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LONG CARBON CHAIN MOLECULES IN CIRCUMSTELLAR SHELLS

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ABSTRACT

Polyynes and grains (presumably carbonaceous) appear to be intimately associated in the circumstellar shells of late-type, carbon-rich stars such as IRC +10°216. These observations have prompted laboratory experiments which have shown that when graphite is vaporized and the resulting gaseous carbon species allowed to condense, long chain molecules (C_3–C_{30}) invariably form at the same time as larger spheroidal carbon clusters (C_{40}–C_{100}) *and* macroscopic carbonaceous particles. When the condensation occurs in the presence of hydrogen *and* nitrogen the long chain cyanopolyynes, actually observed by radioastronomy in IRC +10°216 and interstellar clouds such as TMC 1, are readily produced. The experiments show that high-temperature processes are a viable simultaneous source of polyynes as well as carbonaceous grains. In particular, they suggest that wherever polyynes are abundant, the associated grains are likely to be carbonaceous and that both may be of circumstellar origin.

Subject headings: interstellar: molecules — molecular processes — stars: circumstellar shells

I. INTRODUCTION

The analysis of spectra from interstellar molecules has made significant contributions to a wide range of general astrophysical problems (Winnewisser, Churchwell, and Walmsley 1979; Kroto 1981). Major insights have been gained into the birth of stars and planets, the evolution of galaxies, and the origin of the universe. Many of the important discoveries have been made since 1968 when the field finally blossomed, initiated by the radio detections of NH_3 and H_2O (Cheung *et al.* 1968, 1969).

Much effort has been aimed at understanding the chemical and physical processes that lead to the formation of interstellar molecules themselves. The current view is that most observed species can be accounted for by sequences of bimolecular ion-molecule reactions (Herbst and Klemperer 1973; Dalgarno and Black 1976; Watson 1978; Smith and Adams 1981) supplemented, where necessary, by reactions on the surface of interstellar grains, (Greenberg 1976). Duley and Williams (1984*a*) have surveyed some of the processes that have been proposed.

One particular discovery, that the long chain carbon molecules (cyanopolyynes)—HC_nN with $n = 3$ (Turner 1971), $n = 5$ (Avery *et al.* 1976), $n = 7$ (Kroto *et al.* 1978), $n = 9$ (Broten *et al.* 1978), and also $n = 11$ (Bell *et al.* 1982)—are abundant in various interstellar regions, has given rise to much speculation. Not only was the existence of such relatively complex molecules quite unexpected but their abundance poses a major problem. It is certainly far from clear that species with five to 11 C atoms can be synthesized efficiently from smaller units by the ion-molecule processes which provide the most satisfactory explanations for most of the other (significantly smaller as far as heavy atoms are concerned) molecules that have been discovered. Theoretical models for carbon chain formation have been proposed, such as that of Freed and Oka (1982) which are in need of theoretical confirmation. The recent extensive theoretical calculations of Leung, Herbst, and Huebner (1984), based on a wealth of experimental data only extend reliably to HC_3N and, although HC_5N is included, the authors conclude that a considerably larger model would be necessary for a satisfactory treatment of molecules more complex than HC_3N.

Apart from the fact that chains with more than three carbon atoms have still to be explained, there are other stumbling blocks. One is the interesting fact that there is an apparent relative underabundance of less unsaturated analogues of the polyynes (Kroto *et al.* 1985*b*; Irvine and Hjalmarson 1984; Kroto and Little 1986). The reason for this is not clear since there are expected to be numerous routes to such molecules in an interstellar medium (ISM) in which the ratio C:H is $\sim 10^{-4}$. Even though some may involve endothermic steps (Herbst, Adams, and Smith 1983) this may not necessarily be a bar to reaction. In the cold ISM, in fact, it may in some cases be a positive benefit since a modest amount of endoergicity can lead to collisional energy entrapment yielding complexes sufficiently long-lived to facilitate radiative association processes (Ferguson *et al.* 1984; Smith and Adams 1985).

In ion-molecule reaction schemes the main process which tends to favor the loss of hydrogen, and therefore higher unsaturation is the final cation neutralization step whereby synthesis sequences are terminated. In this step dissociative cation-electron recombination takes place with energy dissipation achieved by the ejection of a fragment which is likely, in general, to be a hydrogen atom. However, it still is not obvious that such a high degree of unsaturation will result, and indeed this critical phase of the ion-molecule route is still hypothetical and in need of experimental confirmation.

It is also not clear that such species are feasible products of the surface catalysis schemes that have been proposed as, even if formed, desorption from the grain surface at the temperatures that obtain in interstellar clouds presents a major obstacle. One route to chain formation in cold molecular clouds that cannot be ruled out has been discussed by Duley and Williams (1984*b*) who have shown that such species may result from grain disruption by shock waves that periodically traverse the ISM (Jura 1986).

To summarize, the existence of the long chains in the ISM has not yet been satisfactorily explained with experimentally supported mechanisms and their abundance implies the possibility of a facile synthesis, at least in some regions. It also seems reasonable to require that any truly satisfying general theory of interstellar molecule formation should provide a convincing explanation of long chain molecules as well as less complex species.

One of the striking aspects of the polyyne observations, and one that has been somewhat neglected, is their exceptional abundance in the circumstellar shell which surrounds the carbon star IRC $+10°216$. Much more attention has been paid to the abundance in molecular clouds such as TMC 1, a cold, quiet, small cloud in Taurus (Avery 1980). The IRC $+10°216$ observations indicate that polyynes are formed efficiently in some circumstellar shells, at relatively high pressures and temperatures, and are being expelled into the general ISM. In addition, IRC $+10°216$ appears to be surrounded by dust (Morris 1975; Kwan and Hill 1977) which also originates in the shell and is being ejected into the general ISM along with the molecules. No ions have yet been detected in IRC $+10°216$.

Loreta (1934) first suggested that the optical behavior of certain irregular variables (such as R Cor B) might be caused by solid particles forming the stars' atmospheres. O'Keefe (1939) was able to show that the physico-chemical conditions were such that carbon particles could form *and* that such particles would be driven out into the general ISM by radiation pressure. Rosen and Swings (1953) and Swings (1953) showed that such a mechanism could also account for the optical properties of late N-type carbon-rich stars. Several authors such as Fix (1969*a*, *b*) and Lucy (1976) have also considered this problem and various aspects have been reviewed by Ney (1971), Kwok (1980), and Savage and Mathis (1979). McCabe, Smith, and Clegg (1979) have considered the molecule/grain relationship in IRC $+10°216$.

Since there is now incontrovertible evidence that carbon chain molecules, together with carbon grains, are being ejected into the ISM by stars, the chemical relationship between these species demands consideration, in particular, under conditions more related to those in stars than the general ISM. The absence of experimentally verifed explanation for the formation of either dust or chains in the general cold ISM and the possibility that they have a common stellar origin together with perhaps a mutually beneficial symbiotic relationship which enables them to survive transport in the ISM should not be overlooked (Kroto 1981, 1982). Without some form of protection during transport molecules are unlikely to survive photodissociation (Duley and Williams 1984*a*) during the millions of years that elapse between formation in a carbon star and the appearance of polyynes in a cold cloud such as TMC 1. The present view that they are destroyed and subsequently reformed in interstellar molecular clouds is a conjecture in need of confirmation.

It has been proposed that the carbon chains can be produced by facile reactions between carbon clusters produced by graphite vaporization and the simpler reagents present in the interstellar medium (Kroto 1982). Recently, laboratory experiments were carried out (Heath *et al.* 1987) which support this hypothesis. The experiments have yielded unequivocal evidence for the formation of such species—in particular, HC_7N and HC_9N as well as very long chain polyynes with as many as 20 or more carbon atoms. Symmetric species such as $H–(C{\equiv}C)_n–H$ and $N{\equiv}C–(C{\equiv}C)_n–C{\equiv}N$, some of which are almost certainly present in the ISM (but not detectable because they do not possess permanent dipole moments), are also readily produced. These laser vaporization experiments have also produced radicals of the type $\cdot C_nH$ similar to those that have been detected in the ISM and IRC$+10°216$ (Guélin and Thaddeus 1977; Guélin, Green, and Thaddeus 1978).

II. SUMMARY OF EXPERIMENTAL DATA ON CARBON CLUSTERS AND THEIR REACTIONS

Pure clusters with as many as 30 or more carbon atoms have long been known to be obtainable by vaporizing solid carbon, and their structures have been the subject of much debate (Palmer and Shelef 1968). The conclusions reached, that linear carbon chains were produced in the original vaporization studies (Pitzer and Clementi 1959; Berkowitz and Chupka 1964), have been supported by recent work (Rohlfing, Cox, and Kaldor 1984).

Recently our laboratory has undertaken a series of studies on carbon clustering. The technique, involving the laser vaporization of carbon from a graphite surface into helium entraining gas, followed by subsequent cooling through supersonic expansion was developed (Smalley 1981) for the study of the clustering behavior of metallic and refractory materials. After expansion the so-produced clusters are skimmed to form a beam which can be interrogated by a second laser which ionizes them so that their mass distribution can be determined by time-of-flight mass spectrometry (TOFMS).

Full details of the results of these studies of carbon vapor nucleation are detailed elsewhere (Kroto *et al.* 1985*a*; Heath *et al.* 1985, 1987; Zhang *et al.* 1986; Liu *et al.* 1986). Although the process is extremely complicated, the experiments have given a new insight into many of its aspects. When pure carbon vapor condenses it appears that small carbon units such as C atoms, we well as C_2 and C_3 radicals, take part in a very fast clustering reaction to form at least three different types of species. We can summarize their properties as follows.

1. *Linear carbon chains.*—Chains with up to 30 atoms are formed. The even-numbered chains probably have polyyne bond configurations ($\cdot C{\equiv}C–C{\equiv}C \cdots C{\equiv}C–C{\equiv}C\cdot$) with highly reactive ends. The odd-numbered chains probably have cumulene-type electronic structures ($:C{=}C{=}C\cdot\cdot C{=}C{=}C:$) which are slightly less reactive than the polyynes. It should be noted that Pitzer and Clementi (1959) calculate that the cumulene-like configuration should be more stable than the polyyne one, even for the *even* clusters. However, the reaction data are most readily interpreted in terms of polyyne products resulting from reactions involving bare carbon polyyne-like species. Cumulene type configurations are not, however, ruled out as electronic reorganization might occur during the formation of the transition state.

2. *Spherical shell carbon clusters.*—A family of even-numbered carbon atom clusters has been discovered which appear to be closed spheroidal hollow shells (Kroto *et al.* 1985*a*). The main chemical characteristic of these species is that they are unreactive (Zhang *et al.* 1986) and one specific one, C_{60} Buckminsterfullerene, appears to be extremely stable. Odd-numbered clusters are also detected which are reactive and disappear rapidly. It appears that partially closed spheroidal shells—such as the odd ones—are intermediates in the rapid formation of macroscopic carbon particles (Zhang *et al.* 1986). The closed shell structures are survivors of this process

as closure has eliminated the reactive edges necessary for further growth.

3. *Macroscopic particles.*—These are large soot-like particles composed of concentric spheroidal shells of graphite-like carbon (Zhang *et al.* 1986). These species are detected indirectly by laser fragmentation into smaller particles. The astrophysical significance of these species is being investigated.

In summary, these studies indicate that carbon clusters belong to three distributions: for C_n with $n < 30$, the carbon clusters appear to be primarily in the form of chains (Heath *et al.* 1986), for $40 < n < 100$, the C_n clusters appear to be closed hollow shell structures (Kroto *et al.* 1986), and there appear to be even larger spheroidal macroscopic soot-like particles (Zhang *et al.* 1986).

Here we are concerned with the formation and reactions of linear chains (Heath *et al.* 1986) with the emphasis on their interstellar significance. It is fairly straightforward to introduce reactants into the entraining He before the vaporization phase. Various gases (H_2, N_2, H_2O, CH_3CN, and NH_3) were introduced as reactants or as atom and radical precursors. The aim was to use such species as H and N atoms as well as $\cdot C{\equiv}N$ radicals, produced by the vaporization plasma, to add to chains which are formed either directly from the graphite or during nucleation.

The results are summarized in Table 1. With a pure graphite target both odd and even bare clusters are detected from C_6–C_{100}. On reaction with small amounts of hydrogen formation of C_nH_2 (n even) species such as C_6H_2 to $C_{20}H_2$ are formed. Similar results are obtained when water vapor is entrained. In this case it is likely that a fast H atom abstraction reaction between carbon chain radicals and H_2O takes place. This is fully consistent with the formation of stable polyynes ($H{-}C{\equiv}C \cdots C{\equiv}C{-}H$) by H atom addition to the highly reactive ends of the even-numbered carbon atom chains. The reaction with N_2 is also consistent, since N atoms are expected to produce dicyanopolyynes, of formula $N{\equiv}C{-}(C{\equiv}C)_n{-}C{\equiv}N$. The reactions with NH_3 and CH_3CN enable the mixed H/C/N molecules, the cyanopolyynes, to form. In Figure 1 the evidence for the formation of HC_7N and HC_9N (Heath *et al.* 1987) is depicted. These particular species, which have been detected by radioastronomy (Kroto *et al.* 1978; Broten *et al.* 1978), were the major stimuli for experiments on carbon.

There is excellent evidence that the nonpolar species are also present in the ISM. For instance the detections of the radicals $\cdot C_4H$ and $\cdot C_3N$ (Guélin and Thaddeus 1977; Guélin *et al.* 1978) strongly support the existence of HC_4H. Similar types of radicals have also been detected under our experimental conditions (Heath *et al.* 1987).

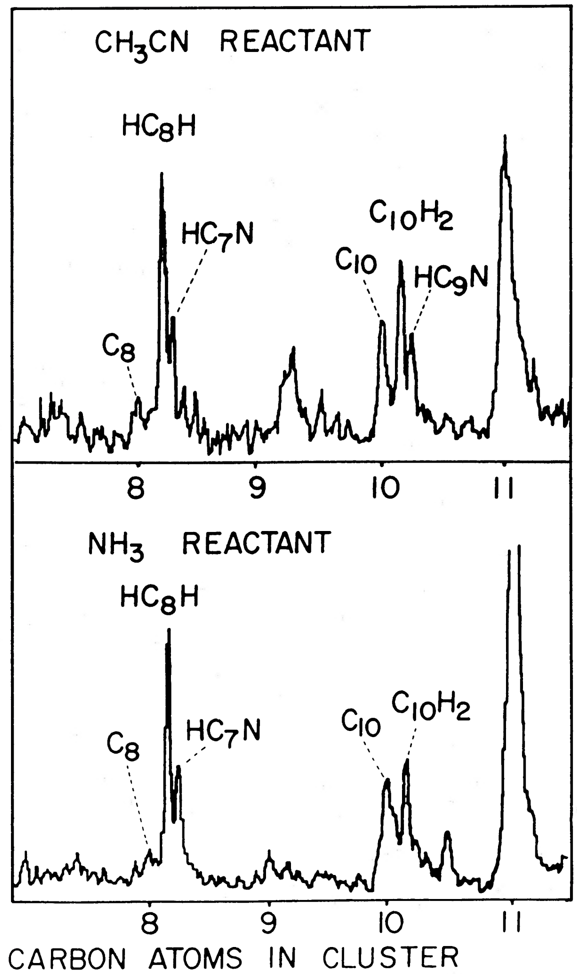

FIG. 1.—*Top*: the result of introducing $CH_3C{\equiv}N$ into the He gas pulse into which the carbon is vaporized. This molecule is expected to provide both H atoms and $C{\equiv}N$ radicals which are expected to react with the even carbon chains to produce the polar cyanopolyynes. In this scan the C_8 and C_{10} peaks are accompanied by peaks at +2 mass units consistent with polyyne formation and also +3 mass units consistent with cyanopolyyne formation. The latter peaks belong to HC_7N and HC_9N, both of which have been detected in the interstellar medium. *Bottom*: the results of introducing NH_3 into the He. In this case H and N atoms are expected to react with the odd carbon cluster population to produce the cyanopolyynes. Clear evidence for HC_7N is observed as well as for HC_8H and $HC_{10}H$. The HC_9N signal is very weak.

TABLE 1

SUMMARY OF CARBON CLUSTER REACTION PRODUCTS[a]

Reactants	Main Products	Range Monitored[a]
H_2[b]	C_6H_2–$C_{22}H_2$	C_6–C_{30}
N_2	C_8N_2–$C_{22}N_2$	C_8–C_{22}
CH_3CN	HC_7N–HC_9N	C_7–C_9
NH_3[c]	HC_7N–HC_9N	C_7–C_9
H_2O	C_8H_2–$C_{20}H_2$	C_8–C_{20}

[a] Heath *et al.* 1987.

[b] These species detected with small amounts of H_2 admixture. Greater H_2 concentration results in higher hydrocarbons. Species such as $\cdot C_6H$, $\cdot C_8H$, and $\cdot C_{10}H$ are also detected. (See Heath *et al.* 1987).

[c] HC_9N signal is weak.

III. DISCUSSION

Although the exact mechanism by which the polyynes are produced during vaporization of graphite has not been fully determined, the ease with which the experiments indicate that they form during nucleation has important implications as far as the existence of such species in the ISM is concerned. To put the results into perspective we note the following.

1. Polyynes are produced in the presence of grains in significant quantities in carbon stars and are subsequently expelled (with grains) into the general ISM.

2. They are also found in significant quantities, protected from photodissociation by grains, in molecular clouds.

3. As was discussed previously, no highly selective process has yet been identified which provides experimental support

for an in situ ion-molecule route to the long chains detected in the molecular clouds.

In the light of these considerations, the carbon cluster reaction results are particularly interesting. They show that there are conditions under which such chains, accompanied by grains, are produced in a *facile* way and therefore provide a plausible mechanism for their formation in space. High temperatures favor the formation of carbon/carbon bonds relative to carbon/hydrogen bonds due to the large difference in bond energies (Stein and Fahr 1985). Although the conditions in our experiments may differ from those in stellar atmospheres in various respects, it is *unlikely* that the main features of the carbon nucleation process are much different. Any species that are observed when carbon nucleates under laboratory conditions are thus likely to occur when carbon particles form under astrophysical conditions.

The results of Schuler and Reinebeck (1954) and Winnewisser *et al.* (1980) have shown that short chains can form in discharges. These may be pertinent experiments as far as processes involving ions are concerned, although the conditions are rather far from those in cold molecular clouds in terms of density and temperature. In fact, they are perhaps not too dissimilar to the conditions in a carbon star, reinforcing the plausibility of a carbon condensation-related mechanism for the production of chains.

Chains are invariably formed at essentially the same time as large particles, and it thus seems that the carbonaceous grains are ideal parents of the polyynes or vice versa. If the chains detected in the cold molecular clouds did not start life in a star then it is conceivable that they resulted from the disruption of a grain that did. It is possible that shock wave disruptive processes might be viable alternative production mechanisms in cold clouds (Duley and Williams 1984*b*). Whichever mechanism is active in giving rise to the polyynes it seems highly likely that their presence signifies the presence of solid carbonaceous aggregates.

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