

RECENT PROGRESS IN ASTROCHEMISTRY

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(Received 22 October, 1988)

Abstract. Models of the four currently recognized regimes of astrochemistry are compared with observations. *Ion-Molecule Gas Phase Chemistry* is fundamental throughout all interstellar and circumstellar molecular clouds, and by itself explains fairly well the simpler molecular species in diffuse and cold quiescent dense interstellar clouds, as well as in the outer envelopes of circumstellar clouds. *Dust-Grain Chemistry* may modify ion-molecule chemistry noticeably in regions containing UV radiation, shocks, or other heating agents which can serve to promote surface reactions and to desorb molecules frozen on grains; it likely plays no role in cold quiescent clouds except to adsorb gas phase molecules. *Shock Chemistry* occurs in regions of star formation and appears important in explaining certain molecular species and in disrupting grains. *Circumstellar envelopes* combine several chemistries, including those of thermochemical equilibrium in the dense inner regions, and ion-molecule in the outer regions, with grain processes also likely. The limitations of all current models are lack of knowledge of reaction rates, of detailed physical conditions (interstellar clouds), and of the relative depletions (onto grains) of the chemical elements, as well as grain surface chemistry in general. In both interstellar and circumstellar objects, ion-molecule gas phase models are now quite successful in explaining, semi-quantitatively, observed species with up to 4 atoms, but difficulties remain for larger species, as well as the state of carbon, and the models are not yet very predictive.

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Space Science Reviews **51**: 235-337, 1989.

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1. Introduction

1.1. OVERVIEW

As of July 1988 there are 82 known interstellar molecules, ranging up to 13 atoms in complexity, and observed in a wide variety of types of objects spanning a wide range of physical and chemical conditions. Because their energy levels are typically characterized by energies of order 1 to 100 K, these molecules have for 20 years served as unique probes of the cool component of the interstellar medium (ISM) and have provided most of our present knowledge of how stars form from the cold, dense interstellar gas and much of our knowledge on how they die and return material to the ISM. Molecules have radically changed our view of the ISM, which we now recognize as being about 50% molecular by mass and containing giant molecular clouds and complexes which are by far the most massive objects in the Galaxy. For a recent review of this aspect of interstellar molecules, see Turner (1988a).

Here we discuss the other major subject of interstellar molecules, their chemistry. The goal of astrochemistry must be ultimately to reach an understanding that allows us to extract from molecular observations the physical nature of the environment, and to work out the consequences of the chemical composition and the variations it may undergo. As we shall see, the evolution of all scales of astrophysical systems, ranging from planetary systems to the early Universe itself, depends as much on the chemical conditions as on the physical conditions. Thus we wish to learn how various astrophysical entities arrived at their present state, how they will evolve, and how they may relate in an evolutionary sequence with other objects. Despite limited insight of these issues, molecules as *physical* probes seem suitable for measuring quite reliably the density, temperature, and mass of the clouds in which they reside. They have provided much information on the life cycles of stars, on interactions of ionization and dissociation fronts, stellar winds and supernova explosions with the ISM, and on collisions of interstellar clouds and even galaxies. As *chemical* probes, it is less clear that molecules currently provide much unique information beyond the presence of the 82 identified species. It seems clear that the chemical composition varies on astrophysically significant timescales, is sensitive to density and temperature, radiation and elemental abundances, and is coupled to the physical evolution of the object, about which it may ultimately yield information. But unfortunately it is also sensitive to reaction rates, few of which are known with certainty, and to interactions with dust grains, about which almost nothing is known.

The early phase of astrochemistry (1972–1977) laid out the basic types of chemistry involved: gas-phase (ion-molecule and neutral); grain (surface catalysis and grain

disruption); shocks; and thermochemical equilibrium. These were developed in some detail with application to specific physical regimes to which they seemed appropriate, and with relatively little coupling between them. The next phase, up to 1983, saw considerable integration of the different chemistries (e.g., low-temperature gas phase and grain chemistries for the colder interstellar clouds) and the input of a rapidly growing reservoir of laboratory data (particularly gas phase reaction rates), as well as detailed attempts to include the time-dependence of the chemistry, and initial efforts to couple it to the physical evolution of the object in question (gravitational contraction for interstellar clouds, constant velocity outflow in circumstellar envelopes (CSEs)). The most recent phase, starting in 1984, has featured the revolution in astrophysical data brought about by the advent of interferometers and large single dishes. We now recognize the ISM as much more complex than the earlier categorization of molecular clouds as cold, warm, diffuse, or circumstellar. Additional physical processes (photo-processes in *dense* clouds, molecular formation in the early universe) are now recognized as important, as is the fact that various types of chemistries proceed with comparable effect in various regimes (CSEs, starforming regions). Thus it is not surprising that, while some aspects of astrochemistry (ion-molecule for interstellar clouds, thermochemical equilibrium for CSEs) have had *qualitative* success, none has had appreciable quantitative success. The situation up to this point is well summarized in several reviews (general: Watson (1976, 1978a), Turner and Ziurys (1988); ion-molecule: Winnewisser and Herbst (1987), Herbst (1988); shock chemistry: Dalgarno (1981, 1985), Hartquist (1986); chemistry in CSEs: Glassgold and Huggins (1986), and there are two important recent books: *Astrochemistry, IAU Symposium* No. 120, 1987, M. S. Vardya and S. P. Tarafdar (eds.), Reidel; and *Interstellar Molecules*, 1984a, W. W. Duley and D. A. Williams, Academic Press).

Here we emphasize important recent observational results and their interpretation in terms of current ideas about astrochemistry.

1.2. CURRENTLY KNOWN INTERSTELLAR* MOLECULES

In Table I we list the currently known molecules in the scheme used by Thaddeus (1981). There are 20 simple inorganics, 26 stable organics, and 36 unstable compounds, the latter including radicals, ions, highly strained rings, isomers, and acetylenic carbon-chains, both organic and inorganic. Among the strictly interstellar species, no inorganic contains more than 4 atoms, so as on Earth it is apparently the carbon bond that is the key to the synthesis of complex species. It is organic chemistry with an apparent difference, however: with two exceptions interstellar organics have simple linear heavy-atom backbones; branched chains and rings in general are not seen.

The differences between Table I and the earlier version given by Thaddeus in 1981 are striking, and reveal observational trends we may expect to persist for several interesting reasons. First, only one addition (and that not yet confirmed) has occurred in the (large) stable organic molecule list. The reason is spectral line crowding: such large

* We will use 'interstellar' to include also circumstellar, but will distinguish them where important.

TABLE I
Known interstellar molecules (1988 July)

(a) Inorganic species (stable)							
Diatomic		Tri-atomic		4-atom		5-atom	
H ₂ ^a	HCl?	H ₂ O ^a		NH ₃ ^a		SiH ₄ ^b	
CO ^a	PN	H ₂ S ^a					
CS ^a	NaCl ^b	SO ₂ ^a					
NO	AlCl ^b	OCS					
NS	KCl ^b						
SiO ^a	AlF ^b						
SiS ^a							
(b) Organic molecules (stable)							
Alcohols		Aldehydes and ketones		Acids		Hydrocarbons	
CH ₃ OH	methanol	H ₂ CO	formaldehyde	HCN ^a	hydrocyanic	C ₂ H ₂ ^b	acetylene
EtOH	ethanol	CH ₃ CHO	acetaldehyde	HCOOH	formic	C ₂ H ₄ ^b	ethylene
		H ₂ CCO	ketene	HNCO	isocyanic	CH ₄	methane
		(CH ₃) ₂ CO?	acetone				
Amides		Esters and ethers		Organo-sulfur			
NH ₂ CHO	formamide	CH ₃ OCHO	methyl formate	H ₂ CS	thioformaldehyde		
NH ₂ CN	cyanamide	(CH ₃) ₂ O	dimethyl ether	HNCS	isothiocyanic acid		
NH ₂ CH ₃	methylaniline			CH ₃ SH	methyl mercaptan		
Paraffin derivatives		Acetylene derivatives		Other			
CH ₃ CN ^a	methyl cyanide	HC ₃ N ^a	cynoacetylene	CH ₂ NH	methylenimine		
EtCN	ethyl cyanide	CH ₃ C ₂ H	methylacetylene	CH ₂ CHCN ^a	vinyl cyanide		
(c) Unstable molecules							
Radicals		Ions		Rings		Carbon chains	
CH	C ₃ H ^{a, c}	CH ⁺		SiC ₂ ^b		C ₃ S ^a	HNC ^a
CN ^a	C ₃ N ^a	HCO ⁺		C ₃ H ₂ ^a		HC ₅ N ^a	CH ₃ NC
OH ^a	C ₃ O	N ₂ H ⁺		C ₃ ^a		HC ₇ N ^a	
SO ^a	C ₄ H ^a	HOCO ⁺				HC ₉ N ^a	
HCO	C ₃ H	HCS ⁺				HC ₁₁ N ^a	
C ₂ ^b	C ₆ H	H ₃ O ⁺ ?				CH ₃ C ₃ N	
C ₂ H ^a	C ₂ S ^a	HCNH ⁺				CH ₃ C ₄ H	
C ₃ ^b	CH ₂ CN	H ₂ D ⁺ ?				CH ₃ C ₅ N?	

^a Seen in CSE as well as ISM sources.

^b Seen only in CSEs.

^c Both linear and cyclic forms.

species radiate many lines and divide their energy among them, so that each is reduced in intensity. At current levels of receiver technology, the observations are fast approaching the line-confusion limit in the richer interstellar sources (SgrB2, Orion (KL)), so that identification of the large species is of increasing difficulty. Second, the category of unstable molecules has grown significantly, from 18 to 36, in only 7 years. This is a direct result of the rapidly growing laboratory techniques both for producing, and for obtaining microwave spectra of, the transient species. These species are basic to the gas-phase chemistry schemes, and serve as definitive tests. Finally, a large number of new species has been detected in CSEs (almost solely the prototypical IRC10216 object) and has added mostly to the list of inorganics. This is as expected if thermochemical equilibrium obtains in the small, hot inner regions of the envelope, which are especially well studied by the new, large mm-wave telescopes brought on line in the past 4 years, although IR techniques have counted heavily also.

2. Morphology of the Molecular ISM

That the ISM is very complex has become increasingly apparent with time. It has many types of 'phases' of very different physical characteristics, and any one of these appears itself to defy a simple morphological description. It is not yet clear whether these differing regions are in pressure equilibrium overall; they are certainly not in thermodynamic equilibrium. Even though the different phases have a wide range of temperature and density, the typical energy density of the important phases is $\sim 1 \text{ eV cm}^{-3}$, or has a typical pressure $nT \sim 3000 \text{ cm}^{-3} \text{ K}$. While the overall pressure may be quite uniform, there are large and important deviations from the mean pressure behind shock waves produced by supernovae, by winds from hot stars, and from most protostellar objects, by expanding H II regions, and from self-gravitating clouds where there is significant compression of the gas even though they appear in quasi-equilibrium (so-called virial equilibrium). The typical energy density of $\sim 1 \text{ eV cm}^{-3}$ characterizes not only the gas component of the ISM, but also starlight, cosmic rays, and the magnetic field. While no theory as yet explains this similarity, this and arguments based on shock speeds, shearing forces from differential galactic rotation, etc., suggest that the ISM is 'well-mixed', that is, a given volume of gas may undergo many 'phases' on time-scales short compared with the lifetime of the Galaxy.

The existence (if not the morphology) of the several physically distinct regimes is fairly unambiguous and is summarized in Table II and in Figure 1.

Consider first the tenuous intercloud components. Their physical distinction from the denser phases is very clear, although the fractional volume of the ISM which they occupy, and their morphology, are poorly known, because they can be observed essentially only along accidental lines of sight to hot stars. The hot intercloud component is believed to arise from the energy input of supernova explosions, and perhaps radiation fields near hot stars. The warm intercloud medium lacks suitable cooling mechanisms to reduce its temperature to values typical of the denser regions. Molecules do not exist in either intercloud phase.

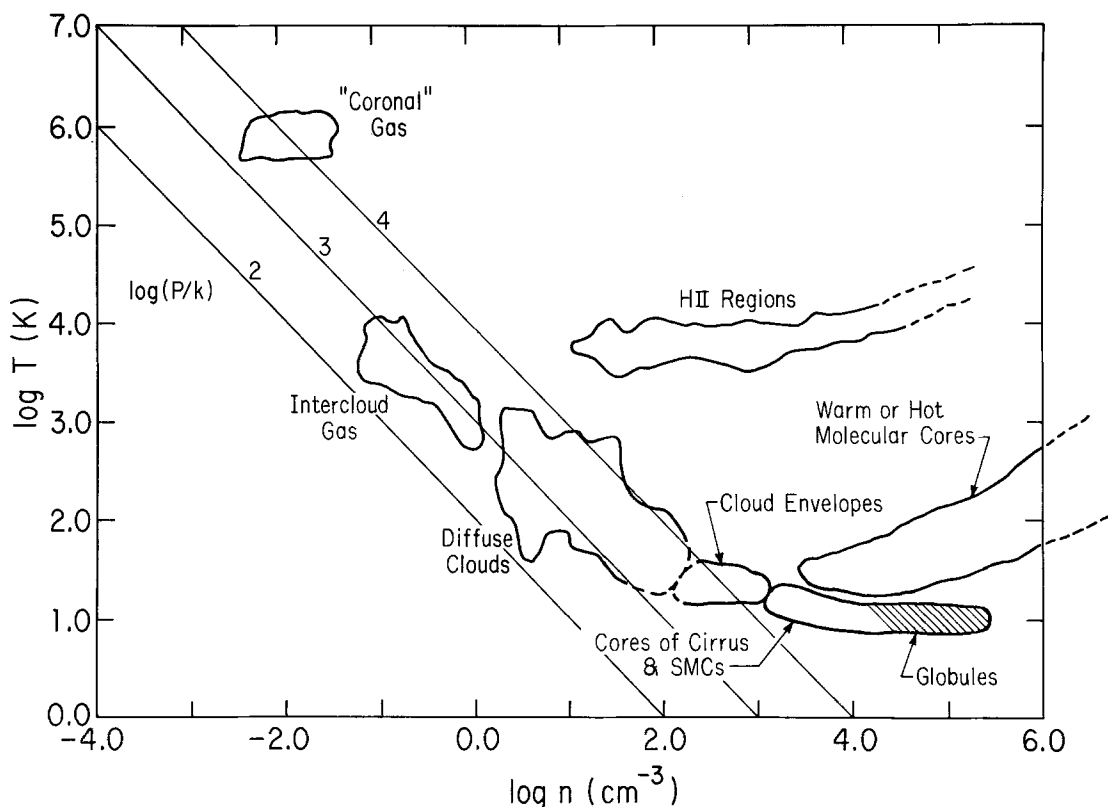


Fig. 1. The physical regimes of the ISM, as currently observed. It is not clear whether cloud envelopes and the denser diffuse clouds are distinct.

The diffuse cloud regime forms the bridge, not necessarily continuous, between the tenuous intercloud, and dense molecular components, of the ISM. The low-density end of the diffuse cloud regime is not well defined physically, but operationally it is where atomic absorption lines of heavy elements (Na, Ca, K, ...) can first be detected in absorption against bright stars. This onset, at $A_v \sim 0.1$ mag, depends on column depth, not density. Temperatures are of order 100 K, and sizes are believed to range from 5 to 35 pc. The high column density end of the diffuse cloud regime is well defined, at $A_v \sim 2$ mag, where simple molecules make their first appearance, being adequately shielded from photodissociation by the average interstellar UV field even though the latter remains important to the chemistry. The cloud temperature drops rapidly to ~ 20 K at this point. The range of density (n) and temperature (T) in Figure 1 applies not only to the ensemble of diffuse clouds, but probably typically to individual clouds as well, whose central densities approach $1(3) \text{ cm}^{-3}$ in several models. Since diffuse clouds are studied mostly via UV absorption spectroscopy toward hot stars, their morphology is poorly known.

The situation is rather different for the 'dense' molecular regimes of the ISM. Here, the morphology can be well studied by mapping emission lines of CO and other simple

TABLE II
The physical regimes of the ISM

Regime	log density	T (K)	Mass (M_{\odot})	Comments/diagnostics
Hot intercloud gas ('coronal')	-2.3 to -1.5	10^6	-	UV absp. lines, soft X-rays, filling factor ~ 0.2 to 0.5 . Contained inside bubbles, shells and supershells.
'Warm' intercloud gas	-1.0 to 0	$\lesssim 10^4$	-	Neutral component: 21 cm line Ionized component: optical emission lines Pulsar dispersion measures
Diffuse clouds	0.5 to 2	10^2	3-300	Opt. absp. lines, 21 cm HI; $A_v < 2$ magn.
Cirrus clouds	2 to 3	?	2-260	IR (100 μm); gal. lat. $> 20^\circ$; $A_v \sim 0.2$ to 2 mag
cores	3.5 to 5	?	0.1-10	IR; radio em. from CO, OH, H ₂ CO; $A_v > 2^m$
Cold clouds				
complex	2 to 3	≥ 10	10^3-10^4	Dark patches, IR, CO, $0.5 \lesssim A_v \lesssim 2$
single	2 to 3	≥ 10	$10-10^3$	Dark patches, IR, simple molecules, $0.5 \lesssim A_v \lesssim 2$
cores	4 to 5	10	$1-10^2$	Many molecules, no massive SF, $\sim 3 \lesssim A_v \lesssim 25^m$
GMCs				
complex	2 to 2.5	15 to 20	$10^5-3 \times 10^6$	Dark regions, IR, CO; $0.5 \leq A_v \lesssim 2$
single	2 to 3	-20	10^3-10^5	Dark regions, IR, simple molecules, $A_v \gtrsim 2$
cores	4.5 to > 9	25 to > 200	$10-10^3$	IR; many complex molecules; nearby massive SF
CSEs	2 to 13	10-100	$\sim 10^{-2}$	IR; many molecules

molecules. The morphology is found to be highly complex and rather ill-defined. The categories given in Table II are therefore rather arbitrary, though generally accepted (e.g., Goldsmith, 1987; Turner, 1988a). Figure 2 shows the outlines of Giant Molecular Clouds (GMCs) in the Orion–Monoceros region as mapped in CO emission by

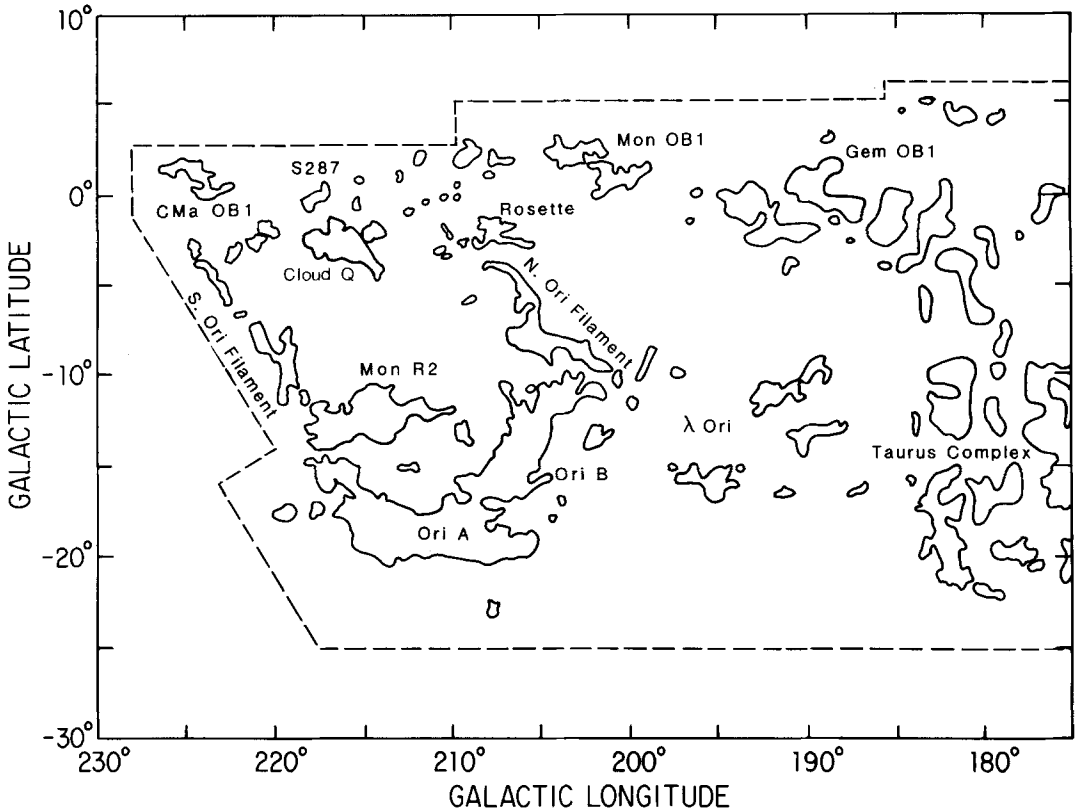


Fig. 2. The Orion system of GMCs (Maddelena *et al.*, 1986).

Maddelena *et al.* (1986). This is an example of a GMC complex; there are at least a dozen other prominent ones. This region illustrates why the definition of a GMC is arbitrary, because it is possible that all the clouds actually form part of a single cloud complex, which might be revealed by mapping at higher sensitivities. The large loop formed by the northern and southern filaments, Mon R2, and Orion A and B, may represent a magnetic bubble expelled from the galactic plane, which lies ~ 100 pc to the north of Orion A. Similarly, the fragmented clouds around the star λ Ori may comprise an expanding shell of molecular gas. Cold cloud complexes have equally complicated morphology. They differ in two important respects from GMC complexes, however. First, the individual clouds are much smaller and less massive, often being called Small Molecular Clouds (SMCs). Second, cold clouds and their complexes are devoid of

massive star formation ($\geq 1 M_{\odot}$). Very crudely, the onset of massive star formation seems to require clouds of mass $1(3)^* M_{\odot}$ or larger. The Taurus region is the best studied example of a Cold Cloud Complex (e.g., Myers and Benson, 1983). It is unclear whether SMCs form from the disruption of GMCs by the effects of massive stars, or whether SMCs coalesce (in spiral arm shocks) to form GMCs (see Turner, 1984, for a review). By contrast with GMC and Cold Cloud complexes, cirrus clouds are morphologically distinguished by lying at high galactic latitudes, although their distances from the Sun (65–200 pc) suggest that they are not physically very distinct from the galactic plane. Since they are so close, they cover large solid angles and have not been systematically mapped in CO emission yet. CO sizes are ~ 2 pc, but sizes determined by their IRAS 100 μm emission are more like 5 pc. Thus cirrus clouds appear to be the smallest type known, and may simply represent the ‘chaff’ of disrupted GMCs expelled from the plane. Since they are smaller and less massive than SMCs, they seem less likely to represent an extension of the SMC distribution out of the plane.

Regarding *physical* properties, the dense molecular regimes are all characterized by low temperatures (10–20 K, except near star forming regions), high extinctions, and much of the gas in molecular form. It is presently difficult to distinguish physically the higher- A_v end of diffuse clouds, cirrus clouds, and the ‘envelope’ gas known to surround SMCs and to comprise most of the volume and mass of GMCs. These categories, taken as a group, have recently been termed ‘translucent’ clouds by van Dishoeck and Black (1988), who take them to represent isolated small clouds (2–5 mag) as well as the outer ‘edges’ of dense molecular clouds. There is indication from CO data that the cirrus cloud temperatures overall are lower than 100 K, but they could well form a continuum with the temperatures of the densest diffuse clouds (Figure 1). A temperature of ~ 20 K is usually regarded as characterizing both envelope gas of galactic plane clouds, and the densest diffuse clouds, and presumably this applies to the cirrus since its extinction is similar. Certain rather simple molecules (HCN, HCO^+ , N_2H^+) seem to be observed in the envelopes of GMCs (although it is not ruled out that they arise from unresolved denser cores along the line-of-sight) but are not observed in the overall cirrus clouds or in diffuse clouds. The envelopes of galactic plane clouds could be somewhat denser than cirrus clouds, or they could be chemically richer as a result of higher metallicity.

A sharp distinction does occur between envelope gas, and dense molecular cores which exist in cirrus clouds, cold galactic plane clouds, and GMCs. Physically, the dense cores of cirrus clouds and cold galactic plane clouds appear indistinguishable except that the cirrus cores are probably less massive (Turner *et al.*, 1988b). Cirrus cores are marginally gravitationally stable and a fraction of them will, therefore, form low-mass stars. In order that the star formation rate not exceed the observed rate, cirrus cores appear to be in virial equilibrium, as are cores of all types of galactic plane clouds. Cold galactic plane cores are definitely gravitationally stable and are sites of low-mass star formation; such stars do not provide significant heating of the cores, whose temperatures therefore remain close to the 10 K value which represents equilibrium between heating

* The notation $a(b)$ stands for $a \times 10^b$.

by cosmic rays and cooling by microwave emission of CO molecules. Unusually low fractional abundances have recently been determined for several molecules in cirrus cores (Turner *et al.*, 1988b), which may establish them as chemically distinct from cold cores in galactic plane clouds, the latter exhibiting a wide variety of molecular species (including species as complex as the cyanopolynes) not apparently present in cirrus cores. By contrast with cirrus cores and cold galactic plane cores, the dense cores in GMCs are far denser, far hotter, and far more massive. These GMC cores are the sites of massive star formation in the Galaxy. They are heated vigorously by embedded massive protostars, or by nearby massive stars in the beginning phases of disruption of the local GMC material. Thus these cores are subject to shocks, massive and highly energetic outflows, and copious far IR radiation. The densities and temperatures listed in Table II for these cores represent only lower limits imposed by limited observational resolution. Temperatures as high as 2000 K occur in the shocked regions at the edges of these cores where the energetic protostellar outflows impact on the adjacent dense molecular cloud. Not surprisingly, these conditions of high temperature and energy are conducive to a much richer chemistry than is found elsewhere, not only because high- T gas phase reactions can occur, but also because grains are volatilized, releasing their rich organic mantle material to the gas phase.

The only other regime comparable in chemical complexity with massive GMC cores is that of CSEs. CSEs form as a result of mass loss from late-type stars, usually semi-regular and regular giants and supergiants. In this way is the stellar gas and dust, now chemically enriched, returned to the ISM. Such stars are generally cool, with surface temperatures of only a few thousand K. They come in two distinct varieties: carbon-rich ($C/O > 1$), and oxygen-rich ($O/C > 1$, comparable to the cosmic ratio). The actual mass loss mechanism is uncertain, but possibilities include radiation pressure on grains (and molecules), shock waves, and various forms of sporadic ejection. Fairly constant mass loss rates, $\sim 1(-5)$ to $1(-4) M_{\odot} \text{ yr}^{-1}$, seem to occur, with expansion velocities of 5 to 30 km s^{-1} (Zuckerman, 1980). A constant mass loss rate means the gas density in the envelope should vary as r^{-2} . Most envelopes appear quite spherical, but some have disk-like structures, and most may contain significant irregularities (large 'clumps') within the envelope, as suggested by recently observed phenomena such as vibrationally excited HCN masers (Guilloteau *et al.*, 1987) and highly unusual spectral profiles in vibrationally excited CS (Turner, 1987a). Envelope sizes vary, but might be represented by the late-type carbon star IRC 10216, with an inner shell radius of 6(14) cm, extending out to 1(18) cm. Densities and temperatures vary throughout the IRC 10216 envelope, with $n \geq 1(11) \text{ cm}^{-3}$, $T \sim 600 \text{ K}$ in the innermost regions, decreasing to $n \sim 1(2) \text{ cm}^{-3}$, $T \sim 10 \text{ K}$ in the outer regions (Rieu *et al.*, 1984). For O-rich envelopes, the stars and hence inner envelopes are somewhat hotter ($\sim 1000 \text{ K}$). The gas is heated by collisions with heated grains driven by radiation pressure at supersonic speeds through the gas, and is cooled by adiabatic expansion and by line emission by abundant molecules (H_2O for O-rich stars, CO for C-rich stars). The shells are almost totally molecular in composition. Relative to any of the ISM systems, the CSEs have reasonably well understood geometries, kinematics, and distributions of n ,

T , and radiation fields. It is not yet clear whether interstellar grains originate solely in the ejecta of evolved stars, but certainly they as well as supernovae account for all of the heavy elements in the ISM, and thus are progenitors of astrochemistry.

Because of the complexities in categorization of the denser components of the ISM, astrochemists have focused on three distinct regimes in modelling the chemistry of the ISM: (i) diffuse clouds, in which photochemistry is of paramount importance; (ii) dense cold clouds, typified by the cores of cold clouds in Table I, in which low- T gas phase ('ion-molecule') chemistry is considered the dominant type; (iii) dense warm cores in star forming regions of GMCs, in which grain and shock (high- T gas phase) chemistry as well as ion-molecule chemistry are important. By contrast, CSEs are well defined objects, and their molecular chemistry is based largely upon thermochemical equilibrium in the inner dense regions of the envelope, with the products being considered 'frozen out' as the envelope expands. These products are then modified by photochemistry in the outer envelope. Grain processes are also important.

3. Ion-Molecule Gas Phase Chemistry

The first known interstellar molecules were CH^+ , CH , and CN , detected in 1937–1941 in diffuse clouds. Early attempts to explain their observed abundances on the basis of non-thermodynamic equilibrium (Kramers and ter Haar, 1946; Bates and Spitzer, 1951) considered radiative association, photoionization and dissociation, and dissociative recombination, but fell far short of reproducing the observed abundances. Because these early gas-phase models encountered such difficulties, subsequent models focused on grain surface processes. Grain chemistry seemed particularly germane when large abundances of H_2 were first directly observed (Carruthers, 1970) because of the longstanding realization that H_2 could not form via radiative association (the manifold of two incident ground state H atoms does not yield a bound state of H_2), and because of the success of grain catalysis models for H_2 (Hollenbach and Salpeter, 1971). But problems quickly arose with grain surface models for other molecules, not only because of large uncertainties related to the unknown composition of the grain surfaces, but also because desorption of molecules heavier than H_2 from the grains appeared difficult, especially in cold clouds (e.g., Watson and Salpeter, 1972a, b). Shortly thereafter, Solomon and Klemperer (1972) and Herbst and Klemperer (1973) realized that gas phase reactions between ions and neutral species could be very rapid at low interstellar temperatures, and gas phase interstellar chemistry was resurrected. The role of shocks in astrochemistry was also recognized early, first as an agent for sputtering grains and explaining the large Ca and Na abundances in some diffuse clouds (Routly and Spitzer, 1952), and later as a trigger for certain high-temperature gas phase reactions which address the CH^+/CH problem in diffuse clouds (Elitzur and Watson, 1978, 1980).

It is now recognized that all of these forms of chemistry are very likely occurring in most regions where molecules are detected, with the probable exception of grain surface catalysis in cold clouds. The subject of astrochemistry is being continuously clarified by new laboratory data but simultaneously is confronted by more and more detailed

observations, which are now revealing a truly bewildering array of chemical complexity. Until a few years ago, astrochemistry was content to explain (largely qualitatively) the mere existence of the observed species. Today, further progress is largely dependent on knowledge of the rates of the myriad chemical processes that are occurring, and on the continuing identification of additional physical processes at work in molecular clouds. This paper is a summary of recent advances over the past few years, drawing attention to new laboratory and observational results which act as tests of current astrochemical models and, where possible, as delimiters between them in the various interstellar morphologies.

3.1. BASIC PROCESSES

As is now well accepted, the chemistry of simple molecules in cool interstellar clouds proceeds largely by a sequence of two-body ion-molecule processes, in which the initial ionization is produced either by photoionization (in diffuse clouds) or by cosmic-ray ionization (in dense clouds). Ion molecule reactions proceed rapidly (at the Langevin rate, $\sim 1(-9) \text{ cm}^{-3} \text{ s}^{-1}$ or even faster at low temperatures) and have no activation energies. Starting with H_2 , which is formed on grains, the initial ionization steps are $\text{H} + cr \rightarrow \text{H}^+ + e$; $\text{He} + cr \rightarrow \text{He}^+ + e$; $\text{H}_2 + cr \rightarrow \text{H}_2^+ + e$, $\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$; and $\text{C} + h\nu \rightarrow \text{C}^+ + e$. Since H and H_2 have by far the greatest fractional abundance, the dominant reactions usually involve hydrogen, whenever possible.

The starting reactions for the C, O, and N families of molecules differ because the ionization potential of carbon is $< 13.6 \text{ eV}$ and thus carbon exists as C^+ except in dense clouds. O and N are not ionized by the ambient UV field. The reaction $\text{C}^+ + \text{H}_2 \rightarrow \text{CH}^+$ is endothermic by $\sim 0.4 \text{ eV}$, so in diffuse clouds carbon chemistry is believed to start via the slow radiative association reaction $\text{C}^+ + \text{H}_2 \rightarrow \text{CH}_2^+ + h\nu$ (Black and Dalgarno, 1973). In dense clouds where carbon is neutral, carbon chemistry is sustained by $\text{C} + \text{H}_3^+ \rightarrow \text{CH}^+ + \text{H}_2$. Oxygen chemistry, by contrast, starts in diffuse clouds with the slightly endothermic reaction $\text{O} + \text{H}^+ \rightarrow \text{O}^+ + \text{H}$ which is efficient at low temperature because the ionization potential of O is only slightly greater than that of H. Then $\text{O}^+ + \text{H}_2 \rightarrow \text{OH}^+$ launches the sequence. In dense clouds the reaction $\text{O} + \text{H}_3^+ \rightarrow \text{OH}^+$ plays the same role. These processes are well established. By contrast the origin of nitrogen chemistry remains uncertain. $\text{N} + \text{H}_3^+ \rightarrow \text{NH}_2^+ + \text{H}$ is exothermic but has been calculated to possess considerable activation energy. $\text{N} + \text{H}_3^+ \rightarrow \text{NH}^+ + \text{H}_2$ is known to be endothermic. However, N^+ can be produced by $\text{N} + cr \rightarrow \text{N}^+ + e$ or, once N-bearing molecules are present, via He^+ dissociative ionization of these molecules (N_2 , CN, etc). $\text{N}^+ + \text{H}_2 \rightarrow \text{NH}^+ + \text{H}$ is also endothermic, but only by 19 meV for H_2 in the $J = 0$ ground state, so it is possible that the reaction can proceed either as a result of rotational energy stored in the reacting H_2 , or because the N^+ itself is not thermalized but possesses excess translational energy as a result of the process $\text{N}_2 + \text{He}^+ \rightarrow \text{N}^{++} + \text{N} + \text{He}$. Models to date have usually assumed $\text{N} + \text{H}_3^+ \rightarrow \text{NH}_2^+$ proceeds.

Once these simple hydride ions of C, O, N are produced, the chemistry proceeds by the coupling of the C, O, N families. The chemical versatility of carbon (its ability to undergo insertion, condensation, and other types of reactions) insures efficient coupling

of the C and N, and C and O families. The direct coupling of the O and N families does not occur in any such way, and the few N–O bonds among interstellar molecules are the result of quite indirect processes. Larger species, and species containing more than one heavy atom, are next formed by a variety of processes including condensation reactions (in which heavy atoms (C) are added), carbon insertion and exchange reactions (with C^+), and radiative association of radicals and radical ions. Of course, dissociative electron recombination (DER) is the process by which neutral species are formed. Though usually slow, some neutral-neutral reactions are also important, especially if the products have very slow destruction rates. Thus CO, N_2 , O_2 , CN have important neutral-neutral formation pathways and high abundances because of their chemical stability.

Figure 3, taken from Turner and Ziurys (1988, adapted from Prasad and Huntress, 1980b), illustrates the basic scheme of ion-molecule chemistry for simple species. In diffuse clouds, C^+ , O^+ , H_3^+ initiate the chemistry through photoionization, and reactions started by He^+ are not important. Their secondary products (HCO^+ , N_2H^+ , H_3O^+ , CH_3^+) quickly recombine with electrons whose abundance is high to yield the simple observed species OH, CO, CH, CH^+ (?), and the chemistry does not likely proceed further. In dense clouds, the reaction chain starting with He^+ may be competi-

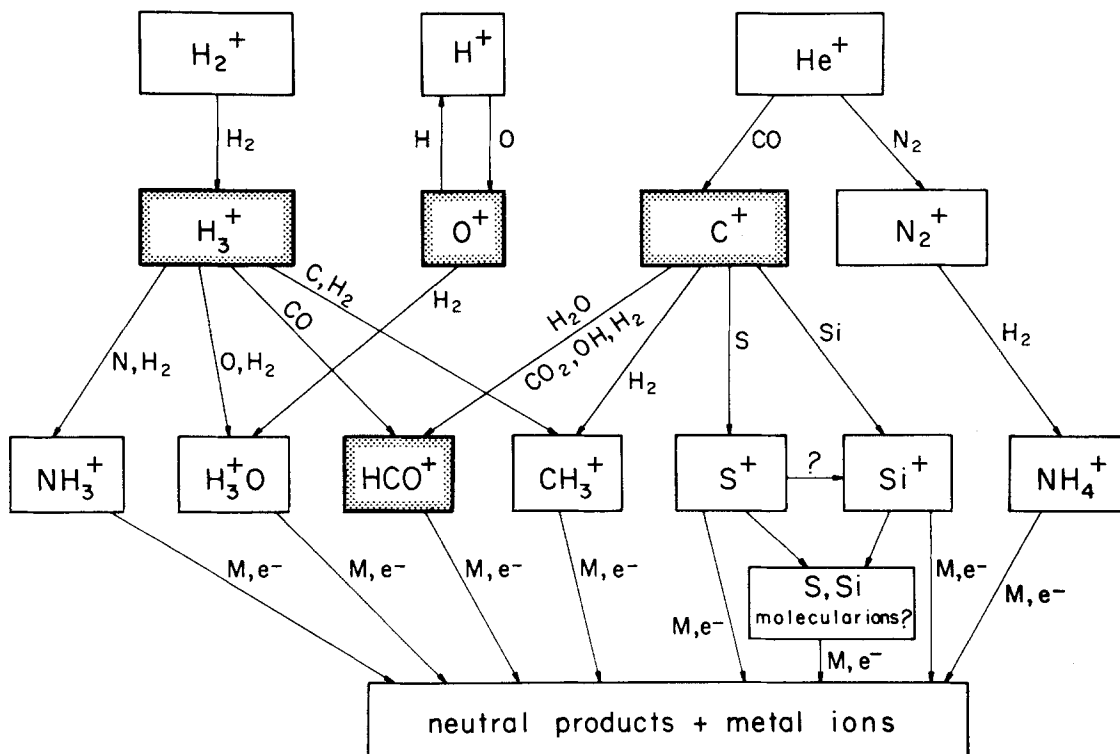


Fig. 3. Schematic of some of the major chemical pathways in the ion-molecule scheme of interstellar molecular synthesis. (Adapted from Prasad and Huntress, 1980b.)

tive with that initiated by H^+ and H_3^+ . Whether it is or not depends on whether C^+ transfers charge rapidly to S^+ , Si^+ (these reaction rates are unmeasured). If it does, ionized metals [M^+] are the major carriers of positive charge if they exist in the gas phase, and x_e , the electron fractional abundance is also high while $x(HCO^+)$, $x(N_2H^+)$, etc., are relatively low. If the charge transfer is not rapid, or if the metal abundances are low, then C^+ reacts mostly with the abundant polyatomic species or with H_2 . Then H_3^+ , HCO^+ will be dominant positive charge carriers, and x_e will be lower than for the first chain. Observed values of $x(HCO^+)$ suggest the second chain, initiated by He^+ , may dominate.

A complicated network of these kinds of reactions constitutes the ion-molecule scheme of interstellar synthesis. The application of this theory involves solving the time-dependent or steady-state differential equations

$$\frac{dn_x}{dt} = \sum_{A,B} k_{AB} n_A n_B - \left[\sum_c k_{xc} n_c + \beta_x \right] n_x$$

for the abundance n_x of species X formed by reaction of A and B and destroyed by reaction with C and by photodestruction β_x . k_{ij} are reaction rates. The early models (Herbst and Klemperer, 1973; Mitchell *et al.*, 1978) were steady-state. Iglesias (1977) and Prasad and Huntress (1980a, b) performed the first detailed pseudo-time-dependent model in which the chemistry evolves under fixed physical conditions. Similar models by Graedel *et al.* (1982) and Langer *et al.* (1984) studied such topics as the dependence of the chemistry on elemental abundances and the nature of isotopic fractionation. More recently, the synthesis of the more complex species has been studied by Leung *et al.* (1984), Millar and Nejad (1985), Herbst and Leung (1986a, b, 1988), and Millar *et al.* (1987a). Finally, attempts have been made to include the time dependence of physical parameters in realistic ways (Gerola and Glassgold, 1978; Tarafdar *et al.*, 1985) such as simulations of hydrodynamic collapse under gravity. As many as 2548 reactions and 273 different atomic and molecular species have been included in the latest models. Different groups using different methods produce results in satisfactory agreement so long as identical reaction schemes are used, and intergroup comparisons (Millar *et al.*, 1987a) have been valuable in establishing how major aspects of the models can be highly sensitive to differing assumptions about one or two key reactions. As has been well documented by all of these studies, the major uncertainties in the models in probable order of severity are: (i) unknown reaction rates; (ii) uncertain physical conditions; (iii) uncertain elemental abundances. The *omission* of important reactions is probably not a significant factor (Dalgarno, 1986). While intelligent guesses can often be made for the $\sim 80\%$ of utilized reactions whose rates are unmeasured, important surprises continue, and new results, both experimental and theoretical, can affect entire classes of reactions. An early example was the realization that radiative association reactions can proceed rapidly when the reacting fragments are large. This opened up a major process by which to explain the most complex of the observed species (Millar and Williams, 1975). A more recent example is the recognition (Clary, 1988; Rowe, 1988)

that ion molecule reactions involving polar species have rates which typically increase dramatically with decreasing temperature down to 10 K. Surprisingly, this development has had only modest effect on the predicted molecular abundances (Herbst and Leung, 1988; Langer and Graedel, 1988), especially at steady state. More isolated but important cases involve the DER of H_3^+ , now known to be 100 times or more slower than other reactions of this type, thus making the H_3^+ chain of reactions in Figure 3 important in diffuse cloud chemistry. Another reaction of key importance to the synthesis of complex molecules is $\text{C} + \text{O}_2 \rightarrow \text{CO} + \text{O}$. If slow at low temperature, large amounts of C will exist in dense clouds, leading to much larger abundances of complex organics. We will discuss points (ii) and (iii) further.

Given these uncertainties, it is surprising how successful ion-molecule chemistry has been, at least for the simpler species (4 atoms and less). There is overall agreement between observed and predicted abundances for most simple compounds containing first-row atoms in both diffuse, and dense quiescent clouds (Watson and Walmsley, 1982; Watson, 1984). Direct evidence of ion-molecule chemistry lies in the observed ions listed in Table I. Relative abundances are predicted quite satisfactorily for these ions, and for simple species such as CO, OH, CN, HCN, H_2CO , and in addition their fractional abundances as a function of density seem reasonably well understood. Perhaps the greatest success of ion-molecule theory has been the quantitative explanation of the large Deuterium fractionation of several species in cold dense clouds ($\text{DCO}^+/\text{HCO}^+ \sim 0.01$, $\text{N}_2\text{D}^+/\text{N}_2\text{H}^+ \sim \text{NH}_2\text{D}/\text{NH}_3 \sim \text{DCN}/\text{HCN} \sim 0.001$ to 0.01 even though $\text{D}/\text{H} = 2(-5)$). This explanation arises naturally from the few ion molecule reactions that govern these species (e.g., Watson, 1978a; Turner and Zuckerman, 1978), provided that the fractional ionization is low ($\lesssim 1(-8)$). In particular, reactions of the type $\text{XH}^+ + \text{HD} \rightarrow \text{XD}^+ + \text{H}_2$ favor production of XD^+ because the forward reaction rate exceeds the back reaction at low T and can compete with the electron recombination of XH^+ at low fractional ionization. This feature of ion-molecule chemistry has been so generally accepted that it has been used to conclude that any species observed to be highly deuterated in cold clouds must be formed by ion-molecule processes (e.g., HC_3N , H_2CO). As we shall see, neutral species that are highly deuterated can also be explained by grain processes (Section 6.5).

The general level of agreement currently recognized between ion-molecule models and observations was established for simpler species (up to 4 atoms) by the models of Graedel *et al.* (1982), which include 'high metals' (as observed by Copernicus in ρ Oph) and 'low metals' (a factor of 100 in depletion). C-O chemistry is successfully explained, as exemplified by CO, OH, and H_2CO for either model. HCO^+ and CS require the low metal model. The high metal case explains only a few abundances in cold clouds but appears to be preferred for C, CO, and HCO^+ in warm clouds even though the adopted temperature are not high enough to affect depletion factors. The conspicuous failures are N_2H^+ and NH_3 , whose observed abundances are at least 100 times those predicted by either model. These discrepancies have been overcome in the recent model by Langer and Graedel (1988), by using new laboratory data on the rates of the nitrogen species reactions at low temperatures. The reaction of H_3^+ with N (which probably does not

occur under interstellar cloud conditions) is not necessary to explain the abundances of the N-species. At early times the reactions of N with CH_3^+ and radicals (e.g., CH) are sufficient.

3.2. LARGER SPECIES

Two important classes of reactions have been recognized in recent years that now seem responsible for building complex interstellar molecules. The first involves the unique ability of carbon to form increasingly complex species by fixation reactions (C with small hydrocarbon ions, e.g., $\text{C} + \text{CH}_3^+ \rightarrow \text{C}_2\text{H}_2^+ + \text{H}$), insertion reactions (C^+ with neutral hydrocarbons, in which the carbon ion is inserted into the hydrocarbon, e.g., $\text{C}^+ + \text{CH}_4 \rightarrow \text{C}_2\text{H}_3^+$; $\text{C}^+ + \text{C}_2\text{H}_2 \rightarrow \text{C}_3\text{H}^+$), and condensation reactions (e.g., $\text{CH}_3^+ + \text{C}_4\text{H} \rightarrow \text{C}_5\text{H}_2^+ + \text{H}_2$) between smaller hydrocarbon ions and neutrals. These reactions are particularly efficient in building up hydrocarbons. An important property of these processes, taken together, is that the products tend to be unsaturated. In addition to these processes, hydrogenation reactions play an important role, but a general feature of these is that they proceed only to a modest degree before becoming kinetically disallowed. The initial hydrogenation step $\text{C}_n^+ + \text{H}_2 \rightarrow \text{C}_n\text{H}^+ + \text{H}$ is efficient for $n = 5$ to 9, but the second step $\text{C}_n\text{H}^+ + \text{H}_2 \rightarrow \text{C}_n\text{H}_2^+ + \text{H}$ does not occur for $n = 5, 7, 9$. High-order hydrogenation appears unlikely for $n > 4$. Hydrogenation by radiative association occurs seldom; Herbst *et al.* (1983) have found that almost all such reactions $\text{C}_n\text{H}_m^+ + \text{H}_2 \rightarrow \text{C}_n\text{H}_{m+2}^+ + h\nu$ have vanishingly small rates for $n > 2$. In an important study of the consequences of these processes, Herbst (1983) has found that steady-state models cannot reproduce observed abundances of complex hydrocarbons such as C_4H unless fixation reactions are important; these require a large amount of atomic C ($x(\text{C}) \sim 1(-5)$), which itself is not predicted by standard ion-molecule models (Section 3.5.1).

Once a family of complex hydrocarbons (ions and neutrals) has been built up, the important cyanopolyne family may be formed by reaction of atomic N with the appropriate hydrocarbon ions. Such reactions have been studied in the laboratory only up to C_3 (Federer *et al.*, 1986) and there is evidence that they may not proceed for higher-order hydrocarbons. Other pathways to the cyanopolyynes are possible, but HC_5N appears to form with difficulty because there is no suitable hydrocarbon (C_5H_3^+ , C_5H_5^+) to react directly with N. The general problem of cyanopolyynes is discussed in Section 3.5.2.

Figure 4 illustrates how the complex hydrocarbons and cyanopolyne families may be formed by the principles just discussed. Reactions are taken from Herbst *et al.* (1983), Herbst (1983, 1988), and Herbst and Leung (1988). We have omitted reactions which do not lead to the observed species because of some of the restrictions discussed. For example, the sequence $\text{C}^+ + \text{C}_3\text{H} \rightarrow \text{C}_4^+$, $\text{C}_4^+ + \text{H}_2 \rightarrow \text{C}_4\text{H}^+$ terminates because C_4H^+ does not react with H_2 . Thus the observed C_4H needs the 'fixation' reaction involving neutral C, which is seen to be important for the higher-order hydrocarbons. These general 'rules' indicate a rather different formation mechanism for HC_5N than for either HC_3N or HC_7N .

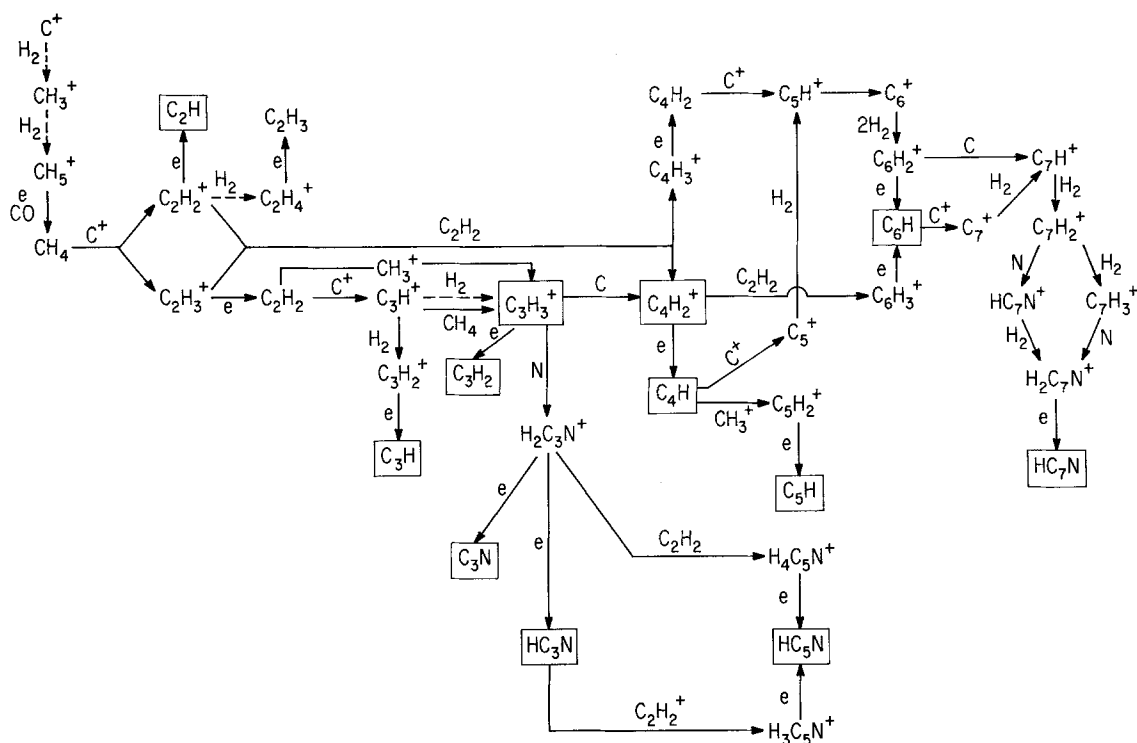


Fig. 4. Reaction scheme for synthesis of long carbon chain molecules in the ISM.

As Table I shows, many complex species other than hydrocarbons and cyanopolynes are observed. To form these requires the second important class of reactions, that of radiative association between complex fragments that contain O and N as well as C. Although radiative association is very slow between small species, it was recognized long ago (Millar and Williams, 1975) that the rates of such reactions should increase dramatically as the size of the reactants increases (because of the large number of possible stabilizing radiative transitions available in all but the smallest species). Also important has been the recent recognition (Clary, 1985; Adams *et al.*, 1985) that radiative association between polar reactants will proceed increasingly rapidly with decreasing temperature, and will reach or probably exceed the Langevin rate ($1(-9) \text{ cm}^{-3} \text{ s}^{-1}$) at cold interstellar temperatures. Thus CH_3^+ has been experimentally verified to radiatively associate rapidly at low temperatures with species such as H_2O , HCN , NH_3 , CO , HC_3N to produce directly the protonated versions of the observed species CH_3OH , CH_3CN , CH_3NH_2 , H_2CCO , and CH_3C_3N , respectively. Although experimental data are lacking, it is likely that larger ions such as CH_5^+ , $C_2H_2^+$, and others shown in Figure 4 will behave similarly. Thus $CH_5^+ + CO$ produces protonated CH_3CHO , $HCO^+ + H_2O$ produces $HCOOH$, $C_2H_5^+ + H_2O$ produces $EtOH$, and so on. The limitations to interstellar molecular complexity as a result of these processes is not known. Theoretical estimates of radiative association of polar species at low T

seem quite reliable, but must be performed for each reaction since the rates can differ by several orders of magnitude (cf. Leung *et al.*, 1984). More unpredictable are the rates of reactions involving higher-order hydrocarbons; the few experimental values that exist are often theoretically quite unexpected (Herbst, 1983). Finally, the interstellar abundances of C and of O, O₂ are crucial to the degree of complexity attainable (Section 3.5.1). It has been speculated that these processes might form molecules as complex as PAHs (Section 3.4.3), or very large condensates which might build into grain-like agglomerates of solid H₂O, alcohols, aldehydes, etc. (Smith and Adams, 1978). However, interstellar clouds might not live long enough for this to happen, even if the chemistry were favorable. Herbst (1985) has suggested that a time of 1(7) yr is required to produce hydrocarbons with 20 C-atoms under favorable conditions.

3.3. TIME DEPENDENCE AND ELEMENTAL ABUNDANCES

As we have mentioned, the major uncertainties in ion-molecule models are unknown reaction rates, uncertain elemental abundances, and uncertain physical conditions. Perhaps chief among the latter is the question of time dependence, which cannot be treated in a realistic manner without tying the chemistry self-consistently to the detailed physical evolution of the cloud (cf. Glassgold and Langer, 1976) about which little is known (cf. Turner, 1984). Current time-dependent models largely ignore these larger evolutionary questions and simply follow the chemistry forward from a switch-on time.

3.3.1. Diffuse Clouds

Traditionally both the chemical composition and the physical conditions in diffuse clouds have been thought to be in steady state, for two reasons. First, models of these clouds indicate that they are stable against gravitational contraction if isothermal collapse is assumed. Second, chemical abundances are assumed to be in equilibrium because the abundances of the important species are controlled by either photodissociation or rapid reactions for which time constants are typically $\leq 1(4)$ yr. Most early models also considered density and temperature to be uniform throughout the cloud, but more recent ones fit these parameters and also allow for the formation of H₂ on grains. An excellent review of diffuse cloud chemistry is given by van Dishoeck and Black (1988), which describes in detail the recent models of these authors. There are certainly residual problems with even these sophisticated steady-state models despite overall good agreement with observations for most species. A number of specific reaction parameters have to be adjusted for a good over-all fit though none violate theoretical or measured bounds. Even with such flexibility, the abundances of three species, CH⁺, CO, and CN are all underestimated. The large observed abundance of CH⁺ has been recognized as a problem for almost 50 years and is now correctly modelled as arising in high-temperature shocked gas, consistent with its peculiar velocities (Section 5.4.1). The difficulty with CO (formed by C⁺ + OH) appears to lie in its destruction rate by photodissociation, which may be satisfactorily reduced by adopting a smaller UV intensity at $\lambda < 1000 \text{ \AA}$ than is usual. The CN problem may reside both in uncertainties in formation reactions and in its photodestruction at

$\lambda < 1000 \text{ \AA}$. Uncertainties in elemental abundances are expected to play an insignificant role in diffuse cloud models. In diffuse clouds depletion from the gas phase of even the heavier non-refractory elements is small and well established (less than a factor of 4 for all elements involved in models of observed species).

Can time dependence of either the chemistry or of physical conditions explain the remaining model discrepancies?

Chemical time-scales are short: $\sim 1(2)$ – $1(3)$ yr at the edges of diffuse clouds, $< 1(5)$ yr even at the centers. The only exception is the H/H_2 chemistry which could require $\sim 5(6)$ yr in a cloud like ζ Oph. Van Dishoeck and Black (1988) argue that, even if clouds evolved significantly on timescales less than a few $1(6)$ yrs (which is unlikely; see, e.g., Turner, 1984), the observable effects of chemical time dependence would be small.

Evolutionary models in which the physical parameters also change with time (e.g., Tarafdar *et al.*, 1985) suggest that clouds spend most of their lifetimes in the diffuse state, and dense cores form on a timescale of a few $1(6)$ yr. The time scales for the chemical processes in the diffuse state are small, and the dynamical effects are found to shorten the approach to chemical equilibrium even further. No significant differences with steady-state models are, therefore, expected in the modelling of the diffuse stage of a contracting cloud.

3.3.2. Dense Clouds

Dense clouds comprise several types (Section 2): quiescent dense cores (non-star forming); slightly energetic dense cores (low-mass star formation); and massive, highly energetic cores (massive star formation). The complexity of the latter defies realistic modelling, and none has been attempted. Low-mass star-forming cores often exhibit supersonic but otherwise fairly simple bipolar flows (producing observed linewidths of $\sim 10 \text{ km s}^{-1}$) and attempts to model these have been made (Charnley *et al.*, 1988), which involve both chemical time dependence and a model of the varying physical conditions. Many aspects are uncertain. Other models treat the time dependency of the chemistry in clouds undergoing hydrodynamic collapse from the diffuse to the dense state (Gerola and Glassgold, 1978; Tarafdar *et al.*, 1985; Prasad *et al.*, 1987). While complex enough to require a supercomputer, these models suffer the difficulty that the physical evolution of clouds is undoubtedly much more complicated than simple hydrodynamic collapse. Indeed, the formation of cores within clouds is thought by many to result from non-elastic collisions of supersonic parcels of gas within the cloud (Blitz and Shu, 1980; Myers, 1983), a process that involves strong shocks among other complexities. A general feature of all dynamically evolving cloud models is that dynamical time-scales are large when the cloud is diffuse, and decrease very rapidly when core densities become $1(4) \text{ cm}^{-3}$ or more. Such behavior is very likely true for shock-formed clumps (cores) as well, and the possibility of a short lifetime (less than the chemical equilibrium time) for such cores should be kept in mind in comparing models with observations.

To test chemical time dependence most precisely requires a so-called pseudo time-

dependent model in which the physical parameters remain time invariant over the time required to reach chemical equilibrium. The source best suited for this purpose is the cold ($T = 10$ K), dense ($n = 1(4)–1(5) \text{ cm}^{-3}$), quiescent ($\Delta v < 0.2 \text{ km s}^{-1}$), i.e. sub-sonic core of TMC-1. The earlier pseudo time-dependent models were not explicitly tailored to the conditions of TMC-1 and similar well-defined dark cores (Iglesias, 1977; Prasad and Huntress, 1980; Henning, 1981) but more recent models either include conditions suitable for TMC-1 (Graedel *et al.*, 1982; Leung *et al.*, 1984; Langer and Graedel, 1988) or are specifically aimed at it (Millar and Nejad, 1985; Herbst and Leung, 1986a, b, 1988; Millar *et al.*, 1987a).

Assuming that a meaningful comparison may be made between ion-molecule pseudo-time-dependent models and observations, the next question is whether the effects of differing element abundances can be separated from those of time dependence. Attempts to explain observed chemical differences between different clouds on the basis of equilibrium models with differing elemental abundances (Millar and Freeman, 1984a, b) probably leave too many variables open to allow definite conclusions, although it is possible that the observed differences between TMC-1 and L183, two dark cloud cores with very similar physical conditions (i.e., age?) can be explained in terms of a greater depletion of C, N, O in L183. The first study that seems capable of an answer is that of Graedel *et al.* (1982) who consider both pseudo time-dependence and two sets of elemental abundances: 'high metal' (normal depleted gas phase abundances), and 'low metal' (additional 100-fold depletions for S, Si, Na, Mg, Fe). For 11 of 13 fundamental species the low metal case explains the observations better, for both steady state ($t \geq 1(7)$ yr) and early times ($t \sim 1(5)$ to $1(6)$ yr). The two species explained better with high metals differ depending on the epoch. The superiority of the low-metals model seems definitive, while the results do not allow a distinction between steady state and early times, for the relatively simple species considered in the model (≤ 4 atoms). An important result is that CI reaches peak abundance at $1(4)$ to $1(6)$ yr, then decreases drastically with time. A recent model by Langer and Graedel (1988) is patterned similarly in that it is restricted to fairly small species and considers conditions appropriate to several types of sources. It uses updated estimates for several key N-reactions, includes photodissociation of CO by cosmic ray induced UV, and considers the time-dependence of the ^{13}C isotope fractionation. The key results of this model are: (i) CI can be very abundant at early times without requiring $\text{C/O} > 1$; (ii) nitrogen is efficiently introduced into the chemistry at early times via $\text{CH}_3^+ + \text{N}$; this leads to a satisfactory explanation of the HNC/HCN ratio, although the large observed abundance of NH_3 is still not well reproduced; (iii) ^{13}C fractionation is significant for CO but not for other C species; (iv) most species reach steady state by $1(5)$ yr, somewhat earlier than other models (primarily because the new low DER rate for H_3^+ is used); N_2H^+ has the longest equilibration time, $\sim 2(6)$ yr, and might be useful as an age indicator for the cloud. Overall good agreement is obtained between the models of Langer and Graedel and those of Herbst and Leung (1986a, b, 1988). In particular, the long-standing problem of underestimating N_2H^+ seems to have been improved. Besides NH_3 , a few other species (C_2 , CN, C_2H , OCS, H_2CS) remain discrepant; the cause is unclear.

The importance of time dependence, and indeed the tantalizing possibility that the chemical composition might be used to age-date molecular clouds, is most clearly revealed in the behavior of the complex molecules (Millar *et al.*, 1987a). Unfortunately, the predictions for the complex species also reflect most sensitively the assumptions about unknown but key reaction rates. Herbst (1988) has discussed the behavior of HC_3N as a function of time as calculated in the models of Herbst and Leung (1986a, b; HL) and Millar and Nejad (1985; MN). The differences between the two groups have been established as arising from different assumptions about unmeasured reaction rates. All three models show a sharp increase in HC_3N abundance (by 3 or 4 orders of magnitude at $t \sim 1(3)$ yr from switch-on and a sharp decline back to the initial levels at $t = 1(6)$ to $1(7)$ yr). Differences between the two HL models are due to inclusion in the latter case of fast rates for ion-polar neutral reactions as recently advocated by Adams *et al.* (1985). The differences are not large for HC_3N (or for most other species, but there are notable exceptions). The discrepancy between MN and HL is large, however, typically 2 to 3 orders of magnitude at all times. Observations do not favor one model over the other because the observed HC_3N abundance agrees reasonably with MN at steady state ($t > 1(7)$ yr) but with HL at early times. The discrepancy arises because of the omission in MN of certain (unmeasured) reactions of O with hydrocarbons, which serve to reduce abundances of complex species, and the inclusion by MN of the reaction $\text{N} + \text{C}_3\text{H}_2 \rightarrow \text{HC}_3\text{N} + \text{H}$, omitted by HL because it may have an activation energy. Certain assumptions about dissociative recombination reactions favorable to the growth of complex species are also made by MN in the absence of data (Section 3.4.1). The lessons are twofold: (i) it is inescapable that certain unmeasured rate coefficients can lead to very large differences in calculated abundances; (ii) despite these limitations, all models currently show very similar time dependence for most carbon species including CI itself. The reason appears fundamental: the early rise in abundance at $t \sim 1(3)$ yr reflects the time needed for C^+ ions to recombine into CI at $n \geq 1(2) \text{ cm}^{-3}$. CI in turn drives the hydrocarbon chemistry. As time progresses C and other C-rich species are lost mainly by neutral-neutral reactions of the type $\text{C} + \text{O}_2 \rightarrow \text{CO} + \text{O}$, $\text{CN} + \text{O} \rightarrow \text{CO} + \text{N}$, etc. The abundances of C and of other complex C-compounds depend critically on the rates of these destructive reactions (the rates are unmeasured at low T) and on the C/O ratio, which determines how much O (or O_2) is available to convert reactive C-species into CO. The neutral-neutral reactions are not as fast as the ion-molecule reactions; this is why the predicted abundances of the C-species peak early in the cloud's history. Eventually, however, all C is tied up in CO by these and other processes, and CI plus complex species assume low equilibrium abundances. In their latent model, Herbst and Leung (1988) extend to species as complex as HC_9N and $\text{CH}_3\text{C}_3\text{N}$, with similar time dependencies but with a persistent underestimation of abundances of up to a factor of 10 relative to the observations.

3.4. ADDITIONAL FACTORS

Several recently recognized factors, not generally incorporated into detailed models as yet, may be important in ion-molecule chemistry, particularly as regards the larger species.

3.4.1. *Dissociative Recombination of Polyatomic Ions: Bates' Theory*

Nearly all neutral species formed by ion-molecule chemistry include a final step of DER of a polyatomic ion, yet very few DER reactions are measured. Although total rate coefficients as functions of temperature are now being measured, very little is known about what neutral fragments are produced and in what ratio. Early theories (Herbst, 1977; Green and Herbst, 1979) argued that removal of one or more H atoms during DR was the favored pathway for ions containing both heavy atoms and H atoms. Current models largely adopt this idea, which is critical to the gas phase synthesis of complex species because it preserves the heavy-atom skeleton. Bates (1986, 1987) has reformulated an older view (Bates, 1950). The polyatomic ion is pictured as involving a valence bond structure. Capture of the electron results in a net anti-bonding character in a single bond involving the atom at the charge center. Only one bond should rupture at a time. Strong bonds between heavy atoms may break, but H-bonds are more susceptible not only because they are weaker but also because pairs of fragments in which one of the neutrals is an H atom separate most readily.

Bates' hypothesis has recently been applied to synthesis models and tested observationally. An application of the hypothesis to chemical models requires (*ab initio*) calculations of the structure of the ion in order to decide where the charge center lies and which bond(s) most likely rupture. Such calculations, as well as subsequent modelling using the results, have been carried out by Millar *et al.* (1988a). The important result of the reaction calculations is that more than one bond may break, with differing probabilities. For example $\text{H}_3\text{CO}^+ + e \rightarrow \text{H}_2\text{CO} + \text{H}$ and $\text{CH}_2 + \text{OH}$ with equal probability. For smaller ions, only one H atom tends to detach, but for larger ions rupture of heavy atom bonds also occurs. Because of this, growth of complex species should be reduced. The results of modelling using the calculated products are complicated. Since the reaction $\text{H}_3\text{O}^+ + e$ now produces mostly H_2O and little or no OH, H_2O becomes the dominant carrier of oxygen, and OH as well as species produced from it (O_2 , NO, N_2) are decreased. C and N are increased at steady state. To meet observations, OH must now be partly formed by photo-dissociation of H_2O via cosmic-ray-induced UV photons (Section 3.4.2). NH_3 is also considerably increased because there is more N, and now agrees with observation (Section 3.1). However, HCN and HNC also increase for the same reason, and become higher than observed. N_2H^+ , until recently (Section 3.3.2) underestimated in models, now suffers a dramatic reduction in abundance, and becomes again unacceptable. Hydrocarbons are reduced significantly only at steady state. A major conclusion of this work is that at early times (3(5) yr) the synthesis of complex species is efficient enough to withstand a small decrease in formation rates. One reason is that the new rules of DR actually open up new pathways for certain hydrocarbons. Other complex species (CH_3OH , CH_3CN , H_2CCO) do not change much, but HC_3N actually increases at steady state because of the increased abundance of N. In summary, the use of Bates' hypothesis does not appear generally to have worsened or improved the agreement between models and observations, although a few key species (N_2H^+ , C_3N , OH) are clearly worsened. It is obviously important that Bates' idea be checked by laboratory or other means.

An observational test of Bates' theory, which confirms it in one case, has been carried out by Turner and Sears (1988). They have placed an upper limit on the abundance of the ketyl radical HCCO in several types of sources, corresponding to $\text{HCCO}/\text{H}_2\text{CCO} < 0.02$ (ketene, H_2CCO is a commonly observed species in many sources). The chemistry of HCCO and H_2CCO is such that both are formed via DR of $\text{H}_3\text{C}_2\text{O}^+$ and thus Bates' rule that only one H should detach implies the formation of H_2CCO but not HCCO. An analysis of the chemistry shows that there are no other ways to form HCCO and that the two species are not chemically coupled, so that $p_2/p_1 \leq \text{HCCO}/\text{H}_2\text{CCO}$, where p_i is the probability of detachment of i H atoms. Other observational tests may be performed, such as the vinoxy radical (CH_2CHO) vs acetaldehyde (CH_3CHO), both deriving from the DR of CH_3CHOH^+ .

3.4.2. Cosmic-Ray Induced UV

Prasad and Tarafdar (1983) recognized that cosmic rays colliding with H_2 generate energetic secondary electrons which in turn excite H_2 into higher electronic states. Upon decay, these produce UV photons of sufficiently low wavelength to dissociate many molecules, the most important being CO because it constitutes a source of free carbon. The photodissociation of CO is a complicated process involving 30 or more photodestruction lines and their overlap with the UV emitting lines of H_2 . Gredel *et al.*, (1987) find the CO dissociation rate to be 10 to 100 times the cosmic ray ionization rate, depending on the CO abundance (self shielding), the CO rotational temperature (number of overlapping transitions), and grain albedo. The important ratio C/CO is estimated to increase from 5(-6) in the absence of photodissociation to 5(-3) in its presence. Recent observations of CI in both its 370 and 610 μm transitions (Zmuidzinas *et al.*, 1988) establish $\text{C}/\text{CO} \sim 0.1$ for several clouds which do not include cold ones. Such a value can be predicted by the model of Gredel *et al.* only if there is a sizable velocity spread (10 km s^{-1}) and a large carbon depletion factor of 100 (which reduces CO even more because of enhanced photodissociation). A clear test will be the observation of C/CO for cold dense clouds ($\Delta v < 0.5 \text{ km s}^{-1}$).

Because of the large uncertainties, the inclusion of *cr*-induced photodissociation into detailed chemical models has only recently begun. Sternberg *et al.* (1987) estimate high rates of photodissociation for several small molecules other than CO. When these results are used in a limited chemical model, the main conclusion of these authors is that formation of complex species (C_3H , C_3H_2) is significantly inhibited and their predicted abundances fall well below observed values. This is the case whether or not $\text{H}_3\text{O}^+ + e$ produces OH as well as H_2O (Section 3.4.1); if OH is produced, then $\text{OH} + h\nu \rightarrow \text{O} + \text{H}$ provides a source of O which reacts efficiently with complex carbon species to reduce their abundances even further. Cosmic ray induced UV photodissociation of CO (but not of other species) is also included in the much more extensive model of Langer and Graedel (1988) but produces $< 10\%$ of the predicted neutral carbon. Since these authors have underestimated the photo-dissociation rate of CO by a factor of 2 to 4, the process can likely account for $\sim \frac{1}{3}$ of the carbon in their models. As the model stands, this process does not greatly affect the predicted abundances of the other small species

either. Cosmic ray induced UV photodissociation is not included in the latest models of Herbst and Leung (1988) since little is known of photodissociation rates for larger species. Any increase in complex molecule abundances at steady state would reflect a dominance of increased C production from CO leading to more efficient synthesis, over a greater depletion brought about by photodissociation and by a potential increase in destructive nascent oxygen. Such a trade-off has been investigated for the case of photodissociation caused by external photons in clouds of low extinction ($A_v \sim 5$ mag; Herbst and Leung 1986a) and found actually to increase steady state abundances of moderately complex species. Since the *cr*-induced UV photodissociation involves only photons in the ~ 1000 Å region covered by the H₂ Werner and Lyman bands, and since photodissociation of larger species involves processes different from those in small species, the conclusion of Herbst and Leung may not be extrapolated.

3.4.3. Polycyclic Aromatic Hydrocarbons (PAHs)

There is now circumstantial evidence for the existence of truly complex interstellar molecules known as PAHs. These are aromatic hydrocarbons of 20 to 100 atoms of unspecified structure (although lattice-like), which are large enough to have grain-like properties. We discuss the evidence in Section 4.7. If PAHs are as abundant as suggested ($2(-7)$), they will affect dense cloud chemistry considerably (Omont, 1986). For ion molecule processes their most important property is charge. Lepp and Dalgarno (1988) list the principle processes involving PAHs as: (i) $M^+ + PAH \rightarrow PAH^+ + M$ (charge transfer); (ii) $e + PAH \rightarrow PAH^- + h\nu$ (radiative attachment); (iii) $PAH^+ + PAH^- \rightarrow PAH$ (neutralization); and (iv) $M^+ + PAH^- \rightarrow M + PAH$ (neutralization). Here, M^+ is a positive ion (atomic or molecular). Because radiative attachment is particularly rapid (see also Omont, 1986), it is found that, for a fractional abundance $x(PAH) = 2(-7)$, 34% of PAHs are PAH^- and 65% are neutral. More importantly, $x(PAH^-)/x(e) \sim 20$, so that if PAHs exist, then $M^+ + PAH^-$ becomes the dominant neutralization process for molecular ions rather than ion-electron recombination processes. If M^+ is a complex molecular ion, the branching ratios for neutral products for $M^+ + PAH^-$ can be expected to differ from those of ion-electron recombination. If M^+ is an atomic ion such as C^+ , recombination with e is very slow because it is radiative, whereas neutralization with PAH^- is rapid. Thus $x(C)$ may be greatly increased, which in turn promotes the formation of both simple and complex organic molecules. In a limited model incorporating these ideas, Lepp and Dalgarno (1988) find that abundances of species such as C_2H , C_2H_2 , C_3H , and C_3H_2 are enhanced by two orders of magnitude if PAHs are present. More complex organic species have not yet been included in PAH models, but it is interesting to note the possible cancellation of the destructive effect of *cr*-induced UV photodissociation and the promotional effect of PAHs, which may offer a way out of the dilemma of complex species. Also, most metals will be neutral in PAH models. The greater the PAH abundance the greater the molecular ion abundances because the rate coefficient for $M^+ + PAH^-$ is about 10 times less than that for $M^+ + e$, and the fraction of e decreases roughly linearly with increase in PAH fraction.

PAHs affect diffuse cloud chemistry importantly as well as dense cloud chemistry. Lepp *et al.* (1988) find a sizable reduction in atomic ions if PAHs exist at $\geq 1(-7)$ abundance, and improved agreement of C^+ and C with observation. A longstanding discrepancy between cloud densities inferred from rotational and fine structure atomic levels and from the ionization balance can also be resolved if PAHs exist at this concentration. Models for ζ Per suggest 1% of all carbon is in PAHs, 40% in the gas phase, and 60% in grains. For ζ Oph the corresponding amounts are 7%, 21%, and 72%. Abundances of many small species are little affected by PAHs, so long as $x(\text{PAH}) \sim 1(-7)$ to $1(-6)$. As in dense clouds, the abundances of more complex species (H_2CO , CH_3 , C_2H_2) are expected to be increased by several orders of magnitude in diffuse clouds if PAHs are included.

It is of great importance to refine the properties of PAHs and to generalize their treatment to pseudo time dependent models involving more complex molecules. In particular, the inclusion of both *cr*-induced photodestruction and PAH chemistry may bear strongly on the apparent distinction between steady-state and early-time chemistry.

3.5. APPARENT PROBLEMS AND LIMITATIONS

3.5.1. The $C^+/C/CO$ Relationship

We have discussed the possible difficulties with the predicted C/CO ratio as compared with observations. A more general problem was recognized many years ago, as soon as the CI line was first observed (Phillips *et al.*, 1980). For uniform clouds immersed in UV radiation fields, models before (Mitchell *et al.*, 1978; Langer, 1976) and since have all predicted spatially a sharp transition zone between the forms C^+ , C, and CO. Virtually all carbon outside dense regions ($A_v \leq 1$ mag) is expected to be ionized, most of it within heavily shielded regions ($A_v \geq 5$ mag) should be in the form of CO, and near the edges of clouds between these two regimes, a fraction of it ($\sim 10\%$) should be in a thin layer of C. All other gas phases of carbon should be negligible. The position of the thin shell of C, and its thickness, is dependent on the intensity of UV illuminating the cloud and the density of the cloud, but not very sensitively (cf. Langer, 1976; Tielens and Hollenbach, 1985). As we have seen, time-dependent models show analogous effects for $C^+/C/CO$ as a function of time. The model of Leung *et al.* (1984) is typical: C^+ is expected to dominate at very early times, CO at late times ($\geq 1(6)$ yr), and C at intermediate times ($\sim 3(2) \leq t \leq 1(5)$ yr). At steady state, $C/CO < 1(-3)$ is predicted.

The early observations of C, involving only the $^3P_1 - ^3P_0$ transition at $609 \mu\text{m}$, suggested $C/CO > 0.1$ for a variety of warm clouds near star forming regions, including some with face-on H II region-molecular cloud interfaces (OMC-1: Phillips and Huggins, 1981), and two with edge-on interfaces (S140, M17: Keene *et al.*, 1985). In several sources comparison of the CI and CO lines suggested large (> 10) optical depths for the single CI line observed, and, hence, $C/CO \sim 1$, a value which poses insurmountable problems for the models. The recent detection of the $^3P_2 - ^3P_1$ transition of CI at $370 \mu\text{m}$ (Jaffe *et al.*, 1985; Zmuidzinas *et al.*, 1988) has permitted a more definitive analysis and an important revision in the observed abundances; in 6 warm clouds

Zmuidzinas *et al.* find optically thin CI lines and C/CO ratios of 0.05 to 0.15, still high enough to raise serious difficulties for current ion-molecule models. It is also established that densities exceed $1(3) \text{ cm}^{-3}$ in CI emission regions, so that C and CO coexist in the dense cores, and the derived values of C/CO pertain to these regions, not to outer envelope gas.

A potentially important observation is that of the ${}^3P_1 - {}^3P_0$ CI line in the dark cloud L183 (Phillips and Huggins, 1981), whose brightness temperature and linewidth appear comparable with those of ${}^{12}\text{CO}$, unlike the situation in the warmer clouds. This suggests that the CI line might be optically thick in L183, corresponding to a C/CO ratio even higher than ~ 0.1 to 0.15.

A second difficulty for the models is posed by Keene (1987). Observations of the ${}^3P_1 - {}^3P_0$ transition of CI in the dense dark cloud associated with the star ρ Oph (Frerking *et al.*, 1988) are combined with UV observations of CI in diffuse clouds (Jenkins and Shaya, 1979). The extinction is known in all of these regions. The diffuse cloud observations ($A_v \leq 4$) indicate a smaller ratio for CI/(H + 2H₂) ($\sim 1(-7)$ or 0.03% of carbon in the form CI) than does the ρ Oph region ($\sim 1(-5)$) for which $4 \leq A_v \leq 20$. The abundance determinations in ρ Oph may have problems, but even a reduction of the observed CI abundance by 1(2) (which seems severe) would imply a constant CI/(H + 2H₂) ratio over the range $0.1 \leq A_v \leq 20$, completely at odds with the models.

Keene *et al.* (1985) have summarized suggestions which might rectify these difficulties. (Both difficulties are resolved if much more CI can be produced in *dense* molecular clouds; the second difficulty also seems to require an enhancement proportional to A_v .) In one category are suggestions that aim at increasing the CI produced in the photodissociating interface region between H II regions and molecular clouds (Tielens and Hollenbach, 1985). This idea has been criticized on the grounds that observations of M17 and S140 are claimed to show CI emission to be widespread throughout these clouds and not to be localized near the H II/cloud interface. However, given the large distances of these objects and the predicted narrowness of the CI zone, it seems doubtful that these observations have adequately resolved the interface. A better example is the nearby bright-rimmed object NGC 1977 which may show an enhanced CI emission at the interface (Wooten *et al.*, 1982a). On the other hand DR210H and ρ Oph exhibit high CI/CO ratios, yet have no nearby H II regions. A second category of hypotheses are those which increase CI in the cloud interior, as seems indicated by the observations. Mechanisms could include changes in the chemical models, a source of UV photons to dissociate CO, the sputtering of carbon from grains due to the passage of shocks, an increase in the assumed C/O abundance, or dynamical effects which keep clouds chemically (if not chronologically) young. In Section 3.4.2 we saw that *cr*-induced UV photodissociation would have difficulty explaining the C/CO ratios, but is possible. Stutzki *et al.*, (1988) observe widespread low-level C⁺ at 158 μm in M17, which demonstrates the presence of UV radiation in this object, regardless of its origin. A number of B-stars embedded in a clumpy cloud is one possible interpretation for M17. More generally, the penetration of external UV into the interior of a clumpy

cloud through the interclump spaces is another, especially if the grain albedo is high. A related idea applies to clouds with active star formation, in which stellar winds might erode cloud clumps and form C from CO (Charnley *et al.*, 1988). Needless to say, the complexity inherent in all such suggestions defies their modelling at the present time.

Dynamical explanations for a high C/CO ratio may take two forms. If there are turbulent transport currents in the clouds which circulate core and envelope material on a time scale short compared to the chemical equilibrium time for $C \rightarrow CO$ (1(6) yr), then C^+ and C can be continually replenished by photodissociation at the cloud edges (Boland and de Jong, 1982). Time scales $Rc/\Delta v$ seem adequate for warm clouds near star forming regions, but are much too long for cold dark clouds whose internal motions are observed to be very small. Alternatively, models of cloud evolution in a simple picture of gravitational collapse indicate short lifetimes in the higher density states, smaller than or on the order of the time needed to complete $C \rightarrow CO$ conversion (Prasad, 1987). Thus C/CO can be enhanced over steady-state conditions throughout the dense cloud regime, for densities up to $1(5) \text{ cm}^{-3}$ ($A_v \sim 10$ to 20 mag) but excluding the very dense core where $n \geq 1(6) \text{ cm}^{-3}$ (see also Tarafdar *et al.*, 1985). The complicated filamentary structures dominating dark cloud regions such as Taurus seem to belie such simple models, however, and suggest instead the formation of cores via supersonic inelastic collisions between parcels of gas. Once such a gravitationally unstable core forms, it collapses in a free-fall time of a few $\times 1(5)$ yr (cf. Turner 1988a) so C/CO might remain above steady state values. In considering all such ideas one should remember that the complex carbon species are particularly abundant in cold dark clouds, where the prospects for any dynamical explanation seem least likely.

Changes in the chemical reaction networks to reflect revised reaction rates may yet explain the problem of atomic carbon. The most important example may be the reaction $C + O_2 \rightarrow CO + O$. In all models to date this reaction is assumed to proceed unimpeded at low T , in which case it is the dominant process that converts C to CO. If there is a small activation barrier, the reaction will not proceed at low T , and the predicted C/CO ratio will be much higher. Observational evidence that such a barrier might exist is the observed limit on O_2 (Liszt and Vanden Bout, 1985): $O_2/CO < 0.1$ in dense clouds. Models predict $O_2/CO \sim 0.3$ to 0.5.

The observed upper limit on O_2/CO has other important consequences. Since models show that the O_2 abundance should drop sharply with increasing C/O ratio, the O_2/CO limit tends to rule out $C/O > 1$. The small O_2 abundance and large H_2O abundance (deduced from HDO) also suggest that oxygen left over from the $C \rightarrow CO$ conversion remains mostly atomic or is locked up as H_2O -ice on grains. A high abundance of O coupled with the observed high abundance of OH indicates that the reaction $O + OH \rightarrow O_2 + H$ must have an activation temperature of ~ 90 K, or else that O_2 must be efficiently dissociated in dense clouds. Both conditions are very difficult to fulfil (Prasad *et al.*, 1987).

In the recent model of Langer and Graedel (1988), larger rates for reaction of He^+ with CN, CS, and C_2 , and C^+ with CH, CH_2 , C_2H produce C at a rate several times larger than previously assumed, which for a normal C/O ratio lead to abundances

possibly consistent with some but not all observations of C. Highest values of C are obtained at low temperature (10 K), which may be relevant to the large abundances of complex organics observed in the coldest clouds. Increasing C/O helps the C/CO problem but tends to over-produce species such as C₂H, C₃H.

In summary, any of several mechanisms may resolve the C/CO question, but some (photodissociation processes for CO) deplete the complex organic species well below observed levels, while others may overproduce smaller organics. It is possible that a combination of *cr*-induced CO photodissociation and the presence of PAHs may resolve the C/CO ratio and the large abundance of complex species. However, problems remain for the cyanopolyynes family quite apart from those we have been discussing.

3.5.2. The Cyanopolyyne Problem

Protonated cyanoacetylene (HC₃NH⁺) has not been detected despite sensitive searches, to a limit HC₃NH⁺/HC₃N < 0.007 in both cold dark clouds and warm star forming clouds (Turner *et al.*, 1988a). By contrast, protonated HCN is detected (Ziurys and Turner, 1986c) at a level HCNH⁺/HCN ~ 0.1, at least 14 times higher. To understand the problem consider Figure 5, a composite of all possible ion-molecule reactions involved in cyanopolyyne chemistry. Reaction rates in units of 1(-9) s⁻¹ cm⁻³ are indicated, those underlined being measured or calculated at 10 K. According to Figure 5, for any ratio HC_{*n*}NH⁺/HC_{*n*}N the determining processes are the fast protonation and DR reactions, and those destruction processes for HC_{*n*}NH⁺ and HC_{*n*}N which do *not* produce HC_{*n*}N and HC_{*n*}NH⁺, respectively. In steady state, HC_{*n*}NH⁺/HC_{*n*}N = {2k'[AH⁺] + k_d[B]}/{α_{*n*}ξ_{*n*}[e] + k_d⁺[D]} where k' is the protonation rate for HC_{*n*}N by AH⁺, and α_{*n*} is the DR rate of HC_{*n*}NH⁺ with branching ratio ξ_{*n*} to HC_{*n*}N, k_d and k_d⁺ are destruction rates for HC_{*n*}N and HC_{*n*}NH⁺ by species [B] and [D], respectively. Recent calculations (Millar *et al.*, 1988a) give ξ₁ = ξ₃ = 1/3, and α₁ ~ 2000 at T = 10 K. Assuming α₃ = 2000 also, one predicts HCNH⁺/HCN ~ 0.018 and HC₃NH⁺/HC₃N ~ 0.023, in disagreement with observations. The steady-state models of Herbst and Leung (1988) confirm this simple analysis. For early epochs these models give ratios of 0.0047 and 0.019, respectively, in even greater disagreement with observations. Generally, also, the detailed models predict only a small fraction of the observed HC₃N.

Possible explanations for the discrepancy in observed and predicted ratios are: (i) HC₃N is being *formed* in an unknown way not involving HC_{*n*}NH⁺. This is unlikely to involve gas phase reactions: any ion-molecule process would have to produce an ion *other* than HC₃NH⁺ yet which must recombine efficiently to form HC₃N. No such ion seems possible. Any neutral-neutral reaction would involve rates which are too slow; e.g., C₃H₂ + N → HC₃N has been suggested but is spin-forbidden. Formation of HC₃N on grains remains a possibility. (ii) HCN is being *destroyed* in an unknown way that does not affect HC₃N. Again, gas phase reactions are unlikely. Radiative association reactions should favor HC₃N, not HCN. Also (see Figure 5) some fairly fast reactions convert HC₃N to HCN, not *vice versa*. Catalytic formation of HC₃N from HCN on grains would relieve the problem but seems unlikely (see Section 4.8.2). (iii) There are

problems with the assumed DR rates or branching ratios. The dilemma is solved if $\alpha_3 > 14 \alpha_1$ and if $\alpha_1[e] \gg k_d^+[D]$. The latter condition is likely. The former condition would be surprising and must be checked by measurement. An error in the calculated value of ξ_3 cannot resolve the problem (Turner, 1988b).

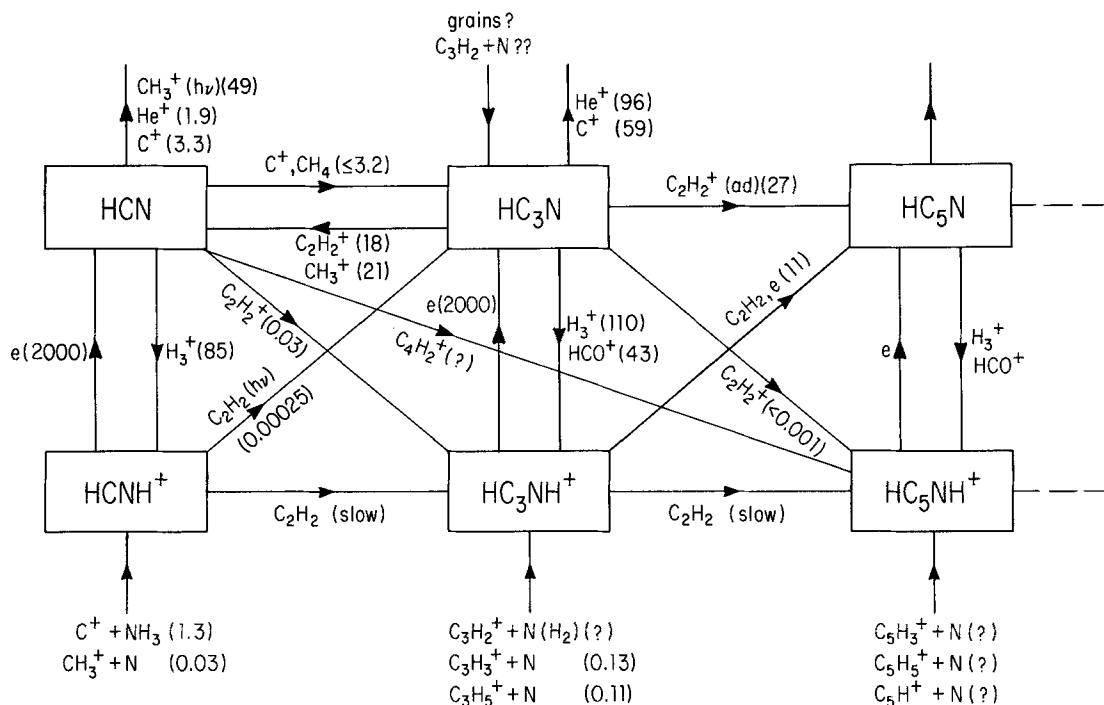


Fig. 5. Reaction scheme for synthesis of interstellar cyanopolyynes. Reaction rates in units of $1(-9) \text{ cm}^{-3} \text{ s}^{-1}$ are shown in parentheses. All rates are calculated or measured at $\sim 10 \text{ K}$.

At present ion-molecule models cannot be said to predict quantitatively or even qualitatively the complex species observed in the ISM. The cyanopolyne family derives most directly from the basic hydrocarbons and must be understood before there is prospect for interpretation of other complex molecules. The problems outlined here do not yield to any one factor (e.g., the reaction $C_3H_2 + N \rightarrow HC_3N$, if allowed, can explain the observed abundance of HC_3N but worsens the discrepant HC_3NH^+/HC_3N ratio; the apparent inefficiency or failure of reactions $C_nH_m^+ + N \rightarrow HC_nN$ for $n \geq 5$ spells trouble for the higher-order cyanopolyynes). The prominence of the cyanopolyynes in cold dark clouds, among interstellar objects, does however point to a low-temperature gas phase formation mechanism.

3.5.3. Chemistry of the Second-Row Elements

It was noticed some time ago (Hartquist *et al.*, 1980) that sulfur molecules are produced only with some difficulty by ion-molecule reactions, because the reactions $S^+ + H_2 \rightarrow$

$\text{SH}^+ + \text{H}$ (diffuse clouds) and $\text{S} + \text{H}_2 \rightarrow \text{SH} + \text{H}$ (dark clouds) are both endothermic. Species such as H_2S , SO , SO_2 have long been recognized as occurring in star-forming regions with abundance levels 100 times those predicted. Additionally, many S-species are overabundant with respect to O-species relative to the cosmic S/O ratio. By contrast with star forming regions, cold dark clouds are known to harbor only the S-species CS, OCS, SO, and SO_2 , and these occur in abundances predicted by ion-molecule models.

The two Si species SiO and SiS are observed only in energetic star forming regions with high-velocity outflows, and in the diffuse post-shock gas of the supernova remnant IC 443. Again this points to an energetic origin. The ion-molecule chemistry of Si is poorly understood (Turner and Dalgarno, 1977), but it seems likely to be initiated very inefficiently if at all at low temperatures by the reactions $\text{Si}^+ + \text{H} \rightarrow \text{SiH}^+ + h\nu$ (diffuse clouds) and $\text{Si} + \text{H}_3^+ \rightarrow \text{SiH}^+ + \text{H}_2$ or $\text{SiH}_2^+ + \text{H}$ in dense clouds. SiH^+ is quickly photodissociated in diffuse clouds, and its further reaction with H_2 may be endothermic. Thus the absence of Si species to very low levels in cold dark clouds is not surprising in terms of ion-molecule chemistry, and a different chemistry seems necessary to explain the Si species in energetic star forming regions.

Phosphorus is so far observed only in the form PN and is absent in species PH_3 , HPO, HCP, PO to levels which are chemically significant. The ion-molecule chemistry of P (Thorne *et al.*, 1984) is very different from that of the related N atom in that PH_n^+ ions react endothermically with H_2 so that PH_n compounds cannot form. P^+ and HP^+ react rapidly with H_2O which is abundant, so that species containing the P–O bond should dominate. To explain the large abundance of PN and the absence of PO, Millar *et al.* (1987b) assume that the exothermic reaction $\text{PO} + \text{N} \rightarrow \text{PN} + \text{O}$ proceeds at low T (has no activation energy). If this is so, PN should occur in cold dark clouds at fractional abundances comparable to those observed in energetic regions, but in fact the PN abundance is at least 10 times lower (Turner *et al.*, 1988a). Further, HPO is less abundant by at least a factor 4 than predicted by Millar *et al.* (Turner *et al.*, 1989). It appears, therefore, that P chemistry does not proceed via ion-molecule processes at low T , and a different chemistry is indicated for the observed PN in star forming regions.

The observed absence of Mg compounds (MgH , MgO) cannot be interpreted as yet because nothing is known of low- T ion-molecule Mg chemistry.

3.6. COLD DENSE CLOUDS: THE DOMAIN OF ION-MOLECULE CHEMISTRY

Cold dense clouds show no evidence of energetic processes such as shocks, and the temperatures are so low that grain chemistry is generally expected to be inoperative (Sections 4.2 and 4.5). Thus low- T gas phase chemistry (i.e., ion-molecule) seems solely responsible for the molecular species observed in these clouds, which accordingly act as test objects for the theory. Therefore, a comparison of observations and theory is useful.

3.6.1. Observations vs Models: General

Despite considerable uncertainties in the molecular abundance data, there seems to be a reasonable uniformity of abundances over a rather wide range of density and tempera-

ture for quiescent clouds (e.g., Irvine *et al.*, 1987) including TMC-1 (cold quiescent cloud), and the Orion extended ridge (a warmer ($T \sim 50$ K) quiescent cloud). Such a conclusion poses two problems: (i) the time-scale for adsorption of molecules onto grains is \ll the estimated cloud ages (Section 4.2) and suggests efficient desorption processes; (ii) abundances are predicted to vary importantly with time, so that all clouds are implied to have similar ages, or more likely, to have reached steady state. For the moment, the conclusion allows us to compare observations with ion-molecule models, as shown in Figure 6. In Figure 6 the range in observed abundances encompasses the

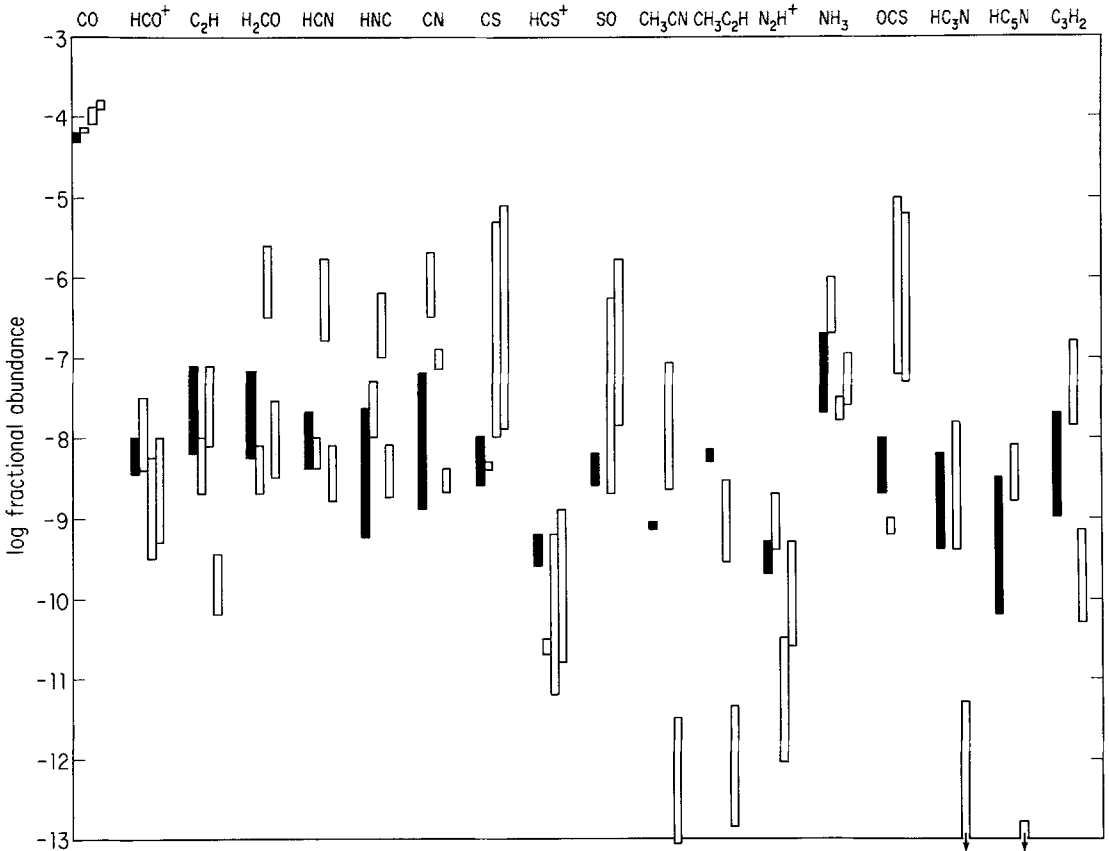


Fig. 6. Comparison of observed and predicted interstellar molecular abundances. Solid bars indicate the observations. The three open bars represent ranges, respectively, for the steady-state models of Langer and Graedel (1988), and for the early-time and steady state models of Herbst and Leung (1988).

sources TMC-1, Orion extended ridge, SgrB2, and 'spiral arm' clouds seen toward W49N (Irvine *et al.*, 1987). These are compared with the models of Langer and Graedel (1988) and of Herbst and Leung (1988). For the Langer–Graedel model, the range represents that of temperature (10–40 K) and density (5(3)–5(4) cm^{-3}), all models

being steady state (1(8) yr). For Herbst and Leung, the range is that covered by low-metal and high-metal models, and by high and low rates for polar neutral-ion reactions. Both early time (3(5) yr) and steady-state models are shown.

For the 12 species covered by both models, the steady state solutions show reasonable agreement except for C_2H , CN, and OCS. Overall, both models fit the observations equally well, although there are differences between the species. There are large differences between early time and steady state solutions in the HL model. Steady state models are clearly superior for H_2CO , HCN, HNC, N_2H^+ , while early time models are better for C_2H , CH_3CN , CH_3C_2H , HC_3N , and HC_5N . The distinction seems to be whether two or more carbon atoms are involved, and the preference for the early time model increases with increasing C number. The emphasis placed on the N-chemistry by Langer–Graedel has not resulted in any obvious improvement for these species. Although not shown in Figure 6, the low-metal model of HL is clearly preferred over the high-metal one for 10 of the species, although the opposite is true for two species. The most important differences occur for the S-compounds, although CS, OCS, SO demand the low-metal case and HCS^+ the high metals. CH_3CN also prefers high metals although all other complex species favor low metals; however, given the major overall problems of the complex organics, it is not clear that this has much significance.

An important subset of molecules is the deuterated species. While it is now recognized that high deuterium fractionation can also occur on grains (Section 3.1), these species still serve as a specific test of certain ion-molecule processes. Millar *et al.* (1988b) have performed the first detailed modelling of the deuterated species, which includes pseudo-time dependence and also both the ‘old’ DR branching ratios (in which one or two H atoms are preferentially ejected), and the ‘new’ branching ratios as advocated by Bates. Of the 10 deuterated species observed in TMC-1, the model is able to explain all but C_3H_2 , whose observed fraction is an order of magnitude larger than predicted. It is not certain that the observed abundance of the C_3H_2 species is reliably estimated as yet. Other species with two or more C atoms are explained well. The two principle conclusions are: (i) observations of the 10 deuterated species toward TMC-1 are explained equally well by the ‘old’ and ‘new’ branching ratios, while the 5 deuterated species observed toward the Orion extended ridge at $T = 70$ K are better explained by the ‘old’ branching ratios. However, both sets of ratios tend to underestimate the fractionation at 70 K (by factors of 2 to 3), so problems other than branching ratios may exist. (ii) the time dependence of the fractionation is small at $T = 10$ K but is pronounced at 70 K for DCO^+ and species derived from it. The observed DCO^+/HCO^+ ratio toward Orion indicates that chemical steady-state has not been reached in the extended ridge.

3.6.2. TMC-1: Large Abundance Gradients

It has long been recognized that complex spatial structure on small scales in dense molecular clouds can introduce serious uncertainties in the estimates of observed abundances (cf. Turner and Ziurys, 1988, for a review). The extreme case of the Ori(KL) region is well known, but only recently have high-resolution observations revealed such complexities in cold quiescent clouds. The first instance of this was the recognition by

Little *et al.* (1979) that the cyanopolyynes and NH_3 have different distributions in TMC-1. A genuine variation of the $\text{NH}_3/\text{HC}_n\text{N}$ abundance ratio as distinct from possible excitation variations along the TMC-1 ridge seems indicated, and is not inexplicable in ion-molecule chemistry, since formation of cyanopolyynes requires much of the nitrogen to be atomic, while formation of NH_3 implies an evolution of N into N_2 as well as into NH_3 (Millar and Freeman, 1984a). However, recent maps of TMC-1 by Olano *et al.* (1988) show that C_4H has yet another distribution, being displaced even further from the NH_3 peak than the cyanopolyynes (Figure 7). The existing observations

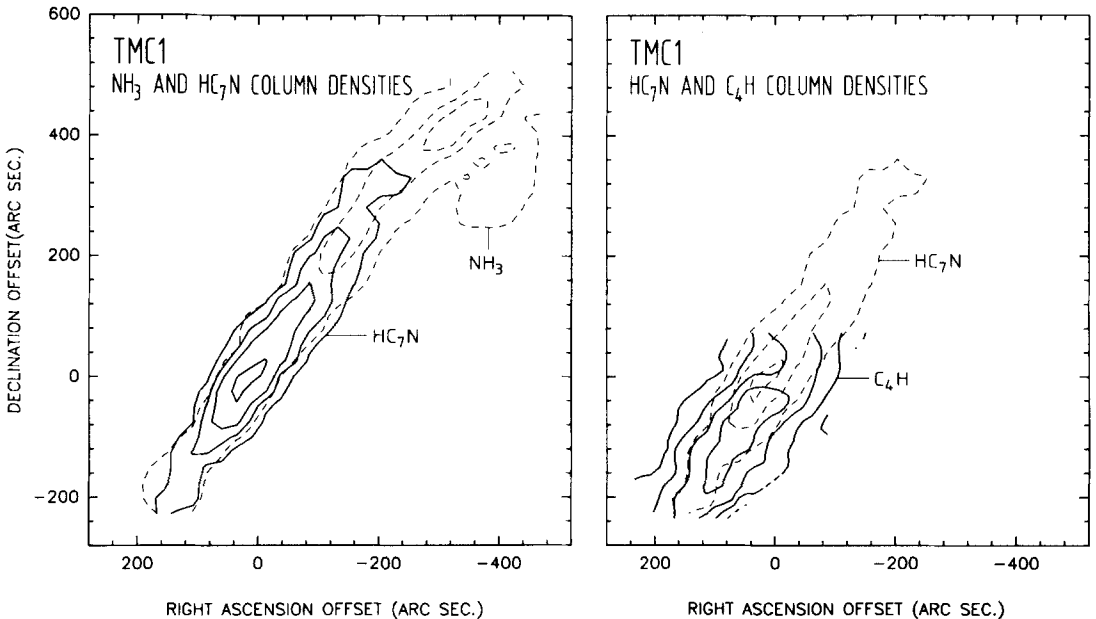


Fig. 7. The spatial distribution of C_4H , HC_7N , and NH_3 in TMC-1. Positions are offset from R.A. $04^{\text{h}}38^{\text{m}}38.0^{\text{s}}$; decl. $25^{\circ}36'00''$.

do not rule out that the $\text{HC}_7\text{N}-\text{C}_4\text{H}$ separation is due to an excitation gradient (a sharp decrease in density at the southern end of the TMC-1 ridge), but an abundance difference seems likely. This has no explanation in terms of current ion-molecule models, since both C_4H and HC_7N require an excess of C to form efficiently (Figure 4).

While the age of the Taurus complex is thought to be $\sim 1(7)$ yr, based on both dynamical arguments ($2(7)$ yr; Olano and Poppel, 1987) and on T Tauri star ages ($\sim 8(6)$ yr; Jones and Herbig, 1979), the dynamical age of the TMC-1 clump is argued to be much younger ($2(5)$ yr; Olano *et al.*, 1988). The pseudo-time-dependent ion molecule models maintain a surplus of C-rich compounds (HC_nN , C_nH) for $> 1(5)$ yr, but require an initial high abundance of C, or at least a 'non-equilibrium' abundance of C. Williams and Hartquist (1984) propose that grains accrete mantles which are predominantly C, CO, and O (but see Section 4.3) and that these grains are subjected

periodically to low-velocity shocks which volatize much of the mantle material back to the gas phase in atomic form. Presumably such a production mechanism for C would be enhanced if PAHs are abundant. Olano *et al.* (1988) suggest that a shock caused by a cloud-cloud collision might be responsible for both the structure of TMC-1 and its C-rich chemistry. A difficulty with this idea is that the relative velocities required to release C from grains are probably larger than those expected from cloud-cloud collisions (Section 4.5). The decrease in HC_nN abundances at the NH_3 peak may be explained by a higher gas density at the NH_3 position, which would accelerate the chemistry and reduce the time-scale over which large organic species can survive. A separation of C_4H and HC_7N may also have an explanation in terms of a density gradient; whether or not the existing models (e.g., Herbst and Leung, 1988) are consistent with this hypothesis, it is obvious from the results for TMC-1 that at least some of the scatter between observed and predicted abundances in Figure 6 may be attributed to observational beam smearing and correspondingly to imprecise resolution of density and temperature parameters in current models.

3.6.3. L183

In this cold, quiescent cloud Swade and Schloerb (1988) observe that NH_3 , C_3H_2 , and the cyanopolynes are concentrated in a core of $n \sim 3(4) \text{ cm}^{-3}$, while SO peaks 4 arc min to the southwest in a lower density region, and H^{13}CO^+ extends over both regions. They interpret these differences in terms of a C/O gradient produced by an O depletion in the denser core due to condensation of H_2O onto grains in regions of highest density. This idea encounters difficulties: (i) H_2O is always a minor carrier of oxygen (Herbst and Leung, 1988), and at all times there is abundant O which should not deplete any faster than any other species including SO; (ii) the depletion time onto grains is only $\sim 3(5) \text{ yr}$ for $n = 1(4) \text{ cm}^{-3}$ (Section 4.2) so steady state should never be reached unless desorption from the grains occurs continuously, which does not lead to a C/O imbalance. However, such a gradient is consistent with strictly gas phase processes, which predict that CS should dominate S-species in a C-rich region, and SO or SO_2 should dominate in an O-rich region. Detailed arguments by Swade (1987) suggest a large C/O ratio in the dense cyanopolyne peak and a low C/O ratio at the SO peak. The reason for the variation in C/O between two regions separated by only 0.23 pc is not clear.

3.6.4. ρ Oph

In the central region of the ρ Oph cloud are several massive cores, most prominent of which are B1 and B2 at 18 and 40 M_\odot . No massive star formation has yet occurred in this region. Although the two cores are only 0.25 pc apart, and have very similar physical conditions ($T \sim 15 \text{ K}$, $n \sim 3(5) \text{ cm}^{-3}$), their chemistry is strikingly different: B1 appears particularly rich in S-species, CS, SO, SO_2 , H_2CS , as well as H_2CO , HCN; B2 exhibits strong deuteration of several species, and high HCO^+ and N_2H^+ abundances. Loren and Wootten (1986) interpret B2 as lying ahead of, and B1 behind, a shock front passing through the region. The compressed gas (B1) has cooled to the original temperature. The

chemical difference is the result of shock (high- T) chemistry, which favors production of S-compounds. While morphological evidence suggests the presence of a shock in ρ Oph, there is no such evidence in L183, and the similar chemical differentiation in the latter case needs an alternate explanation.

In summary, these cases indicate the need for high-resolution observations and for detailed mapping in order to compare ion molecule models reliably with observed abundances. In particular, certain salient conclusions, such as that cyanopolyynes/hydrocarbon abundances are much smaller in L183 than in TMC-1, and that L183 exhibits a separation in NH_3 and the complex hydrocarbons similar to that in TMC-1, need modification. It is likely that models (e.g., Millar and Freeman, 1984a, b; Herbst and Leung, 1988) can be adjusted within the uncertainties of the free parameters to account for the more detailed current observations, but these models do not yet suggest whether the striking chemical differences between nearby dense cores within these clouds can result strictly from evolutionary differences, or whether there must have been a differentiation of atomic element abundances by some as yet unknown process.

3.7. CIRRUS CLOUDS

Despite the apparent similarity in physical conditions of cores in cirrus clouds and in cold quiescent galactic plane clouds (Section 2), there appear to be intriguing differences in the chemistry. Magnani *et al.* (1988) find fractional abundances of CO and H_2CO to be similar in cirrus and galactic plane clouds, but find OH to be 10 times more abundant in cirrus clouds. By contrast, Turner *et al.* (1988b) find the abundances of H_2CO , C_3H_2 , and HC_3N to be 10 times *less* in cirrus clouds than in galactic plane clouds. (The discrepancy in H_2CO determinations is explainable by a more detailed analysis used by Turner *et al.*, utilizing the 2 cm transition as well as the 6 cm transition used by Magnani *et al.*). The OH observations of Magnani *et al.* are low resolution ($18'$) and employ extinction measures over $8'$ regions to derive fractional abundances. Since the extinction is known to be ~ 10 times larger in the cores (Turner *et al.*, 1988b), the OH fractional abundance may be ~ 10 times smaller there, i.e., comparable to that in galactic plane clouds.

Systematically lower abundances are deduced in the cirrus cores for all the major chemical families (H_2CO : carbon-oxygen family; C_3H_2 : hydrocarbon family; HC_3N : nitrogen chemistry). There is no obvious explanation in terms of ion-molecule chemistry. It has been speculated that the cirrus clouds might be very young ($\leq 1(6)$ yr), in which case the cores may be formed by shocks. Shock chemistry models (Sections 5.3 and 5.4) predict a greatly *increased* fractional abundance for H_2CO , however, as well as sizable increases for C_3H_2 and HCN (HC_3N has not been analysed as yet). Alternatively, the shock chemistry may be quickly eclipsed by ion-molecule chemistry in the cirrus cores once the densities caused by the shocks become large enough. In this case, the ion-molecule chemistry would be early phase, not steady-state. All models at early times predict that species such as H_2CO , C_3H_2 , and HC_3N have fractional abundances that are much *enhanced* (by factors of 1(2) to 1(4); Herbst and Leung, 1988). Thus an

explanation for the reduced observed abundances lies neither in shock chemistry, nor in non-steady state ion-molecule chemistry. The only general explanation that applies to all chemical types of species is that the metallicity of the cirrus clouds is significantly less than for galactic plane clouds. This could occur if cirrus clouds have failed to form massive stars over their history; the masses found for the cirrus cores do seem insufficient to form such stars (Turner *et al.*, 1988b), but on the other hand the lack of metallicity mixing between cirrus and galactic plane clouds, separated by ≤ 100 pc, seems puzzling.

3.8. DIFFUSE CLOUDS

Quiescent cold dense clouds have been identified as the domain of pure ion-molecule chemistry, but diffuse clouds may offer an even better test. Although photoprocesses and shocks complicate ion-molecule processes in diffuse clouds, their physical conditions are better understood than those of cold dense clouds, because they can be studied in the optical by absorption lines of atoms and molecules, and because depletion of the elements onto grains is negligible. Thus a good understanding of their chemistry is a prerequisite for having any confidence in the chemistry occurring in dense clouds. An excellent review of diffuse cloud chemistry has been given by van Dishoeck and Black (1988). Here we merely summarize successes and limitations of ion molecule chemistry in diffuse clouds. The observed species which provide the test are H, H₂, C, C⁺, CH, CH⁺, CN, C₂, OH, CO, with upper limits for many other species.

As for dense clouds, in which variations in physical conditions along the line of sight are unknown, many models of diffuse clouds have considered only relative abundances for fixed values of the physical conditions in order to reproduce general trends in the observations (cf. Federman, 1987). At this level the ion-molecule/photodissociation models reproduce observations very well in steady state, with the well known exception of CH⁺ which evidently is formed in shocks (Section 5.4.1). Recent models have considered spatial variations of physical conditions and abundances, and have attempted to reproduce a wide variety of observed features in specific clouds (notably ζ Oph, ζ Per). The physical conditions (n , T , I_{uv}) are derived from the rotational excitation and abundance of H₂, the rotational excitation of C₂ and CO, and relative populations in the fine structure levels of C, C⁺, O. These physical conditions are imposed on the chemical reaction network, which is solved at each depth into the cloud, resulting in column densities to be compared with observations. Generally the agreement is very good, although for every species there is at least one model parameter which can be adjusted for best fit. These parameters include unknown reaction rates (e.g., C⁺ + H₂ → CH₂⁺ + $h\nu$), branching ratios (especially for the C₂/CH ratio), cosmic-ray ionization rate (which determines the OH abundance and those of other O-species), and photodissociation rates (especially for CO). Two problems remain, however. The CH⁺ abundance is not explained by steady-state ion molecule processes. When shocks are invoked to explain CH⁺ they tend to be in conflict with observations of other species. Recent estimates of large photodissociation rates for CO lead to predictions of CO

abundances that are 100 times lower than observed. An increased density or decreased I_{uv} could reduce the problem, but would be in conflict with the diagnostic species (H_2 , C_2 , etc.).

3.9. SUMMARY

Ion-molecule chemistry is the only existing theory of interstellar molecules with reasonable predictive capacity. It has had considerable qualitative success at explaining the smaller species (≤ 4 atoms), under steady state conditions, but becomes very speculative about the origins of complex species in dense clouds. Quantitative tests of the theory are difficult because of uncertain physical conditions, reaction rates, and observed abundances. These problems are minimized in diffuse clouds, for which the steady state theory has some success in explaining the simple species. Further developments of time-dependent, shock, and evolutionary models of diffuse clouds with various assumptions about the history of the clouds appear necessary to test whether the remaining problems of purely gas phase models have satisfactory explanations in the framework of ion-molecule and photodissociative processes alone.

In cold dense clouds, which often are more remote from regions of massive star formation than are diffuse clouds, there is less evidence for shocks, and less uncertainty about radiation fields, but the role of grains becomes important. Observations are much less definitive than for diffuse clouds, despite the much larger array of species observed. Thus current attempts to compare models and observations are in a primitive state, with modest detail existing only for TMC-1. Taking into account the differences between existing models, the general conclusion is that steady-state gas phase models can reproduce the observed abundances of several simple species, but they fail to produce enough complex species (C_3H_2 , C_3H , C_4H , HC_3N) unless the most optimistic assumptions are made about key reaction rates (Millar and Nejad, 1985). The models also generally produce too little NH_3 unless the reactions of N with H_3^+ and N^+ with H_2 (Section 3.1) are much faster at low temperatures than expected. Generally, O_2 and H_2O are overproduced. Finally (Section 3.5.1) the models cannot produce the large CI abundances inside dense clouds. The CI and complex hydrocarbon problems appear to be related. Differences between models and observations may well result from neglect of other astrophysical processes, which have been discussed. Differing physical or chemical conditions seem clearly to occur over small distances at the limits of current observational resolution. The crude agreement between observations and prediction for even small species involving first-row elements is likely illusory, especially as long as the carbon question remains unsettled. Formation of second-row species clearly requires energetic processes beyond the scope of low-temperature gas phase chemistry. Many aspects of complex species, exemplified by the cyanopolyynes, are not explained by ion molecule models, even when time dependence is considered. Lack of knowledge about many reaction rates may cause the problems, but perhaps equally likely is the prospect that grains are involved. Finally the recent observations of cirrus clouds reveals new problems that reaffirm the general lack of predictive ability of current astrochemical theory.

4. Grain Chemistry

A molecular species X may be removed by reaction with an ion Y^+ or by adsorption onto a grain. The latter occurs at a rate $A \times s \times v \times n$ (Section 4.2), where $A = 2(-21) \text{ cm}^{-2} (\text{cm}^{-3})^{-1}$ is the grain surface area per H atom cm^{-3} , and s is the sticking coefficient (0.1 to 1). Thus the ratio of grain adsorption rate to gas phase reaction rate is $r_{gr}/r_{gas} \sim 2.3(-8) \times s/[Y^+]$ where $[Y^+]$ is the fractional abundance of Y^+ , and a gas reaction rate coefficient of $1(-9)$ has been assumed. In diffuse clouds, $[Y^+] \sim 1(-4)$ and condensation on grains is not competitive with gas phase reactions. In dense clouds $[Y^+] \sim 1(-8)$ for an abundant ion, and the rates become comparable. Grain chemistry thus needs to be included in astrochemical models of dense interstellar clouds. Once photoionization becomes unimportant, r_{gr}/r_{gas} does not depend directly on gas density but the relative contribution of grain processes to the composition of the gas phase will be particularly significant for those species that are produced slowly in the gas phase (small $[Y^+]$).

In addition to acting as a sink for gas phase molecules, grains may be involved in several formation mechanisms: (i) surface catalytic reactions; (ii) evaporation of grain mantles; (iii) UV processing of grain mantles; (iv) grain disruption by shocks.

4.1. GRAIN COMPOSITION

Despite 50 years of research, there are no generally accepted answers to the two basic questions about interstellar grains: what is their composition? and where and how are they formed? A comprehensive summary of current thinking is given by Tielens and Allamandola (1987). As revealed by IR spectroscopy, there appear to be two basic types of grains: 'stardust' (silicates, graphite, PAHs, and amorphous carbon), which form in the outflows of late-type giant stars and planetary nebulae; and 'interstellar' components, formed in the ISM itself. The latter include 'icy' grain mantles consisting of simple molecules (H_2 , NH_3 , CO , CH_3OH) inside dense clouds, and an organic refractory component consisting of more complex molecules, in the diffuse ISM. The icy mantles seem to occur in all dense clouds while the organic refractories have so far been seen only toward the galactic center, and are thought to be formed by energetic processing (UV photolysis or cosmic-ray bombardment) of the icy grain mantles (e.g., Greenberg, 1976; d'Hendecourt *et al.*, 1985). Both icy mantles and organic refractories are presumed to reside on top of silicate or carbon/graphite cores. An approximate composition as given by Tielens and Allamandola (1987) for grains in diffuse clouds is: silicates (100% of Si; mass $9(-27) \text{ g H}^{-1}$); amorphous carbon (5–10% of C; $0.6(-27) \text{ g H}^{-1}$); PAHs (1% of C, $0.08(-27) \text{ g H}^{-1}$); organic refractories (24% of C, 6% of O, $3(-27) \text{ g H}^{-1}$); graphite (25% of C, $2(-27) \text{ g H}^{-1}$). These add up to $14.5(-27) \text{ g H}^{-1}$, while $\sim 16(-27) \text{ g H}^{-1}$ is required by models of the extinction curve. In dense clouds one must add the icy mantles (5–40% of O and C), which can double the net grain mass, but which are not observed outside dense clouds, presumably because they are easily destroyed by interstellar shocks or UV photodesorption. These estimates suggest that silicates and organic refractory material dominate, and models based on this idea are

proposed by Greenberg and Hong (1974) and Greenberg and Chlewicki (1984). However, the estimated mass of the organic refractory component is quite uncertain; if it is much less than estimated, then most of the dust would have to be in a form without detectable IR or UV absorption features, a property of large graphite particles. There are important models based on this idea (Mathis *et al.*, 1977; Draine and Lee, 1984). It is not presently possible to choose between these two classes of model, and the actual situation probably lies between these extreme cases (Tielens and Allamandola, 1987).

4.2. THE PROBLEMS OF ACCRETION AND DESORPTION

It has been realized for many years that the time scale for deposition of a grain mantle is short relative to both probable molecular cloud lifetimes, and to at least some of the timescales of gas phase chemistry. If molecules heavier than H_2 are not easily returned to the gas phase, then the question may be posed: why does a gas phase exist? (Winnewisser and Herbst, 1987). The timescale for a gas phase molecule to encounter a grain is $t_{gr} = (n_{gr} n_x \pi r_{gr}^2 \times v \times s)^{-1} \sim 3(9)/n_{H_2}$ yr, since $n_{H_2}/n_g \sim 4(11)$, $r_{gr} \sim 0.1 \mu\text{m}$, and $s \sim 1$ (as indicated by experiment). Thus $t_{gr} \sim 3(5)$ yr for a typical dense cloud with $n_x \sim 1(4) \text{ cm}^{-3}$. By contrast, dense cloud lifetimes, based on OB star formation rates, are at least 1(7) yr (Turner, 1984), and the time needed to reach chemical steady state is $\sim 1(7)$ yr. The dilemma is resolved only if there is an efficient desorption mechanism, or if there is a continuous influx of gas into molecular clouds which is converted into molecules by a process as rapid as that of grain accretion, i.e., ion-molecule reactions.

To preserve a gas phase ISM in general, desorption of some kind must occur, on either a local or 'microscopic' scale, or globally, as when a cloud is violently disrupted (by the effects of OB stars or cloud-cloud collisions). Both local and global phenomena evidently occur, since cold dark clouds have no nearby OB stars, and since there is ample evidence that OB stars, once formed within GMCs, cause massive disruption (e.g., Elmegreen and Lada, 1977).

On the microscopic scale, desorption might occur as a result of the heat of formation of surface reactions, or it might involve thermal evaporation as a result of grain heating by photoabsorption, or photochemical grain explosions. Because of its low-mass and low-binding energy, the heat of formation of H_2 from two physically adsorbed H atoms is sufficient to eject the H_2 molecule. This appears not to be the case for any other molecule (Section 4.6). Thus thermal evaporation or photochemical grain explosions seem necessary to return mantles to the gas phase in quiescent clouds. The latter process, championed by Greenberg (1984, 1987) involves storing up chemical energy in the form of adsorbed free radicals on the grain surface; these radicals are produced by UV irradiation of the grain material and do not react at ~ 10 K owing to activation energies. If the grain is then heated to a critical temperature, ~ 27 K according to experiment (Greenberg, 1984; d'Hendecourt *et al.*, 1982), the radicals may suddenly react, releasing enough energy to explode the grain. The necessary UV may not exist in dense molecular clouds (but see Section 3.4.2), and in any case might dissociate the molecules once they are released from the grain. Heating of the grains may occur via grain-grain collisions (d'Hendecourt *et al.*, 1982) or via heavy nuclei cosmic-ray

bombardment, or X-rays (Leger *et al.*, 1985). It is not known whether X-rays or cosmic rays can provide the necessary photo-processing of the mantle. Thus these agents (particularly heavy cosmic rays) are considered merely to provide a heating mechanism which can allow thermal evaporation of the mantle. Leger *et al.* find that if grain mantles are CO-rich, cosmic-ray heating of typically sized grains ($< 0.25 \mu\text{m}$) produces limited desorption to the extent that t_{gr} is effectively raised to $1(11)/n_{\text{H}_2}$ yr, still marginal in that condensation will still overwhelm desorption after $\sim 1(7)$ yr. If the mantles are mainly refractory ices (H_2O , NH_3 , H_2CO) with higher heat capacities, desorption via cosmic rays is negligible.

On the macroscopic scale, desorption may be effected by interstellar shocks, or by an enhanced UV field such as provided by a supernova flash. In addition to photochemical grain explosions, the UV photons might directly desorb a given molecule (Barlow, 1978) or they could merely heat the grain and produce thermal evaporation (Dopita, 1977; Draine and Salpeter, 1979). Boland and de Jong (1982) find that supernova flashes dominate other suitable UV sources, and estimate that for a cloud with $n = 1(3) \text{cm}^{-3}$ and $A_v = 6 \text{mag}$, $\geq 10\%$ of heavy elements should be retained in the gas phase for reasonable assumptions about the surface binding energy (0.1 eV). The situation is less favorable for denser regions, posing the question of whether there is observational evidence for increased depletion at higher density. For volatile species such as CO, Frerking *et al.* (1982) find no correlation between molecular column densities and dust extinction; Wadiak *et al.* (1985) find fractional abundances of H_2CO do not decrease in high density clumps where $n > 1(6) \text{cm}^{-3}$. (Since the cosmic rays responsible for evaporating grain mantles are identical to those which ionize the gas and initiate ion molecule chemistry, these observations suggest limits on cosmic ray induced desorption.) Conversely, there is evidence that molecules containing highly refractory elements such as P and Si are more heavily depleted in cold clouds than in warm ones (Section 3.5.3).

Since catalytic surface reactions in which the newly formed molecules are desorbed by the heat of reaction appear inoperative (Section 4.6.1), the problem of deciding what chemical signature grain chemistry imposes on the gas phase becomes the problem of assessing the chemical composition of grain mantles and how this composition may be modified by alternative desorption processes such as we have discussed. Some progress has been made in these areas in recent years. We summarize this next.

4.3. ICY GRAIN MANTLES

Inside dense molecular clouds, IR observations between 3 and $12 \mu\text{m}$ have identified several components of icy grain mantles: NH_3 (Knacke *et al.*, 1982); H_2O (e.g., Tielens *et al.*, 1984); CO and CO complexed with other molecules (Lacy *et al.*, 1984), the C \equiv N group in various molecules (Lacy *et al.*, 1984), and possibly CH_3OH (Tielens *et al.*, 1984) although there is ambiguity in the identification of saturated hydrocarbons such as CH_3OH . Approximately 20 times more NH_3 is frozen in grains than exists in the gas phase. A significant, although probably not dominant, fraction of the total CO appears to be frozen on grains. Frozen H_2O and CH_3OH (which exemplifies the presence of

several possible saturated hydrocarbons) accounts for $\sim 30\%$ of all available carbon and oxygen.

Theoretically, several models have been constructed of the molecular composition of accreting grain mantles. Dominant species are expected to be H_2O , H_2O_2 , H_2CO , CO , CO_2 , N_2 , O_2 , and NH_3 in varying ratios depending on the physical conditions in the gas phase (Tielens and Hagen, 1982; d'Hendecourt, 1984). The predicted fraction of C and O locked up in these mantles ranges from 1 to 40%, so that the accretion of these icy mantles actually doubles the total grain mass or volume. The physical basis of such models rests on the fact that at low temperatures (~ 10 K), only H and H_2 are sufficiently lightly bound to an icy surface that they can evaporate. All other species incident from the gas phase (C, N, O, S, CO, N_2 , O_2 , CH_4 , H_2O) are more tightly bound and have sticking coefficients of \sim unity. Once on the surface, species with a migration time-scale \ll the accretion time-scale can diffuse on the surface until they find a coreactant (at 10 K, these are H, H_2 , C, N, O, S). Otherwise they are trapped in their site and can only react with migrating coreactants that visit their sites (e.g., CO, N_2 , O_2 , CH_4 , NH_3 , and H_2O at 10 K). Thus at 10 K the grain mantle reaction network contains reactions of the migrating atoms H, C, N, O among themselves and with the nonmigrating atoms or radicals (Tielens and Hagen, 1982). Because of their low mass, H atoms can tunnel through activation barriers as high as 4000 K and react with closed-shell species such as CO, O_2 , H_2CO , H_2O_2 , H_2S , and O_3 , although the probability for such a reaction can be shown to be small ($\sim 5(-9)$). Thus a series of H-addition reactions may occur, such as $\text{H} + \text{CO} \rightarrow \text{HCO}$, $\text{H} + \text{HCO} \rightarrow \text{H}_2\text{CO}$, and $\text{H} + \text{H}_2\text{CO} \rightarrow \text{CH}_3\text{OH}$, although the latter has not yet been studied in the laboratory. Similar reactions involving H_2 are also possible although they have even smaller probability. If the surface is essentially covered with coreactants, even O atoms can react with a few species such as O_2 and CO which have only modest activation barriers (< 450 K). Thus O_3 and CO_2 may be formed.

In harmony with the IR observations, which show significant fractions of CO residing in icy grain mantles, models indicate that CO in the gas phase will fully condense onto pure CO-covered grains for $T < 17$ K if thermal evaporation is the only desorption mechanism (Leger, 1983). Such a depletion has recently been measured directly via $4.6 \mu\text{m}$ observations of the CO $v = 0 \rightarrow 1$ band by Hall (1984), who finds a marked decrease in $N(\text{CO})/A_v$ for $T_{\text{rot}}(\text{CO}) < 20$ K compared to clouds for which $T_{\text{rot}} > 20$ K (note the apparent conflict of this result with evidence cited in Section 4.8.1). If there are other organic species on the surface, the critical temperature will be raised, and the amount of carbon and oxygen locked up will depend on how CO and other organics are formed and destroyed. Such considerations are just one reason why use of CO as a tracer of total gas density in dense molecular clouds is hazardous. Another reason involves the fact that H_2 does *not* form on icy surfaces by the process $\text{H} + \text{H}$, because the binding energy is only ~ 350 K on such physically adsorbed surfaces, so the thermal evaporation rate of H becomes less than the accretion time-scale for H atoms. Stronger binding is needed. Surface species such as H_2CO , H_2S , N_2H_2 , N_2H_4 , and metal hydrides can act as enhanced binding sites (Tielens and Hagen, 1982). Then

H-abstraction ($\text{H} + \text{HX} \rightarrow \text{H}_2 + \text{X}$) may occur (the H atom may tunnel through the activation barrier of the reaction). However, if there are radicals on the surface, an H atom will react with them rather than tunnel through an activation barrier and form H_2 , since radical-radical reactions are activation-less. Reaction of H even with non-radicals such as O_2 and CO can also be important in this respect (Tielens and Allamandola, 1987). Thus when the gas phase atomic H abundance decreases below the abundance of heavier species such as O, CO, and O_2 , then H_2 formation on grain surfaces will stop. This occurs at a density of $\sim 3(4) \text{ cm}^{-3}$. The remaining H will now be incorporated in H_2O , NH_3 , H_2CO , etc. In cold dense cores, therefore, gas phase fractional abundances may differ markedly from those predicted by gas phase models as a result of grain chemistry, even if the grain molecules are not returned to the gas. In particular, the CO/ H_2 ratio may be very different, rendering CO a poor tracer of gas density or mass.

One other class of species, the deuterated analogues of the simple icy mantle species, are expected to have high abundances in the icy mantles (Tielens, 1983). Within the mantles, XD/XH is a reflection of D/H in the gas phase, since the grain-surface reaction networks are very similar. As total density increases, $(\text{D}/\text{H})_{\text{gas}}$ increases sharply because, although most hydrogen is in the form H_2 , much of the deuterium remains as D. This can be seen as follows. Initially, $\text{HD}/\text{H}_2 \sim 2 \text{ D}/\text{H}$ as a result of reactions on grain surfaces. However the sequence $\text{HD} + \text{H}_3^+ \rightarrow \text{H}_2\text{D}^+ + \text{H}_2$; $\text{H}_2\text{D}^+ + \text{CO} \rightarrow \text{DCO}^+ + \text{H}_2$; $\text{DCO}^+ + e \rightarrow \text{CO} + \text{D}$ restores atomic deuterium, while no analogous process restores H. Tielens (1983) estimates that roughly one of every 20 cosmic-ray ionizations of H_2 (producing H_3^+) will destroy HD, a rate much larger than that of H_2 .

To assess the contribution of icy mantles to gas phase abundances, desorption processes must be considered. If icy grain mantles are subjected to gentle warming, as by an IR source associated with a protostar, the mantles may heat to $> 90 \text{ K}$, typical of the sublimation temperature of H_2O ice. The simple molecules that make up the mantle (CO , N_2 , O_2 , H_2O , NH_3 , H_2CO , CO_2 , H_2O_2) and their deuterated counterparts may be expected to desorb intact, increasing the local gas phase abundances of these species by large factors. Note that molecules produced in this way by grain surface chemistry are typically neutral, saturated, small, and highly hydrogenated. By contrast, molecules produced by ion-molecule gas phase reactions may be large or small, but are often highly unsaturated, radicals, or ions.

If unprocessed icy grain mantles are subject to photodesorption, somewhat different products would likely be returned to the gas phase, for two reasons: (i) while photodesorption may well be efficient for small molecules, it will be inefficient for larger species, both because they may have a larger binding energy, and because there are many more channels for decay of the electronic excitation energy imparted by the UV photon other than an induced momentum perpendicular to the surface which is necessary for desorption (Nishi *et al.*, 1984); (ii) the necessary UV flux for photodesorption would also be sufficient to photoprocess the mantle, altering it fundamentally from our simple icy mantle picture (Section 4.4).

In summary, icy mantles result from a complex interplay of gas phase and grain surface reactions. Tielens and Allamandola (1987) identify three regimes. For low

densities ($n < 5(4) \text{ cm}^{-3}$), atomic H is more abundant in the gas phase than heavy species, so the atmosphere is 'reducing', in which most of the accreting gas phase species are saturated through reactions with atomic H on the grain surfaces (e.g., CO saturates to HCO, H₂CO, and possibly CH₃OH; note, however, that N₂ does not react with H, so NH₃ must start with atomic N, and will be a trace species on grains). At higher densities ($n > 5(4) \text{ cm}^{-3}$), gas phase H falls below gas phase CO, N₂, etc., so most accreting species are not hydrogenated. Now, atomic O becomes the most abundant, mobile surface radical. If gas phase O/O₂ is high (oxidizing atmosphere), then O + CO → CO₂ dominates and CO₂ becomes the major mantle constituent. If gas phase O/O₂ is low (inert atmosphere) then few surface reactions occur and the grain mantle composition will reflect that of the gas phase (i.e., CO, O₂, N₂ dominant). In both high density cases, saturated species (H₂O, H₂CO) are only trace constituents. Since the IR observations show H₂O and CH₃OH to be dominant mantle species, with CO and NH₃ in lesser amounts, then on this picture grain mantles would appear to be formed in a 'reducing' atmosphere, and thus at low densities ($\sim 1(4) \text{ cm}^{-3}$).

4.4. REFRACTORY GRAIN MANTLES

The only direct observational evidence for an organic refractory grain component comes from IR spectroscopy in the 4–8 μm band toward the galactic center. This evidence is sparse, consisting of a single unidentified absorption feature at 3.48 μm (Willner *et al.*, 1979; Allen and Wickramasingh, 1981; Butchart *et al.*, 1986). The absence of other IR features seen in this band in molecular clouds, and the belief that the IR extinction toward the galactic center arises in the general ISM rather than in molecular clouds (Soifer *et al.*, 1976; Becklin *et al.*, 1978) leads to the conclusion that the 3.48 μm feature arises in the diffuse ISM. Laboratory simulations suggest that the carrier might be CH₂ or CH₃ groups (Willner *et al.*, 1979), UV tholins (Sagan and Khare, 1979), synthesized organic residue (Greenberg, 1982), or hydrogenated amorphous carbon (Duley and Williams, 1984b).

Indirect observational evidence for an organic refractory component comes from IR spectroscopy of protostars embedded inside dense molecular clouds which suggests that mantle composition is more complex than explained by grain surface reactions alone. Lacy *et al.* (1984) observe a broad wing on the blue side of the well-known 4.61 μm feature which they identify in the laboratory with one or more species containing C ≡ N bonds. Tielens *et al.* (1984) observe complexities in the well-known 6.0 μm feature (normally attributed to OH bending in H₂O) and 6.8 μm feature (normally deformation modes in saturated hydrocarbons such as CH₃OH, H₂CO) which are not identified but which seem to fit a mixture of complex saturated (e.g., acetone) and unsaturated (e.g., C₂H₂) hydrocarbons, or a mixture of saturated hydrocarbons with and without strongly electronegative groups. Such species could occur as a result of simple grain surface reactions only if the accretion rate of C exceeds that of H and O together, an impossibility in terms of current understanding of gas phase chemistry.

Grain surface reactions alone (Sections 4.3 and 4.6) form only simple saturated hydrides. The formation of an organic refractory dust compound, which probably

includes long carbon chains (i.e., polymeric carbon), is difficult to understand in such a reducing environment as the ISM. Thus the presence of refractory organic material in grain mantles argues for the occurrence of energetic processes which change the molecular composition. UV photolysis of grain mantles to produce larger molecules was originally suggested by Greenberg and Yench (1973) and Greenberg (1976), and later demonstrated in the laboratory (Hagen *et al.*, 1979). The UV photolysis produces radicals in the bulk material which at low T can reach concentrations of $\sim 1\%$. If the grain is then warmed up to a critical temperature of ~ 27 K, the frozen radicals will diffuse and react upon encounter. If the mantles are poorly connected thermally to the substrate, they will explosively eject most of the mixture (d'Hendecourt *et al.*, 1982). The critical temperature of 27 K seems to be a general property of irradiated ices, as it is independent of the mixture. The explosions are not the result of a chain reaction, that is, the heat liberated by one reaction does not promote reaction of other stored radicals because the grain does not heat up much, and cools very rapidly. Rather, the critical temperature seems to be a result of a sudden change in the heat conductivity of an amorphous material at ~ 25 K.

Although the processes during photolysis and warmup are poorly understood, typical radicals produced experimentally are HCO, HOCO, OH, NH₂; only simple molecules are subsequently formed with reasonable efficiency. Most products are expected to be volatile and to survive only a short time in the diffuse interstellar gas phase (e.g., H₂CO, CO₂, CH₃OH). Very complex molecules will form only with low efficiency. A general conclusion seems to be that aliphatic rather than aromatic hydrocarbon mixtures are readily formed. Oxygen-rich mixtures lead to residues containing large amounts of carboxylic acids. If NH₃ is present, amino groups also form (Hagen *et al.*, 1979; d'Hendecourt *et al.*, 1985).

Given the UV absorption cross section of H₂O ice below 1600 Å, it can be shown (Tielens and Allamandola, 1987) that a typical H₂O molecule in a mantle will absorb at least one UV photon over a cloud lifetime of 3(7) yr if the extinction $A_v < 7$ mag. Other sources of UV exist for larger extinctions inside dense clouds. During the 'transition' from the diffuse cloud regime to a denser condensation within a molecular cloud, accretion and photolysis are efficient and the photolyzed grain mantle can be partly built up during this early cloud state (Greenberg, 1976). Also, photolysis will always be important at the outer parts of dense molecular clouds. Boland and de Jong (1982) suggest that cloud material circulates from the deep interior to the surface and back again, on time-scales comparable to or shorter than cloud lifetimes, in which case all grains are exposed to UV light during their lifetimes. Finally, a constant steady flux of UV arises from the cosmic-ray ionization of H₂ (Section 3.4.2). The energetic ejected electrons electronically excite other H₂ molecules, and those that decay to $v \neq 0$ states in the ground electronic state produce photons able to penetrate the clouds. For cloud extinctions > 6 mag, this 'cosmic-ray UV flux' will dominate the external UV flux. Lacy *et al.* (1984) estimate that such a flux will require a photoprocessing time-scale of $\sim 7(8)$ yr, longer than the cloud lifetime, to completely photoprocess every molecule in a grain mantle. This timescale may be conservative, as it corresponds to every H₂O

molecule absorbing 20 UV photons over the cloud lifetime. However, not every absorption leads to radical production, and estimates of the efficiency (Tielens and Allamandola, 1987) suggest that UV photolysis, while quite efficient for producing smaller species, will not be efficient for the larger ones. For instance, photolysis of H_2O leads to reactions of its photolysis products, H, O, OH with neighboring simple species such as CO, forming CO_2 , H_2CO , CH_3OH . Molecules containing CH_2 , CH_3 , NH_2 groups can also be photolysed, increasing the complexity of the resultant products. However, the efficiency (number of radicals produced per UV photon absorbed) of producing a molecule consisting of N building blocks can be estimated to be $f_{uv} = 20(0.005)^n$ where $n = \log_2 N$ (Tielens and Allamandola 1987) over the lifetime of the cloud (3(7) yr). Thus UV photolysis alone cannot account for the presence of an abundant complex organic refractory dust component in the ISM.

Photoprocessing by cosmic rays is fundamentally less efficient than by UV photons, because of a smaller absorption cross section by surface molecules. Also, one UV photon is generated for every cosmic ray ionization of H_2 , which occurs at a much faster rate than that of cosmic rays colliding with grains.

4.5. EVAPORATION PROCESSES

Molecules may be released from grain mantles in quiescent dense clouds by energetic release of stored chemical energy, discussed above, or by the action of shocks.

Grains may be heated to ≥ 25 K, necessary to release the photoprocessed stored energy, by cosmic-ray impact, grain-grain collisions, warming by nearby protostars, or by shocks. Tielens and Allamandola (1987) have estimated the amount of mantle material evaporated by one cosmic-ray event or by a grain-grain collision within a dense cloud. For either process, they assume enough energy is deposited to raise the grain temperature to 27 K. The mantle is composed mostly of H_2O ice, with a 1% concentration of radicals that start to diffuse and react at 27 K. The reaction energy liberated is calculated to raise the grain temperature to 170 K, well above the 90 K evaporation temperature of H_2O ice. The amount of material evaporated is estimated by equating the reaction heat with the heat loss through evaporation; $\sim 40\%$ of the H_2O will evaporate before T_{gr} falls below 90 K. Cosmic-ray heating seems to dominate the transient grain heating process with a time-scale of 3(4) yr for $0.1 \mu\text{m}$ sized grains. Grain-grain collisions will become dominant for $n \geq 1(6) \text{ cm}^{-3}$. Thus the ejection timescale for a molecule is $\sim 1(5)$ yr for these processes. Similar conclusions are reached by Leger *et al.* (1985). X-ray heating is less important than *cr* heating. CR fluxes would need to be larger in very dense regions ($n \geq 1(6) \text{ cm}^{-3}$) than considered by Leger *et al.* to maintain desorption. Note that the cosmic rays involved in evaporating grains are the same as those that ionize the gas.

Evaporation rates due to nearby protostars fall into two categories. If the incident radiant energy heats the grains to > 27 K but less than 90 K, the evaporation efficiency is the same as for cosmic-ray heating. In many sources (e.g., Ori(KL), Section 6.5) the grain temperature is maintained well above 90 K by the nearby protostar, in which case all of the icy mantle evaporates.

A grain subjected to a strong shock will likely lose all of its icy grain mantle, at least some of its refractory mantle (if any), and possibly suffer vaporization of its refractory core (Seab, 1987). Grains are destroyed in shocks by 3 principle mechanisms: thermal sputtering (which occurs only in the high temperature of fast, non-radiative adiabatic shocks), and by nonthermal sputtering and grain-grain collisions (which dominate in slower, radiative shocks). In radiative shocks, additionally, icy grain mantles may be photodesorbed by the UV flux which precedes the shock, although estimates of this effect for a shock of $v_s = 40 \text{ km s}^{-1}$ range from total (Barlow, 1978) to negligible (Draine and Salpeter, 1979). Sputtering is the ejection of atoms from a solid by the impact of high-energy ions. Thermal sputtering occurs as a result of the thermal motions of the gas particles. Non-thermal sputtering is due to the grain motion causing (non-isotropic) impacts with the gas. Thermal sputtering of refractory grains requires $T > \text{few} \times 1(5) \text{ K}$ and, hence, will occur in the hot coronal phase of the ISM. Here the density is low and the sputtering rate is only $1(-6) \text{ \AA yr}^{-1}$ (Draine and Salpeter, 1979), so that an $0.1 \text{ }\mu\text{m}$ grain will survive for $1(9) \text{ yr}$. Thermal sputtering behind fast shocks ($v_s \geq 200 \text{ km s}^{-1}$) in warm clouds can be important since both n and T are high. Of course such thermal sputtering easily destroys icy grain mantles completely in both the diffuse ISM and in shocked gas near protostellar outflows in dense clouds. For both silicate and graphite materials, models (Draine and Salpeter, 1979) suggest a destruction rate of $\sim 1(-3) n \text{ \AA yr}^{-1} \text{ cm}^{-3}$ for $T \sim 5(5) \text{ K}$, as may characterize a fast ($v_s \sim 130 \text{ km/s}^{-1}$) shock. Since the density n may be $1(6) \text{ cm}^{-3}$ in such a shock, an $0.1 \text{ }\mu\text{m}$ grain will survive only $\sim 1 \text{ yr}$, hence will be completely destroyed before the shock significantly cools. Most shocks in star forming regions are slower, and may have magnetic precursors. In slower, radiative shocks, the charged grains are betatron-accelerated in the magnetic field component parallel to the shock front as they enter the shock. This acceleration vanishes deeper into the shock where the ionized hydrogen recombines ($T \leq 1(4) \text{ K}$), and drag forces then halt the grains relative to the gas. Large grains are little accelerated and, hence, little nonthermally sputtered, while smaller ($\leq 0.25 \text{ }\mu\text{m}$) grains are effectively accelerated and destroyed in radiative shocks (Seab, 1987). Again, volatile mantles will be completely destroyed in all cases. In typical models (Seab and Shull, 1983), $\sim 25\%$ of silicate and $\sim 2-3\%$ of graphite grain material is sputtered away nonthermally during passage through typical radiative shocks (graphite has higher binding energy). Laboratory data suggest that silicate sputtering rates depend little on the particular compound involved. By contrast to nonthermal sputtering, grain-grain collision processes are more complicated and less understood. Grains gyrating in the magnetic field with random phase velocities can meet head-on at relative speeds up to 200 km s^{-1} yielding an energy of $\sim 1000 \text{ eV}$ per atom. This compares with a binding energy of 5 to 10 eV for refractory grains. If only 1% of the collision energy goes into breaking chemical bonds, then both grains would be vaporized. Laboratory data on grain-grain collisions at these energies is completely lacking, so models are highly uncertain, especially with respect to shattering vs nonthermal sputtering, and the degree of partial sputtering as a function of grain size. Nevertheless, models (Seab and Shull, 1983) suggest that grain-grain collisions are more destructive in radiative shocks

than is nonthermal sputtering, for grains larger than 0.1 μm . In total, 37% of the silicate and 4% of the graphite grain material is destroyed in these models, which neglect shattering.

4.6. CATALYTIC SURFACE REACTIONS

Many types of reactions, including radical-radical, radical-molecule, and possibly molecule-molecule can occur on the surfaces of grains at low temperatures. The question is whether the reaction products can be returned to the gas phase, and what may be their nature. We have discussed photoprocesses in some detail. Here we briefly summarize the older viewpoints of grain surface contributions which do not rely on photoprocesses, and, hence, can be termed catalytic in the usual sense.

The simplest idea is that the products may be directly desorbed if enough of the formation energy flows into center-of-mass translational energy perpendicular to the surface (Watson and Salpeter, 1972a, b; Hunter and Watson, 1978). This process has always been recognized as marginal at best for all heavy species and perhaps even for H_2 , since most of the formation energy will be transferred to neighboring molecules through multipolar-multipolar interactions, will flow into local rotational modes, or will be radiated away (Tielens and Hagen, 1982). More complicated from the point of view of predicting products returned to the gas phase is the idea of Allen and Robinson (1975, 1977) that a fraction of the formation energy will be converted into heat. The resulting temperature rise depends on the grain size, but if large enough will evaporate all weakly adsorbed species. The required grain size depends on the amount of energy transferred to the delocalized lattice phonons of the grain, which is unknown. If all the energy is converted into heat, then the limiting grain size is $\sim 50 \text{ \AA}$.

In terms of these simpler (non-photo) processes, can we hope for more definitive predictions about the products, for certain limiting grain types or physical conditions which may be tied to experiment? It does appear possible to identify two limiting extremes of physical conditions, as follows.

4.6.1. *Cold Clouds*

In clouds with $T_{gr} \leq 20 \text{ K}$ the binding energy to grains of saturated molecules, and probably also of atoms and radicals will be weak, corresponding to physical adsorption. The reason is that even if grains do not initially contain ice mantles or low-binding monolayers of H_2 , they will soon accumulate them. On initially more strongly binding surfaces, evaporation is certainly not possible, so condensation of H_2 or of ices of H_2O , NH_3 , ... will occur, on top of which the binding is weak. These statements are true whether grains are silicates or graphite. The grain temperatures above which such icy mantles will evaporate are $\sim 17 \text{ K}$ for pure CO (Leger, 1983) and 90 K for pure H_2O . Regarding photodesorption, the ambient UV field will fail to prevent buildup of icy mantles for $A_v > 3 \text{ mag}$ (Tielens and Hagen, 1982). In cold, opaque clouds, we conclude that under static conditions grains act only as repositories of gas phase molecules, with the exception of H_2 , although formation of even H_2 on grains ceases at $n \geq 3(4) \text{ cm}^{-3}$ (Section 4.3). The small UV flux from cosmic-ray ionization of H_2 is inconsequential.

Shocks do not penetrate significantly into dark clouds. Grain-grain collisions at low speeds ($\sim 10 \text{ km s}^{-1}$) deposit $\sim 2.5 \text{ eV}$ per atom, and heat a grain only slightly (unless there is stored photoprocessed energy). The cooling time via evaporative heat loss is fast if any evaporation (e.g., of CO) can occur. Thus grain-grain collisions are important only at high densities ($\geq 1(6) \text{ cm}^{-3}$) and only if photoprocessing has occurred (Tielens and Allamandola, 1987). Similar statements are true for cosmic-ray heating.

Thus grain accretion in dark clouds is easily fast enough to explain the observed depletion of refractory elements. The question is how to explain the observed presence of any heavy elements at all in the gas phase (Greenberg, 1984). The controlling time-scale for accretion becomes the mixing time for the accreted grains to re-enter the diffuse phases of the ISM. This time is not well known, but is generally taken to be approximately the galactic rotation time, $\sim 1(8) \text{ yr}$. The overall grain destruction time is otherwise $\sim 5(8) \text{ yr}$ in dark clouds (Seab, 1987).

4.6.2. Warm Clouds

Near protostars in warm GMC cores, IR observations indicate T_{gr} is often high enough to evaporate ice mantles or H_2 layers, so that grain surfaces will be chemically active. A necessary condition for a catalytic surface reaction is that an accreted atom must find a reaction partner on the surface, or another reaction partner must arrive, before it evaporates. Since interstellar accretion times are slow, relatively strong binding such as occurs between radicals and chemically active surfaces is needed in the interstellar context to insure this condition, although raising problems for desorption. Three types of refractory grain material which provide such binding sites have been considered.

(i) *Silicate surfaces.* At high temperatures ($\geq 1000 \text{ K}$) such surfaces are actually hydrophobic (bind H_2O only weakly) but at warm interstellar cloud temperatures they are expected to bind H_2O and other polar species relatively strongly by H-bonding to silanol (Si-OH) groups. Reactions among surface species are strongly inhibited by the strong binding, at warm interstellar cloud temperatures. Experiments (Anders *et al.*, 1974) show that a large variety of organic molecules can be catalysed on silicate surfaces, at $T \sim 500 \text{ K}$. These Fisher-Tropsch type reactions are inoperative at the lower temperatures of warm interstellar cloud cores, but may well be productive in the immediate vicinity of protostellar objects. These reactions predict a fall-off in abundance with increasing number of C atoms that appears much steeper than observed in interstellar species. This, and the failure to detect many other species predicted to be abundant, suggests at least that the 'protostellar nebula' cannot have ejected enough material into the surrounding molecular cloud to alter its molecular composition significantly.

(ii) *Graphite, PAHs, amorphous carbon grains.* These are injected into the ISM from evolved stars, and will already have the edges of the aromatic ring system largely saturated by aromatic H. There is some uncertainty about the binding energy of H on the basal plane of graphite, but it is at least 800 K and possibly higher. Experiments at 78 K using graphite surfaces (Bar-Nun, 1975) show that CO, CO_2 , and hydrocarbons are catalysed from reaction of H, N, O, and S. These reactions abstract C atoms from

the lattice so that warm graphite grains would be eroded, on a time-scale $\sim 3(5)$ yr, much shorter than cloud lifetimes. Such a process does not constitute catalysis in the normal sense, but might be relevant near protostars for short times, without affecting the overall warm cloud chemical composition noticeably.

(iii) *Metallic oxide grains.* Alkaline-earth oxides are well-known catalysts whose reactivity is associated with defect surface sites in the crystalline structure consisting of trapped holes, electrons, and anion or cation vacancies, particularly OH^- sites. Based on experiments at 77 K, Duley *et al.* (1978) have modelled the active sites on MgO/FeO/SiO/CaO grains. $\text{M}^+ + \text{O}^-$ pairs on these surfaces have broad resonances at 2175 Å, which may explain the well-known 2200 Å bump in the interstellar extinction curve. Reactions of ions X^+ with the OH^- sites produce species XOH . The resonance absorbs the energy of XOH if it lies near 2200 Å, preventing its escape. If such energy transfer is not effective, XOH or some fragment of it will escape. Neutral species react with such sites with much less energy, and atomic rearrangement is unlikely. For neutrals, OH^- sites have binding intermediate between physical and chemical bonding. An important property of metal oxide surfaces is that the chemistry on them is expected to be much more specific than on other surface types, leading possibly to several well defined products rather than the wide range generally assumed for surface catalysis. In particular, Duley *et al.* find that reactions involving H atoms lead, in addition to H_2 , to HCO , H_2O or OH . C^+ reactions will produce H_2CO , N atoms will result in NH , NH_2 , NH_3 , NO ; C atoms yield CH and possibly CH_4 ; CO reactions produce HCO . H_2 does not react with any of the sites on oxide grains. The specific nature of these OH^- sites is also what leads to the highly selective depletion of gas phase heavy elements (Fe, Mg, Ca, Al, etc.) in accordance with the observations (Duley and Millar, 1978). Another important aspect is that the defect reaction sites must be maintained, presumably by UV or cosmic rays, since they are being continuously lost by chemical reactions with ambient species if the products do not desorb. The same UV may be required to desorb at least some of the species. In dense clouds, even if warm, prospects for catalysis on oxide grains appear dim. H_2 formation ceases at lower densities than for other surfaces because of the low abundance of gas phase H, needed not only to form H_2 but to keep certain types of grain sites from being poisoned. Only heavy-atom species can then be formed, and their desorption is highly problematic. Poisoning of all active sites may then occur, halting the catalytic process.

In summary, except for H_2 , catalytic processes in static, cold dark clouds appear unable to contribute to gas phase chemistry and serve only to deplete the gas phase irrespective of the basic grain constituents. In warm cores of star-forming clouds, catalysis appears likely on silicate and graphite surfaces, but only at high temperatures so that insignificant contributions are made to the overall cloud. Metal oxide grain catalysis appears unlikely in any except diffuse clouds.

4.7. PAHs

There is growing evidence for a new and important component of the ISM, namely clusters of atoms of size intermediate between the relatively small molecules ($N \leq 13$

atoms) currently observed, and the conventional small grains ($N \sim 1(5)$ atoms). Such particles have been speculated for a long time (Platt, 1956) as possible carriers of the diffuse interstellar bands. The idea has recently reemerged from two separate directions. First, a large near-IR continuum excess has been observed in 3 reflection nebulae (Sellgren *et al.*, 1983) which corresponds to a color temperature of 1000 K. Excess emission at 12 μm was later revealed as a common feature of the cirrus clouds observed by IRAS (e.g., Beichman *et al.*, 1984), again implying a temperature of ≥ 1000 K for the emitter. Such temperatures are completely excluded for conventional grains under equilibrium with UV absorption for the extended sources. Sellgren (1984) has proposed that the emission arises from small clusters of ≤ 100 atoms during temperature spikes following absorption of a UV photon (so-called stochastic heating of 'small grains').

The second proposal involved attempts to identify the carriers of several IR spectral emission features, at 3.28, 6.1, 7.7, 8.6, and 11.3 μm , which have been known since 1973 in a wide variety of interstellar objects (Allamandola, 1984). Many authors (e.g., Leger and Puget, 1984) have proposed PAHs as the carriers of these bands, based both upon their great stability against photodissociation, and the resemblance of laboratory IR fluorescence spectra of such species with the astrophysical spectra. They may also be carriers of the visible diffuse interstellar bands (e.g., Leger and d'Hendecourt, 1985).

PAHs are mainly hydrocarbons with 20 to 100 C atoms. They are extremely stable because of the large binding energy of aromatic C atoms in their planar hexagonal lattices. If PAHs are actually responsible for the excess IR continuum and the IR emission features, they contain a few percent of interstellar carbon, and probably have a total surface area comparable to that of interstellar grains. Thus they can both act as small grains in promoting reactions on their surfaces, or they themselves may be accreted onto conventional grains. They are probably formed mostly in the hot, dense envelopes of evolved stars, are ejected into the ISM and are able to survive photodissociation for long timescales if they contain ≥ 20 C atoms. On the other hand, if they contain ≥ 50 atoms, they could not be heated to ~ 1000 K by a single UV photon. They might also form by the cleavage of carbon grains during grain-grain collisions in moderate shocks. Generation of PAHs appears very naturally in the cleavage of graphite, requiring only relatively small amounts of energy. Less likely is their synthesis from small carbon molecules, because the deduced fractional abundance of PAHs, 1.5(-7), implies 30 times more carbon than is contained in all carbon molecules observed in TMC-1, the richest known carbon-molecule region. The destruction of PAHs is mainly by sputtering in strong shocks and in hot, diffuse interstellar gas on timescales of a few 1(8) yr, comparable to destruction timescales for grains. A thorough review of the physics and chemistry of interstellar PAHs is given by Omont (1986).

Chemically, PAHs have a potentially strong effect on both grain-surface and gas phase chemistry. For ion-molecule chemistry their most important property is their negative charge, which supplants electrons as the principle neutralization agent for molecular ions (Section 3.4.3). Since ordinary grains also acquire a negative charge in molecular clouds, the fact that $\sim \frac{1}{3}$ of PAHs are negatively charged at any time only slows the rate of accretion of PAHs onto grains by a factor of 3. In dense clouds Omont

(1986) estimates a coagulation time for PAHs onto grains of $\sim 3(10)/n$ yr, so the process is significant only in dense cores, and even there does not exceed accretion times for smaller species. PAHs bind by physical adsorption onto grains in dense regions.

As catalytic surfaces, PAHs exhibit several much more specific properties than ordinary grains, even those of graphite. Although the total surface area of PAHs is comparable to that of grains, most of it, namely the surfaces of the C-lattices, is less suited to surface reactions. This is because physical adsorption of at least closed shell species is negligible on the lattice surface owing to the low density of PAH energy levels for the ≤ 0.1 eV energies of physical adsorption. Thus the initial kinetic energy cannot be easily dissipated at the surface. In this property, PAHs differ from graphite which allows dissipation of ~ 0.1 eV energies via soft phonons propagating perpendicular to the basal planes. Thus closed-shell species will desorb very quickly, and in addition, activation energies prevent their reaction on the surface. The situation is much less clear for neutral atoms and possibly radicals. H appears to adsorb on graphite lattices with ~ 1 eV of energy (≥ 2 eV on PAH^+); O, N, and C probably have greater binding energies. Since the density of PAH energy states is much higher at 1 eV, the incident atom is much more likely to transfer its kinetic energy and stick. Under such chemisorption, it can diffuse over the surface before it evaporates, at least during a heating event. Thus formation of H_2 , and other hydrides (OH, CH, NH, ...) may be possible by surface reactions on the C-lattice. As is the case for grains, it is unclear whether such hydrides (H_2 excepted) will be desorbed by stochastic heating, but ejection is more likely for PAHs because of the higher temperatures reached. Certainly desorption will occur for saturated hydrides (H_2O , NH_3 , CH_4).

The situation regarding binding is clearer for the active sites at the periphery of PAHs caused by their interaction with UV and with positive ions. The most active sites are C atoms which have just lost their H atoms via impulsive heating or ion recombination. This creates a radical PAH, and the percentage of these can be quite high. On these, incident atoms will likely enter a bound complex without activation energy (closed-shell incident species have activation energy). H will be most frequent, but other atoms or ions can also attach to the C-skeleton with large binding energies and await reaction with H atoms diffusing over the surface, or other incident atoms arriving at the heavy atom site. There may be activation energy against such reactions if the PAH is neutral, but not for PAH^- for which the reaction becomes ionic. The products of these reactions are presently unclear. O will be the most frequently bound heavy atom, and could go on to form ketones, phenols, epoxys, or CO but the relevant activation energies are uncertain, as are the products that would desorb during a heating event. Similar uncertainties exist for incident N or C atoms. Reaction of ions with PAHs involves enough energy to overcome the activation barrier of addition or substitution reactions. The reaction rate is uncertain ($> 1\%$ of all collisions is likely) but H^+ will chemisputter PAHs, forming H_2 or CH_4 ; C^+ appears able to produce condensation reactions with products including small hydrocarbons, especially from PAH^- . C^+ ions may also produce carbon side-chains followed by growth of the hexagonal carbon lattice itself.

In summary, although the total surface area of PAHs roughly equals that of grains,

the effect of PAHs on the gas phase composition is probably smaller. Physisorption is probably negligible. Chemisorption of atoms on the graphite carbon lattice is possible, and will be important if it occurs. The reactivity of peripheral radical sites is high. Products are unknown, but it is likely that small, saturated, neutral, and highly hydrogenated species are favored, just as for surface reactions on grains.

4.8. OBSERVATIONS AND GRAIN CHEMISTRY

One may conclude from this section that i) all aspects of the chemistry of interstellar grains are highly uncertain compared with those of gas phase processes; and ii) grains are expected to produce few if any types of molecules that cannot also be produced by gas phase reactions. Thus it is difficult to establish observationally that grains are an *important* source of astrochemistry, and the task is rather to determine whether they have *any* discernable effect other than as (passive) sinks of the gas phase.

4.8.1. *The Dependence of Abundances on Density*

Despite considerable uncertainties in the observational determination of molecular abundances (cf. Turner and Ziurys, 1988), there is an apparent uniformity of abundances for many species over a rather wide range of density and temperature for quiescent clouds (Irvine *et al.*, 1987). If molecules adsorb efficiently onto grains at low temperatures, a general inverse dependence of gas phase abundance on density might be expected. In detailed studies of dark clouds, Frerking *et al.* (1982) find no evidence for CO depletion for extinctions up to $A_v \sim 20$ mag. Similarly, Guelin (1987) finds that the fractional abundance of CO is independent of depth into the TMC-1 cold cloud, at least up to $A_v = 7$ mag, the limit of star counting procedures. Schloerb *et al.* (1987) find that the ratio of $C^{18}O$ column density to dust column density in the energetic molecular clouds in Orion, W49N, and W51 is the same as that found by Frerking *et al.* (1982) for two quiescent dark clouds. Thus the CO fractional abundance does not appear to decrease even in the high-density cores of star forming regions, and remains quite constant between the cold, lower density dark clouds and the much higher density star forming cores. Similarly the H_2CO fractional abundance does not seem to decrease appreciably with increasing density in dark clouds and in star-forming clouds (Wilson, 1985). Further, Wootten *et al.* (1984) find a uniform $H^{13}CO^+ / ^{13}CO$ abundance ratio among a large number of clouds including Ori(KL) and L183 at two extremes. Finally, Huggins *et al.* (1984) find a fairly constant $C_2H / ^{13}CO$ ratio among GMCs.

Because CO may not freeze out above ~ 20 K (Section 4.3), the CO observations may not directly test the adsorption facility of grains. For the other species, with higher critical temperatures, the rate of formation and destruction by gas phase should not exceed the rate of adsorption on grains if the species is to serve as a test of grain depletion. H_2CO is a good test because its formation ($CH_3 + O$) and destruction (C^+) are both dependent mainly on the ion abundances (C^+ , He^+ , H_3^+) which scale similarly with density, so the equilibrium abundance of H_2CO under gas phase processes is not an important function of density. For H_2CO , the ratio of rates $r_{gr}/r_{gas} \sim 1(-8)/[C^+] \sim 1$ (Section 4), so a noticeable decrease of H_2CO abundance

with increasing (grain) density should occur. The available observational data are only marginally able to refute this prediction. An additional complication is possible in tests of this sort: since formation of H_2 on grains stops for $n \geq 3(4) \text{ cm}^{-3}$ (Section 4.3), fractional abundances of other species formed in gas phase should be expected to *increase* with increasing n , *unless* the existing gas phase H_2 does not adsorb on grains as efficiently as the heavier species. In fact, the time-scale for evaporation of an H_2 molecule accreted on an icy grain (dense clouds) is only 1 yr, even for $T_{gr} = 10 \text{ K}$; in addition, H_2 molecules do not react with other surface species. Thus the failure to observe a decrease in H_2CO abundance with increasing density serves to substantiate the argument that efficient desorption mechanisms must exist (on time-scales shorter than the formation time-scale of the dense regions), assuming that accretion is as efficient as believed.

4.8.2. Signatures of Grain Chemistry

Diffuse clouds. The debate over the importance of grain chemistry in diffuse clouds has been a long one. Hydrogen is largely atomic, and impinges on grains at about 1000 times the rate of C, N, O atoms. Under conditions near physical adsorption, where surface mobilities are largely unrestrained, hydrides should be formed predominantly over other species on grain surfaces. In particular, NH and OH should form about equally per atom (Watson, 1978b), so that if the optically observed OH in diffuse clouds is produced on grains, then NH should be present in moderate abundances. A search for NH (Crutcher and Watson, 1976) gives $\text{NH/OH} \leq 0.01$. This result does not auger well for surface chemistry dominating at the diatomic level, although the fact that $\text{N/O} \sim 0.14$ as well as other uncertainties (unrestricted mobilities?) do not allow ruling out grain reactions at this level. In a more detailed study, Mann and Williams (1984, 1985) compare observations of CH, OH, NH, CO, CN, H_2O toward several diffuse clouds with models with and without grain chemistry, and conclude that the uncertainties in both observations and models are too large to make a distinction.

Molecules containing metals offer another test, principally because they are difficult to form by ion-molecule processes (Oppenheimer and Dalgarno, 1974; Smith *et al.*, 1983). The case of Na is representative (Tielens and Allamandola, 1987). Unlike O, N, C, Na may not form simple hydrides, because hydrogen abstraction reactions can be important for Na on surfaces: $\text{NaH} + \text{H} \rightarrow \text{Na} + \text{H}_2$ (the activation energy associated with bond breakage is easily overcome on a surface). H addition and abstraction reactions continue to form H_2 with Na acting as a chemical bonding site, until NaH eventually reacts with another migrating species, most likely O because it is the next most abundant mobile radical. Thus NaOH forms, and further reactions with Na are inhibited because $\text{NaOH} + \text{H}$ does not form $\text{NaO} + \text{H}_2$ owing to a large activation energy. In diffuse clouds, the expected abundances of NaH and NaOH are much too low to be detectable via microwave rotational transitions, and that of NaH is below even optical observational limits.

Dense clouds. Because of the low grain temperatures in dense clouds, the reaction $\text{NaH} + \text{H} \rightarrow \text{Na} + \text{H}_2$ might be inefficient owing to its activation energy, so NaH might

form on grains rather than NaOH. Also, NaH will not be photodissociated in the gas phase. If every Na or Na⁺ atom encountering a grain returns an NaH molecule to the gas phase, which in turn is destroyed by C⁺, Mg⁺, then the fractional abundance of NaH should be $\sim 1(-9)$, while the predicted abundance via ion molecule reactions initiated by Na⁺ + H₂ → NaH₂⁺ + hν is $\leq 1(-10)$. Plambeck and Erickson (1982) have observed upper limits of $\leq 1(-11)$ in Ori(KL) and ρ Oph. NaOH has also not been observed. Consistency with the grain model is possible only if NaH and NaOH are not formed, or are not returned to the gas phase. A recent analysis of the chemistry of sodium in dense clouds (Turner, 1987b) concludes that it does not occur significantly in the gas phase as Na I, Na II, or in molecules, but that it resides on grains, from which it is not returned to the gas phase in any form.

Grain chemistries of all types are predicted to form molecules which are typically neutral, saturated, small, and highly hydrogenated. By contrast ion molecule gas phase processes form radicals and ions as well as neutrals, favor unsaturated species, and seem able to produce large molecules. Can we identify a grain chemistry from these differences?

The fractional abundances of H₂O and alcohols (presumably CH₃OH) as observed in the IR in grain mantles range from 4(-6) to 2(-4), much larger than their predicted gas phase abundances (Tielens and Allamandola, 1987). One may deduce little from this about desorption efficiencies, because (i) H₂O (HDO) and CH₃OH are largely unobserved in quiescent regions (CH₃OH is seen in TMC-1, with an abundance that is uncertain but probably consistent with gas phase models); (ii) the net material contained in icy mantles is uncertain; if 5–40% of O and C are in mantles (Section 4.1) then the enhancement in gas phase H₂O and CH₃OH caused by the release of all mantle material would lie well within the uncertainties of determining their observed abundances. In energetic regions such as Ori(KL) where there is good evidence for the evaporation of icy grain mantles (Section 6.5), the observed enhancement of abundances of H₂O and CH₃OH in the gas phase in fact suggests that much more than 5–40% of O and C must have been locked up in grains. Among the other small, saturated, highly hydrogenated species predicted for grain chemistry, many (NH, HOCO, HNO, H₂O₂) are not seen, and the rest are predicted sufficiently well by ion-molecule models that grain processes are neither indicated nor countered by the observations.

The observed properties of complex molecules (cyanopolynes) are not in accord with ion-molecule models, and it was speculated in Section 3.5.2 that grain reactions might be involved. UV photolysis is the only known mechanism for producing such species on grains, and appears much less likely to form species like HC₃N as efficiently as gas phase models (Section 4.4).

Indirectly, grain processes might help explain the C-rich complex molecule problem, by effectively altering the gas phase C/O ratio via selective desorption. Blake *et al.* (1987) speculate that, among the fully hydrogenated products CH₄, NH₃, H₂O which might contain most of the C, N, O on grain surfaces, CH₄ will most easily evaporate from cold grain surfaces due to its nonpolar nature. H₂O would evaporate least easily. CH₄ would then be free to form complex species (Section 3.2) while much of the destructive O would

be bound on grains. The problems with this hypothesis are: (i) CH_4 is not expected to be an important C-compound on icy grain surfaces (Section 4.3); and (ii) the binding energies of CH_4 and H_2O on H_2O -ice surfaces are 2600 K and 4000 K, respectively (Tielens and Allamandola, 1987), so that neither would evaporate during a cloud lifetime except under the influence of energetic desorption processes, which would be unlikely to discriminate between them.

Both ion-molecule and grain surface chemistry can lead to large deuteration effects, in both cases essentially as a result of a large D/H ratio in the gas phase, resulting from the more efficient conversion of HD to D than of H_2 to H by cosmic rays. The fractionation ratio XD/XH for some species is predicted to behave somewhat differently as a function of density for grain models than for ion-molecule models, but there are insufficient observations over suitable density ranges to serve as a test. Typical values of XD/XH do not differ enough between the models to permit a distinction. One species, however, may be revealing. Tielens and Allamandola (1987) predict that for grain chemistry $\text{ND}_3/\text{NHD}_2 = \text{NHD}_2/\text{NH}_2\text{D} = \text{NH}_2\text{D}/\text{NH}_3 = n(\text{D})/n(\text{H})$. Ion-molecule models of deuteration such as that of Millar *et al.* (1988b) will have to be extended to see whether they make similar predictions. In any case, the deuterated species will require an evaporating agent such as IRc2 in Ori(KL) before they can be observed in the gas phase. Their concentrations will reflect the fractionation process at an earlier time when the gas and grains were very cold.

A final test of grain processes involves the ortho/para abundance ratio of species which have such forms (H_2 , H_2O , NH_3 , CH_4 , H_2CO , H_2CCO , etc.). Either radiative or gas phase collisional transitions between ortho (parallel nuclear spins) and para (antiparallel spins) are highly forbidden because a nuclear spin flip must occur. Ortho states lie higher in energy than para states. When such species are formed on grains, the ortho/para ratio should equal the high- T limit (i.e., the ratio of statistical weights) because of the large reaction heat available upon formation and the considerable rearrangement of the H nuclei during reactions. According to Tielens and Allamandola (1987), subsequent ortho-para transformation on the grain will occur on a time-scale of a day because of the interaction of the nuclear spins of neighboring molecules. Since the residence time of molecules formed on surfaces is expected to be $\sim 1(5)$ yr, their ortho-para ratio will reflect the grain temperature, and will not change during the rapid ejection process to the gas phase. The ratio may then be affected by gas phase reactions, principally by reaction with H_3^+ , but only on a timescale $3(9)/n$ yr, or about the time-scale for accretion onto grains. However gas phase processes can produce H_2CO ortho/para ratios of ~ 3 to 5 at 10 K and ~ 3 at ≥ 70 K (Kahane *et al.*, 1984). Thus observations of the ratio may indicate whether grains are involved. Kahane *et al.* find a ratio of 3 in Orion and ~ 1 to 2 in TMC-1 and L183. The 15 K energy difference between ortho and para levels of H_2CO is equivalent to a ratio of 1.5 at $T \sim 10$ –15 K. Thus the observed ratios suggest that H_2CO may have equilibrated with the expected grain temperature (10–15 K) in the dark clouds, although observational difficulties involving self-absorption of the H_2CO emission lines, and beam dilution, render this conclusion uncertain. In the hotter (70 K) Orion cloud, both gas and grain processes

predict a ratio of 3 : 1 as observed. Observed ortho-para ratios of 1.5 to 2 for H_2CCO in SgrB2 (Turner, unpublished data) also imply grain equilibration for H_2CCO since the ortho-para energy difference is similar to that of H_2CO , but the beam dilution is probably severe for the H_2CCO observations.

The limited observational evidence relevant to the role of grains in astrochemistry suggests that they act only as passive sinks for gas phase molecules. Desorption appears unlikely except under the action of energetic external mechanisms. Efficient desorption processes appear necessary, with recurrence on short timescales ($\sim 1(5)$ yr), yet observed gas phase abundances provide no clear evidence of this except in a few star forming regions where gentle evaporation is apparently occurring, with products that seem to be as predicted by grain models.

4.8.3. Refractory Compounds

Since grains are composed chiefly of refractory compounds, we may use the observations of such species in the gas phase as a potential diagnostic of grain composition and destruction processes. The only refractories observed are SiO and SiS. Observations of MgO place limits of $\text{MgO}/\text{SiO} \leq 1(-3) * \text{Mg}/\text{Si}$ (Turner and Steimle, 1985). In this context, the elements Na, P, and their compounds are not considered refractory since they are not expected to constitute the core grain material.

The silicate cores of interstellar grains are believed to originate in mass loss from cool stars (Section 7), though direct condensation in the ISM also might be possible (Snow, 1975; but see Section 8.1). When adsorbed upon these silicate surfaces, any residual gas phase atoms of Si, P, Mg, Na, K are expected to form volatile, fully-hydrogenated molecules which in diffuse clouds are easily photodesorbed, then photodissociated. Thus depletions of these elements are expected to be modest in diffuse clouds, as observed. Ca forms a tightly bound $\text{Ca}(\text{OH})_2$ surface molecule and is not photo-desorbed, explaining the large Ca depletion in normal diffuse clouds. In dense clouds, all of these refractory compounds would remain on the grain surfaces. In the energetic Orion star forming core (Section 6), the powerful 100 km s^{-1} shock is observed to have disrupted grains and restored an undepleted abundance of Si (Haas *et al.*, 1986). Since $\sim 100\%$ of Si is estimated to be locked up in the silicate grain cores (Tielens and Allamandola, 1987), the Orion shock is evidently atomizing most or all of the underlying grain cores. The cosmic abundances of Mg and Si are equal. Since the silicate cores have composition $(\text{Mg, Fe})\text{SiO}_3$ or $(\text{Mg, Fe})_2\text{SiO}_4$, even partial disruption returns a ratio $\text{Mg}/\text{Si} \geq 0.5$ to the gas phase. Once in the gas phase at high temperature, SiO can be formed via $\text{Si} + \text{OH} \rightarrow \text{SiO} + \text{H}$. Similarly $\text{Mg} + \text{OH} \rightarrow \text{MgO} + \text{H}$. Then we expect $\text{MgO}/\text{SiO} \geq 0.5$ contrary to observation. Several explanations are possible: (i) Mg could become more highly ionized than Si, but against this possibility is the fact that there are few molecular ions in the dense shocked gas, and the reaction time with OH is very short; (ii) there is a much larger activation barrier for the Mg reaction, though this appears unlikely; (iii) neither reaction operates, and SiO is formed by other processes. Leung *et al.* (1984) find that ion molecule processes form SiO abundances in accord with those observed assuming a depletion factor of 100. In the dense shocked

core of Orion, Si is probably much less depleted, but the abundance of H_3^+ necessary to initiate the ion molecule reactions would also be much less than assumed. It is unknown whether the corresponding reaction $\text{Mg} + \text{H}_3^+ \rightarrow \text{MgH}^+ + \text{H}_2$ proceeds.

An intriguing possibility to explain the MgO/SiO dilemma has been raised by Duley and Boehlau (1986). Laser experiments simulating disruption of interstellar grains by a 100 km s^{-1} shock yield SiO, MgO, and atomic species when MgSiO_3 (enstatite) is heated, but only SiO plus atoms when Mg_2SiO_4 (forsterite) is heated. This result is consistent with the bonding of Si–O within Mg_2SiO_4 being stronger than that of Mg–O, as pointed out by Turner and Steimle (1985). Since $\text{SiO/Si} \sim 0.04$ is observed, only a small molecular yield is required. Alternatively, if grains consist of metal oxide solids as advocated by Duley and Millar (1978), then the stronger, crystalline bonding in the MgO solid should make it less easily disrupted by a shock than the weaker bonding that characterizes the amorphous SiO solid expected under the reducing properties of the ISM.

Compounds of other refractory elements expected to reside on grain surfaces are PH_3 , SiH_4 , MgH_2 , NaH, and $\text{Ca}(\text{OH})_2$. Only $\text{Ca}(\text{OH})_2$ is strongly bound. Under the non-shocked heating of the Orion hot core source by the IRc2 protostar (Section 6.5) one expects these compounds to be readily desorbed just as NH_3 and H_2O are observed to be. Neither NaH (Section 4.8.2) nor PH_3 (Turner *et al.*, 1989) are observed to significantly low levels. Since $\text{PN/P} \sim 5(-4)$, essentially all cosmic P should be available to form PH_3 . Apparently the $\sim 300 \text{ K}$ temperature of the Orion hot core is sufficient to evaporate copious quantities of H_2O , NH_3 , and HCN (Section 6.5), but essentially no NaH or PH_3 , contrary to expectation. SiH_4 and MgH_2 are not amenable to searches at present. The failure to observe MgH (Ziurys, unpublished) is not surprising in these terms.

5. Shock Chemistry

5.1. THE NATURE OF INTERSTELLAR SHOCKS

Shocks are supersonic compressions that occur when the bulk fluid velocity of the gas exceeds the local sound velocity. In neutral interstellar gas the sound speed is only 0.3 km s^{-1} at 10 K and 1 km s^{-1} at 100 K. A variety of interstellar processes produces velocities much in excess of these values: expanding H II regions and cloud-cloud collisions ($\geq 10 \text{ km s}^{-1}$); galactic spiral density wave ($\sim 100 \text{ km s}^{-1}$); bipolar outflows from protostars (10 to 140 km s^{-1}); supernova explosions (1000 km s^{-1}); stellar winds from OB stars ($\geq 1000 \text{ km s}^{-1}$). Thus shocks are expected to be a common phenomenon throughout the ISM, not only in neutral gas, but also in ionized and in hot coronal gas. Shock waves heat and compress the gas. The extent of this depends in part on the shock velocity v_s , and in part on the presence or absence of magnetic fields. Observations thus far show that shocked gas can attain temperatures of several kK and densities on order $1(10) \text{ cm}^{-3}$, although these values could be higher.

Shocked gas is identified observationally by the presence of high-velocity components

and/or broad spectral lines, as well as by vibrationally excited H_2 (which implies $T \geq 2000$ K). In diffuse clouds two lines of evidence indicate shocks. One is the velocity difference characteristically observed between CH^+ and CH (CH^+ is formed in shocked gas; Sections 5.3.3 and 5.4.1), which indicates shock speeds of typically $10\text{--}15 \text{ km s}^{-1}$ (Federman, 1982, although recent determinations (Federman, 1987) reduce this significantly). The other evidence is that the abundance of Ca II suddenly becomes undepleted at a threshold Ca II line velocity $> 20 \text{ km s}^{-1}$ even for clouds with A_v as high as ~ 1 , a result usually explained by the disruption of grains by shocks. In dense warm star-forming molecular cores, shocks are observed in the form of energetic bipolar flows generated by pre-Main-Sequence protostars of both low and high mass. Over 70 such flows are known, with velocities ranging from 10 to 140 km s^{-1} . These flows are accompanied by the near-IR ($2 \mu\text{m}$) lines of H_2 , excited behind shock waves moving with $v_s \sim 7$ to 30 km s^{-1} into dense ($n \geq 1(5) \text{ cm}^{-3}$) gas. In a few cases neutral H has been observed to mimic the bipolar distribution of $2 \mu\text{m}$ H_2 (Bally and Stark, 1983), indicating that the H_2 is being dissociated into HI by the bipolar shock.

The simple theory of non-magnetic shocks tells us (cf. Duley and Williams, 1984a) that the gas behind a shock is compressed by a factor of 4, and heated to a temperature $T = 2900 (v_s/10 \text{ km s}^{-1})^2 \text{ K}$ for a neutral atomic gas, or $T = 1400 (v_s/10 \text{ km s}^{-1})^2 \text{ K}$ for an ionized gas. If v_s is high enough, the gas is ionized, and the process $\text{H}^+ + e \rightarrow \text{H} + h\nu$ provides a radiative precursor which may both ionize and dissociate gas ahead of the shock, and also inhibit molecular formation in the post-shock region. If a magnetic field is present with a component perpendicular to v_s , then ions and electrons in the gas tend to follow the field lines. For sufficiently large fields, ‘magnetic precursor’ effects force ions and electrons upstream of the shock to move rapidly through the neutral gas, heating and compressing it, and reducing the jump in the neutral flow parameters. High temperatures may not be attained, although $T > 1(3) \text{ K}$ is still likely. We shall first consider non-magnetic shocks, which may be either dissociative or non-dissociative depending on whether molecules are dissociated in the post shock region. Once the shock has passed the gas cools quickly (a few 100 years) by fine structure transitions of O and by rotational and vibrational transitions of H_2 and CO. As it cools the pressure tends to remain constant, so the density rises, possibly by a factor of 100 (in non-magnetic shocks). This affects the chemistry also. Since cooling is rapid, the shock chemistry is ‘frozen in’. It is subsequently modified by ion-molecule processes on time-scales of $\geq 1(5) \text{ yr}$, but for regions of recent star formation such as Ori(KL) the present composition may well reflect the signature of shock chemistry.

5.2. DESTRUCTIVE PROCESSES IN SHOCKS

5.2.1. Gas Phase Destructive Processes

These include collisional dissociation ($M + XY \rightarrow M + X + Y$ with $M = \text{H}$ or H_2), electron impact dissociation, and chemical reactions (Dalgarno, 1981). Collisional dissociation is relatively unimportant even for temperatures as high as 10 kK. Electron impact will completely dissociate H_2 for $v_s > 50 \text{ km s}^{-1}$ if $n \leq 1(2) \text{ cm}^{-3}$, and for

$v_s > 25 \text{ km s}^{-1}$ if $n > 1(4) \text{ cm}^{-3}$ (Hollenbach and McKee, 1980). Other molecules are similarly destroyed by energetic electrons, and none survive a fast shock even in low density gas where the effect of radiative stabilization of the molecules through radiative decay is greater. If even a small fraction of H_2 is dissociated, the resultant H will react efficiently with other molecules and lead to their destruction. Dissociation of a molecule XY occurs via $\text{H} + \text{XY} \rightarrow \text{HX} + \text{Y}$ and $\text{H} + \text{HX} \rightarrow \text{H}_2 + \text{X}$. Only species with large dissociation energy such as CO can persist after the dissociation of H_2 is initiated. Finally, fast shocks produce X-rays and UV which dissociate molecules in the preshock gas and retard formation in the post shock gas. Because of radiative trapping by H, much of the UV will emerge as $\text{Ly}\alpha$, which is absorbed strongly by OH, H_2O , CH_4 , but not by CO. $\text{L}\alpha$ also photoionizes some species (e.g., NO, HCO).

In diffuse clouds, sufficient hydrogen exists as H because of the ambient UV field that the elevated shock temperatures will insure the complete destruction of existing molecules by reaction with H when even a modest shock passes. In dense star forming cores, a large fraction of bipolar flows have sufficient velocity to dissociate H_2 . While not all H_2 is destroyed (as indicated by the $2 \mu\text{m}$ emission), enough H is produced to destroy all other existing molecules except apparently CO.

5.2.2. Destruction of Grains

In Section 4.5 it was argued that icy grain mantles will be completely destroyed by passage through a shock in diffuse or dense clouds. The constituent grain molecules will be destroyed also. Of importance is the release of heavy refractory elements from the silicate grain structures. It was pointed out (Section 3.5.1) that ion-molecule chemistry fails systematically to produce abundances of molecules containing second-row atoms (S, Si, P) as large as those observed. These species are most likely formed in warm star-forming cores as a result of shocks, which first release the refractory atoms from grains, and then provide the high temperatures necessary for their reactions in the gas phase, which are characteristically endothermic. The efficiency with which refractories are released from grains is important. Some but not all of graphite and silicate grains will be destroyed in typical radiative shocks with magnetic precursors (Section 4.5). However, a much more destructive J -type shock seems to be present in the high-velocity outflow of Ori(KL), where *all* of the Si seems to have been returned to the gas phase, as observed in the fine structure transition of Si^+ (Haas *et al.*, 1986).

In summary, shocks in both diffuse clouds and in dense star-forming cores are expected to dissociate most of the existing gas phase molecules in $\leq 100 \text{ yr}$, and to vaporize all of the grain mantles and perhaps $\frac{1}{3}$ of the cores. The problem is now to assess the subsequent chemistry of the dense, high-temperature atomic region that remains once the shock has passed.

5.3. FORMATION OF MOLECULES IN SHOCKS

Even in the absence of grains, H_2 can be formed in a hot, ionized gas by a sequence of reactions beginning with $\text{H} + e \rightarrow \text{H}^- + h\nu$ (Dalgarno, 1981). If the post shock gas is not ionized, H_2 is reformed on grains (Hollenbach and McKee, 1979). In general, the

heating of the gas by the shock overcomes activation barriers and also allows normally endothermic reactions to occur. This has significant consequences for the gas phase chemistry of first-row atoms (C, N, O) as well as second-row atoms. Some examples follow.

5.3.1. Oxygen Chemistry

At low temperature, O does not react with H_2 , and O^+ must react with H_2 to form OH and H_2O . At high T , $O + H_2 \rightarrow OH + H$ and $OH + H_2 \rightarrow H_2O + H$ are rapid, and the abundances of both OH and H_2O are greatly increased. While substantial abundances of OH are predicted in diffuse clouds by this process (Elitzur and Watson, 1980), its main utility is probably to explain the high abundances necessary in the powerful OH and H_2O masers associated with massive star formation. This is the basis of the earliest shock models (Elitzur and de Jong, 1978). Later refinements (Draine *et al.*, 1983) indicated that for magnetic shocks with v_s between 5 and 50 $km\ s^{-1}$ nearly all the oxygen not contained in CO is converted to H_2O . This suggests that OH masers may result from the collisional dissociation of H_2O by shocks, so that such masers would occur in the initial destructive shock phase. In diffuse clouds, OH/CO is observed with a 100-fold enhancement in the supernova remnant IC 443, which also exhibits vibrationally excited H_2 . Models of a 10 $km\ s^{-1}$ shock incident on a diffuse cloud reproduce the observed OH/CO (Mitchell and Deveau, 1983). Elaborate models of nonmagnetic shocks with $5 \leq v_s \leq 20\ km\ s^{-1}$ (Mitchell, 1984) indicate large increases for several other O-species such as HO_2 and H_2O_2 over short periods of time.

5.3.2. Nitrogen Chemistry

All of the simple reactions of N and N^+ with H_3^+ or H_2 , which are problematic at low T (Section 3.1), will proceed at shock temperatures. Thus all N is processed into NH_3 and N_2 . CN is converted to HCN by reaction with H_2 . For $5 \leq v_s \leq 10$, NH_3 and HCN are the dominant species, while at $v_s = 15\ km/s$, CN becomes highly abundant also because its destruction by H_2 turns off (Mitchell 1984).

5.3.3. Carbon Chemistry

While C^+ initiates low-temperature hydrocarbon reactions by its slow radiative association reaction with H_2 , at shock temperatures the endothermic reaction $C^+ + H_2 \rightarrow CH^+$ proceeds rapidly and in diffuse clouds produces the large abundances of CH^+ that are observed (Elitzur and Watson, 1978, 1980). In dense clouds with substantial abundance of C (i.e., immediately after passage of the dissociating shock), the endothermic reaction $C + H_2 \rightarrow CH + H$ starts a sequence of H-abstraction reactions which produces the hydrides CH, CH_2 , CH_3 . Another sequence, initiated by $C + H_3^+ \rightarrow CH^+$, produces transient CH_2^+ , CH_3^+ , CH_5^+ ions which form CH_4 . For non-dissociative shocks ($v_s \leq 15\ km\ s^{-1}$ in the models of Mitchell, 1984), the neutral hydrides are all predicted to have high abundance for $v_s \geq 10\ km\ s^{-1}$. Many higher-order neutral hydrocarbons are also predicted in large quantity, including H_2CO and C_3H_2 among observed species. For dissociative shocks (e.g., $v_s = 17.5\ km\ s^{-1}$ in the model of

Mitchell) the abundances of all of these species actually decrease with respect to preshock conditions.

5.3.4. Chemistry of Second-Row Elements

The endothermic reactions of S^+ and S with H_2 can proceed in heated gas, followed by reaction of SH with H_2 and O to form H_2S and SO. In turn SO can form SO_2 by reaction with OH, while CS can form by several routes. Models incorporating these processes (Hartquist *et al.*, 1980) appear capable of producing the observed high abundances of S-compounds in dense shocked regions, though the details depend on the nature of the shock, especially whether magnetic precursors exist (Hartquist, 1986).

The fact that SiO is observed *only* in spatially confined regions associated with high velocity outflows (Downes *et al.*, 1982) virtually assures a shock origin. In shocks with enhanced abundance of OH, the reaction $Si + OH \rightarrow SiO + H$ will produce the necessary SiO (Hartquist *et al.*, 1980) if a source of Si is available, presumably the disruption of silicate grains. Formation of SiS in shocks, with a ratio $SiS/SiO \sim S/O$ as observed, is not so easily explained.

PN also seems present *only* in shocked regions. Unlike Si, P is not highly depleted in the ISM (e.g., Dufton *et al.*, 1986), so disruption of grains to produce gaseous P appears unnecessary. Most likely, the reaction $PO + N \rightarrow PN + O$ (Millar *et al.*, 1987b) has an activation barrier which prevents conversion of PO into PN in cold clouds, but insures that PN will be the dominant P-species in heated gas. Alternatively, stable closed-shell species such as PN, SiS, and SiO could be formed in quasi-thermochemical equilibrium if both densities and temperatures are high enough. This might explain the observed $SiS/SiO \sim S/O$; in C-rich environments the predominant P-compound would likely be HCP (Tsugi, 1988), but might be PN in O-rich regions. It is doubtful, however, that thermochemical equilibrium conditions are realized in shocks even in dense clouds (Section 8.1).

In the Ori(KL) core, one observes that $SiO/Si = 3(-4)$, $PN/P = 5(-4)$, and $\sum S\text{-species}/S \sim 2(-2)$. The similarity of the Si and P fractions, and the much larger S fraction, may point to two distinct mechanisms, although the similarity in depletions of S and P (in diffuse clouds) might caution against speculation that grain disruption is involved for Si, P but not for S.

5.3.5. Catalysis and Desorption on Shocked Grains

Silicate and graphite cores of grains partially survive all but the fastest shocks ($v_s \geq 200 \text{ km/s}^{-1}$). The cores are heated mostly by the UV emitted by the cooling gas. The important question for neutral post shock gas is whether the grain temperature exceeds the critical temperature T_{cr} above which H_2 cannot form on grain surfaces. The value of T_{cr} is uncertain, depending strongly on the nature of the surface binding sites. $T_{cr} \sim 20 \text{ K}$ is the nominal value for 'pure' surfaces, but impurities or defect sites raise T_{cr} ; a value $\sim 100 \text{ K}$ is representative for the post-shock problem (Hollenbach and McKee, 1979). When cooling processes are considered, Hollenbach and McKee find that H_2 catalysis on post-shock grains proceeds efficiently for conditions of column

depth, density, and shock speeds such as describe star forming regions. Catalysis of other molecules seems possible also, since the grain temperatures may reach ~ 400 K if $n > 1(6) \text{ cm}^{-3}$. However, the grains are not significantly heated by collisions with the hot gas, and since they cool much faster than the gas, there is only a short time (~ 100 yr) in which grain catalysis rates of molecules other than H_2 can be comparable with high- T gas phase rates.

After the grains are reduced by the shock, releasing refractory elements for gas phase processing, these refractories immediately begin to coagulate again on the grains. The time for accretion is $\sim 3(9)/n$ yr for a Si atom at $T \sim 1000$ K. The time for a Si atom to react with an OH molecule at maximum fractional abundance $1(-5)$ (Mitchell, 1984) is $1(8)/n$ yr. Thus the vaporized Si will participate fully in gas phase reactions before being accreted onto grains.

5.4. SUMMARY OF MODELS AND PREDICTIONS

Fundamental to the resultant chemistry of any shock is whether it is dissociating or not, and if not, what is the preshock form of carbon (i.e., C^+ in diffuse clouds, CO in dense clouds) and of hydrogen (H in diffuse clouds, H_2 in dense clouds). In addition, peak-shock temperatures depend on whether a magnetic field is present, and, hence, on pre-shock densities since these affect the strength of the magnetic precursor. Finally, overall column depth of the shocked gas affects the role of UV in radiative shocks. Thus several types of models are needed, and give quite different overall results.

5.4.1. Diffuse Cloud Shocks

As is the case for ion-molecule chemistry, diffuse clouds provide the best tests of shock models. The condition for a magnetic precursor ($v_s < B_0/\sqrt{4\pi\rho_i}$ where B_0 is the preshock field, ρ_i is the mass density of ions; see Hartquist, 1986) appears often not satisfied in diffuse clouds. Thus the early model of Mitchell and Deveau (1983) for a $v_s = 10 \text{ km s}^{-1}$ shock in a $n = 1(2) \text{ cm}^{-3}$ cloud was chosen to be purely hydrodynamic. The shock is not dissociating, and initial molecule abundances are taken as those of the Prasad and Huntress (1980) model for diffuse clouds in which C^+ and H are dominant. The results depend strongly on whether the post-shock gas is shielded ($A_v = \infty$) or unshielded ($A_v = 1$) from the ambient UV. Most species which are markedly shock-enhanced decrease rapidly after the gas has cooled ($> 1(3)$ yr) and are not suitable as observational diagnostics. In the shielded case species which retain an enhanced abundance over $> 1(5)$ yr are CH_4 , C_2H_2 , H_2O , CO_2 , H_2CO , HCN, CN, NH_3 . In the unshielded case CO and HCN attain stable high abundances. This model appears quite successful in explaining some abundances in the shocked gas of the supernova remnant IC 443, with the notable exception of HCO^+ , whose large observed abundance requires special postulates.

Mitchell (1983) has extended his hydrodynamic calculations for a cloud with $n = 1(2) \text{ cm}^{-3}$ to include complex hydrocarbons containing up to 6 carbon atoms. Provided the initial abundance of C^+ and C is high (as in diffuse cloud conditions), substantial amounts of complex hydrocarbons are produced for $t \geq 1(5)$ yr and there

is little decrease in predicted column abundance with increasing number of C atoms. Since the final post-shock density is $3(4) \text{ cm}^{-3}$, the shock has transformed a diffuse cloud into a moderately dense one, so the omission of photoprocesses behind the shock may be justified.

The observed large abundance of CH^+ , which originally inspired shock models, is still a key diagnostic in diffuse clouds (Hartquist, 1986). Purely hydrodynamic shocks predict too little CH^+ in clouds where most of the hydrogen is H_2 and where the UV field is noticeably attenuated. If there is appreciable H as well as H_2 it is found that observed CH^+ and OH abundances can be predicted but only if $\text{H}_2/\text{H} \sim 0.1$ (Elitzur and Watson, 1980), which is an unlikely 'transition' condition. The way out may be MHD shocks. Detailed MHD models using modest ($\sim 5 \mu\text{G}$) transverse field strengths have been compared to observations of several diffuse clouds containing CH^+ (Pineau des Forets, 1986a; Draine, 1986; Draine and Katz, 1986), though with differing results. The basic endothermic reaction is driven by ambipolar diffusion through an extended acceleration zone (magnetic precursor). Unlike hydrodynamic shocks, MHD models do not overproduce neutral species such as OH, and do not seriously constrain the H_2/H ratio. However the two groups disagree on whether enough CH^+ can be produced, and in general poor agreement is achieved with observed excited rotational states of H_2 . Pineau des Forets *et al.* conclude that the observed CH^+ cannot be accounted for, while Draine and Katz contend that models can be found which are in reasonable agreement with observations. The difference in model results is due partly to differences in assumed shock parameters, and partly to different adopted rates for the reaction of C^+ with H_2 . Draine and Katz find that MHD shocks may also be important in the formation of CH, OH, and CO in diffuse clouds.

A test of the presence of MHD shocks has been proposed by Millar *et al.* (1986) and by Pineau des Forets *et al.* (1986b) in an analysis of S-chemistry in highly diffuse clouds ($n \sim 10 \text{ cm}^{-3}$). They find that SH^+ will form in observable quantities ($\text{SH}^+/\text{CH}^+ \rightarrow 1$) in MHD shocks with $v_s \sim 10\text{--}16 \text{ km s}^{-1}$, and over a wide range of H_2/H , but that SH^+ will be far below observable abundances in hydrodynamic shocks. A recent search for SH^+ (Millar and Hobbs, 1988) was unsuccessful but the limits are only slightly below the predicted SH^+ abundance and are within uncertainties in the MHD model.

Pineau des Forets *et al.* (1987) have also considered shock formation of complex hydrocarbons in an MHD shock of $v_s = 15 \text{ km s}^{-1}$ in diffuse clouds of $n = 20$ and 100 cm^{-3} . The latter has extinction $A_v \sim 2$ mag through the shocked gas. Ambipolar diffusion drives endothermic ion-neutral reactions such as $\text{C}_3\text{H}^+ + \text{H}_2 \rightarrow \text{C}_3\text{H}_2^+$ and $\text{C}_3\text{H}_2^+ + \text{H}_2 \rightarrow \text{C}_3\text{H}_3^+$, leading to substantial column densities of species such as C_2 , C_2H , C_2H_2 , C_3 , C_3H , and C_3H_2 . A key factor is the large pathlength of the precursor of the MHD shock which is possible if the magnetic field is sufficiently large ($5 \mu\text{G}$) and if the ambient UV field is sufficiently attenuated. Owing to the long precursors, observable column depths of C_3H_2 and C_3H are predicted. In fact, C_3H_2 has recently been detected in several rather diffuse interstellar regions (Cox *et al.*, 1988) at fractional abundances comparable to those in dense clouds ($1(-9)\text{--}1(-8)$). The densities in the C_3H_2 clumps range from ~ 500 to $5(3) \text{ cm}^{-3}$, greater than exist even in the post-shock

region of the Pineau des Forets models. However, C_3H_2 is sometimes observed at velocities where no other molecules exist, suggesting that it indeed forms in low extinction ($A_v \sim 1$) regions, thus requiring a large formation rate to counter the high photo-dissociation rate. Since ion-molecule models underproduce C_3H_2 , at least in dense clouds, shock production deserves serious consideration.

5.4.2. *Absence of Shocks in Cirrus Clouds?*

It has been speculated that the filamentary structures and the cores themselves in cirrus clouds have been formed by shocks (Section 2). The observed chemistry may argue against this. Although the abundance of C_3H_2 is observed to be the same in the semidiffuse ISM ($A_v \leq 2$) and in dense clouds, it appears to be ~ 10 times smaller in cirrus cores, even though their densities ($\sim 4(4) \text{ cm}^{-3}$) are similar to those found in galactic plane dense cloud cores (Turner *et al.*, 1988b). Differing formation mechanisms might be indicated. Both the hydrodynamic model of Mitchell (1983) and the MHD model of Pineau des Forets *et al.* (1987) predict similar abundances for C_3H_2 (1(-7.2) and 1(-7.5), respectively); the post-shock density in Mitchell's model is $3(4) \text{ cm}^{-3}$, appropriate for both cirrus cores and cold dark galactic plane cores. A possible explanation of the observations is that shocks produce C_3H_2 in galactic plane clouds (both diffuse and dense) while ion-molecule processes alone operate in the cirrus cores. The smaller observed abundance in the cirrus cores is in good agreement with predictions of steady state (low metal) ion-molecule models (Herbst and Leung, 1988), while the shock models may overestimate C_3H_2 somewhat in galactic plane clouds. Although the TMC-1 object is generally interpreted as a disk (Olano *et al.*, 1988), its highly elongated morphology also seems suggestive of a shock. In this regard, we note that the cyanopolyne abundances are considerably less in L183 (more in line with ion-molecule predictions) where there is no morphological suggestion of a shock.

A possible test of these ideas involves C_3H . If only ion-molecule processes operate, $C_3H^+ + H_2 \rightarrow C_3H_3^+ + h\nu$, then according to Bates' rule, C_3H should not be formed. If shocks dominate, i.e., $C_3H^+ + H_2 \rightarrow C_3H_2^+ + H$ and $C_3H_2^+ + H_2 \rightarrow C_3H_3^+ + H$, then both C_3H and C_3H_2 should form, from $C_3H_2^+$ and $C_3H_3^+$, respectively. C_3H has indeed been detected in galactic plane clouds, but has not yet been the object of searches in cirrus cores.

5.4.3. *Dense Cloud Shocks*

Early models of dense cloud shocks were non-magnetic and were based primarily on the processes $X + H_2 \rightarrow XH + H$; $XH + Y \rightarrow XY + H$; and $XH + Y^+ \rightarrow XY + H^+$. The models of Iglesias and Silk (1978) and Mitchell (1984) are particularly useful to compare, as hydrodynamic shocks are relatively simple to model, and the dependence of the results on assumed initial compositions (these models are non dissociative) can be assessed. Both models have $v_s \sim 10 \text{ km s}^{-1}$ and $n = 1(4) \text{ cm}^{-3}$. The most important difference is the assumed form of carbon: all in CO (Iglesias and Silk, 1978), and $CI = CO$ (Mitchell, 1984). Both models find the abundance of CO unchanged by the shock, HCO^+ reduced substantially, and H_2O , CH_4 greatly enhanced. However, the

assumption $C/CO = 0$ leads to a reduction in H_2CO while $C/CO \sim 1$ leads to an enhancement of H_2CO . (It is still observationally unclear whether the observed CI resides in a thin layer in the outer layer of dense molecular clouds, or whether it is mixed throughout the cloud.) Serious discrepancies exist between the two models for the N-species CN, HCN, NH_3 , which can be traced to improved knowledge of certain reactions as used by Mitchell. Therefore, his conclusion that these species are enhanced by shocks should be adopted.

The early hydrodynamic non-dissociative model of Hartquist *et al.* (1980) focuses on S-chemistry in dense clouds, and adopts $v_s = 8 \text{ km s}^{-1}$, $n = 1(6) \text{ cm}^{-3}$. H_2S , SO, and SiO are strongly enhanced by the shock, as is H_2O . Although a relatively limited reaction network is used, Hartquist *et al.* find that post-shock abundances of O species depend only weakly on shock conditions, while S-species are highly sensitive to v_s ($5 \leq v_s \leq 10 \text{ km s}^{-1}$ is required for enhancement) and to n . In addition, S-species are suppressed if H/H_2 is appreciable (H removes SH and H_2S).

If the magnetic field is zero, shocks with $v_s \sim 25 \text{ km s}^{-1}$ or even less will dissociate H_2 (and, hence, all other species) in a dense cloud. The existence of molecular gas spanning a velocity range of $\geq 100 \text{ km s}^{-1}$ in many star forming regions (e.g., Ori(KL)) is incompatible with the simple picture of a hydrodynamic shock of a single speed propagating into a quiescent dense cloud, and thus indicates the necessity of considering MHD shocks in dense clouds. Unfortunately, this has proved difficult, because of the fundamental aspect of MHD shocks that the ionized and neutral fluids have differing flow velocities (it is this differential velocity that drives the endothermic reactions $C^+ + H_2 \rightarrow CH^+ + H$, etc.). The problem is actually more complex than a 2-fluid situation; although they have equal velocities, electrons and positive ions develop differing kinetic temperatures because their scattering processes differ, so that a 3-fluid model is actually needed. The difficulty is that the degree of ionization affects all processes controlling the shock structure critically. Diffuse clouds offer the simplest case, where the ionization fraction is high (allowing certain approximations, e.g., in the cooling rates) and also is 'controlled' (set by the ambient UV and not by the chemistry). In dense clouds the fractional ionization is low and is controlled by the chemistry which in turn is determined by the adopted shock parameters. For these reasons, current dense cloud MHD models (Draine and Roberge, 1982; Chernoff *et al.*, 1982; Draine *et al.*, 1983) do not include ion-molecule chemistry, although a simple scheme for the neutral O-chemistry is included. The inclusion of even a simple ion-molecule scheme involving only a few simple hydrocarbon reactions into a diffuse cloud formulation of MHD shocks was shown by Flower *et al.* (1985) to have a profound effect on the structure of an MHD shock, by enhancing the width of the magnetic precursor and reducing the maximum temperature of the neutral gas. Thus it is not surprising that the more ambitious ion-molecule models even for diffuse clouds are only now beginning to reach some agreement (Flower *et al.*, 1988; see also Draine, 1986, Flower and Pineau des Forets, 1986), and still leave certain aspects of even the classic CH^+ problem uncertain. A much more complex set of reactions will be necessary for dense clouds, as well as more precise modelling of the shock. The role of grains in modifying dissipation

processes must also be included, requiring fluid equations for each grain charge state. Grains will be of particular importance in dense cloud shocks where the fractional ionization is low. At present it seems likely that abundances of simple species such as H_2O and OH will be enhanced, as well as those of some S-species, although the abundances of several S-species (e.g., SO , SO_2) are expected to depend critically on shock parameters (Hartquist, 1986). Detailed comparison with molecular observations in shocked, dense star forming regions is currently not possible.

Two recent observations have pointed to the strong effects of shocks on first-row molecules in dense regions. Rotationally excited CH has been detected in several galactic plane dense clouds, all regions of star formation (Ziurys and Turner, 1986a), and an analysis (Turner, 1988c) has determined CH -abundances ~ 15 times higher than previously recognized, $\geq 2(-8)$ in regions where $n \geq 2(4) \text{ cm}^{-3}$. Ion-molecule models at early times (3(5) yr) (Herbst and Leung, 1988) can at best marginally reproduce the observed CH at these densities; steady-state models are insufficient by two orders of magnitude. Shock enhancement of CH in these energetic regions seems indicated. Even clearer evidence of shock chemistry is the observation of enormous quantities of OH at the interfaces between energetic bipolar flows and ambient cold quiescent clouds (Clark and Turner, 1987). Here the OH fractional abundance is 1000 times greater than in quiescent clouds, and its column depth exceeds that of the entire surrounding cloud. The shock speeds appear to be dissociative ($\sim 30 \text{ km s}^{-1}$). For non-dissociative shocks the model of Elitzur and de Jong (1978) produces OH from $\text{O} + \text{H}_2$, then H_2O from $\text{OH} + \text{H}_2$. Finally $\text{H} + \text{H}_2\text{O}$ restores OH . The model predicts $\text{OH}/\text{H}_2 \sim 7(-4)$, a 700 fold increase over 'ambient', and in good agreement with the observations.

All detailed shock chemistry models to date are non-dissociating. Current hydrodynamic models are, therefore, restricted to $v_s \leq 25 \text{ km s}^{-1}$ (Hollenbach and McKee, 1980) and MHD models to $v_s \leq 40\text{--}50 \text{ km s}^{-1}$ for $n = 1(6) \text{ cm}^{-3}$ (Draine *et al.*, 1983). In dissociative models H_2 will reform on grains and also in the gas phase at high T (Hollenbach and McKee, 1979). According to Dalgarno (1985) species such as OH , H_2O , NH_3 , CH_4 will be dissociated by $L\alpha$ photons from the shock precursor radiation, allowing CO to form preferentially. Any O left over will form OH , H_2O , and O_2 . Sulfur will be transformed mostly to H_2S and N to NH_3 . If all oxygen not in CO is in the form OH , OH/H_2 would have roughly the value observed in bipolar flow shocks by Clark and Turner (1987).

6. The Complex Chemistry of Star-Forming Regions: The Orion Core

Stars of all ages, from pre-Main-Sequence protostellar objects to evolved stars with Circumstellar Envelopes (Section 7), lose mass in the form of supersonic outflows. They also generate intense radiation, usually in the IR while still embedded in dense molecular clouds. Especially if the stars are massive, these stellar activities profoundly affect the dynamical conditions and the chemistry of the surrounding dense cloud. The GMC in Orion is $\sim 500 \text{ pc}$ in distance, and is the nearest region of massive star formation (Section 2). A smaller, dense core lies roughly behind the H II region M42 which itself

is at the near edge of the GMC. The core contains several young, massive, embedded stars which are completely obscured in the visible by dust. This central core is known as OMC-1 and includes the KL nebula. Here we shall be concerned with OMC-1 and Orion (KL). Although the Ori(KL) object demonstrates the complexity of interstellar chemistry, it also serves as the currently best test object for aspects of grain and shock chemistry. Its chemistry has been discussed in detail by Blake *et al.* (1987) and its morphology, which rests largely on the pioneering interferometric studies of Plambeck *et al.* (1982, 1985) and Vogel *et al.* (1984) has been discussed in reviews by Irvine *et al.* (1987) and Prasad *et al.* (1987).

6.1. OBSERVED MORPHOLOGY

A schematic of the Ori(KL) region, adapted from Irvine *et al.* (1987), is shown in Figure 8. Each of the source regions has a distinctive spatial and spectral distribution. The *extended ridge* cloud of largely quiescent gas extends ~ 3 arc min (0.4 pc) north and south of the central IR sources and has a temperature of 20–70 K, density $1(4)\text{--}1(6)\text{ cm}^{-3}$ and mass 100–1000 M_{\odot} . It produces narrow molecular spectral lines ($\Delta v \sim 2.5\text{--}4\text{ km s}^{-1}$) and is nicknamed the ‘spike’ component. It is warmest near IRC2, and contains several dense clumps ($\sim 1(6)\text{ cm}^{-3}$) throughout its extent which may be incipient protostars. The southern ridge contains a localized warmer clump ($T = 70\text{--}150\text{ K}$, $n \sim 1(7)\text{ cm}^{-3}$) often called the ‘*southern condensation*’ or ‘compact ridge’. It is chemically very distinct from the extended ridge cloud. The inner, highly energetic core region (the ‘*plateau*’ source because of its broad flat line profiles) contains several IR sources, of which IRC2 appears to drive the powerful outflows. Data from both interferometers and large single dishes indicates the plateau source, $\sim 20''$ in extent, consists of three distinct regions: (i) a disk or ‘*doughnut*’ at lower velocity ($v = 9\text{ km s}^{-1}$, $\Delta v \sim 18\text{ km s}^{-1}$) seen as a clumpy, expanding ring in SO_2 emission, centered on IRC2; (ii) a *high velocity* bipolar outflow ($\Delta v \sim \pm 30\text{--}100\text{ km s}^{-1}$), $\sim 50''$ in extent, which is orthogonal to the disk and is presumably channelled by it. This outflow apparently produces the more spatially extended vibrationally excited H_2 emission and highly excited CO (J up to 30) where the outflow drives shocks into the surrounding quiescent material; (iii) a low-velocity ‘*hot core*’ ($v = 5\text{ km s}^{-1}$, $\Delta v \sim 5\text{--}10\text{ km s}^{-1}$) which is spectrally distinct but difficult to resolve spatially from the high-velocity outflow. The hot core (of size $6\text{--}10''$, $T \sim 150\text{--}230\text{ K}$, $n \geq 1(7)\text{--}1(10)\text{ cm}^{-3}$, $\sim 10 M_{\odot}$) appears to be heated radiatively by IRC2.

All of these components are related, in one way or another, with the mass loss from one or more of the protostellar objects formed in the plateau. The hot core has traditionally been viewed as a large clump left over from the collapse of the inner ambient ridge which formed IRC2 and BN. It is argued to be very close to IRC2 ($\leq 3(16)\text{ cm}$, Section 6.5) and to be undergoing continued disruption by the strong isotropic outflow from IRC2. It appears to be gravitationally bound to IRC2 (Masson and Mundy, 1988). An important unanswered question is whether the molecular gas seen in the high-velocity outflow has been swept up from the hot core by the outflow wind, or is actually formed in the high-velocity flow. At a distance $\sim 10''$ northeast and southwest of IRC2, the

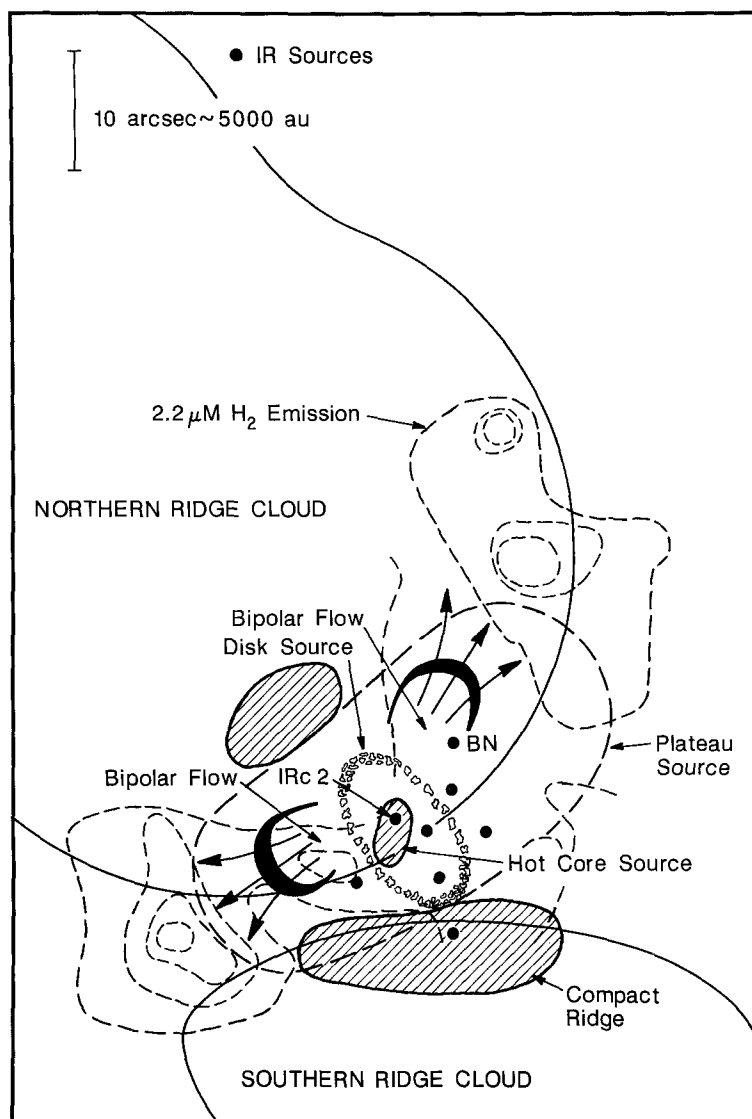


Fig. 8. Schematic of the Orion (KL) region showing the source regions discussed in the text. (Adapted from Irvine *et al.*, 1987.)

$\sim 100 \text{ km s}^{-1}$ isotropic wind has swept up material to form the clumpy ($n \sim 1(5) \text{ cm}^{-3}$) doughnut. The shocked doughnut gas is the 'lower velocity outflow'. The wind pressure deduced from the stability of the hot core (Masson and Mundy, 1988) yields an expected shock velocity of $\sim 10 \text{ km s}^{-1}$ at the doughnut, consistent with observed linewidths. In directions perpendicular to the doughnut the wind expands faster and further because of the lower density or larger density gradient in this direction. Vibrationally excited H_2 probes a thin shell of the hottest (2000 K) gas within the outflow-produced high-velocity

shock, while high- J CO emission samples the cooler (~ 750 K) post-shock gas. Masson and Mundy (1988) argue that little of the material in the plateau need have come from the original wind; it may be largely swept up from the surrounding ambient cloud or ablated from the hot core and ridge.

Some of the slowed outflow appears to penetrate the doughnut and interact with the ambient ridge both south and north of IRC2. A large region is rather strongly affected to the south (the ‘compact ridge’), with corresponding alterations in the chemistry. Interferometric maps of H_2CO (Mangum *et al.*, 1989) indicate that the compact ridge constrains the high-velocity flow to the south, explaining why its centroid appears to lie slightly north of IRC2. A weaker interaction takes place to the north producing the so-called ‘ 10 km s^{-1} feature’ or Northern Condensation. Here the density ($\sim 3(5) \text{ cm}^{-3}$) and temperature (~ 55 K) are enhanced (Mangum *et al.*, 1989), but the chemistry is largely unaltered from that of the ambient ridge.

6.2. THE AMBIENT RIDGE: PURE ION-MOLECULE CHEMISTRY?

We have seen that observed abundances of many simple species are well described by ion-molecule chemistry and do not vary much from one cloud to another, nor depend much on density or temperature (at least for $T \leq 70$ K) (Section 4.8.1). The ambient ridge cloud is no exception. Thus, like other clouds, it seems dominated by ion-molecule chemistry, and exhibits the two major shortcomings of such models: the ‘carbon problem’ (observed abundances of C and C-rich species exceed predicted steady-state abundances), and the ‘desorption problem’ (some mechanism must exist to remove adsorbed molecules from grains deep within quiescent clouds without significantly altering the composition of the gas). For large complexes like Orion the ages of stellar associations formed from the molecular gas may be used to set lower bounds for the cloud lifetime, and are generally $\sim 1(7)$ yr (Kutner *et al.*, 1977). The age of the Orion H II region (M42) can be set at $1(5)$ yr (Field, 1982) and serves as an upper limit to the age of the KL region if both star forming sites evolved on similar time-scales. Thus an ‘early time’ scenario is entirely possible for KL. The general gradient in temperature and density along the ridge might provide an interesting case in which to look for differing grain/gas-phase contributions to the chemistry, but the necessary data are generally lacking outside of the innermost region. However, in several ridge clumps quite far from Ori(KL), Menten *et al.* (1988) find that CH_3OH has fractional abundances similar to those in dark clouds. Nonetheless, there are a few striking differences between the Orion ridge and dark cloud chemistries. For Orion ridge and TMC-1, respectively, one finds (Irvine *et al.*, 1987): $\text{C}_2\text{H}/\text{C}_4\text{H} > 33, 3$; $\text{HC}_3\text{N}/\text{HC}_5\text{N} \sim 7, 2$; $\text{HCN}/\text{HNC} = 50, 1$; $\text{CH}_3\text{OH}/\text{H}_2\text{CO} \sim 5, 0.2$. The abundances of the C-rich species for the Orion ridge agree quite well with early time ion-molecule models (Herbst and Leung, 1988); it is the TMC-1 abundances that are difficult to explain. Since O-rich species (CH_3OH , H_2CO) are much more abundant in Orion, and also agree well with (early time) model predictions, it seems tempting to suggest that C/O is ‘normal’ in the Orion region, and is anomalously high in TMC-1. A more efficient recycling of carbon in TMC-1 is possible, but seems unlikely owing to the much lower temperatures there.

6.3. THE SOUTHERN CONDENSATION

Although the gas in this region is much warmer than in the ridge, observed linewidths indicate that it is quiescent. The object has been interpreted as a region where the IRC2 outflow interacts with the ambient molecular cloud (cf. Irvine *et al.*, 1987). However the strong peak in the 400 μm continuum (Keene *et al.*, 1982), together with high excitation lines of NH_3 by Mauersberger *et al.* (1986) which indicate a temperature of ≥ 270 K, suggest the presence of an internal heating source which must be deeply embedded because of lack of an IR peak at shorter IR wavelengths.

The southern condensation is characterized by unusually large abundances of several complex oxygen-rich species (Johansson *et al.*, 1984; Olofsson, 1984; Blake *et al.*, 1987). Most such species have larger abundances here than in any other Orion region. We may compare O-rich species in the Southern Condensation, in SgrB2 (also an O-rich source), and in the latest models (Herbst and Leung, 1988; cf. Blake *et al.*, 1987). The southern condensation chemistry is thus found to be very selective: the simplest species H_2CO , HCOOH , CH_3CHO have similar abundances in the two sources and are reasonably well predicted, requiring steady state rather than early time; however, H_2CO and CH_3CHO require low metal models, while HCOOH seems to need high metals. By contrast the species CH_3OH , $(\text{CH}_3)_2\text{O}$ and CH_3OCHO are strongly enhanced relative to other Orion regions, SgrB2, and the model predictions. (Relative to predictions, these latter 3 species are overabundant in SgrB2 also, as is CH_3CN in both sources.) These observations can be explained by standard ion-molecule processes if there is an overabundance of H_2O and HCN , as is the case in the core of Ori(KL). Using estimated radiative association rates, Blake *et al.* (1987) argue that the reactions $\text{CH}_3^+ + \text{HCN}$, $\text{CH}_3^+ + \text{H}_2\text{O}$ produce the observed high abundance of CH_3CN and CH_3OH , respectively. Similarly, the lower abundance of HCOOH and CH_3CHO result because both $\text{HCO}^+ + \text{H}_2\text{O}$ and $\text{HCO}^+ + \text{CH}_4$ are slow. The low abundance of C_2H_5^+ means that $\text{C}_2\text{H}_5^+ + \text{H}_2\text{O}$ results in only modest amounts of EtOH . The exceptionally large abundances of $(\text{CH}_3)_2\text{O}$ and CH_3OHCO follow directly from the equally large abundance of CH_3OH , whose precursor ion CH_3OH_2^+ reacts with CH_3OH and H_2CO , respectively, to produce $(\text{CH}_3)_2\text{O}$ and CH_3OHCO . The latter reaction does *not* produce acetic acid (CH_3COOH), an isomer of CH_3OHCO , and it is not observed. An important aspect of this idea is that rates for radiative associative reactions decrease rapidly with increasing temperature or with decreasing fractional ionization, thus explaining why these complex species are not observed in the plateau and hot core regions. The considerable quantities of H_2O required by this picture may result from evaporation of grains in the warm southern condensation, or from the interaction of the strong O-rich 'plateau' shock with the same gas. In the latter case, abundant OH should also result; type I OH masers show no discernable concentration near the southern condensation, but do occur in the vicinity. The 100-fold enhancements of OH have been observed in the IR at low-spatial resolution (Melnick *et al.*, 1988) but cannot be assigned to the southern condensation.

6.4. THE PLATEAU SOURCE (HIGH-VELOCITY BIPOLAR FLOW PLUS DOUGHNUT)

The two components of the plateau source which we consider together are actually separable both spectrally and spatially, but current interferometry of the doughnut has not yet included the entire complement of species assigned to it, and in any case the chemistry of both components should be dominated by shocks. Species which map like the bipolar flow (with $\Delta v \geq 50 \text{ km s}^{-1}$) are vibrationally excited H_2 , HCO^+ , CO , SiO , SO , SO_2 , HCN , HDO ; relatively little is presently known about their abundances because of confusion with the inner disk or doughnut in single-dish beams. HCO^+/CO appears to reach a maximum in the extreme spatially extended high-velocity flow which coincides with vibrationally excited H_2 . The 100-fold abundance enhancements of OH observed in the IR are reasonably consistent with hydromagnetic shock models for OH in the hottest parts of the post-shock gas, although definite assignment of the OH emission spatially to the high-velocity flow is not possible; models suggest the observed OH would have to exist in dense clumps within the flow. Vibrationally excited H_2 has line wings out to $\pm 90 \text{ km s}^{-1}$, and since H_2 would be dissociated in a hydrodynamic shock with $v_s \geq 25 \text{ km s}^{-1}$, magnetic precursors seem necessary (e.g., Draine and Roberge, 1982). However, the $90 \text{ km s}^{-1} \text{H}_2$ wings are difficult to model without postulating condensations in a bulk flow (Shull and Beckwith, 1982), and such condensations are surely needed to explain the existence of HCO^+ in 2000 K gas, as well as being suggested by the OH observations. Interferometry isolates the doughnut (and innermost high-velocity flow) and establishes that relative to the ambient ridge: (i) SO , SO_2 , H_2S , SiO are *greatly* enhanced (~ 1000 -fold); (ii) HDO , HCN , HC_3N are strongly enhanced (100-fold); (iii) CS , OCS , and perhaps H_2CO are ~ 10 -fold enhanced; (iv) the highly reactive species C , CN , C_2H are *diminished* 10 times or more relative to the ridge (they are undetectable).

Unlike the ambient ridge and most other molecular clouds, the plateau abundances which are dominated by O- and S-rich species, suggest a region with $\text{O}/\text{C} > 1$, as expected for an outflow from an O-rich star, or for rapid desorption from grains. A large oxygen abundance is also seen in OI at $63 \mu\text{m}$ (Werner *et al.*, 1984).

Category (i) indicates an amplified S (and Si) chemistry in general (the modest enhancement of CS is consistent with an O-rich environment, in which $\text{CS} + \text{O} \rightarrow \text{CO} + \text{S}$ removes the CS at high T). Although enhanced S-species have commonly been considered as diagnostics of shock chemistry (Section 5.3.4), Prasad and Huntress (1982) find that the plateau abundances of SO , SO_2 , SiO , SiS can, in fact, be produced by ion-molecule models if S and Si are not strongly depleted. These authors deduce that the observed S-species abundances in quiescent dense clouds imply depletion factors of 100 to 1000, but this depends on the assumption that the reaction $\text{S} + \text{O}_2 \rightarrow \text{SO} + \text{O}$ proceeds uninhibited at low T . If there is an activation barrier, or if O_2 is not abundant, then S may exist mostly as neutral atoms in dense quiescent clouds. In this case, the role of shocks in an energetic region like Ori(KL) would be only to raise the temperature. Conversely if S is highly depleted, the shock must also release sulfur from the grains, presumably by sputtering. As usual, the choice between these possibilities is ambiguous.

Shock models produce too little SO_2 because of the high O abundance and the reaction $\text{SO}_2 + \text{O} \rightarrow \text{SO} + \text{O}_2$, while ion-molecule models reproduce the observed SO/SO_2 ratio well (Blake *et al.*, 1987). This might argue that shocks are not needed at all for the S chemistry, and indeed Blake *et al.* remark that it is unclear from the observed chemistry in the doughnut that shocks have had much effect. Rather, some species seem to have been formed very close to IRC2 in what may more closely resemble the chemistry of CSEs (Section 7) (e.g., the SiO masers which lie only 70 AU from IRC2). On the other hand, all reactions leading to H_2S are highly endothermic, and shocks seem necessary to produce the observed high abundances. A different perspective seems necessary for Si chemistry. Ziurys (1988) has detected SiS with a linewidth characteristic of the 'low-velocity' flow inside the doughnut, and an abundance such that $\text{SiO}/\text{SiS} \sim \text{O}/\text{S} = 40$, in sharp contrast to predictions of either ion-molecule models (≥ 1000) or of CSE chemistry (≥ 1000 for O-rich stars: Slavsky and Scalo, 1987). The observed ratio seems consistent with thermal equilibrium chemistry. Near IRC2 grains are presumably at least partly sputtered, by the low velocity (18 km s^{-1}) flow, releasing Si as well as S and O into the gas phase. The high temperatures and densities might suggest at least quasi-thermochemical equilibrium, allowing stable species like SiO and SiS to form with abundances proportional to those of the constituent atoms. Temperatures in the low-velocity flow fall rapidly away from IRC2 and soon shut off formation of SiO and SiS, which then are destroyed further out by other processes. Thus such species are not seen in the hot core or ambient ridge. The presence of SiO in the high-velocity flow well away from IRC2 is a result of complete grain destruction by a dissociative *J*-type shock, producing a near-cosmic abundance of Si in the gas phase (Haas *et al.*, 1986). Finally, we consider phosphorus. Ion molecule models easily produce the observed abundance of PN in the plateau region even if phosphorus is depleted by up to 1000 times, so long as the reaction $\text{PO} + \text{N} \rightarrow \text{PN} + \text{O}$ proceeds (Section 5.3.4). The observed absence of PN in cold dark clouds then implies a depletion factor $> 1(4)$ in these clouds. If the above reaction does not proceed at low T , the shock provides the necessary energy, but is needed neither to drive the overall P-chemistry, nor to release phosphorus from grains. A problem with this scheme is that a depletion factor of ~ 1000 for P is required to produce the observed PN, while $\text{Si}/\text{SiO} \sim 100$, implying that even if all Si is in the form of SiO, the depletion factor for Si cannot exceed 100. It seems inconceivable that P can be more depleted than Si, since it is far less refractory. In general, the existence of refractory compounds (SiO, SiS, PN) in the high-velocity flow, along with their absence in the hot core, does not indicate whether or not the high-velocity material is swept up from the hot core. If it is swept up, it is also chemically transformed, starting with the disruption of the grains.

Category (ii) species pose different questions. Certainly H_2O and HCN (Mitchell, 1984) and presumably HC_3N can be greatly enhanced by shock chemistry. However, deuterium fractionation as strongly enhanced as suggested by the HDO abundance, cannot occur at high T as a result of either gas phase reactions or grain processes under an excess of atomic D. The highly abundant HDO in the plateau gas, therefore, reflects the cool pre-shock conditions and suggests that a sizable fraction of the outflow material

is in high density clumps whose composition has not yet been altered by the shock. (It is unlikely that such fragile species could be sputtered intact off grains.) Thus the observed HDO abundance cannot be used to infer an H₂O abundance, because pre-shock H₂O may exist in the same clumps as HDO and additional H₂O may subsequently have been formed by the shock. Like HDO, HCN, and other species of high abundance may have explanations other than shocks. Blake *et al.* (1987) point out that a combination of high temperature chemistry such as found in CSEs (Section 7), governing the outflow chemistry close to IRC2, together with some ion-molecule and neutral-neutral processing in the outer outflow, can mimic the large enhancements found in most shock models.

It has been suggested that shocks may be responsible for the large apparent abundance of CI in some molecular clouds (Williams and Hartquist, 1984). The idea is that mantles on grains are removed every $\sim 1(6)$ yr by shocks, and if the mantles are largely atomized by the shocks, large C/CO ratios (~ 0.1) can be maintained. Can the high-velocity outflow in Orion have produced any effect on the C/CO ratio? The recent CI observations of Zmuidzinas *et al.* (1988) establish an upper limit of $C/CO \leq 0.12$ in the high-velocity gas, and thus do not indicate whether C is depleted or enhanced relative to CO, given their results for quiescent clouds (Section 3.5.1).

An overall scenario for the plateau chemistry might be as follows. SiO, OH, and H₂O masers close to IRC2 suggest a typical O-rich CSE chemistry (Section 7). The outflow also liberates refractory elements such as Si, S, P from the smaller grains (this may be unnecessary for S and P). The shock formed where the outflow strikes the dense material at the edge of the partially evacuated cavity surrounding IRC2, produces high abundances of SO, SO₂, HCN, H₂O, etc. Embedded in the outflow are dense clumps containing HDO, H₂CO, HC₃N. The temperature in these clumps may be sufficient to evaporate these species from grains but not to dissociate them, whereas they would be destroyed in the shocked, less dense gas outside the clumps.

6.5. THE HOT CORE

Considerable evidence (Townes *et al.*, 1983; Ziurys and Turner, 1986b) suggests that the hot core is physically close to IRC2, probably encased in the wall of the cavity surrounding IRC2. The small distance, $\sim 7(16)$ cm, and the minimal extinction of the cavity gas, allow IRC2 to vibrationally excite HCN (Ziurys and Turner, 1986b) and radiatively to heat the hot core gas to 150–230 K. Thus the heating mechanism is very different from that of the plateau and gives rise to substantially different chemistry. Two features are similar to the plateau case: (i) simple fully hydrogenated species such as H₂O, HCN, (and also NH₃) are highly overabundant (50–100 times relative to the ridge); (ii) reactive C-species such as C, CN, CS, C₂H, HCO⁺ are underabundant (10–100 times) relative to the ridge. The major differences are: (i) SO, SO₂, SiO are much less abundant in the hot core (they are undetected) than in the plateau; (ii) in addition to HCN, several complex, hydrogenated N-species (CH₃CN, HC₃N, EtCN, HNCO, VyCN) are 10 to 500 times more abundant in the hot core than in the ambient ridge or plateau. Interferometer maps show that HDO, HC₃N, and EtCN peak precisely with the hot core center, 2" southeast of IRC2.

Primarily because of its proximity to the heating source IRc2, and because of its lack of SiO and H₂S (species which require high temperatures to form), the hot core has been regarded for some time as the 'classic' case of gentle evaporation of icy grain mantles, particularly since the species first recognized as being highly abundant (NH₃, HDO, HCN) are just those expected to be prominent in icy mantles. The observed temperature of the hot core (150–300 K) is ideal to evaporate H₂O and NH₃ from mantles, while not destroying the more refractory grain cores which contain Si. Apparently the hot core temperature is insufficient to release S, P to the gas phase. Temperatures of 150–300 K would also enhance the gas phase abundance of HCN and decrease that of CS (as observed) by the reactions $\text{CN} + \text{H}_2 \rightarrow \text{HCN} + \text{H}$ and $\text{CS} + \text{O} \rightarrow \text{CO} + \text{S}$, while insufficient S resides in CS to subsequently form much SO, SO₂, H₂S. As is the case for the Southern Condensation, the HDO in the hot core is fossilized from the earlier cooler environment. Since no shocks process hot core material, the HDO in this case is a measure of the H₂O abundance, estimated at $\geq 1(-4)$, or containing 15% of the total oxygen. Blake *et al.* (1987) have compared the hot core abundances with those expected in models of icy grain mantles (Tielens and Hagen, 1982). If most of the C and N adsorbed onto grains is molecular, then CO₂ is predicted to contain most of the total C and O. If a significant atomic population initially resides on grains, H₂O, NH₃, CH₄ should dominate. The large observed H₂O and NH₃ abundances favor the latter case, and also indicate a high efficiency of hydrogenation on grain surfaces.

Based on the ion-molecule picture (Section 6.1), the lack of complex O-species in the hot core, such as occur in the Southern Condensation, may be explained by a significantly smaller abundance of H₂O in the hot core, since shocks do not assist in its production. Alternatively, the radiative association reactions needed to form the complex O-rich species may be inoperative at the higher densities (which reduce ion abundances) or higher temperatures (which reduce rate coefficients) that characterize the hot core. An important species to test ion-molecule vs grain processes is CH₃OH, which can be formed efficiently either on grains (Section 4.3) or by the reaction $\text{CH}_3^+ + \text{H}_2\text{O}$, which is the favored mechanism in the Southern Condensation. Recent interferometer maps of HDO (Plambeck and Wright, 1987) and of CH₃OH (Plambeck and Wright, 1988) indicate high abundances of both species in both the Southern Condensation and the hot core. Importantly, these maps show a rather poor spatial correlation between CH₃OH and HDO. Since HDO almost certainly originates on the grains, one concludes that CH₃OH may not. The tendency for CH₃OH to peak farther from IRc2 (to the southwest) than HDO might be because CH₃OH evaporates at a lower temperature (~ 70 K) than HDO (~ 90 K), but this argument is countered by the fact that NH₃ evaporates at even lower temperatures (~ 60 K) but is observed very close to IRc2 (Genzel *et al.*, 1982). The argument also assumes that each species evaporates at its own sublimation temperature even though the grain mantles are 'dirty ice' mixtures. More likely, the evaporation of the more volatile NH₃ and CH₃OH are inhibited by being trapped by the dominant H₂O, and only when H₂O evaporates does it also release the other species, much as envisaged for Comet Halley (A'Hearn *et al.*, 1987). Thus the data tend to argue in favor of the ion-molecule scheme of Blake *et al.* (1987) for

producing CH_3OH ; such processes would increase in efficiency away from IRC2 because of decreasing temperature and increasing abundance of ions. Since CH_3OH abundances cannot be reliably estimated from the single transition observed interferometrically, it is unclear whether these results are consistent or not with the abundance of CH_3OH expected in icy grain mantles.

The large abundance of complex N-species in the hot core might be expected from grain processes, especially because the observed species are fully hydrogenated (Sections 4.3 and 4.8.2), but also because ion-molecule processes such as $\text{HC}_3\text{NH}^+ + \text{H}_2 \rightarrow \text{C}_2\text{H}_3\text{CN}^+ + \text{H}$ and $\text{C}_2\text{H}_3\text{CN}^+ + \text{H}_2 \rightarrow \text{C}_2\text{H}_4\text{CN}^+ + \text{H}$ (to form VyCN) are highly endothermic (Herbst *et al.*, 1983). Even HC_3N has problems in ion-molecule schemes (Section 3.5.2). On the other hand, the hydrogenation of HC_3N to form $\text{H}_3\text{C}_3\text{N}$ (VyCN) and $\text{H}_5\text{C}_3\text{N}$ (EtCN) could in principle proceed efficiently on grains, especially since there is no rearrangement of the CCCN skeleton. Blake *et al.* (1987) argue that the observed ratios of $\text{HC}_3\text{N}/\text{VyCN}$ and $\text{HC}_3\text{N}/\text{EtCN}$ in the hot core and in the ambient ridge cloud suggest that the hydrogenation process tends to saturate any HC_3N adsorbed onto grains with a conversion efficiency of 25–75%. Note, however, that such a loss process for HC_3N exacerbates the cyanopolyne problem as discussed in Section 3.5.2. A more fundamental problem with this scheme is that VyCN has been detected in the cold cloud TMC-1 (Irvine, 1987). Since there are no heating sources in TMC-1 to evaporate grain mantles, VyCN must have been formed by gas phase processes at least in TMC-1. As for HC_3N itself, although there are problems with its formation in gas phase (Section 3.5.2), it is even more difficult to see how it could form on grains, since it is so highly unsaturated. (A grain reaction between adsorbed C_2H and CN might be the most likely pathway, but nearly every CN should form HCN .) Recent interferometric maps of HC_3N (Masson and Mundy, 1988; Plambeck and Wright, 1988) show a strong concentration spatially coincident with HDO within $2''$ of IRC2, but also weaker emission coincident with the position and velocities of the plateau source, as earlier seen by Goldsmith *et al.* (1982). The hot core source of HC_3N must lie very close to IRC2 to explain the observed vibrationally excited HC_3N , similar to that observed in HCN . The plateau HC_3N gas, at higher velocities, is not centered on IRC2 and, therefore, must be being swept up from the hot core by the high velocity flow (it is unlikely that the plateau HC_3N is formed within the high velocity flow).

With the exception of HDO , NH_3 , and HCN , it is not possible to decide on chemical grounds whether the species that are clearly associated with the hot core are formed on grains or in the gas. Other clues may help. Plambeck and Wright (1987) estimate that most of the hot core HDO has evaporated from the grains within the last 1(3)–1(4) yr, the estimated age of the outflow. Any species released from grains into the now warm gas will survive only $\sim 1(3)$ yr before being destroyed by gas phase reactions. Since this is comparable with the outflow age, such species could still be overabundant. Brown *et al.* (1988) have modelled the Orion hot core in terms of the collapse of a cold clump to a density of $1(7) \text{ cm}^{-3}$, requiring a free fall time of $\sim 1(6)$ yr so that the gas phase chemistry does not reach steady state; thus some atomic C, N, O are available, and their accretion onto grains, followed by processing (hydrogenation) also occur rapidly during

the collapse. No other grain reactions are considered. Except for H_2O , CH_4 , NH_3 , the grains serve in the model only as repositories although this does affect the predicted gas phase abundances. Good agreement is achieved with observations where relevant, including the species HC_3N , CH_3OH , and CH_3CN (more complex species are not considered). The exception is NH_3 , for which the model produces 10 to 100 times more than observed. If the hot core H_2O abundance is $\geq 5(-5)$ (Blake *et al.*, 1987), then the model also overproduces H_2O , by ~ 10 times. Insofar as the model represents the gas phase quite realistically, one might conclude that gas phase chemistry (in the presence of passive grain accretion) explains hot core abundances well, and that grain processing, as distinct from storage, has played little role.

6.6. SUMMARY

An enormous variety of species are observable in Orion, as a result of its proximity. Only SgrB2 exhibits a comparable number. Only in Orion, however, can the many physical processes at work be isolated and correlated with the resultant chemistry. Not all of the causes and effects are unambiguous, but progress is continually being made, particularly on the observational front, and it is clear that Orion will remain the test source upon which much of our knowledge of interstellar chemistry is based. Thus it is useful to conclude our discussion with a summary (Table III) of the apparent roles of each of the chemistries among the various regions of the Orion star forming core.

TABLE III
Chemistries within the Orion core^a

Region	Ion-mol.	Shock	Grains	
			Storage only	Processing
Ambient ridge	✓	-	-	-
Southern condensation	✓	✓ (excess H_2O)	✓ (HDO)	-
Plateau:				
sulfur	✓	✓ (H_2S)	-	-
silicon	?	✓ (sputter grains)	-	-
phosphorus	✓	?	-	-
other	✓	-	✓ (HDO)	-
Hot core	✓	-	✓ (HDO, NH_2D)	×

^a '✓' (explains observed species); '-' (not applicable or not testable); '×' (fails to explain observed species).

The designations we have assigned may well change with further understanding. The deuterated species in the hot core offer the only compelling argument at present for *any* role of the grains in affecting observed species, and the prospects of grain processing remain uncertain at best. Shocks may be less dominant in Orion core chemistry than generally believed; they are certainly needed to return *highly* refractory elements (Si) to

the gas, but could have little other effect. Gas phase ('ion-molecule') processes seem to dominate, just as in cold clouds. In the case of Orion they demonstrate the quite different products that result from O- and C-rich environments; the cooler, spatially extended outer regions contain most of the C-rich species, while the energetic star forming core disrupts grain mantles, restoring the cosmic O/C > 1 ratio, and producing O-rich species in abundance.

7. The Chemistry of Circumstellar Envelopes

Because the inner regions of CSEs are hot (~ 1000 K) and dense ($n > 1(10) \text{ cm}^{-3}$), activation energy barriers are overcome and 3-body collisions can occur. Molecules thus form under conditions of thermochemical equilibrium (TE). The expansion of the inner shell to its outer edges is rapid enough (1(4) yr for IRC 10216) that the 'equilibrium' abundances in the inner shell have traditionally been thought to be 'frozen in' throughout the shell. That is, on the time-scale of shell expansion chemical reactions cannot occur quickly enough to alter significantly the abundances established in the inner regions before the molecules arrive at the shell edge. TE is thought to prevail near the photosphere, where $n \sim 1(15) \text{ cm}^{-3}$, and 'freeze-out' is taken to occur at $n < 1(10) \text{ cm}^{-3}$. At this point, grains are believed to start forming as well, so the possibility of adsorption of gas phase molecules onto grains must be considered. The products of the freeze-out will be primarily stable species, not radicals or ions. Finally, interstellar UV photons will penetrate the outer envelope, where photodestruction will occur. Both radicals and ions will result. Thus ion-molecule chemistry comes into play. Although all of the chemistries we have discussed are relevant to CSEs (there is even evidence for shocks in many cases), one hopes that CSEs may serve as the best test objects for models of astrochemistry, because of their simple structures (some of the most-studied objects are reasonably spherical and uniform) and well defined physical conditions. In addition, CSEs are a major source of element enrichment and of dust grains in the ISM, returning enriched material at a large enough rate ($\sim 1 M_{\odot} \text{ yr}^{-1}$) to insure a major role in galactic chemical evolution. Thus it is important to understand the chemistry of both their dust and gas. Since this chemistry is very different in C- and O-rich CSEs, we consider them separately.

7.1. C-RICH CSEs

Most of what is known of these objects results from studies of IRC10216, which is unusually nearby (~ 200 pc) and has unusually large mass loss rate ($2(-5) M_{\odot} \text{ yr}^{-1}$), hence, a large, dense envelope. The list of molecules currently detected in this object numbers 36 (Table I). There are several noteworthy properties of this list. First, the 12 species seen *only* in CSEs fall into two groups: (i) those observable only in absorption in the IR (they have no permanent dipole moment) and thus unobservable in the ISM because of lack of suitable continuum sources; most of these are undoubtedly highly abundant in the ISM also; (ii) those containing highly refractory elements (Si, Na, Al, K); these argue strongly for TE chemistry at high T . Second, the complex hydrocarbons

C_nH and cyanopolyynes HC_nN , so notable in cold ISM clouds, are also highly abundant in IRC 10216. Third, no ions have yet been observed. Fourth, with the exception of the C_nH and HC_nN families, most molecules are relatively simple. Only CH_3CN and $VyCN$ approach the complexity of interstellar species.

Glassgold and Huggins (1986) have reviewed the observed abundances of molecular species in IRC 10216, and the uncertainties for some species can be a factor of 10. Nevertheless, some specifics about the chemistry can be inferred immediately: (i) the oxygen (i.e., CO) abundance is approximately solar; (ii) HCN is strongly enhanced, by a factor 100–1000, over interstellar clouds; (iii) unobserved O-species are apparently underabundant but their limits are not much smaller than their observed levels in interstellar clouds; (iv) HNC/HCN is lower than seen in any interstellar clouds; (v) if Si and S are mostly in the observed Si- and S-molecules, then both Si and S must be highly depleted (> 95%); (vi) the highly abundant radicals CN, C_2H , C_3N , C_4H argue strongly against a simple freeze-out formation in the inner envelope as their source.

7.1.1. Thermochemical Equilibrium Chemistry

All TE models predict that hydrogen is almost entirely converted to H_2 by 3-body reactions as long as $n > 1(11) \text{ cm}^{-3}$ and the photosphere temperature is $< 2500 \text{ K}$ (Glassgold and Huggins, 1983). These conditions are expected for most late-type giants, and in fact HI is generally undetected in CSEs (Knapp, 1987). Abundances of all other molecules are predicted to depend critically on the C/O ratio. If $C/O > 1$ (C-rich), essentially all available O is tied up in CO, and the remaining C is mostly in HCN and C_2H_2 . If $C/O < 1$ (O-rich), all available C is in CO, and the remaining O is in the form H_2O . N_2 is the dominant form of nitrogen in either case.

TE models for C-rich CSEs have been performed by Tsugi (1973, 1987), McCabe *et al.* (1979), and Lafont *et al.* (1982). In comparing these models with observations, several problems with simple freeze-out must be kept in mind. First, most models use a single freeze-out location for all species, whereas less reactive species (H_2 , CO) will tend to freeze out close to the inner envelope, while more reactive species (radicals) may not become 'frozen' until well out in the shell. Also, some molecules may be heavily adsorbed onto grains, a process which models have not yet generally included. The most extensive models (McCabe *et al.*, 1979; Lafont *et al.*, 1982) agree quite well with each other. Without accounting for either adsorption onto grains, or photochemistry, a comparison with observations of models with $T \sim 1200 \text{ K}$ and $C/O = 2$ can be summarized as follows:

- (1) Simplest C, N, O species and hydrocarbons: (i) models work well for CO and HCN; (ii) models fail for C_2H_2 (predicted 10 times too high) and for NH_3 and CH_4 (predicted 10 times too low).
- (2) S and Si species: (i) CS is predicted somewhat too low; (ii) SiO, SiS are predicted too large by factors of ~ 20 .
- (3) P species: all P should be in the form HCP, which is not observed
- (4) Complex C species: (i) HC_3N is predicted at least 10 times too low; (ii) HC_5N is predicted 6 orders of magnitude too low.

(5) Radicals: all radicals are predicted too low by large factors, CN and C₂H being the worst cases.

The Si problem strongly suggests grain adsorption, although the model of McCabe *et al.*, performed with and without graphite formation, agrees *less* well with observations for most other species if graphite grain formation (acting to deplete carbon) is allowed.

The recent detection of the highly refractory species NaCl, KCl, AlCl, and AlF in IRC 10216 (Cernicharo and Guelin, 1987) provides the best evidence of TE chemistry in the inner cores of CSEs. Such low abundance elements as Na and Cl can combine to form appreciable quantities of species like NaCl only because NaCl is one of the most stable Cl molecules. Compounds with high dissociation energies are strongly favored in TE chemistry, but not in the other astrochemistries. These metallic compounds seem restricted to the inner 15 arc sec (4(16) cm) of the CSE, in which case the fractional abundance of NaCl is $\sim 1(-10)$ assuming a column depth for H₂ of 6(22) cm⁻² (Keady and Hinkle, 1988). If, however, these species are confined to the inner acceleration zone of radius $\sim 1(15)$ cm (as seems true for vibrationally excited SiS), then the abundances must be revised upward by a factor of 40. Even this value seems well below the value of 1(-7) predicted by Tsugi (1973) for O-rich CSEs, and probably applicable to C-rich CSEs as well. For the other metal compounds, the observed (and predicted) abundances are KCl: (3(-11)/5(-8)); AlCl: (3(-9)/1(-8)); and AlF: (7(-10)/6(-8)). For all of these except possibly AlCl, condensation onto grains at a radius of $\leq 4(16)$ cm ($T_{gr} \geq 100$ K) is indicated. The column densities of these species seem to be 2 to 3 orders of magnitude smaller than those of SiO and SiS when compared to values of the latter species deduced for the outer envelope.

Only one other molecular species seems to be directly observed in the innermost envelope: SiS via its vibrationally excited states (Turner, 1987c). As with the metallic compounds, the narrow observed linewidths of this form of SiS indicate its confinement to the inner acceleration zone of the envelope, where its abundance is estimated at $> 7(-7)$. The predicted abundance is 36 times higher (Tsugi, 1987). Also, SiS/CS > 20 is found for the inner core; the predicted value is 1(5). The SiS abundance is, however, found to decrease by at least 3 times outside the acceleration zone, which has a radius of only 1(15) cm. Again, loss of the Si species onto grains is suggested. An observed ratio SiS/(metal species) ~ 6 to 600 is deduced if both SiS and metal compounds coexist in the inner acceleration zone, while the predicted ratios range from 200 to 2500. Within large uncertainties, Si and metal compounds all seem to be satisfactorily explained by TE formation, and to be severely depleted onto grains, by roughly similar factors, by the time they have reached a distance of only $\sim 1(15)$ cm (8 stellar radii) from the central star, where the grain temperature is ~ 750 K (Keady *et al.*, 1988).

Recent TE calculations by Tsugi (1988) for phosphorus species in a C-rich environment predict that all P should be in the form of HCP, whose fractional abundance should then be 3(-7). Such an abundance should be detectable in IRC 10216 unless concentrated within a very small region, for which observational beam dilution becomes excessive. A recent search for HCP (Turner *et al.*, 1989) was unsuccessful to an abundance limit of 2(-7) if HCP is confined to a region of 15" size, or to a much less

sensitive limit if the HCP is confined to the inner acceleration zone of size $0.4''$. Since the condensation temperature of P is 1300 K, just below that of Si (1340 K), sufficient P should survive in the gas phase to form molecules, but detection of any species capable of testing predictions appears difficult.

The accepted conclusion at present is that TE accounts for the production of the heavy refractories (allowing for grain depletion), and of a few of the most strongly bound species with the largest abundances (CO, HCN, C_2H_2) and possibly a few others (Lafont *et al.*, 1982).

7.1.2. Grains

In C-rich CSEs, grains are usually believed to consist mainly of graphite and SiC (with condensation temperatures as high as 2000 K and 1670 K, respectively: Gilman, 1969). Detailed models of the IR continuum spectral distribution of IRC10216 (Sutton *et al.*, 1979) find that the dust cannot have an inner radius less than $5 R_*$. This value is also obtained by Ridgway and Keady (1988). At this radius the equilibrium temperature of graphite grains would be ~ 1000 K, well below the condensation temperature. Possibly, carbon condenses out in amorphous form, although this seems to require lower, not higher temperatures and pressures (Clegg, 1980). Current models (Ridgway and Keady, 1988) assume this to be the major grain constituent. The possibility that carbon condenses as SiC would explain the underabundance of the Si compounds including that of SiS observed at $r < 8 R_*$. Although the $11.2 \mu\text{m}$ signature of SiC suggests that it is only a minor grain constituent, it could certainly lock up most of the Si. Thus the current view is that SiC grains could form before graphite grains and that graphite forms further out than expected. McCabe *et al.* (1979) find that SiC condenses out before C if $C/O \leq 1.1$, although they are not able to explain good agreement with observed molecular abundances in general when C/O is this low. It seems possible that SiC grains deplete Si, and that freeze-out occurs before carbon grains form.

An important question for the chemistry of the CSE as a whole is whether adsorption of molecular species onto grains is important throughout the outer envelope. Indications (Section 7.1.1) are that significant depletion ($\sim 97\%$ in the case of SiS, higher for the metallic compounds) already occurs in the innermost core of IRC 10216. The derived total mass loss rate of SiO is estimated by Morris *et al.* (1979) at $4(-11) M_\odot \text{yr}^{-1}$; taking into account that $\text{SiS}/\text{SiO} \sim 4$ and contributions from other species (SiC_2 , SiH) observed or calculated to have abundances comparable to that of SiO in C-rich envelopes, the total mass loss rate in Si molecules is $\sim 4(-10) M_\odot \text{yr}^{-1}$. Since the total mass loss rate is $2(-5) M_\odot \text{yr}^{-1}$, a net depletion of 98.5% of the Si over the cosmic abundance is deduced. Taken literally, these values imply some additional adsorption (from 3% to 1.5%) in the outer envelope, but this is clearly very uncertain, and in any case cannot be considered representative for more volatile species. Recent interferometer maps of SiO and SiS (Likkell *et al.*, 1987; see also Biegging, 1988) show these species to be spatially extended but to have abundances 100 times lower than TE predictions. The SiS abundance seems roughly independent of radius, with a possible enhancement (factor of ~ 5) at $r = 3(16)$ cm. A large initial depletion of Si onto grains at $r < 1(15)$ cm is indicated, with a possible formation of SiS in the outer envelope.

The recent discovery of C_3 in IRC 10216 (Hinkle *et al.*, 1988) has raised the possibility that grains may consist at least partly of large carbon clusters similar in some respects to PAHs. These clusters would condense near the stellar photosphere and be eventually photodissociated in the outermost envelope. Other such species (C_4 , C_5 , ...) would have to be formed also. A difficulty is that the C_3 excitation implies its occurrence deep enough in the envelope to preclude penetration of dissociating photons. Alternatively, C_3 could be formed on carbon-rich grains, possibly by catalytic reactions as is thought to be the case for NH_3 , CH_4 , SiH_4 . Hinkle *et al.* estimate that the observed C_3 abundance would constitute 0.1% of the grain mass on such a picture. (A small fraction of C_3 would arise from photodissociation of C_3H .)

A general assessment of the condensation of molecules onto grains can be made in terms of their binding energies and the grain temperature, which govern rates of evaporation, and flow velocities, which govern rates of grain encounter and, hence, adsorption. In this way Jura and Morris (1985) find that species such as H_2 , N_2 , CO , CH_4 , H_2S , C_2H_2 , HCN , NH_3 will not be appreciably depleted for a wide range of assumptions. H_2O may be noticeably condensed, and heavier species such as SiO will require sticking probabilities < 0.2 in order not to be depleted well below the observed level. Such estimates are useful in assessing the chemistry of the outer envelope (Section 7.1.3) but may be misleading owing to the necessary but severe assumptions about grain-molecule interactions. For example, there is observational evidence that the abundance of C_2H_2 decreases by a factor of 5 from $\sim 100 R_*$ to $\sim 1000 R_*$, perhaps by accretion onto grains (Keady and Hinkle, 1988).

7.1.3. Chemistry of the Outer Envelope

Several failures of TE have been noted, all of which point to the importance of non-equilibrium gas phase (or possible grain surface) chemistry in the IRC 10216 envelope. The most obvious of these are (i) the existence of large abundances of complex organic species: (a) long-chain carbon species (HC_nN with odd n up to 11; C_nH with n up to 6); (b) organic rings (C_3H_2 , SiC_2); (ii) an NH_3 abundance much greater than TE predictions. In addition, the ratios of radicals to parent molecules (i.e., CN/HCN , C_2H/C_2H_2 , C_3N/HC_3N , etc.) are much larger than expected on the basis of TE and suggest that the radicals are made by some process directly from their parents.

As the highly abundant TE species CO , C_2H_2 , HCN , and others flow out through the envelope, neutral gas phase reactions, and perhaps dust grain reactions, become important. Eventually the gas becomes exposed to ionizing sources (interstellar UV, cosmic rays). Because these sources of ionization are external to the CSE, species which depend on ion-molecule processes may be expected to peak in the outer envelope and hence to exhibit a shell structure. Interferometric observations of IRC 10216 show that this is indeed the case, for HNC , C_2H , and HC_3N (Bieging and Rieu, 1988b). The UV field will also sharply limit the radial extent of certain species such as HCN (Bieging *et al.*, 1984), as well as explaining the large radial extent of other photodissociation products such as CN and C_2H (Wootten *et al.*, 1982b; Huggins *et al.*, 1984).

Grain surface chemistry may well be important also in the outer envelope, but the

densities and temperatures of the outer regions ($r > 1000 R_*$) are similar to those in warm interstellar molecular clouds, and thus gas phase reactions have been emphasized in outer envelope studies. Notwithstanding the lack of ions, the array of observed molecules in the outer envelope seems even more suggestive of gas phase chemistry than in interstellar clouds, as it lacks heavily hydrogenated species except for simple ones.

Ion-molecule models for IRC 10216, while based on the same reaction schemes as for interstellar clouds, start with significantly different 'inputs'. High-fractional abundances of CO (3–4(–4)), C_2H_2 (2–3(–5)), and HCN (6(–6)), and similarly large abundances for N_2 , NH_3 , CH_4 , supplied by the inner envelope TE chemistry, have been adopted by all detailed models to date (Glassgold *et al.*, 1986, 1987; Nejad and Millar, 1987). Under these input conditions, quite different reactions are dominant in the CSE case than in the interstellar case. In Figure 9 we show the scheme (slightly modified from Glassgold *et al.*, 1986) used in all these models. The central role of the highly abundant

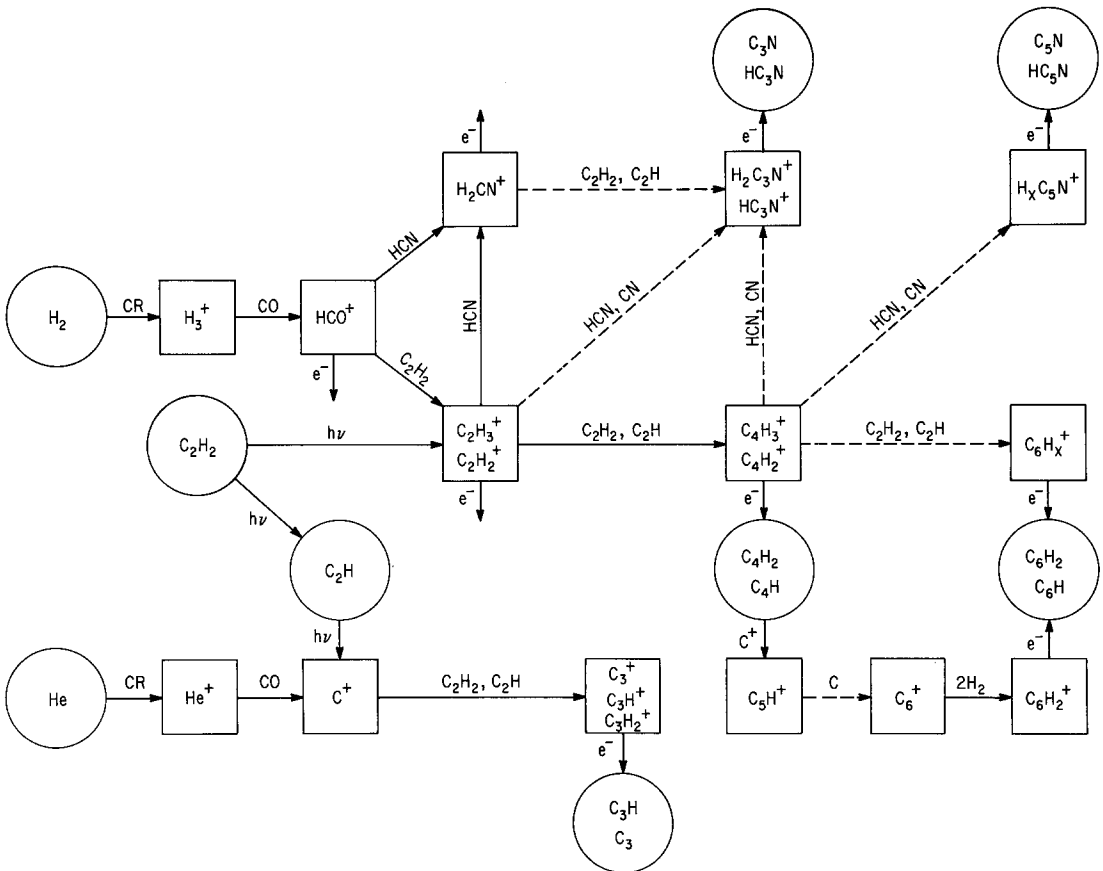


Fig. 9. Reaction scheme for the chemistry of the outer envelopes of C-rich CSEs. Taken from Glassgold *et al.* (1986) with slight modification. The reaction $HCNH^+ + C_2H_2 \rightarrow H_2C_3N^+$ has been retained despite its low rate (Section 3.5.2.; Turner *et al.*, 1988a) because of the high C_2H_2 abundance of IRC 10216.

C_2H_2 and HCN is obvious, these species being > 100 times more abundant than in interstellar clouds (TMC-1). The rather different role of cosmic-ray and UV upon the ion-molecule products is noted also. Cosmic-ray processes alone seem clearly able to produce molecular ions with at least four, and probably six, carbon atoms. However, although many of the steps in producing these species are uncertain, Glassgold *et al.* (1986) estimate that only a small fraction (~ 0.1) of the observed species with ≥ 4 carbon atoms can be produced by *cr*-initiated processes involving H_2 , assuming a standard *cr* ionization rate and reasonable photodissociation rates. The He/*cr* branch, by contrast, can produce the observed abundance of C_3H but not of C_3 , which is 60 times more abundant. By contrast, processes initiated by the photoionization of C_2H_2 are able to produce the observed quantities of most species containing 3, 4, and 6 C atoms, including the highly abundant C_3 species, which indicates that the photoionization sequence $C_2H_2 \rightarrow C_2H \rightarrow C_2 \rightarrow C \rightarrow C^+$ is highly efficient. In fact, the photoionization processes seem to overpredict the complex C species (with the notable exception of the HC_nN family) unless the abundance of C_2H_2 is $\leq 1(-5)$, about 5 times lower than the most recent determinations (Keady and Hinkle, 1988). However, the discrepancy does not exceed one order of magnitude, which is within the uncertainties of the model. The overall success in abundance predictions of the scheme shown in Figure 9 seems to indicate that adsorption onto grains of volatile species in the outer envelope is not likely of great importance, with one important exception: C_2H_2 , the basic species of most of the chemistry. Recent observations of C_2H and C_2H_2 by Keady and Hinkle (1988) show that the C_2H is concentrated at $\sim 1200 R_*$ (8(16) cm) from the star, so that a photospheric or TE origin is unlikely. The C_2H_2 abundance averaged over 14 to $100 R_*$ is 5(-5), and is shown to produce ~ 10 times higher peak abundance of C_2H by photodissociation than is observed. Thus the C_2H_2 abundance must decrease by a factor ~ 10 from $100 R_*$ to the radius where photodissociation begins, $\sim 1000 R_*$. Depletion onto grains seems most likely. A reduction of the C_2H_2 abundance by such a factor will bring into better agreement the predicted and observed abundances of most other species, with the glaring exception of the HC_nN family, which if actually produced in the photodissociation zone, will now be predicted more than 100 times lower than observed.

Several other molecular observations of IRC 10216 serve to test the model in other ways, and to provide insight into the envelope structure as well.

(1) *Ion abundances*: The only molecular ion of significant predicted abundance which is accessible to current observational techniques is HCO^+ ; it is produced by the *cr* reaction chain. Its abundance depends on the mass loss rate, the *cr* ionization rate, and the CO/C_2H_2 abundance ratio. Upper limits for the observed HCO^+ abundance are within the predicted model range, and constrain the mass loss rate to $\leq 4(-5) M_\odot \text{ yr}^{-1}$, the *cr* ionization rate to $\leq 5(-18) \text{ s}^{-1}$ (with some uncertainty), and the C_2H_2 abundance to $\geq 3(-5)$. Changes in each of these limits can to some extent be compensated by changes in the others; the C_2H_2 abundance now seems fairly well established observationally.

(2) *Outer radii and shell structure*: It is a fundamental prediction of TE plus ion-molecule models of CSEs that species which are formed by ion-molecule processes and

destroyed by photodissociation will exhibit a shell structure, with peak abundances at radii of typically 1(17) cm. Examples are C_2H , C_2 , C_3H_2 , C_3 , C_3H , HNC, HC_3N , CH_3CN , C_3N . Other species, not formed by ion-molecule reactions, will show a sharp cutoff in their distributions, at $\sim 1(17)$ cm (NH_3 , HCN, C_2H_2 , CH_4). The observations confirm these predictions extremely well. Bieging *et al.* (1984) find a sharp cutoff in HCN emission at $\sim 1(17)$ cm. The models of Glassgold *et al.* (1986, 1987) predict that HCN decreases sharply to 10% its inner abundance, between $r = 7(16)$ and $1(17)$ cm, while CN peaks at $7(16)$ cm. Thus photodissociation models account for the observed size of HCN as well as the product CN species. Recent interferometer maps of C_2H , HNC, HC_3N show a marked shell structure for all three species (Bieging and Rieu, 1988b). The maps of C_2H and HNC clearly show a reduced abundance at $r < 1(16)$ cm and an annular ring with inner and outer half power intensity at $\sim 3(16)$ and $8(16)$ cm. The derived abundances and radial distribution are in good agreement with the models (the model of Nejad and Millar (1987) predicts a radius of peak abundance for HNC ~ 3 times larger than that of Glassgold *et al.*, and 3 times larger than observed, giving some idea of the uncertainty in the models themselves). Both models predict the peak radius of C_2H well, but underestimate the peak abundance by a factor of 2 to 5. The overall good agreement between observations and models indicates that (i) C_2H is solely a photodissociation product of C_2H_2 and is produced only in the outer envelope at radii $> 3(16)$ cm; (ii) HNC is produced also by ion-molecule reactions and not by the freeze-out of TE abundances as earlier suggested (McCabe *et al.*, 1979). Freeze-out would predict $HCN/HNC > 6000$ (Glassgold *et al.*, 1987) whereas ion-molecule processes predict $HCN/HNC \sim 100$ at the peak radius for HNC, consistent with observations. HNC may be formed either from the reaction $HCO^+ + HCN \rightarrow HCNH^+$ or the reaction $C^+ + NH_3 \rightarrow H_2NC^+$, which can form *only* HNC. The observed distribution and abundance of HNC favor the first of these, since HNC does not show a large peak at $1(17)$ cm such as predicted from reaction with NH_3 .

(3) *Central abundances of ion-molecule products and the HC_3N problem*: The distribution of HC_3N is ringlike with peak abundance at $r \sim 3(16)$ cm. It also has a filled center with abundance about half that at the peak. This suggests two pathways for formation of HC_3N . Outside $\sim 2(16)$ cm, where UV photons penetrate, HC_3N is produced by the reaction $C_2H_2^+ + HCN \rightarrow H_2C_3N^+$. Inside $\sim 2(16)$ cm where UV does not penetrate, Glassgold and Mamon (1988) have modelled HC_3N as formed by $HCNH^+ + C_2H_2 \rightarrow H_2C_3N^+$ and report that it produces a substantial abundance further into the envelope. This contribution arises solely from *cr*-initiated ionization, and it would seem doubtful that it can produce the observed quantities of HC_3N deep within the envelope. In fact, as is the case in interstellar clouds (Section 3.5.2), CSE models have great difficulty producing sufficient HC_3N at any radius; the model of Nejad and Millar (1987) produces only 2% of the observed peak HC_3N and $\sim 10\%$ of all HC_3N averaged over the envelope. Glassgold and Mamon (1987) predict HC_3N abundances ~ 5 times too low at the peak. This deficiency is particularly serious given that the models tend to overestimate abundances of most other species. It should be emphasized that the problem is with the HC_nN and C_nN families, not the C_nH species. To explain both the

overall shortfall of HC_3N and the central abundance problem, one must consider the possibility of neutral-neutral reactions for the HC_nN family in general. Lafont *et al.* (1982) point out that reactions with radicals R of the type $R + \text{C}_{2n}\text{H}_2 \rightarrow \text{RC}_{2n}\text{H} + \text{H}$, of possible importance in Titan's atmosphere, may also be relevant to CSE chemistry. Thus HC_3N could be formed via $\text{C}_2\text{H} + \text{HCN} \rightarrow \text{HC}_3\text{N} + \text{H}$ and $\text{CN} + \text{C}_2\text{H}_2 \rightarrow \text{HC}_3\text{N} + \text{H}$. Sufficient C_2H and CN in the inner envelope is a problem unless the star possesses a warm chromosphere, which can produce significant UV emission (cf. Glassgold, 1986). Such a source could easily rival or exceed interstellar dissociation rates and thus have a profound effect upon models. Alternatively, the HC_nN family may actually be formed in the inner envelope in TE. A TE abundance of $\sim 3(-8)$ has been calculated for HC_3N by Lafont *et al.* (1982), assuming $\text{C}/\text{O} = 2$. This is only about twice the abundance predicted by the ion-molecule models, and is thus still well below the observed value. Furthermore, the TE abundance for HC_5N is ~ 6 orders of magnitude below the observed value!

The cyanopolyne problem appears even more fundamental in CSEs than in interstellar clouds. In the latter the problem is resolved if the C abundance is sufficiently high, and the HC_nN family is not after all prominent in very many interstellar clouds. HC_3N seems prominent in all C-rich CSEs. The synthesis of the HC_nN species by ion-molecule reactions may be fundamentally inadequate in CSEs because: (i) the electron fraction must remain small enough to prevent dissociative recombination of the precursor molecular ions, yet in CSEs it is much higher ($\sim 1(-5)$) than in interstellar clouds; (ii) the condensation reactions $\text{HCNH}^+ + \text{C}_2\text{H}_2 \rightarrow \text{H}_2\text{C}_3\text{N}^+$ (and higher order), not essential in interstellar clouds, are required in CSEs, yet have not been demonstrated beyond 4 heavy atoms; (iii) reactions of suitable ions with HCN and other N-species may be less efficient than with hydrocarbons. We are left with the possibility of grain processes. Given the higher temperatures, such processes are more likely than in interstellar clouds. It is worth noting that the total amount of carbon in HC_nN species is $< 1\%$ of the carbon in the grains.

With the exception of the HC_nN problem, and the uncertainty about grain processes, the observed chemistry of IRC 10216 seems quite well explained by a combination of TE, ion-molecule, and photo-chemistry.

7.1.4. How Typical Is IRC 10216?

How typical is IRC 10216 of C-rich GSEs? Surveys have by now detected CO emission in ~ 130 cool CSEs (cf. Zuckerman and Dyck, 1986) about half of which are C-rich even though these stars constitute a small fraction of evolved objects. The significance of this has not been fully evaluated yet. HCN has been seen in ~ 30 objects (Zuckerman, 1987), with an average abundance $\geq 3(-6)$, compared with $\sim 2(-8)$ in the ISM. Obviously the C-rich environment could favor the high CSE abundance via TE processes, but other mechanisms may be at work (Section 7.2). Finally, a few other molecules (HC_3N , CS) have been detected in the half-dozen nearest CSEs and seem generally representative.

Among the few objects observed in quite a number of species are CIT-6 (HCN ,

HC₃N, CS, CN, C₃N, SiS) and AFGL 2688 (HCN, HC₃N, NH₃, HC₇N, CS, C₂H, SiS). These objects are unfortunately much more complex structurally than IRC10216 (which seems to be quite unique in its simplicity), and therefore have contributed little to our understanding of CSE chemistry as yet because of the obvious difficulty of modelling them. AFGL 2688 (the Egg Nebula) is an F-type supergiant with mass loss rate comparable to that of IRC 10216. It has a highly symmetric bipolar nebula with CO present in and well beyond the optical bipolar lobes. NH₃ is concentrated in the optical dark lane which is presumably a dense disk around the central star, perpendicular to the bipolar flow. HCN is also concentrated in the disk, while HC₇N is very extended (Bieging and Rieu, 1988a). Interferometric maps (Ball, 1987) show CS to be distributed along the lobes of the bipolar flow, and to be absent in the dense disk, contrary to expectations. CN, conversely, is extended in the disk direction as is expected if the denser outflow material there shields the gas to greater radii from the interstellar UV. CIT-6 is an extreme late-type carbon star with only ~3% of the mass loss rate of IRC 10216, and is known to be clearly anisotropic with a possible torus seen edge-on. It has undergone dramatic changes of its visible emission recently with evidence of shock emission. Strong HCN masers occur in this object, and it exhibits quite abundant SiO and SiC₂, as well as SiS. This could indicate that depletion onto grains is relatively incomplete, perhaps as a result of shock processes. CN and HCO⁺ are also seen, the latter possibly produced by shocks. Interferometry of CN and CS in CIT-6 (Ball, 1987) show that its structure consists of a resolved bright core (in CS) with irregular extended emission that is broken up into a number of dense clumps with no regular velocity pattern. The mass loss appears clearly to be asymmetric and episodic. The CN distribution is also centrally peaked, not at all as expected if CN is a photochemical product in the outer envelope.

Despite the complexity of these objects, the intensities of their molecular lines relative to CO are quite similar to those in IRC10216. There is no strong evidence for a different chemistry. The tentative detection of CI in AFGL 2688 (Beichman *et al.*, 1983) but not in IRC 10216 or CIT-6 might suggest differences in chemistry (although an excess of C would be expected to associate quickly to C₂). It would be desirable to trace the chemical consequences of a varying C/O ratio from extreme C-rich objects (AFGL 2688?) through S-stars (C/O ~ 1) but at present there is very little data on very few objects. Models will have to include shocks and probably hydromagnetic effects (Bieging and Rieu, 1988a) as well as complex geometry.

7.2. O-RICH STARS

The list of molecules detected in the expanding CSEs of M and S stars is rather limited: OH, H₂O, CO, SiO, H₂S, SO, SO₂, HCO⁺, HCN, HNC, and NH₃. There is no O-rich object equivalent to IRC 10216 in the sense of being nearby and exhibiting a rich O-dominated chemistry. Thus the overall picture of the chemistry in O-rich CSEs is rather incomplete. Of particular disadvantage is the fact that OH, H₂O, and largely SiO are observed only under strong masing conditions, so that they reveal little about the chemistry other than that they are present at sufficient abundances to produce maser

gain. VLBI mapping (e.g., Bowers *et al.*, 1983) and phase-lag measurements (e.g., Herman and Habing, 1981) show that the OH emission arises in a shell of radius $\sim 1(16)$ – $1(17)$ cm. Interior to this, OH would be rapidly converted to H_2O by reaction with H_2 , so that photodissociation of H_2O by external UV is thought to explain the OH distribution. Non-maser SiO is seen in many O-rich CSEs (Knapp and Morris, 1985) where in fact it is much more readily detected than in C-rich objects, consistent with the simplest ideas of the differences of O and C dominated chemistries. SiS is not seen ($\text{SiS}/\text{SiO} < 1$), again as expected on the basis of simple TE freeze-out in an O-rich environment. Si is heavily depleted, $\sim 99\%$, as in C-rich stars. Since such depletion is unlikely in the innermost regions where the SiO masers occur, Si must condense onto grains between $r \sim 1(14)$ and $1(16)$ cm (Zuckerman, 1980), which is consistent with the overall picture determined from observations of the dust. The presence of HCN in large abundances in some O-rich envelopes cannot be understood in terms of freeze-out of TE products, and thus must be produced by other processes (ion-molecule, shocks, photochemistry).

7.2.1. Thermochemical Equilibrium Chemistry

Virtually all carbon is expected to be tied up in CO for O-rich conditions, and all nitrogen is in the form N_2 . The leftover oxygen is mostly in H_2O ($> 80\%$) and SiO ($\sim 18\%$).

Among refractory elements, the calculations of Tsugi (1973, 1987) predict that the major compounds (and the logarithms of their fractional abundances) should be SiO (-4.4), MgOH (-4.8 for $T \leq 700$ K), CaOH (-5.6), AlOH (-5.6), PS (-6.4), NaCl (-6.8), AlCl (-7.2), AlF (-7.2), KCl (-7.3). Thus several compounds are 1 to 2 orders of magnitude more abundant than those (NaCl, AlCl, KCl, AlF) already detected in the C-rich object IRC 10216. Nearly all of the Mg and Ca, and most of the Al are tied up in the hydroxides. A search for CaOH (Turner and Steimle, 1989) in both IRC 10216 and several O-rich CSEs was unsuccessful. In IRC 10216 upper limits for the CaOH abundance are less than those observed for NaCl, KCl, etc., but may be expected in C-rich objects (in lieu of existing calculations) because of the lack of oxygen. The failure to detect CaOH in O-rich objects may be attributed to their generally large distances. A search for PS in CSEs (Ohishi *et al.*, 1988) has also been unsuccessful; PS may be more reactive in the outer envelope than the more refractory compounds. SiS is predicted to be ~ 10 times less abundant than SiO and is consistent with present observations which establish that $\text{SiS}/\text{SiO} < 1$. The presence of strong maser emission from vibrationally excited states of SiO implies a large abundance of gas phase SiO near the stars. Abundances of SiO derived from ground state emission imply abundances of SiO 100 to 1000 times less than the TE predictions. These differences imply that SiO is quickly depleted onto grains, probably just outside the SiO maser zone at $r \leq 1(15)$ cm. The grains are probably silicates, as deduced from the $9.7 \mu\text{m}$ spectral feature (Jones, 1987).

The more abundant volatile species predicted by TE are CO (-3.2), H_2O (-3.5), N_2 (-4.2), and H_2S (-4.8). Thus the detection of H_2S in these objects is not surprising, but observed species such as SO, SO_2 (and OH) must be formed by other processes.

At $T < 600$ K CH_4 becomes highly abundant, since it is then the most stable form of carbon.

Unfortunately the lack of an equivalent 'IRC 10216' among O-rich CSEs appears to be a major handicap in testing O-rich circumstellar chemistry. What few observations exist are consistent with predictions for those species expected to be dominated by TE chemistry (and grain depletion).

7.2.2. Grains

H_2O ice and silicates have been observed via their features at 3, 6, and 11 μm (Soifer *et al.*, 1981). The equal strengths of these features indicate roughly equal masses of O are in H_2O ice and silicate grains. Rather indirect arguments based on mass estimates for the envelope suggest that at $r \sim 2(17)$ cm the H_2O is more or less equally distributed between gas phase and grains. Thus the oxygen content at this radius is probably distributed equally between gas phase OH and H_2O , and silicate and H_2O ice grains. No other grain constituents are suggested by the observations, nor are they expected in appreciable amounts.

7.2.3. Chemistry of the 'Outer' Envelope

The types of chemistry which can occur outside the TE zone are neutral-neutral gas phase reactions among abundant species, where T and n are still quite high, and photochemistry in the outer regions. In the inner shells reactions between closed shell species freeze out quickly because of their high activation energies. Reactions between radicals then dominate, the most important being those involving H such as $\text{XH} + \text{H} \leftrightarrow \text{X} + \text{H}_2$ ($\text{X} = \text{OH}, \text{O}, \text{C}_2\text{H}, \text{CN}, \text{SH}, \text{S}, \text{etc.}$). Thus the system $\text{OH} + \text{H} \leftrightarrow \text{H}_2\text{O} + \text{H}$ is fundamental to the chemistry of O-rich CSEs. Of somewhat lesser importance is $\text{O} + \text{H}_2 \leftrightarrow \text{OH} + \text{H}$. In general all radicals whose binding energy to H exceeds that of H_2 (e.g., CN, C_2H) will have rapidly decreasing abundances as T decreases. On the other hand, the hydrides with low binding energy such as H_2S or NH_3 are rapidly destroyed if H is present. Thus the H/H_2 ratio is critical. Most radical reactions have modest activation energies, so that they freeze out for $T < \text{few } 100$ K. These considerations are of much greater importance in O-rich CSEs because of the large abundance of the reactive radical OH throughout the envelope (no such abundant radical exists in C-rich objects, even in the photodissociated outer envelope). In fact, the production of many species in O-rich shells is dominated by reactions with OH, for two reasons. First, the OH abundance is large, owing to photodissociation of H_2O (either by external interstellar UV or photospheric UV from the central star, which is considerably hotter than C-rich stars). Much OH is formed at a radius $R(\text{OH})$ beyond which the temperature is too low for the reaction $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O}$ to proceed, and photodissociation by the interstellar UV becomes dominant. Second, neutral reactions with OH proceed even in the cooler outer parts of the envelope, owing to the small activation barrier for most OH reactions (except $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O}$). Thus abundances of many other molecules should rise sharply around $R(\text{OH})$ as well as OH itself.

Detailed models based on these principles have been carried out by Scalo and Slavsky

(1980), Clegg *et al.* (1983), and Slavsky and Scalo (1987), who solve the coupled continuity equations for each molecular species travelling outward in a uniform flow. The key parameters in such models are the radii R_1 and R_2 : for $R < R_1$ the abundance of H_2O is controlled by the basic neutral-neutral reaction; the H_2O abundance is then essentially frozen in until R_2 , beyond which the time-scale for photodissociation is smaller than the expansion time-scale R/v .

In addition to OH and H_2O , these models predict large abundances of SO and SO_2 . These arise from $\text{S} + \text{OH} \rightarrow \text{SO} + \text{H}$ and $\text{OH} + \text{SO} \rightarrow \text{SO}_2 + \text{H}$. The latter reaction proceeds rapidly, and the SO_2 abundance remains large far out into the envelope because of its small photodissociation rate. Similarly, CO_2 is formed at abundances comparable to SO_2 by the reaction $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$, but is destroyed by photodissociation more rapidly than SO_2 . Other S-species are formed via $\text{S} + \text{H}_2 \rightarrow \text{SH}$ and $\text{SH} + \text{H}_2 \rightarrow \text{H}_2\text{S} + \text{H}$; since these are highly endothermic, the abundances of SH and H_2S are predicted to be small ($\leq 1(-9)$).

Si chemistry seems unable to proceed beyond the products of TE (SiO). SiO reacts only very slowly with OH (to produce SiO_2). Any Si^+ or Si which might exist close to a hot chromosphere may react with H_2 to form SiH, followed by $\text{S}^+ + \text{SiH} \rightarrow \text{SiS}$.

NH_3 is strictly an inner envelope species in the theory, requiring high temperatures necessary for the series of H-abstraction reactions $\text{N} + \text{H}_2 \rightarrow \text{NH}$, ..., $\text{NH}_2 + \text{H}_2 \rightarrow \text{NH}_3$, all of which have activation barriers. Thus NH_3 is frozen-out deep within the envelope, and its abundance slowly decreases with n as it is dissociated. A similar distribution characterizes H_2S , for the same reasons.

With the exception of H_2S and NH_3 , the other species considered here have spatial distributions similar to that of OH. Most species (OH, SO, SO_2 , SiS, CO_2) peak at $r \sim 1(16)$ cm in typical models, with OH and SO_2 persisting out to $\sim 3(17)$ cm. H_2O , CO, SiO have roughly constant abundances throughout the envelope, with H_2O and SiO cutting off sharply at $\sim 3(16)$ cm. Peak abundances are predicted as: CO, H_2O , OH ($\sim 3(-4)$); SO_2 , CO_2 , SiO, SO ($3(-7)$ – $2(-6)$). The centrally condensed species NH_3 , H_2S have low abundances ($1(-11)$ – $1(-10)$).

7.2.4. Comparison with Observations

We shall not discuss the SiO, OH, and H_2O masers except to remark that abundance estimates for these species are very difficult (see Walmsley, 1987, for a review) and are not inconsistent with the model predictions. VLBI imaging and phase-lag measurements of the OH and H_2O masers locate them in the outer envelope, as predicted. SiO masers are found close to the stellar photosphere, judging from the large excitation required for the vibrationally excited states (e.g., the $v = 3$ level is > 5000 K above ground). VLBI results show that these masers are sometimes a few stellar radii above the photosphere (Lane, 1984), so that they may form just inside the dust condensation region where much of the SiO probably condenses into grains. NH_3 is seen only in the IR (Betz, 1987), establishing its location near the central star, as predicted.

The sulfur compounds are generally observed in accordance with the theory, but there are discrepancies. The most commonly observed O-rich CSE, OH 231.8 + 4.2, as well

as OH 26.5 ± 0.6 , have high abundances of SO_2 and SO commensurate with an undepleted S abundance and in ratio $\text{SO}_2/\text{SO} \gg 1$ that agrees with the models. On the other hand, SO_2 is observed to have much lower abundance (by at least a factor 10) in most other O-rich CSEs examined (Lucas *et al.*, 1986; Guilloteau *et al.*, 1986), suggesting a S-depletion in the gas phase. Such a depletion is puzzling in O-rich systems, however, because S is quite volatile, the grains are warm, and most metals are in oxides or in silicate grains and are unavailable to form the relatively refractory sulfides. There could be problems with the UV radiation field as assumed in the models, but this cannot explain the sharply differing SO_2 abundances in the observed CSEs unless the strength of the UV varies from object to object. An overestimate of the UV field, along with the invocation of shock phenomena in OH 231.8 ± 4.2 (which has a well-known bipolarity and large velocities) is also unsatisfactory, because the warm temperatures that drive the neutral-neutral chemistry in O-rich CSEs are similar in effect to conditions provided by shocks, and are common to all CSEs. The fact that OH 231.8 ± 4.2 is unique in the number of S-species detected (SO, SO_2 , H_2S , CS, OCS (see Morris *et al.*, 1987)) might suggest an 'over-abundance' of sulfur, since H_2S samples a quite different part of the envelope than SO or SO_2 , and since CS and OCS are predicted to have low abundance ($1(-9)$). However, shocks also seem involved, and the total abundance of S-species, dominated by SO_2 , implies that almost all of the S is accounted for if the mass loss rate is $\sim 1(-4) M_\odot \text{yr}^{-1}$.

Thirteen molecular species (5 of them sulfurous) are now known in OH 231.8 ± 4.2 , far more than in any other O-rich envelope. Despite its distance (1300 pc) and the presence of a high velocity bipolar flow ($\pm 140 \text{ km s}^{-1}$) as well as the evident complication of a hot companion star (Cohen *et al.*, 1985), OH 231.8 ± 4.2 serves as the best test object for O-rich CSE chemistry currently available. Molecular spectra consist of two kinematic components (Morris *et al.*, 1987), one with triangular profile $\sim 80 \text{ km s}^{-1}$ wide, presumably arising from the thick equatorial disk; the other a flat-topped profile $\sim 200 \text{ km s}^{-1}$ wide, representing the fast flow.

Nitrogen: With an abundance $> 1(-6)$, NH_3 is more than 100 times as abundant as predicted by TE at 1000 K, and suggests either a lower temperature for TE or more likely an internal source of N atoms (UV, shocks) which could be readily converted to NH_3 in the warm inner layers by successive reactions with H_2 (if H/H_2 is small). HCN is then formed from the abundant NH_3 via $\text{C}^+ + \text{NH}_3 \rightarrow \text{HCNH}^+ + \text{H}$, which also produces HNC. C^+ is photoproduced from CO. The observed abundance of HCN ($4(-7)$) can result if C^+ has abundance $\geq 1(-2)$ in the outer shell, as is predicted even if there is only an external source of UV (Mamon *et al.*, 1987). The presence of HNC with abundance $\text{HNC}/\text{HCN} \leq 0.3$ (typical of interstellar clouds), presumably reflects the branching ratios of the DR of HCNH^+ . Alternatively, even if HCN is somehow formed in the interior of the envelope, its subsequent reaction with HCO^+ or H_3O^+ will produce HCNH^+ and, hence, HNC. An upper limit for CN of $< 2(-7)$ indicates that HCNH^+ forms mostly HCN and HNC; this limit is not sufficient to test Bates' conjecture rigorously (Section 3.4.1).

HCO⁺: arises in the fast outflow where UV radiation is likely enhanced. Thus it is

produced by $C^+ + H_2O \rightarrow HCO^+ + H$ or $C^+ + OH \rightarrow CO^+ + H_2 \rightarrow HCO^+ + H$. Mamon *et al.* (1987) predict an abundance of HCO^+ slightly smaller than observed. The discrepancy is easily explained by an increase in the rate of production of C^+ . The failure to detect N_2H^+ , even though the envelope has been claimed to be nitrogen-rich (Cohen *et al.*, 1985), is then explained by a slow formation via $H_3^+ + N_2$ (H_3^+ is produced only by cosmic rays) and a fast destruction of N_2H^+ by H_2O and CO .

Sulfur: although all observed S-species can be accounted for by assuming a cosmic abundance for S and a mass loss rate $\sim 1(-4) M_\odot \text{ yr}^{-1}$, the question remains whether S itself could be enhanced. The mass of the central star ($\sim 3 M_\odot$) argues against nucleosynthesis past the He-burning stage, so the relative mass of S should not be affected (CNO processing could explain a N-rich envelope). If a nova episode has occurred in the past (Jura and Morris, 1985) and the system has somehow retained the nucleosynthetic products of the nova, then S could very well be enhanced. Observations of sulfur isotope ratios would serve to check this possibility. As for the chemistry, no S-species are seen in the high velocity outflow, even though S itself is not lacking. Presumably the flow is dissociative. Given the observed H_2S , CS might be produced via $C^+ + H_2S \rightarrow HCS^+ + H$. There seems no satisfactory production mechanism for OCS other than shocks.

SiO: Apart from the outer bipolar flow region, the envelope of OH 231.8 + 4.2 is very cold and contains a very high dust content (Jura and Morris, 1985). Thus the condensation of SiO onto grains should be complete. In fact, (non-maser) SiO is observed at an abundance $SiO/Si \sim 1(-3)$, indicating considerable, but not complete condensation. The SiO is observed in both the high-velocity outflow and the narrower disk component. The high-velocity SiO would be subjected to high velocity shocks which could sputter SiO off the grains. High-velocity grain-grain collisions could also occur. Or, the streaming motion of the grains through the gas could inhibit adsorption of SiO if the streaming exceeds $\sim 4 \text{ km s}^{-1}$, the equivalent binding energy of SiO. The first two of these processes are of interest because of the implication that molecules such as SiO could survive an energetic desorption process intact (Section 4.5 and 4.8.3).

Summary: OH 231.8 + 4.2 lacks the large complement of molecular species observed in IRC 10216, and also contains internal ionization sources and high-velocity shocks, so that it is probably not a typical circumstellar environment. These processes seem to promote the reaction chains that produce many of the observed species, so OH 231.8 + 4.2 is a test object for several types of chemistry at once, but a rather ambiguous one. OH 26.5 + 0.6 is probably a similarly energetic object. In more common types of O-rich CSEs, such as OH/IR stars, the ionization is predominantly external and the shocks that may be present are weaker. Unfortunately none of these objects is both nearby and has so large a mass loss rate as IRC 10216. Despite these disadvantages, OH 231.8 + 4.2 seems at least qualitatively to confirm the basic premises of the chemical models, but cannot yet constrain them appreciably. Ultimately, the principle reward for understanding the chemistry of both O- and C-rich CSEs may well be to understand the products ejected into the ISM, in particular the heavy, refractory elements. This requires understanding the interactions of products produced in TE with

grains as they pass through the envelope. Based on only two objects, IRC 10216 and OH 231.8 + 4.2, current observations seem to bear out the predictions of TE in the innermost envelope. However, the interactions of the TE products with grains remain obscure in both types of object.

8. Global Questions in Astrochemistry

As discussed in Section 2, the ISM appears to have reached a state of quasi-equipartition of energy densities. It also appears to be chemically homogeneous on a large scale, although perhaps not on local scales (Section 4.8.1). These properties raise questions about the physical and chemical evolution of the ISM and, hence, the global issues of (i) the origin of interstellar molecules and grains, and which came first; and (ii) how stars (or galaxies) initially formed.

8.1. THE EVOLUTION OF THE ISM

To make progress on the issues just mentioned, one must understand the sources and sinks of the ISM. Jura (1987) has summarized what is known of these at the present time. The principle sink is star formation. Its rate is somewhat uncertain for two reasons. First, the rate of formation of stars with $M < 0.4 M_{\odot}$ is not directly measurable, though it can be estimated quite reliably from models of the Initial Mass Function, and leads to a local rate of $0.01 M_{\odot} \text{ kpc}^{-2} \text{ yr}^{-1}$. Second, this local rate must be extrapolated over the Galaxy. This step is more uncertain, and leads to a total rate of $3\text{--}10 M_{\odot} \text{ yr}^{-1}$.

The sources of interstellar material are:

- (i) AGB stars and planetary nebulae: $0.3\text{--}1 M_{\odot} \text{ yr}^{-1}$;
- (ii) early-type stars: $0.08\text{--}0.5 M_{\odot} \text{ yr}^{-1}$;
- (iii) supernovae: $0.03 M_{\odot} \text{ yr}^{-1}$;
- (iv) novae: $0.003 M_{\odot} \text{ yr}^{-1}$;
- (v) infall of intergalactic gas: $\leq 1.4 M_{\odot} \text{ yr}^{-1}$.

The rates for (i)–(iv) are relatively well established compared with (v) or with the star formation rate. A non-zero infall is suggested by the existence of interstellar deuterium, at an abundance greater than expected from the combined effects of formation by spallation reactions in supernovae, and destruction by processes of astration (the measured D/H ratio of $\sim 2(-5)$ is commonly believed to be the primordial ratio). The infall rate of $1.4 M_{\odot} \text{ yr}^{-1}$ assumes all observed high-velocity HI represents material being accreted by the Galaxy; other arguments suggest the accretion rate could be close to zero.

The first important conclusion is, therefore: the net loss rate of the ISM likely exceeds the net rate of increase. (The only uncertainty in this conclusion is that of the infall rate, because the existence of white dwarfs and other low-mass stars, which represent an evolutionary endpoint, constitutes a deficit of the ISM due to stellar processing alone, at a rate of \sim one white dwarf per year.)

The second important quantity in this discussion is the recycle time of interstellar material through stars. The local rate of return of material to the ISM from evolved

giants is $> 3.5(-10) M_{\odot} \text{ yr}^{-1} \text{ pc}^{-2}$ (Knapp and Morris, 1985). The local gas density, in both HI and H₂, is $\sim 5.3 M_{\odot} \text{ pc}^{-2}$ (Gordon and Burton, 1976). Thus the recycling time for the local ISM is $\leq 1.5(10) \text{ yr}$.

The third important point concerns gas/dust ratios. Knapp (1985) finds mass ratios of 160 : 1 for O-rich stars (assuming silicate grains) and 400 : 1 for C-rich stars (assuming graphite grains) averaged over many mass-losing stars. O-rich stars dominate by number, and the ratio 160 : 1 for these objects is very close to that estimated for the ISM (147 : 1). The similarity of values does not indicate that interstellar grains come from O-rich stars, but only that essentially all the heavy elements are condensed into grains in both O-rich envelopes and in the ISM. (The value 160 : 1 thus merely reflects current cosmic abundances.) An important question is: can heavy elements condense (i.e., nucleate) out of the gas phase in the ISM, do they accrete onto existing grains, or do the interstellar grains indeed originate solely in stellar mass loss. Certainly it is *possible* that all interstellar grains come from O-rich stellar mass loss because (i) at observed ejection velocities, the grains can diffuse throughout the ISM in $\sim 1(8) \text{ yr}$ or $< 1\%$ of the lifetime of the Galaxy; (ii) the total mass of dust in the ISM, $\sim 1(8) M_{\odot}$, will be ejected from evolved stars at the current rate of $\sim 0.006 M_{\odot} \text{ yr}^{-1}$ for the dust in $1(10) \text{ yr}$, approximately the age of the Galaxy. Arguments exist for and against the condensation of refractory elements in the ISM. Field (1974) noted a strong correlation between the condensation temperature of an element and its depletion and, therefore, concluded that the depletions occur mainly within the outflows of mass losing red giants (one might argue that shock heating and compression of grain-less interstellar gas also creates conditions suitable for condensation). Jura (1987) notes that mass loss from early-type stars apparently accounts for $\geq 10\%$ of all matter ejected into the ISM, and that grains cannot form in the fast outflows from these stars. Therefore any element observed to be depleted by more than 90% (i.e., Fe, Ca, Ti) must actually stick to grains in the ISM itself. (The time required for such an atom to find a grain in a 100 K interstellar gas of mean density 1 cm^{-3} is $5(9) \text{ yr}$, or less than the lifetime of the Galaxy.) Other evidence that grain 'processing' of refractories occurs in the ISM includes: (i) the depletion of highly refractory elements like Fe is correlated with cloud density (Jenkins *et al.*, 1986); (ii) P and Fe have nearly the same condensation temperature, but P is much less depleted than Fe (Jura and York, 1978). TE does not appear to govern the depletion of these two elements. We conclude from this discussion that a significant fraction of the depletion of the most refractory elements occurs within the ISM itself, rather than in red giant outflows. These arguments do not indicate that these elements *condense* in the TE sense, only that they are at least accreted onto existing interstellar grains. In the general ISM, about 25% of the available oxygen is depleted, just the amount needed to form silicates such as olivine and enstatite using essentially all the available Si, Mg, Fe, and other refractories. If sticking or even condensation of refractory elements occurs in the ISM, it apparently is able to do so by processes resembling TE. On the other hand, the process of nucleation requires densities of $\geq 1(9) \text{ cm}^{-3}$ while the temperature is less than the typical condensation temperature of 1000–2000 K. While these conditions exist in outflows from red giants, and possibly in clumps or knots in supernova ejecta, they seem difficult to achieve in the ISM, even via shocks.

An analysis of the sources and sinks for interstellar *grains* casts additional light on these questions. Seab (1987) finds that destruction of grains in supernova shocks occurs on a shorter time-scale than any other process including the injection of new grains from red giants and supernova ejecta. The time-scales for the interstellar grain population are $\sim 1.7(8)$ yr for destruction in shocks, $3(9)$ yr for replenishment by condensation in supernova ejecta, and $\sim 1(10)$ yr for replenishment by red giant ejecta. This implies that most of the grain mass in the ISM was formed by accretion (or condensation) in the ISM rather than by thermal condensation in stellar envelopes and supernova ejecta. The direct accretion time for a refractory element onto existing grains is very short, $\sim 5(7)$ yr in a diffuse loud ($n \sim 20 \text{ cm}^{-3}$) and $3(6)$ yr in a dense molecular cloud ($n = 1(3) \text{ cm}^{-3}$). Since depletion is not observed to be complete, the *controlling* accretion time-scale is actually the mixing time for accreted grains to re-enter the more diffuse interstellar regions from dense clouds, where they can return material to the gas phase. This time-scale is $\sim 1(8)$ yr but is poorly known. A suggested lifecycle and evolution of interstellar grains is therefore as follows (cf. Seab, 1987):

(i) Refractory grain cores nucleate in cool stars and supernova ejecta, then mix into the general ISM.

(ii) Grains ejected into the diffuse ISM ($n \leq 20 \text{ cm}^{-3}$) are destroyed by shocks; some fraction of the gas phase refractories make their way to dense clouds. Other grains from cool stars are injected directly into dense clouds.

(iii) Dense clouds re-accrete grain materials into a refractory form probably distinct from the high-temperature condensates from step (i). Small grains coagulate into larger ones.

(iv) Some dense cloud material is mixed back into the diffuse ISM. Go to step (ii).

(v) some dense cloud material forms new stars. Go to step (i).

The cycle time between dense and diffuse interstellar regimes is $\sim 1(8)$ yr. The cycle time back through new star formation is $\sim 1(10)$ yr.

8.2. PRIMORDIAL ASTROCHEMISTRY

The foregoing discussion has indicated that nucleation of refractory grains in the ISM does not occur, and that cool stars are the source of all grains. Yet interstellar chemistry seems to require grains (as a formation mechanism for H_2) and stars (as a source of ionization, either UV or cosmic ray). How did stars, and hence grains, form in the primordial universe without the presence of a chemistry which could alter the cooling mechanisms of the gas and thus permit gravitational instabilities in an expanding universe?

The chemical processes which led to the formation of molecules in the early universe are described by Dalgarno and Lepp (1987). The primordial elements H, D, ^4He , ^3He , ^7Li , ^6Li can enter a chemistry when the radiation temperature of the expanding universe falls below ~ 4000 K, allowing what was a fully-ionized state to become a nearly neutral one by the process $e + \text{H}^+ \rightarrow \text{H} + h\nu$. This is the recombination phase, after which matter and radiation evolve independently. The chemistry begins with the radiative association process $\text{H} + \text{H}^+ \rightarrow \text{H}_2^+ + h\nu$. The presence of He allows several processes:

$\text{H}_2^+ + \text{He} \rightarrow \text{HeH}^+ + \text{H}$ and $\text{H}^+ + \text{He} \rightarrow \text{HeH}^+ + h\nu$. Once photodissociation ceases to be rapid, the reaction $\text{H}_2^+ + \text{H} \rightarrow \text{H}_2 + \text{H}^+$ can occur. A second sequence can also form H_2 ; $\text{H} + e \rightarrow \text{H}^- + h\nu$ followed by $\text{H} + \text{H}^- \rightarrow \text{H}_2 + e$. The HD molecule is formed by an analogous system of reactions, and also by the direct process $\text{H} + \text{D} \rightarrow \text{HD} + h\nu$, which is possible because HD has a permanent dipole moment. Of greater importance is the sequence $\text{H}^+ + \text{D} \rightarrow \text{H} + \text{D}^+$, $\text{D}^+ + \text{H}_2 \rightarrow \text{HD} + \text{H}^+$, which is the main source of HD in diffuse clouds. Finally a Li chemistry occurs via $\text{Li}^+ + \text{H} \rightarrow \text{LiH}^+ + h\nu$, and, less importantly, $\text{Li} + \text{H} \rightarrow \text{LiH} + h\nu$.

Thus the first species were formed in an almost neutral atomic gas of H and He, with fractional ionization $\sim 1(-4)$ and a fractional molecular abundance of $\sim 3(-6)$ with trace amounts of D, Li^+ , HD, and LiH^+ . The importance of these molecules lies in their cooling function. The expanding universe inevitably contained anisotropies with masses exceeding the Jeans mass, which therefore formed collapsing pregalactic clouds. The earliest of these were probably only $\sim 1(6) M_\odot$. Under adiabatic collapse, $T \propto \rho^{2/3}$ and the Jeans mass increases. If the collapse is to continue, the gravitational energy released must be radiated away. The formation of H_2 facilitated this. When densities exceeded $1(9) \text{ cm}^{-3}$, 3-body recombination $\text{H} + \text{H} + \text{H} \rightarrow \text{H}_2 + \text{H}$ converted the remaining hydrogen to H_2 . The temperature then rose slowly until the cloud became optically thick to the cooling radiation, at which time collisionally induced dissociation of H_2 occurred, reducing the cloud to atomic form and briefly cooling it before the temperature rise resumed. Eventually the cloud became ionized, via any of the processes $\text{H} + \text{H} \rightarrow \text{H}^+ + \text{H} + e$, $\text{H} + \text{H} \rightarrow \text{H}^- + \text{H}^+$, or $\text{H} + \text{H} \rightarrow \text{H}_2^+ + e$, and the resultant $L\alpha$ cooling permitted continued collapse. Finally, stars formed (Palla *et al.*, 1983; Villere and Bodenheimer, 1987) over a wide range of masses whose spectrum depended on the nature of the shocks produced from colliding fragments in a turbulent collapsing cloud. Such shocks heat the gas and raise the Jeans mass, leading to massive star formation. Massive stars lead eventually to supernova explosions. Many of the original sub-galactic sized condensations may have terminated in such explosions which then drove blast waves into the surrounding intergalactic medium, producing compressed shells of heated gas in the adjacent intergalactic gas (Ostriker and Cowie, 1981). If these shells cooled sufficiently, the gas could become gravitationally unstable and fragment into additional clouds larger than the original one. This 'amplification' factor (final shell mass/original cloud mass) and the gravitational instability depend on the details of the cooling and on the time available for the expansion. The formation of molecules in the cooling shocked gas may, therefore, have been critical in determining the resulting galactic sizes. These explosions may also have injected heavy elements into the expanding universe. Cooling in the swept-up intergalactic shell may then have been enhanced by the formation of additional molecules by endothermic reactions such as $\text{C}^+ + \text{H}_2 \rightarrow \text{CH}^+ + \text{H}$ and $\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$.

Whether or not these models for the formation of galaxies are valid, it appears likely that grains play a secondary role with respect to molecules in astrochemistry (certainly forming later in the early history of the universe); the first galaxies, which formed at $z \sim 5$, would contain very little if any dust). It also appears certain that molecular processes play a central role in galaxy formation, as they do in star formation.

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