Electron Capture Negative Ion and Positive Ion Chemical Ionization Mass Spectrometry of Polychlorinated Phenoxyanisoles

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Several polychlorinated phenoxyphenols with three to nine chlorine atoms were examined as their methyl ethers by electron capture negative ion and positive ion chemical ionization and electron impact mass spectrometry. In chemical ionization studies methane, hydrogen, nitrogen, helium and argon were used as reagent gases. Selected compounds were also examined with deuteriomethane, ammonia and deuterioammonia as reagent gases. Utilization of chemical ionization spectra in conjunction with electron impact spectra provides substantial structural information about these compounds. Chemical ionization spectra provide information about chlorine atom substitution. The position of phenoxy substitution can be established from electron capture negative ion and positive ion spectra.

INTRODUCTION

Significant concentrations of a large number of chlorinated by-products have been detected in the analyses of technical pentachlorophenol (PCP).[1] Polychlorinated phenoxyphenols are among the major impurities in technical PCP.[2–5] The three nonachlorophenoxyphenols have been isolated from technical PCP and identified by electron impact (EI) mass spectrometry.[4] Five octachlorophenoxyphenol isomers were identified by utilization of a combination of EI and electron capture negative ion chemical ionization (ECNICI) mass spectrometry.[5] Alkyl ethers of these polychlorinated phenoxyphenols were utilized in these gas chromatographic mass spectrometric analyses.

In this investigation, methyl ethers of polychlorinated phenoxyphenols (polychlorinated phenoxyanisoles) were studied by ECNICI, positive ion chemical ionization (PICI) and EI mass spectrometry. Methane, hydrogen, nitrogen, helium and argon were used as reagent gases in chemical ionization (CI) studies of all fourteen compounds. Spectra of selected compounds were also obtained utilizing deuteriomethane, ammonia and deuterioammonia as reagent gases. Structures of the compounds studied are shown in Fig. 1.

RESULTS AND DISCUSSION

ECNICI

Negative ion chemical ionization mass spectra of 14 polychlorophenoxyanisoles were obtained using CI source conditions with methane, hydrogen, nitrogen, helium and argon as reagent gases. For selected compounds ammonia and deuterioammonia were also used as reagent gases. However, none of these gases acts as true negative ion chemical ionization agents for these compounds. Rather, the reagent gases primarily moderate the energy of the electrons to thermal energies.[6] Thus, negative ion spectra of polychlorinated phenoxyanisoles primarily result from fragmentations by electron capture processes under these conditions. Results are summarized in Table 1.

The only peaks in the negative ion spectra of these compounds resulting from chemical ionization are the $[M+35]^-$ chloride attachment peaks observed in some of the spectra of phenoxyanisoles containing six or fewer chlorine atoms and the $[M+21]^-$ peaks corresponding to addition of hydrogen chloride with loss of methyl radical. In both cases, chemical ionization by the species itself is involved rather than chemical ionization by the reagent gas. Chloride attachment peaks observed in methane–oxygen enhanced negative ion spectra of tetrachlorinated diphenyl ethers have been attributed to chloride anion attachment or to HCl_2^- attack on the molecule.[7] Both of these species are abundant in the negative ion spectra of polychlorinated phenoxyanisoles, particularly the lower chlorinated analogs. $[M+HCl-CH_3]^-$ anion peaks are observed only in spectra of phenoxyanisoles in which one of the rings contains one or no chlorine substituents and only when inert reagent gases (nitrogen, argon or helium) are used. Formation of $[M+HCl-CH_3]^-$ anions is particularly significant for 2-(pentachlorophenoxy)anisole (Cl_0-2-(Cl_5P)A). When helium is used as the reagent gas, the ion cluster based at *m/z* 391 arising from this anion contains the base peak.

Hydrogen chloride elimination by molecular anions of these polychlorinated phenoxyanisoles is a significant process for a number of compounds and seems to

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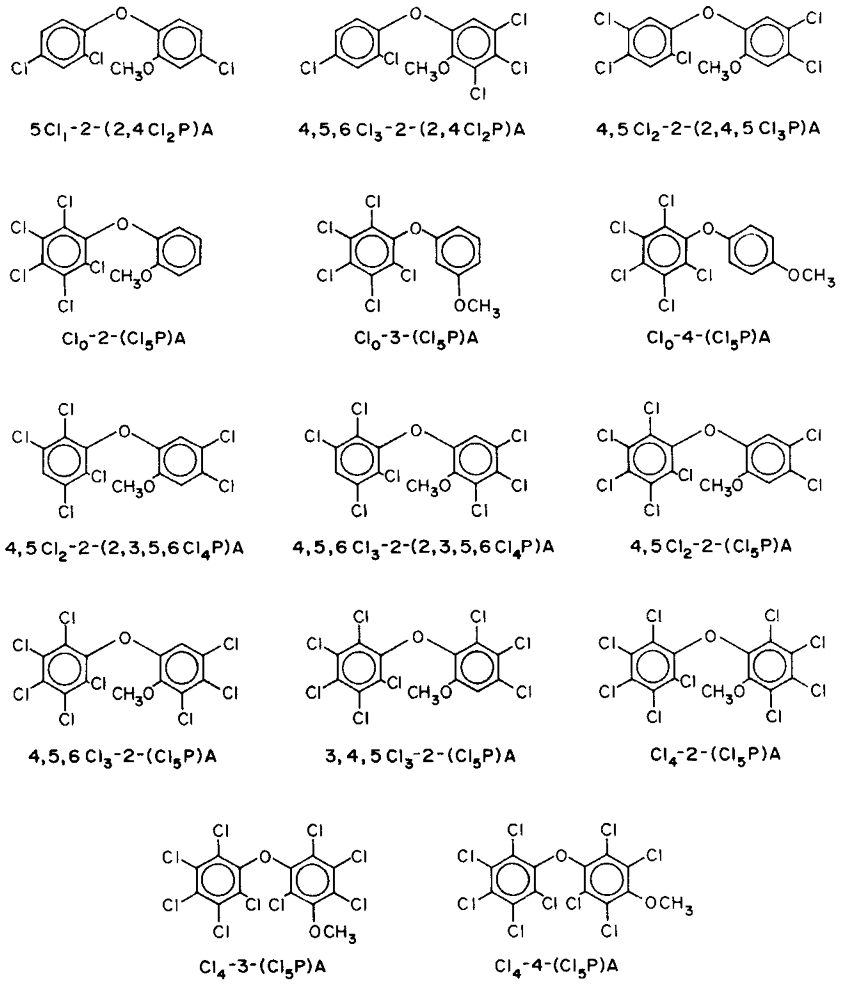


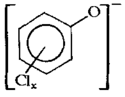
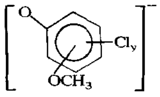
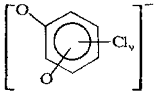
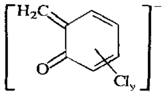
Figure 1. Structures of polychlorophenoxyanisoles. The abbreviations used to describe the compounds are derived from the nomenclature of the compounds, e.g. $5Cl_1$-2-($2,4Cl_2P$)A represents 5-chloro-2-(2′,4′-dichlorophenoxy)anisole. Where no confusion as to the position of chlorine substitution on the rings is possible, the numbers indicating position of chlorine atom substitution are dropped from the abbreviations.

occur by an interannular process in which a methoxypolychlorinated dibenzofuran is formed. The intensity of $[M-36]^{-\cdot}$ anion peaks is quite significant in the spectra of all of these compounds containing a hydrogen atom adjacent to the phenoxy linkage on one ring and a chlorine atom adjacent to the phenoxy linkage on the other ring (Fig. 2). An exception to this rule is, however, observed for 3-(pentachlorophenoxy)anisole (Cl_0-3-(Cl_5P)A) (Fig. 3).

Ion clusters at *m/z* 319 and 298 for Cl_0-3-(Cl_5P)A and for 4,5-dichloro-2-(2′,4′,5′-trichlorophenoxy)-anisole ($4,5Cl_2$-2-($2,4,5Cl_3P$)A) (Fig. 2) correspond to loss of methyl radical $[M-36-15]^-$ and hydrogen chloride $[M-36-36]^{-\cdot}$, respectively, from the methoxypolychlorodibenzofuran anion. As expected, since elimination of HCl and loss of the alkyl radical are characteristic fragmentations of alkoxypolychlorodibenzofurans,[8] these anions are observed in the spectra of all the compounds studied which could undergo interannular hydrogen chloride elimination to form a polychlorodibenzofuran anion. Interannular elimination of hydrogen chloride by Cl_0-3-(Cl_5P)A, which may occur but is not evident from the spectra, would result in the formation of a 1- or 3-methoxytetrachlorodibenzofuran anion (Scheme 1). The molecular anions in ECNICI spectra of 1- and 3-alkoxypolychlorodibenzofurans are very weak, if they are observed at all. Rather $[M-R]^-$ anions are observed.[8] An interannular hydrogen chloride elimination by the phenoxyanisoles which exhibit $[M-36]^{-\cdot}$ anions, all of which have the phenoxy linkage in the 2- or 4-position, would lead to formation of 2- or 4-methoxypolychlorodibenzofurans (Scheme 2). The 2- and 4-alkoxy isomers of polychlorinated dibenzofurans form molecular anions which are readily observed in ECNICI spectra.[8]

Although some of these compounds meet the criteria reported for HCl elimination in other compounds, i.e. a chlorine atom *ortho* to methoxy in polychloroanisoles[9] or a chlorine atom *ortho* to the phenyl ether linkage with an adjacent *meta* hydrogen in polychlorodiphenyl ethers,[7] neither of these criteria is met by some of the compounds which exhibit peaks corresponding to the loss of HCl. Elimination of HCl

Table 1. ECNICI mass spectra of some polychlorophenoxyanisoles[a]

Compound	$[M+Cl]^-$	$[M]^{-\cdot}$	$[M-H]^-$	$[M-HCl]^{-\cdot}$	$[M-HCl -CH]^{-\cdot}$	$[M-HCl -HCl]^-$					$[HCl_2]^{-\cdot}$	$[Cl]^{-\cdot}$	Other
$5Cl_1$-2-(2,4Cl_2P)A													
CH_4	<1[b]	1		22			3	1	10	<1	2	100	
H_2	23	5		100	18	<1	12		7		18		$[M-CH_3]^-$, 3
N_2	14	21		100			27	11	31		15		$[M+H]^-$, 25; $[M-CH_3]^-$, 10
Ar	29			100	42		17		16				$[M+HCl\text{-}CH_3]^-$, 3; $[M-CH_3]^-$, 23
He	67	6		100	30	2	15		8		27		$[M+HCl-CH_3]^-$, 22; $[M+H]^-$, 9; $[M-CH_3]^-$, 91; $[M-HCl\text{-}CH_3\text{-}Cl]^{-\cdot}$, 17
4,5,6Cl_3-2-(2,4Cl_2P)A													
CH_4	<1	100		75		26	38	26	5	1	7	47	$[H-Cl]^-$, 28; $[M-CH_3Cl]^{-\cdot}$, 10
H_2	<1	100		31	9	8	10	8	<1		3		
N_2		100		39	2	3	2	3	<1				
Ar	<1	100		50	7	6	<1	2					$[M-CH_3]^-$, 2
He	1	100		45	4	8	9	9	<1		1		$[M-CH_3]^-$, 2; $[M-Cl]^-$, 17; $[M-CH_3Cl]^{-\cdot}$, 7
4,5Cl_2-2-(2,4,5,Cl_3P)A													
CH_4		100		81	23	56	89	5	25	13	15	81	$[M-OCH_3]^-$, 24
H_2	<1	100		60	13	9	66	4	5		10		$[M-CH_3Cl]^{-\cdot}$, 29
N_2		100		44	12	7	28	2	2		1		$[M-CH_3Cl]^{-\cdot}$, 20
Ar	1	100		47	12	6	24	2	1				$[M-CH_3]^-$, 2; $[M-CH_3Cl]^{-\cdot}$, 21
He	7	100		52	15	7	72	6	5		9		$[M-CH_3]^-$, 4; $[M-CH_3Cl]^{-\cdot}$, 26
4,5Cl_2-2-(2,3,5,6Cl_4P)A													
CH_4		5		13		10	44		1	1	15	100	$[M-CH_3Cl]^{-\cdot}$, 5; $[C_6HCl_4]^-$, 25
NH_3	<1	5	15	100	21		90				31	13	$[M-OCH_3]^-$, 22; $[C_6HCl_4]^-$, 27
H_2	<1		20	62	15	47	100		6		40		$[M-CH_3Cl]^{-\cdot}$, 36; $[Cl_2]^{-\cdot}$, 4
N_2	<1		24	58		50	100		5		7		$[M-CH_3Cl]^{-\cdot}$, 41; $[C_6HCl_4]^-$, 39
Ar	<1		30	91	40	60	100	6	5				$[C_6HCl_4]^-$, 57
He	3		98	56	20	47	100	4	5		23		$[M-CH_3]^-$, 5; $[M-CH_3Cl]^{-\cdot}$, 29 $[C_6HCl_4]^-$, 41
4,5,6Cl_3-2-(2,3,5,6Cl_4P)A			<1	25		57	100	19		5	2	41	$[M-Cl]^-$, 5; $[M-2HCl-CH_3]^-$, 27
CH_4		2		5	31	51	100	7					$[M-OCH_3]^-$, 10; $[C_6HCl_4]^-$, 2
NH_3				10	54	72	100	8	2				$[M-Cl]^-$, 8
H_2				16	75	100	25						$[M-Cl]^-$, 22
N_2				17	100	95	84	9	2				$[M-CH_3]^-$, 2; $[M-Cl]^-$, 21
Ar			<1	12	51	77	100	10					$[M-Cl]^-$, 10; $[C_6HCl_4]^-$, 4
He													

[a] Spectra of additional compounds are available directly from authors.

[b] Per cent relative abundance. The most intense peak of ion cluster is reported.

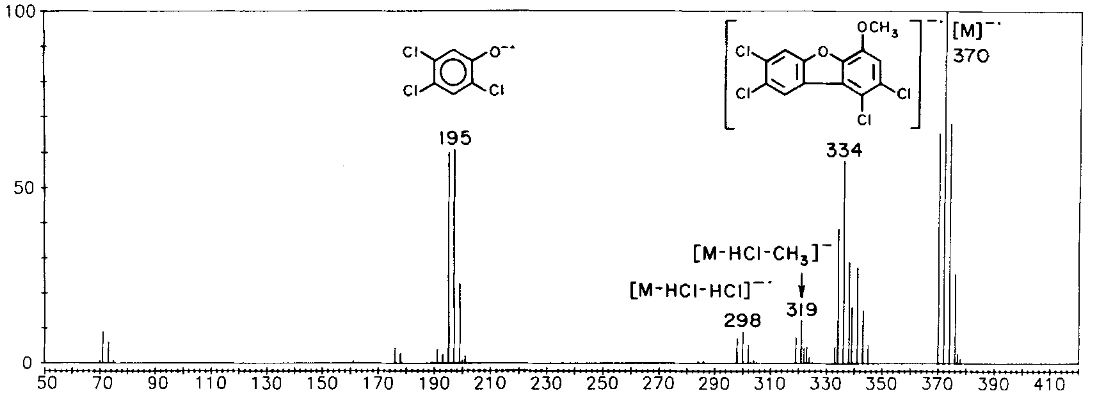


Figure 2. ECNICI mass spectrum of 4,5Cl$_2$-2-(2,4,5Cl$_3$P)A. Hydrogen reagent gas.

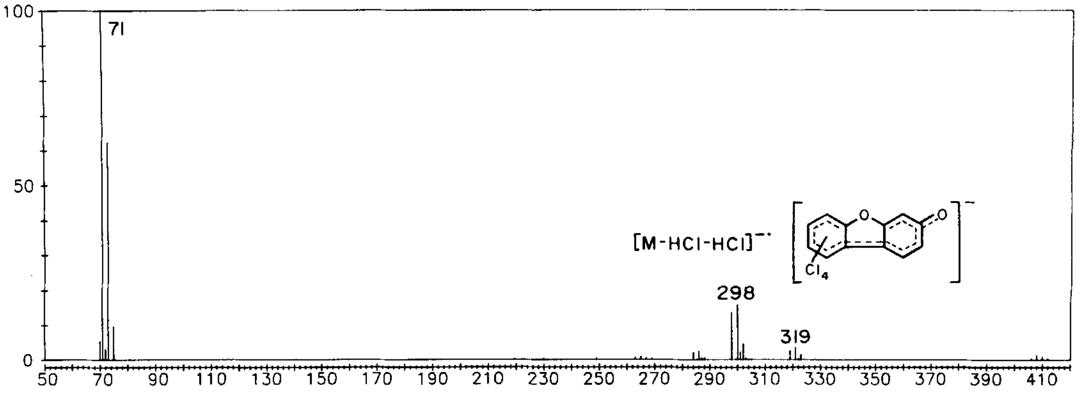
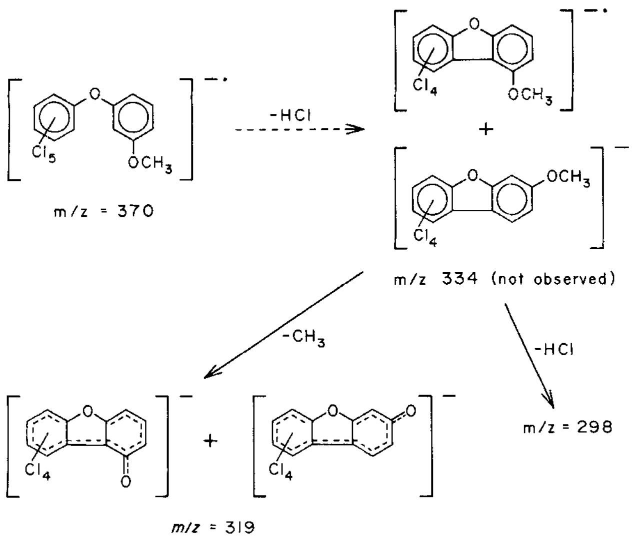


Figure 3. ECNICI mass spectrum of Cl$_0$-3-(Cl$_5$P)A. Hydrogen reagent gas.

by some polychlorodiphenyl ethers[7] and polychlorophenoxyphenols[10] has been attributed to an unspecified type of interannular process.

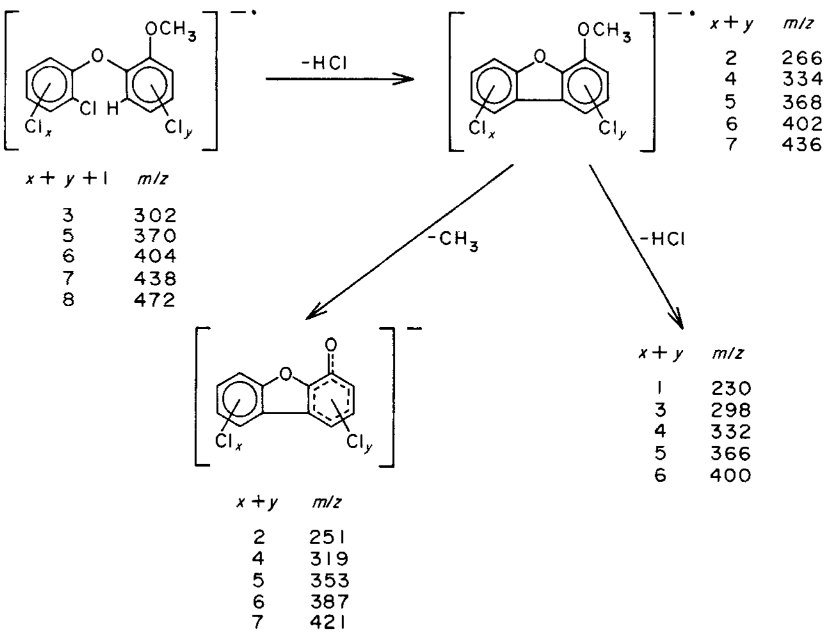
There are four polychlorinated phenoxyanisoles which exhibit no $[M-36]^{-\cdot}$ anions in their spectra. These include the three nonachlorophenoxyanisole isomers and 3,4,5-trichloro-2-(pentachlorophenoxy)-anisole (3,4,5Cl$_3$-2-(Cl$_5$P)A). There is also no evidence for $[M-HCl-CH_3]^{-\cdot}$ or $[M-HCl]^{-\cdot}$ anion formation in the spectra of these compounds. This is consistent with the fact that methoxypolychlorodibenzofurans cannot be formed by interannular HCl elimination because there are no hydrogen atoms *ortho* to the phenoxy linkage. None of the criteria for HCl elimination, either previously reported[7] or proposed here, are met by 3,4,5Cl$_3$-2-(Cl$_5$P)A, thus this polychlorophenoxyanisole would not be expected to undergo such an elimination.



Scheme 1.

Loss of HCl by polychlorophenoxyanisoles to form methoxypolychlorodibenzofuran anions with subsequent loss of methyl radical and HCl indicates the presence of at least one hydrogen atom *ortho* to the phenoxy linkage in one ring and at least one chlorine atom *ortho* to the phenoxy linkage in the other ring of the compound. Thus, this series of fragmentations in ECNICI spectra of these compounds is useful in the assignment of chlorine atom ring position.

Cleavage of the phenyl ether linkage in polychlorinated phenoxyanisoles may occur through two routes. The process which results in the phenoxide anion without the methoxy substituent (Scheme 3) predominates. Chlorinated phenoxide anions formed in this manner are significant in polychlorinated phenoxyanisole ECNICI spectra measured in all reagent gases. This is particularly true of highly chlorinated compounds. The base peak in the spectra, measured in all reagent gases, of those compounds containing eight or more chlorine atoms is attributable to this process.

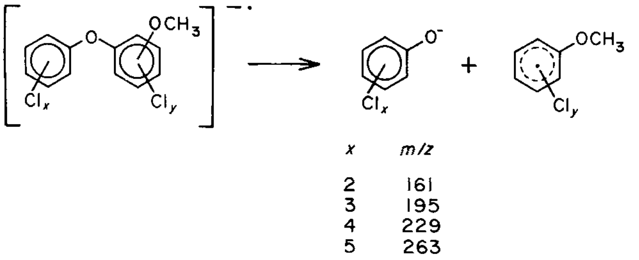


Scheme 2.

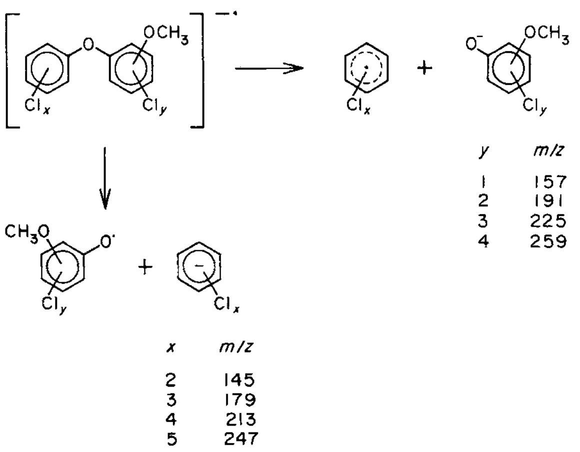
Formation of these phenoxide anions is significant for lower chlorinated analogs as well. It is observed to varying degrees in all reagent gases for all compounds studied. The loss of chlorine from the anions occurs for a few of the compounds with some reagent gases. The structural significance of this loss cannot be established from this group of compounds. From these phenoxide anions, chlorine atom distribution between the aromatic rings of the molecule can be established.[5]

Anions formed by the process in which the phenyl ether linkage is cleaved in such a way that the oxygen atom remains on the ring with the methoxy group (Scheme 4) are detected in the spectra of several of these compounds. In this case the negative charge may reside on either half of the molecule. Although neither anion formed in this manner is as significant as the phenoxide anion formed in Scheme 3, in general one or the other is observed in all spectra. For nonachloro analogs both are observed.

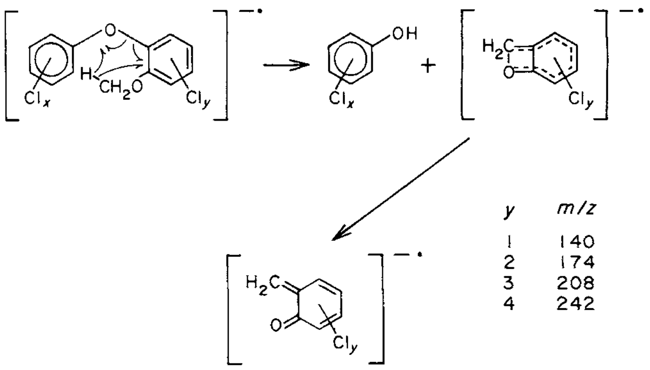
Anions formed by elimination of a neutral chlorophenol molecule formed by hydrogen atom abstraction from the methoxy group by the chlorophenoxy group (Scheme 5) are characteristic of methane ECNICI spectra of most polychloro-2-phenoxyanisoles. Hydrogen atom abstraction from the methoxy group of polychloroanisoles by *ortho* chlorine atoms has been demonstrated.[9] Peaks arising from this anion are most intense in the spectrum (Fig. 4) of tetrachloro-2-(pentachlorophenoxy)anisole (Cl_4-2-(Cl_5P)A) at *m/z* 242. Ammonia and deuterioammonia spectra of Cl_4-2-(Cl_5P)A also exhibit peaks attributed to this anion which is unique to spectra of chlorinated 2-phenoxyanisoles.



Scheme 3.



Scheme 4.



Scheme 5.

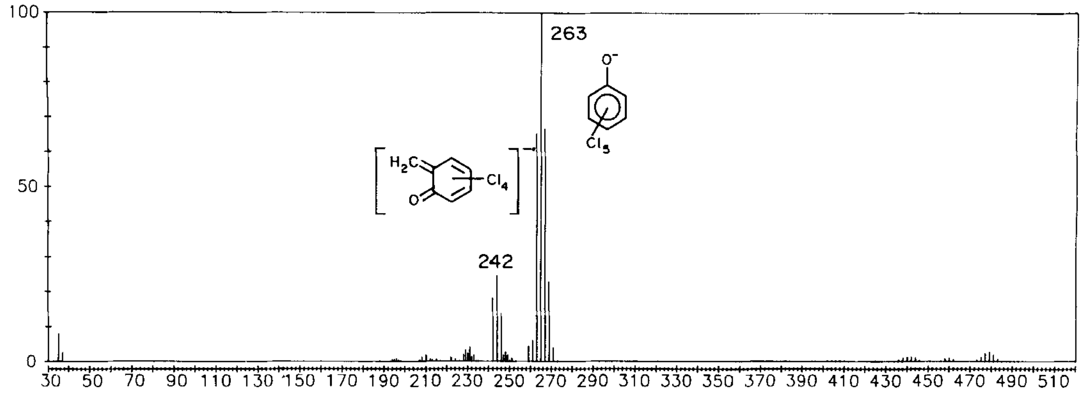


Figure 4. ECNICI mass spectrum of Cl_4-2-(Cl_5P)A. Methane reagent gas.

Generally, when methane is used as the reagent gas, peak intensities at *m/z* 35 and 37 corresponding to chloride increase with decreasing number of chlorine substituents. For 5-chloro-2-(2′,4′-dichlorophenoxy)-anisole (5Cl_1-2-(2,4Cl_2P)A) and most pentachloro isomers *m/z* 35 represents the base peak in the spectrum. For the nonachloro isomers, chloride anion peak intensities are 2% or less. This region of the spectrum was not scanned for other reagent gases except those cases where ammonia or deuterioammonia was used. Spectra obtained with these two reagent gases appear to follow the trend established in methane.

HCl_2^- anions, characterized by peaks at *m/z* 71, 73 and 75 are also widely observed in chlorinated phenoxyanisole spectra. Formation of this species in negative ion chemical ionization mass spectrometry of polychlorinated insecticides has been attributed to secondary reactions of chloride anions.[11] In general, the same trend is observed for HCl_2^- ion formation in all reagent gases except argon, in which the ion is observed only for Cl_0-2-(Cl_5P)A, as is observed for Cl^- ion formation in methane.

Molecular anion peaks and $[M-H]^-$ anion peaks are generally weak or not observed. In particular, the absence of these peaks is notable in negative ion chemical ionization spectra of highly chlorinated analogs. The exceptions are 4,5,6-trichloro-2-(2′,4′-dichlorophenoxy)anisole (4,5,6Cl_3-2-(2,4Cl_2P)A) and 4,5Cl_2-2-(2,4,5ClP)A which exhibit strong molecular ion peaks (base peak) in all reagent gases and 4,5-dichloro-2-(2′,3′,5′,6′-tetrachlorophenoxy)anisole (4,5Cl_2-2-(2,3,5,6Cl_4P)A) which exhibits relatively intense $[M-H]^-$ anion peaks.

Other minor fragment ions observed include $[M-15]^-$, $[M-31]^-$, $[M-35]^-$, $[M-50]^{-\cdot}$ and $[M-70]^{-\cdot}$ arising from loss of CH_3, OCH_3, Cl, CH_3Cl and Cl_2, respectively. From this set of compounds there does not appear to be any specific structural requirements for these losses and no significant structural information is derived from them.

In general, fragmentation patterns in ECNICI spectra of polychlorinated phenoxyanisoles are not greatly affected by the choice of reagent gas. General trends in relative abundances resulting from variation of the reagent gas are not observed. However, the overall detectability of a given compound is affected. The order of sensitivity for these compounds is hydrogen > methane ≈ ammonia ≈ deuterioammonia > nitrogen > argon > helium. Enhancement of molecular negative ion current in nitrobenzene by hydrogen has been reported.[12] These differences in sensitivity may be due to varying energy content of electrons. The use of different reagent gases gives rise to varying electron energy.[13]

Chemical ionization by the species itself appears to be enhanced by using inert reagent gases. This may result from the inability of reactive species formed in fragmentation processes to react with the reagent gas.

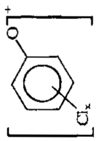
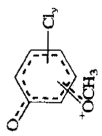
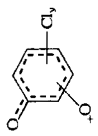
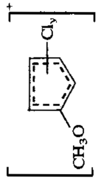
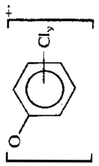
PICI and EI

In positive ion chemical ionization mass spectrometry polychlorinated phenoxyanisoles undergo ionization by charge exchange in nitrogen, argon and helium whereas ionization takes place predominantly by chemical means in methane, deuteriomethane, ammonia and deuterioammonia. When hydrogen is used as the reagent gas, fragmentations characteristic of both processes are observed.

Since nitrogen, argon and helium act as charge exchange reagent systems, the fragmentation reactions are essentially the same as those observed in EI mass spectrometry of polychlorophenoxyanisoles (Table 2). Variations in spectral intensities arise from differences in the internal energies of the molecular ions formed and from variations in reagent gas pressures. In EI ionization molecular ions having a distribution of internal energies are formed, while molecular ions formed by charge exchange have a discrete internal energy dependent on the recombination energy of the reactant ion in the reagent gas.[14]

As reported for the EI spectra of nonachlorophenoxyanisoles[4,15] and di- and tri-chlorophenoxyanisoles[16] the position of the chlorophenoxy substituent is indicated by unique fragmentations from the molecular ion. EI and charge exchange spectra of polychloro-2-(polychlorophenoxy)anisoles are dominated by intense molecular ion peaks and $[M-50]^+$ peaks resulting from the formation of polychlorodibenzo-*p*-dioxin ions by elimination of CH_3Cl (Fig. 5(b)). Fragments formed by loss of Cl, COCl and 2 COCl from polychlorodibenzo-*p*-dioxin ions are also observed to varying degrees in some of the EI and charge exchange

Table 2. Positive ion mass spectra of some polychlorophenoxyanisoles[a]

Compound	$[M+H]^+$	$[M]^{+\cdot}$	$[M-Cl]^+$ [c]	$[M-CH_3Cl]^{+\cdot}$	$[M-CH_3Cl-Cl]^+$	$[M-CH_3Cl-COCl]^{+\cdot}$	$[M-Cl_2]^{+\cdot}$ [d]						Other
5Cl$_1$-2-(2,4Cl$_2$P)A													
CH_4	57[b]	13	22					9	100	7			$[M+CH_3]^+$, 1; $[M+C_2H_5]^+$, 2; $[M+C_2H_5-C_6H_3Cl_2O]^{+\cdot}$, 14; $[M+C_3H_5]^+$, 2; $[M+C_3H_5-C_6H_3Cl_2O]^{+\cdot}$, 4; $[M+H-Cl_2]^{+\cdot}$, 8; $[M-C_6H_3Cl_2-Cl]^{+\cdot}$, 13
H_2		97	32	23				14	100	22	6		
N_2	13	59	10	100			12	12	62	5	12		
Ar		33	3	100			10		11		6		
He		100	3	50			6	6	16		5	7	
EI		91		100	7	25	14	17	16		15	32	$[C_6H_3Cl_2O]^+$, 17; $[C_6H_3Cl_2]^+$, 27
4,5,6Cl$_3$-2-(2,4Cl$_2$P)A													
CH_4	100	7	10					60	98	7			$[M+C_2H_5]^+$, 3; $[M+C_2H_5-C_6H_3Cl_2O]^{+\cdot}$, 20; $[M+C_3H_5]^+$, 2; $[M+C_3H_5-C_6H_3Cl_2O]^{+\cdot}$, 5; $[M+H-Cl_2]^+$, 4; $[M-C_6H_3Cl_2-Cl]^{+\cdot}$, 3; $[M-C_6H_3Cl_2-CH_3Cl]^+$, 3
H_2		89	9	36				47	100	15	4		$[M+H-CH_3]^{+\cdot}$, 18; $[M+H-Cl]^{+\cdot}$, 6
N_2		37	4	100			8	15	13				
Ar		21		100		11	6		4		<1	1	
He		100	4	79		10	7	4	1			7	
EI		61		100	5		8	15				2	$[C_6H_3Cl_2]^+$, 15
4,5Cl$_2$-2-(2,4,5Cl$_3$P)A													
CH_4	47		10					25	100	86			$[M+C_2H_5]^+$, 3; $[M+C_2H_5-C_6H_2Cl_3O]^{+\cdot}$, 46; $[M+C_3H_5-C_6H_2Cl_3O]^{+\cdot}$, 15; $[M+H-Cl_2]^+$, 5
H_2		100	47	23			7	18	81	58	5	2	
N_2		45	11	100			11	9	20	9	5		
Ar		26	10	100		12	11	4	7	1	3	2	
He		100	3	44		9	6	2	4		2	2	
EI		84		100	7	24	16	17	22		16	29	$[C_6H_2Cl_3]^+$, 31
Cl$_0$-2-(Cl$_5$P)A													
CH_4	21	10	18						100	59			$[M+C_2H_5]^+$, 1; $[H+C_2H_5-C_6Cl_5O]^{+\cdot}$, 27; $[M+C_3H_5-C_6Cl_5O]^{+\cdot}$, 13; $[M+H-Cl_2]^+$, 24
NH_3		80		20			55						$[M+NH_4]^{+\cdot}$, 100; $[M+NH_4-Cl]^{+\cdot}$, 7; $[M-HCl]^{+\cdot}$, 10
ND_3		47		10									$[M+ND_4]^+$, 100; $[M+D-HCl-Cl]^{+\cdot}$, 37;
H_2		43	5	10			7		100	78	11	3	$[M+H-CH_3]^{+\cdot}$, 2; $[M+H-Cl]^{+\cdot}$, 10;
N_2		46	9	100		26	38		50	17	40	25	$[M-HCl]^{+\cdot}$, 9
Ar		55	5	100		17	23		13	3	13	8	
He		100	10	42		6	13		2		3	7	
EI		100		56		1	37		4		16	49	

[a] Spectra of additional compounds are available directly from authors.

[b] Per cent relative abundance. Most intense peak of ion cluster is reported.

[c] $[M+H-HCl]^+$ for methane, ammonia and hydrogen.

[d] $[M+H-HCl-Cl]^{+\cdot}$ for methane, ammonia and hydrogen.

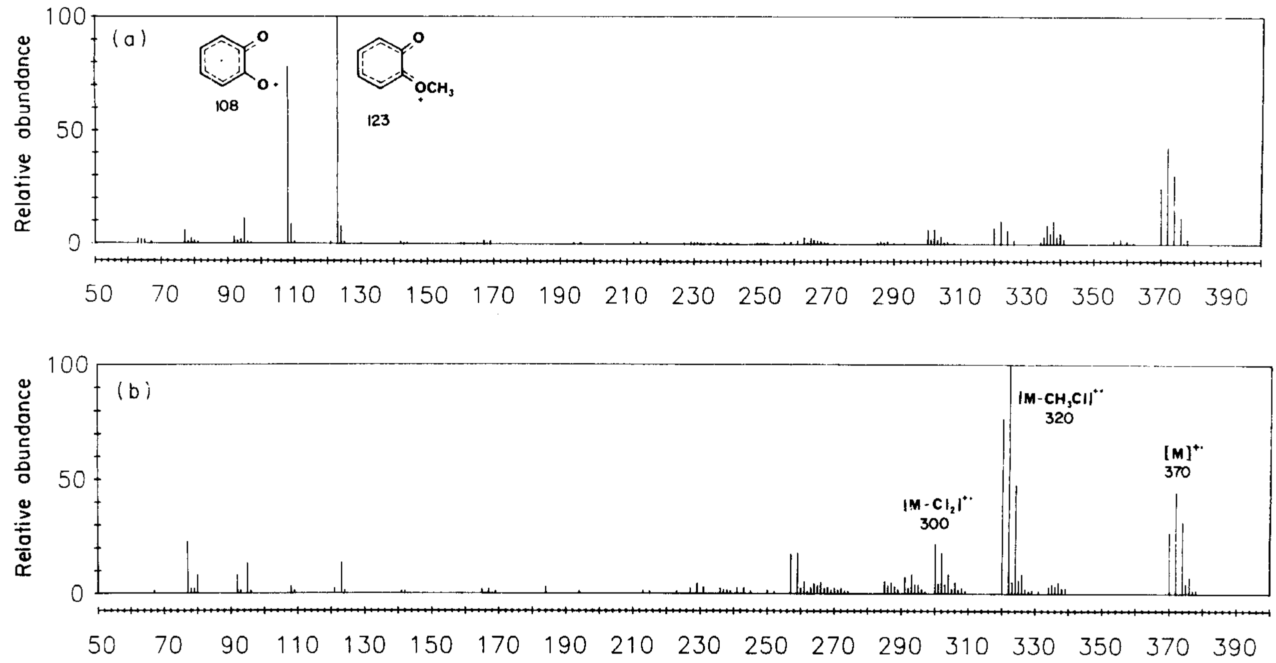


Figure 5. PICI mass spectra of Cl_0-2-(Cl_5P)A. (a) Hydrogen reagent gas; (b) argon reagent gas.

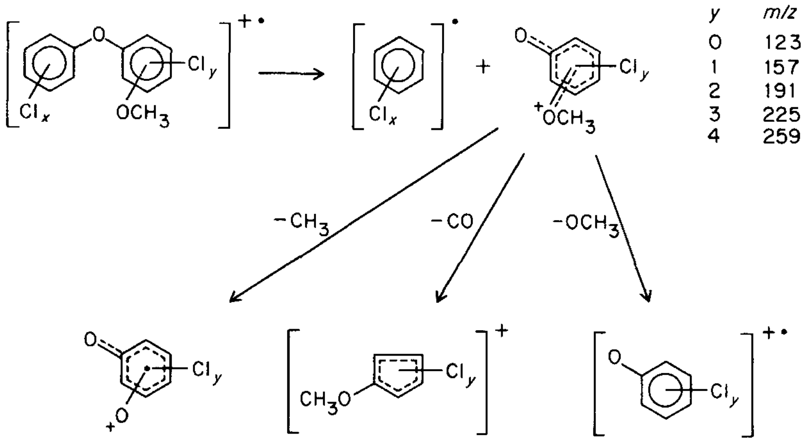
PICI spectra of compounds containing polychlorophenoxy substituents in the 2-position. Fragmentations corresponding to these have been reported in the EI spectra of chlorinated dibenzo-*p*-dioxins.[17,18]

Charge transfer and EI spectra of tetrachloro-3-(pentachlorophenoxy)anisole (Cl_4-3-(Cl_5P)A) and Cl_0-3-(Cl_5P)A are characterized by strong molecular ion peaks and $[M-70]^+$ peaks due to the loss of Cl_2 from the molecular ion. In the EI spectra of Cl_4-3-(Cl_5P)A this ion at *m/z* 436 has been attributed to formation of methoxyheptachlorodibenzofuran (CH_3OCl_7DBF) ions by concerted or stepwise loss of Cl_2.[4] This is supported by the presence of peaks characteristic of chlorinated dibenzofuran fragmentations[13] at *m/z* 421 $[CH_3OCl_7DBF-CH_3]^+$ and at 393 $[OCl_7DBF-CO]^+$ in nitrogen, argon, helium and EI spectra and at *m/z* 358 $[OCl_7DBF-COCl]^+$ in helium and EI spectra. The loss of Cl_2 by Cl_0-3-(Cl_5P)A to form the ion at *m/z* 300 must occur by a different route since no dibenzofuran ion could be formed by such a loss. There is an absence of fragment ions attributable to dibenzofurans in the Cl_0-3-(Cl_5P)A spectra. The relatively high abundance of $[M-Cl]^+$ ions at *m/z* 371 suggests a stepwise loss of two chlorine atoms.

The structurally significant feature of EI[4] and charge transfer spectra of the anisoles substituted with phenoxy in the 4-position is the presence of relatively intense $[M-15]^+$ ions due to loss of methyl radical. Molecular ion peaks are very intense in these spectra. The formation of $[M-70]^+$ ions by 4-(pentachlorophenoxy)anisole (Cl_0-4-(Cl_5P)A) and tetrachloro-4-(pentachlorophenoxy)anisole (Cl_4-4-(Cl_5P)A), though not as significant a process as for Cl_0-3-(Cl_5P)A and Cl_4-3-(Cl_5P)A should be noted. As for Cl_4-3-(Cl_5P)A, $[M-70]^+$ peaks at *m/z* 436 in Cl_4-4-(Cl_5P)A spectra apparently result from $[CH_3OCl_7DBF]^+$ ion formation as indicated by the existence of significant dibenzofuran-like fragmentations from the ion at *m/z* 436.

Other fragment ions of structural interest in charge exchange and EI spectra of these compounds result from cleavage of the phenoxy linkage. However, these ions are generally more evident in spectra obtained with more reactive reagent gases such as methane and hydrogen (Table 2). This is illustrated by a comparison of the spectra of Cl_0-2-(Cl_5P)A in hydrogen and argon (Fig. 5). Cleavage of the phenoxy linkage results in the formation of the 2-methoxyphenoxy cation (*m/z* 123) which subsequently loses a methyl radical forming a quinoid cation (*m/z* 108) or a methoxy radical to form a phenoxy cation (*m/z* 91) or extrudes carbon monoxide to form the ion at *m/z* 95 (Scheme 6). Generally, methoxyphenoxy cations formed by initial cleavage of the phenoxy linkage and the ions resulting from loss of methyl radical from these cations dominate hydrogen and methane PICI spectra of polychlorophenoxyanisoles. Cations resulting from loss of OCH_3 and CO from methoxyphenoxy cations are generally present in low abundance. They are more prevalent in EI and charge exchange spectra. In addition, chlorinated phenoxy cations formed by cleavage of the phenoxy linkage adjacent to the ring with the methoxy substituent are detected (Scheme 7). Examination of isotopic profiles of ions formed by phenoxy linkage cleavage provides information about the distribution of chlorine atoms between the rings of the compound. Spectra obtained with methane and hydrogen chemical ionization conditions are particularly useful for this purpose since significant abundances of these ions are formed by most polychlorophenoxyanisoles under these conditions.

Ions resulting from the reaction of polychlorophenoxyanisole molecules with reagent gas ions are detected when methane or ammonia are used as reagent gases in chemical ionization experiments (Table 3). In spectra obtained with methane as the reagent gas, minor peaks attributed to $[M+C_2H_5]^+$ and $[M+C_3H_5]^+$ ions are observed for most polychloro-



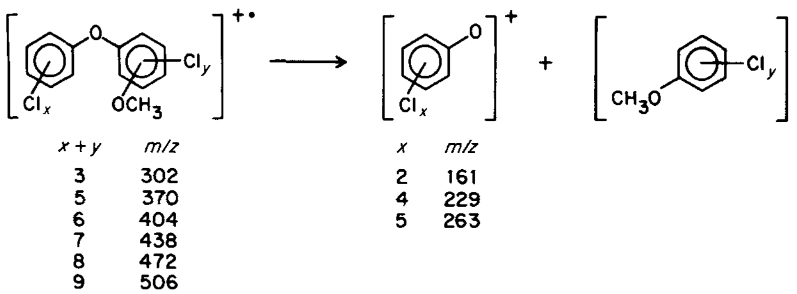
Scheme 6.

phenoxyanisoles. Peaks at m/z ($M+15$) arising from $[M+CH_3]^+$ ions are of very low intensity for the few spectra in which they are observed. Comparison of the methane spectrum with the deuteriomethane spectrum of 4,5Cl_2-2-(2,3,5,6Cl_4P)A (Fig. 6) indicates the formation of fragment ions by interaction of sample molecules with reactive components of the ionized reagent gas. The peaks at m/z 204 and m/z 216 in methane are shifted five mass units to m/z 209 and m/z 221, respectively, in deuteriomethane, revealing the presence of five hydrogen (or deuterium) atoms from the reagent gas in each of these ions. The significant quantities of $[C_2H_5]^+$ and $[C_3H_5]^+$ ions in methane reagent plasmas[14] suggests that interactions of these ions with sample molecules may be responsible for the formation of ions at m/z 204 and m/z 216. Isotopic profiles of the ions at m/z 204 and 216 in methane and m/z 209 and 221 in deuteriomethane indicate that they contain two chlorine atoms (the same number of chlorine substituents as the ring with the methoxy group). These fragment ions may be formed by either of two pathways: (i) from $[M+C_2H_5]^+$ and $[M+C_3H_5]^+$ ions by cleavage of the phenoxy linkage adjacent to the ring with the methoxy substituent, the reagent ion and charge remaining with that ring or (ii) from sample molecules by loss of chlorophenoxy radical (e.g. 4,5Cl_2-2-(2,3,5,6Cl_4P)A loses the tetrachlorophenoxy radical) upon attack by $[C_2H_5]^+$ or $[C_3H_5]^+$ ion in a concerted fashion (Scheme 8). This process is a general fragmentation pathway for methane CI of chlorinated phenoxyanisoles, although much less significant for Cl_0-3-(Cl_5P)A and Cl_0-4-(Cl_5P)A.

Under ammonia CI conditions, several ions resulting from the interaction of sample molecules with ammonium ions are observed. As reported for a number of classes of compounds[19] $[M+NH_4]^+$ adduct ions are formed. Although generally of low abundance, for Cl_0-3-(Cl_5P)A the base peaks at m/z ($M+18$) in the ammonia spectrum and m/z ($M+22$) in the deuterioammonia spectrum result from adduct ion formation. Frequently these adduct ions may undergo sequential loss of chlorine atom and ammonia to form $[M+NH_4-Cl]^{+\cdot}$ and $[M+NH_4-Cl-NH_3]^{+\cdot}$ ions. In addition, the strong peaks at m/z corresponding to ($M-70$) observed in the ammonia spectra of all the polychlorophenoxyanisoles studied under these conditions may result from fragmentation of the adduct ion, rather than loss of two chlorines from molecular ions. The relative abundances of these ions in ammonia spectra is higher than expected for chlorinated 2- and 4-phenoxyanisoles. Under deuterioammonia CI conditions, this ion is shifted to m/z corresponding to (M-69) for chlorinated 2- and 4-phenoxyanisoles. For these compounds, no ($M-70$) peaks are observed in deuterioammonia spectra. On the other hand, the deuterioammonia spectrum of the 3-phenoxy analog, which would be expected to form $[M-Cl_2]^{+\cdot}$ ions in significant quantities from the molecular ion, contains peaks at m/z corresponding to ($M-70$) and ($M-69$) with about equal relative intensities (30%).

CONCLUSIONS

While fragmentation patterns in ECNICI spectra of polychlorinated phenoxyanisoles are not greatly



Scheme 7.

Table 3. Positive ions formed by reaction of polychlorophenoxyanisoles with chemical ionization reagent gases

	Reagent gases: CH_4 (CD_4)					Reagent gases: NH_3 (ND_3)			
	$[M+CH_3]^+$ ($[M+CD_3]^+$)	$[M+C_2H_5]^+$ ($[M+C_2D_5]^+$)	$[M+C_3H_5]^+$ ($[M+C_3D_5]^+$)	$[M+C_2H_5-Cl_xC_6H_{5-x}O]^+$ ($[M+C_2D_5-Cl_xC_6H_{5-x}O]^+$)	$[M+C_3H_5-Cl_xC_6H_{5-x}O]^+$ ($[M+C_3D_5-Cl_xC_6H_{5-x}O]^+$)	$[M+NH_4]^+$ [$[M+ND_4]^+$)	$[M+NH_4-Cl]^{+\cdot}$	$[M+NH_4-Cl-NH_3]^{+\cdot}$	$[M+NH_4-Cl-NH_3-HCl]^{+\cdot}$ ($[M+ND_4-Cl-ND_3-HCl]^{+\cdot}$)
$5Cl_1$-2-(2,4Cl_2P)A	1[a]	2	2	14	4				
4,5,6Cl_3-2-(2,4Cl_2P)A	<1	3	2	20	5				
4,5Cl_2-2-(2,4,5Cl_3P)A		3		46	15				
Cl_0-2-(Cl_5P)A	<1	1	<1	27	13	100	7		55 $[M-70]^{+\cdot}$
						(100)			(37 $[M-69]^+$)
4,5Cl_2-2-(2,3,5,6Cl_4P)A		3		50	17	1	3	11	100 $[M-70]^{+\cdot}$
	(<1)		(<1)	(10)	(7)				
4,5,6Cl_3-2-(2,3,5,6Cl_4P)A		2	<1	20	7	4	4	9	26 $[M-70]^{+\cdot}$
		(<1)	(<1)	(11)	(6)				
4,5Cl_2-2-(Cl_5P)A		6		43	17	3	3	15	100 $[M-70]^{+\cdot}$
4,5,6Cl_3-2-(Cl_5P)A		1		41	15	8	8	16	77 $[M-70]^{+\cdot}$
3,4,5Cl_3-2-(Cl_5P)A		2	<1	23	14				
Cl_4-2-(Cl_5P)A	<1	1	<1	21	8				
Cl_0-3-(Cl_5P)A		14	5	1					34 $[M-70]^{+\cdot}$
									(29 $[M-69]^+$)
Cl_4-3-(Cl_5P)A		8	8	25	8				
Cl_0-4-(Cl_5P)A		1	<1	46	13				37 $[M-70]^{+\cdot}$
									(36 $[M-69]^+$)
Cl_4-4-(Cl_5P)A			1	4	1				

[a] Per cent relative abundance. The most intense peak of ion cluster is reported.

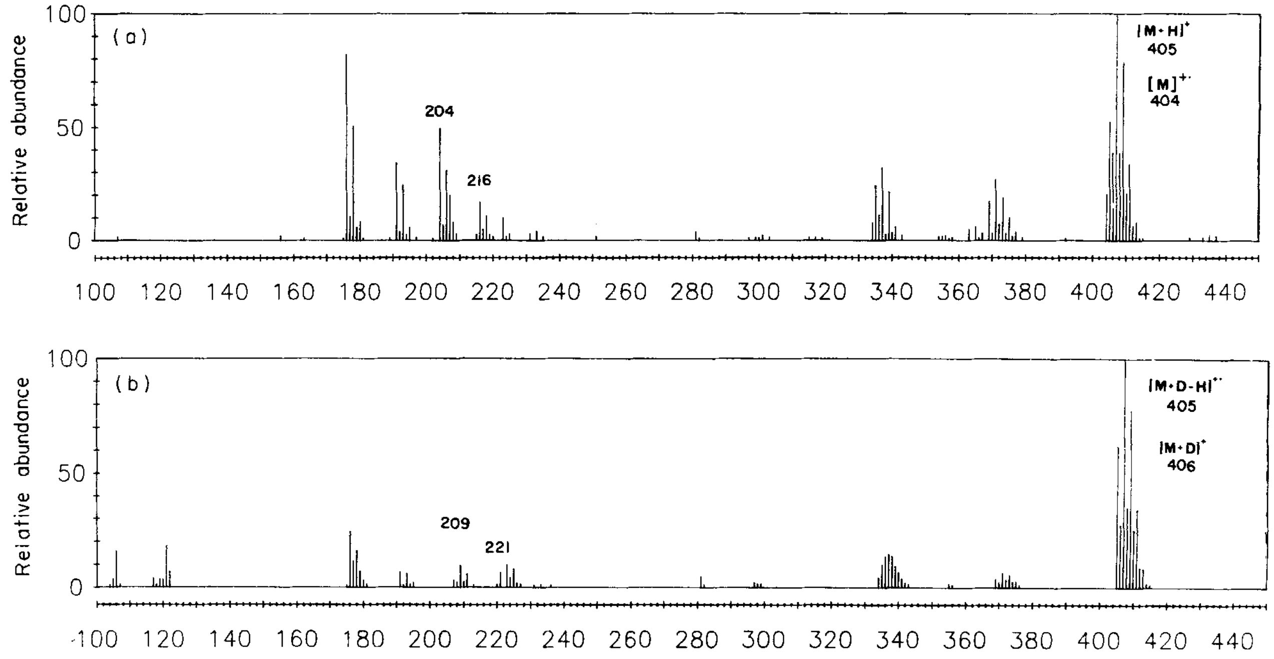


Figure 6. PICI mass spectra of 4,5Cl$_2$-2-(2,3,5,6Cl$_4$P)A. (a) Methane reagent gas; (b) deuteriomethane reagent gas.

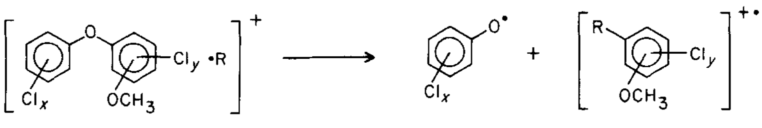
affected by the choice of reagent gas, noticeable differences are observed between PICI spectra obtained utilizing inert reagent gases and PICI spectra obtained utilizing reactive reagent gases. Positive ion spectra obtained in the presence of inert reagent gases (helium, nitrogen and argon) result from charge exchange and resemble EI spectra. Utilization of more reactive reagent gases (methane and ammonia) results in spectra dominated by ions which are formed by chemical means, including a number of ions formed by ion–molecule reactions. Positive ion hydrogen spectra contain peaks resulting from ions characteristic of spectra obtained in the presence of inert and reactive reagent gases though no ion–molecule reactions are identified.

The distribution of chlorine atoms in polychlorinated phenoxyanisoles is most readily established from ECNICI and reactive reagent gas PICI spectra because ions arising from phenoxy linkage cleavage dominate these spectra. Additional information about chlorine atom position is available from examination of ECNICI spectra for $[M-36]^{-\cdot}$ anions and subsequent fragmentation ions characteristic of alkoxypolychlorodibenzofurans. Although assignment of the position of phenoxy substitution in polychlorophenoxyanisoles is best made from EI or charge exchange PICI spectra, polychlorinated 2-phenoxyanisoles can be distinguished from polychloro-3- and -4-phenoxyanisoles by the presence, in methane ECNICI spectra, of the anion arising from elimination of a neutral chlorophenol molecule formed by hydrogen abstraction from the methoxy group by the *o*-chlorophenoxy group. Of those polychlorophenoxyanisoles which meet structural requirements for methoxypolychlorodibenzofuran formation by HCl elimination; i.e. compounds containing a hydrogen atom adjacent to the phenoxy linkage on one ring and a chlorine atom adjacent to the phenoxy linkage on the other ring, polychloro-3-phenoxyanisoles may be distinguished from polychlorinated 2- and 4-phenoxyanisoles by the absence of $[M-HCl]^{-\cdot}$ anions in the presence of $[M-HCl-CH_3]^{-}$ and $[M-HCl-HCl]^{-\cdot}$ anions in ECNICI spectra.

EXPERIMENTAL

Gas chromatography mass spectrometry

Gas chromatographic (GC) mass spectrometric studies were carried out on a Finnigan 4023 instrument with a



y	*m/z* R = C$_2$H$_5$	*m/z* R = C$_3$H$_5$
0	136	148
1	170	182
2	204	216
3	238	250
4	272	284

Scheme 8.

Model 625-pulsed positive–negative ion chemical ionization module. Methane (Matheson, Ultra High Purity, 99.97%), hydrogen (Industrial Air Products, High Purity), nitrogen (Industrial Air Products, Prepurified), helium (Industrial Air Products, High Purity) and argon (Industrial Air Products, High Purity) were used as reagent gases in chemical ionization investigations of all 14 compounds studied. Selected compounds were also examined with ammonia (Matheson, Anhydrous) and ammonia-d_3 (Merck Sharp Dohme Canada Ltd, 99 atom %D) as reagent gases. For each reagent gas, Pirani gauge pressure was 0.25 Torr for the pulsed positive ion negative ion chemical ionization (PPNICI) mode. The source temperature was routinely set at 300 °C. Electron energy was 70 eV. The GC column used in these experiments was a 2 mm i.d. × 3.05 m Pyrex column packed with 7% OV-101 on High Performance Chromosorb W (100–120 mesh). Column temperature was programmed during the run from 250–310 °C at 8° min^{-1}.

Preparation of chemicals

4-(Pentachlorophenoxy)anisole, 3-(pentachlorophenoxy)anisole, 2-(pentachlorophenoxy)anisole, 4,5-dichloro-2-(2′,3′,5′,6′-tetrachlorophenoxy)anisole, 4,5-dichloro-2-(pentachlorophenoxy)anisole and 3,4,5-trichloro-2-(pentachlorophenoxy)anisole were prepared by the reaction of the appropriate potassium phenoxide with the appropriate activated aromatic substrate in the presence of a crown ether.[20]

4,5-Dichloro-2-(2′,4′,5′-trichlorophenoxy)anisole was prepared by the method of Nilsson and Andersson.[21]

4,5,6-Trichloro-2-(2′,4′-dichlorophenoxy)anisole, 4,5,6-trichloro-2-(2′,3′,5′,6′-tetrachlorophenoxy)anisole and 4,5,6-trichloro-2-(penta-chlorophenoxy)anisole were prepared from the corresponding phenols by treatment with an etheral solution of diazomethane prepared from Diazald (Aldrich Chemical Co.). The phenols were prepared by chlorination[22] of 5-chloro-2-(2′,4′-dichlorophenoxy)phenol (commercially available as Irgasan DP 300), 4,5-dichloro-2-(2′,3′,5′,6′-tetrachlorophenoxy)phenol and 4,5-dichloro-2-(pentachlorophenoxy)phenol[20] respectively.

5-Chloro-2-(2′,4′-dichlorophenoxy)anisole, 3,4,5,6-tetrachloro-2-(pentachlorophenoxy)anisole, 2,4,5,6-tetrachloro-3-(pentachlorophenoxy)anisole and 2,3,5,6-tetrachloro-4-(pentachlorophenoxy)anisole were prepared by treatment with diazomethane of 5-chloro-2-(2′,4′-dichlorophenoxy)phenol, nonachloro-2-phenoxyphenol,[23] nonachloro-3-phenoxyphenol[24] and nonachloro-4-phenoxyphenol[25] respectively.

Each compound was dissolved in acetone for injection into the GC column.

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