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# Dissociative recombination of $C_3H_4^+$: preferential formation of the $C_3H_3$ radical

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## Abstract

Branching ratios and absolute cross sections have been measured for the dissociative recombination of $C_3H_4^+$ using the CRYRING ion storage ring. The pre-eminent channel involves the production of $C_3H_3$ and H, whereas processes involving rupture of carbon–carbon bonds are clearly disfavoured. The cross section of the reaction could be fitted to the expression $\sigma = 5.5 \pm 0.2 \times 10^{-15}\ E^{-1.01\pm0.02}$, which leads to a thermal reaction rate of $k(T) = 2.95 \pm 0.1 \times 10^{-6}\ (T/300)^{-0.67\pm0.02}\ \mathrm{cm^3\ s^{-1}}$.

*Keywords:* Dissociative recombination; Ion chemistry; Molecular astrophysics

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## 1. Introduction

Dissociative recombination (DR) is one of the most important destruction mechanisms of molecular ions in plasmas of low temperature and number density, such as those that exist in combustion processes and in the interstellar medium or the upper layers of planetary atmospheres. In many systems, the high kinetic energy release of the DR reaction can enable different fragmentation pathways of the intermediate neutral molecule. Knowledge of the branching ratios of the different pathways is therefore crucial to accurately model large reaction networks in these media [1]. This holds especially for the DRs of hydrocarbon ions like $C_3H_4^+$, since the number of exoergic channels available in these reactions tends to be high. The exoergicity of the formation of one or two hydrogen molecules brings about that enough energy is available for different fragmentation pathways of the rest molecule which leads to a multitude of different channels. Small aliphatic hydrocarbons are also seen as important intermediates in the construction of hydrocarbon molecules containing long carbon chains and polycyclic aromatic hydrocarbons (PAHs), which are found or predicted to be present in various interstellar environments. Generation of PAHs is also interesting from a terrestrial point of view, since it finally leads to soot formation in combustion processes.

Furthermore, the $C_3H_4^+$ ion is thought to be an important intermediate in the chemistry of Titan's atmosphere, and it is expected that it is produced by the photoionisation of $C_3H_4$ and other hydrocarbons [2]. Models of Titan's ionosphere predict a density of $\sim 13\ \mathrm{cm^{-3}}$ for this species at an altitude of 1055 km [3,4]. $C_3H_4^+$ has also been produced in a laboratory gas mixture similar to that of Titan's atmosphere by lightning discharge [5] and the ion has also been found to react with phenyl radicals in a probably barrierless process [6], thus being able to get involved in the build-up of higher hydrocarbons. The parent molecule, propyne (methylacetylene) has been detected in various interstellar environments, e.g. in dark and translucent interstellar clouds [7]. Moreover, it has been unambiguously identified in the atmosphere of both Jupiter and Titan [8,9], while, in laboratory studies, it has also been readily produced through the UV irradiation of pure methane, which constitutes an important component in the atmosphere of giant planets [10].

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Dissociative recombination reactions of hydrocarbon ions deserves special interest, since it is regarded as the final step in producing hydrocarbons in the interstellar medium [11], therefore investigations into the rates and branching ratios of such processes are important for the quality of the predictions of astrophysical model calculations. Earlier it was expected by Bates that the bond, or bonds, disrupted in the DR reaction are those involving the significant positive partial charges on the ion and that simultaneous breakage of several bonds is unlikely [12,13]. Calculations of Breneman (CHELPG) charge distributions at the UMP2/6-311++G(2d,p) level using the Gaussian programming package [14] yielded that the three hydrogen atoms of the $CH_3$ group carry a partial charge of +0.16 and the one located in CH group one of +0.33. The only carbon atom with a positive charge is the 2-C atom, which is unlikely to be ejected in the DR process. Therefore, in case of $C_3H_4{}^+$, this would mean that the most likely pathway in a DR process would be the splitting off of a hydrogen atom or, maybe the formation of a hydrogen molecule, both of which processes would leave the carbon chain intact. Recent research into the DR of many molecular species, however, has shown that many reactions do not follow this prediction. For example, unexpected pathways like rupture of the C–C bond in the DR of hydrocarbon ions and three-body break-ups in triatomic molecules are, in fact, very common, and branching ratios turn out to be far less predictable than previously assumed [15]. In the DR of $C_2H_2{}^+$, the channels involving the breaking of the carbon bond make up 18% of the total reaction rate [16]; for $C_2H_3{}^+$ the respective figure is 6% [17]. Furthermore, even a three-body break-up has been observed, namely in the DR of $CH_2{}^+$ [18].

In the DR of $C_3H_4{}^+$ (propynylium form) the following exoergic reaction channels can be found:

$$C_3H_4{}^+ + e^- \rightarrow C_3H_3 + H \qquad \Delta H = -6.51\,\text{eV} \tag{1a}$$

$$C_3H_4{}^+ + e^- \rightarrow C_3H_3 + H_2 \qquad \Delta H = -6.14\,\text{eV} \tag{1b}$$

$$C_3H_4{}^+ + e^- \rightarrow C_2H_3 + CH \qquad \Delta H = -3.03\,\text{eV} \tag{1c}$$

$$C_3H_4{}^+ + e^- \rightarrow C_2H_2 + CH_2 \qquad \Delta H = -5.93\,\text{eV} \tag{1d}$$

$$C_3H_4{}^+ + e^- \rightarrow C_2H_2 + CH_3 \qquad \Delta H = -5.83\,\text{eV} \tag{1e}$$

$$C_3H_4{}^+ + e^- \rightarrow C_3H_2 + 2H \qquad \Delta H = -1.61\,\text{eV} \tag{1f}$$

$$C_3H_4{}^+ + e^- \rightarrow C_2H_2 + CH + H \qquad \Delta H = -1.51\,\text{eV} \tag{1g}$$

$$C_3H_4{}^+ + e^- \rightarrow C_2H + H_2 + CH \qquad \Delta H = -1.18\,\text{eV} \tag{1h}$$

$$C_3H_4{}^+ + e^- \rightarrow C_2H + CH_2 + H \qquad \Delta H = -1.07\,\text{eV} \tag{1i}$$

$$C_3H_4{}^+ + e^- \rightarrow C_2H_2 + C + H_2 \qquad \Delta H = -2.50\,\text{eV} \tag{1j}$$

$$C_3H_4{}^+ + e^- \rightarrow C_3 + 2H_2 \qquad \Delta H = -3.78\,\text{eV} \tag{1k}$$

$$C_3H_4{}^+ + e^- \rightarrow C_2H_4 + C \qquad \Delta H = -4.31\,\text{eV} \tag{1l}$$

$$C_3H_4{}^+ + e^- \rightarrow CH_4 + C_2 \qquad \Delta H = -4.38\,\text{eV} \tag{1m}$$

$$C_3H_4{}^+ + e^- \rightarrow C_3H + H_2 + H \qquad \Delta H = -2.42\,\text{eV} \tag{1n}$$

The quoted enthalpies have been calculated using the ionisation energy of propylene (10.36 eV) [19] and using experimental reference data [20] for the formation enthalpies of propyne and the products under standard conditions. In the cases where no experimental data was available for the heat of formation for one of the products ($C_3H_2$ and $C_3H$), the values calculated by Guadagnini et al. [21] have been employed. If more than one isomer of one the products exists, the values for the most stable linear products have been used.

Despite the multitude of exoergic pathways available, only a few of these processes are considered in models of astronomical reaction networks, which might negatively affect the quality of the predictions made by them. For example, in a model of a dark cloud, only reactions (1a) and (1d) have been included, and for both a branching ratio of 0.5 has been assumed [1]. This paper presents a full analysis of the branching ratios in the DR of $C_3H_4{}^+$ together with a determination of the reactive cross section in the collisional energy range relevant to the interstellar medium as well as a calculation of the temperature dependence of the overall reaction rate.

## 2. Experimental

The DR experiments have been performed at the heavy-ion storage ring CRYRING at the Manne Siegbahn Laboratory, Stockholm University. The experimental procedure has been described in detail elsewhere [22] and is only briefly summed up here. $C_3H_4{}^+$ ions were produced in a hot filament Penning discharge ion source (Nielsen m/57) from propyne (methylacetylene). After extraction of the ions from the source at 40 keV, they were mass selected, injected into the ring and accelerated to 2.4 MeV translational energy. The stored ion beam was merged with a mono-energetic electron beam in an electron cooler, the length of the interaction region being 0.85 m. During the first 4 s after acceleration, the electron and the ion beam were kept at the same average velocity to allow heat transfer from the ion to the electron beam in order to reduce the translational temperature of the ions, which results in an increase of their density in phase space. Furthermore, such storage time enables radiative vibrational cooling of the ions.

Neutral products generated by DR reactions in the electron cooler leave the ring tangentially and were detected by an energy-sensitive silicon surface barrier detector (SBD) with a diameter of 34 mm mounted at a distance of 3.85 m from the centre of the interaction region. A background signal due to neutral products emerging from collisions of the ions with residual gas was also present; and this was measured with the relative translational energy of ions and electrons tuned to 1 eV, where the DR cross section is very low and the observed neutral fragments are therefore almost exclusively produced by rest gas collisions. This background was subsequently subtracted from the total SBD signal and amounted to less than 8% of the total measured signal at 0 eV relative translational energy in all experiments.

### 2.1. Branching ratios

The fragments produced by a DR event reached the detector within a very short time interval compared with the integration time of the detection system. The pulse height of the SBD signal was therefore proportional to the kinetic energy carried by the products of the reaction and, consequently, the mass. To measure the branching ratios of the DR channels a metal grid with a transmission $T = 0.297 \pm 0.015$ was inserted in front of the detector [22]. Particles stopped by the grid do not reach the detector, and DR events where one of the fragments has been stopped by the grid results in a signal whose amplitude is proportional to the detected fragment's kinetic energy. The registered DR spectrum therefore splits into a series of peaks with different energies, the intensities of which can be expressed in terms of the branching ratios and the probabilities of the particles passing the grid. For example, the intensity of the 2H ($H_2$) peak emerging from Reaction (1b) is proportional to $T(1 -$

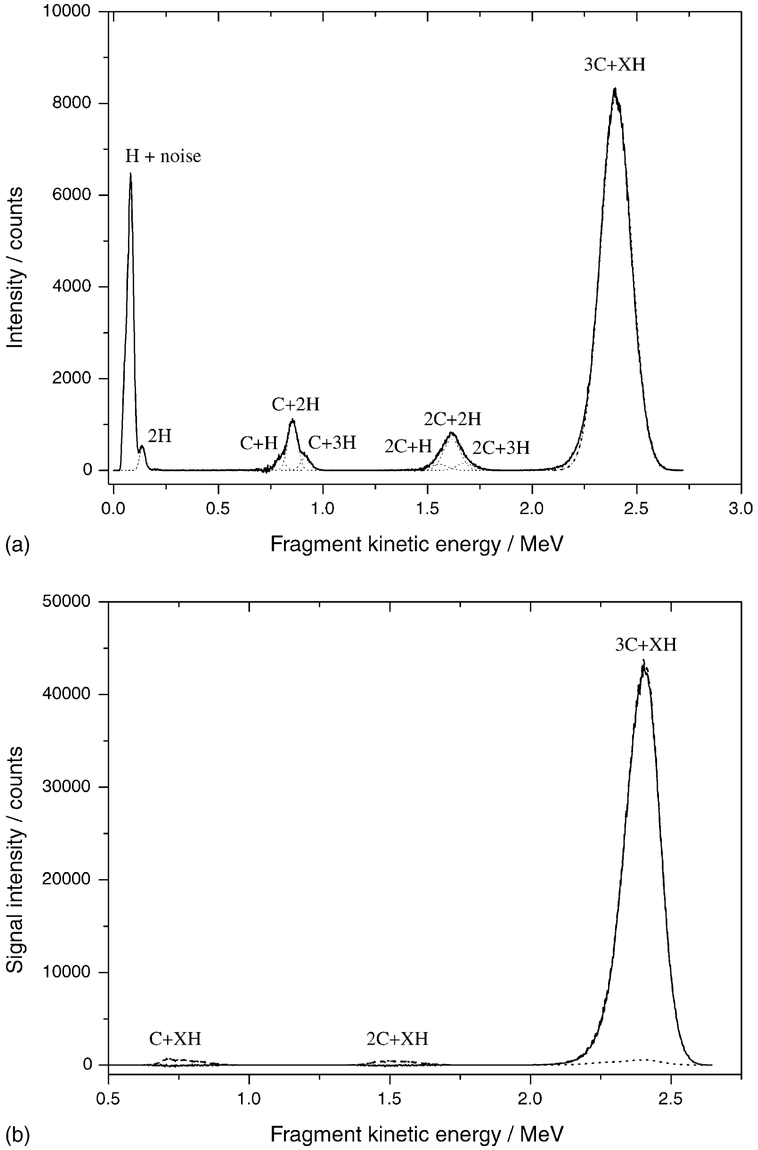


Fig. 1. (a) Energy spectrum of the neutral fragments of the dissociative recombination of $C_3H_4^+$ (signal from the surface barrier detector) with the grid (transmission = 0.297) in place. The solid line shows the data, whereas the double-gaussian fitting curves are shown as dashed lines and the total fit as dotted line. (b) Energy spectrum of the neutral fragments of the dissociative recombination of $C_3H_4^+$ (signal from the surface barrier detector) with the grid removed. The dashed lines shows the spectrum obtained at 0 eV collision energy, the dotted line the one at 1 eV (rest gas collisions), and the solid line the spectrum after correction for the rare gas collision background.

$T$)$b$, with $b$ being the branching ratio of reaction (1b) and $T(1-T)$ the probability of only the $H_2$ fragment passing the grid. The energy spectrum of the DR reaction is shown in Fig. 1a. For the mass signals up to $m = 27$, the peaks were fitted to Gaussian functions. In the case of the signals corresponding to detector hits of three carbon atoms the bad resolution and the asymmetry of the peaks prevented an unambiguous fit of the curve to the different mass signals. Since the peaks are very large, small changes of their positions will change their relative intensity quite dramatically, which is likely to be detrimental to the further analysis. Therefore, it was decided to treat the feature emerging from $C_3H_x$-signals as a single peak, i.e. summing up three different Gaussian functions. As can easily be seen in Fig. 1a, the final fitting curve is in very good agreement with the data. The first peak in the spectrum is the signal from hydrogen atoms, which is overlapping with noise from the detector and therefore was not taken into account in the data reduction. The energy calibration is performed as follows: the well-defined maxima of the C + 2H ($m = 14$ amu) and 2C + 2H ($m = 26$ amu) peaks are used to calibrate the mass spectrum. The full energy of the beam (96 MeV) then defines the kinetic energy of the unfragmented molecule. Thus, the energy of the C+2H ($E = 96/40 \times 14/40 = 0.86$ MeV) and 2C+2H ($E = 96/40 \times 26/40 = 1.56$ MeV) masses is obtained.

By examining the mass signals present in the fragment energy spectrum (Fig. 1a) several of the reaction pathways can already be dismissed, simply because one ore more of their products have not been detected. This includes all the processes leading to atomic carbon (reactions (1j) and (1l)), $C_2$ (reaction 1m), and $CH_4$ (also reaction (1m)). Furthermore, channels producing more than $H_2$ + H or two $H_2$ molecules (reactions 1k, and 1n), which would lead to a signal in the 3H and/or 4H mass channel, are not present.

Using the transmission probabilities mentioned above, the matrix Eq. (2) is formulated for the relative intensities of the different energy channels,

$$\begin{bmatrix} T & T & T^2 & T^2 & T^2 & T & T^3 & T^3 & T^3 \\ 0 & 0 & T(1-T) & 0 & 0 & 0 & T^2(1-T) & T^2(1-T) & 0 \\ 0 & 0 & 0 & T(1-T) & 0 & 0 & T(1-T)^2 & 0 & T^2(1-T) \\ 0 & 0 & 0 & 0 & T(1-T) & 0 & 0 & T(1-T)^2 & T(1-T)^2 \\ 0 & 0 & 0 & 0 & T(1-T) & 0 & 0 & T^2(1-T) & T^2(1-T) \\ 0 & 0 & 0 & T(1-T) & 0 & 0 & T^2(1-T) & 0 & T(1-T)^2 \\ 0 & 0 & T(1-T) & 0 & 0 & 0 & T(1-T)^2 & T^2(1-T) & 0 \\ 0 & T(1-T) & 0 & 0 & 0 & T(1-T) & 0 & T^2(1-T) & 0 \end{bmatrix} \begin{pmatrix} a \\ b \\ c \\ d \\ e \\ f \\ g \\ h \\ i \end{pmatrix} = \begin{pmatrix} I_{3C+XH} \\ I_{2C+3H} \\ I_{2C+2H} \\ I_{2C+H} \\ I_{C+3H} \\ I_{C+2H} \\ I_{C+H} \\ I_{2H} \end{pmatrix} = \begin{pmatrix} 0.880 \pm 0.024 \\ 0.009 \pm 0.002 \\ 0.040 \pm 0.003 \\ 0.008 \pm 0.002 \\ 0.010 \pm 0.001 \\ 0.035 \pm 0.005 \\ 0.008 \pm 0.001 \\ 0.010 \pm 0.001 \end{pmatrix} \tag{2}$$

where $a$–$i$ denote the branching ratios of reaction channel (1a)–(1i), respectively. Note that the features emerging from signals of three carbon atoms have been summed up into one peak. The probability of obtaining a signal in the 3C + $X$H channel from reaction 1a is therefore the sum of the probability of obtaining a 3C + 4H signal ($T^2$) and the one of getting a 3C + 3H signal ($T(1-T)$), also $T$. By taking a first look at this matrix, further reaction channels can be excluded. Only reactions 1e, 1h and 1i contribute to the 2C + H and C + 3H mass signal. Since the contribution of 1e is the same ($T(1-T)$) for both channels, and channels (1h) and (1i) contribute more to 2C + H than C + 3H, existence of the latter two channels should augment the 2C + H signal compared to C + 3H. Such an increase is not found and it can therefore be concluded that the branching ratios h and i are 0. If that is the case, channel (1g) can be disregarded through a similar reasoning by comparing the 2C + 3H and C + H mass signals. Therefore, the matrix is reduced to:

$$\begin{pmatrix} T & T & T^2 & T^2 & T^2 & T \\ 0 & 0 & T(1-T) & 0 & 0 & 0 \\ 0 & 0 & 0 & T(1-T) & 0 & 0 \\ 0 & 0 & 0 & 0 & T(1-T) & 0 \\ 0 & 0 & 0 & 0 & T(1-T) & 0 \\ 0 & 0 & 0 & T(1-T) & 0 & 0 \\ 0 & 0 & T(1-T) & 0 & 0 & 0 \\ 0 & T(1-T) & 0 & 0 & 0 & T^2(1-T) \end{pmatrix} \begin{pmatrix} a \\ b \\ c \\ d \\ e \\ f \end{pmatrix} = \begin{pmatrix} I_{3C+XH} \\ I_{2C+3H} \\ I_{2C+2H} \\ I_{2C+H} \\ I_{C+3H} \\ I_{C+2H} \\ I_{C+H} \\ I_{2H} \end{pmatrix} = \begin{pmatrix} 0.880 \pm 0.024 \\ 0.009 \pm 0.002 \\ 0.040 \pm 0.003 \\ 0.008 \pm 0.002 \\ 0.010 \pm 0.001 \\ 0.035 \pm 0.005 \\ 0.008 \pm 0.001 \\ 0.010 \pm 0.001 \end{pmatrix} \tag{3}$$

Since this matrix contains three pairs of identical rows, we obtain a system with six variables and five equations. However, from the small size of the 2H signal it can be concluded that the branching ratios of both channel (1b) and (1f) will be rather minute. Therefore one can probably be content with determining the maximum branching ratio for both channels by calculating the matrix once with $b = 0$ and once with $f = 0$. In the first case the branching ratio of channel (1f) is 0.02, in the second case the one of (1b) amounts to 0.05. If both channels are open, the sum of their contributions should lie between those values. In conclusion, the branching ratios listed in Table 1 have been obtained.

Since some of the reactions have negative enthalpies, some (especially lighter) particles might gain a high transversal reaction velocity and thus, miss the detector. This holds especially for reactions 1a and 1b. However, every loss of H atoms or $H_2$ by detection leads to an augmentation of the signal in the 3C + 3H, respectively, 3C + 2H channel on the cost of the 3C + 4H channel. Therefore the

Table 1
Branching ratios of the dissociative recombination of $C_3H_4^+$

| Reaction pathway | Products | Branching ratio |
|---|---|---|
| 1a | $C_3H_3 + H$ | 0.87 ± 0.04 |
| 1b | $C_3H_2 + H_2$ | ≤0.02 |
| 1c | $C_2H_3 + CH$ | 0.01 ± 0.01 |
| 1d | $C_2H_2 + CH_2$ | 0.06 ± 0.02 |
| 1e | $C_2H + CH_3$ | 0.01 ± 0.01 |
| 1f | $C_3H_2 + 2H$ | ≤0.05 |

total effect of these losses on the analysis is 0, because we treat the 3C features as one peak. From the other reactions some produce either heavy fragments, which lead to a low transversal product velocity (reactions 1c, 1d, 1e, 1l and 1m) and consequently to no loss of detection. Others have a too low exoergicity to allow any loss (reactions 1f–1j). In the remaining reactions 1k and 1n, the kinetic energy has to be divided amongst three fragments, making a considerable loss unlikely. Also, the branching ratios of the latter processes have been found to be 0 because of the absence signals with mass three and four. The loss of fragments can also be estimated from a fragment energy spectrum obtained at 0 and 1 eV relative kinetic energy of the reactants obtained without a grid. Such a spectrum is shown in Fig. 1b. As can be seen the signal intensity at 1 eV, where the cross section of the dissociative recombination is very low, and the signal mostly consists of rest gas collisions is small compared to the one at 0 eV. Subtraction of the latter contribution yields a spectrum consisting exclusively of the 3C+*X*H peak. This shows that loss of heavier fragments (containing at least one carbon atom) is nonexistent in the present experiment.

### 2.2. Absolute cross section and thermal reaction rate

During cross section measurements, the relative translational energy between the ions and the electrons was continuously varied between 1 and 0 eV. This was achieved by changing the cathode voltage of the electron cooler over 1 s from a high-value corresponding to a centre-of-mass energy of 1 eV, the electrons being faster than the ions, down to a low-value also corresponding to 1 eV but where the electrons were slower than the ions. Thus, a voltage corresponding to a centre-of-mass energy of 0 eV is reached during the scan. Before the measurement was started, 4 s of cooling, with the electrons tuned to 0 eV collision energy, was carried out. The signal from the SBD was monitored by a single channel analyser. Signal intensities at different times during the scan of the relative kinetic energies of ions and electrons (and therefore at different collision energies) were thereafter recorded by a multi-channel scaler, yielding the number of DR events (counts on the SBD detector) during a defined time window (2 ms).

The experimental DR rate coefficient in the electron cooler is expressed by the formula:

$$\langle v_{cm}\sigma\rangle = \left(\frac{dN}{dt}\right)\frac{v_i v_e e^2 r_e{}^2 \pi}{I_e I_i l} \tag{4}$$

where d*N*/d*t* is the number of counts per unit time; $v_i$ and $v_e$ are the electron and ion velocities, respectively; $r_e$, the radius of the electron beam; *l*, the length of the interaction region and; $I_e$ and $I_i$ are the electron and ion currents, respectively. Simultaneously with this measurement, the ion current was monitored using an AC integrating current transformer in combination with a multichannel plate detector installed at the end of one of the straight sections of the ring. Continuous measurement of neutral products arising from the ion-rest gas collisions also allowed the decay of the ion beam to be followed during each injection. The following corrections to the measured data had to be performed: (a) the voltage of the electron cooler cathode (and therefore $v_e$) had to be corrected for space charge effects; (b) the measured rate coefficient $\langle\sigma v_{cm}\rangle$ had to be adjusted because of the toroidal effect [23]. This toroidal effect stems from the zones at both ends of the interaction region where the electron beam is bent into or out of the ion beam. In these regions, the transversal electron velocity is higher than in the merged interaction region leading to larger collision energies; (c) since the electron beam has (in contrast to the ion beam) a non-neglectible energy spread, the measured reaction rate $\langle\sigma v_{cm}\rangle$ has to be deconvoluted according to the formula:

$$\langle v_{cm}\sigma\rangle = \int_{-\infty}^{\infty} v_e f(v_e)\sigma(v_e) d^3 v_e \tag{5}$$

where $f(v_e)$ is the velocity distribution; (d) drag force effects [24] were neglected due to the relatively large weight of the investigated ion. The cross section can then be obtained as a function of the collision energy and follows the expression $\sigma = 5.5 \pm 0.2 \times 10^{-15}\ \mathrm{E}^{-1.01\pm0.02}\ \mathrm{cm}^2$. The thermal reaction rate can be deduced from the cross sections applying the following formula:

$$k(T) = \frac{8\pi m_e}{(2\pi m_e kT)^{3/2}} \int_0^{+\infty} E\sigma(E)\mathrm{e}^{-E/kT}\mathrm{d}E \tag{6}$$

where $m_e$ is the mass of the electron and is depicted as a function of the temperature in Fig. 2. During the measurement of the cross sections an energy discriminator was applied and set in a way that only the 3C + *X*H peak was regarded as DR signal, excluding the small contributions of other mass channels, which consisted of rest gas collisions (see Fig. 1b). Since the contribution of such collisions only made up less than 2% of the 3C + *X*H peak at 0 eV collision energy, the contribution of rest gas collisions to the measured cross section at low energies could also be minimized. As the cross section of the DR is very low at 1 eV collision energy, and the rest gas collisions are independent of the electron velocity, the neutral particles measured at this energy were assumed to be due solely to charge-transfer. This small contribution was subsequently subtracted.

The reaction rate depending on the electron energy can be expressed with the formula $k(T) = 3.25 \pm 0.2 \times 10^{-9}\ \mathrm{E(eV)}^{-0.52\pm0.02}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$. Assuming a Maxwell distribution of the kinetic energy of the electrons, the temperature de-

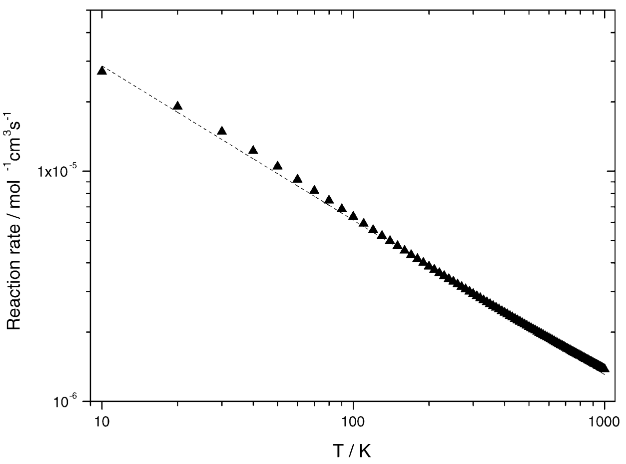


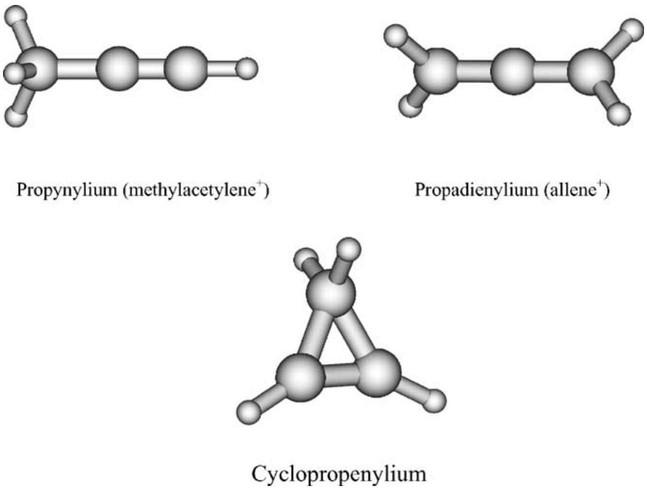
Fig. 2. Reaction rate coefficient, the dissociative recombination of $C_3H_4^+$, as a function of temperature. The dashed line shows the best fit with $k = 2.95 \times 10^{-6}$ $(T/300)^{-0.67}$ cm$^3$ s$^{-1}$.

pendence of the rate can finally be fitted by the equation $k(T) = 2.95 \pm 0.1 \times 10^{-6}$ $(T/300)^{-0.67\pm0.02}$ cm$^3$ s$^{-1}$ (see Fig. 2).

## 3. Discussion

Three stable isomers of $C_3H_4^+$ have been detected in the gas phase, the propynylium ($CH_3CCH^+$), allenylium ($CH_2CCH_2^+$) and the cyclopropenylium (*cyc*-$C_3H_4^+$) cation [25]. They are schematically displayed in Fig. 3. Since different cross sections have been obtained for charge-transfer reactions of the allenylium and propynylium ion [20], it cannot be excluded that the DR rates are also different for these two ions.

The most stable $C_3H_4^+$ species is the allenylium ion ($\Delta H_F = 1126$ kJ/mol) followed by the propynylium ($\Delta H_F = 1186$ kJ/mol) and the cyclopropenylium ion ($\Delta H_F = 1210$ kJ/mol) [19]. Theoretical calculations of the barrier for interconversion between allenyl and propynyl have predicted it to lie 196 kJ/mol above the allenyl ion: the respective barrier for the conversion from alenyl to cyclopropenyl was found to be 192 kJ/mol above the propynylium cation [26]. A later study by van der Hart [27] confirmed these values. Also, isomerisation of propynylium to allenylium has been observed in a photoionisation study of propyne [28]. Given the high electron energies involved in the production of these ions in the source (∼160 eV) isomerisation of propynylium to allenylium cannot be ruled out and we expect the ion beam to contain a mixture of these isomeric ions. Rearrangement to the less stable cyclopropenylium ion is less probable, since in a Coulomb explosion study of $C_3H_4^+$ ions no evidence for cyclic structures has been found [29].


Propynylium (methylacetylene$^+$)

Propadienylium (allene$^+$)

Cyclopropenylium

Fig. 3. Schematic view of the three most stable $C_3H_4^+$ ions.

Interconversion between different isomers is not restricted to the ionic states in the present experiment. The DR can follow an indirect mechanism, in which the electron attachment first forms a Rydberg state of the neutral, which then subsequently decays. This may occur over a timescale favourable to molecular rearrangement. The potential surface for $C_3H_4$ has recently been investigated by Guadagnini et al. [21]. Their calculations predicted that propyne can rearrange to allene via cyclopropene with an overall barrier of 86.1 kcal/mol (3.73 eV), which is well below the ionisation energy of propyne (10.36 eV) and allene (9.69) [30], so rearrangement of the intermediately produced neutral is at least energetically possible. The presence of channel (1c), whose products are likely to be formed from an allenic structure, indicates that such a structure is potentially involved in the present experiment.

Despite these ambiguities, there is a clear dominance of the pathway leading to $C_3H_3$ and H (1a). It is tempting to ascribe this behaviour to the fact that this pathway is, from a thermodynamical view, the most favoured one. Therefore, it is worthwhile to compare the branching ratios obtained in our experiment with those observed in the DR of other unsaturated hydrocarbon ions. In the acetylene ion, the analogous channel producing $C_2H$ has been identified as the major pathway with a branching ratio of 0.50. Conversely, in the DR of ethylene and $C_2H_3^+$ [16,17], the thermodynamically disfavoured three-body fragmentation leading to $C_2H_2 + 2H$, dominates [31]. Whereas in these three systems channels preserving the carbon–carbon bond are predominant, this does not hold for $C_4H_5^+$, where break-up into two C–C fragments is about as probable as the thermodynamically advantageous preservation of the carbon chain [32] with the stable 1-Butaene-3-yne as product. Also in the DR of $C_4H_7$ the obvious pathway leading to butadiene and H accounts for only 20%, whereas in $C_4H_9^+$ the carbon chain is mostly preserved. From these data it follows that a simple pattern to predict the branching ratios of the DR of unsaturated hydrocarbons cannot be established, which clearly underlines the need for further research in this matter.

Concerning the overall reaction rate, it should be noted that our total reaction rate is a factor of 2–3 higher than those observed for other related unsaturated hydrocarbons like $C_3H_3^+$ and $C_5H_3^+$ [33]. With regard to branching ratios, our results can be compared with those obtained in charge inversion mass spectra of $C_3H_4^+$ isomers obtained by Hayakawa et al. [34], where electronically excited $C_3H_4$ isomers have been produced by collision of $C_3H_4^+$ ions with alkali metals. Also in these investigations a large predominance of hydrogen loss over break-up of the C–C bond has been observed. Moreover, lower excitation of the interim molecule has been found to favour the loss of one hydrogen atom over the loss of $H_2$ or 2H, which makes it probable that the former process is favoured at the collision energy of 0 eV employed in the present experiment. As the charge inversion experiment was also carried out with a partly deuterated parent molecule ($CD_3CCH$), it could be established that the formation of the propargyl radical ($CD_2CCH$) is strongly preferred over that of of $CD_3CC$. Thus, we expect the propargyl radical to be the major product also in the titular reaction.

Finally, the possibility of radiative recombination:

$$C_3H_4^+ + e^- \rightarrow C_3H_4 + h\nu \qquad (7)$$

can be discussed. Radiative recombination is an important process in atomic ions. However, the rate coefficients in atomic ions with low charges (for molecules the data is very sparse) at 0 eV relative kinetic energy are usually in the range of $10^{-11}$ to $10^{-9}$ $cm^3\,s^{-1}$ [35,36] and thus, much lower than the DR rate coefficients of molecules at low collision energies. Although energetically viable it is therefore thought to be a much slower process than DR in molecules and is only considered to play a role in very large molecules [37].

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