Branching ratios for the dissociative recombination of hydrocarbon ions

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Abstract. Branching ratios for the recombination of hydrocarbon ions have been measured using the ASTRID storage ring electron cooler. These studies have concentrated upon the competition of channels where the carbon skeleton of the molecule is left intact with other channels where carbon-carbon bonds are broken. A discussion of the effects of initial molecular structure on the resulting dissociation pattern is given.

1. Introduction

The dissociative recombination of hydrocarbon ions is a subject of importance to many areas including nuclear fusion research [1], plasma deposition techniques [2], interstellar chemistry [3, 4] and combustion chemistry [5]. Cross sections for the dissociative recombination of light hydrocarbon ions have been measured using the single pass merged beams technique [6] and the storage ring method [5]. Rate coefficients for a wide variety of hydrocarbon ions have been measured using flowing afterglow experiments and these are reviewed in [7]. Up until now there has been a lack of information concerning the branching ratios for the final channels for these processes but recent experiments at the CRYRING and ASTRID storage rings have largely rectified this situation. The latter experiments are discussed in this paper while those at CRYRING are reviewed in [5].

2. Experimental method

Branching ratios for the dissociative recombination of hydrocarbon ions with the general formula C2Hm+3, C3Hm+4 (m = 1–8) and C4Hm+5 (m = 1–9) have been measured by us using the electron cooler at the ASTRID ion storage ring [8–10], shown in figure 1, and full details of the measurement technique have been given in these references.

Briefly, mass selected ions were injected into the storage ring where they were accelerated to 2.5 MeV, a process that takes about 4 seconds to achieve. An electron beam is merged with the ion beam in the electron cooler and the velocity of the electrons can be varied to yield a range of center-of-mass collision energies from 0 to tens of eV. Neutrals, produced during passage of the ion beam in the straight section, A–D, pass undeflected through the dipole magnet D and are detected by an energy sensitive surface barrier detector. These neutrals arise due to electron-ion interactions but also through charge changing
processes with the background gas in the ring. The latter are minimized by maintaining the ring at ultra high vacuum ($10^{-11}$ Torr) and are separated from the electron-ion signal by chopping the electron beam on and off and modulating the detection system so that signals are separately counted with the electrons on and off, respectively. The neutral fragments arising from the various collision processes carry kinetic energy to the detector that is proportional to their mass. The detector is energy sensitive and so can distinguish the total mass of the neutral fragments, when they arrive for individual events by emitting pulses whose height is proportional to the deposited energy.

Figure 2 shows the pulse height spectra obtained when $C_4H^+$ ions are used. The points are obtained when the electron beam is on while the solid curve shows the spectrum with the electrons off. The surface barrier detector used did not have sufficient energy resolution to distinguish hydrogen atoms either free or attached to carbon atoms. The measurements therefore determined just the relative distributions of carbon atoms among the dissociation products. When the molecular ion collides with the background gas forming both neutral and ionic fragments, the latter are deflected by the dipole magnet D and do not reach the detector so the fragments are dispersed across the pulse height spectrum according to their mass as shown in the figure, giving rise to peaks I to III. In recombination collisions (and in ion-gas charge exchange collisions) however, the molecular ion is completely neutralized to form fragments that will arrive simultaneously, yielding signals in peak IV that correspond to the primary beam energy (2.5 MeV). The difference seen in peaks IV of the two spectra (electrons on – electrons off) is due to the recombination signal and can be used to determine the relative recombination cross section. It provides no information, however, about the branching ratios for the various possible final dissociation channels for the recombination process.
In order to distinguish between the final channels of the recombination reactions, a grid (transmission \( T \)) was placed in front of the detector to prevent some of the recombination products from arriving. Omitting the H atoms, one can represent the reactions as follows:

\[
\begin{align*}
e^- + C_2^+ & \rightarrow C_2 \quad (1a) \\
& \rightarrow C + C \quad (1b) \\
\end{align*}
\[
\begin{align*}
e^- + C_3^+ & \rightarrow C_3 \quad (2a) \\
& \rightarrow C_2 + C \quad (2b) \\
& \rightarrow C + C + C \quad (2c)
\end{align*}
\[
\begin{align*}
e^- + C_4^+ & \rightarrow C_4 \quad (3a) \\
& \rightarrow C_3 + C \quad (3b) \\
& \rightarrow C_2 + C_2 \quad (3c) \\
& \rightarrow C_2 + C + C \quad (3d)
\end{align*}
\]

where it must be remembered that the channels 1a, 2a and 3a involve the loss of one or more hydrogens and that hydrogen atoms can be attached to the products in the other channels, appear as separate atoms, or be combined in hydrogen molecules according to the particular ion species under study. If we consider the recombination processes associated with for example \( C_4^+ \), i.e. reactions 3a–3d, we can write down a series of equations that yield the number of counts that appear in peaks I–IV, respectively:

\[
\begin{align*}
N_I &= T(1-T)N_{3b} + 2T(1-T)N_{3d} \quad (4a) \\
N_{II} &= 2T(1-T)N_{3c} + \{T(1-T)^2 + T^2(1-T)\}N_{3d} \quad (4b) \\
N_{III} &= T(1-T)N_{3b} + 2T^2(1-T)N_{3d} \quad (4c) \\
N_{IV} &= TN_{3a} + T^2N_{3b} + T^2N_{3c} + T^3N_{3d} \quad (4d)
\end{align*}
\]

where \( N_{3a}, N_{3b}, N_{3c} \) and \( N_{3d} \) are the fractions of the total number of recombinations that yield channels 3a, 3b, 3c and 3d, respectively. If some of the lighter fragments with only a single carbon atom fly apart too far from the primary beam direction and are not counted by the detector, this loss can be taken account of by modifying the above equations [8]. As seen in figure 2, however, there is no indication there of such a loss as differences appear only in peak IV when no grid is used. This was checked for all the measurements presented here.

Figure 3 shows a typical pulse height spectrum with a grid in place. The spectrum shows only the difference between the data collected with the electrons on and the electrons off, i.e. only recombination signals. It is seen that the signals are now distributed between peaks II and IV with little signal appearing in peaks I and III. Just by inspection, one can say, therefore, that in this case (\( C_4^+ \)) the main recombination channels are those that leave the \( C_4 \) skeleton intact (probably involving a loss of one or more hydrogens) and those where two \( C_2 \) fragments are formed, arising from the breaking of a carbon-carbon bond. The exact branching ratio can be determined from equations (4a)–(4d). In this case it was found that 78% of recombinations involved leaving the \( C_4 \) skeleton intact and 18% yielded \( C_2 \) pairs. Just 4% of recombinations yielded a \( C_3 + C \) pair.

3. Results and discussion

The results obtained for the branching ratios for recombination of \( C_2H^+_m \), \( C_3H^+_m \) \((m = 1–8)\) and \( C_4H^+_m \) \((m = 1–9)\) are listed in tables 1–3. All of the above data were taken at zero center-of-mass energy, i.e. where the electron velocity was equal to the ion velocity. Values in parentheses are data from CRYRING.
It is seen that, once a third carbon atom is added, the possibility of breaking a carbon-carbon bond increases, and this becomes especially true the more hydrogens are present. Two notable exceptions are \( \text{C}_3\text{H}^+ \) and \( \text{C}_4\text{H}^+ \) which exhibit much more C-C breaking than when the carbon skeleton has a few more hydrogen atoms attached. These ions would be very good candidates for theoretical study and their recombination is very important for astrophysical models since \( \text{C}_3 \) and \( \text{C}_4 \) have been identified in the interstellar medium.

**Table 1.** Branching ratios for carbon skeleton structures in DR of \( \text{C}_2\text{H}^+_3 \) ions determined in this work (Values in parentheses are from CRYRING [11])

| Species    | \( \text{C}_2 \) | \( \text{C} + \text{C} \) |
|------------|-----------------|-----------------|
| \( \text{C}_2\text{H}^+_3 \) | 0.965 (0.964) | 0.035 (0.036) |

**Table 2.** Branching ratios for carbon skeleton structures in DR of \( \text{C}_3\text{H}^+_m \) ions determined in this work (Values in parentheses are from CRYRING [12, 13])

| Species    | \( \text{C}_3 \) | \( \text{C}_2 + \text{C} \) |
|------------|-----------------|-----------------|
| \( \text{C}_3\text{H}^+ \) | 0.66 | 0.34 |
| \( \text{C}_3\text{H}_2^+ \) | 0.875 | 0.125 |
| \( \text{C}_3\text{H}_3^+ \) | 0.91 | 0.09 |
| \( \text{C}_3\text{H}_4^+ \) | 0.9 (0.87) | 0.1 (0.08) |
| \( \text{C}_3\text{H}_5^+ \) | 0.87 | 0.13 |
| \( \text{C}_3\text{H}_6^+ \) | 0.69 | 0.31 |
| \( \text{C}_3\text{H}_7^+ \) | 0.67 (0.63) | 0.33 (0.32) |
| \( \text{C}_3\text{H}_8^+ \) | 0.68 | 0.32 |

**Table 3.** Branching ratios for carbon skeleton structures in DR of \( \text{C}_4\text{H}^+_m \) ions determined in this work

| Species    | \( \text{C}_4 \) | \( \text{C}_3 + \text{C} \) | \( \text{C}_2 + \text{C}_2 \) |
|------------|-----------------|-----------------|-----------------|
| \( \text{C}_4\text{H}^+ \) | 0.44 | 0.28 | 0.28 |
| \( \text{C}_4\text{H}_2^+ \) | 0.78 | 0.04 | 0.18 |
| \( \text{C}_4\text{H}_3^+ \) | 0.76 | 0.06 | 0.18 |
| \( \text{C}_4\text{H}_4^+ \) | 0.77 | 0.06 | 0.17 |
| \( \text{C}_4\text{H}_5^+ \) | 0.46 | 0.09 | 0.45 |
| \( \text{C}_4\text{H}_6^+ \) | 0.59 | 0.09 | 0.32 |
| \( \text{C}_4\text{H}_7^+ \) | 0.20 | 0.65 | 0.15 |
| \( \text{C}_4\text{H}_8^+ \) | 0.30 | 0.64 | 0.06 |
| \( \text{C}_4\text{H}_9^+ \) | 0.58 | 0.4 | 0.02 |

**Figure 3.** The difference in the pulse height spectra (electrons-on minus electrons-off) for \( \text{C}_4\text{H}_7^+ \) taken with a grid in place. This ion recombines to yield primarily fragments with four carbon atoms (\( \text{C}_4 \)) or with two carbon atoms each (\( \text{C}_2 + \text{C}_2 \)).
For most of the ions that were in linear isomeric form, the fragmentation patterns were predictable from the structure of the parent ion. In the absence of other information, we shall assume that the ion \( \text{C}_4\text{H}_2^+ \) in its lowest state has a similar isomeric form to that of the neutral radical \( \text{C}_4\text{H}_2 \), the structure of which is shown in figure 4. It would seem natural then that this ion would either recombine by losing one or more hydrogen atoms, leaving the carbon skeleton intact (i.e., to form a \( \text{C}_4 \) fragment) or that the central single bond would break yielding a pair of \( \text{C}_2 \) fragments. This is reflected in the branching fractions with 78\% going to \( \text{C}_4 \) and 17.7\% to \( \text{C}_2 + \text{C}_2 \).

For the case of \( \text{C}_4\text{H}^+ \), the situation is less obvious. The most stable isomeric forms of this ion are shown in figure 5 and since they are very close in energy we must assume that both are present in our ion beam. Clearly the cyclic form is most likely to fragment by losing one or more hydrogen atoms, while leaving the carbon skeleton intact. For the linear form however, one could say that it has also the possibility of breaking the central single bond while the fracture of one of the triple bonds would seem unlikely. In fact it is found (see table 3) that the channel that involves breaking one of the triple bonds (i.e. \( \text{C}_3 + \text{C} \)) is just as likely as the \( \text{C}_2 + \text{C}_2 \) channel. It must be remembered, however, that the structures shown in figure 5 refer to the ion and that if the recombination occurred by the indirect process, i.e., via the formation of a high lying Rydberg state, this might rearrange to another isomeric form of the neutral prior to dissociation so that the dissociation pattern could be quite different. Indeed, it has been shown by calculation that, as the \( \text{C}_4\text{H} \) radical becomes electronically excited, the triple bonds elongate (become weaker) while the single bond maintains its length. Thus, for highly excited states, the triple bonds might be more likely to break, yielding the \( \text{C}_3 + \text{C} \) products.

For cyclic isomers the situation is also not clear and indications are that ring opening may occur prior to dissociation. \( \text{C}_3\text{H}_3^+ \) is an ion that in its most stable form, cyclopropenyl, is cyclic though it does have a linear isomer, propargyl. These are shown in figure 6. The measured branching ratios for this ion (table 2) indicate that 90.7\% of products yield \( \text{C}_3 \) fragments and this would be surprising if only the cyclic form, which is more stable, circulated in the ring. Talbi (private communication) has examined the potential energy curves for the \( \text{C}_3\text{H}_3^+/\text{C}_3\text{H}_3 \) system and found that, while the cyclic isomer of the ion has a neutral state that intersects it near its minimum, thus providing excellent conditions for direct
recombination, and therefore a large rate coefficient, the linear form has a neutral state that intersects the ion away from the minimum in the curve. It thus can only undergo indirect recombination and Talbi predicts therefore a much lower recombination rate for this isomer. This has been confirmed by recent studies by Adams and co-workers [7]. Given the uncertainty concerning the isomeric state of the ions in the experiment, it is not possibly to say with conviction that this ion displays a ring opening prior to dissociation.

The ion C₄H₅⁺ is rather similar to C₃H₃⁺ with its principal isomer having a triangular carbon skeleton with an attached methyl group in place of one of the hydrogen atoms in C₃H₃⁺ (figure 7). In this case, it was found that the ion recombines almost with equal probability to form either C₄ fragments or C₂ + C₂ fragments with the C₃ + C channel accounting for less than 10% of the total recombinations. This is difficult to explain in terms of mixed isomer populations since the linear form 3 lies almost 2.5 eV in energy above the cyclic form 1. This suggests that in fact a ring opening occurs prior to recombination in this case. Unfortunately we have no means of positively identifying the isomeric structure of the ions in our studies and so we refer this question to theoretical analysis to provide further guidance.

4. Concluding remarks

This series of experiments reviewed here have provided insight into the recombination of complex hydrocarbon ions and have provided basic data, needed for the modelling of a variety of plasma processes. Measurements for the branching ratios of C₂H₃⁺, C₃H₄⁺ and C₃H₇⁺ have also been performed at CRYRING [11–13] and, as seen from the tables, their results are in excellent agreement with ours. In their case however, their energy resolution was superior and this allowed them to distinguish channels involving the loss of different numbers of hydrogen atoms. In our most recent experiments, we have examined the recombination of fluorocarbon ions including CF⁺, CF₂⁺ and CF₃⁺. These are necessary for the modelling of semiconductor processing plasmas and a number of papers are currently in preparation regarding these ions.

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