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A New Mechanism for the Formation of Meteoritic Kerogen-Like Material

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The carbon in ancient carbonaceous chondritic meteorites is mainly in a hydrocarbon composite similar to terrestrial kerogen, a cross-linked structure of aliphatic and aromatic hydrocarbons. Until recently, the composite has been commonly thought to have been produced in the early solar nebula by a Fischer-Tropsch-type process, involving the catalytic synthesis of hydrocarbons from carbon monoxide and hydrogen on grain surfaces. Instead, the aromatic hydrocarbons may form in gas-phase pyrolysis of simple aliphatics like acetylene and methane by a mechanism developed recently to explain formation of soot in combustion and of aromatic molecules in circumstellar envelopes. Nonequilibrium chemical kinetic calculations indicate that this mechanism can produce meteoritic aromatics if the initial concentration of simple hydrocarbons in the solar nebula was sufficiently but not unreasonably high.

THE COMPLEX NATURE OF C-BEARING material in carbonaceous chondritic meteorites has been a subject of great interest for several decades. Components such as racemic mixtures of prebiological amino acids and tiny refractory particles of presolar diamond constitute only a small amount of the C in these meteorites (1). Most C resides in the matrix as a hydrocarbon composite similar to the terrestrial material "kerogen," which is an acid-insoluble material comprised of aliphatic and aromatic hydrocarbons found in coal and humic soil (2). The meteoritic material is variously referred to as "kerogen-like material," "insoluble carbon," or "macromolecular carbon." The aromatic fraction can reach 75% and is comprised mainly of 1- to 8-ring molecules (3).

Attempts to explain the origin of meteoritic kerogen-like material generally assumed

(as we do) that it formed in the early solar nebula, although recent evidence for polycyclic aromatic hydrocarbon (PAH) molecules in the interstellar medium (4) permits that some material could have been inherited from the parent interstellar cloud. The two formation mechanisms generally considered have been: (i) photolysis of various combinations of CH₄, C₂H₆, NH₃, H₂S, and H₂O by energetic radiation, as in Miller-Urey experiments (5); and (ii) the reaction of CO and H₂ on the surface of mineral catalysts through Fischer-Tropsch-type (FTT) reactions (6).

The FTT synthesis has attracted the most attention (7), but it has several drawbacks. Foremost among them, and directly motivating our work, is that the FTT process under terrestrial conditions typically produces almost exclusively aliphatic hydrocarbons (8). In experiments simulating solar nebula conditions, Studier *et al.* (9) reported up to a 35% yield of aromatics, but only after reheating to about 1200 K when aliphatic hydrocarbon species were already present. These aliphatics, rather than CO, are more likely to be the precursors of the aromatic product under their experimental conditions. Also, the reported prevalence of

certain meteoritic aliphatic species, which closely matched FTT predictions (9), probably resulted from terrestrial contamination (10). Because the most widely discussed explanation for the formation of this material has encountered such difficulties, there is considerable motivation to investigate alternatives.

We propose that aromatic hydrocarbon formation takes place in the gas phase by pyrolysis of simple hydrocarbons present in the solar nebula, such as acetylene (C₂H₂) or methane (CH₄). Our model is based on the detailed chemical kinetic mechanism developed recently by Frenklach and colleagues to explain the early stages of soot formation in hydrocarbon pyrolysis and combustion (11). The first aromatic ring can be formed through one of several possible pathways. The principal growth pathway of the mechanism is the abstraction of H atoms, followed by the addition of C₂H₂ molecules to the resulting aromatic radical. Essentially the same mechanism has been applied to investigate PAH formation in the dense atmospheres of carbon-rich red-giant stars (12, 13). At high temperatures ($T \sim 2000$ K), where PAH molecules form in terrestrial flames, aromatic formation does not occur in stars because ambient H₂ inhibits the abstraction step. However, at lower temperatures ($900 \text{ K} \leq T \leq 1100 \text{ K}$) the H-abstraction is no longer the rate-limiting step, and the reaction is driven by the irreversibility of the C₂H₂ addition. For sufficiently dense and slow winds, the aromatic yield in C stars can approach 100% of the initial C in C₂H₂ (12).

The chemical reaction mechanism is composed of two parts. The first (14) is responsible for the interconversion between CH₄ and C₂H₂ and determines the concentration of H atoms, the main reaction carrier under the conditions studied. The second reaction subset (12) describes the formation and growth of PAH molecules starting from C₂H₂. Altogether the model contains more than 200 reactions and computes the time-

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Table 1. Calculated PAH yields for solar nebula models after 10^6 years. The quoted yield is the fraction of C atoms present in the initial gas incorporated into PAHs of one or more rings. Blank entries indicate yields less than 10^{-6} ;

(a) C_2H_2 - H_2 mixture; (b) CH_4 - H_2 mixture; (c) C_2H_2 - CH_4 - H_2 mixture; initial $[CH_4]/[H_2]$ ratio is 10^{-5} ; (d) the mixture described in (16). P , pressure.

P (atm)	(a) $[C_2H_2]/[H_2]$			(b) $[CH_4]/[H_2]$			(c) $[C_2H_2]/[H_2]$			(d) $[C_2H_2]/[H_2]$		
	10^{-5}	10^{-6}	10^{-7}	10^{-4}	10^{-5}	10^{-6}	10^{-5}	10^{-6}	10^{-7}	10^{-5}	10^{-6}	10^{-7}
10^{-4}										2×10^{-6}		
10^{-5}	2×10^{-4}			3×10^{-3}			1×10^{-4}			4×10^{-2}	4×10^{-3}	3×10^{-3}
10^{-6}	0.26	2×10^{-6}		0.91	2×10^{-6}		0.52	2×10^{-4}	4×10^{-6}	0.40	0.30	0.29
10^{-7}	8×10^{-2}			0.57	2×10^{-5}		9×10^{-2}	6×10^{-4}	9×10^{-5}	0.35	0.12	0.11
10^{-8}	2×10^{-5}						1×10^{-5}			6×10^{-4}	8×10^{-5}	6×10^{-5}

dependent abundances of more than 60 chemical species including H, H_2 , C, O, oxides of H and C, hydrides of C and O, linear hydrocarbons with up to six C atoms, and aromatic hydrocarbons with one or two rings. The growth of PAH molecules beyond two rings is described by a linear lumping algorithm. The reactions take place in the gas phase: no grains are assumed to be present, and no catalysis is included. Reaction rate coefficients are derived from experimental data and theoretical calculations, when available, and are otherwise set equal to known rates of similar reactions (11, 12). The dependence of rate coefficients on pressure was expanded to cover pressures from 10^{-8} to 10^{-4} atm, appropriate for solar nebular models. Lumping, thermodynamic assumptions, computational method, and other details are described in (12) and references therein. The chemical reaction mechanism has considerable uncertainty. The aromatic yields obtained could either increase or decrease severalfold, depending on conceivable adjustments of critical reaction rate coefficients.

The predictions of this mechanism are sensitive to the initial abundances of CH_4 and C_2H_2 , which were often thought to be low in the solar nebula. However, studies of interstellar clouds now indicate that simple hydrocarbons are present in more than trace amounts. Acetylene has been directly detected in interstellar clouds at levels from about 10^{-4} to greater than 10^{-3} times that of CO

(15). Recent theoretical nonequilibrium chemical models of interstellar clouds (16, 17) predict that the $[C_2H_2]/[CO]$ ratio is $\sim 10^{-2}$ and that the $[CH_4]/[CO]$ ratio is 0.01 to 0.1, considerably above predictions in earlier equilibrium models. The observed $[CH_4]/[CO]$ ratio of P/Comet Halley was ~ 0.03 to 0.3, and $[C_2H_2]$ inferred from the Swan bands of C_2 (18) was an order of magnitude lower than that in interstellar clouds. The relevance of all such studies to the conditions in the inner solar nebula is quite uncertain because of the complex chemistry that might occur during interstellar cloud collapse (19) and possible chemical inhomogeneities in the nebula (20). But they indicate that around 1 to 10% of the initial gaseous C in the solar nebula may have been in the form of small aliphatic hydrocarbons.

We used two approaches to estimate the initial chemical abundances of the solar nebula. First, we calculated models based on mixtures of CO, CH_4 , and C_2H_2 diluted in molecular hydrogen. On the basis of the evidence discussed above, we adopted the following values and ranges: $[CO]/[H_2] = 10^{-4}$ (a standard value for interstellar clouds), $[CH_4]/[H_2] = 10^{-6}$ to 10^{-4} , and $[C_2H_2]/[H_2] = 10^{-7}$ to 10^{-5} . Secondly, we took the result of a recent nonequilibrium chemical model of a dense interstellar cloud (16). Our goal was to see whether a more complex combination of input chemical species would significantly affect the trends

found in the first approach.

Gas densities were obtained from astrophysical models of the solar nebula evaluated in the temperature range $900 \text{ K} \leq T \leq 1100 \text{ K}$, where our earlier studies (12, 13) showed that PAH molecules form in H-rich environments. Recent nebula models indicate that temperatures of 900 to 1100 K may have occurred over a wide region of the inner solar nebula because of compressional heating during collapse. The PAH molecules could also have been produced above or below the plane of the nebula where densities were lower than in the nebular plane. From the models described in (21), we considered gas pressures in the wide range of 10^{-8} to 10^{-3} atm. Effects of vertical convection or radial mixing, which would cause pressure and temperature variations, were neglected.

The chemical reactions are computed for times ranging from 10^5 to 10^6 years, representing estimates of the time scale of planet building and meteorite formation in the solar nebula (22). However, we continued some calculations for longer times to investigate the kinetic behavior of the reaction system.

Several hundred runs of the chemical model were made covering the ranges of solar nebular pressures, temperatures, and initial abundances. On typical time scales of $\sim 10^6$ years for runs including only C_2H_2 and H_2 (Table 1a), the acetylene was largely depleted; some polymerized into PAH molecules and some reverted to CH_4 (Fig. 1). For runs with only CH_4 and H_2 (Table 1b), CH_4 was converted to C_2H_2 and then polymerized into PAH molecules. For such a run, conversion of CH_4 typically took 10^5 to 10^6 years (Fig. 2). For runs with C_2H_2 , CH_4 , and H_2 (Table 1c), as in the other runs, PAH molecules were formed in substantial quantities. Thus, significant PAH yields can occur for high but not unreasonable initial concentrations of hydrocarbons.

Whereas a higher concentration of initial hydrocarbons always yielded higher PAH production, as expected, higher pressures suppressed the yields (see Table 1). Highest yields typically appeared around 10^{-7} atm,

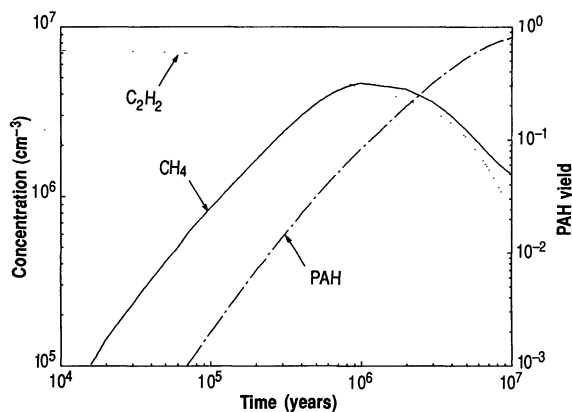


Fig 1. Temporal evolution of C_2H_2 and CH_4 concentration and of PAH yield obtained for a run with initial H_2 and a $[C_2H_2]/[H_2]$ ratio of 10^{-5} at a pressure of 10^{-7} atm and temperature of 1000 K.

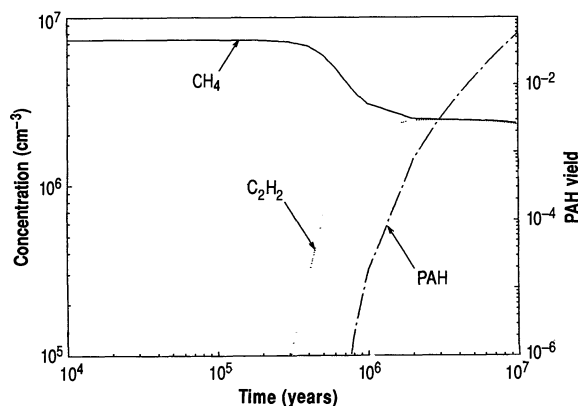


Fig 2. Temporal evolution of C_2H_2 and CH_4 concentration and of PAH yield obtained for a run with initial H_2 and a $[CH_4]/[H_2]$ ratio of 10^{-5} at a pressure of 10^{-7} atm and temperature of 1000 K.

which might have been the pressure somewhat away from the plane of the solar nebula. The behavior can be understood by examining detailed time dependencies for a typical run with initial C_2H_2 (Fig. 3). Although the PAH yields at high pressures were always suppressed, at low pressures high yields were only delayed. The yield approached unity for pressures below $\sim 10^{-6}$ atm when the calculation was extended to 10^7 to 10^8 years. Yields at high pressures are suppressed because C_2H_2 , the key reactant for PAH growth, was converted to CH_4 .

We also examined the effect of temperature on the formation of PAH molecules. Peak production occurred around 1000 to 1050 K, and dropped off significantly below ~ 900 K and above ~ 1100 K. This temperature window is caused by kinetic-thermodynamic coupling of key PAH-forming reactions in H-rich atmospheres (12, 13).

For a more elaborate initial chemical mixture (16), PAH yields above 10% were obtained for a considerably wider range of pressures and C_2H_2 abundances than seen in the models with simpler initial conditions (Table 1d). This increase in yields arose principally from the presence of atomic C in the initial mixture. After 10^4 years, atomic C disappeared, and instead much of the C was in C_2H_x species. When C was removed from the initial mixture, the yield fell two orders

of magnitude.

The average PAH size increased along with the increase in PAH yield. For example, a run at a pressure of 10^{-8} atm and with a yield of 10^{-5} had an average PAH size of about 100 C atoms, whereas a run with the same conditions except at a pressure of 10^{-6} atm and with a yield of 0.52 had an average PAH size of 9×10^3 C atoms. This increase in size indicates that the conditions under which the PAH yield peaked in the runs promote molecular growth rather than simply increasing the population of small aromatic rings. However, such aromatic growth is likely to be accompanied by coalescence into soot-like turbostratic particles or by reactions with aliphatics creating the mixed-structure polymer characteristic of kerogen-like material.

The basic finding can be summarized simply: gas-phase pyrolysis of simple hydrocarbons present in the solar nebula could have, under reasonable nebular conditions, produced considerable amounts of aromatic structures. However, the process may not have been effective under all solar nebular conditions. First, directly in the nebular plane where the density is highest, hydrocarbons may have converted preferentially to CH_4 . Second, PAH production may also have been low if meteoritic formation or nebular gas cooling was very rapid ($< 10^5$ years) before most of the CH_4 was convert-

ed to C_2H_2 . Third, the model predicts that PAH production would have been low if the initial hydrocarbon abundance was low; initial abundances of CH_4 or C_2H_2 of order 10^{-1} to 10^{-2} times that of CO are needed. The required hydrocarbon abundance could be inherited from the parent molecular cloud, or result from partial conversion of CO to CH_4 in the solar nebula (7, 20).

There are several outstanding issues. First, the model could be enhanced to include the coalescence of aromatic molecules and reactions between aromatics and aliphatics forming kerogen-like structures. Second, our proposed mechanism does not include any isotopic fractionation effect, which is needed to explain the four isotopically distinct components of meteoritic kerogen-like material (3). Although extensive data are not available, there are indications that gas-phase C chemistry could have produced some isotopic fractionation (23). Third, the model might be applied to more complex, and perhaps more realistic, nebular conditions. Cycling of density and pressure due to convection and application to conditions of the Jovian subnebulae might be examined.

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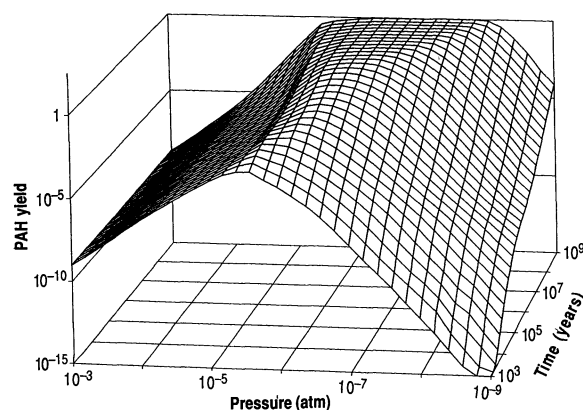


Fig 3. PAH yield as a function of time (extended to 10^9 years) and pressure, computed with initial H_2 and a $[C_2H_2]/[H_2]$ ratio of 10^{-5} .

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Energetics of Caterpillar Locomotion: Biomechanical Constraints of a Hydraulic Skeleton

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Power input increased linearly with speed and was closely associated with changes in cycle frequency. Minimum cost of transport of gypsy moth caterpillars was 4.5 times as high as predicted for vertebrates and arthropods with jointed framework skeletons. Reduced locomotor economy was associated with stride length only one-third or less than that for animals with solid skeletons.

FROM THE NOW CLASSIC WORK OF Taylor, Schmidt-Neilsen, and Rabb (1), investigations on the cost of terrestrial locomotion have been conducted on birds (2), reptiles (3), and amphibians (4), as well as adult insects (5) and other arthropods (6). Remarkably, aerobic metabolism during continuous submaximal performance is essentially a linear function of speed in all these groups, and the minimum cost of transport (M_{run}), obtained from the slope of metabolism versus speed relationships, is surprisingly insensitive to differences in morphology, mechanics, or phylogenetic history (7, 8). All of the animals in the studies outlined above possess muscles attached to solid skeletal elements, and muscle contraction against the skeleton produces limb movement. Caterpillars depart markedly from such organization. Their muscles surround a continuous, fluid (or hydraulic) skeleton. Muscle contraction against an incompressible fluid causes movements by elongation of the body. I report that the soft body of caterpillars reduces their range of speeds and the range of stride lengths pos-

sible yielding energetic costs of locomotion, which are about four to five times as great as for arthropods and vertebrates that use solid skeletons.

Oxygen consumption of gypsy moth caterpillars (*Lymantria dispar*) walking on a motor-driven treadmill was continuously monitored with an S-3A oxygen analyzer attached to an analog to digital channel of a microcomputer (BBC Acorn Model B). Air flow through the chamber was approximately 130 ml/min. Before entry into the sensor, the air passed through a desiccant to remove water vapor. Performance stabilized within 3 to 5 min, and data were only taken for such performances. Oxygen consumption (standard temperature and pressure, dry) was calculated by standard open flow respirometry equations (9).

Movements of the caterpillars during locomotion were recorded by placing a video camera (with macro lens) besides the treadmill, allowing continuous recording of side view (10). Body wave production (stride frequency) was determined by counting the movements of the terminal prolegs during specified time intervals. Stride length was calculated by dividing the speed by the frequency of body wave production. Movement of prolegs was obtained by videoanal-

ysis from below as caterpillars walked across a perspex sheet.

Terrestrial locomotion by caterpillars occurs as a result of a progressive series of body waves proceeding from posterior to anterior. Body movement occurs only in a horizontal and a vertical plane. The terminal prolegs move forward and anchor the body. Once these prolegs are set, the body wave proceeds forward and muscles from each body segment contract serially. The movement of different body regions is confined to distinct intervals of the cycle. Once a particular proleg pair has moved and been "planted," there is no further movement by that proleg or body segment until the next cycle (Fig. 1). The head, which moves as a result of hydraulic pressure sweeping forward, is moving almost continuously rather than cyclically (Fig. 1). Only a single wave occurs in the body at any one time.

As speed increases, both stride frequency

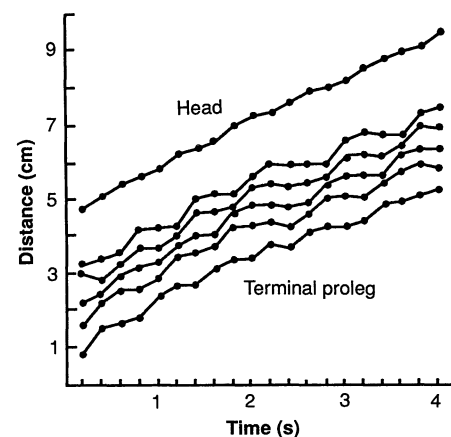


Fig. 1. Movement of the five proleg pairs and the head during several locomotor cycles. As movement is bilaterally symmetrical only the right prolegs are shown.

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