

# Chapter 11

## Chemistry of the C<sub>2</sub> and C<sub>3</sub> parent molecules

### 11.1 Chemistry of possible C<sub>2</sub> parents

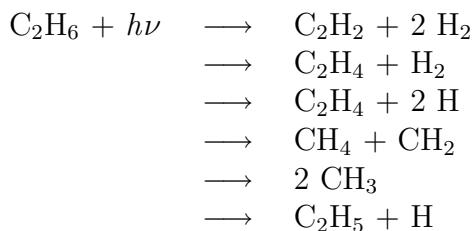
The emission of C<sub>2</sub> has been detected in numerous comets. However, no known parent molecule was found which would produce C<sub>2</sub> in a single step photodissociation, except possibly C<sub>2</sub>H<sub>2</sub>. Jackson [1976] was the first to propose this molecule as a parent species for the C<sub>2</sub> radical. His reasoning was the fact that C<sub>2</sub>H<sub>2</sub> is the smallest stable hydrocarbon able of forming C<sub>2</sub> in few reaction steps.

Using a different approach Yamamoto [1981] showed, that the C<sub>2</sub> radical is a second generation product, originating from a different parent molecule than C<sub>3</sub>. He based this result on an analysis of the variation of the density profiles of C<sub>2</sub> with nucleocentric and with heliocentric distance. He concluded that C<sub>2</sub>H<sub>2</sub> would be a plausible grandparent molecule.

After the first detection of C<sub>2</sub>H<sub>2</sub> in comet Hyakutake by Tokunaga *et al.* [1996], Sorkhabi *et al.* [1997] presented an explanation for the formation of C<sub>2</sub> based on photo chemistry. However they included only C<sub>2</sub>H<sub>2</sub> as parent and based their results on measurements of the C<sub>2</sub> Mulliken system obtained in the UV using the Hubble Space telescope. The small geocentric distance of comet Hyakutake made these measurements possible.

#### 11.1.1 C<sub>2</sub>H<sub>6</sub> chemistry

The photodissociation of ethane (C<sub>2</sub>H<sub>6</sub>) was studied early by Calvert and Pitts [1966]. The main products of the photolysis are C<sub>2</sub>H<sub>2</sub> and CH<sub>4</sub>. Unfortunately the exact branching ratios are still unknown. They seem however to depend on the wavelength of the irradiating photon. While at 1236 Å the first process is dominant, at large wavelengths the second process becomes increasingly important.



The C<sub>2</sub>H<sub>5</sub> produced in the last reaction dissociates almost immediately to C<sub>2</sub>H<sub>4</sub>. For this reason some authors do not even list this reaction (for example Lias *et al.* [1970] or Moses [2000]).

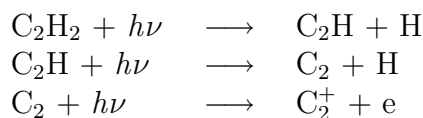
The photodissociation rate coefficients have been obtained mainly from Huebner *et al.* [1992] (see also section 12.2). While the cross section for wavelengths below 250 Å is derived from the atomic cross sections of C and H, there are measurements for the cross sections from 354-1127 Å, from 1160 to 1200 Å, from 1200 to 1380 Å and from 1380 to 1600 Å (see Huebner *et al.* [1992] and references therein). Branching ratios leading to dissociation and ionization have been measured by Lias *et al.* [1970] at 1055, 1236 and 1470 Å. The photodissociation rate coefficients derived by Huebner *et al.* [1992] are in good agreement with recent data by Moses [2000].

Little is known about the electron impact dissociation of C<sub>2</sub>H<sub>6</sub>. There are no reaction coefficients available, neither theoretical nor measured. Even the reaction pathways are unknown. One might assume that the electron impact dissociation of C<sub>2</sub>H<sub>6</sub> will form similar products as the photodissociation reactions. At the current time electron impact dissociation reactions of C<sub>2</sub>H<sub>6</sub> are not included in the reaction network discussed in section 12.2. This will be changed as soon as measurements become available. However as will be shown later (see section 18), C<sub>2</sub>H<sub>6</sub> is not the main source of C<sub>2</sub>. This result will hold true for a reaction network including electron impact dissociation of C<sub>2</sub>H<sub>6</sub>, unless these reactions are by magnitudes more effective than the photodissociation reactions.

### 11.1.2 C<sub>2</sub>H<sub>2</sub> chemistry

The photodissociation of C<sub>2</sub>H<sub>2</sub> was studied by a number of authors, for example Jackson [1976]; Jackson *et al.* [1996].

The main proposed sequence for dissociation of C<sub>2</sub>H<sub>2</sub> is



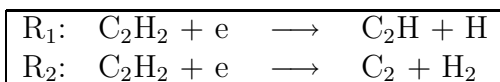
While this is the main photolytic channel for the production and destruction of the C<sub>2</sub> radical by C<sub>2</sub>H<sub>2</sub>, there is a second production channel by direct photodissociation of C<sub>2</sub>H<sub>2</sub>



However based on Wodtke and Lee [1985] this reaction has a very low efficiency at a wavelength of 1930 Å. Integrated over the whole solar spectrum this reaction is about one order of magnitude less important than the dissociation in C<sub>2</sub>H (see Huebner *et al.* [1992]).

In addition to ionization of C<sub>2</sub>, the photodissociation of C<sub>2</sub> is the second channel for the destruction of this radical. In general it is difficult to measure the photoabsorption cross sections of small radicals. Pouilly *et al.* [1983] have studied the photodissociation in the range from 918-1210 Å. Based on their results and the values for atomic carbon Huebner *et al.* [1992] calculated the reaction rates.

The photodissociation rate coefficients have been obtained mainly from Huebner *et al.* [1992] (see also section 12.2). Up to 500 Å the cross section is derived from the cross sections of atomic C and H. The cross section has been measured from 600 to 1000 Å and from 1050 to 2011 Å (see Huebner *et al.* [1992] and references therein). The derived values are in good agreement with recent data by Moses [2000]. For C<sub>2</sub>H<sub>2</sub> Wu [2000] has provided recent preliminary laboratory measurements of absorption cross sections at low temperatures. A comparison of the resulting dissociation rate coefficients showed only difference of less than a factor of two compared to the values obtained by Moses [2000] and Huebner *et al.* [1992]. For this work the values by Huebner *et al.* [1992] have been used for the C<sub>2</sub>H<sub>2</sub> photodissociation. Once the complete measurements by Wu [2000] are available these values can be updated. The electron impact dissociation of C<sub>2</sub>H<sub>2</sub> was studied in the laboratory by Pang *et al.* [1987]. There are two branches for the electron impact dissociation of C<sub>2</sub>H<sub>2</sub>.



Based on cross sections determined from the laboratory measurements and theoretical studies by Keady (see [Boice *et al.*, 1986] and [Schmidt *et al.*, 1988] and references therein) the temperature dependent cross sections given in table 11.1 can be determined. For the definition of k see equation (4.4).

T[K]	k(R <sub>1</sub> ) [cm <sup>3</sup> /s]	k(R <sub>2</sub> ) [cm <sup>3</sup> /s]
10000	1.37·10 <sup>-11</sup>	9.32·10 <sup>-12</sup>
15000	1.15·10 <sup>-10</sup>	2.13·10 <sup>-10</sup>
20000	3.35·10 <sup>-10</sup>	1.01·10 <sup>-9</sup>
25000	6.32·10 <sup>-10</sup>	2.57·10 <sup>-9</sup>
30000	9.55·10 <sup>-10</sup>	4.77·10 <sup>-9</sup>

Table 11.1: Reaction rate coefficients estimated by Boice *et al.* [1986]

All cross sections are for excitation and ionization, with some electronic excitation possibly leading to dissociation, but the branching ratio for this process is not given. However based on the known cross sections for small hydrocarbons Alman and Ruzic [2000] made some general estimates for the branching ratios for hydrocarbons.

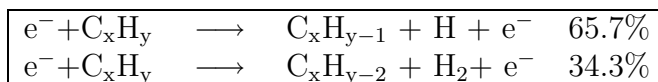


Table 11.2: Estimates for the branching ratio for electron impact dissociation of hydrocarbons (Alman and Ruzic [2000])

Alman and Ruzic [2000] approximated the electron impact cross sections using an approach developed for the study of cold plasma. Based on this estimated cross sections a new set of temperature dependent rate coefficients can be calculated

T[K]	k(R <sub>1</sub> ) [cm <sup>3</sup> /s]	k(R <sub>2</sub> ) [cm <sup>3</sup> /s]
10000	2.14·10 <sup>-10</sup>	8.44·10 <sup>-11</sup>
15000	2.10·10 <sup>-9</sup>	1.13·10 <sup>-9</sup>
20000	6.85·10 <sup>-9</sup>	4.30·10 <sup>-9</sup>
25000	1.43·10 <sup>-9</sup>	9.85·10 <sup>-9</sup>
30000	2.37·10 <sup>-8</sup>	1.74·10 <sup>-8</sup>

Table 11.3: Reaction rate coefficients based on estimates by Alman and Ruzic [2000]

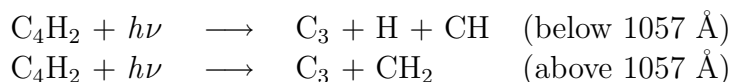
The new rate coefficients are about a factor 10 larger. It should be pointed out that the measurements of the cross section leading to R1 are almost constant near the upper energy limit and the measurements are terminated before the cross section decreases again. The code used to determine the reaction coefficients extrapolates the cross section, but since it is constant, the extrapolation is also constant. So there is some uncertainty about this result.

### 11.1.3 HC<sub>3</sub>N as possible further C<sub>2</sub> parent molecule

As has been shown in section 5.3 on page 47 cyanoacetylene HC<sub>3</sub>N, is another possible parent for C<sub>2</sub>. For the photodissociation reactions see the section 5.3 on the chemistry of the CN parent molecules. Following the discussion presented there HC<sub>3</sub>N is a parent of C<sub>2</sub> as well as a parent of CN.

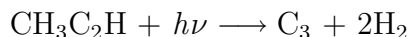
## 11.2 Chemistry of the C<sub>3</sub> parent molecules

The search for the parent molecules of C<sub>3</sub> is a longstanding discussion in the literature. Swings [1965] proposed already in 1965 diacetylene C<sub>4</sub>H<sub>2</sub> as a possible parent for C<sub>3</sub>. The relevant reactions are given as



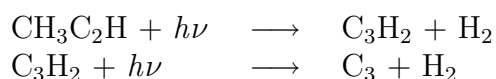
However, as was pointed out by Stief *et al.* [1972], below 1057 Å the solar flux is too weak for the first photodissociation process to take place. So only the second formation process

would be possible. This process is however not plausible, because the lifetime of C<sub>4</sub>H<sub>2</sub> is much higher than the measured lifetime of the C<sub>3</sub> parent. (e.g. Krasnopolsky [1991]). Stief *et al.* [1972] examined various potential parents, and proposed propyne (CH<sub>3</sub>C<sub>2</sub>H) as the plausible candidate. According to his work C<sub>3</sub> is formed via



This would mean a formation in a single step process. This is however in contradiction to the results by Yamamoto [1981] and Krasnopolsky [1991] which indicate a formation as a second generation radical.

Jackson [1976] proposed the following two-step mechanism



While most early work focused on propyne, there are two isomers of C<sub>3</sub>H<sub>4</sub>, allene H<sub>2</sub>CCCH<sub>2</sub> and propyne CH<sub>3</sub>C<sub>2</sub>H. Both forms are possible grandparents of C<sub>3</sub>.

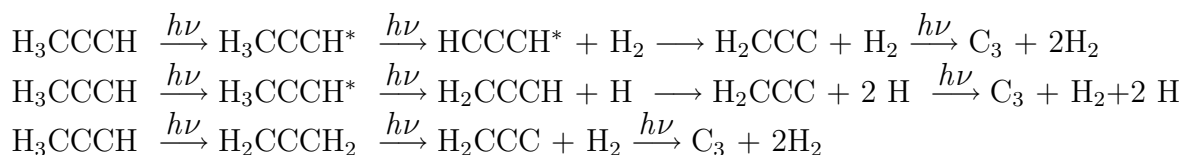
For the photodissociation of propyne at 1930 Å Mebel *et al.* [1998] predicted that it occurs via a fast pathway including internal excitation and a slow pathway including internal isomerization into allene. In the fast pathway propyne is excited and eliminates fast the acetylenic hydrogen. This is followed by a dissociation to H<sub>3</sub>CCC+H. The slow pathway includes the internal conversion into the vibrationally excited ground electronic state. The vibrationally excited propyne then dissociates to produce either H<sub>2</sub>CCCH+H or HCCCH+H<sub>2</sub>, or isomerize to allene, which, in turn, dissociates to H<sub>2</sub>CCC+H<sub>2</sub>. The HCCCH produced from propyne can have sufficiently high internal energy to rearrange to H<sub>2</sub>CCC.

The most likely mechanism for the photodissociation of allene at 1930 Å is to produce C<sub>3</sub>H<sub>2</sub>+H<sub>2</sub> via a vibrationally excited state of allene. It can also produce C<sub>3</sub>H<sub>3</sub>+H. The branching ratio was already determined by Jackson *et al.* [1991] experimentally to be 0.19 for the first and 0.81 for the latter reaction. The atomic hydrogen production channel dominates over the molecular hydrogen channel.

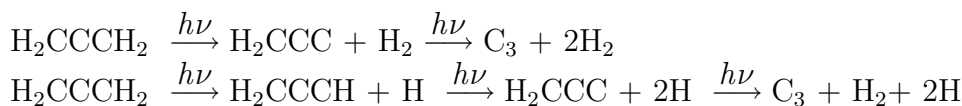
In both cases, the formation of C<sub>3</sub>+H<sub>2</sub> from propyne and allene goes via the same intermediate. This is in agreement with the fact that the same rotational distribution of the C<sub>3</sub> products is observed in the laboratory. Unfortunately this excludes the possibility to deduce the C<sub>3</sub> parent from the observed C<sub>3</sub> excitation spectrum.

Both scenarios can be summarized to

Propyne:



Allene:

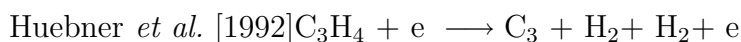


( $\xrightarrow{h\nu}$  is used as a short notation for  $+ h\nu \longrightarrow$ , the asterisk marks an excited state)

Within these reaction schemes only few cross sections are available. For the dissociation of allene there are measurements by Sutcliffe and Walsh [1952], Rabalais *et al.* [1971] and Fuke and Schnepf [1979]. For the dissociation of propyne (CH<sub>3</sub>C<sub>2</sub>H) also known as methylacetylene there are some measurements available by Fahr and Nayak [1996], Stief *et al.* [1971], Hamai and Hirayama [1979], and Nakayama and Watanabe [1964].

Jackson *et al.* [1992] discussed the implications of recent laboratory studies on the photochemistry C<sub>3</sub>H<sub>2</sub> on the cometary chemistry. Only recently some laboratory work on the photodissociation of C<sub>3</sub>H<sub>2</sub> has been published by Fahr *et al.* [1998]). However, the data is still too sparse to determine a reaction rate for this process. For this work a photodissociation rate of C<sub>3</sub>H<sub>2</sub> is determined from the observed spatial column density profiles of C<sub>3</sub> (see section 14.2.2).

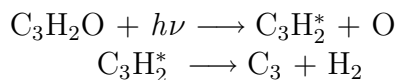
For the electron impact dissociation of C<sub>3</sub>H<sub>4</sub> there are no measurements available. In fact even the reaction pathways are unclear. One might assume a similarity to the photodissociation reactions. Alman and Ruzic [2000] give some general estimates for branching ratios for electron impact dissociation of smaller hydrocarbons as given in Table 11.2. However without measurements of electron impact reactions for any of the C<sub>3</sub>H<sub>4</sub> isomers it is nearly impossible to estimate reaction rates. As an estimate for the effect of electron impact dissociation on the formation of C<sub>3</sub> a hypothetical reaction



was included in the reaction network. For this reaction Huebner *et al.* [1992] gives an estimate for an effective dissociation rate. This reaction can be replaced by the individual electron impact dissociation reactions if reaction rates become available.

### 11.2.1 Possible more complex C<sub>3</sub> parent molecules

Krasnopolsky [1991] proposed propynal C<sub>3</sub>H<sub>2</sub>O as another possible parent. The dissociation of propynal is depending on the wavelength range considered. Krasnopolsky [1991] assumed that at 121.6 nm the dissociation is similar to that of propyne with one oxygen atom (rather than two hydrogen atoms) removed in the first step. The asterisk marks an excited state.



In the near ultraviolet region, the photodissociation occurs mainly via



The intensity of the solar flux is very low in the ultraviolet wavelength range. Therefore, the total yield of  $C_3$  produced from propynal is only approximately 0.01 compared to the production by  $C_3H_2$  [Krasnopolsky, 1991].

