

## Dust formation in circumstellar shells

### ABSTRACT

The mechanisms responsible for dust formation and grain growth in dust shells of late type stars are discussed. Pure SiO or MgO clustering seems to be the starter process responsible for the onset of condensation around early or late-type M-stars, respectively. Silicates can be formed only by chemical surface reactions on these initial condensates. For C-stars, dust formation is similar to soot formation in laboratory acetylene flames with some modifications due to a large excess of free H atoms in the stellar wind material.

### 1. Introduction

Dust formation in circumstellar shells has been discussed several times during the last two decades (Donn et al., 1968, Tabak et al., 1975, Salpeter, 1977, Draine and Salpeter, 1977, Yamamoto and Hasegawa, 1977, Draine, 1979, Gail et al., 1984, Gail and Sedlmayr, 1986, 1987, 1988, Keller, 1987, Frenklach and Feigelson, 1989). Most of these discussions are based on classical homogeneous nucleation theory which assumes (i) that grains of all sizes down to the molecular region have the same material properties and (ii) that the lower bond energy of atoms at the surface of grains can be accounted for by the concept of surface tension. This concept, however, is invalid for small particles and usually results in predictions for dust formation rates which are seriously in error (Donn and Nuth, 1985).

The dust formation problem, in principle, has to be studied by means of reaction kinetics to determine the possible chemical pathways from molecules to dust. Little has been done up to now for M-stars (Donn et al., 1981), mainly because the required data for molecular properties and rate coefficients are not available. For carbon stars, however, considerable progress has recently been achieved in determining the microscopic processes responsible for soot formation in these stars (Keller, 1987, Frenklach and Feigelson, 1989). In the following sections

we give a brief description of the problem and of the results obtained up to now.

### 2. Principles of the dust formation process

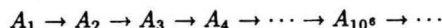
If a gas with a given chemical composition cools down, it becomes unstable against formation of a condensed phase at a certain temperature. This occurs if the cooling trajectory of the gas in the pressure-temperature plane crosses the stability limit curve of the condensate given by

$$\frac{1}{\prod_i p_i} = \exp \left( -\frac{\Delta G}{RT} \right) \quad (1)$$

with  $p_i$  being the partial pressures of the molecules (or atoms) from the gas phase, from which the condensate can be formed and  $\Delta G$  is the difference between the free enthalpy of formation of the solid and the free enthalpies of formation of the molecules.

Usually for a complex mixture of molecules as in a stellar wind more than one kind of condensed material can be formed from the gas species. Then there exist several different stability limits for formation of these condensates. In the past, it has often been assumed (i) that material is formed for which the chemical system first becomes unstable against a phase transition and (ii) that this material forms immediately after crossing of the stability limit. Laboratory experiments, however, show that often it is not the thermodynamically most stable condensate which is formed and that secondly condensation occurs only if the gas has cooled for several hundred K below the stability limit.

The requirement of a strong supercooling results from the fact, that the condensation process is a long chain of chemical reactions



in which molecules and clusters of increasing size and complexity are formed by association processes with atoms and molecules from the gas phase until finally they grow to particles macroscopic size. The onset of condensation requires that the whole sequence of reactions becomes possible and this requires that all members of the reaction chain can be formed in sufficient quantities in order that association reactions to the next member on the chain proceed sufficiently fast that the whole sequence of reactions from molecules to macroscopic particles is passed through in a finite time. If only one member of the chain is readily disassociated for the given temperature-pressure conditions, condensation does not occur under these conditions. Thus, the abundance of the least stable member on the reaction chain decides on the possibility or impossibility of condensation. Usually, the small molecules on the

initial part of the reaction chain are more weakly bound than the condensate. They are formed in sufficient quantities only, if the temperature is reduced far below the stability limit of the condensate.

This consideration shows that the rate of formation  $J_*$  of condensation nuclei is given by

$$J_* = n_{gr} v \sigma \alpha n_{cr} \quad (2)$$

with  $n_{cr}$  being the particle density of the least abundant intermediate cluster on the reaction chain from molecules to dust – the critical cluster – which forms the bottleneck of the whole process.  $n_{gr}$  is the particle density of the growth species responsible for the transition from the critical cluster to the next, more stable member of the reaction chain,  $v$  the average thermal velocity of the growth species,  $\sigma$  the collision cross-section and  $\alpha$  the association probability. For condensation under near stationary conditions it can be shown that  $n_{cr}$  can be calculated from the law of mass action

$$\frac{p_{cr}}{\prod_i p_i} = \exp \left( -\frac{\Delta G}{RT} \right) \quad (2)$$

where  $p_{cr}$  is the equilibrium partial pressure of the critical cluster and the  $p_i$  are the partial pressures of the molecules from which it is formed (Gail and Sedlmayr, 1988).

If there exist several competing reaction chains, obviously the most efficient one with the highest nucleation rate  $J_*$  wins. This means, that not necessarily the most stable condensate is formed, which first becomes stable during the cooling process, but the one for which an efficient reaction chain first starts to operate.

The process of formation of the critical cluster depends on the chemical properties of the molecules and the small clusters. These may be quite different from that of the final condensate. This means that the dust formation process and the process of growth of macroscopic particles have to be treated separately since both may involve quite different molecules. Especially, the grains may incorporate molecules into their lattice, which do not participate in the grain formation process, thereby changing their chemical nature.

Thus, if we intend to unravel out the processes responsible for dust formation in circumstellar shells, we have to go through the following steps.

1) We have to determine the molecular composition of the gas. This determines the raw material, from which the condensate has to be formed.

2) We have to determine the possible condensates which might be formed from these molecules by means of (1).

3) We have to find out the possible reaction path's from molecules to large clusters and to deter-

mine the corresponding critical cluster by means of (3). Then we have to determine the most efficient reaction chain operating at the highest temperature by means of (2). This determines the dust formation process.

4) For this most efficient nucleation process we have to determine the growth processes from large clusters to macroscopic sized grains. This determines the kind of dust material finally formed in the condensation process.

Up to now, it has not been possible to follow this program in complete generality. Only very preliminary results have so far been obtained. They are discussed in sections 4 and 5.

### 3. Chemical composition of the gas

Observation shows that nucleation and grain growth is a very efficient process in circumstellar shells – at least for mass loss rates above  $\dot{M} \approx 10^{-6} M_{\odot} \text{yr}^{-1}$ . This requires that very abundant and reactive molecules are responsible for the process. Hence we can concentrate on the chemistry of the most abundant elements H, C, N, O, Si, Fe, Mg and S. Less abundant elements have to be considered for the nucleation process only if it should turn out that there exists no efficient nucleation path involving only the more abundant elements. For grain growth, the less abundant elements can presently be neglected, since we know from observations that circumstellar dust is formed mainly from the most abundant elements capable of forming condensates under circumstellar conditions (O, Si, Mg, Fe in M-star shells, C in C-star shells). The less abundant elements can either be incorporated as impurities into the main dust component or form separate but less important dust components (SiC and MgS in C-stars) and can be neglected at the present state of the art.

If the molecular abundance in the outflowing gas would be as in chemical equilibrium then the chemical composition of the gas is rather simple. For each element, only simple molecules with the highest bond energies are present in large amounts. A key role for the chemistry plays the CO molecule due to its exceptional high bond energy (cf. Fig.1). The less abundant of the two elements C and O is completely tence of a chromosphere. Second, all stars showing circumstellar dust shells seem to be variables with periods ranging from  $\approx 200$  d to  $\approx 1500$  d. The pulsation of the outer layers of the star lead to shock waves running through the photosphere and far out into the stellar envelope. These shocks disassociate all molecules, which then have to be newly formed. If the timescale for molecule formation is short compared to the time between passage of subsequent shocks through a specific gas parcel, the chemistry will settle to the equilibrium composition described above, which is mainly determined by element abun-

dances and bond strength's and (in absence of UV-radiation) depends little on the specific molecule formation processes.

The most difficult step in molecule formation is radiative association of two free atoms to a diatomic molecule. The typical rate coefficient for this process is  $k_{rad} \approx 10^{-17} \text{ cm}^3 \text{ s}^{-1}$  (cf. Duley and Williams, 1984). The timescale of formation of a molecule of type AB from A and B (B being the less abundant element) is

$$\tau_{form} = \frac{1}{k_{rad} n_A} \approx \frac{10^{17}}{n_A} \quad (4)$$

This has to be compared with typical shock passage times of  $10^7 \dots 10^8 \text{ s}$ . Down to particle densities  $n_A \approx 10^{10} \dots 10^{11} \text{ cm}^{-3}$  this process is sufficiently fast for reformation of diatomic molecules. Thus, hydrogen compounds like CH or OH are readily formed down to densities typical for the dust condensation and growth region. From these, other molecules then are easily formed by exchange or association reactions since radical reactions involving at least one diatomic or polyatomic molecule proceed much faster with rate coefficients of the order of  $k \approx 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ .

Hydrogen, however, cannot recombine by this process, since radiative association of homonuclear molecules is strongly forbidden. The three-particle reaction  $\text{H} + \text{H} + \text{H} \rightarrow \text{H}_2 + \text{H}$  is efficient only down to particle densities of  $n_H \approx 10^{13} \text{ cm}^{-3}$ . Indirect formation by reactions like  $\text{O} + \text{H} \rightarrow \text{OH}$ ,  $\text{OH} + \text{H} \rightarrow \text{O} + \text{H}_2$  proceeds on a timescale (eq.(4)) determined by the density of oxygen atoms, i.e., it is efficient only down to densities of  $n_H \approx 10^{12} \text{ cm}^{-3}$ . Then, hydrogen only incompletely associates to  $\text{H}_2$  between passage of two shocks and we expect a strong excess of free hydrogen atoms compared to chemical equilibrium. Unfortunately, no model calculation exists for this problem and we do not know the exact degree of deviation from equilibrium.

The free hydrogen radicals are strongly reactive and hydrogen abstraction reactions of the type  $\text{X-H}$  consumed by forming CO and only the excess of the more abundant of the two elements is available for forming additional molecules. In M-stars, for this reason no carbon compounds can be formed while in C-stars no oxygen compounds can be formed. This is the origin of the completely different chemistry of M- and C-stars. The nitrogen molecule  $\text{N}_2$ , too, has an exceptional high bond energy with the result that all N is blocked in this molecule. Both, CO and  $\text{N}_2$  are very unreactive and cannot be involved in the dust formation process.

With respect to dust formation we are interested in the molecular composition for temperatures below  $\approx 1500 \text{ K}$ . Then in M-stars, the silicon is completely associated to  $\text{SiO}$  due to its very strong bond energy. The excess of O over Si forms mainly OH

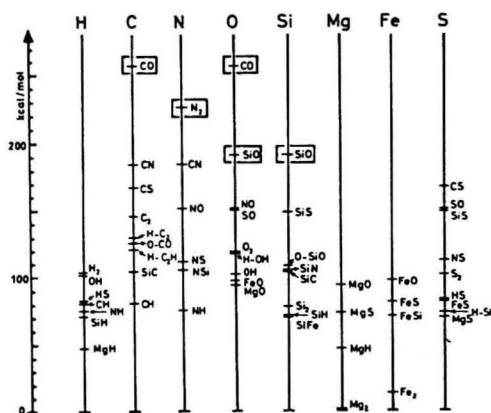


Fig. 1. Bond strength of diatomic molecules and of some bonds in polyatomic molecules.

or  $\text{H}_2\text{O}$ . Magnesium is mainly present as Mg and  $\text{MgOH}$  and small amounts of  $\text{MgO}$ . Iron is essentially present as free atom and sulphur as free S and  $\text{H}_2\text{S}$ . In carbon stars, essentially all carbon is bound in  $\text{C}_2\text{H}_2$  and in small amounts of HCN. The remaining less abundant elements are probably unimportant for the formation of the observed carbon dust.

There are two reasons, however, which may be responsible for deviations from a chemical equilibrium composition. First, the central star may have a chromosphere. Its UV-emission then is the source of ionization and dissociation of gas particles in the wind, thus driving a chemistry far from chemical equilibrium (Clegg et al., 1983). This is important for early-type M-stars, but probably unimportant for the much cooler late-type M-stars and C-stars, which generally show no indications for the  $\text{exis} + \text{H} \rightarrow \text{X} + \text{H}_2$  are very efficient, since they usually involve only minor or no activation energy barrier if the indicated reaction is exothermic. From simple kinetic considerations the equilibrium abundance of radical sites is given by

$$\frac{n_X}{n_{X-H}} = \frac{n_H}{n_{H_2}} \frac{p_X \cdot p_{H_2}}{p_{X-H} p_H} \quad (5)$$

where the  $p$ 's are partial pressures in chemical equilibrium. For M-stars this means, that hydrides will not exist, if there is a strong excess of H over  $\text{H}_2$  compared to chemical equilibrium. For C-stars this means, that the usually rather unreactive hydrocarbons are partially stripped of their hydrogen atoms and become very reactive radicals. This has severe consequences for the chemistry of the dust formation process.

Molecules with very strong bonds like CO,  $\text{N}_2$  and  $\text{SiO}$ , however, are not attacked by the free H

atoms since breaking of their bonds to form hydrides would be a strongly endothermic process. They will be formed in quantities like in equilibrium.

#### 4. Dust formation in shells of M-star

For M-stars, the chemical composition of the gas phase depends on the spectral type.

Early-type M-stars have small mass-loss rates and form only small amounts of dust. They have a warm chromosphere with a non-negligible UV output (Carpenter et al., 1985). The chemistry of the outflowing gas then is far from chemical equilibrium and determined by ionization, recombination and ion-molecule reactions. This has been discussed in detail by Clegg et al., 1983, Goeres et al., 1988, Henkel, 1990. The most abundant neutral species are O, Fe and SiO. The elements Si, Fe, Mg and S are present mainly as ions.

Late-type M-stars show high mass-loss rates and copious dust formation. They show no indication for the existence of chromospheres but shocks are running through their outer layers, since they are variables. The chemistry in these stars probably is determined by neutral radical reactions. As has been argued above, the most stable molecules CO, N<sub>2</sub> and SiO of the abundant elements will then be formed in quantities as in chemical equilibrium while less stable molecules like MgOH (very abundant in equilibrium) will be reduced by the excess of free H atoms. From (5) one shows (thermochemical data from JANAF-tables)

$$\frac{n_{\text{MgO}}}{n_{\text{MgOH}}} = 5.8e^{-277/T} \frac{n_{\text{H}}}{n_{\text{H}_2}} \quad (6)$$

Then  $n_{\text{MgO}}/n_{\text{MgOH}} \approx 4n_{\text{H}}/n_{\text{H}_2}$  at  $T=1000\text{K}$ . MgO, thus, is an abundant molecule.

The type of dust material formed in both cases seems to be clear from observation. The  $9.7\mu$  and  $18\mu$  features clearly point to silicates while the width of these features and the absence of structures in it points to a strongly amorphous structure of the condensate. It is very likely that the abundant elements Fe and Mg can easily be incorporated into the dust material, i.e., we expect the formation of amorphous Mg-Fe-silicates.

This material, however, cannot be formed directly from the gas phase. It is known from the laboratory that all silicates on vaporization decompose into free atoms and SiO. Very small silicate molecules are unstable; they are stabilized in a large lattice by Coulomb attraction within an ionic lattice. Thus, silicates can only grow on preformed stable condensation nuclei of a different nature, which collect the necessary atoms and molecules from the gas phase and form a silicate structure by chemical surface reactions.

The reaction chain for dust formation then has to start with formation of some kind of stable clusters from the abundant and reactive molecules present in the gas phase. The most attractive possibility is clustering of SiO to pure (SiO)<sub>n</sub> clusters since this molecule is very abundant in the gas phase. Clustering of the abundant free Fe (in early and late-type M-stars) or Mg (in late-type M-stars) can be ruled out since (i) the dimers Fe<sub>2</sub> and Mg<sub>2</sub> have extremely low bond energies (these molecules don't exist until the temperature becomes very low) and (ii) formation of these molecules by radiative association or three-particle collisions is extremely slow.

Condensation of pure SiO has been studied in the laboratory by Nuth and Donn (1982, 1983) and theoretically by Donn et al., 1981. Extrapolating the results of Nuth and Donn (1982) to circumstellar conditions one obtains a condensation temperature of  $\approx 600\text{K}$ . This fits well to observed dust condensation temperatures (c.f. Rowan-Robinson and Harris, 1982, 1983a) in shells of early type M-stars. Hence, SiO clustering is a possible and likely process for formation of the first stable polyatomic clusters in the outstreaming gas of early type M-stars, which later grow to silicates by chemical surface reactions.

For late-type M-stars, however, clustering of SiO definitely starts at a much lower temperature than the observed condensation temperature of  $\approx 1000\text{K}$  (Rowan-Robinson and Harris, 1982, 1983a). A different process for initiation of condensation operates in these shells, since the much higher condensation temperature needs different thermochemical properties of the critical cluster (cf. eqs. (2) and (3)). The most attractive possibility then is clustering of MgO since (i) this molecule is abundant and (ii) association reactions between molecules with ionic bonds are fast. Additionally clusters of molecules with ionic bonds tend to be more strongly bound than the free molecules or even the solid condensate (cf. Martin, 1983, for NaCl clusters). In this case, the critical cluster is the free molecule and the onset of condensation then coincides with the formation of the molecule. Definite results for this nucleation mechanism are not yet available but model calculations for the properties of such clusters (Köhler and Gail, 1991) indicate, that clustering of ionic molecules may be responsible for formation of the first stable polyatomic clusters in winds of late type M-stars.

#### 5. Dust formation in shells of C-stars

The main dust component formed in carbon stars is some kind of soot. This material has to be formed from acetylene, since (i) this is the major carbon bearing gas species (in addition to the unreactive CO molecule) and (ii) the observed high efficiency of the dust formation process requires that a very abun-



dant molecule is responsible for soot formation. Soot formation from acetylene flames has been subject of intense laboratory research (Harris and Weiner, 1985, Wieschnowsky et al., 1988, Bockhorn et al., 1989). These experiments show that the soot consists of large fused aromatic ring systems. At least part of the smaller soot particles formed in flames are PAH's. The larger particles observed in the laboratory are formed by coagulation of smaller particles.

We can safely expect that the dust material formed in the winds of C-stars is similar to that in flames. The precise formation mechanisms, however may be somewhat different due to differences in the formation and growth conditions: (i) the hydrogen is strongly in excess over carbon, contrary to flames, (ii) there exists a strong excess of free H compared to chemical equilibrium and (iii) coagulation is not important in stellar winds.

The presence of free hydrogen atoms results in large amounts of radical sites due to hydrogen abstraction reactions. From eq.(5) one shows (using thermochemical data from Benson, 1976)

$$\begin{aligned} \frac{n_{C_2H}}{n_{C_2H_2}} &= 15. e^{-7900/T} \frac{n_H}{n_{H_2}} \\ \frac{n_{C_2}}{n_{C_2H}} &= 2.5 e^{-12500/T} \frac{n_H}{n_{H_2}} \end{aligned} \quad (6)$$

For  $T=1000K$  we obtain  $n_{C_2H}/n_{C_2H_2} \approx 10^{-3} n_H/n_{H_2}$  and  $n_{C_2}/n_{C_2H} \approx 10^{-5} n_H/n_{H_2}$ , i.e., depending on the actual  $H/H_2$ -ratio which is not well known at present, we have a small to large fraction of  $C_2H$  radicals, but certainly no bare C-chains. For hydrogen attached to PAH's one shows (X denotes a PAH with a stripped H atom)

$$\frac{n_X}{n_{X-H}} = 4.5 e^{-3300/T} \frac{n_H}{n_{H_2}},$$

i.e.,  $n_X/n_{X-H} \approx n_H/n_{H_2}$  at  $T=1000K$ . At the edge of PAH's then we have a significant fraction of radical sites. They easily allow attachment of  $C_2H_2$  by means of one of the reactions  $X \cdot + H-C \equiv C-H \rightarrow X-C \equiv C-H + H$  or  $\rightarrow X-(CH)=\dot{C}-H$ , which proceed nearly at the collisional rate. This suggests a mechanism of addition of a new ring to an existing PAH shown in Fig.2, which has been proposed for PAH growth in flames by Frenklach and Warnatz (1987). In stellar winds this is a natural consequence of the strong excess of free H atoms.

Not definitely solved is the problem of formation of the first rings in stellar winds. The obvious starting process is formation of polyacetylenes by reactions like  $C_2H_2 + C_2H \rightarrow C_4H_2 + H$ ,  $C_4H_2 + C_2H \rightarrow C_6H_2 + H$ , .... The corresponding polyacetylene radicals  $C_{2n}H$  are observed in stellar winds. Additionally by such reactions one obtains the cyanopolyacetylenes  $NC-C_{2n}H$  if a chain reacts with the less

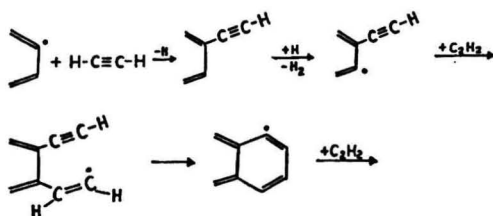


Fig. 2. The sequence of hydrogen abstraction and acetylene addition reactions responsible for PAH growth in shells of carbon stars.

abundant but not rare molecule HCN or radical CN. Such molecules are observed in circumstellar shells.

The polyacetylenes are linear molecules. To obtain ring structures, at least one of the triple bonds has to be changed to a double bond to form a bent molecule which closes to the first ring. Two different reaction chains involving such steps have been proposed by Keller (1987, see also Gail and Sedlmayr, 1987) and Frenklach and Feigelson (1989).

Keller has calculated the thermal equilibrium abundances of all possible small intermediate molecules between  $C_2H_2$  and small PAH's and worked out the most efficient reaction path under circumstellar conditions (cf. Fig. 2 of Keller, 1987). A preliminary model calculation (Gail and Sedlmayr, 1987) shows that this nucleation path approximately reproduces the observed condensation temperature.

Frenklach and Feigelson proposed a different reaction path for PAH formation based on solving numerically the chemical reaction network including a large number of intermediate molecules possibly involved in formation of the first rings from  $C_2H_2$  and many reaction types. From the solution, the most efficient reaction path can be determined (cf. Fig.2 of Frenklach and Feigelson, 1989).

Both results differ only in the mechanism responsible for formation of the first two 6-rings. Beyond that step, the reaction paths for formation of multiple fused 6-rings are identical. The origin of the difference between the two proposed reaction paths up to the  $C_{10}H_7$  radical seems to be the degree of disequilibrium of the  $H_2$  dissoziation. Frenklach and Feigelson started the numerical integration of the chemical reaction network with nearly chemical equilibrium abundances at the base of the wind. The small degree of dissoziation disequilibrium in their calculation then results from the freeze out of the slow  $H_2$ -formation reactions in the expanding and diluting wind. Keller (1987) determined reaction paths both for near equilibrium  $H/H_2$  ratio and for a strong disequilibrium due to shock dissoziation and inefficient recombination processes. For a near equilibrium  $H/H_2$  ratio, he obtained a similar re-

action path from  $C_2H_2$  to  $C_{10}H_7$  as Frenklach and Feigelson (1989), while for a strong disequilibrium he obtained a quite different reaction path due to the high abundance of reactive radicals.

Which of the two mechanisms is the correct one, presently cannot be decided until reliable calculations for the H/H<sub>2</sub>-ratio in the wind become available. The inefficient production of PAH's in the model of Frenklach and Feigelson (1989) seems to indicate, however, that the efficiency of the growth process is severely underestimated due to the rather low abundance of free H atoms in their model calculation which in turn points to a much higher abundance of free H in a real stellar wind. The whole picture of the mechanism of ring closure, however, may change drastically if improved reaction rates become available since the details of both mechanisms critically depend on the often not very accurately known rate coefficients.

With respect to grain growth, up to now only the formation of planar PAH-structures has been discussed. Keller (1987) has pointed out, however, that the inclusion of 5-ring structures is favourable. In real grain growth, thus, the carbon network probably contains a certain fraction of pentagons, which will result in growth of non-planar structures. As an extreme case, one might form the famous C<sub>60</sub> footballs (which, however, would form an endpoint of the particle growth process). The formation of this molecule is discussed by Goeres and Sedlmayr (1991). Additionally, the less abundant (a few percent) HCN or CN could be attached to the boarder of PAH's, inhibiting the formation of new rings at this place due to the unreactive N-atom at the end of this group. This probably will favour the growth of irregular networks of fused carbon 5- and 6-rings.

## 6. Concluding remarks

In the preceding sections we have discussed chemical pathways to circumstellar dust condensation. It is shown that the conditions under which dust is formed strongly restricts the number of possibilities for the actual condensation mechanism:

- 1) Pure SiO clustering in early-type M-stars where dust condenses around 600K.
- 2) Probably pure MgO clustering in M-stars where dust condenses around 1000K.
- 3) A mechanism for formation of the first 6-rings followed by repeated steps of hydrogen abstraction and acetylene addition similar to but not identical with the soot formation process in laboratory acetylene flames for carbon stars.

Many problems, however, have not yet been solved. Thus, presently we have some ideas about what is going on in dust forming circumstellar shells, but much future work is required to obtain a quantitative understanding of dust formation in such objects.

## References

- Benson, S.W., 1976 - Thermochemical Kinetics (New York: John Wiley & Sons)
- Bockhorn, H., Fetting, F., Knümann, R., Schäfer, T., Wieschnowsky, U., 1989 - in: Joint meeting of the German and Italian sections of the Combustion Institute
- Carpenter, K.G., Brown, A., Stencel, R.E., 1985 - *Astrophys. J.* 289, 676
- Clegg, R.E.S., van IJsendorn, L. J., Allamandola, L.L., 1983 - *Monthly Notices Roy. Astr. Soc.* 203, 125
- Donn, B., Wickramasinghe, N. C., Hudson, J. R., Stecher, T.P., 1968 - *Astrophys. J.* 153, 451
- Donn, B., Khanna, R., Nuth, J., Stranz, D., Anderson, A.B., 1981 - *Surface Science* 106, 576
- Donn, B., Nuth, J.A., 1985 - *Astrophys. J.* 288, 187
- Draine, B.T., 1979 - *Astrophys. Space Sci.* 65, 313
- Draine, B.T., Salpeter, E.E., 1977 - *Journ. Chem. Phys.* 67, 2230
- Duley, W. W., Williams, D. A., 1984, *Interstellar Chemistry* (London: Academic Press)
- Frenklach, M., Warnatz, J., 1987 - *J. Comb. Sci. Tech.* 51, 265
- Frenklach, M., Feigelson, E.D., 1989 - *Astrophysical J.* 341, 372
- Gail, H.-P., Keller, R., Sedlmayr, E., 1984 - *Astron. Astrophys.* 133, 320
- Gail, H.-P., Sedlmayr, E., 1986 - *Astron. Astrophys.* 166, 225
- Gail, H.-P., Sedlmayr, E., 1987, in: *Physical Processes in Interstellar Clouds*, G.E. Morfill, M. Scholer Eds., Reidel, Dordrecht, p. 275
- Gail, H.-P., Sedlmayr, E., 1988 - *Astron. Astrophys.* 206, 153
- Goeres, A., Sedlmayr, E., 1991 - *Chem. Phys. Lett.*, in press
- Goeres, A., Henkel, R., Sedlmayr, E., Gail, H.-P., 1988 - *Rev. Modern Astron.* 1, 231
- Harris, J.H., Weiner, A.M., 1985 - *Ann. Rev. Phys. Chem.* 36, 31
- Henkel, R., 1990 - Thesis, Technische Universität Berlin
- JANAF-tables: National Bureau of Standards (US). NSRDS-NBS 37
- Keller, R., 1987 - in: *Polycyclic Aromatic Hydrocarbons and Astrophysics*, A. Léger, L.d'Hendecourt, N. Boccarda Eds., Reidel, Dordrecht, p. 387
- Köhler, M., Gail, H.-P., 1991 - in preparation
- Martin, T.P., 1983 - *Phys. Rep.* 95, 167

Nuth, J.A., Donn, B., 1982 – J. Chem. Phys. 77, 2639  
 Nuth, J.A., Donn, B., 1983 – J. Chem. Phys. 78, 1618  
 Rowan-Robinson, M., Harris, S., 1982 – Monthly Notices Roy. Astron. Soc. 200, 197  
 Rowan-Robinson, M., Harris, S., 1983a – Monthly Notices Roy. Astron. Soc. 202, 767  
 Rowan-Robinson, M., Harris, S., 1983b – Monthly Notices Roy. Astron. Soc. 202, 797  
 Salpeter, E.E., 1977 – Ann. Rev. Astron. Astrophys. 15, 267

Wieschnowsky, U., Bockhorn, H., Fetting, F., 1988 – Twenty-Second Symposium (International) on Combustion / The Combustion Institute, p. 343

Yamamoto, T., Hasegawa, H., 1977 – Progr. Theor. Phys. 58, 816

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