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FEATURE ARTICLE

Chemistry of Star-Forming Regions

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The space between stars is not empty but contains gas-phase and particulate matter under varying conditions. Neutral matter is found mainly in large regions of the interstellar medium known as “clouds”, the largest of which, termed “giant molecular clouds”, are essentially molecular in nature. Stars and planetary systems form inside these giant clouds when portions collapse and heat up. The details of the collapse can be followed by observation of the chemical changes in the molecular composition of the gas and dust particles. Moreover, an understanding of the chemical processes yields much information on the time scales and histories of the assorted stages. Among the most recent additions to our chemical knowledge of star formation are a deeper understanding of isotopic fractionation, especially involving deuterium, and a realization that the role of neutral–neutral reactions is more salient than once thought possible.

1. Introduction

The universe started as a Big Bang and within a relatively brief astronomical period cooled and expanded to form an undifferentiated ooze consisting overwhelmingly of hydrogen and, to a lesser extent, helium.[1] Eventually, the ooze condensed into relatively concentrated large portions of material known as protogalaxies, and local matter in these objects collapsed to form the first generation of stars. Much of the matter in the universe is now to be found in galaxies, which are large assortments of stars, interstellar matter, and so-called “hidden” matter, necessary to understand the dynamics of galaxies but not directly detectable. Our own galaxy, the Milky Way, has a typical spiral structure, with a dense center that may contain a black hole, and spiral arms that trace out both stars and interstellar matter. The interstellar matter is composed of a variety of low-density phases. In addition to rather hot and rarefied matter, there is much neutral material, typically concentrated in regions known as “interstellar clouds”, and containing both gaseous and particulate phases.[2]

The nuclei of stars both heat and stabilize stellar matter by exothermic nuclear fusion reactions that produce elements more complex than hydrogen. This matter eventually finds its way into interstellar space because older stars lose much of their matter either explosively, as in supernovae, or more gently. Under the influence of gravity, interstellar clouds are formed from the stellar ejecta. The relationship between stars and interstellar matter is cyclical because, as clouds evolve, portions of them collapse to form new generations of stars, which start life with considerable portions of non-hydrogenic matter in their outer regions.[3] Some chemistry and condensation into dust particles can then occur in relatively cool stellar atmospheres, especially as stars age. The matter emanating from these older stars contains atoms, molecules, and tiny dust particles composed either of silicates or carbon. The harsh radiation field in interstellar space quickly dissociates most molecules formed in stellar atmospheres, and the material that leads to yet new generations of interstellar clouds becomes mainly atomic and particulate in nature, although any very large molecules formed in stars may survive relatively unscathed.

Given this cycling, one can expect that the elemental makeup of stars and clouds in our galaxy is on average rather similar.

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TABLE 1: Cosmic and Solar Abundances[a] of Some of the More Important Elements Normalized to Hydrogen

element	cosmic	solar
He	1.0(−01)	8.5(−02)
C	2.1(−04)	4.0(−04)
N	6.6(−05)	1.1(−04)
O	4.6(−04)	8.5(−04)
Mg	2.5(−05)	3.8(−05)
Si	1.9(−05)	3.6(−05)
S	1.2(−05)	1.6(−05)
Fe	2.7(−05)	4.7(−05)

[a] Note: $a(-b)$ refers to $a \times 10^{-b}$.

The relative abundances of each element are best determined via stellar absorption spectra, in which cooler atmospheric layers absorb radiation from the nearly blackbody radiation emitted from high-density interior regions of stars. Although all stars do not show the same elemental abundances, an average of many nearby young and middle-aged stars, known as “cosmic abundances”, can be defined.[4] The most abundant elements are shown here in Table 1 for the cosmic and solar cases, with the numbers given relative to hydrogen, which is dominant for almost all bodies except gravitationally insignificant ones such as the earth. It can be seen that although helium is close in abundance to hydrogen, the chemically important elements carbon, oxygen, and nitrogen are lower in abundance by factors of 10^{3-4} and heavier elements are lower by even greater factors. The elemental abundances in the solar atmosphere lie very close to the cosmic values but tend to be somewhat greater for the heavier elements.

The detailed nature of interstellar clouds is still only partially understood, even in our own galaxy. Relatively nearby “diffuse” clouds can be studied by optical and ultra-violet spectroscopic absorption using background stars as lamps; the matter in such regions is relatively transparent and has a typical gas density n of approximately 10^2 cm^{-3}, a gas temperature of 50 K, and a dust temperature of 20 K.[2,5] Except for hydrogen, which is roughly evenly divided between its neutral atomic and molecular forms, most of the gas is atomic in nature, with small concentrations of diatomic species and a few polyatomic ones. The elemental abundances pertaining to the gas show depletions for elements heavier than helium relative to stellar values because of the existence of dust.

More important chemically are dense clouds, where the gas density rises to 10^4 cm^{-3} and the temperature plunges to 10 K, for both gas and dust. Note that the density of so-called “dense” clouds is only relatively high; on an absolute scale it is so low that the material is more vacuous than the best laboratory vacuum! Here the hydrogen is overwhelmingly molecular in nature, and many polyatomic molecules can be detected.[6] The elemental abundances in the gas are highly uncertain but observations indicate moderate to strong depletions of heavy elements. The density of dust particles, typically 1% of the matter by mass and 10^{-12} by number, is sufficiently great to “extinguish” most background stellar radiation in the visible and UV, but not in the infrared and longer wavelengths, because the extinction goes roughly as $1/\lambda$. Indeed, dense clouds can look like holes in the sky if they are relatively nearby so that there are few foreground stars. Figure 1 shows a visible picture of the so-called “black cloud” Barnard 68. Infrared absorption studies can be performed to study both gaseous and particulate matter in dense clouds such as Barnard 68, but the terrestrial atmosphere renders such studies difficult and telescopes mounted on satellites improve the signal-to-noise ratio dramatically.[7,8] The major spectroscopic technique for studying dense clouds is radio astronomy, which probes the rotational spectra of gas-phase molecules, and can be performed from the ground at wavelengths as short as 0.3 mm. Rotational spectra are generally seen in emission both because of the relative paucity of continuous background sources and because collisional excitation is efficient. Such spectra do not probe the condensed phase. In addition, nonpolar molecules do not possess a strong rotational spectrum, and only the very abundant molecule H_2 has been detected in this manner, via its quadrupolar transitions.

Figure 1. The so-called black cloud B68, 500 light years distant and 0.5 light years across, is really a dense core that extinguishes most background visible radiation. Permission to reproduce the figure has been granted by ESO. Taken from web site http://antwrp.gsfc.nasa.gov/apod/ap990511.html.

Use of all of the above high-resolution spectroscopic techniques has resulted, by comparison with laboratory spectra, in the detection of well over 120 gas-phase interstellar molecules (excluding isotopomers), which are mainly organic in nature. Most of these species are detected only in dense sources. Infrared spectral studies of dense clouds show that dust particles possess a core−mantle structure, with cores of silicates and carbon surrounded by mantles of simple ices composed mainly of water, CO, and CO_2.[6,9,10] The detected gas-phase species comprise molecules that are both normal by terrestrial standards and those (molecular ions, radicals, unusual isomers) that are quite exotic.[6] In dense clouds, the most abundant gas-phase molecule after molecular hydrogen is CO, which possesses a concentration approximately 10^{-4} that of H_2, taking up a significant portion of the elemental abundances of both carbon and oxygen. Other species have even smaller relative concentrations known as “fractional abundances”. The largest molecule detected in the gas phase is $HC_{11}N$, a very unsaturated nitrile known as a cyanopolyyne. A list of some gaseous molecular fractional abundances in the well-studied dense cloud TMC-1 is shown in Table 2.[11] The organic chemistry of cold dense clouds such as TMC-1 is dominated by very unsaturated species such as the radicals C_nH ($n = 1-9$) and the cyanopolyynes.

Dense clouds can be detected as single objects often called globules, but they tend to be associated with much larger and heterogeneous agglomerations of gas and dust known as

TABLE 2: Some Observed Fractional Abundances[a] in TMC-1 with Respect to H_2

species	abundance	species	abundance
CO	8(−5)	HCCCN	2(−8)
OH	2(−7)	Cyclic-C_3H_2	1(−8)
CCCCH	9(−8)	HCO^+	8(−9)
HCN	2(−8)	HCS^+	4(−9)
HNC	2(−8)	$HCNH^+$	2(−9)
NH_3	2(−8)	$HCCCNH^+$	1(−10)

[a] Note: $a(-b)$ refers to $a \times 10^{-b}$.

"complexes" or "giant molecular clouds", depending on size, location, and the type of stars being formed. The denser portions of these assemblies are often known as "dense cores" rather than "dense clouds" whereas the relatively diffuse material surrounding them is often referred to as "translucent" because it lies in a density regime in between the cores and standard diffuse clouds.[12] TMC-1, for example, is located in a much larger and generally less dense structure known as the Taurus Molecular Cloud. The spectra of dense cores are highlighted by rotational emission from polar molecules with large spontaneous emission rates, because only at relatively higher densities can such species be collisionally excited sufficiently rapidly. The molecule CO, on the other hand, possesses a very small dipole moment and a low rate of spontaneous emission so that, thanks in part to its large abundance, it can be excited and detected throughout a giant cloud, especially in its lowest-lying ($J = 1 \rightarrow 0$) transition.[13] Giant molecular clouds contain large populations of young stars, some even with dark pre- (or proto-) planetary disks of dense dust surrounding them, and it is now regarded as certain that these stars are formed within the clouds from dense cores when the material collapses.[14] Initially isothermal, the collapse eventually produces a condensation that is sufficiently dense that further collapse becomes adiabatic. We use the term "protostar" for the ensuing stage, in which the central condensation increases in temperature until nuclear reactions turn on, the exothermicity of which stabilizes the collapse. The heat from protostars and newly formed stars influences the host dense cloud core in a complex variety of ways, changing the chemical makeup of the nearby gas and leading, at the least, to the evaporation of the grain mantles.

The series of stages leading to star formation depends strongly on whether a low-mass or high-mass star is being formed. The formation of a low-mass star, with a mass approximately that of the sun, is better understood because it takes longer. The formation of a high-mass star is far more spectacular, however, because it eventually leads to the creation of a hot ionized gas around the newly formed star, which lights up the vicinity. Although no molecules are found in these ionized areas, known as HII regions after the spectroscopic notation for protons, molecules are found nearby under relatively warm conditions in areas labeled PDR's, an acronym for "photon-dominated regions".[15] Figure 2 shows perhaps the most famous HII region in the sky, the Orion Nebula, which lies in the forefront of the Orion molecular cloud and is powered by the newly formed Trapezium stars. Right at the border of the visible region in the southwest region lies the so-called Orion Bar source, which is probably the best-known PDR. Broad infrared spectra from PDR's seen in fluorescent emission indicate the existence of aromatic matter, most probably in the form of large polycyclic aromatic hydrocarbons.[16] There is also some evidence for these species in still-unassigned diffuse spectra in the visible seen in absorption as starlight passes through diffuse interstellar clouds.[17]

Of course, we do not witness actual star formation in real time but detect many objects that can be regarded as existing along an "evolutionary track" that leads to star formation. Much of what we know about these stages comes from our observation of what molecules are present, how abundant they are, and what chemical processes lead to their formation and destruction. Indeed, the use of chemistry to study regions of star formation as well as a host of other objects has become a very important field in astronomy in the last thirty years or so, ever since polyatomic molecules were first detected.

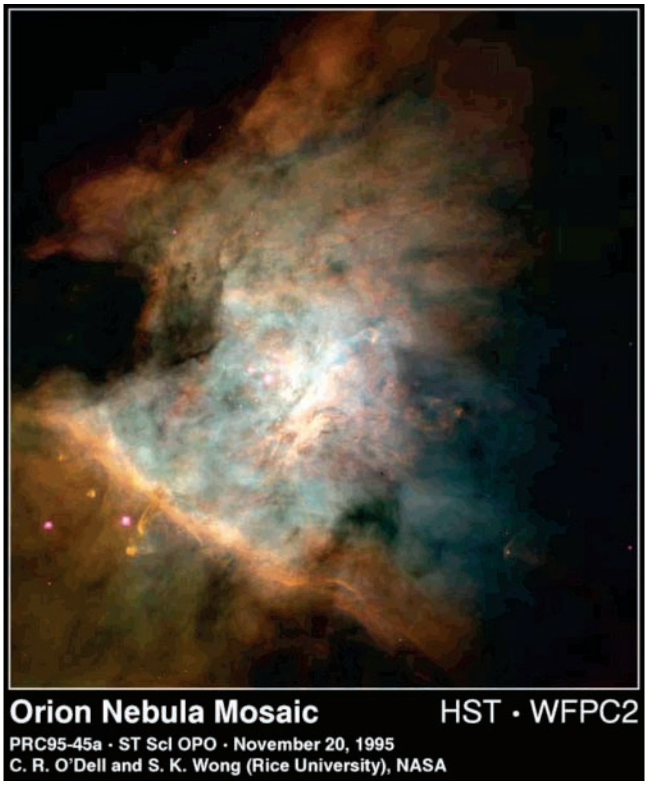

Figure 2. Orion Nebula, a hot plasma caused by high-mass star formation within the Orion molecular cloud. Image courtesy of NASA. Modified by C. R. O'Dell. Taken from web site http://antwrp.gsfc.nasa.gov/apod/ap970511.html.

In the remainder of this article, we will first discuss the formation of molecular hydrogen on granular surfaces in both diffuse and dense interstellar sources, as part of a general introduction to surface chemistry in clouds. The production of H_2 is a precursor to subsequent gas-phase chemistry. We will then discuss recent advances concerning the chemistry occurring in some of the stages associated with the formation of a solar-mass type star and its associated planetary system. Our discussion of the initial stage—dense, or starless, cores—will be used to review briefly some of the basic aspects of low-temperature gas-phase interstellar chemistry. In addition, we will touch upon some chemical aspects of high-mass star formation. More detailed studies can be found in the relevant literature cited throughout the article. Although work from our group will be emphasized, the field of astrochemistry is a worldwide one with many practitioners.

2. Formation of Molecular Hydrogen: An Introduction to Astronomical Surface Chemistry

A substantial amount of molecular hydrogen is found even in diffuse interstellar clouds, so its formation is efficient at exceedingly low densities. Given the inefficiency of gas-phase radiative association between two hydrogen atoms and the impossibility of three-body association at the low density, it has been thought for many years that the formation of H_2 occurs on the surfaces of interstellar dust particles.[18] Recent temperature-programmed desorption (TPD) experiments on ultra-cold olivine (silicate) and amorphous carbon substrates show that the process does indeed happen on realistic analogues of granular surfaces, occurring via a diffusive, or Langmuir−Hinshelwood, mechanism, in which physisorbed hydrogen atoms move from lattice site to lattice site until finding one another.[19−21] With most but not all of the reaction exothermicity transferred to the solid, the molecular product can then be immediately desorbed from the surface or, if thermalized, soon evaporate except at the lowest temperatures. In addition, a relatively simple analysis of the TPD data yields the binding energies of both atomic hydrogen reactant and molecular hydrogen product to the surface, the barrier against diffusion of atomic hydrogen, the fraction of product immediately ejected from the surface, and the fact that diffusion occurs via classical hopping rather than quantum mechanical tunneling.[22] As shown by other investigators, however, more complex models invoking some chemisorption and tunneling can also be used to fit the data.[23] Similar experiments on amorphous low-density ice require more detailed analyses partially because the ice is porous and exceedingly irregular.[24]

The parameters determined from analyses of the experiments on olivine and amorphous carbon can be used to estimate the efficiency of the conversion of atomic to molecular hydrogen on interstellar grains under a variety of conditions. The efficiency is defined as twice the number of hydrogen molecules produced divided by the number of hydrogen atoms landing on a grain under steady-state conditions. The simplest approach to determine the efficiency is to utilize rate equations. Rather than use surface (areal) densities or monolayers, as is common in the field of surface chemistry,[25] we prefer to use actual number of species on a grain in these equations. Let $N(\mathrm{H})$ be the average number of H atoms on a grain. The rate of change of $N(\mathrm{H})$ is given by the rate law[26]

$$\mathrm{d}N(\mathrm{H})/\mathrm{d}t = k_{\mathrm{ads}}n(\mathrm{H}) - k_{\mathrm{H-H}}N(\mathrm{H})\,N(\mathrm{H}) - k_{\mathrm{evap}}N(\mathrm{H}) \quad (1)$$

where $n(\mathrm{H})$ is the gas-phase concentration of H atoms, k_{ads} is the second-order rate constant for collisions between H atoms and grains leading to sticking, k_{evap} is the first-order rate constant for evaporation, and $k_{\mathrm{H-H}}$ is the reactive rate constant for two hydrogen atoms. It is typically assumed that sticking is 100% efficient.

To determine an expression for the reactive rate constant, consider a hydrogen atom moving from one lattice site to another. Its rate of reaction is simply the rate of diffusion k_{diff} (s^{-1}) to a nearest neighbor site multiplied by the probability $N(\mathrm{H})/N$ of finding another H atom at the site, where N is the total number of lattice sites. If one remembers that there are $N(\mathrm{H})$ hydrogen atoms looking for partners and that both atoms of a future partnership are moving, the formula for $k_{\mathrm{H-H}}$ is derived to be

$$k_{\mathrm{H-H}} = 2k_{\mathrm{diff}}/N \quad (2)$$

For a typical grain of radius 0.1 μm, there are roughly 10^{5-6} surface sites for adsorption using standard lattice-site areal densities.[22,25] If tunneling can be neglected and there is only one diffusive barrier,[22] the diffusive rate constant is given by the expression

$$k_{\mathrm{diff}} = \nu \exp(-E_{\mathrm{b}}/kT) \quad (3)$$

where ν is a typical attempt frequency (10^{12} s^{-1}), E_{b} is the barrier between lattice sites, which are represented as potential minima, k is the Boltzmann constant, and T is the absolute temperature. The rate constants for adsorption and evaporation are considered below. Using an analogous rate law for $N(\mathrm{H_2})$, one can determine the efficiency of $\mathrm{H_2}$ formation under steady-state conditions as a function of the gas-density $n(\mathrm{H})$.[26]

Although a rate equation analysis is adequate for modeling laboratory experiments on regular surfaces, one cannot just utilize rate equations for the interstellar reaction because the small sizes of dust particles (1 nm to 1 μm) and the low rate of adsorption onto grains lead to very small average surface populations $N(\mathrm{H})$ of H atoms, often less than unity, requiring an analysis that treats the discrete aspects of the problem as well as its fluctuations. To perform such an analysis generally requires a stochastic treatment. In the stochastic master equation method, for example, one focuses on the time derivatives of probabilities that certain numbers of species are present on an individual grain rather than on time derivatives of average abundances.[26,27] The equations look somewhat similar to eq 1 but expressions such as $N(\mathrm{H})$ are replaced by probabilities $P_n(\mathrm{H})$ for $n = 0, 1, 2, ...$ H atoms on a grain. Such an approach is superior to rate equations for regular grain surfaces, which are described by individual values of E_{b} and E_{D}, especially in situations where the average abundance of atomic hydrogen is less than unity. If, as determined from the laboratory experiments with a simple model, single binding energies and diffusive barriers for hydrogen atoms represent the adsorption and diffusion, then the calculated interstellar reaction efficiency is high (greater than 50%) only in narrow temperature ranges, typically much lower than the surface temperature of diffuse clouds.[22] One method of alleviating this problem is to use a model with some chemisorption to explain the laboratory data, and use the determined parameters to model the interstellar analogue.[23]

We have preferred to study inhomogeneous surfaces in which only physisorption occurs. Silicate and carbonaceous surfaces are considered to be inhomogeneous if either continuous distributions or multiple but discrete values of binding energies and diffusive barriers for H atoms exist.[28,29] These two types of inhomogeneities result, respectively, from amorphous substrates and irregularities including kinks and terraces.[25] Whether or not such inhomogeneities pertain to laboratory samples, it is likely that they pertain to interstellar particles. To model $\mathrm{H_2}$ formation on inhomogeneous surfaces with a careful attention to the nature of random walk, we have used a Monte Carlo treatment to follow the motions of individual hydrogen atoms on square lattices representing the surfaces of interstellar grains.[28] With this approach, the calculated efficiency of reaction in diffuse clouds is found to depend severely on the inhomogeneity of the surface. Using sufficiently inhomogeneous surfaces, we have found that the temperature range for high efficiency of $\mathrm{H_2}$ formation under the conditions of diffuse interstellar clouds extends to temperatures higher than surface temperatures relevant to these sources. We are also currently attempting to reanalyze the laboratory experiments by using models of inhomogeneous surfaces that are patterned on microscopic pictures of those surfaces used in the laboratory.

The formation of molecular hydrogen on grain surfaces in dense clouds is a more complex process because it occurs on the surfaces of mantles that grow via both simple adsorption from the gas and via granular chemistry. Nevertheless, observations and theory indicate that virtually all of the hydrogen is molecular in these sources, with a residual atomic abundance of 10^{-4} that of $\mathrm{H_2}$, so that surface hydrogenation on icy mantles is still efficient. The formation of water ice in cold dense regions is thought to occur by a surface process in which primeval oxygen atoms landing on grains react twice with hydrogen atoms, again via a diffusive mechanism. Analogous hydrogenation reactions convert atomic carbon and nitrogen into methane and ammonia, respectively.[29] There is even laboratory evidence for the slow conversion of CO, when it lands on a grain, into formaldehyde and subsequently methanol although here there are several reactions with small activation energies.[30] Thus, surface chemistry acts to make saturated molecules because atomic hydrogen, because of its low binding energy to the surface and consequent rapid rate of diffusion, is the dominant reactant. Unlike the case of molecular hydrogen formation, however, heavy products formed on grain surfaces cannot evaporate efficiently, basically because they are bound too strongly. This result is seen easily by considering the first-order rate constant for evaporation k_{evap}, which is given by the Polanyi−Wigner relation[25]

$$k_{\mathrm{evap}} = \nu \exp\{-E_{\mathrm{D}}/kT\} \tag{4}$$

where ν is the same frequency used for diffusion (see above), typically 10^{12} s^{-1} for physisorbed species, and E_{D} is the binding energy of the adsorbate to the surface. The binding energy E_{D}/k of H to olivine, a metallic silicate, has been measured to be 373 K.[22] At a temperature of 10 K, the rate constant is 6×10^{-5} s^{-1}, leading to a half-life against evaporation of 1×10^4 s, or 3 h. Contrast this for the case of a heavier species with typical binding energy of 1000 K, in which case the half-life against evaporation at 10 K rises dramatically to 2×10^{31} s (6×10^{23} yr), much greater than the lifetime of the universe.

A variety of nonthermal desorption processes for heavy species have been considered by ourselves and other groups, including immediate ejection following reaction, ejection via the heat generated by a reaction exothermicity, energetic particle desorption, and photodesorption, but no detailed laboratory analyses are available.[31,32] Given the large mantles detected in cold dense regions, nonthermal desorption cannot be particularly efficient. The chemistry that forms detected gas-phase molecules in cold dense sources is thus mainly gas-phase in nature, starting from H_2 and primeval atoms. Once a star is born, or nearly born, and heating occurs in the nearby region, the mantle species evaporate into the gas and change the character of the gas-phase chemistry from a nonsaturated to a saturated one.[33]

3. Starless Cores

We now switch to the adjective "starless" to refer to dense cores with the standard conditions ($n = 10^4$ cm^{-3}, $T = 10$ K) and with no obvious evidence of a central condensation of higher density formed by collapse. The basic gas-phase chemistry occurring in such regions has been reasonably well understood for some time, and is dominated by exothermic ion−molecule reactions.[34] Rarely possessing any activation energy barriers, these reactions have very large rate constants down to low temperatures. For nonpolar neutral reactants, the rate constant can be approximated quite well by the Langevin expression k_{L}, which is derivable from a consideration of long-range forces leading to capture. It is given by the formula[35]

$$k_{\mathrm{L}} = 2\pi e\{\alpha/\mu\}^{1/2} \approx 10^{-9}\ \mathrm{cm}^3\ \mathrm{s}^{-1} \tag{5}$$

where, in cgs-esu units, e is the electronic charge, α is the polarizability, and μ is the reduced mass of reactants. There is no temperature dependence in the formula at all! Ionization occurs via bombardment by cosmic rays, which are bare nuclei, mainly protons, traveling at relativistic speeds and able to penetrate dense clouds with a small but significant cross section for ionization.[34] The rate of ionization is normally expressed in terms of a first-order ionization rate constant ζ for atomic hydrogen, with rate constants for other neutral species such as H_2 expressed in terms of ζ. An estimate for ζ in starless cores is 10^{-17} s^{-1}, so that an average time between ionization events per H atom is 10^{17}s $= 3 \times 10^9$ yr. Nevertheless, cosmic ray "bombardment" leads to an overall fractional ionization of perhaps $10^{-8} - 10^{-7}$ within a reasonable time period according to recent chemical models.[36]

In starless cores, the major ionizing event occurs for the dominant species H_2 and leads mainly to the production of H_2^+. This ion is short-lived, reacting with H_2 in an average time period of approximately 10^5 s (1 day) and producing the longer-lived H_3^+ ion, a well-known interstellar molecule detected via infrared absorption.[7] The H_3^+ ion is depleted by dissociative recombination reactions with electrons, and by reactions with neutral species such as atomic oxygen:

$$\mathrm{O} + \mathrm{H}_3^+ \rightarrow \mathrm{OH}^+ + \mathrm{H}_2 \tag{6}$$

mainly via proton-transfer processes. A similar process produces CH^+ from atomic C. Both OH^+ and CH^+ react quickly with H_2 via H-atom transfer processes:

$$\mathrm{X}^+ + \mathrm{H}_2 \rightarrow \mathrm{XH}^+ + \mathrm{H} \tag{7}$$

to form OH_2^+ and CH_2^+, respectively, whereas subsequent H-atom transfer leads to H_3O^+ and CH_3^+. The oxonium ion, a relatively stable and detected interstellar species, is mainly destroyed by dissociative recombination:

$$\mathrm{H}_3\mathrm{O}^+ + \mathrm{e}^- \rightarrow \mathrm{H}_2\mathrm{O} + \mathrm{H};\ \mathrm{OH} + 2\mathrm{H};\ \mathrm{OH} + \mathrm{H}_2 \tag{8}$$

It has been known for some time that dissociative recombination reactions have very large rate constants, typically 10^{-6} to 10^{-7} cm^3 s^{-1} at room temperature with an inverse temperature dependence, but only recently have storage-ring experiments given us a sense of the branching fractions for assorted products.[37,38] These reactions produce both normal species such as water and unusual ones such as the hydroxyl radical. In reaction 8, the OH + 2H channel has the largest branching fraction, 0.60. As another example, the dissociative recombination of the linear ion $HCNH^+$ produces both HCN and the isomer HNC, probably in equal proportions.

The methyl ion does not react with H_2 in the normal sense because the H-atom transfer is endothermic; nevertheless, reaction occurs by the slower mechanism of radiative association:

$$\mathrm{CH}_3^+ + \mathrm{H}_2 \rightarrow \mathrm{CH}_5^+ + h\nu \tag{9}$$

in which the intermediate complex is stabilized by emission of a photon. According to a statistical theory of ours,[39] the rate constant for this process is approximately 10^{-13} cm^3 s^{-1} at 10 K, corresponding to about one in 10^4 Langevin-type collisions. Nevertheless, because H_2 is so dominant, the process is competitive with dissociative recombination. Two ion-trap experiments have been performed on this reaction and are only in qualitative agreement with theory and with each other.[40,41] Once protonated methane is synthesized, it undergoes a dissociative recombination reaction to produce an assortment of single-carbon hydrocarbons. Many other chains of ion−molecule and dissociative recombination reactions have been invoked to form and destroy most of the gas-phase molecules seen in starless cores.[11,34,36] To use these reactions to determine the concentrations of interstellar molecules, it is important to remember that because the gas-phase chemistry is powered by external energy in the form of cosmic rays and/or photons, the chemistry is kinetically controlled. Involving mainly ionic processes, large chemical networks, including perhaps 4000 reactions and involving 400 species, have been formulated and used to model the gas-phase chemistry of starless cores by numerical integration of coupled rate equations starting from atomic gas except for molecular hydrogen. Such models, if suitably adapted, can also be used for diffuse cloud chemistry, although the chemistry is not as complex and photoprocesses are quite important.

Our current network of reactions and rate constants can be found at http://www.physics.ohio-state.edu/∼eric/research.html, which also contains a link to the comparable network of the UMIST (now University of Manchester, U.K.) group, known as RATE99. With the assumptions of homogeneous and static physical conditions, models based on these networks are most successful at times of approximately 10^5 yr, at which time they can reproduce the abundances of perhaps 50−80% of the observed molecules to within their uncertainties, depending on the source studied.[11,34,36] At longer periods of time, most heavy molecules stick to dust particles and are removed from the gas.[42] If adsorption is ignored, the system will reach a steady-state situation in 10^{7-8} yr, which is unrealistic (and still not to be confused with thermodynamic equilibrium). Moreover, the steady-state solutions are typically worse than those obtained at so-called early time. In addition to their partial quantitative success at the earlier time, the models show qualitatively why normal molecules, radicals, isomers, and molecular ions are all detected. In addition, the unsaturated nature of the organic chemistry is reproduced, mainly because as the molecular ions become larger in size, they tend to be unreactive with H_2. Nevertheless, the failure of the models to reproduce 100% of the molecular abundances should be probed. This failure stems from a variety of astronomical and chemical reasons.

The major chemical reasons for the lack of total success are uncertainty in reaction rate constants and incompleteness of the networks. Two other chemical problems arise from actual errors in the network and the possibility of nonthermal events. The major astronomical reasons are the lack of physical homogeneity and the possibility that physical conditions change with time on time scales comparable with the chemistry, rendering the initial conditions and chemical abundances obscure. Progress is currently being made on reducing all sources of error. The lack of homogeneity becomes apparent with telescopic techniques of high spatial resolution; TMC-1, for example, is now known to consist of four cloudlets, named A−D, respectively. At the simplest level, models can now be constructed for each cloudlet. More ambitiously, new models are being constructed in which both the formation and destruction of dense cores in a more diffuse medium occur.[43] Other models consider the role of nearby star formation in changing physical conditions on a temporal basis; nearby star formation can lead among other changes to desorption of mantle material.[44]

Regarding the chemical deficiencies, a salient issue is that most of the reactions in the networks have not been studied in detail in the laboratory or via ab initio means. Under such circumstances, one might assume that we and other astrochemists have just been lucky in getting any concentrations correct. The percentage of critical reactions that have been measured, however, is significantly higher than the overall percentage. Moreover, the networks are dominated by ion−molecule reactions, and these typically fall into classes where both rate constants and products can be estimated accurately. Ironically, the largest uncertainty concerns the role of neutral−neutral reactions in the low-temperature chemistry.[11] Of course, even studied rate constants possess uncertainties, and several groups have recently tried to estimate how uncertainties, both measured and estimated, in rate constants propagate to uncertainties in calculated abundances.[45] The result is that the smaller molecules tend to have the smaller uncertainties, whereas the larger ones in the model can have several-order-of-magnitude uncertainties. Because the larger species are typically the ones with abundances that cannot be calculated accurately, it would appear that the problem is simply one of uncertainty. That this is not the case, however, is shown by the fact that the calculated abundances for complex molecules are almost always too low.[11] It is likely then that the incompleteness of models plays an important role.

One source of incompleteness might be neglect of the nonthermal desorption of molecules from grain mantles. For example, consider the case of methanol. The only gas-phase synthesis of this molecule in networks consists of the radiative association reaction

$$CH_3^+ + H_2O \rightarrow CH_3OH_2^+ + h\nu \qquad (10)$$

followed by dissociative recombination:

$$CH_3OH_2^+ + e^- \rightarrow CH_3OH + H \qquad (11)$$

Recent measurements indicate that our calculated value of the rate constant for reaction 10 is too high by at least 2−3 orders of magnitude,[46] indicating the importance of correcting errors. With the newly measured rate constant, we cannot come close to reproducing the observed abundance of methanol in the gas phase in sources such as TMC-1. The only alternative possibility we currently know of is that methanol, having been formed on granular surfaces by the hydrogenation of CO, desorbs into the gas with some low efficiency.[30] Our current unpublished estimate is that 1 out of every 10^3 CO molecules landing on grains must come off as methanol to explain the observed abundance in TMC-1. If it is true that grain mantles must be included, then it makes sense to run gas-grain models in which surface chemistry and gas-phase chemistry occur simultaneously with both adsorption and nonthermal desorption. Although we have constructed models based on such combined networks, the difficulty in modeling surface reactions via correct stochastic methods plus the unknown efficiency of nonthermal desorption mechanisms has limited their usefulness for starless cores.[12,42,47]

Another source of incompleteness in gas-phase models may lie in our treatment of neutral−neutral reactions in the networks. It has been recognized for some time that radical−radical reactions typically do not possess activation energy and should be included. The problem lies in what to do with the discovery over the past decade that certain reactions between radicals and nonradicals do not possess activation energy and indeed increase in rate as the temperature is lowered. [11] Studied to low temperatures mainly by groups in Birmingham, U.K., and Rennes, France, using the CRESU technique[48] and by the Bordeaux group with a merged beam apparatus,[49] these reactions have rate constants nearly as large as the Langevin value at temperatures near 10 K. The main radicals studied—atomic carbon, CN, and CCH—react rapidly with unsaturated hydrocarbons and generally produce more complex products. For example, the following reactions with acetylene:

$$C + C_2H_2 \rightarrow C_3H + H; C_3 + H_2 \tag{12}$$

$$CN + C_2H_2 \rightarrow HCCCN + H \tag{13}$$

$$CCH + C_2H_2 \rightarrow C_4H_2 + H_2 \tag{14}$$

are all rapid and quite important in starless cores. The problem with this class of reactions is the small number of systems studied. Generalization to the many possible reactions needed to describe the chemistry of starless cores is difficult without laboratory or theoretical studies because activation energies may indeed exist. An example is the reaction

$$CCH + HCN \rightarrow HCCCN + H \tag{15}$$

which was included in our network on the basis of the suggestion of the Birmingham group until it was determined to have a significant activation energy.[50]

Undaunted by this mistake, we have recently attempted to include a sizable number of unstudied radical-neutral reactions likely to be of importance into our network based mainly on chemical intuition and studies of analogous systems.[11] The new network − labeled osu.2003 − can be found on our web page (http://www.physics.ohio-state.edu/~eric/research.html). Using this network to model starless cores leads to smaller calculated abundances of the more complex molecules and worsens agreement with observation for the well-studied source TMC-1.[11] A sensitivity analysis shows, however, that the poor results are dependent on our choices of reaction rate constants for some poorly understood neutral−neutral reactions involving atoms and either unsaturated radicals or bare carbon clusters. For example, it is assumed that the radiative association reactions

$$C + C_{2n+1} \rightarrow C_{2n+2} + h\nu \tag{16}$$

for $n = 1-3$ occur at the collisional rate ($k \approx 10^{-10}$ cm^3 s^{-1}) on the basis of simple statistical theories. These reactions compete with hydrogenation processes that produce the unsaturated species detected.

3.1. Deuterium Fractionation. A notable success of gas-phase models of starless cores is their reproduction of exceedingly large isotope effects involving deuterium. The ratio of elemental deuterium to hydrogen is not constant throughout even our galaxy but can be approximated as 10^{-5} in most sources of interest. In starless cores, the deuterium is mainly in the form of HD, so the ratio of HD to H_2 is 2×10^{-5}. When one observes deuterated isotopomers of trace species such as HCN and HCO^+, however, the ratio of the deuterated to the normal species is in the range 0.01−0.10, a 3−4 order-of-magnitude enhancement over the HD/H_2 ratio. The explanation of this extraordinary isotope effect concerns a small number of ion−molecule exchange reactions in which small energy changes due to zero-point energy become important at low temperatures.[51]

Consider, for example, the reaction system

$$H_3^+ + HD \leftrightarrow H_2D^+ + H \tag{17}$$

Both forward and backward exchange reactions are known to occur, but the left-to-right reaction is the exothermic one, by the rather small amount of 230 K (1.91 kJ/mol). This small exothermicity is large compared with thermal energy at 10 K, so that the backward (endothermic) reaction becomes immeasurably slow if thermal conditions prevail. As a result, the equilibrium constant becomes quite large at this temperature. Indeed, if the system could reach thermal equilibrium, the predicted abundance ratio H_2D^+/H_3^+ would exceed unity! Such a situation does not occur because H_2D^+ is destroyed by reactions with electrons and by ion−molecule reactions with heavy species such as CO:

$$H_2D^+ + CO \rightarrow DCO^+ + H_2; HCO^+ + HD \tag{18}$$

The ion−molecule reactions serve to reduce the H_2D^+/H_3^+ abundance ratio to ≈0.1 and spread the deuteration around so that abundance ratios such as DCO^+/HCO^+ also reach high values. Other important ions that undergo exothermic deuteron-exchange with HD include CH_3^+ and $C_2H_2^+$.

In 1989, we extended the chemical network to include deuterium exchange reactions such as reaction 17 as well as reactions such as (18) in which deuterons go from one species to another.[52] For these latter reactions, we assumed that the placement of the deuteron is determined via a simple statistical analysis. For example, in reaction 18 the assumption is made that DCO^+ is produced on 1/3 of the collisions. With this assumption, our extended model was able to predict successfully most of the abundance ratios between singly deuterated isotopomers and normal species. In addition, the predictions are "robust" in the sense that they show little time dependence compared with predictions for the absolute concentrations of each species. Models including fractionation of ^{13}C and ^{15}N have also been attempted, but here the effects are much smaller because the zero-point energy differences are not large compared with thermal energies even at 10 K.[53]

4. Prestellar Cores

Prestellar cores are objects in which collapse has started, as can be detected by both the Doppler patterns of the spectral lines and the existence of a central condensation with a total gas density 10^{6-7} cm^{-3}. The temperature remains near 10 K throughout both this condensation and its "envelope." The easiest way to think of prestellar cores is in terms of onions, with shells of increasing density located closer to the center. Observations of molecules indicate that with few exceptions, abundances peak in regions outside of the central condensation, where the residual gas is overwhelmingly H_2 and He.[54] For example, it is thought that the fractional abundance of CO in the center of such objects is perhaps 1−2 orders of magnitude reduced from its value in starless cores. Of course, the depletion detected by astronomers is less than this value because even if one observes toward the center of a prestellar core, one is also looking at both background and foreground material at lower densities.[55] To obtain actual depletions as a function of radius requires a nontrivial de-convolution of the data.[54]

The detection of depletions is not too surprising, given the short time scale for adsorption onto grains. If it is assumed that the sticking probability is near unity, this time scale τ (1/e time) is given by the standard kinetic-type expression

$$\tau = \{\sigma v n_{gr}\}^{-1} = \{k_{ads} n_{gr}\}^{-1} \tag{19}$$

where σ is the granular cross section, v is the average velocity of a gas-phase species, and n_{gr} is the granular density. Making the standard assumptions that grains have a radius of 0.1 μm, so that $\sigma = 3 \times 10^{-10}$ cm^2, and a fractional abundance of 1×10^{-12}, we obtain that the time scale τ for CO at 10 K to stick to a grain is a little over 100 yr at a gas density of 10^7 cm^{-3}, which is quite short compared with the time scale of collapse and star formation. Those residual gas-phase species either do not remain on grains because they can evaporate efficiently at 10 K, as is the case for H, H_2, and He, or are desorbed with small efficiency by nonthermal means such as cosmic ray collisions with grains. The efficiency of cosmic-ray desorption has been estimated by calculating the peak temperature and cooling rate of grains, using the formula for evaporation as a function of temperature (see above), and averaging the result over a duty cycle.[56] Interestingly, it appears from observations that N_2 (traced by the polar ion HN_2^+) remains in the gas to higher densities than does CO, a result that seems somewhat strange given the close relationship in properties between the two species.[54]

A dramatic effect that supports the result that depletions are exceedingly large in the centers of prestellar cores is even stronger deuterium fractionation than occurs in starless cores, including the detection of multiply deuterated species.[55] The analysis of deuterium fractionation in the gas is the same as in starless cores but the depletions at the center of starless cores mean that the destruction of H_2D^+ by reactions with heavy species is much slower.[57] Moreover, the electron abundance also decreases at higher densities so that reaction system (17) approaches chemical equilibrium and H_2D^+ achieves a greater concentration than H_3^+. A caveat must be made, however: we are assuming that H_2D^+ reaches thermal equilibrium before back reaction with H_2. This assumption is not obviously true, and nonthermal considerations in this and other instances need to be considered in more detail. In particular, the forward reaction might lead to rotationally excited H_2D^+ which, if forbidden from relaxing radiatively to the ground rotational state by ortho/para considerations, can react exothermically with rotationally excited ($J = 1$, ortho) H_2. If there is a significant nonthermal abundance of ortho-H_2, then the backward reaction rate constant in (17) will be much larger than the thermal value, and deuterium fractionation will be less dramatic at low temperatures.[58]

The extent of this particular problem is still unclear because the state-to-state rate constants needed have not yet been studied, and the extent of ortho-H_2 is not known. Moreover, the detection of H_2D^+ at high abundance toward the center of the prototypical prestellar cores L1544 supports the thermal analysis.[59]

But, if H_2D^+ has a greater concentration than does H_3^+, one must consider further deuteration via the processes

$$H_2D^+ + HD \leftrightarrow HD_2^+ + H_2 \tag{20}$$

$$HD_2^+ + HD \leftrightarrow D_3^+ + H_2 \tag{21}$$

for both of which the left-to-right reaction is the exothermic one. A simple model of the center of starless cores with static physical conditions shows that D_3^+ is actually the most abundant ion of the four isotopomers.[57] Moreover, D_3^+ is most efficient at deuteration, because unlike the cases of the partially deuterated ions, it does not protonate as well as deuterate. For example, when D_3^+ reacts with CO, the result is 100% production of DCO^+, rather than 33% and 67% with H_2D^+ and HD_2^+ reactants, respectively. A medium with a high abundance of D_3^+ leads to significantly more deuteration than occurs in starless cores, including the production of multiply deuterated isotopomers. Because D_3^+ is nonpolar, its detection must come from infrared measurements, which will be difficult given the atmospheric problems and the small sizes of prestellar cores. Nevertheless, the polar species HD_2^+ can be detected via its rotational spectrum, and was seen via a submillimeter-wave rotational transition in one prestellar core, as soon as the spectral line had been measured in the laboratory.[60]

The production of multiply deuterated isotopomers such as D_2CO, detected in prestellar cores, can occur via sequences of reactions such as

$$H_2CO + D_3^+ \rightarrow H_2DCO^+ + D_2 \tag{22}$$

$$H_2DCO^+ + e^- \rightarrow HDCO + H \tag{23}$$

$$HDCO + D_3^+ \rightarrow HD_2CO^+ + D_2 \tag{24}$$

$$HD_2CO^+ + e^- \rightarrow D_2CO + H \tag{25}$$

if the deuterons in the ions can be regarded as mobile so that statistical product branching fractions can be obtained in the dissociative recombination reactions. For example, in reaction 23, the probability of forming HDCO would be twice that of forming H_2CO. There is some uncertainty, however, that the statistical model is valid in this case. It is most probable, according to ab initio calculations, that the deuteration of formaldehyde leads to a species with the well-defined structure H_2COD^+.[61] If so, it is not at all obvious that dissociative recombination can lead to HDCO. Experiments are clearly needed! We use doubly deuterated formaldehyde as an example, because this species has been detected in a number of prestellar cores, and its abundance found to correlate with the observed depletion of CO.[55] Other detected isotopomers include both the doubly deuterated and triply deuterated forms of ammonia.[62] The production of these species from ammonia via deuteration sequences as in reactions 22−25 is straightforward.

Another consequence of high abundances of ions such as D_3^+ is the production of deuterium atoms by dissociative recombination with electrons. This is important because adsorption of deuterium atoms onto dust grains can lead to surface deuteration processes analogous to the hydrogenation processes discussed earlier involving atomic hydrogen. For example, doubly deuterated formaldehyde can be synthesized on surfaces by deuteration of CO:

$$CO + D \rightarrow DCO; DCO + D \rightarrow D_2CO \tag{26}$$

It is unlikely under the conditions of prestellar cores that much of the D_2CO formed on grain surfaces could make its way into the gas phase.[63]

Chemical models of prestellar cores must take depletion from the gas into account in some manner. Because deuteration is so important a phenomenon, the normal models must be extended to include many deuterated isotopomers. To do this without undue difficulty, the number of larger molecules in the networks is normally reduced. The simplest models are those that consider only gas-phase chemistry and depletion in the central condensation and assume static and fixed physical conditions. We have performed such a model for the prestellar core L1544, with the additional ad hoc assumption that N_2 does not freeze out.[57] Such a model is useful only for the short time between when significant accretion starts for CO and when there is virtually no CO left. Over this range of times, our findings are that (a) D_3^+ is slightly more abundant than the other ions of this series, (b) the calculated abundances of the ions N_2D^+, N_2H^+, and H_2D^+ are in reasonable if not perfect agreement with observation, but (c) the calculated D_2CO/H_2CO ratio is much too low until almost all of both species are depleted. In other words, the theory is only partially successful in a quantitative sense, although it certainly reproduces the main qualitative features of the chemistry.

TABLE 3: Calculated and Observed Column Densities (cm^{-2})[a] for the Prestellar Core L1544[64]

species	calcd	obsd
H_2	1.2(23)	1.6(23)
CO	5.5(17)	9.0(17)
H_2D^+	5.4(13)	5.0(13)
HCO^+	4.0(13)	1.0(14)
DCO^+	6.8(12)	4.0(12)
N_2H^+	6.7(12)	2.0(13)
N_2D^+	7.8(12)	4.0(12)
H_2CO	1.0(14)	2.5(13)
D_2CO	3.1(12)	9.0(11)
HNC	9.0(13)	9.0(13)
DNC	2.3(13)	3.0(12)

[a] Note: $a(b)$ refers to $a \times 10^b$.

To reproduce observations of prestellar cores more accurately, one needs to consider an onion model, as discussed above. One also needs to calculate the actual measured quantities, known as column densities N, which are defined as the integral of the concentration over the line of sight to the observer or, put alternately, the number of molecules in a cylinder with cross section 1 cm^2. The column density N of species X as a function of distance r from the center of a spherical source is given by the integral

$$N = \int n(l)\, dl \tag{27}$$

where the integration extends from the back to the front of the sphere along a path that is distant from the center by r at its closest approach. For $r = 0$, the integration is from $-R$ to $+R$, where R is the radius, whereas for $r = R$, the column density is 0.

We have recently published a static onion model in which collapse is not treated, and in which gas-phase chemistry and depletion occur at different rates in different shells.[64] The earlier assumption that N_2 is not adsorbed onto grains is replaced by a more modest assumption that its binding energy is low enough for evaporation. For our model of L1544, shells range in density from 2×10^4 cm^{-3} in the outermost portion of the envelope to 2×10^6 cm^{-3} at the center, whereas the temperature runs from 17 K in the envelope to 8 K at the center, on the basis of a previous analysis. The higher temperatures away from the center increase the rate of evaporation for species such as CO so that they remain in the gas longer. The column density of each species through the center of the source is calculated and compared with observation. In addition, the dependence of concentration on distance from the center is followed. The time scale is as follows: we initially run a model for the outer envelope for the typical time of 10^5 yr, using the calculated abundances as initial abundances for the higher density shells. The calculation is then run an additional 2×10^4 yr, at which time the agreement with observation is best. Table 3 contains calculated and observed results for the detected species in L1544, including deuterated isotopomers.[64] It can be seen that the agreement is excellent for most column densities, where the adjective "excellent" really means within a factor of a few. Moreover, the abundance patterns versus distance from the center at least qualitatively reproduce the observations that CO and HCO^+ are strongly reduced at the center but N_2H^+ is less strongly so. Remaining problems with this model, however, are (a) that it does not include surface chemistry, and (b) it does not include collapse. These objections are met by our latest model, which includes both surface chemistry and hydrodynamical collapse.[65] Even this complex model, however, does not reproduce all of the observed chemical and dynamical data, showing that collapse is probably more complicated than the treatment allows.

TABLE 4: Abundances of Deuterated Methanols in the Protostellar Core IRAS 16293-2422 with Respect to Normal Methanol[71]

isotopomer	abundance ratio
CH_3OD	0.02
CH_2DOH	0.30
CHD_2OH	0.06
CD_3OH	0.01

5. Protostellar and Hot Cores

The next stages of star formation involve a central condensation that begins to heat up and continues to do so until nuclear reactions onset and the life of a star begins.[3] Meanwhile the environment around the so-called protostellar object is changed in a variety of ways. Perhaps the most noticeable is the emergence of what is known as a "bipolar flow" of rapidly moving jet-like material that shoots out of the protostellar object in opposite directions from the poles, entraining some of the material in the envelope.[66] The interaction leads to shock waves with a unique high-energy chemistry.[67] Another notable feature is the development of a protoplanetary disk of dense gas and dust in the equatorial plane rotating around the protostar (see below). But, perhaps equally importantly, the envelope surrounding the protostars is heated gently to temperatures of 50 K or more, depending on position and the mass of the star being formed.[68]

Observations of warm envelopes show clearly that the chemistry changes from the previous stage, with large abundances of formaldehyde, methanol, and significant abundances of more complex species such as methyl formate detectable.[68−70] It seems reasonable to conclude that material is being evaporated from the mantles of dust grains. One of the most unusual aspects of the observations concerns the strong deuterium fractionation detected for methanol in the envelope of the protostellar source IRAS 16293-2422. Table 4 shows the abundance ratios of the various deuterated isotopomers of methanol detected in this source.[71] These large values cannot be explained by gas-phase processes because methanol itself is not produced efficiently in the gas. The production of the deuterated methanols probably occurs via the earlier production of large abundances of atomic deuterium in the gas (see above) followed by surface deuteration and hydrogenation of CO. Our detailed chemical model of the surface chemistry followed by evaporation is not totally successful in reproducing the observed abundance ratios, and it seems likely that a gas-phase chemistry occurring in the 50−100 K range following evaporation must occur as well.[72−74]

Although the study of low-mass protostellar envelopes is in its infancy, with only a few sources studied, the examination of a similar phenomenon in high-mass protostars is well advanced.[75] In these sources, the warm envelope is heated to a temperature close to 300 K and extends over a much wider region with a typical density of 10^7 cm^{-3}. Known as "hot molecular cores", these objects contain a variety of saturated gas-phase organic species not detected elsewhere including dimethyl ether, acetic acid, acetone, and glycolaldehyde.[76] In addition, the abundance of methyl formate, now also detected in protostellar envelopes, is large and its spectrum very rich. The chemistry of hot cores has been studied for some time.[77,78] The basic idea, as in protostellar envelopes, is that in prior, colder eras, an active surface chemistry occurs to produce species such as water, ammonia, methane, formaldehyde, and methanol. These species, and perhaps some more complex ones as well, remain mainly in the grain mantles until the temperature rises and the mantles evaporate. The evaporation is more thorough than in the low-mass protostellar case. The gas-phase species present immediately after evaporation then undergo a gas-phase chemistry at the temperature of 300 K, which allows some weakly endothermic reactions and exothermic reactions with small barriers to occur at competitive rates. In fact, it is felt that the age of the hot core can be determined from the abundances of gas-phase species that can only be formed by chemistry in the post-evaporation era. Sulfur-containing molecules (H_2S, SO_2, OCS) are thought to be especially useful in this regard.[79] Different hot cores also have somewhat different abundances of complex molecules; examples are two such sources in the Orion Molecular Cloud known as the Hot Core and the Compact Ridge.[77] It is our view, however, that the chemistry of hot cores is not understood as well as most astrochemists seem to think. In the last year, we looked carefully at the synthesis of methyl formate, because the spectrum of this internal rotor is a salient feature of hot cores.[80]

According to the standard view of hot core chemistry, methyl formate ($HCOOCH_3$) is produced from precursor methanol by the sequence of reactions:

$$XH^+ + CH_3OH \rightarrow CH_5O^+ + X \tag{28}$$

$$CH_5O^+ + H_2CO \rightarrow HCO(OH)CH_3^+ + H_2 \tag{29}$$

$$HCO(OH)CH_3^+ + e^- \rightarrow HCOOCH_3 + H \tag{30}$$

where XH^+ is a protonating ion such as HCO^+ or H_3^+. Reaction 29 had not been studied in detail in the laboratory or theoretically until our recent work, which shows conclusively by two experimental techniques and detailed ab initio calculations that protonated methyl formate is not a major product of the reaction. We have tried to find replacement gas-phase syntheses for methyl formate but cannot find one efficient enough to account for its observed abundance. Based on this result, it might be useful to study some of the proposed reaction pathways leading to other organic species.

If gas-phase processes cannot produce methyl formate, what can? There are several alternative mechanisms, including a more complex thermal surface chemistry,[81] a high-energy surface chemistry caused by bombardment of photons or high-energy electrons or protons,[81] and a catalytic process such as the Fischer−Tropsch synthesis.[82] The second alternative is the best studied; numerous laboratory studies on assorted ices containing some organic species at low temperature show that intense irradiation over a short period of time leads to more complex organic molecules.[83] The important question, however, is how the intense irradiation and short times of the laboratory relate to the weak irradiation and long time scales of hot molecular cores. An example of a possible problem is the following. In the laboratory, irradiation of water ice can lead to the production of hydroxyl radicals, which can recombine to form HOOH if the H atoms are desorbed away. In hot cores, where the atmosphere contains a residual supply of H atoms, it is quite probable that some of the newly formed hydroxyl radicals will react with adsorbing H atoms to reform water ice. In a simple simulation of the surface photochemistry in dense clouds as well as the laboratory, we found that the efficiency of formation of HOOH is indeed reduced in space compared with laboratory studies.[84] More detailed simulations of the more complex organic surface photochemistry are urgently needed.

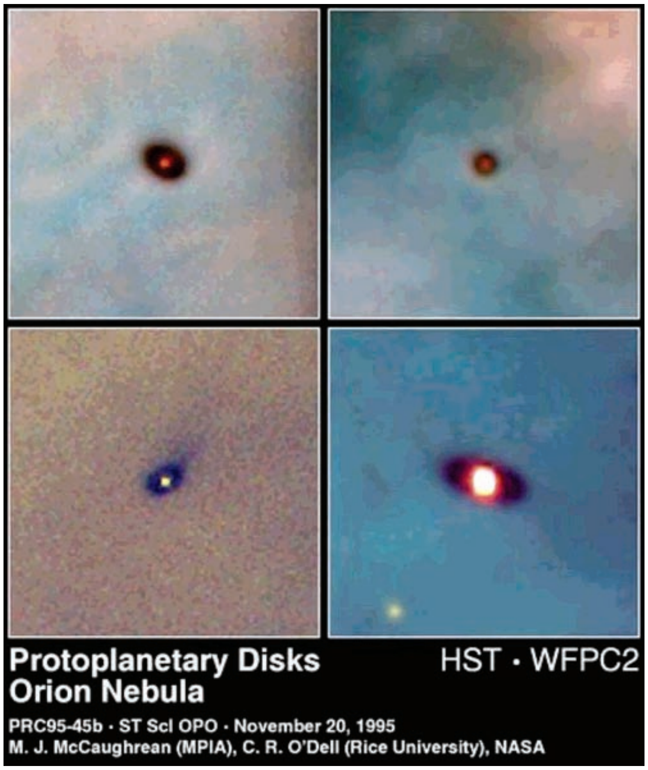

Figure 3. Protoplanetary disks and newly born (T Tauri) stars seen in the visible against light from the Orion Nebula. Image courtesy of NASA. Modified by C. R. O'Dell. Taken from web site http://www.oarval.org/OriProp4.htm.

Experiments on thermal surface chemistry at low temperatures leading to species more complex than methanol are also needed. A perhaps fanciful synthesis of methyl formate from precursor CO, O, C, and H landing on dust particles might consist of the processes

$$CO + H \rightarrow HCO \tag{31}$$

$$C + H \rightarrow CH;\ CH + H \rightarrow CH_2;\ CH_2 + H \rightarrow CH_3 \tag{32}$$

$$CH_3 + O \rightarrow CH_3O \tag{33}$$

$$CH_3O + HCO \rightarrow HCOOCH_3 \tag{34}$$

6. Protoplanetary Disks

Eventually a low-mass protostar collapses and heats sufficiently to form a young reddish star, known as a T Tauri star. Such adolescent stars are unstable and are often found in the center of so-called protoplanetary disks, which contain gas and dust at much higher densities than found in dense cloud or prestellar cores. These disks have masses of 0.01−0.1 times the mass of the sun, and the material in them is undergoing Keplerian rotation.[85] In some if not most cases, the jets from the previous protostellar stage have driven much of the natal interstellar cloud away.[86] Figure 3 shows optical pictures of four such disks rotating around stars located in front of the Orion Nebula and so seen in the visible. Radio and infrared astronomers can also look at these disks and probe their molecular content.[87] Unfortunately, these objects are small (approximately 500−1000 AU in diameter, where 1 AU is the mean distance between the earth and the sun), so that with current telescopes it is very difficult to probe structure within the disks. A future large array of radio telescopes, to be located in the Andean mountains of Chile and known as ALMA, will enable small structures such as disks to be spatially resolved by the use of interferometric techniques.[88] Protoplanetary disks are of great interest because they lead to planetary systems in some if not most cases. The details of this conversion, taking something more than one million years, are not well understood; it is known though that the next stage of evolution is the debris disk, in which much of the dust has disappeared, presumably used up in the formation of planets and other macroscopic bodies.

Although one can get the impression from Figure 3 that protoplanetary disks are flat, resembling old-fashioned LP's, detailed studies indicate that the material spreads out in a vertical direction (perpendicular to the midplane) as the distance from the star increases so as to trap much of the light from the central star. The three-dimensional structure still has cylindrical symmetry; to imagine the structure, start with a cone lying in the XY plane with its apex at the origin and rotate the cone around an azimuthal angle of 2π radians. The predicted temperature and density profiles of protoplanetary disks are quite inhomogeneous. Along the so-called midplane, both temperature and density decrease as one travels outward from the star. Models indicate that at a distance of 1 AU from the star, $n = 10^{14}$ cm^{-3} and $T = 600$ K, whereas at 100 AU from the star, $n = 10^9$ cm^{-3} and $T = 20$ K. At this latter distance, if one leaves the midplane in the vertical direction, the density gradually decreases whereas the temperature increases. At a height of 100 AU, the density has reached a typical dense core value of 10^4 cm^{-3} whereas the temperature has risen to 80 K.[89]

The chemistry is clearly dependent on the local physical conditions. Our models have been mainly concerned with the outer regions of disks ($\geq$100 AU from the star) because these regions are large and dominate the observed molecular abundances. According to our models, the density of dust is so high in the midplane that accretion is rapid and the gas phase consists only of species such as H_2 that can evaporate efficiently at such low temperatures.[89] As one travels in a vertical direction off the midplane, the temperature increases, allowing evaporation so that gas-phase chemistry can occur. Finally, at large distances from the midplane, any gas-phase molecules produced are destroyed rapidly by photons from the central star and from interstellar radiation. So, the abundances of gas-phase molecules are predicted to peak at intermediate heights.[89] Of course, this prediction is a relatively safe one for the time being because current telescopes cannot detect abundance variations. When ALMA becomes operational, within the next decade, the models will be put to a much sterner test. For now, to compare observation and theory, one must integrate out some of the calculated structure. If one integrates along the vertical coordinate, one can get a column density at a given radial distance from the star. Even these integrated densities possess a radial dependence although it is not severe in the outer disk. If one divides the column densities at a given radial distance from the center by the H_2 column density, one determines fractional abundances for heavy gas-phase species much lower than found in dense cores because of the accretion of heavy species near the midplane, an effect similar to that found in prestellar cores. Because these fractional abundances do not have a strong radial dependence, they can be compared with observational values. The observed results for a well-studied disk named DM Tau are in reasonable if hardly perfect agreement with the outer disk model, as can be seen in Table 5.[89] It can also be seen by comparison with the results for TMC-1, also shown in Table 5, that most of the fractional abundances are lower in the disk.

TABLE 5: Comparison of Observed and Calculated Fractional Abundances[a] in the outer Portions of DM Tau[89]

species	obsd abundance DM Tau	calcd abundance DM Tau	obsd abundance TMC-1[11]
CO	2(−5)	1.4(−4)	8(−5)
CN	3(−9)	4.0(−9)	5(−9)
CS	3(−10)	3.3(−10)	4(−9)
CCH	1(−8)	1.8(−9)	2(−8)
HCN	6(−10)	3.5(−10)	2(−8)
HNC	2(−10)	3.5(−10)	2(−8)
HCO^+	4(−10)	1.1(−9)	8(−9)
H_2CO	3(−10)	8.8(−10)	5(−8)

[a] Note: $a(-b)$ refers to $a \times 10^{-b}$.

Once the chemistry of protoplanetary disks is better understood, it should be possible to create models with both chemistry and the formation of planetary bodies.

7. PDR's

A final stage to discuss is the photon-dominated region,[15] which consists of material sufficiently distant from the newly formed star to not be involved directly in star formation, but sufficiently close to be affected by the electromagnetic radiation from the star once it turns on. PDR's can be dense or diffuse, can be found near HII regions such as the Orion Nebula or near low-mass stars with much less radiation. Indeed, a picture of any giant molecular cloud complex will show a significant portion of the complex with radiation penetrating through the gas and dust.

To model PDR's, astrochemists typically consider a one-dimensional grid of slabs representing the different physical conditions as the radiation penetrates the cloud, often starting on the outside with low-density, high-temperature outer layers and ending at the center with high-density, low-temperature inner layers.[5,15] The radiative transfer problem must be looked at carefully in the outer layers because radiation is extinguished by both dust particles and abundant gas-phase species. The case of H_2 is particularly interesting because it is photodissociated by line absorption: discrete absorption into an excited bound state is followed by emission into the continuum of the ground electronic state. Because the process of photodissociation only utilizes discrete frequencies, the amount of radiation in these bands is soon exhausted, and H_2 manages to shield itself efficiently.[90] A similar situation happens with CO.

Our main interest in PDR's is to determine if radiation helps or hinders the development of organic molecules.[91] Starting from abundances representative of dense cloud cores, we can show that high abundances of very unsaturated species such as the linear radicals C_nH are maintained in outer regions of PDR's with modest photon fluxes.

8. Conclusion

The role of molecules and molecular spectra in the study of astronomy has become a significant research area in the 30+ years since polyatomic species were first discovered in the interstellar medium. The term "astrochemistry" is no longer a noun known only to a few cognoscenti, and molecules are studied in a wide variety of regions in the universe, ranging back in time to epochs close to the Big Bang. In this article, we have focused on some recent progress in our understanding of the chemistry occurring during the formation of stars, a process that happens only in giant interstellar clouds full of molecules. In each stage of star formation, the molecular makeup of the gas and dust particles reflects both the physical conditions and the time-scale of the stage, so that an understanding of the chemistry deepens our knowledge of the forces at work as stars are formed from precursor cloud cores. Yet our knowledge of the chemical processes that occur is still incomplete.

What will the future bring? Within the next decade, new telescopes will expand our knowledge of molecules in space in two different ways. First, nonground-based telescopes will explore for the first time the far-infrared region of the electromagnetic spectrum, a region in which rotational transitions among excited rotational states and low-frequency bending vibrations are likely to occur.[92,93] Such transitions will be especially strong in star-forming regions. Second, arrays of radio telescopes such as ALMA will be used to study rotational spectra from small-scale objects such as protoplanetary disks with a spatial resolution sufficient to resolve inhomogeneities in these objects.[88] The two advances will doubtless require improvements in our current generation of chemical models to handle the richness of the new data and to focus on small-scale features.

How can our current models of all types of sources be improved to make the chemistry more secure? If we confine ourselves initially to gas-phase networks, there are four major problems: (i) unacceptably large uncertainties in individual rate constants, (ii) incomplete networks, (iii) incorrect chemistry, and (iv) possible nonthermal processes. To correct problem (i), it would be nice if all rate constants in the networks could be known to infinite accuracy. This goal is obviously an impossible task, so a better strategy is to use sensitivity analyses to determine the important reactions to know accurately and then to study these in more detail. Work on sensitivity analyses has gotten ahead of the work on the corollary study of individual reactions,[11,79] but a new large-scale European network known as The Molecular Universe and funded by the European Community is bringing together astrochemists and laboratory physical chemists to try to alleviate the gap.[94] There is no general solution to problem (ii) except to add new types of reactions such as rapid radical-neutral processes and to look carefully for additional syntheses of under-produced molecules, testing them, if necessary, in the laboratory or via theoretical means. As for the problem of incorrect chemistry, this too can be remedied by individual experiments. An example discussed earlier concerns the synthesis of methanol in low-temperature dense cores via the radiative association between methyl ions and water (reaction 10), with a rate constant calculated from statistical theory. Experiments now indicate that the reaction is intolerably slow,[46] leading to the conclusion that the only viable synthesis of methanol occurs on grain surfaces via the hydrogenation of CO followed by nonthermal desorption into the gas. Another example is the incorrect synthesis of methyl formate used in hot core models until recently.[80] Here, however, the debunking of one synthesis has not led to the adoption of another.

Finally, there is the problem that thermal equilibrium is frequently a poor assumption to make for low-density objects such as interstellar clouds. The problem is especially acute for reactive species produced in chemical reactions with excess energy; if cooling and reaction are comparable, thermal equilibrium may play little consideration in the rate of reaction. As discussed in the text, an example of the problem is the uncertain rate of the backward reaction in system (17) at low temperatures.[58] Another cause for anxiety is that there might be enough nonthermal energy to power other slightly endothermic reactions.

Compared with gas-phase chemistry, the problem of understanding diffusive surface chemistry on small, poorly understood interstellar dust particles is an immense one. Yet here progress is certainly being made: in the past decade a number of studies of important reactions on cold, realistic surfaces have been undertaken and the results have generally been close to what had been anticipated by astrochemists.[19−24] Much more work remains to be done in the laboratory to probe individual reaction mechanisms in more detail, to determine energy parameters unambiguously, and to explore the role of irregular surfaces. The possible formation of complex species via diffusive surface reactions represents an interesting problem to study soon. In addition, alternative approaches to thermal diffusive chemistry should be investigated, including the Eley−Rideal mechanism, in which stationary adsorbates are struck by gas-phase species,[25] and the role of photon and high-energy particle bombardment. Bombardment needs to be modeled to determine its efficiency under the low irradiation levels of interstellar clouds, even those portions near young stars.

As these chemical problems begin to be tackled and our knowledge of chemistry under the unusual conditions of interstellar space improves, the chemical networks will be used more confidently by astrochemists to model complex heterogeneous objects undergoing dynamical change. At the current stage of development of astrochemistry, however, much basic work on relevant reactions in the gas phase and on cold surfaces is still necessary to make our window into the cosmos a more transparent one.

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