Origin of adduct ions in the electron capture mass spectrum of tetracyanoethelyne [i.e. tetracyanoethylene]
by John Allen Culbertson

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 high pressure electron capture (HPEC) mass spectrum of tetracyanoethylene (TCNE) is dominated by unusual hydrogen atom and hydrocarbon radical adduct ions when methane is used as the buffer gas. The origin of these unusual ions is investigated here by four separate mass spectrometric experiments. These are: (1) the electron capture rate constant of TCNE is determined and integrated into a previously developed kinetic model of HPEC ion source events, (2) electron impact mass spectra of TCNE are obtained following exposure of the ion source to irradiated methane and irradiated carbon dioxide, (3) the HPEC mass spectrum of TCNE in ammonia buffer gas is obtained shortly after the ion source has been exposed to irradiated methane, (4) and the temporal profiles of TCNE are obtained and analyzed by gas chromatographic introduction to the ion source with multiple ion monitoring. All of these experiments suggest that the reactions leading to the unusual adduct ions in the HPEC mass spectrum of TCNE are initiated by alterations of TCNE on the walls of the ion source rather than in the gas phase.

ORIGIN OF ADDUCT IONS IN THE ELECTRON CAPTURE MASS SPECTRUM OF TETRACYANOETHELYNE

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John Allen Culbertson

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For the ongoing support, love, and understanding, this thesis is dedicated to my wife, Melinda.

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ABSTRACT

The high pressure electron capture (HPEC) mass spectrum of tetracyanoethylene (TCNE) is dominated by unusual hydrogen atom and hydrocarbon radical adduct ions when methane is used as the buffer gas. The origin of these unusual ions is investigated here by four separate mass spectrometric experiments. These are: (1) the electron capture rate constant of TCNE is determined and integrated into a previously developed kinetic model of HPEC ion source events, (2) electron impact mass spectra of TCNE are obtained following exposure of the ion source to irradiated methane and irradiated carbon dioxide, (3) the HPEC mass spectrum of TCNE in ammonia buffer gas is obtained shortly after the ion source has been exposed to irradiated methane, (4) and the temporal profiles of TCNE are obtained and analyzed by gas chromatographic introduction to the ion source with multiple ion monitoring. All of these experiments suggest that the reactions leading to the unusual adduct ions in the HPEC mass spectrum of TCNE are initiated by alterations of TCNE on the walls of the ion source rather than in the gas phase.

INTRODUCTION

The ability of certain molecules to capture thermalized electrons has been greatly exploited by High Pressure Electron Capture Mass Spectrometry (HPECMS), which had its first origins in experiments performed by Doughetry in 1972[1]. HPECMS, coupled with capillary gas chromatography, has proven to be a powerful analytical tool due to its high chemical specificity and sensitivity. Quite often the HPEC mass spectra contain the molecular ion in high relative abundance, lending it to be a valuable tool for molecular weight information. The negative ion to be detected is formed by the capture of an electron of thermal energy, which can then lead to one of two electron capture (EC) products shown in reactions 1a and 1b.

$$MX + e(\text{thermal}) \longrightarrow [MX^-]^* \rightarrow MX^- \quad (1a)$$

$$[MX^-]^* \rightarrow M + X^- \quad (1b)$$

The resonance EC product and dissociative EC product, reactions 1a and 1b respectively, can be formed only if the following two conditions are met[2]. First, the electron affinity of the analyte molecule, MX, must be positive, and second, the excited intermediate molecular negative ion must be sufficiently long lived so that either the excess energy can be quenched or bond rupture can occur. Only a small portion of molecules have high enough electron affinities so that they may capture an electron and be detected. This can lead to a great advantage when attempting to detect molecules

in a complex mixture. For certain molecules whose electron affinity are too low, simple derivatization procedures can be performed with fluorinated reagents which can increase the electron affinity of the molecule to a high enough value so that it may then form a negative ion under HPECMS conditions.

Some of the molecules that can be analyzed by HPECMS happen to be of environmental[3,4] and biomedical[5] importance. Molecules which possess these high electron affinities can be much more sensitive to HPECMS as opposed to positive chemical ionization or electron impact. Hunt and coworkers[6] have demonstrated with pulsed positive negative ion chemical ionization experiments, employing methane as the buffer gas, that the negative ion signal can be three orders of magnitude larger than the positive ion signal for compounds that have high EC rate coefficients. This is explained by the fact that the rate coefficients for the electron-molecule reactions are often greater than those of ion-molecule reactions by two orders of magnitude[7].

HPECMS employs a buffer gas at ion source pressures of 0.1 to 1 torr. The buffer gas serves two basic purposes: to thermalize the secondary electrons being created by the source filament, and to stabilize the excited intermediate molecular negative ions shown in reaction sequence 1. Table 1 shows the electron thermalization rates and the number of collisions required for vibrational quenching for a number of different buffer gases.

Table 1. Electron Thermalization Rates[8] (k_e) and Number of Collisions Required for Vibrational Quenching[10] (Z) for Various Buffer Gases.

Gas	k_e cm^3 s^{-1}	Z	Gas	k_e cm^3 s^{-1}	Z
Ar	1.3×10^{-13}	77	O_2	1.0×10^{-10}	30
Ne	2.5×10^{-13}	100	CH_4	8.6×10^{-10}	40
He	6.4×10^{-12}	150	CO_2	5.8×10^{-9}	18
N_2	2.2×10^{-11}	70			

Warman and Saurer[8] have shown that the electron thermalization efficiency generally increases with increasing complexity of the buffer gas. Factors such as molecular size, the presence of pi bonds, and dipole moment increase the electron thermalization efficiency as they themselves increase. CO_2, however, is exceptionally efficient at thermalizing electrons. This is attributed to the fact that CO_2 can form an intermediate negative ion, CO_2^-, which then rapidly autodetaches to yield a low energy electron and vibrationally excited CO_2[9]. The ability of the buffer gas to quench the excess energy of the excited intermediate has also been shown to increase with increasing complexity of the gas, as demonstrated in Table 1. The quenching efficiency is thought to be governed by two principal factors[10]: the strength of the ion-neutral collision, and the heat capacity of the quenching neutral.

Methane is probably the most commonly used buffer gas for HPECMS due to its high electron thermalization rate and

because it is also commonly used for positive CI work. Upon careful examination of CH_4 - HPECMS spectra, however, one often observes ions that cannot be explained solely by the simple EC reactions 1a and 1b. These "unusual" ions often comprise a majority of the ions observed in the spectrum and can dominate the relative ion signal. They are typically thought to originate from a reaction of the analyte molecule with hydrogen atoms (H) or hydrocarbon free radicals (R). The radicals are produced from the e-beam irradiation of the methane (or other hydrocarbon buffer gas). Reactions 2-7 show some of the formation pathways for these radicals in methane.

$$CH_4 + e \longrightarrow CH_4^{+\cdot} \quad (2)$$

$$CH_4^{+\cdot} \longrightarrow CH_3^+ + H\cdot \quad (3)$$

$$CH_4^{+\cdot} + CH_4 \longrightarrow CH_5^+ + CH_3\cdot \quad (4)$$

$$CH_5^+ + e \longrightarrow CH_3\cdot + H_2 \quad (5)$$

$$CH_3^+ + CH_4 \longrightarrow C_2H_5^+ + H_2 \quad (6)$$

$$C_2H_5^+ + e \longrightarrow C_2H_5\cdot \quad (7)$$

Several classes of compounds such as unsaturated halogen and cyano compounds[2,3,11], polycyclic aromatic hydrocarbons[11,12], and organo-metallic complexes[13,14] have produced H-adduct and R-adduct ions in their HPEC mass spectrum. One compound that McEwen and Rudat[11] have shown to be particularly susceptible to the formation of both H-adduct and R-adduct negative ions in CH_4-HPECMS is tetracyanoethylene (TCNE). This compound has been studied in depth here as to determine the origin of these unusual adduct ions and the results will be reported in the

Results and Discussion section.

Sears, Campbell, and Grimsrud[2] have developed a model that describes four potential routes that lead to the formation of unusual negative ions, which is shown in Figure 1. Routes A and B were proposed by Sears et al. to be possibly important pathways to unusual ion formation, while routes C and D have been previously reported by others.

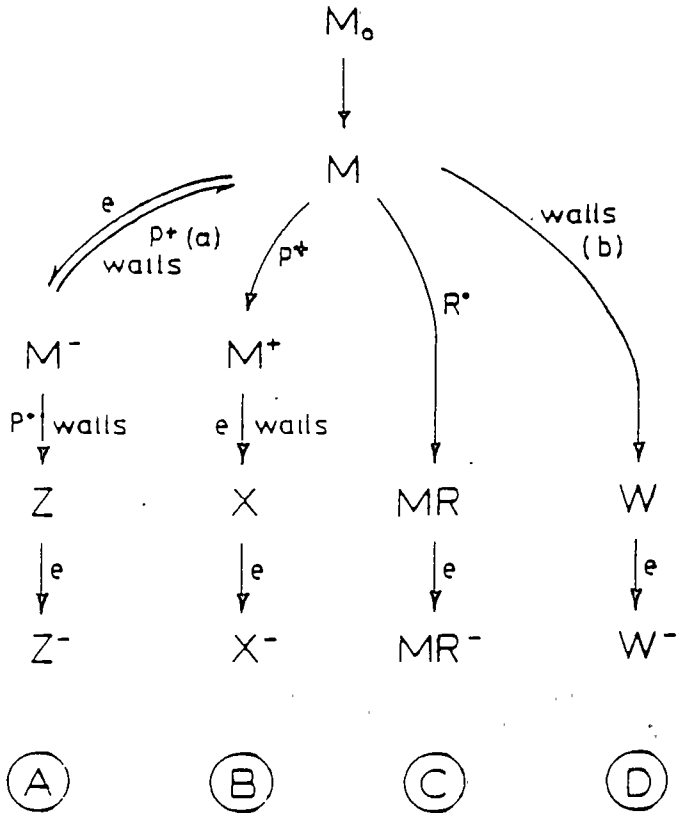

Figure 1. Four possible routes to the formation of unusual ions as proposed by Sears, Campbell, and Grimsrud[2].

Route A is initiated by electron attachment to the analyte molecule M, which upon neutralization by reaction with a positive ion and/or contact with the wall of the ion source, can produce the altered neutral species Z. Z may then attach an electron to form the unusual ion Z^-. If M^- has undergone resonance EC, thereby having the same structure as M, neutralization of M^- will simply regenerate the original analyte M. The coefficient, a, is indicative of which one of these reactions will occur. If a=1, the regeneration of M will result, and if a=0 species Z will be formed. Intermediate values allow both M and Z to be formed.

Route B is initiated by an ion molecule reaction to form M^+. These types of positive ions are analogous to those that constitute the normal positive CI mass spectrum. Upon neutralization by recombination with an electron or contact with the walls, M^+ is converted to the neutral species X. X can then undergo EC to form the unusual ion X^-.

Route C was first proposed by McEwen and Rudat[11], in which M first reacts with a gas phase radical to form the neutral MR, which can then attach an electron to give the unusual ion MR^-. McEwen and Rudat thought this to be a good way of determining the radical species that are present upon the irradiation of hydrocarbon buffer gases by using compounds like TCNE as the radical trapping agent.

Kassel and coworkers[15] have described a surface-assisted

pathway (Route D) to unusual negative ions whereby the neutral analyte is altered on the walls of the ion source to produce the species W. W can then attach an electron to form one or several unusual ions, collectively termed W^-. In their work, Kassel and coworkers witnessed $(M+Cl)^-$ ions under normal CH_4-HPECMS conditions, however, no chlorine containing compounds were present in the source. They proposed that the $(M+Cl)^-$ ion originated from a reaction of the neutral analyte, M, with a Cl radical on the walls of the ion source, which had been deposited from previous use of CCl_4. The (M+Cl) neutral then came off the wall and attached an electron to form the negative ion.

STATEMENT OF RESEARCH OBJECTIVE

The goal of this research is to determine the origin of unusual adduct ions that appear in the high pressure electron capture (HPEC) mass spectrum of tetracyanoethylene (TCNE). This will be accomplished by employing the model developed by Sears, Campbell, and Grimsrud which was discussed in the previous section and by several mass spectrometric experiments. These experiments include the following: determination of the electron capture rate constant of TCNE; obtaining the electron impact and HPEC-ammonia mass spectrum of TCNE after exposure of the ion source to irradiated methane; analyzing the chromatographic time profiles of TCNE under HPEC conditions with multiple ion monitoring.

THEORY

In this section the processes that contribute to ion source dynamics will be individually described. These events are important and must be considered when attempting to determine the mechanism by which unusual ions are formed.

Ventilation

Ventilation of an ion source is given by F/V, where F(cm^3 sec^{-1}) is the volumetric flow rate of gas through the detector and V(cm^3) is the ion source volume[2]. The volume of the CI ion source used in this study is 1 cm^3. The flow rate is independent of the buffer gas pressure in the source and is equal to the conductance of the source. Knowing the areas of the electron entrance aperture and the ion exit slits, one can make a good estimate of the conductance from the expression provided by Dushman[16]:

$$F(cm^3\ sec^{-1}) = 3.64 \times 10^3\ A\ (T/M)^{1/2} \qquad (8)$$

where A(cm^2) is the total area of the slits and aperture, T(K) is the source temperature, and M(g mol^{-1}) is the molecular weight of the buffer gas. Thus for the ion source used here, at 150°C, methane as the buffer gas, and the total area of the slits and aperture equal to 0.018 cm^2, the total volumetric flow rate is about 340 cm^3 sec^{-1}. This corresponds to a residence time of about 3 msec.

Diffusion to the Walls

An ion source operated under typical HPECMS conditions will have ion and electron densities too high for them to undergo free diffusion to the walls[20]. Therefore, these species will diffuse through the plasma under ambipolar conditions. When an ion or electron comes in contact with the walls of the ion source it will be neutralized. The rate coefficient for the diffusional process depends on whether the species is charged or neutral. For negative ions, positive ions, and electrons the rate of diffusion is given by $D_a l_0^{-2}$ [2], where D_a is the ambipolar diffusion coefficient which applies to both ions and electrons, and l_0 is the characteristic diffusion length of the ion source[20]. The free diffusion coefficient of electrons is much greater than that of positive ions, but because the two are coupled in their diffusion, the electrons will diffuse about three orders of magnitude slower than if free and the positive ions about twice as fast[2]. A general expression for D_a has been provided[2] in equation 9 for an ion of 100amu and methane as the buffer gas.

$$D_a(cm^2\ sec^{-1}) = 0.11\ (T/273)^2\ (760/P) \qquad (9)$$

The above expression for D_a is very dependent on temperature (T, in K), and pressure (P, in torr). For the ion source used in this study at 0.5 torr methane and 150°C, D_a=400 $cm^2\ sec^{-1}$. The diffusion length, l_0, has been estimated[2] to be 0.13 cm. Therefore, the rate of diffusion of ions and electrons equals $400/(0.13)^2 = 2.4 \times 10^4\ sec^{-1}$.

Neutral molecules and radicals also diffuse to the walls of the ion source. Their rate of diffusion can be expressed as above by Dl_0^{-2}, where D is the diffusion coefficient of the neutral radical or molecule and l_0 is the same as above. An expression for D has been provided[2] and is given by:

$$D(cm^2\ sec^{-1}) = 0.063\ (T/273)^{3/2}\ (760/P) \qquad (10)$$

If a the diffusion length of 0.13 cm is used, a pressure of 0.5 torr methane, and 150°C, the rate of diffusion for neutrals is then 1.1×10^4 sec^{-1} and will again be very dependent on temperature and pressure.

Electron Capture and Ion-Molecule Reaction Rate Coefficients

As was mentioned in the Introduction, the reason HPECMS can be so much more sensitive than positive CI is that the EC rate coefficient can be much larger than the rate coefficient of ion-molecule reactions. For example, an ion-molecule reaction involving relatively large molecules and being favored thermodynamically will have a second order rate coefficient of approximately 2×10^{-9} cm^3 sec^{-1}. On the other hand, molecules which undergo exothermic electron attachment can have a wide range of rate coefficients[17] and can be as high as 4×10^{-7} cm^3 sec^{-1} for those molecules that attach electrons most rapidly[2]. HPECMS is most powerful for selectively detecting these types of molecules.

Positive Ion and Radical Production

Many pathways for radical production in methane have already been shown in reactions 2-7. It is sufficient to say, for our purposes here, that for each ion pair produced from the irradiation of methane 2 to 4 free radicals will be produced[2]. Reactions 11-14 show the sequence by which three radicals, H· and two CH_3·, are formed from the initial ion pair.

$$CH_4 \xrightarrow{e_i} CH_4^{+\cdot} + e_{th} + e_i \quad (11)$$

$$CH_4^{+\cdot} \longrightarrow CH_3^+ + H\cdot \quad (12)$$

$$CH_4^{+\cdot} \xrightarrow{CH_4} CH_5^+ + CH_3\cdot \quad (13)$$

$$CH_5^+ \xrightarrow{e} CH_3\cdot + H_2 \quad (14)$$

An estimation of the radical production rate, S_R, can be made by the following expression:

$$S_R \text{ (radicals sec}^{-1}) = 5 \times 10^{11} \text{ (I x E)} \quad (15)$$

where I(uA) is the intensity of the e-beam entering the ion source and E(eV) is its energy. The efficiency of entry of the e-beam into the source used in this study is about 5%[2]. Thus, I must be multiplied by 5% to obtain the true e-beam intensity in the source. Sears, Campbell, and Grimsrud have derived an equation to calculate the steady state radical concentration in a CI plasma and is given by:

$$[R] = \frac{-(F/V) + [(F/V)^2 + 4k_R S_R/V]^{1/2}}{2k_R} \quad (16)$$

where k_R is the rate of radical recombination. All other terms have previously been discussed.

For the ion source conditions used in this study the

radical concentration was calculated to be about 4 x 10^{12} radicals cm^{-3}. A similar equation for the steady state concentration of positive ions is given by:

$$[P] = \frac{-(D_a/l_0^2 + F/V) + [(D_a/l_0^2 + F/V)^2 + 4qS/V]^{1/2}}{2q} \quad (17)$$

where S = 1.7 x 10^{11} (I x E) which is the ion production rate[2] and q is the rate of ion-electron recombination (a typical value for q is 8 x 10^{-7} cm^3 sec^{-1})[23].

A value of [P] = 3.5 x 10^{10} ions cm^{-3} was calculated for the source conditions used in this study. Thus, the concentration of radicals in the CI ion source used here is over 100 times greater than the ion concentration.

As can be seen from reaction 11, for each positive ion formed one low energy electron is also formed. Thus, we can conclude the concentration of low energy electrons [e_{th}] and positive ions are equal. The ionizing electron, e_i, loses about 30eV of energy during the ionizing process[21] and can lose further energy by subsequent nonionizing collisions with neutral methane molecules. However, e_i may still have sufficient energy to ionize several additional methane molecules. The 30eV of energy lost by e_i in the ionization step is distributed between the ion pair. This excess energy is quickly quenched either through fragmentation (of the radical cation) or by collision with the buffer gas.

Radical Reactions

In an attempt to determine the origin of radical adduct

ions that are present in the HPEC mass spectrum of TCNE, it will be useful to know the rate at which gas phase radical reactions proceed. The rate coefficients for these reactions will be very dependant on the nature of the reactant pair and will vary over many orders of magnitude[2]. For a very fast radical-neutral reaction[18] the rate coefficient could possibly be as high as 1 x 10^{10} cm^3 sec^{-1}, which is about one order of magnitude slower than a fast ion-molecule reaction. These gas phase reactions will be further discussed as a possible pathway for unusual ion formation in a later section.

Radical Losses

Free radicals produced by the irradiation of a hydrocarbon buffer gas can be lost by at least three processes. They are: diffusion to the walls of the ion source; reaction with a neutral molecular species; or by radical-radical recombination. The radical-neutral and diffusion rate coefficients have already been discussed. The recombination coefficient, (k_R), for methyl radicals has been shown to be[19] 4 x 10^{-11} cm^3 sec^{-1}, which is approximately one order of magnitude slower than a fast radical-neutral reaction. This value is used throughout this study to represent all radical recombinations.

EXPERIMENTAL

All mass spectra reported in this study were obtained using a double focusing, medium resolution mass spectrometer (VG Analytical, model 7070E-HF). The buffer gas was ionized by using a 150eV electron beam generated from a tungsten filament with an emission current of 0.2 mA. Methane, ammonia (anhydrous), and carbon dioxide were used as buffer gases and all were at least 99.97% pure. Methane and carbon dioxide were passed through molecular sieve, water, and oxygen traps. The flow rate of buffer gas through the ion source was approximately 10-20 cm^3 atm sec^{-1}. The port in the ion source for the direct insertion probe was plugged to prevent variations in source conductance. The repeller was grounded to prevent any electric fields within the source which could effect ion population. Ion source pressure was maintained between 0.1 and 0.5 torr and was measured by a capacitance manometer (MKS, model 270B). The temperature of the ion source used in this study was 150°C and was measured by a thermocouple attached to the ion source block. The ions were accelerated by 5000 volts into the analyzer region and then detected by an off axis discrete dynode electron multiplier (ETP, model AEM-1200).

TCNE (98% pure) was diluted in acetonitrile (HPLC grade) and introduced directly into the ion source using a gas

chromatograph (Varian, model 3700) equipped with a capillary column (J&W Scientific, DB-5 30m x 0.25mm). The typical injection size was 100ng. A temperature of 200°C was maintained in the injection port and all interface heaters. The temperature program used for the GC had an initial temperature of 50°C, which was held for 4 minutes, then increased by 10°C per minute. High purity helium was used as the carrier gas with a flow rate of about 30 cm^3 sec^{-1}.

Experiments to determine the EC rate coefficient of TCNE (performed by Dr. Berk Knighton) were done using a home built pulsed high pressure mass spectrometer (PHPMS). The ion source of the PHPMS has an electron gun that provided 10 pulses per second of 3kV electrons to the ion source. The intensity of each ion of interest was monitored as a function of time between the e-beam pulses by a multichannel scaler (Ortec, model 913). The gaseous mixture under study was prepared in carbon dioxide in an associated gas handling plant and then leaked continuously through the ion source of the PHPMS. The total ion source pressure was 3 torr. Negative ions were detected by a channeltron electron multiplier (Galileo Electro-optics, model 4870E) that was operated in the ion counting mode.

RESULTS and DISCUSSION

Routes to Unusual Ion Formation

TCNE has a very high electron affinity (3.2 eV[24]) and is therefore expected to capture thermalized electrons very rapidly. Upon EC, TCNE would also be expected to form a stable molecular anion by resonance EC, reaction 1a. However, as can be seen in Figure 2, the molecular anion, M^-, constitutes only a small fraction of the total negative ion signal and the spectrum is dominated by H-adduct and R-adduct negative ions.

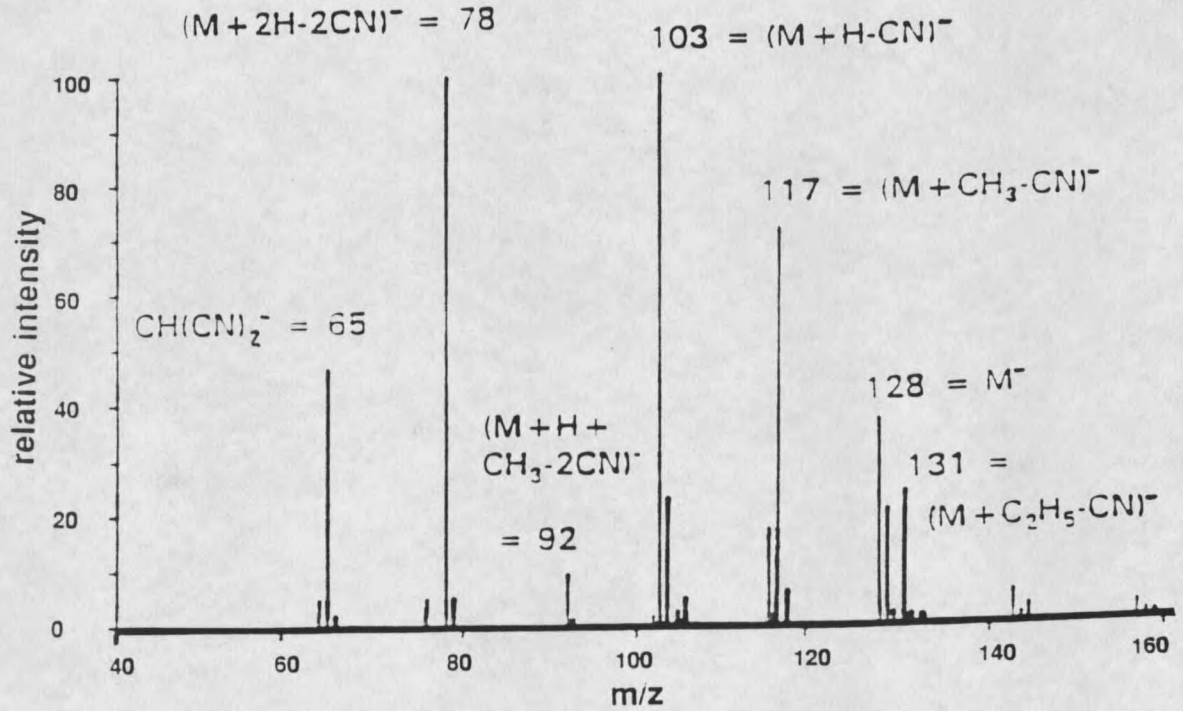

Figure 2. HPEC-CH_4 mass spectrum of TCNE at 150°C and 0.5 torr.

For comparison Figure 3 shows the HPEC mass spectrum of TCNE when CO_2 has been used as the buffer gas. No unusual ions are formed under HPEC-CO_2 conditions.

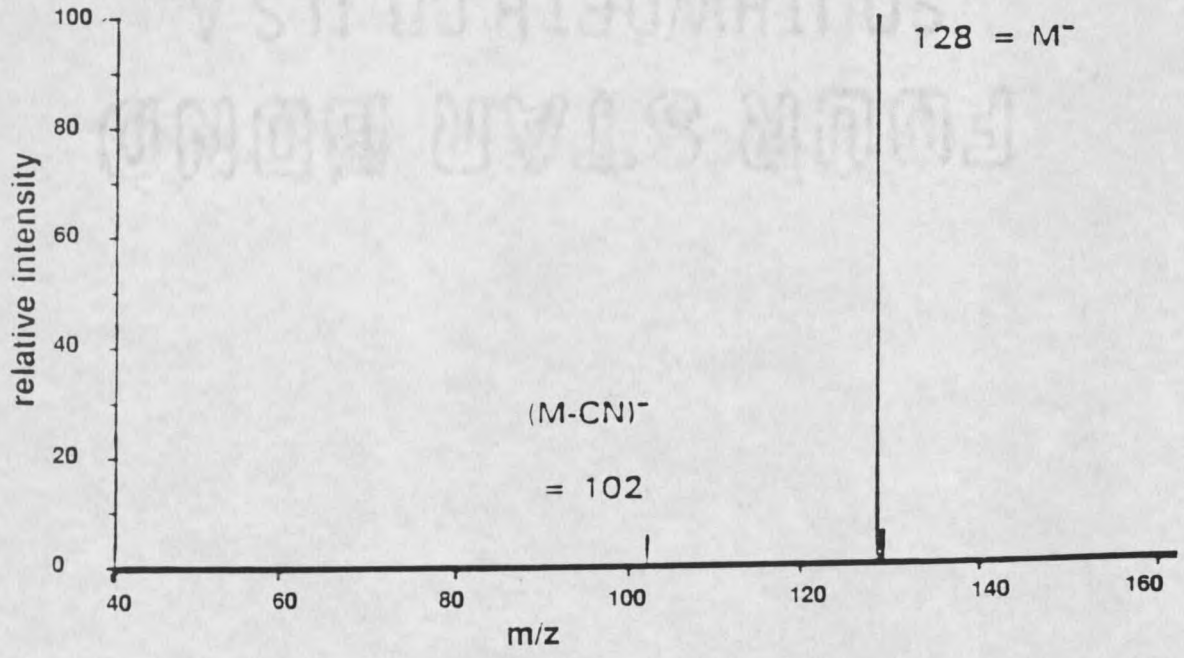

Figure 3. HPEC-CO_2 mass spectrum of TCNE at 150°C and 0.5 torr.

In order to determine how the unusual adduct ions are formed in the HPEC-CH_4 mass spectrum of TCNE, all four routes of the model developed by Sears et al.[2] must be considered. Table 2, which shows calculated[2] amounts for the species of Figure 1, will aid in the discussion to follow, in which three of these routes will be ruled out.

Table 2. Calculated Relative Amounts (x 10^2) of Ionic and Neutral Species of Figure 1 Under Most Favorable Conditions.

Route	Conditions ($k = (cm^3\ sec^{-1})$)	Relative Amounts					
A	$k_{eM} = 3 \times 10^{-7}$	M	M^-	Z	Z^-		
	$k_{eZ} = 3 \times 10^{-7}$	7.3	1.2	6.6	1.1		
B	$k_+ = 2 \times 10^{-9}$	M	M^-	Z	M^+	X	X^-
	$k_{eX} = 3 \times 10^{-7}$	7.2	1.2	84	0.0059	0.044	0.0076
	$k_{eM} = 3 \times 10^{-7}$						
C	$k_R = 1 \times 10^{-10}$	M	M^-	Z	MR	MR^-	
	$k_{eMR} = 3 \times 10^{-7}$	6.8	1.2	85	0.47	0.081	
	$k_{eM} = 3 \times 10^{-7}$						
D	b = 1	M	M^-	Z	W	W^-	
	$k_{eW} = 3 \times 10^{-7}$	2.2	0.37	27	5.1	0.88	

Route A

Table 2 shows that if the analyte molecule, M, has a high EC rate coefficient ($k_{eM} = 3 \times 10^{-7}$ cm^3 sec^{-1}) and the altered neutral, Z, also undergoes rapid EC, that the unusual ion Z^- does not exceed the molecular anion, M^-, in intensity. Calculations have shown[2] that even if $k_{eZ} > k_{eM}$, the concentration of Z^- can never exceed that of M^-. This allows route A to be ruled out right away because most of the unusual ions in the EC mass spectrum of TCNE are greater in intensity than the molecular anion.

Route B

If the ion-molecule reaction that initiates route B is given a high rate constant ($k_+ = 2 \times 10^{-9}$ cm^3 sec^{-1}), and both the altered neutral, X, and analyte, M, capture electrons very fast, the relative amount of the unusual ion, X^-, formed is very small. If route B were operative the EC mass spectrum would be dominated by the molecular anion, which is not the case for TCNE. Therefore, this route cannot compete with a fast EC reaction. It can, however, give fairly sensitive signals to the unusual ions if k_{eM} is not too large.

Route C

McEwen and Rudat[11] have proposed this gas phase reaction route to be the mechanism by which the unusual adduct ions are formed in the EC mass spectrum of TCNE. However, the results in Table 2 show that route C is not predicted to be dominant over a fast EC reaction. Even with optimal rate coefficients chosen, the relative concentration of the unusual ion, MR^-, is more than an order of magnitude less than the molecular anion. Route C can provide sensitive signals to MR^- for compounds that react with radicals very fast but attach electrons with only modest speed.

Route D

The results in Table 2 for this reaction sequence show that it can indeed be competitive with a fast EC reaction. If all neutral analyte molecules that come in contact with the wall are converted to W (b = 1), and both M and W are allowed

to capture electrons very rapidly, sensitive signals to the unusual ion, W^-, can be achieved. For the case here, W^- is more than twice as large as M^-. These results agree with the intensities of the ions that are present in the EC mass spectrum of TCNE. At this point it appears as if route D is the likely mechanism to unusual ion formation for TCNE.

Electron Capture Rate Constant of TCNE

In order for the above discussion to be valid, the EC rate constant of TCNE at 150°C must be known. This rate constant has been determined here from pulsed high pressure mass spectrometry (PHPMS) measurements such as the one shown in Figure 4. For the experiment shown, the ion source contains 0.068 mtorr TCNE and 0.027 mtorr $CFCl_3$ in 3 torr CO_2 buffer gas. After an e-beam pulse of 20 usec duration and 3 kV energy, the secondary electrons within the source are very quickly thermalized and then undergo competitive electron capture with either TCNE or $CFCl_3$. EC by TCNE produces the molecular anion, $TCNE^-$. After 5 msec, all of the electrons have been captured and $TCNE^-$ then decreases in concentration due to first order diffusion to the walls of the ion source. EC by $CFCl_3$ initially produces Cl^-. However, Cl^- then undergoes an irreversible reaction with TCNE, reaction 18.

$$Cl^- + TCNE \longrightarrow TCNE\text{-}Cl^- \qquad (18)$$

The Cl^- decreases rapidly in concentration with time as $TCNE\text{-}Cl^-$ is produced. The slope of the relative $[Cl^-]$ versus time

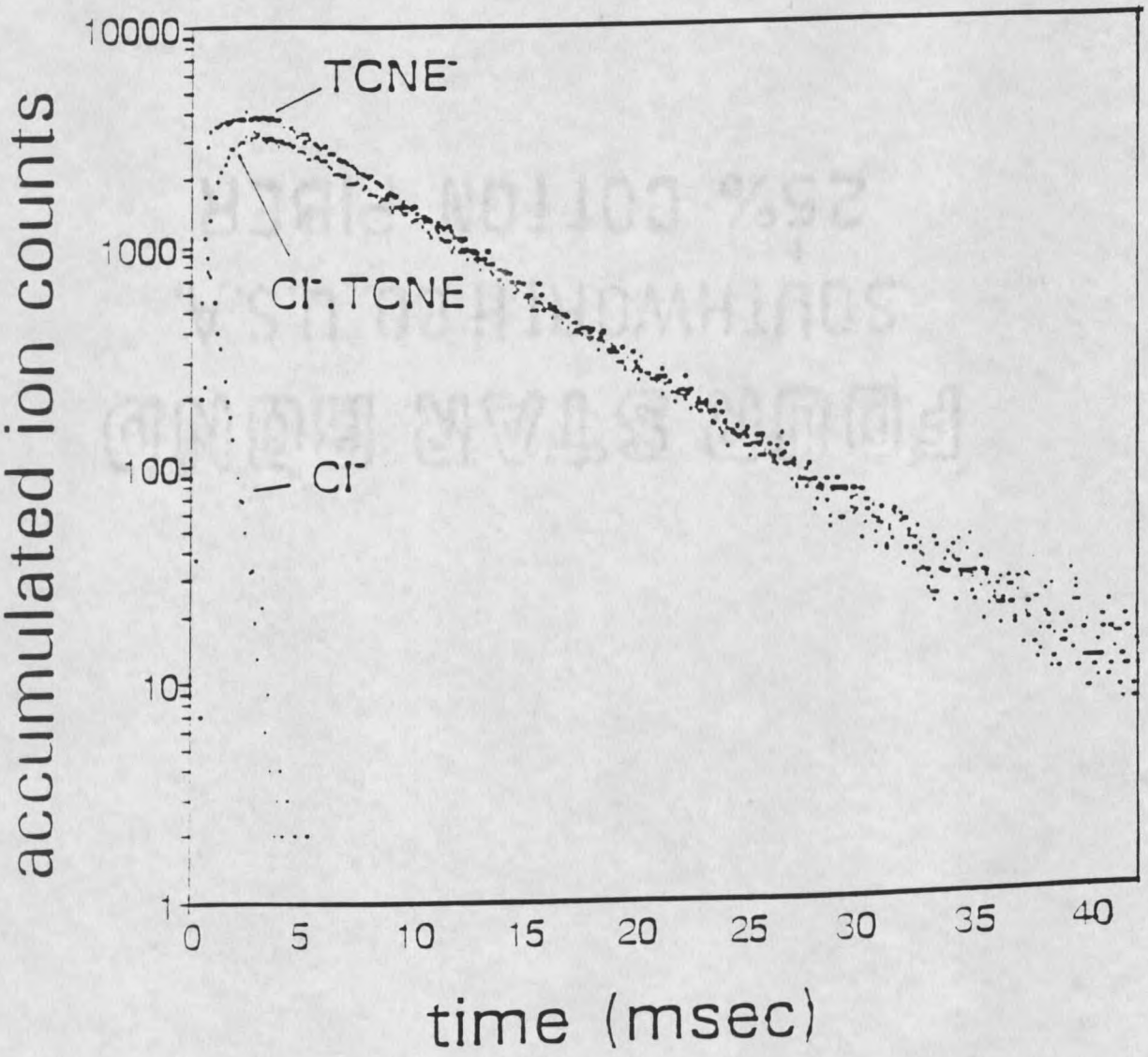

Figure 4. A pulsed e-beam high pressure mass spectrometric measurement for the determination of the EC rate constant of TCNE.

in Figure 4 indicates that the second order rate constant for the reaction between Cl^- and TCNE is 1 x 10^{-9} cm^3 sec^{-1}. After 5 msec, all the Cl^- has been converted to TCNE-Cl^- and the decay of TCNE-Cl^- then also occurs by first order diffusion to the walls of the ion source. Due to the greater mass of the TCNE-Cl^-, its diffusional loss to the walls occurs slightly more slowly than $TCNE^-$.

In view of the above interpretation of Figure 4, it is assumed that the ratio of intensities of the two ions, $TCNE^-$ and TCNE-Cl^-, at about 5 msec after the e-beam pulse will reflect the relative EC rates of TCNE and $CFCl_3$. This relative intensity ratio (1.3) multiplied by the ratio of $CFCl_3$ and TCNE concentrations in the ion source (0.40) indicates that the ratio of EC rate constants for TCNE and $CFCl_3$ is 0.5. Since the EC rate constant of $CFCl_3$ is known[25] to be 3.0 x 10^{-7} cm^3 sec^{-1}, multiplication of this by the ratio of EC rate constants yields the EC rate constant of TCNE, which is 1.5 X 10^{-7} cm^3 sec^{-1}. Multiple repetitions of this experiment resulted in an average value of 1.3 x 10^{-7} cm^3 sec^{-1} for the EC rate constant of TCNE.

The previous argument in which three of the possible routes to unusual ion formation were ruled out was based on the assumption that TCNE had a high electron capture rate coefficient. The PHPMS experiment described above showed that TCNE does in fact have a very high EC rate coefficient, thus validating the argument and suggesting that the H and R adduct

ions in Figure 2 are formed by a wall-assisted pathway and not by a gas phase reaction.

H Atom Adduct Ions in the Electron Impact Spectrum of TCNE

Persuasive evidence for the ease with which TCNE can be converted to a H-adduct species by a wall-assisted reaction is provided in Figure 5.

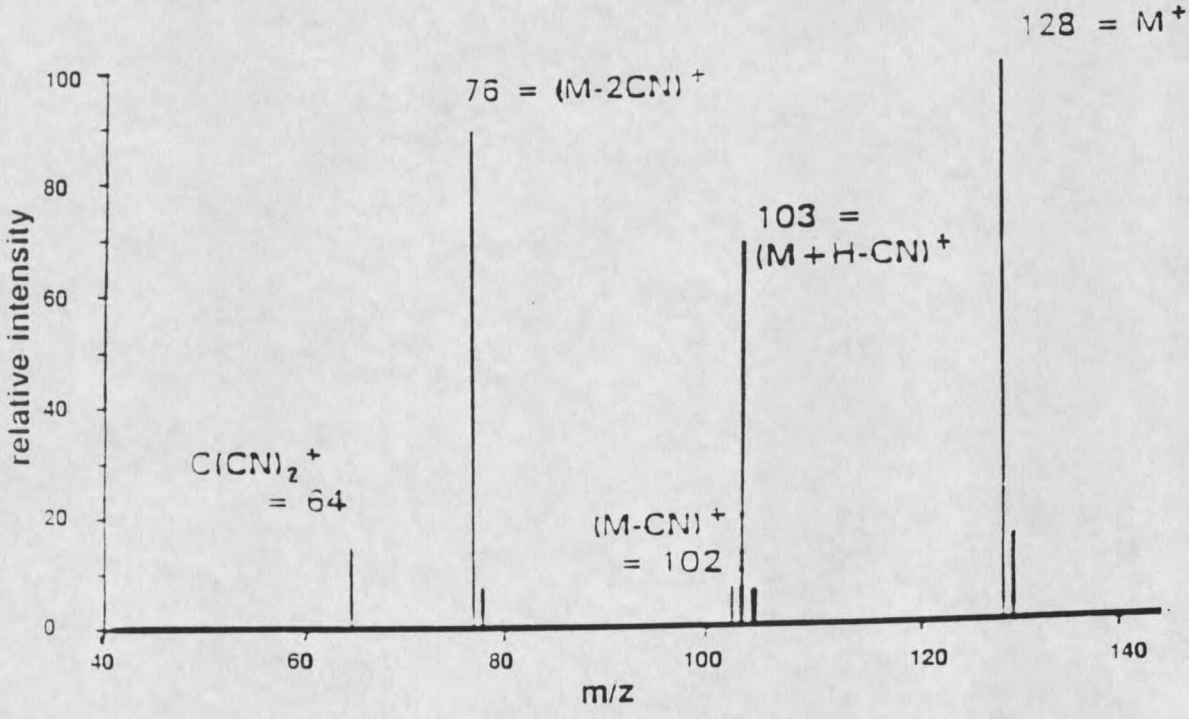

Figure 5. Electron impact mass spectrum of TCNE obtained after exposure of the ion source to HPEC-CH_4 conditions.

This figure shows the electron impact mass spectrum of TCNE obtained about 10 minutes after the ion source was exposed to HPEC-CH_4 conditions. The spectrum consists of a dominant molecular ion, M^+, three typical fragment ions, $(M-CN)^+$, $(M-2CN)^+$, $C(CN)_2^+$, and an unusual ion corresponding to the species $(M+H-CN)^+$. The only plausible explanation for the presence of this unusual ion is that an H-adduct neutral species is being formed by contact of TCNE on the walls of the ion source, and that the ion source walls have retained hydrogen atoms which were deposited by earlier exposure of the source to irradiated methane. Since the efficiencies of ionization by EI for the H-adduct species and TCNE can be expected to be similar, the intensity of the $(M+H-CN)^+$ ion in Figure 4 indicates that the concentration of the H-adduct neutral species in the ion source is approximately one-third that of M. This suggests that the wall-assisted conversion of M to the H-adduct species is a very efficient process when the ion source walls have been activated by prior exposure to irradiated methane.

Figure 6 shows the electron impact mass spectrum of TCNE after the source had been used in the HPEC mode with CO_2 as the buffer gas. The H-adduct ion is not present and the expected EI spectrum of TCNE was obtained. CO_2 is thought[26] to effectively scrub the walls of the ion source, getting rid of any radical species deposited from prior use of other buffer gases. This has proven to be an effective way of cleaning the ion source without physically removing it from the instrument.

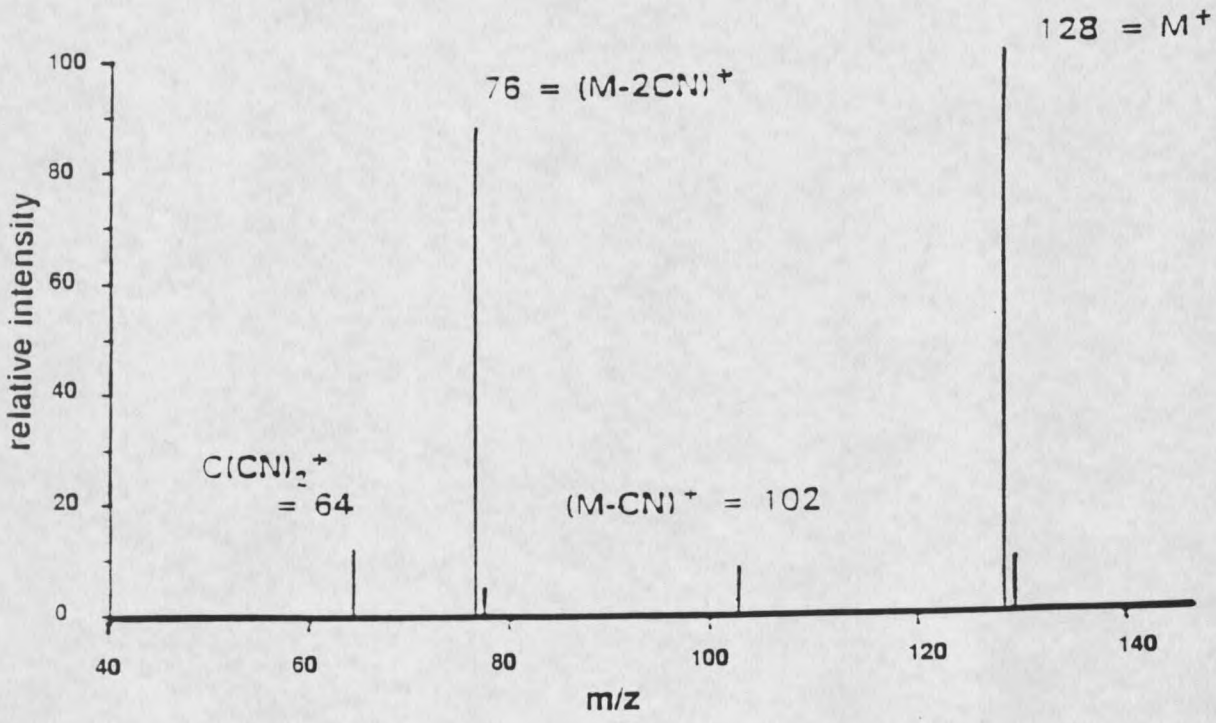

Figure 6. Electron impact mass spectrum of TCNE in a clean ion source.

In attempting to identify what the neutral species is that has led to the unexpected ion, $(M+H-CN)^+$, in the EI spectrum of Figure 5, perhaps the simplest possibility is that the neutral is (M+H), and that the $(M+H-CN)^+$ ion is formed from it by a dissociative EI process with the elimination of CN. However, it has been previously shown[2] that when other compounds are introduced into an EI ion source that has been previously exposed to HPEC-CH_4 conditions, a neutral species corresponding to the addition of two H atoms is formed on the walls of the ion source. It is therefore reasonable to also consider the following possibility for the formation of the $(M+H-CN)^+$ in the EI spectrum in Figure 5.

$$M \xrightarrow{\text{walls}} (M+2H) \xrightarrow{EI} (M+H-CN)^+ + HCN \qquad (19)$$

In the first step of reaction sequence 19, the addition of 2 H atoms across the double bond of TCNE could be envisioned to occur on the surface of the ion source walls. This would lead to the formation of 1,1,2,2-tetracyanoethane, (M+2H), which would subsequently be released back into the gas phase. If this mechanism has merit, electron impact of 1,1,2,2-tetracyanoethane must lead primarily to $(M+H-CN)^+$ and elimination of HCN. The EI mass spectrum of 1,1,2,2-tetracyanoethane could not be found in the literature. However, that of 1,1-dicyanoethane was found[27] and is shown in Figure 7.

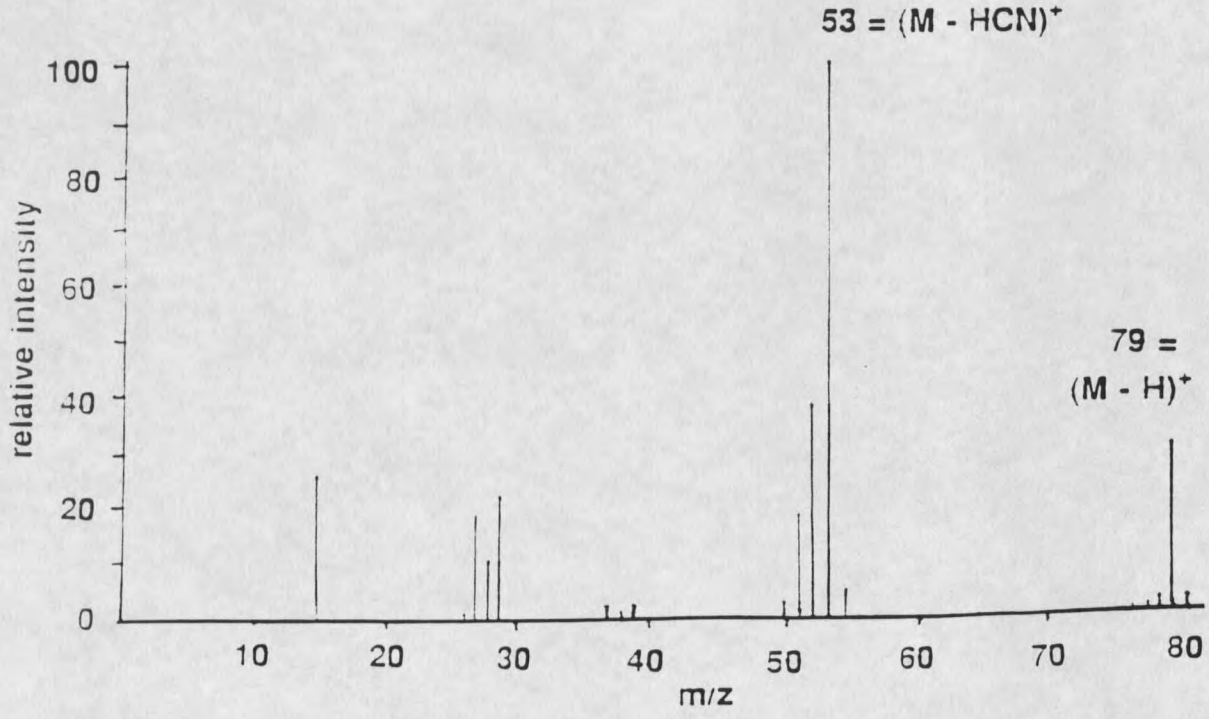

Figure 7. Electron impact mass spectrum of 1,1-dicyanoethane.

The dominant EI process for 1,1-dicyanoethane is the dissociative mechanism involving loss of HCN. No molecular ion is observed in Figure 7 and the fragment ion due to the loss of an H atom is only 0.35 relative intensity. It is reasonable to expect that these features would also be present in the EI spectrum of 1,1,2,2 tetracyanoethane and that the ion at m/z = 103 in the spectrum of Figure 5 would indeed be prominent if this compound were present. Also, it is noted that the ion at m/z = 129 in the same spectrum is somewhat larger than expected from the ^{13}C content of M^+. This would also be consistent with the minor EI fragment ion expected due to the loss of one H-atom from 1,1,2,2-tetracyanoethane. These observations, along with the precedence set by previous studies[2] with other compounds, support the suggestion that 1,1,2,2-tetracyanoethane is formed by contact of TCNE on the walls of the ion source that has been or is being exposed to irradiated methane.

Methyl and Ethyl Adduct Ions in the HPEC-NH_3 Spectrum of TCNE

The fact that H-atom adduct ions are present in the EI mass spectrum of TCNE (Figure 5) shows quite convincingly that hydrogen atoms are being retained and reacting with TCNE on the walls of the ion source. However, no methyl or ethyl adduct ions are present in this spectrum. A possible explanation as to why this is the case could be that methyl and ethyl radicals simply do not adhere to the walls of the

ion source as well as hydrogen atoms. If this were the case, when the ion source was switched from the high pressure, methane CI conditions to the low pressure EI conditions, the methyl and ethyl radicals would come off the walls and be pumped away while the hydrogen atoms would be retained on the surface of the ion source walls. The experimental results shown in Figure 8 support this theory quite well.

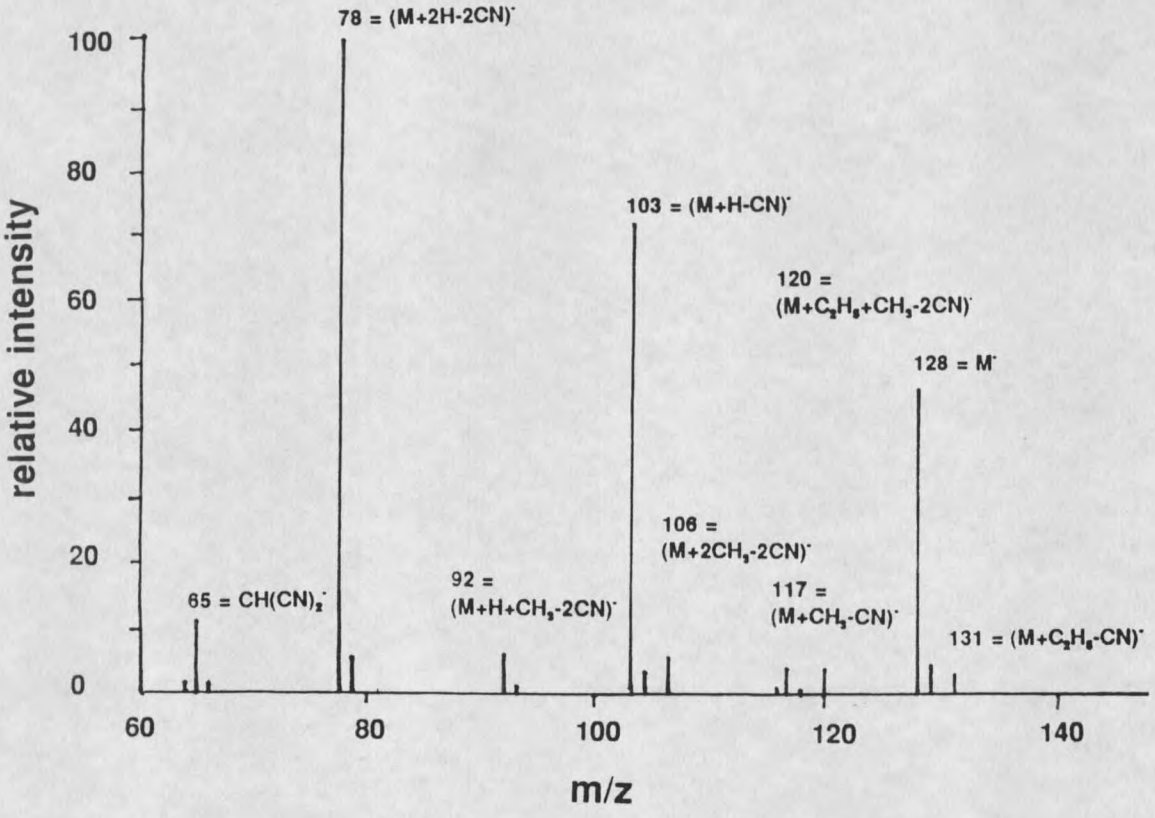

Figure 8. The HPEC-NH_3 mass spectrum of TCNE at 150°C and 0.5 torr.

Figure 8 is the HPEC mass spectrum of TCNE with ammonia used as the buffer gas. The ammonia was introduced into the ion source approximately 30 seconds after the source had been

exposed to irradiated methane and the mass spectrum was obtained approximately 7 minutes after that. The spectrum contains two intense hydrogen atom adduct ions that correspond to $(M+H-CN)^-$, and $(M+2H-2CN)^-$. Not surprisingly, these are the same two hydrogen atom adduct ions that appear in the HPEC spectrum of TCNE when methane is used as the buffer gas. This can be attributed to the fact that hydrogen atoms are also produced upon the irradiation of ammonia. What is very unusual, however, is the presence of both CH_3 and C_2H_5 adduct ions in the spectrum of Figure 8. The following reasoning will demonstrate why the only possible way these ions can be formed is by a reaction between TCNE and CH_3 or C_2H_5 radicals that have been previously deposited on the walls of the ion source. The time period at which the ion source was at a low pressure after the methane was pumped out and before the ammonia was introduced was 30 seconds. This is ample time for any gas phase radicals produced from the irradiated methane to be pumped away. Therefore, the only place alkyl radicals could be present under the ammonia conditions is on the walls of the ion source. The fact that hydrogen atoms are produced in irradiated ammonia would result in their concentration being much higher than that of the previously deposited alkyl radicals. This, along with the fact that many, or a majority of the alkyl radicals probably had enough time in that 30 second low pressure period to come off the walls and be pumped away would explain the relative low intensities of the alkyl

adduct ions in Figure 8.

Temporal Displacements of Unexpected Ions in HPECMS Chromatograms

Convincing evidence of wall-assisted reactions occurring within the HPECMS has also been obtained from multiple ion monitoring experiments in which the intensities of several negative ions under HPEC-CH_4 conditions were "simultaneously" recorded as a sample of TCNE was introduced into the ion source by capillary column gas chromatography. The intensities of the selected ions were measured by rapidly jumping the magnetic field to the m/z values of two or more selected ions. Typically, two to five ions were included in a given analysis and each ion was measured in order of increasing mass for 80 milliseconds each. By this method, five cycles of measurement for five ions or ten cycles for two ions were obtained per second. The reconstructed ion chromatograms obtained by this method provide a profile of the intensity of each ion in real time over the course of the chromatographic peak.

An illustration of the single ion chromatograms obtained in this way is provided in Figures 9 and 10. Figure 9 contains signals for the M^- and $(M+H-CN)^-$ ions. It is seen that the M^- and $(M+H-CN)^-$ ions have distinctly different temporal profiles. While the peak maximum for $(M+H-CN)^-$ occurs at the same time as that of M^-, the $(M+H-CN)^-$ signal then persists in time long after M^- has returned to baseline.

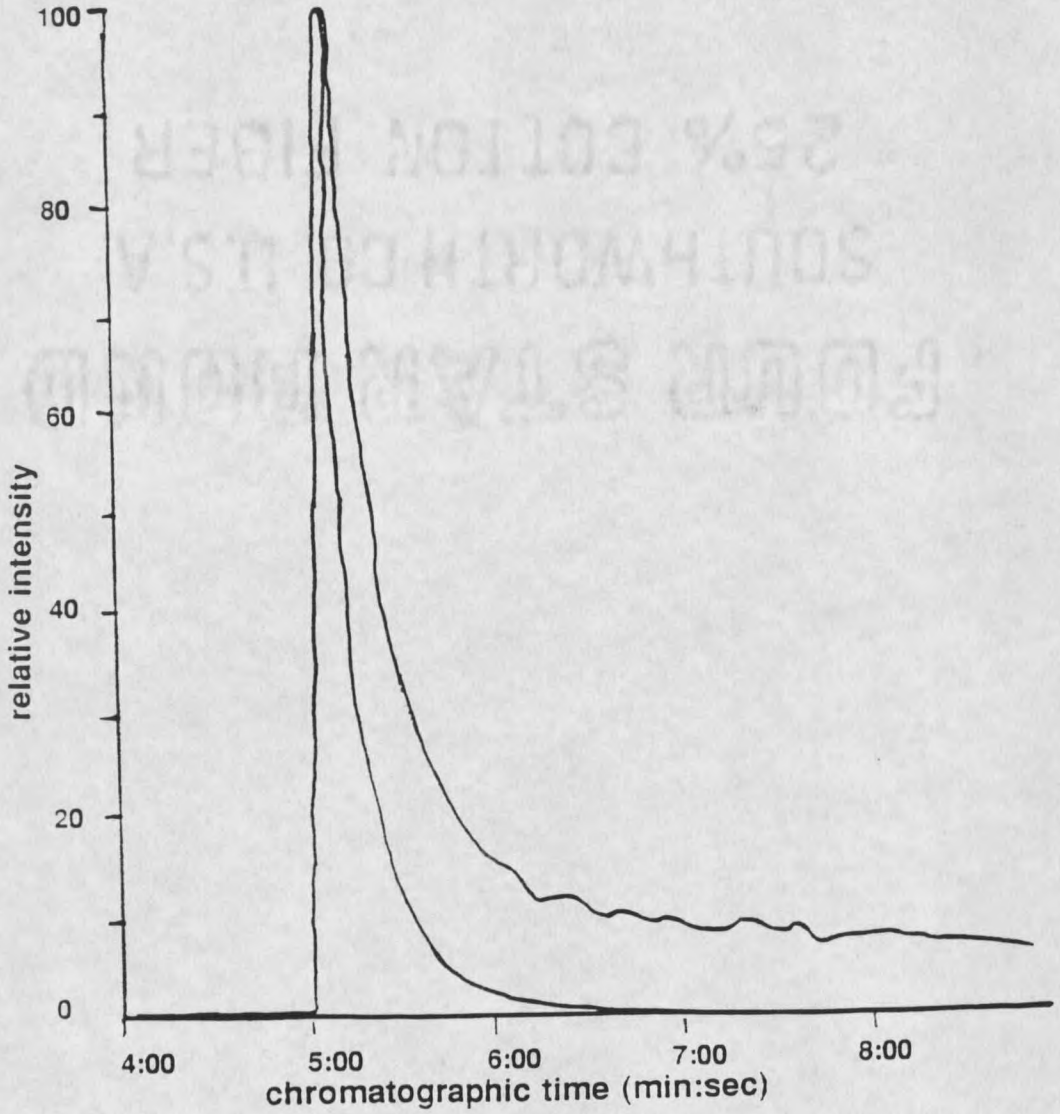

Figure 9. HPECMS-CH_4 single ion chromatograms of the M^- and $(M+H-CN)^-$ ions of Figure 2.

In Figure 10 the signals for the M^- and $(M+H+CH_3-2CN)^-$ are shown. Here the peak maximum for $(M+H+CH_3-2CN)^-$ occurs about 5 seconds after that of M^-. Again, the intensity of $(M+H+CH_3-2CN)^-$ persists long after M^- has returned to baseline. By comparisons of single ion chromatograms such as these, most of the major ions in the HPEC mass spectrum of TCNE (Figure 2) were found to have unique time dependencies. Only the chromatograms of $(M+CH_3-CN)^-$, $(M+H-CN)^-$, and $CH(CN)_2^-$ were indistinguishable. The order in which these ions appear and recede is as follows: 1st, M^-; 2nd, $(M+C_2H_5-CN)^-$; 3rd, $(M+H-CN)^-$, $(M+CH_3-CN)^-$, and $CH(CN)_2^-$; 4th, $(M+H+CH_3-2CN)^-$; and 5th, $(M+2H-2CN)^-$.

Since the M^- ion is known to be formed from the gas phase resonance EC reaction (reaction 1a), the intensity of the M^- ion can be assumed to provide a direct measure of the relative concentration of TCNE over the time of the chromatographic peak. Therefore, if the unexpected ions were also being formed totally by gas phase processes, such as in route C (Figure 1), the temporal profile of the unexpected ions would have been expected to be indistinguishable from that of M^-. This is because the time required for gaseous ventilation of the ion source is only about 3 msec. Therefore, on the relatively short time scale of the chromatograms, it is impossible to accumulate intermediates in the gas phase by route C so that the concentration of species MR and its EC products, MR^-, could continue to remain high after M has already passed

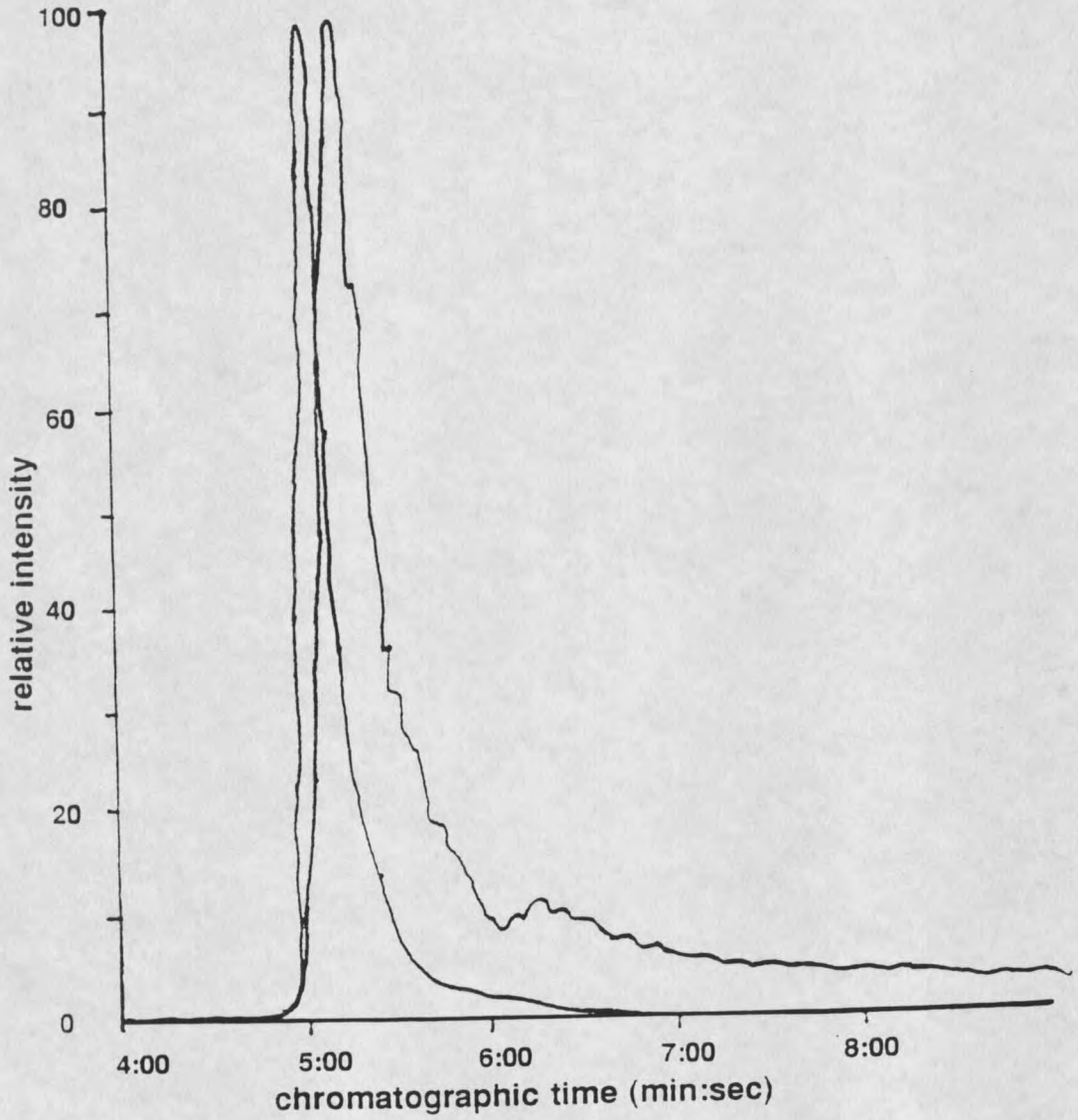

Figure 10. HPECMS-CH_4 single ion chromatograms of the M^- and $(M+H+CH_3-2CN)^-$ ions of Figure 2.

through the ion source. In order to account for the large time lags in the temporal profiles of the unexpected ions, it is necessary to invoke some sort of wall interaction that allows the concentration of the altered neutral species to remain high long after the parent molecule has reached its maximum concentration.

One possible way that a wall effect might occur is that following the gas phase production of the neutral species MR, a reversible adsorption process of MR on the walls of the ion source occurs. In view of the experiments previously described in this report, however, the single ion chromatograms in Figures 9 and 10 appear to be most readily explained by route D. By this mechanism, the intermediates MW become available for EC only after the following events have occurred: M has been adsorbed onto the wall, M has been converted to MW, and MW has been released back into the gas phase. The time required for these events to occur is not dependent on the gaseous ventilation of the ion source and, therefore, the concentrations of MW in the gas phase can be held high or can even increase long after gas phase M has passed through the ion source.

In the previous discussion of the EI spectrum of Figure 5, it was shown that the neutral most likely formed upon contact of TCNE with an ion source surface that had previously been activated by exposure to irradiated methane was 1,1,2,2-tetracyanoethane, (M+2H). It is reasonable to suggest then

that the same neutral is formed when TCNE comes in contact with the walls of the ion source under HPEC-CH_4 conditions. This neutral could then lead to the unexpected ion, $(M+H-CN)^-$ by the reaction sequence 20:

$$M \xrightarrow{\text{walls}} (M+2H) \xrightarrow{e} (M+H-CN)^- + HCN \qquad (20)$$

in which 1,1,2,2-tetracyanoethane is formed and then undergoes dissociative EC (reaction 1b) with elimination of HCN. A previous study[2] has shown an analogous reaction to occur in two other compounds. It is also reasonable to suggest that the ion, $CH(CN)_2^-$, in Figure 2, might also be formed by electron capture of the neutral species (M+2H) = 1,1,2,2-tetracyanoethane by the following reaction sequence.

$$(M+2H) \xrightarrow{e} CH(CN)_2^- + CH(CN)_2 \qquad (21)$$

The fact that the single ion chromatograms of $CH(CH)_2^-$, and $(M+H-CN)^-$ have identical time profiles provides supporting evidence that these two ions are formed by a branched EC reaction from the same gas phase neutral species , (M+2H), as shown in reactions 20 and 21.

Further comparison of the results obtained with that of the previous study[2] mentioned above leads to the suggestion that the $(M+2H-2CN)^-$ ion in Figure 2 might be formed from the reaction sequence 22:

$$(M+H-CN)^- \xrightarrow{\text{walls}} (M+3H-CN) \xrightarrow{e} (M+2H-2CN)^- + HCN \qquad (22)$$

in which the negative ion of reaction 20 goes back to the wall of the ion source where it undergoes neutralization and hydrogenation. The neutral product, (M+3H-CN), =

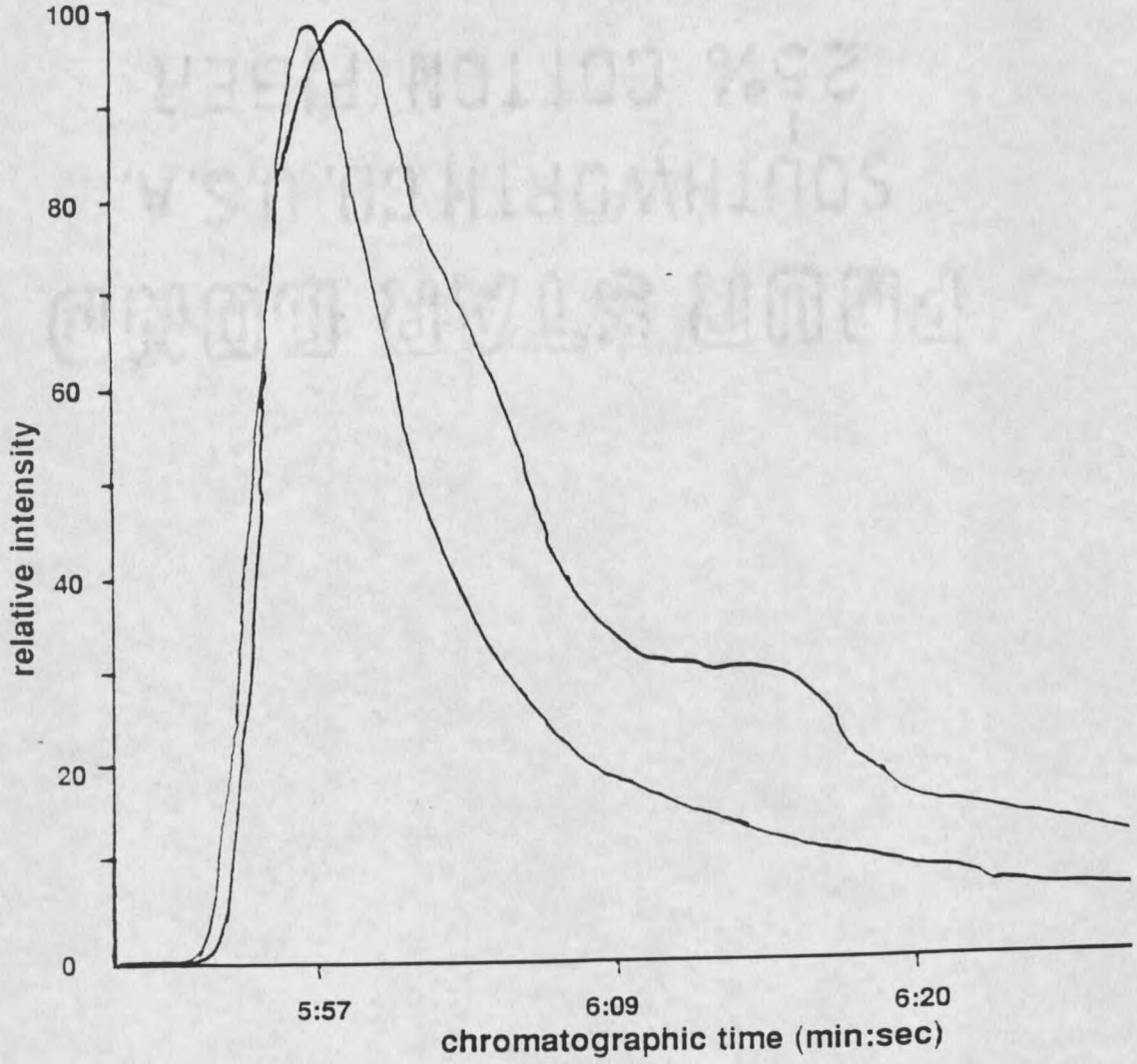

Figure 11. HPECMS-CH_4 single ion chromatograms of the $(M+H-CN)^-$ and $(M+2H-2CN)^-$ ions of Figure 2.

1,1,2-tricyanoethane, would again be expected to undergo dissociative EC with elimination of HCN as in reaction sequence 20. The consecutive nature of reaction 22 is consistent with the temporal profiles of the $(M+H-CN)^-$, and $(M+2H-2CN)^-$ ions, which are shown in Figure 11. This figure demonstrates that the two ions reach maximum concentrations at distinctly different times.

Figures 12 and 13 are the single ion chromatograms for the sets of ions $(M+H-CN)^-$, $(M+CH_3-CN)^-$, and $(M+2H-2CN)^-$, $(M+H+CH_3-2CN)^-$ respectively. Both figures show the strong resemblance in time profiles for their respective ions. This indicates that the rates of formation of these sets of ions are similar and that their mechanisms of formation might be the same. It is reasonable to suggest, therefore, that the R-adduct ions are formed through the analogous process as shown for the H-adduct ions in reactions 20 and 22. This reaction sequence is shown as follows.

$$M \xrightarrow{\text{walls}} (M+H+R) \xrightarrow{e} (M+R-CN)^- + HCN \qquad (23)$$

$$(M+H-CN)^- \xrightarrow{\text{walls}} (M+2H+R) \xrightarrow{e} (M+H+R-CN)^- + HCN \qquad (24)$$

Reactions 23 and 24 would occur if an H atom and a hydrocarbon radical, R, instead of two H atoms, were added to the adsorbed TCNE in reaction 23 or to the (M+H-CN) species in reaction 24. By this mechanism, all of the unexpected ions observed in Figure 2 could be explained by surface-assisted hydrogenation and alkylation across the double bonds of the substrate species, followed by a dissociative EC reaction with the

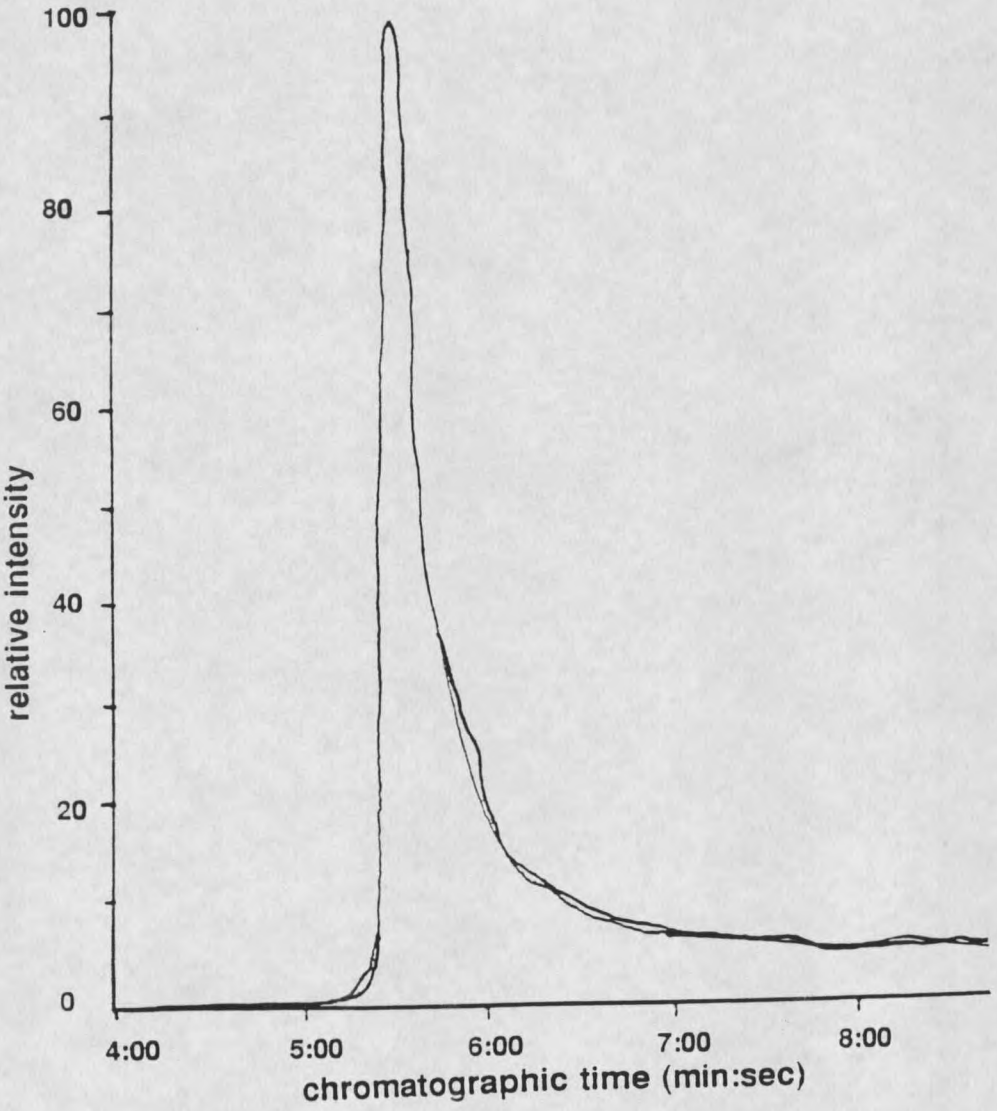

Figure 12. HPECMS-CH_4 single ion chromatograms of the $(M+H-CN)^-$ and $(M+CH_3-CN)^-$ ions of Figure 2.

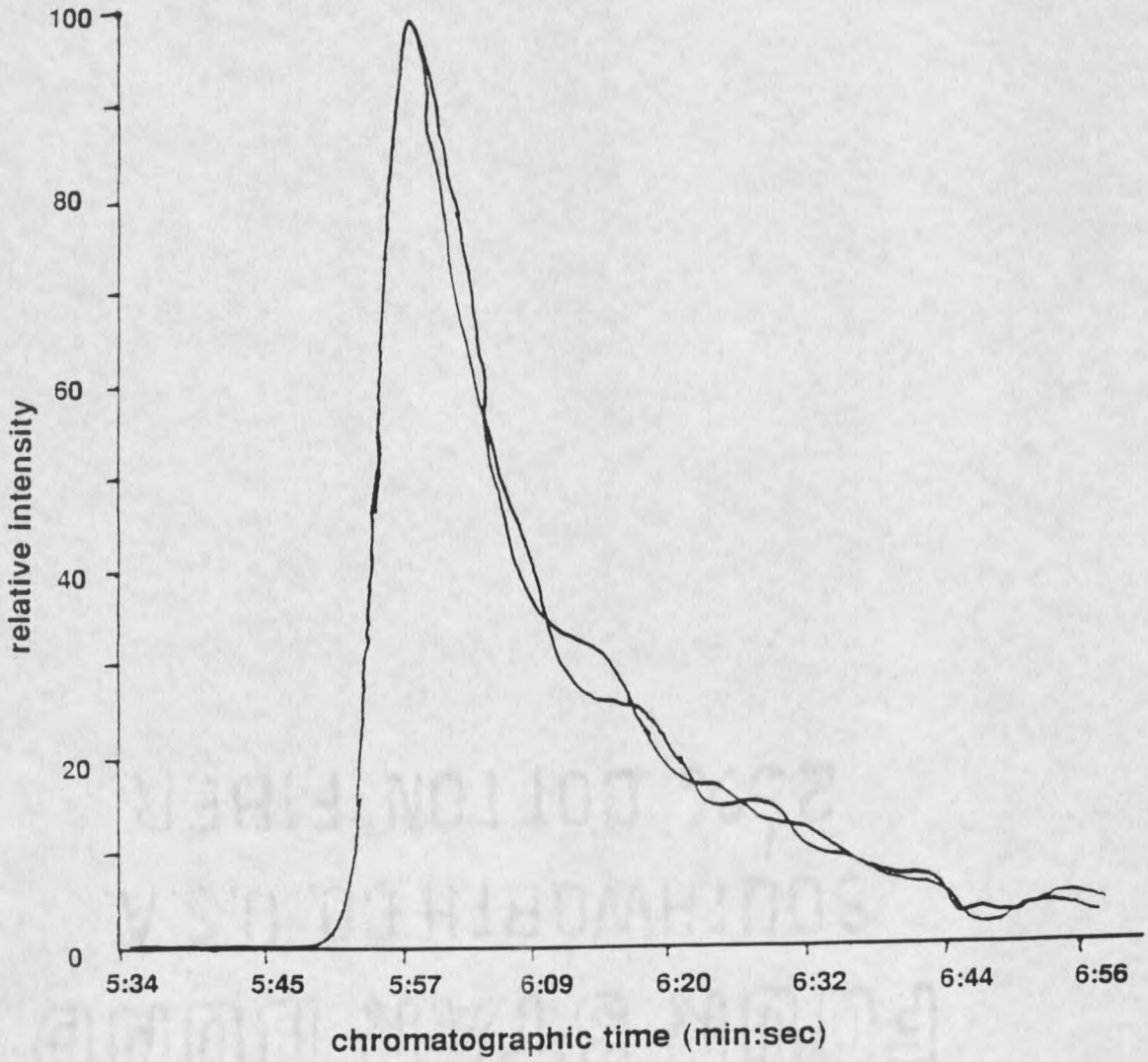

Figure 13. HPECMS-CH_4 single ion chromatograms of the $(M+2H-2CN)^-$ and $(M+H+CH_3-2CN)^-$ ions of Figure 2.

elimination of HCN or RCN. The alternate possibility, that R-adduct ions are formed by the addition of a single radical, R, to an adsorbed TCNE molecule, followed by desorption and EC of the neutral (M+R) to form $(M+R-CN)^-$ and CN, cannot be ruled out by the evidence provided here. However, since it has been shown here that the initial reaction occurs on the ion source walls, where an abundance of R and H species exist, the mechanism by which an R and H are simultaneously added across the double bond of TCNE is considered to be more likely.

SUMMARY

By employing the model developed by Sears, Campbell, and Grimsrud, and evaluating the experimental results reported in this study, evidence is provided that strongly suggests that all of the unexpected ions that appear in the HPEC-CH_4 mass spectrum of TCNE (M) are formed by a wall-assisted process. The formation of these ions is initiated by a reaction between TCNE and hydrogen atoms or alkyl radicals on the walls of the ion source. The first step in the formation of the $(M+H-CN)^-$ ion is wall-assisted hydrogenation across the double bond of TCNE to form 1,1,2,2-tetracyanoethane (M+2H). The (M+2H) species is then released back into the gas phase where it undergoes a branched EC reaction to produce two unexpected ions, $(M+H-CN)^-$ and $CH(CN)_2^-$. Following adsorption and neutralization of $(M+H-CN)^-$ on the walls of the ion source, a repetition of the wall and EC reactions just described is responsible for the production of the $(M+2H-2CN)^-$ unexpected ion. The formation of CH_3 and C_2H_5 (R) adduct ions could possibly occur by addition of a single R to TCNE on the walls of the ion source, followed by desorption, EC and elimination of CN. However, it is more likely that the R-adduct ions are formed by an analogous reaction as that described above for the formation of H-adduct ions. That is, a H and R species are added to TCNE in a wall reaction to form (M+H+R), as opposed to (M+2H). The (M+H+R) then desorbs and undergoes EC to form

$(M+R-CN)^-$ and HCN. Analogous to the sequence described above for $(M+H-CN)^-$, adsorption and neutralization of $(M+R-CN)^-$ leads to the unexpected ion of the type $(M+H+R-2CN)^-$.

The adduct ions in the HPEC mass spectrum of TCNE have previously been suggested as a means of identifying gas phase radicals that are produced in a gaseous plasma. This work has shown that the adduct ions are formed, not by direct addition of a single radical, but by an indirect process in which two radical species are added to TCNE only after they have been deposited on the ion source walls. Therefore, care must be taken if this technique is to be used for the identification of radical species in a gaseous plasma.

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