

than by catalysis on grain surfaces or the dissociation of even longer molecules formed in stellar atmospheres, in the richest source of polycyanoacetylenes, the Heiles cloud 2 region of the Taurus molecular cloud complex. The evidence is the detection of deuterated cyanoacetylene, DC₃N, in an interstellar cloud. Further observations of DC₃N are necessary to clarify the role of ion-molecule chemistry in the formation of HC₃N in sources other than the one position observed in Taurus.

As noted by Watson *et al.* (3), measurement of the relative abundances of the deuterated and protonated forms of a molecule in an interstellar cloud can discriminate between formation by gas phase reactions and by grain catalysis. The presence of large abundances of deuterated molecules can only be explained in terms of an ion-molecule gas phase model of the interstellar chemistry. In addition to DC₃N, the following molecules have been observed in interstellar clouds in their deuterated form and have been shown to derive from ion-molecule reactions: HCO⁺, HCN, N₂H⁺, and H₂CO (4).

Furthermore, Hayatsu *et al.* point out that Fischer-Tropsch reactions predict a decrease in relative abundance of successive homologs of the polycyanoacetylenes (HC_{2n+1}N/HC_{2n-1}N ~ 1/4), which they argue agrees with the observed ratios. Recent studies show that HC₅N/HC₃N ~ 1 (5) and so may rule out grain catalysis by this method entirely.

We would not assert that only gas phase ion-molecule reactions produce molecules in interstellar clouds. In fact, it is clear that there are places, such as the star IRC + 10216, where the long carbon chains are formed in the absence of ion-molecule chemistry. Yet unambiguous evidence for catalytic formation of molecules on grains in clouds exists only for the special case of H₂ and no other molecule.

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We fully agree with Langer *et al.* that the deuterium in interstellar cyanopolyacetylenes such as DC₃N was grafted on by ions such as H₂D⁺ or DCO⁺. But this was only the last embellishment of a long carbon chain; the crucial question is how this carbon chain formed in the first place.

We do not share the belief of Langer *et al.* that these chains formed by ion-molecule reactions in the gas phase. A telling clue is the relatively high abundance of heavier cyanopolyacetylenes; for example, in TMC-1, successive homologs from HC₃N to HC₉N decrease in abundance by a mean factor of 0.27 (1, 2). This means that the probability of chain growth by two carbon atoms is 0.27, whereas the probability of chain destruction is 0.73. In other words, conversion to the next homolog is one-third as likely as all other fates combined: hydrogenation, branching, dissociation, ionization, chain termination, and so on.

Several authors have proposed ingenious schemes for gas-phase buildup of cyanoacetylenes, using intermediates that themselves are rare, such as C₂H₂. However, it remains to be shown, by a truly comprehensive review of all relevant reactions, that so hydrogen-poor a series as H-(C≡C)_n-CN can be made and preserved, with a net growth probability of 0.27, in a gas phase where H outnumbered C by a factor of 1000.

On the other hand, grain surfaces have the proven ability to catalyze the growth of carbon chains, either by the well-known Fischer-Tropsch reaction (yielding hydrocarbons, alcohols, and so on) or by the disproportionation of CO [yielding free C, up to at least C₆ (3)]. The slope of the distribution depends on reaction conditions, but typically corresponds to a decline of 0.35 to 0.8 times for every two carbon atoms. This range

encompasses all astronomically observed ratios reported to date, including the HC₅N/HC₃N ratio of ~ 0.7 (4) that Langer *et al.* claim "rule[s] out grain catalysis . . . entirely."

A logarithmic distribution of similar slope can also arise by another process: fragmentation of larger molecules or polymers. We have suggested (2, 3) that the primary products of grain catalysis may first polymerize, and later break down to smaller fragments on some type of provocation.

A serious problem with grain catalysis is that it requires relatively high temperatures and densities. But there are possible solutions to this problem (2, 5).

We strongly agree with Langer *et al.* that the occurrence of cyanopolyacetylenes in the infrared star IRC +10216 (6) shows that nature knows how to make these compounds by a nonionic mechanism. But being disciples of William of Ockham, we would like to go a step further and note that this mechanism may well be the dominant one even in molecular clouds where ions are present. If ions are irrelevant for cyanoacetylenes in one place, perhaps they are irrelevant for them in all places, except for the final deuteration. Of course, we have no quarrel with the role of ions in building smaller molecules.

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