

Isomerization of Linear $C_3H_3^+$ in Its Reaction with Acetylene, and Collisional Stabilization of the $[C_5H_5^+]$ * Collision Complex in a Quadrupole Ion Trap Mass Spectrometer

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The isomerization of linear $C_3H_3^+$ in its reaction with acetylene to cyclic $C_3H_3^+$ was studied with a quadrupole ion trap mass spectrometer. The reaction of linear $C_3H_3^+$ with $^{13}C_2H_2$ shows that isomerization takes place via a $[C_5H_5^+]$ * activated complex that is unstable relative to disproportionation back into the cyclic and linear forms of $C_3H_3^+$ and acetylene. The formation of carbon-13 labeled cyclic and linear $C_3H_3^+$ indicates that isomerization involves skeletal exchange. Collisional stabilization of the $[C_5H_5^+]$ * collision complex was achieved at a helium pressure of approximately 1 mtorr. (*J Am Soc Mass Spectrom* 1992, 3, 631–636)

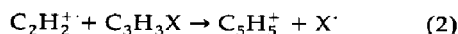
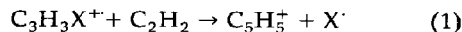
Recent experimental and theoretical studies have sought to characterize the structure and reactivity of the isomeric forms of $C_3H_3^+$ produced from a variety of precursors inside the ion source of mass spectrometers. This research is of special interest because of the high concentration of $C_3H_3^+$ ions in sooting flames [1, 2] and the fact that it is a common fragment ion of many compounds, including aromatics and alkyl halides.

The reaction of $C_3H_3^+$ with acetylene and diacetylene has been suggested as an initial step in soot formation, followed by sequential condensation and condensation-elimination reactions, forming successively larger ions and eventually nucleating soot particles [3]. Understanding the structure and reactivity of $C_3H_3^+$ with acetylene, therefore, is important to the testing of the hypothesis.

Baer and co-workers [4] used photoion-photoelectron coincidence spectroscopy to study the isomeric forms of the $C_3H_3^+$ ions formed from propargyl chloride and propargyl bromide. They concluded that there are two accessible isomeric forms of $C_3H_3^+$ within the energy range of their experiment. Holmes and Lossing [5], using propargyl halides to generate $C_3H_3^+$ ions, interpreted the composite metastable peak shape for the loss of Cl and Br due to the formation of two different $C_3H_3^+$ product ions. The broad and narrow components of the composite peak shape were as-

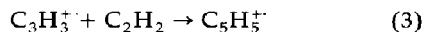
signed to cyclic (cyclopropenylium ion) and linear (propargylium ion) isomers, respectively. They also reported [5] the importance of different precursors in the reactivity of $C_3H_3^+$. Smyth et al. [6] differentiated the isomers of $C_3H_3^+$ ions in terms of their reactivity. They demonstrated that the cyclopropenylium ion was relatively unreactive toward simple hydrocarbon fuels, whereas the linear propargylium ion was quite reactive. Ausloos and Lias [7] formed $C_3H_3^+$ by dissociative charge exchange ionization of propargyl chloride and propargyl bromide. They showed that the ratios of the linear to the cyclic isomer can be affected by charge transfer reactions of small ions (Ar^+ , Xe^+ , CO^+ , etc.). Eyler and co-workers [8] later reported that a high proportion (90–95%) of the linear isomer can be obtained with propargyl iodide, either by electron impact or charge exchange with Xe^+ . Burgers et al. generated and identified four stable isomers of $C_3H_3^+$ by dissociative ionization or by charge reversal of anions [9].

Reaction of $C_3H_3^+$ with acetylene has been studied by Smyth et al. [6]. They reported that the linear propargylium ion reacts with acetylene to produce $C_5H_3^+$ and $C_5H_5^+$ ions. Later, Ozturk et al. [10] demonstrated that within the pressure range of Fourier transform ion cyclotron resonance (FT-ICR), when propargyl halides were used as the precursor of $C_3H_3^+$, the main reactions leading to $C_5H_5^+$ formation were



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and not



where X is Cl, Br or I.

In the case of propargyl bromide, the only source of C_5H_5^+ formation was reaction 1. Although no C_5H_5^+ was formed within the pressure range of FT-ICR when linear C_3H_3^+ reacted with acetylene, C_3H_3^+ became unreactive toward its precursor neutrals. Unreactivity was interpreted as the isomerization of linear C_3H_3^+ to the cyclic form. Further understanding of this isomerization was achieved when C_2D_2 was used as the neutral reactant. Deuterium exchange to form $\text{C}_3\text{H}_2\text{D}^+$, C_3HD_2^+ , and C_3D_3^+ was observed. It was concluded that the isomerization of C_3H_3^+ ions by collision with acetylene is a reactive process, that is, the reactants produce a C_5H_5^+ collision complex that dissociates to give unreactive C_3H_3^+ , that is, the cyclic form [10]. The reaction of C_3H_3^+ with C_2H_2 has also been studied [11] in a variable-temperature selected-ion flow tube over a helium pressure range of 0.3 to 0.8 torr. In this pressure range C_5H_5^+ was produced. According to this study, both linear C_3H_3^+ and cyclic C_3H_3^+ react with C_2H_2 , although with widely different rate coefficients.

The isomeric structures of C_3H_3^+ and their reactivity have also been the subject of several theoretical studies. Radom et al. [12] studied the relative stability of many C_3H_3^+ structures. More accurate results than theirs were later published by Zerner and co-workers [13], who gave the relative energies obtained for five structures of C_3H_3^+ . Zerner's calculation predicts that the cyclopropenylium ion is lowest in energy, followed by the propargylium cation, with a difference in energy of 27.7 kcal/mol. This difference agrees with an experimental estimate of 25 ± 4 kcal/mol [14]. The other isomers were calculated to be at least 72 kcal/mol higher in energy than the cyclopropenylium ion.

Zerner and co-workers [15] also examined theoretically the reactions between the isomers of C_3H_3^+ and acetylene. They predicted that the cyclic form does not react with acetylene, whereas the linear form does. In addition, they found that only one of the reactions between the propargyl ion and acetylene leads to a product that is thermodynamically stable relative to disproportionation back into the cyclic form of C_3H_3^+ and acetylene.

Wiseman et al. [16] studied the isomerization of the reactive C_3H_3^+ with acetylene and deuterioacetylene using kinetic modeling of the reactions of C_3H_3^+ with acetylene and deuterioacetylene. Their results suggest a bonding rearrangement in the transition-state structure leading to the formation of C_5H_5^+ .

To further investigate this isomerization mechanism, that is, to examine whether the isomerization involves skeletal exchange, we studied the reaction of linear C_3H_3^+ with $^{13}\text{C}_2$ -acetylene in a quadrupole ion trap mass spectrometer (ITMS). The effect of pressure

on collisional stabilization of the $[\text{C}_5\text{H}_5^+]^*$ collision complex was also studied.

Experimental

The study used a commercial Finnigan ITMS (Finnigan MAT, San Jose, CA). C_3H_3^+ was produced by the charge transfer reaction of propargyl bromide with Xe^+ formed by electron impact ionization. Propargyl bromide was used for these experiments because among the commercially available propargyl halides it gives the highest yield of linear C_3H_3^+ upon reaction with Xe^+ . The application of appropriate radiofrequency (rf) and direct current (dc) voltage pulses to the electrodes of the ion trap enabled isolation of the desired reactant ions as well as storage of the reactant ions and their ionic products during the reaction period. The ejection capabilities of the ITMS were used for the charge transfer reaction and for the isolation of C_3H_3^+ . Propargyl bromide was distilled before use to remove the toluene stabilizing agent. Propargyl bromide (Aldrich Chemical Co., Milwaukee, WI), $^{13}\text{C}_2$ -acetylene (Cambridge Isotope Laboratories), and xenon (Air Products) were introduced into the mass spectrometer through Granville-Phillips leak valves after multiple freeze-pump-thaw cycles. Neutral gas pressures were measured with an ionization gauge in the vacuum manifold. The nominal pressures of the samples were as follows: $P(\text{C}_3\text{H}_3\text{Br}) = 2$ or 5×10^{-7} torr; $P(^{13}\text{C}_2\text{H}_2) = 0$ or 4×10^{-7} torr; $P(\text{Xe}) = 1.5 \times 10^{-6}$ torr. Except where noted, the helium pressure was adjusted to give a total ionization gauge reading of 8×10^{-5} torr, equivalent to an estimated pressure of 1 mtorr (Finnigan MAT Corp.). The experimental sequences were as follows: (1) electron impact ionization; (2) Xe^+ isolation by the appropriate rf; (3) a delay of 50 ms for the charge exchange reaction of Xe^+ with the background gases; (4) isolation of C_3H_3^+ by application of appropriate rf and dc voltage sequences; and (5) monitoring the products of C_3H_3^+ reactions with the neutral gases at variable reaction times of 1 to 1000 ms.

Results and Discussion

Effects of Helium Buffer Gas Pressure on Total Ion Intensity

Stafford et al. [17] reported that buffer gases with low atomic or molecular weight, such as helium, have an effect on the resolution and sensitivity of the quadrupole ITMS. They found that collisions of the helium buffer gas with trapped ions cool them translationally to the center of the trap, where field homogeneity is optimum and therefore ion loss is at a minimum. The collisions with helium buffer gas also prevent the gradual displacement of trapped ions during the rf voltage sweep. On the other hand, an increase in the pressure of the buffer gas beyond the optimum pressure produces scattering and therefore

loss of ion signal. Because the translational cooling and scattering processes of the ions are mass dependent, there is an optimum pressure at which mass discrimination will be minimum for the mass range of interest.

While effort has been expended to optimize total ion intensities in conventional ITMS, less attention has been paid to optimum pressure in ion-molecule reactions. In the reaction of $C_3H_3^+$ with propargyl bromide, as is the usual case in ion-molecule reaction studies, higher mass ions are produced from lower mass ones. At longer reaction times, as higher mass ions are produced from lower mass ions, any parameter that favors lower or higher mass ions will cause the apparent total ion signal to decrease or increase, respectively [18]. In studying ion-molecule reaction kinetics, and in the quantitation of the isomeric forms of the ions based on their reactivity, it is important to have a constant total ion intensity across the range of the reaction times—typically between 1 and 1000 ms in the quadrupole ITMS. To obtain this optimum pressure for the reaction of $C_3H_3^+$ with propargyl bromide in the reaction range of 1 to 1000 ms, the pressure of helium buffer gas was adjusted while observing the total intensity in the range of 1 to 1000 ms reaction times. The total ion intensity in the present experiments could be kept constant at all reaction times at the nominal pressure range of 5×10^{-5} to 8×10^{-5} torr, consistent with the suggested range of operating pressure of the mass spectrometer.

Reactivity of $C_3H_3^+$

Identification of the isomeric forms of ions according to their reactivity is a technique commonly used in ITMSs. The reactivity of different isomers can be used for their identification if other factors that can affect this reactivity, for example, differences in the ions' internal energies, have been ruled out. The effect of the internal energy can be ruled out by cooling the ions with neutral gases prior to reaction, so long as the ion of interest does not isomerize upon collision with neutral gases.

Only two of the several stable isomers of $C_3H_3^+$, the cyclopropenylum and propargylum ions, can be formed by the charge exchange reaction of Xe^+ (ionization energy of approximately 12.1 eV) with propargyl bromide [9]. The results of several FT-ICR studies in the pressure range of up to 1×10^{-5} torr indicate that, among commercially available propargyl halides, the dissociative charge exchange reaction of Xe^+ with propargyl bromide gives the highest percentage of the reactive (linear) isomer of $C_3H_3^+$ [6-8, 10]. To confirm that the difference in reactivity resulted from structural differences rather than internal energy differences of one isomer, the reactivity of $C_3H_3^+$ was studied in an ITMS with operating pressures of at least two orders of magnitude higher than FT-ICR. In this experiment, $C_3H_3^+$ formed by chemical ionization charge transfer from Xe^+ was isolated by using the ejection

capability of the quadrupole ion trap. No acetylene was present in this experiment. The isolated $C_3H_3^+$ reacted with its precursor neutral molecules in the range of 1 to 1000 ms reaction time. The result is shown in Figure 1. The reaction products, for example, $C_6H_6^+$, $C_7H_7^+$, $C_7H_7^+$, $C_9H_7^+$, etc., were similar to those reported earlier [10].

At a propargyl bromide pressure of 5×10^{-7} torr the intensity of $C_3H_3^+$ peak reached its steady-state value at approximately 750 ms. The attenuation of the signal at m/z 39 from 392 to 89 arbitrary units (about 77%) is assumed to be due solely to removal by reaction of all of the linear isomer [6-8, 10]. The 25% unreactive form of the $C_3H_3^+$ at long times in reactions with propargyl bromide (Figure 1, bottom graph) is based on the assumption that on the time scale of this experiment the contribution of the reverse reactions, that is, of products reacting back to form $C_3H_3^+$, is insignificant [10]. The 75% reactive form of $C_3H_3^+$ is consistent with the results of the FT-ICR study [10]. Observation of a similar linear-to-cyclic isomer ratio in two different instruments with two different operating pressures supports our previous observation that the difference in reactivity of these series of compounds does derive from the existence of the two isomeric forms and not from differences in the internal energies of one isomer. This observation also demonstrates that for the time scale and operating pressure of this experiment, collision with the helium buffer gas does not convert linear $C_3H_3^+$ to the cyclic form.

Isomerization of Linear $C_3H_3^+$

After ejection of all ions except $C_3H_3^+$, the ion-molecule reactions of $C_3H_3^+$ with $^{13}C_2H_2$ were monitored

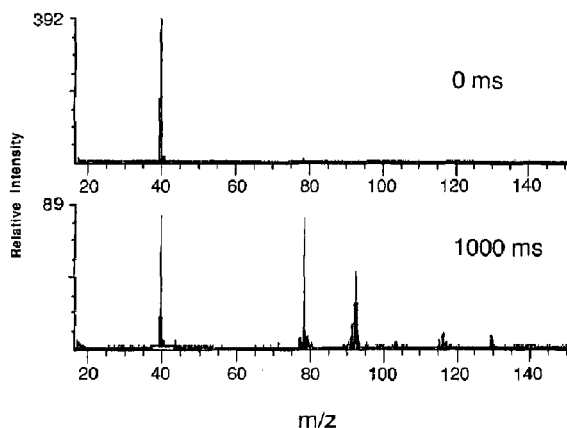
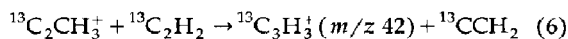
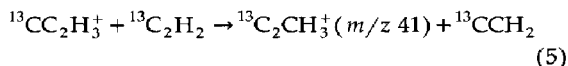
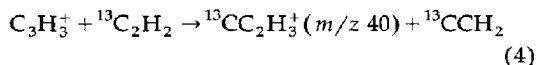


Figure 1. Reaction of $C_3H_3^+$ produced from propargyl bromide by chemical ionization charge transfer with Xe^+ , with its precursor neutral (propargyl bromide). The top graph was obtained with no reaction time, while the bottom one resulted from 1000 ms reaction time. No acetylene was present in this experiment. The nominal pressures of the propargyl bromide and xenon were, respectively, 5×10^{-7} and 1.5×10^{-6} torr.

as a function of time. As shown in Figure 2, at low reaction times $C_3H_3^+$ (m/z 39) and $^{13}CC_2H_3^+$ (m/z 40) were observed. At 100-ms reaction time, $^{13}CC_2H_3^+$ and $^{13}C_2CH_3^+$ (m/z 41) were formed in addition to $C_3H_3^+$. At higher reaction times, for example, 200 ms, $^{13}C_3H_3^+$ (m/z 42) was also produced and at ca. 750 ms the intensity of the $C_3H_3^+$ peak reached its steady-state value. The major net reactions can be summarized as follows:



It was observed that reactions of $C_3H_3^+$ with $^{13}C_2H_2$ led to the isomerization of linear $C_3H_3^+$ to the nonreactive cyclic $C_3H_3^+$. At the steady state (Figure 2, bottom

graph) approximately 25% of the $C_3H_3^+$ remained unreactive. This percentage is the same as that in Figure 1, in which no $^{13}C_2H_2$ was present. Therefore, only reactive (linear) $C_3H_3^+$ participates in the isomerization process; that is, on the time scale and under the experimental conditions employed in this experiment, cyclic $C_3H_3^+$ does not react with acetylene. This result is consistent with the quantum mechanical calculation of Zerner and co-workers.

It was also observed that isomerization of linear $C_3H_3^+$ occurs through a $C_5H_5^+$ reaction complex via skeletal exchange, producing $^{13}CC_2H_3^+$, $^{13}C_2CH_3^+$, and $^{13}C_3H_3^+$. $^{13}C_3H_3^+$ (m/z 42) is formed mainly from the reactive component of $^{13}C_2CH_3^+$ (m/z 41) (reaction 6), which itself is formed mainly from the reactive component of $^{13}CC_2H_3^+$ (m/z 40) (reaction 5). Therefore, the sum of the intensities at m/z 41, 42, and 79 ($^{13}CC_5H_6^+$, which is a product of the reaction of reactive $^{13}CC_2H_3^+$ with C_3H_3Br), depicted in the bottom graph of Figure 2, represents the reactive portion, and the intensity at m/z 40 represents the unreactive portion of $^{13}CC_2H_3^+$. Therefore, approximately one third of the $^{13}CC_2H_3^+$ produced from the $C_5H_5^+$ complex remains unreactive, while two thirds react further with $^{13}C_2H_2$ to produce a mixture of linear and cyclic $^{13}C_2CH_3^+$. The linear isomer in turn reacts further with $^{13}C_2H_2$ to form a mixture of linear and cyclic $^{13}C_3H_3^+$ (Figure 2). The quantum mechanical calculation of Zerner and co-workers suggests that the acetylene initially drifts to the most positive end-carbon atom of the propargylium cation, then attaches to this atom to form a three-member ring. This complex is unstable relative to disproportionation into the cyclic isomer and acetylene. Unfortunately, in the quantum mechanical calculation only the disproportionation of the activated $[C_5H_5^+]^*$ complex formed from the reaction of linear $C_3H_3^+$ with acetylene to cyclic $C_3H_3^+$ and C_2H_2 was studied; the dissociation of the $C_5H_5^+$ complex to linear $C_3H_3^+$ and acetylene was not considered. However, the kinetic modeling of Wiseman et al. [16] predicts that $C_5H_5^+$ fragments to linear $C_3H_3^+$ at a rate three times faster than it fragments to cyclic $C_3H_3^+$. This is consistent with the present results. A similar interconversion of the linear to the cyclic form was reported by Bowers and co-workers [19], who demonstrated that linear $C_4H_4^+$ isomerizes to the cyclic form in its reaction with acetylene. They used isotopically labeled C_2H_2 to show that the isomerization takes place via complex formation.

Collisional Stabilization of the $[C_5H_5^+]^*$ Collision Complex

In the pressure regime of FT-ICR (10^{-9} to 10^{-5} torr), no $C_5H_5^+$ ion was observed when $C_3H_3^+$ was reacted with acetylene, indicating that most of the $[C_5H_5^+]^*$ collision complex dissociated to give $C_3H_3^+$ and acety-

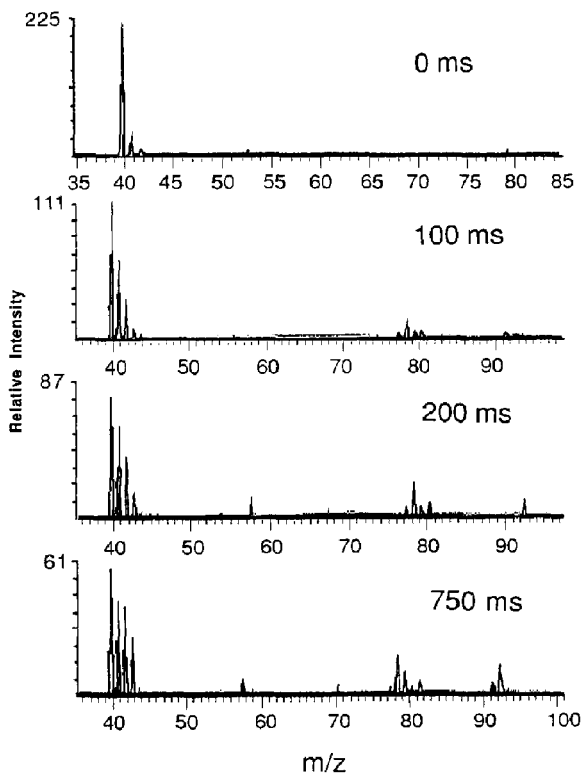


Figure 2. Isotope exchange reaction of $C_3H_3^+$ with $^{13}C_2$ -acetylene after 0, 100, 200, and 750 ms reaction time. Peaks at m/z 39, 40, 41, and 42 are $C_3H_3^+$, $^{13}CC_2H_3^+$, $^{13}C_2CH_3^+$, and $^{13}C_3H_3^+$, respectively. $C_3H_3^+$ ions were produced by charge transfer reactions of propargyl bromide with Xe^+ . The nominal pressures of propargyl bromide, acetylene, and xenon were, respectively, 2×10^{-7} , 4×10^{-7} , and 1.5×10^{-6} torr.

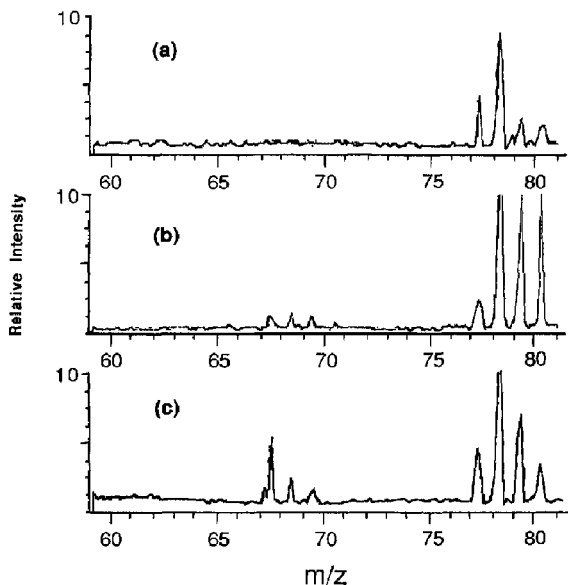


Figure 3. The effect of helium buffer gas pressure on the stabilization of the $[C_5H_5^+]^*$ collision complex, formed from the reaction of $C_3H_3^+$ with $^{13}C_2H_2$ after 200 ms reaction time. The results were obtained at nominal total pressures of approximately (a) $5-8 \times 10^{-6}$, (b) 8×10^{-5} , and (c) 1.2×10^{-4} torr, respectively (see text for experimental details).

lene. Because quadrupole ion traps operate in a higher pressure range (10^{-5} to 10^{-3} torr), the effect of buffer gas pressure on the stabilization of $[C_5H_5^+]^*$ collision complex could be studied using helium for third-body stabilization of the $[C_5H_5^+]^*$ collision complex.

The experimental procedure for this experiment was similar to that used for the experiment described in the previous section, that is, $C_3H_3^+$ was isolated following charge transfer chemical ionization by Xe^+ of a mixture of $^{13}C_2H_2$ and propargyl bromide. Figure 3 shows the effect of helium buffer gas pressure on the stabilization of $[C_5H_5^+]^*$ after 200-ms reaction time. In this experiment $C_6H_6^+$ (m/z 78), formed from the reaction of $C_3H_3^+$ with propargyl bromide, was used as an internal standard. Figure 3b was obtained at the optimum buffer gas pressure, about 1 mtorr (ionization gauge reading of 8×10^{-5}). Figure 3a was acquired at a pressure of approximately an order of magnitude lower than the optimum pressure (ionization gauge reading pressure of ca. $5-8 \times 10^{-6}$ torr), while Figure 3c was obtained at a pressure higher than the optimum pressure (an ionization gauge reading pressure of ca. $1.0-1.2 \times 10^{-4}$ torr). As shown in Figure 3, the threshold for the stabilization of the $C_5H_5^+$ collision complex is approximately 1 mtorr. At a higher buffer gas pressure the intensity of the reference peak at m/z 78 decreases, indicating scattering phenomena as described above. The increase in the intensity of the $^{13}C_2C_3H_5^+$ (m/z 67) ions at pressures above the opti-

um indicates that the rate of collisional stabilization of $[C_5H_5^+]^*$ is greater than the rate of its scattering, and therefore an increase in intensity is observed. In addition, higher pressures further cool the reactant ions, i.e., $C_3H_3^+$, which can contribute to the formation of stable $C_5H_5^+$ [20, 21].

Conclusion

The results show that isomerization of linear $C_3H_3^+$ to the cyclic form is frequently accompanied by carbon exchange through a $[C_5H_5^+]^*$ collision complex. Third-body stabilization of $[C_5H_5^+]^*$ occurs at pressures above 1 mtorr, supporting the existence of the collision complex formation mechanism.

An implication of these results with regard to the ionic mechanism of soot formation is that, although at low pressures the isomerization of linear $C_3H_3^+$ to cyclic $C_3H_3^+$ is the dominant process, at pressures comparable to that of a sooting acetylene flame linear $C_3H_3^+$ can react with acetylene to produce $C_5H_5^+$. At this time neither the structure nor the reactivity of the $C_5H_5^+$ formed in this reaction is known sufficiently to enable one to predict whether $C_5H_5^+$ can react further with acetylene to form aggregates with higher carbon content, as has been postulated for the ionic mechanism of soot formation.

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References

- Goodings, J. M.; Bohme, D. K.; Ng, C.-W. *Comb. Flame* **1979**, *36*, 27.
- Olson, D. B.; Calcote, H. F. In *Eighteenth Symposium (International) on Combustion*; Combustion Institute, 1981, p 453.
- Calcote, H. F. *Comb. Flame* **1981**, *42*, 215.
- Tsai, A. S.; Werner, A. S.; Baer, T. *J. Chem. Phys.* **1975**, *63*, 4384.
- Holmes, J. C.; Lossing, F. P. *Can. J. Chem.* **1979**, *57*, 249.
- Smyth, K. C.; Lias, S. G.; Ausloos, P. *Combust. Sci. Tech.* **1982**, *28*, 147.
- Ausloos, P. J.; Lias, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 6505.
- Ozturk, G.; Brill, F. W.; Eyler, J. R. *Combust. Sci. Tech.* **1986**, *45*, 233.
- Burgers, P. C.; Holmes, J. L.; Mommers, A. A.; Szulejko, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 21.
- Ozturk, F.; Baykut, G.; Moini, M.; Eyler, J. R. *J. Phys. Chem.* **1987**, *91*, 4360.
- Smith, D.; Adams, N. G. *Int. J. Mass Spectrom. Ion Phys.* **1987**, *76*, 307.
- Radom, L.; Hariharan, P. C.; Pople, J. A.; Schleyer, P. V. R. *J. Am. Chem. Soc.* **1976**, *98*, 10.

13. Leszczynski, J.; Weiner, B.; Zerner, M. C. *J. Phys. Chem.* **1989**, *93*, 139.
14. Lossing, F. P. *Can. J. Chem.* **1972**, *50*, 3973.
15. Feng, J.; Leszczynski, J.; Weiner, B.; Zerner, M. C. *J. Am. Chem. Soc.* **1989**, *111*, 4648.
16. Wiseman, F. L.; Ozturk, F.; Zerner, M. C.; Eyler, J. R. *Int. J. Chem. Kinet.* **1990**, *22*, 1189.
17. Stafford, G. C. Jr.; Kelley, P. E.; Syka, J. E. P.; Reynolds, W. E.; Todd, J. F. *Int. J. Mass Spectrom. Ion Proc.* **1984**, *60*, 85.
18. Moini, M.; Eyler, J. R. *Int. J. Mass Spectrom. Ion Proc.* **1989**, *87*, 29.
19. Jarrold, M. F.; Wagner-Redeker, W.; Illies, A. J.; Kirchner, N. J.; Bowers, M. T. *Int. J. Mass Spectrom. Ion Proc.* **1984**, *58*, 63.
20. Basic, C.; Yost, R. A.; Eyler, J. R. In *Proceedings of the 38th Annual Conference of the American Society of Mass Spectrometry*, June, 1990, Tucson, AZ; p 858.
21. McLuckey, S. A.; Glish, G. L.; Asano, K. G.; Bartmess, J. E. *Int. J. Mass Spectrom. Ion Proc.* **1991**, *109*, 171.