

Pathways to Molecular Complexity

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Abstract. Pathways leading to the formation of complex organic molecules are described. Gas-phase processes that may build large carbon-chain species in cold molecular clouds are summarised. Catalytic reactions on grain surfaces can lead to a large variety of organic species, and model calculations of mantle formation by atom additions to multiply-bonded molecules are presented. The subsequent desorption of these mixed molecular ices can initiate a distinctive organic chemistry via ion-molecule pathways. The predictions of this theory are briefly compared with observations to show how possible organic formation pathways in the interstellar medium may be constrained.

Keywords. astrobiology — astrochemistry — ISM: chemistry — ISM: molecules

1. Introduction

Well over one hundred molecules have been discovered in the interstellar medium† (ISM), with the largest molecule detected to date containing 13 atoms (HC_{11}N ; Bell *et al.* 1997). A large variety of different types of species are present, including alcohols, aldehydes, ethers, carboxylic acids, amines, nitriles, etc. Several of these organic molecules have also been observed in the gaseous comae of comets (e.g., Bockelée-Morvan *et al.* 2000), including the recent detection of ethylene glycol in comet Hale-Bopp (Crovisier *et al.* 2004). Laboratory analysis of meteoritic material has revealed a complex organic component (Botta, this volume), including numerous amino acids (Cronin & Chang 1993). The enhanced D/H ratios in both cometary and meteoritic molecules suggest an interstellar heritage for some solar system material, and raise the question of how much of the prebiotic organic material present on the young Earth can be traced to interstellar precursors (Ehrenfreund & Charnley 2000). The detection in the ISM of the smallest sugar and amino acid (Hollis *et al.* 2000; Kuan *et al.* 2003), indicates that significant complexity can arise in interstellar gas before planetary systems begin to form.

Several of the molecules observed in the ISM are isomers (e.g., ethylene oxide, acetaldehyde, vinyl alcohol); others correspond to more or less reduced forms of the same heavy-atom ‘backbone’ (e.g., hydrogen cyanide, methanimine, methylamine). A key challenge in astrochemistry is to determine the chemical mechanisms that lead to large molecules, whilst also explaining the relative abundances of different isomers and the differing degrees of hydrogenation. In this paper we discuss three pathways that have been proposed to account for the formation of complex molecules: (i) cold gas-phase processes occurring in dark clouds which lead to the growth of long carbon chains, (ii) atom addition reactions on the surfaces of interstellar dust grains, leading to more reduced species such as aldehydes and alcohols, and (iii) gas-phase processes in warm gas where icy grain mantles have evaporated, seeding the gas with large abundances of specific molecules, which proceed to react to form more complex species.

† See http://www.molres.org/astrochymist/astrochymist_mole.html for a current list of all detections.

2. Carbon Chains and Carbonaceous Dust

2.1. Formation Mechanisms

The rapid condensation of carbonaceous dust in the outflows of evolved stars is thought to be initiated by the formation of small polycyclic aromatic hydrocarbons (PAHs) driven by reactions of acetylene molecules (Frenklach & Feigelson 1989; Cherchneff *et al.* 1992). An important recent development has been the realization that nitrogen heterocycles (a.k.a. PANHs) may be abundant in space (see Hudgins, this volume; Charnley *et al.* 2005). Ricca *et al.* (2001) showed how additions of HCN as well as C_2H_2 can lead to PANHs rather than PAHs—Figure 1 illustrates this process for the formation of the two-ring PANHs quinoline and isoquinoline. Alternatively, grains may form via carbon-chain growth, followed by spontaneous ring closure (e.g., Tielens & Charnley 1997). The growth of small C-chains is driven by neutral-neutral reactions involving C_2H and C_2 (Cherchneff & Glassgold 1993; Millar *et al.* 2000). Cyanopolyne formation is initiated by neutral-neutral reactions involving the CN radical (Fukuzawa *et al.* 1998). Similar processes are also able to form the observed abundances of carbon-chain molecules in dark interstellar clouds, following the removal of acetylene and methane from grain mantles (Markwick *et al.* 2000).

2.2. Dust Destruction in PDRs and Comets

Observations of hydrocarbons in photodissociation regions (PDRs) have revealed large abundances of many species, greatly elevated above the amounts predicted by traditional chemical models. For example, Teyssier *et al.* (2004) derive a C_6H abundance of 10^{-10} in the Horsehead nebula. These observations have been interpreted as being caused by UV-driven fragmentation of PAHs or small C-rich grains (Pety *et al.* 2005). Guélin *et al.* (1999) suggested that UV destruction of dust grains could be responsible for enhanced abundances of small C-chains in the outer regions of circumstellar envelopes.

Destruction of large organic macromolecules as a source of smaller species has also been proposed to occur in the comae of comets close to the Sun. Measurements by the Giotto probe as it passed through the coma of comet Halley showed that much of the H_2CO seen in the coma was not sublimating from the nucleus, but must have an extended coma source (e.g., Meier *et al.* 1993). This fact, together with regularly spaced peaks in the mass spectrometer data, led Huebner (1987) to suggest that the formaldehyde polymer polyoxymethylene (POM) was an important constituent of the refractory organic component of cometary dust. Laboratory experiments on the thermal

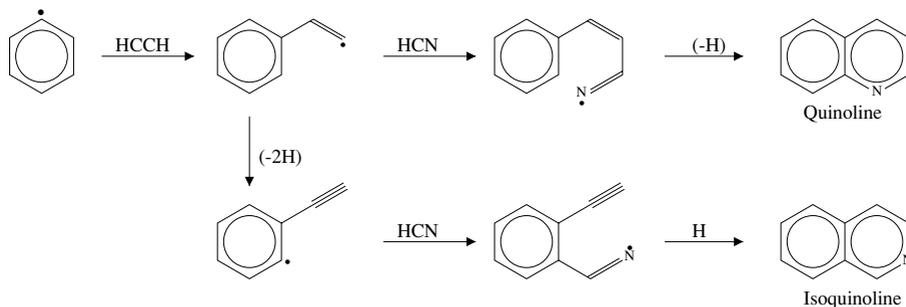


Figure 1. PANH formation via C_2H_2 and HCN addition to phenyl radicals (from Charnley *et al.* 2005). The position of the N in the final molecule depends on the details of the reaction mechanism (Ricca *et al.* 2001; Peeters *et al.* 2005).

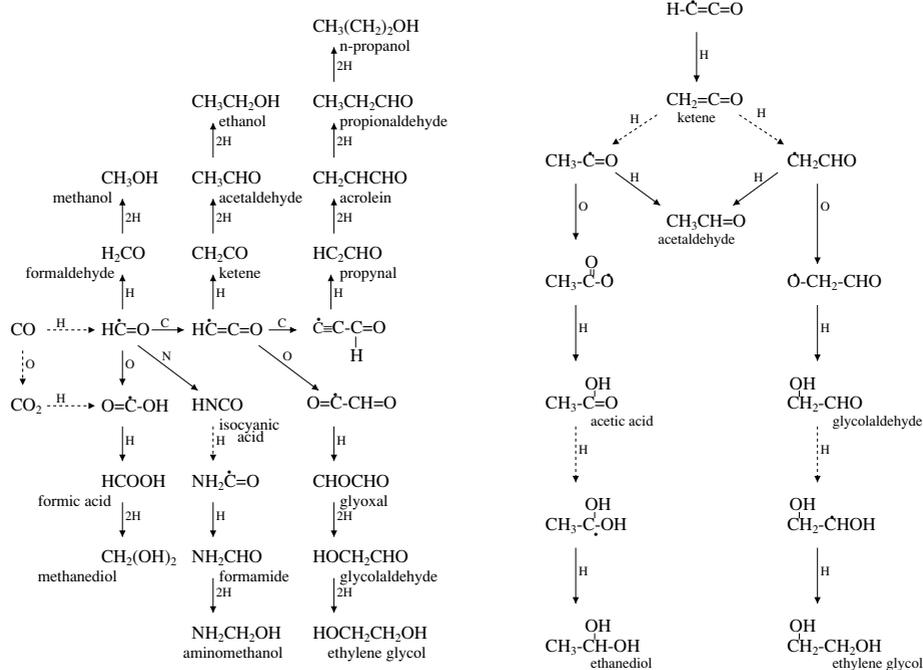


Figure 2. Grain-surface atom addition reactions starting from CO. The right hand side shows the alternative pathways that can arise if an O rather than an H atom adds to the $\text{C}_2\text{H}_3\text{O}$ radical.

degradation of POM confirm that this scenario is feasible (e.g., Cottin *et al.* 2004), and POM is known to be produced when H_2CO -rich ices are warmed to 40–80 K (Schutte *et al.* 1993). Erosion of N-bearing macromolecules has been proposed to account for the excess HNC and CN production seen in comets at small heliocentric distances (Rodgers *et al.* 2003; Fray *et al.* 2005). This idea is corroborated by the large $\text{C}^{15}\text{N}/\text{C}^{14}\text{N}$ ratios detected in several comets—around twice that of the $\text{HC}^{15}\text{N}/\text{HC}^{14}\text{N}$ ratio—which have been ascribed to the destruction of ^{15}N -rich presolar material (Manfroid *et al.* 2004).

3. Grain-Surface Chemistry

3.1. Atom Addition Reactions

As species freeze out onto the surfaces of interstellar dust grains, they can combine with other species to form larger molecules. At the low temperatures in the ISM, only atoms are likely to be mobile on grains, and the dominant reaction mechanism will be atomic addition reactions. Laboratory experiments have demonstrated that H atoms can tunnel through barriers to react with stable species such as C_2H_2 , CO and H_2CO (Hiraoka *et al.* 2000; Watanabe *et al.*, this volume), and it is probable that interstellar CO_2 ice forms via oxidation of CO (e.g., Roser *et al.* 2001). The type of chemistry occurring will depend on the relative accretion rates of different atoms: if the accretion rate of C atoms is high, unsaturated C-chains will result, whereas at late times after most heavy atoms have frozen out, the accretion will be dominated by H atoms and so we expect the upper layers of ice mantles to be dominated by reduced species such as H_2CO and CH_3OH .

An important constraint that will influence the type of molecules formed on the surface is that at each stage the most stable radical will be formed. Unfortunately, very little

is known about the relative stability of many radical isomers, with the exception of the $\text{CH}_2\text{OH}/\text{CH}_3\text{O}$ system (Jodkowski *et al.* 1999). An additional constraint is that H atoms will break double and triple bonds in sequence so that weaker bonds are broken first; $\text{C}\equiv\text{O}$, $\text{C}=\text{C}$, $\text{C}\equiv\text{C}$, $\text{C}=\text{O}$ (Charnley 2001a). Figure 2 shows an example of some of the surface pathways that are allowed under these constraints. Extensions to this scheme involving larger molecules or the addition of nitrogen atoms are also possible (e.g., Charnley 1997; Ehrenfreund *et al.* 2005). Finally, a further complication that can arise is that back reactions can occur, *i.e.*, rather than simply adding to a radical, an H atom may abstract another H to form H_2 . These types of reactions may be particularly important in determining the deuterium fractionation in certain molecules, as D abstraction may be energetically inhibited (e.g., Tielens 1983; Nagaoka *et al.* 2005).

3.2. Stochastic Simulation

Although numerous models have been developed to model grain-surface chemistry, almost all suffer from two problems. The first is that these models typically solve the chemical evolution using the mass action kinetics (*i.e.*, systems of coupled ordinary differential equations) used to follow gas-phase chemistry. However, when the typical number of atoms on the surface of each individual dust grain is small, the use of mean abundances leads to gross errors in the model predictions (Charnley *et al.* 1997; Tielens & Charnley 1997). In this case, accurate solutions can only be obtained via stochastic simulation of the chemical master equation (Charnley 1998, 2001b). The second problem is that only species on the surface may take part in the chemical processing. Models which assume that all solid molecules are available to react will therefore give incorrect results, and are unable to follow the chemical differentiation that arises in sequential ice layers as the relative accretion rates of gas-phase species vary.

In order to accurately calculate the grain-surface chemistry it is essential that both the gas-phase and surface chemistry are followed simultaneously. We have developed a coupled gas-grain model that solves the master equation using the Monte Carlo algorithm of Gillespie (1976) (Rodgers & Charnley 2005). In addition to gas-phase and surface processes, we include accretion and desorption, and we also consider the covering and uncovering of surface species, assuming that there are 10^6 surface sites available. To resolve a single dust grain requires that a gas volume containing $\sim 10^{12}$ H_2 molecules is considered. Figure 3 shows the results for the surface abundances and bulk mantle fractions for a model in which surface species as large as propanol are considered. At early times, C atoms compete effectively with H atoms, and C-chain radicals are formed and subsequently hydrogenated. At late times, H additions dominate the surface chemistry, and methanol becomes the primary product.

3.3. Secondary Processing: Photolysis and Radiolysis

Many experiments have been performed on the photolysis of interstellar ice analogs. UV irradiation can lead to the production of complex molecules such as HMT ($\text{C}_6\text{H}_{12}\text{N}_4$; Bernstein *et al.* 1995) and amino acids (Bernstein *et al.* 2002; Muñoz-Caro *et al.* 2002). However, all these experiments require methanol, yet photolysis of simple ices is unable to produce methanol. Hence, if UV processing is indeed important in interstellar ices, there must exist a previous phase of grain-surface chemistry to produce the CH_3OH required to initiate the formation of more complex species. Radiolysis of laboratory ices by energetic protons, simulating the processing of interstellar ice by cosmic rays, has also been investigated in many experiments (e.g., Moore & Hudson, this volume). Unlike photolysis, radiolysis is able to produce CH_3OH from mixed CO and H_2O ice (Hudson & Moore 1999). Another difference between photolysis and radiolysis is that the latter

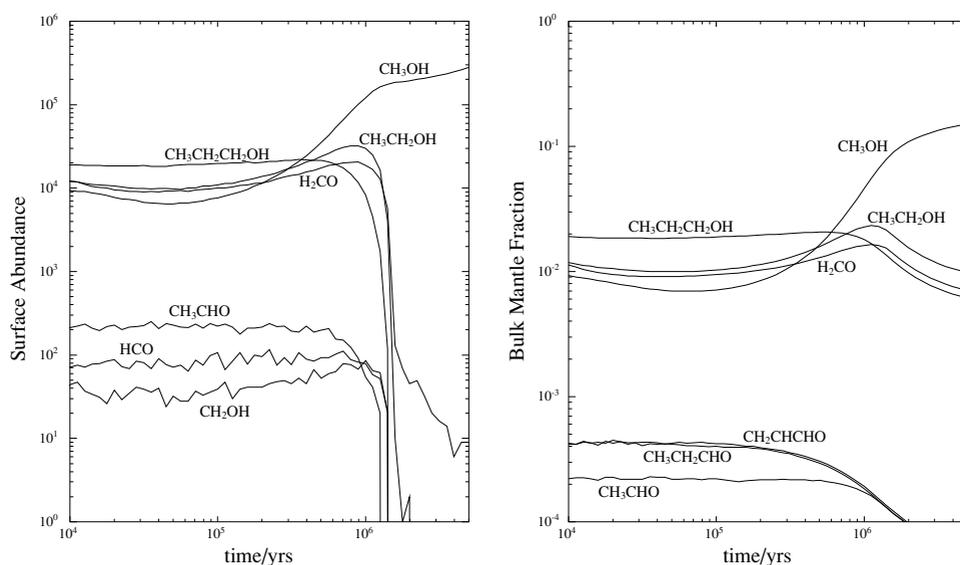


Figure 3. Solid-phase abundances calculated by our surface chemistry model (Rodgers & Charnley 2005). *Left:* surface populations. *Right:* fractional composition of the bulk ice.

appears to be much more effective in breaking the $\text{N}\equiv\text{N}$ bond in molecular nitrogen, and so may be a source of nitriles (Moore & Hudson 2003). Although both photolysis and radiolysis are capable of producing complex molecules, quantitative models of the yield of specific molecules expected from these processes in interstellar ices are currently lacking.

4. Mantle-Seeded Gas: Hot Cores and Hot Corinos

Hot molecular cores are warm, dense regions of the ISM with large abundances of many complex molecules. They are thought to represent one of the earliest stages in massive star formation, where the growing protostar becomes sufficiently luminous to heat a significant mass of its natal cocoon, leading to the evaporation of interstellar ices (e.g., Kurtz *et al.* 2000). It is now known that similar regions surround low-mass protostars, albeit on a smaller scale, so-called ‘hot corinos’ (Kuan *et al.* 2004; Bottinelli *et al.* 2004). In this paper we are concerned principally with the chemical pathways to large molecules, which are similar in both hot cores and hot corinos, and hereafter we use the term hot core generically to refer to any region where interstellar ice mantles have recently evaporated.

Models of the chemistry in hot cores have demonstrated that reactions in the warm post-evaporation gas can lead to large abundances of second-generation species produced from the evaporated ‘parent’ species (e.g., Millar *et al.* 1991; Charnley *et al.* 1992, 1995). Small-scale chemical differentiation is often observed in hot cores (e.g., Kuan *et al.* 2004), and this is thought to be related to different dynamical and thermal histories of specific regions (Rodgers & Charnley 2001, 2003). A detailed description of the kinds of coupled dynamical-chemical models used to analyse protostellar envelopes appears in the chapter by Doty. Below, we describe the most important classes of chemical reactions leading to the production of large organics in hot cores.

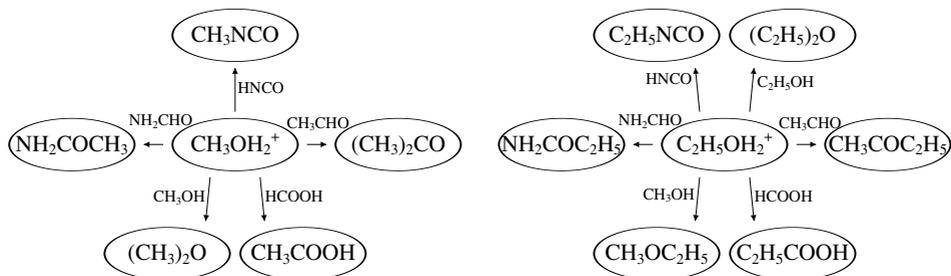


Figure 4. Alkyl cation transfer reactions from protonated methanol (*left*) and ethanol (*right*) can lead to a variety of large organic molecules.

4.1. Reactions of Protonated Methanol and Ethanol

Laboratory experiments involving protonated alcohols reacting with neutral coreactants have shown that, when the direct proton transfer channel is endothermic, transfer of the ionized alkyl group often proceeds rapidly (Karpas & Mautner 1989). Thus, protonated methanol and ethanol can respectively add CH_3^+ and C_2H_5^+ side groups to other species. Self-alkylation of alcohols can lead to large abundances of ethers in the gas phase, in particular dimethyl ether (Charnley *et al.* 1995). Similar reactions with other species can lead to a large variety of complex organic molecules. Considering reactions with several species which are thought to be formed on grain surfaces, Figure 4 shows some of the second-generation species that can be formed in the hot core.

Reactions of protonated alcohols with HCN have also been demonstrated to result in alkyl cation transfer (Mautner & Karpas 1986). In this case, protonated isocyanides are formed, *i.e.*,



Recombination will most likely lead to the isocyanide rather than the cyanide. Therefore, observations of the isomer pairs CH_3CN and CH_3NC may be able to assess the importance of reaction (4.1) in hot cores.

4.2. Interstellar Acids

Alkyl cation transfer reactions from protonated methanol and ethanol to formic acid have been shown to lead to acetic acid and propanoic acid respectively (D. Bohme, private communication), *e.g.*,



It is possible that similar reactions involving protonated aminoalcohols (which are readily formed via the putative surface chemistry scheme of the previous section; see Figure 2) and formic acid may lead to protonated amino acids, *e.g.*,



(Charnley 2001a).

Alternatively, the experiments of Blagojevic *et al.* (2003) showed that protonated amino acids are formed via reactions of protonated hydroxylamine with carboxylic acids, *i.e.*,



Although NH_2OH has not yet been detected in space, models of gas-grain processing suggest it should be abundant in interstellar ices (Charnley *et al.* 2001). In this scenario,

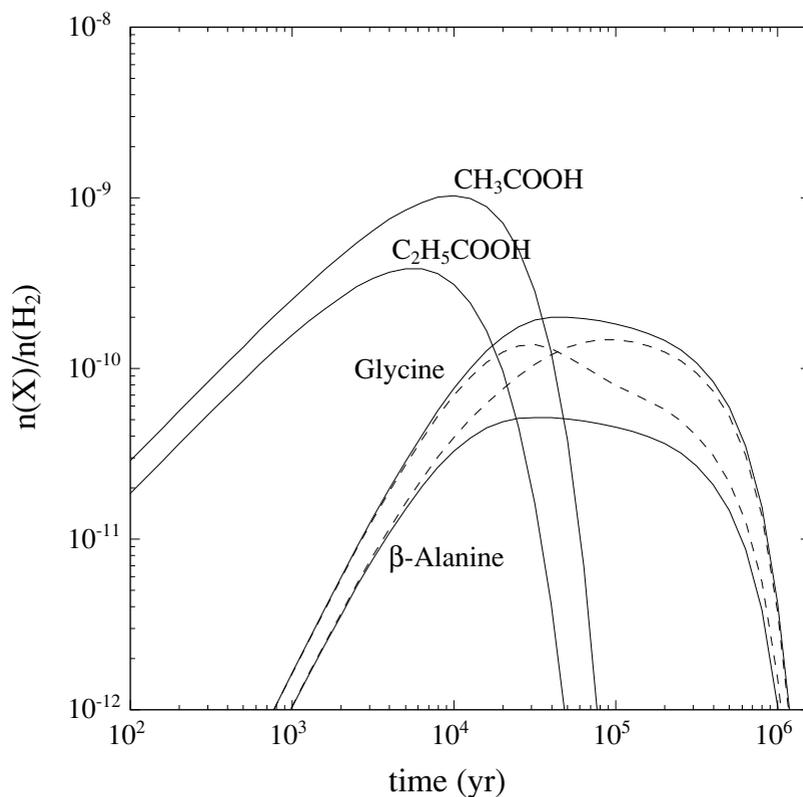


Figure 5. Abundances of organic acids produced via gas-phase chemistry following the evaporation of ices rich in CH_3OH , HCOOH , and NH_2OH (Charnley *et al.* 2005). Solid lines are for the standard model, and dashed lines show the effects of including a CH_3^+ transfer channel from protonated methanol to glycine.

evaporation of alcohols and HCOOH leads to the formation of carboxylic acids via reactions such as (4.2), and subsequent reactions with NH_3OH^+ lead to amino acids. To test this hypothesis, we ran our standard hot-core model (Rodgers & Charnley 2001) with these reactions included, and with initial abundances of CH_3OH , HCOOH , and NH_2OH of 10^{-7} . We also included an additional channel to β -alanine via alkyl cation transfer from CH_3OH_2^+ to glycine. Even though in this case the competing proton transfer channel is exothermic, it is possible that a few per cent of collisions result in CH_3^+ transfer (D. Bohme, private communication). The resulting abundances of the acids of interest are shown in Figure 5. The inclusion of the additional channel results in a β -alanine/glycine ratio greater than unity. Such a large ratio has been measured in the Orgeuil meteorite, and led to the suggestion that this carbonaceous chondrite originated from a cometary, as opposed to an asteroidal, parent body (Ehrenfreund *et al.* 2001). If correct, a cometary origin would strengthen the connection with the type of organic chemistry proposed here.

4.3. Methyl Formate, Acetic Acid and Glycolaldehyde

Methyl Formate (CH_3OCHO), acetic acid (CH_3COOH) and glycolaldehyde (HOCH_2CHO) are isomers, and all three have been detected in hot cores (Remijan *et al.* 2003; Hollis *et al.* 2004). However, the abundances and spatial distributions of the molecules are different. The reason for this is that each of these species is produced

by a different mechanism. Acetic acid can be synthesized post-evaporation in the gas phase, via reaction (4.2). Glycolaldehyde, on the other hand, can be formed on grain surfaces by simple atom addition reactions (see Fig. 2), and so will evaporate directly from the ice mantles. The origin of methyl formate is less certain. Blake *et al.* (1987) proposed that methyl cation transfer from CH_3OH_2^+ to H_2CO could lead to protonated methyl formate. However, both experiment and theory have demonstrated that this reaction leads to $\text{CH}_3\text{OCH}_2^+$ (Karpas & Mautner 1989; Charnley 1997; Horn *et al.* 2004). Grain-surface chemistry via atomic addition is also unable to form methyl formate. One possibility is that grain-surface chemistry is more complicated than described above, and that radicals such as HCO and CH_3O are able to encounter each other and combine directly. Another possibility is that these type of radical-radical reactions occur efficiently in the wake of cosmic ray particle passing through the ice, where it is expected that many radicals will be formed in close proximity via the hot secondary electrons generated by the cosmic ray.

5. Conclusions

We have discussed several pathways to molecular complexity in the ISM. In circumstellar envelopes and dark clouds, neutral-neutral reactions driven by small C-bearing radicals can generate long carbon chains and small aromatic molecules. Some of these species will coagulate to form C-rich dust particles, and the erosion of this dust by UV photons may be an important source of several species in PDRs and cometary comae. Grain-surface chemistry via atomic addition reactions can lead to the growth of larger molecules. When surface chemistry schemes are limited by realistic constraints, such as radical stability and the penetration of multiple bonds in order of activation energy, we find that these reactions tend to lead to aldehydes and alcohols. The degree of hydrogenation will depend on the competition between accretion of H atoms and other heavy atoms, and may be greater in the upper layers of interstellar ice mantles. When these ice species are evaporated in hot cores, subsequent gas-phase processing can synthesize a variety of new, even larger molecules. Ethers, carboxylic acids, and amino acids are all signatures of this type of gas-phase chemistry. Finally, there are some molecules that cannot be generated efficiently by any of these mechanisms, such as methyl formate and dihydroxyacetone. For these molecules, a possible origin is direct reactions of functional groups, driven by energetic processing of the ices.

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Discussion

DOTY: The identification of pathways for complex molecules is very interesting. To make quantitative predictions for comparison with observations, however, the results presumably depend upon the structure of the grain surface and mantles. Could you comment on what you assume, and how changing these assumptions would affect the predicted abundances?

CHARNLEY: In these particular calculations a regular lattice of surface binding sites was assumed. Recent simulations by Cuppers, Chang and Herbst, reported at this meeting, consider the kinetics of H₂ formation on more realistic porous surfaces.

MILLAR: Do you know of any laboratory experiments, which indicate that the destruction of carbonaceous grains or PAH molecules which result in the efficient production of carbon chains.

CHARNLEY: I seem to recall a paper by Duley & Williams, where the discussion was based on the results of laboratory experiments. Carbon chains were reported to be produced from laser processing of solid carbonaceous material.

MÜLLER: Many of the species you have proposed may be present in the interstellar medium. The question is: will we ever be in the position to detect these species unambiguously? (E.g., because of issues such partition function, vapor presences, low lying vibrational rates.)

CHARNLEY: This is more a question for Aldo (Apponi).