$C_3H_3^+$ Isomers: Temperature Dependencies of Production in the H_3^+ Reaction with Allene and Loss by Dissociative Recombination with Electrons

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Received: December 8, 2004; In Final Form: April 4, 2005

A technique has been developed to simultaneously determine recombination rate coefficients, α_e, and initial concentrations of ion types that coexist in a flowing afterglow plasma. This was tested using the H_3^+ + allene reaction in which two different $C_3H_3^+$ isomers are produced. Use of an electrostatic Langmuir probe enabled the $C_3H_3^+$ isomer branching ratios for propargyl and cyclic $C_3H_3^+$ from this allene reaction and their α_e to be determined over the temperature range 172−489 K. The study showed that the cyclic $C_3H_3^+$ to propargyl $C_3H_3^+$ branching ratios from the allene reaction varied from 50/50 at 172 K to 18/82 at 489 K. Over this temperature range, the α_e for both isomers change only slightly. The room temperature α_e values for propargyl and cyclic $C_3H_3^+$ are $(1.15 \pm 0.2) \times 10^{-7}$ and $(8.00 \pm 0.1) \times 10^{-7}$ cm^3/s, respectively. The data are discussed relative to current theories and in relation to fuel-rich flame chemistry, interstellar molecular synthesis, and modeling of Titan's atmosphere.

Introduction

A variable temperature flowing afterglow with an electrostatic Langmuir probe (VT-FALP) has previously been used in our laboratory to obtain temperature dependencies of recombination rate coefficients (α_e), including those for a series of hydrocarbon ions relevant to the interstellar medium[1]and Titan's atmosphere,[2,3] i.e., CH_5^+, $C_2H_5^+$, and $C_6H_7^+$ (protonated benzene),[4] as well as a calibration reaction with O_2^+. In these and all of our previous studies, situations have been chosen where one ion type has been dominantly produced in a proton-transfer reaction with H_3^+. However, in the H_3^+ dissociative proton-transfer reaction with allene ($H_2C_3H_2$), two isomeric ion types dominate the plasma, propargyl, and cyclic $C_3H_3^+$. This reaction has previously been studied by Milligan et al.[5] in a selected ion flow tube (SIFT) at room temperature, where the two isomeric forms of $C_3H_3^+$ were distinguished by their different reactivities with CH_3OH yielding a cyclic/propargyl $C_3H_3^+$ product ratio of 30/70. For flowing afterglow plasmas, we have developed techniques to separately determine the proportions of the two ion types coexisting in the plasma and their respective α_e values. Techniques have been developed previously by Rebrion-Rowe et al.[6] to determine α_e's for minority ions in flowing afterglow plasmas, but this requires use of a movable mass spectrometer together with the Langmuir probe. Our technique has been applied to the $C_3H_3^+$ isomers produced in the allene reaction over the temperature range 172−489 K. Over this range, the previously studied O_2^+, CH_5^+, $C_2H_5^+$, and $C_6H_7^+$ recombinations all show temperature-dependent behavior consistent with theoretical calculations.[4] In the present studies, the observed almost temperature independent behavior of the α_e is inconsistent with early theories of the direct[7] and indirect mechanisms,[8,9] but the observed behavior could be obtained if there was initial rovibrational excitation in the $C_3H_3^+$ isomers.[10] This temperature independent behavior of $C_3H_3^+$ is contrary to theoretical calculations of potential curves that have shown that there is a favorable dissociative curve crossing in the cyclic case,[11] implying that the direct mechanism would occur efficiently. No such crossing was predicted for the propargyl form.[12] From an applications point of view, $C_3H_3^+$ is an important ion in fuel-rich flame chemistry[13] and in complex hydrocarbon plasmas (see Table 1). It could also play an important role in the chemistry of the Titan ionosphere and in the interstellar synthesis and recombination of the two isomeric forms of $C_3H_3^+$ to form the ubiquitous cyclopropenylidene C_3H_2 in dense molecular clouds,[14] as well as a linear form (propadienylidene).

Experiment

A VT-FALP technique was used for all the present measurements, and this has been described in detail in the literature.[15,16] Thus, only an overview of the most important features of the technique will be given here. The available temperature range is 100−500 K for these experiments. Helium ions were generated using a microwave discharge to create ionization in a flowing helium carrier gas. Hydrogen was then added to the flow downstream of the discharge to produce a plasma with H_3^+ as the dominant ion by a standard reaction sequence.[4] Detailed models of the ion chemistry have been used to ensure that H_3^+ was the dominant ion present at the point where allene was injected into the flow and a downstream quadrupole mass filter was used to identify all ions present in the flow. At room temperature, H_3^+ reacts rapidly with allene by the dissociative proton transfer,[5]

$$H_3^+ + C_3H_4 \rightarrow c\text{-}C_3H_3^+ + 2H_2 \qquad [30\%] \qquad (1a)$$

$$\rightarrow p\text{-}C_3H_3^+ + 2H_2 \qquad [70\%] \qquad (1b)$$

where c-$C_3H_3^+$ and p-$C_3H_3^+$ are the cyclic and propargyl $C_3H_3^+$ ions, respectively.

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10.1021/jp0444159 CCC: $30.25

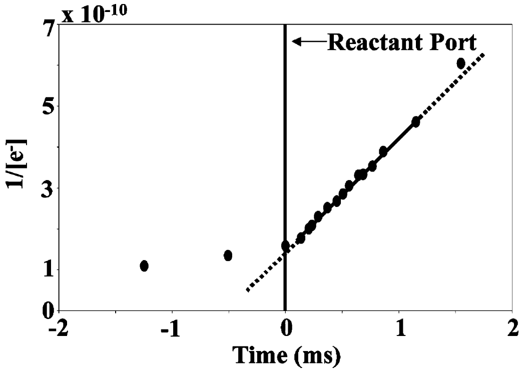


Figure 1. Plot of 1/[e^-] vs time showing the one linear region caused by the presence of a single ion $C_2H_5^+$ recombining at 400 K. Time zero is where the C_2H_6 was introduced into the flow and where subsequent recombination of the $C_2H_5^+$ begins. The upcurving at late times and low [e^-] is due to the increasing importance of diffusive ion loss.

These ions then begin to recombine with electrons simultaneously,

$$\text{c-}C_3H_3^+ + e^- \rightarrow \text{neutral products} \qquad (2)$$

$$\text{p-}C_3H_3^+ + e^- \rightarrow \text{neutral products} \qquad (3)$$

The ability to measure the electron density at any point along the flow tube, the reaction coordinate, using a Langmuir probe illustrates the beauty and simplicity of this technique (see Figures 1 and 2) and allows both recombination rate coefficients to be determined simultaneously. Techniques have been described previously in detail and used for the recombination of a single ion type.[4,15,16] Here, when the loss of a single ion type, x^+, is dominated by recombination, then

$$\frac{d[e^-]}{dt} = -\alpha_e[x^+][e^-] \qquad (4)$$

where [e^-] is the electron density and [x^+] is the ion density. For a quasi-neutral plasma, [e^-] = [x^+] and eq 4 can be integrated to yield

$$\frac{1}{[e^-]_{t,z}} - \frac{1}{[e^-]_0} = \alpha_e \frac{z}{v} \qquad (5)$$

where v is the ion velocity. Thus a linear plot (for example, Figure 1) of 1/[e^-]$_z$ versus time (z/v) would be expected, enabling the α_e to be determined.

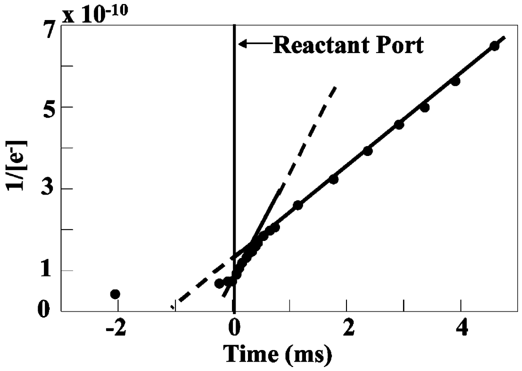


Figure 2. Plot of 1/[e^-] vs time showing two approximately linear regions caused by the presence of two simultaneously recombining isomers of $C_3H_3^+$ at 300 K. Time zero is where the allene was introduced into the flow and where simultaneous recombination of the $C_3H_3^+$ isomers begins.

However, in Figure 2, for $C_3H_3^+$ recombination, the 1/[e^-]$_z$ profile is not linear but reveals two approximately linear regions. This indicates the presence of two recombining ion types and further analysis for these particular recombinations was required.

Because the recombination of both ions is occurring simultaneously, eq 4 is not valid and numerical integration of the kinetic differential rate equation for the recombinations must be used to obtain an accurate determination of the individual α_e values; an analytical solution is not possible. For this situation, the kinetic differential rate equation is

$$\frac{d[e^-]}{dt} = -\alpha_{e,p}[p^+][e^-] - \alpha_{e,c}[c^+][e^-] \qquad (6)$$

where [p^+] and [c^+] are the ion densities, and $\alpha_{e,p}$ and $\alpha_{e,c}$ are the recombination rate coefficients for the propargyl and cyclic isomers, respectively. Numerically integrating eq 6 to fit the experimental data requires that the initial ion ratio and the recombination rate coefficients ($\alpha_{e,p}$) and ($\alpha_{e,c}$) are treated as unknowns.

$$\frac{d[p^+]}{dt} = -\alpha_{e,p}[p^+][e^-] \qquad (7a)$$

$$\frac{d[c^+]}{dt} = -\alpha_{e,c}[c^+][e^-] \qquad (7b)$$

The initial ion ratios [p^+]$_0$ and [c^+]$_0$ (the product ion ratios from the precursor H_3^+ + allene reaction) are related by the expressions

$$[c^+]_0 = f_c[e^-]_0 \qquad (8a)$$

$$[p^+]_0 = f_p[e^-]_0 \qquad (8b)$$

where f_c and f_p are the initial fractions of the cyclic and propargyl isomer (because there are only two ions created in the precursor reaction, $f_c = (1 - f_p)$). The analysis is only possible because of the charge neutrality:

$$[c^+] + [p^+] = [e^-] \qquad (9)$$

In the analysis, the three unknowns $\alpha_{e,c}$, $\alpha_{e,p}$, and $f_{c\text{ or }p}$, ([e^-]$_0$ and thus [c^+]$_0$ + [p^+]$_0$ are known, eqs 8a and 8b) were given numerical values and the changes in [e^-], [c^+], and [p^+] were determined for a small time interval (see eqs 6 and 7). From this, new [e^-], [c^+], and [p^+] were determined and again used in eq 6 to determine the changes in [e^-], [c^+], and [p^+] for the next time interval. In this way, variations of [e^-], [c^+], and [p^+] with time were generated. The values of the three unknowns were then varied to optimize the fit to the 1/[e^-] versus time experimental data. The best fit of this model to the experimental data at 300 K is shown in Figure 3 and was repeated on data at various temperatures.

In this way, $\alpha_{e,c}$, $\alpha_{e,p}$, [c^+]$_0$, and [p^+]$_0$ were determined as a function of temperature. The upward curvature of the data above the fit in Figure 3 (see also Figure 1) at lower densities occurs because diffusion becomes increasingly more important relative to recombination as the process of [e^-] decay proceeds. Because of the number of variables involved in the integration of eq 6, further fitting was performed at each temperature to determine the amount of error that is associated with this type of analysis. This sensitivity analysis showed that, if the initial ion distribution ($f_{c\text{ or }p}$) was varied by more than 3%, the experimental electron density profile could not be accurately fitted. In addition,

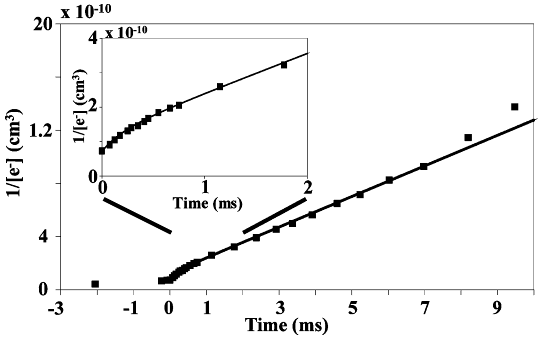


Figure 3. Plot of $1/[e^-]$ vs time showing the fit of two simultaneously recombining isomers of $C_3H_3^+$, at a temperature of 300 K. (α_e are $(1.15 \pm 0.2) \times 10^{-7}$ and $(8.00 \pm 0.1) \times 10^{-7}$ cm^3/s for propargyl and cyclic $C_3H_3^+$, respectively.) The fit was obtained by numerically integrating the differential rate eq 6. The inset is a magnified part of the plot at early times.

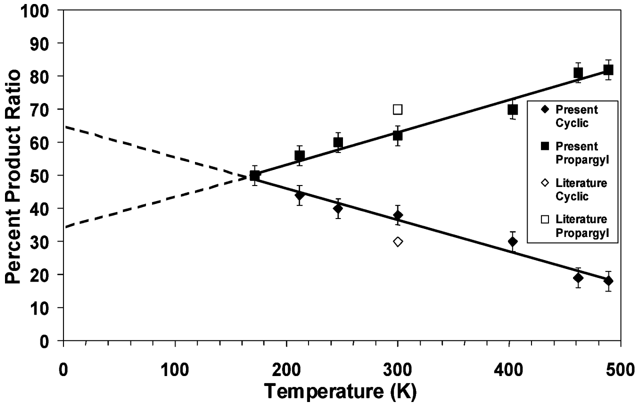


Figure 4. Temperature dependence of the ion distribution percentages for the propargyl and the cyclic $C_3H_3^+$ produced in the H_3^+ dissociative proton transfer with allene (C_3H_4). The linear fits are extrapolated to interstellar molecular cloud temperatures. Open symbols indicate previous data.[5]

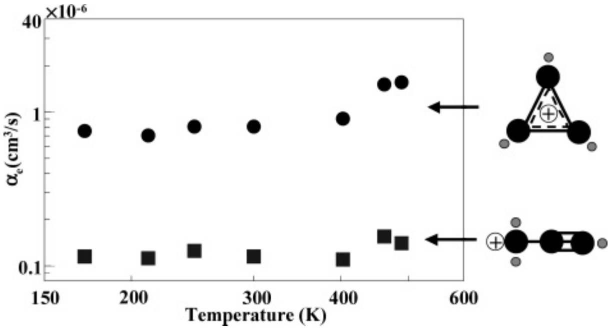


Figure 5. Plot of α_e versus temperature for the propargyl and cyclic $C_3H_3^+$ isomers.

changing the values of $\alpha_{e,p}$ and $\alpha_{e,c}$ by more than 8% also caused a poor fit, and with larger percentages the data could not be fitted at all. Measurements were made at temperatures varying from 172 to 489 K to determine the temperature dependencies of the α_e's (Figure 5) and of the initial ion concentrations $[c^+]_0$ and $[p^+]_0$, as generated in the H_3^+ + allene reaction (see Figure 4). All recombination rate coefficients are accurate to within ±15% at 300 K, and ±20% at all other temperatures. The initial ion distributions are accurate to within ±5 in the percentage.

Results and Discussion

$H_3^+ + C_3H_4$. The reaction of H_3^+ with allene has been studied previously at 300 K,[5] and this showed that two isomers of $C_3H_3^+$ are formed in a distribution of 30% cyclic to 70% propargyl $C_3H_3^+$. At room temperature, our initial ratio of the small α_e product to the large α_e product is 62% to 38% (see Figures 4 and 5), identifying the ions and showing that the less abundant cyclic form has the larger α_e. The product ion distribution at the lowest temperature of 172 K is 50/50. Then, these distributions show a trend tending toward a ratio of the cyclic over the propargyl form of 18/82 at the highest temperature of 489 K.

Pathways to the production of both isomers are exothermic, with the cyclic isomer formation having about 100 kJ/mol more excess energy than the propargyl ion formation. This is because the cyclic ion is more stable than the propargyl ion, so at low temperatures, production of the cyclic isomer is likely to dominate. Increasing the temperature of the reaction reduces the lifetime of the reaction intermediate complex and allows less time for the cyclic isomer to be produced, leaving the product as more of the less stable propargyl ion form. Thus, the propargyl form begins to dominate the plasma at $T > 172$ K.

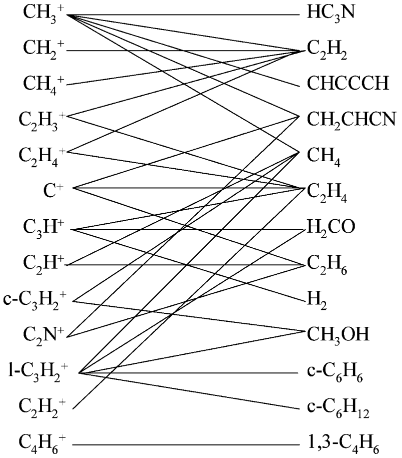
c/p-$C_3H_3^+ + e^-$. The α_e's for the c/p-$C_3H_3^+$ isomers show a slight increase at the higher temperatures (Figure 5). This is different from previous hydrocarbon data,[4] where the temperature dependence can be written as a simple power law dependence:

$$\alpha_e(T) = \alpha_e(300K)\left(\frac{T}{300K}\right)^X \tag{10}$$

Simple theoretical models have indicated X to be around −1.5 for the indirect mechanism,[8,9] and −0.5 for the direct mechanism.[7] Note that the calibration of the technique was checked by determining the temperature dependence of the well-known O_2^+ recombination and the data are absolutely in agreement with previous data.[4,17,18] However, temperature dependencies different from theory are not unique because they have been observed recently in flowing afterglow measurements for the N_2H^+ and HCO^+ recombinations.[19,20] The temperature dependence of the N_2H^+ data are consistent with previous data at $T \leq 300$ K,[21−24] but recent storage ring measurements of Geppert et al.[23] indicate that this trend continues at $T > 300$ K. Note that the N_2H^+ recombination rates obtained close to room temperature by Amano[21] and Geppert et al.[23] differ significantly, and in the opposite directions from four independent flowing afterglow measurements that are in good agreement.[19,22,24,25] In the N_2H^+ and HCO^+ recombinations, a tunneling mechanism could be invoked.[20] Alternatively, several Rydberg states could be accessed sequentially for which case, to the authors' knowledge, the X dependence in eq 8 has not been accurately determined theoretically.[26]

For $C_3H_3^+$, previous experimental values of α_e have been obtained which were concluded to be for c-$C_3H_3^+$ at 300 K[27] and at 2000 K[13] and were found to be $(7 \pm 2) \times 10^{-7}$ and 1×10^{-7} cm^3/s, respectively. Thus the α_e at 300 K is consistent with the present study. No information is available to compare with the high-temperature measurements. The cyclic isomer recombines at a consistent rate that is a factor of 6 larger than that of the propargyl isomer; α_e's at room temperature are $(8.00 \pm 0.2) \times 10^{-7}$ and $(1.15 \pm 0.1) \times 10^{-7}$ cm^3/s for the cyclic and the propargyl $C_3H_3^+$, respectively. This difference is not unexpected because there is evidence that a favorable dissociative curve crossing exists for the cyclic[11] and not for the propargyl[12] form. At the highest temperature of 489 K, there is a thermal vibrational population above the vibrational ground state of 33% (the vibration spacings were obtained from previous

TABLE 1: Hydrocarbon Ion−Molecule Reactions That Produce $C_3H_3^+$ as the Dominant Ion[31,a]



[a] The lines join the reacting combinations.

work by Rehfuss et al.[28]) and this could explain the slight increase in the α_e at the higher temperatures, but at the lower temperatures the thermal vibrationally excited population is negligible and yet there is still temperature independent behavior. The initial rovibrational population from the reaction is difficult to determined experimentally, although the recombining ions are expected to be thermalized in collisions with allene; why both of these hydrocarbon ions have little to no temperature dependence, compared to previous work for other recombinations,[4] is still an open question.

$C_3H_3^+$ has been shown to be an important ion in fuel-rich flames.[29] The production of this ion has been considered to be a precursor to soot formation.[30] Its abundance is not surprising because it can be produced in a large number of hydrocarbon reactions (Table 1).[31] The present recombination data should provide insight into the mechanisms that occur in combustion flames.

The data have relevance to the observed abundance ratio of the cyclic-C_3H_2 to linear H_2CCC (propadienylidene) forms in the cold cloud TMC-1, where the ratio is about 30/1.[14] A possible formation mechanism for these species has been attributed to the association reaction $C_3H^+ + H_2$ followed by dissociative recombination of the $C_3H_3^+$ isomers.[32] The recombination products of $C_3H_3^+$ (isomeric form not identified) have been determined experimentally in a storage ring showing C_3H_X channels to be dominant, where X could be 1 or 2.[33] However, it is also possible that the H_3^+ + allene reaction and a myriad of other reactions[31] (see Table 1) could also contribute.

This observed abundance ratio might be not only due to the difference in the recombination rate coefficients, i.e., a factor of 6 larger for the cyclic isomer, but also due to the ion distribution trend for reactions such as the allene reaction (see Figure 4), which if extrapolated to low temperatures (around 10 K for a cold molecular clouds), would give cyclic/propargyl ratios of 65/35 in the direction of the observations.

$C_3H_3^+$ has been included in models of the Titan ionosphere as a major ion.[2] $C_3H_3^+$ has also been observed as the dominant ion produced in many ion−molecule hydrocarbon reactions including those of the hydrocarbon ions and neutrals thought to be present in the Titan atmosphere and is produced in numerous other ion−molecule reactions (Table 1).[31] As in the allene reaction, $C_3H_3^+$ might be expected to be produced in different isomeric forms in these other reactions. c-$C_3H_3^+$ ion is very stable and does not react with many abundant neutrals within that atmosphere, i.e., not with H_2, N, N_2, NH_3, CH_4, C_2H_2, C_2H_4, C_3H_4, or c-C_6H_6, and would thus be available for recombination. Note though that p-$C_3H_3^+$ reacts at about the gas-phase kinetic rate with NH_3, C_2H_2, C_2H_4, and c-C_6H_6,[31] and could thus be rapidly destroyed.

Conclusions

The recombination rate coefficients, α_e's, for cyclic and propargyl $C_3H_3^+$ and the $C_3H_3^+$ product ion distributions for the reaction of H_3^+ with C_3H_4 (allene) have been obtained over the temperature range 172−489 K. The α_e of the cyclic isomer exceeds the α_e of the propargyl isomer by a factor of 6, α_e's averaging 8.5×10^{-7} and 1.5×10^{-7} cm^3/s for the cyclic and the propargyl $C_3H_3^+$, respectively, over this temperature range. This difference is consistent with recent theoretical work on the ion and dissociative neutral potential curves crossings.[11,12] However, that the α_e for the two $C_3H_3^+$ isomers have little temperature dependence over this temperature range, is inconsistent with simple theory. This may be attributed to an initial thermal vibrational excitation of the $C_3H_3^+$ ions, but this is the first time that such behavior has been observed experimentally for hydrocarbon ions using a VT-FALP. It is interesting that the product ion distributions for the precursor $H_3^+ + C_3H_4$ reaction could be obtained by numerical analysis of the recombination differential rate equation, and that these distributions change with temperature from a 50/50 cyclic/propargyl ratio at the lowest temperature of 172 K to a ratio of 18/82 at the highest temperature of 489 K. This is the first time that recombination rates and isomeric product ion distributions of ion−neutral reactions have been simultaneously obtained.

Acknowledgment. Funding under NASA Grant No. NAG5-8951 is gratefully acknowledged.

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