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# Association reactions at low pressure. III. The $C_2H_2^+/C_2H_2$ system

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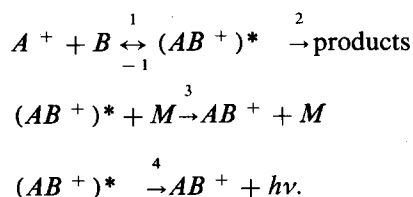
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The association reactions,  $C_4H_2^+ + C_2H_2$  and  $C_4H_3^+ + C_2H_2$  have been examined at pressures between  $8 \times 10^{-8}$  and  $1 \times 10^{-4}$  Torr at 298 K in an ion cyclotron resonance mass spectrometer. Association occurred via two different mechanisms. At pressures below  $\sim 2 \times 10^{-6}$  Torr, the association was bimolecular having rate coefficients  $k_2 = 2.7 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  and  $2.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  for  $C_4H_2^+$  and  $C_4H_3^+$ , respectively. At pressures above  $\sim 2 \times 10^{-6}$  Torr, termolecular association was observed with rate coefficients,  $k_3 = 5.7 \times 10^{-23} \text{ cm}^6 \text{ s}^{-1}$  and  $1.3 \times 10^{-23} \text{ cm}^6 \text{ s}^{-1}$  for  $C_4H_2^+$  and  $C_4H_3^+$ , respectively, when  $M = C_2H_2$ . The termolecular rate constants with  $N_2$ , Ar, Ne, and He as the third body,  $M$ , are also reported. We propose that the low pressure bimolecular association process was the result of radiative stabilization of the complex and the termolecular association process was the result of collisional stabilization. Elementary rate coefficients were obtained and the lifetime of the collision complex was  $\geq 57 \mu\text{s}$  for  $(C_6H_4^+)^*$  and  $\geq 18 \mu\text{s}$  for  $(C_6H_5^+)^*$ . At pressures below  $1 \times 10^{-6}$  Torr,  $\sim 11\%$  of the  $(C_6H_4^+)^*$  were stabilized by photon emission and the remaining  $\sim 89\%$  reverted back to reactants, while  $\sim 24\%$  of the  $(C_6H_5^+)^*$  were stabilized by photon emission and the remaining  $\sim 76\%$  reverted back to reactants. The ionic products of the  $C_2H_2^+ + C_2H_2$  reaction,  $C_4H_2^+$  and  $C_4H_3^+$ , were found to be formed with enough internal energy that they did not react by the radiative association channel until relaxed by several nonreactive collisions with the bath gas.

## INTRODUCTION

The ion-molecule reactions under investigation in this series of studies are association reactions which may be represented by the scheme

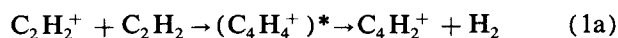


$AB^+$  is the stabilized association product of  $A^+ + B$ ,  $(AB^+)^*$  is the unstable excited complex which undergoes unimolecular dissociation back to reactants (step -1) or on to products (step 2). Competing with the two dissociation channels are two association steps: one has collisional stabilization of the complex (step 3) and the other has radiative stabilization of the complex (step 4) by emission of a photon,  $h\nu$ . Association processes provide a mechanism for efficient synthesis of larger molecules from relatively simple ion and neutral precursors. Such processes are relevant to molecular synthesis in interstellar clouds and planetary atmospheres.

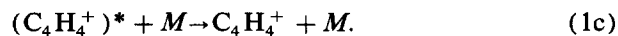
In our first paper in this series<sup>1</sup> we examined systems that only exhibited association via collisional stabilization,

without steps 2 and 4, occurring at measurable rates. In our second study<sup>2</sup> we examined the  $CH_3^+ + CH_3CN$  system in which unimolecular dissociation of  $(CH_3NCCH_3^+)^*$  to exothermic channels  $H_2CN^+ + C_2H_4$  and  $C_2H_5^+ + HCN$  (step 2) competed with step -1 back to reactants, and steps 3 and 4 leading to the stable product  $CH_3CNCH_3^+$ . At the lowest pressures in that system, the bimolecular (radiative) stabilization process was the only association step observed. In the present study we examine two systems in which step 2 is absent and steps 3 and 4 compete with step -1 for removal of  $(AB^+)^*$ .

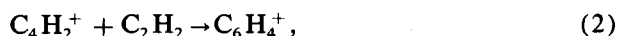
The characteristic reactions of the parent radical cation of acetylenes ( $C_xH_2$ ,  $x = 2, 4, \dots$ ) are condensation reactions leading to higher molecular weight hydrocarbons.<sup>3-8</sup> When the condensation ion is formed with excess energy, then H or  $H_2$  may be lost from the adduct as in Reaction (1).



At higher pressures of the parent gas, some collisional stabilization of the adduct takes place before loss of hydrogen occurs [Reaction (1c)].<sup>8</sup>



Subsequent association of the secondary ions  $C_4H_2^+$  and  $C_4H_3^+$  with  $C_2H_2$  has been observed to occur efficiently even at pressures as low as  $10^{-7}$  Torr.<sup>7,9,10</sup>



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One of the most interesting aspects of these very low pressure associations is the mechanism of the stabilization of the  $(\text{C}_6\text{H}_x^+)^*$  complex. In 1974, Miasek and Beauchamp<sup>9</sup> using trapped-ion mass spectrometry noted that the associations represented by Eq. (2) and (3) were bimolecular. They attributed the bimolecular kinetics to radiative emission as the process responsible for dissipation of energy from the complex. Later, Brill and Eyler<sup>10</sup> studied the same reaction using ion cyclotron resonance (ICR) and also observed bimolecular kinetics leading to association. Brill and Eyler argued that the  $(\text{C}_6\text{H}_x^+)^*$  complex required 1 or 2 collisions for stabilization and that the observed bimolecular kinetics was a consequence of the association reaction being in the saturated regime even though the measured rate coefficient was much less than the Langevin capture rate. In a recent ICR study in our laboratory<sup>7</sup> we measured bimolecular rate coefficients for Reactions (2) and (3). The rate coefficients were independent of pressure over the range  $2 \times 10^{-6}$  to  $1 \times 10^{-5}$  Torr and had measured values of  $1.4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  and  $2.4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ , respectively. A minor (5%) reaction channel leading to  $\text{C}_6\text{H}_3^+$  was observed in addition to the association adduct  $\text{C}_6\text{H}_4^+$ . Finally, Knight *et al.*<sup>8</sup> in a selected ion flow tube (SIFT) investigation of association reactions in acetylene using a helium buffer gas at pressures between 0.2 Torr and 0.4 Torr, observed much larger rate coefficients for association of  $1.3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  and  $9.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  for Reactions (2) and (3), respectively. Under these conditions the association proceeded essentially at the Langevin rate, and Knight *et al.* concluded that the reaction proceeded by association at, or close to, the high pressure saturation limit.

The present experimental study was undertaken in an endeavor to elucidate the mechanism responsible for low pressure, bimolecular association.

## EXPERIMENT

The Jet Propulsion Laboratory ICR spectrometer has been described previously.<sup>1,7</sup> The following brief description is given as a summary. The instrument is based on a 12 in. electromagnet which was typically operated at a constant magnetic field of 1.5 T. The cyclotron frequency of the ions is utilized to monitor ion concentrations within the cell and detected using a bridge of the Wronka and Ridge design.<sup>11</sup> The cell is of the trap/drift design after McMahon and Beauchamp<sup>12</sup> and gas pressures within the cell are measured by an ion gauge calibrated against an MKS Baratron capacitance manometer. The experiments were conducted at 298 K. The second-order reaction rate constants have an estimated error of  $\pm 15\%$ , which is due principally to the inaccuracy of the pressure determination and control. The third-order rate constants have an expected error of  $\pm 30\%$ .

## Data analysis

Data was obtained from the ICR spectrometer in either of two modes of operation: the trap-mode or the drift-mode. Each mode allows for the examination of the same reaction

under a different pressure and time regime. Any difference between the data obtained in the two modes is useful in the elucidation of the reaction mechanism.

Analysis of the varying signal intensity plots with time was carried out using either of two methods. In the normal method, the decay of the reactant ion was plotted semilogarithmically versus time. As the neutral reactant concentration was always orders of magnitude larger than the ion concentration, pseudo first-order kinetics prevailed and linear decays were observed as in Fig. 1. The signals from the bridge detector are proportional to the ion density within the cell and with no known mass discrimination. This method will be referred to as the method of "simple ion loss." It was used to calculate a rate constant at a specific pressure and so a series of measurements each at a different pressure allowed for the study of the rate coefficient as a function of pressure. This "simple ion loss" method can be applied to the decay of primary or secondary ions, except in the latter case it is necessary to allow sufficient time for most of the primary ion to be converted to the secondary ion by reaction before the data is analyzed for linearity. The "simple ion loss" method is only concerned with the loss of the reactant ion of interest and neglects completely the product ions.

An alternative method of analysis of the time-density data is to monitor both the reactant and product ions with time. The ratio of the two peaks at a specified trapping time and pressure is used to calculate a rate constant. A set of such data can be used to generate plots of the rate coefficient as a function of either time or pressure. This method will be referred to as the "peak ratio" method. This "peak ratio" method has the advantage over the "simple ion loss" method in that it gives a balanced ion budget. In principle, both methods of analysis should yield the same results, however as we have learned in this work, any differences between the two methods gives additional understanding of the pro-

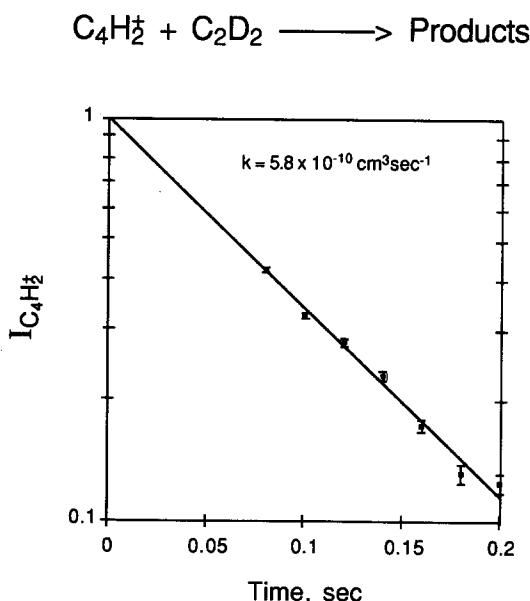


FIG. 1. Typical semilogarithmic decay of  $\text{C}_4\text{H}_2^+$  signal against trapping time in the ICR cell used in the trap-mode of operation. The pressure of  $\text{C}_2\text{H}_2$  was  $5.5 \times 10^{-7}$  Torr.

cesses. In particular the “peak ratio” method assumes a constant rate coefficient from  $t = 0$ , whereas the “simple ion loss” method allows all data points affected by excess energy in the reactant ion to be ignored. In a variation of the “peak ratio” method, a kinetic model of the reactions is developed and used to determine the proper rate constants by varying the rate constants until the modelled ion intensities agree with the experimentally observed time-dependent ion intensities. The kinetic model variation requires a complete inventory of all ions in the cell and examines their chemical production and loss processes. It allows for the detailed fitting of each of the ion intensity versus time curves. More complicated models may be used that include changes in the reaction rate constant with time.

In the trap-mode of operation the ion of interest was trapped for up to 500 ms before being allowed to drift for  $\sim 1$  ms through the detection region. Rate coefficients for total ion loss via all channels were measured primarily in this mode by monitoring the ion loss of the ion of interest continuously with the bridge detector, the “simple ion loss” method. The alternate methods of using “peak ratios” and kinetics plots were used in several cases to either reproduce or evaluate differences between the “simple ion loss” and “peak ratio” method.

In the drift-mode of operation of the spectrometer, ions were continuously drifted through the ICR cell. The ions typically require 1–3 ms to transit both the reaction region and the detection region. In this mode, the “peak ratio” technique was the only mode of analysis that could be used. Drift times were measured by the method of McMahon and Beauchamp.<sup>13</sup>

A critical parameter in the study of association reactions is not only the number of collisions the complexes undergo, but also the time between collisions. It is therefore important to distinguish between the different experimental conditions under which the cell is operated in the two modes of operation. In the trap-mode the pressure range was typically  $5 \times 10^{-8}$  to  $5 \times 10^{-6}$  Torr and trapping times were in the range 0.05 to 0.5 s. In the drift-mode, the pressure range was  $5 \times 10^{-6}$  Torr to  $1 \times 10^{-3}$  Torr and drift times were in the range  $5 \times 10^{-4}$  to  $3 \times 10^{-3}$  s. As a consequence the times between collisions in the drift-mode were very much less than in the trap-mode.

Primary ions were generated by electron impact on the parent gas at energies just above the ionization threshold.  $C_4H_2^+$  and  $C_4H_3^+$  were formed from Reactions (1a) and (1b) in acetylene or alternatively by electron impact on diacetylene and vinylacetylene, respectively. Acetylene gas was obtained from Matheson Gas Products with a reported impurity of 99.6%. Small traces of acetone were found and these were removed by repeated freeze-pump-thaw cycles. Deuterated acetylene was obtained from MSD Isotopes and was used without further purification. Diacetylene and vinylacetylene were synthesized using standard procedures.<sup>14,15</sup>

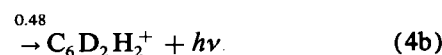
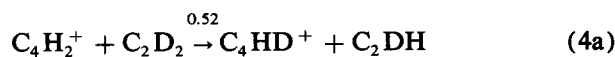
## RESULTS

In the previous section we pointed out differences in the experimental conditions pertaining to the trap-mode and the drift-mode of operation of the ICR cell. In the trap-mode of

operation ions are stored for up to 500 ms before mass analysis whereas in the drift-mode, ion residence times of  $< 3$  ms are typical. Another crucial parameter influencing the outcome of an excited complex in an association reaction is the time between collisions. At pressures below  $5 \times 10^{-6}$  Torr, the average time between collisions is  $> 5$  ms. If the lifetime of the complex with respect to unimolecular dissociation is of the order of the radiative lifetime of the complex (or longer) then under these low pressure conditions, stabilization may result from photon emission. At higher pressures collisional stabilization becomes the dominant process, because then the times between collisions are much shorter and the radiative process has a diminishing probability of occurring. The ambient pressure will thus influence the type of stabilization process observed and we therefore list the results of the trap- and the drift-modes of operation, separately.

### Trap-mode results

The results obtained using the method of “simple ion loss” for the total rate of reaction of the  $C_4H_2^+$  (produced by near threshold electron impact on  $C_4H_2$ ) and  $C_2D_2$  via the Reactions (4a) and (4b)



are shown in Fig. 1, where the disappearance of  $C_4H_2^+$  is followed at a single pressure with time. By repeating the measurement at different pressures the results for Fig. 2 were obtained. The overall reaction rate constant [Reactions (4a) and (4b)] was determined to be  $5.9 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ . The branching ratios of channel (4a) and (4b) were measured to be 0.52 and 0.48, respectively. This means that the isotopic exchange rate constant is  $3.1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  and

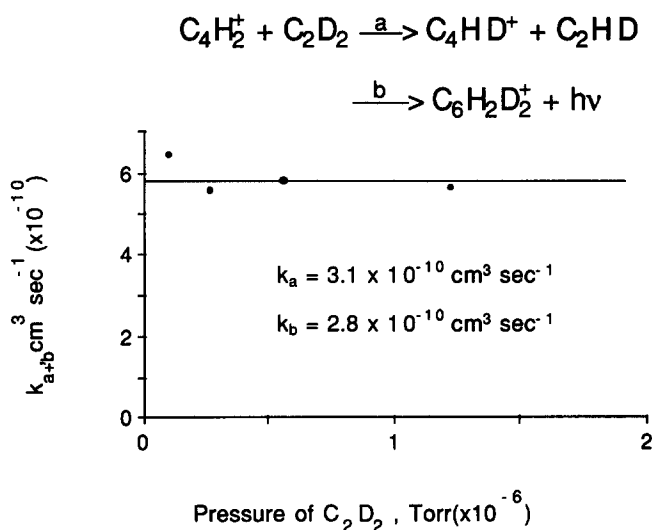


FIG. 2. The dependence of  $k_2$ , the observed bimolecular rate coefficient for Reaction (4) on  $C_2D_2$  pressure.  $k_2$  was measured in the trap-mode of operation and the data was analyzed according to total ion loss.

the bimolecular association rate constant is  $2.8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ . When allowance is made for isotopic substitution in channel (4a) these results are twice as large as our earlier measurement<sup>7</sup> of  $1.4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  for the association channel, Reaction (2), where the  $\text{C}_4\text{H}_2^+$  ion was produced by the reaction of  $\text{C}_2\text{H}_2^+$  and  $\text{C}_2\text{H}_2$ .<sup>7</sup> This difference will be discussed below. We observed that even at the lowest pressures, the association product  $\text{C}_6\text{D}_2\text{H}_2^+$  was present and was verified by double resonance spectrometry. Using the trap-mode and the "kinetic plot" method a reaction rate constant of  $2.7 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  was measured for the  $\text{C}_4\text{H}_2^+/\text{C}_2\text{H}_2$  reaction.

It was possible to use the "peak ratio" method on Reaction (2), and the results are shown in Fig. 3 for the  $\text{C}_4\text{H}_2^+/\text{C}_2\text{H}_2$  system. This "peak ratio" study showed a markedly smaller measured reaction rate constant than had been measured by "simple ion loss." These results are in better agreement with our earlier measurement of  $1.4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ , for the association channel, Reaction (2), where the  $\text{C}_4\text{H}_2^+$  ion was produced by the reaction of  $\text{C}_2\text{H}_2^+$  and  $\text{C}_2\text{H}_2$ .<sup>7</sup> We believe that the smaller rate coefficient results from  $k_2$  being averaged over a time when the rate coefficient was not constant. This will be discussed below.

The absence of any significant pressure dependence and nonzero intercept in Figs. 2 and 3 is strongly indicative of a bimolecular mechanism for association. The most likely process responsible for stabilization is the emission of infrared photons (i.e., radiative stabilization).

Similar results were found for the association between  $\text{C}_4\text{H}_3^+$  and  $\text{C}_2\text{D}_2$  and these are shown in Fig. 4. The overall reaction rate constant of Reactions (5a) and (5b) was measured to be  $\sim 3.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ . The branching ratio between (5a) and (5b) was determined by use of double resonance in the drift-mode to be 0.3 and 0.7, respectively.

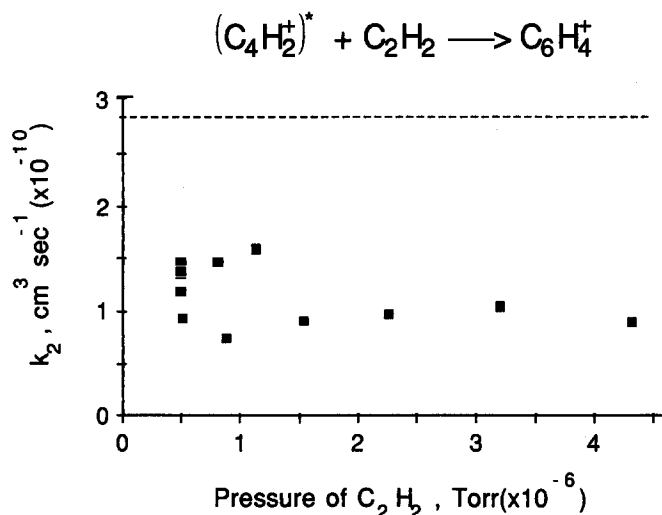


FIG. 3. The dependence of  $k_2$ , the observed bimolecular rate coefficient for the reaction  $\text{C}_4\text{H}_2^+ + \text{C}_2\text{H}_2 \rightarrow \text{C}_6\text{H}_4^+$  on  $\text{C}_2\text{H}_2$  pressure.  $k_2$  was obtained using the "peak ratio" method of analysis but in the trap-mode of operation. ( $t = 160\text{--}470 \text{ ms}$ )

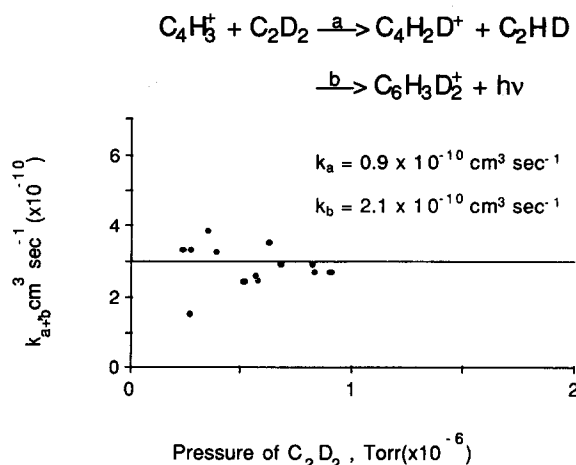
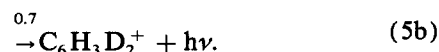
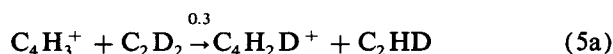
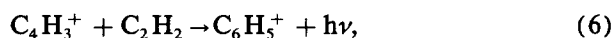


FIG. 4. The dependence of  $k_2$ , the observed bimolecular rate coefficient for Reaction (5), on  $\text{C}_2\text{D}_2$  pressure analyzed according to total ion loss. The crosses are for  $\text{C}_4\text{H}_3^+$  derived from  $\text{C}_2\text{H}_2^+ + \text{C}_2\text{H}_2$  and the open circles for  $\text{C}_4\text{H}_3^+$  derived from electron impact on vinyl acetylene. The solid circles represent data obtained under conditions where the partial pressure of  $\text{C}_2\text{D}_2$  was  $3.5 \times 10^{-7} \text{ Torr}$  and the partial pressure of argon was  $1.0\text{--}1.5 \times 10^{-6} \text{ Torr}$ .

This gives a value for the isotopic exchange reaction rate constant of  $9 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  and a value for the radiative association reaction rate constant of  $2.1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ .



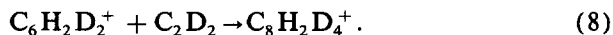
The rate coefficient for low pressure bimolecular association, Reaction (6), was found to have a mean value of  $2.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$



which is consistent with other measurements,  $2.4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  and  $2.1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  of this rate coefficient.<sup>7,10</sup>

#### Drift-mode results: $\text{C}_4\text{H}_2^+/\text{C}_2\text{D}_2$

The influence of the reactant gas pressure on the rate coefficient for association of  $\text{C}_4\text{H}_2^+$  (from diacetylene) with  $\text{C}_2\text{D}_2$  is shown in Fig. 5. Each rate coefficient in the figure was determined by the "peak ratio" method as described earlier, after first correcting for isotopic substitution and subsequent association as in Reactions (4), (7), and (8).



The intercept of the pressure-dependent curve shown in Fig. 5 provides the contribution to stabilization from the bimolecular process. This intercept yields a bimolecular rate coefficient of  $3.3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  for the Reaction (4b), which is similar to the trap-mode rate coefficient measured directly at low pressure discussed previously. We attribute the bimolecular kinetics for the association process to radiative stabilization [Reaction (4b)].

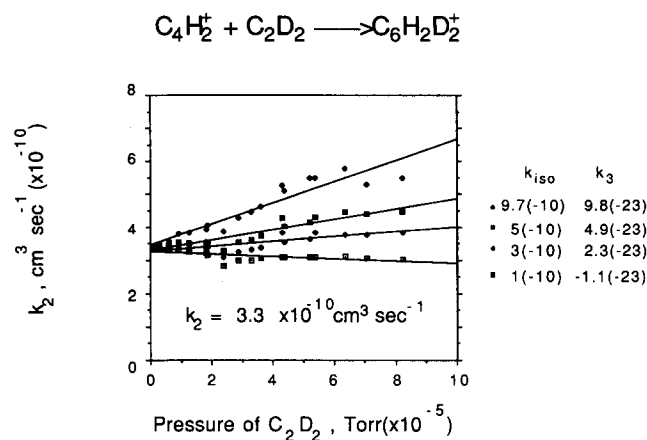


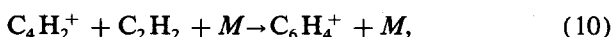
FIG. 5. The dependence of  $k_2$ , the observed bimolecular rate coefficient for Reaction (7) on  $C_2D_2$  pressure.  $C_4H_2^+$  was derived from  $C_4H_2$ . The  $k_2$ s were obtained using the "peak ratio" method in the drift-mode. The non-zero intercept corresponds to a bimolecular association process with a rate coefficient of  $3.3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ . Correction in the data have been made for the isotopic dilution of the product ion. Four different isotopic dilution rates were used ranging from the collision rate to near zero.

Four different reductions of the data set is shown in Fig. 5 using different values of the reaction rate constant of Reaction (7). Since we were unable to measure this reaction rate constant we have reduced the data using four values, ranging from the collision rate constant to zero. This approach can only give an upper limit to the overall rate constant of  $\leq 9.8 \times 10^{-23} \text{ cm}^6 \text{ s}^{-1}$  for Reaction (9) where  $M$  was the parent neutral  $C_2D_2$ .



#### Drift-mode results: $C_4H_2^+/C_2H_2$

The dependence of the rate coefficient for association of  $C_4H_2^+$  on the pressure of  $C_2H_2$  is shown in Fig. 6. In this case  $C_4H_2^+$  was generated by the reaction of  $C_2H_2^+ + C_2H_2$  ( $k = 4.9 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  for the  $C_4H_2^+$  channel). Electron impact on  $C_2H_2$  was used to form the  $C_2H_2^+$  ion. All of the kinetics were incorporated in the calculation of the rate coefficient from "peak ratios" at each pressure. The pressure dependence of the "peak ratio" rate coefficient yielded a value for the three body rate coefficient for collisional stabilization [Reaction (10)] of  $k_3 = 5.7 \times 10^{-23} \text{ cm}^6 \text{ s}^{-1}$ .



when  $M = C_2H_2$ . This value has an estimated experimental error of  $\pm 30\%$ . (The rate coefficients,  $k_3$ , for other stabilizing gases were:  $2.9 \times 10^{-23} \text{ cm}^6 \text{ s}^{-1}$  ( $M = N_2$ );  $2.8 \times 10^{-23} \text{ cm}^6 \text{ s}^{-1}$  ( $M = Ar$ );  $2.3 \times 10^{-23} \text{ cm}^6 \text{ s}^{-1}$  ( $M = Ne$ ); and  $1.0 \times 10^{-23} \text{ cm}^6 \text{ s}^{-1}$  ( $M = He$ ). The zero intercept in the curve for Fig. 6 is noticeably different than the nonzero intercept found in Fig. 5 and this will be discussed in the next section. The relative efficiencies of the third bodies,  $\beta_{rel}(M)$ , can be compared by using the following formula

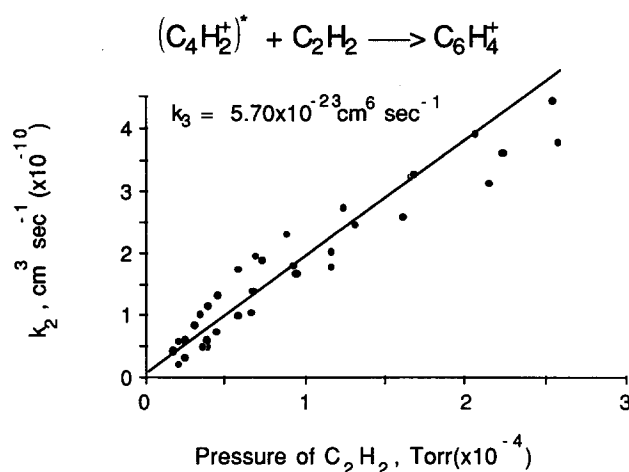


FIG. 6. The dependence of  $k_2$ , the observed bimolecular rate coefficient for Reaction (10), on  $C_2H_2$  pressure.  $C_4H_2^+$  was derived from  $C_2H_2$ . The  $k_2$ s were obtained using the "peak ratio" method in the drift-mode and  $k_3$  from the pressure dependence of  $k_2$ .

$$\beta_{rel}(M) = \frac{k_3(M)/k_{coll}(M)}{k_3(C_2H_2)/k_{coll}(C_2H_2)}.$$

The values thus calculated are shown in Table I.

#### Drift-mode results: $C_4H_3^+/C_2H_2$

The dependence of the rate coefficient for association of  $C_4H_3^+$  on the pressure of  $C_2H_2$  is shown in Fig. 7. As in the preceding case,  $C_4H_3^+$  was produced from  $C_2H_2$  and it was necessary to include the formation process of  $C_4H_3^+$  (*viz*  $C_2H_2^+ + C_2H_2$ ,  $k = 9.1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  for  $C_4H_3^+$  formation) in the kinetic scheme used to evaluate peak ratios for rate coefficients. The rate coefficient for collisional stabilization

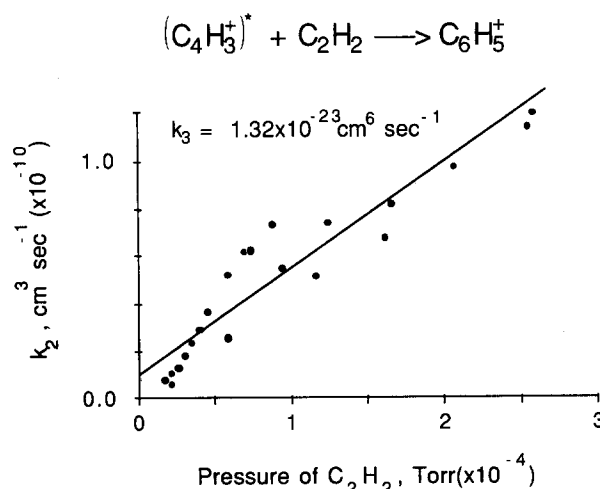


FIG. 7. The dependence of  $k_2$ , the observed bimolecular rate coefficient for Reaction (11), on  $C_2H_2$  pressure.  $C_4H_3^+$  was derived from  $C_2H_2$ . The  $k_2$ s were obtained using the "peak ratio" method in the drift-mode and  $k_3$  from the pressure dependence of  $k_2$ .

TABLE I. Bimolecular rate coefficient  $k_2$  (in units of  $10^{-9} \text{ cm}^3 \text{ s}^{-1}$ ) and termolecular rate coefficients  $k_3$  (in units of  $10^{-23} \text{ cm}^6 \text{ s}^{-1}$ ) for association reactions measured in this work.

	$k_2$	$k_3^c$	$\beta_{\text{rel}}$			
$\text{C}_4\text{H}_2^+ + \text{C}_2\text{H}_2 \rightarrow \text{C}_6\text{H}_4^+$	0.14, <sup>a</sup> 0.27 <sup>b</sup>	5.7	1.0	( $M = \text{C}_2\text{H}_2$ )		
		2.9	0.73	( $M = \text{N}_2$ )		
		2.8	0.81	( $M = \text{Ar}$ )		
		2.3	1.1	( $M = \text{Ne}$ )		
		1.0	0.32	( $M = \text{He}$ )		
$\text{C}_4\text{H}_2^+ + \text{C}_2\text{D}_2 \rightarrow \text{C}_4\text{HD}^+ + \text{C}_2\text{DH}$ $\rightarrow \text{C}_6\text{H}_2\text{D}_2^+$	0.31 <sup>d</sup> 0.28, <sup>c</sup> 0.28 <sup>d</sup>	<9.8	1.0	( $M = \text{C}_2\text{D}_2$ )		
$\text{C}_4\text{H}_3^+ + \text{C}_2\text{H}_2 \rightarrow \text{C}_6\text{H}_5^+$	0.24, <sup>a</sup> 0.17 <sup>b</sup>		1.0	( $M = \text{C}_2\text{H}_2$ )		
			0.6	0.66	( $M = \text{N}_2$ )	
			0.4	0.51	( $M = \text{Ar}$ )	
			0.5	1.0	( $M = \text{Ne}$ )	
		0.26	0.36	( $M = \text{He}$ )		
$\text{C}_4\text{H}_3^+ + \text{C}_2\text{D}_2 \rightarrow \text{C}_4\text{H}_2\text{D}^+ + \text{C}_2\text{DH}$ $\rightarrow \text{C}_6\text{H}_3\text{D}_2^+$	0.09 <sup>d</sup> 0.21 <sup>d</sup>					

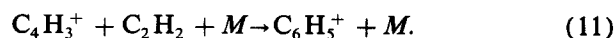
<sup>a</sup>Our earlier measured values from Ref. 7.

<sup>b</sup>Measured by the "kinetic plot" method in trap-mode.

<sup>c</sup>Measured by the "peak ratio" method in drift-mode.

<sup>d</sup>Measured by the "simple ion loss" method in trap-mode.

tion has termolecular kinetics at low pressure, and was found to be  $1.3 \times 10^{-23} \text{ cm}^6 \text{ s}^{-1}$  for  $M = \text{C}_2\text{H}_2$ .



The rate coefficients,  $k_3$ , for other stabilizing gases were:  $0.6 \times 10^{-23} \text{ cm}^6 \text{ s}^{-1}$  ( $M = \text{N}_2$ ),  $0.4 \times 10^{-23} \text{ cm}^6 \text{ s}^{-1}$  ( $M = \text{Ar}$ ),  $0.5 \times 10^{-23} \text{ cm}^6 \text{ s}^{-1}$  ( $M = \text{Ne}$ ), and  $0.26 \times 10^{-23} \text{ cm}^6 \text{ s}^{-1}$  ( $M = \text{He}$ ). Figure 7 shows a zero intercept for the  $\text{C}_4\text{H}_3^+/\text{C}_2\text{H}_2$ , similar to that found in Fig. 6. The relative efficiencies of the third bodies,  $\beta_{\text{rel}}(M)$ , were calculated as those for the  $\text{C}_4\text{H}_2^+/\text{C}_2\text{H}_2$  system and the values thus calculated are shown in Table I.

A summary of the experimental data obtained in the present work is included in Table I.

## DISCUSSION

### A summary of the results

In addition to the present investigation in the low to intermediate pressure range, experimental data were also available from a higher pressure SIFT study of Knight *et al.*<sup>8</sup> in which much larger rate coefficients for association were measured. These rate coefficients were  $1.3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  for  $\text{C}_4\text{H}_2^+/\text{C}_2\text{H}_2$  and  $9.4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  for  $\text{C}_4\text{H}_3^+/\text{C}_2\text{H}_2$ , which are close to the Langevin capture rates of  $1.1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  for these reactions. It is reasonable to conclude therefore, that in the flow tube at helium pressures  $\sim 0.3$  Torr, almost all of the collision complexes formed are stabilized by collision before they can revert back to reactants. In the SIFT work, as in this study, only the association products were observed. Under flow-tube conditions the association is in the near saturated regime and bimolecular kinetics for association are observed.<sup>8</sup>

At three orders of magnitude lower pressure than the SIFT study, the present drift-mode study does not observe this saturation effect. We would expect the apparent bimo-

lecular rate coefficient for association to start out at a much lower value and then increase with pressure, as the number of complexes collisionally stabilized are proportional to the pressure as the pressure tends to zero. Such a variation in the apparent two body reaction rate constant with pressure was observed (Figs. 5, 6, and 7). The slope of the line (in the limit of the pressure going to zero) is a measure of the overall three body reaction rate constant and the intercept is a measure of the overall two body reaction rate constant.

At six orders of magnitude lower pressure than the SIFT study, the time between collisions increased to the point where collisional stabilization no longer competed with the radiative (noncollisional stabilization) process. Under the conditions of the trap-mode measurements, the primary stabilization process is radiative and the kinetics of association changes to bimolecular (Figs. 2, 3, and 4).

### Bimolecular (radiative) association is verified in this study

The condition where radiative association becomes a significant and therefore identifiable process in the ICR cell occurs when the unimolecular dissociation lifetime of the association complex is of the order of the radiative lifetime of the complex or longer. Under these conditions the association process exhibits bimolecular kinetics at low pressures.

The trap-mode results (Figs. 2 through 4) provide evidence for a stabilization process of the association complex that follows bimolecular kinetics at the low end of the pressure range of these studies and this process was assumed to be radiative.

The drift-mode results for the association between  $\text{C}_4\text{H}_2^+$  and  $\text{C}_2\text{D}_2$ , Fig. 5, were also entirely consistent with this view as the intercept at zero pressure of  $\text{C}_2\text{D}_2$  corresponded to the same bimolecular rate coefficient as that observed in the trap-mode results.

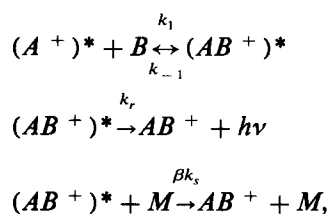
### Energetic effects in the radiative association channels

The drift-mode results of Figs. 5, 6, and 7 show the onset of collisional stabilization as it manifests itself through termolecular kinetics. What is immediately apparent is that Fig. 5, and Figs. 6 and 7 are contradictory. Figures 6 and 7 have zero intercepts at zero pressure, for Reactions (2) and (3). In contrast, Fig. 5 has a nonzero intercept which is indicative of bimolecular association and which is consistent with the trapped-mode results shown in Figs. 2 and 4.

The explanation for the apparent contradiction in these figures lies in the different mechanisms for production of the  $C_4H_x^+$  ion. In Fig. 5, the  $C_4H_2^+$  reactant ion was produced by low energy (11 eV) electron impact on diacetylene. Electron impact ionization is a vertical process. The ground state configuration of the  $C_4H_2^+$  ion is little different than that of the neutral  $C_4H_2$ <sup>16</sup> and the process of ionization should not produce an ion with large amounts of internal energy.

On the other hand, the reactant ions  $C_4H_2^+$  and  $C_4H_3^+$  in Figs. 6 and 7 were produced by Reactions (1a) and (1b) in pure acetylene. The formation processes are exothermic reactions with heats of reactions  $-134 \text{ kJ mol}^{-1}$  and  $-121 \text{ kJ mol}^{-1}$ , respectively. Some H atom rearrangement occurs in the  $(C_4H_4^+)^*$  complex and it is reasonable to assume that the product ions,  $C_4H_2^+$  and  $C_4H_3^+$ , are formed with internal energies which amount to a reasonable fraction of the exothermicity of the reactions. In principle there is sufficient internal energy to populate vibrational levels of the  $A^2\Pi_u$  electronic state of  $C_4H_2^+$ , but lifetime measurements have shown that radiative and nonradiative decay of this state to the ground,  $X^2\Pi_g$ , electronic state occurs in less than  $10^{-6} \text{ s}$ .<sup>17</sup> We must therefore be concerned with vibrationally excited ground state ions. This excess vibrational energy is carried into the collision complexes, the  $(C_6H_4^+)^*$  and  $(C_6H_5^+)^*$  ions, and elevates their total energies above the dissociation limit by this same amount. In contrast, the collision complexes made from the  $C_4H_2^+$  and  $C_4H_3^+$  ions produced by electron impact on diacetylene and vinylacetylene, form complexes that have energies around the dissociation limit.

The influence of excess energy within the  $(AB^+)^*$  complex formed in the reaction



must now be considered. In particular we consider the effect of energy on  $k_{-1}$ , the unimolecular rate coefficient for dissociation back to reactants, on  $k_s$ , the rate coefficient for stabilization by collision and on  $k_r$ , the rate coefficient for stabilization by photon emission. It is well established that the unimolecular lifetime,  $\tau (= 1/k_{-1})$ , is sensitive to internal energy and decreases with increasing energy.<sup>18</sup> The observation of very fast three body rates in Figs. 6 and 7 indicate however, that at the level of excitation present in the  $(C_6H_n^+)^*$  complexes,  $\tau$  was not shortened sufficiently to

influence  $k_3$ , the rate coefficient for termolecular association by more than a factor of two. The results are qualitatively consistent with the work of Baer<sup>19</sup> who found in 10 systems studied, that  $k_{-1}$  increased by a factor of  $3.3 \pm 1.0$  for a 0.2 eV increase in vibrational energy.

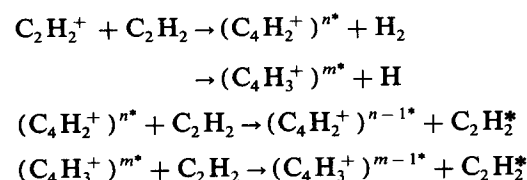
We examine next the effect of excess vibrational energy in the complex on  $k_r$ . If the collision complex contains excess energy it will most likely be in the form of several quanta of vibrational energy. Therefore, the radiative relaxation process will require the emission of *several* vibrational quanta within the lifetime of the complex in order to stabilize the complex before it dissociates back to reactants. It is much less probable that this will happen compared to a single or double photon emission. Therefore, the vibrationally excited complexes may emit a photon (or possibly two), but if they have several vibrational quanta of energy to start with they will dissociate back to reactants before radiative emission can lower the total energy below the threshold for dissociation. The net effect of the added internal energy is to close down the radiative association channel. Herbst<sup>20</sup> has modeled the radiative process and found that the radiative lifetime decreases somewhat with increase in vibrational energy, but the exact rate is not going to be important if it does not stabilize the complex. He also found that emissions from overtones and combination bands become significant with increased vibrational energy, but only one and two quanta may be lost at a time.

By modeling the reactions using Runge-Kutta techniques we have shown that, in the 1 ms of the drift-mode experiment the reactant  $C_4H_n^+$  ion never relaxes enough to allow the radiative association channel to compete with the collision stabilized channel. The data in Fig. 6 thus represents the process of collisional stabilization of the complex formed from the reaction of  $(C_4H_2^+)^*$  and  $C_4H_2$ . The lack of any great variation in  $\beta k_s$  between Fig. 5 and Fig. 6 is an indication that the amount of internal energy resident in the complex is less than about 0.2 eV. Four or so collisions, each removing on the average  $250 \text{ cm}^{-1}$  per collision<sup>21</sup> are sufficient to stabilize the  $C_6H_4^+$  complex.

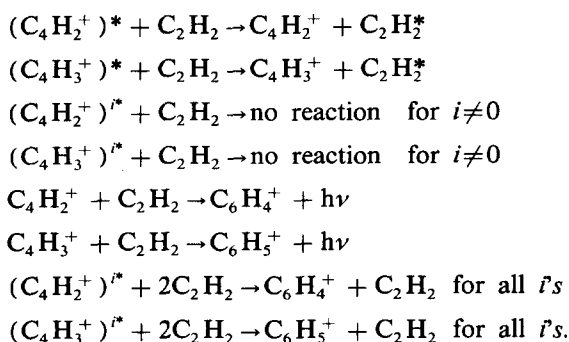
The interesting conclusion from these data is that in the  $C_4H_2^+/C_2H_2$  system, it is the rate coefficient  $k_r$  for the process of radiative stabilization that has the most sensitive response to internal energy within the complex.

### Experimental test of energetic reactant ion hypothesis

To test the hypothesis we monitored the ion abundances in acetylene as a function of time at two  $C_2H_2$  pressures. The data were obtained by monitoring all of the ions in the system by measuring the peaks at  $m/e = 26$  ( $C_2H_2^+$ ), 50 ( $C_4H_2^+$ ), 51 ( $C_4H_3^+$ ), 76 ( $C_6H_4^+$ ), and 77 ( $C_6H_5^+$ ) in the trap mode of operation. The following kinetic model was assumed







In this scheme, the symbol,  $(\text{C}_4\text{H}_3^+)^i$ , describes a  $\text{C}_4\text{H}_3^+$  ion which has excess internal energy. The amount of excess energy,  $i^*$ , is a measure of  $i$  quantities of the average energy lost in a collision with the  $\text{C}_2\text{H}_2$  neutral. The system of differential equations evaluated numerically using the data of Table I and rate coefficients for the  $\text{C}_4\text{H}_2^+$  and  $\text{C}_4\text{H}_3^+$  production from  $\text{C}_2\text{H}_2^+$  as  $4.9 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  and  $9.1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ , respectively.<sup>7</sup> Figures 8 and 9 show the results for ions derived from acetylene at  $\text{C}_2\text{H}_2$  pressures of  $5.3 \times 10^{-7}$  Torr and  $1.35 \times 10^{-6}$  Torr, respectively. The points are experimental and the solid curves present the computer fit of the model to the experimental points. Significant amounts of the association product  $\text{C}_6\text{H}_4^+$  and  $\text{C}_6\text{H}_5^+$  were observed only at the higher  $\text{C}_2\text{H}_2$  pressure of  $1.35 \times 10^{-6}$  Torr. In the latter case a good fit to the experimental data was obtained for all ions other than the association products  $\text{C}_6\text{H}_4^+$  and  $\text{C}_6\text{H}_5^+$  at  $m/e = 76$  and  $77$ , respectively. In order to achieve a fit to the experimental data for  $\text{C}_6\text{H}_4^+$  and  $\text{C}_6\text{H}_5^+$  it was necessary to include a delay time for the onset of the tertiary products. This delayed onset of the tertiary products was also manifested as an increased secondary abundance prior to the onset. We chose to model this with a number of non reactive collisions between the appropriate  $(\text{C}_4\text{H}_x^+)^*$  species and  $\text{C}_2\text{H}_2$ . The number of nonreactive collisions required are shown in Fig. 10 for  $\text{C}_4\text{H}_2^+$  (4 collisions) and Fig. 11 for  $\text{C}_4\text{H}_3^+$  (5 collisions). The number of nonreactive collisions found represent a lower limit since we used unit

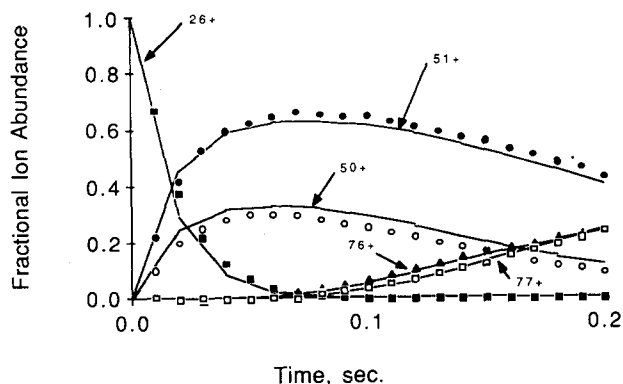
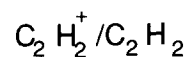


FIG. 9. A comparison of the computer model fit (solid curves) with the ion density data obtained from a pure  $\text{C}_2\text{H}_2$  system in the trap-mode of operation. The  $\text{C}_2\text{H}_2$  pressure was  $1.35 \times 10^{-6}$  Torr.

efficiency for each collisional relaxation step. It was assumed in deriving the curves in these figures, that the nonreactive collisions occur at the collision limit,  $k = 1.1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ . We attempted to fit the data without including the nonreactive collisions and were unsuccessful in matching the delayed onset and the secondary ion abundances. This is demonstrated in Figs. 10 and 11.

### Test results

We conclude that the lack of evidence for association via bimolecular kinetics (radiative association) in the drift-mode for  $\text{C}_4\text{H}_2^+$  and  $\text{C}_4\text{H}_3^+$  ions obtained from  $\text{C}_2\text{H}_2$  is because these ions contain excess vibrational energy in this experiment. The excess energy can not be relaxed by either photon emission or collisions in the time of the experiment (1–2 ms). This effect is demonstrated by the zero intercept in Figs. 6 and 7. Therefore, Figs. 6 and 7 represent the reactions

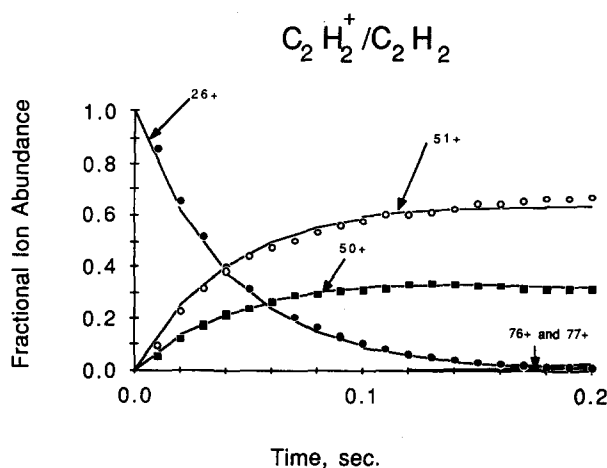


FIG. 8. A comparison of the computer model fit (solid curves) with the ion density data obtained in a pure  $\text{C}_2\text{H}_2$  system in the trap-mode of operation. The  $\text{C}_2\text{H}_2$  pressure was  $5.3 \times 10^{-7}$  Torr.

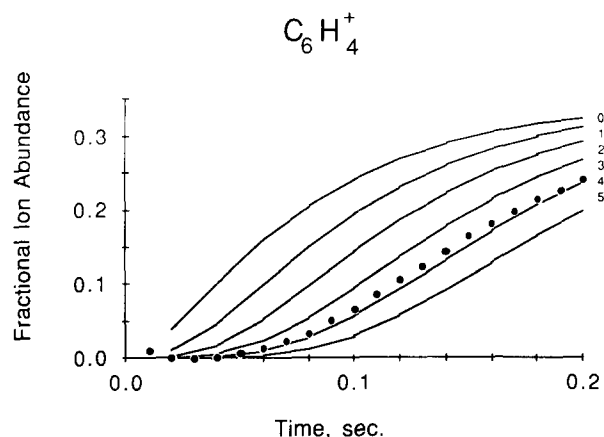


FIG. 10. A comparison of the computer model fit (solid curves) with the appearance of the association product  $\text{C}_6\text{H}_4^+$  showing the effect of internal energy in the reactant  $\text{C}_4\text{H}_2^+$  ion. The numbers by each curve refer to the number of nonreactive collisions between  $\text{C}_4\text{H}_2^+$  and  $\text{C}_2\text{H}_2$  used in the model. The  $\text{C}_2\text{H}_2$  pressure was  $1.35 \times 10^{-6}$  Torr.

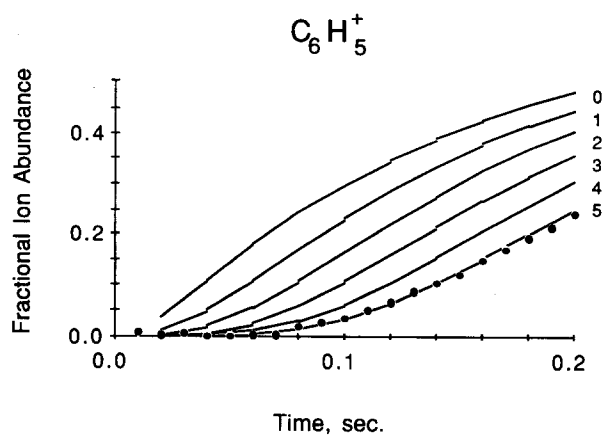
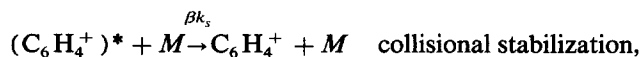
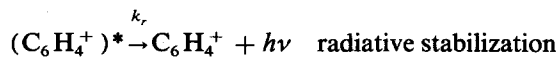
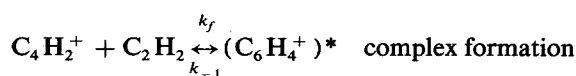


FIG. 11. A comparison of the computer model fit (solid curve) with the appearance of the association product  $C_6H_5^+$  showing the effect of internal energy in the reactant  $C_4H_3^+$  ion. The numbers by each curve refer to the number of nonreactive collisions between  $C_4H_3^+$  and  $C_2H_2$  used in the model. The  $C_2H_2$  pressure was  $1.35 \times 10^{-6}$  Torr.

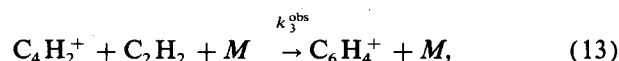
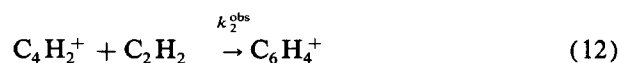
of the excited species  $(C_4H_2^+)^*$  and  $(C_4H_3^+)^*$ . The trap-mode results in Fig. 3 determined by the "peak ratio" method have rate constants that are well below the  $2.8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  measured for the ground state  $C_4H_2^+$  ion (trap mode, "simple ion loss"), because they are measured at a time when there were still a substantial number of excited species. In a typical rate constant measurement a plot like that shown in Fig. 1 is produced. It will be noticed that the first two data points are missing. A typical loss plot like Fig. 1 will have several initial points which lie below the regression line and they will usually be discarded. We believe that the ICR is generally able to measure reaction rate constants of ions having a near Boltzmann distribution of rotation and vibrational energies because we can wait long enough to allow the ions to relax in the ICR. Practically this is done by taking only the last points on the decay curve that have a linear decay. Figure 3 shows that if not enough time is allowed then an "incorrect" rate constant is determined. In this case, the rate constant measured is an average value and is slower than that expected because during the time of the experiment most of the ions are reacting at slower than the "thermal" rate. This is also assumed to be the reason why the measured rate constant for the  $C_4H_2^+/C_2H_2$  reaction in Ref. 7 was only  $1.4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ . These results are contrary to those found in most other types of ion-molecule reactions. Most other ion-molecule reactions are exothermic and have rates that proceed at the collision limit and are not very energy sensitive. In systems that exhibit bimolecular association, excess energy in the complex may hinder the radiative stabilization process.

#### Limits can be determined for the elementary rate coefficients in this model

The bimolecular and termolecular association reactions in the  $C_4H_2^+/C_2H_2$  system may be represented by the mechanism:



where  $\beta$  represents the fraction of collisions effective in producing stabilization. Solving the appropriate differential equations, we find that the observed rate coefficients  $k_2^{\text{obs}}$  and  $k_3^{\text{obs}}$  defined in the reactions



may be expressed in terms of the elementary rate coefficients,  $k_f$ ,  $k_{-1}$ ,  $k_r$  and  $k_s$  such that, as  $[M] \rightarrow 0^2$

$$k_2^{\text{obs}} = k_f k_r / (k_{-1} + k_r) \quad (14)$$

and

$$k_3^{\text{obs}} = k_f k_{-1} \beta k_s / (k_{-1} + k_r)^2. \quad (15)$$

It is possible to establish values for the elementary rate coefficients from the SIFT and ICR data available provided the following approximations are made

(i)  $k_s = k_{\text{coll}}$  where  $k_{\text{coll}}$  is the calculated collision rate for  $C_6H_4^+$  with the bath gas ( $k_{\text{coll}} = 9.7 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  for  $M = C_2H_2$ ).

(ii)  $\beta_{\text{abs}}(C_2H_2) \leq 1.0$ , for the parent gas.

(iii)  $k_2^{\text{obs}}$  ("saturated rate") in the SIFT  $\leq k_f$ . In the present case, the SIFT association rate of  $1.3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  has reached the Langevin rate and we therefore assume  $k_f = 1.3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  and define  $\tau = 1/(k_r + k_{-1})$ .

With these assumptions and approximations, the following conclusions are made for the  $C_4H_2^+/C_2H_2$  system. For  $\beta_{\text{abs}}(C_2H_2) = 1.0$

$$k_{-1} = 1.39 \times 10^4 \text{ s}^{-1}; k_r = 3.64 \times 10^3 \text{ s}^{-1}; \tau = 57 \mu\text{s}.$$

For  $\beta_{\text{abs}}(C_2H_2) = 0.1$

$$k_{-1} = 1.39 \times 10^3 \text{ s}^{-1}; k_r = 3.64 \text{ s}^{-1}; \tau = 570 \mu\text{s}.$$

The same quantities for the  $C_4H_3^+/C_2H_2$  system are

For  $\beta_{\text{abs}}(C_2H_2) = 1.0$

$$k_{-1} = 4.3 \times 10^4 \text{ s}^{-1}; k_r = 1.36 \times 10^4 \text{ s}^{-1}; \tau = 18 \mu\text{s}.$$

For  $\beta_{\text{abs}}(C_2H_2) = 0.1$

$$k_{-1} = 4.3 \times 10^3 \text{ s}^{-1}; k_r = 1.36 \times 10^3 \text{ s}^{-1}; \tau = 180 \mu\text{s}.$$

Studies on this system and other similar systems<sup>2</sup> show that collision complexes in association reactions that have relatively long lifetimes exhibit large termolecular rate coefficients for association. In the present case  $\tau \geq 57 \mu\text{s}$  for  $(C_6H_4^+)^*$  and  $\geq 18 \mu\text{s}$  for  $(C_6H_5^+)^*$ . Long lifetimes also favor radiative stabilization of the complex at low pressures and in the case of the  $C_4H_2^+/C_2H_2$  system, we find  $\sim 11\%$  of the collision complexes are stabilized by a bimolecular process and  $\sim 89\%$  revert to reactants at room temperature. Similarly, in the case of the  $C_4H_3^+/C_2H_2$  system, we find  $\sim 24\%$  of the collision complexes are stabilized by a bimo-

lecular process and  $\sim 76\%$  revert to reactants at room temperature. We note that the values calculated from the experimental data for  $k_{-1}$  and  $k_r$  depend on the collision efficiency  $\beta$ . It is usual to assume values of  $\beta$  close to 1.0 when vibrational energy is being transferred from the ion complex to the parent neutral but occasions can arise when very small values of  $\beta$  occur ( $< 0.1$ ), even for large parent neutrals with large dipole moments such as  $\text{CH}_3\text{CN}$ .<sup>22</sup>

## CONCLUSIONS

The association of  $\text{C}_4\text{H}_2^+$  and  $\text{C}_4\text{H}_3^+$  with  $\text{C}_2\text{H}_2$  exhibits its classical behavior in the pressure range  $5 \times 10^{-8}$  Torr to 0.4 Torr. At the very lowest pressures ( $10^{-8}$ – $10^{-6}$  Torr), bimolecular association is the major process and stabilization of the complex is presumed to occur by photon emission. As the pressure increases, more complexes are stabilized by collision than by radiation so the association exhibits termolecular kinetics. Under SIFT conditions with flow tube pressures ( $\sim 0.3$  Torr), almost all complexes are stabilized by collision before they can revert back to reactants and the association moves into the "pressure-saturated" regime thus exhibiting bimolecular kinetics. The termolecular associations observed in the systems studied in this work are all very rapid ( $> 10^{-23} \text{ cm}^6 \text{ s}^{-1}$ ) indicating long lifetimes with respect to unimolecular dissociation. Unimolecular lifetimes [ $\tau = 1/(k_r + k_{-1})$ ] estimated from the experimental data were  $> 57 \mu\text{s}$  for the  $\text{C}_4\text{H}_2^+/\text{C}_2\text{H}_2$  system and  $> 18 \mu\text{s}$  for the  $\text{C}_4\text{H}_3^+/\text{C}_2\text{H}_2$  system. Long lifetimes are a consequence of a deep potential well for the stabilized complex with respect to the reactant energies, and a large number of modes in the complex in which energy may be stored. In the  $\text{C}_4\text{H}_2^+ - \text{C}_2\text{H}_2$  reaction, the well depth is  $\sim 339 \text{ kJ mol}^{-1}$  and in the  $\text{C}_4\text{H}_3^+ - \text{C}_2\text{H}_2$  reaction it is  $\sim 318 \text{ kJ mol}^{-1}$  assuming in each case that the stabilized association products are the cyclic isomeric forms.<sup>23</sup> Internal energy in the reactant ion [ $(\text{C}_4\text{H}_2^+)^*$  or  $(\text{C}_4\text{H}_3^+)^*$ ] when produced by reaction of  $\text{C}_2\text{H}_2^+$  and  $\text{C}_2\text{H}_2$  prevents the complex surviving long enough in the drift-mode of operation for radiative stabilization to compete with unimolecular dissociation.

At low temperatures and pressures such as are found in interstellar clouds we would expect radiative association to be the major outcome of encounters between acyclic unsaturated hydrocarbon cations and unsaturated hydrocarbons

such as acetylene. We have found therefore that an efficient route via radiative association exists for unsaturated hydrocarbon cations to convert to aromatic structures in the presence of acetylene.

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