Chemistry in the Inner Regions of Protoplanetary Disks

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Abstract. Interstellar material is highly processed when subjected to the physical conditions that prevail in the inner regions of protoplanetary disks, the potential birthplace of habitable planets. Polycyclic aromatic hydrocarbons (PAHs) are abundant in the interstellar medium, and they have also been observed in the disks around young stars, with evidence for some modification in the latter. Compounds such as C_2H_2, HCN and CO_2 have been observed in high abundances within the central 3 AU in some disks as well. Using chemical models for sooting flames, we have investigated the thermally-driven reactions involving PAHs to understand the chemical evolution of these compounds as they are incorporated into the region where habitable planets may eventually form. We find that PAHs are destroyed over disk timescales at temperatures ~1000 K and higher. In the process, high abundances of C_2H_2 persist due to the kinetic inhibition of reactions that drive the carbon into CO and CH_4. We also find that relatively high abundances of CH_4 and CO_2 are to be expected at chemical equilibrium at typical disk temperatures, pressures and C/O ratios. We suggest that PAH destruction in inner warm zones of protoplanetary disks is important and is the origin of abundant C_2H_2, CH_4 and CO_2.

1. Introduction

PAHs are pi-bonded cyclic aromatic hydrocarbons. They are extremely stable, in oxidizing or reducing conditions, at high temperatures, and in the presence of intense, high-energy UV radiation, allowing them to persist in a very wide range of astrophysical and planetary environments. In particular, PAHs have been observed in the ISM and, at much-reduced abundances, in the planet-forming disks around young stars (e.g. Bouwman et al 2008, Geers et al 2008, Boersma et al 2008). Some observations indicate that the PAHs have been modified in disk environments (e.g. Sloan et al 2007).

Observations indicate that PAHs account for up to 10% of the carbon in interstellar space (e.g. Allamandola 1996); most of the rest is CO. PAHs are also present in the most primitive meteorites – in both ordinary and carbonaceous chondrites (Clemett 1996). Deuterium fractionation associated with carbon phases in carbonaceous meteorites attests to an interstellar heritage. PAHs' stability against both heat and radiation contributes to their survival from carbon stars, into the ISM, through the solar nebula, and ultimately into meteorites, interplanetary dust particles and comets (Allamandola 1996).

The most abundant PAHs identified in the Murchison CM2 carbonaceous chondrite include pyrene, acenaphthene, naphthalene, and phenanthrene. Meteoritic PAHs are enriched in deuterium from +244 to 468 $^o/_{oo}$, indicating an interstellar heritage (Cronin & Chang 1993).

In this work, we do not attempt to present a complete picture of the chemical evolution of the entire disk. Instead, we investigate the thermally-driven chemical pathways that PAHs may take when subject to the hot inner regions of disks. These novel chemical pathways are the result of recent studies of combustion and sooting flames (Smith et al 2000; Appel et al 2000). It is our hope and intent that these reactions will be incorporated into future chemical kinetic models for the solar nebula and other protoplanetary disks.

2. Modeling the Kinetics of PAH Chemistry

We implement a computational combustion model to investigate the chemical kinetics of PAHs and nitrogen compounds within a parameter space of nebular timescales, pressures, temperatures, C/O ratios and other factors to understand the reactions that modify PAHs in the inner disk environment. Historically (e.g. Lewis 1972), chemical abundances in the solar nebula have been calculated using thermodynamic equilibrium models, which usually neglect aromatics altogether.

While Lewis-style equilibrium models explain inorganic mineral abundances in meteorites well, they fail when trying to explain the organics. The gas-phase reactions that involving breaking the CO bond are kinetically inhibited under nebular conditions. Therefore, in Lewis' classic picture of the solar nebula as a disk cooling from a hot (> 2000 K) state, no organics should form in the gas phase when the C/O < 1.

Today's view of planet-forming disks and the chemistry therein involves more than simple condensation from a very hot gas. The most primitive meteorites contain organic compounds, often with substantial isotopic enrichments, that strongly indicate a pre-solar origin. Therefore, it is clear that a substantial fraction of the material coming in from the ISM did not completely lose its interstellar heritage. (For a good recent review of meteorites and their relationship to the early solar system, see Aleon 2008 and references therein.)

While thermodynamic equilibrium models are generally not useful for calculating the abundances of organics in disks, they can be used to address the relative stability of

different species. For instance, Zolotov & Shock (2001) use thermodynamic models to address the stability of PAHs under disk conditions, and find that they are more stable than their alkylated and/or aliphatic counterparts with the same carbon number.

The chemistry of PAHs has been well studied under combustion conditions (P ~ 1 atm, T > 1000 K). In this work, we apply a state-of-the-art combustion kinetics model (Smith et al 2000 and Appel et al 2000). This model was originally developed to describe the chemistry of sooting flames. The combustion model only considers thermally-driven reactions involving H, C, O and N. The reaction mechanism that was used in the calculations presented here has been tailored to the comparatively low temperatures and low pressures of disks. The largest PAH considered in this model is pyrene ($C_{16}H_{10}$, see Figure 1) because it is the smallest "stabilomer" (extremely stable PAH).

3. Model results: Stability of PAH, CH_4, C_2H_2, HCN and NH_3 in disks

In the terrestrial-planet forming region of disks, models indicate that the temperature at ~2 AU ranges from 1200-800 K between 10^5 and 10^6 years, or from 2-4 AU at 10^5 years (Bell et al 1997). To illustrate the pathways and timescales to destroy PAH, HCN, and NH_3 under these conditions, the temperature and pressure are kept constant and the ensuing chemistry is followed for 10^6 years. There is no mixing: the parcel of gas is allowed to evolve thermally over time, which allows us to determine the timescales for PAH destruction and other key reactions.

In Figures 2-7, we show the chemical abundances vs. time for temperatures of 1000 K (Figs. 2, 3 and 4) and 1200 K (Figs. 5, 6 and 7). Abundances are given as mole fractions (approximately equal to the abundance relative to hydrogen). In all cases, the pressure is kept constant at 10^{-6} atm. In all cases, the initial abundances of CO and H_2O are both $3x10^{-4}$. 10% of the total carbon is initially in the form of the four-aromatic-ring molecule, pyrene (the largest PAH considered in this reaction mechanism). The initial pyrene abundance corresponds to a mole fraction of $2x10^{-6}$. The solar nitrogen abundance gives an N_2 mole fraction of $5x10^{-5}$ when all of the nitrogen is initially in the form of N_2.

In Figures 2 and 5, all of the nitrogen is initially in the form of N_2. In Figures 3 and 6, 10% of the nitrogen is initially in the form of NH_3 (mole fraction $5x10^{-6}$) and the rest is N_2. In Figures 4 and 7, 10% of the nitrogen is initially in the form of HCN (mole fraction $5x10^{-6}$) and the rest is N_2.

The most important general result is that even after one million years at 1000 K, the thermally-driven reactions proceed slowly enough that equilibrium is not reached for most molecular species – with a notable exception being CO_2, which reaches its equilibrium abundance in less than a year. At 1200 K, most species are at least approaching their equilibrium abundances; for instance, all of the carbon has been converted into CO and CH_4.

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Our results show that PAH destruction occurs within a disk's lifetime for temperatures in excess of 1000 K. The destruction of PAH heralds a rise in acetylene, C_2H_2, to an abundance of approximately 2×10^{-6} relative to hydrogen. In other modeling efforts, high abundances of acetylene are usually achieved by having this (or a closely related compound) evaporate directly from grain mantles. While this is an interesting suggestion, there is no strong indication that acetylene is present at similarly high abundances in interstellar clouds.

Our model results indicate that a high abundance of acetylene is a natural by-product of the thermally-driven reactions of PAHs with H atoms and OH radicals. All of the PAHs are converted to acetylene, which persists before being converted to methane and CO via kinetically-inhibited reactions.

Thermally-driven reactions that convert HCN and NH_3 to N_2 are also slow compared to the disk lifetime, for T < 1000 K. At 1200 K, however, the conversion occurs over about 3000 years. A notable result here is that, when starting with 10% of the nitrogen initially in NH_3, HCN briefly reaches a high abundance before the nitrogen is eventually driven into N_2. And when starting with 10% of the nitrogen in HCN, NH_3 also reaches a high abundance – and persists for a significantly longer time – before ultimately ending up as N_2.

4. Conclusions

We find that the destruction rate of PAHs is extremely temperature-dependent. At T = 1000 K, they can survive over disk timescales, while at T = 1200 K, they are destroyed within a few thousand years. Both HCN and NH_3 are relatively stable at 1000 K, while at 1200 K, they are both destroyed about as rapidly as the PAHs. The chemical pathways to destroy these compounds involve OH as well H atoms.

We conclude that protoplanetary disks will exhibit a "soot line," within which gas has reached temperatures above 1200 K and PAHs are rapidly destroyed. Outside of the soot line, PAHs can 'happily' survive. The sharpness of this transition will depend on the cooling history as well as the degree of radial mixing of the gas in the disk.

Large abundances of acetylene (C_2H_2) form as the PAHs are destroyed, persisting over the lifetime of the disk at 1000 K. Carr & Najita (2008) observed significant abundances of acetylene, hot water vapor, HCN, and CO_2 in AA Tauri, a classical T Tauri star with a gaseous disk. They found a H_2O/CO ratio of 1.3 in the inner few AU, and a C_2H_2/CO ratio of 0.016. In our calculations, the maximum C_2H_2/CO ratio is only a factor of ~2 smaller than the observed value.

When HCN is included as an input species, a large amount of NH_3 is produced, which can survive over long timescales at 1000 K. The converse is also true, although the HCN forms later and lasts for a shorter time. In either case, at thermal equilibrium, most of the

nitrogen will be in the form of N_2, and other nitrogen compounds will be at negligible abundances.

A more complete treatment of disk chemistry, one that includes photochemistry and ion-molecule reactions, will keep the chemistry even further from equilibrium. Together with our results, we conclude that thermodynamic equilibrium models will be unable to explain the abundances of observed species such as HCN and acetylene, because the reactions involving these compounds are kinetically inhibited even at the high temperatures of the inner disk. Chemical models of disks would benefit from incorporating this novel and detailed reaction mechanism involving PAHs. Future observations of PAHs in disks will help to reveal the complex environment of the planet-forming region of disks and perhaps also allow us to understand their connection to PAHs found in primitive meteorites.

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Zolotov, M. Yu., & Shock, E.L. 2001, Icarus, 150, 323.

Figure 1. A few examples of the aromatics and other important hydrocarbons considered in the chemical model, followed by their labels (see model results in Figures 2-7).

Cyclopropene
AC3H4
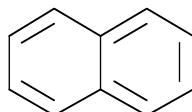
Naphthalene
A2
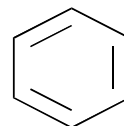
Benzene
A1
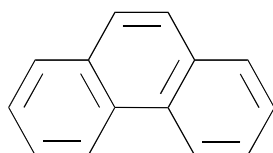
Phenanthrene
A3
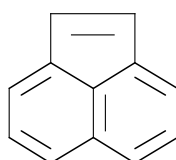
Acenaphthene
A2R5
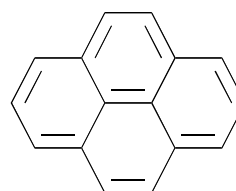
Pyrene
A4

Figure 2. T = 1000 K; P = 10^{-6} atm. The input abundances (expressed as mole fractions) are: H_2O = CO = 3×10^{-4}, pyrene(A4) = 2×10^{-6} (such that 10% of the carbon is initially in the form of the largest PAH considered in the model), N_2 = 5×10^{-5}. The chemistry is allowed to evolve for 10^6 years.
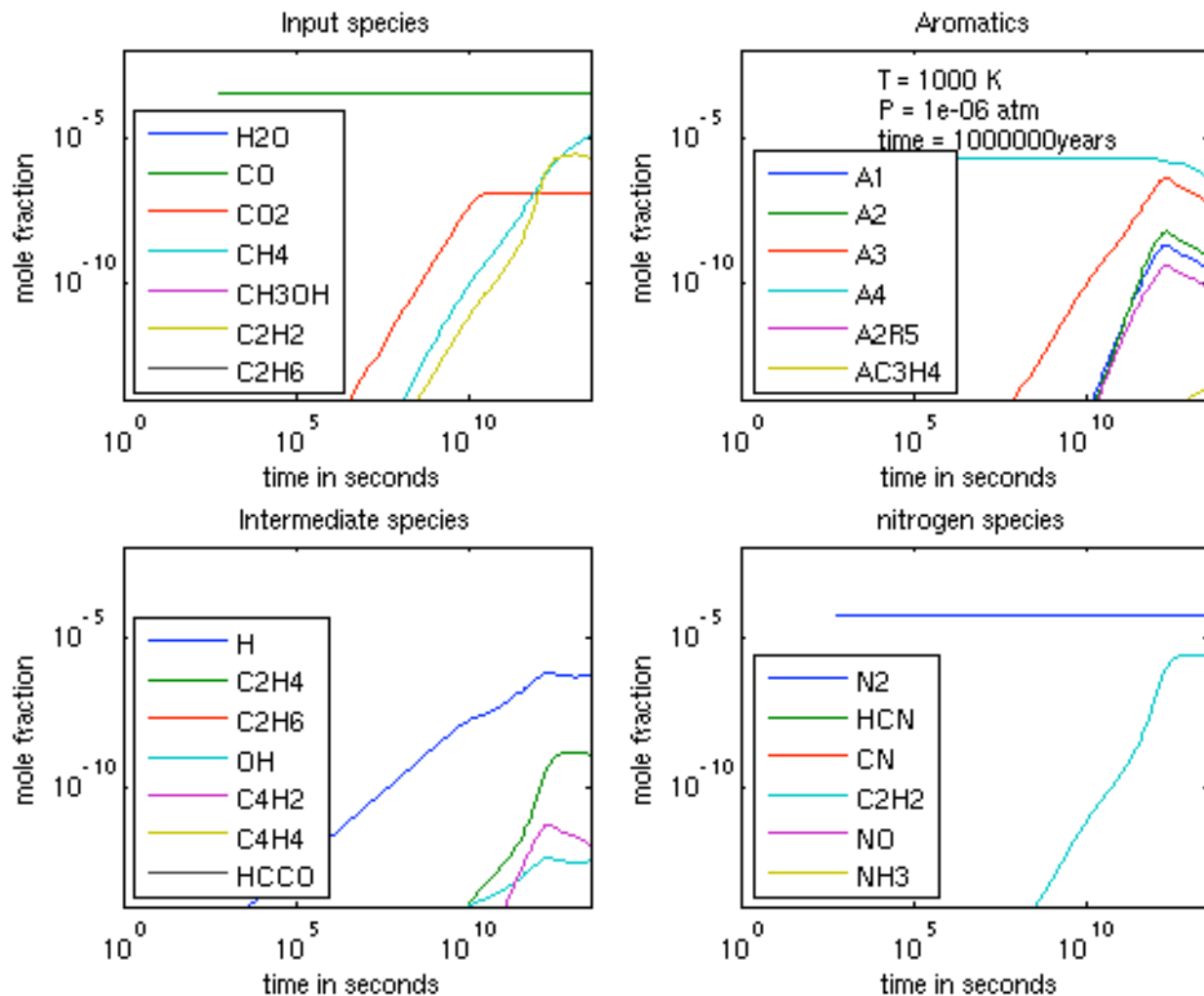
Figure 3. T = 1000 K, P = 10^{-6} atm. The input abundances (expressed as mole fractions) are: H_2O = CO = 3x10^{-4}, pyrene(A4) = 2x10^{-6} (such that 10% of the carbon is initially in the form of the largest PAH considered in the model). 10% of the N is initially in HCN. The rest is N_2. The chemistry is allowed to evolve for 10^6 years.
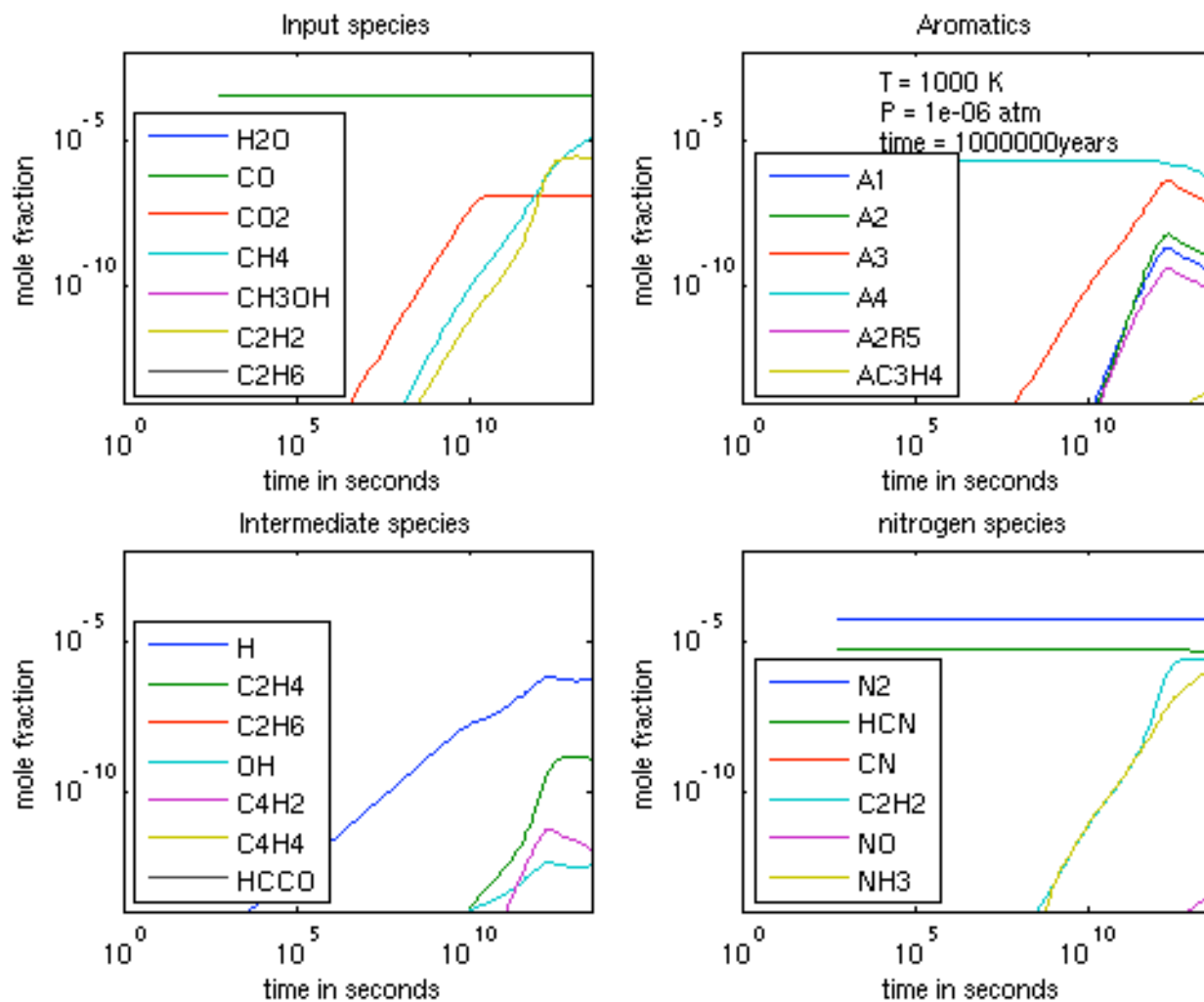
Figure 4. T = 1000 K, P = 10^{-6} atm. The input abundances (expressed as mole fractions) are: H_2O = CO = 3×10^{-4}, pyrene(A4) = 2×10^{-6} (such that 10% of the carbon is initially in the form of the largest PAH considered in the model). Here, 10% of the N is initially in NH_3. The rest is N_2. The chemistry is allowed to evolve for 10^6 years.

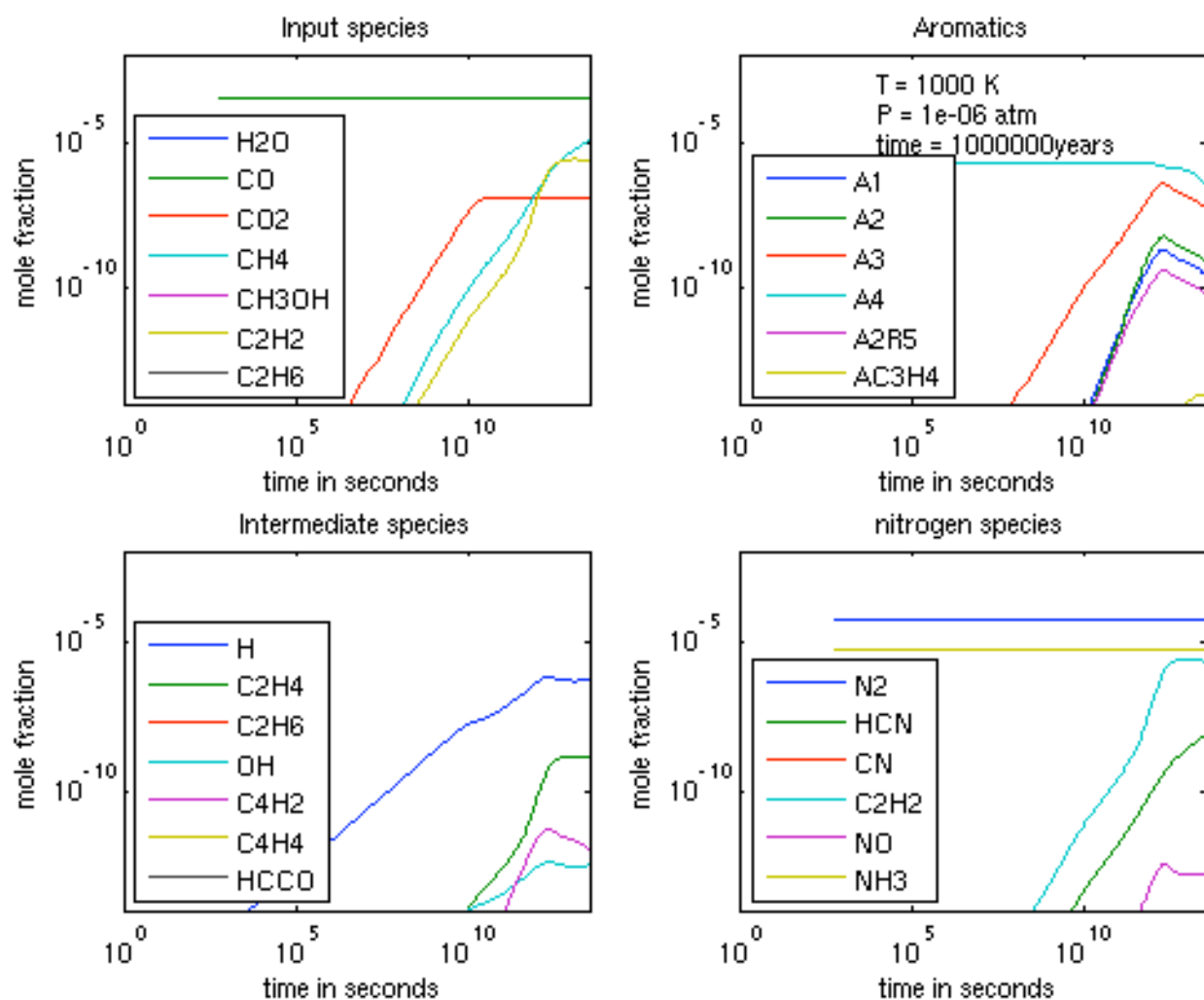Figure 5. T = 1200 K; P = 10^{-6} atm. The input abundances (expressed as mole fractions) are: H_2O = CO = 3×10^{-4}, pyrene(A4) = 2×10^{-6} (such that 10% of the carbon is initially in the form of the largest PAH considered in the model). N_2 = 5×10^{-5}. The chemistry is allowed to evolve for 10^6 years.

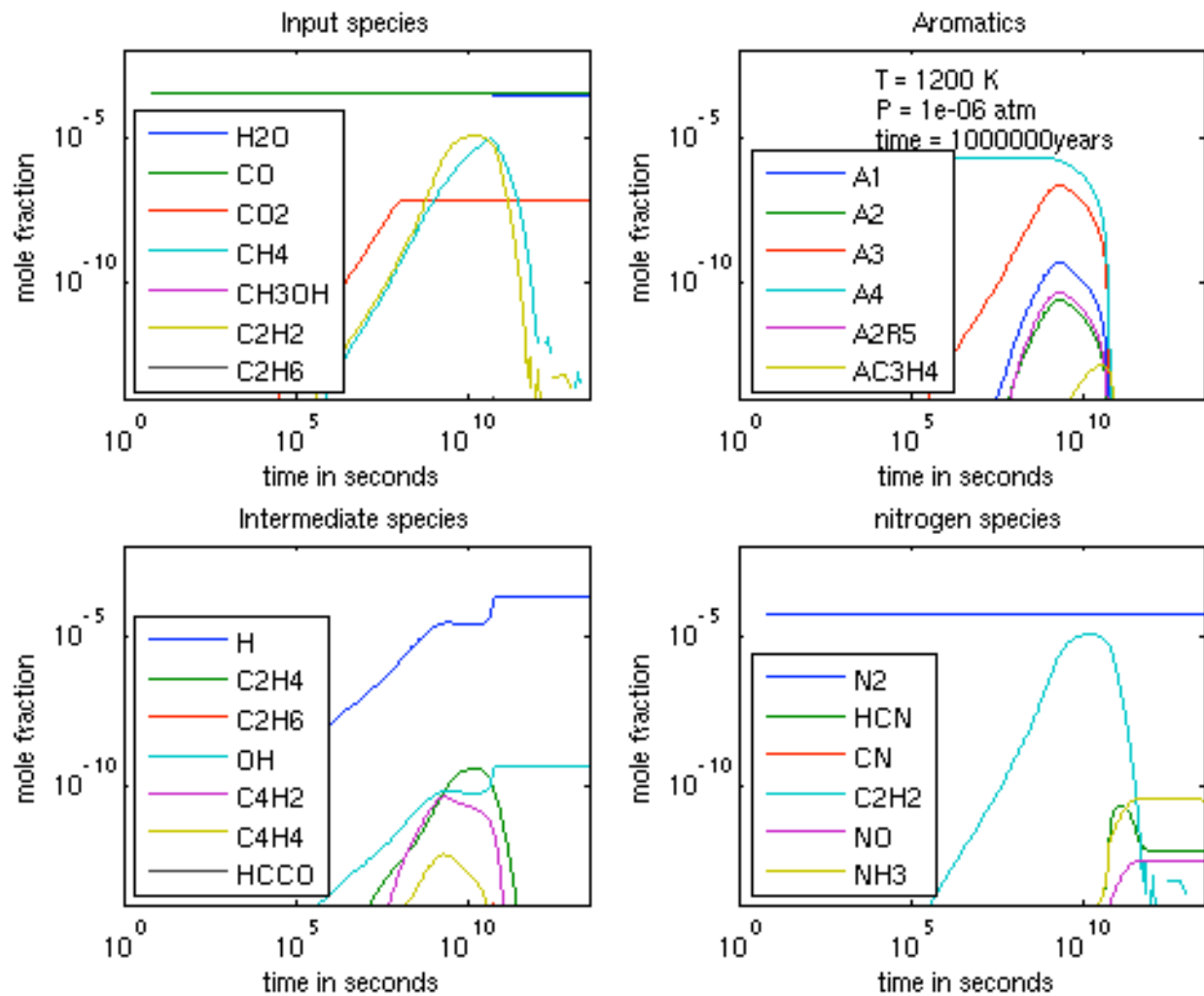Figure 6. T = 1200 K; P = 10^{-6} atm. The input abundances (expressed as mole fractions) are: H_2O = CO = $3x10^{-4}$, pyrene(A4) = $2x10^{-6}$ (such that 10% of the carbon is initially in the form of the largest PAH considered in the model). 10% of the N is initially in HCN. The rest is N_2. The chemistry is allowed to evolve for 10^6 years.
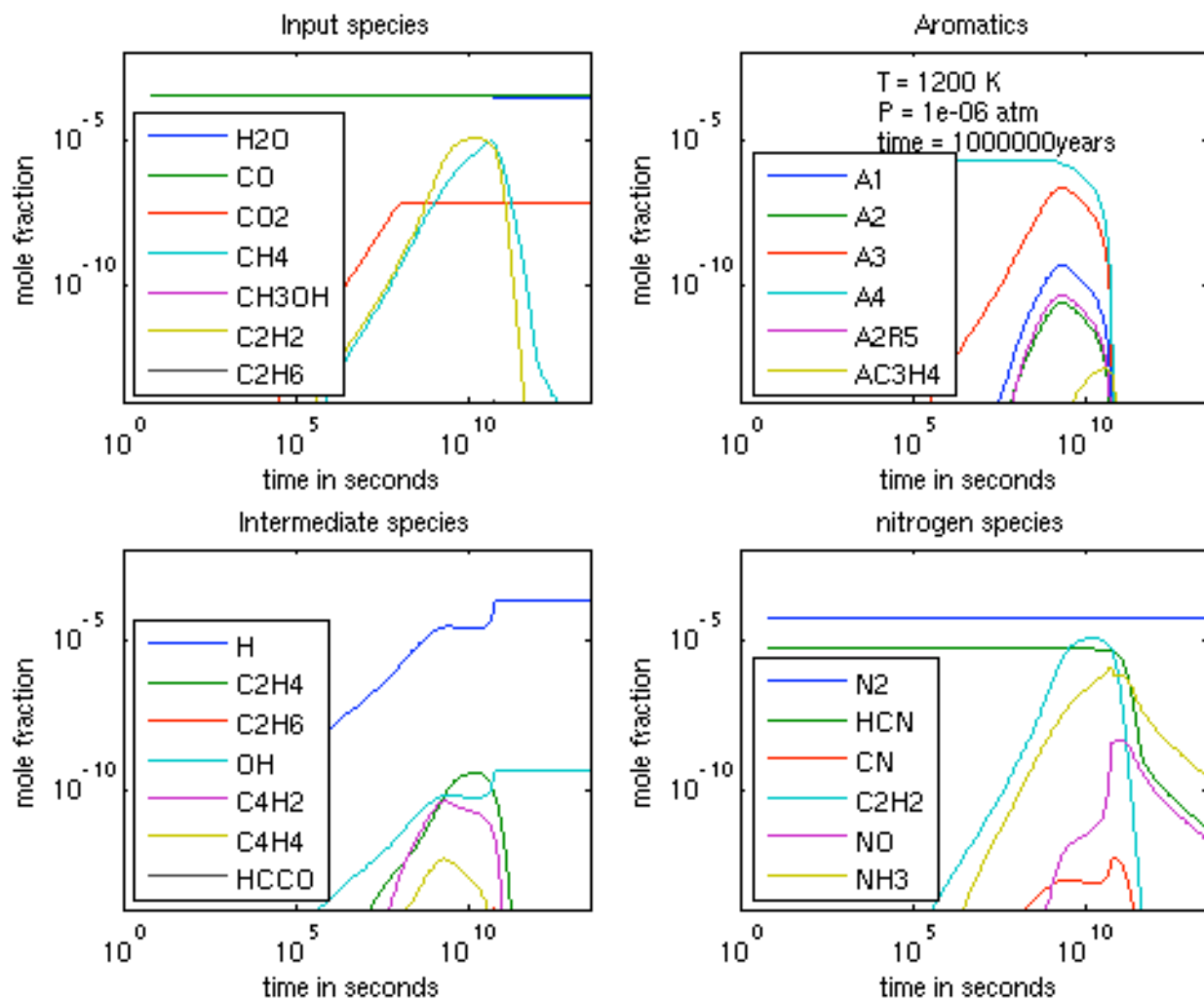
Figure 7. T = 1200 K; P = 10^{-6} atm. The input abundances (expressed as mole fractions) are: $H_2O = CO = 3 \times 10^{-4}$, pyrene(A4) = 2×10^{-6} (such that 10% of the carbon is initially in the form of the largest PAH considered in the model). Here, 10% of the N is initially in NH_3. The rest is N_2. The chemistry is allowed to evolve for 10^6 years.