

Figure 19. Calculated in-plane and out-of-plane spin distributions for $[\text{TCNQ}]^{\bullet-}$.

The presence of the two negative charges has significant effects on the infrared intensities. As discussed above, there are greater atomic charges on some atoms than on others and the charge separation between bonded atoms is increased in some cases. Since $I(\nu) \propto \partial\mu/\partial x_i$ (μ = dipole moment) a normal mode involving bonded atoms with a larger charge separation will have enhanced intensities. This will be especially so for modes involving $\text{C}_4\text{-N}$ motion and $\text{C}_1\text{-C}_2$ motion. Thus, the two IR-active CN stretches have increased intensities over those in the neutral and two very strong bands are predicted. The B_{3u} band (1483 cm^{-1} scaled) involving the C-H bend significantly mixes with the asymmetric

$\text{C}_1\text{-C}_2$ stretch. Since this latter motion involves a large charge separation the intensity of this band is enhanced. Similarly the B_{3u} band at 1353 cm^{-1} (scaled) which is predominantly the asymmetric coupling of the $\text{C}_1\text{-C}_2$ stretches is even more intense. Two intense bands should be observed in these regions in the IR spectrum, and the B_{3u} band at 1353 cm^{-1} (scaled) should be the most intense band in the spectrum. There are a number of other moderately intense bands as shown in Table XX, and the B_{2u} band at 1061 cm^{-1} (scaled) and the B_{1u} band at 584 cm^{-1} should be the next most intense transitions.

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Supplementary Material Available: Atomic coordinates for the dimeric phase $[\text{Fe}(\text{C}_5\text{Me}_5)_2]_2^{\bullet+}[\text{TCNQ}]_2^{2-}$ (Table II); bond angles for dimeric phase $[\text{Fe}(\text{C}_5\text{Me}_5)_2]_2^{\bullet+}[\text{TCNQ}]_2^{2-}$ (Table IV); least-squares planes in the $[\text{Fe}(\text{C}_5\text{Me}_5)_2]_2[\text{TCNQ}]_2$ dimer phase (Table V); atomic coordinates and general temperature factor expressions for the 1-D $\text{Fe}(\text{C}_5\text{Me}_5)_2\text{TCNQ}$ phase (Tables VI and VII); bond angles and weighted least-squares planes for 1-D $[\text{Fe}(\text{C}_5\text{Me}_5)_2]_2^{\bullet+}[\text{TCNQ}]^{2-}$ (Tables IX and X); positional parameters, general displacement parameters, rms amplitudes of thermal vibration, bond angles, and weighted least-squares planes for $[\text{Co}(\text{C}_5\text{Me}_5)_2]_2[\text{TCNQ}]$ (Tables XI-XIII, XV, and XVI) (20 pages); structure factors for $[\text{Fe}(\text{C}_5\text{Me}_5)_2]_2[\text{TCNQ}]_2$, $[\text{Fe}(\text{C}_5\text{Me}_5)_2]_2[\text{TCNQ}]$, and $[\text{Co}(\text{C}_5\text{Me}_5)_2]_2[\text{TCNQ}]$ (36 pages). Ordering information is given on any current masthead page.

Reactions of C_3H_3^+ with Acetylene and Diacetylene in the Gas Phase

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The reactions of linear C_3H_3^+ with acetylene, diacetylene, and deuteriated acetylene were investigated with a Fourier transform ion cyclotron resonance (FTICR) mass spectrometer. A rate coefficient of $(1.4 \pm 0.7) \times 10^{-9}\text{ cm}^3/\text{s}$ was obtained for the reaction of linear C_3H_3^+ with diacetylene while no production of larger ions was observed with acetylene. The ejection capabilities of FTICR were used to study the reactions of different C_3H_3^+ precursors with C_2H_2 in order to investigate the possible production of C_5H_5^+ from ionic sources other than C_3H_3^+ present in the reaction medium. Linear C_3H_3^+ isomerized to the cyclic form in reactions with both acetylene and diacetylene. The isomerization was shown to take place via a long-lived C_5H_5^+ complex by isotope exchange reactions between linear C_3H_3^+ and deuteriated acetylene. Results are discussed in relation to previous work involving C_3H_3^+ reactions and a proposed ionic route to soot formation.

Introduction

The C_3H_3^+ ion has received considerable attention in recent years as a possible soot precursor because it is found in quite high abundance in fuel-rich and sooting flames.¹⁻³ Although substantial uncertainty remains as to C_3H_3^+ formation mechanisms in flames,^{4,5} the ion is postulated^{4,6} to react with neutrals such as acetylene, diacetylene, and C_2H in rapid, sequential conden-

sation and condensation/elimination reactions, forming successively larger ions, which can rearrange to cyclic species during the ion/molecule reaction chain.

Michaud et al.³ have made an alternate suggestion that direct reactions of C_3H_3^+ with aromatic neutrals such as benzene, toluene, naphthalene, methylnaphthalenes, and indene may be more important in forming polycyclic ions than sequential reactions involving acetylene and diacetylene. In fact, recent ion cyclotron resonance (ICR) studies of reactions of C_3H_3^+ with aromatic neutrals showed⁷ that these reactions are fast enough to be considered as possible bypass channels in ionic soot formation pathways in fuel-rich hydrocarbon flames.

Two isomeric structures of C_3H_3^+ are important in discussing the role of C_3H_3^+ in ion/molecule reaction mechanisms. The first is the cyclopropenyl cation, recognized as the most stable isomer, which has a theoretically calculated heat of formation of 253

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kcal/mol,^{8,9} in quite good agreement with the 256 ± 2 kcal/mol determined by experiment.¹⁰ A second and potentially more important C₃H₃⁺ structure is that of the linear propargylium ion with a calculated^{8,9} heat of formation 31 to 34 kcal/mol higher than that of the cyclopropenylium ion, in fair agreement with the 25 kcal/mol difference found experimentally by Lossing.¹⁰ Recent calculations⁹ have shown several other stable isomeric structures of the C₃H₃⁺ ion with higher heats of formation relative to the cyclopropenylium and propargylium ions.

The importance of different precursors in affecting the reactivity of C₃H₃⁺ ions was reported in a thermochemical study of Holmes and Lossing.¹¹ In an ICR study of C₃H₃⁺ reactions, Ausloos and Lias¹² showed that significant fractions of the linear isomer can be produced by charge-transfer reactions of small ions (Ar⁺, Xe⁺, CO⁺, Ne⁺, etc.) with propargyl chloride and bromide. Later it was reported⁷ that even higher proportions of the propargylium isomer relative to the cyclopropenylium isomer can be obtained with propargyl iodide either by electron impact or charge exchange using Xe⁺.

A study by Smyth et al.¹³ demonstrated that the cyclopropenylium ion was relatively unreactive toward simple hydrocarbon fuels whereas the linear, propargylium ion was quite reactive. In particular, reaction of propargylium ions with acetylene was reported to produce C₅H₃⁺ and C₅H₅⁺ ions with an overall C₃H₃⁺ disappearance rate coefficient of 1 × 10⁻⁹ cm³/s. Since this sequence of reactions is a critical one in the initial stages of the postulated ion/molecule mechanism of soot formation, it was studied as a part of ongoing work^{7,14} in our laboratory related to reactivity and structures of small hydrocarbon ions. Results substantially different from those reported earlier were found and the study was thus expanded to investigate possible production of C₅H₅⁺ ions from ionic sources other than C₃H₃⁺ present in the reaction media using the ejection capabilities of Fourier transform ion cyclotron resonance (FTICR) mass spectrometry. Reactions of propargylium ions with C₂D₂ were also studied in order to delineate further a proposed mechanism for the C₃H₃⁺/acetylene interaction.

Diacetylene is another important flame neutral which has been postulated to react with C₃H₃⁺ ions in an ion/molecule soot formation mechanism.⁶ Reaction pathways and the rate coefficient for the reaction of propargylium ions with diacetylene near room temperature were thus also investigated. In this paper, results for the reactions of C₃H₃⁺ ions with acetylene, deuterated acetylene, and diacetylene are reported and discussed in relation to previous work involving C₃H₃⁺ reactions^{7,12,13} and the proposed^{4,6} ionic route to soot formation.

Experimental Section

A Nicolet FTMS-1000 Fourier transform ion cyclotron resonance (FTICR) mass spectrometer with a superconducting magnet of fixed magnetic field (3.0 T) was used for the work reported here. Basic principles of the technique and its applications in ion/molecule reaction studies have been reviewed in several recent articles.¹⁵⁻¹⁷ Reaction pathways were delineated by using the ejection capabilities¹⁸ of FTICR which make it possible to eject one ion from a complicated reaction mixture to determine its contribution to the mass spectrum of all the other ions.

Reaction rate coefficients were determined by monitoring the intensity of the C₃H₃⁺ ions as a function of time (typically at least 2 s) after ejection of all other ions from the analyzer cell. Neutral gas pressures were measured with an ionization gauge. Ionization gauge readings were then corrected by constructing calibration curves of ionization gauge vs. capacitance manometer (MKS-Baratron) readings in the 1 × 10⁻⁶ to 1 × 10⁻⁴ Torr range. In order to correct for the fact that the ionization gauge and capacitance manometer were located at different points on the vacuum system, somewhat removed from the FTICR analyzer cell, a correction factor was required. This was obtained by determining the rate coefficient of a well-studied reaction (C₂H₄⁺ + C₂H₄ → products, *k*_{av} = (1.0 ± 0.3) × 10⁻⁹ cm³/s),¹⁹⁻²⁴ where the ionization gauge pressure readings were corrected by using the capacitance manometer. This experimentally determined rate coefficient was then compared with the average of published values¹⁹⁻²³ and the ratio of the published value to the measured, which was 3.3 ± 1.1,²⁵ was used as a correction factor. This factor was used in calculating the absolute rate coefficients reported in this article. All calculations of rate coefficients and 95% confidence limits were performed with a menu-driven Fortran computer program (available from the authors on request).

Reactive and nonreactive C₃H₃⁺ ions were produced by charge-transfer reactions of various precursors with Xe⁺, formed with an electron beam pulse of 5-ms duration at an ionizing electron energy of ca. 15 eV. Propargyl iodide was used as a precursor for C₃H₃⁺ in studies of the reaction of this ion with acetylene, deuterated acetylene, and diacetylene, while a number of different precursors (propargyl iodide, propargyl bromide, propargyl chloride, propyne, and allene) were used to investigate the reaction mechanisms leading to C₅H₅⁺ ion formation. In some studies C₃H₃⁺ ions were produced directly from the above-mentioned precursors by electron impact to compare the effect of ionization technique on the ratio of reactive to unreactive isomers.

Propargyl iodide was prepared from propargyl chloride by a halogen exchange reaction.²⁶ The details of purification are given elsewhere.⁷ Propargyl chloride, propargyl bromide, allene, propyne, and acetylene were obtained commercially and their purity was checked by obtaining wide mass range spectra. In the case of acetylene, some production of protonated acetone was observed at long delay times indicating the presence of a small amount of acetone as an impurity. Propargyl bromide was distilled before use in order to remove toluene which was present as a stabilizing agent. Deuterated acetylene was prepared from D₂O and CaC₂. Diacetylene was prepared by the method of dehydrochlorination of 1,4-dichloro-3-butyne in aqueous potassium hydroxide/dioxane solution.²⁷ All the samples were used after multiple freeze-pump-thaw cycles.

Results

C₃H₃⁺ Reactions with Acetylene. Despite an earlier report¹³ that linear C₃H₃⁺ is quite reactive with acetylene, only very low intensities of C₅H₃⁺ and C₅H₅⁺ produced via this reaction could be found in this work. Experimental conditions of the earlier study were duplicated as closely as possible, and then varied substantially with respect to relative pressures of neutrals (from 1:1 to 8:1

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(24) The uncertainty given is the 95% confidence limit of the mean of five determinations. Reported uncertainties for the correction factor and rate coefficients throughout this paper are also 95% confidence limits.

(25) The large uncertainties reported for the correction factor and rate coefficients calculated using it in this work are primarily due to the wide range of reported values for the C₂H₄⁺ + C₂H₄ reaction used to determine the correction factor. The even more widely studied "standard" calibration reaction of CH₄⁺ with CH₄ could not be employed because the lowest mass-to-charge ratio accessible to the FTMS-1000 instrument is *m/z* 18.

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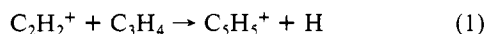
TABLE I: Production of $C_5H_5^+$ and $C_5H_3^+$ Ions in Mixtures of Various Neutrals and Acetylene^a

neutral	ionic sources ^b of $C_5H_5^+$	ratio of $C_5H_5^+$ prod ^c	ionic sources ^b of $C_5H_3^+$	int of $C_5H_5^+$ vs. $C_5H_3^+$	% reactive $C_5H_3^+$ ions
allene	$C_2H_2^+$ (40%) $C_3H_4^+$ (60%)	1.0			<5
propyne	$C_2H_2^+$ (40%) $C_3H_4^+$ (60%)	0.75			30
propargyl chloride	$C_2H_2^+$ (40–50%) $C_3H_3Cl^+$ (50–60%)	0.25	$C_3H_3Cl^+$ (20%) $C_3H_3^+$ (20%) $C_2H_2^+$ (60%)	3.0	15
propargyl bromide	$C_3H_3Br^+$ (90–100%)	0.08	$C_2H_2^+$ (70%) [$C_3H_3^+$ + $C_3H_3Br^+$] (30%)	2.0	85
propargyl iodide	$C_2H_2^+$ (40%) $C_3H_3^+$ (60%)	<0.02	$C_2H_2^+$ (50%) $C_3H_3^+$ (50%)	1.7	90

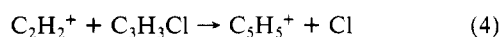
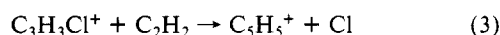
^a All ions were produced by chemical ionization charge transfer from Xe^+ . ^b Ionic sources of $C_5H_5^+$ after Xe^+ charge-transfer ionization of a mixture of the neutral and acetylene. Percentages show the relative contributions to $C_5H_5^+$ and $C_5H_3^+$ prodn. as detd. by double resonance expts. and have an estd. uncertainty of $\pm 10\%$. ^c Ratio relative to that in the allene case. Neutral reactants all had the same pressure (7×10^{-7} Torr) as measured by the ionization gauge. Xenon and acetylene pressures were 5.6×10^{-6} and 1.8×10^{-6} Torr, respectively.

$C_2H_2:C_3H_3I$) and overall system pressure (from 5×10^{-7} to 3×10^{-5} Torr). $C_3H_3^+$ ions were formed from propargyl chloride, bromide, and iodide by both charge transfer using Xe^+ and electron impact. In order to determine other possible sources of $C_5H_5^+$ observed under the earlier reaction conditions, binary mixtures of acetylene and one of the $C_3H_3^+$ precursors reported^{7,12,13} earlier were used. Intensities of $C_5H_5^+$ and $C_5H_3^+$ were first measured after a 125-ms reaction time. Then the parent ion, $C_2H_2^+$, and $C_3H_3^+$ were each ejected separately during the 125-ms reaction period to assess their contribution to $C_5H_5^+$ and $C_5H_3^+$ formation.

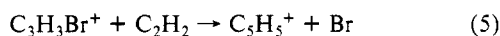
For each different neutral precursor, the sources and amounts of $C_5H_5^+$ ions produced were found to be different. Propyne and allene were similar in producing large amounts of $C_5H_5^+$ and no $C_5H_3^+$ ion. However, the $C_3H_3^+$ + C_2H_2 reaction was not responsible for $C_5H_5^+$ formation. The main reactions leading to $C_5H_5^+$ were



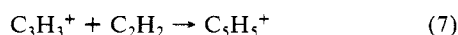
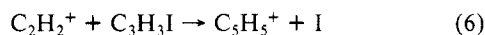
in both cases. On the other hand, when propargyl iodide, propargyl bromide, and propargyl chloride were used as precursors, relatively smaller amounts of $C_5H_5^+$ ion formation were observed along with $C_5H_3^+$ ion production. In the propargyl chloride case



were the major reactions leading to $C_5H_5^+$ formation. For propargyl bromide the



reaction was the only source of $C_5H_5^+$ ions observed. Any contribution to $C_5H_5^+$ formation from linear $C_3H_3^+$ was less than the experimental uncertainty. Finally, very little (almost negligible) amounts of $C_5H_5^+$ ions were observed when propargyl iodide was used as a precursor and the reactions



were the major contributors in this case. An upper limit for the rate constant, k , for reaction 7 was estimated as 5×10^{-12} cm³/s by assuming that the very small $C_5H_5^+$ signal observed resulted from this reaction, and using the expression $[C_3H_3^+](t) = [C_3H_3^+](0) - [C_5H_5^+](t) = [C_3H_3^+](0)e^{-nk}$, where n is the C_2H_2 number density. Overall results for the production of $C_5H_5^+$ and $C_5H_3^+$ ions with different neutrals which have been reported^{7,12,13} as precursors of $C_3H_3^+$ are summarized in Table I.

Because propargyl iodide was shown to produce the highest reactive/unreactive ratio of $C_3H_3^+$ ions in both earlier^{7,11} and the present work (see Table II), it was used as a precursor for $C_3H_3^+$ ions in these reaction kinetics studies. Since the precursor neutral molecule was always present in the FTICR analyzer cell, it was

TABLE II: Percentages^a of Reactive $C_3H_3^+$ Found from Various Precursors by Various Ionization Techniques

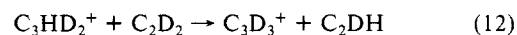
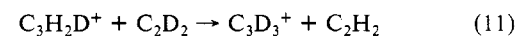
ionizing technique	precursor		
	propargyl iodide	propargyl bromide	propargyl chloride
electron impact (15 eV)	90	40	10
chemical ionization charge transfer with Xe^+	90	85	15

^a Monitored by observing reaction with the precursor neutral. Estimated error is $\pm 5\%$.

a competitor with the reactant neutral of interest in ion/molecule reactions involving $C_3H_3^+$. In order to determine the rate coefficient of reactions of $C_3H_3^+$ with the neutral reactant, it was necessary first to monitor the reactions of this ion with C_3H_3I and then to subtract the rate coefficient for this reaction from the total rate coefficient observed in the presence of both the precursor neutral and the reactant of interest. Reactions of $C_3H_3^+$ with propargyl iodide were monitored as a function of time following charge-transfer chemical ionization of C_3H_3I by Xe^+ and ejection of all ions but $C_3H_3^+$ from the analyzer cell. Results obtained were identical with $C_3H_3^+$ reaction channels with propargyl iodide which have been reported elsewhere.⁷

Isomerization of Linear $C_3H_3^+$. In addition to the absence of any significant $C_5H_3^+$ and $C_5H_5^+$ formed by reaction of linear $C_3H_3^+$ with C_2H_2 , it was also observed that C_2H_2 led to the isomerization of linear $C_3H_3^+$ ions to their cyclic form, thus rendering them unreactive toward their parent neutral (C_3H_3I) as well as toward C_2H_2 . This isomerization was followed as a function of C_2H_2 pressure and a direct pressure dependence was found, as can be seen in Figure 1.

$C_3H_3^+$ Reactions with C_2D_2 . To achieve a better understanding of the isomerization of linear $C_3H_3^+$, C_2D_2 instead of C_2H_2 was used as the neutral reactant. The following isotope exchange reactions were observed:



With the FTICR ejection capabilities, it was found that reactions 9 and 10 contribute equally to the production of $C_3HD_2^+$ while reaction 12 produces more of the $C_3D_3^+$ (80%) than reaction 11 (20%).

Ion intensity vs. time curves for the $C_3H_3^+/C_2D_2$ reaction are shown in Figure 2. The overall rate coefficient for the disappearance of $C_3H_3^+$ was calculated by subtracting the observed rate coefficient for the reaction with propargyl iodide from the total observed rate coefficient in the presence of C_2D_2 . This

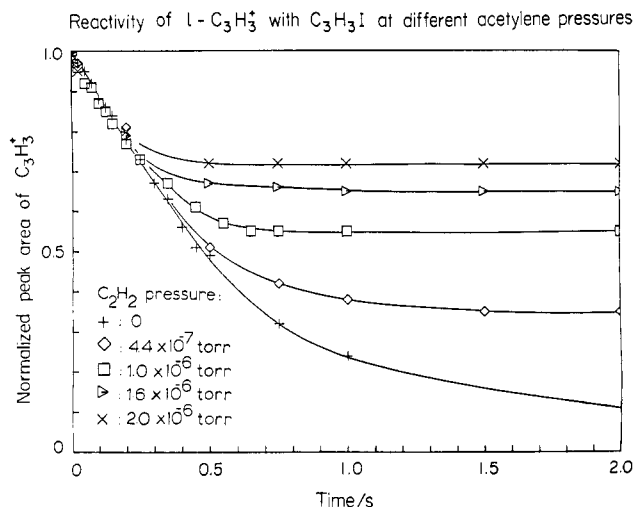


Figure 1. Isomerization of linear C₃H₃⁺ ions at different pressures of C₂H₂. C₃H₃⁺ ions were produced by charge-transfer reactions with Xe. $p_{\text{C}_3\text{H}_3\text{I}} = 1.1 \times 10^{-7}$ Torr; p_{Xe} was adjusted to maintain a constant total pressure of 2.6×10^{-6} Torr as measured on the ionization gauge. (All pressures are capacitance-manometer corrected.)

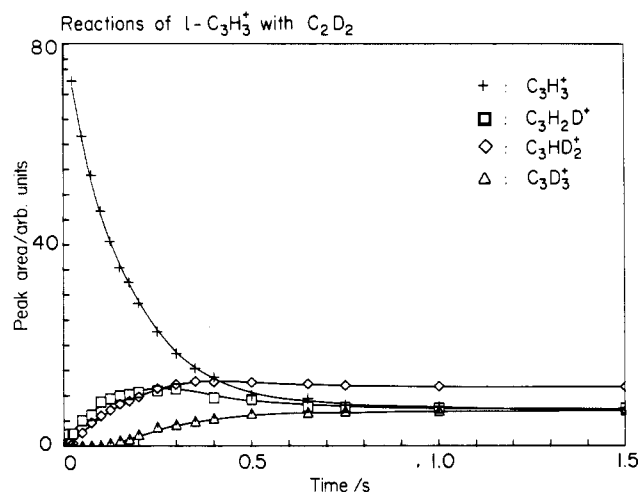


Figure 2. Isotope exchange reactions of C₃H₃⁺ with C₂D₂. Disappearance of C₃H₃⁺ ion includes reactions with propargyl iodide. Note that the sum of all isotopic forms of C₃H₃⁺ remaining at the end of the reaction with C₂D₂ approximately equals the total unreactive C₃H₃⁺ when C₂H₂ is used as a neutral reactant at the same pressure (see Figure 1). $p_{\text{C}_3\text{H}_3\text{I}} = 1.1 \times 10^{-7}$ Torr; $p_{\text{C}_2\text{H}_2} = 1.2 \times 10^{-6}$ Torr; $p_{\text{Xe}} = 6.2 \times 10^{-6}$ Torr.

observed rate coefficient was then converted to the true rate coefficient by using the corrected pressure of C₂D₂. A value of $(4.5 \pm 1.9) \times 10^{-10}$ cm³/s was found at a cell temperature of 373 K for the disappearance of C₃H₃⁺ (reactions 8 and 9). In Figure 3, ion intensity vs. time curves of C₃H₃⁺ are compared for reactions with and without C₂D₂.

C₃H₃⁺ Reactions with Diacetylene. After ejection of all ions except C₃H₃⁺ following charge-transfer chemical ionization by Xe⁺ of a mixture of diacetylene and propargyl iodide, the ion/molecule reactions as a function of time were monitored. Consecutive C₂ and C₄H₂ addition reactions were observed:

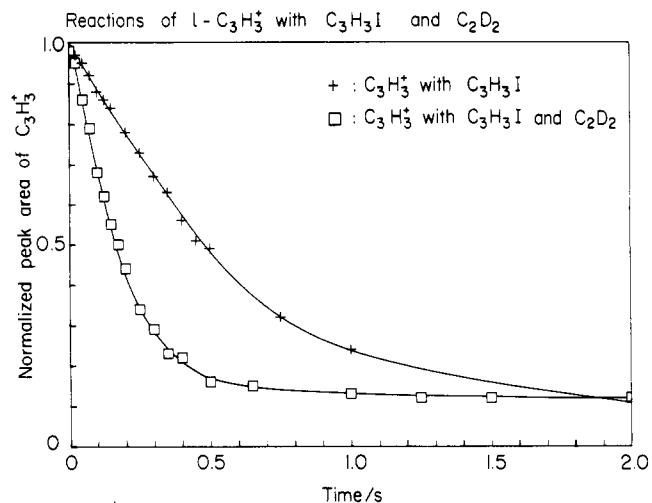
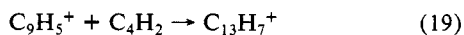
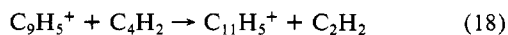
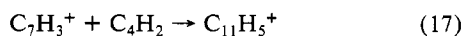
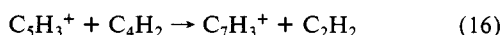
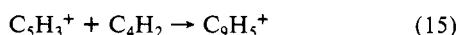
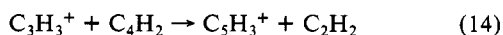


Figure 3. C₃H₃⁺ ion decay curves for reaction with C₃H₃I and C₂D₂. (Pressures are the same as given for Figure 2.)

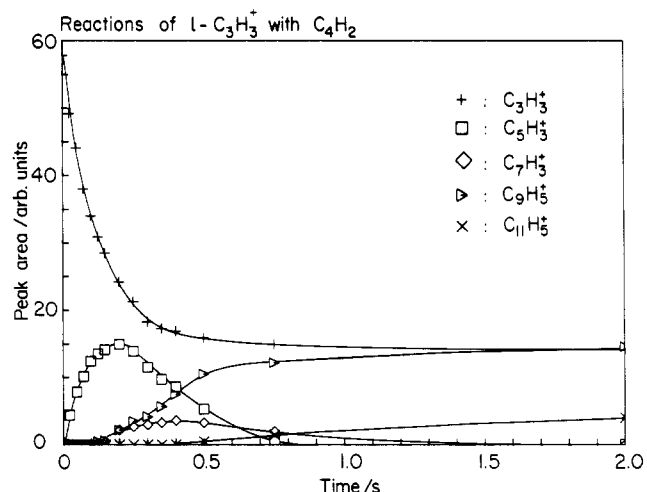
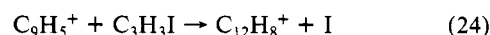
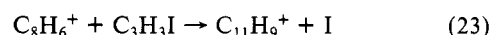
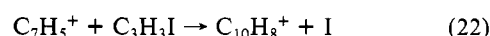
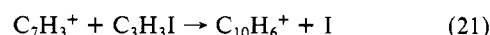


Figure 4. Reactions of C₃H₃⁺ with C₄H₂. Disappearance of C₃H₃⁺ and product ions include reactions with propargyl iodide. $p_{\text{C}_3\text{H}_3\text{I}} = 1.1 \times 10^{-7}$ Torr; $p_{\text{C}_4\text{H}_2} = 4.8 \times 10^{-7}$ Torr; $p_{\text{Xe}} = 6.2 \times 10^{-6}$ Torr. (All pressures are capacitance-manometer corrected.)

Some of these product ions were seen to react further with propargyl iodide by displacement of atomic iodine:



Ion intensity vs. time curves for the C₃H₃⁺/C₄H₂ reaction are shown in Figure 4. The rate coefficient for the disappearance of C₃H₃⁺ (reactions 13 and 14, Figure 5) was calculated as described earlier, and a value of $k = (1.4 \pm 0.7) \times 10^{-9}$ cm³/s was found.

Propargyl iodide, bromide, and chloride were all used as precursors of C₃H₃⁺ in studying its reactions with diacetylene. For each precursor, both electron impact and charge-transfer chemical ionization techniques were used. The percentages of reactive isomer in the reaction with diacetylene are shown in Table III. When these percentages of reactive isomer were compared to those in the absence of C₄H₂ (see Table II), it was clear that some isomerization of the reactive linear C₃H₃⁺ ion, as well as reactions 13 and 14, had taken place (see also Figure 5). This isomerization was followed as a function of C₄H₂ pressure and a direct pressure

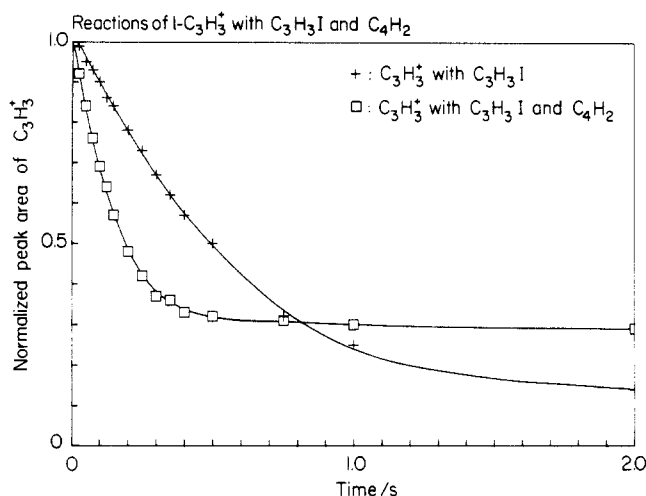


Figure 5. $C_3H_3^+$ decay curves for the reactions with C_3H_3I and C_4H_2 . (Pressures are the same as given for Figure 4.)

TABLE III: Percentages^a of Reactive $C_3H_3^+$ Observed in the Reaction with C_4H_2 ^b

ionization technique	precursor		
	propargyl iodide	propargyl bromide	propargyl chloride
electron impact (15 eV)	75	30	5
charge transfer by Xe^+	75	65	5

^a Estimated error is $\pm 5\%$. ^b $P_{C_4H_2} = 4.8 \times 10^{-7}$ Torr.

TABLE IV: Changes in $C_3H_3^+$ Reactivity^a at Different Pressures of Diacetylene^b

C_4H_2 press./ 10^{-7} Torr	% unreactive $C_3H_3^+$
0.8	16
1.6	17
4.8	25
7.2	32
8.0	35
9.6	40

^a $1-C_3H_3^+$ ions were produced from propargyl iodide by chemical ionization charge transfer with Xe^+ . ($p_{C_3H_3I} = 1.1 \times 10^{-7}$ Torr; p_{Xe} was adjusted to maintain a constant total pressure of 2.6×10^{-6} Torr as read on the ionization gauge). ^b All pressures are capacitance-manometer corrected.

dependence was found, as can be seen in Table IV.

Discussion

Although the results of this work are not in agreement with the earlier report¹³ of $C_3H_3^+/C_2H_2$ reactivity, the discrepancy is most likely due to limitations of the older pulsed ICR¹³ instrumentation for studying ion/molecule reaction pathways in complicated systems when compared to newer FTICR capabilities. Facile ejection of all ions except the one whose ion/molecule reactions are being investigated offers a very clean monitoring opportunity for product-parent relationships even in complicated consecutive and competitive reaction systems. Various alternative pathways for the production of $C_5H_3^+$ and $C_5H_5^+$ which have been described above probably contributed significantly to the intensities of these ions seen in the earlier work. Additional support for the low reactivity of $C_3H_3^+$ with C_2H_2 is found in a recent report²⁸ of the rate coefficient for this reaction as less than 0.01×10^{-9} cm^3/s , although the isomeric form of $C_3H_3^+$ was not given. It is also possible that the highest pressures used in this work did not reach those of the earlier study¹³ due to differences in the location of capacitance manometers, ionization gauges, etc. Thus

third-body stabilization of $C_5H_5^+$ collision complexes might have been occurring to some extent in the earlier work and not in that reported here.

The most likely mechanism of the observed isomerization of $C_3H_3^+$ ions by collisions with acetylene is a "reactive" rather than a "nonreactive" one. That is, it results from an intimate encounter of the ion and neutral in the $C_5H_5^+$ collision complex. This hypothesis is confirmed by the fact that deuterated forms of $C_3H_3^+$ were produced when C_2D_2 was the neutral reactant (see Figure 3). In most cases the $C_5H_5^+$ collision complex dissociates to give the cyclic, unreactive, $C_3H_3^+$ isomer, instead of the reactive, linear form which reacted initially. The possibility of nonreactive collisional isomerization of linear $C_3H_3^+$ to the cyclic isomer has been ruled out because experiments at elevated pressures of xenon (to ca. 1×10^{-5} Torr) showed no interconversion. Similar interconversion of $C_4H_4^+$ ions from a linear to cyclic form has also been reported²⁹ in the reaction with C_2H_2 and has also been shown to take place via complex formation by using isotopically labeled C_2H_2 . To confirm the hypothesis that energetically less stable, reactive, (linear) $C_3H_3^+$ ions interconvert to more stable, unreactive ones, cyclic $C_3H_3^+$ ions were also reacted with C_2D_2 and no isotope exchange reactions were observed.

Plots of $C_3H_3^+$ ion intensity vs. time for reaction with diacetylene (C_4H_2) (Figure 5) indicate a 10–12% increase in the intensity of the unreactive isomer relative to the reaction when the parent precursor only is present. Isomerization of reactive $C_3H_3^+$ was also seen when different precursors were used (compare Tables II and III). A similar mechanism involving complex formation may be responsible for this isomerization as well, although it was not investigated in any detail.

The extensive ion/molecule condensation reaction sequences (reactions 13–19) observed when $C_3H_3^+$ reacts with C_4H_2 suggest that this aspect of the proposed^{4,6} ionic path to soot formation is quite credible. The rate coefficient determined in this work for $C_3H_3^+$ disappearance ($(1.4 \pm 0.7) \times 10^{-9}$ cm^3/s) is in good agreement with that determined earlier¹³ ($(1.0 \pm 0.5) \times 10^{-9}$ cm^3/s). Some of the product ions formed (e.g. $C_5H_3^+$ and $C_7H_5^+$) have been seen to be abundant in both nonsmoking and smoldering flames.² On the other hand, the observation of $C_3H_3^+$ isomerization and not condensation with acetylene suggests that the proposed sequential acetylene addition reactions to $C_3H_3^+$ in the ionic soot formation mechanism be reconsidered. Other channels such as direct reaction of neutral aromatics with $C_3H_3^+$ ^{3,7} may be as important in the formation of small polycyclic ions.

These experiments and those reported earlier¹³ were carried out at relatively low pressures ($p \leq 5 \times 10^{-5}$ Torr). It is thus quite possible that third-body collisions in atmospheric pressure flames can stabilize a fraction of the $C_5H_5^+$ reaction complexes before the "reactive" deactivation observed in this work can take place. However, direct bimolecular reaction of linear $C_3H_3^+$ with acetylene to form $C_5H_3^+$ and $C_5H_5^+$ does not appear to take place readily.

Reactivity studies involving other small hydrocarbon ions and flame neutrals, including determination of rate coefficients at elevated temperatures, are in progress and will be reported in subsequent publications.

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Registry No. $C_5H_5^+$, 29661-18-5; C_2D_2 , 1070-74-2; D_2O , 7789-20-0; $C_2H_4^+$, 34470-02-5; $C_3H_3^+$, 24858-94-4; C_2H_2 , 74-86-2; CaC_2 , 75-20-7; C_2H_4 , 74-85-1; diacetylene, 460-12-8; cyclopropenium, 26810-74-2; propargyl iodide, 659-86-9; propargyl bromide, 106-96-7; propargyl chloride, 624-65-7; propyne, 74-99-7; allene, 463-49-0; 1,4-dichloro-3-butyne, 83682-45-5.

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