Pergamon

Chemosphere, Vol. 37, No. 7, pp. 1395–1410, 1998

0045-6535/98 $19.00+0.00

Effects of Temperature and Sample Amount on the Electron Capture Negative Ion Mass Spectra of Polychloro-*n*-alkanes.

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(Received in USA 18 February 1998; accepted 25 March 1998)

Abstract

Ion source temperature, sample amount and the positions of the chlorine atoms attached to the neutral molecule all had profound effects on the appearance of the ECNI mass spectra of a number of synthesized polychloro-*n*-alkanes (PCAs). Increases in the ion source temperature resulted in a decrease in the abundances of both the $[M + Cl]^-$ and $[M - Cl]^-$ ions, while the abundances of the structurally non-characteristic ions, HCl_2^- and $Cl_2^{-}\bullet$, increased. An increase in the amount of the injected PCA resulted in an increase in the abundance of the $[M + Cl]^-$ ion, most notably for congeners containing chlorine atoms only 1,2-substituted at both ends of the alkane chain. The abundance of the $[M - Cl]^-$ ion increases with decreasing ion source temperature down to 120°C, the lowest temperature easily maintained with our instrument. For analytical purposes we recommend that this source temperature be used.

Introduction

Polychloro-*n*-alkanes (PCAs) are a class of industrially prepared mixtures of the general formula $C_nH_{2n+2-z}Cl_z$, used commercially as high-temperature lubricants in metal-working industry and as flame-retardant plasticizers in vinyl plastics [1]. Their more limited applications

include use as flame retardants in rubber, paints, adhesives, and sealants [1]. Also known industrially as chlorinated paraffins (CPs), they are formed by direct chlorination of *n*-alkane feedstocks with molecular chlorine under forcing conditions. These reactions, which have low positional selectively, yield complex mixtures of congeners (*i.e.*, homologues and their isomers). Based on the principal *n*-alkane feedstocks, which are derived from petroleum fractions, commercial PCA mixtures fall into three categories: C_{10}-C_{13} (short), C_{14}-C_{17} (medium), and C_{20}-C_{30} (long). The extent, and conditions, of chlorination used depend ultimately on the desired applications [2,3].

In the United States, PCAs have been placed on the Environmental Protection Agency (EPA) Toxic Release Inventory (TRI), and in Canada are classified as Priority Toxic Substances under the Canadian Environmental Protection Act (CEPA). Of particular interest are the C_{10}-C_{13} PCAs, which have the greatest potential for environmental release [4], appear to exhibit the highest toxicity [5-7], and, because of their environmental mobility, persistence and their appearance in industrialized countries, could have adverse effects on terrestrial and aquatic organisms and on humans [4,8].

To date, there has been limited information on the environmental concentrations of these compounds. This arises, in part, from the difficulty associated with quantifying PCAs because of the inherent complexity of commercial formulations [9,10]. These mixtures, which may contain thousands of positional isomers [9], generally elute over a wide retention time range [9,11-17], and components are not resolved to baseline even with high resolution gas or liquid chromatographic columns [11].

The lack of individual PCA congeners has precluded an understanding of the behaviour of these compounds in the ion source of the mass spectrometer under electron capture negative ion (ECNI) conditions, a necessary prerequisite before sensitive analytical methods for PCA analysis can be developed. Apart from the study by Tomy *et al.* (1997), in which the behaviour of a hexachlorodecane PCA congener was reported at two ion source temperatures [9], no extensive information exists regarding the effects of temperature and sample amount upon the appearance of the ECNI mass spectra of PCA congeners. Therefore, we have made a comprehensive study to address these knowledge gaps; the suitability of the $[M - Cl]^-$ ion as the

quantitation ion for environmental measurement purposes was also assessed.

Experimental

Materials. Chlorine gas (99.5%), 1,9-decadiene, 1,5,9-decatriene, sodium hydroxide and magnesium sulfate were purchased from Aldrich Chemical Co. (Oakville, ON), and 1,10-undecadiene from Wiley-Organics (Coshocton, OH).

Synthesis. PCA congeners were synthesized by bubbling chlorine gas, at room temperature, into neat solutions of the respective *n*-alkenes, contained in a flask wrapped in aluminium foil to exclude light. In the absence of light, these conditions were expected to lead, predominantly, to chlorine addition at the double bond(s). Reaction mixtures were shaken with NaOH (0.05M), the aqueous phase was then removed and then the organic phase was dried with $MgSO_4$. The drying agent was removed by filtration, and the filtrate was diluted with hexane to give a final PCA concentration of ~ 0.5% (v/v) prior to GC/MS analysis.

The notation $M_{x,y}$, used hereafter, denotes the number of carbon (x) and chlorine atoms (y) present in the PCA molecule; in addition, numerical prefixes indicate the known positions of chlorine atoms. When necessary the position of a chlorine atom at an unknown position will be indicated with the prefixes *x* and *y*; these species are formed by the substitution of hydrogen atom(s) by chlorine atom(s) *via* free radical chlorination.

Gas chromatography mass spectrometry. Separations were performed on a Hewlett-Packard (HP) (Mississauga, ON) 5890 Series II gas chromatograph, fitted with a high resolution 5% phenyl-substituted methylpolysiloxane stationary phase (DB-5MS) fused silica column (30 m x 0.25 mm i.d., 0.25 μm film thickness; Chromatographic Specialities, Brockville, ON, Canada), connected to the mass spectrometer through a heated transfer line maintained at 280°C. All sample injections were made by a CTC A200SE (Leap Technologies, Chapel Hill, NC) autosampler under data system control. The injector port temperature was 220°C and a helium carrier gas flow rate of 0.75 mL/min was maintained by an electronic pressure program. The column temperature program was: initial 100°C; hold 0 mins; ramp to 280°C at 10°C min^{-1}; hold for 20 mins.

Electron ionization (EI) mass spectra of GC effluents were obtained in the positive ion mode with a Kratos Concept (Kratos Analytical, Manchester, England) high resolution double focussing mass spectrometer (EBE geometry) controlled by a Mach 3 data system. Operating conditions were as follows: electron beam energy adjusted for maximum sensitivity (~55eV), electron beam current 500 μA, ion acceleration voltage 8 kV and an ion source temperature of 220°C, measured by a thermocouple located in the ion source body . The scan range was *m/z* 400 to *m/z* 40, at a fixed rate of 0.7 sec per decade. Perfluorokerosene (PFK) was the mass calibrant.

ECNI mass spectra at nominal resolution, were generated at 1 sec per decade over the mass range *m/z* 600 to *m/z* 65, with argon as the moderating gas, at an ambient gas pressure of ~2 x 10^{-4} torr, as recorded by the source ion gauge located adjacent to the source. The electron emission current was 100 μA, the initial electron beam energy was ~180 eV, and the ion accelerating voltage was 5.3 kV. Mass spectra were recorded at different ion source temperatures ranging from 120°C (the lowest easily maintained temperature with the instrument) to 220°C.

Results and Discussion

1. Products of the chlorination reactions. Figures 1-3 show the HRGC/EI -MS total ion chromatograms of the reaction products formed by the reaction of molecular chlorine with 1,9-decadiene, 1,5,9-decatriene and 1,10-undecadiene, respectively. The general features of the EI mass spectra (not shown) have been described elsewhere [18]. In addition to the expected products formed by chlorine additions to each double bond, a number of by-products were observed that resulted from: (*i*) chlorine additions to only one double bond, resulting in the formation of chlorinated olefins, and (*ii*) free radical substitution of hydrogen atom(s) by chlorine atom(s). The ECNI mass spectra of the latter products were also investigated. The sections that follow will, therefore, discuss the general features and the effects of ion source temperature and sample amount upon the appearance of the ECNI mass spectra of the chlorinated products highlighted in Figures 1-3, *viz.*, 1,2,9,10-$M_{10,4}$, 1,2,x,9,10-$M_{10,5}$, 1,2,5,6,9,10-$M_{10,6}$, 1,2,5,6,x,9,10-$M_{10,7}$, 1,2,10,11-$M_{11,4}$, 1,2,x,10,11-$M_{11,5}$ and 1,2,x,y,10,11-$M_{11,6}$.

2. General features of the ECNI mass spectra. Figure 4 shows the ECNI mass spectrum of a

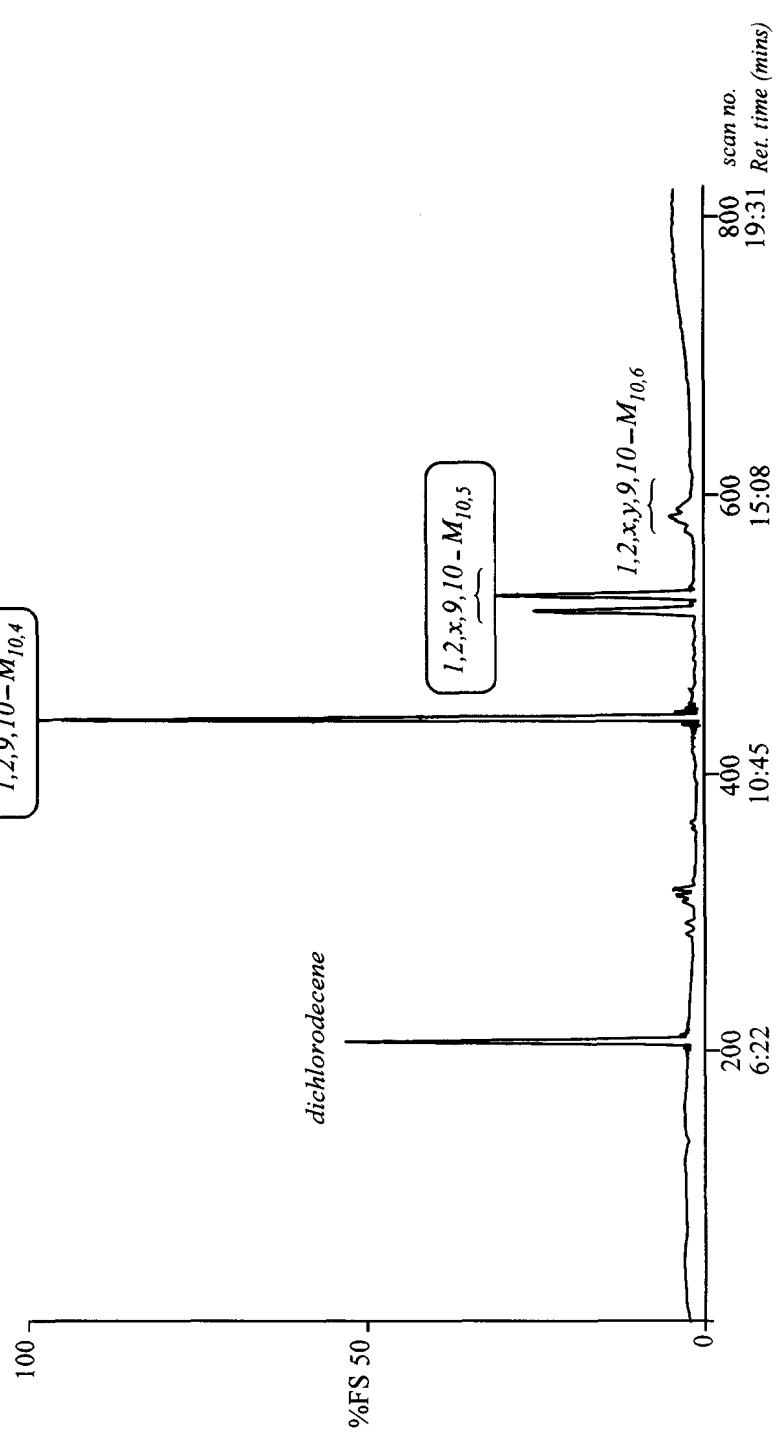


Figure 1. HRGC-EI/MS total ion chromatogram of reaction products formed by the reaction of molecular chlorine with 1,9-decadiene.

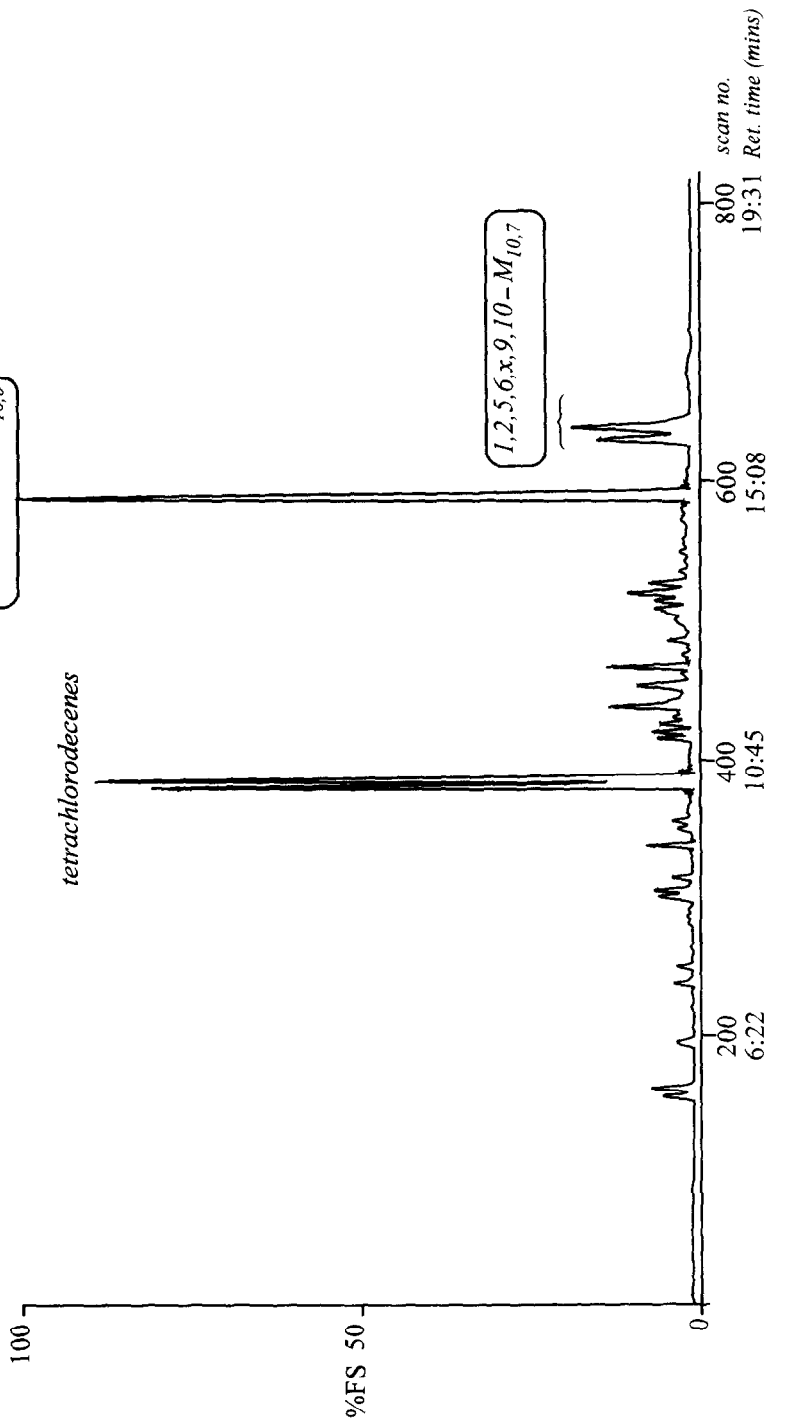


Figure 2. HRGC-EI/MS total ion chromatogram of reaction products formed by the reaction of molecular chlorine with 1,5,9-decatriene.

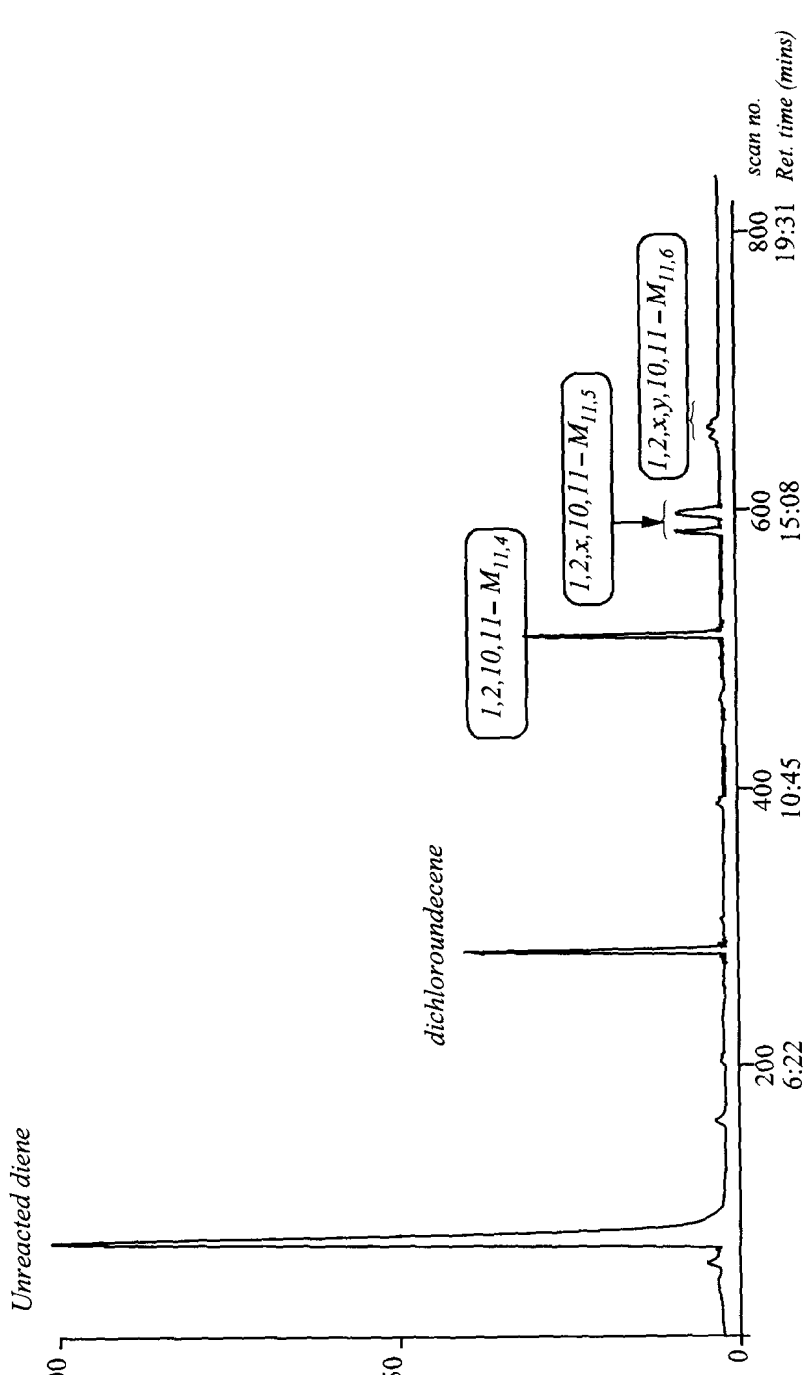


Figure 3. HRGC-EI/MS total ion chromatogram of reaction products formed by the reaction of molecular chlorine with 1,10-undecadiene.

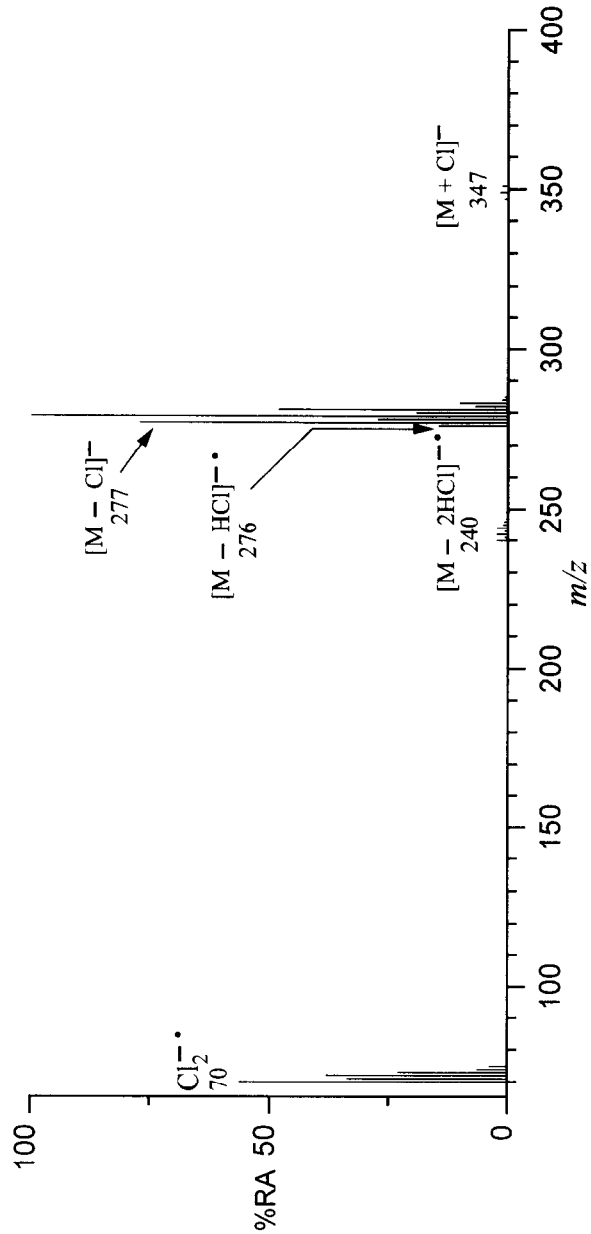


Figure 4. ECNI mass spectra of 1,2,x,9,10-pentachloro-*n*-decane at an ion source temperature 120°C.

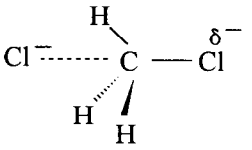
representative PCA congener, *viz.*, 1,2,x,9,10-$M_{10,5}$, at a source temperature of 120°C. The spectrum is highlighted by four groups of peaks. At low mass we observe the ubiquitous ions (in organochlorine negative ion mass spectra) corresponding to $Cl_2^-\bullet$ (m/z 70/72/74) and HCl_2^- (m/z 71/73/75) [19-21]. The ion groups starting at *m/z* 276 and *m/z* 277 correspond to the molecular formulae $C_{10}H_{16}Cl_4^-\bullet$ and $C_{10}H_{17}Cl_4^-$, respectively, and are derived by respective losses of HCl and Cl• from the molecular ion. The low abundance group starting at *m/z* 240 corresponds to a loss of 2HCl from the molecular ion. In addition, the ion group starting at *m/z* 347, corresponds to the $[M + Cl]^-$ ion.

The observation of adduct ions, $[M + Cl]^-$, especially at low ion source temperatures, in the mass spectra of a few chlorohydrocarbons has been previously reported [20,22-25]. The generation of $[M + Cl]^-$ ions is thought to occur by steps 1 and 2 shown below.

$$M + e^-_{thermal} \rightarrow [M - Cl]\bullet + Cl^- \quad [1]$$

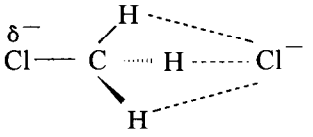
$$M + Cl^- \rightarrow [M + Cl]^- \quad [2]$$

In our case, neutral analyte PCA molecules in the ion source under ECNI conditions yield chloride ions by dissociative electron capture (reaction 1), which subsequently attach to neutral PCA molecules (reaction 2). Originally, chloride attachment to a carbon atom as, for example, in chloromethane (structure A) was thought to occur [25], but later this structure was shown to be less stable than the hydrogen bonded structure (B) [26] (*see below*).



A

carbon bonding



B

hydrogen bonding

Factors which may influence the abundance of chloride adduct ions include, *(i)* ion source temperature, *(ii)* ion source pressure, *(iii)* concentration of sample molecules, *(iv)* number and position of chlorine atoms already on the molecule, *(v)* reagent gas, *(vi)* the rate of electron

capture vs. the rate of chloride attachment, *(vii)* instrumentation, *(viii)* lifetime of the adduct and *(ix)* the concentration of electrons and their energy distribution [23]. The next sections will discuss the effect of ion source temperature on the general appearance of the ECNI mass spectra of PCAs, and the effects of sample amount and positions of chlorine atoms on the relative abundance of the $[M + Cl]^-$ ion.

3. Effects of ion source temperature. Variations in the relative abundance of negative ions that occur because of changes in the temperature of the ion source are well documented [9,22,23,27-31]. In general, a lower ion source temperature decreases fragmentation and enhances the abundance of molecular anions [19,22]. This effect has been attributed to a decrease in internal energy of the ionized molecule and subsequently lowers the propensity for dissociative reactions [22].

The effects of ion source temperature on the appearance of the ECNI mass spectra of the PCAs under investigation are shown in Table 1. In general, at 220°C, spectra are dominated by the low mass fragment ions corresponding to $Cl_2^{-}\bullet$ and HCl_2^-. As the temperature in the ion source is lowered, the relative abundances of the $[M - Cl]^-$ ions increase; there are also groups of smaller peaks, in some cases, which arise from further losses of HCl and/or Cl•. Also observed, in some cases, in particular at lower source temperatures, are ions corresponding to the adduct ion, $[M + Cl]^-$.

The domination of $Cl_2^{-}\bullet$ and HCl_2^- ions in the mass spectra of the synthesized PCA congeners at higher ion source temperatures, is problematic for analytical purposes for two reasons. First, they are not characteristic of any one PCA congener and, second, other persistent chlorohydrocarbon contaminants fragment to yield such ions, *e.g.*, *p,p'*-DDT, *p,p'*-DDE, lindane, dieldrin, aldrin and endrin [19-21]. Thus, if these contaminants are not *selectively* removed completely from sample matrices during extraction or clean-up procedures, they would ultimately contribute to the response of the quantitation ion, $Cl_2^{-}\bullet$ (*m/z* 70), and lead to an overestimation in the level of PCAs in samples [10].

From an analytical perspective, therefore, in order to *selectively maximize* the abundance of the structurally specific $[M - Cl]^-$ ions, relative to the abundance of the $Cl_2^{-}\bullet$ and HCl_2^- ions,

Table 1. Effect of temperature on the % relative abundance of ions in the ECNI mass spectra of PCA congeners.

Source Temperature→	120°C	175°C	220°C	120°C	175°C	220°C	120°C	175°C	220°C	120°C	175°C	220°C
Congeners→	1,2,9,10-$M_{10,4}$			1,2,x,9,10-$M_{10,5}$			1,2,5,6,9,10-$M_{10,6}$			1,2,5,x,6,9,10-$M_{10,7}$		
$Cl_2^{-\bullet}$	87.3	93.2	100	65	100	100	35.3	96	100	31.6	100	100
HCl_2^-	100	100	95	41	60.7	57.8	42.3	100	90.9	10.7	31	37.9
$[M - Cl]^-$	73.2	10.9	2.7	100	23.1	1.2	100	36.2	13.7	100	48.4	21.3
$[M - HCl]^-$	16.8	0.9	0	26.4	3.8	0	65.6	10.7	2.2	40.4	10.7	1.7
$[M - HCl - Cl]^-$	-	-	-	-	-	-	5.8	0.8	0.3	-	-	-
$[M - 2HCl]^-$	-	-	-	2.6	0	0	9	1.1	0	5.2	2.1	0
$[M - HCl - Cl_2]^-$	-	-	-	-	-	-	2.2	0	0	3.4	0.6	0
$[M - 3Cl]^-$	-	-	-	-	-	-	7.3	1	0.3	10.4	2.1	0.7
$[M + Cl]^-$	11.6	4.4	0.1	0.2	0.2	0	0	0.7	0.3	-	-	-
	1,2,10,11-$M_{11,4}$			1,2,x,10,11-$M_{11,5}$			1,2,x,y,10,11-$M_{11,6}$			1,2,x,y,z10,11-$M_{11,7}$		
$Cl_2^{-\bullet}$	81.4	85	100	100	100	100	100	100	100	100	100	100
HCl_2^-	100	100	85.6	69.3	66.7	53.8	39.7	41.5	35.5	19	17	27.6
$[M - Cl]^-$	11.9	1.4	1.2	26.4	2.9	3.9	32.5	8.2	10.9	29	11.2	15.4
$[M - HCl]^-$	4.8	0	0.2	9.7	0.2	0.6	15.1	1	0.2	13.7	0.3	2.9
$[M - 2Cl]^-$	-	-	-	0.7	0	0	-	-	-	-	-	-
$[M - 2HCl]^-$	-	-	-	-	-	-	0.4	0	0	0.8	0.2	1.4
$[M + Cl]^-$	3.2	0.6	0.4	-	-	-	-	-	-	-	-	-

a low ion source temperature is recommended.

4. Effects of sample amount. Tannenbaum *et al.* (1975) have shown that the formation of chloride adduct ions can be enhanced by using methylene chloride as the reagent gas [25]. The chloride ion in this case is generated by dissociative electron capture by the reagent gas:

$$CH_2Cl_2 + e^-_{thermal} \rightarrow CH_2Cl\bullet + Cl^- \quad [3]$$

In ECNI (*i.e.*, generation of thermal electrons by a non-reactive moderating gas) the chloride ions are generated from a chlorine-containing sample during the few seconds the sample spends in the ion source as it elutes from the GC column. The concentration of the sample in the source depends upon the sample amount, carrier gas flow rate, GC peak broadness, and volume of the ion source. These parameters have received little attention, but Stemmler and Hites (1985) have studied the effects of the amount of sample introduced on the appearance of the ECNI mass spectrum of α-chlordane [23]. When low quantities (10 ng or less) of the sample were introduced, *via* a GC-column, $M^-\bullet$ and a few fragment ions were observed. However, when microgram quantities of the sample were introduced, *via* a direct insertion probe, $[M + Cl]^-$ ions dominated the mass spectrum.

For this study, because we are dealing with mixtures, introduction of large numbers of analytes into the ion source *via* the direct insertion probe was not feasible. Instead, three solutions from the products derived from the chlorination of 1,9-decadiene, 1,5,9-decatriene and 1,10-undecadiene, based on approximately 0.5% concentration (v/v) of *starting material* in hexane were prepared, and 0.1, 0.5 and 1.0 μL samples were separately injected onto a GC column by means of an autosampler. Owing to incomplete and competing reactions we do not know the precise amounts of sample injected but, roughly, 1 μL of 0.5% solution corresponds to 5 μg of starting material, or about 1-10 μg of the various products. Thus, injection of the three different sample volumes gives information on the *relative* amounts of sample in the 0.1-10 μg range. Figure 5 shows the effect of injected solution volume on the relative abundance of the $[M + Cl]^-$ for a number of the reaction products at three ion source temperatures. A strong effect of injected sample amount is not observed for 1,2,9,10-$M_{10,4}$, 1,2,10,11-$M_{11,4}$ and

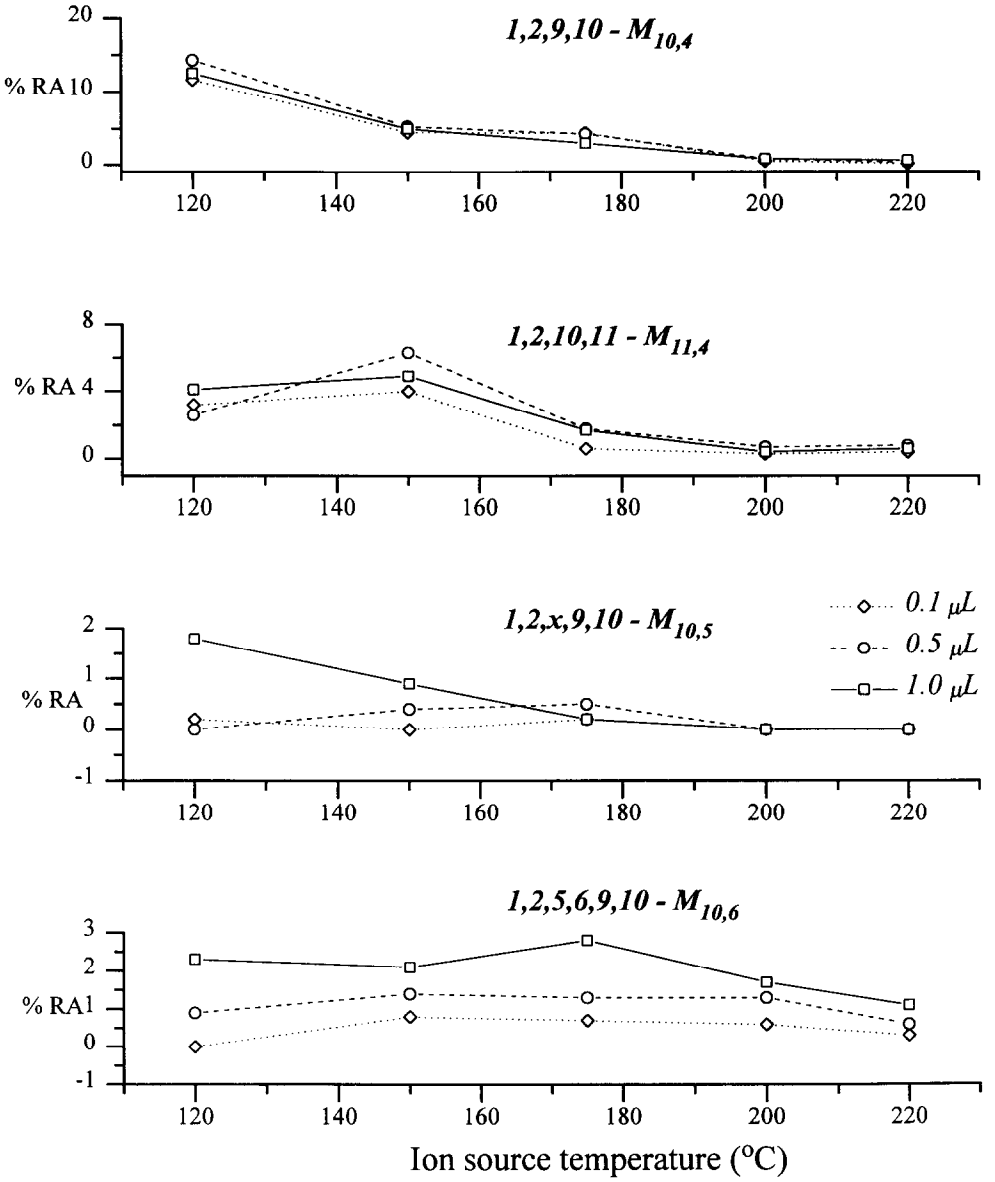
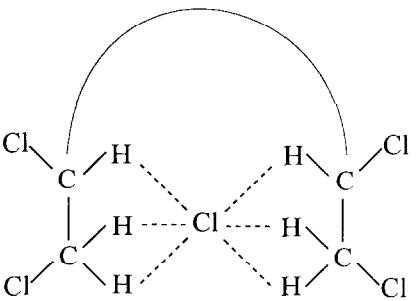


Figure 5. Effect of ion source temperature and volume of injected solution (see text) on the relative abundance of the $[M + Cl]^-$ ion.

1,2,x,9,10-$M_{10,5}$ (except at low temperature) but a trend to increasing abundance with increasing sample amount is observed for 1,2,5,6,9,10-$M_{10,6}$.

5. Effects of number and positions of chlorines on the relative abundance of adduct ions. Little is known about these effects. Figure 5 shows that the relative abundance of the adduct is much higher for 1,2,9,10-$M_{10,4}$ and 1,2,10,11-$M_{11,4}$ than for the more highly substituted compounds. We suggest that this arises because the first two compounds can adopt conformations, as in structure C, that can maximize hydrogen bonding interactions, and that such conformations are less sterically favorable for the compounds having chlorine atoms in the interior of the carbon chain. Subtle changes are observed, however, for the abundances of the $[M + Cl]^-$ ions because of a change in volume of injected solution. In all but one instance, the abundance of the $[M + Cl]^-$ ion is highest when 1.0 μL of sample was injected, as to be expected.



C

Conclusions

Clearly, quantifying PCAs based on the response of the ubiquitous $Cl_2^{-}\bullet$ ions is unsuitable. In addition, the variability observed in the relative abundances of the $[M + Cl]^-$ ion in the ECNI mass spectra of the PCA congeners, because of (*i*) changes in the ion source temperature, (*ii*) changes in sample amount, and (*iii*) changes in the number and positions of the chlorine atoms in the molecules; this variability illustrates that the adduct ion is not suited for

analytical purposes. Although the relative abundances of the $[M - Cl]^-$ ions were shown to be dependent on ion source temperature they showed very little change when the sample concentration was varied. In most cases, to maximize the abundance of the $[M - Cl]^-$ ion, an ion source temperature of ~120°C is required. For maximum sensitivity and specificity, therefore, quantitation of environmental concentrations of PCAs is best carried out by monitoring the $[M - Cl]^-$ ion at an ion source temperature of ~120°C.

Acknowledgements

The authors would like to thank the Natural Sciences and Engineering Research Council of Canada (NSERC) and the Canadian Chlorine Coordinating Committee for their financial support.

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