

Stability of Condensed Hydrocarbons in the Solar Nebula

Mikhail Yu. Zolotov and Everett L. Shock

Department of Earth and Planetary Sciences, Washington University, Campus Box 1169, One Brookings Drive, St. Louis, Missouri 63130-4899
E-mail: zolotov@zonvark.wustl.edu

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Thermodynamic calculations of metastable equilibria in the H–C–O system are used to evaluate the stability of condensed polycyclic aromatic hydrocarbons (PAHs) and normal alkanes in the solar nebula. The effects of temperature, total pressure (governed by H₂), the abundances of gaseous CO and H₂O, as well mass accretion rate into the Sun and viscous efficiency at the nebula midplane are explored. We show that the inhibited formation of graphite and methane permits metastable existence of hydrocarbons with respect to the inorganic gases H₂, CO, and H₂O. Low temperatures, high pressures, high abundances of CO, low abundances of H₂O, low accretion rates, and low viscous efficiencies favor stability of hydrocarbons. Condensed PAHs are stable relative to nominal abundances of the inorganic gases at temperatures below ~450 K depending on the physical parameters adopted for the nebula. Normal alkanes with carbon numbers > 10 are stable at temperatures 30–60 degrees lower. During the evolution of the nebula, hydrocarbons have a thermodynamic potential to form in a narrow zone, which moved toward the Sun as the accretion rate decreased. At radial distances of 2–4 AU, hydrocarbons had a potential to form at the time when the accretion rate was 10^{-6.3}–10^{-7.7} solar mass yr⁻¹, depending on the viscous efficiency. High temperature, low pressure, and a high CO/H₂O ratio in the nebula increase the stability of PAHs compared with their alkylated versions and relative to their aliphatic counterparts with the same carbon number. The calculations reveal the thermodynamic possibility for nebular Fischer–Tropsch type (FTT) synthesis of condensed hydrocarbons on the surface of mineral grains from CO and H₂ in an H₂O-depleted and/or CO-rich environment. © 2001 Academic Press

Key Words: solar nebula; organic chemistry.

INTRODUCTION

High molecular weight condensed hydrocarbons are widely present in the universe. In particular, polycyclic aromatic hydrocarbons (PAHs) are believed to be among the most abundant organic molecules in space. These compounds have been identified in carbonaceous and ordinary chondrites (Studier *et al.* 1968, Pering and Ponnampereuma 1971, Hayatsu *et al.* 1977, Basile *et al.* 1984, Hahn *et al.* 1988, Zeboni *et al.* 1992, Kovalenko *et al.* 1992, Krishnamurthy *et al.* 1992), in interplanetary dust particles (Clemett *et al.* 1993, Thomas *et al.* 1995), and in presolar grains from chondrites (Messenger *et al.* 1998). In all of these objects,

PAHs predominate over other organic compounds and are represented by a multicomponent mixture of species with variable degrees of alkylation. PAHs are supposed to be constituents of the atmospheres of Jupiter and Titan (Sagan *et al.* 1993) and can exist in other reduced atmospheres of the outer Solar System as well. They are probably present on the surfaces of low-albedo asteroids (Moroz *et al.* 1998) and in nuclei of comets (Moreels *et al.* 1994, Joblin *et al.* 1997). Outside the Solar System, partially ionized gaseous PAHs could be a major group of organic compounds responsible for the unidentified infrared emission bands (UIRs) and some of the diffuse interstellar bands (DIBs) observed in interstellar molecular clouds and planetary nebulae (e.g., Allamandola *et al.* 1989, Salama *et al.* 1996). Contrasting with the immense structural diversity of biologically derived terrestrial PAHs, the majority of space PAHs are represented by a more limited variety of two- to four-ring compounds with low to moderate degrees of alkylation. The following species and their alkyl derivatives are among the most abundant PAHs in space objects: biphenyl (C₁₂H₁₀), naphthalene (C₁₀H₈), phenanthrene (C₁₄H₁₀), anthracene (C₁₄H₁₀), pyrene (C₁₆H₁₀), and chrysene (C₁₈H₁₂). The chemical structures of these and other compounds are shown in Fig. 1.

Meteorites provide the most complete direct evidence concerning the presence of high molecular weight condensed hydrocarbons in the Solar System, but multiple processes are likely to have influenced the composition of meteoritic organic compounds. In chondrites, condensed aliphatic hydrocarbons are much less abundant than polyaromatic molecules and include structurally diverse, branched, alkyl-substituted alkanes of carbon number greater than 10 and aliphatic polycyclic compounds (Cronin and Chang 1993). In acid-insoluble macromolecular polymeric organic material, aliphatic structures link 2–4 ring aromatic clusters (Hayatsu *et al.* 1977, Cronin *et al.* 1988). Other chains between polyaromatic molecules include O-, N-, and S-bearing functional groups.

The inferred presence of isotopically distinct components in organic compounds in meteorites indicates a multi-path complex history for this organic material (Kerridge 1983, Kerridge *et al.* 1987, Alexander *et al.* 1998). It is quite possible that the speciation of PAHs and other hydrocarbons found in meteorites and IDPs represents a mixture of compounds formed through a variety of processes of synthesis and alteration, some of which

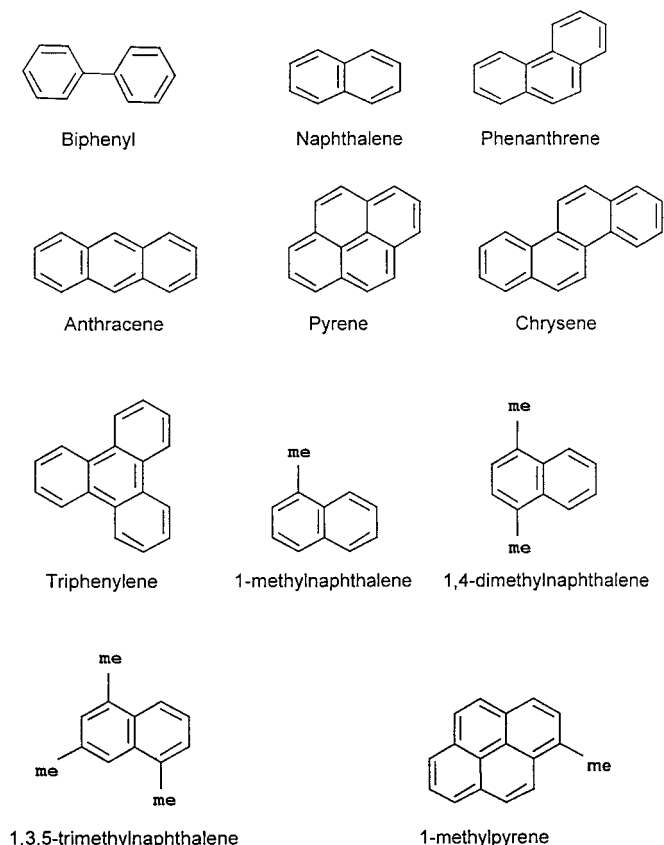


FIG. 1. Chemical structures of several PAHs and their methylated derivatives considered in this paper. Methyl ($-\text{CH}_3$) group is denoted "me".

are listed in Table I. PAHs could also be modified in secondary processes such as alkylation/dealkylation, hydrogenation, polymerization and graphitization, oxidation, and ionization, some of which can occur in the interstellar media, in the solar nebula, on parent bodies of meteorites, during entry into the terrestrial atmosphere, and on the ground.

The popularity of catalytic hydrogenation of CO gas on mineral grains, known as Fischer–Tropsch type (FTT) synthesis, as a reaction responsible for the formation of solar system hydrocarbons has waxed and waned since the suggestions made by Urey (1953) and Oró (1965). Extensive experimental efforts by Anders and colleagues (e.g., Studier *et al.* 1968, 1972, Anders *et al.* 1973, 1974, Hayatsu *et al.* 1977, Hayatsu and Anders 1981) supported FTT synthesis of solar system hydrocarbons. The speciation of normal (straight-chain) alkanes in the products of their simulated FTT reactions was similar to contemporary results of extracting organic compounds from carbonaceous chondrites. In addition, these experimental data showed that aromatic hydrocarbons are secondary products formed from primary alkanes by dehydrogenation on the catalyst surface. An association of carbonaceous material with Fe–Ni metal in ordinary chondrites and IDPs (Christofferson and Buseck 1984, Bradley *et al.* 1984, Brearley 1990, Bradley 1994) indirectly supported a nebular, possibly grain-catalyzed, hydrocarbon synthesis.

However, through time, new meteoritic and experimental data showed inconsistencies with nebular FTT syntheses. Normal alkanes in carbonaceous chondrites were found to be terrestrial contaminants (Cronin and Pizzarello 1990). Magnetite and hydrous silicates that were initially considered as catalysts for FTT reactions are now thought to have formed in parent bodies of meteorites (e.g., Zolensky and McSween 1988). Detailed isotopic studies of separated organic compounds and carbonates in carbonaceous chondrites (Chang *et al.* 1978, Yuen *et al.* 1984) showed that carbon fractionation in FTT reactions (Yuen *et al.* 1990) could not explain the observed carbon isotopic variations. Finally, large D/H and ^{15}N enrichments in acid-insoluble macromolecular organic material in meteorites indicated a very low temperature origin of organic compounds (e.g., Kolodny *et al.* 1980, Yang and Epstein 1983, Kerridge 1983, Kerridge *et al.* 1987), consistent with extremely isotopically selective ion–molecule reactions (Bohme 1992) in cold interstellar molecular clouds and/or in low-density parts of the solar nebula (Aikawa *et al.* 1998). Although FTT reactions cause fractionation of hydrogen isotopes (Kellner and Bell 1981), available experimental data show that synthesis does not lead to profound deuterium enrichments. Isotopic fractionation of N in FTT reactions was found to be ineffective (Kung *et al.* 1979). Indeed, the enrichment in D and ^{15}N in chondritic organic material is considered by some to be a strong argument for an extrasolar origin of the insoluble organic polymer in meteorites and IDPs (e.g., Yang and Epstein 1983, Kerridge 1983, Alexander *et al.* 1998), and it has been argued that the small variation in presolar nanodiamond to organic carbon abundance ratios in various chondrite groups

TABLE I
Possible Stages of a Complex History of PAHs
from Chondrites and IDPs

Location	Processes affecting PAH formation and transformation
Envelopes of carbon-rich stars	Condensation on SiC grains. Grain-catalyzed reactions. Pyrolysis of acetylene, methane, and other organic compounds.
Interstellar medium	Ion–molecule reactions leading to PAH synthesis. Ionization and polymerization.
Solar nebula	Fischer–Tropsch type synthesis. Miller–Urey reactions. Ion–molecule reactions. Pyrolytic aromatization of hydrocarbons. Pyrolytic/irradiative dealkylation and polymerization.
Meteorite parent bodies	Aqueous separation and redeposition. Aqueous and gas phase hydrogenation of interstellar and/or nebular PAHs. Aqueous and/or gas phase Fischer–Tropsch type synthesis of hydrocarbons. Oxidative dealkylation. Pyrolytic dealkylation, polymerization, and graphitization during thermal metamorphism.
Earth	Oxidative dealkylation, oxidation, aqueous separation, and contamination.

is consistent with most of the organic material being presolar (Alexander *et al.* 1998).

Nevertheless, the current lack of strong evidence for FTT syntheses in meteorites is not evidence that this process was absent in the nebula and that all organic compounds in meteorites and IDP are presolar. The solar nebula was probably a very complex and dynamic system in which conditions favorable for FTT reactions could have existed. In fact, H₂ and CO were the major nebular gases, the FTT-effective Fe-metal catalyst was present in the nebula, and temperatures of 400–600 K in some nebular locations would have favored FTT reactions (Prinn and Fegley 1989, Fegley and Prinn 1989, Fegley 1988, Kress and Tielens 2001). Recent experiments of Llorca and Casanova (1998, 2000) and Ferrante *et al.* (2000) show a possibility for FTT synthesis of light hydrocarbons in simulated nebular conditions. In addition, formation of carbonaceous deposits with aliphatic and aromatic hydrocarbons on the surface of catalysts seems to be unavoidable during FTT reactions (Galyshzka *et al.* 1992, Llorca and Casanova 1998). The general similarity of carbon isotopic composition in meteoritic organic material, the Sun, and other solar system objects cannot be accidental and is consistent with the origin of meteoritic organic compounds from a gas of solar composition. The outer Solar System, typified, for example, by low albedo asteroids, is rich in organic compounds and it is hard to believe that all these compounds are presolar. In chondrites, presolar mineral grains are not volumetrically abundant compared with the organic polymer, indirectly indicating the presence of organic compounds formed in the Solar System. In addition, survival of interstellar organic compounds in high-temperature nebular processes in which meteorites formed is questionable. If a majority of organic material in meteorites represent solar material, the isotopic anomalies of H and N could have been caused by ion–molecule reactions or other irradiation-driven mechanisms during the final stages of the evolution of the solar nebula, when the nebula had a low density and the Sun went into the T-Tauri stage (Aikawa *et al.* 1998). This scenario can accommodate the work of Alexander *et al.* (1998) who showed that isotopic anomalies of H and N are mostly present in aliphatic chains that link polyaromatic molecules in the meteoritic organic polymer.

Therefore, the possibility exists that condensed aliphatic and polyaromatic molecules could have formed in part coincident with the formation of other major constituents of meteorites in the nebula. Thermodynamic modeling of nebular condensation of metals, silicates, and oxides (e.g., Grossman 1972, Grossman and Larimer 1974, Petaev and Wood 1998, Ebel and Grossman 2000) provides reliable explanations of observations from meteorites. It follows that a thermodynamic assessment may also prove worthwhile for modeling the chemistry of condensed organic compounds in the nebula.

Thermodynamic calculations in the H–C–O system made by Dayhoff *et al.* (1964, 1967) and Eck *et al.* (1966) demonstrated that PAHs and other high molecular weight hydrocarbons may form as metastable products if the formation of graphite is ki-

netically inhibited. It has been suggested that low-temperature zones of the solar nebula would have provided that prohibition. Succeeding models and observations support this general concept. As an example, high-temperature quenching in the H–C–O system, together with inhibition of the formation of graphite below temperatures of about 900 K, has been observed experimentally and inferred from observations of natural terrestrial systems (Ziegenbein and Johannes 1980, Luque *et al.* 1998). Methane can be a stable form of carbon in the cold outer part of the nebula. However, formation of methane at low temperatures is slow and this synthesis was probably inhibited over the lifetime of the solar nebula, as speculated by Urey (1953) and first shown quantitatively by Lewis and Prinn (1980) and Mendybaev *et al.* (1986). These data allowed several authors (Lewis and Ney 1979, Hayatsu *et al.* 1980, Hayatsu and Anders 1981, Fegley 1988, Prinn and Fegley 1989, Fegley and Prinn 1989, Fegley 1993) to conclude that inhibition of graphite and methane formation could have enabled hydrocarbon synthesis within the stability field of graphite.

Evidently, in chondrites the predominance of organic matter over graphite, which is thermodynamically stable with respect to organic compounds, indicates the lack of complete H–C–O thermochemical equilibrium in the nebula but does not exclude metastable equilibria among organic compounds and nebular gases. This concept of metastable equilibria has been applied by Lewis and Ney (1979) to model hydrocarbon synthesis in envelopes of carbon-rich stars. Hayatsu *et al.* (1980) and Hayatsu and Anders (1981) have applied this idea in order to consider the stability of organic matter in low-temperature zones of the nebula. In particular, Hayatsu *et al.* (1980) presented the saturation curve for the *n*-alkane eicosane (C₂₀H₄₂) with respect to H₂ and CO in *P*–*T* coordinates relevant to the solar nebula. However, a detailed consideration of the stability of a variety of hydrocarbons found in meteorites and IDPs has not been published. Nevertheless, in recent years, the concept of metastable equilibrium in the low-temperature H–C–O system has been developed and applied to explain organic acid and hydrocarbon speciation in sedimentary basins (Shock 1988, 1989, 1994, Helgeson *et al.* 1993) and hydrothermal systems (Shock 1992, Shock and Schulte 1990, 1998, Zolotov and Shock 1999), as well as in igneous and impact rocks (Zolotov and Shock 2000a, 2000b). It has also been realized that inhibition of methane formation below 600–900 K would provide conditions for synthesis of a variety of metastable organic compounds in natural systems.

For these reasons, a thermodynamic approach can be applied to model the stability of hydrocarbons at nebular conditions if the formation of graphite and methane are suppressed. Efforts to provide quantitative tests of nebular organic synthesis have been enhanced by the recent summary, critique, and prediction of thermodynamic data for hydrocarbons by Helgeson *et al.* (1998) and Richard and Helgeson (1998). Here we evaluate the stability of condensed PAH species and *n*-alkanes under the conditions of the solar nebula with respect to the most abundant nebular gases: H₂, CO, and H₂O. We explore the effects of total pressure,

temperature, and concentrations of CO and H₂O, and we consider relative stabilities of PAHs, their methylated counterparts, and alkanes.

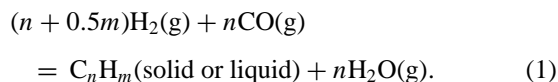
THERMOCHEMICAL EQUILIBRIUM CALCULATIONS

A model for metastable equilibrium in the H–C–O system. We use the free energy minimization method (Van Zeggeren and Storey 1970) to calculate metastable thermochemical equilibria in the H–C–O system as functions of temperature, total pressure, and bulk composition in the nebula. In these calculations, the formation of CH₄ and graphite are prohibited. The compounds considered include gaseous H₂, CO, and H₂O, condensed *n*-alkanes with carbon number from 10 to 20, and the condensed PAHs.

The calculations of strict metastable equilibria in the H–C–O system result in the predominance of one condensed PAH (usually pyrene) which has the lowest H/C ratio among the aromatic and aliphatic hydrocarbons considered. We obtained similar results in terms of the stability of condensed hydrocarbons in the model of complete thermochemical equilibrium and in models that involved fixed abundances of CO and H₂O. Calculations of this type do not tell us much about the stability of various condensed hydrocarbons because the evaluation of metastable equilibria tends to be dominated by a single compound of the highest stability, rather than a variety of hydrocarbons as observed in meteorites and IDPs. This would indicate that complete metastable equilibrium was not achieved during synthesis of hydrocarbons.

Saturation conditions for individual condensed hydrocarbons. In this set of calculations we evaluate the stability of individual hydrocarbons by considering reactions that involve the most abundant nebular gases. In contrast to modeling metastable equilibrium in the first set of calculations, the consideration of distinct reactions does not necessarily require the assumption of strict metastable equilibrium in the H–C–O system, which may or may not have been attained in the nebula. Moreover, nebular conditions may not have matched the equilibrium conditions for the reactions. Nevertheless, thermodynamic consideration of individual reactions provides a means to estimate the *P–T*-composition conditions at which formation of metastable hydrocarbons might have been possible and to evaluate the energetic drives for the formation of distinct hydrocarbon species.

We calculate the hydrocarbon saturation conditions for temperature, total pressure, and abundances of gases for the net equilibria by considering reactions of the type



Although reactions of this type correspond to FTT synthesis, the approach we have adopted considers only hydrocarbon stability with respect to the major nebular gases and does not necessarily require a particular reaction mechanism such as FTT synthesis.

In addition, these results can be considered for evaluation of stability of presolar hydrocarbons in the nebula.

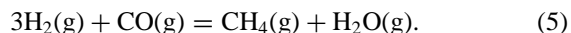
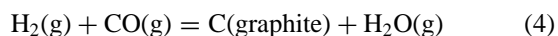
We assume the activities of condensed hydrocarbons to be unity and that the gases behave ideally. For reaction (1), at the *equilibrium* conditions

$$K_r = f_{\text{H}_2\text{O}}^n f_{\text{CO}}^{-n} f_{\text{H}_2}^{-(n+0.5m)} \cong X_{\text{H}_2\text{O}}^n X_{\text{CO}}^{-n} P^{-(n+0.5m)}, \quad (2)$$

where K_r designates the equilibrium constant, f and X represent the fugacity and mole fraction of the subscripted gas, and P stands for the total pressure, which roughly equals the hydrogen pressure. Values of K_r are calculated from standard Gibbs energies (ΔG_r°) of reactions via

$$\ln K_r = -\Delta G_r^\circ / (RT)^{-1}, \quad (3)$$

where R stands for the ideal gas constant, and T designates temperature in kelvin. Equation (2) allows us to calculate the equilibrium *T–P–X_i* conditions for reaction (1), which correspond to saturation of nebular gas with condensed hydrocarbons. In our modeling, we neglect the effect of the mutual solubility of hydrocarbons on their activities. In a solution of hydrocarbons the activity of individual species would be decreased, and their stability would increase. Although the formation of graphite and methane is disallowed in our model, to compare with the hydrocarbons, the stabilities of pure graphite (activity = 1) and methane can be calculated via the following equilibria:



In order to characterize the oversaturation of graphite, its activity can be calculated with Eq. (2b) from Lewis *et al.* (1979).

A model for hydrocarbon oversaturation. The occurrence of meteoritic hydrocarbons as a multicomponent mixture is consistent with simultaneous synthesis of several compounds, which could have happened if oversaturation was achieved with respect to several hydrocarbons at once. For a numerical approach to the oversaturation disequilibrium state, we evaluate thermodynamic drives for reaction (1) at conditions which do not match equilibrium. For this purpose, values of thermodynamic affinities (A_r) are calculated via

$$A_r = RT \ln (K_r Q_r^{-1}), \quad (6)$$

where K_r is taken from Eq. (3). The value of Q_r corresponds to the reaction quotient, which for *disequilibrium* conditions with respect to reaction (1) is calculated from

$$Q_r = f_{\text{H}_2\text{O}}^n f_{\text{CO}}^{-n} f_{\text{H}_2}^{-(n+0.5m)} \cong X_{\text{H}_2\text{O}}^n X_{\text{CO}}^{-n} P^{-(n+0.5m)}, \quad (7)$$

where mole fractions of gases and pressure can be taken from nebular models. At *equilibrium*, $Q_r = K_r$ and $A_r = 0$. At *disequilibrium*, $Q_r \neq K_r$ and A_r will be either positive or negative

depending on the ratio. Combining Eqs. (6) and (7) yields the affinity expression for reaction (1):

$$A_{(1)} = RT \ln \left\{ K_{(1)} X_{\text{H}_2\text{O}}^{-n} X_{\text{CO}}^n P^{(n+0.5m)} \right\}. \quad (8)$$

The value of affinity is negative of that for the overall Gibbs free energy and shows how much energy is required or released during the formation of the reaction products. The more positive the affinity, the higher the thermodynamic drive needs to be to form these products. The affinities we calculate refer to one mole of a hydrocarbon, methane, or graphite produced in reactions (1), (4), and (5). These calculations allow us to compare the extent of oversaturation for a variety of compounds in energetic terms.

Alkylation and aromatization equilibria. In this set of calculations, we assess P - T conditions that can favor alkylation/dealkylation of PAHs and aromatization of aliphatic hydrocarbons by evaluating relative stabilities of alkyl-substituted and parent PAHs and the relative stabilities of PAHs and n -alkanes. This is done by calculating the equilibrium $f\text{H}_2$ values for the dehydrogenation reactions shown in Table II. Carbon is conserved in these reactions and the abundances of CO and H_2O will not affect the stabilities. These overall reactions do not represent reaction mechanisms but permit us to evaluate relative stabilities as functions of temperature and $f\text{H}_2$, where the latter is equivalent to the total pressure.

Sources of data. The equilibrium constants used in this study are calculated from the thermodynamic data for gases from Gurvich *et al.* (1989–1994) and condensed hydrocarbons from Helgeson *et al.* (1998) and Richard and Helgeson (1998). In our modeling, the nominal H_2/CO and $\text{H}_2/\text{H}_2\text{O}$ molecular ratios are 1409 and 1815, respectively. These ratios are calculated from the solar abundances of the elements (Grevesse and Noels 1993) assuming that all carbon is present in the form

TABLE II
Overall Reactions Used to Represent Dehydrogenation among Alkylated PAHs, Parent PAHs, and n -Alkanes

<i>Demethylation reactions</i>	
10	1-methylnaphthalene = 11 naphthalene + 6 H_2
14	2-methylphenanthrene = 15 phenanthrene + 9 H_2
16	1-methylpyrene = 17 pyrene + 11 H_2
18	2-methylchrysene = 19 chrysene + 12 H_2
<i>Aromatization reactions</i>	
	Cyclohexane (C_6H_{12}) = benzene + 3 H_2
	Decane ($\text{C}_{10}\text{H}_{22}$) = naphthalene + 7 H_2
	Dodecane ($\text{C}_{12}\text{H}_{26}$) = biphenyl + 8 H_2
	Tetradecane ($\text{C}_{14}\text{H}_{30}$) = phenanthrene + 10 H_2
	Tetradecane ($\text{C}_{14}\text{H}_{30}$) = anthracene + 10 H_2
	Hexadecane ($\text{C}_{16}\text{H}_{34}$) = pyrene + 12 H_2
	Octadecane ($\text{C}_{18}\text{H}_{40}$) = chrysene + 13 H_2
	Octadecane ($\text{C}_{16}\text{H}_{40}$) = triphenylene + 13 H_2

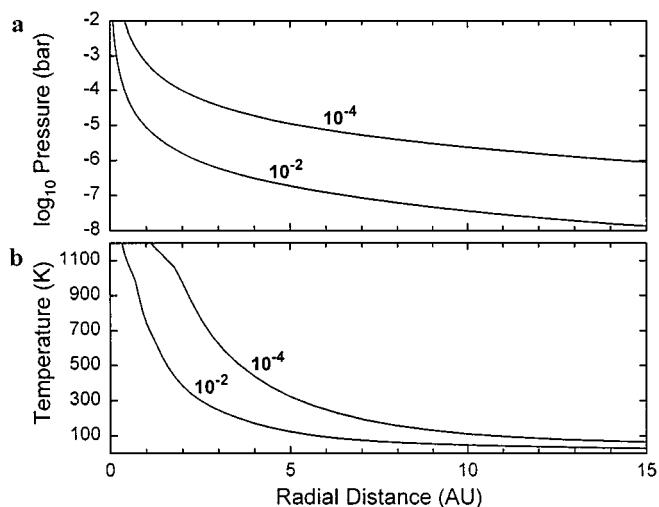


FIG. 2. Pressure (a) and temperature (b) at the solar nebular midplane as a function of radial distance at mass flux of $10^{-7} M \text{ yr}^{-1}$ from the model of Bell *et al.* (1997).

of CO and that 15% of the oxygen in a low-temperature nebula is present in silicates. We consider variations in these ratios based on the composition of comets and changes in the abundances of gases during chemical and physical processes in the nebula.

The physical model for the nebula midplane we adopt (Bell *et al.* 1997) provides P - T -radial distance estimates as functions of the mass flux (F) into the proto-Sun and the viscous efficiency (α) of the disc. We consider fluxes of solar mass (M) from 10^{-5} to 10^{-9} yr^{-1} and viscous efficiencies of 10^{-2} and 10^{-4} . Figure 2 illustrates how temperature and pressure vary with radial distance in the nebula model at fixed values of F and α . For nominal values, we use the flux of $10^{-7} M \text{ yr}^{-1}$ and $\alpha = 10^{-4}$ because they lead to P - T conditions where meteorites could have formed at radial distances between about 1 and 5 AU. These results are compared with those for the P - T models of Lewis (1974) and Cameron (1995) for the nebular midplane (Table III). In addition, we use 10^{-5} bar as the nominal midplane pressure for the inner part of solar nebula, as recommended by Wood and Morfill (1988).

TABLE III
Parameters for the Midplane of Solar Nebula Used in the Present Study

Radial distance (AU)	Lewis (1974)		Cameron (1995)		Bell <i>et al.</i> (1997) ^a	
	T (K)	P (bar)	T (K)	P (bar)	T (K)	P (bar)
0.1	7600	0.7	2200	3×10^{-2}	2820	0.43
1	600	10^{-4}	470	4×10^{-5}	1240	6.6×10^{-4}
10	80	10^{-7}	100	6×10^{-8}	110	2.3×10^{-6}

^a At $F = 10^{-7} M \text{ yr}^{-1}$ and $\alpha = 10^{-4}$.

RESULTS

Role of Pressure and Temperature

We found that in the solar nebula hydrocarbons have saturation temperatures within the stability field of graphite, under conditions where CH_4 would predominate over CO if stable equilibrium was reached. For example, at the saturation condition for pyrene the CH_4/CO ratio would be as high as 10^7 if reaction (5) is not prohibited. At saturation conditions of pyrene (435 K and 1.8×10^{-5} bar calculated with the nebular model of Bell *et al.* 1997 at $\alpha = 10^{-4}$), the activity of graphite is about 13,500, indicating severe oversaturation conditions. At the nominal abundances of CO and H_2O in the nebula and total pressure of 10^{-4} to 10^{-6} bar, PAHs have saturation temperatures below ~ 450 – 390 K, but about 20–40 K greater than saturation temperatures of *n*-alkanes, as shown in Fig. 3. This figure also shows that the saturation temperatures for hydrocarbons decrease as pressure decreases. Note that the nominal *P*–*T* nebular model of Bell *et al.* (1997) gives roughly similar results for hydrocarbon stability when compared with those of Lewis (1974) and Cameron (1995). At the conditions of the nebular midplane given by these models, condensed PAHs become metastable phases at temperatures below ~ 440 K and pressures below $\sim 4 \times 10^{-5}$ bar. Other calculations also show that at pressures higher than 10^{-3} bar, representative of the subnebulas of giant planets (Prinn and

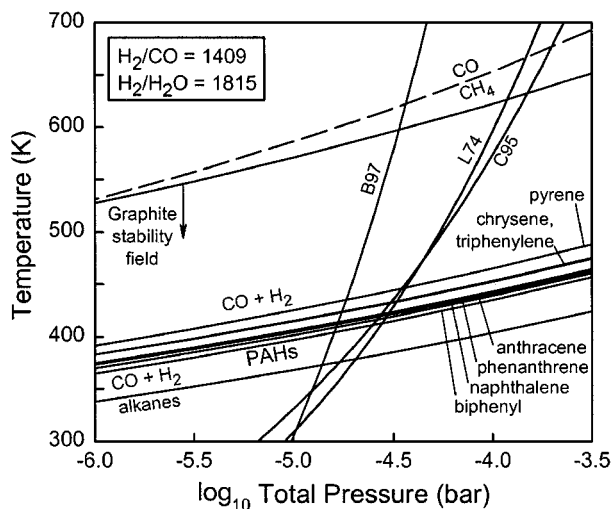


FIG. 3. Saturation temperatures of hydrocarbons and graphite as functions of total pressure under the conditions of the solar nebula. The saturation curves for hydrocarbons correspond to metastable equilibria like Eq. (1). The compounds have a thermodynamic potential to form below these curves. The high-temperature boundary of the stability field of graphite represents Eq. (4). The dashed line corresponds to equal fugacities of CH_4 and CO if stable Eq. (5) is attained. The curve labeled “alkanes” represents *n*-alkanes with carbon number 10 to 20. The curve labeled B97 stands for the *P*–*T* model of nebular midplane at $F = 10^{-7} M \text{ yr}^{-1}$ and $\alpha = 10^{-4}$ from Bell *et al.* (1997). Curves labeled L74 and C95 represent models for the nebula midplane of Lewis (1974) and Cameron (1995), respectively. The abundances of CO and H_2O correspond to the nominal solar-based values adopted in this study (see text).

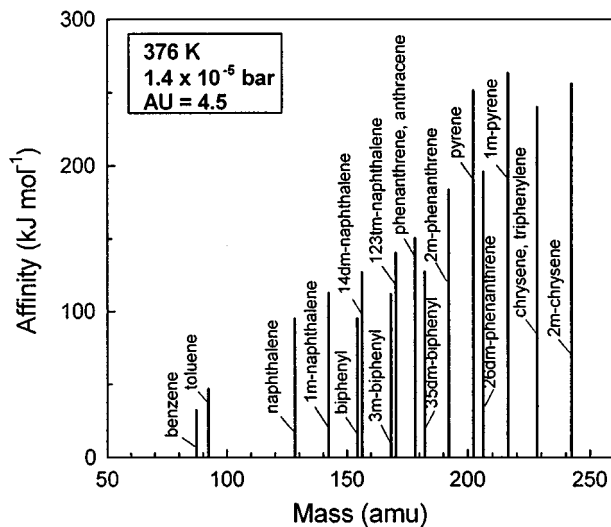


FIG. 4. Affinities for aromatic hydrocarbons in the solar nebula. The affinities correspond to reactions like Eq. (1) at the H_2/CO ratio of 1409, the $\text{H}_2/\text{H}_2\text{O}$ ratio of 1815, 1.4×10^{-5} bar, and 376 K. In the midplane model of Bell *et al.* (1997) these *P*–*T* conditions correspond to a radial distance of 4.47 AU. Among PAH isomers (e.g., phenanthrene and anthracene), the results are for the most stable species with the highest affinity.

Fegley 1981), PAHs have saturation temperatures above ~ 500 K. In other words, high pressures in the subnebulas favor hydrocarbon stability.

Over the pressure range from 10^{-7} to 10^{-3} bar, the sequence of the saturation of PAHs remains unaltered for both unalkylated and methylated species. Within these sequences, the saturation temperatures increase as the H/C atomic ratio in the species decreases. For example, pyrene ($\text{C}_{16}\text{H}_{10}$) has a higher saturation temperature than either naphthalene (C_8H_{10}) or chrysene ($\text{C}_{18}\text{H}_{12}$). The PAHs with lower H/C atomic ratios resemble graphite more closely than species with higher H/C ratios.

Consideration of affinities, which represent thermodynamic drives for hydrocarbon supersaturation, would be more effective for modeling the speciation of hydrocarbons than would an evaluation based on a strict equilibrium analysis. An assessment of this type is illustrated by Fig. 4, which shows the affinities of hydrocarbons as a function of their molecular mass, at the particular *P*–*T* conditions in the nebula midplane located within the field where hydrocarbons are metastable phases. All of the PAHs shown in Fig. 4 can form, but their different affinities mean that they have different thermodynamic drives to form. Note that many PAH affinities are close to one another, suggesting that the formation of a metastable mixture is more likely than the formation of a single PAH.

Thermodynamic affinities of PAHs generally increase with an increase in the C/H ratio in the species. This can be seen in Fig. 5, which shows affinities for hydrocarbon formation as a function of midplane temperature at 10^{-5} bar. The affinities increase as temperature decreases, but relative affinities for various PAHs change with temperature. Note that slightly below the saturation

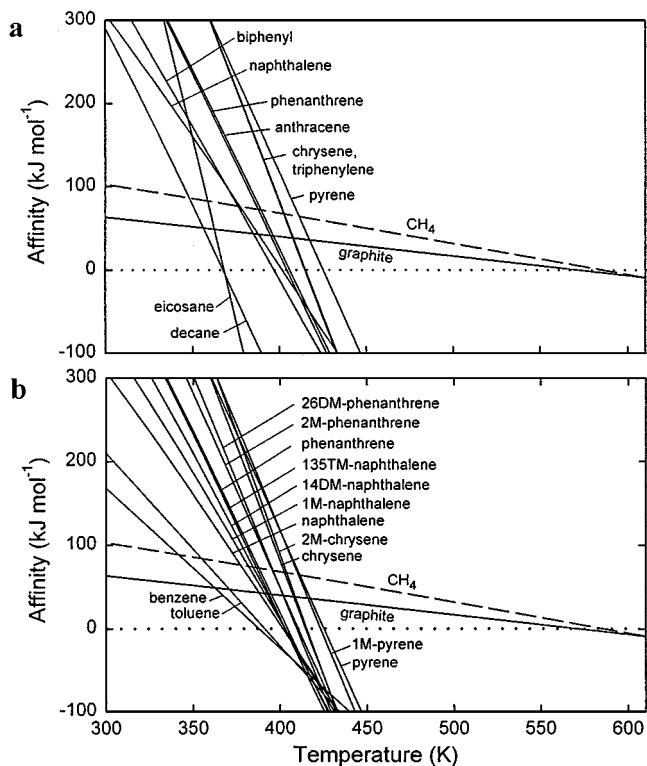


FIG. 5. Affinities for hydrocarbons and graphite in the solar nebula at 10^{-5} bar and solar-based abundances of CO and H₂O. (a) Unalkylated PAHs, eicosane (C₂₀H₄₂), and decane (C₁₀H₂₂); (b) methylated aromatic hydrocarbons. The affinities refer to reaction (1) for hydrocarbon synthesis, reaction (4) for graphite formation, and reaction (5) for methane. Zero affinity shown by the dotted line corresponds to equilibrium for these reactions. Positive values of affinity represent supersaturation. The dashed line corresponds to equal fugacities for CH₄ and CO if equilibrium with respect to Eq. (5) is attained.

temperatures PAHs reach affinities that are *higher* than those of graphite or methane. This provides an energetic explanation for the low-temperature formation of metastable hydrocarbons instead of graphite and methane.

Despite similar results for PAH stability obtained with the P - T models of Lewis (1974) and Cameron (1995), these models lead to different results in terms of the actual distances from the Sun at which hydrocarbons could have achieved saturation. Figure 6 shows that in the calculations based on the model of Cameron (1995), PAHs become stable somewhere between 1 and 1.3 AU. The model of Lewis (1974) leads to the saturation of PAHs at radial distances of about 1.4–1.5 AU that are closer to the asteroid belt from which some meteorites come.

Results obtained with the model of Bell *et al.* (1997) at $F = 10^{-7} M \text{ yr}^{-1}$ depend on viscous efficiency of the disc. The α value of 10^{-4} leads to the stability of hydrocarbons at radial distances >4 AU and temperatures $<\sim 450$ K, as shown in Fig. 7. Although a viscous efficiency of 10^{-2} favors stability at >2 AU, hydrocarbons become stable only at temperatures less than 400 K, and hydrocarbon synthesis can be inhibited compared to the case of lower α . This can be seen in Fig. 8, which

illustrates the effect of viscous efficiency on the saturation conditions of pyrene. Pyrene has the highest saturation temperature among the hydrocarbons considered in this study. Figures 8a and 8b demonstrate that at a fixed flux a viscous efficiency of 10^{-4} provides saturation temperatures ~ 50 degrees higher than at $\alpha = 10^{-2}$. Figure 8b shows that lower accretion rates favor higher saturation temperatures. Although fluxes $<10^{-8} M \text{ yr}^{-1}$ lead to saturation temperatures of pyrene higher than 450 K (at $\alpha = 10^{-4}$), at these low fluxes pyrene can be stable only at radial distances $<\sim 1.5$ AU, as shown in Fig. 8c. At high fluxes, pyrene and other hydrocarbons are stable at radial distances >15 AU. At radial distances of 2–4 AU they can form at fluxes of $10^{-6.3}$ – $10^{-7.7} M \text{ yr}^{-1}$ at $\alpha = 10^{-4}$ and 10^{-2} , respectively.

Saturation temperatures of methylated PAHs are similar to those of the parent compounds; however, the relative stability of methylated compounds increases with decreasing temperature and/or increasing distance from the Sun. Comparison of Figs. 5b and 7b shows that alkylated PAHs are stable at higher hydrogen pressures compared to their parent compounds. This corresponds to higher H/C ratios in alkylated species.

The condensed n -alkanes we consider have similar saturation temperatures that are 20–40 degrees below those of PAHs, as shown in Fig. 3. This is reflected in their lower affinities

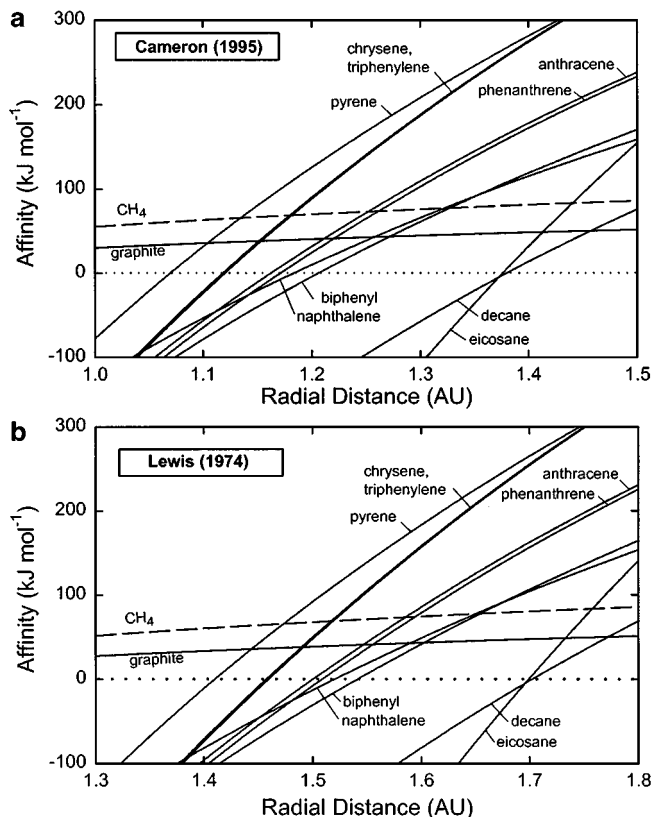


FIG. 6. Affinities for hydrocarbons and graphite in the solar nebula as a function of radial distance for the midplane model of Lewis (1974) (a) and Cameron (1995) (b) at nominal H₂/CO and H₂/H₂O molecular ratios. The definition of lines is the same as for Fig. 5.

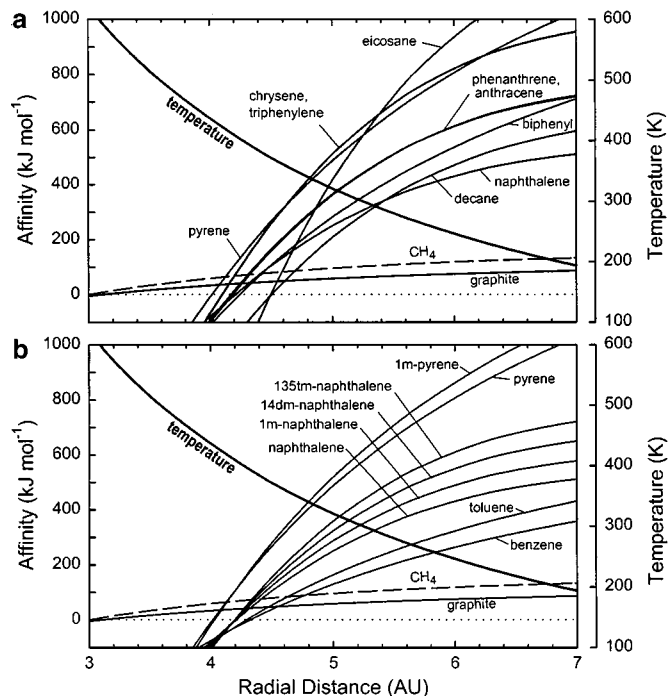


FIG. 7. Affinities for hydrocarbons in the solar nebula as a function of the distance from the Sun for the midplane model of Bell *et al.* (1997) at mass flux of $10^{-7} M \text{ yr}^{-1}$, $\alpha = 10^{-4}$, and the nominal H_2/CO and $\text{H}_2/\text{H}_2\text{O}$ ratios adopted in this paper. (a) Unalkylated PAHs, eicosane, decane, methane, and graphite; (b) methylated aromatic hydrocarbons. The bold curve represents midplane temperatures read from the right axis. The definition of lines is the same as for Fig. 5.

compared with PAHs. However, as temperature decreases, affinities of heavy *n*-alkanes (exemplified by eicosane, $\text{C}_{20}\text{H}_{42}$) increase more sharply than those of PAHs and reach affinities of naphthalene and biphenyl at about 50 degrees below the saturation temperatures (see Fig. 5a). It follows that heavy alkanes might form simultaneously with low molecular weight PAHs, if synthesis of both groups is accompanied by similar kinetic inhibitions.

Effects of the Abundances of CO and H_2O

In the previous section, we showed how the H_2 content expressed as total pressure affects the stability of hydrocarbons. Here we explore the influence of possible variations in the abundances of CO and H_2O . In the nebula, the abundance of CO can be lower than the solar-based value because of the formation of some amount of methane, other hydrocarbons, and carbides (Lewis and Prinn 1980, Simonelli *et al.* 1989, Llorca and Casanova 1998, 2000, Ferrante *et al.* 2000), as well as the incorporation of carbon in iron–nickel grains (Lewis *et al.* 1979) during their formation. Water is produced during synthesis of CH_4 , other hydrocarbons, and carbides and would decrease the $\text{CO}/\text{H}_2\text{O}$ ratio below the solar-based value of about 1.3. The low $\text{CO}/\text{H}_2\text{O}$ ratio of 0.035 in the nucleus of Comet Halley (Eberhardt 1998) may result from this type of process (if the

nucleus is not made of extrasolar material). In addition, the $\text{CO}/\text{H}_2\text{O}$ ratio in the nebula can be locally higher than that of a solar gas because of incorporation of oxygen from water to oxides and silicates, and because of addition and subsequent evaporation and/or oxidation of interstellar carbonaceous dust (see Krot *et al.* 2000 for a review).

In addition to the effects of chemical reactions, the $\text{CO}/\text{H}_2\text{O}$ ratio might have increased locally because of a decrease in water vapor content in the inner part of the nebula caused by transport toward colder zones of the nebula where water ice formed (Stevenson and Lunine 1988, Cyr *et al.* 1998, 1999). From reaction (1) and Eq. (8), one can conclude that higher abundances of CO facilitate hydrocarbon synthesis, but higher abundances of H_2O do not. The stability and saturation temperatures of hydrocarbons decrease as the H_2/CO ratio increases and as the $\text{H}_2/\text{H}_2\text{O}$ ratio decreases, as shown in Fig. 9 for a total pressure of 10^{-5} bar. The calculations show that if the abundances of CO and H_2O differ from the solar-based abundances within about one order of magnitude, the corresponding changes in the saturation temperatures do not exceed one hundred degrees.

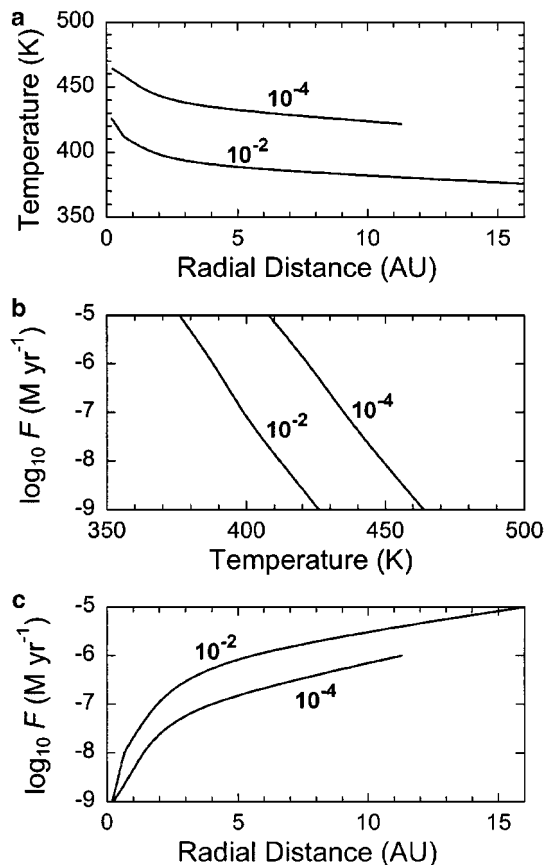


FIG. 8. Saturation conditions for pyrene ($\text{C}_{16}\text{H}_{10}$) for the solar nebula midplane model of Bell *et al.* (1997). Saturation conditions refer to reaction (1) for pyrene synthesis. The labels at the curves represent α . (a) Saturation temperature as a function of radial distance. (b) Saturation temperature as a function of mass flux. (c) Mass flux and the radial distance that represent conditions of pyrene saturation.

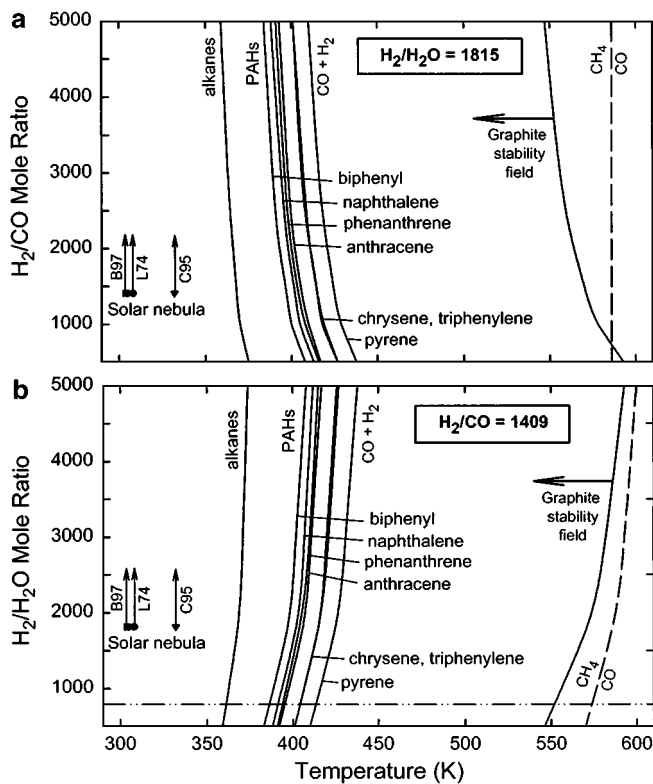


FIG. 9. Saturation temperatures for hydrocarbons at 10^{-5} bar as functions of (a) H_2/CO and (b) H_2/H_2O ratios in the solar nebula. Filled black symbols represent the midplane temperatures from the models of Bell *et al.* (1997), Lewis (1974), and Cameron (1995) at 10^{-5} bar and the nominal solar-based H_2/CO and H_2/H_2O ratios. For Bell *et al.* (1997), the temperature corresponds to $F = 10^{-7} M \text{ yr}^{-1}$ at $\alpha = 10^{-4}$. The arrows above these symbols show directions of possible changes in nebular composition from solar-based abundances. The horizontal dash-dotted line in (b) shows a lower limit for the H_2/H_2O ratio in the nebula that corresponds to the case when all C is present as CH_4 . The definition of other curves is the same as for Fig. 3.

An increase in the CO/H_2O ratio would favor the stability of hydrocarbons, allowing them to saturate at lower total pressures or at higher temperatures. In turn, a decrease in the CO/H_2O ratio leads to saturation of hydrocarbons at higher pressures and lower temperatures, as shown in Fig. 10. Figure 10a illustrates that at 400 K and the low CO/H_2O ratio representing the dust of Comet Halley (0.035, Eberhardt 1998), PAHs can saturate only at pressures $>10^{-4.5}$. These pressures are higher than those in nebular models at 400 K. In fact, at Comet Halley's low CO/H_2O ratio and 10^{-5} bar, PAHs have saturation temperatures as low as 360–380 K, and their formation would be inhibited, as shown in Fig. 10b. On the other hand, Fig. 10 shows that at CO/H_2O ratios above the solar-based value of 1.29, PAHs can saturate at pressures as low as $\sim 10^{-6}$ bar and at temperatures that could be high enough to prevent significant kinetic inhibition. If 90% of the water vapor were consumed in a cold-trapping process (indicated by the dashed vertical lines labeled “10% of solar H_2O ”), PAHs could form at pressures ~ 0.7 log units below and at temperatures ~ 30 degrees above those at the solar-based CO/H_2O

value. Other calculations show that if only 1/1000 of the water were left in the inner nebula, the condensation temperature of pyrene would be as high as 530 K (at 10^{-5} bar). Note that an increase in the CO/H_2O ratio further decreases the relative stability of n -alkanes compared to PAHs, as shown in Fig. 10.

The variations in the abundances of CO and H_2O do not change the saturation sequence of unalkylated PAHs, but they do slightly affect the relative stabilities of alkylated species with respect to their parent compounds. Our results show that the relative stabilities of methylated PAHs decrease somewhat as the CO/H_2O ratio increases. For example, if the CO/H_2O ratio exceeds ~ 5 , naphthalene becomes slightly more stable than the methylated naphthalenes. Other calculations show that the

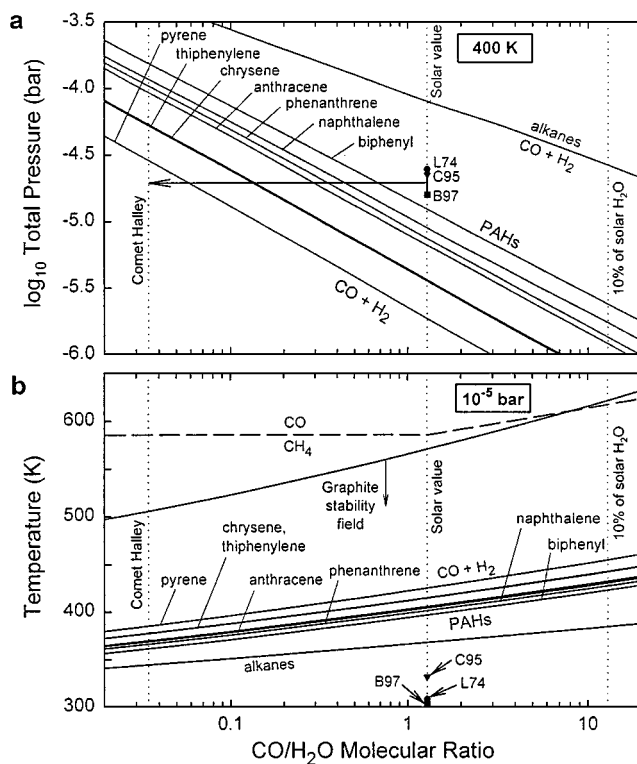


FIG. 10. Saturation conditions for PAHs and alkanes as functions of the CO/H_2O ratio in the solar nebula at 400 K (a) and 10^{-5} bar (b). The saturation curves for hydrocarbons correspond to equilibrium conditions with respect to reactions like Eq. (1). The dotted lines represent the CO/H_2O ratios in the nucleus of Comet Halley (0.035), the solar-based value adopted in this paper (1.29), and the value of 12.9 that corresponds to 10% of the original water abundance in the nebula (see text). Filled symbols represent the midplane pressures from the models of Bell *et al.* (1997), Lewis (1974), and Cameron (1995) and the solar-based CO/H_2O ratio. For Bell *et al.* (1997), the temperature corresponds to $F = 10^{-7} M \text{ yr}^{-1}$ at $\alpha = 10^{-4}$. Curves represent total pressure and temperature that allow saturation of the hydrocarbons, and hydrocarbons are stable at pressures above the curves. The horizontal arrow in (a) represents hypothetical changes of the CO/H_2O ratio during synthesis of high molecular weight PAHs that currently are present in the nuclei of Comet Halley. In calculations of Eqs. (1), (4), and (5), we use the H_2/H_2O ratio of 1815 at $CO/H_2O < 1.29$ and the H_2/CO ratio of 1409 at $CO/H_2O > 1.29$. The curves labeled alkanes represent n -alkanes with carbon number 10 to 20.

stabilities of alkylated PAHs increase as the CO/H₂ ratio in the nebula decreases. Parent PAHs have lower H/C ratios compared to the corresponding alkylated compounds and the increase in their stabilities would correspond to a decrease in the H/C ratio in the H–C–O system as the CO/H₂O ratio increases (see Fig. 14 in Zolotov and Shock 2000a).

DISCUSSION

Where, When, and How Could Hydrocarbons Have Formed in the Solar Nebula?

There is a restricted interval of temperature over which condensed hydrocarbons can form in the nebula. The upper temperature limit is controlled thermodynamically and corresponds to the saturation temperature of hydrocarbons. The lower limit for hydrocarbon synthesis is controlled kinetically and would be set by the appropriate value of reaction progress over the lifetime of the solar nebula. A limit of such type for hydrocarbons formed through FTT reactions was estimated by Fegley (1988, 1993) as 440–510 K for 10% conversion of CO. Lower extents of CO conversion lead to higher quench temperatures. These theoretical estimations are consistent with laboratory studies of FTT reactions showing that they are effective down to about 375 K (Anders *et al.* 1973). The calculated saturation temperatures for the hydrocarbons we consider at 10⁻⁵ bar match closely with these lower temperature limits for effective hydrocarbon synthesis. This agreement does not exclude synthesis of condensed hydrocarbons via FTT reactions in the nebula but would indicate a low efficiency of these reactions, at least at low pressures.

The increasing thermodynamic drives for hydrocarbon synthesis with increasing radial distance are consistent with darkening of asteroids outward across the asteroid belt, which may be caused by an increasing amount of organic matter on their surfaces (e.g., Jones 1988, Gradie *et al.* 1989). Nevertheless, the *P–T* models of the nebula midplane provide relatively narrow belts in radial distance that are favorable to grain-catalyzed hydrocarbon synthesis from CO and H₂. The midplane model of Cameron (1995) leads to values of about 1.05 to 1.4 AU, and the model of Lewis (1974) results in values of 1.4–1.7 AU. The outer boundaries of these belts correspond to 373 K (100°C), which would barely provide kinetic inhibition of FTT reactions according to experimental data of Anders *et al.* (1973, 1974). Lewis's model appears more realistic because the zone of potential hydrocarbon synthesis is located closer to the asteroid belt. However, neither model provides the high-temperature conditions in the asteroid belt required for the formation of the metal, oxide, and silicate constituents of meteorites. In contrast, the model of Bell *et al.* (1997), in which *P–T* profiles for the nebula midplane vary with the mass flux, provides conditions for hydrocarbon synthesis at distances between Mars and Jupiter (see Fig. 8c). Assuming that the mass flux decreased during the evolution of the nebula (Bell *et al.* 2000), hydrocarbons could have formed in a narrow zone that moved toward the proto-Sun. Toward the proto-Sun from this zone, hydrocarbon synthesis is limited by

thermodynamic reasons (high temperature). Outward from the proto-Sun, kinetic factors (low temperature) prevent synthesis. The temperature below which hydrocarbons are stable increases as the accretion rate decreases, and the inner part of the nebula is more favorable for FTT synthesis during the final stages of the evolution of the solar nebula. Similar conclusions have been obtained by Kress (2000) and Kress and Tielens (2001) in their kinetic model for FTT synthesis of methane.

Prinn and Fegley (1981) showed that if subnebulas of giant proto-planets had pressures several orders of magnitude higher than surrounding nebula values, the synthesis of methane would have been facilitated because reaction (5) would not have been inhibited. Our calculations demonstrate a significant increase in the saturation temperatures for condensed hydrocarbons under pressures that exceed typical nebular values.

Variations in Nebula Chemistry and Hydrocarbon Formation

Simonelli *et al.* (1989) estimated that only 10% of the solar CO was actually converted to methane and other organic compounds. This indicates that low-temperature metastable equilibrium involving hydrocarbons did not occur in the nebula. Therefore, hydrocarbon synthesis could not change significantly the solar CO/H₂O ratio. In addition, small changes should not have suppressed hydrocarbon synthesis if it were controlled by the kinetics of FTT reactions.

Nevertheless, we do not exclude the possibility that in some places in the nebula the progress of reactions like Eq. (1) could be greater than 10%. The presence of a carbonaceous dust component (Schulze *et al.* 1997) and the low CO/H₂O ratio of 0.035 in the nucleus of Comet Halley (Eberhardt 1998) indicate that as much as 94% of nebular CO could have been converted to organic compounds and water, if this comet is representative of solar system material. In this particular case, further synthesis of organic compounds that compose the nucleus of Comet Halley might have been suppressed by a decrease in the CO/H₂O ratio in the gas phase. Achieving metastable thermochemical equilibrium with respect to Eq. (1) seems to be possible but would require relatively high pressures (> 10^{-4.5} bar) even at the lowest temperatures at which hydrocarbon synthesis is kinetically possible.

Engel *et al.* (1990) and Fegley (1993) suggested that organic compounds in the nucleus of Comet Halley could have formed from gases of solar composition in Fe-grain-catalyzed reactions, such as FTT synthesis. It is plausible that the observed low CO/H₂O ratio in the nucleus of Comet Halley is a result of profound synthesis of organic compounds from a gas with initially solar composition. The horizontal arrow in Fig. 10a shows possible changes of the CO/H₂O ratio during hydrocarbon synthesis. The base of the arrow represents the solar-based ratio (1.29) and the point corresponds to the cometary ratio (0.035). Near the tip of the arrow, the cometary CO/H₂O ratio roughly matches saturation conditions of PAHs with a low H/C ratio (e.g., pyrene), at pressures governed by the nebular models we consider. This match allows us to speculate that the low CO/H₂O

ratio observed in the nucleus of Comet Halley represents a locally “frozen” equilibrium between high molecular weight organic compounds, which can be preserved in the nucleus, and the H₂O–CO mixture. More data on the chemistry of cometary nuclei are needed to test this hypothesis.

Stability and Abundances of Alkylated PAHs

Our thermodynamic assessment indicates an increase in stability of unalkylated aromatic compounds as temperature increases, as total nebular pressure decreases, and as the CO/H₂O ratio increases. However, under the nominal conditions of the solar nebula, alkylated PAHs appear to be more stable than parent species, with the exception of pyrene. This causes us to ask why PAHs in meteorites and IDPs have low degrees of alkylation, and whether the observed PAH speciation in these objects is relevant to nebular processes at all.

A variety of processes can be suggested to explain this inconsistency: (1) The low extent of alkylation can be caused by the peculiarities of reaction mechanisms, which do not allow for the formation of methylated PAHs. (2) Local depletion of water vapor and/or incorporation of interstellar carbonaceous dust in the nebula changed the solar CO/H₂O ratio resulting, in part, in the low extent of alkylation of PAHs. (3) Pyrolytic dealkylation could have occurred during post-formational heating in the solar nebula and/or in parent bodies of meteorites (see details in the next section). (4) A decrease in total pressure, which means a decrease in H₂ pressure, expected during the quiescent phase of nebula history, would have favored dealkylation. (5) Finally, alkyl side chains might have been oxidized in aqueous processes on carbonaceous chondrite parent bodies. Indeed, the final stages of hydrothermal alteration on parent bodies of CI and CM carbonaceous chondrites were fairly oxidizing and allowed the stability of sulfates (e.g., Zolensky and McSween 1988). As an example, at temperatures of ~410 K in aqueous processes, oxidation of alkyl groups can proceed at and above the oxidation state of the quartz–fayalite–magnetite buffer (Zolotov and Shock 1999). The oxidation of alkyl chains during hydrothermal alteration is consistent with the low degree of alkylation of PAHs in the Murchison CM2 chondrite (Tingle *et al.* 1991). Highly alkylated PAHs in the Allende CV3 carbonaceous chondrite (Tingle *et al.* 1991) may reveal more reduced conditions during hydrothermal alteration than in Murchison.

Pyrolysis of Aliphatic Hydrocarbons

Despite the fact that aromatic and polyaromatic molecules are typical byproducts of Fischer–Tropsch syntheses that form carbonaceous films on the surfaces of catalysts (e.g., Galuszka *et al.* 1992), aliphatic hydrocarbons predominate in the experimental reaction products in contrast to the predominance of PAHs among organic compounds in meteorites and IDPs. Our results demonstrate a greater drive to form PAHs than to form alkanes. Studier *et al.* (1965) and Prinn and Fegley (1989) proposed that a decrease in the H₂/CO ratio in the nebula or else-

where would have increased the aromatic/aliphatic ratio in FTT products. Our calculations demonstrate the possible role of increased CO/H₂ and CO/H₂O ratios in the nebula relative to a gas of solar composition (see Figs. 9 and 10). Indeed, a decrease in the H/C bulk ratio should favor the stability of hydrocarbons with higher C/H atomic ratios as shown by Zolotov and Shock (1999, 2000a, 2000b). The presence of specific catalysts (Al₂O₃, Cr₂O₃, etc.; Studier *et al.* 1968, Galuszka *et al.* 1992) in nebular grains might also have increased the aromatic/aliphatic ratio in FTT reactions.

Another possible way to explain the prevalence PAHs over other hydrocarbons in meteorites is secondary alteration of aliphatic hydrocarbons. Pyrolytic aromatization of aliphatic FTT products is among the more probable causes, as suggested by Studier *et al.* (1968, 1972), Anders *et al.* (1973), Hayatsu and Anders (1981), and Basile *et al.* (1984). It has been shown that aromatization of FTT products proceeds in about a day on the surface of a catalyst at temperatures of 620–670 K but that longer times are needed at lower temperatures (Studier *et al.* 1968, 1972). Equilibrium curves for the dehydrogenation-aromatization reactions listed in Table II indicate that the potential for aromatization increases above ~350 K, as shown in Fig. 11b. In addition, it can be seen in this figure that a decrease in total pressure at constant temperature favors aromatization of alkanes. Usually high pressure favors aromatization, but in the nebula a decrease of pressure corresponds with decreases of f_{H_2} and the C/H ratio, both of which increase the stability of aromatics. It is possible that nebular temperatures of 350–400 K

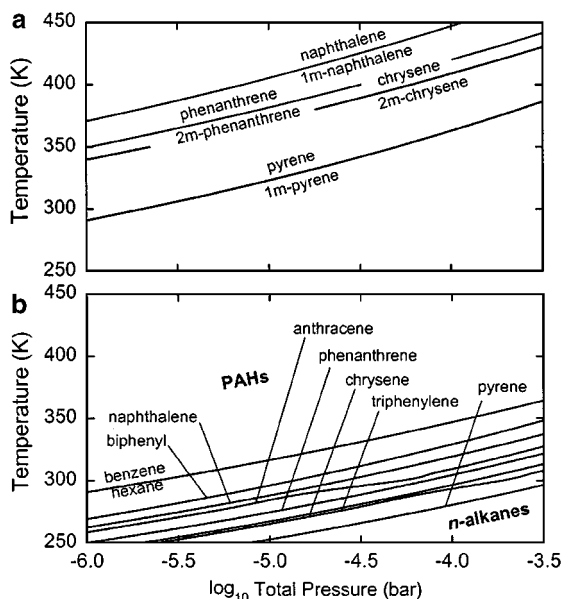


FIG. 11. Metastable equilibria between (a) methylated and parent PAHs and between (b) PAHs with *n*-alkanes as functions of temperature and pressure. The curves represent metastable demethylation and aromatization equilibria from Table II. In (b), PAHs are stable above equilibrium curves and alkanes are stable below the curves. The abundances of CO and H₂O correspond to the nominal values.

alone may have been enough for aromatization over the 10^5 – 10^7 year lifetime of the solar nebula. In addition, several thermal events in the nebula could have driven pyrolysis of FTT products, including density–temperature inhomogeneities caused by turbulence, collisions, and shock waves in spiral arms (Wood 1996), as well as the event(s) that caused chondrule formation. Convection of nebula midplane gases (Meibom *et al.* 2000) at a distinct radial distance could have led to periodic heating of dust material above and below the midplane. Sagan and Khare (1979) pointed out that UV irradiation should lead to formation of polymerized aromatic molecules from simple organic molecules in several space environments. Strong irradiation during solar T-Tauri phase flares of the sort seen in the Orion nebula (Hartmann *et al.* 1993) could have led to pyrolysis of aliphatic hydrocarbons and alkylated PAHs, and this could have left a residue of essentially unalkylated PAHs. Note that UV irradiation is much more important for its direct chemical effects than for its heating effect. Finally, thermal metamorphism on parent bodies of meteorites should have contributed to aromatization, as well as dealkylation, polymerization, and graphitization of PAHs (Brearley 1990).

CONCLUDING REMARKS

Our calculations of metastable equilibria show that there is a thermodynamic drive to form condensed PAHs through hydrogenation of CO in the solar nebula within the stability field of graphite, and under conditions where CH_4 would predominate over CO if stable equilibria were reached. If the formation of graphite, methane, and CO_2 is prohibited, condensed PAHs become stable at temperatures below ~ 450 K with respect to nebular gases H_2 , CO, and H_2O . The stabilities of PAHs increase as the H/C ratio in the species decreases. Low temperatures, high pressures, high CO abundances, and low H_2O contents favor hydrocarbon stability in the nebula and increase the temperatures where saturation of condensed hydrocarbons become possible. Low accretion rates of nebula material into the proto-Sun and low viscous efficiencies of the disc also favor hydrocarbon stability. Model results show that hydrocarbons could have formed in a narrow zone, which moved toward the proto-Sun as the accretion rate decreased during the evolution of the nebula. At radial distances of 2–4 AU, PAHs could have formed at the time when the accretion rate was $10^{-6.3}$ – $10^{-7.7}$ solar mass year $^{-1}$. The stabilities of the PAHs considered in our models do not differ significantly, and the formation of a metastable mixture at supersaturation conditions is more likely than formation of a single PAH. Note that solubility of hydrocarbons in each other increases their stability and makes condensation easier.

Kinetic constraints inhibited complete metastable equilibria between condensed hydrocarbons and nebular gases, resulting in the conversion of only a small part of the nebular CO to hydrocarbons. Grain-catalyzed Fischer–Tropsch type synthesis on mineral surfaces provides a reliable mechanism for nebular

formation of condensed hydrocarbons from CO and H_2 . Alternatively, or additionally, thermodynamic calculations show that PAHs could have formed through subsequent pyrolysis of aliphatic hydrocarbons. Unalkylated PAHs in meteorites and interplanetary dust particles could be a product of pyrolysis and/or oxidation of alkylated PAHs and aliphatic hydrocarbons which formed earlier. Conditions for nebular FTT synthesis of condensed hydrocarbons could have been spatially and/or temporally limited, and several presolar, other nebular, giant planet subnebular, and parent-body processes could also have contributed to the hydrocarbon inventory in the Solar System.

At nebula conditions, methylated aromatic hydrocarbons usually have higher stabilities than unalkylated species; however, depletion of nebular water vapor and/or an excess of CO compared to solar gas composition would have favored unalkylated PAHs. If they do not represent presolar organic matter, the unalkylated compounds found in meteorites and IDPs could represent nebular products that could have been modified by such nebular and parent-body processes as pyrolysis and oxidation.

Although our thermodynamic calculations do not prove that PAHs from meteorites and IDPs formed in the solar nebula, they demonstrate the energetic drive for such a possibility. Nebular synthesis of hydrocarbons could have been one episode in the complex history of synthesis and transformation of these compounds. Note that our calculations of hydrocarbon stability can also be used to evaluate the fate of presolar PAHs in the solar nebula.

We conclude by suggesting several studies that could provide insight into the processes responsible for PAHs and other hydrocarbons in the Solar System.

1. Expansion of this study to include thermodynamic assessment of the formation of gaseous hydrocarbons in the nebula. It is plausible that PAHs could have formed in the gas phase and then condensed as temperature decreased. Thermodynamic models of Eck *et al.* (1966) and Stein (1978) show that hydrocarbons could exist stably in the gas phase above the saturation temperatures of condensed phases.

2. Theoretical and experimental study of other nebular processes that could be responsible for hydrocarbon syntheses or alteration. In particular, the role of lightning and nebular flares in synthesis through Miller–Urey reactions could be explored from a thermodynamic perspective.

3. Laboratory analysis of hydrocarbon speciation and isotopic composition of separated fractions of the organic material in meteorites, in IDPs, and on the surfaces of presolar grains. This effort could include searches for correlations of aromatic to aliphatic ratios, PAH speciation, and degree of PAH alkylation with the extent of secondary alteration in meteorites and the local mineralogical environment. The goal of these efforts would be to resolve the differences among presolar, nebular, and parent-body processes of hydrocarbon formation and alteration.

4. Experimental study of carbonaceous deposits formed through hydrogenation of CO and pyrolysis of aliphatic

hydrocarbons and PAHs at simulated nebular and subnebular conditions in order to model solar system synthesis and survival of presolar hydrocarbons.

5. Theoretical and experimental modeling of hydrocarbon transformation and synthesis on parent bodies of chondrites. Previous research (e.g., Shock and Schulte 1990, 1998, Hartman *et al.* 1993, Zolotov and Shock 1999) provides the theoretical framework to explore synthesis of organic compounds during the hydrothermal alteration of meteorites.

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