

# The formation of carbon chain molecules in IRC + 10216

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## SUMMARY

This paper considers the formation of carbon-chain molecules, including  $C_{2n}H$ ,  $C_nS$ ,  $HC_{2n+1}N$  ( $n = 1-3$ ) and  $SiC_n$  ( $n = 1-4$ ), in the outflowing envelope of the late-type carbon star IRC + 10216. The results suggest that the organo-sulphur species  $C_2S$  and  $C_3S$  can be formed in ion-molecule reactions involving acetylenic ions and parent CS and SiS molecules. In addition to ion-molecule processes, neutral-neutral reactions can play a significant role in the formation of hydrocarbons and cyanopolynes with up to six heavy atoms and in the formation of  $SiC_4$ , and suggest that  $SiC_3$  might be observable. However, the short time-scales available in the outflow are such that the observed abundances of the cyanopolynes larger than  $HC_5N$  cannot be reproduced using the parent molecules and abundances adopted here.

## 1 INTRODUCTION

The circumstellar envelope of the high mass-loss carbon star IRC + 10216 (CW Leo) contains many molecules, particularly complex species which are also detected in cold, dense interstellar clouds. The radial variation of temperature, density and visual extinction in the outflow ensure that a variety of chemical processes, including LTE, grain surface reactions, photochemistry and ion-molecule reactions, are important in determining the chemical composition of the envelope (McCabe, Smith & Clegg 1979; Lafont, Lucas & Omont 1982; Nejad, Millar & Freeman 1984; Glassgold, Lucas & Omont 1986; Nejad & Millar 1987).

In recent years a growing number of carbon chain molecules have been detected. These include the organo-sulphur species  $C_2S$  and  $C_3S$  (Cernicharo *et al.* 1987b; Saito *et al.* 1987; Yamamoto *et al.* 1987), the hydrocarbons  $C_nH$ ,  $n = 2-6$  (Cernicharo *et al.* 1987a; Bieging & Rieu 1988) and the cyanopolynes  $HC_{2n+1}N$ ,  $n = 1-5$ , though  $HC_5N$  has not been detected as yet. Recently Ohishi *et al.* (1989) have observed the linear  $SiC_4$  molecule while Cernicharo *et al.* (1989) have detected  $SiC$ . The presence of the cyclic  $SiC_2$  molecule in IRC + 10216 has been known for some time (Thaddeus, Guélin & Linke 1984). Previous chemical models (e.g. Glassgold *et al.* 1986; Nejad & Millar 1987) did not consider the organo-sulphur species, the organo-silicon species, nor  $C_nH$  ( $n > 4$ ). In this paper we apply some new laboratory data on both ion-molecule and neutral-neutral reactions to a model of the external envelope of IRC + 10216, thereby extending the work of Glassgold *et al.* (1986) and Nejad & Millar (1987).

## 2 MODEL

We have assumed that the gas in the envelope of IRC + 10216 expands in a spherically symmetric outflow at a

velocity of  $16 \text{ km s}^{-1}$  and a hydrogen mass-loss rate  $\dot{M} = 5 \times 10^{-5} M_{\odot} \text{ yr}^{-1}$  for a distance of 200 pc although, since the star may be closer than this (Zuckerman, Dyck & Claussen 1986), this may be too large by a factor of 2–3. The kinetic temperature profile,  $T(r) = 3.2 \times 10^4 r^{-0.79} \text{ K}$ , is taken from Glassgold *et al.* (1986). In our calculation of the photorates at a distance  $r$  from the star, we have adopted the approach suggested by Morris & Jura (1983), that is

$$\beta(r) = \beta_0 \exp\{-1.644[bA_v(r)]^{0.86}\} \text{ s}^{-1},$$

where  $\beta_0$  is the unshielded photodissociation rate due to the interstellar radiation field,  $A_v(r)$  is the visual extinction in the radial direction from a point  $r$  to infinity and is calculated using a gas-to-dust mass ratio of 200, and  $b$  is a coefficient which relates  $A_v$  to the effective optical depth for each photoprocess. For CO and  $H_2$  the photorates are calculated with the inclusion of self-shielding.

Parent species, whose initial fractional abundances with respect to  $H_2$  are given in Table 1, and dust are assumed to have formed rapidly before the material has travelled  $\sim 10^{15} \text{ cm}$  from the star. Our calculation of the radial distribution of molecular abundances starts at a radius of  $4.75 \times 10^{15} \text{ cm}$ , at which point cosmic-ray ionization, photo-ionization and photodissociation begin to drive the chemical evolution. Abundances are determined to an outer radius of  $5.25 \times 10^{17} \text{ cm}$ .

In addition to the calculation of abundances per unit volume, we have also determined the resulting column densities for comparison with observation. Where the distribution of a particular molecule is unresolved, one can calculate the total number of particles of the species and divide by the estimated area,  $\pi r_b^2$ , of the beam to obtain a beam-averaged column density. However, our models usually predict distributions which would be resolved, i.e. larger in extent than the telescope beam,  $r_b$ . In the case of species produced and destroyed in the photochemical, i.e. outer, region

**Table 1.** Adopted fractional abundances of parent species.

species	abundance
H <sub>2</sub>	1.0
He	0.15 <sup>a</sup>
CO	4(-4) <sup>b</sup>
C <sub>2</sub> H <sub>2</sub>	2(-5) <sup>b</sup>
SiS	1(-6) <sup>c</sup>
HCN	6(-6) <sup>b</sup>
CH <sub>4</sub>	2(-6) <sup>b</sup>
NH <sub>3</sub>	2(-6) <sup>b</sup>
N <sub>2</sub>	1.84(-5) <sup>b</sup>

Notes: <sup>a</sup>Assumed; <sup>b</sup>from Nejad & Millar (1987); <sup>c</sup>from fit to observations. a(-b) signifies a  $\times 10^{-b}$ .

of the envelope, their formation occurs at radii  $r \lesssim r_b$  and the column densities were calculated assuming a telescope beam radius smaller than the formation radius. However, for parent species, this method overestimates the true column density and a different approach was adopted. In general, the fractional abundances of parent species remain roughly constant in the outflow until a radius is reached, beyond which the fractional abundances decrease rapidly due to photoprocesses. To estimate column densities for parent species which have a spatial distribution larger than  $r_b$ , we assume a constant fractional abundance between sharply defined inner and outer radii,  $r_i$  and  $r_o$ , respectively ( $r_i$  being taken as  $10^{15}$  cm and  $r_o$  the radius at which the fractional abundance decreases by a factor of  $1/e$ ). The column density can then be estimated by integrating analytically the radial distribution over the volume intersected by the telescope beam, assuming a sharp-edged beam centred on the star. This yields the following equation for the beam-averaged column density,  $\bar{N}$ , of a parent species

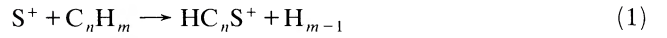
$$\bar{N} = \frac{\dot{M}x_i}{m(\text{H}_2)v\pi r_b^2} [r_b\theta + r_o(1 - \sin\theta) - r_i],$$

where  $r_b$  is the beam radius ( $r_o > r_b \geq r_i$ ),  $\theta = \cos^{-1}(r_b/r_o)$ ,  $x_i$  is the initial fractional abundance with respect to H<sub>2</sub> and the other quantities have their usual meanings.

### 3 RESULTS

#### 3.1 The organo-sulphur species

The C<sub>n</sub>S species,  $n=1-3$ , have been observed in IRC+10216 and in interstellar clouds (Cernicharo *et al.* 1987; Saito *et al.* 1987; Yamamoto *et al.* 1987). Millar & Herbst (1990) have discussed the interstellar chemistry of C<sub>2</sub>S and C<sub>3</sub>S and suggested that ion-molecule reactions of the type (Smith *et al.* 1988; Wlodek, Bohme & Herbst 1989)

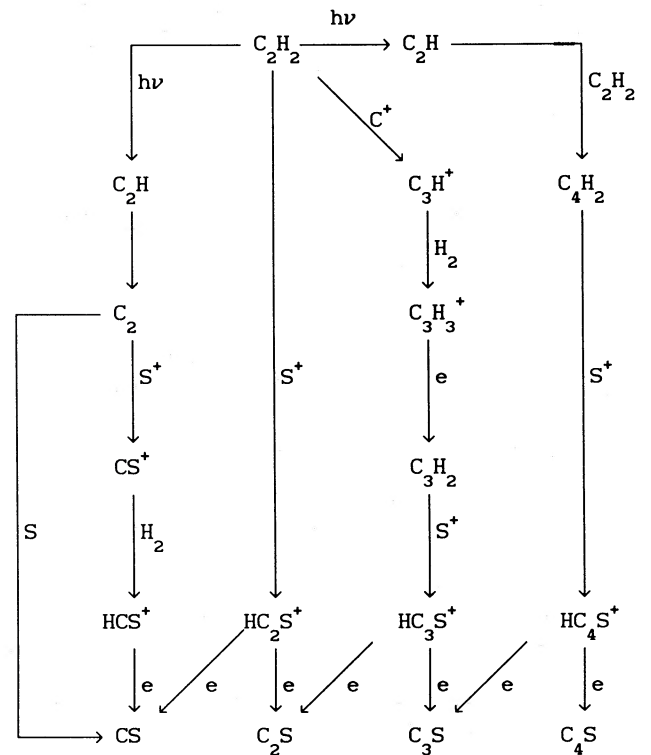


are the major formation mechanism. If such a scheme also occurs in IRC+10216, the S<sup>+</sup> ions originate as photo-products from parent SiS and/or CS molecules, in agreement with LTE photospheric abundance estimates (Tsuji 1973; McCabe *et al.* 1979). Observations of SiS in IRC+10216 (Sahai, Wootten & Clegg 1984; Bieging & Rieu 1989; Cernicharo *et al.* 1989) demonstrate convincingly that it is a parent, while the evidence for CS as a parent is less clear (Cernicharo *et al.* 1987b). The observed column density of SiS ( $7 \times 10^{15}$  cm<sup>-2</sup>) can be reproduced using an initial fractional abundance of  $10^{-6}$  consistent with the observations of Bieging & Rieu (1989) – although they assumed a lower mass-loss rate of  $2.1 \times 10^{-5} M_\odot \text{ yr}^{-1}$ . In order to see if SiS can account entirely for the CS, C<sub>2</sub>S and C<sub>3</sub>S observations, we have included reactions (1) and (2) in a detailed numerical model. We have also considered a reaction involving S atoms,



with rate coefficients of  $1.5 \times 10^{-10}$  cm<sup>3</sup> s<sup>-1</sup>, though this made only a small contribution to the formation of the C<sub>2</sub>S species.

Fig. 1 shows a schematic diagram of this chemistry, and the calculated abundances are compared with observations in Model 1 of Table 2. One sees immediately that the calculated abundances of C<sub>2</sub>S and C<sub>3</sub>S are typically two orders of magnitude less than those observed. These discrepancies occur because of the low parental abundance of SiS and because of the dependence of the scheme on S and S<sup>+</sup> which



**Table 2.** Observed and modelled column densities for  $C_nS$ .

species	$N_{\text{obs}} (\text{cm}^{-2})^a$	$N (\text{cm}^{-2})$		
		model 1 <sup>b</sup>	model 2 <sup>c</sup>	model 3 <sup>d</sup>
SiS	$7 \times 10^{15}$	$7 \times 10^{15}$	$7 \times 10^{15}$	$7 \times 10^{15}$
CS	$4 \times 10^{15}$	$3 \times 10^{14}$	$7 \times 10^{15}$	$7 \times 10^{15}$
$C_2S$	$1.5 \times 10^{14}$	$2 \times 10^{12}$	$1.4 \times 10^{14}$	$7 \times 10^{13}$
$C_3S$	$1.1 \times 10^{14}$	$4 \times 10^{11}$	$1.4 \times 10^{14}$	$8 \times 10^{13}$

Notes: <sup>a</sup>Cernicharo *et al.* (1987b); <sup>b</sup>parent SiS at  $10^{-6}$ ,  $C_nS$  ( $n=1-3$ ) formed as in Fig. 1; <sup>c</sup>parent SiS and CS at  $10^{-6}$ , parent  $C_2S$  and  $C_3S$  at  $2 \times 10^{-8}$ ; <sup>d</sup>parent SiS and CS at  $10^{-6}$ ,  $C_2S$  and  $C_3S$  formed via ion-molecule reactions between CS and hydrocarbon ions.

form in the outer envelope where, because densities are low, collision times are long. It thus appears necessary to propose a mechanism for  $C_nS$  formation in IRC+10216 different from that proposed for dense interstellar clouds. LTE calculations suggest that CS, and even  $C_2S$  and  $C_3S$ , may be formed in or near the photosphere. If indeed CS,  $C_2S$  and  $C_3S$  are parents then initial fractional abundances of  $10^{-6}$ ,  $2 \times 10^{-8}$  and  $2 \times 10^{-8}$ , respectively, ensure good agreement with observations (see Model 2 of Table 2). Interferometric observations of these molecules would be useful in this regard.

While it does appear difficult to account for the CS abundance unless it is assumed to be a parent species, we have performed calculations which support the suggestion made by Cernicharo *et al.* (1987b) namely that  $C_2S$  and  $C_3S$  are formed from parent CS via ion-molecule reactions in the photochemical region of the envelope. If one assumes that suitably rapid reactions exist between CS and the more abundant photochemical products of  $C_2H_2$ , for example,



then the observed abundances of  $C_2S$  and  $C_3S$  may be reproduced (Model 3 of Table 2). On the other hand, the large proton affinity of CS may ensure that



rather than  $HC_3S^+ + H$ . As yet, there have been no laboratory studies of any ion-molecule reactions involving CS.

### 3.2 The hydrocarbons $C_nH$ , $n=1-3$

Observations of  $C_2H$  provided some of the earliest evidence that photochemistry played an important role in the envelope of IRC+10216 (Huggins & Glassgold 1982). Bieging & Rieu (1988) have determined the radial distribution of  $C_2H$  from interferometric observations finding that it has a maximum fractional abundance of  $2.6 \times 10^{-6}$  at a radius of  $6 \times 10^{16}$  cm, with half maxima at  $2.5 \times 10^{16}$  and  $8.5 \times 10^{16}$  cm. On the assumption that  $C_2H$  is produced in the photodissociation of parent  $C_2H_2$ , with a rate from Lee (1984),



our model calculation gives a maximum fractional abundance of  $1.1 \times 10^{-5}$  at  $3.7 \times 10^{16}$  cm, with half maxima at

**Table 3.** Observed and modelled column densities for  $C_nH$ .

species	$N_{\text{obs}} (\text{cm}^{-2})^a$	$N (\text{cm}^{-2})$	
		model 4 <sup>b</sup>	model 5 <sup>c</sup>
$C_2H$	$10^{16}$	$3.5 \times 10^{16}$	$2.7 \times 10^{16}$
$C_4H$	$5 \times 10^{15}$	$5.5 \times 10^{13}$	$1.0 \times 10^{15}$
$C_6H$	$3 \times 10^{14}$	$1.3 \times 10^{14}$	$7.0 \times 10^{14}$

Notes: <sup>a</sup>Cernicharo *et al.* (1987a); <sup>b</sup>no neutral formation mechanisms; <sup>c</sup>including neutral mechanisms.

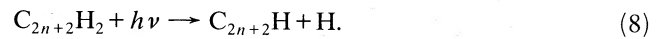
$2.4 \times 10^{16}$  and  $5.5 \times 10^{16}$  cm, reasonable agreement given the uncertainties in both the modelling and observations.

Column densities of  $C_4H$  and  $C_6H$  in IRC+10216 have been determined by Cernicharo *et al.* (1987a) and are listed in Table 3. We have modelled the formation of these species using successive reactions of  $C_2H_2$  and  $C_2H$  with ions such as  $C_2H_2^+$  and  $C_4H_2^+$ , as described by Glassgold *et al.* (1986) with rate coefficients taken from the experimental results of Anicich, Huntress & McEwan (1986) and Dheandano *et al.* (1986). This calculation, the results of which are given as Model 4 in Table 3, was able to account for  $C_6H$ , but not for  $C_4H$ . The column density of  $C_6H$  may be an upper limit since we made the optimistic assumption that all  $C_6H_x^+$  gave  $C_6H$  upon dissociative recombination with electrons.

Alternative routes to  $C_4H$  and  $C_6H$  may involve neutral reactions, such as



followed by



For the reactions of type (7) we adopted rate coefficients of  $6.7 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ , as determined by the high-temperature laboratory measurements of Tanzawa & Gardiner (1978). This value is somewhat larger than that measured at room temperature by others for the reaction between  $C_2H_2$  and  $C_2H - 5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  (Lange & Wagner 1975) and  $3.1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  (Laufer & Bass 1979). The column densities of  $C_4H$  and  $C_6H$ , found using the largest rate coefficient, are given as Model 5 in Table 3, and show good agreement with the observations. Use of the smallest rate coefficient above roughly halves the estimated column densities of  $C_4H$  and  $C_6H$ .

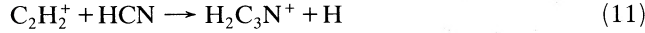
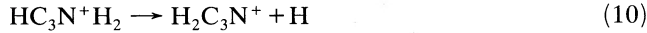
### 3.3 The cyanopolyynes, $HC_{2n+1}N$ , $n=1-3$

With the exception of  $HC_9N$ , all the cyanopolyynes in the series up to  $HC_{11}N$  have been detected in IRC+10216, with column densities which reduce only by a factor of about 10 in going from  $HC_3N$  to  $HC_{11}N$ , indicating that a very efficient mechanism for forming large molecules must be operative.

Detailed interferometric observations of  $HC_3N$  have been made by Bieging & Rieu (1988) who have determined its radial distribution, finding a small, but significant, fractional abundance of  $6 \times 10^{-8}$  close to the star, at  $10^{16}$  cm, rising to

a maximum of  $3 \times 10^{-7}$  at a radius of  $4.5 \times 10^{16}$  cm, with half maxima at  $2 \times 10^{16}$  and  $7 \times 10^{16}$  cm. They suggest that neutral processes may account for the  $\text{HC}_3\text{N}$  observed close to the star, while ion-molecule reactions driven by the photon field determine the distribution in the outer envelope.

$\text{HC}_3\text{N}$  can be formed in reactions between  $\text{C}_2\text{H}_2^+$  and CN or HCN (Glassgold *et al.* 1986; Nejad & Millar 1987)



This scheme, which is shown in Fig. 2, gives a maximum in the fractional abundance of  $\text{HC}_3\text{N}$  at a radius of  $4.5 \times 10^{16}$  cm, in good agreement with the observations, with the peak abundance of  $\text{HC}_3\text{N}$  about 20 per cent of that determined by Bieging & Rieu (1988), using ion-dipolar rate coefficients. The column density of  $\text{HC}_3\text{N}$  calculated using this scheme is given in Table 4 (Model 6) and is much less than the value of  $3 \times 10^{15} \text{ cm}^{-2}$  (for a 25 arcsec source size) determined by Cernicharo *et al.* (1987a). Millar (1988) found  $N(\text{HC}_3\text{N}) = 10^{14} \text{ cm}^{-2}$ , our smaller value being due largely to the use of a smaller photo-ionization rate for acetylene (Herbst & Leung 1986).

This discrepancy suggests that other routes to  $\text{HC}_3\text{N}$  need to be considered. One possibility is that neutral reactions are important. Lichtin & Lin (1986) have measured the rate coefficient of

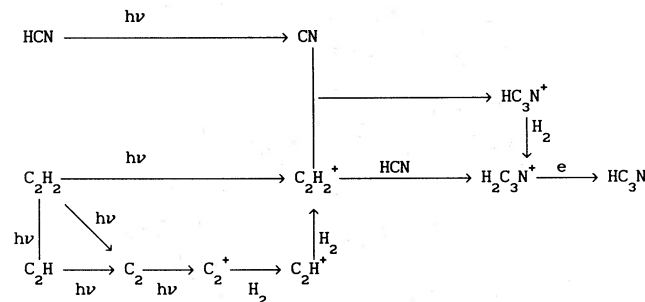


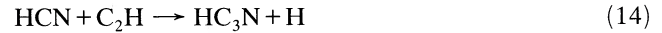
Figure 2. The major  $\text{HC}_3\text{N}$  formation routes used in our model 6.

Table 4. Observed and modelled column densities for  $\text{HC}_{2n+1}\text{N}$ .

species	$N_{\text{obs}} (\text{cm}^{-2})^a$	$N (\text{cm}^{-3})$	
		model 6 <sup>b</sup>	model 7 <sup>c</sup>
$\text{HC}_3\text{N}$	$3 \times 10^{15}$	$5 \times 10^{13}$	$1.4 \times 10^{15}$
$\text{HC}_5\text{N}$	$6 \times 10^{14}$	$2 \times 10^{13}$	$1.6 \times 10^{14}$
$\text{HC}_7\text{N}$	$3 \times 10^{14}$	—	$1.7 \times 10^{13}$

Notes: <sup>a</sup>Cernicharo *et al.* (1987a); <sup>b</sup>no neutral reactions; <sup>c</sup>as model 6 but including the neutral reactions (13)–(15).

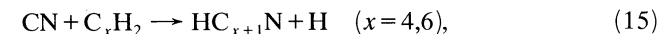
finding  $k_{13} = 2.3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  at 294 K and  $6.85 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  at 700 K, while Becker & Hong (1983) have measured the reaction



with  $k_{14} = 2.2 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ , according to Yung, Allen & Pinto (1984). We have included these two reactions in our model, using the room temperature rate coefficient for (13) in the absence of any knowledge of its low temperature behaviour, and obtained a column density of  $1.4 \times 10^{15} \text{ cm}^{-2}$ , in good agreement with the observed value (see Model 7 of Table 4). Reaction (13) provides over 90 per cent of the  $\text{HC}_3\text{N}$  formed in this model. In addition, the  $\text{HC}_3\text{N}$  fractional abundance distribution has a maximum value of  $5.8 \times 10^{-7}$  at  $3.2 \times 10^{16}$  cm, with half maxima at  $2.3 \times 10^{16}$  and  $4.5 \times 10^{16}$  cm in reasonable agreement with the values determined by Bieging & Rieu (1988), although, since we have not included any chemical processes in the inner envelope, we do not reproduce the observed abundance at  $10^{16}$  cm.

We have investigated the possibility that the larger cyanopolynes are formed in both ion-molecule and neutral-neutral reactions. The ion-molecule scheme is similar to that suggested by Glassgold *et al.* (1986) and involves reactions between  $\text{C}_4\text{H}_2^+$  and  $\text{C}_4\text{H}_3^+$  with CN. No reactions of HCN with  $\text{C}_4\text{H}_x^+$  were used since these are endothermic for  $x > 1$  (Anicich *et al.* 1986). This ion-molecule scheme produced only about 1 per cent of the observed column density of  $\text{HC}_5\text{N}$  (Model 6 of Table 4), a discrepancy which is likely to be greater for the larger cyanopolynes if similar ion-molecule schemes are invoked. This is due to the competition between ion-molecule and fast dissociative recombination processes in the outer envelope. For large molecules in which chain growth is via ion-molecule reactions acting sequentially, dissociative recombination is the dominant loss process for ions in the outer envelope, thus hindering severely the growth of long chain molecules.

We have therefore modelled the formation of  $\text{HC}_5\text{N}$  and  $\text{HC}_7\text{N}$  using neutral reactions analogous to reaction (13)



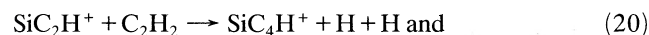
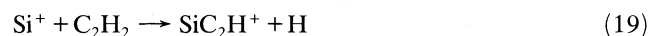
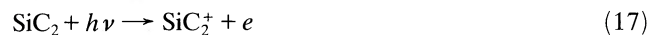
with  $k_{15} = k_{13}$ . This scheme has recently been shown to be efficient in the formation of the cyanopolynes in cold, dense interstellar clouds (Herbst & Leung 1990). Our results, Model 7 in Table 4, give a column density of  $\text{HC}_5\text{N}$  about 25 per cent of that observed and of  $\text{HC}_7\text{N}$  about 5 per cent of that observed. Considering the uncertainty in the rate coefficients this may indicate that  $\text{HC}_5\text{N}$ , at least, is formed in neutral-neutral reactions in the outer envelope of IRC + 10216.

### 3.4 The organo-silicon species

Two new organo-silicon molecules have been detected recently in IRC + 10216. Cernicharo *et al.* (1989) observed SiC and obtained a column density, averaged over a 17 arcsec beam, of  $6 \times 10^{13} \text{ cm}^{-2}$ . The distinct line profiles observed imply that SiC has a spatial extent much larger than that of  $\text{SiC}_2$  (Thaddeus, Guélin & Linke 1984). This, together with the higher  $\text{SiC}_2$  column density observed, led Cernicharo *et al.* to suggest that SiC is formed as a photo-dissociation product of  $\text{SiC}_2$ . In addition Ohishi *et al.* (1989)



have detected the linear  $\text{SiC}_4$  molecule with a column density of  $7 \times 10^{12} \text{ cm}^{-2}$  averaged over a 25 arcsec beam and suggested that it might be formed in either ion-molecule or neutral-neutral reactions. In order to quantify these suggestions we have modelled the formation of the  $\text{SiC}_n$  chain under the assumption that  $\text{SiC}_2$  is a parent species with an initial fractional abundance of  $1.5 \times 10^{-7}$ .  $\text{SiC}$  and  $\text{SiC}_4$  are then formed in the reactions



The neutral species so produced are photodissociated, resulting in the formation of  $\text{SiC}_3$



In this scheme, the ion-molecule reactions (19) and (20) have had rate coefficients determined experimentally at room temperature (Bohme, Wlodek & Fox 1988). Using photodissociation rates of  $\text{SiC}_n$  equal to that of  $\text{SiS}$  [ $10^{-10} \exp(-2.3 A_\nu) \text{ s}^{-1}$ , Prasad & Huntress 1980], we were able to reproduce the observed  $\text{SiC}$  column density, but the observed  $\text{SiC}_4$  column density is too small by a factor of 5 (see Model 8 of Table 5).

Ohishi *et al.* (1989) have suggested that  $\text{SiC}_4$  might be produced in either of two neutral-neutral reactions



Because reaction (24) involves two parent species, it would, if efficient, be a major destruction mechanism for  $\text{SiC}_2$  and result in an  $\text{SiC}_2$  column density much below that observed. The inclusion of reaction (23), with a small rate coefficient of  $5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ , in Model 9 of Table 5, is sufficient to reproduce the observed  $\text{SiC}_4$  abundance. In our calculations,  $\text{SiC}_3$  has a column density of, at most,  $2 \times 10^{12} \text{ cm}^{-2}$ ,

although this value depends on some unknown photodissociation rates. None the less, our calculations suggest that, once laboratory frequencies are known,  $\text{SiC}_3$  may be detectable in IRC + 10216.

## 4 DISCUSSION AND CONCLUSIONS

The expansion of circumstellar envelopes leads to a rich chemistry in which large carbon chain molecules grow through ion-molecule and neutral-neutral reactions initiated by the external ultraviolet radiation field. However, our calculations have shown that there are a number of factors which hinder chain growth. First, since the kinematic time-scale is short,  $\sim 2000 \text{ yr}$  for IRC + 10216, chain growth via a sequence of reactions must be quite fast as each member of the chain tends to occur slightly further out in the envelope than the previous member. Thus collision rates are reduced, while at the same time the increasing photon flux can destroy potential reactants as well as limit the extent of product distributions. In addition, the electron abundance increases in the outer envelope and rapidly destroys molecular ions, thereby diminishing the efficiency of chain growth via ion-molecule reactions.

Our detailed calculations show that ion-molecule reactions may be able to account for the observed  $\text{C}_2\text{S}$  and  $\text{C}_3\text{S}$  if  $\text{CS}$  and  $\text{SiS}$  are parent species, and if one or both of these are capable of suitably fast reactions with the more abundant ionic products of the acetylene photochemistry. On the other hand, ion-molecule processes do not seem able to explain the observed column densities of the cyanopolynes. Neutral-neutral reactions are probably important in this regard, as well as in the formation of the hydrocarbon species and the organo-silicon molecules, although the low-temperature behaviour of the neutral rate coefficients adopted here remains unknown.

The small but significant amount of  $\text{HC}_3\text{N}$  observed in the inner envelope, where the external radiation field cannot penetrate, suggests that carbon-chain molecules can be formed by processes close to the star, either in the photosphere, or early in the outflow via neutral reactions, or in grain surface processes.

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## REFERENCES

- Anicich, V. G., Huntress, W. T. & McEwan, M. J., 1986. *J. Phys. Chem.*, **90**, 2446.
- Becker, R. S. & Hong, J. H., 1983. *J. Phys. Chem.*, **87**, 163.
- Biegging, J. H. & Rieu, N. Q., 1988. *Astrophys. J.*, **329**, L107.
- Biegging, J. H. & Rieu, N. Q., 1989. *Astrophys. J.*, **343**, L25.
- Bohme, D. K., Wlodek, S. & Fox, A., 1988. In: *Rate Coefficients in Astrochemistry*, p. 193, eds Millar, T. J. & Williams, D. A., Kluwer, Dordrecht.
- Cernicharo, J., Guélin, M., Menten, K. M. & Walmsley, C. M., 1987a. *Astr. Astrophys.*, **181**, L1.
- Cernicharo, J., Guélin, M., Hein, H. & Kahane, C., 1987b. *Astr. Astrophys.*, **181**, L9.
- Cernicharo, J., Gottlieb, C. A., Guélin, M., Thaddeus, P. & Vrtilek, J. M., 1989. *Astrophys. J.*, **341**, L25.
- Dheandano, S., Forte, L., Fox, A. & Bohme, D. K., 1986. *Can. J.*

**Table 5.** Observed and modelled column densities for  $\text{SiC}_n$ .

species	$N_{\text{obs}} (\text{cm}^{-2})^a$	$N (\text{cm}^{-2})$	
		model 8 <sup>b</sup>	model 9 <sup>c</sup>
$\text{SiC}$	$6 \times 10^{13}$	$6 \times 10^{13}$	$6 \times 10^{13}$
$\text{SiC}_2$	$2 \times 10^{15}$	$1.5 \times 10^{15}$	$1.5 \times 10^{15}$
$\text{SiC}_3$	—	$3 \times 10^{11}$	$2 \times 10^{12}$
$\text{SiC}_4$	$7 \times 10^{12}$	$1.5 \times 10^{12}$	$1.5 \times 10^{13}$

Note: <sup>a</sup>Observed column densities taken from Cernicharo *et al.* (1987b, 1989) and Ohishi *et al.* (1989); <sup>b</sup>no neutral-neutral reactions; <sup>c</sup>the  $\text{SiC}_2\text{--C}_2\text{H}$  reaction has been included.

- Chem.*, **64**, 641.
- Glassgold, A. E., Lucas, R. & Omont, A., 1986. *Astr. Astrophys.*, **157**, 35.
- Herbst, E. & Leung, C. M., 1986. *Mon. Not. R. astr. Soc.*, **222**, 689.
- Herbst, E. & Leung, C. M., 1990. *Astr. Astrophys.*, in press.
- Huggins, P. J. & Glassgold, A. E., 1982. *Astrophys. J.*, **252**, 201.
- Lafont, S., Lucas, R. & Omont, A., 1982. *Astr. Astrophys.*, **106**, 201.
- Lange, W. & Wagner, H. G., 1975. *Ber. Bunsenges. Phys. Chem.*, **79**, 165.
- Laufer, A. H. & Bass, A. M., 1979. *J. Phys. Chem.*, **83**, 310.
- Lee, L. C., 1984. *Astrophys. J.*, **282**, 172.
- Lichtin, D. A. & Lin, M. C., 1986. *J. Chem. Phys.*, **104**, 325.
- McCabe, E. M., Smith, R. C. & Clegg, R. E. S., 1979. *Nature*, **281**, 263.
- Millar, T. J., 1988. In: *Rate Coefficients in Astrochemistry*, p. 287, eds Millar, T. J. & Williams, D. A., Kluwer, Dordrecht.
- Millar, T. J. & Herbst, E., 1990. *Astr. Astrophys.*, in press.
- Morris, M. & Jura, M., 1983. *Astrophys. J.*, **264**, 546.
- Nejad, L. A. M. & Millar, T. J., 1987. *Astr. Astrophys.*, **183**, 279.
- Nejad, L. A. M., Millar, T. J. & Freeman, A., 1984. *Astr. Astrophys.*, **134**, 129.
- Ohishi, M. *et al.*, 1989. *Astrophys. J.*, **345**, L83.
- Prasad, S. S. & Huntress, W. T., 1980. *Astrophys. J. Suppl.*, **43**, 1.
- Sahai, R., Wootten, A. & Clegg, R. E. S., 1984. *Astrophys. J.*, **284**, 144.
- Saito, S., Kawaguchi, K., Yamamoto, S., Ohishi, M., Suzuki, H. & Kaifu, N., 1987. *Astrophys. J.*, **317**, L115.
- Smith, D., Adams, N. G., Giles, K. & Herbst, E., 1988. *Astr. Astrophys.*, **200**, 191.
- Tanzawa, T. & Gardiner, W. C., 1978. *Proc. Symp. (Int.) Comb.*, **17**, 563.
- Thaddeus, P., Guélin, M. & Linke, R. A., 1984. *Astrophys. J.*, **283**, L45.
- Tsuji, T., 1973. *Astr. Astrophys.*, **23**, 411.
- Wlodek, S., Bohme, D. K. & Herbst, E., 1988. *Mon. Not. R. astr. Soc.*, **235**, 493.
- Yamamoto, S., Saito, S., Kawaguchi, K., Kaifu, N., Suzuki, H. & Ohishi, M., 1987. *Astrophys. J.*, **317**, L119.
- Yung, Y. L., Allen, M. & Pinto, J. P., 1984. *Astrophys. J. Suppl.*, **55**, 465.
- Zuckerman, B., Dyck, H. M. & Claussen, M. J., 1986. *Astrophys. J.*, **304**, 401.