associated with the data analysed, only those multiple regression analysis results with correlation coefficient (R²) value greater than 0.990 were considered. Furthermore, the standard deviation of all the percent-label-lost values for a given congener (with an R² > 0.990) was used to verify that no variation with instrument parameters occurred. A standard deviation less than 5 was taken to indicate no significant variation.

Results and Discussion

The average percent-label-lost values and associated standard deviations are presented in Table 1. In order to explain the structure regioselective dechlorination relationships that were observed in this investigation, it is useful to describe and classify PCBs in the following way. Each of the two phenyl rings was considered to be a substituent of the other and they interact with each other to produce a united effect. This implied specific labelled congeners should be grouped into certain sets or classes. In Table 1, labelled congeners are presented in sets defined by which pure PCB isomers were used as the starting material to produce the labelled products. For the most part, this grouped labelled congeners with the same chlorination pattern in the more highly chlorinated phenyl ring together. For discussion purposes, the more highly chlorinated

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phenyl ring will be referred to as ring "A", the less highly chlorinated phenyl ring as ring "B"

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 less than a random loss. Each measured percent-label-lost value was considered to have a \pm range of two times the reported standard deviation. All the congeners with the 3,4,5- pattern on ring "A" (BZ 38 set) had loss-of-label values which were classified as 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 values which were classified 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 values which were classified as less than a random loss. None of the other sets of ring "A" patterns had loss-of-label values within a set that could be classified as being similar to one another. In the three sets which did have similar classifications, there was a common structural property on ring "A", the presence of chlorines at positions 3,4, and 5.

The labelled congeners presented in Table 1 have also been sorted by the chlorine pattern on ring "B". In this case, all the congeners with the 3,4- pattern on ring "B" had loss-of-label values which were classified as greater than a random loss, whereas none of the other sets had loss-of-label values which could be classified as being similar to one another. For example, the seven congeners with the 3,4- pattern on ring "B" had an average percent-label-loss value of 13% with a standard deviation of only 3 (in % units), whereas all the congeners with the 2,3- pattern on ring "B" had percent-label-loss values which ranged from 3% to 73%. It is worth noting that the 3,4- configuration is also common to the three ring "A" sets that induce common dechlorinations.

The similarity of the four types of configurations: 3,4- ; 3,4,5- ; 2,3,4,5- ; and 2,3,4,5,6- which were able to dominate the overall observed chlorine loss, implied that there was only one type of dominant configuration, the 3,4- configuration. This configuration directed the loss of chlorine such that this configuration was maintained. The addition of other chlorine to the same aromatic ring simply modified the influence of this group. For instance, the presence of a chlorine at the meta-position (5-) enhanced this effect, while the presence of chlorine at only ortho-positions negated this effect unless a meta-chlorine (5-position) was also present. Thus, the 2,3,4- ; 2,4,5- ; and 2,3,4,6- structures do not also show the same type of dominance as 3,4- while the 2,3,4,5- ; and 2,3,4,5,6- structures do.

The reason why the 3,4- configuration has such unique and dominating effects is explained by a combination of factors. In a biphenyl structure the presence of a para-chlorine (position 4-) plays an important role. A chlorine induces resonance effects at positions ortho- and para- to its location on an aromatic system. For a para-chlorine in a biphenyl system, a resonance effect is induced at the biphenyl linkage. If the two aromatic rings are in a planar conformation, this resonance effect could be transferred to the second aromatic ring, and thus to the ortho- and para-positions on the second aromatic ring. Evidence for this effect has been demonstrated in NMR investigations³. If the two aromatic rings of a biphenyl molecule are orthogonal to each other, no resonance transfer from one ring to the other can occur. Therefore, even though an ortho-chlorine on a biphenyl system can have a resonance effect at the biphenyl-carbon (ie., the 1- or 1'-position), the presence of this chlorine also restricts planar conformation formation. The meta-chlorine (position 3 or 5) is ortho- to the para-carbon (at position 4) and thus stabilizes this site. Therefore, in a PCB the 3,4- configuration on one phenyl ring can influence the aromatic electron densities in the other phenyl ring while at the same time being particularly stable.

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All the congeners with a 2,3,4,5,- structure on ring "A" had loss-of-label values which were similar to a random loss. However, an analysis of the three members of this set that were produced from two different starting congeners indicated otherwise. In BZ 86 the chlorine at position 2- was lost 34% of the time. In BZ 106 the chlorine at position 2- was lost 52% of the time. Both of these losses are significantly greater than the 20% expected from a random chlorine loss. In BZ 114, the two para-positions were labelled and each were lost 16% of the time. Thus BZ 114 could also have a greater than random loss of chlorine from position 2-.

The observed directing effect and stability of the 3,4,5- and 3,4- structures has an unexpected, yet intriguing, coincidence, in that the three most toxic PCBs ^{4,5}, 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 configurations on both aromatic rings.

Table 1 : Percent Label Lost in Forming [M-X]- (Labels Indicated by Bold and Underline)

Products from BZ 21 (2,3,4-) Starting Material			
Congener	Structure	Percent Label Lost	Replicate Measurements (STD**)
BZ 60	2,3,4, <u>4</u> ,-	26% (Random 25%)	3 (1)
BZ 87	2, <u>2</u> ',3,4, <u>5</u> '-	28% (Random 40%)	3 (1)
BZ 82	2, <u>2</u> ',3, <u>3</u> ',4-	45% (Random 40%)	1 (0)*
BZ 105	2,3, <u>3</u> ',4, <u>4</u> '-	11% (Random 40%)	3 (2)
Products from BZ 23 (2,3,5-) Starting Material			
Congener	Structure	Percent Label Lost	Replicate Measurements (STD**)
BZ 63	2,3, <u>4</u> ',5-	27% (Random 25%)	2 (15)*
BZ 92	2, <u>2</u> ',3,5, <u>5</u> '-	64% (Random 40%)	5 (5)
BZ 83	2, <u>2</u> ',3, <u>3</u> ',5-	46% (Random 40%)	1 (0)
BZ 117	2,3, <u>4</u> ',5, <u>6</u> '-	53% (Random 40%)	5 (3)
BZ 107	2,3, <u>3</u> ', <u>4</u> ',5-	13% (Random 40%)	4 (2)
BZ 114	2,3, <u>4</u> ', <u>4</u> ',5-	32% (Random 40%)	4 (2)
Products from BZ 24 (2,3,6-) Starting Material			
Congener	Structure	Percent Label Lost	Replicate Measurements (STD**)
BZ 64	2,3, <u>4</u> ',6-	58% (Random 25%)	3 (2)
BZ 95	2, <u>2</u> ',3, <u>5</u> ',6-	4% (Random 40%)	5 (5)
BZ 110	2,3, <u>3</u> ', <u>4</u> ',6-	20% (Random 40%)	1 (0)*
Products from BZ 29 (2,4,5-) Starting Material			
Congener	Structure	Percent Label Lost	Replicate Measurements (STD**)
BZ 74	2,4, <u>4</u> ',5-	74% (Random 25%)	5 (3)
BZ 101	2, <u>2</u> ',4,5, <u>5</u> '-	79% (Random 40%)	5 (3)
BZ 97	2, <u>2</u> ', <u>3</u> ',4,5-	73% (Random 40%)	2 (1)
BZ 118	2, <u>3</u> ',4, <u>4</u> ',5-	16% (Random 40%)	3 (4)

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Table 1 : Percent Label Lost in Forming [M-X]- (continued)

Products from BZ 30 (2,4,6-) Starting Material			
Congener	Structure	Percent Label Lost	Replicate Measurements (STD**)
BZ 75	2,4, <u>4'</u> ,6-	14% (Random 25%)	3 (1)
BZ 103	2, <u>2'</u> ,4, <u>5'</u> ,6-	74% (Random 40%)	4 (3)
BZ 88	2, <u>2'</u> , <u>3'</u> ,4,6-	24% (Random 40%)	3 (5)
BZ 109	2, <u>3'</u> , <u>3'</u> ,4,6-	31% (Random 40%)	2 (2)
BZ 115	2, <u>3'</u> , <u>4'</u> , <u>4'</u> ,6-	54% (Random 40%)	4 (6)*
Products from BZ 38 (3,4,5-) Starting Material			
Congener	Structure	Percent Label Lost	Replicate Measurements (STD**)
BZ 76	3,4, <u>2'</u> ,5-	62% (Random 25%)	1 (0)*
BZ 81	3,4, <u>4'</u> ,5-	58% (Random 25%)	1 (0)*
BZ 86	<u>2'</u> , <u>2'</u> ,3,4,5-	58% (Random 40%)	5 (1)
BZ 124	<u>2'</u> ,3,4,5, <u>5'</u> -	77% (Random 40%)	4 (4)
BZ 106	<u>2'</u> ,3, <u>3'</u> ,4,5-	87% (Random 40%)	2 (3)
BZ 122	<u>2'</u> ,3, <u>3'</u> ,4,5-	73% (Random 40%)	4 (5)
Products from BZ 61 (2,3,4,5-) Starting Material			
Congener	Structure	Percent Label Lost	Number Measured (Standard Deviation)
BZ 86	2, <u>2'</u> ,3,4,5-	24% (Random 20%)	8 (3)
BZ 106	2,3, <u>3'</u> ,4,5-	25% (Random 20%)	8 (6)*
BZ 114	2,3,4, <u>4'</u> ,5-	16% (Random 20%)	8 (5)
BZ 141	2, <u>2'</u> ,3,4,5, <u>5'</u> -	30% (Random 33%)	3 (5)
Products from BZ 62 (2,3,4,6-) Starting Material			
Congener	Structure	Percent Label Lost	Replicate Measurements (STD**)
BZ 88	2, <u>2'</u> ,3,4,6-	2% (Random 20%)	4 (2)
BZ 109	2,3, <u>3'</u> ,4,6-	20% (Random 20%)	6 (5)
BZ 115	2,3,4, <u>4'</u> ,6-	13% (Random 20%)	6 (1)
BZ 144	2, <u>2'</u> ,3,4, <u>5'</u> ,6-	30% (Random 33%)	6 (5)
BZ 158	2,3, <u>3'</u> , <u>4'</u> , <u>4'</u> ,6-	12% (Random 33%)	4 (4)
Products from BZ 65 (2,3,5,6-) Starting Material			
Congener	Structure	Percent Label Lost	Replicate Measurements (STD**)
BZ 93	2, <u>2'</u> ,3,5,6-	9% (Random 20%)	4 (8)*
BZ 112	2,3, <u>3'</u> ,5,6-	45% (Random 20%)	5 (6)*
BZ 117	2,3, <u>4'</u> ,5,6-	21% (Random 20%)	7 (5)
BZ 151	2, <u>2'</u> ,3,5, <u>5'</u> ,6-	43% (Random 33%)	3 (5)
BZ 163	2,3, <u>3'</u> , <u>4'</u> ,5,6-	10% (Random 33%)	1 (0)*

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Table 1 : Percent Label Lost in Forming [M-X]- (continued)

Products from BZ 116 (2,3,4,5,6-) Starting Material			
Congener	Structure	Percent Label Lost	Replicate Measurements (STD**)
BZ 142	2, <u>2</u> ',3,4,5,6-	3% (Random 17%)	13 (1)
BZ 160	2,3, <u>3</u> ',4,5,6-	6% (Random 17%)	13 (2)
BZ 166	2,3,4, <u>4</u> ',5,6-	5% (Random 17%)	14 (2)
BZ 185	2, <u>2</u> ',3,4,5, <u>5</u> ',6-	12% (Random 29%)	13 (3)
BZ 173	2, <u>2</u> ',3, <u>3</u> ',4,5,6-	12% (Random 29%)	3 (2)
BZ 190	2,3, <u>3</u> ',4, <u>4</u> ',5,6-	11% (Random 29%)	6 (3)

* indicates possible variation in percent label lost values with instrument parameters.

** STD indicates Standard Deviation.

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