

CHEMISTRY IN THE INTERSTELLAR MEDIUM

Eric Herbst

Department of Physics and Department of Astronomy, The Ohio State
University, 174 W. 18th Avenue, Columbus, Ohio 43210-1106

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ABSTRACT

Over the past 25 years, astronomers have discovered a large number of gas-phase molecules in space, ranging in size up to more than 10 atoms. The molecules, which are mainly organic in nature and comprise both normal and abnormal species, are located between stars, in regions known as interstellar clouds, which contain both gaseous material and material in the form of dust particles. The gas is well characterized by high-resolution spectroscopy, whereas the dust is less well characterized by low-resolution infrared spectroscopy and the scattering of visible radiation. The gaseous molecules are synthesized in situ from precursor atomic material, which derives from the mass loss of previous generations of stars. The chemical reactions involved in this synthesis are discussed in some detail as are the models that seek to reproduce the observed abundances of molecules.

INTRODUCTION

Galactic Astronomy

The universe is organized in a hierarchical structure in which matter is concentrated into large organizations known as galaxies, which occupy only a small fraction of space (1). Galaxies come in a variety of shapes and forms; the three main types of galaxies are spirals, ellipticals, and irregulars. Our own Milky Way galaxy is a fairly normal spiral, with much of the detectable matter located in planar spiral arms rotating around the galactic center. The solar system is located in one such spiral arm, situated

approximately 8.5 kpc (pc stands for parsec; 1 pc = 3.26 light years) from the center. The detectable matter consists of stars and interstellar material; the latter is organized into large structures, 1–100 pc in size, known as interstellar clouds (1). Galactic matter is thought to cycle between stellar and interstellar periods.

Using spectral studies of absorption lines formed in the atmospheres of stars, astronomers are able to deduce the so-called cosmic abundances, or average elemental composition, of stellar material. The material is dominated by hydrogen, with helium approximately 10% of the hydrogen abundance by number. The elements carbon, nitrogen, and oxygen have fractional abundances with respect to hydrogen of 4×10^{-4} , 9×10^{-5} , and 7×10^{-4} , respectively. The lightest two elements were formed in the Big Bang, which occurred $\approx 2 \times 10^{10}$ years ago, while the heavier elements, often referred to by astronomers as “metals,” are synthesized in the interiors of stars (1). The average elemental abundances do not apply to all astronomical objects; for example, stars in certain stages of evolution can be carbon rich, i.e. containing more carbon than oxygen.

Interstellar clouds consist of matter in the gaseous form and in the form of tiny dust particles, or grains, with a size distribution peaking at a radius $r \approx 0.1 \mu\text{m}$. The dust particles contain 1% of the mass of the interstellar medium. The gaseous matter can be studied via high-resolution spectroscopic observations, whereas the dust particles are more difficult to characterize (2, 3). Particulate matter scatters and absorbs the radiation emitted by stars. Astronomers refer to scattering and absorption as extinction; the extinction is inversely dependent on wavelength (3), so as starlight passes through a cloud, it tends to be reddened. There is so much dust in the plane of our galaxy that visible astronomy is quite limited in how far it can probe; the center of our galaxy is totally undetectable in the visible (1).

Interstellar clouds can be classified as diffuse or dense. Diffuse clouds possess gas densities n in the range $10 \leq n \leq 1000 \text{ cm}^{-3}$, low extinction in the visible, and temperatures in the range 50–100 K. The gas is mainly atomic in nature. Dense (molecular) clouds possess “high” gas densities in the range $10^3 \leq n \leq 10^6 \text{ cm}^{-3}$, large visible extinction, and temperatures under 50 K. Clouds between these two limiting cases are referred to as translucent. Dense interstellar clouds are not homogeneous, with cores of higher-density material sitting in envelopes of somewhat lower density. In some dense-cloud complexes, there is little evidence of star formation; such regions are referred to as quiescent. In other complexes, known as giant clouds, both regions of star formation and newly formed stars can be detected; in these regions the temperature and gas density are elevated. If sufficiently hot, the young stars can form bright HII regions around

them, where the hydrogen is ionized (1, 2). Farther removed from hot young stars are so-called photon-dominated regions, in which the material can be both warm and mainly neutral (4). Also associated with the process of star formation are both maser emission and outflowing shock waves (2, 5).

Spectral Observations

Characterization of the atoms and molecules in the gas requires a knowledge of the laboratory spectra. In diffuse clouds, visible absorption spectroscopy can be performed by using background stars as light sources. The diatomic molecules CH, CH⁺, and CN were observed in this manner more than 50 years ago (6). In more recent years, observations in the ultraviolet have permitted the detection of H₂ and CO (7, 8). Other diatomic molecules now known to exist in the diffuse-cloud gas are C₂, OH, and NH (9, 10). In addition to the sharp features assigned to atoms and diatomic molecules, many diffuse features exist that have remained unassigned for over 50 years (11) but that may be due to complex molecules immune to the harsh radiation field pervading interstellar regions of low gas and dust density (12).

In the last 25 years, dense interstellar clouds have primarily been studied via radio astronomy. Astronomers use the term radio to refer to wavelengths as short as those possessed by millimeter- and even submillimeter-wave radiation. Although dense clouds are dark in the visible, they do not extinguish radio waves. Indeed, in these regions, radio astronomers can detect thousands of sharp emission features (13, 14) assignable to molecular rotational transition frequencies. The emission spectra are excited both collisionally and, in warm regions, via absorption of infrared radiation (2). A list of all known (≈ 106) gaseous interstellar molecules is contained in Table 1; the list contains detections in all regions of the spectrum and includes identifications from carbon-rich circumstellar clouds existing around old stars. Molecules of up to 13 constituent atoms have been detected in interstellar sources (15, 16). In addition to the species shown, there are numerous isotopomers containing D, ¹³C, ¹⁸O, ³⁴S, and other isotopes. The species seen are mainly organic, reflecting the high abundance of elemental carbon, and almost equally divided between rather well-known species and positive molecular ions, radicals, and metastable isomers seen in terrestrial laboratories under unusual conditions (17, 18). Simple internal rotors such as methanol and methyl formate are especially prominent, with large numbers of lines. Astronomers are able to use molecular spectra to determine the physical conditions (e.g. temperature, density) of the interstellar material and to probe inhomogeneities in these conditions (19). Molecular hydrogen is the dominant molecule; the second

Table 1 Gas-phase interstellar molecules in order of increasing complexity (November 1994)^a

H ₂	KCl	HNC	NH ₃	C ₃ S	C ₅	C ₆ H
CH	AlCl	HCO	H ₃ O ⁺	CH ₄	CH ₃ OH	HC ₄ CN
CH ⁺	AlF	HCO ⁺	H ₂ CO	SiH ₄	CH ₃ SH	HCOOCH ₃
NH	PN	HOC ⁺ ?	H ₂ CS	CH ₂ NH	C ₂ H ₄	CH ₃ C ₂ CN
OH	SiN	HN ₂ ⁺	HCCH	H ₂ C ₃ (lin)	CH ₃ CN	(CH ₃) ₂ O
C ₂	SiO	HNO	HCNH ⁺	c-C ₃ H ₂	CH ₃ NC	C ₂ H ₅ OH
CN	SiS	HCS ⁺	H ₂ CN	CH ₂ CN	HC ₂ CHO	C ₂ H ₃ CN
CO	CO ⁺	C ₃	C ₃ H(lin)	NH ₂ CN	NH ₂ CHO	CH ₃ C ₄ H
CSi	SO ⁺	C ₂ O	c-C ₃ H	CH ₂ CO	HC ₃ NH ⁺	HC ₆ CN
CP	H ₂ D ⁺ ?	C ₂ S	HCCN	HCOOH	H ₂ C ₄ (lin)	(CH ₃) ₂ CO?
CS	CH ₂	SiC ₂	HNCO	C ₄ H	C ₃ H	CH ₃ C ₄ CN?
NO	NH ₂	SO ₂	HOCO ⁺	HC ₂ CN	CH ₃ NH ₂	NH ₂ CH ₂ COOH?
NS	H ₂ O	OCS	HNCS	HCCNC	CH ₃ CCH	HC ₈ CN
SO	H ₂ S	MgNC	C ₂ CN	HNCCC	CH ₃ CHO	HC ₁₀ CN
HCl	C ₂ H	NaCN	C ₃ O	C ₄ Si	CH ₂ CHCN	
NaCl	HCN	N ₂ O				

^a Ambiguous detections are followed by question marks. The designation "lin" means a linear skeleton, whereas the prefix "c-" stands for a cyclic molecule. Molecules detected in circumstellar outflows are included.

most abundant molecule, CO, is four orders of magnitude less abundant. All polyatomic molecules are trace constituents of the clouds, with the most complex organic species possessing fractional abundances by number of 10^{-8} – 10^{-10} . Because the quadrupolar rotational transitions of H₂ are both weak and lie in the infrared rather than the radio, radio astronomers use the strong transitions of CO to map out interstellar clouds in our galaxy and others. Indeed, CO spectra have recently been detected in objects at high redshift as distant as quasars (20).

Dense clouds have also been studied in the infrared. Until recently, detected absorption and emission spectra in this wavelength region had been mainly confined to low-resolution vibrational studies. Some broad features assigned to grains indicate that these particles are composed of a core of silicate-type material and graphite that in dense clouds is covered with a mantle of assorted ices, including water, carbon monoxide, carbon dioxide, methanol, methane, ammonia, and hydrogen sulfide (21). The dominant constituent of the mantle is water ice, which is far more abundant than its gas-phase counterpart. Other low-resolution emission spectra, seen at 3050, 1610, 1300, 1150, and 885 cm⁻¹, have been detected in the vicinity of stars inside clouds and are thought to arise from optical pumping followed by internal conversion (22). Although these bands cannot be assigned to any single molecule, their wavelengths and relative intensities

indicate that they are most likely caused by polycyclic aromatic hydrocarbons (PAHs), possibly in an ionized and dehydrogenated state, with perhaps 50–100 atoms (22, 23). The PAH hypothesis had been preceded by the more general suggestion of nonequilibrium emission from very small grains (24). An alternative hypothesis is that the spectra are emitted by hydrogenated amorphous carbon (HAC) (25). The existence of very large molecules or very small grains under typical cool interstellar conditions is uncertain.

Lacy and coworkers have successfully undertaken high-resolution infrared absorption studies of a variety of polar and nonpolar (e.g. C_2H_2 , H_2) gas-phase interstellar molecules (26, 27). Bernath et al had previously undertaken high-resolution infrared studies of carbon-rich circumstellar clouds (28).

GAS-PHASE REACTIONS IN CLOUDS

Given the strength of the radiation field in unshielded interstellar space and the short 10- to 300-year lifetime for small molecules in such a field (29), it is unlikely that the interstellar molecules in Table 1 are formed in stellar atmospheres and transported to interstellar clouds. Rather, the chemistry that forms (and destroys) these molecules occurs in interstellar clouds and synthesizes the molecules from precursor material of stellar origin consisting of atoms and the cores of dust particles. Interstellar molecules can be synthesized via gas-phase processes and via reactions occurring on the surfaces of the dust particles. Of these two types of reactions, the former has been given more consideration because much more is known about gas-phase reactions. Still, gas-phase reactions cannot by themselves account for all observed molecules, and increasing attention is being paid to surface chemistry (3).

Perhaps the biggest weakness of gas-phase chemistry is its inability to convert atomic hydrogen efficiently into molecular hydrogen under low-density, low-temperature conditions. The gas-phase reaction $\text{H} + \text{H} \rightarrow \text{H}_2$ is an exceedingly unlikely case of a type of binary process known as radiative association (30, 31). Although ionic routes involving H^+ and H^- are available (30), the production of interstellar H_2 occurs predominantly via recombination of adsorbed H atoms on the surfaces of dust particles, followed by desorption of H_2 back into the gas (3, 30, 32). Gas-phase reactions can produce most of the observed gas-phase interstellar molecules, however, and are considered first. After a discussion of the types of reactions that occur, I consider how they form and destroy the observed molecules.

Constraints

The interstellar gas is a vacuum, by laboratory standards. The low densities require all chemical reactions to be binary in nature; ternary processes do not take place. Although ternary association reactions between species A and B in the presence of bath gas C ($A + B + C \rightarrow AB + C$) cannot be utilized to synthesize more complex interstellar molecules, radiative association reactions ($A + B \rightarrow AB + h\nu$) are quite permissible, although their efficiency is normally low for small species (31).

The low temperatures of most interstellar cloud material pose an even stronger constraint; endothermic reactions or exothermic reactions with even small activation energy barriers are too slow in almost all instances to be competitive, as can be deduced from the Arrhenius rate law for the rate coefficient k :

$$k(T) = A(T) \exp(-E_a/k_B T),$$

where $A(T)$ is the preexponential factor and E_a is the activation energy.

Virtually all exothermic reactions involving only stable neutral molecules possess sufficient activation energy to render them useless in interstellar synthesis. When consideration of the synthesis of interstellar molecules began (33), there was little understanding of the low-temperature reaction rates for processes involving one or two neutral radicals. Although several atom-radical reactions were considered, attention focused on positive ion-molecule reactions because positive ions are produced in even the most dense clouds by a small flux of bare atomic nuclei known as cosmic rays (33, 34) and because ion-molecule processes generally occur without activation energy (35). Today the situation has changed markedly. Sims & Smith (35a) describe recent work on the very-low-temperature reactivity of radicals such as CN and OH with assorted stable neutral reactants. It now appears that many radical-neutral reactions are surprisingly rapid at low temperature and must be considered in interstellar chemistry (36, 37). Unlike the case of ion-molecule reactions, however, the new studies do not generally reveal the reaction products.

Ion-Molecule Reactions

Exothermic ion-molecule reactions are surprisingly simple; the vast majority of reaction rates are governed by long-range considerations tempered perhaps by adiabatic-diabatic subtleties in cases with multiple potential surfaces (35, 38). For reactions in which the neutral species is nonpolar, the dominant long-range, charge-induced dipole potential is isotropic and leads to the well-known temperature-independent Langevin rate coefficient,

$$k = 2\pi e[\alpha/\mu]^{1/2} \approx 10^{-9} \text{ cm}^3 \text{ s}^{-1},$$

where e is the electronic charge in esu, α is the polarizability in cubic centimeters, and μ is the reduced mass in grams. Many experimental studies from room temperature down to 10 K confirm the validity of the Langevin expression (39, 40), which is derived from a simple capture theory (41).

For ion-molecule reactions in which the neutral species has a permanent dipole, the long-range potential is no longer isotropic, and capture theories are more complex. The results of several such theories (40, 42, 43) show that predicted thermal reaction rate coefficients are dependent on temperature T , varying typically as $T^{-1/2}$ and reaching values as large as $10^{-7} \text{ cm}^3 \text{ s}^{-1}$ at 10 K. Experiments at low temperature often support the results of these calculations (40).

Some ion-molecule reactions do have short-range potential energy barriers. If one of the reactants is H_2 , however, tunneling through this barrier can be important in low-temperature interstellar clouds because of the large relative abundance of this species. One system that has been studied in some detail is the reaction $\text{NH}_3^+ + \text{H}_2 \rightarrow \text{NH}_4^+ + \text{H}$ (44, 45), which is slow at room temperature ($k < 10^{-12} \text{ cm}^3 \text{ s}^{-1}$), becomes even slower as temperature is reduced, and then gets more rapid at temperatures under 100 K. The dependence on temperature has been reproduced by a theory incorporating phase-space dynamics with a one-dimensional tunneling correction on an ab initio potential surface (46). The enhancement in rate at low temperature is caused by the transient existence of a weakly bound, long-range complex from which tunneling occurs; the same mechanism has been postulated for the neutral-neutral reaction between the radical CCH and H_2 (47) and may also pertain to the reaction between C_2H_2^+ and H_2 (48, 49).

Radiative association between positive ions and neutral reactants has been studied at low pressure and temperature in the laboratory (50–52), following suggestions that such processes may reach high efficiencies at low temperature for systems with 5–10 atoms or more if their potential surfaces possess deep wells (31). Laboratory studies at higher pressures on ternary association reactions have also led to some information about the rate of the analogous radiative association reactions (51). In general, for radiative association to occur, the complex AB^{+*} formed in the initial collision between species A^+ and B must relax via emission of vibrational infrared radiation to stable levels, although electronic emission can sometimes enhance the rate (53). Given a typical vibrational emission rate of 10^2 s^{-1} for a complex formed several electron volts above its potential minimum, the complex must last a considerable amount of time for the

radiative association rate coefficient to approach the collision rate coefficient (54). Measured radiative association rate coefficients, occurring over a range of many orders of magnitude with a strong inverse temperature dependence (T^{-k} ; $k > 1$), typically agree well with the results of a variety of statistical theories (31, 51, 52, 55). Although most association reactions are efficient only in the absence of competitive normal exothermic product channels, there are systems in which the two channels compete (39). Two mechanisms for this competition have been studied (51, 56).

In interstellar chemistry, two classes of ion-molecule radiative association can be distinguished. Reactions between positive molecular ions and H_2 comprise the first class; such reactions need not be very efficient. Examples of this first class include $C^+ + H_2$ and $CH_3^+ + H_2$, both of which have been studied theoretically and experimentally (51) and possess reaction rates well below the Langevin limit. Reactions between positive ions and heavy neutrals comprise the second class; such reactions must, in general, be more efficient to be competitive. One example is the reaction between CH_3^+ and NH_3 to produce protonated methyl amine, the precursor of methyl amine. This reaction is calculated to proceed at a near collision rate at 30 K, despite a competitive exothermic channel (56).

Recombination Reactions

Neutral species are produced via recombination reactions between positive molecular ions and electrons, which are presumed to be the dominant carrier of negative charge. Recombination reactions are dissociative and tend to be quite rapid; typical rate coefficients at room temperature range from $10^{-7} \text{ cm}^3 \text{ s}^{-1}$ to $10^{-6} \text{ cm}^3 \text{ s}^{-1}$ (57, 58). There is a small inverse dependence of rate on temperature (57, 58). A controversy has ranged concerning the rate of the reaction between thermal H_3^+ and e^- , with experimental results ranging over many orders of magnitude (57). The discrepancy has currently been lowered to only one order of magnitude; the weight of evidence now favors a value at room temperature somewhat in excess of $10^{-7} \text{ cm}^3 \text{ s}^{-1}$ (59–61). Two mechanisms, labeled direct and indirect, have been deduced for dissociative recombination reactions (62, 63). The direct mechanism proceeds via a curve crossing between the attractive ionic potential surface and a repulsive neutral one, whereas the indirect mechanism involves intermediate Rydberg states of the parent neutral.

Although the rates of dissociative recombination reactions are well studied, the product channels have proved more elusive to experimentalists and theoreticians. Only within the last few years have spectroscopic techniques been used to measure selected product channels, mainly H atoms and OH radicals (64–66). The results obey no simple theoretical model (66).

There is still little evidence regarding the product channels for reactant ions larger than four atoms in size; it is unclear whether large positive ions will recombine dissociatively by ridding themselves of at most a few atoms or by more significant disruption of the molecular structure. Interstellar modelers assume the former.

Several authors have suggested that dissociative recombination reactions can produce metastable isomers as efficiently as normal structures (67); a well-known case is



The existence of a large number of metastable isomers in interstellar clouds (see Table 1) appears to buttress this suggestion.

If a large fractional abundance of complex molecules, such as PAHs, exists in dense interstellar clouds, and if the electron affinities of these species are sufficiently large, it is possible that the sticking efficiency of electrons to the large molecules will be high enough that the large negative ions will be the major carrier of negative charge (68). In this case, positive molecular ions will recombine with negative ions rather than electrons, leading to less dissociation (68, 69).

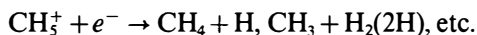
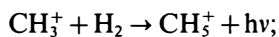
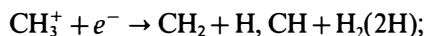
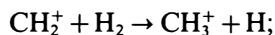
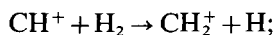
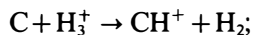
Neutral-Neutral Reactions

The extent of the role of neutral-neutral reactions in interstellar chemistry is highly uncertain, given recent experimental results showing very large reaction rate coefficients ($\geq 10^{-10} \text{ cm}^3 \text{ s}^{-1}$) for selected atom-stable neutral and radical-stable neutral systems at room temperature and below. A generalization of the laboratory results requires an understanding of the reaction dynamics, which is currently incomplete. The recent experimental results are not in good agreement with the results of long-range capture theories, which might be expected to be successful for such rapid reactions, although the divergence is least at very low temperatures (70, 71). A variational statistical calculation on the rapid reaction $\text{CN} + \text{O}_2$, including short-range effects, reproduces the rate coefficient for this system above 50 K (72). More such studies are needed.

The existence of activation energy barriers in many reactions involving one radical or atom as inferred from their slow reaction rates presents an additional complication (73). It is well known, for example, that atomic oxygen does not react efficiently (on every collision) with stable neutrals at room temperature, although it does react readily with many radicals (73). On the other hand, atomic carbon appears to react efficiently with a variety of stable hydrocarbons (70, 74). There would appear to be a large role for ab initio studies in elucidating the reasons for dichotomies such as this as well as in determining reaction products (72).

The Synthesis and Destruction of Interstellar Molecules

The gas-phase synthesis of polyatomic molecules in dense interstellar clouds starts from the cosmic ray-induced ionization of molecular hydrogen and, to a lesser extent, atomic helium. Direct cosmic-ray ionization of other species is less efficient than chemical ionization. The cosmic ray-induced ionization rate ($\zeta \approx 10^{-17} \text{ s}^{-1}$) leads to a theoretical ionization fraction of 10^{-6} – 10^{-8} , depending on the degree to which metallic elements are present in the gas phase (33, 75, 76). In diffuse clouds, gas-phase processes involving atomic hydrogen are also critical (9, 77). The ionization of H_2 produces mainly H_2^+ , which reacts with H_2 to form H_3^+ and H via a well-studied ion-molecule reaction. The H_3^+ ion subsequently reacts with a variety of the atoms present initially in the gas, starting a rich ion-molecule chemistry. The reaction with atomic carbon initiates a reaction sequence that forms methane, methyl radical, methylene, and methyldiene:



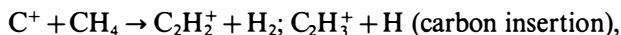
Of the ion-molecule processes, the first reaction has not yet been studied in the laboratory, although it has been studied theoretically (78). The H -abstraction reactions have been measured (39). The CH_3^+ ion does not react exothermically with H_2 but does undergo a slow but competitive association reaction (50, 51). Analogous syntheses lead to hydroxyl, water, NH_2 , and ammonia through the protonated ions H_3O^+ and NH_4^+ . The branching ratios for the dissociative recombination reactions are not fully measured (66).

Once formed, methane, ammonia, water, and all other neutral molecules can be depleted chemically by ion-molecule reactions and, possibly, neutral-neutral reactions with atoms and radicals. Ions such as H_3^+ tend to protonate neutral species (39), leading to protonated ions that can then reform the parent neutral species on some fraction of dissociative recombination reactions. The He^+ ion is far more efficient at breaking chemical bonds in the neutral species with which it reacts (39). Although external photons are strongly excluded from dense interstellar clouds, photons are provided by a mechanism in which energetic electrons produced from

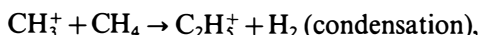
cosmic-ray bombardment excite H_2 molecules, leading to fluorescence (79, 80). These secondary photons can photodissociate and photoionize neutral molecules at rates slightly slower than chemical destruction (80).

The ubiquitous CO molecule is formed via a variety of processes, including the (unstudied) atom-radical reaction $\text{CH} + \text{O} \rightarrow \text{CO} + \text{H}$. Once CO is formed, the abundant formyl ion (HCO^+) is produced by (39) $\text{H}_3^+ + \text{CO} \rightarrow \text{HCO}^+ + \text{H}_2$. Similar protonation reactions lead to the HN_2^+ and H_3O^+ ions, which have been detected by radio astronomers (Table 1) along with the formyl ion. The C^+ ion, important in complex molecule synthesis, is formed from CO via the reaction (39) $\text{He}^+ + \text{CO} \rightarrow \text{C}^+ + \text{O} + \text{He}$.

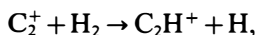
The production of complex hydrocarbons via ion-molecule pathways occurs via (a) carbon-insertion reactions, (b) condensation reactions, and (c) radiative association reactions. For example, two-carbon hydrocarbons can be formed via processes (39) such as



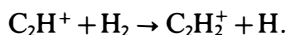
and



followed by H-abstraction and association reactions with H_2 (if they occur) and dissociative recombination reactions to form neutrals. In general, it is difficult to hydrogenate hydrocarbon ions significantly despite the large abundance of H_2 because H-abstraction reactions between C_nH_m^+ and H_2 for $n > 1$ and m greater than a few typically do not occur rapidly due to endoergicity or barriers (81, 82). For two-carbon hydrocarbon ions, the following H-abstraction reactions are known to occur:



and



The exothermicity and rate of the reaction to produce C_2H_3^+ are in dispute (48, 49), although the radiative association between $\text{C}_2\text{H}_2^+ + \text{H}_2$ has been measured (51). Dissociative recombination of C_2H_n^+ ($n = 2-4$) leads to the species C_2 , C_2H , C_2H_2 , and C_2H_3 , while the more saturated C_2H_4 is formed from C_2H_5^+ , the product of a condensation reaction. For three-carbon and larger hydrocarbon ions, hydrogenation is even more difficult. Because the carbon insertion mechanism, which leads to the loss of hydrogen, is the dominant one, ion-molecule syntheses tend to produce strongly unsaturated hydrocarbons, a prediction that matches most of the data in

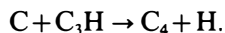
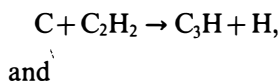
Table 1. The more saturated hydrocarbons and other organic molecules seen in this table are detected in star formation regions and may derive from hydrogenation processes on grain mantles followed by desorption caused by rising temperatures (83, 84).

Radiative association between heavy species becomes important as larger molecules are produced. One series of proposed synthetic reactions leading to complex molecules involves C^+ and bare carbon clusters C_n (85–87; RPA Bettens & E Herbst, in preparation), which are chains and rings for small n : $C^+ + C_n \rightarrow C_{n+1}^+ + h\nu$.

Organic molecules that contain nitrogen are generally produced via syntheses that include N-hydrocarbon ion reactions. For example, the synthesis of cyanoacetylene (HC_2CN) occurs via (88) $N + C_3H_3^+ \rightarrow HC_2CNH^+ + H$, followed by dissociative recombination.

More extensive discussions of ion-molecule interstellar chemistry exist in the literature (33, 75, 76, 89). In general, syntheses have been found for most major classes of unsaturated molecules found in interstellar clouds, including molecules with second-row elements, such as sulfur (90). Although many of the ion-molecule reactions utilized in models have been studied in the laboratory, much work remains to be accomplished, especially involving the larger reactants.

The ion-molecule synthesis of hydrocarbons and other organic species is strongly affected by neutral-neutral reactions. Based on recent work concerning the reactivity of C atoms with neutral hydrocarbons (70, 74), these neutral-neutral reactions may play a significant role in molecular synthesis if they proceed via carbon insertion. For example, starting from interstellar acetylene, the following sequence of reactions produces C_4 :



Neutral-neutral reactions between the radical CN and acetylenes are probably a major source of cyanopolynes ($HC_{2n}CN$), which are well-known interstellar molecules (91); the rate of the reaction $CN + C_2H_2 \rightarrow HC_2CN + H$ has been studied down to 25 K, although the products have not been confirmed (92).

In addition to these classes of reactions, condensation reactions involving hydrocarbon radicals and stable neutrals can synthesize more complex species. One such reaction found to be rapid at room temperature (73) is $C_2H + C_2H_2 \rightarrow C_4H_2 + H$. These reactions are critical in the synthesis of hydrocarbons in carbon-rich circumstellar shells, where acetylene and its photodegradation product C_2H are in high abundance (93–95). Interstellar

neutral-neutral syntheses are discussed in more detail in the literature (96, 97).

Isotopic Fractionation

Ion-molecule chemistry can produce large isotopic fractionation effects at low temperature, especially involving deuterium (30, 98–100). The deuterium-to-hydrogen ratio, a remnant of the Big Bang, is a few times 10^{-5} . In dense clouds, deuterium resides chiefly in the form of HD. Despite the rather low HD:H₂ abundance ratio, the relative abundances of other singly deuterated isotopomers can reach up to a few percent or more of their parent species. This many-order-of-magnitude isotope effect is thermodynamic rather than kinetic in origin. Consider the reactions $\text{H}_3^+ + \text{HD} \rightleftharpoons \text{H}_2\text{D}^+ + \text{H}_2$. The left-to-right reaction is exothermic by an amount $\Delta E_0/k_B \approx 227 \text{ K}$ (101), so the backwards reaction becomes increasingly ineffective as the temperature drops below 100 K. Even though thermal equilibrium cannot be reached because of the presence of side reactions, the abundance of H_2D^+ relative to H_3^+ is much larger than that of the sink HD relative to H_2 . The H_2D^+ ion has probably been detected in space; its daughter DCO^+ , formed in the reaction $\text{H}_2\text{D}^+ + \text{CO} \rightarrow \text{DCO}^+ + \text{H}_2$, is a well-known interstellar isotopomer, with an abundance reaching a few percent of HCO^+ for the lowest-temperature clouds. The dissociative recombination of DCO^+ leads to a significant abundance of atomic D, which starts another cycle of fractionation reactions (102). In general, models including isotopic fractionation are fairly successful at reproducing the abundances of isotopomers (99, 100). The problem is made manageable by the fact that HD does not react rapidly with many ions because of activation energy barriers (103).

SURFACE CHEMISTRY IN CLOUDS

Dust particle surfaces are assumed to start out as mixtures of silicates and graphitic material and, as the clouds age, become ice rich (3, 32, 104). It is generally assumed that reactive processes occur between mobile physisorbed species via a diffusive, or Langmuir-Hinshelwood, mechanism (3, 30, 32, 104, 105). The chemistry on very small grains of ≈ 100 atoms is likely to be different (106, 107), and it may be profitable to consider these species individual molecules (108).

The production of molecules on large ($R \approx 0.1 \mu\text{m}$) grain surfaces requires reactants to stick, a process that is known to occur with high efficiency at low temperatures (30, 104) once a gas-phase species strikes a dust particle. Because the number density of dust particles is only 10^{-12} that of gaseous species (30, 32), even with the assumption of 100% sticking

efficiency, a typical time scale for an atom or molecule to stick to a grain is $10^9 m^{1/2} n^{-1}$ per year, where m is the mass (amu) of the gaseous species and n (cm^{-3}) is the gas density. For H atoms in a typical cloud of gas density $n \approx 10^4 \text{ cm}^{-3}$, the adsorption time scale is 10^5 years. Because H atoms do not stick with 100% efficiency and heavier species travel more slowly in the gas, large-scale depletion of the gas in the absence of desorption requires perhaps 10^6 years or more.

Following adsorption, at least one of the reactants should be both mobile and reactive. Diffusion of surface species from one potential minimum to another can occur via classical or quantum mechanical means. The classical "thermal hopping" mechanism (32) occurs with a rate k_{hop} (s^{-1}) given approximately by the expression $k_{\text{hop}} = \nu_0 \exp(-E_b/k_B T)$, where ν_0 is the vibrational frequency of the adsorbate, typically in the range $10^{12-13} \text{ s}^{-1}$, and E_b is the potential barrier between the two sites of minimum energy. As a general assumption, E_b can be regarded as 25–30% of the adsorption energy of a molecule on the surface, which we label E_D . Given a dense-cloud grain temperature of 10 K, only species with the smallest adsorption energies can hop about the surface with appreciable rates. For example, for a heavy species with an adsorption energy of 0.2 eV (e.g. CO on ice) and a surface vibrational frequency of 10^{12} s^{-1} , $k_{\text{hop}} \approx 6 \times 10^{-14} \text{ s}^{-1}$ ($E_b \approx 0.25 E_D$), whereas for H atoms ($E_D \approx 0.03 \text{ eV}$ on ice), $k_{\text{hop}} \approx 2 \times 10^9 \text{ s}^{-1}$ if $\nu_0 \approx 10^{13} \text{ s}^{-1}$. In general, classical diffusion is limited to light, mainly atomic species, with H, He, and H_2 dominating. An exception pertains to the nonthermal products of chemical reactions and photoprocesses; these species may translate on the surface before thermalizing, even if they are heavy (109, 110). The quantum mechanical tunneling rate must also be considered for thermal adsorbates. With a rectangular barrier of thickness a , the rate k_{tun} for tunneling through a potential barrier between adjacent sites by a surface species of mass m is given by the expression (111) $k_{\text{tun}} = \nu_0 \exp[(-2a/\hbar)(2mE_b)^{1/2}]$. With some standard assumptions, tunneling is more rapid than thermal hopping at 10 K for the lightest species.

In addition to the diffusion rate, the probability for a species to undergo reaction via thermal hopping or tunneling is proportional to the fraction of surface sites N_s ($N_s \approx 10^6$) occupied by a potential reaction partner (30). The overall rate R_{ij} ($\text{cm}^{-3} \text{ s}^{-1}$) for surface chemical reactions between species i and j is then given by the formula (105)

$$R_{ij} = \kappa_{ij} (k_{\text{hop},i} + k_{\text{hop},j} + k_{\text{tun},i} + k_{\text{tun},j}) N_i N_j n_d / N_s,$$

where N_i and N_j are the average number of molecules of species i and j , respectively, on a grain; n_d is the grain number density; and κ_{ij} is an efficiency factor. Although simple addition of the four diffusion rates may

not be warranted, normally one of them dominates. The efficiency factor is of the order of unity for exothermic reactions without activation energy and can be approximated for reactions with activation energy by the expression $\kappa_{ij} = \exp [(-2a/\hbar)(2\mu E_a)^{1/2}]$, where μ is the reduced mass, and it has been assumed that only tunneling through the activation energy barrier E_a contributes at low temperatures. The reaction rate R_{ij} can also be expressed in a quasi-gas-phase formulation, $R_{ij} = K_{ij} n_s(i) n_s(j)$, where the surface abundances (cm^{-3}) are given by the equation $n_s(q) = N_q n_d$ ($q = i, j$) and the second-order rate coefficient K_{ij} ($\text{cm}^3 \text{s}^{-1}$) is defined by $K_{ij} = \kappa_{ij} (k_{\text{hop},i} + k_{\text{hop},j} + k_{\text{tun},i} + k_{\text{tun},j})/N_s n_d$.

A variety of views of the important surface reactions in addition to the formation of H_2 have been expressed (30, 32, 105, 107, 109–112). The dominant view is that the most important chemical reactions involve H as long as there is a sufficient surface abundance of this reactive species. In this view, heavy atoms such as C, N, and O striking and sticking to grains will be hydrogenated efficiently to saturated forms (CH_4 , NH_3 , H_2O) via association reactions without activation energy, unless the intermediate radicals formed are desorbed before they can react with H. The large abundance of water ice appears to indicate such a mechanism (21) as does the large abundance of gas-phase ammonia in star formation regions, where the grains have been heated (83, 84). Other association reactions involving atomic H possess at least some activation energy, such as $\text{H} + \text{CO} \rightarrow \text{HCO}$, for which $E_a/k_B = 1000 \text{ K}$ (111). However, the surface hydrogenation of many unsaturated molecules sticking to grains is thought to proceed relatively rapidly. The surface hydrogenation of CO via successive addition reactions to form methanol through formaldehyde does not appear to occur in a facile manner (113), although the high abundance of methanol on grain surfaces as well as in the gas phase of star formation regions can best be explained by such a mechanism (114). If the saturated molecules formed via H-atom association reactions themselves react with atomic hydrogen, viz, $\text{H} + \text{H}_2\text{S} \rightarrow \text{H}_2 + \text{HS}$, then a catalytic cycle occurs that acts as a mechanism for atomic to molecular hydrogen conversion (111).

The reactivity of surface H_2 is of some importance because, despite its low adsorption energy, it appears to be an important constituent of cold grains (115). Hydrogen abstraction reactions between radicals and H_2 possess significant ($E_a/k_B \approx 2000\text{--}5000 \text{ K}$) amounts of activation energy but can occur competitively on surfaces via tunneling once $\text{H}_2 \gg \text{H}$ (112) to produce relatively unreactive, saturated species. The production of complex molecules on very cold grain surfaces probably occurs only under nonthermal conditions in which radicals are continually generated, such as photon bombardment (109). Grain mantles grown under dense-cloud

conditions and then subjected to radiation from newly formed stars are sites for an active photochemistry.

Grain chemistry is also a contributor to observed isotopic fractionation of gas-phase species in star formation regions. Deuterium atoms are formed in high abundance in the gas via dissociative recombination of ions such as DCO^+ and then stick to grain surfaces, so the atomic D:H ratio is high. Association reactions with unsaturated species then lead to high abundances of singly deuterated and even doubly deuterated surface species, such as NH_2D and D_2CO (116–118). Rising temperatures occurring in the area of star formation then disrupt the grain mantles leading to high gaseous abundances of the isotopomers.

In low temperature quiescent sources, evaporation of surface species is inefficient, except for the most weakly bound molecules, as can be seen from the equation for the evaporation rate $k_{\text{evap}}(\text{s}^{-1})$ (32): $k_{\text{evap}} = \nu_0 \exp(-E_D/k_B T)$. For H on 10 K ice, $k_{\text{evap}} = 0.01 \text{ s}^{-1}$, whereas for CO on ice, k_{evap} is unmeasurably small at 10 K. Thus if heavy molecules are to exist in the gas phase past the adsorption time of $\approx 10^6$ years, nonthermal desorption mechanisms must be invoked. Investigators have considered a variety of such mechanisms, which can be divided into intermittent and continuous varieties (104).

Intermittent mechanisms involve astronomically significant events that raise the temperature over large distance scales. One example is a shock wave that propagates outward from a protostar (119). Another example is a cloud-cloud collision. The problem with such intermittent mechanisms is their frequency of occurrence; if the frequency is too low, then they do not affect many of the normally cold dust particles.

Continuous mechanisms involve excitation of the surface molecules by photons, cosmic rays, or the exoergicity of chemical reactions. The effects of cosmic rays have been considered by several investigators (112, 120). Depending on the size of the grain, spot heating can occur, or the whole grain can be heated by the passage of a cosmic ray. For the case of whole-grain heating, desorption rates for assorted molecules have been tabulated (112). Ultraviolet (UV) photons, created deep inside clouds via the excitation of H_2 by secondary electrons (79, 80), can photodissociate surface molecules such as water, leading to spot heating or ejection from the surface (104). Alternately, large-scale diffusion can expose fresh cloud surfaces to external UV photons (121, 122). Infrared photons, unextinguished by dust particles to any significant extent, can cause vibrational excitation of surface species, which can couple into physisorption-libration modes of adjacent molecules, leading to their desorption (F Dzegilenko & E Herbst, in preparation). The exoergicity of individual chemical reactions such as $\text{H} + \text{H} \rightarrow \text{H}_2$ can produce enough heat to cause at least local

desorption or, in the case of small grains, general desorption (107, 123). There is also the possibility that the energy of exoergic reactions can couple directly to the ejection of product molecules from the surface (30). In general, these mechanisms, although studied to some extent in terrestrial laboratories, cannot yet be readily quantified.

CHEMICAL MODELS

Quiescent Dense Clouds

The simplest chemical models of dense clouds contain only gas-phase reactions; the production of H_2 from H atoms on grain surfaces is an exception. In these models, the coupled kinetic equations are solved for chemical concentrations, with the results normally expressed as fractional abundances with respect to the overall density. Although investigators at first solved the equations only in the steady-state limit (33), today there is little difficulty in solving hundreds of coupled "stiff" equations as a function of time with the assumption of constant and homogeneous physical conditions (75, 76, 124, 125). Such models are often referred to as pseudo-time dependent. Normally investigators choose as initial conditions either atomic abundances or abundances relevant to diffuse clouds, in which a significant amount of H_2 is already present. The extinction of radiation caused by dust particles and, for H_2 and CO, by self-shielding caused by line photodissociation (9, 126, 127) is assumed to be sufficiently large that photodestruction via external photons is unimportant. Photodestruction caused by internally generated photons can be included, with uncertainties caused by the lack of laboratory data on cross sections and products (80). At present, pseudo-time-dependent models contain up to 4000 gas-phase reactions involving 400 molecules through 10 atoms in size composed of the elements H, C, N, O, Si, P, S, Cl, and assorted metals (97, 124). The elemental abundances for elements heavier than He in the gas are normally depleted from their standard cosmic values, which pertain to the combined gas and dust. The oxygen-to-carbon elemental abundance ratio in the gas is typically assumed to be greater than unity.

The results of these models show that with standard quiescent dense-cloud conditions ($T = 10\text{--}50\text{ K}$, $n = 10^4\text{--}10^5\text{ cm}^{-3}$), steady-state abundances are reached within $10^7\text{--}10^8$ years, an unphysically long time given the time scales for changes in physical parameters. Interestingly, the steady-state abundances can be many orders of magnitude different from those pertaining to thermodynamic equilibrium. In general, a strong dichotomy exists between the calculated abundances of small and large molecules as regards their time dependence. The former tend to approach their steady-state values by 10^5 years, whereas the latter tend to possess peaks at this

so-called early time and then decline sharply. The time behavior of the larger molecules derives from the oxygen-rich nature of the gas; by steady state most of the carbon has found its way into the form of carbon monoxide, while at earlier times much of the carbon is still atomic and reactive. The calculated abundances in the vicinity of early time are typically in order-of-magnitude agreement with observed fractional abundances (76). However, when a large number of rapid neutral-neutral reactions were recently added to the interstellar gas-phase chemical codes, it was found that they reduce the effectiveness of the models in producing complex molecules (96). The reduction occurs because destructive reactions between hydrocarbon radicals and carbon clusters with abundant oxygen atoms seem to outweigh synthetic reactions involving atomic carbon (125). Of course, because both the rates and products for most of the atomic oxygen reactions are not known, the estimates of their influence on interstellar chemical models must be taken cautiously. If, for example, it is assumed that carbon clusters do not react rapidly with atomic oxygen, then the efficiency of the models in producing complex species is high, even if all other radicals react rapidly with atomic oxygen (97). Even if all of the neutral-neutral reactions added to the model codes do in fact proceed rapidly, the production of complex molecules still occurs efficiently if H-abstraction reactions between C_nH_m ($m = 0, 1$) and H_2 proceed at a moderate rate (97). If the dense-cloud gas is assumed to be carbon rich, then the O-atom abundance is low, and large abundances of complex molecules exist for all times past 10^5 years, whether or not many rapid neutral-neutral reactions are included (97, 128).

Because the differential equations are nonlinear, the existence of only one physically reasonable solution cannot be proved. Indeed, recent work shows that at least two steady-state solutions are possible in selected regions of parameter space (129, 130). Although the parameter space over which two solutions are obtained is controversial, it appears to be associated with somewhat lower densities and somewhat higher elemental abundances of gas-phase sulfur than used in most models. One of the two solutions corresponds to the standard molecule-rich solution, but the other solution has much lower abundances of molecules and much higher abundances of atoms such as C, offering an alternative explanation to cloud inhomogeneity for the high abundance of C detected in many dense clouds (130).

Models of diffuse clouds also show low molecular abundances; external photons penetrate such clouds appreciably (9, 131). Steady-state results of these models can be compared closely with observational results of diatomic abundances. Currently, disagreement centers on CH^+ (131–133) and NH (134). The CH^+ ion may be formed in shocks, while the NH

radical may be formed on dust particles. Clouds in between the diffuse and dense categories are often labeled translucent (131). This category probably applies to many clouds found at high galactic latitudes that appear to be dense but small enough for some photon penetration (131).

A strong objection to the homogeneous gas-phase dense-cloud models is their neglect of adsorption of gaseous species onto dust particles. Given the time necessary for adsorption to occur, gas-phase model predictions for times greater than 10^6 years would seem meaningless unless desorption is efficient. A variety of investigators have included grain chemical processes in their models (105, 107, 110–112, 114, 135–139). The most passive approach is to include adsorption and desorption but to assume that nothing happens (except $2\text{H} \rightarrow \text{H}_2$) while the molecules reside on the grains (140). More detailed approaches contain varying sets of surface reactions. General predictions of a high surface abundance of water ice are in agreement with observations, but in the absence of possible photochemistry, there are serious problems regarding surface CO and methanol (135, 139).

The predicted contributions to gas-phase abundances of the gas-grain models occur mainly at late times in the chemical evolution of dense clouds and depend critically on poorly understood desorption rates. In some models, a steady-state solution can eventually be reached (138, 139). In other models, it is only the lighter molecules such as CO, bound more loosely to the dust particle surfaces, that desorb to any extent, and ice-grain mantles tend to grow with time, as long as the temperature remains low (136). If grain mantles grow, then it is necessary to consider whether or not chemistry inside of these mantles has a significant role (136).

Another objection to one-phase models, whether or not they include dust processes, is that clouds are not homogeneous. In the simplest view, clouds consist of shells of material with increasing density and decreasing temperature as one progresses from the outermost layers to the core. The one-phase dense-cloud models then pertain to the core, while the outer layers are closer to diffuse or translucent cloud conditions, with appreciable external photon penetration. Some observations of molecules along the lines of sight to dense clouds are better understood if the molecules are located in such external regions (141). One can take this increasing complexity into account with time-independent steady-state models in which the conditions in the layers are governed by hydrostatic equilibrium or by an assumed density, temperature profile. Slabs are often used for simplicity instead of spherical shells. The existence of layers of differing physical conditions may not be stable; turbulent diffusion can mix the layers and lead to interesting chemical effects (122). One can also regard the development of cloud structure as a time-dependent hydrodynamic process. A series of physical-chemical models incorporating hydrodynamics and time-

dependent gas-phase chemistry explores the relationship between collapse and chemistry (142, 143).

Recent observations of atoms such as C and C⁺ plus highly excited CO confirm to most investigators that a more complex form of inhomogeneity often persists throughout dense clouds (4, 144), where clumps of denser material exist within a more diffuse atomic medium, and there are clumps inside clumps, leading to a fractal-type picture (145). Diffusion can occur, in which case the flow of atomic carbon into the dense gas can prolong early-time abundances of one-phase models, leading to large steady-state abundances of complex molecules (146).

Active Regions

Active regions possess unusual physical conditions that vary with relatively short time scales. Shocked portions of clouds were the first type of active region studied, initially as an attempt to explain the high abundance of CH⁺ in diffuse clouds (132). As a shock front of a certain velocity crosses a medium, the temperature rises dramatically, depending upon the square of the velocity. At sufficiently high velocities, molecules are dissociated (147). The subsequent cooling is rather slow, allowing a high-temperature chemistry to occur for a finite period of time. Different chemical signatures of shock waves in diffuse and dense clouds have been worked out (148), and the chemistry of some turbulent sources, such as the plateau source in Orion, has been assigned to shock chemistry (149). It has become apparent, however, that shocks are diverse and depend on the magnetic field in the interstellar object. Two classes of shocks, J-type and C-type, have been distinguished (148, 150, 151). In the first, there is a rapid jump in temperature, but in the second, the temperature increases in a more continuous manner, and there is a streaming of the ions relative to the neutral species; in general, the chemical effects are more modest. Shock periods have been included in cyclic models of the physics and chemistry of clouds and stars (152).

Models of photon-dominated regions (PDRs) have also been undertaken. Previously referred to as photodissociation regions, PDRs comprise a variety of regions subjected to an intense radiation field, typically because a young bright star resides nearby (4). Both diffuse and dense PDRs have been studied; the dense variety are best thought of as the borders of dense clumps of material inside clouds. The models contain information on the excitation and chemical nature of such sources, such as the C⁺, C, CO balance (153–156). A proper treatment of self-shielding effects in the radiative transfer of external photons is very critical to such models.

Star formation regions are yet a third class of active region of interest to modelers. This material, with $T \approx 200\text{--}300\text{ K}$, $n \approx 10^{5-6}\text{ cm}^{-3}$, lingers

in the vicinity of newly formed stars or advanced protostars, perhaps owing to a balance between gravity and outflowing winds. The regions often go under the name of hot cores, following the original description of one such region in the Orion Nebula. Surprisingly large chemical differences are found among hot cores; the best known case concerns the closely spaced Hot Core and Compact Ridge sources in Orion (19), which despite their proximity, show different chemical abundances. Hot core models include both gas-phase and surface chemistry in a time-dependent picture that contains an initial low-temperature phase, followed by a phase of increasing temperatures (during which the grain mantles are lost), followed by a phase of constant high temperature (83, 84, 114, 116, 157, 158). This general picture explains both the high deuterium fractionation at relatively high temperatures (116, 117) and the general increase in saturation. Small differences in original temperature lead to large changes in the dust chemistry; such differences may explain the subsequent abundance variations (114). Rawlings et al (159) have considered the gas-grain chemistry occurring during the actual protostellar collapse phase.

Carbon-Rich Circumstellar Envelopes

Outflowing circumstellar envelopes are important molecule factories if the stars are carbon rich. The best-studied of these envelopes, IRC+10216, has almost as rich a chemistry as well-studied interstellar clouds (160). The chemistry in such C-rich regions has aspects similar and dissimilar to interstellar chemistry (93–95). In the innermost portion of the envelope, near the border of the star proper, a few basic parent molecules—such as CO, HCN, CH₄, C₂H₂, N₂, NH₃, and SiH₄—are produced in thermodynamic equilibrium under hot and dense conditions. As material in the envelope expands outward, it cools and rarefies. Eventually, at lower temperatures and densities, external ultraviolet photons and cosmic rays penetrate the material and produce some radicals and ions from the parent species (93). The stage is now set for both ion-molecule and radical neutral-neutral chemistry. The chemistry may resemble a low-temperature acetylene discharge, with condensation reactions between hydrocarbon radicals and stable neutrals efficient in building up larger clusters (specifically linear chains) and unsaturated hydrocarbons. Cyanopolynes (HC_{2n}CN) can be produced via reactions between CN (a daughter of HCN) and polyacetylenes, as well as via reactions between HCN and C_{2n}H radicals (93–95). As in interstellar models, a caveat must be raised because the products of many of the most important neutral-neutral reactions have not been studied, nor are their rates often known. Models must account for both abundances and spatial extents of the molecules. If produced as daughter species, the molecules show a ring-like structure that may or may not be

spherically symmetric (161). Although there are disagreements, gas-phase models of the outer envelope appear to be successful in interpreting observations of molecules through perhaps 10 atoms in size.

As circumstellar shells expand outward, they can evolve into objects known as protoplanetary nebulae and planetary nebulae. These objects also exhibit molecules, but the chemistry is by now less rich than in the circumstellar phase (160). Molecules are even found in the ejecta of supernovae, which represent a still later stage of massive stars; Dalgarno et al have proposed a chemical model for Supernova 1987a (162).

LARGE MOLECULES

The spectral evidence for the existence of truly large interstellar organic molecules consists of the more than 150 diffuse interstellar bands (DIBs) seen in the visible by Herbig (11) and others (163) in absorption against the light of background stars and the broad infrared features seen in emission toward a variety of objects (22). Diffuse visible features in emission have also been detected (164).

Although the DIBs have still not been unambiguously identified, their explanation in terms of the electronic spectra of complex molecules (12, 165) is in vogue. With this hypothesis, the diffuseness of the spectra arises from a combination of intramolecular relaxation (e.g. internal conversion) and unresolved rotational substructure. Bill Klemperer, who earlier had proposed the carrier of the DIBs to be S_n^- ions ($n = 2, 3$) in oxide glasses (166), has written in a letter to John Maier that "... there is no better way to lose a scientific reputation than to speculate on the carrier of the diffuse bands," so some caution is required. In particular, a condensed-phase origin for the DIBs has yet to be completely ruled out. Nevertheless, classes of molecules such as porphyrins (165), PAHs (167), carbon clusters (chains and rings) (12, 87), fullerenes (168), and fulleranes (169) have been proffered. Within the last year, two of the DIBs have been tentatively assigned to C_{60}^+ (170). One promising recent laboratory investigation shows a reasonable statistical correlation between DIBs and spectra obtained from a mixture of highly unsaturated hydrocarbons with 6–12 carbon atoms (171). Other laboratory investigations involve aromatic species (172). Many investigations have been undertaken on species in matrices such as argon and neon; care must be taken in interpreting matrix shifts between such spectra and gas-phase spectra, which are far more difficult to obtain (173).

From the theoretical point of view, the most difficult aspect of the large-molecule hypothesis is that the DIBs are seen along many lines of sight to stars, including some with very little extinction. One possibility is that

seeds for the large molecules were produced in a dense cloud, which then dispersed into a larger portion of diffuse gas (87). Once molecules reach a critical size, they are relatively stable against photodissociation (if not photoionization) assuming Rice-Ramsperger-Kassel-Marcus (RRKM)-type statistical considerations to be at all relevant. Synchrotron experiments on PAH photodissociation appear to support this view (174). We (RPA Bettens & E Herbst, unpublished data) are currently running very large model calculations of dispersing clouds in which we utilize ion-molecule and neutral-neutral reaction pathways to produce molecules containing as many as 64 carbon atoms; these are mainly unsaturated linear chains, single and triple rings, and fullerenes.

The formation of PAHs has been considered by several investigators (175–177) to occur in the acetylene-rich expanding envelopes of old carbon-rich stars, at temperatures around 1100 K. Small rings are formed first via Diels-Alder-type processes. The growth of PAHs then occurs via condensation reactions involving aromatic radicals A, which are formed at high temperatures by reactions with atomic hydrogen: $AH + H \rightarrow A + H_2$. These latter reactions are close to thermoneutral and have activation energy barriers, so production of the radicals does not occur at low temperatures. As the material flows outward, cools, and interacts with external photons, smaller molecules are produced from the still abundant parent molecules (see above), and they and the more complex species are cata-pulted into interstellar space. The PAHs may well preserve their skeletal structure against attack by interstellar photons (174, 175).

SUMMARY

The field of interstellar chemistry is a rich one, with continuing advances from observers working in different regions of the electromagnetic spectrum, from laboratory spectroscopists and kineticists studying unusual species and temperature ranges, from theoreticians working on reaction potential surfaces and rates, and from modelers trying to incorporate all of these advances in knowledge. In many ways, interstellar chemistry has motivated basic chemical research, such as the recent work on the rate of neutral-neutral reactions at low temperature. It has thus had a salutary effect on pure chemistry, which in turn, has helped to increase our understanding of the interstellar medium. Although much has been learned in the 25 years since polyatomic molecules were first detected in the interstellar medium, much remains to be learned.

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