Is acetylene essential for carbon dust formation?

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ABSTRACT

We have carried out an investigation of the chemical evolution of gas in different carbon-rich circumstellar environments. Previous studies have tended to invoke terrestrial flame chemistries, based on acetylene (C$_2$H$_2$) combustion to model the formation of carbon dust, via polycyclic aromatic hydrocarbons (PAHs). In this work, we pay careful attention to the accurate calculation of the molecular photoreaction rate coefficients to ascertain whether there is a universal formation mechanism for carbon dust in strongly irradiated astrophysical environments. A large number of possible chemical channels may exist for the formation of PAHs, so we have concentrated on the viability of the formation of the smallest building block species, C$_2$H$_2$, in a variety of carbon-rich stellar outflows. C$_2$H$_2$ is very sensitive to dissociation by UV radiation. This sensitivity is tested, using models of the time-dependent chemistry. We find that C$_2$H$_2$ formation is sensitive to some of the physical parameters and that in some known sources of dust formation it can never attain appreciable abundances. Therefore, multiple (and currently ill-defined) dust-formation channels must exist.

Key words: astrochemistry – molecular processes – stars: AGB and post-AGB – dust, extinction – ISM: molecules.

1 INTRODUCTION

The observational properties of dust and the physical consequences of its presence in the interstellar medium are extremely well known and well documented (Draine 2003). However, its composition, structure and size-distribution are still subjects of much discussion. Even though there are no direct samples of interstellar dust, carbonaceous dust deposits found in meteorites give us an indication of what structure and composition we might expect. These grains consist of a core of microcrystalline aromatic moieties surrounded by a crystalline graphite mantle (Bernetowicz, Croat & Daulton 2006). Significantly, the precise chemical kinetic pathways leading to the (relatively simple) case of carbon dust formation are almost entirely speculative.

The recent observations of higher-than-expected dust masses around high-redshift quasars (Bertoldi et al. 2003; Dwek, Galliano & Jones 2007) and local supernovae (Matsuura et al. 2011) have caused a resurgence of interest in the issues of dust-formation mechanisms and efficiencies. In the local universe, dust is observed mainly in two environments: dense interstellar clouds and circumstellar media. The main sources of interstellar dust are believed to be evolved red giants, novae and supernovae (Salpeter 1977; Dwek 2004; see Tielens 2008 for a review). There are thus two questions that we address in this paper: (i) What is the chemical pathway for the formation of macromolecular species that leads to the formation of dust-nucleation sites? (ii) What range of physical parameters determines viability of these pathways?

For the sake of (relative) simplicity, we limit our discussion to the formation of carbon dust in carbon-rich circumstellar environments, making the simplifying assumption that the oxygen is completely locked up in the relatively inert form of CO. In such an environment the C:O ratio is $\gtrsim 1$ and is a crucial parameter. However, it should be noted (see below) that this usually assumed approximation has been challenged by relatively recent observational and modelling efforts (e.g. André, Dr Chefel & Starrfield 1994).

Some of the earliest attempts at modelling carbon dust formation concentrated on novae, some of which are seen to produce very optically thick (carbon) dust shells on time-scales of days. Rawlings (1988) developed a proto-PDR model of the chemistry in nova ejectae, and found that molecule formation requires the presence of H$_2$ and carbon neutrality (C). The presence of C$^+$ (and the carbon ionization continuum) inhibits molecule formation. Chemical equilibrium is established very fast (within $\sim 10$ s). Rawlings & Williams (1989, hereafter RW89) extended this and proposed a non-LTE chemical kinetic model of (carbon) dust formation in nova ejectae which proceeds via a limited hydrocarbon chemistry – totally dominated by the photophysics, and requiring all oxygen to be locked up in CO. This latter finding has been challenged – both by the observations that suggest that carbon dust is formed in oxygen-rich (O $>$ C) environments (e.g. André et al. 1994) – and also models of the chemistry in nova outflows (Ponetfrac & Rawlings 2004).

In these models, C$_2$ (for which the more significant of the two pre-dissociation bands is shielded against photodissociation in a C$^+$...
region) is the key building block species, rather than C$_2$H$_2$ which is susceptible to photodissociation. As such, nucleation of dust was found to be possible only in a C$_1$ region, but requires some source of ionization to drive the chemistry.

Pontefract & Rawlings (2004) extended the work by RW89 by including oxygen and nitrogen chemistry and updated the photoreaction rates. Surprisingly, they found that the overall chemistry is not as dependent on the photochemistry as earlier studies had suggested and that carbon dust could be formed even when all of the oxygen is not ‘locked’ in CO. The work highlighted that CN, CO and C$_2$ are key molecular species in the formation pathways of larger species. Although C$_2$H$_2$ was included, its chemistry was not closely scrutinized.

More generally, it has been proposed that polyacetylene aromatic hydrocarbon (PAH) molecules are key intermediates in carbon dust formation and act as nucleation sites for dust grains (Cherchneff, Barker & Tielens 1992; Helling et al. 1996; Cherchneff 2011). This inferred link is due to the close relationship between the molecular structure of PAHs and the carbon structure of graphite. Also, observations of the far-IR continuum due to carbon dust are accompanied by strong PAH features (Tielens 2008). However, some caution should be exercised with the interpretation of these features. For example, PAH (and/or hydrogenated amorphous carbon) emission is also detected in some carbon-dust-producing novae but in all cases it is only seen well after dust formation and in an environment where it would be susceptible to photodissociation. This indicates that – for novae at least – the PAHs are transitory products of dust destruction, rather than intermediates to dust formation (Evans & Rawlings 2008).

Gail & Sedlmayr (1987) proposed chemical mechanisms required to form PAH molecules in stellar winds. The acetylene molecule (C$_2$H$_2$) was found to be crucial in the formation pathway. An important contribution came from Frenklach & Feigelson (1989, hereafter FF89). They investigated a mechanism of PAH formation, using a chemical kinetic approach. The chemistry network was based on soot production in terrestrial hydrocarbon flames, which they applied to astrophysical conditions, i.e. much lower pressure and densities. They confirmed that the complex network of chemical reactions can essentially be described by a sequence of hydrogen abstraction followed by acetylene addition. Following a study by Miller & Melius (1991), Cherchneff et al. (1992) then found the dominant pathway for closure of the first aromatic ring in flames is via the recombination of propargyl.

Acetylene does not possess a permanent dipole moment and so does not have a rotational spectrum observable at radio wavelengths. It is therefore somewhat elusive; detections rely on rovibrational transitions, observable in the mid-infrared. For this reason, detections tend to be limited to the warm gas (~1000 K) along the lines of sight towards young stellar objects (e.g. Boonman et al. 2003). There is also strong evidence for the presence of C$_2$H$_2$ in evolved carbon stars within the dust-formation region (1–5 stellar radii); the most well known of which – IRC+10216 – exhibits a forest of C$_2$H$_2$ lines in the 11–14 μm window (Fonfría et al. 2008). Indeed, after H$_2$ and CO, C$_2$H$_2$ is determined to be the most abundant species in the gas – with a fractional abundance of ~8 × 10$^{-5}$ – although this is primarily detected outside the dust-formation zone and so is not necessarily associated with the dust-formation process. There may even be some evidence of C$_2$H$_2$ freeze-out into icy mantles at larger radii in IRC+10216, and an icy mantle-based origin for interstellar C$_2$H$_2$ is strongly suggested by Spitzer observations of the correlation between C$_2$H$_2$ and gas-phase CO$_2$ towards Cepheus A East (Sonnentrucker, González-Alfonso & Neufeld 2007).

Cherchneff et al. (1992) addressed the issue of PAH chemistry and dust formation in the carbon-rich envelopes of late asymptotic giant branch (AGB) stars; driven by stellar pulsations and (strong, density enhancing) shocks. Although extremely dense, the gas is much cooler and not subject to the intense FUV radiation field that is present in a nova, so the chemical model was based on a terrestrial neutral gas acetylenic-burning soot chemistry. In such environments, the carbon budget is largely split between CO and C$_2$H$_2$. The chemistry was largely based on well-studied flame chemistries (e.g. FF89), expanded and augmented to include free radicals. It was found that C$_2$H$_2$ is the key species in macro-molecular growth and (especially) ring closure/cyclization to form aromatic hydrocarbon rings, as well as the polymerization to multiple ring PAHs. The formation of the first aromatic ring is often recognized as the main ‘bottleneck’ in macro-molecular growth/dust nucleation. In this, as in later studies (e.g. Cherchneff & Cau 1999), ring closure was found to proceed following reactions of two propargyl radicals (C$_3$H$_2$) or via a lesser channel involving reaction of acetylene with 1,3 butadiyne (C$_4$H$_2$) (e.g. see figs 3 and 4 in that paper). In either case, C$_2$H$_2$ initiates the reaction. Reaction networks need to include both two-body and three-body reactions, but did not include photoreactions, or an ion–molecule chemistry. Although they were able to identify the presence of a temperature window (900–1100 K) in which the formation of PAHs is possible, the formation efficiency is too low – possibly due to the lack of inclusion of the effects of a local UV radiation field and/or an ion–molecule chemistry.

Considering a different class of object Woods et al. (2002) modelled the formation of benzene (C$_6$H$_6$) in a protoplanetary nebula (CRL618) where the chemistry is characterized by high densities, temperatures and ionization rates – although photoreactions were significantly inhibited throughout the molecule-formation zone due to the assumed presence of dust. This chemistry is somewhat different to the Cherchneff et al. schemes due to the presence of a degree of ionization and an efficient ion-molecule chemistry. However, even in these conditions, C$_2$H$_2$ plays a crucial role – mainly through the initiating reaction of

HCO$^+$ + C$_2$H$_2$ → products . . .

All of the above models and reaction schemes have made extremely simplistic assumptions about the radiation field and the photoreaction rates; either by only considering the chemistry in low-luminosity environments (or external to an optically thick dust-formation zone) – in which case they are ignored, or by simply ‘scaling up’ interstellar photoreaction rates in a way that does not properly take into account the specific nature of the radiation field and/or the significance of ionization continua. The overall aim of this work is therefore to include an ion–molecule chemistry and a careful recalculation of the photoreaction rates using local radiation fields and accurate cross-sectional data to reassess the viability of C$_2$H$_2$ formation in a variety of carbon-rich circumstellar environments. As C$_2$H$_2$ is fundamental to the formation of PAH molecules, we try to determine if the amount of C$_2$H$_2$ produced in carbon-rich AGB and nova environments is enough to seed dust formation. We use a specially adapted chemical network for high temperatures and densities, paying particular attention to a more accurate account of the photochemistry involved in non-interstellar conditions, which (as explained above) previously had been highly oversimplified. We investigate a broad range of dust-forming objects which includes carbon stars with effective temperatures higher than AGB stars (e.g. CH subgiants), AGB stars and novae. By doing this, we aim to establish the range of parameter space within which effective C$_2$H$_2$ formation is possible. It is worthwhile noting that the presence of
C$_2$H$_2$ is a necessary, but not sufficient condition for PAH growth in H-rich circumstellar outflows. Therefore, we will establish a parameter space in which it is possible to form PAH-rich outflows.

In Section 2, we describe the model that was implemented. Section 3 specifies the physical and chemical parameters used for the three different carbon-rich circumstellar environments that we have modelled. We describe the results and analysis in Section 4. Finally, in Section 5, we summarize our results and their implications.

2 THE MODEL

The nucleation sites for dust-grain formation are formed in the gas phase in a cooling, expanding atmosphere, such as in the outflow from a red giant (Cadwell et al. 1994). Therefore, if PAHs are the key intermediate molecules to carbonaceous dust they should also be formed in the stellar winds that feed the circumstellar environment. We therefore model the time-dependent chemistry that occurs in an appropriately located gas parcel. This will be the part of the envelope whose temperature lies within the range that is appropriate for dust formation – corresponding to the `condensation radius’ in previous studies (e.g. Clayton & Wickramasinghe 1976).

As explained above, the main chemical pathway to form a PAH molecule starts with the polymerization of C$_2$H$_2$ (Gail & Sedlmayr 1987) and we therefore identify acetylene as being the key molecule in the formation of larger species, such as PAHs. We investigate the viability of acetylene formation as being the controlling factor in the formation of dust-nucleation sites via PAHs as intermediate macro-molecules.

The gas in stellar outflows is dense ($n > 10^3$ cm$^{-3}$) and warm ($T > 1000$ K), so that (providing the gas is not too hot, such that bond-breaking, collisional dissociation reactions can occur), molecules can be formed efficiently and quickly. As the gas expands and its density falls, the chemical reaction rates are quenched. However, the geometrical dilution time-scale is typically many orders of magnitude larger than the chemical kinetic time-scale (Rawlings 1988) and this is not a critical factor in determining the dust-formation efficiency. Despite the possible presence of shocks, etc., and although the gas is very far from thermal equilibrium, the characteristic timescale of the outflow is often much larger than the chemical kinetic timescale. We therefore assume that both the circumstellar environment and the stellar wind are spherically symmetric around the star. We model the time-dependent chemistry that would occur during the period of a single shock.

The chemistry is evolved for a period of time that corresponds to the dynamical age of the dust-forming region (e.g. the shock period or expansion time-scale) by which time the molecular abundances are often – but not always – fairly close to being in chemical equilibrium. We have investigated the sensitivity of the equilibrium abundances to the physical conditions. The key free parameters that we have varied are: the total abundances of the elements, the photospheric temperature of the star, the density and the temperature of the gas. Other parameters, such as the dilution factor for the radiation field, are taken to be defined by the observed location of dust formation. The C/O ratios are given in Table 4. The cosmic ray ionization rate is set to $10^{-17}$ s$^{-1}$, which is representative of the assumed galactic background rate (Dalgarno 2006).

2.1 The chemistry

The chemical network includes 1537 reactions between 102 gas-phase species involving eight elements (H, He, C, N, O, S, Na and Si). These species are listed in Table 1.

Table 1. Chemical species.

| Species          |
|------------------|
| H, H$_2$, H$^+$, H$^-$, H$_2^+$, H$^+_2$ |
| C, C$^+$, CO, CO$^+$, CH, CH$^+$, CH$_2$, CH$_2^+$ |
| CH$_4$, CH$_2^+$, C$_2$, C$_2^+$, C$_2$H, C$_2$H$^+$, C$_2$H$_2$, C$_2$H$_2^+$ |
| N, N$^+$, NH, NH$^+$, NH$_2$, NH$_2^+$, NH$_3$, N$_2$, N$_2^+$, N$_2^+_3$ |
| O, O$^+$, O$_2$, O$_2^+$, OH, OH$^+$, OH$_2$, H$_2$O, H$_2$O$^+$, H$_2$O$^+_2$ |
| HCO, HCO$^+$, H$_2$CO, H$_2$CO$^+$, CO, CO$^+$ |
| CN, CN$^+$, CN$^-$, HCN, HCN$^+$, HNC, HCN$^+$ |
| NO, NO$^+$, HNO, HNO$^+$, NO$_2$, NO$_2^+$, OCN |
| He, He$^+$, He$^-$, Na, Na$^+$, e$^+$ |
| S, S$^+$, S$^-$, HS, HS$^+$, H$_2$S, H$_2$S$^+$, H$_2$S$^+_3$ |
| CS, CS$^+$, HCS, HCS$^+$, H$_2$CS$^+$, SO, SO$^+$, SO$_2$, SO$_2^+$, OCS, OCS$^+$ |
| NS, Si, Si$^+$, SiH, SiH$^+$, SiH$_2$, SiO, SiO$^+$, SiOH$^+$, SiO$_2$ |

The chemical complexity of the reactants was limited as we only concentrate on the initiating steps in the formation of larger molecular species.

The ratefile is an adapted set of reactions, applicable to high densities, high temperatures and intense radiation fields. Many of the reactions and rate coefficients ($k_r$) were taken from the UMIST Database for Astrochemistry (e.g. Woodall et al. 2007) where the formulation for the rate coefficients is valid in the operative temperature range. Additional data were taken from data bases that are relevant to high-temperature/high-density environments (e.g. Rawlings, Drew & Barlow 1993; Lim et al. 2002; Pontefract & Rawlings 2004, etc.). Although the densities are very much larger than those applicable to interstellar studies. We have not included three-body reactions as the main formation reactions are not dependent on molecular hydrogen. Reaction types that are included in the chemistry are charge transfer, ion–molecule, radiative association, neutral exchanges, radiative recombination, dissociative recombination and negative ion reactions. Reactions which are particularly significant in addition to those applicable to interstellar clouds are neutral–neutral reactions, reactions with significant activation energy barriers, and reactions between rovibrationally excited species, due to the high temperatures that exist in circumstellar outflows.

The main formation and destruction reactions for C$_2$H$_2$ in normal interstellar environments are given in Table 2.

2.1.1 Photochemical reactions

In circumstellar environments, irradiated by the central star, the UV radiation field is typically very much stronger and has quite a different spectral shape to that which pertains in the interstellar medium. It is therefore important that we pay particular attention to the correct evaluation of the photoreaction rate coefficients: The rates for all photodissociation, photoionization and photodetachment reactions are calculated ab initio.

In these conditions, the key factor in determining the viability of any chemical kinetic pathway that leads to dust formation is therefore the stability of the intermediates against photodissociation/photoionization by the stellar radiation field.

The calculation of the photorates by a time-dependent non-interstellar radiation field in an expanding atmosphere is a non-trivial task. There are two components to the calculation of the photoreaction rate-coefficients in the local radiation field:

(i) a basic ‘photospheric’ rate, calculated for the specific photoreaction and radiation field;
(ii) a time-dependent geometrical dilution, due to the expansion of the wind.
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In earlier models, and for the sake of simplicity, photoreaction rates were calculated by scaling the unshielded interstellar photorates by a ratio of the stellar flux to that of the interstellar radiation field, either by a single scaling factor, or by a value appropriate to a single characteristic wavelength for each reaction in question (Rawlings 1988). In this study, we use a more accurate approach that can encompass the variety of situations that we wish to investigate: photoreactions are calculated by fully integrating the known cross-sections and oscillator strengths for a certain temperature range over the specified radiation field. Following van Dishoeck (1988), we treat the contributions to the photodissociation rate arising from continuous absorption and those arising from absorption in discrete transitions as separable. These can be written as

\[ k_{\text{cont}} = \int \sigma(\lambda) I(\lambda) d\lambda \, s^{-1} \]  

and

\[ k_{\text{line}} = \frac{\pi e^2}{m c^2} \frac{\lambda^2}{f_0 d \eta_0 x_1 I(\lambda_{\text{ul}}) s^{-1}}, \]

respectively, where \( k \) is the photoreaction rate coefficient, \( \lambda \) is the wavelength, \( I_0 \) is the flux, \( \sigma(\lambda) \) is the cross-section for the reaction, \( f_0 \) is the oscillator strength and the other symbols have their usual meanings. Photoreaction cross-sectional data and oscillator strengths were taken from a variety of sources (e.g. van Dishoeck 1988; Rawlings et al. 1993) as described in Rollins & Rawlings (2012). We assume that the gas is within the carbon-neutral zone (equivalent to being behind the photodissociation region: as was shown in Rawlings (1988), complex chemistries are unsustainable in C \( \odot \) regions). We therefore assume that H\(_2\) and CO are fully self-shielding and that carbon photoionization is effectively suppressed. The lower limit of the integral in equation (1) is therefore set to the ionization threshold for C \( \odot \) (1102 Å).

This study is too generalized to consider the radiation fields of individual sources so we instead opt to characterize the radiation field by that of an (appropriately diluted) single-temperature blackbody (\( T_{BB} \)). In addition, as we have investigated a wide range of \( T_{BB} \) which may also be time dependent, we have utilized a parametric fit to the dependence of the photoreaction rates to \( T_{BB} \). Thus, after calculating the photoreaction rates for several values of \( T_{BB} \) we fit a simple quadratic to the logarithm of the rates

\[ \log(k) = a + b \log(T_{BB}) + c \log(T_{BB})^2, \]

where the coefficients \( a \), \( b \) and \( c \) are specific to each reaction and are defined for a certain temperature range. The ranges used are as specified in Table 4.

For the geometrical dilution, we assume simple spherical symmetry, in which case, at a distance \( R \) from the star, the dilution factor is given by

\[ W = \left( \frac{R_s}{2R} \right)^2 R \gg R_s, \]

where \( R_s \) is the photospheric radius of the star.

Finally, we include a (small) contribution to the photorate deriving from the local internally generated UV field induced by cosmic ray ionizations (Prasad & Tarafdar 1983; Gredel et al. 1989).

### 3 Physical and Chemical Parameters

We have investigated three different carbon-rich (C > O) astrophysical environments. We have studied acetylene formation in the outflows from

(i) thermally pulsing AGB stars,
(ii) novae, and
(iii) pulsating G/K-type carbon stars.

The physical conditions are quite different in these three classes of objects, yet they are each known to be prolific sources of carbon dust.

First, we have extended the work of Cherchneff et al. (1992), which modelled PAH formation in the post-shock gas in thermally pulsing AGB stars. These are well-known dust production sites. Including a more complete photochemistry has allowed us to determine more accurately the stability of C\(_2\)H\(_2\) in this environment. We have applied our model to examine the viability of PAH formation

| Reaction | Reaction rate |
|----------|---------------|
| 1        | \( k_1 = 1.80 \times 10^{-10} \, \text{e}^{-1000/T} \) |
| 2        | \( k_2 = 2.63 \times 10^{-11} \, \text{e}^{-1500/T} \) |
| 3        | \( k_3 = 1.00 \times 10^{-9} \) |
| 4        | \( k_4 = 5.00 \times 10^{-10} \) |
| 5        | \( k_5 = 1.00 \times 10^{-10} \) |
| 6        | \( k_6 = 1.45 \times 10^{-10} \) |
| 7        | \( k_7 = 1.45 \times 10^{-10} \) |
| 8        | \( k_8 = 5.40 \times 10^{-10} \) |
| 9        | \( k_9 = 3.80 \times 10^{-10} \) |
| 10       | \( k_{10} = 8.39 \times 10^{-12} \) |
| 11       | \( k_{11} = 5.30 \times 10^{-9} \) |
| 12       | \( k_{12} = 7.70 \times 10^{-9} \) |
| 13       | \( k_{13} = 1.61 \times 10^{-9} \) |
| 14       | \( k_{14} = 8.75 \times 10^{-9} \) |
| 15       | \( k_{15} = 2.54 \times 10^{-9} \) |
| 16       | \( k_{16} = 2.20 \times 10^{-9} \) |
| 17       | \( k_{17} = 9.50 \times 10^{-9} \) |
| 18       | \( k_{18} = \) (see text) |
| 19       | \( k_{19} = \) (see text) |
in the ejecta around novae, some of which (but not all) are also known to be efficient dust producers. We have also investigated the outflows from stars that are somewhat hotter than AGB stars, so that we can ascertain the possibility of soot chemistries operating in these circumstellar environments. The initial conditions selected for each of these three scenarios are discussed below, and the values for the key physical and chemical parameters are summarized in Table 3. In this table, the chemical time-scale refers to the time-scale on which dust is seen to form (in the case of novae) or the period for shocks, within which dust must form (in the case of AGB and G–K stars).

There are considerable variations (and uncertainties) in the observationally inferred elemental abundances for each source type. However, the C:O ratio is a key parameter. This determines the efficiency of the hydrocarbon chemistry and, hence (whatever reaction pathway is followed) the viability of carbon dust formation. To effect the requisite variations in the C:O ratio, we have adopted cosmic abundance values for all elements other than carbon; 0.85, 6.0 × 10⁻³, 4.6 × 10⁻⁴, 1.4 × 10⁻⁴, 3.5 × 10⁻⁵ and 3.2 × 10⁻⁵ for He, N, O, S, Na and Si, respectively. The abundance of carbon is then varied to give the (observed) C:O ratio as specified in Table 3.

### 3.1 Case I: AGB stars

High carbon–oxygen ratios (>2) are unlikely in the Galaxy (although common in the Large Magellanic Cloud) and are excluded. Lower ratios of C:O ~ 1.5 are expected for most carbon stars (Bergeat, Knapik & Rutily 2001). Lambert et al. (1988) found slightly subsolar values for the oxygen and nitrogen abundances in AGB stars, but our approximation of using solar abundances is essentially valid. This is consistent with the abundances used by Cherchneff et al. (1992) and Cherchneff (2012) to model an AGB star that is similar to the well-known source IRC+10216.

We assume the shocks form at 1.5 stellar radii from the star and the gas has a kinetic temperature of 2000 K with a maximum density of 10¹⁴ cm⁻³. The outflows undergo periodic shocks due to stellar pulsations. We model the time-dependent chemistry that would occur in a single shock with a period of 650 d. This follows the physical parameters used by Cherchneff (2012), allowing us to compare our results to distinguish the effects of including a complete photochemistry. In a study of 390 carbon-rich stars by Bergeat et al. (2001), the highest effective temperature evaluated was 3870 ± 1080 K. We have therefore investigated photospheric temperatures in the range T = 1500–3500 K. The initial conditions and parameter ranges that we consequently adopt for AGB outflows are given in Table 3.

### 3.2 Case II: novae

It has long been established that dust is sometimes formed, rapidly and efficiently, in nova outflows (e.g. Gallagher 1977). In the most extreme circumstances, a steep decrease in the visual emission occurs, accompanied by a strong rise in thermal infrared emission – as an optically thick dust shell is formed (Clayton & Wickramasinghe 1976). Following Rawlings (1988), we adopt the following relations between the physical parameters:

\[ \Delta m_v = m_v \times t_0, \]

\[ L_{\text{nova}} = 1.036 \times 10^6 \times m_v, \]

\[ r_{\text{phot}} \sim 9.97 \times 10^6 \times L_{\text{nova}}, \]

\[ T_{\text{phot}} = 15280 \times 10^5 \frac{\Delta m_v}{\Delta t_0}, \]

where \( m_v \) is the rate of magnitude decline in the optical, \( r_{\text{phot}} \) is the initial photospheric radius, \( L_{\text{nova}} \) is the nova luminosity and \( t_0 \) is the number of days post-outburst.

The values for the rate of visual decline from maximum \( m_v = 0.03 \text{ mag d}^{-1} \) and time at start of calculation \( t_0 = 30 \text{ d post-outburst} \) were adopted following RW89. Novae can be classed by the time taken for a nova to diminish by 2 mag below maximum visual brightness. Generally, ‘slower’ novae (i.e. those with smaller values of \( m_v \)) are more effective at producing optically thick shells of carbon dust. RW89 estimated the density in the dust-forming zone to be of the order of 10⁹–10¹⁰ cm⁻³, based on simple arguments relating to the time when dust-formation starts, geometric expansion and the likely spatial extent of the dust-forming zone. However, this could be a lower limit and the actual density may be substantially larger, especially if significant clumping is occurring in the ejecta. Expected parameters for a typical dust-producing nova are given in Table 4. The parameter range investigated and initial conditions are given in Table 3. The fractional abundance of carbon is much higher than in the case of AGB stars (RW89). This is due to the thermonuclear processing of the gas and dredge-up of white dwarf material that occurs following the thermonuclear runaway that drives the nova outburst.

### 3.3 Case III: carbon stars in spectral class G–K

We investigate stars with photospheric temperatures in the range 3750–6000 K. Low-mass main-sequence stars are not likely to have a high C:O ratio. However, CH subgiants are low-luminosity peculiar giants, which have a high C:O ratio in their atmosphere as a
result of mass transfer from an evolved companion (Smith, Coleman & Lambert 1993). The upper limit of C:O observed in these stars is 1.5 (Luck & Bond 1982). The parameter ranges chosen to represent these objects are given in Table 3. We have optimized the parameters for dust production by only considering the highest values possible for the C:O ratio and the gas density. These stars are also known to pulsate, with periods of up to 135 d (Good 2003). Again, to investigate the most conducive conditions for C$_2$H$_2$ formation, we have used this upper limit of the period in our models (see Table 3).

4 RESULTS

C$_2$H$_2$ formation is a necessary, but not sufficient, criterion for carbon dust formation via PAH chemistry in hydrogen-rich environments. Therefore, we need to establish the conditions needed for a positive result, i.e. the minimum fractional abundance of C$_2$H$_2$ that will explain the requisite abundance of dust-nucleation sites. To do this, we follow RW89; where the number of grains is equated to the number of nucleation sites. Considering the case of a nova, the number of grains, $N_c$, inferred from infrared observations is $\sim 7 \times 10^{38}$ (Clayton & Wickramasinghe 1976). The dust shell condenses at a radius $r_c \sim 8 \times 10^{15}$ cm, and has a typical thickness of $\sim r_c/10$. The shell volume is therefore $V \sim 6 \times 10^{44}$ cm$^3$, implying a number density of grains of $\sim 10^{-6}$ cm$^{-3}$. Note that this is a lower limit, subject to the ejecta configuration. The gas density is $\sim 10^6$ cm$^{-3}$, hence the minimum fractional abundance of nucleation sites needed is $10^{-15}$.

On the assumption that each C$_2$H$_2$ molecule is efficiently converted into a nucleation site (i.e. that there are no kinetic bottlenecks in the formation of larger molecules), we can very crudely adopt this value as the threshold for the minimum fractional abundance of acetylene which can promote a PAH-driven dust-formation pathway. Of course, this number may vary significantly if the gas is more dense; but since it is based on the required total number of nucleation sites, rather than their fractional abundance, it should be reasonably robust to variations in the morphology of the dust-forming region.

We understand that for this, and other considerations, this is a very crude assumption, as C$_2$H$_2$-rich environments may not always translate to efficient PAH formation. However, this acts as a primary filter allowing us to establish which environments which will almost certainly not be effective in forming PAHs.

Results from our models are shown in Figs 1–3 as contour plots of the equilibrium abundance of C$_2$H$_2$ as a function of density and photospheric temperature. We discuss the results for the three cases in Sections 4.1–4.3.

4.1 Case I: AGB

The results for AGB winds are presented in Fig. 1. The upper figure shows that the C$_2$H$_2$ abundance is not strongly sensitive to the density. There is, however, a strong dependence on the photospheric temperature. For photospheric temperatures $T_{\text{phot}} \leq 2500$ K, C$_2$H$_2$ can be produced with the requisite efficiency for any density within the range explored (i.e. $10^{11}$--$10^{14}$ cm$^{-3}$). The lack of sensitivity to density implies that if C$_2$H$_2$ leads to PAH formation, then the production of dust will not be critically limited to the geometrical dilution of the wind.

From this figure, it is apparent that, even at the lower end of the range of the photospheric temperature, a significant abundance of the C$_2$H$_2$ abundance on $T_{\text{phot}}$ is discernable. To test this, we have run a model in which the (internal) radiation field is completely suppressed. Table 5 gives a comparison of the C$_2$H$_2$ abundances that are obtained from this model to one in which $T_{\text{phot}} = 1500$ K. A small difference is noticeable, most significantly at the lowest densities, but the results show that the C$_2$H$_2$ abundance is approaching its asymptotic limit for $T_{\text{phot}} < 1500$ K.

To illustrate the variety of chemical pathways that may be operating, we can consider an analysis of the output from a typical model in our grid, for which the density is $9 \times 10^{13}$ cm$^{-3}$ and the temperature is 2500 K. We find that the main formation channel for C$_2$H$_2$ is

\[ \text{C} + \text{H}_2 \rightarrow \text{CH} + \text{H} \]

\[ \text{CH} + \text{C} \rightarrow \text{C}_2 + \text{H} \]

\[ \text{C}_2 + h\nu \rightarrow \text{C}_2^+ + \text{e}^- \]
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C is highly susceptible to photodissociation by 2500 K and densities $10^{13}$–$10^{16}$ cm$^{-3}$. After 135 d in the circumstellar environment of a star with spectral class G–K, the abundance is always many orders of magnitude below the nominal threshold value.

The photospheric temperatures of novae are 10 times higher than for AGB stars so that, even after significant geometrical dilution is taken into account, and despite the high abundance of carbon in Starrfield, Truran & Sparks (2000), C$_2$H$_2$ is found to be highly susceptible to photodissociation; its abundance is always many orders of magnitude below the nominal threshold value. This is a strongly negative result and supports the findings of previous studies (e.g. RW89) – C$_2$H$_2$ cannot be produced in irradiated nova environments at abundance levels sufficient to seed dust formation via PAH chemistry.

4.3 Case III: stars in spectral class G–K

Results applicable to the circumstellar environment of carbon-rich stars with photospheric temperatures of 3750–6000 K are presented in Fig. 3. Although the critical fractional abundance of C$_2$H$_2$ is not reached, the abundance is closer to the threshold than was found to be the case for the nova outflows; especially for the lowest photospheric temperatures ($T < 4400$ K) and highest densities ($n > 10^{13}$ cm$^{-3}$).

Thus, we can conclude that, whilst efficient C$_2$H$_2$ formation seems unlikely in the spherically symmetric approximation, conditions may be more conducive in a density-enhanced, clumped environment. However, as this conclusion is more marginal, it would seem to suggest that these clumps would have to be dynamically stable over a period of time that is consistent with the epoch during which the physical conditions (temperature and density) are appropriate for PAH and dust formation.

5 CONCLUSIONS

We have used a simple model of the time-dependent chemistry of several different astrophysical dust-forming environments to consider the stability of acetylene (C$_2$H$_2$). In previous studies of dust formation, based on terrestrial flame chemistries, this molecule is a precursor to PAH formation and so its presence at appreciable abundance levels can be used to establish the viability of PAH formation and, by inference, dust formation based on PAH condensation chemistry. However, C$_2$H$_2$ is highly susceptible to photodissociation by stellar ultraviolet. The novel approach in this study is that we have carefully calculated the photodissociation rates for the molecular species involved in the C$_2$H$_2$ chemistry, subject to the local radiation field. Previous studies had made major simplifying assumptions in this respect.

In each case, we have investigated the dependence of the C$_2$H$_2$ abundance as a function of gas density and photospheric temperature. In general, we find that the inclusion of accurate photorates significantly restricts the parameter space within which efficient C$_2$H$_2$ formation (and hence, presumably, PAH formation) can occur.

In the case of the winds driven by thermally pulsing AGB stars, we find that – as in previous studies – C$_2$H$_2$ can be formed very efficiently indeed and that a PAH chemistry is therefore at least a viable pathway for carbon dust formation in these environments. This is an interesting result as some previous studies (which have not

C$_2$H + H$_2$ → C$_2$H$_2$ + H

followed by charge exchange with neutral species to give C$_2$H$_2$. A secondary channel involves the C$^-$ anion

CH + H$_2$ → CH$_2$ + H

CH$_2$ + C$^-$ → C$_2$H$_2$ + e$^-$.

The primary loss route of C$_2$H$_2$ is, as expected, photodissociation to C$_2$H, together with a contribution from reactions with oxygen atoms at higher temperatures: C$_2$H$_2$ + O → CO/C$_2$H. Clearly, the chemistry of C$_2$H$_2$ is somewhat different to what applies in molecular clouds (as specified in Table 2) and, in particular, demonstrates the importance of both ion–molecule reactions, even in the high-density regime, and photoreactions for photospheric temperatures $T_{\text{phot}} > 2500$ K and densities $n < 10^{13}$ cm$^{-3}$. Previous studies, which have not included ion–molecule reactions or photoreactions, may therefore have overestimated the C$_2$H$_2$ abundances by several orders of magnitude.

4.2 Case II: novae

The results for nova outflows are presented in Fig. 2. As discussed in Section 3.2, and specified in Table 3, the gas density in the dust-forming zone of novae is poorly constrained. For the purpose of our studies, we have considered the extreme upper limit of this range, which will be the most conducive for acetylene formation. This is confirmed in Fig. 2 where it can be seen that – even in the most propitious conditions – the modelled C$_2$H$_2$ abundance is extremely low. Compared to AGB winds, different trends are found; there is a stronger dependence on density, but a weaker dependence on photospheric temperature over the investigated range.

Table 5. Fractional abundances of C$_2$H$_2$ in AGB winds obtained with and without a low-temperature photospheric radiation field component.

| Density (cm$^{-3}$) | $X(C_2H_2)$ with phot. $T_{\text{phot}}$ | $X(C_2H_2)$ without phot. $T_{\text{phot}}$ |
|---------------------|--------------------------------------|--------------------------------------|
| $10^{11}$           | $1.62 \times 10^{-9}$                 | $1.9 \times 10^{-9}$                |
| $10^{12}$           | $9.58 \times 10^{-9}$                 | $1.0 \times 10^{-8}$                |
| $10^{13}$           | $1.55 \times 10^{-8}$                 | $1.6 \times 10^{-8}$                |

Figure 3. Contour plot showing the logarithm of the fractional abundance of C$_2$H$_2$ after 135 d in the circumstellar environment of a star with spectral class G–K. The density and photospheric temperature are treated as free parameters. All other parameters are fixed and given values as specified in Table 4.
included photochemistry in their modelling) have not been so successful at producing C$_2$H$_2$ (e.g. Cherchneff et al. 1992; Helling et al. 1996). However, we find that this positive result only holds for photospheric temperatures that are $\sim 2500$ K. There are dust-producing carbon AGB stars with photospheric temperatures $\sim 3500$ K (e.g. Eglitis & Eglite 1995). If we were to include a more accurate physical model of the outflows, including shocks and clumping, a PAH chemistry may also be viable in these objects. In their models, which incorporated a neutral-neutral shock chemistry, Cherchneff (2012) predicted C$_2$H$_2$ fractional abundances as high as 10$^{-4}$. However, these models did not include the effects of photodissociation by the stellar radiation field which, as shown in this study, may result in significantly reduced abundances.

As compared to the dust-forming environment of AGB stars, the ejecta of novae are subject to a much stronger radiation field with a significantly higher blackbody temperature. The photodissociation rates for unshielded molecular species, such as C$_2$H$_2$, are very much larger than in the other sources considered in this study (e.g. RW89). As a result C$_2$H$_2$ can never attain significant abundances. Of course, other factors should be taken into account – such as possible variations in the elemental abundances in the ejecta – but the extreme clumping required is incompatible with the observed spherical coverage of the optically thick dust shell in these objects. In this case, it seems that other (non PAH-based) formation channels must be operating – involving species that can survive the intense radiation field (e.g. C$_2$, which is partly shielded by the carbon ionization continuum, RW89).

Finally, CH subgiants have physical characteristics that are closer to main-sequence stars than stars in the giant phase. They have lower luminosities than equivalent stars on the main sequence and are known to be chemically peculiar (Smith et al. 1993), having a carbon overabundance. The winds from these stars are not expected to have such extreme shock-generated density enhancements as in the AGB outflows. Thus, even with the extreme parameters we have chosen, we still obtain a marginally negative result within the inner wind. Again, an environment that is conducive to C$_2$H$_2$–PAH chemistry may exist in the outer winds if significant clumping occurs, but it would seem that alternative dust-formation pathways are more likely in these environments.

In summary, we find that C$_2$H$_2$ (and PAH) formation is at least viable in AGB outflows, but is only possible in the winds of CH subgiants if significant clumping is present in outer winds, and is not possible at all in nova winds. It is evident that although the physical parameters of the gas are similar in all three cases – the spectrum of the radiation field has a significant effect on acetylene production. Therefore, on the basis of these studies, it is evident that the formation pathway for (carbon) dust cannot be the same in all environments; in particular, the modified flame-PAH chemistries that provide a plausible formation channel in the dust-rich winds of thermally pulsing AGB stars cannot be applied to environments such as novae. It would therefore seem that multiple (and, as yet, largely undefined) pathways for the kinetic formation of carbon dust exist.

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