Dissociative recombination of hydrocarbon ions

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Abstract. Rate constants and product distributions have been measured for a number of hydrocarbon ions at the CRYRING facility at the Stockholm University. Rate constants at 300 K are about 5×10⁻⁷ cm⁻³ s⁻¹. The electron temperature dependences are also roughly constant and follow a power law. The products appear to correlate with reaction exothermicity.

1. Introduction
Dissociative recombination of hydrocarbon ions is important to a number of applications including interstellar chemistry (see several papers in this volume) and plasma assisted combustion [1]. Flying reusable aircraft at hypersonic speeds (> Mach 5) using airbreathing engines is very difficult, particularly if a hydrocarbon fuel is used. Plasmas injectors are being considered in order to help speed the combustion and improve performance. In this scheme, air is ionized as it is introduced into the engine, and the air plasma ions react with the hydrocarbon fuel to produce various hydrocarbon ions. The chemistry involved has been modeled and the ignition delay time has been calculated as a function of the ionization level [1,4]. The modeling has assumed that the termination step for neutralizing the plasma involves dissociative recombination where a single H atom is released. Ionization levels >10⁻⁶ were found to improve performance. Approximately 80% of the improvement in performance was attributed to production of free radicals; much of that through dissociative recombination. The type of radical had only a small effect. Thus, an important parameter is the number of radicals formed. The first product measurements of dissociative recombination showed that three-body breakup was much more important than previously considered [2] by modelers [3]. Since it has been difficult to determine even overall trends, it has therefore become necessary to measure as many reactions as possible.

We began a systematic study of the dissociative recombination of hydrocarbon ions, starting with C₂ species and recently progressing to s-C₃H(D)₇⁺ and t-C₄D₉⁺. The latter ion is large enough that it is not possible to experimentally identify all product channels, i.e. the number of H(D) atoms lost. Therefore, finding ways to extrapolate the low mass results is important. Here we present an overview of the results, paying particular attention to trends that might lead to a predictive capability and also to the number of radicals produced in a recombination.

2. Experimental
The experiments were performed at CRYRING [5]. The techniques used are standard for that facility, and only a few details are described here. Ions are created in an external source, injected into the ring, and accelerated to the maximum beam energy for that particular mass. Electrons are produced and merged with the ions in an electron cooler. The electrons have a transverse and longitudinal velocity...
spread corresponding to 2 and 0.1 meV, respectively. The ions are allowed to cool radiatively and through collisions with the electrons for several seconds, after which time they are assumed to have a 300 K vibrational temperature and an unknown rotational temperature. Ions and electrons interact for 85 cm per revolution. Cross sections were measured as a function of energy by varying the electron energy, which also requires that absolute measurements of both the ion and electron current are made. Low energy cross sections are obtained by a deconvolution process that includes an end correction for the toroidal field of the electron magnet. Rate constants are derived as a function of electron temperature by integrating the cross sections over Boltzmann energy distributions.

Branching fractions are measured at nominally zero energy by inserting a 30% transparent grid just before the surface barrier detector. For each recombination event, all, some, or none of the particles may pass through the grid and reach the detector. Since the detector is sensitive to the total amount of energy deposited in a short time a probability matrix involving the possible fragment masses and product channels allows the branching fractions to be determined. For example, if all the particles pass through the grid, a signal is found at the full beam energy and if an H atom hits the grid, the signal is found at \((X-1)/X\) of the full beam energy, where \(X\) is the total mass of the ion. For small molecular systems the detector has enough resolution to distinguish between channels that lose one and two hydrogen atoms. More massive ions are injected into the ring at a lower beam energy, which also reduces the ability to distinguish such channels. Resolution is regained by substituting D for H. However, for \(\text{C}_4\text{D}_9^+\) it was not possible to separate such channels (unpublished data). The isomers were controlled by appropriate choice of the precursor molecule, e.g. \(\text{t-C}_4\text{D}_9\text{-Br}\) was used to generate \(\text{t-C}_4\text{D}_9^+\).

3. Results and discussion

Derived rate constants for dissociative recombination of hydrocarbon ions containing at least two carbon atoms are shown in table 1. Both the measured 300 K rate \(k_{300}\) and the \(n\) value in a power law fit, \(\alpha = k_{300} (300/T)^n\), are shown. Generally, the 300 K rate constants are in the mid \(10^{-7}\) range, and the variation is within a factor of two. The notable exception is the value for \(\text{s-C}_3\text{H}_7^+\) which is considerably larger. This is in contrast to the rate constant for the deuterated species, which is almost four times smaller. Rate constant measurements made elsewhere are more in line with the other species, perhaps suggesting there may have been an error in that measurement at CRYRING. In re-examining the data, it was found that the normal procedure used to derive the absolute rate constant could not be used in that case; a double normalization of the signal was used instead to place the measurements on an absolute basis. This may have caused a larger error than was believed at the time of the measurements.

The electron temperature dependence is also remarkably similar for all species. The range of \(n\) varies only from 0.59 to 0.84. The average value is 0.74 with a standard deviation of only 0.08. While

| Species        | \(k_{300} [10^{-7}\text{ cm}^{-3}\text{s}^{-1}]\) | \(n\) | Reference | Other results for \(k_{300}\) [10^{-7} cm^{-3}s^{-1}] |
|----------------|---------------------------------------------|---|-----------|-------------------------------------------------|
| \(\text{C}_2\text{H}^+\) | 2.7 | 0.76 | [6] |  |
| \(\text{C}_2\text{H}_3^+\) | 5.0 | 0.84 | [7] |  |
| \(\text{C}_2\text{H}_4^+\) | 5.6 | 0.76 | [6] |  |
| \(\text{C}_2\text{D}_5^+\) | 2.8 | 0.81 | [8] | (6.0; 9.0; 7.512)* [9-11] |
| \(\text{s-C}_3\text{H}_7^+\) | 19 | 0.68 | [13] | 8.3 [9] |
| \(\text{s-C}_3\text{D}_7^+\) | 5.8 | 0.73 | unpublished |  |
| \(\text{t-C}_4\text{D}_9^+\) | 5.8 | 0.59 | unpublished | 8.3* [9] |

* for the non-deuterated species
this difference is outside the error of the measurements, it appears reasonable to use the average value for species for which no measurement exists. The recent work of Adams and coworkers [11] shows a true temperature dependence below 300 K that is in good agreement with this value, indicating that internal temperature does not change the dependence to a significant degree below 300 K. In contrast, they measured a steeper temperature dependence above 300 K, which may indicate that vibrational excitation decreases the rate constants.

Most of the complete product distributions for hydrocarbon ions were made at CRYRING. Table 2 shows the product distributions for the entire C2Hn+ series (n = 1-5) where the channels are described by the type of chemical process taking place. Loss of a single H atom is the dominant channel for n = 1 and 2 and decreases substantially for the largest species. Loss of two H atoms becomes important as soon as it is possible (n = 2) and becomes the dominant channel for n = 3 and 4. For C2H4+ this channel by far dominates at 84%. At first glance it appears that this channel decreases substantially for C2D5+. However, that is because other multiple H loss channels become important. Particularly interesting is the observation of the first four-body breakup for a molecular ion, producing C2H2 and three H atoms. Equally intriguing is the observation of a large (29%) related channel producing H2 and H. Breaking the C-C bond is infrequent, accounting for less than 18% in all ions except C2H+. As mentioned in the introduction, a key parameter for combustion modeling is the number of radicals produced in a recombination. The average number of radicals produced has a surprisingly narrow range, 1.9-2.3. There is no obvious reason for this consistency. Three and four body dissociation channels dominate for n = 3 and larger.

Table 3 shows the product distributions for C3H7+ [13] and C3D7+ (paper in preparation). The derivation for C3H7+ was very difficult since the detector did not allow the congested pulse-height spectrum to be well resolved and because of the need to estimate the fraction of H atoms that missed the detector due to the large exothermicities. Due to these limitations, it was difficult to distinguish between channels that differ only in the number of hydrogen atoms lost. Therefore, what appears to be major differences between the two ions can best be ascribed to problems in determining the number of H atoms lost for C3H7+. However, the difference in the fraction where a C-C bond breaks appears to be real. Using the C3D7+ branching fractions, we have not been able to reproduce the amount of C-C bond breaking in C3H7+ raw data. The amount of C-C bond breaking in C3H7+ (35%) agrees well with the value of Angelova et al. [14] who found 33%. The C3D7+ value is 44%. The C3D7+ results show no channel that clearly dominates over the others. Two channels account for about 21-22% each of the products and numerous other channels account for the remainder. A large amount of D2 is formed, 42%. The number of radicals formed per recombination event is 1.7 for both systems.

| Channel description       | C2H+ [6] | C2H2+ [12] | C2H3+ [7] | C2H4+ [6] | C2D5+ [8] |
|---------------------------|---------|-----------|-----------|-----------|-----------|
| H loss                    | 43      | 50        | 29        | 11        | 12        |
| 2 H loss                  | n/a     | 30        | 59        | 66        | 27        |
| H2 loss                   | n/a     | 2         | 6         | 6         | 0         |
| H + H2 loss               | n/a     | n/a       | 3         | 10        | 29        |
| 3 H loss                  | -       | -         | -         | -         | 13        |
| C-C break                 | 39      | 13        | 3         | 4         | 17        |
| C-C break + H loss        | 18      | -         | -         | -         | -         |
| C-C break + other         | n/a     | 5         | 0.6       | 3         | -         |
| Sum C-C break             | 57      | 18        | 3.6       | 7         | 17        |
| Sum 3-body                | 18      | 30        | 62        | 76        | 71        |
| <# Radicals>              | 2.17    | 2.27      | 2.27      | 1.89      | 1.98      |

* includes four body channel
The data set for small hydrocarbon ion recombination is now large enough that trends may be examined in order to predict results for species that have not yet been measured. Because ratios of the branching into different channels are more sensitive than branching fractions or percentages, we have made a number of correlations of the measured branching ratios with exothermicities. For hydrocarbon ions, figure 1 shows the ratio of the sum of all channels that lose at least two H’s to the single H atom channel. Channels that lose H\textsubscript{2} are included in the numerator. The data fit a linear function quite well if CH\textsubscript{5}\textsuperscript{+} is excluded. That ion has a non standard structure so there is reason it might be excluded. A smaller deviation is found for C\textsubscript{2}D\textsubscript{5}\textsuperscript{+}, for which three H atom loss was quite important. We attach no particular theoretical significance to the correlation at present. An exponential correlation also provided reasonable results.

Figure 1 also includes several non-hydrocarbon species involving only first row elements. In general, these show the same general trend but with larger deviations. NH\textsubscript{2}\textsuperscript{+} is an obvious exception. The fact that both CH\textsubscript{2}\textsuperscript{+} and NH\textsubscript{2}\textsuperscript{+} deviate negatively from the line may be related to the fact that the multiple H loss channel does not leave a molecular species. In that case, kinematic constraints become important since all energy must be deposited into translation or discrete quanta of electronic excitation, i.e. rotations and vibrations are not available to soak up small amounts of energy.

Figure 2 shows the ratio of single H-C bond breaking to C-C bond breaking vs. the ratio of the exothermicities for the two channels. Only channels where more than a single H bond was broken are included but all C-C bond breaking channels are included. Again, the data appear to satisfy an exponential relationship to which we attach no particular significance at present. The correlation coefficient is high (R=0.95), and the data vary from a ratio of 0.3 to 7, a wide range. Over that range, the exothermicity ratio changes from under 1 to over 5. No point is more than 50% from the fit and many are better than that. Possibly, the broad range will make the fit applicable to most hydrocarbons.

In order to further improve the fit, we tried several simple corrections to account for the complexities of the various ions. The most successful one was to multiply the exothermicity ratio by the number of atoms in the ion. The results are shown in figure 3. If one excludes C\textsubscript{2}H\textsuperscript{+}, the data follow a power law; the correlation coefficient is 0.99. A correction for the complexity of the ion allows for internal excitation of the molecular fragments. More atoms allow for much more vibrational excitation. We did not find that a similar correction for the number of H atoms lost produced a better fit.
Figure 1. Product ratio for channels where two or more hydrogens are lost to the one for a single H loss vs. exothermicity for 2 H loss. Channels that lose H₂ are counted in the numerator. Hydrocarbon ions are shown as solid points and other systems as open circles [6-8,12,16-20]. The line is a linear least squares fit to the hydrocarbon data excluding CH₅⁺.

Figure 2. Ratio of the branching fraction for single H loss to that of simple C-C cleavage vs. the ratio of the exothermicities for the two processes. The line is a least squares fit to an exponential function.
Figure 3. Ratio of the branching fraction for single H loss to that of simple C-C cleavage vs. the ratio of the exothermicities for the two processes times the number of atoms in the ion. The line is a least squares fit to a power function and excludes the C$_2$H$^+$ datum.

4. Conclusions

We have attempted to identify trends with predictive power for rates and product distributions of hydrocarbon ion dissociative recombination. The 300 K value of the rate constants measured at CRYRING have been found to vary little with species and the electron temperature dependences follow power laws $T^{-n}$ with $n$ in the range of 0.59-0.84. Flowing afterglow Langmuir probe data [11] as a function of true temperature indicate a break in the data above 300 K, which may indicate that vibrational excitation diminishes the rate constants. In any case, the range is narrow, and taking average values should enable good estimates for unknown species.

Product ratios appear to be governed primarily by exothermicities. The ratio of multiple H loss to single H loss increases with the exothermicity for the second H atom loss. Three atom systems appear to be exceptions, possibly due to kinematic constraints. Similarly, the ratio of simple H loss to C-C bond breaking increases exponentially with the ratio of the exothermicities. The correlation is improved further if one accounts for the complexity of the ion.

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