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A voyage from dark clouds to the early Earth

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Stellar nucleosynthesis of heavy elements, followed by their subsequent release into the interstellar medium, enables the formation of stable carbon compounds in both gas and solid phases. Spectroscopic astronomical observations provide evidence that the same chemical pathways are widespread both in the Milky Way and in external galaxies. The physical and chemical conditions—including density, temperature, ultraviolet radiation and energetic particle flux—determine reaction pathways and the complexity of organic molecules in different space environments. Most of the organic carbon in space is in the form of poorly-defined macromolecular networks. Furthermore, it is also unknown how interstellar material evolves during the collapse of molecular clouds to form stars and planets. Meteorites provide important constraints for the formation of our Solar System and the origin of life. Organic carbon, though only a trace element in these extraterrestrial rock fragments, can be investigated in great detail with sensitive laboratory methods. Such studies have revealed that many molecules which are essential in terrestrial biochemistry are present in meteorites. To understand if those compounds necessarily had any implications for the origin of life on Earth is the objective of several current and future space missions. However, to address questions such as how simple organic molecules assembled into complex structures like membranes and cells, requires interdisciplinary collaborations involving various scientific disciplines.

1. Introduction

Life in the Universe is the consequence of the increasing complexity of chemical pathways which led to stable carbon compounds assembling into cells and higher organisms. The starting point of this fascinating evolution is the synthesis of elements that play key roles in life as we know it: hydrogen, carbon, oxygen, nitrogen, sulfur and phosphorus. Whereas hydrogen is primordial, having been formed during the Big Bang together with helium and traces of other species, the more heavy elements such as carbon, oxygen and nitrogen have been formed by nucleosynthesis in stellar interiors. During the course of stellar evolution those heavy elements are redistributed into the interstellar medium (ISM) and are incorporated into solid and gaseous chemical networks. The elemental abundances in space, scaled to the most abundant element, hydrogen, are listed in Table 1.

Understanding interstellar organic chemistry may yield important insights into the chemical conditions prevalent at the birth of the Solar System (see Ehrenfreund & Charnley 2000, Ehrenfreund et al. 2002a for reviews). Observations of the interstellar medium, primarily at microwave frequencies, have led to the identification of 123 molecules (Wootten 2002). Most of these molecules are organic and many of them have also been detected in the outgassing comae of comets, supporting the view that cometary ices contain some pristine interstellar matter (Bockelée-Morvan et al. 2000). The high isotopic fractionation of deuterium found in extracts of carbonaceous meteorites indicates that they represent a highly processed sample of interstellar material (Cronin & Chang 1993). Material from cometary and asteroidal impacts is believed to have been important for providing the

Element	Abundance
H	1
He	7.5×10^{-3}
O	8.3×10^{-4}
C	4.0×10^{-4}
N	1.0×10^{-4}
Ne	0.8×10^{-4}
Si	4.3×10^{-5}
Mg	4.2×10^{-5}
S	1.7×10^{-5}
Fe	4.3×10^{-5}
Na	2.1×10^{-6}
P	3.0×10^{-7}

TABLE 1. Elemental abundances in space

molecular inventory available at the beginning of prebiotic evolution on the early Earth (e.g. Chyba et al. 1990). Hence, studies of the organic chemistry in the interstellar medium and the Solar System form the interface between astrochemistry and prebiotic evolution. They are an active area of research in Astrobiology (Ehrenfreund & Charnley 2000) and address issues such as the chemistry of molecules which could act as precursors or building blocks of biologically-important molecules, e.g. amino acids for proteins, purines and pyrimidines for RNA and DNA bases (Ehrenfreund et al. 2002a).

2. Organic molecules in dense interstellar clouds

In cold molecular clouds, simple molecules form through a chemistry network dominated by gas phase ion-molecule and neutral-neutral reactions (e.g. Herbst 2000). As external starlight is not penetrating into the cloud interior, cosmic ray ionization of molecular hydrogen is the process which energetically drives this chemistry. Rather large organic molecules can form in these environments, and it appears that the production of long carbon chain species is favored (e.g. Langer et al. 2000). Infrared observations show that ice mantles cover interstellar dust grains and indicate that a rich catalytic chemistry is possible on them (Ehrenfreund & Charnley 2000). The efficient adsorption due to the low temperatures in these molecular clouds, diffusion of atoms and small molecules, subsequent reactions on the grain surface and desorption are the prevailing processes responsible for the formation of new molecules and the enrichment of the gas phase inventory, see Figure 1.

The infrared satellite *Infrared Space Observatory (ISO)* observed a large number of high-mass star-forming regions and allowed to establish an inventory of the most abundant ice species in dense clouds (Ehrenfreund & Schutte 2000, Gibb et al. 2000). A few low-mass star-forming regions, representative of Sun-type stars have also been observed (e.g. Boogert et al. 2000). Apart from water ice, CO, CO₂ and CH₃OH are the most abundant ice species which were observed with the *ISO*. Ice species which show a tentative signature and/or low abundances are CH₄, NH₃, H₂CO, OCS and OCN⁻, see Table 2. On cold grain surfaces, reactions occur in two steps: after accretion atoms and molecules diffuse (by tunneling or hopping) and react following essentially Langmuir-Hinshelwood kinetics. For molecular hydrogen formation on bare silicates or carbon grains, which is relevant for the diffuse ISM, experiments indicate that H diffusion appears to be slower

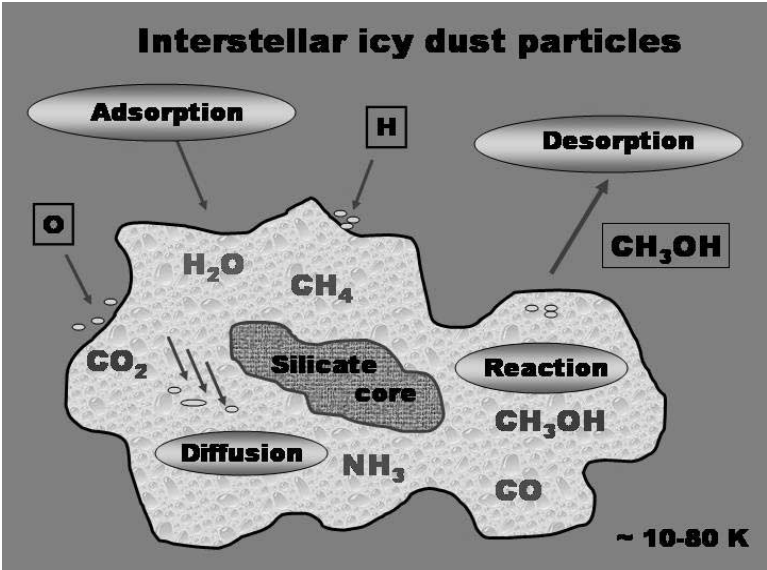


FIGURE 1. The catalytic surface of an interstellar icy grain. The efficient accretion of all atoms and molecules in dense clouds (H_2 excluded) leads to an active surface chemistry forming molecules which can not be produced via gas-phase reactions.

	W33A	Elias 29	Elias 16
Ice species	high-mass protostar	low-mass protostar	field star
H ₂ O	100	100	100
CO	9	5.6	25
CO ₂	14	22	15
CH ₄	2	<1.6	–
CH ₃ OH	22	<4	<3.4
H ₂ CO	1.7–7	–	–
OCS	0.3	<0.08	–
NH ₃	3–15	<9.2	<6
C ₂ H ₆	<0.4	–	–
HCOOH	0.4–2	–	–
O ₂	<20	–	–
OCN [–]	3	<0.24	<0.4

TABLE 2. Abundances of interstellar ices

(Pirronello et al. 1997, 1999) than expected by quantum diffusion. This may raise difficulties for producing H_2 in diffuse media. However, in dense molecular clouds at temperatures around 10 K, after formation of at least one molecular ice monolayer (Manico et al. 2001), quantum diffusion by H atoms is very rapid, and an H atom will almost always meet a coreactant before another particle arrives from the gas, i.e. to scan the entire surface. Reduction of O, N and C atoms by H addition reactions with zero activation energy form water, ammonia, and methane (Ehrenfreund & Charnley 2000). Direct accretion of CO forms molecular ices which can in principle be reduced and deuterated by quantum tunneling of H and D atoms through the activation energy barriers (Tielens & Hagen 1982; Charnley et al. 1997). This hydrogenation of CO is understood to be the source of the large abundances of solid methanol seen in many lines of sight, as

well as for the extremely large deuterium fractionation observed in both formaldehyde and methanol (Loinard et al. 2001; Parise et al. 2002). Experimentally, hydrogenation of CO to form formyl radical, formaldehyde and methanol can occur at low temperatures (van Ijzendoorn 1985; Hiraoka et al. 1994, 1998), but the high efficiencies required to fit the observations have yet to be demonstrated unequivocally (cf. Watanabe & Kouchi 2002). Carbon dioxide can also be formed from CO in an oxygen addition reaction that appears to possess a small activation barrier (Grim & d'Hendecourt 1986; Roser et al. 2001; Charnley 2001a).

A surface chemistry based on these kinetics, with the additional constraint of radical stability (cf. Allen & Robinson 1977), leads to surface schemes like that of Figure 2. This shows how methanol as well as other simple alcohols and aldehydes could be formed by a sequence of reactions starting from CO. The surface reaction network of Figure 2, and extensions of it (e.g. Charnley 2001b), have several promising characteristics. From the perspective of the organic composition in the Murchison meteorite, the scheme depicted in Figure 2 is consistent with the decline in concentration observed within homologous series, such as amino acids, with increasing number of carbon atoms, as some of these compounds (e.g. aldehydes, ketones) are believed to have been precursors for the formation of these species during aqueous alteration (Cronin & Chang 1993).

Hot molecular cores are dense, warm regions heated by young protostars (Brown, Charnley & Millar 1988). Observations show that they are particularly rich in molecules believed to have been synthesized on grains, as well as in larger, more complex, organic molecules. These include methanol, ethanol, dimethyl ether, methyl formate, ketene, formaldehyde, acetaldehyde, formic acid and several nitriles (Langer et al. 2000). These regions are a natural laboratory in which the most complex molecules observable in the interstellar medium can be studied and therefore provide an important point of contact for comparative studies of Solar System organics, such as those found in meteorites and comets (Cronin & Chang 1993; Crovisier 1998). Several of the larger organic species probably formed in ice mantles. However, many more probably formed after the evaporation of simple molecular mantles, through ion-molecule reactions in the warm gas (Charnley, Tielens & Millar 1992; Charnley et al. 1995). In particular, alkyl cation transfer reactions involving surface-formed alcohols and other products of grains surface chemistry could form an extensive suite of very large interstellar molecules (Figure 3). Recent support for this picture comes from observations which indicate that methyl formate (HCOOCH_3) and acetic acid (CH_3COOH) have a common formation mechanism (Remijan et al. 2002), from correlations between formic acid (HCOOH) and CH_3COOH (Liu et al. 2001), as well as from the detection of many molecules predicted to form in grain-surface schemes similar to that of Figure 2 (see Charnley 2001b): vinyl alcohol (CH_2CHOH ; Turner & Apponi 2001), glycolaldehyde (HOCH_2CHO ; Hollis et al. 2000) and ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$; Hollis et al. 2002).

3. Interstellar amino acids?

The most abundant amino acids found in meteorites are typically Glycine (Gly, $\text{NH}_2\text{CH}_2\text{COOH}$), β -Alanine (β -Ala, $\text{NH}_2\text{CH}_2\text{CH}_2\text{COOH}$), α -Alanine (α -Ala, $\text{NH}_2(\text{CH}_3)\text{CHCOOH}$), α -aminoisobutyric acid (AIB, $\text{NH}_2\text{C}(\text{CH}_3)_2\text{COOH}$), and 2-amino-*n*-butyric acid (α -ABA, $\text{NH}_2(\text{C}_2\text{H}_5)\text{CHCOOH}$); their presumed interstellar precursors for Strecker-cyanohydrin synthesis are formaldehyde, acetaldehyde, acetone and propionaldehyde. Figures 2 and 3 show that interstellar chemistry can clearly provide all the required amino acid precursors to start parent body chemistry. The question naturally

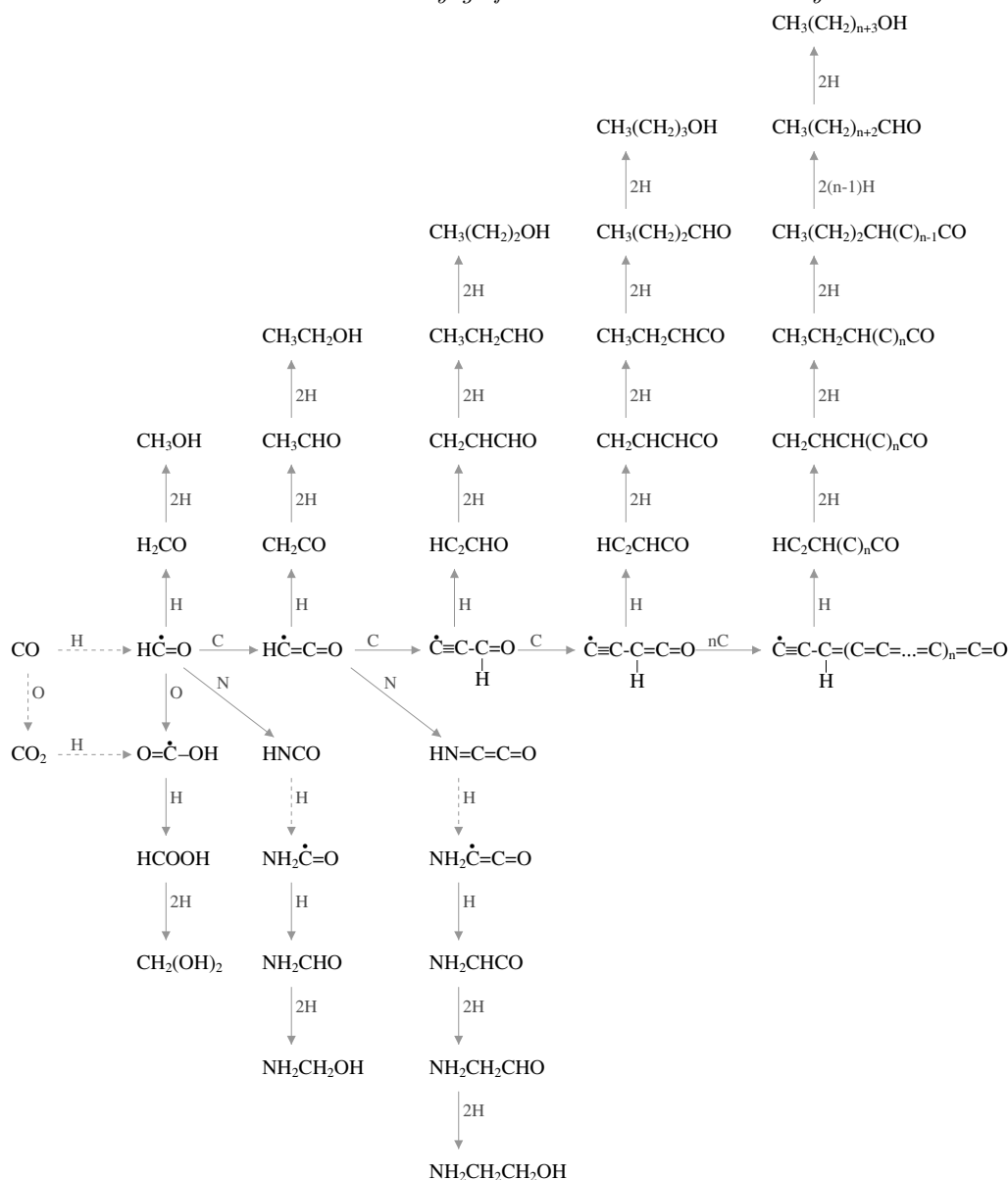


FIGURE 2. Interstellar grain surface chemistry. Hydrogen atom addition to unsaturated molecules creates reactive radicals and a rich organic chemistry seeded by carbon monoxide ensues. Broken arrows indicate reactions with activation energy barriers; where $2H$ is shown, a barrier penetration followed by an exothermic addition is implicitly indicated (adapted from Charnley 1997).

arises as to whether amino acids could actually form in the interstellar medium and then become directly incorporated in meteorites.

3.1. Grain-surface synthesis of amino acids?

Interstellar ice mantles are also subject to energetic processing in dense clouds by a weak ambient flux of UV photons (Prasad & Tarafdar 1983). This processing potentially opens up more pathways for surface organic chemistry. Recent experimental and theo-

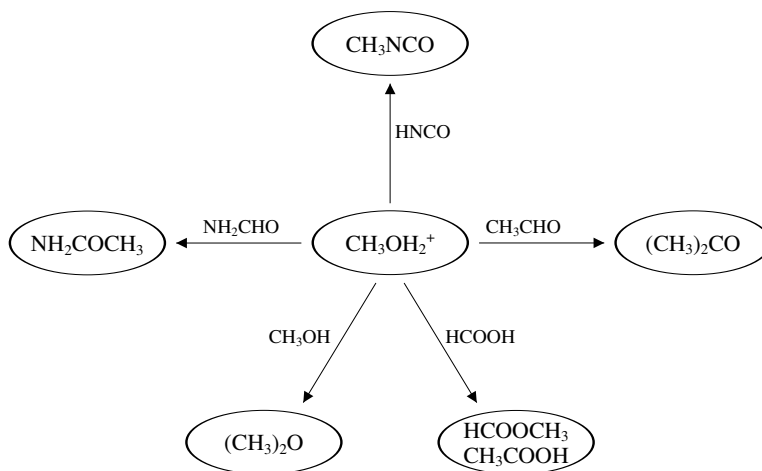


FIGURE 3. Methyl cation transfer in hot cores (Charnley 2001b). For clarity, formation of the molecular ion and the subsequent electron recombination step have both been omitted.

retical work suggests that UV photolysis of interstellar ice analogs produces amino acids (Bernstein et al. 2002; Munoz-Caro et al. 2002; see also Sorrell 2001 and Woon 2002). However, the applicability of these results to the interstellar medium is compromised by the need for a large UV flux in molecular clouds, and the fact that amino acids are photochemically very unstable (Ehrenfreund et al. 2001a).

We find that it is not possible to form amino acids in highly-restrictive surface reaction schemes like that of Figure 2. Although many of these pathways have unknown, and probably large, energy barriers, isomerization could be relevant for the production of some organic precursors. For example, in Figure 2 N atom addition to the ketyl radical ($\text{HC}=\text{C}=\text{O}$) has been depicted to lead to $\text{HN}=\text{C}=\text{C}=\text{O}$, and further C additions to longer cumulenone radicals will generally generate HNC_nO compounds. Saturation of these compounds leads, in analogy to the alcohols (see Figure 2), to aminoalcohols such as aminomethanol ($\text{NH}_2\text{CH}_2\text{OH}$), which was identified as a component of Comet Halley's tail (Kissel & Krueger 1987), and aminoethanol ($\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}$). An isomer of HNCCO is formyl cyanide ($\text{HCOC}\equiv\text{N}$). It has been demonstrated experimentally that cold H atoms cannot add efficiently to the nitrile bond (Hiraoka et al. 1998) and, in this case, the end product will be cyanomethanol. Hence, this route could lead to interstellar cyanohydrins and could perhaps allow part of the Strecker-cyanohydrin route to hydroxy acids to be bypassed. However, it does not seem possible to efficiently produce the corresponding Strecker intermediates for amino acid synthesis in this way.

3.2. Gas phase synthesis of amino acids?

As there are no routes to amino acids in surface schemes based on Figure 2, we consider gas phase synthesis. Evaporation of alcohols, aminoalcohols and formic acid in hot molecular cores may produce amino acids through exothermic alkyl and aminoalkyl cation transfer reactions analogous to those of Figure 3 (Charnley 1997; 2001b). Gas phase synthesis of amino acids provides an important counterpoint to the recent work on solid-state production of interstellar amino acids (Bernstein et al. 2002; Munoz-Caro et al. 2002). Hot cores were identified as one of the few regions where the UV flux was sufficiently low (about 300 mag of extinction) that amino acids could survive in the gas (Ehrenfreund et al. 2001a).

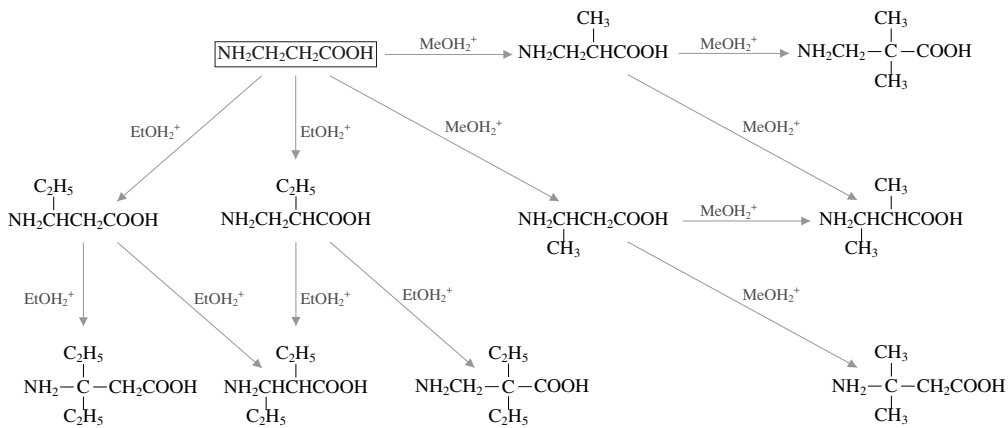


FIGURE 4. Possible amino acids formed from β -Alanine (Charnley 2001b).

A first possible step is the formation of protonated Gly and β -Ala via aminoalkyl cation transfer from aminomethanol and aminoethanol



followed by electron recombination producing the neutral acid. Further alkylation can theoretically produce a large suite of amino acids (see Figure 4) and could in principle explain the high degree of branching seen in the Murchison amino acids. Generally, the proposed reactions involve the hydrogen atoms of amino acids being replaced by alkyl groups, through elimination of a water molecule, as occurs between the alcohols themselves (Charnley et al. 1995).

In theory one can calculate the distribution of amino acids expected in such a scheme. Precursor abundances can be determined based on observations or from model calculations. Clearly, based on Figure 4, there are interrelationships between specific amino acids. However, one can ‘solve’ the networks (e.g. Figure 4) by inspection. There is no experimental information currently available, therefore one must simply assume similar rates for all amino acid formation and destruction processes (e.g. Mautner & Karpas 1986). Furthermore, one generally expects that surface-formed molecules will be less abundant the more heavy atoms they contain. Observations do show that $\text{MeOH}/\text{EtOH} > 1$, and we also expect that $\text{NH}_2\text{CH}_2\text{OH}/\text{NH}_2\text{CH}_2\text{CH}_2\text{OH} > 1$. In this case, the scheme of Figure 4 predicts the same distribution of amino acids as Strecker-cyanohydrin synthesis, i.e. $\text{Gly} > \alpha\text{-Ala} > \text{AIB} > \alpha\text{-ABA}$. Hence, although this chemistry may produce interstellar amino acids, as it stands it cannot account for either the similarity of the Gly and AIB abundances in Murchison, or the prevalence of β -Ala in Orgueil.

Although most of the reactions depicted in Figure 4 are exothermic, the existence of activation energy barriers is unknown. In fact, the lack of good experimental or theoretical ‘ground truths’ for any of the proposed reactions, means that any hot core chemistry modeling of amino acid chemistry would be largely unconstrained. For example, variation of reaction rates could reproduce a different amino acid distribution than that inferred above. It has been assumed that electron dissociative recombination of these large organics leads only to the loss of a hydrogen atom (e.g. Herbst 1978); different branching ratios would also have a significant effect. Specifically, we need to know the molecular structure of the product ions, whether or not energy barriers exist, the product branching ra-

tios, and also the rate coefficients. These quantities could be measured experimentally or estimated theoretically to allow us to develop reliable the amino acid reaction networks.

A prime motivation for constructing this scheme was that proton transfer to HCOOH from protonated alcohols and aminoalcohols is endothermic, whereas alkyl or aminoalkyl cation transfer is exothermic (Lias et al. 1984; Hunter & Lias 2001), hence the latter process should be favored in hot cores. This fact also makes these ion-molecule reactions amenable to study in the laboratory. Preliminary studies using a flow reactor/tandem mass spectrometer have confirmed the general viability of the proposed aminoalkyl transfer reactions (using aminoethanol, D. K. Bohme, private communication). These results indicate that, contrary to Figure 4, significant molecular rearrangements can occur, and that some product channels possess large energy barriers. This has important consequences as it means that the amino acid distribution can be much different from that naively expected by inspection (see above).

Acetic acid is present in hot cores at abundances that make compounds formed from it relevant for meteoritic composition. The observation of HCOOH/CH₃COOH ~ 1 (Remijan et al. 2002) could have important consequences for the proposed theory (see Figure 3). It suggests that the kinetics can be such that a ‘parent’ (HCOOH) can form a ‘daughter’ (CH₃COOH) which persists longer due to differences in the destruction rates of the molecules. It has already been noted that there is a significant discrepancy between high abundances of HCOOH in interstellar ices (Schutte et al. 1996) and gaseous HCOOH in hot cores (Ehrenfreund et al. 2001b). This process, as well as molecular rearrangements in ion-molecule reactions involving CH₃COOH, could also play a role in amino acid synthesis. Hopefully, these issues will be quantified experimentally in the near future to allow an accurate calculation of the possible amino acid distribution in hot cores.

4. Complex organic molecules in diffuse interstellar clouds

Diffuse clouds have moderate extinctions (<1 mag), densities of roughly 100–300 cm⁻³ and are dominated by photochemistry. Lines of sight through diffuse clouds allow measurements of the extinction curves (Jenniskens & Greenberg 1993). The extinction curve measured towards many targets seems rather constant in the long wavelength part ($\lambda > 2500$ Å). However, substantial changes characterize the short wavelength behavior, including the 2200 Å bump. The differences in the extinction curve reflect changes in the composition and size distribution of local dust particles (Draine 1990). Hydrogenated amorphous carbon (HAC) is considered as a potential carrier for the 2200 Å bump observed in the interstellar extinction curve (Mennella et al. 1998), while a variety of complex aromatic networks are likely to be present on carbonaceous grains (see Papoular et al. 1996 and Henning & Salama 1998 for reviews).

Organic molecules present in the diffuse medium can be formed by gas phase reactions, either directly or indirectly through formation in circumstellar envelopes followed by subsequent mixing into the diffuse medium, or by photoreactions of carbonaceous particles and sputtering by grain-grain collisions. Since the initial discovery of simple diatomic molecules in interstellar space, many more gas phase molecules have been detected in the diffuse medium, such as HCO⁺, CO, OH, C₂, HCN, CN, CS, H₂C, C₃H₂ (Lucas & Liszt 1997, 2000) and C₃ (Roueff et al. 2002).

Among the large organic molecules observed or suspected in diffuse clouds are polycyclic aromatic hydrocarbons (PAHs), fullerenes, carbon-chains, diamonds, amorphous carbon (hydrogenated and bare), and complex kerogen-type aromatic networks. The formation and distribution of large molecules in the gas and solid state is far from understood. In the envelopes of carbon-rich late-type stars, carbon is mostly locked in CO and

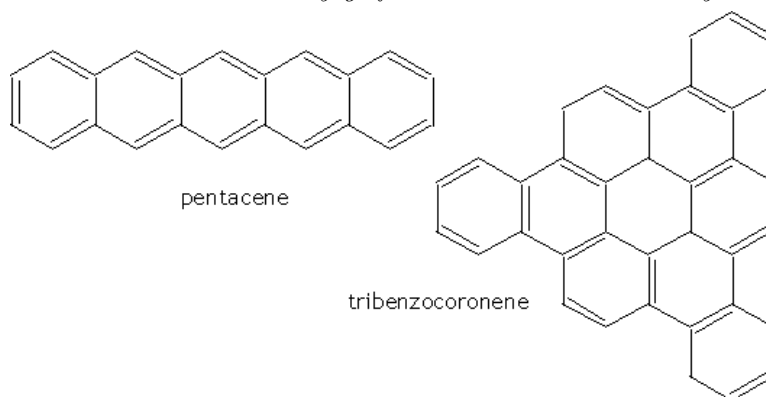


FIGURE 5. Examples of polycyclic aromatic hydrocarbons (PAHs), probably the most abundant organic gas phase molecules in space.

acetylene (C_2H_2). Soot formation involves polymerization of C_2H_2 in these envelopes, with PAHs as important intermediates (Frenklach & Feigelson 1989). PAHs are observed ubiquitously in our galaxy and beyond (Tielens et al. 1999) through their signature in the near and mid-infrared bands. They seem to be stable and abundant components in diffuse clouds and other space environments (see Figure 5).

4.1. *The diffuse interstellar bands*

The diffuse interstellar bands (DIBs) are a large number of absorption lines between 4000–10000 Å that are superimposed on the interstellar extinction curve (Herbig 1995). Since the discovery of the first two DIBs in the 1920s, their identification remains an important problem in astronomy (Herbig 1995, Ehrenfreund et al. 2001c). In the last 75 years DIBs have been observed toward more than a hundred stars. The number of known DIBs present in current observational data is ~ 300 and continuously increases due to the higher sensitivity of detectors (Jenniskens et al. 1994, O’Tuairisg et al. 2000). At present, no definitive identification of any of the carriers of the DIBs exists. The detection of substructures in some of the narrow, strong DIBs strongly suggests a gas phase origin and a stable nature of the carrier molecules. Consequently, good candidates are large carbon-bearing molecules which reside ubiquitously in the interstellar gas (Ehrenfreund & Charnley 2000). Polycyclic Aromatic Hydrocarbons (PAHs), fullerenes and carbon chains are among the most promising carrier candidates (see Ehrenfreund & Charnley 2000 for a review). The same unidentified absorption bands are also observed in extragalactic targets (Snow 2002). We have recently observed with the VLT/UVES at unprecedented spectral resolution the absorption spectrum toward reddened stars in the Magellanic Clouds. This range covers the strong transitions associated with neutral and charged large carbon molecules of varying sizes and structures. We reported the first detection of diffuse interstellar bands (DIBs) at 5780 and 5797 Å in the Small Magellanic Cloud (SMC), (see Figure 6) and measured the variation of DIBs in the SMC, the Large Magellanic Cloud (LMC) and our galaxy (Ehrenfreund et al. 2002b). The variation of DIBs in the Magellanic Clouds compared to Galactic targets may be governed by a combination of the different chemical processes prevailing in low metallicity regions and the local environmental conditions. However, the formation pathways of the DIB carriers seems to be ubiquitous throughout the universe.

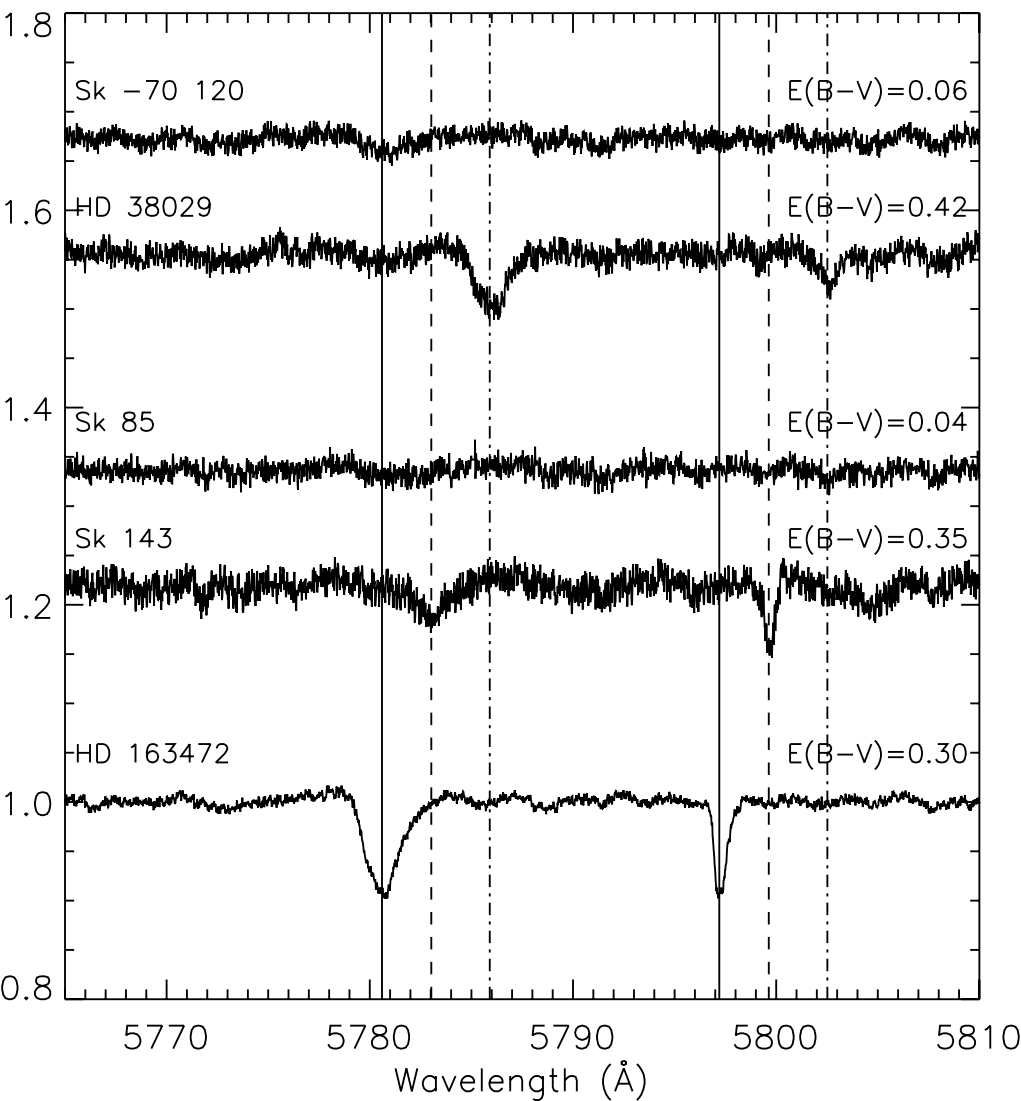


FIGURE 6. This figure shows spectra of the two best known DIBs, the $\lambda\lambda 5780$ and 5797 DIB. All spectra are normalized to the continuum, and shifted for display. The spectrum at the bottom shows a Galactic translucent cloud source (HD 163472). The two middle spectra show an SMC target Sk 143 (AzV456) and an unreddened SMC standard Sk 85 (AzV242); the two top spectra show an LMC target (HD 38029) and an unreddened LMC standard Sk -70 120. The full vertical lines indicate the Galactic rest wavelengths for those DIBs, the dashed lines indicate the wavelengths expected for these DIBs at SMC velocities, as determined from the NaD lines and the dash-dotted lines are the same for the LMC velocities. Both DIBs are clearly detected in both the SMC and LMC reddened targets (Ehrenfreund et al. 2002b).

5. The evolution of organic molecules during Solar System formation

The interstellar gas and dust (discussed in Sections 2 and 3) provide the raw material for the formation of stars and planetary systems as outlined in the following scenario. Interstellar clouds undergo a gravitational collapse to form protostars. During the proto-