BIOMOLECULES IN THE INTERSTELLAR MEDIUM
AND IN COMETS

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ABSTRACT

We review recent studies of organic molecule formation in dense molecular clouds and in comets. We summarise the known organic inventories of molecular clouds and recent comets, particularly Hale-Bopp. The principal chemical formation pathways involving gas phase reactions, as well as formation by catalytic reactions on grain surfaces or through dust fragmentation, are identified for both dense clouds and cometary comae. The processes leading to organic molecules with known biological function, carbon chains, deuterium fractionation, HNC and S-bearing compounds are described. Observational searches for new interstellar organics are outlined and the connection between observed interstellar organics and those detected in comets Hale-Bopp and Hyakutake are discussed.

INTRODUCTION

The birth sites of solar-mass stars and their planetary systems are dense interstellar clouds. Such clouds provide the building blocks, in the form of interstellar molecules and dust, for the formation of planets, comets, asteroids, and other macroscopic bodies in protostellar disks (Ehrenfreund & Charnley 2000; Irvine et al. 2000; Lunine et al. 2000). These clouds are the site of an extremely active and complex chemistry; to date over 100 molecules have been detected in them. Many of these molecules are also observed in protoplanetary disks and comets. A central question in the fields of astrochemistry and astrobiology is how much of the material present in primitive bodies, such as comets and asteroids, is pristine interstellar material? In other words, to what extent does the chemical inventory of these objects and the planets reflect chemical processing, firstly in the collapsing cloud, and subsequently in the protoplanetary disk (e.g. van Dishoeck & Blake 1998; Langer et al. 2000)?

Answering this question is of fundamental concern to two areas of research. Firstly, chemical abundances, together with isotopic and ortho-para ratios, are sensitive tracers of the molecule formation conditions and so differences between the chemical inventory of the interstellar medium (ISM) and the solar system can be used to constrain models of low-mass star formation, many aspects of which are not well understood. Secondly, the molecules in the early solar nebula provided the seed from which life eventually formed. It is thought that a great deal of organic material was deposited on the young Earth by cometary and asteroid impacts (Chyba et al. 1990). Many of the organic molecules detected in dense interstellar clouds have important functions in terrestrial biochemistry. The presence of extraterrestrial amino acids in meteorites (e.g. Cronin & Pizzarello 1983) shows that extremely complex molecules are able to form in space. In order to assess the implications for life elsewhere in the universe, we need to understand if such complexity is a general feature of interstellar and/or protoplanetary disk chemistry, or if these molecules arose due to specific conditions in our solar system. We can obtain clues to the above question by comparing observations of comets – thought to be the most pristine objects in our solar system – with those of protoplanetary disks, protostellar cores, and interstellar clouds (Ehrenfreund et al. 1997; Ehrenfreund 2000; Ehrenfreund & Charnley 2000; Bockelée-Morvan et al. 2000; Irvine et al. 2000).
Table 1. Representative compositions of the gas in a cold molecular cloud (L134N), protostellar ices (NGC7538:IRS9), protostellar hot core gas (Sgr B2(N)), and in a cometary coma (Hale-Bopp).

| Molecule       | L134N | NGC7538:IRS9 | Sgr B2(N) | Hale-Bopp |
|----------------|-------|--------------|-----------|-----------|
| H$_2$O         | <3    | 100          | >100      | 100       |
| CO             | 1000  | 16           | 1000      | 20        |
| CO$_2$         | -     | 20           | -         | 6-20      |
| H$_2$CO        | 0.25  | 5            | >0.005    | 1         |
| CH$_3$OH       | 0.04  | 5            | 2         | 2         |
| NH$_3$         | 2.5   | 13           | -         | 0.7-1.8   |
| CH$_4$         | -     | 2            | -         | 0.6       |
| C$_2$H$_2$     | -     | <10          | -         | 0.1       |
| C$_2$H$_6$     | -     | <0.4         | -         | 0.3       |
| HCOOH          | 0.004 | 3            | >0.003    | 0.06      |
| CH$_3$CO       | <0.009| -            | 0.002     | <0.03     |
| CH$_3$CHO      | 0.008 | -            | 0.002     | 0.02      |
| c-C$_2$H$_4$O  | -     | -            | 0.001     | -         |
| CH$_3$CH$_2$OH | -     | <1.2         | 0.01      | <0.05     |
| CH$_3$OCH$_3$  | -     | -            | 0.03      | <0.45     |
| HCOOCH$_3$     | <0.02 | -            | 0.02      | 0.06      |
| CH$_2$COOH     | -     | -            | 0.0008    | -         |
| CH$_2$OHCHO    | -     | -            | 0.003     | -         |
| OCN$^-$        | -     | 1            | -         | -         |
| HNCO           | -     | -            | 0.006     | 0.06-0.1  |
| NH$_2$CHO      | <0.001| -            | 0.002     | 0.01      |
| HCN            | 0.05  | -            | >0.05     | 0.25      |
| HNC            | 0.08  | -            | >0.001    | 0.04      |
| CH$_3$CN       | <0.01 | -            | 0.3       | 0.02      |
| CH$_3$NC       | -     | -            | 0.015     | -         |
| HC$_3$N        | 0.002 | -            | 0.05      | 0.02      |
| C$_2$H$_5$CN   | -     | 0.6          | -         | -         |
| C$_2$H$_7$CN   | -     | 0.006        | -         | -         |
| H$_2$S         | 0.01  | -            | -         | 1.5       |
| OCS            | 0.02  | 0.05         | >0.02     | 0.5       |
| H$_2$CS        | 0.008 | -            | 0.2       | 0.02      |
| SO             | 0.25  | -            | 0.2       | 0.2-0.8   |
| SO$_2$         | 0.005 | -            | 0.3       | 0.1       |

NOTES: Abundances for interstellar ices and cometary volatiles are normalized to H$_2$O. Gaseous abundances for Sgr B2(N) and L134N are normalized to CO. Original references for the abundances in L134N and NGC7538 appear in Charnley et al. (2001b). Values for Sgr B2(N) and comet Hale-Bopp are taken from Nummelin et al. (2000) and Crovisier & Bockelée-Morvan (1999) respectively.

THE INTERSTELLAR-COMET CONNECTION

Table 1 compares the abundances of a number of molecules in a dark cloud, ices toward a protostar, a star-forming ‘hot molecular core’ where ices have recently evaporated, and a cometary coma. Whilst the analysis is complicated by factors such as the probable depletion of CO and CO$_2$ in cometary ices (Yabushita 1995), and the fact that some of the molecules in hot cores and comets are likely to be daughter species formed via post-evaporation chemistry in the warm gas, it is clear that there are many fundamental similarities between the different regions. However, there are also a number of differences between cometary and interstellar abundances, which suggests that whilst solar system objects may consist of some purely interstellar material, other constituents have undergone significant processing. It is also apparent that there are substantial differences between molecular abundances in interstellar dark clouds and warm protostellar regions. This can be explained in terms of surface chemistry occurring as atoms and molecules freeze out onto dust grains in the cold cloud, followed by a complex gas-phase hot core chemistry which is initiated when the grain mantles are evaporated by the nearby protostar. A similar chemistry is thought to occur as material falls onto the disks surrounding low-mass stars, and the products will then refreeze and be incorporated into cometesimals and planetesimals (Lunine et al. 2000). Therefore, it is clear that in order to address the above question in a quantitative manner, we require a detailed understanding of the relevant chemical reactions and physical processing that interstellar material experiences as it suffers the violent passage from a cold dense cloud into a protoplanetary system.
ORGANIC ASTROCHEMISTRY: OBSERVATIONS AND THEORY

Interstellar Medium

Cold Dark Clouds

The two most intensively studied dark clouds are TMC-1 and L134N (see Table 1 of Ehrenfreund & Charnley 2000). Because of the low temperatures in these clouds, the chemistry is driven by exothermic ion-molecule reactions, initiated by cosmic ray ionization. In general, chemical models are able to give reasonable agreement with the observed abundances, although there remain problems with sulphurretted molecules and carbon-chain species (e.g. Millar et al. 1997). It is also possible that grain surface chemistry may contribute to the formation of molecules seen in dark clouds. Although these clouds are cold, a number of possible non-thermal desorption mechanisms have been proposed to return material from grains to the gas phase (e.g. Markwick et al. 2000); these proposals are motivated by the fact that in dense clouds one would expect heavy elements to be almost totally depleted from the gas on timescales much less than the estimated ages of the clouds (cf. Charnley et al. 2001a). The largest molecules observed in dark clouds are linear carbon chain molecules, such as C₈H and HC₁₁N (e.g. Bell et al. 1997, 1999). However, the decline in abundance with increasing chain length suggests that only a small fraction of interstellar carbon is locked up in longer chains. Nevertheless, it is likely that a significant fraction of the carbon is in the form of large aromatic molecules (see below). After atoms and molecules accrete onto grains to form ice mantles, it is likely that the resulting ices are subsequently processed by UV photons and/or energetic cosmic ray impacts. Laboratory experiments involving irradiation and radiolysis of interstellar ice analogs have demonstrated that relatively simple ices can be processed into much more complex molecules such as ethanol, formamide, carbonic acid, lactic acid, urea, and even larger molecules (Agarwal et al. 1985; Bernstein et al. 1995; Moore & Hudson 1998). Greenberg (1998) has proposed that over the lifetime of a molecular cloud a substantial fraction of the ice is converted into complex organic material, and that when planetary systems form this material is eventually incorporated into comets.

Hot Molecular Cores

The first hot molecular cores to be discovered were the Hot Core and Compact Ridge sources in Orion-KL, which are characterised by large abundances of small saturated molecules (e.g. NH₃, H₂O, CH₃OH) in warm (T ≥ 100 K), dense (n ∼ 10⁷ cm⁻³) gas, with anomalously high molecular D/H ratios for such high temperatures (e.g. Blake et al. 1987). Many other hot cores have since been identified and studied, and many molecules have been detected in them (see Table 1). The relation of many hot cores with ultracompact H II regions confirms that they are associated with the earliest stages of high-mass star formation (Kurtz et al. 2000), and their composition is thought to result from the evaporation of interstellar ices by the newly-formed protostars (Brown et al. 1988).

In addition to water, ammonia and methanol, hot cores also contain lesser abundances of larger saturated species such as ethanol and ethyl cyanide, which are not detected in dark clouds. On the other hand, the long unsaturated chain species which are observed in dark clouds, such as the larger of the cyanopolyynes, are absent from hot cores. This is generally taken to be evidence for a limited surface chemistry occurring on interstellar grains. The prevalence of hydrogen in the ISM, and the much greater mobility of H atoms on the grain surface, ensures that hydrogenation is the principal reaction for surface molecules (Tielens & Hagen 1982); saturated alkanes and alcohols are the end result of H addition to the linear chain molecules observed in dark clouds (e.g. Charnley 1997a). After the evaporation of the initial ices, a rich gas phase chemistry can occur, and large abundances of new molecules can be formed (Charnley et al. 1992, 1995). Although broadly similar, the detailed chemical composition of the gas is seen to vary between different hot cores. For example, the Orion Hot Core appears to be enriched in N-bearing species, whereas the Compact Ridge has enhanced levels of O-bearing species (Blake et al. 1987); similar spatial differentiation is seen in a number of other sources (e.g. Nummelin et al. 2000). Charnley et al. (1992) showed that the N/O differentiation can be explained by differing ammonia/methanol ratios in the original ices, since many of the large O-bearing species are formed in the hot gas via reactions involving protonated methanol, and the presence of ammonia suppresses the CH₃OH⁺ abundance since NH₃ acts as a sink for protons. Caselli et al. (1993) proposed a mechanism to account for the initial differentiation in the ices, but recent observations suggest that NH₃ and CH₃OH do in fact coexist in interstellar ices (Gibb et al. 2000). Rodgers & Charnley (2001a) showed that the N/O differentiation may actually be an age/temperature effect, since ‘cool’ (T ≈ 100 K) cores will eventually
lose their NH$_3$ after $\sim 10^5$ yrs, whereas at higher temperatures endothermic reactions become rapid enough to ensure that the NH$_3$ abundance never drops substantially, and hence large abundances of O-rich organics never evolve. Similar age/temperature effects may also be apparent in the sulphur chemistry, since the presumed parent molecule, H$_2$S, is processed into HS, S, S$_2$, SO, SO$_2$, H$_2$CS, and CS, the peak abundances of which depend on the core temperature (which controls the O$_1$ abundance) and age. Therefore, observed abundance differences in sulphuretted hot core molecules may be used to constrain the age of the cores, and place limits on the time-scale for this phase of the star formation process (Charnley 1997b).

Finally, an alternative explanation for the chemical variety amongst hot cores lies in the nature of the source which drives the mantle evaporation and the gas phase chemistry. All the models discussed above assume temporally constant temperatures and densities. This will be (roughly) appropriate for cores which are heated radiatively, but it is likely that many hot cores have experienced the passage of shock waves caused by the impact of protostellar outflows into the surrounding natal cloud material. In this case the postshock temperature can reach values higher than 1000 K (e.g. Draine & McKee 1993), this permits many reactions which are endothermic, or have activation energy barriers, to occur. For example, Charnley & Kaufman (2000) showed that the low abundances of CO$_2$ observed in hot cores can be explained if these regions are heated by shocks. Shock waves can also erode the refractory grain cores and the release of silicon, observed to be highly depleted in cold clouds, is now understood to account for the presence of SiO in star-forming regions (Schilke et al. 1997). These considerations ensure that a thorough understanding of hot core chemistry requires detailed chemical modelling, since only when all possible gas phase production routes have been investigated and ruled out, is it possible to infer that a particular molecule is a parent in the original ice. Through this type of modelling, we can gradually build up a secure inventory of interstellar ices (cf. Ehrenfreund & Charnley 2000). Comparison of inferred ice composition with that observed by the ISO satellite will allow us to determine the processing that the ices undergo as they are irradiated and evaporated by nearby protostars.

Comets

The modern view of comets began with the work of Whipple (1950), who proposed the ‘icy conglomerate’, or ‘dirty snowball’ model of comet nuclei. Over the years this model has been refined, particularly after the discovery in comet Halley of large, so-called ‘CHON’, organic particles (Kissel et al. 1986), and comets are now known to consist of roughly equal parts by mass of ice (mainly water, with $\sim 10\%$ CO and CO$_2$), inorganic refractories (mainly silicates), and organic refractories (CHON particles and other carbonaceous material) (Greenberg 1998). The ices also contain trace amounts of other molecules at the $\sim 1\%$ level or less (Table 1) – although only a minor constituent of the comet as a whole, these species are very important, since they can be used to trace the conditions under which comets were formed. The recent detection of Argon in comet Hale-Bopp (Stern et al. 2000) is proof that this comet has undergone very little thermal processing since its formation, as Ar sublimates at $T \approx 35$ K.

Based on their orbital characteristics it is possible to divide comets into two distinct populations: long- and short-period comets. A more strict classification is based on the Tisserand invariant, $T$; comets with $T > 2$ (short-period comets) are thought to originate from the Kuiper belt (located at a heliocentric distance $30 < r_h \lesssim 50$ AU), whereas long-period comets come from the Oort cloud ($r_h \sim 5 \times 10^4$ AU). The current consensus is that Kuiper belt comets most probably formed near their current location, whereas Oort cloud comets were formed somewhere in the giant planet region of the protosolar nebula ($5 \lesssim r_h \lesssim 30$ AU), before being ejected to their present position via gravitational interaction with these planets (Weissman 1999). If this picture is correct, one would expect to see chemical differences between the two populations. This indeed seems to be the case for carbon chains; A’Hearn et al. (1995) showed that short-period comets are much more likely to be depleted in C$_2$ and C$_3$ than long-period comets. More recently, Mumma et al. (2000) observed ethane in the short period comet Giacobini-Zinner, and showed that it too is depleted relative to the long-period comet Hale-Bopp.

Our detailed knowledge of the molecular inventory of comets has been revolutionised in the past few years by the apparitions of the bright comets Hyakutake and Hale-Bopp; many of the molecules listed in Table 1 were observed for the first time in Hale-Bopp (Bockelée-Morvan et al. 2000). The use of interferometers allowed the first detailed maps to be made of the distributions of molecules in the coma (e.g. Blake et al. 1999; Kuan et al. 2001a). Mapping of ions such as HCO$^+$ also allowed the structure of the cometary ionosphere
to be determined (e.g. Lovell et al. 1997), and showed that ion-molecule chemistry may be important in the coma since, for example, HCO$^+$ is formed from proton transfer to CO. The results of this mapping showed that, in addition to a nuclear source, some molecules also appeared to have an extended source in the coma. Although this was previously known to be the case for formaldehyde in comet Halley (Meier et al. 1993), it is now known that CO, OCS, HCN, and HNC also had extended sources in Hale-Bopp. Various theories exist to explain these distributions; it may be that these molecules are formed via photodissociation of some unknown parent, or they may be sublimating directly from icy grains in the coma. Alternatively, as in hot cores, these species and many others could possibly have been produced via post-sublimation gas-phase chemistry occurring in the coma.

In order to quantitatively assess the potential for chemical reactions to alter the composition of the coma, we have developed a model of the chemistry and physics in the coma (Rodgers & Charnley 2001d). Despite the differences in the physical parameters and the molecular lifetimes, the chemistry taking place in the coma is analogous in many ways to that which occurs in hot cores. However, because the physical conditions change throughout the coma, it is necessary to calculate the hydrodynamics in tandem with the chemistry and this ensures that the development of realistic coma models is a far more demanding task. Briefly, the model simultaneously solves the conservation equations for abundances, mass, momentum and energy appropriate for a steady spherical outflow. Endothermic chemical reactions driven by suprathermal H atoms are included, along with all the important microphysical processes that determine the heating and cooling in the coma. As described below, we have used this model to investigate possible production routes for HNC and complex organics, as well as the potential of gas-phase chemistry to alter D/H ratios in the coma (Rodgers & Charnley 1998, 2001b,c,d).

**COMPLEX ORGANICS**

**Interstellar Medium**

It has become clear in recent years that the ISM contains a large population of polycyclic aromatic hydrocarbon (PAH) molecules (e.g. Léger & Puget 1984; Allamandola et al. 1985), with a typical size of ∼20–100 C atoms. PAHs are thought to account for ∼10% of the interstellar carbon budget, and are most likely formed in the outflows of evolved stars (Frenklach & Feigelson 1989). However, it has not yet proved possible to definitively identify specific PAH molecules. The largest positively-identified molecule thus far detected in the ISM is HC$_{11}$N (Bell et al. 1997). Yet, despite containing 13 atoms, structurally this is a simple linear chain molecule. In terms of structure the most complex interstellar molecules are seen in hot cores, where molecules such as ethanol, dimethyl ether, ethylene oxide, methyl formate, acetic acid, and glycolaldehyde have been detected. The latter three molecules are isomers of each other, as are ethanol and dimethyl ether. It is clear that any comprehensive theory of interstellar chemistry should be able to explain the prevalence of some isomers over others. In the previous section we discussed how the molecular abundances in hot cores are determined by two different chemical processes; surface chemistry in the cold gas prior to the formation of the hot core, and hot post-evaporation gas phase chemistry. Here we briefly describe a unified scheme to explain the observed molecular complexity in these regions (cf. Charnley 1997a, 2001; Charnley et al. 2001b).

Unconstrained grain surface reactions can potentially produce many molecules (e.g. Caselli et al. 1993), however, such models cannot account for the specific abundances seen in hot cores. We therefore limit the surface chemistry to consist of atomic addition reactions (one atom at a time), with the further constraint of radical stability imposed on the intermediate organic radicals. This results in surface production of alcohols and amines, although the existence of energy barriers for H addition to double and triple bonds may mean not all molecules are fully reduced, resulting in some aldehydes, ketones, and nitriles. This scheme naturally accounts for the methanol, formaldehyde, ethanol, ketene, acetaldehyde, vinyl cyanide, and ethyl cyanide seen in hot cores (Charnley 1997a). It can also explain the existence of the ring molecule ethylene oxide (c-C$_2$H$_4$O) via O atom addition to the C$_2$H$_3$ radical, which is formed when H atoms react with acetylene. If instead of an O atom an N atom is added to C$_2$H$_3$, either methyl cyanide or vinylmine can result; however a ring structure is also possible and this results in the azirines 1-H azirine (H(c–C=N–C)H$_2$) and 2-H azirine (H(c=C=C=NH)H). Complete reduction via addition of two further H atoms will result in aziridine (H$_2$(C–NH–C)H$_2$). We therefore searched for these molecules in several hot cores with the NRAO 12m telescope (Kuan et al. 2001b; Charnley et al. 2001b). Figures 1 and 2 show tentative detections of the
azaheterocycles 2-H azirine and aziridine in Orion-KL, Sgr B2(N) and W51.

Whilst surface chemistry can account for the molecules discussed above, there are other molecules observed in hot cores that cannot be explained by this mechanism, such as dimethyl ether and methyl formate. Such molecules must therefore be formed in the warm gas; a plausible mechanism is alkyl cation transfer reactions, whereby a protonated alcohol transfers an alkyl group to a neutral base i.e.

$$\text{ROH}^+ + \text{R}'\text{X}\rightarrow \text{R}'\text{XR} + \text{H}_2\text{O}$$

Many of these reactions have been measured in the laboratory and found to be rapid (e.g. Mautner & Karpas 1986), and methanol and ethanol are known to be abundant in hot cores. Thus, dimethyl ether can be formed via self-methylation of methanol, and methyl formate may arise from reactions of $\text{CH}_3\text{OH}^+$ with $\text{H}_2\text{CO}$ or HCOOH (Charnley et al. 1995, 2001b). Transfer of methyl groups to other common hot core species can produce many other large molecules, e.g. $\text{CH}_3\text{NCO}$, $(\text{CH}_3)_2\text{CO}$, $\text{NH}_2\text{COCH}_3$, $\text{CH}_3\text{OC}_2\text{H}_5$, isocyanides and large amides (Ehrenfreund & Charnley 2000; Charnley & Rodgers, in preparation). Another predicted product is diethyl ether, which was tentatively detected by Kuan et al. (1999).

Finally, it is possible that the type of reactions we have discussed may lead to glycine, the simplest amino acid. The surface chemistry scheme we described can lead to aminomethanol, via hydrogenation of HNCO. Alternatively, aminomethanol is thought to be formed when ices containing $\text{H}_2\text{O}$, $\text{NH}_3$, and $\text{H}_2\text{CO}$ are heated (Woon 1999). In either case, one would expect significant abundances of aminomethanol to be evaporated into hot cores, and subsequent protonation followed by reaction with HCOOH may form glycine (Charnley 1997a). Despite many searches over the years, glycine has yet to be detected in the ISM, but recent tentative identification of several lines suggest that it may soon be conclusively identified (Charnley et al. 2001b).
Comets

The brightness of comet Hale-Bopp means that it is the only comet in which many large organic molecules have been positively detected. The largest molecule observed in Hale-Bopp is methyl formate (HCOOCH$_3$) (Bockelée-Morvan et al. 2000), and Kuan et al. (2001a) reported a tentative detection of its structural isomer acetic acid (CH$_3$COOH). As discussed above, these molecules are also seen in hot cores where they are thought to be daughter species. Thus, it is possible that the HCOOCH$_3$ (and CH$_3$COOH) seen in Hale-Bopp were actually created in the coma. In order to investigate this possibility, we used our comet model to follow the organic chemistry which occurs in the coma following the sublimation of methanol rich ices from the nucleus (Rodgers & Charnley 2001b). We find that chemical reactions cannot form sufficient quantities of HCOOCH$_3$ and other organic molecules detected in Hale-Bopp: HCOOH, HC$_3$N and CH$_3$CN. Therefore, these species must be present in the nuclear ice. Hence it appears that cometary ices are more processed than their interstellar counterparts, which is consistent with primordial interstellar ices being evaporated, perhaps within the protosolar nebula, undergoing a hot core-like phase of chemical processing, then refreezing onto pre-cometary grains. However, we cannot be absolutely certain that these large organics are daughter molecules in hot cores, and they may also be present in interstellar ices. One way to determine the origin of these molecules may be to use D/H and $^{13}$C/$^{12}$C ratios (Rodgers & Millar 1996; Rodgers & Charnley 2001e; Charnley et al. 2001c).

Photo-fragmentation of cometary CHON particles, first detected by the Giotto probe in the coma of comet Halley, has been proposed to account for the extended sources seen for many molecules and radicals in the coma, in particular CO, C$_2$, H$_2$CO, CN and NH$_2$. Specifically, to account for the coma sources of CO and H$_2$CO, and also the regular peaks in the mass spectra of CHON particles seen by Giotto, it has been proposed that a substantial fraction of the CHON material consists of the formaldehyde polymer, polyoxymethylene (POM, $[-\text{CH}_2\text{O}-]_n$) (e.g. Huebner 1987). Other potential candidates include hexamethylenetetramine (HMT, C$_6$H$_{12}$N$_4$; Bernstein et al. 1995), polyaminocynaomethylene (PACM, $[-(\text{NH}_2)\text{C(CN)}-]_n$; Rettig et al. 1992), and PAHs (specifically phenanthrene, C$_{14}$H$_{10}$; Moreels et al. 1994). It is likely that a mixture of many types of organic particles are actually present in comets, but we may be able to constrain the amounts of the different types if we can model the predicted production rates for daughter molecules, and compare them with the observations.

THE HNC/HCN RATIO

Interstellar Medium

The HNC/HCN ratio varies a great deal in the ISM, with an inverse temperature dependence: in cold dark clouds the ratio is typically $>1$, whereas in hot cores it is low. This was previously thought to be caused by three factors; i) low temperature ion-molecule reactions preferentially forming HNC via the H$_2$NC$^+$ ion, ii) proton transfer reactions cycling between the two isomers via the HCNH$^+$ ion, and iii) high temperature isomerization reactions transforming HNC into HCN. However, recent quantum chemical calculations have showed that assumptions (i) and (iii) are incorrect (e.g. Talbi et al. 1996).

In hot cores, HCN and HNC are thought to be daughter species, since HCN is produced efficiently from reactions of NH$_3$ and C$^+$; at high temperatures ($>250$K) the reaction of CN with H$_2$ ensures that the net destruction rate of HCN is extremely small (Rodgers & Charnley 2001a). Proton transfer to HCN to form HCNH$^+$ followed by recombination or proton transfer to ammonia forms HNC, and models predict HNC/HCN ratios of $\sim 0.007$–0.05 for a 300 K core, depending on the age and the initial NH$_3$ abundance. This is in reasonable agreement with the observed value in these regions, but we are still unable to explain the excess of HNC in cold clouds.

Comets

HCN has been seen in many comets, but HNC was detected for the first time in comet Hyakutake, where it was present with an abundance relative to HCN of 6% (Irwin et al. 1996). HNC was subsequently detected in comets Hale-Bopp and Lee, and the HNC/HCN ratio in Hale-Bopp showed a strong increase as the comet approached perihelion, from $<0.02$ at 2.5 AU to $\sim 0.16$ at 1 AU (Irwin et al. 1998). The Hyakutake results were originally interpreted as proof that cometary ices contain unprocessed material from the ISM, but the observations of Hale-Bopp proved conclusively that HNC must be a daughter species, and that its production is related to the solar photon flux and/or coma temperature.

We have used our comet model to investigate possible chemical production routes to HNC in the coma.
(Rodgers & Charnley 1998, 2001c). We find that ion-molecule chemistry is unable to synthesise the observed quantities of HNC, but that endothermic isomerisation reactions of HCN, driven by suprathermal H atoms produced in the photodissociation of parent molecules, may be efficient in large, active comets such as Hale-Bopp. However, in comets Hyakutake and Lee we demonstrated that HNC must be produced via the photodestruction of some unknown parent. Possible molecular candidates are HNCO and CH$_2$NH, but the former is thought to be photodissociated into NH + CO and/or H + OCN, whereas the latter is not observed in comets. Hence, we consider it most likely that HNC is coming from CHON particles in the coma, and conclude that the most likely candidate is PACM (cf. Rettig et al. 1992). This source of HNC may also account for the extended sources of HCN and CN in the coma.

**CARBON CHAINS**

**Interstellar Medium**

Carbon chain molecules appear to be almost equally abundant in both the diffuse ISM and dense clouds (Allamandola et al. 1999), and it has been proposed that C-chain anions may be responsible for some of the diffuse interstellar bands (Tulej et al. 1998). The overall abundance of long C-chains ($\gtrsim 10$ C atoms) in diffuse clouds is $\sim 10^{-10}$ with respect to hydrogen, and they are thought to account for a few parts per million of the total cosmic carbon. In comparison, $\sim 10\%$ of the total cosmic carbon is in PAHs (see above). Carbon chains are thought to be formed via neutral-neutral C-insertion reactions involving CN and C$_2$H radicals (Fukuzawa et al. 1998).

The overall abundances of chain molecules are derived from infrared observations of C=C vibrational transitions; in order to identify specific molecules one must look at rotational transitions at millimeter wavelengths. The largest molecule identified to date is HC$_{11}$N which was seen in the dark cloud TMC-1 (Bell et al. 1997). The abundances decrease with increasing chain length, and this detection is at the limit of current telescope capabilities, making the detection of longer chains difficult in the near-term. However, in recent years the spectra of a large number of chain molecules have been accurately characterised in the laboratory (e.g. McCarthy et al. 2000), and so future observations may be able to distinguish the precise molecular nature of the smaller chains ($\leq 10$ C atoms).

**Comets**

Although there is no direct evidence for carbon chains in comets, the presence of the C$_2$ and C$_3$ radicals suggests that they are fairly abundant. The longest chain molecule positively detected in a comet is HC$_3$N, which is a parent species in Hale-Bopp (Rodgers & Charnley 2001b). This suggests that longer cyanopolyynes may also be present in the nucleus, albeit in lower abundances. It is interesting that C$_2$ and C$_3$ are observed to be depleted in some Kuiper belt comets (A’Hearn et al. 1995), implying that C-chain molecules are more abundant in Oort cloud comets. This can be explained if these chains were formed more efficiently in the warmer, giant planet region of the protosolar nebula than the Kuiper Belt region. Alternatively, chain molecules may form readily in both regions, but undergo further processing in the outer region, perhaps involving saturation or the formation of ring molecules and fullerenes. We previously discussed the probable contribution of polymeric material to the CHON particles in comets (e.g. Huebner 1987; Rettig et al. 1992). However, this material cannot be unequivocally identified via spectroscopy of the coma, and we must wait until the Stardust mission returns a sample of comet dust to the Earth for laboratory analysis before we can properly understand the nature of the CHON grains.

**DEUTERIUM FRACTIONATION**

**Interstellar Medium**

The overall D/H ratio in our galaxy is $\approx 1.6 \times 10^{-5}$, but the D/H ratios in some molecules can be up to $10^4$ times larger, since at low temperatures small zero-point energy differences result in the fractionation of ions such as H$_2$D$^+$, C$_2$HD$^+$, and CH$_2$D$^+$. Ion-molecule chemistry spreads the D-enrichment to a variety of molecules, and the observed D/H ratios can be used to constrain the gas temperature, the electron fraction, and the depletion of heavy elements (e.g. Millar et al. 2000). In addition, spatial variations in D/H ratios may allow the propagation of Alfvén waves to be traced in molecular clouds (Charnley 1998). The D/H ratios observed in interstellar molecules can also be used to probe the chemical mechanisms which form those molecules. Rodgers & Millar (1996) showed that D/H ratios in hot cores trace the values in the precursor ice, and Charnley et al. (1997) used this fact to show that the hot core abundances of the two isotopomers
of deuterated methanol – CH$_2$DOH and CH$_3$OD – should always have a ratio of 3:1 if methanol is formed on grains via hydrogenation of CO. Rogers & Charnley (2001e) considered NH$_3$ production in dense cores, and showed that although the total fractionation of ammonia may vary from source to source, for a specific chemical production mechanism the ratio of the multiply deuterated isotopomers should be constant, and may be used to distinguish between gas phase and surface production of ammonia.

Comets

To date, the only deuterated molecules observed in comets are HDO and DCN. HDO was detected in Halley, Hyakutake, and Hale-Bopp, and the observed HDO/H$_2$O ratios lie in the range 5.7–6.6$\times$10$^{-4}$ (e.g. Meier et al. 1998a). DCN was seen only in Hale-Bopp, where a DCN/HCN ratio of 0.002 was determined (Meier et al. 1998b), although Blake et al. (1998) showed that the DCN/HCN ratio was a factor of ten larger in the dust jets. We have used our comet model to follow the deuterium chemistry which occurs in the coma and find that, as in hot cores, post-evaporation chemistry does not significantly alter the initial D/H ratios (Rodgers & Charnley 2001d). Therefore, for parent species we can use the observed coma ratios to infer the nuclear D/H ratio, and for daughter species we can use these ratios to constrain the nature of the parent and the chemical mechanism by which the species are formed. In particular, if the DNC/HNC ratio can be determined in a comet, we may be able to ascertain the origin of cometary HNC, which is currently not well understood (see above).

Comparison of cometary D/H ratios with interstellar values may be used to determine the physical conditions in the protosolar nebula, since it is likely that the original interstellar values were altered by chemical processing and/or mixing in the nebula (Aikawa & Herbst 1999; Mousis et al. 2000). The observed D/H ratios in comets are similar to the values in hot cores, but since HCN could possibly be a daughter species in hot cores, this leaves only one molecule, HDO, for which comparisons are currently possible. Future observations of other deuterated cometary molecules are therefore vital. An exciting recent development is the first tentative detection of HDCO in a comet, Hale-Bopp (Kuan et al. 2001a). A determination of the HDCO/H$_2$CO ratio, when combined with the known D/H ratios in water and hydrogen cyanide, will further constrain models of cometary origin. It is also useful to compare cometary D-enrichment with that seen in the Earth’s oceans – it appears that comets have twice as much deuterium as the Earth, which casts doubt on the assertion that comets brought the bulk of the volatiles to the Earth. On the other hand, Delsemme (2000) has argued that the Earth’s water was deposited mainly by deuterium-poor comets formed in the inner region of the protosolar nebula; such comets should account for ~4% of the Oort cloud’s population.

CARBON AND NITROGEN FRACTIONATION

Interstellar Medium

Heavy isotopes of carbon and nitrogen, $^{13}$C and $^{15}$N, are formed in low- to intermediate-mass stars, and so their abundances relative to $^{12}$C and $^{14}$N increase toward the galactic center (e.g. Boogert et al. 2000). Langer et al. (1984) modelled the fractionation in $^{13}$C occurring in interstellar molecules, and concluded that it is preferentially locked up in CO, and hence depleted in species such as C$^+$, H$_2$CO, CS, CH, and HCN. Terzieva & Herbst (2000) modelled the fractionation occurring in $^{15}$N, and concluded that in typical dark clouds the resulting fractionation is negligible. However, there is growing evidence for the presence of ‘depletion cores’ in some clouds, where most of the molecules have frozen out onto grains, but some N$_2$ remains in the gas phase (e.g. Charnley 1997c; Caselli & Walshes 1999; Bergin et al. 2001). In this case, only simple N-bearing molecules are present in the gas, and significant fractionation can occur (Charnley & Rodgers 2001).

Comets

No significant fractionation is seen in cometary dust (Jessberger 1999), except for some grains which are strongly depleted in $^{13}$C, which are thought to be unprocessed presolar grains formed in the outflows of massive stars. In cometary volatiles, the $^{12}$C/$^{13}$C ratios have been determined from observations of C$_2$, CN, and HCN in a number of comets (Wyckoff et al. 2000), and are found to lie in the range 85–93, consistent with the terrestrial value of 90. The cometary $^{14}$N/$^{15}$N ratio has been measured in CN and HCN (Crovisier & Bockelée-Morvan 1999), and is found to equal 323, slightly larger than the terrestrial value of 272. However, the $^{15}$N/$^{14}$N ratio is seen to vary amongst different solar system objects, and the initial protosolar value is uncertain (e.g. Kallenbach et al. 1998). Large $^{15}$N enhancements are seen in some
meteoritic and interplanetary dust particle material (Messenger & Walker 1997), and the measurement of a large $^{15}\text{NH}_3/^{14}\text{NH}_3$ ratio in a comet would provide positive evidence for the interstellar fractionation scenario proposed by Charnley & Rodgers (2001).

**SULPHURETTED MOLECULES**

**Interstellar Medium**

The sulphur chemistry in cold clouds is not fully understood. Gas phase sulphur appears to be depleted in dark clouds by a factor of 100-1000 relative to its cosmic abundance, whereas it is undepleted in the diffuse ISM (e.g. Ruffle et al. 1999). It is clear that somehow sulphur must become preferentially incorporated into refractory material as compared with C, N and O. The only solid phase sulphuretted molecule detected to date is carbonyl sulphide (OCS) which has an abundance relative to H$_2$O of 0.04–0.1% (Palumbo et al. 1997). In hot cores, a wide variety of S-bearing molecules are observed. Charnley (1997b) modelled the sulphur chemistry occurring after the evaporation of H$_2$S, and showed that all the observed sulphuretted species except OCS can be formed in the hot gas from this one parent molecule. The predicted abundances of different S-bearing daughter molecules depend on the core age and temperature, which means that observations of species such as SO and SO$_2$ may be used as ‘chemical clocks’ to determine the ages of the cores (e.g. Hatchell et al. 1998).

**Comets**

To date, eight S-bearing molecules have been detected in comets, four of them solely in Hale-Bopp (Crovisier & Bockelée-Morvan 1999). Many of these are also observed in hot cores, so it is possible that sulphuretted cometary molecules are formed in the coma from reactions of H$_2$S. We have previously discussed the fact that the organic molecules seen in Hale-Bopp cannot have been formed via coma chemistry, which appears to suggest that the S-bearing molecules in Hale-Bopp must also have been present in the nucleus. However, hot core organic chemistry is driven by ion-molecule reactions, whereas the sulphur chemistry is initiated by the reaction of H$_2$S and H to form SH, which has a barrier of $\sim 860$ K. The large abundances of suprathermal H atoms in the inner coma may therefore be instrumental in rapidly converting H$_2$S into other molecules (cf. Rodgers & Charnley 1998).

**CONCLUSIONS**

In this article we have presented a review of our current understanding of the organic chemistry that can occur in dense molecular clouds and in comets. By comparing the respective molecular inventories of interstellar and cometary environments we can begin to elucidate the degree of alteration of the interstellar material as it becomes incorporated into protostellar nebulae. In the next decade, astronomical observations of distant star-forming regions, combined with analyses of meteoritic and cometary samples, should allow the relative degree of pristinity of cometary material to be determined. Space-based telescopes of relevance to interstellar and cometary chemistry include SIRTF, FIRST-Herschel, NGST, and SOFIA. Although cometary H$_2$O can be detected from the ground through radiatively pumped ‘hot-band’ lines (Dello Russo et al. 2000), space-based observatories are essential to overcome the telluric extinction affecting most water lines. SWAS has observed H$_2$O in comets Lee and McNaught-Hartley (Neufeld et al. 2000), and FIRST-Herschel should allow the determination of HDO/H$_2$O in a large sample of comets, including both short and long period comets. The Stardust mission, although still some years from its encounter with comet P/Wild 2, has already detected interstellar dust particles. Preliminary results indicate that these particles are very similar to the complex organics seen in comet P/Halley, providing further evidence for a link between interstellar and cometary materials; such particles are understood to be destroyed in cometary comae to provide the observed ‘extended sources’ of molecules (e.g. Huebner 1987; Meier et al. 1993). Finally, the Rosetta mission will be launched in 2003 and is due to rendezvous with comet P/Wirtanen in 2011. The Rosetta lander module will allow the first in situ examination of the nature of a cometary nucleus, including the determination of the elemental, molecular and isotopic composition of the surface and subsurface layers. Assimilation and interpretation of the data returned by each of these missions will represent a significant advance in the quest for a detailed understanding of the connection between interstellar and cometary organic material.
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