CHEMICAL EVOLUTION OF PROTOSTELLAR MATTER

William D. Langer
Jet Propulsion Laboratory, California Institute of Technology

Ewine F. van Dishoeck
Leiden Observatory

Edwin A. Bergin
Smithsonian Astrophysical Observatory, Harvard University

Geoffrey A. Blake
California Institute of Technology

Alexander G. G. M. Tielens
Kapteyn Astronomical Institute

Thangasamy Velusamy
Jet Propulsion Laboratory, California Institute of Technology

and

Douglas C. B. Whittet
Rensselaer Polytechnic Institute

We review the chemical processes that are important in the evolution from a molecular cloud core to a protostellar disk. These cover both gas phase and gas grain interactions. The current observational and theoretical state of this field are discussed.

I. INTRODUCTION

The study of chemical evolution from interstellar gas and dust to planetary systems is a key to understanding the pathways and the processes leading to solar origins. The formation of stars and planetary systems begins with the collapse of a dense interstellar cloud core, a reservoir of gas and dust from which a protostar and circumstellar disk are assembled. Throughout these evolutionary stages, simple and complex molecules that are formed deplete onto grains and a portion of these ices is ultimately incorporated into stars and planetary bodies. There is now substantial observational evidence of chemical evolution throughout the formation and evolution of protostars and protostellar disks. Clues to the degree of chemical processing also come from studies of comets in our own solar system (see chapter by Irvine et al.). Much of the interest is driven by the inventory of carbon-bearing species which, likely, formed one stepping stone towards the organic inventory of comets, meteorites, and planetary bodies in the solar system and, by inference, in other planetary systems as well.

The wealth of new observations at various wavelengths show the need for chemical evolutionary models that cover the history of the formation of the proto-solar nebula, from the forming dense core, to gas infalling onto and evolving in an accretion disk, onward to the planetary disk. Over the last decade, the following scenario has emerged. In the cold molecular cores prior to star formation, much of the chemistry is dominated by low-temperature gas-phase reactions leading to the formation of small radicals and unsaturated molecules. Small amounts of long carbon-chains form at early times if the material is initially atomic-carbon rich. Gas–grain interactions are also important as observations show that ices form in cold molecular clouds prior to star formation. Surface reactions play an important role in the formation of the ices. However, it is during the collapse phase, that the density becomes so high that most molecules accrete onto the grains and are incorporated into an icy mantle. After the new star has formed, its radiation heats up the surrounding envelope, so that the molecules evaporate back into the gas phase, probably in a sequence according to their sublimation temperatures. In addition, the outflows from the young star penetrate the envelope, creating high temperature shocks and lower temperature turbulent regions in which both volatile and refractory material can be returned. These freshly evaporated molecules then drive a rich chemistry in the "hot cores" for a period of 10^5 yr. Some of this gas-phase and icy material can be incorporated through accretion into the circumstellar disks surrounding the young star. Finally, the envelope is dispersed by winds and/or ultraviolet photons, leading to the appearance of photon-dominated regions in the case of high-mass young stars.

In this chapter, the chemistry of the pre-stellar cores, collapse envelopes and circumstellar disks is briefly discussed. The emphasis lies on a discussion of those species that are most characteristic of a particular evolutionary phase, but which are not necessarily the dominant species in terms of elemental abundances. More detailed reviews of various aspects include Tielens and Charnley (1997), van Dishoeck and Blake (1998), Hartquist et al. (1998), van Dishoeck (1998b) and van Dishoeck and Hogerheijde (1999).

II. OBSERVATIONS OF CORES AND ENVELOPES

A. Gas-phase Species

Nearly 120 different molecules have been detected in the interstellar and circumstellar gas, not counting the different isotopic varieties (see Ohishi 1997 for an overview). Most have been observed through their rotational transitions at (sub)millimeter wavelengths, but species like CH_4 and CO_2 can only be measured through infrared absorption lines. One of the most important detections of the last decade is the H_3^+ ion, a key player in the ion-molecule chemistry networks (Geballe and Oka 1996, McCall et al. 1998). New species continue to be discovered, either through systematic line surveys or through dedicated searches based on laboratory frequencies. For example, the frequency measurements of more than thirty new carbon-chains in the laboratory (McCarthy et al. 1997) has stimulated deep searches for them in interstellar clouds (Langer et al. 1997).

A large number of different carbon chain molecules (including, e.g., ring chain carbenes $C_{2n+1}H_2$, cumulene carbenes H_2C_n, cyanopolyynes $HC_{2n+1}N$, methylpolyynes $H_2C_{2n+1}N$, methylcyanopolyynes $H_2C_{2n}N$; free radicals C_nH) have been detected in dark cloud cores with typical abundances of 10^{-9} with respect to hydrogen. Laboratory spectra of long carbon chains may reproduce observed features of some Diffuse Interstellar Bands (DIBs) (Kirkwood et al. 1998) and, hence, carbon chains may be ubiquitously present in the diffuse interstellar medium as well. The infrared emission spectrum of interstellar clouds is dominated by the vibrational modes of large Polycyclic Aromatic Hydrocarbon molecules (PAHs) and, as a class, these species lock up a few percent of the elemental carbon (i.e., an abundance of $\sim 10^{-7}$). Both these classes of species are likely to be pervasive and stable components of the chemistry of protosolar systems and indeed PAHs are known to be abundant in carbonaceous meteorites (Henning and Salama 1998).

A.1. Pre-stellar cores. The cold, dark cloud cores are important sites with which to probe the interstellar chemistry prevailing prior to the onset of collapse. More than 100 dark cores have been identified through optical extinction and molecular line studies (c.f. Benson et al. 1998 and references therein, Turner et al. 1998). The best studied dark cores in terms of their chemical composition are TMC-1 and L134N. About half of the known interstellar molecules have been detected in TMC-1 (Ohishi et al. 1992, Ohishi and Kaifu 1998). Detailed maps in a number of species have most recently been provided by Pratap et al. (1997). The southern part of TMC-1 is particularly rich in unsaturated, long carbon chains, whereas the northern part is chemically similar to the high-latitude cloud L134N, consisting mostly of simple radicals and ions. In both clouds, significant chemical gradients have been found across the cores, which have been attributed either to age effects (see §III.A) or differential depletion of elements like O, C and S.

Figure 1 illustrates the richness of complex species detected in TMC-1, including the cumulene carbene H_2C_6 ($H_2C{=}(C{=})_4C$) (Langer et al. 1997), the carbon chain radical C_8H (Velusamy and Langer 1998), the shorter cumulene carbene chains H_2C_3, H_2C_4, and several other complex molecules. Although the relative abundances of the cumulene carbenes are distributed similarly to those of other complex carbon compounds such as $HC_{2n+1}N$ and C_nH, the spectral shapes in Figure 1 show that there are at least three pre-stellar fragments along this line-of-sight with different intensity ratios among these molecules. Indeed very high spectral resolution, well sampled, CCS maps, confirm that the emission comes from a highly clumped gas, loosely associated with pre-protostellar structures (Peng et al. 1998). Thus, chemical differentiation among the velocity components is large, indicating chemical evolution on small spatial scales (10,000 AU) owing, perhaps, to the density and grain-dependent chemical processing. It seems unlikely that fragments formed so close together in relative isolation should have such intrinsically different chemical composition without some chemical evolution, in which some of the fragments have evolved more rapidly because of initially higher density or dynamical factors.

Systematic surveys of characteristic molecules in a larger number of dark cores have been performed by Suzuki et al. (1992) using C_2S, HC_3N and NH_3, and by Benson et al. (1998) in C_2S, c-C_3H_2 and N_2H^+. In both studies, the carbon-chain molecules are found to correlate well with each other, but not with NH_3 nor N_2H^+. The C_2S/NH_3 or C_2S/N_2H^+ abundance ratios have been proposed as indicators of the amount of time that has passed since the gas was atomic-carbon rich, as illustrated in Figure 2 (Bergin and Langer 1997). In this scenario TMC-1 is found to be one of the youngest clouds yet studied.

A long-standing question concerns the amount of depletion in these dark cores. An illustrative example is provided by the quiescent core L1498, studied by Kuiper et al. (1996) (see Figure 3). The C_2S, CS and NH_3 maps show a chemically differentiated structure, with the carbon-rich molecules more abundant in the diffuse outer part, and NH_3 dominant in the denser cloud center. Observationally, depletion is very difficult to prove, because every cloud has a "skin" in which the abundances are close to normal (Mundy and McMullin 1997). Even if the skin contains only a few percent of the total column density, the higher abundances can effectively mask any depletions deep inside. The case of L1498 provides some evidence for depletion of CO at the core center, since offsets between the $C^{18}O$ emission (Lemme et al. 1995) and the far-infrared continuum have been found (Willacy et al. 1998a). Another interesting example is provided by the dark cloud IC 5146, for which the comparison of the extinction A_V derived from infrared star counts with the $C^{18}O$ emission suggests depletion at $A_V > 20$ mag (Kramer et al. 1998). Direct observations of ices in dark clouds indicate that the column density of solid CO may be comparable to that of gas-phase CO, and that up to 40% of the heavy elements may be condensed onto the grains (Chiar et al. 1998, Schutte 1999).

A.2. Cold collapse envelopes. The increasing densities and decreasing temperatures during collapse result in enhanced depletion of gas-phase molecules in the envelopes. The dust obscuration is too high at this stage for direct observations of ices with current instrumentation. Careful modeling of the line and dust emission on various scales appears the only way to probe the abundances in this phase. One of the best-studied cases is that of the deeply embedded YSO NGC 1333 IRAS4, where depletions of more than a factor of 10 have been inferred (Blake et al. 1995). Studies of other class 0 YSOs suggest that this phase of high depletion is short lived, however (Hogerheijde et al. 1999).

Chemical differentiation such as seen toward L1498 is still observed in the outer, less dense parts of the collapsing envelopes. An example is provided by the deeply embedded object B335 (Velusamy et al 1995), where CCS and other radicals are located predominantly in the outer infall envelope. CS is abundant further in, while NH_3 is more abundant close to the circumstellar disk. Thus, we can trace the sequence by which these simple species are chemically transformed and freeze out onto dust to form icy grain mantles that populate planet-forming disks.

Systematic observations of molecules other than CO have been performed for only a few deeply embedded YSOs. For NGC 1333 IRAS4A, only weak emission from other species is found, and most of it is associated with the outflow (Blake et al. 1995). In contrast, a wealth of molecular lines has been detected in the circumbinary envelope of IRAS 16293 –2422 (Blake et al. 1994, van Dishoeck et al. 1995), including organics such as CH_3OH and CH_3CN in the warm, inner part of the envelope on scales of a few hundred AU that result from the interaction with the outflow. The optically thin lines of $H^{13}CO^+$ and $H^{13}CN$ trace the dense envelope on scales up to a few thousand AU, whereas the optically thick HCO^+ and HCN outline the walls of the outflow cavity. Apparently, a larger fraction of the envelope has been affected for IRAS 16293 –2422 than for NGC 1333 IRAS4A. A similar trend is found for three deeply-embedded YSOs in Serpens, SMM1, SMM3 and SMM4 studied by Hogerheijde et al. (1999).

A systematic high resolution study of the HCO^+ and CS lines in the envelopes of a set of more evolved, but still embedded low-mass objects in Taurus has been performed by Ohashi et al. (1991, 1996) and Hogerheijde et al. (1997, 1998) using a combination of single dish and interferometer data. As for the deeply embedded objects, HCO^+ is found to be an excellent tracer of the inner envelope structure and mass, whereas N_2H^+ appears to trace preferentially the quiescent outer envelope (Bachiller and Peréz-Gutierrez 1997, Benson et al. 1998). N_2H^+ may be destroyed by proton transfer to CO and H_2O in regions where these molecules are not significantly condensed onto grains (Bergin et al. 1998). In B5 IRS1, HCN, but not HCO^+, also appears to avoid the inner part of the envelope (Langer et al. 1996), as does CS (Langer and Velusamy 1999). This distribution is consistent with the result of Blake et al. (1992), who found the CS/CO ratio in the inner envelope of HL Tau to be a factor to 25 to 50 less than that of the surrounding dense core.

Detailed chemical studies of the envelopes of high-mass YSOs have been performed for several objects, including W 3 IRS5 (Helmich & van Dishoeck 1997), NGC 2264 IRS1 (Schreyer et al. 1997) and AFGL 2591 (Carr et al. 1995, van der Tak et al. 1999). Most of them show a simple chemistry, with little or no evidence for high abundances of complex organic molecules such as those found in hot cores (Blake et al. 1987, Sutton et al. 1995). These studies are interesting because they can be combined with direct observations of solid-state species for the same line-of-sight (see see §II B below).

B. Ices

Interstellar ices have been detected in absorption by their vibrational bands in the infrared, either toward background field stars, or, more often, embedded young stars (see Whittet 1993, Tielens and Whittet 1997 for overviews). The YSOs heat their surrounding dust to a few hundred K, providing a bright continuum against which the ices in the colder envelope can be seen in absorption. The availability of a grating-resolution spectrometer in space, the *Short Wavelength Spectrometer* (SWS) carried by the *Infrared Space Observatory* (ISO), represents an advance in our observational capability at least as significant as that which occurred when such instruments were first used on ground-based telescopes more than two decades ago, and allows an almost complete inventory of the major constituents of ices and organics.

B.1. Inventory of ices. A sample spectrum taken with the ISO-SWS covering the wavelength range 2.5–20 μm at a mean resolving power $\lambda/\Delta\lambda \approx 1000$ toward the well-known embedded massive young star W 33A is shown in Figure 4. The spectrum is dominated by strong, broad features centered near 3 and 10 μm, attributed to H_2O-ice and silicates, the primary constituents of the mantles and cores of the grains, respectively. H_2O-ice is represented by its bending mode at 6.0 μm as well as the stretching mode at 3 μm. The spectral signatures of various carbon-bearing molecules are also present in the spectrum. Prominent amongst these are the CO stretching mode at 4.67 μm and the stretching and bending modes of $^{12}CO_2$ at 4.27 and 15 μm, as well as the stretching mode of $^{13}CO_2$ at 4.39 μm. It is notable that signatures of CH-bonded carbon are less in evidence: only CH_3OH and CH_4 are securely identified.

Absorption at 4.62 μm is associated with CN bonds in an unidentified molecule or ion ('XCN'), and a weak feature at 4.9 μm is most likely identified with OCS. Unidentified features include a shallow absorption at 3.47 μm buried in the 'wing' of the deep ice feature, and the more prominent 6.85 μm band; these seem likely to be caused by CH stretching and deformation modes in hydrocarbons (Allamandola et al. 1992; Schutte et al. 1996) but no convincing fits with laboratory analogs have yet been reported. Solid NH_3 is difficult to detect as the N–H feature at 2.95 μm is effectively blocked in objects with deep 3.0 μm H_2O-ice bands like W 33A. A tentative detection of the 9.6 μm band has been made by Lacy et al. (1998) toward NGC7538 IRS9, indicating an abundance of $\sim$10% with respect to H_2O ice. Observations of other lines of sight suggest that the NH_3 abundance is no more than a few percent (Smith et al. 1989; Whittet et al. 1996). From theoretical considerations, O_2 and N_2 are also expected to be abundant, but since these species have no intrinsic dipole moment, they very hard to detect in the infrared (Ehrenfreund and van Dishoeck 1998, Vandenbussche et al. 1999).

As SWS data reduction techniques continue to be refined, detailed analysis becomes feasible, encompassing also the weaker features of less abundant species in ice-rich sources like W 33A and NGC7538 IRS9. Of greatest interest are organic molecules of potential exobiological significance. Tentative evidence for an organic acid (R-COOH, most likely formic acid, HCOOH) has recently been presented (Schutte et al. 1996, 1999), and preliminary analysis indicates that it may be ubiquitous (Keane et al. 1999). Finally, detailed studies of the CH stretch region have placed upper limits on the abundances of ethane (C_2H_6) and ethanol (CH_3CH_2OH) in the mantles (Boudin et al. 1998).

B.2. Heating and evaporation of ices. The sensitivity of the mantle material to environment is studied by comparing observations for different sources. A problem is that both processed and unprocessed material may be present at different locations along the line of sight toward YSOs, so that it is also important to observe background field stars to give a measure of unprocessed mantle properties. Table 1 compares the ice abundances for five interstellar lines of sight: one quiescent dark cloud and four YSOs. All abundances are normalized to $N(H_2O) = 100$. Elias 16 is a field star behind the Taurus Dark Cloud in a line of sight close to TMC–1, where the kinetic gas temperature is $T_{\rm gas} \approx 10$ K (Pratap et al. 1997). Each of the four YSOs has both cold and warm/hot gas and dust components in the line of sight (Mitchell et al. 1990). Sources are ordered from left to right in Table 1 in a sequence of declining solid CO abundance. Since CO is the most volatile of the primary constituents of the ices (in pure form, it sublimes at ~ 16 K), its abundance varies inversely with the degree of thermal processing. Estimates of $T_{\rm gas}$ (Table 1) are consistent with this conclusion: solid CO is most abundant in the quiescent cloud, and undetected toward GL2591, where $T_{\rm gas} > 30$ K.

Modeling the solid state features of molecules such as CO and CO_2 allow not only their abundances but also their molecular environment within the mantles to be examined. Distinct 'polar' and 'non-polar' ice phases, dominated by H_2O and CO, respectively, have been identified (Tielens et al. 1991; Chiar et al. 1995, 1998; de Graauw et al. 1996; Boogert et al. 1999; Gerakines et al. 1999). These ices evidently form under distinctly different conditions: polar, H_2O-rich mantles accumulate in regions where atomic H has appreciable abundance in the gas, so that accreting CNO-group species typically become hydrogenated; non-polar mantles accumulate in regions where essentially all the H is molecular, including species such as CO, O_2 and N_2 which may freeze directly out of the gas as well as form by surface catalysis (see §III B).

The bending mode of $^{12}CO_2$ near 15 μm is an especially sensitive diagnostic of the ice environment and the degree of thermal processing (Ehrenfreund et al. 1996, 1998; Gerakines et al. 1999). SWS observations of four representative sources, ordered in sequence of increasing $T_{\rm gas}$, are illustrated in Figure 5; also shown are fits based on laboratory data. In polar ice mixtures, the 15 μm feature is broad (FWHM $= 10$–25 cm^{-1}) with no substructure; however, sharp peaks (FWHM $=$ 2–4 cm^{-1}) near 15.27 μm and 15.15 μm appear in non-polar molecules containing CO_2, or in pure annealed CO_2. The systematic evolution of the profile with temperature evident in Figure 5 provides a strong indication that thermal processing is an important process (perhaps the dominant process) in the environments of embedded YSOs. The presence of a non-polar CO_2 component only in YSOs suggests that some segregation of mantle constituents (especially H_2O, CH_3OH and CO_2) might be taking place as the grains are warmed. Further evidence for thermal processing arises from detailed study of the $^{13}CO_2$ stretch feature (Boogert et al. 1999) which shows structure consistent with segregation between CO_2 and polar molecules.

The overall abundance of CO_2 is surprisingly similar (Table 1) in contrasting environments. As CO_2 forms easily in the laboratory by UV photolysis of ice mixtures containing CO, it might be assumed that the CO_2 abundance should measure the degree of radiative processing. The detection of CO_2 ice in the dark cloud environment (Whittet et al. 1998) was thus something of a surprise: CO_2 formation can evidently occur in clouds remote from local embedded sources of radiation. Because CO_2 is located almost exclusively in the polar (H_2O-dominated) component of the ices in dark clouds, it must form simultaneously with H_2O. If surface catalysis is the primary route, a problem for chemical models (§ III.B) is to explain why CO_2 is generally much more abundant than CH_3OH or CH_4, given that it must form in a hydrogenating environment. If photolysis is the primary route to CO_2, it must be driven by ambient photons from the interstellar radiation field, or by cosmic rays.

An important motivation for the study of interstellar ices is to allow detailed comparison with comets (see Table 1). Information on the composition of comets comes both from observations with ground-based and space-based telescopes and from in situ studies (see chapter by Irvine et al. for an in-depth review). Note that cometary abundances in Table 1 represent typical values/ranges and do not refer to any individual comet. Although preliminary, these results do suggest that cometary and interstellar abundances are broadly similar. Interstellar and nebular models for cometary origins predict systematically different abundances for many species: the generally low NH_3 and CH_4 abundances measured in comets, together with high CO/CH_4 and CH_3OH/CH_4 ratios, and deuterium enrichment (see chapter by Irvine et al.), are suggestive of a substantial contribution from interstellar ices.

III. CHEMICAL MODELS

A. Gas-phase Chemistry

The basic gas-phase molecular processes and chemical networks developed to explain the observed abundances have been described extensively in the literature (see Herbst 1995, van Dishoeck 1998 for recent overviews). At the low densities of interstellar clouds, only two-body reactions are important. Processes such as radiative association, photodissociation, dissociative recombination and ion-molecule reactions can form, destroy and rearrange molecular bonds.

Chemical models of star-forming regions require the specification of the initial chemical and physical conditions, namely density, temperature, radiation field, initial elemental abundances, and even geometry (e.g., Millar et al. 1997, Lee et al. 1996a). Of these the density and temperature can be constrained through observations, while the radiation field is typically parameterized in terms of a "standard" interstellar radiation field (e.g., Habing 1968) attenuated according to the depth (e.g. visual extinction). The initial elemental abundances are based on observations of diffuse clouds such as ζ Oph (see Meyer 1997), but often additional depletion is assumed for dark clouds.

One of the principal aims of the modeling efforts is to develop sets of tracers that can be used to discriminate between various stages of dense core evolution. For pure gas-phase chemical models the main time-dependent aspects depend on how the various elemental pools (e.g. C, O, N, S, etc..) interact, both internally and with each other. The main driver of the chemistry starts with cosmic-ray ionization of the dominant molecular species, H_2, with an estimated rate of $\zeta_{H_2} \approx (1-5) \times 10^{-17}$ s^{-1} (Lepp 1992; van Dishoeck and Black 1986, Plume et al. 1998). Ionization of H_2 produces H_2^+, which reacts rapidly with H_2 forming H_3^+ and H. The H_3^+ ion then reacts with numerous atoms and molecules leading to a rich chemistry.

The most important transition in the chemistry is the eventual production of CO from neutral and ionized atomic carbon. If dark cores are assumed to evolve from diffuse gas, the carbon is initially present as C^+. Since the $C^+ + H_2 \rightarrow CH^+ + H$, reaction is endothermic, C^+ can recombine with electrons to form neutral carbon within a few hundred years. C then reacts with H_3^+, OH, and O_2 to produce CO within 10^5 - 10^6 years at typical cloud densities of $10^4 - 10^5$ cm^{-3}. This multistage process is quite important since the creation of more complex organic species and carbon chains (e.g., CCS, HC_3N) requires large abundances of C and C^+ for carbon insertion reactions to be effective. Thus, the concentrations of complex molecules tend to peak at early times ($\sim 10^5$ years) and decline as equilibrium is approached (see Figure 2). C^+ also reacts slowly via a radiative association reaction, $C^+ + H_2 \rightarrow CH_2^+ + h\nu$, providing another molecular formation pathway during the neutralization phase. It competes with carbon recombination only after the electron fractional abundance has decreased by 1–2 orders of magnitude.

The main time-dependent aspects of the other elemental pools, O, N, and S, depend on how their chemistry is linked to that of carbon. The oxygen chemistry begins with $H_3^+ + O \rightarrow OH^+ \rightarrow H_2O^+ \rightarrow H_3O^+$, where the latter dissociatively recombines to form OH, H_2O, and O with a branching ratios that have only recently been measured in the laboratory (Williams et al. 1996; Vejby-Christensen et al. 1997). O_2 is produced through reaction of O and OH. The abundances of these simple oxygen-bearing molecules are low at early times, as OH, O_2, and H_2O react with C and C^+. The primary N-bearing molecules (N_2, NH_3) form via simple ion-molecule and neutral-neutral reactions and have slow, steady buildup in concentration until equilibrium is reached. The most abundant sulfur-bearing molecules, CS and SO, exhibit slight evolutionary differences because SO is produced mainly through a reaction of S with OH and O_2, and is destroyed by atomic carbon producing CS. Thus, the chemistry of CS is linked to the carbon network which leads to slightly higher abundances at earlier times compared to steady state, while SO has large concentrations in equilibrium. The reaction of SO with OH is expected to produce SO_2. However, the observed SO_2 abundance is generally low in dark clouds, indicating an incomplete understanding of the sulfur chemistry and the depletion of sulfur

(Palumbo et al. 1997).

The above scenario leads to a dichotomy in the chemistry: (i) Species linked to the carbon chemistry such as CS, CN, HCN, complex carbon chains, and organics have larger abundances at earlier evolutionary stages; (ii) Molecules that are independent or destructively linked to the carbon chemistry such as N_2, NH_3, N_2H^+, and SO exhibit higher concentrations near equilibrium. It is these aspects of the chemistry that have been used to interpret observations of molecular clouds in terms of evolution in sources such as TMC-1 or L134N (Lee et al. 1996 a,b; Millar et al. 1997; Pratap et al. 1997; Taylor et al. 1998). In the case of L1498 the chemical structure (Figure 3) reflects this dichotomy and is very well explained by the time dependent models of Bergin and Langer (1997). Note however that this "chemical age" does not necessarily reflect the age of the core since its formation from the diffuse gas; it basically measures the time since a dynamical event destroyed molecules and effectively reset the chemical clock (e.g., Langer et al. 1995, Bergin et al. 1997). Other dynamical processes, such as turbulence (Xie, Allen, and Langer 1995) or outflows (Norman and Silk 1989) can also bring fresh atomic carbon inside the cores and lead to a "young" appearance.

B. Grain chemistry

Four processes contribute to the composition and evolution of the observed interstellar ices in molecular clouds: surface chemistry of species accreted on interstellar grains, thermal processing of ice mantles driven by nearby newly formed stars, energetic processing of ices by FUV photons and/or particle bombardment, and depletion of molecules produced in the gas phase and in shocks. Evidence for the importance of each of these has been claimed in the observational characteristics of interstellar ice mantles (see, e.g., Tielens and Whittet 1997, Schutte 1999 for reviews).

B.1. Grain surface chemistry. Grain surface chemistry is dominated by hydrogenation and oxidation reactions of simple species accreted from the gas phase. While many of these reactions have activation barriers, they may still proceed on grain surfaces in view of the long timescale (~ 1 day) available for reaction between two reactive species on a grain surface before another reactive species is accreted from the gas phase (Tielens and Hagen 1982). In the gas phase, CO is the dominant C-bearing species. Other C-bearing compounds have observed (or calculated) abundances $\lesssim 10^{-4}$ relative to CO, except perhaps for atomic C which may be as abundant as 0.01 (Bergin et al. 1997). Hence, the chemistry of CO is particularly relevant for the organic reservoir of interstellar ices.

The key step in the surface chemistry of CO is hydrogenation to

HCO (Figure 6), which has a measured activation barrier of 1000 K (Tielens and Hagen 1982), which is known to occur in low-temperature matrices (van IJzendoorn et al. 1982). The resulting radical HCO will react on a grain with H to form H_2CO. Formaldehyde may be unstable to further hydrogenation to form methanol (Tielens and Allamandola 1987) and there is some experimental support for this (Hiraoka et al. 1994, 1998). Because of the high H flux in these experiments, most of the H formed H_2 and the measured efficiency of methanol formation was low. In contrast, CH_3OH is calculated to be the preferred endpoint of the hydrogenation of CO under typical dark cloud conditions (Charnley et al. 1997).

The intermediate HCO (formyl) and CH_3O (methoxy) radicals in this route can also react with various other accreted C, N and O atoms, leading to a variety of complex species (Fig. 6, Tielens and Hagen 1982), including CH_3CHO (acetaldehyde) and CH_3OCH_3 (dimethyl ether). Like H_2CO, the former may be unstable to hydrogenation leading to CH_3CH_2OH (ethanol) (Charnley 1998). Reaction of HCO with O results in the formation of HCOOH (formic acid). The reaction of N with HCO will lead to NCHO, which might be further hydrogenated to $HCONH_2$ (formamide; Tielens and Hagen 1982), or isomerize to its more stable form, HNCO (Charnley 1998). Observations of hot cores near massive stars, where the ices have evaporated off the grains, can form significant tests of these models.

The long timescale between the accretion of reactive radicals on grain surfaces may also allow oxidation of CO to occur. Laboratory studies by Tielens and Hagen (unpublished) and Grim and d'Hendecourt (1986) are somewhat contradictory, but the reaction of O with CO may well be the predominant grain surface chemistry route towards CO_2 in dark clouds (Tielens and Hagen 1982).

If atomic O indeed reacts readily with CO on a grain (or if the reaction of O with O_2 dominates), there will always be a reaction partner for atomic O and the surface reaction of O and H forming H_2O is then blocked. Hydrogenation of O_2 (through H_2O_2) and its oxidation product, O_3 (through OH), are then the dominant routes towards H_2O in theoretical calculations of grain surface chemistry (Tielens and Hagen 1982). In the O_3 route, O_2 plays a catalytic role.

B.2. Thermal processing. Thermal processing of interstellar ice mantles is important in star-forming regions and the experimental data have recently been reviewed by Tielens and Charnley (1997). When an ice mantle is heated to a temperature near its sublimation point, outgassing will occur. Sublimation temperatures of a variety of mixed molecular ices have been measured in the lab (Sandford and Allamandola 1990; 1993; Kouchi 1990). In view of the difference in timescales, these sublimation temperatures have to be scaled down somewhat for the interstellar case and representative values are summarized in Table 2. In a mixed molecular ice where two (or more) components have similar concentrations but different sublimation temperatures, the evaporation of each component is largely regulated by its own sublimation behavior (Kouchi 1990; Sandford and Allamandola 1990). Thus, sublimation experiments on $CO/H_2O=1/2$ and $CO_2/H_2O=1/1$ ices show early release of CO (around 25 K) and CO_2 (around 85 K). A small fraction of the CO or CO_2 stays behind and is (partly) released during phase transformations in which the whole H_2O ice-crystal structure rearranges. This phase transformation may be associated with the amorphous to cubic (or more properly, clathrate formation) transition of H_2O ice (around 120–130 K in lab experiments).

CH_3OH has a sublimation temperature ($\simeq$ 140 K in the lab) above the clathrate formation temperature. Hence, H_2O/CH_3OH mixtures when heated to $\simeq$ 130 K will segregate into rather pure CH_3OH and H_2O–clathrate domains (Blake et al. 1995) whose evaporation behavior (necessarily) follows that of the pure substance: CH_3OH and H_2O evaporation at 140 and 150 K, respectively, in the lab, or 80 and 90 K in space. Recent experiments have shown that CH_3OH/CO_2 and $H_2O/CH_3OH/CO_2$ mixtures show similar segregation behavior (Ehrenfreund et al. 1998). The profiles of the interstellar CO_2 bands show evidence for this process around luminous protostars (Boogert et al. 1999; Gerakines et al. 1999, see Fig. 5).

B.3. Processing by ultraviolet photons. UV photolysis of ices containing H_2O, CO, NH_3, and CH_4 produces small radicals such as H, O, OH, N, NH, NH_2, C, CH, CH_2, and CH_3. These react with each other and the parent species resulting in, for example, H_2O_2, N_2H_2, N_2H_4, CO_2, and radicals such as HCO, HO_2, C_2H_3, which are available for further reactions (e.g., Hagen et al. 1980; Gerakines et al. 1996; Bernstein et al. 1995). In mixtures with CO, the HCO channel leads to various interesting complex molecules such as H_2CO, HCOOH, $HCONH_2$, and $HCOCH_3$ (Allamandola 1987). This chemistry is very much akin to the surface hydrogenation scheme for CO, which also runs through HCO and hence gives rise to the same species. For the surface chemistry scheme, the relative abundances of the various end products reflect the relative accretion rates of the migrating radicals, H, C, N, and O (Tielens and Hagen 1982). In the photolysis scheme, this is convolved with the UV destruction rate of the parent species which can vary by an order of magnitude (Hagen et al. 1980; Gerakines et al. 1996). No quantitative comparison between these different formation routes has yet been made.

Mixtures containing CH_3OH (and H_2CO) are of particular interest for molecular complexity. UV photolysis of methanol leads to formaldehyde which can thermally polymerize, particularly in the presence of

NH_3, to polyoxymethlene POM (see above; Schutte et al. 1993; Bernstein et al. 1995). In this process, many of the H atoms may be replaced by other functional groups. Furthermore, reactions of simple radicals such as CH_3 with the double-bonded O in formaldehyde can lead to products such as CH_3OCH_3. Similar reactions involving CO_2, another important (second order) product of methanol photolysis, will lead to, for example, CH_3OCHO. The presence of NH_3 in these mixtures has important consequences. Besides facilitating thermal polymerization of H_2CO (Schutte et al. 1993), photolysis will lead to efficient carbon–nitrogen bond formation (Bernstein et al. 1995). Analysis of residues shows that hexamethylenetetramine (HMT) is the dominant product of the photolysis of mixtures containing CH_3OH and NH_3, locking up to 40% of the initial nitrogen. For comparison, POM–like species lock up less than 1% of the carbon initially in methanol. Other compounds in the residue include ethers, ketones, and amides, which lock up about 5% of the C.

C. Gas-grain models

Both the gas-phase and grain-surface processes have been incorporated into chemical models which take the exchange between the two phases into account. For gas densities of more than 10^4 cm^{-3}, all the gas phase molecules (except H_2, H_3^+, CO, N_2, and a few other weakly polar molecules) should accrete onto grain surfaces in 10^5 yr, a time scale short compared to the ages of molecular clouds, but comparable to the time scales for protostar formation. At the densities characteristic of disk material, $> 10^6$ cm^{-3}, the depletion rate is even faster since it scales inversely with density. Chemical history may be even more complicated as molecules which freeze onto grain surfaces can be reinjected into gas phase by the desorption of grain mantles (e.g., Willacy & Williams 1993, Shalabiea & Greenberg 1994, Bergin & Langer 1997). Each of these scenarios makes specific predictions regarding the chemistry in the gas phase and frozen icy grain mantles in the disk accretion and early evolutionary phases, which eventually determines the makeup of solar system objects.

Two different regimes have been considered in the gas-grain models (Tielens and Charnley 1997). In the "accretion limited" regime (Tielens and Hagen 1982), reactions are limited by the rate at which species are "delivered" to the grain surface where they rapidly migrate and react. In the "reaction limited" regime (e.g. Hasegawa and Herbst 1993), the opposite holds: many reactive species are present on a grain surface and reaction is controlled by surface concentrations (as well as kinetic parameters). Most of the chemical models including gas–grain interactions have been formulated in the "reaction limited" regime using rate equations which mirror those used for gas-phase chemistry (e.g. Hasegawa and Herbst 1993, Shalabiea and Greenberg 1995). This approach is only accurate when a large number of reactive species exist on a single grain surface, since only average abundances are calculated. This condition is usually not met in interstellar clouds, since the accretion times are long, grains are small, and reactions are fast, so that at most one reactive species is present on a grain at any time. The grain surface chemistry is therefore in the accretion limited regime and can only be properly treated by a Monte–Carlo method, which determines the likelihood of two such species arriving from the gas in succession onto a particular grain in a steady-state model. Recently, an ad hoc reformulation of the reaction-limited approach has been proposed by Caselli et al. (1998) to remedy its shortcomings, and the consequences for the models have been discussed by Shalabiea et al. (1998). So far, no Monte-Carlo method has been developed for use in time-dependent codes due to computational restrictions.

In addition to the thermal desorption discussed above, other non-thermal desorption processes involving cosmic-ray spot heating, heating by the energy liberated by molecule formation or photodesorption by ultraviolet or infrared radiation. Grain-grain collisions may play a role if stored radicals, produced for example by ultraviolet photolysis, are present in the ice (see Schutte 1996 for overview). These processes are only effective for volatile molecules, but not for H_2O- and CH_3OH-rich ices which contain strong hydrogen bonds. The outcome of the models then depends strongly on the adopted desorption mechanisms. For example, if the non-thermal mechanisms are assumed to be ineffective, N_2 is one of the few heavy species which is not significantly condensed onto grains in cold cores with $T \approx 10$ K, leading to significant N_2H^+ and NH_3 (see Figures 2 and 3).

Models appropriate for the cold outer envelopes which include collapse dynamics have been presented by Rawlings et al. (1992), Willacy et al. (1994), Shalabiea and Greenberg (1995), and Bergin and Langer (1997). The ions HCO^+ and N_2H^+ are good tracers of the envelopes, because their abundances remain high owing to the increase in the H_3^+ abundance when its main removal partners (CO, O, ...) are depleted. Since CO and H_2O are also the main removal partners of N_2H^+, this ion avoids the warmer inner envelopes where these molecules have been returned to the gas phase. In contrast, HCO^+ is removed primarily by electrons, making it a better tracer of the inner envelope, consistent with observations (Hogerheijde et al. 1997). Studies of the temperature structure and chemistry in the warmer, inner envelopes have been presented by Ceccarelli et al. (1996) and Doty and Neufeld (1997).

Gas-grain interactions and the formation of ices can also be significant in regions which have recently been subjected to shocks due to outflows from young stars. Bergin et al. (1998) predict that large quantities of water vapor are produced in shocked gas, as supported by ISO observations of strong emission from gaseous water towards Orion

BN-KL (Harwit et al. 1998). In the cold postshock gas the abundant H_2O vapor will condense onto the dust grain surface producing a water-dominated mantle. This mechanism, which requires some shielding from photodissociating photons, may also be able to reproduce the observed deuterium fractionation of water in comets. Further studies of species such as CH_3OH are needed to test the importance of this mechanism compared with other processes.

IV. Circumstellar Disks

As shown in the previous sections, substantial variations in chemical abundances occur as the circumstellar envelope evolves. What happens to these species when they are incorporated into the dense circumstellar disks? With the increased sensitivity of telescopes, it is now also possible to probe the chemistry in the disks themselves on scales of a couple hundred AU.

A. Observations

The best objects for study are YSOs which have already dispersed their envelopes and cloud cores, so that no confusion with the surrounding material is possible. Excellent examples are provided by DM Tau and GG Tau (Dutrey et al. 1997) and TW Hya (Kastner et al. 1997), where molecules such as CN, HCN, HNC, CS, HCO^+, C_2H, and/or H_2CO have been detected with single dish telescopes. These molecules appear underabundant with respect to the standard pre-stellar cores, probably due to depletion of gas phase molecules onto the surfaces of cold dust grains. An issue here is whether the molecules are passively stored on the grains during this period, or whether grain surface chemistry modifies their composition.

The available single dish data are suggestive of a scenario in which the distance at which depletion occurs is species-dependent, with the most volatile species remaining in the gas phase furthest from the central star. Further characterization of the chemistry in circumstellar disks would benefit from a combination of high spectral and spatial resolution observations. Current millimeter-wave interferometric arrays are now capable of imaging the more abundant molecules in circumstellar disks, as is illustrated by the observations of the ^{13}CO, CN, HCO^+, and HCN $1 \rightarrow 0$ transitions toward the T Tauri star LkCa 15 presented in Figure 7 (Qi et al. 1999). Even at 2-3$''$ resolution (or a disk diameter of $\sim$ 300 AU), there appear to be interesting morphological differences between species expected to follow different (photo)chemical paths such as ^{13}CO and CN. The HCO^+ emission provides an important lower bound to the gas fractional ionization of a few $\times\ 10^{-10}$, while the ratio of the HCN, HCO^+, and ^{13}CO $1 \rightarrow 0$ emission to that of higher J transitions detected with submillimeter telescopes indicates low kinetic temperatures of less than ~30 K. Future observations of disks around T Tauri and Herbig Ae stars at even higher spatial resolution will be able to measure directly any gas phase chemical gradients that may exist in the icy planetesimal formation zone of circumstellar disks. In favorable cases, the millimeter-wave images may also be combined with infrared spectroscopy to constrain the icy budget.

B. Chemistry of Disks

Densities in the outer disk are typically greater than 10^6 cm^{-3} (they rise to 10^9 cm^{-3} at 100 AU), and temperatures are around 10 K so that depletion takes place in a short time, $< 10^4$ years. The timescale for desorption by cosmic ray spot heating is about 10^6 years so the chemistry is not able to reach equilibrium. Thus, it is necessary to consider the dynamical chemical evolution as material is transported inwards, and to consider a variety of desorption mechanisms (c.f., Aikawa et al. 1997, 1998). The transport needs to be calculated along with the chemistry because of the changing physical conditions and time scales as material moves inwards. Several groups have considered the chemical composition of a parcel of gas transported towards the center of the disk (c.f., Bauer et al. 1997, Duschl et al. 1996) from 1,000 AU inwards. However, their major focus was on the very central regions where the dust is destroyed (< 10 AU), and a very limited set of initial conditions and gas-grain chemistry were considered.

Aikawa et al. (1997, 1998) and Willacy et al. (1998b) have calculated more comprehensive chemical and gas-dust models. For example, in the models of Aikawa et al. cosmic ray ionization drives the chemistry beyond 10 AU, since the surface density is too small to attenuate the cosmic rays there. These produce the $H_3{}^+$ and He^+ ions that initiate the chemistry and convert CO and N_2, initially the most abundant species, into CO_2, CH_4, NH_3, and HCN. In the cold regions the reaction products are depleted onto grains as part of the ice mantle. As matter accretes towards the inner, warmer regions, the ice mantle evaporates. Therefore, in regions beyond 20 AU species such as CH_4 are in the form of ice. Inside 20 AU the methane is desorbed and converted into larger hydrocarbons. Clearly, the details of the transport and heating are critical for understanding the chemical distribution in the early stages of disk formation and evolution.

At small disk radii (< 100 AU), irradiation by the central star will be significant, and possible sources of grain heating include disk surface heating by stellar photons and stellar X-rays. The impact of heating by stellar optical and UV photons on the vertical temperature structure has yet to be considered in the context of desorption. Chiang & Goldreich (1997) show that even at 100 AU distances, grains at disk surfaces that are irradiated by an (unattenuated) T Tauri star will be heated to temperatures in excess of the disk effective temperature due to the mismatch in the optical absorption and far-infrared emission efficiencies of grains. The high grain temperature (80 K for 1000 Å grains) will likely result in significant CO desorption. Photons absorbed in the surface layer will be reradiated down toward lower layers, producing a potentially significant column density of warm dust. Disk chemistry models are in their infancy and much work remains to produce realistic 2-D disk chemistry models.

V. SUMMARY

A great deal of progress in understanding interstellar chemistry has been made in the last several years since the *Protostars and Planets III* reviews. In large measure this progress has been due to the increased instrumental capabilities of interferometers, the thrust into space from ISO, new laboratory results for grain chemistry, and better theoretical models which couple dynamics and chemistry. We expect further improvements in the coming years with the advent of new larger millimeter arrays, and space–based missions such as the Far Infrared Submillimeter Telescope (FIRST) and the Next Generation Space Telescope, and the advent of more sensitive ground based near-IR instruments.

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FIGURE CAPTIONS

Figure 1. Examples of spectra (antenna temperature, T_A(K), versus frequency, as measured in velocity offset from V_{lsr}) of complex molecules taken at the CCS peak emission (Langer et al. 1997; Velusamy and Langer 1998). Note the differences in the intensity ratios among these molecules at different velocities.

Figure 2. Time-dependent chemistry for the evolution in a collapsing dense core including depletion (based on Bergin and Langer, 1997). This shows the 'late time' chemistry where species such as CS and C_2S are depleting onto grains while the nitrogen species such as N_2H^+ and NH_3, as well as HCO^+, survive.

Figure 3. The top panel shows L1498 in the ISO continuum emission at 200 μm (dashed line) which traces out the dense core (Willacy et al. 1998a). The solid lines are a $C^{18}O$(1-0) map showing a minimum at this position. This indicates that even CO is strongly depleted in the center of cold dense cores. The bottom panel traces the structure of the L1498 core in CS, CCS, and NH_3 emission (Kuiper et al. 1996). The molecules and telescopes used are indicated. These interferometer data highlight limb brightened emission indicating that these molecules trace shells around the center. The ammonia data also peak at the continuum position.

Figure 4. ISO SWS spectrum of the deeply embedded source W33A in the wavelength range 2.4 – 20 μm. The mean spectral resolving power is approximately 1000. Various absorption features arising in silicate dust and icy mantles along the line of sight are labelled.

Figure 5. ISO SWS spectra of the CO_2 bending mode near 15 μm, illustrating thermal evolution of interstellar ices. The sources are displayed in order of increasing gas temperature ($T_{\rm gas}$ = 16 K, 23 K, 26 K and 28 K for SgrA*, W33A, NGC7538 IRS9 and S140, respectively). Solid lines are fits based on laboratory data for an ice mixture (H_2O:CH_3OH:CO_2 = 1:1:1) at various temperatures (Gerakines et al. 1999). The strengths of the narrow features near 15.12 and 15.25 μm increase systematically with temperature.

Figure 6. Grain surface chemistry routes involving CO (adapted from Tielens and Hagen 1982). Hydrogenation of CO mainly leads to the formation of H_2CO and CH_3OH. The accreted C, N, and O can also lead to the formation a variety of complex species whose abundances only depend on the relative accretion rates of these species.

Figure 7. OVRO Millimeter Array observations of the ^{13}CO, CN, HCN, and HCO^+ 1–0 emission from LkCa 15 (Qi et al., 1999). The synthesized beam is depicted in the lower left hand corner of each panel, and is approximately

$4.''5 \times 3''$ ($\sim$700 $\times$ 500 AU). Contour levels are spaced by roughly 0.6, 0.6, 0.35, and 0.4 K km s^{-1}, respectively, and begin at twice this level. In each case, the emission is centered on, or very close to, the position of the star, as measured by the thermal continuum emission from dust. The velocity ranges measured for the observed emission are similar to or less than those of CO (2-1), and arise from gas bound to the star.