

# Chapter 18

## Analyzing the formation chemistry of the C<sub>2</sub> and C<sub>3</sub> radical

One of the advantages of the ComChem model is the ability to investigate the processes for the production and destruction of each species. The model produces at five given nucleocentric distances a list of the ten most important reactions forming and destroying each species. In this chapter the information which can be extracted is discussed for one night as an example.

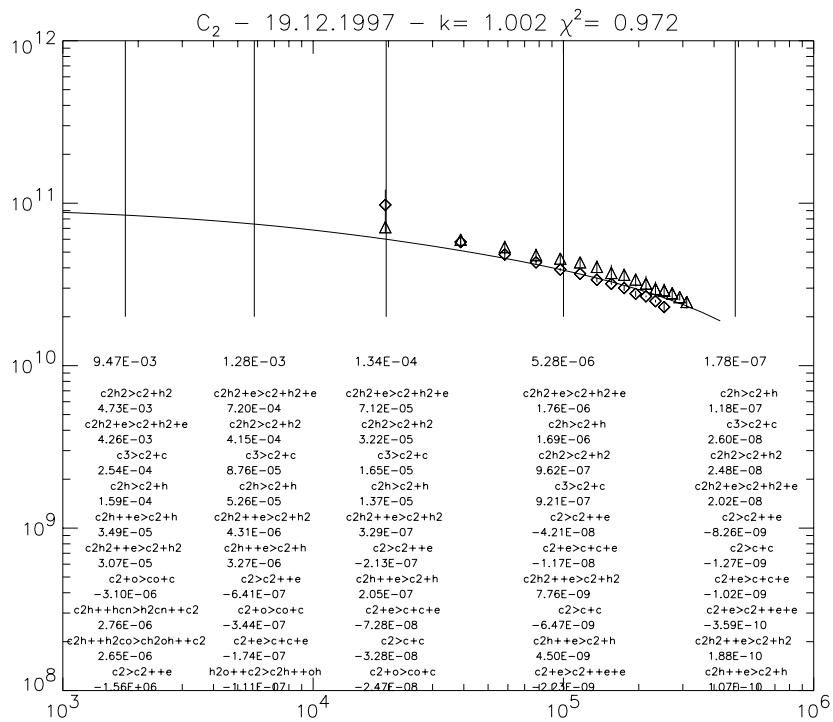


Figure 18.1: Example history output for the C<sub>2</sub> profile at r<sub>h</sub>=3.78AU

Figure 18.1 is an example of a 'history plot' for the modeled C<sub>2</sub> profile for the night of Dec. 19, 1997. These are semi-graphical representations of the information obtained at the five given nucleocentric distances. The lists at the bottom of the plot show the net production rate (negative if destruction) at the corresponding nucleocentric distance, followed by the ten most important reactions with their corresponding production- and destruction rate, respectively. Using this type of plot it is possible to study the details of the chemical network.

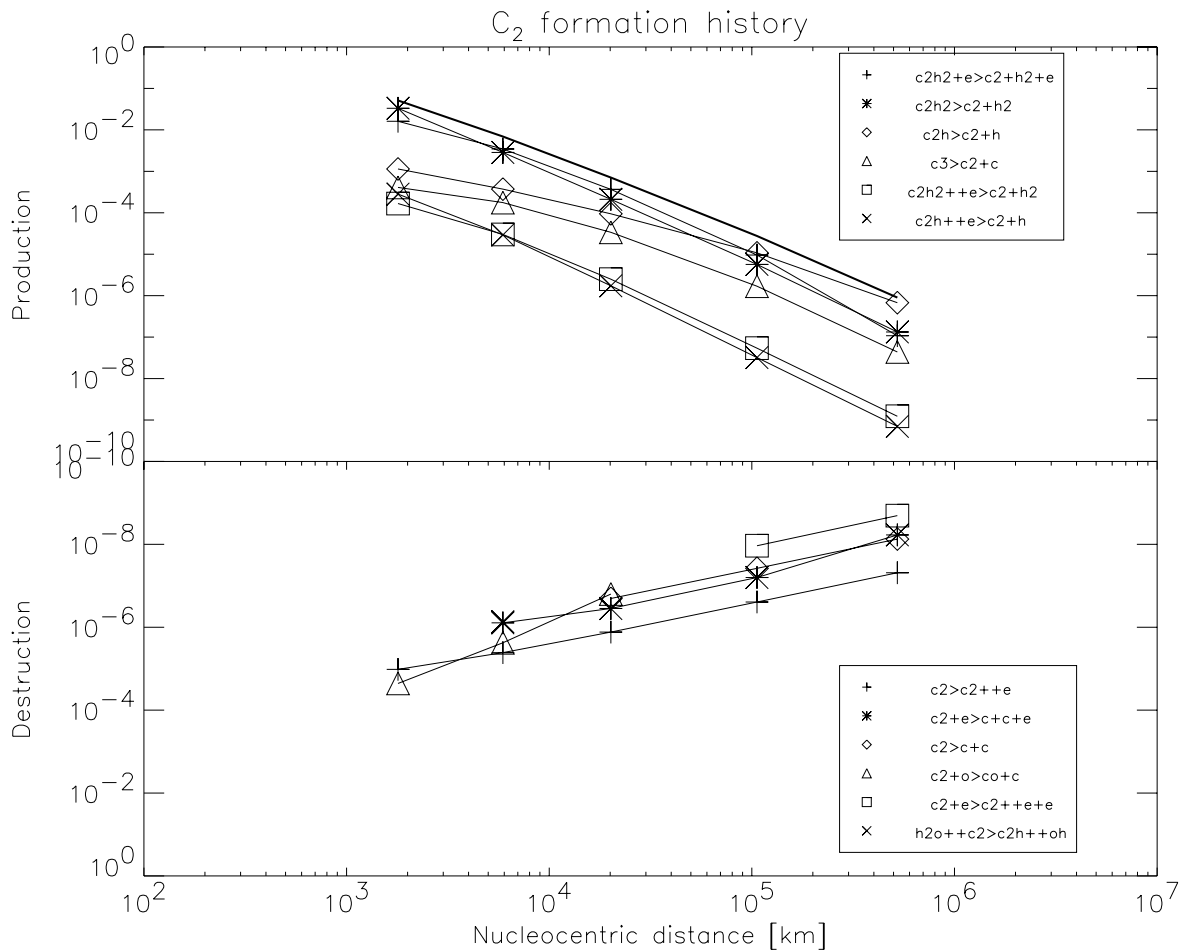


Figure 18.2: C<sub>2</sub> formation at  $r_h=3.78\text{AU}$

Figures 18.2 and 18.3 show a graphical way of displaying the same information. Instead of listing the production or destruction rates they are plotted versus nucleocentric distance with each line representing one reaction. Production reactions are plotted in the upper panel, destruction reactions are plotted in the lower panel. In this type of plot only reactions contributing more than 1% to the net production rate are presented to enhance the readability of the plot. The thick line corresponds to the net production- or destruction rate.

Both types of plots can be used to extract the details of the formation chemistry of  $C_2$  and  $C_3$  from the complete reaction network. However for practical use the graphical representation given in Figures 18.2 and 18.3 is easier to interpret than the lists given in the semi-graphical representation.

Based on the information given in Figure 18.2 there is a net production of  $C_2$  up to at least  $1 \cdot 10^6$  km shown by the thick line which remains always in the upper panel. The main production process changes with nucleocentric distance. Close to the nucleus photodissociation of  $C_2H_2$  is the main source of  $C_2$ . Starting from a nucleocentric distance of about  $1 \cdot 10^4$  km electron impact dissociation of  $C_2H_2$  becomes about equally important, for some distances even slightly dominant. In the graphical representation of Figure 18.2 this is shown by the line corresponding to the electron impact dissociation of  $C_2H_2$ , marked with crosses which is slightly above the line for the photodissociation of  $C_2H_2$  (marked by stars) outward of  $6 \cdot 10^3$  km nucleocentric distance. Closer to the nucleus the electrons are cooled effectively by collision with water molecules, but from a distance of  $1 \cdot 10^4$  km from the nucleus outward the electrons have enough kinetic energy to dissociate  $C_2H_2$  (for details see also Figure 12.1 in section 12). The decreasing density of the electrons with nucleocentric distance reduces the influence of the electron impact processes for larger nucleocentric distances.

The photodissociation of  $C_2H$  becomes more important for larger nucleocentric distances. Far out in the coma at about  $1 \cdot 10^6$  km this process is the dominant source for  $C_2$ . This corresponds to the fact that  $C_2H$  has to be formed in the coma and is not a constituent of the initial composition.

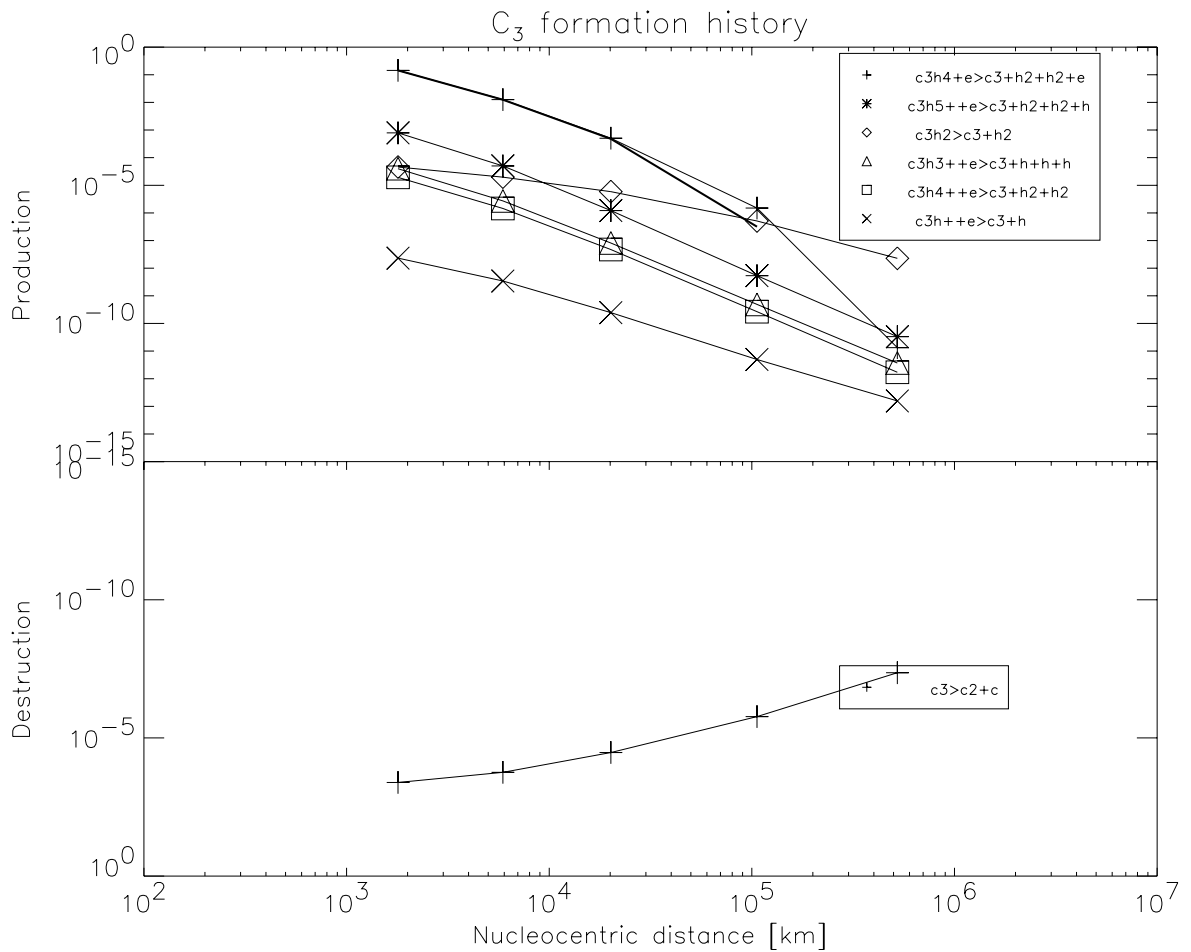
Dissociative recombination of  $C_2H_2^+$  and  $C_2H^+$  plays only a minor role, producing about four orders of magnitude less  $C_2$  than the dominant processes.

The main destruction process for  $C_2$  is ionization, followed by photodissociation and electron impact dissociation with about equal importance. Close to the nucleus the densities are high enough for neutral-neutral reactions of oxygen and  $C_2$  forming CO and a carbon atom.

The formation processes of  $C_3$  show also a strong variation with nucleocentric distance. Figure 18.3 shows that the electron impact dissociation of  $C_3H_4$  is the dominant source at small nucleocentric distances, while outward of about  $1 \cdot 10^5$  km the photodissociation of  $C_3H_2$  dominates. Because  $C_3H_2$  is not part of the initial composition it has to be formed first, mainly by a two step photodissociation of  $C_3H_4$ . A minor source for  $C_3$  is the dissociative recombination of  $C_3H_5^+$ . The sole destruction process for  $C_3$  in the model is by photodissociation, forming  $C_2$ .

Appendix D shows the plots of the formation chemistry for all main species contributing to the formation of  $C_2$  and  $C_3$ .  $C_2H_6$  is part of the initial composition. Figure D.5 shows its chemistry over nucleocentric distance. There are no formation processes for  $C_2H_6$ . So it has a net loss over the whole coma. Three channels for the destruction are of about equal importance, the photodissociation to  $C_2H_4$ ,  $C_2H_5$  and to  $CH_2+CH_4$ . This last channel removes part of the  $C_2H_6$  from the formation chemistry of  $C_2$ . It is interesting to note that a small amount of  $C_3H_5^+$  is formed by positive ion-atom interchange. As has been just discussed  $C_3H_5^+$  is a minor source for  $C_3$ . However looking at the absolute numbers this is only a very minor link between  $C_2H_6$  and  $C_3$ .

$C_2H_4$  (see Figure D.4) is mainly produced from  $C_2H_6$ . It has three about equal important

Figure 18.3:  $C_3$  formation at 3.78AU

dissociation channels, two forming  $C_2H_2$  and the main one forming  $2 CH_2$ . This means that another part of  $C_2H_6$  is removed from the formation chemistry of  $C_2$ . Overall more  $C_2H_6$  goes into the formation of  $CH_2$  than into the formation  $C_2H_2$  which forms  $C_2$ . The detailed study of the chemistry shows that  $C_2H_6$  is not a major parent of  $C_2$ .

Figure D.3 shows that for nucleocentric distances greater than about  $1 \cdot 10^4$  km  $C_2H_2$  is formed via the two photodissociation channels of  $C_2H_4$ . However  $C_2H_2$  is also part of the initial composition as well. Comparing the rate of formation of  $C_2H_2$  with the rate of destruction shows that there is a net loss of  $C_2H_2$ . Therefore most of the  $C_2H_2$  which goes into the formation of  $CH_2$  and  $C_2$  is native material sublimated from the nucleus and is not a result of the formation process via  $C_2H_4$ . This is another strong indicator that  $C_2H_2$  is the main parent of  $C_2$ , while  $C_2H_6$  is only of minor importance. Four destruction channels for  $C_2H_2$  are of about equal importance, two forming  $C_2$  by photodissociation and electron impact dissociation and two forming  $CH_2$  via the same processes.

Figure D.2 shows that  $C_2H$  is predominantly formed by photo- and electron impact dissociation of  $C_2H_2$ . Nearly all  $C_2H$  contributes to the formation of  $C_2$ . All other destruction channels are several orders of magnitude less important.

$C_3H_4$  is part of the initial composition. However there is a very minor channel producing this molecule by dissociative recombination of  $C_3H_5^+$  as can be seen in Figure D.9. The destruction of  $C_3H_4$  is dominated by photodissociation into  $C_3H_3$ . The photodissociation into  $C_3H_2$  and the direct formation of  $C_3$  by electron impact dissociation are of about equal importance. It is important to remember that the direct electron impact dissociation used here is only an approximation of the real reactions (see section 11.2). However up to now there are no laboratory studies on the electron impact dissociation of allene or propyne. All other destruction channels of  $C_3H_4$  are of minor importance.

Figure D.8 shows that  $C_3H_3$  is only an intermediate step in the photodissociation of  $C_3H_4$  and it is forming  $C_3H_2$  by a photodissociation reaction as discussed in section 11.2.  $C_3H_2$  is formed by  $C_3H_4$  and  $C_3H_3$  as shown in Figure D.7. It forms  $C_3$  by photodissociation.

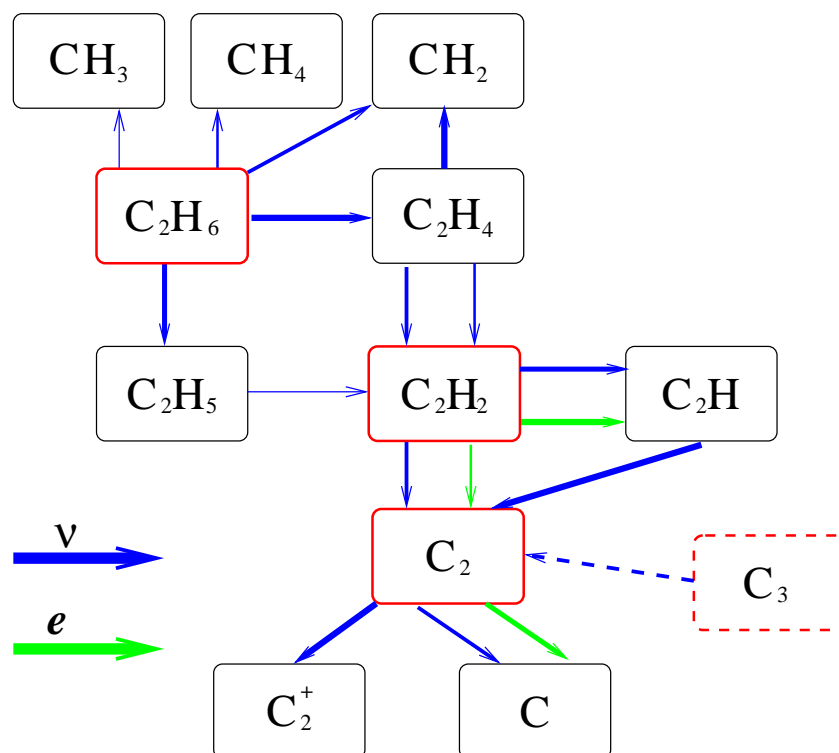


Figure 18.4: Formation of the  $C_2$  radical

The same detailed analysis of the  $C_2$  and  $C_3$  formation chemistry has been performed for several other nights studied in this work. As examples Figures D.10 and D.11 in appendix D show the history plots for  $C_2$  and  $C_3$  from the observations at 2.86 AU pre-perihelion, Figures D.12 and D.13 are the same plots for the observations obtained at 4.74 AU post-perihelion. Comparing these two plots and including Figures 18.2 and 18.3 shows that the chemistry changes very little over the whole range of heliocentric distances covered in this study.

Based on the detailed analysis of the reaction network it is possible to determine the 18 reactions dominating the formation of  $C_2$ . This is an important simplification compared to the over 200 reactions related to the hydrocarbon chemistry. The resulting main reaction network is shown in Figure 18.4. Red boxes denote observable species, the blue arrows are photodissociation reactions, the green arrows electron impact dissociation reactions.

For the formation of the  $C_2$  radical photodissociation and electron impact dissociation of  $C_2H_2$  play an about equal important role.

Looking at the two parent molecules  $C_2H_2$  and  $C_2H_6$  it has been stated already that the main destruction pathway of  $C_2H_6$  leads to  $C_2H_4$  and  $C_2H$ . Therefore  $C_2H_6$  is only a minor source for the  $C_2$  radical. This is in agreement with the fact, that the abundance of  $C_2H_6$  can be varied over a wide range without a significant effect on the modeled  $C_2$  profile (see section 15).  $C_2H_2$  is the main source for the  $C_2$  radical. This is important for estimating the errors on the production of  $C_2H_6$  compared the errors of  $Q(C_2H_2)$  in the following section.

For  $C_3$  the main reaction network is given in Figure 18.5. This network contains, apart from photodissociation and electron impact dissociation, also electron recombination of  $C_3H_5^+$ .

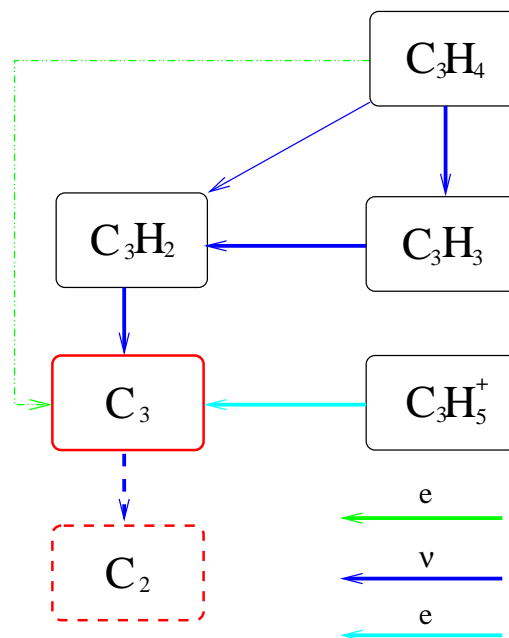


Figure 18.5: Formation of the  $C_3$  radical

The network has been simplified in the sense that allene and propyne are combined to a general  $C_3H_4$  parent molecule. This simplification is made, since it is not possible to determine the abundance ratios of the two isomers from the measurements.

A word of caution is necessary here. The simplified reaction networks as given in Figures 18.4, 18.5 and combined in Figure 18.6 can not replace the full chemistry network in general. The sole purpose of determining them is to find the main channels of formation and to support the following error analysis. At other heliocentric distances, the importance of reactions may change significantly or reactions which are not even included in the simplified network might

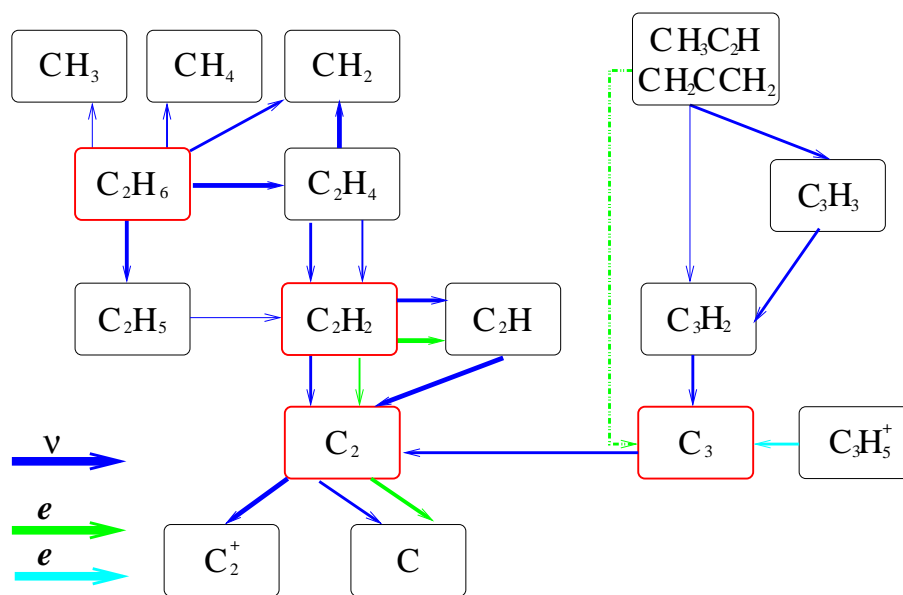


Figure 18.6: Formation of the  $C_2$  and  $C_3$  radical

become important.

