



Ion source surface activity in high pressure electron capture mass spectrometry
by Christopher Martin Pace

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in
Chemistry

Montana State University

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Abstract:

The negative ion mass spectra of 61 Environmental Protection Agency (EPA) priority pollutants using high pressure electron capture mass spectrometry (HPECMS) revealed that many of the compounds produced ions that could not have been formed by classical resonance and dissociative electron capture. Two general types of unusual ions arose out of the initial examination of the negative ion mass spectra produced by the pollutants. One of the two types of unusual ions was produced by many of the polychlorinated pollutants. These unusual ions corresponded to $[M-Z+nH-nCl]^-$ where M is the parent analyte molecule and Z is either a fragment of M whose mass depends on its composition or is zero. The value of n was found to range between 1 and 5. The other type of unusual ion observed corresponded to $[M+R]^-$ where R was thought to be predominantly CH₂, CH₃, or some other small alkyl species. Most of the polycyclic aromatic hydrocarbons (PAH's) examined displayed unusual ions of the type $[M+R]^-$. Normalized reconstructed single ion chromatograms (NRSIC) are shown to provide a useful probe into the nature of the two types of unusual ions discussed here. From examining the HPEC mass spectra and NRSIC at various ion source conditions, it is shown that both types of unusual ions result from interactions of an analyte species with the ion source wall. The theory of HPECMS shows that reactions occurring at the ion source surface provide a likely pathway for the production of unusual negative ions.

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MASS SPECTROMETRY

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A thesis submitted in partial fulfillment
of the requirements for the degree

of

Master of Science

in

Chemistry

MONTANA STATE UNIVERSITY
Bozeman, Montana

March 1988

N378
P1132

ii

APPROVAL

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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ACKNOWLEDGMENT

This research was funded in part by Cooperative Agreement CR-813424 with the U.S. Environmental Protection Agency, Environmental Research Laboratory, Athens, Georgia; and the National Science Foundation under Grant No. CHE-854029.

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ABSTRACT

The negative ion mass spectra of 61 Environmental Protection Agency (EPA) priority pollutants using high pressure electron capture mass spectrometry (HPECMS) revealed that many of the compounds produced ions that could not have been formed by classical resonance and dissociative electron capture. Two general types of unusual ions arose out of the initial examination of the negative ion mass spectra produced by the pollutants. One of the two types of unusual ions was produced by many of the polychlorinated pollutants. These unusual ions corresponded to $[M-Z+nH-nCl]^-$ where M is the parent analyte molecule and Z is either a fragment of M whose mass depends on its composition or is zero. The value of n was found to range between 1 and 5. The other type of unusual ion observed corresponded to $[M+R]^-$ where R was thought to be predominantly CH_2 , CH_3 , or some other small alkyl species. Most of the polycyclic aromatic hydrocarbons (PAH's) examined displayed unusual ions of the type $[M+R]^-$. Normalized reconstructed single ion chromatograms (NRSIC) are shown to provide a useful probe into the nature of the two types of unusual ions discussed here. From examining the HPEC mass spectra and NRSIC at various ion source conditions, it is shown that both types of unusual ions result from interactions of an analyte species with the ion source wall. The theory of HPECMS shows that reactions occurring at the ion source surface provide a likely pathway for the production of unusual negative ions.

INTRODUCTION

Background

High Pressure Electron Capture Mass Spectrometry (HPECMS) is a term used to describe the analytical method of detecting negative ions produced in a chemical ionization (CI) ion source containing about 0.1 to 1.0 Torr of buffer gas. This method of mass spectrometry evolved from its counterpart, Positive Chemical Ionization Mass Spectrometry (PCIMS), developed by Munson and Field¹ in 1966. While the production and detection of positive ions was well understood in 1966, negative ion mass spectrometry was not. The slower development of negative ion mass spectrometry was due in part to a lack of instruments capable of detecting negative ions. One of the first reports of HPECMS was in 1972 when Dougherty and Dalton² published their negative ion mass spectra of 10 polycyclic chlorinated insecticides using methane as the buffer gas. Since this time, and especially in the last decade, HPECMS has evolved into a widely used technique. HPECMS in conjunction with capillary column gas chromatography has become a powerful tool to those working in areas of chemistry where a need exists for a highly sensitive and/or selective means of compound identification.

The reason for the success of HPECMS stems from the reaction of thermalized gas phase electrons with gas phase molecules. It has been shown³ that the sensitivity of HPECMS versus PCIMS depends to a large degree upon the second order rate coefficients of the primary reactions involved. The second order rate coefficient for electron-molecule reactions is up to two orders of magnitude greater than that of the positive ion-molecule reactions associated with PCIMS.⁴ In order for an organic molecule to undergo electron capture, it must possess a positive electron affinity (EA)⁵⁻⁸ and be able to stabilize its excess energy, obtained from the electron capture process, by collisions with neutral gas molecules before electron autodetachment can occur.^{7,8} Only a small fraction of all organic molecules possess a positive EA, thus making HPECMS a very useful tool for detecting certain compounds in complex matrixes.^{3,9} In some instances it is possible to derivatize a compound with a negative or slightly positive EA to form one which captures electrons readily.¹⁰ One example of the derivatization technique is in the quantitation of octopamines and synephrines in urine¹¹ where the molecules were first derivatized with pentafluoropropionic anhydride.

The buffer gas in the HPECMS ion source serves two purposes. First, the buffer gas provides a medium in

which the energy of the initial electron beam and that of the secondary electrons produced by the beam are quickly reduced by collisions with neutral buffer gas molecules. This produces a large population of low energy electrons^{1 2} increasing the probability of electron capture occurring. Secondly, the buffer gas provides collisional stabilization to the initially formed excited negative ion.^{1 3} Several different monotomic and diatomic gases, including He, Ne, Ar, Kr, Xe, N₂, CH₄, i-C₄H₁₀ and CO₂, have been used as the buffer gas in HPECMS.^{1 3} All of the above gases have unique characteristics. In the remainder of this work we will be concerned primarily with methane as the buffer gas.

Although many of the organic molecules that capture electrons do so by the classical resonance and/or dissociative electron capture processes, some organic molecules exhibit HPEC mass spectra that must have had their origins from reactions other than or in addition to electron capture.^{1 2} Several reasons can be stated for the appearance of unusual ions observed in the HPEC mass spectra of certain compounds. First, the electron capture process is sufficiently fast as to allow several events to occur during the residence time that the analyte molecule spends in the ion source.⁸ The high source pressure can possibly cause reactions between analyte molecules and buffer gas ions^{1 2} and between analyte molecules and buffer

gas radicals prior to ionization.^{14,15} Both gas phase ions and radicals are produced in high abundance by irradiation of the buffer gas with the primary electron beam. Finally, the presence of trace impurities, such as oxygen and water, that find their way into the ion source of the mass spectrometer can possibly lead to the formation of unusual ions.¹² The processes leading to the formation of negative ions inside the HPEC ion source are strongly dependent upon experimental parameters such as temperature, pressure, emission current, and the energy of the primary electron source.¹⁶

Numerous examples appear in the literature which exhibit HPEC mass spectra that arose from processes other than simple resonance and/or dissociative electron capture. The HPEC mass spectra of the polycyclic chlorinated insecticides published by Dougherty and Dalton² displayed unusual ions of the type $[M+O-Cl]^-$ and $[M+Cl]^-$ (where M is the parent analyte molecule). The $[M+O-Cl]^-$ ion appears elsewhere in the literature^{6,16,17} and has been shown¹⁸ to be a displacement reaction between the molecular anion, M^- , and trace amounts of oxygen present in the mass spectrometer.

The $[M+Cl]^-$ ion mentioned above is thought to arise from reaction between the parent molecule and the primary dissociative electron capture product, chloride ion.¹⁹ The $[M+Cl]^-$ ion in this case can be minimized, if not

eliminated, by reducing the sample concentration initially introduced into the ion source.¹⁹ The introduction of analyte molecules under normal capillary column GC/MS conditions will, under most conditions, eliminate the production of $[M+Cl]^-$ ions. Kassel, Kayganich and Watson²⁰ displayed HPEC mass spectra that also contained $[M+Cl]^-$ ions, but in this case the analyte molecules did not contain any chlorine atoms. Here the ion source was pretreated with carbon tetrachloride (CCl_4) for a short time (five minutes) before being returned to the normal mode of HPECMS operation, methane at 1 Torr. A five- to ten-fold increase in relative response for a wide range of compounds was observed when the CCl_4 pretreatment method was applied. The unusual $[M+Cl]^-$ ions were described as arising from a chloride radical (Cl^\cdot) attachment prior to ionization by electron capture. The source of the Cl^\cdot radical was thought to be the metallic surfaces inside the ion source which had been pretreated with CCl_4 . The observation of very low levels of Cl^- ions and the decrease in the $[M+Cl]^-$ ion with increases in both time and temperature strongly supported the idea of Cl^\cdot species bound to the source walls. The authors summed up this work with the following:

For unsaturated organic compounds there appears to be sufficient interaction between analyte, Cl^\cdot radicals, and the source volume surface for production of very intense $[M+Cl]^-$ ions.

The $[M+nH-nX]^-$ ion, where X refers to a halogen, is prevalent in the HPEC mass spectra of many polyhalogenated organic molecules.^{8, 16, 17, 22, 23}

Sears, Campbell and Grimsrud⁸ recently published a paper which addressed the formation of unusual ions of the type $[M+nH-nX]^-$ and concluded that these ions resulted from interaction of the species of interest with the walls of the ion source. Evidence supporting this idea was presented and will be briefly described here.

When the compound fluoranil was introduced into the ion source of a mass spectrometer which had previously been filled with methane under normal HPECMS conditions, the electron impact (EI) spectrum of this compound displayed an ion which was not present in the EI spectrum when the compound was introduced into a clean ion source. This ion corresponded to the molecular ion plus two hydrogens, $[M+2H]^+$. The $[M+2H]^+$ ion was thought to result from a reaction where a double bond containing two halogens was hydrogenated. Other evidence shown in this work displayed the apparent sticking of certain species to the ion source walls. The sticking effect was displayed by the use of normalized reconstructed single ion chromatograms (NRSIC) which showed that the unusual ions of the type $[M+nH-nX]^-$ were persisting in time well after the disappearance of the parent molecular anion, M^- . This result suggested that some species adhere to the walls of

the ion source for some time after the analyte passed through the source. The mechanism proposed by Sears, Campbell and Grimsrud for the production of the $[M+nH-nX]^-$ ions is shown in Figure 2 and takes the above evidence into consideration.

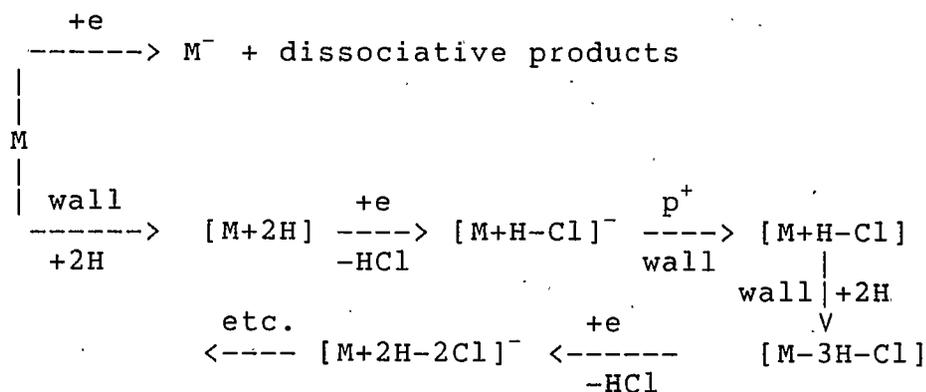


Figure 2. The Proposed Mechanism for Unusual Ion Production Suggested by Sears, Campbell and Grimsrud.

Also, in this same study the HPEC mass spectra of trifluoroacetic derivatives of isomers of aminoanthracene and aminophenanthrene were shown to contain unusual ions of the type $[M-0]^-$. These ions are considered unusual because the only oxygen present in these molecules is doubly bonded to a carbon atom. The $[M-0]^-$ ion was drastically reduced in abundance by adding triethylamine to the methane buffer gas. Triethylamine has a very high proton affinity and reacts quickly with the positive reagent ions found in the methane plasma by abstraction of

a proton. The protonated amines, thereby formed, do not react with the analyte. Their conclusion was that the unusual ion in this case arose from a positive ion-molecule reaction followed by neutralization and then electron capture. These researchers also applied triethylamine to the compounds discussed above that show unusual ions of the type $[M+nH-nX]^-$. They found that no changes in the spectra were observed, indicating that these ions do not depend on positive ion-molecule interactions.

Another type of unusual ion found in HPECMS literature is the ion corresponding to $[M+R]^-$, where R is a hydrogen or other alkyl species. McEwen and Rudat¹⁵ were the first investigators to report radical addition reactions taking place in the ion source of a mass spectrometer under HPECMS conditions. They used 7,7,8,8-tetracyanoquinodimethane (TCNQ) as a radical trap inside the ion source and showed that this compound gave complex HPEC mass spectra which displayed ions of the type $[M+R]^-$, where R in this case was predominantly $\cdot H$, $\cdot CH_3$, and $\cdot C_2H_5$. They concluded that the addition products observed for TCNQ under HPECMS conditions were due to the gas phase addition of radicals prior to electron capture.

Other examples appear in the literature where it is believed that the $[M+R]^-$ ions observed resulted from gas phase radical attachment prior to electron capture. A study done by Stockl and Budzikiewicz¹⁴ concerning

molecule-radical reactions under HPECMS conditions showed that 4-hydroxyquinoline-2-carboxylic acid, phenzaine-1-carboxylic acid, and related compounds produced spectra that included ions of the type $[M+C_nH_{2n}]^-$. They concluded that these ions resulted from methyl radical ($\cdot CH_3$) attack on the analyte molecule followed by abstraction of a hydrogen by another radical species ($R\cdot$) prior to ionization. Hilpert, Byrd, and Vogt²⁴ showed that some of the polycyclic aromatic hydrocarbons (PAH's) they tested produced HPEC mass spectra that included ions of the type $[M+CH_2]^-$. An interesting feature of the work shown by these investigators was the differing relative abundance of the $[M+CH_2]^-$ ions between different compounds. The studies of other investigators^{25, 26} on the HPEC mass spectra produced by PAH's exhibit general disagreement with respect to the ionization process involved.

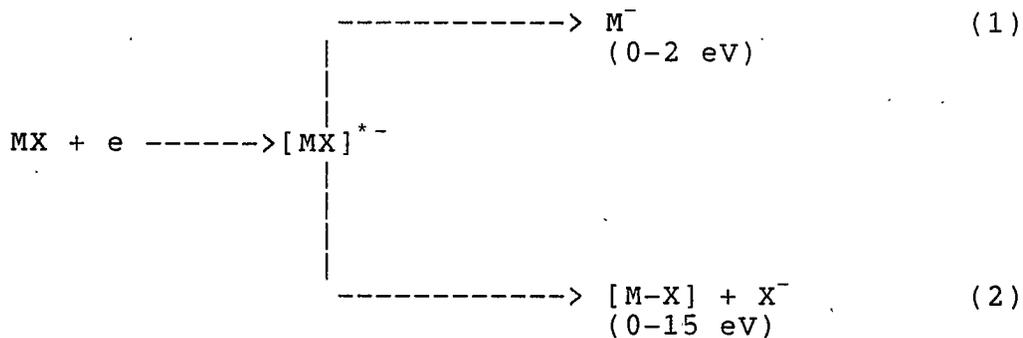
The examples given above of unusual ions occurring in HPECMS indicate that the ion source is a place where chemical events, in addition to resonance and dissociative electron capture, can be responsible for the observed spectra. In order to determine the origins of the unusual ions found in the HPEC mass spectra of some of the EPA priority pollutants examined in Chapter 4 of this study, a detailed look at the existing theory concerning the possible chemical events occurring inside the CI ion source will be presented.

Theory

According to the present theory of HPECMS, several chemical events are possible inside the ion source that can potentially lead to the negative ions detected. These chemical events will be systematically reviewed in the following sections. After the review of chemical events, the importance of each will be presented.

Formation of Negative Ions

Negative ions may be formed by resonance and dissociative electron capture.⁷ These processes are shown by reactions 1 and 2:



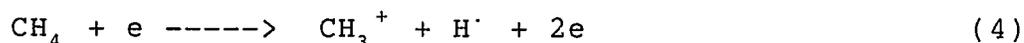
Reaction 1, resonance electron capture, occurs between molecules having a positive electron affinity and electrons which have energies in the range of 0-2 electron volts (eV). The vibrationally excited negative ion initially produced, $[\text{MX}]^{*-}$, must be stabilized by collisions with neutral gas molecules before it undergoes

autodetachment of the electron or dissociation. Reaction 2, dissociative electron capture, can occur by a rapid bond cleavage or by a slower process which may involve a molecular rearrangement.⁷ These reactions occur between analyte molecules and electrons with energies in the range of 0-15 eV. The electrons inside the ion source under HPECMS conditions are thought to be of near thermal energy (0 eV).⁸ In addition to the electron's energy, the product generated by electron capture can also be dependent upon the ion source temperature and pressure. For some molecules higher ion source temperature promotes dissociative electron capture resulting in an increase in fragment ions, such as Cl^- for chlorinated compounds, while lower temperatures favor the production of molecular anions formed by the resonance electron capture process.¹⁷ Other molecules, such as the PAH's, show a much smaller degree of HPEC mass spectral variation with changes in temperature.²⁶ Increasing the ion source pressure will increase the number of ion-electron pairs that are produced until the electron beam is stopped by gas molecules. Increasing the ion source pressure will also increase the collisional frequency, affecting the rate of electron thermalization and collisional stabilization of the vibrationally excited negative ions. In most cases increasing the ion source pressure increases the negative ion response until a maxima is reached.^{5, 13} The second

order rate coefficient for the electron capture process is around $2 \times 10^{-7} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ for molecules which undergo this process most rapidly,⁴ and a wide range of coefficients can generally be expected.

Positive Ions, Radicals,
and Electrons

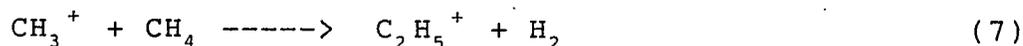
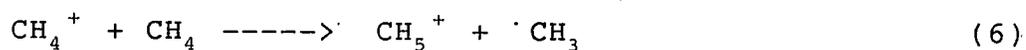
The HPEC ion source contains between 0.1 and 1.0 Torr methane which is used for the purpose of reducing the energy of the initial electron beam and to provide collisional stabilization of the negative ions formed by electron capture.¹³ The interaction of the electron beam with neutral methane gas molecules inside the ion source produces a high abundance of positive ions, radicals, and low energy electrons.^{13, 15} As indicated in equations 3 and 4:



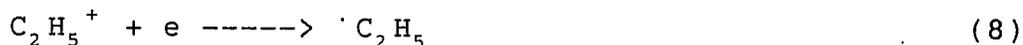
formation of each positive ion is accompanied by the production of a low energy electron. Each ionizing event removes about 30 eV from the bombarding electron,²⁷ typically between 70-300 eV, and the energy of the incident electron beam is further reduced by additional nonionizing collisions with neutral methane molecules.²⁸ The production rate, S , of positive ions and low energy electrons is given by:

$$S \text{ (pairs/sec)} = 2.1 \times 10^{11} (I \times E) \quad (5)$$

where I (μA) is the intensity of the electron beam entering the ion source and E (eV) is its energy. For the ion source used in this study the value of I has been estimated to be 5% of the set emission current.⁸ The positive ions produced by reactions 3 and 4 are rapidly converted into CH_5^+ and C_2H_5^+ ions¹ as shown below:



Recombination of positive ions with electrons also occurs under HPECMS conditions¹⁵ producing radical and neutral products. Examples of recombination are given by equations 8-10:



The production rate for radical species, S_R , can be obtained by modification of equation 5. The modification takes into account the observation made from equations 3, 4 and 6 through 10 that between 2 and 3 radicals are produced for every positive ion-electron pair produced by the interaction of the primary electron beam with methane gas molecules. The production rate for radicals inside the HPEC ion source is given by:

$$S_R \text{ (radicals/sec)} = 5.3 \times 10^{11} (I \times E) \quad (11)$$

where I (μA) and E (eV) are the same as equation 5.

The second order rate coefficients for positive ion-molecule reactions under HPECMS conditions are around $2 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ for exothermic reactions.⁴ For radical-molecule reactions the second order rate coefficient is around $1 \times 10^{-10} \text{ cm}^3 \text{ radicals}^{-1} \text{ sec}^{-1}$ for the very fastest of these reactions.¹⁵

In addition to reacting with neutral molecules, positive ions can also recombine with electrons or negative ions. The second order rate coefficient for positive ion-electron recombination, α_e , has been shown to be fairly constant for different organic positive ions²⁹ and is given by:

$$\alpha_e \text{ (cm}^3 \text{ sec}^{-1}\text{)} = 9 \times 10^{-7} (300/T)^{1/2} \quad (12)$$

where T (K) is the temperature of the ion source. For positive ion-negative ion recombinations under HPECMS conditions, the second order rate coefficients, α_- , have been shown to be approximately equal for all reactions of this type regardless of the interacting species.³⁰ The second order rate coefficient for all positive ion-negative ion recombinations is given by:³⁰

$$\alpha_- \text{ (cm}^3 \text{ sec}^{-1}\text{)} = 6.8 \times 10^{-7} T^{-0.4} \quad (13)$$

The radical species produced inside the ion source can undergo radical-radical recombination. The second order rate coefficient for methyl-methyl radical recombination, K_R , will be used for all recombinations of this type and is $4 \times 10^{-11} \text{ cm}^3 \text{ radicals}^{-1} \text{ sec}^{-1}$.³¹

Diffusion to the Walls

An ion source operated under HPECMS conditions fits Langmuir's definition of a plasma,³² and the diffusional characteristics of charged species are ambipolar as opposed to free. The chemical species present in the ion source can diffuse through the plasma and come into contact with the source wall. A charged species upon contact with an ion source wall will lose its charge. The rate coefficient for the diffusion process depends upon whether the species under consideration is charged or neutral. For positive ions, negative ions and electrons the rate coefficient for diffusion is given by $D_a r_o^{-2}$, where D_a is the ambipolar diffusion coefficient⁸ and r_o is the characteristic diffusion length³³ of the ion source. The ambipolar diffusion coefficient, D_a , is used here for all charged species because the ionic plasma does not permit the free diffusion of individual species. Inside the ion source of the HPEC mass spectrometer a positive ion will diffuse twice as fast as the electrostatically free positive ion, and the electron will diffuse 500 times

slower than when free in order to meet the conditions of charge neutrality required by ionic plasmas of this type.³ An equation for D_a has been provided,⁸ which is strongly dependent on changes in both temperature and pressure and is given by:

$$D_a \text{ (cm}^2\text{sec}^{-1}\text{)} = 0.11 \text{ (T/273)}^2 \text{ (760/P)} \quad (14)$$

where T (K) is the temperature of the ion source and P (Torr) is the pressure.

For neutral molecules and radicals the rate coefficient for diffusion is given by $D r_o^{-2}$, where D is the diffusion coefficient for neutrals^{3,4} and r_o is the characteristic diffusion length^{3,3} of the ion source. An equation for D has been provided^{8,3,4} and is given by:

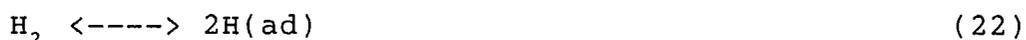
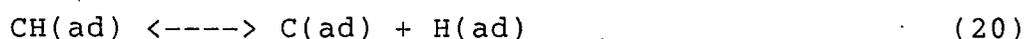
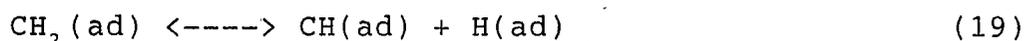
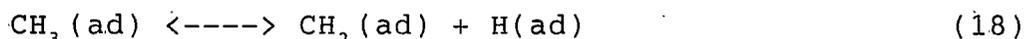
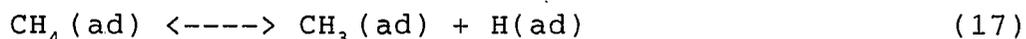
$$D \text{ (cm}^2\text{sec}^{-1}\text{)} = 0.063 \text{ (T/273)}^{3/2} \text{ (760/P)} \quad (15)$$

The characteristic diffusion length, r_o , has been estimated⁸ at 0.13 cm for the ion source used in this work.

Ion Source Surface Activity

If a species is chemically altered upon contact with the metallic surface (or wall) inside the ion source and subsequently detected as a negative ion, there then is a need to know what type of activity takes place at this surface. For most gas-metal combinations absorption is a

remarkably efficient process, and the probability that a normal background constituent of a vacuum system, such O₂, CO, N₂ or H₂, will become adsorbed during a single collision with a clean metal surface (the "sticking probability") is high, often between 0.1 and 1.³⁵ When the methane plasma interacts with the typical HPEC ion source of stainless steel construction, a series of surface reactions are possible. Some of the surface reactions that could possibly take place at the methane plasma-metal interface³⁶ are shown below:



From equations 16 through 22 it can be seen that the ion source surface has on it a complex array of methane derived species. In addition to the methane gas interaction with the ion source surface, it can now be envisioned that some of the radicals and positive ions shown earlier to be produced inside the ion source under HPECMS conditions could also adsorb onto the surface.

If an analyte species, neutral or charged, comes into contact with the ion source wall there are several possible outcomes. The species could potentially react with one of the methane derived species thought to be present on the source surface followed by desorption and possible electron capture to result in the observation of an unusual ion.

Another fate of collision of an analyte species with the ion source surface might be a dissociative reaction which consumes the species of interest as was shown³⁷ to be the case for ethylene and selected halogeno-substituted alkenes on an iron surface at 300 K. The species could also adsorb onto the ion source surface then desorb without any change in structure.

If any sticking is occurring at the ion source surface by analyte species, a means of showing this type of behavior is needed. The normalized reconstructed single ion chromatogram (NRSIC) is probably the best method available for this type of observation and will be used in this study.

Ventilation

For the chemical events described earlier to occur inside the ion source they must do so before the species of interest is vented from the source. The rate coefficient for ventilation is given by F/V where

F ($\text{cm}^3 \text{ sec}^{-1}$) is the volumetric flow rate of gas through the detector and V (cm^3) is the source volume. The volumetric flow rate is determined from an equation by Dushman³⁸ and is shown below:

$$F = 3.64 \times 10^3 A (T/M)^{1/2} \quad (24)$$

where A (cm^2) is the sum of the electron beam entrance aperture and the ion exit slit, T (K) is the temperature of the ion source, and M is the molecular weight of the buffer gas. The volumetric flow rate is independent of the ion source pressure and is equal to the conductance out of the source. For the ion source used in this work the value of A is 0.018 cm^2 , and the value of M is 16, the molecular weight of methane.

Steady State Equations

In order to determine the importance of the chemical events listed earlier in this chapter, the concentration of electrons, positive ions and radicals needs to be determined. The equation Siegal³ derived for the positive ion concentration under CI conditions in the absence of sample molecules and assuming steady state conditions is given by:

$$\frac{d[I^+]}{dt} = S - \frac{F[I^+]}{V} - \frac{Da[I^+]}{r_o^2} - \alpha_e [I^+][e] = 0 \quad (25)$$

where all the terms for this equation have been described earlier. A similar equation can be derived¹⁵ to calculate the steady state radical population in a CI plasma and is given by:

$$\frac{d[R]}{dt} = S_R - \frac{F[R]}{V} - \frac{kD[R]}{r_o^2} - K_R[R]^2 = 0 \quad (26)$$

where k is the reactivity between radicals and the ion source walls. For the case in which every collision with the wall results in loss of the radical, $k=1$. The other terms found in equation 26 have been described earlier in this chapter.

Equations 25 and 26 can be rearranged into quadratic equations and subsequently solved. In solving equation 25 the positive ion and electron concentrations were taken as being equal as was shown in an earlier section of this chapter. For equation 26 it will be assumed that all radicals upon contact with the source surface will not be destroyed, $k=0$. The resulting equations in terms of positive ion and electron concentration and radical concentration are shown by:

$$[e] = [I^+] = \frac{\left(\frac{D_a}{r_o^2} + \frac{F}{V} \right) + \left[\left(\frac{D_a}{r_o^2} + \frac{F}{V} \right)^2 + \frac{4\alpha_e S}{V} \right]^{1/2}}{2\alpha_e} \quad (27)$$

$$[R] = \frac{\frac{(F)}{(V)} \left[\frac{(F)^2}{(V)} + \frac{4K_R S_R}{V} \right]^{1/2}}{2 K_R} \quad (28)$$

where the values of the components of each equation have been given in absolute or equation form in previous sections of this chapter. Table 1 lists the value of each component of equations 27 and 28 at the specified ion source conditions. From the values given in Table 1 the concentration of positive ions and electrons is found to be 8×10^9 pairs cm^{-3} , and the concentration of radicals is 2×10^{12} radicals cm^{-3} . Thus at these conditions the radicals exceed positive ions and electrons by a factor of 250.

Table 1. Values for Components of Equations 27 and 28 at 473 K, 0.3 Torr, 200 μA , and 200 eV.

Component	Value
F	$356 \text{ cm}^3 \text{ sec}^{-1}$
V	1 cm^3
S	$4.2 \times 10^{14} \text{ pairs sec}^{-1}$
S_R	$1.1 \times 10^{15} \text{ radicals sec}^{-1}$
D_a	$8.3 \times 10^2 \text{ cm}^2 \text{ sec}^{-1}$
D	$3.6 \times 10^2 \text{ cm}^2 \text{ sec}^{-1}$
r_o^2	0.0169 cm^2
α_e	$7 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$
K_R	$4 \times 10^{-11} \text{ cm}^3 \text{ radicals}^{-1} \text{ sec}^{-1}$

Chemical Events versus
Ventilation

From the concentrations of positive ions, electrons, and radicals found in the previous section, it is now possible to determine the time needed for individual chemical events to occur inside the ion source. Table 2 lists the time that is needed, by way of pseudo first order rate constants, for the two-body reactions at the ion source conditions given. Table 3 lists the time required for single body events to occur inside the ion source.

Table 2. Time Required for Two Body Reactions Inside the Ion Source at 473 K, 0.3 Torr, 200 μ A, and 200 eV.

Event	Rate Const. $\text{cm}^3 \text{sec}^{-1}$	Time Req. (msec)
Electron capture	2×10^{-7}	0.5
Positive ion-molecule	2×10^{-9}	60
Radical-molecule (K_R)	1×10^{-7}	5
Positive ion-electron (α_e)	7×10^{-7}	0.2
Positive ion-negative ion (α_-)	5.8×10^{-8}	2

Table 3. Time Required for Single Body Processes Inside the Ion Source at 473 K, 0.3 Torr, 200 μ A, and 200 eV.

Event	Rate Const. sec^{-1}	Time Req. (msec)
Ventilation (F/V)	356	3
Neutral Diffusion ($D_r r_o^{-2}$)	2.1×10^4	0.05
Charged Diffusion ($D_a r_o^{-2}$)	4.9×10^4	0.02

It is apparent that the time required for ventilation, about 3 msec, is slow enough to allow several reactions to occur while the analyte is still inside the ion source. For example, the analyte molecule could diffuse to the source wall (0.05 msec), desorb and capture an electron (0.5 msec), then diffuse to the source wall again (0.02 msec) followed by desorption and electron capture. This sequence of diffusion, desorption, and electron capture could theoretically occur approximately six times before the analyte is vented from the source.

Because the rates of reactions given earlier were for specific cases the values given in Table 2 could possibly be in large error for certain cases. Nevertheless, this view of ion source events has proven to be useful in the past⁸ and will be used in this work to help explain the unusual ions found to be present in the HPEC mass spectra of a number of the EPA priority pollutants.

STATEMENT OF PROBLEM

In the previous chapter the current literature concerning the observation of unusual ions in HPECMS was presented which showed that events other than electron capture must have been responsible for the unusual ions. The current theory concerning HPECMS was then presented and clearly showed that many chemical events in addition to electron capture can possibly occur inside an ion source operated under HPECMS conditions. The objective of this study was to examine the HPEC mass spectra of a majority of the EPA priority pollutants³⁹ and to use the present theory of HPECMS described in the Introduction to explain any unusual ions observed.

EXPERIMENTAL PROCEDURES

All HPEC mass spectra and chromatograms shown in this study were obtained on a VG 7070E-HF double focusing mass spectrometer which was directly coupled to a Varian 3700 gas chromatograph using a 30 m x 0.25 mm DB-5 fused silica column (J&W Scientific, Rancho Cordova, California). Helium was used as the GC carrier gas at a flow rate of about 1 to 2 cm³- atm sec⁻¹. The flow rate of methane gas through another port depended upon the ion source pressure desired and was typically ten times greater than the flow of helium. Ion source pressure was determined with a MKS 270B capacitive manometer. In this study source pressures between 0.1 and 0.5 Torr were used. The opening where the direct insertion probe entered the source was plugged to avoid variations in source conductance. The ion source temperature was determined by a thermocouple which was attached to the ion source block. Source temperatures between 80°C and 260°C were used. The electron energy was either 200 eV or 250 eV and the emission current was either 200 μ A or 500 μ A. The detection of negative ions was achieved by the use of a conversion dynode and an analog electron multiplier.

All compounds used in this study were obtained from Chemical Services, Inc., West Chester, Pennsylvania. Methanol was used as the solvent except in the case of the polynuclear aromatic hydrocarbons (PAH's) where toluene was used. All compounds were introduced into the ion source via the capillary column in the splitless mode for 30 seconds at concentrations between 1 and 10 ng/ μ L.

RESULTS AND DISCUSSION

This study began with the examination of the HPEC mass spectra produced by the EPA priority pollutants listed in Table 4. From this initial examination two distinct types of spectra arose which displayed negative ions that could not have resulted from the classical resonance and dissociative electron capture processes alone. One of the two types of spectra mentioned above shows unusual ions of the type $[M-Z+nH-nCl]^-$, where M is the analyte molecule and Z is either a fragment of M whose mass depends on its composition or is zero. A number of the polychlorinated pollutants listed in Table 4 display negative ions corresponding to $[M-Z+nH-nCl]^-$. The other type of unusual negative ions observed in the spectra of some of the EPA priority pollutants corresponds to $[M+R]^-$, where R is thought to be H, CH_2 , CH_3 or some other small alkyl species. Most of the PAH's listed in Table 4 show ions of the type $[M+R]^-$.

The normalized reconstructed single ion chromatograms (NRSIC), which were mentioned briefly in Chapter 1, will be used extensively throughout this study to prove the existence of interactions between analyte species and the ion source walls. Theoretically, the ions produced in the

