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# Branching ratios for the dissociative recombination of hydrocarbon ions. I: The cases of $C_4H_9^+$ and $C_4H_5^+$

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## Abstract

Branching ratios for C–C bond breaking during the dissociative recombination of $C_4H_9^+$ and $C_4H_5^+$ ions, produced from *n*-butane gas in a Nielsen source, have been measured using the merged beam method at the ASTRID storage ring. These results show that while $C_4H_9^+$ recombines to form $C_4$ and $C_3 + C$ products, $C_4H_5^+$ recombines to form $C_4$ and $C_2 + C_2$ products. A discussion of how these fragmentation patterns may be related to the isomeric forms of the ions undergoing recombination is presented.

*Keywords:* Dissociative recombination; Isomers; Branching ratios

## 1. Introduction

Reactive hydrocarbon plasmas are found in combustion [1,2], industrial reactors [3], thermonuclear reactor divertors [4], the ionospheres of Titan and Jupiter [5,6] and the interstellar medium [7]. A critical reaction in determining the chemical and physical nature of such plasmas is dissociative recombination namely

$$e^- + ABC^+ \rightarrow AB + C$$

where $ABC^+$ is a polyatomic molecular ion that fragments upon recombination with an electron yielding an array of products. There have been a number of merged beam studies of simple hydrocarbon ions [8] and in some cases, recombination products have been identified [9–13]. In the case of alkyl ions, DR can either affect the carbon skeleton (C–C bond breaking) or lead to the loss of hydrogen atoms (C–H bond breaking). A number of total rate coefficients for such reactions involving complex aliphatic, aromatic and polyaromatic hydrocarbon ions have been measured using the flowing afterglow Langmuir probe-mass spectrometer (FALP-MS) technique [14–18]. For these types of molecules, the reacting ion can exist in a variety of different isomeric forms but up until now the form of the ion undergoing recombination in these experiments has been uncertain and there has been no determination of the recombination products.

In the present work, the recombination of $C_4H_9^+$ and $C_4H_5^+$ ions have been examined. These are dominant ions in plasmas derived from alkanes and alkene

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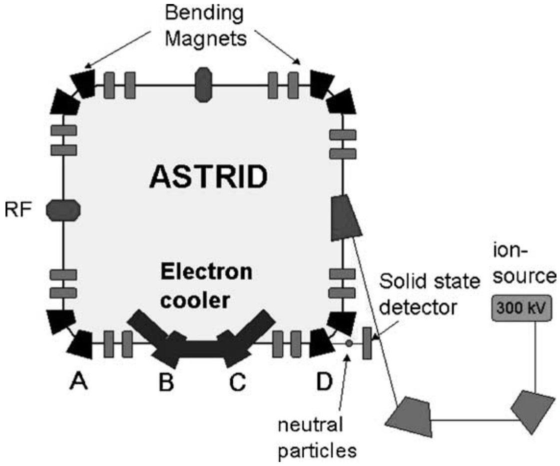

Fig. 1. Layout of ASTRID storage ring showing beam injection, electron cooler and neutral particles detection system. Magnets are labeled A–D.

parent gases. Room temperature rate coefficients for these ions have already been measured by some of us [15,16] and they were found to have the same value ($8.3 \times 10^{-7}$ cm$^3$ s$^{-1}$). The particular goal of this study has been to determine the branching ratios for the recombination of these ions. Details of these measurements and a discussion of the results are presented below.

## 2. Experimental method

The experiment was performed using the heavy-ion storage ring ASTRID at the University of Aarhus, Denmark. A Nielsen source was used to produce the ions with both linear *n*-butane and branched *iso*-butane as the source gas. The ions were extracted from the source, mass selected and accelerated to 150 keV, prior to injection into the storage ring.

The electrons are produced in the electron cooler assembly, shown in Fig. 1. A hot barium oxide cathode emits electrons via thermionic emission and these are attracted by the anode to produce an electron beam. A negative potential is applied to the cathode to accelerate the electrons to the desired energy and the beam is merged with and de-merged from the ions using the dipole magnets shown in the figure. The field of these magnets is rather weak and has little effect on the fast heavy ion beam.

In ASTRID the ions are accelerated to an energy of 2.7 MeV. This process takes about 4 s to accomplish. At this point the electron beam is turned on by removing the bias from a grid in front of the cathode and the electrons collide with the ions.

Neutrals, formed in the straight section between magnets A and D (Fig. 1) pass undeflected through magnet D and are detected by a surface barrier detector located at a distance of 6 m from the exit of the electron cooler magnet C. There are two sources for these neutrals. One is dissociative collisions involving interaction of the stored ion beam with the background gas in the storage ring which is maintained at a vacuum pressure of about $10^{-11}$ Torr. The other source is due to interaction of the ions with the electron beam. For low center-of-mass collision energies, this interaction is only due to dissociative recombination. When molecular ions dissociate in a storage ring, the resulting fragments carry away with them, kinetic energies that are distributed according to the fragment mass. This is because they continue their passage through the machine with essentially the same velocity as the primary ion (velocity changes due to the release of dissociation energy are small compared with the primary ion velocity and for the purposes of the present discussion, can be neglected). The surface barrier detector is energy sensitive and so is capable of distinguishing between fragments having differing masses provided they do not arrive simultaneously.

This is illustrated in Fig. 2 that shows the pulse height spectrum, obtained in the present experiment, using $C_4H_9{}^+$ ions (the spectrum for $C_4H_5{}^+$ is very similar). The resolution of the detector used, was insufficient to distinguish hydrogen atoms and so the four peaks correspond to molecular fragments with 1, 2, 3 or 4 carbon atoms. There should be a fifth peak due to released hydrogen atoms and molecules but this lies low in energy and falls into the electronic noise of the detector that is removed using a discriminator. We are thus unable to determine by direct means, the number of hydrogen atoms that are distributed between the

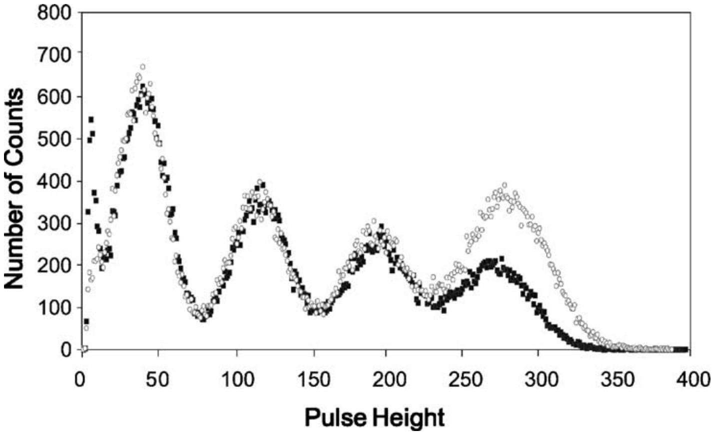

Fig. 2. Pulse height spectrum arising from $C_4H_9{}^+$ ions with and without the electron beam on with no grid in front of the detector.

fragments resulting from the recombination process. We can however observe the scission of C–C bonds.

In order to distinguish between ion-background gas processes and ion–electron processes, the electron beam is chopped electrostatically and measurements of the neutrals are performed when the electrons are on and when they are off. Neutrals due to recombination are thus determined by subtracting the two measured count rates. Fig. 2 shows the pulse height spectra accumulated with the electrons on and off. It can be seen that the number of counts accumulated in the fourth (highest energy) peak, is different depending upon whether the electrons are turned on or off. For the other peaks, however, the number is the same. The reason for this is as follows.

The four peaks correspond to neutral fragments containing 1, 2, 3 or 4 carbon atoms. These fragments arise due to recombination processes such as:

$$e^- + C_4{}^+ \rightarrow C_4 \tag{1a}$$

$$e^- + C_4{}^+ \rightarrow C_3 + C \tag{1b}$$

$$e^- + C_4{}^+ \rightarrow C_2 + C_2 \tag{1c}$$

and background gas reactions such as:

$$C_4{}^+ + X \rightarrow C_4 + X^+ \tag{2a}$$

$$C_4{}^+ + X \rightarrow C_3 + C^+ + X \tag{2b}$$

$$C_4{}^+ + X \rightarrow C_2 + C_2{}^+ + X \tag{2c}$$

$$C_4{}^+ + X \rightarrow C + C_3{}^+ + X \tag{2d}$$

where X is a background gas molecule and we have ignored the hydrogen atoms. By inspection of these equations it is realized that the background corrected signal only contains one peak with a total of four C atoms hitting the detector corresponding to reactions (1a)–(1c) since these channels all result in a total of four carbon atoms hitting the detector.

### 2.1. Branching ratio measurement

The goal of the present experiment is to determine the branching ratios, i.e., the relative proportions of the three dissociation channels (1a)–(1c). In order to do this, it is necessary to separate the contributions from each channel. In fact this can be achieved using a method [19] that involves placing a mesh grid with a known transmission $T$ in front of the detector. This method has been used in a large number of branching ratio measurements with polyatomic molecular ions at ASTRID [9,20] and also at CRYRING [10,13]. The probability of one atom or molecule reaching the detector is $T$, for two atoms or molecules it is $T^2$, etc. This means that when not all particles from a given channel arrive at the detector, those that do will therefore fall into lower energy channels since not all the energy is deposited. We can analyze the contributions from each of the channels (1a)–(1c) that fall into peaks

1–4 but one must take into account the probability that a particle will not arrive as well as the probability for a particle to arrive and the number of ways that a given situation can occur. Thus the number particles in peaks 1–4 being $N_1$, $N_2$, $N_3$, and $N_4$ is given by:

$$N_1 = T(1-T)N_{1b}$$

$$N_2 = 2T(1-T)N_{1c}$$

$$N_3 = T(1-T)N_{1b}$$

$$N_4 = TN_{1a} + T^2 N_{1b} + T^2 N_{1c}$$

where $N_{1a}$, $N_{1b}$, and $N_{1c}$ are the fractions of the total number of recombinations that yield channels (1a), (1b), and (1c), respectively.

In fact the analysis is not quite as simple as this for it is possible for light fragments, that leave the recombination center with most of the dissociation energy, to fly off at an angle to the primary ion beam and so miss the detector. This represents a loss that must be accounted for. In the present measurement, this loss concerned fragments containing a single carbon atom and this amounted to about 10% of all products (loss of $C_2$, $C_3$, and $C_4$ fragments was negligible). We therefore include such a loss factor, $L_c$ as follows:

$$N_1 = T(1-T)(1-L_c)N_{1b}$$

$$N_2 = 2T(1-T)N_{1c}$$

$$N_3 = [T(1-T) + L_c]N_{1b}$$

$$N_4 = TN_{1a} + T^2(1-L_c)N_{1b} + T^2 N_{1c}$$

The actual measurement was performed using a grid with nominal transmission values $T_1 = 0.67$ and one with $T_2 = 0.25$. This allows the branching ratios to be over-determined and so one can apply a numerical $\chi^2$ routine, treating the transmission factors as free parameters, in order to obtain more accurate values for $T_1$ and $T_2$ [20]. This is important for the resulting determination of the branching ratios which is very sensitive to the transmission factors. It was found using this procedure that $T_1 = 0.675$ and $T_2 = 0.235$ to an accuracy of about ±0.5%.

## 3. Results and discussion

### 3.1. Results

The branching ratios were measured at zero relative energy and the results are presented in Table 1.

In other experiments [9–13], it has been found that such branching ratios are weakly dependent upon center-of-mass collision energy.

### 3.2. $C_4H_9{}^+$—branching ratio

From an energetic point of view [21,22], only three types of reactions can be observed:

$$C_4H_9{}^+ + e^- \rightarrow C_4H_8 + H$$

$$C_4H_9{}^+ + e^- \rightarrow C_4H_7 + H_2$$

$$C_4H_9{}^+ + e^- \rightarrow C_nH_m + C_pH_q,$$

where $(n+p) = 4$ and $(m+q) = 9$

corresponding respectively to the rupture of one or two C–H bonds or one C–C bond.

Upon inspection of Table 1, it is striking that the dominant decay channels are those that produce either a $C_4$ structure, that will probably have lost at least one hydrogen atom (the loss of a hydrogen molecule is also energetically possible) or a $C_3$ and a C fragment with attached hydrogen atoms. The channel leading to a pair of $C_2$ structures has a negligible probability.

When *n*-butane is used as the source gas in this experiment, it would be expected that the ionization of this gas in the source would produce the *s*-butyl cation structure shown in Fig. 3.

The C–C bond strengths in a hydrocarbon are quite similar, independent of their position in the molecule. If $C_4H_9{}^+$ were in its linear form only, one might expect

Table 1
Branching ratios for the dissociative recombination of $C_4H_9{}^+$ and $C_4H_5{}^+$

| Dissociation channel | $C_4H_9{}^+$ (%) | $C_4H_5{}^+$ (%) |
|---|---|---|
| $C_4$ | 61.5 ± 0.1 | 52.6 ± 0.2 |
| $C_3$ + C | 38.4 ± 0.1 | 0.1 ± 0.2 |
| $C_2$ + $C_2$ | 0.1 ± 0.2 | 47.3 ± 0.2 |

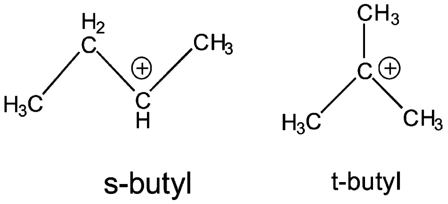

Fig. 3. Isomeric forms for $C_4H_9{}^+$ ions.

the $C_3 + C$ and $C_2 + C_2$ channels, both to be present, in a 2:1 statistical ratio. As this is not the case, one might deduce that most of the ions, initially in the secondary butyl isomeric form, have undergone a rearrangement, to the *t*-butyl form (Fig. 3) prior to the recombination reaction. This supposition conforms with what is widely accepted [23] namely that the initial secondary butyl cation rapidly undergoes rearrangement to the more stable *t*-butyl cation. The unimolecular reaction rate for this isomerization is unknown but is thought to be fast [24]. When the experiment was repeated using *iso*-butane as source gas, the branching ratios were found to be very similar to those obtained for *n*-butane.

An alternative explanation for the observed branching ratio is that an isomeric rearrangement to the *t*-butyl structure occurs following electron capture. This possibility cannot a priori be ruled out and is discussed further below.

### 3.3. $C_4H_5{}^+$—branching ratio

The branching ratios for this ion are also listed in Table 1 and it is seen that recombination occurs via $C_4$ and $C_2 + C_2$ channels only. Changing to *iso*-butane as source gas produced no noticeable change in the measured branching ratio. The low lying isomeric forms of $C_4H_5{}^+$ are illustrated in Fig. 4 [25]. All of these isomers can of course contribute to the $C_4$ channel. Since from energy considerations one can say that probably only one C–C (and most likely a single, rather than a double) bond is broken during the recombination, then isomers 1, 4, and 5 might be expected to lead to $C_3 + C$ fragments and isomers 3 and 5 to $C_2 + C_2$. The observed branching ratios with no $C_3 + C$ channel being seen, (only $C_4$ and $C_2 + C_2$) indicate that in the present experiment, if we take the isomeric form of the ion as being indicative of the subsequent dissociation pathways, then the $C_4H_5{}^+$ ions are mainly in the isomeric forms 2 and 3. In our

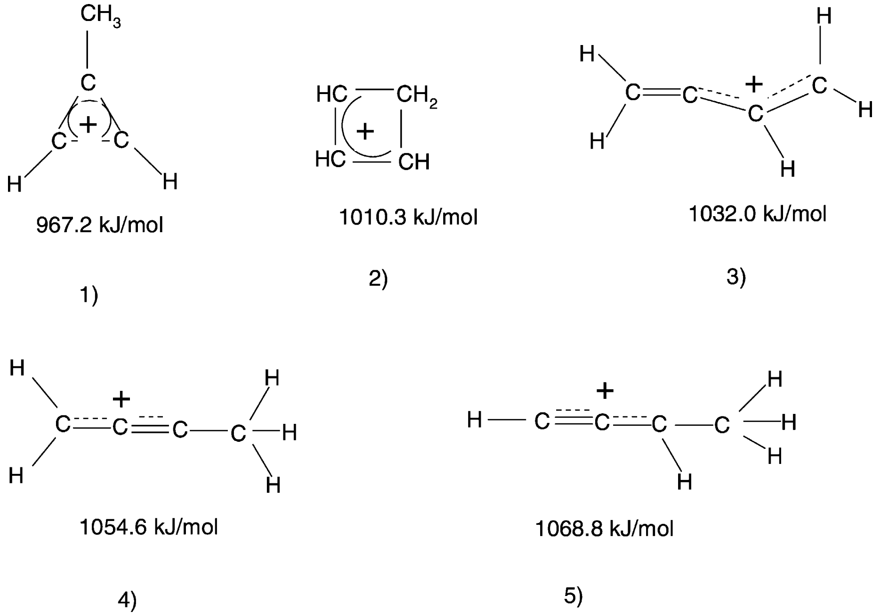

Fig. 4. Isomeric forms of $C_4H_5{}^+$ ions and their enthalpies of formation [25].

previous, flowing afterglow experiment, where the ions were formed from acetylene, we argued from thermochemical principles, that the cyclic form, 1, would be the most likely form of the ion undergoing recombination but this would give rise to a $C_3+C$ dissociation. Certainly during the ionization process there is sufficient energy available to populate excited states of the ion and hence different isomeric forms can exist in the beam. As explained above, the ions are stored in the storage ring during a period of 4 s prior to reacting with the electron beam and one might imagine that they would relax to the most stable isomeric form. In a storage ring, such a de-excitation of the ions occurs via radiative relaxation processes since there are few collisions under the ultra high vacuum conditions in the ring. It may be, however, that an energy barrier exists between isomer 3 and lower energy isomers.

An alternative explanation could be that an isomeric rearrangement occurs following electron capture. Examination of the lowest energy isomeric forms of the neutral $C_4H_5$ molecule [26–28] offers little assistance here for it is not obvious that one structure would be produced that would dissociate to $C_2 + C_2$ but not $C_3 + C$. Dissociative recombination is a complex process however, involving capture of an electron to form an excited state of the neutral molecule that ultimately undergoes dissociation. How this is accomplished for hydrocarbon species such as those studied here is a subject for future theoretical examination.

## 4. Conclusions

The difference in the branching fractions for these two hydrocarbon ions is striking despite the fact that they were previously shown to have identical recombination rates [15,16]. As discussed above, it can be argued that the branching ratios reflect the structure of the ions undergoing recombination. The situation may be more complicated than this, however, for it is possible that the isomerization occurs during the actual dissociation process, i.e., following electron capture. In recent measurements made at the TSR storage ring in Heidelberg, it has been observed that $H_3^+$ ions, initially triangular in form, recombine to form products that reflect the dissociation of a linear form of the neutral molecule [29,30]. A similar phenomenon has been seen in experiments at CRYRING in Stockholm concerning the dissociative recombination of $H_2O^+$ ions. The products of this reaction appear to come from a linear neutral $H_2O$ molecule while $H_2O^+$ ions have a bent configuration [31–33]. Our knowledge of the mechanism via which the neutralized hydrocarbon ions proceed to dissociation is insufficient for us to say definitively at this time, which explication is valid though certainly that concerning the isomeric state of the recombining ion is attractive.

The branching fractions measured here are essential input data to models of hydrocarbon plasma chemistry and this technique represents therefore a very useful complement to the afterglow method that yields absolute, thermal recombination rate coefficients. In future experiments, other $C_4$ hydrocarbon ions will be studied and experiments are being planned to study C–H bond breaking during dissociative recombination of even larger species.

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