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# Abundances of Linear Carbon-Chain Molecules in Supernovae

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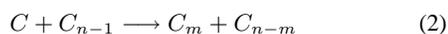
**ABUNDANCES OF LINEAR CARBON-CHAIN MOLECULES IN SUPERNOVAE.** D.D. Clayton, E. Deneault, B. S. Meyer, L.-S. The, *Department of Physics and Astronomy, Clemson University, Clemson SC 29634-0978.*

**Introduction.** This paper continues our effort to understand the condensation of carbon solids in a gas of pure C and O atoms when these exist within the interior of an expanding young supernova. This setting has a sufficiently large number of energetic electrons that the CO molecule is disrupted with a lifetime of a few months, causing the abundance of CO to be no greater than 1% or so of the C abundance. As a consequence, the CO molecule cannot consume the available C atoms, even when the O abundance exceeds that of C. The maintenance of free C atoms is the driver for condensation of carbon (1,2). Clayton et al. (2) presented a sweeping picture of the chemical sequence that enables large micron-sized carbon grains to condense even when  $C < O$ . We adopt this same sequence: (1) carbon association reactions balanced approximately by rapid destruction reactions determine the abundance of linear  $C_n$  molecules within the gas; (2) given sufficient length, the chain molecules isomerize to ringed molecules, for which further C associations become more rapid than oxidations; (3) monocyclic rings grow to bicyclic and multicyclic sizes, including fullerenes; (4) multicyclic rings seed the inexorable growth to macroscopic particles owing to very fast C association. In this picture, the large  $C_n$  linear chains and their ringed isomers constitute seed nucleations for the growth of macroscopic grains of carbon; therefore the key chemistry governs the abundances of those linear  $C_n$  molecules. Because the destruction reactions (oxidation, C association, or C-induced fission) for  $C_n$  occur very rapidly (about 1 sec when  $N(C) = N(O) = 10^{10} \text{cm}^{-3}$  with destruction rate coefficient  $k = 10^{-10} \text{cm}^3 \text{s}^{-1}$ ), destructive reactions limit the abundance of linear  $C_n$  to a small steady state value. Steady state is achieved more rapidly than environmental changes (density and temperature), which occur only over month timescales after one year, when condensation mostly happens. For that reason, we evaluate in this work the stationary abundances of  $C_n$  and seek to understand what chemical rates are of importance to that abundance. Our approach may be likened to that of classical nucleation theory, except that the nucleation abundances are determined by the balance of kinetic rates for creation and destruction rather than by the more restrictive assumption of chemical equilibrium (the usual assumption of nucleation theory). Indeed, the abundances of  $C_n$  molecules are vastly greater than would obtain in thermal equilibrium, for in that case CO molecule formation would consume the carbon.

**Reaction Rates.** We take as our standard set of kinetic rates those given by (2) in their Table 1. The destruction rate for even linear molecules  $C_{2n}$  reaches the maximum kinetic rate  $k = 10^{-10} \text{cm}^3 \text{s}^{-1}$  by both oxidation



and by association-induced fission



The odd chains  $C_{2n+1}$  are also destroyed at the maximum

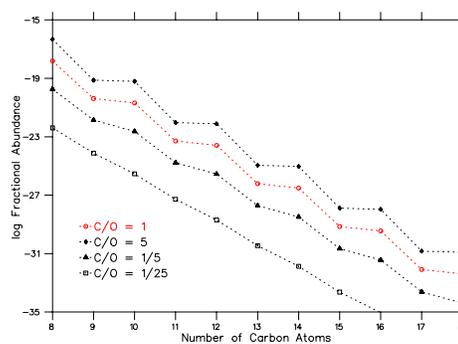
kinetic rate, but instead by C association reactions



whereas their oxidation is slower  $k_O = 10^{-13} \text{cm}^3 \text{s}^{-1}$  and fission is taken to be even slower yet. Association rates are fast because the larger chains do not have to radiate immediately to conserve energy, but instead simply exist in states of high excitation to be stabilized eventually by photon emission. This greatly increases the association rate  $k_C$  above the value required if radiative stabilization must be prompt. The C association rate  $k_C$  is slower for even- $n$  chains owing to the competition by the fast C-induced fission (2). Using this basic set of rates for reference calculation we solve for the steady state abundances. The reference calculation takes the number densities to be  $10^{10} \text{cm}^{-3}$  for both C and O; but the dependence on the C/O ratio is determined by numerical solutions.

Setting the rate of change of each molecular abundance to zero yields a matrix equation for the abundance vector  $[N_n] = [C_2, C_3, C_4, \dots, C_{24}]$ . With  $[M]$  being the matrix of reaction rates, the abundance equation can be written  $[M] \times [N_n] = 0$  except in its first row, which equals instead the production of  $C_2$  from C atoms (which lie outside the elements of the vector  $[N]$ ). The solution is straightforward and will be described more completely in a work in progress (3).

**Results.** Figure 1 displays stationary abundances of the



linear molecules as fractional abundances  $N(C_n)/N(C)$  relative to free C atoms, which prior to condensation constitute roughly 99% of the total density of C atoms. The standard calculation has ambient ratio  $C/O = 1$ ; but results for  $C/O = 5, 1/5$  and  $1/25$  are also shown for comparison. For the range shown ( $C_8$  to  $C_{18}$  only) the fractional abundance drops steeply from about  $10^{-18}$  for  $C_8$  to about  $10^{-31}$  for  $C_{18}$ . To appreciate such small numbers consider that a fractional abundance near  $10^{-20}$  is needed for the final micron-sized graphites if each contains  $10^{15}$  C atoms (say) and if they are to constitute about  $10^{-5}$  of all C by mass in the ISM. This will require isomerization rates into ringed C that produce about  $10^{-20}$  rings per C atom during roughly the first year of expansion. This might

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be achieved in various ways: a chain with abundance  $10^{-20}$  isomerizing at the rate  $10^{-7}\text{s}^{-1}$  would yield  $3 \times 10^{-20}$  rings per year; or an abundance  $10^{-28}$  isomerizing at rate  $10\text{s}^{-1}$  would also give  $3 \times 10^{-20}$  rings per year. These possibilities will be explored by (3). Note that the abundances of Fig. 1 do not include depletion by the unknown isomerization rates.

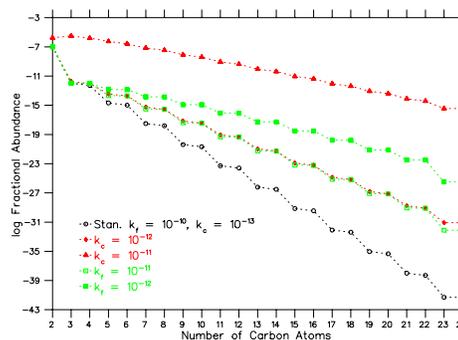
Another conclusion from Fig. 1 is that different C/O ratios produce parallel results; but reduction of C/O by factor 5 reduces the fractional abundances of  $C_n$  only by a factor near 100. Although this makes already small abundances even smaller, it is important to note that the abundances are not zero for C/O = 1/5. This illustrates the kinetic non-LTE nature of this problem. Were one to instead calculate chemical thermal equilibrium at C/O = 1/5, the abundance of  $C_n$  would be vanishingly small! Secondly, even if C/O = 1/5,  $10^{-20}$  rings may be produced per year from  $C_{14}$ , say, if its isomerization rate is near  $10\text{s}^{-1}$ . On the other hand, a carbon-rich C/O = 5 produces no great increase of abundances in the supernova problem whereas it is a huge facilitator in equilibrium condensation calculations because when C/O=5 one has free carbon in the equilibrium calculation; but carbon is maintained free by radioactivity in the supernova problem. These ideas clarify immediately that graphite grains may grow even if C<O (2).

**Population Control.** Having more abundant nucleations does not imply more large particles. The nucleations must not be too abundant or there will not exist enough C atoms for them to grow into large graphite particles. The kinetic destruction of the linear molecules controls their population, which in turn allows them to grow large before free C is depleted. Sufficient collisions to deplete all of the carbon do occur within an expanding supernova interior. If the ringed nucleation molecules were as abundant as  $10^{-12}$  they could grow no larger than 1 micron ( $10^{12}$  atoms) before depleting all of the C into graphite. They would thus be too abundant to give mass fraction  $10^{-5}$  to 1 micron particles. We call this principle "population control", and we note that for this problem ringed-isomer abundance near  $10^{-20}$  appears to be about right.

**Rate Survey.** Because supernova condensation is controlled by kinetic rates it is of interest to examine which reaction rates are the most critical for the outcome. In what follows we increase or decrease all of the reaction rates of specified type. Fission rates are very important. We have taken their rates to be as fast as oxidation in the destruction of the even-n chains. Figure 2 shows the standard reference calculation as well as a comparison result if the fission rate is slowed from the fast  $k_f = 10^{-10}\text{cm}^3\text{s}^{-1}$  to  $10^{-11}\text{cm}^3\text{s}^{-1}$  and then even more to  $10^{-12}\text{cm}^3\text{s}^{-1}$  with all other rates held at the reference values (green curves). It is clear that despite the continued rapid destruction by oxidation, the abundances increase greatly (about 15 powers of ten for  $C_{20}$ ) by the slow-down factor (100) in these even-n fission rates. Fission is so destructive owing to the high probability that the smaller fragment may be lost altogether by oxidizing it down to  $C_2$  where another oxidation removes a molecule.

The carbon association rate with linear  $C_{2n}$  is also important but unknown. Because we have taken the C association rate to be small for even  $C_{2n}$ , only 1/1000 of the fission rate,

we explored that high sensitivity as well in Fig. 2 (red curves). Increasing  $k_C$  from  $10^{-13}\text{cm}^3\text{s}^{-1}$  to  $10^{-11}\text{cm}^3\text{s}^{-1}$  while



holding other rates fixed vastly increases the abundances. Increasing association tenfold to  $k_C = 10^{-12}\text{cm}^3\text{s}^{-1}$  is almost identical to slowing the fission rate by a factor 10. This shows that it is the branching ratio  $k_C/k_f$  that governs the abundances as long as modest variations are involved. But further increase to  $k_C = 10^{-11}\text{cm}^3\text{s}^{-1}$  results in huge abundance increase. Even though that association rate remains smaller than both destruction rates of  $C_{2n}$  by a factor ten, it produces a much flatter abundance curve. With such a flat curve, the doubling of molecule number accomplished by each fission plays an important new role in the steady state abundances, which become even greater than those that would obtain were there no fission at all. Inefficient population control resulting from that value of  $k_C$  creates too many particles (unless isomerization to ringed structure is much slower than expected), resulting in a large number of small graphite grains rather than a smaller number of large ones (as observed). We have also shown that the assumption of fast  $k_C$  for the odd-n linear chains  $C_{2n+1}$  is not so crucial. This is because C association dominates destruction of odd-n molecules; decreasing all such rates would therefore increase their abundances but for its also decreasing the creations of the even-n  $C_{2n}$  by compensating factors. These compensate within the general decline. We find that even two powers of ten decrease of  $k_C$  leaves the same general decline in abundances, although it does smooth out the odd-even effect.

We have taken the oxidation rate for odd-n chains to be  $k_O = 10^{-13}\text{cm}^3\text{s}^{-1}$ , which is much smaller than the C association rate for odd-n. But that is not a critical unknown. We find that increasing the value of  $k_O$  by even a factor 100 does not alter the abundance curve. By such results we propose to clarify for chemists the identity of chemical rates that govern the supernova presolar-grain problem.

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**References.** (1) Clayton, D.D. (1998) *LPSC* 29. (2) Clayton, D.D., Liu, W. and Dalgarno, A. (1999) *Science*, 283, 1290-1292. (3) Clayton, D.D., Deneault, E., Meyer, B.S. and The, L.-S. (2001) *ApJ*, to be submitted.