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Electron Capture Negative Ion Mass Spectrometry of ^{37}Cl -Labeled 2,2',3,4,5,6-Hexachlorodiphenyl Ether

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There have been intense interest over the past decade in the polychlorinated diphenyl ethers (PCDPEs) because of their high toxicity as contaminants in the environment.¹ Electron capture negative ion (ECNI) mass spectrometry has been an important technique for analysis of the polychlorinated diphenyl ethers along with many other halogenated aromatic compounds in environmental samples largely due to

its inherent sensitivity and specificity.² In the case of polychlorinated diphenyl ethers, however, their mass spectra obtained from ECNI-MS are highly dependent on the ion source temperature.³ This dependence was argued on the basis of time-dependent electron thermalization as it affects the relative cross sections for resonance and dissociative electron capture process as well as secondary reaction such as radical cyclization to form polychlorinated dibenzofurans (PCDFs).⁴ Nevertheless, the variation of mass spectra by different instrument conditions often raises difficulties for the interpretation of spectra.

For mono-, di-, and trichlorinated compounds, the major detectable ions are Cl^- , $[\text{HCl}_2]^-$, and $[\text{M-H}]^-$ which are probably derived from dissociative electron capture process.⁵ In tetrachlorodiphenyl ethers, $[\text{M-HCl}]^-$ is also observed along with the expected ions. The formation of $[\text{M-HCl}]^-$ ions are unique in the ECNI-MS of PCDPEs since they are not observed from polychlorinated dibenzo-*p*-dioxins and dibenzofurans. Hass *et al.* suggested that the loss of HCl from the tetrachlorinated compounds is only from an intra-annular loss of an *ortho* chlorine and the adjacent *meta* hydrogen since the 2,3,5,6-isomer does not show a loss of HCl.⁶ On the contrary, Hites and Stemmler have observed the loss of HCl from 3,4,3',4' isomer which does not meet this criterion.⁷ For the higher chlorinated compounds there is insufficient information to deduce the structural requirement for the loss of HCl. We suggested that the isotope labeling experiment (^{37}Cl and/or deuterium) would give us an insight information for the loss of HCl. We report here a successful synthesis of ^{37}Cl labeled 2,2'(^{37}Cl),3,4,5,6-hexachlorodiphenyl ether and propose a mechanism for the formation of $[\text{M-HCl}]^-$ from the interpretation of isotope enrichment under ECNI mass spectrometry conditions.

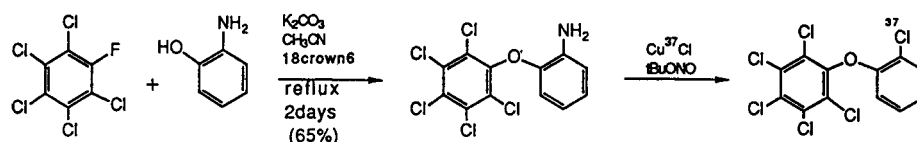
Experimental

Synthesis of the title compound was carried out by the selective ^{37}Cl substitution of the corresponding pentachlorodiphenyl ether with NH_2 group (Scheme 1).⁸ The Cu^{37}Cl was prepared from Na^{37}Cl .⁹ The theoretical isotopic cluster patterns of the molecular ions and the fragmentation ions were obtained directly from DS-90 computer program. The calculation should be based on the equation $(x+y)^m(a+b)^n$, where m is the number of natural chlorines with percent abundance $x:y$ and n is the number of isotope-rich chlorines with the percent abundance $a:b$.¹⁰

Mass spectrometric measurements were made on a Finnigan 4023 (4500 ion source) instrument employing a quadrupole electric field. Isotope enrichments were measured under 70 eV electron impact conditions and 140 °C ion source temperature. For ECNI-MS methane was used as a reagent gas under the pressure of 0.5 Torr. Source temperature was varied from 90 to 200 °C. Peak sizes varied, but there was no effect on the isotopic ratios. Samples were introduced into the instrument by splitless injection through a DB-5 30 M \times 0.25 mm i.d. GC column.

Results and Discussion

The ECNI mass spectrum of 2,2',3,4,5,6-H₆PCDE with 0.5 Torr CH_4 at 100 °C is shown in Figure 1. Lowering the ion



Scheme 1.

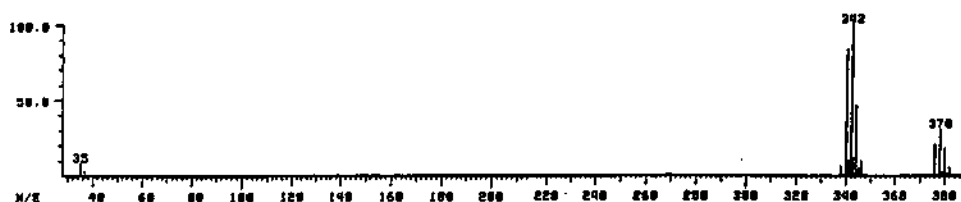


Figure 1. Electron capture negative ion mass spectrum of 2,2'(^{37}Cl),3,4,5,6-hexachlorodiphenyl ether, methane as reagent gas, 0.5 torr, 100 $^{\circ}\text{C}$.

source temperature in the ECNI mass spectrometer is generally found to enhance molecular ion abundance by decreasing the degree of fragmentation. This effect has been attributed to a decrease in ion internal energy and subsequently the rate of dissociative processes.⁴ The results showed that the abundance of $[\text{M}-\text{HCl}]^-$ and chloride fragment ions from the radical anion increased as the ion source temperature was increased, however, a large reduction in the abundance of the molecular ion was observed (Figure 2). Note that, although the relative abundance of $[\text{M}-\text{HCl}]^-$ increases with the ion source temperature, the ratio of $[\text{M}-\text{HCl}]^-$ to Cl^- decreases with the ion source temperature (Figure 3). This temperature effect suggests that the formation of $[\text{M}-\text{HCl}]^-$ is related to the loss of Cl^- . A similar phenomenon was rationalized by Hites *et al.* for 2,2',4,4',5-isomer that the reduction in ion source temperature affects the ion source residence time, providing more time for reactions and diffusional process to occur.¹¹

Comparison of the calculated (A) and experimental (B) isotopic cluster patterns for $[\text{M}-\text{HCl}]^-$ anions shows an excellent agreement having 95% enrichment of ^{37}Cl , which is the same to that of molecular anions (Figure 4). This indicates that there is no loss of ^{37}Cl with the adjacent *meta* hydrogen. In an effort to provide a basis for the development of a mechanistic rationale, three pathways were considered (Scheme 2). In the first case (path a), the fragmentation involves the most important resonance structure leading to the formation of pentachlorophenoxy anion, however, there is no indication for the formation of this anion in the mass spectrum (Figure 1). A second mechanistic pathway involves a heterolytic dissociation of the chloride ion generating an aryl radical followed by an intramolecular substitution to give a cyclized product (path b). This type of mechanism is well suited with the classic Pschorr cyclization of intramolecular aromatic radical substitution.^{12,13} However, this mechanism would not be a major one because the relative abundance of chloride ion compared to $[\text{M}-\text{HCl}]^-$ ion is very small. Therefore, we believe that a concerted process leading to the formation of the radical anion of pentachlorodibenzofuran (m/z 342) is the most probable one (path c). Capture of an electron to the higher chlorinated ring, which has a lower LUMO energy level, induces the distortion of the molecule.

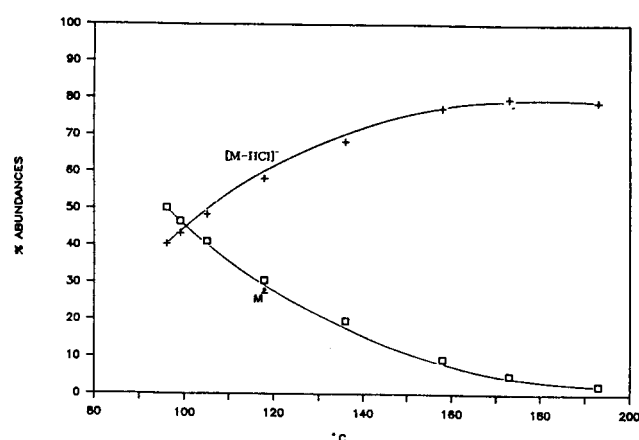


Figure 2. Ion source temperature effect of abundances for molecular radical anion (\square) and $[\text{M}-\text{HCl}]^-$ ion (+) from 2,2'(^{37}Cl),3,4,5,6-hexachlorodiphenyl ether under ECNI-MS conditions.

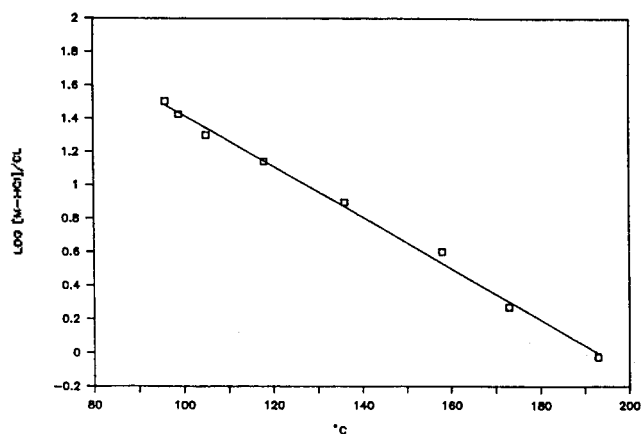


Figure 3. Ion source temperature effect of abundance ratios for $[\text{M}-\text{HCl}]^-$ ion and Cl^- ion from 2,2'(^{37}Cl),3,4,5,6-hexachlorodiphenyl ether under ECNI-MS conditions.

This leads to an effective overlapping of π orbitals of two *ortho* carbons from both phenyl rings. The common photocyclization of PCDPEs to make PCDFs has the same structural

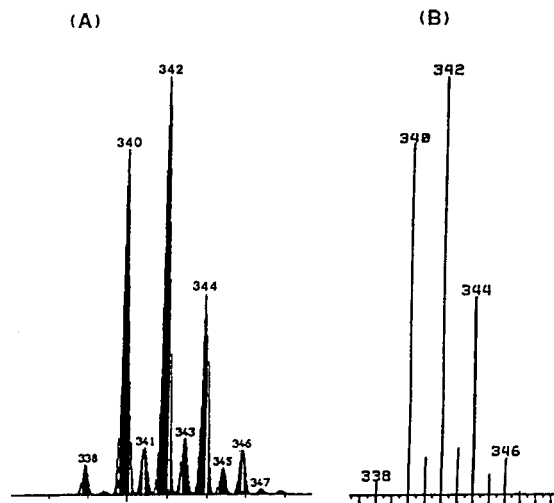
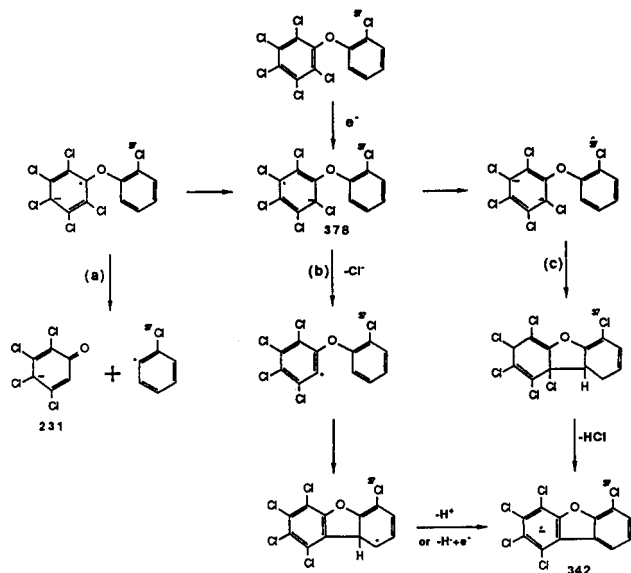


Figure 4. Computer simulated (A) and ECNI mass spectrum (B) of $[M-HCl]^-$ ion.



Scheme 2.

requirement to this criterion.^{14,15} The photolytic cyclization product of this compound was 1,2,3,4,6-pentachlorodibenzofuran which had the same ^{37}C enrichment as $[M-HCl]^-$ cluster has.

In conclusion, the formation of $[M-HCl]^-$ in the ECNI mass spectrometry of 2,2',3,4,5,6-HxCDFE does not involve the loss of *ortho* chlorine and *meta* hydrogen. The concerted dehydrochlorination leading to a cyclized product of pentachlorodibenzofuran (PeCDF) seems to be the probable pathway for the formation of $[M-HCl]^-$.

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Enantioselective Complexation of Amino Ester Salts with Chiral Crown Ether

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A large number of chiral crown ethers have been prepared for enantioselective recognition of optically active organic guests, usually primary ammonium cations.¹⁻² The chirality of the crown ethers was created by introduction of optically pure diols into the macrocyclic ring. The limited diols such as tartaric acid, hydrobenzoin, and diols derived from carbohydrates have been mostly used for the preparation of chiral crown ethers due to synthetic difficulties of the optically pure 1,2-diols.¹ Now, almost all of the chiral *cis*-1,2-diols can be synthesized as an optically pure form through Sharpless's AD method.³ We were particularly interested in 1-phenyl-*cis*-1,2-cyclohexanediol (**1**) as a chiral building block due to its conformational rigidity, steric environment, and easy availability. In fact, the diol **1** has been already utilized by K. Naemura *et al.* for the preparation of several synthetic hosts including crown ether **2**.⁴ Two C_2 -symmetric hosts **2** and **3** are composed of the exactly same molecular components,