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Interstellar Molecules

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1 Introduction

During the past decade, molecular line astronomy has contributed substantial new information about a variety of long standing astronomical problems such as (i) the distribution of matter within our galaxy and others, (ii) the mass loss associated with old and young stars, (iii) the formation of young stars occuring in dense molecular clouds and, (iv) the determination of isotope ratios as a useful indicator of the past chemical history of the Galaxy. Thus molecular line astronomy has opened several new areas of research and has widened our understanding of the cosmos. The most fascinating of these new research activities certainly seems to be cosmochemistry, the chemistry prevailing in the highly diluted medium of space as compared to terrestrial conditions. This is for the simple reason that we all share a certain curiosity in understanding of (i) how the cosmically most abundant elements H, C, N, O (with the exception of He) bind together under the extreme conditions of interstellar space to form simple and fairly complex molecules and (ii) how these rather recent interstellar results relate to and influence our knowledge of the origin and early history of the solar system.

Although some of the organic interstellar molecules are by far not as complex as biologically important molecules such as deoxyribonucleic acid (DNA) or ribonucleic acid (RNA), which govern the process of reproduction, the most basic property of life, they are however fairly exotic even when compared with present day organic chemistry since not all interstellar molecules have been synthesized in the laboratory. Among the known interstellar molecules, one finds all the smaller molecules or functional groups out of which larger molecules and eventually the biologically complex molecules can form. All the ingredients are produced there in the hostile environment of interstellar space, awaiting conditions which allow the formation of even biologically important molecules. Whether these conditions are ever met by interstellar space seems unlikely, or whether they are only found in atmospheres of certain planets in the close neighbourhood of stars remains an intriguing question.

On the other hand one finds interstellar molecules such as water, H_2O, methyl- or ethylalcohol CH_3OH, CH_3CH_2OH respectively which are well known to us from common day life.

The aim of this article is to give a short outline of current theories of molecule formation and destruction in interstellar clouds, together with a short summary of the observational material which has been accumulated up to early 1981. Although this article will address itself predominantly to simple molecules a section on complex molecules has been added. We will, therefore, discuss some general aspects of cosmochemistry and then turn to molecule formation in diffuse clouds followed by a discussion of the chemistry of dense interstellar clouds. A section has been added to summarize recent observational results and theoretical proposals in understanding the formation of intermediate and complex molecules, an area of considerable current activity. Finally the article closes with a short summary of the molecular species found in planetary atmospheres and a short discussion of what the relation might be to the interstellar molecules.

The subject of molecule formation and destruction has been reviewed by several authors (e.g. Herbst and Klemperer 1976, Watson 1976, Herbst 1978 and Watson 1978). In this cosmochemistry series "Topics in Current Chemistry", Winnewisser, Mezger and Breuer 1974 have given a general review of interstellar molecules, with some consideration of molecule formation mechanisms. Recently Winnewisser, Churchwell and Walmsley 1979 have given a detailed account of the "Astrophysics of Interstellar Molecules" with a chapter specially devoted to molecule formation mechanisms. This article is based on these earlier reviews with emphasis on some of the more recent developments.

We will not mention effects on molecular formation due to shocks and shock fronts in dense molecular clouds, nor will we discuss the chemistry of the circumstellar environment, where an abundance of molecular species has been detected during the past several years. In the warm, dense envelopes of stars the abundances can be matched by chemical-equilibrium calculations, in contrast to the chemical reactions which can take place in the cold interstellar molecular clouds. For example theoretical calculations based on chemical equilibrium have been performed for the expanding molecular envelope of the cool carbon star IRC +10216 by McCabe et al. (1980), in agreement with the observed molecular column-densities.

2 Astrophysical Scenario

Our Galaxy consists of stars and matter which has either not yet participated in the formation of stars or has already been expelled by them, i.e. interstellar matter is probably composed of original material and the "ashes" from the nuclear burning processes returned by stars in their final stages of evolution. This matter constitutes together with the radiation field covering all wavelengths from γ-rays to the metre-wavelength radio background, the interstellar medium. In the Galaxy interstellar matter comprises presently 10% of the total galactic mass which is estimated to be about 1.1×10^{11} $M_{\odot}$, with one solar mass 1 $M_{\odot} \sim 2 \times 10^{33}$ g.

The dawn of the galaxy probably started with its entire mass in the form of hydrogen gas (and possibly helium), 90% of which has since been converted into stars. The remaining mass comprises now the matter between the stars. Interstellar matter proper consists of gas and dust which are heterogeneously dispersed between the stars. It is now known from the observational data that the distribution of interstellar matter on a galactic scale always follows closely that of the stars indicating their intimate connection: stars do form in regions of high concentration of interstellar matter. While stars are concentrated in a thin flat disk about 500 to 600 pc in width (where 1 pc = 1 par sec = 3.26 light years = 3.09×10^{18} cm) and about 40 kpc in diameter, interstellar matter is even more closely confined to the galactic plane. Within the galactic disk interstellar matter is not distributed uniformly, it is very clumpy and patchy giving rise to the interstellar clouds.

The principal constituents of interstellar matter are fine dust particles (with a diameter of several μm) and gas. One therefore believes that the dust-to-gas ratio is about constant throughout the galaxy with the possible exception of the galactic centre. Table 1 which is adopted from Winnewisser et al. (1979) summarizes the various components of interstellar matter and also indicates the methods by which they can be investigated.

With practically no exception, observational data indicate that interstellar dust and gas always appear simultaneously. The extinction of starlight i.e. the combined effect of absorption and scattering at optical wavelength is still the main evidence for the existence of interstellar dust, although observations of infrared emission from heated dust grains near young stars furnish us with independent but strong evidence for its wide distribution. Their chemical composition is presently far from being settled, but there is now strong evidence that silicate and graphite are the main constituents with ice and traces of heavier elements surrounded by envelopes containing carbon nitrogen and oxygen. There are several fine reviews of the physical and chemical properties of interstellar grains (Aanestad and Purcell 1973) and the observational data which pertains to them (Savage and Mathis, 1979). It has however to be noted that although the interstellar dust particles account for only 1% of the interstellar matter, they seem to play a vital but still uncertain role in the formation of interstellar molecules. In fact ever since the first attempts to understand the mechanisms which govern interstellar cloud chemistry, the question has arisen whether molecules are formed through gas-phase reaction sequences or by the alternative process, i.e. formation of molecules on grain surfaces. Although in this review there will be no attempt made to settle this issue, results are described which have some bearing on this question. To assess the intrinsic difficulties encountered in this fundamental issue of molecule formation mechanisms one should bear in mind that the strongest evidence for the importance of grain chemistry is the existence of H_2 the most abundant molecule in space, whereas the existence of HD furnishes us with the strongest evidence for the importance of gas phase chemistry. In addition, interstellar grains are also important because they shield the molecules from dissociation by UV radiation. Thus interstellar dust and gas seem to be connected like the master and his slave, but the question remains which of the two assumes the role of the master.

Table 1 indicates that the interstellar gas consists essentially of two components: the ionized and the neutral form. It is the investigation of the neutral component which is of special interest in an attempt to understand the general process of molecular formation and reactions in interstellar space. One estimates that about 50% of the neutral component is in molecular form, with molecular hydrogen H_2 being the most abundant interstellar molecule followed by carbon monoxide, CO, as has become evident from recent large-scale CO surveys of the Galaxy. Estimates of the galactic mass of H_2 and CO can now be given with reasonably accuracy $M(H_2) = 2 \times 10^9\ M_\odot$, $M(CO) = 2 \times 10^6\ M_\odot$.

Table 1. Interstellar matter (Winnewisser et al., (1979))

Total mass of Interstellar matter		$\sim 5 \times 10^9\ M_\odot$	Probes for investigation
1% dust			Starlight extinction Far IR emission, Polarization
99% gas	3% ionized	(H II, He II, C II, ...)	Recombination lines Nebular emission lines Continuum emission Pulsars
	97% neutral	Atomic (H I, He, ...)	21 cm H line Optical absorption line
		Molecular (H_2, CO, ...)	Molecular lines

Although the average density of the interstellar gas within the Galaxy is about one hydrogen atom per cubic centimetre, it does vary considerably with galactic radius (see for example Winnewisser et al. 1979). However, the gas density is not uniformly distributed on the contrary it shows local concentrations of gas (and dust) with gas densities as high as 10^6 to 10^8 cm^{-3}. It is in these regions of higher than average gas density, called interstellar clouds where many different molecules are currently being found. Although by now a large variety of molecular clouds has been detected in interstellar space, there exists nothing like a standard molecular cloud. However, it has been widely accepted that one can describe the gas component as composed of three different phases: (i) the diffuse interstellar clouds with an average density of about 1 to 100 particles cm^{-3} and a temperature of $\lesssim 100$ K. (ii) the dense molecular clouds (density $\sim 10^3$-10^6 cm^{-3}, all hydrogen is essentially in molecular form) and (iii) a very diluted (< 0.1 particle cm^{-3}) but hot ($10^3\ K \lesssim T \lesssim 10^4\ K$) intercloud medium. Only simple molecules are found in the diffuse interstellar clouds whereas the bulk of the molecular detections pertain to the dense molecular clouds. From the molecular point of view the intercloud medium is of little importance and will not be discussed further.

The dense molecular clouds span a wide scale of physical parameters such as size (1 — 200 pc) density ($10^3 \lesssim n_{H_2} \lesssim 10^8$ cm^{-3}), temperature $5 \lesssim T_{kin} \lesssim 150$ and total masses between $10 \lesssim M_{cloud} \lesssim 10^6\ M_\odot$. Recently Winnewisser et al. 1979 have attempted a cloud classification on the basis of the observed molecular line-widths. This classification is reproduced in Table 2. Since the line-width carries a large amount of intrinsic information about the physical properties of the clouds, from which the lines emanate, this classification also serves as a good indicator of the chemical reaction schemes assumed to prevail in the individual cloud types. Thus we assume that certain reaction schemes are associated with specific types of molecular clouds.

We will therefore consider in the following sections some basic ideas and observations of the chemistry pertaining to diffuse interstellar clouds and cold dark and dense clouds.

3 General Aspects of Interstellar Chemistry

Since the first attempts to cast the subject of interstellar chemistry into quantitative terms by Bates and Spitzer (1951) in understanding the abundance of CH and CH$^+$, there has been considerable discussion about the relative importance of gas phase chemistry versus catalytic processes on interstellar grain surfaces. This issue has remained the great unknown in interstellar chemistry and has assumed new importance by being shifted to the question to which extent both mechanisms contribute to the formation of larger organic molecules. Ever since the early success in under-

Table 2. Interstellar molecules detected by optical techniques in diffuse clouds (Winnewisser et al., (1979))

Molecule	Transition	Wavelength (Å)	Other transitions	Column densities (cm^{-2})	Source	Year of discovery
^{12}CH	$A^2\Delta - X^2\Pi(0, 0)\ R_2(1)$	4300	Y	$\sim 10^{13}$	~40	1937
	$B^2\Sigma^- - X^2\Pi(0, 0)\ ^PQ_{12}(1)$	3890	Y			1941
	$C^2\Sigma^+ - X^2\Pi(0, 0)\ ^PQ_{12}(1)$	3146	Y			1960
$^{12}CH^+$	$A^1\Pi - X^1\Sigma(0, 0)\ R(0)$	4233	Y	10^{13}	~60	1937
$^{13}CH^+$	$A^1\Pi - X^1\Sigma(0, 0)\ R(0)$	4232	Y	10^{13}	~ 2	1969
CN	$B^2\Sigma^+ - X^2\Sigma^+(0, 0)\ R(0)$	3875	Y	10^{12}	14	1938, 39
CO	$A^1\Pi - X^1\Sigma(1, 0)$	1510	Y	10^{15}	ζ Oph	1971
	$C^1\Sigma^+ - X^1\Sigma^+(0, 0)\ R(0)$	1088	Y	$\sim 10^{13}$	3	1973
	$E^1\Pi - X^1\Sigma^+(0, 0)\ R(0)$	1076	Y	$\sim 10^{13}$	3	1973
^{13}CO	$A^1\Pi - X^1\Sigma(2, 0)$	1476	Y	$\sim 10^{13}$	ζ Oph	1971
H_2	$B^1\Sigma_u - X^1\Sigma_g(0, 0)$	1108	Y	10^{20}	15	1970
HD	$B^1\Sigma_u^+ - X^1\Sigma_g^+(3, 0)\ R(0)$	1066	Y	$\sim 10^{14}$	9	1973
OH	$A^2\Sigma^+ - X^2\Pi$	3078			2	1976
	$D^2\Sigma - X^2\Pi(0, 0)\ Q_1(3/2)$	1222	Y	$\sim 10^{14}$	ζ Oph	1976
C_2	$A^1\Pi_u - X^1\Sigma_g^+(2, 0)\ R(0)$	8758	Y	$\sim 10^{13}$	ζ PER	1980

standing the formation of molecular hydrogen by association on the surfaces of grains (Hollenbach and Salpeter 1971, Hollenbach, Werner and Salpeter, 1971), surface chemistry has been hampered seriously by the lack of predictability. This is connected with the intrinsic difficulties of the process itself. Firstly there is still now a great lack of detailed knowledge of what precisely grains are made of, and secondly the details of the catalytic processes remain rather uncertain and speculative. Although there are essentially three steps involved in the molecular formation on grain surfaces[1], (each associated with is own uncertainty) it is the final step which poses the central problem. With the exception of H_2 it has not been shown convincingly for other molecular species how the product molecule could acquire sufficient kinetic energy to escape from the grain surface. A summary of reactions on the surfaces of dust grains is given by Watson, 1978.

On the other hand gas-phase reactions between positive ions and neutrals have been recognized in the early 70's to be a basic process giving birth to interstellar molecules (Herbst and Klemperer, 1973, 1976). No activation energies and exothermicity for most of these reactions produces appreciable reaction rates even at the low temperatures ($T \lesssim 100$ K) of interstellar clouds. It therefore gives them preference over neutral-neutral reactions, which are usually hampered by problems of activation energy. Negative-ion neutral reactions suffer from the fact that for most cases they are endothermic and are therefore of limited signifiance to astrophysical problems. Thus based on the idea of positive-ion chemistry it has become possible to predict quantitatively the abundances of simple and some intermediate size interstellar molecules. With laboratory measured and/or calculated and estimated reaction rates, the results of positive-ion gas phase chemistry in the diluted medium of interstellar space have become predictable, a commodity which has certainly contributed to the success of ion molecule reactions. Based on this concept the early prediction of the formation of HCO^+ and N_2H^+ were key-successes for the ion-molecule scheme. The properties of such reactions have been discussed by McDaniels et al. 1970, and their astrophysical significance by Dalgarno and Black 1976. Huntress 1976 discusses and summarises recent laboratory measurements.

In summary we may then note concerning the question of the relative importance of catalytic processes on grain surfaces versus gas phase reactions that the results for simple molecules lend a certain preference to ion molecule reactions over the competing surface chemistry models. Strong evidence for catalytic surface reactions comes from the formation of molecular hydrogen. Recombination of hydrogen atoms on grain surfaces according to the reaction

$$H + H + \text{grain} \rightarrow H_2 + \text{grain}$$

with a formation rate ($cm^{-3}\,sec^{-1}$) $k_i n$ (HI) n where $n = n\,(HI) + 2n(H_2)$ and $k_i \sim 10^{-17}\,cm^3\,sec^{-1}$ is reasonably well understood and will not be repeated here although there are still problems associated with it (see for example recent summaries: Winnewisser et al. 1979, Hollenbach and McKee, 1980). For instance,

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[1] In short the three steps are: the sticking ability of a molecule to the surface, subsequent mobility on the grain surface to encounter a reaction partner and finally reaction and ejection from the surface.

the initial rotational and vibrational distribution of newly created H_2 molecules cannot be predicted with certainty (Hunter and Watson 1978) which expresses itself in the observed rotational distribution of H_2 and affects the associated analysis and the calculation of the heating rate.

For the case of high temperatures found in the vicinity of hot stars, or in cloud regions under the influence of a shock wave, or in ionized nebulae, several authors have suggested (c.f. Jura, 1975, Dalgarno and McCray 1973) a gas phase formation scheme which could be a significant source for molecular hydrogen, H_2. The associative detachment reaction

$$H + H^- \rightarrow H_2 + e$$

has a measured rate constant of 1.3×10^{-9} cm³ sec⁻¹ (Schmeltekopf et al. 1967). From the formation rate of H^- via the reaction

$$H + e \rightarrow H^- + h\nu ; \qquad k = 5 \times 10^{-17}\ \mathrm{cm^3\ sec^{-1}}$$

and the estimated lifetime of H^- against photodestruction (5×10^6 sec) one can deduce that this gas phase mechanism is likely to be less effective by two orders of magnitude than surface reactions in areas with a ratio of electron density n_e to hydrogen density $n = n(HI) + 2n(H_2)$ $n_e/n < 10^{-3}$, which is typical for interstellar clouds.

Although it would really be surprising if H_2 were to remain the only molecule to be produced on grain surfaces, it has emerged that the formation of other simple molecules can now be explained satisfactorily – not without problems though – by gas phase reactions. Evidence but not proof for positive-ion gas-phase reactions comes from several rather independent areas (c.f. Watson, 1980)

(i) the formation of HD and OH in diffuse clouds
(ii) abundance predictions for HCO^+ and N_2H^+ in dense clouds
(iii) the nearly equal interstellar abundance ratio of HCN and HNC
(iv) deuterium enchancement in the deuterium to hydrogen ratio in molecules
(v) the apparent fractionation of carbon isotopes observed in several clouds for various molecules
(vi) the agreement between prediction and deduced electron densities in dense clouds.

The next chapter will present a short outline of the basic ideas which have gone into the model of gas-phase chemistry centered around positive-ion reactions and we will illustrate the reaction paths of some selected simple interstellar molecules. In this case one has to consider two limiting cases of interstellar sources, (i) the diffuse interstellar cloud and (ii) the dense molecular clouds which themselves will have to be subdivided into several different cloud types.

4 Chemistry in Molecular Clouds

The primary energy source behind the ion-molecule scheme in interstellar molecular clouds is the cosmic ray ionization of H, H_2 and He, which can be transferred efficiently to less abundant atoms or species, notably C, N and O. Thus their effective time scale for ionization is reduced by a factor proportional to their abundance. In addition, exothermic reactions between positive ions and neutrals occur with no activation energy and with rate coefficients near 10^{-9} cm³ sec⁻¹ at room temperature. Since these rates usually do not change with temperature (some increase at low temperatures) they remain fast at low temperatures. These general characteristics make ion-molecule reactions important for interstellar cloud chemistry, i.e. for the diffuse interstellar clouds as well as for the cool dense dark molecular clouds.

4.1 Diffuse Interstellar Clouds

The chemical composition of diffuse interstellar clouds is simple and essentially limited to diatomic molecules which have been summarized in Table 2, together with the wavelength region where detection was made. It has to be noted, however, that there is a marginal detection of H_2O at about the 2σ level by Snow (1980). If confirmed a new H_2O mechanism has to be thought of.

Diffuse clouds are tenuous concentrations of interstellar gas and dust that do not block entirely the light of stars which are located behind them. They can be studied by absorption spectroscopy and as seen from Table 2, they were already studied as early as 1940. Although diffuse clouds are chemically simpler than are dense molecular clouds the assessment of the formation and destruction mechanisms has its own difficulties associated with it. Just because of the lower density, photoionization and photodissociation processes play a significant role in altering the otherwise simple chemistry of the diffuse clouds. The formation of HD may serve as a standard example.

Cosmic ray ionization of H leads to the formation of HD through a sequence of reactions. The resonant charge-exchange reaction, whose rate constant has been given (Watson et al. 1978)

$$H^+ + D \rightarrow D^+ + H \qquad (\sim 10^{-9}\ \mathrm{cm^3\ sec^{-1}})$$

furnishes an important source of D^+, which reacts by the gas-phase reaction

$$D^+ + H_2 \rightarrow HD + H^+ \qquad (\sim 10^{-9}\ \mathrm{cm^3\ sec^{-1}})$$

whose rate constant has been measured by Fehsenfeld et al. 1973. The observed column density ratio HD/H_2 is 10^{-6} with about an order of magnitude variation about this value. The D/H abundance ratio has been measured for a distance up to 200 pc from the sun directly in the ultraviolet and is 10^{-5} (York and Rogerson 1976). It may be noted that the HD abundance is directly proportional to the cosmic ray flux and the cosmic D/H ratio. The latter ratio can be determined once the cosmic ray flux is known. This has been done from the OH abundance via the charge exchange reaction

$$H^+ + O \rightarrow O^+ + H$$

followed by

$$O^+ + H_2 \rightarrow OH^+ + H$$

which transfers the ionization to a molecule that is subject to rapid neutralization (Watson 1973). For ζ Oph, ζ Per, and o Per the D/H ratio has been determined to be 4×10^{-5} (Hartquist, Black and Dalgarno, 1978), in agreement with the value from York and Rogerson.

Other important reactions take place between C^+ and H_2. Black and Dalgarno 1973 suggested that radiative association

$$C^+ + H_2 \rightarrow CH_2^+ + h\nu$$

can occur and can trigger an entire reaction sequence with the end products CH, CH^+, C_2, C_2H and $C_2H_2^+$. The latter two species are important species for the formation of complex carbon chain molecules in dense clouds as will be discussed in the next section. CN and molecular carbon C_2 are other important species. While CN is produced by various reaction sequences involving atomic nitrogen ($CH^+ + N \rightarrow CN + H^+$, or $C_2^+ + N \rightarrow CN + C^+$) and the CH cycle, C_2 is produced by reaction of C^+ with the CH cycle ($CH + C^+ \rightarrow C_2^+ + H$) (Black and Dalgarno 1977 and Black et al. 1979). The observational value of the column density of 1.4×10^{13} cm^{-2} towards ζ Per (Chaffee Jr. et al. 1980) is in remarkable good agreement with the predicted value from the model by Black et al. 1979. Table 3 which gives a summary of predicted and observed column densities for five molecular species has been taken from Dalgarno 1980. It is noted that there is generally good agreement between theoretical prediction and observational results with the exception of CH^+. The chemical model produces too little CH^+. Dalgarno 1980 discusses several possibilities all of which encounter difficulties, such as that the rate constant of $C^+ + H_2 \rightarrow CH_2^+ + h\nu$ is too low or the destruction mechanisms are not taken into account properly.

It is also of interest to note that the chlorine chemistry in diffuse clouds has been discussed (Dalgarno et al. 1974, and Black and Dalgarno, 1977) showing that Cl^+ will react with H_2:

$$\begin{aligned} Cl^+ + H_2 &\rightarrow HCl^+ + H \\ HCl^+ + H_2 &\rightarrow H_2Cl^+ + H \\ H_2Cl^+ + e &\rightarrow HCl + H \end{aligned}$$

with the destruction of hydrogen chloride by either photodissociation or with C^+

$$HCl + C^+ \rightarrow CCl^+ + H\,.$$

Table 3. Column densities log N (cm^{-2}) (Dalgarno, 1980)

	ζ Oph		ζ Per		o Per	
	Obs	Th	Obs	Th	Obs	Th
CO	15.0–15.2	15.0	14.7–15.0	15.0	14.7–15.0	15.1
CH	13.5–13.6	13.6	13.0–13.4	13.6	13.4–13.6	13.5
CN	12.94	12.95	12.6	12.5	12.3–12.7	11.9
C_2	12.9	12.9	13.1	13.1	—	13.3
CH^+	13.0	11.4	12.2	11.5	12.7	11.5

Furthermore several authors point out that for a hot environment gas phase chemistry is altered drastically in that endothermic reactions with H_2 become progressively more important (Iglesias and Silk 1978; Elitzur nach De Jong 1978, Hartqvist, Oppenheimer and Dalgarno 1980), and molecular ions such as SiH^+, SH^+, NaH^+, MgH^+, FeH^+ and HCl^+ may become detectable.

4.2 Dense Molecular Clouds

Dense molecular clouds, often also called dark clouds, block entirely the light of stars which lie behind them, and can therefore be studied observationally only by radio astronomy or infrared techniques. These clouds have a visual extinction in excess of $A_v \gtrsim 10$ which corresponds to a gas density of $n_{H_2} \sim 10^4$ cm^{-3} and a kinetic temperature usually well below $T \sim 100$ K, typically between 10 and 25 K. Within the last ten years, the investigation of these dark molecular clouds has become almost entirely the domain of radio astronomy although now the first very promising results by infrared astronomy reveal the power of this new branch of spectroscopy.

The dark molecular clouds are chemically very rich in comparison to the diffuse clouds. They harbor all of the presently observed more than 50 chemical species which are summarized in Table 4. Clearly dark clouds are a very heterogenous group which have been classified by Winnewisser, Churchwell and Walmsley 1979. We will reproduce this classification here which is based on observed physical and astronomical parameters. Table 5 groups the dark clouds into four different classes according to observed molecular line-widths, size of the cloud and other astronomical parameters with which the cloud is associated. The first class are the giant molecular clouds, those clouds which are associated with ionized regions of gas, H^+ regions (or often referred to as H II regions). The large molecular line width is a typical characteristic of these clouds. Together with the dark dust clouds which form the second category they are the clouds in which star formation is occuring and probably only there. The third and fourth group are intrinsically connected with the immediate neighbourhood of stars. The protostellar environment is associated with the formation of young stars whereas the envelopes of late type stars describes the molecular clouds which can form around old stars which are losing processed mass to the interstellar medium. Although we will not discuss the chemistry of the protostellar environment or the chemistry of late type stars, it is of interest to note here that the abundance ratios of the molecular species (also isotopic) in circumstellar envelopes can be quite different from that of the interstellar medium. For example in IRC +10216 the observed circumstellar (HCN)/(HNC) ratio (~100) is very much different from the observed interstellar ratio (~1), where both species are about equally abundant. The circumstellar ratio is in agreement with calculated values assuming chemical equilibrium at ~1000 K. A summary on the chemical composition and physical properties of the envelopes of late type stars is given by Zuckerman 1980.

In the following two sections the discussion will be confined to the chemistry of dense molecular clouds, where one can assume that effects of photodissoziation and photoionization are unimportant, quite in contrast to diffuse clouds. Furthermore, in dense clouds hydrogen is predominantly in the molecular form, H_2, and reactions

Table 4. Interstellar Molecules

2	3	4	5	6	7	8	9	10	11
H_2 OH SO SiO SiS NO NS	H_2O H_2S N_2H^+ SO_2 HNO O_3	NH_3							
CH^+ CH CN CO CS	HCN HNC C_2H HCO HCO^+ OCS HCS^+	H_2CO HNCO H_2CS HNCS C_3N	HC_3N C_4H H_2CNH NH_2CN HCOOH H_2C_2O	CH_3OH CH_3CN CH_3SH NH_2CHO	HC_5N CH_3CCH CH_3NH_2 CH_3CHO H_2CCHCN	$HCOOCH_3$	HC_7N $(CH_3)_2O$ CH_3CH_2OH CH_3CH_2CN	–	HC_9N

Isotopically substituted molecules

By optical techniques			
H_2	H_2, HD	H_2O	$H_2{}^{16}O$, $HD^{16}O$, $H_2{}^{18}O$
CH^+	$^{12}CH^+$, $^{13}CH^+$	N_2H^+	$^{14}N^{14}NH^+$, $^{14}N^{14}ND^+$
CO	$^{12}C^{16}O$, $^{13}C^{16}O$	HCO^+	$H^{12}C^{16}O^+$, $H^{13}CO^+$, $D^{12}C^{16}O^+$, $H^{12}C^{18}O$
		HCN	$H^{12}C^{14}N$, $H^{13}C^{14}N$, $H^{12}C^{15}N$, $D^{12}C^{14}N$
		HNC	$H^{14}N^{12}C$, $H^{14}N^{13}C$, $D^{14}N^{12}C$
By radio techniques		NH_3	$^{14}NH_3$, $^{15}NH_3$
OH	^{16}OH, ^{18}OH, ^{17}OH	H_2CO	$H_2{}^{12}C^{16}O$, $H_2{}^{13}C^{16}O$, $H_2{}^{12}C^{18}O$, HDCO
SiO	$^{28}Si^{16}O$, $^{29}Si^{16}O$, $^{30}Si^{16}O$	HC_3N	$H^{12}C^{12}C^{12}C^{14}N$, $H^{13}C^{12}C^{12}C^{14}N$, $H^{12}C^{13}C^{12}C^{12}C^{14}N$, $H^{12}C^{12}C^{13}C^{14}N$, DCCCN
CO	$^{12}C^{16}O$, $^{13}C^{16}O$, $^{12}C^{18}O$, $^{12}C^{17}O$, $^{13}C^{18}O$		
CS	$^{12}C^{32}S$, $^{13}C^{32}S$, $^{12}C^{34}S$, $^{12}C^{33}S$	CH_3OH	$^{12}CH_3{}^{16}OH$, $^{13}CH_3OH$, CH_3OD

Table 5. Classification of molecular line sources (Winnewisser et al. 1979)

Class	Linear size (pc)	Typical linewidths (km s^{-1})[a]	Density (cm^{-3})	Temperature (K)	Mass ($M_\odot$)
Molecular clouds associated with H II regions (giant)	1-50	3-30	10^4–10^6	20–80	10^5 10^6
Dark dust clouds	1-10	1	10^3–10^5	10–20	10^2 10^4
Envelopes of late type stars	0.01-0.5	25	10^4–10^6	100-1000	$\sim 10^{-2}$
Masers in a "proto-stellar" environment	10^{-5}–10^{-3}	0.1-2	$>10^5$	100-1000	$\lesssim 10$

[a] From the Doppler relation $\Delta v/v = -\Delta\upsilon/c$, 1 km s^{-1} corresponds to a linewidth (kHz) of 3.336ν (GHz).

between molecular species are of importance particularly for the formation of larger molecules. In addition, physical conditions in dense clouds are considerably more complicated than in diffuse clouds and thus the observational data are often difficult to assess precisely. In particular, there are always problems associated with the conversion of observed line intensities to molecular abundances, numbers which are of primary interest to the chemist. The observational data have recently been reviewed by Winnewisser et al. 1979. The proceedings of the recent IAU Symposium No. 87 on Interstellar Molecules (B. H. Andrew, Ed. 1980) is an excellant compendium to the current observational and theoretical knowledge, the success and failures of astrophysics and astrochemistry and in understanding interstellar molecules.

4.3 The Ion-Molecule Scheme: HCO^+, N_2H^+, H_2O and NH_3

According to the ion-molecule scheme, the chemistry in dense molecular clouds is driven by the assumed cosmic ray ionization of the most abundant species: i.e. H, H_2 and He. The cosmic ray ionization rate ξ_{CR} should be 10^{-17} sec^{-1} based upon the cosmic ray flux measured at earth.

Ionization of the main gas component H_2, the most important basic process, leads essentially to H_3^+ which then either recombines or reacts further with molecules or molecular fragments. Thus the latter destruction mechanism of H_3^+ is of fundamental importance to ion chemistry in dense clouds by transferring the ionization to molecular or less abundant elements.

A likely sequence is

$$H_2 + \text{C.R.} \xrightarrow{98\%} H_2^+ + e + \text{C.R.}$$

$$\xrightarrow{2\%} H^+ + H + e + \text{C.R.}$$

This reaction is followed by

$$H_2^+ + H_2 \rightarrow H_3^+ + H$$

There are several pathways for the destruction of H_3^+.

Dissosiative recombination with an electron

$$H_3^+ + e \rightarrow H_2 + H$$

competes with reactions of the form

$$H_3^+ + A \rightarrow AH^+ + H_2$$

and

$$H_3^+ + AB \rightarrow HAB^+ + H_2$$

Carbon monoxide is known to be next to H_2 one of the most abundant molecules. In addition, it is highly probable that in dense molecular clouds most of the gas-phase carbon is in the form of CO (there could also be large amounts of C_2). It has been suggested that the reaction

$$H_3^+ + CO \rightarrow HCO^+ + H_2$$

should produce a large fraction of the interstellar HCO^+ through the destruction of H_3^+. Similarly one would expect

$$H_3^+ + N_2 \rightarrow N_2H^+ + H_2$$

and

$$H_3^+ + C_2 \rightarrow C_2H^+ + H_2$$

The prediction and identification of HCO^+ and N_2H^+ as key molecules of the positive-ion gas-phase chemistry paved the way to its general acceptance.

Interesting examples of the formation of intermediate molecules are illustrated by the possible exothermic reactions of H_3^+ with O and N and the reaction paths leading finally to H_2O and NH_3:

$$\begin{aligned} &H_3^+ + O \rightarrow OH^+ + H_2 \\ &OH^+ + H_2 \rightarrow OH_2^+ + H \\ &H_2O^+ + H_2 \rightarrow H_3O^+ + H \\ &H_3O^+ + e \begin{array}{l} \nearrow H_2O + H \\ \searrow OH + H_2 \end{array} \end{aligned}$$

Support for these reactions comes from laboratory measurements which show that their reaction rates are fast. Yet the interstellar importance of these reactions is not completely clear since the reaction of H_3^+ with atomic oxygen has to compete with the dissociative electron recombination of H_3^+.

Similarly, the reaction with atomic nitrogen produces NH_3, NH_2 and NH:

$$\begin{aligned} &H_3^+ + N \rightarrow NH^+ + H_2 \\ &NH^+ + H_2 \rightarrow NH_2^+ + H \\ &NH_2^+ + H_2 \rightarrow NH_3^+ + H\,. \end{aligned}$$

The reaction

$$NH_3^+ + H_2 \rightarrow NH_4^+ + H$$

is important in spite of the fact that the rate constant is small ($\sim 10^{-13}$ cm^3 sec^{-1}). NH_3 can also be formed by either charge exchange reactions with heavy atoms of low ionization potential, i.e. Fe, He, Ca, Na according to:

$$NH_3^+ + Mg\,, \ldots \rightarrow NH_3 + Mg^+\,, \ldots$$

or by the dissociative electron recombination reaction of NH_5^+:

$$\begin{aligned} NH_3^+ + H_2 + h\nu \rightarrow\ & NH_5^+ \\ & NH_5^+ + e \rightarrow NH_3 + H_2\,. \end{aligned}$$

Most of these reactions have been measured and their rates are thus reasonably well known (Fehsenfeld et al. 1967). In comparing the two reaction schemes, it is interesting to note that H_3O^+ does recombine dissociatively with an electron to form H_2O and OH, but that the analoguous reaction sequence with NH_4^+ seems to take place. The branching ratio of the H_3O^+ dissociative recombination is not accurately known. In this connection, it is also important to note that reactions of H_3^+ with atomic carbon seem to be endothermic (Burt et al. 1970 and references therein), and thus the carbon chemistry in dense molecular clouds can not start this way.

So far we have summarized some basic reactions starting with the cosmic ray ionization of H_2. However cosmic ray ionization of He, which is considerably less abundant in dense clouds than H_2 (about $^1/_4$) seems to be important for two reasons: firstly, an activation energy barrier (Johnsen and Biondi, 1974) is likely to keep the reaction rates of H^+ with H and H_2 anomalously small (reaction rate $\sim 8 \times 10^{-16}$ cm^3 $\cdot$ sec^{-1}; Sando et al. 1972), and therefore He^+ remains available for the ionization of neutral molecules. Secondly, in most cases, the charge transfer from He^+ to diatomic molecules dissociates them, producing essentially ionized heavy elements, such as C^+, N^+, O^+. The reaction sequence has the general form: (see note added in proof).

$$He + C.R. \rightarrow He^+ + e + C.R.$$

followed by

$$He^+ + AB \rightarrow A^+ + B + He$$

with the specific examples

$$\begin{aligned} He^+ + CO &\rightarrow C^+ + O + He \\ He^+ + N_2 &\rightarrow N^+ + N + He \\ &\rightarrow N_2^+ + He \\ He^+ + O_2 &\rightarrow O^+ + O + He \\ He^+ + C_2 &\rightarrow C^+ + C + He \end{aligned}$$

whereby the latter reaction is of uncertain significance due to the unknown relative abundances of C_2 compared with the CO abundance.

Ionized C^+, N^+, O^+ in turn can be used for the formation of simple ions by reacting with H_2 according to

$$O^+ + H_2 \rightarrow OH^+ + H$$
$$N^+ + H_2 \rightarrow NH^+ + H$$

or they can be involved in formation of more complex molecules.

4.4 Formation of HCN, HNC, CN, and H_2CO

Soon after the discovery of the unidentified molecular emission line U 89.190 and its subsequent identification as HNC is was recognized from the astrophysical data that HNC has comparable abundance to HCN and that this almost equal abundance ratio should be a likely consequence of an ion-molecule reaction mechanism. HCN and HNC are thought to be produced fairly directly from the reaction of C^+ with NH_3 through the following reaction sequences:

$$NH_3 + C^+ \begin{array}{l} \nearrow H_2CN^+ + H \\ \searrow HCN^+ + H_2 \end{array}$$

and

$$H_2CN^+ + e \begin{array}{l} \nearrow HNC + H \\ \searrow CN + H_2 \end{array}$$

whereby the branching ratio of the latter equation is unknown. However molecular orbital calculations of Conrad and Schaefer 1978 indicate that H_2CN^+ rearranges itself to the energetically lower isometric form $HCNH^+$. Subsequent dissociative electron recombination forms HNC, HCN in equal abundances since there seems to be no obvious preference in the branching ratio (see note 2 added in proof).

$$H_2CN^+ \rightarrow HCNH^+ + e \begin{array}{l} \nearrow HCN + H \\ \searrow HNC + H \end{array}$$

HCN and HNC are likely to be destroyed by reaction with C^+ according to

$$HCN + C^+ \rightarrow C_2N^+ + H$$

followed by

$$C_2N^+ + e \rightarrow C + CN\,.$$

If these reactions are the main destruction process one can estimate a model independent value for the abundance ratios of $([HCN] + [HNC])/[NH_3] \leqq 0.6$ (e.g. Watson, 1976) for a cloud density of $n_{H_2} \sim 10^6\ cm^{-3}$. This ratio can also be determined from the laboratory measured reaction rate (Huntress and Anicich, 1976) to be $[HCN]/[NH_3] \sim 0.4$. Within errors the observationally determined ratios do tend to confirm this value (e.g. Winnewisser et al., (1979)), although it is still not easy to confirm or deny this estimate on the basis of the present interstellar observations.

Formaldehyde, H_2CO, is a widely distributed interstellar molecule which occurs in diffuse and in dense molecular clouds. Specific gas phase reactions have been proposed. But formaldehyde has remained a test case molecule where gas-phase reactions cannot completely explain the observed interstellar abundances and where surface reactions might play a role. However, the recently observed HDCO shows that its abundance (Langer et al., (1979)) is not in disagreement with the proposed reaction mechanisms for H_2CO. Three mechanisms have been proposed (Watson, (1976), Herbst and Klemperer (1973)):

$$CH_3 + O \rightarrow H_2CO + H$$

which is followed by charge transfer with low ionization metals. Herbst and Klemperer suggested:

$$HCO^+ + H_2 \rightarrow H_3CO^+ + h\nu$$
$$HCO_3^+ + e \rightarrow H_2CO + H\,.$$

The deuterated compound HDCO can be produced by reaction of

$$CH_3^+ + HD \rightarrow CH_2D^+ + H_2 + \Delta E$$

where ΔE is the binding energy difference between the deuterated and the non deuterated species ($\Delta E/k \sim 300\ ^\circ K$). This difference in binding energy is generally held responsible for isotope fractionation, also in cases of observed ^{13}C fractionation.

These examples already illuminate the difficulties encountered by gas phase mechanisms even at the level of intermediate sized molecules such as NH_3, HCN, HNC or H_2CO. With each additional reaction and possible associated branching ratio the uncertainties grow. Despite these difficulties it seems, however, that molecules such as HD, CN, HCO^+, HCN, HNC, NH_3 and probably also H_2CO are preferentially formed through ion-molecule reactions. It seems, however, certain that in the formation of ions and/or radicals the final step in the formation scheme has to occur through gas-phase reaction rather than surface reaction.

5 Formation of Complex Molecules and Carbon Chemistry

5.1 Complex Molecules

The understanding of the formation of complex organic molecules in the interstellar environment is a tantalizing field of interstellar chemistry. Presently it is a very active area for both theoretical and experimental research for it has resisted so far all attempts to even obtain a good qualitative understanding and it promises to remain an area of great challenge and optimism. Despite impressive progress, it has not been possible to overcome the question of whether ion-molecule reactions or surface reactions are the predominant contributors of complex molecules. There are advocates for either mechanism.

The fact that catalytic processes on grain surfaces cannot be neglected does not have its justification in that these processes are easier to understand in the case of complex molecules than for simple ones, but rather that ion-molecule reactions become harder to track, since the uncertainties compound: for converting atoms into complex molecules the number of reaction steps have to increase, whereby reaction rates and branching ratios are less well known. For a large number of supposed reactions rates simply have not even been measured in the laboratory. However progress seems to come in mainly three areas. (i) Extensive studies have been made on reactions of the form

$$AX^+ + BY \rightarrow AB^+ + XY$$

where AB^+ is assumed to be more complex than AX^+.

Applications of this reaction will be specifically discussed for the carbon chain molecules. (ii) the radiative association of larger molecules has been studied by measurements of analogous three body associations (McEwan et al. 1980).

$$A^+ + B + M \rightarrow (AB^+)^* + X \rightarrow AB^+ + M + h\nu$$

with the two distinct intermediate steps

$$(AB^+)^* + M \rightarrow AB^+ + M$$
$$(AB^+)^* \rightarrow AB^+ + h\nu\,.$$

Detailed studies show that the rate coefficients for 3-body association increase with decreasing temperature (Smith and Adams, 1978) probably due to the longer lifetime of the excited complex $(AB^+)^*$. Arnold (1979) suggested that radiative association of H_2 to molecular ions may proceed with high rate constants at the low temperatures of dense molecular clouds. (iii) Laboratory observation of a large number of chemical reactions which lead to the formation of complex molecules. Often though, it is not easy to assess the precise relevance of these new data to the interstellar conditions.

On the other hand, the fundamental problem associated with grain production, the return of molecules to the interstellar gas is caused by the low grain temperatures and is certainly not facilitated for complex molecules. On the contrary, the vapour pressure of molecules usually decreases with with increasing molecular complexity as is the case for carbon chain molecules. H_2 overcomes this problem and both CO and N_2 also have sufficient vapour pressure to prevent them from freezing out entirely onto grains. Both molecules serve therefore as reservoirs for atoms and ions through charge transfer reactions discussed earlier.

Infrared observations however have established that local areas of heated dust (T ~ 40 — 100 K) are wide spread. In addition it has been observationally noted that emission of infrared radiation tends to correlate with molecular line emission from these areas, although notable exceptions exist. In Table 6, the presently known molecules in two selected sources ORIA, and TMC1 are summarized, indicating from the point of view of complexity of molecules, that the temperature does not seem to be the only essential parameter. In the present series, Hayatsu and Anders (1981) review some aspects of complex molecule formation "with an admitted bias towards grain surfaces".

It remains here to point out that various authors (see Hayatsu and Anders 1981 and references therein) have suggested that warm grains could alleviate some of the

Table 6. Molecules Detected in the Orion Molecular cloud and the Taurus Molecular cloud

	Orion (OMC1)	Taurus (TMC1)
Simple hydrides	H_2 CH OH H_2O H_2S NH_3 NNH^+	CH OH NH_3 NNH^+
Oxides, sulfides	CO SiO O_3 CS SO SO_2 OCS HCS^+	CO SO CS
Acetylene derivatives	CN HCN HCCCN H_3C-CN H_2C_2HCN H_3CCH_2CN CCH H_3CCCH HNCO HNC H_3CNH_2	CN HCN HCCCN HCCCCCN HCCCCCCCN HCCCCCCCCCN CCH CCCN HNC
Aldehydes, Alcohols, Acids and ethers	H_2CO H_3CCHO H_2CS $HCOOCH_3$ CH_3OH $(CH_3)_2O$ HCO^+	H_2CO HCO^+

The following molecules habe been detected only in the Galactic center sources:
NO, NS, HNO, HCO, CH_3SH, HNCS, HCOOH, CH_2NH, NH_2CHO, CH_3CH_2OH

problems associated with surface mechanisms, in particular the ejection process. Yet even warm grains are far from delivering the complete answer. Observations show that a number of intermediate sized molecules occur in diffuse clouds without known infrared emission (e.g. H_2CO) and secondly large complex chain molecules do occur in cold, dense clouds without any embedded infrared sources and/or small compact H^+ regions. The best studied example of the latter category are probably the Taurus Molecular Clouds in particular TMC1. These sources show a high abundance of complex molecules, expecially the cyanopolyynes, a series of carbon chain molecules with the general formula $HC_{2n+1}N$ with $n = 0, 1, 2, \ldots$

After these more general comments, we would like to discuss within the context of recent laboratory data some of the progress which has been made specifically in the area of complex molecules such as cyanopolyynes. The interstellar carbon chemistry in dense molecular clouds ($n_{H_2} \sim 10^4\ \mathrm{cm}^{-3}$) is used as an example.

5.2 Carbon Chemistry

Reactions of C^+ with H, H_2 are of fundamental importance to the carbon chemistry in interstellar clouds, and some of the reaction paths prevalent in dense interstellar clouds may also be of significance in the reducing atmospheres of the outer planets. These reactions initiate a complex sequence which produce CH, CH^+ and lead eventually to molecules such as CH, $C_2H_2^+$. These molecules are important precursors to the formation of complex carbon chain molecules found in a large number of astronomical sources.

The explanation of the carbon chemistry took its start with the first attempts by Bates and Spitzer in 1951 to explain the abundances of CH and CH^+. They pointed out that CH^+ in diffuse clouds can be formed by the radiative association process in the gas phase:

$$C^+ + H \rightarrow CH^+ + h\nu\,.$$

The rate coefficient $\alpha \sim 10^{-17}\ \mathrm{cm}^3\ \mathrm{sec}^{-1}$ has been and is a matter of controversy. Similarly CH can be formed

$$C^+ + H \rightarrow CH + h\nu$$

with a similar rate constant but since carbon is mainly ionized in diffuse clouds, this process does not seem likely. (Reactions for OH, NH have even smaller rate constants). CH can be formed from CH^+ by radiative recombination

$$CH^+ + e \rightarrow CH^*(^2\Sigma^+) \rightarrow CH + h\nu\,.$$

There is also the possibility that the CH^+ ion dissociates by electron capture into C and H:

$$CH^+ + e \rightarrow C + H \qquad (10^{-7}\ \mathrm{cm}^3\ \mathrm{sec}^{-1}?)\,.$$

On the other hand photoionization can convert CH into CH^+, i.e.

$$CH + h\nu \rightarrow CH^+(X'\Sigma) + e\,.$$

$$CH + h\nu \rightarrow CH^+(A^3\Pi) + e\,.$$

In dense clouds however reactions with H_2 are of importance: Black and Dalgarno (1973) suggested the radiative association reaction between C^+ and H_2

$$C^+ + H_2 \rightarrow CH_2^+ + h\nu \qquad (4 \times 10^{-17}\ \mathrm{cm}^3\ \mathrm{sec}^{-1})$$

initiating a complex network of reactions leading to larger molecules, as is summarized in Fig. 1. This figure follows the reaction scheme for CH^+ and CH given by Dalgarno 1976 but has been extended to incorporate the starting point of the presumed carbon chain chemistry. Huntress (1977) has published a large number of bimolecular reactions of positive ions which are supposed to be of importance to the chemistry of interstellar clouds, comets and planetary atmospheres of reducing composition.

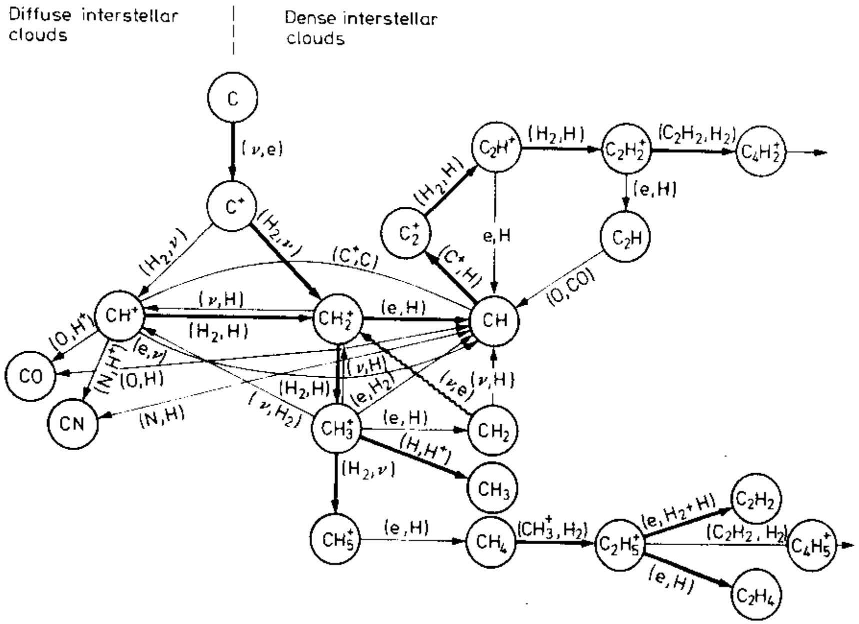


Fig. 1. Interstellar formation scheme illustrating the CH, CH^+, C_nH^+ and higher hydrocarbon cycle. The left side of the reaction cycle pertains to tenous clouds ($n_{N_2} \sim 100\ \mathrm{cm}^{-3}$), whereas the right hand side is more appropriate to areas where H_2 is present, i.e. dense molecular clouds ($n_{N_2} \sim 10^4$–$10^6\ \mathrm{cm}^{-3}$). The thick arrows indicate assumed preferential reaction paths leading to the higher order hydrocarbons. The following processes are involved: (ν, e) photoionization; (ν, H) photodissociation; (e, ν) radiative recombination; (H); (H_2, ν) radiative association; (e, H), (e, H_2) dissociative electron recombination. (H_2, H) hydrogen abstraction reaction; (C^+, H) charge exchange: (M, M^+) metal charge exchange: metal = Mg, Fe, Ca, Na, . . .

For most of the reactions, rate constants have been determined. In dense clouds, CH^+ is efficiently destroyed by the hydrogen abstraction reaction

$$CH^+ + H_2 \rightarrow CH_2^+ + H \qquad (1 \times 10^{-9}\ \mathrm{cm^3\,sec^{-1}})$$

which is followed by

$$CH_2^+ + e \rightarrow CH + H$$

and

$$CH_2^+ + H_2 \rightarrow CH_3^+ + H \qquad (0.7 \times 10^{-9}\ \mathrm{cm^3\,sec^{-1}})$$

which terminates the hydrogen abstraction sequence, since the reaction $CH_3^+ + H_2$ is endothermic. There are several ways in which CH_3^+ can be destroyed.

Neutralisation of CH_3^+ can be achieved, — as in the case NH_3^+ — by charge exchange reaction with low ionization metals, such as Fe, Ca, Mg, Na, . . . In dense clouds there is also the possibility of radiative association followed by dissociative electron recombination to reach neutral CH_4.

The more complex hydrocarbon molecules can be produced either by reaction of CH with C^+ according to the sequence

$$C^+ + CH \rightarrow C_2^+ + H$$
$$C_2^+ + H_2 \rightarrow C_2H^+ + H$$
$$C_2H^+ + H_2 \rightarrow C_2H_2^+ + H$$

where $C_2H_2^+$ can now react by dissociative electron recombination to form C_2H (Watson 1974):

$$C_2H_2^+ + e \rightarrow C_2H + H$$

or in those clouds with an acetylene rich environment:

$$C_2H_2^+ + C_2H_2 \rightarrow C_4H_2^+ + H_2\,.$$

Another likely possibility for the formation of hydrocarbon molecules starts with methane CH_4 and CH_3^+

$$CH_4 + CH_3^+ \rightarrow C_2H_5^+ + H_2$$

which then by dissociative electron recombination could produce the simplest hydrocarbon chain molecules:

$$C_2H_5^+ + e \begin{array}{l} \nearrow C_2H_2 + H_2 + H \\ \searrow C_2H_4 + H \end{array}$$

Follow-up steps in this series would be further reactions between CH_3^+ and C_2H_2, C_2H_4 and C_2H_6. These initial steps leading to the formation of complex hydrocarbon molecules are indicated in Fig. 1.

It remains however to mention that the reactive CH_3^+ ion can react with other atoms and molecules. Some of these reactions are with N, NH_3 or H_2CO leading essentially to the formation of HCN and HCO^+ (Huntress 1977):

$$CH_3^+ + N \begin{array}{l} \nearrow HCN^+ + H_2 \\ \searrow H_2CN^+ + H \end{array}$$
$$CH_3^+ + H_2CO \rightarrow HCO^+ + CH_4$$
$$CH_3^+ + NH_3 \rightarrow CH_2NH_2^+ + H_2$$
$$CH_2NH_2^+ \begin{array}{l} \nearrow HCN + H_2 + H \\ \searrow CN + 2H_2 \end{array}$$

This presents a short summary of the reactions which are supposed to be important gas-phase reactions leading to the complex hydrocarbon molecules, and some of their derivatives. In interstellar space the cyanopolyynes constitute an important class, since only molecules with a permanent dipole moment can be observed in radioastronomical measurements. Thus hydrocarbons which have no dipole moment elude radioastronomical detection.

The detection of cyanopolyyne molecules in interstellar space and their wide distribution seem to have revived the discussion of the fundamental question of how and where molecules form. The discussion centers around the question whether the origin of the molecules is to be interpreted as an *in situ* synthesis from interstellar gas or if the opposite hypothesis is correct. In this picture the observed large organic molecules are dissociation products of much more complex molecules or, in effect, they are the result of spallation of interstellar grains which are composed of or covered by organic matter. In the present volume on cosmochemistry, Hayatsu and Anders (1981) have discussed organic compounds in meteorites and their origin, and have given arguments for the formation of cyanopolyynes on grain surfaces.

Before discussing the possibility of gas-phase cyanopolyyne chemistry, it seems necessary to summarize the present status of carbon chain molecule detections in interstellar space. Table 7 presents an overview of where these molecules are found and their respective abundances. These tables are an abbreviated update from Table I taken from Winnewisser and Walmsley (1979). It is seen that these molecules are found essentially in every type of molecular cloud from the cold dark cloud to the warm circumstellar environment, underlining the trend which has been observed over the past few years: namely that complex organic molecules are not limited to a few sources only (in particular to the galactic center sources) but that they are spread over sources with rather different physical conditions. A qualifying statement may be in order here.

In contrast to the dark cloud chemistry, the molecules in circumstellar envelopes (IRC +10216) seem to be created continuously in a small, high temperature high density layer- which allow fast thermodynamic equilibrium- and subsequently expelled into the lower density cool envelope. There they are observed with an

Table 7. Distribution of carbon chain molecules

Molecule	Cloud type								
	Dark clouds				clouds with assoc. H^+ region			Circum stellar	
	TMC 1	L 1544	L 183	ϱ Oph.	Sgr B2	Ori A	W 51	IRC + 10216	CRL 2688
CN	•			•	•	•	•	•	
HCN	•		•	•	•	•	•	•	•
HC_3N	•	•	•	•	•	•	•	•	•
HC_5N	•	•	•		•			•	
HC_7N	•				•			•	
HC_9N	•								
C_2H	•				•	•		•	
C_4H								•	
C_3N	•							•	
HCCH								•	
C_2								•	•
C_3									•

Molecular abundances of carbon chain molecules in selected sources (Winnewisser a. Walmsley 1979)

Source	Distance d (kpc)	Density n (H_2) (cm^{-3})	Temperature T_K (K)	Molecular column densities (cm^{-2})									
				CN	HCN	HC_3N	HC_5N	HC_7N	HC_9N	C_2H	C_4H	C_3N	C_2H_2
TMC 1	0.1	3×10^4	10	$\sim10^{13}$		6×10^{13}	7×10^{13}	2×10^{13}	0.3×10^{13}	–	–	7×10^{12}	–
L 183	0.1	3×10^4	10	$<3.6\times10^{13}$	$\sim3\times10^{12}$	$\sim10^{12}$	–	–	–	$<6\times10^{12}$	–	–	–
ORI A	0.45	$\sim10^5$	50–70	3×10^{13} -9×10^{14}	10^{15}	2×10^{13}	–	–	–	2×10^{14} 3×10^{15}	–	–	
SGR B2	10	$\sim10^4$–10^6	50	3×10^{14}	–	2×10^{14}	2×10^{14}	–	–	–	–	–	–
IRC + 10216	0.29		~300	1×10^{15}	10^{15}	2×10^{14}	4×10^{14}	10^{14}		$\sim5\times10^{14}$	4×10^{14} 3×10^{15}	1×10^{14} 8×10^{14}	3×10^{19}

essentially "frozen-in" chemical equilibrium. It seems that grains are produced and ejected simultaneously with the molecules. In this picture, the large organic molecules might be spallation products of interstellar grains.

However, the present discussion pertains to dark cloud chemistry. The experimental interstellar observations clearly indicate that the distribution of carbon chain molecules is correlated, and that the column densities of the longer chain members decreases about linearly with increasing chain length. Several mechanisms have been proposed for the chain building. For cool dark clouds Churchwell et al. (1978) and in further detail Walmsley et al. (1979) have proposed a formation scheme by which the longer chain molecules are formed via the acetylene "backbone" reaction:

$$C_2H_x^+ + C_2H_2 \rightarrow C_4H_y^+ + C_2H_2 \rightarrow C_6H_z^+ + C_2H_2 \rightarrow \ldots$$

where then the appropriate cyanopolyyne species is formed from $C_2H_2^+$, $C_4H_4^+$, ... with notably CN or HCN as abundant nitrogen bearing molecules:

$$C_2H_2^+ + HCN \begin{cases} \nearrow HC_3NH^+ + H \\ \searrow H_2C_3N^+ + H_2 \end{cases}$$

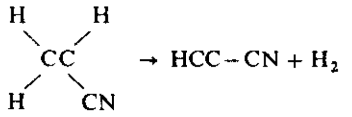
followed by dissociative electron recombination. Huntress et al. 1980 discusses in further detail the synthesis of very complex organic molecules by ion-molecule reactions.

Huntress 1977 also points out that the reaction is slow and could have a significant temperature dependence. However if this mechanism contributes the major part of the cyanopolyyne chemistry than one has to conclude (Winnewisser et al. 1980) (i) that the abundance of the cyanopolyyne molecules will decrease with increasing length of the carbon chain, (ii) that long chain molecules with other functional groups such as CH_3, NH_2, ... should be observable (iii) that molecules with no permanent dipole moment such as the hydrocarbons (saturated and unsaturated) acetylene, HCCH, diacetylene, HCCCCH, ... should have high abundance in the interstellar medium (iv) that unstable species such as HCCN, H_2CCN should also be abundant in the appropriate molecular clouds. Some of the unidentified interstellar lines could have these reactive species as their carrier. Similar to interstellar HCN higher cyanopolyyne members are likely to be destroyed by C^+.

It was noticed during the acetylene-hydrogen cyanide discharge experiments that they are always accompanied by a fairly rapid formation of a brown deposit. A similar polymerization product has been observed in the pure acetylene discharge of Vasile and Smolinsky. Sagan and Khare (1979) have analysed a presumably similar residue, the "intractable polymer", or what they call "tholin" (Greek "muddy"), which they obtained by discharging CH_4, C_2H_2, NH_3, H_2O and H_2CO. They find that their "tholins" contain a large fraction of the presently known interstellar molecules and argue that tholins are a major constituent of the interstellar grains. The observed large interstellar molecules could be produced by spallation from such grains. Molecular abundance arguments are used to favour this view rather than in situ synthesis from interstellar gas. However, the largest organic molecules, the cyanopolyynes, show a decline in abundance with increasing length (Broten et al., 1978). In this connection it is highly interesting to note that Sakata et al. (1977) have found spectroscopic evidence that "an extract of organic material" (mainly aromatic polymers from the Murchison carbonaceous chondrite) shows absorption features near 2000 Å with a half-width ~300 Å. Organic molecules with conjugated multiple bonds such as $C{\equiv}C{-}C{\equiv}N$, $H{-}C{\equiv}C{-}C$, $C{=}C{=}O$ are known to absorb near 2200 A. Douglas (1977) has suggested that the diffuse interstellar bands observed by optical astronomy could be caused by long carbon chain molecules C_n ($5 \leq n \leq 15$) which would not be easily photodissociated, since they can transform excess energy by internal conversion.

Although there seems to be no doubt that such molecules are abundant in the brown deposit of the discharge products or the "tholins", or more colloquially the "laboratory grains", the coincidence between their absorption and the observed interstellar spectra of sources such as NGC7538E, NGC7027 are at best suggestive, but not conclusive. Thus the idea that grains consist of tholins or a variety of organic compounds, polysaccharides or carbonaceous compounds is speculation. In fact, quite to the contrary, Duley and Williams (1979) very recently concluded that there is little spectroscopic evidence to support the contention that much of the interstellar dust consists of organic material. In particular, grains made of organic material might be expected to show the C-H stretching vibration between 3.3 and 3.4 µm. The carbynes, a triply bonded, linear allotrope of elemental carbon could be an interesting alternative grain (see for example Hayatsu and Anders, this issue).

Although Fischer-Tropsch-type reactions have so far failed to produce the heavier cyanopolyynes — the reason may be technical (Hayatsu and Anders this issue) — HC_3N and HC_5N have been produced in a discharge, starting from HCCH and HCN (Winnewisser et al. 1978). More recently it was noticed that in other (presumed) gas-phase reactions HC_3N can be observed as well: decomposition of vinylcyanide by action of a discharge splits off hydrogen to yield the unsaturated HC_3N (Winnewisser et al. 1981):



A similar reaction of vinylcyanide H_2C_2HCN with HCCH yields HC_5N. In this context the reaction of acetylene, HCCH, with fulminic acid, HCNO, is of interest, since it produces HCCCN but not HCC-CNO (Winnewisser et al. 1981):

$$\begin{array}{lll} HCCH + HCNO & \xrightarrow{\text{r.f. discharge}} & HCCCN + H_2O \\ & \xrightarrow{\hspace{3em}} & HCC{-}CNO + 2H \end{array}$$

In a reducing environment hydrogen atoms will scavenge the oxygen atoms from molecules with NO bonds. This might be the reason that molecules, such as HCNO, N_2O are absent in interstellar space or have fairly low abundances such as NO.

Hayatsu and Anders (this volume) point out from a comparison of the relative abundance pattern of cyanopolyynes $H(C{=}C)_nN$ (n = 1, 2, 3, 4) with that of alcohols $C_nH_{2n-1}OH$ (Fig. 13 of their contribution) that the probability of the cyano polyyne carbon chains growing by one C unit is equal to the "Fischer-Tropsch-type" alcohols. Clearly if the proposed gas-phase mechanism operative in interstellar clouds is the only contributor to the formation of the cyanopolyyne chemistry, and if this mechanism feeds only on itself without other contributing reactions, one would expect an exponential decrease in the abundance. This is not observed. However, several searches for $HC_{11}N$ has so far remained negative. The recent discovery of the high abundance of DC_3N in TMC1 suggests that gas phase reactions must be involved.

In this sense one can only agree with the conclusion of Hayatsu and Anders "that a truly comprehensive review-study of *all* relevant reactions" could reveal the relative importance of gas phase versus surface reactions. It may then turn out that the "truth" is achieved by employing both mechanisms at different stages during the interstellar formation process.

In summary it seems that in situ synthesis of long chain carbon molecules is presently the most convincing of the various formation mechanisms. In particular, spallation of organic grains seems rather unlikely in the cold dark clouds such as TMC 1. We note, incidentally, that the dark clouds produce an absolutely "clean chemistry", in the sense that many types of reactions which occur in terrestrial chemistry are excluded. Shocks, for example, appear not to be present if one can judge from the observed narrow line profiles. The gas is very quiescent and cold. On the other hand, ions such as HCO^+ and N_2H^+ (Guélin et al., 1977) are present within these condensations and we therefore think that molecular-ion production schemes should be investigated further. Some consequences of an ion-molecule formation scheme for the cyanopolyynes have already been discussed. Green and Herbst (1979) point out that even if molecules are produced, say, on grain surfaces, secondary processing by molecular ions is liable to have observable consequences. For example, if, as we have suggested, acetylene, HCCH, is very abundant in TMC 1, then it is likely that its isomer $H_2C{-}C$ (vinylidene) will be produced via the sequence

$$C_2H_2 + H_3^+ \rightarrow C_2H_3^+ + H_2$$

$$C_2H_3^+ + e \begin{cases} \nearrow HC{\equiv}CH + H \\ \searrow H_2C{=}C + H \end{cases}$$

Vinylidene, unlike acetylene, should have a dipole moment and hence may be observable at radio wavelengths. In a similar fashion, one might expect that a high abundance of HC_3N would go together with a large concentration of the isomers HC_2NC and C_3NH. An obvious goal of future research is to attempt to detect isomers and determine their relationship to those already known. The isomers of isocyanic acid, HNCO, cyanuric acid, HOCN, and fulminic acid, HCNO, furnish a particularly interesting example: HNCO has been detected in interstellar space, a tentative assignment of interstellar HOCN exists (Guélin et al., 1981), and HCNO has not been found in agreement with the generally low abundance of molecules with one or more NO bonds.

6 Molecules in Comets and Planetary Atmospheres

Although it is clearly beyond the scope of this review to discuss in detail the composition and chemistry of comets and planetary atmospheres, it seems proper to give a short summary of the molecular species which have been detected there. From Table 8 and 9, it is evident that remarkable similarities exist between the composition of the interstellar medium, comets and the atmospheres of the outer planets which is, in part, based on the reducing environment (with the exception of the inner planets) and the carbon based chemistry. The ability of carbon atoms to combine with as many as four other atoms and its ability to form long chains in which the carbon atoms form the "backbone" of the entire molecule gives them their fundamental importance. The list of detected molecules (interstellar, cometary and planetary) contains a large number of molecules with one or more carbon atoms. In fact, the most complex molecules safely identified in interstellar space are carbon based molecules and even in the highly reducing atmospheres of Jupiter and Saturn hydrocarbons have been identified. Thus the carbon chemistry in interstellar space is not only interesting in its own right but also because the more complex interstellar molecules are found in meteorite materials, in comets, and in the primordial atmospheres of the outer planets. They also resemble closely the basic building blocks of living matter on earth. Despite these similarities, it is not clear, however, how the existence of interstellar molecules relates to the existence of molecules in comets and planetary atmospheres. Recently, Larson 1980 and Prinn and Owen 1976 (and references therein) have summarized in detail the atmospheres of the outer planets. From Table 9, it becomes clear that next to molecular hydrogen, methane CH_4, is the major constituent in the atmospheres of the outer planets, and its photodissociation yields CH and CH_2 radicals in a ratio of about 8 to 92. CH_2 reacts with H_2 to form CH_3 which, in turn, captures H to form CH_4. About 20% of the photo-dissociated CH_4 is then converted to the hydrocarbon chain molecules C_2H_2, C_2H_4 and C_2H_6, two of which have been detected in the jovian atmosphere. In the ionosphere of Jupiter and in the regions of discharges in the cloudy zones of the atmosphere, the higher-order hydrocarbon ions are the likely precursors of C_2H_2, C_2H_4, . . . which could form according to the reactions:

$$C_2H_5^+ + C_2H_4 \rightarrow (C_4H_9^+)^* \rightarrow C_4H_5^+ + CH_4$$
$$C_2H_5^+ + C_2H_2 \rightarrow (C_4H_7^+)^* \rightarrow C_4H_5^+ + H_2$$

followed by dissociative electron recombination which is similar to the interstellar mechanism. The hydrocarbon reaction scheme for Jupiter, illustrated in Fig. 2 (according to Prim and Owen), reveals the similarities between the interstellar and planetary chemistry in a reducing environment. The longer hydrocarbons produced in the ionospheres and higher atmospheres of the giant planets Jupiter and Saturn are convectionally transported down to the hot lower atmosphere. There they are converted back into CH_4 most likely by thermochemical reactions. In this sense it is "raining crude oil" in the atmospheres of Jupiter and Saturn. The hydrogen abundance in Uranus and Neptune is lower than that of Jupiter and Saturn, indicating that they have lost some hydrogen and helium in the course of their

Table 8. Observed composition of comets (Whipple and Huebner (1976))

Head:	H, C, C_2, C_3, CH, CN, $^{12}C^{13}C$, HCN, CH_3CN, NH, NH_2, O, OH, H_2O, Na, K, Ca, V, Cr, Mn, Fe, CO, Ni, Cu.
Tail:	CH^+, CO^+, CO_2^+, N_2^+, OH^+, H_2O^+, Ca^+.
	Continuum from particles including Silicate 10- and 18 µm bands in head and tail.

Table 9. Molecules detected in Planetary Atmospheres

Planet	Molecules	
Mercury	No definite identification	
Venus	CO_2 (96%), N_2 (3.5%), H_2O, HCl, HF, H_2SO (droplets), Ar	(90 Earth Atm.)
Earth	N_2 (80%), O_2, $_{=2}O$, CO_2, CH_4, H_2, CO; Ar, Xe, Ne, Kr, N_2O, O, O_2, O_3	
Mars	CO_2 (95%), N_2 (2.7%), Ar, O_2, H_2O	(0.01 Earth Atm.)
Jupiter	H_2, He, CH_4, NH_3, H_2O, PH_3, GeH_4, CO, C_2H_2, C_2H_6	
Saturn	H_2, CH_4, NH_3, PH_3, C_2H_2, C_2H_6; (He assumed)	
Uranus	H_2, CH_4	
Neptun	H_2, CH_4	
Pluto	No identifications	

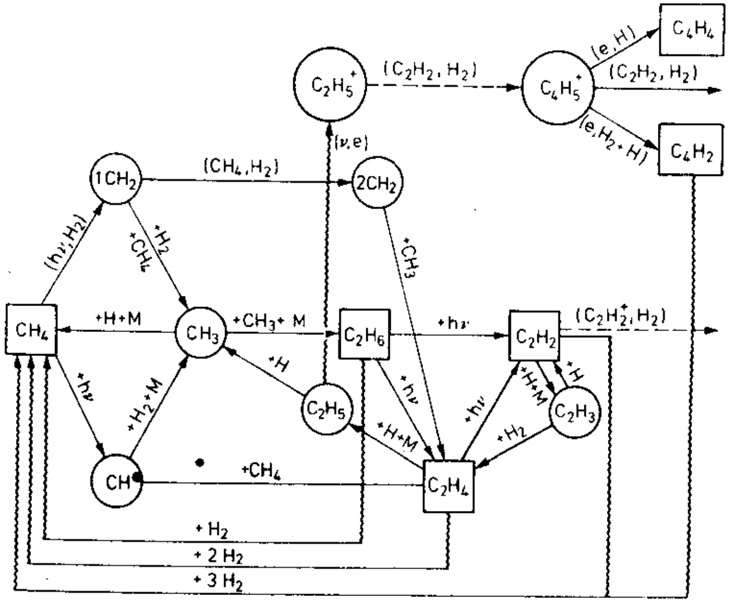


Fig. 2. Planetary methane and higher order hydrocarbon cycle in Jupiter's mesosphere and stratosphere (from Prinn and Owen, (1976)) and upper atmosphere. Vertical transport is represented by vertical wavy lines. Squares enclose stable molecules, whereas ions, radicals and unstable molecules are encircled.

history. Contrary to the reducing primordial atmospheres of the outer planets, the inner planets (notably Venus and Earth) have oxidizing secondary atmospheres, which were made after the planets had been formed and most of primordial hydrogen and helium was lost.

Comets offer the chance, each time they come to close encounter with the sun, to investigate early primitive solar system material which presumably was formed directly from the gas and dust of the solar nebula. It is assumed that the nucleus of comets consists of large grains of rocky material (meteoroidal material) which is mixed and/or covered with ices, molecules and atoms which are bonded to the ices (clathrates). Although the true nucleus of a comet is rarely observed, the comets are extensively being studied by the material they lose under the action of solar radiation during close solar encounter, i.e. at distances of less than 5 AU (1 AU = 1 astronomical unit = 1.5×10^{13} cm). The matter comets lose in this process are mainly gases and meteorites. Table 8 summarizes all so far detected cometary molecules. It is seen that the head of the comet contains molecules, radicals and atoms, whreas the tail shows only ions. Practically all of these molecules and ions are also interstellar species. For further detail on cometary spectra and the prevailing physical processes, the reader is referred to an excellent review by Whipple and Huebner (1976). All of the present knowledge has come from the analysis of cometary spectra but the planned space probe mission (if carried out) to Halley's comet in 1986 would be of superb scientific value.

7 Conclusion

The past decade of interstellar research has established that the most widely distributed and most abundant interstellar molecules (OH, CH, H_2O, H_2CO, HCN, NH_3) are found in molecular clouds within our Galaxy and in other galactic systems, i.e. in extragalactic sources such as the Andromeda Nebula (M31) the spiral Galaxy NGC 253 and others. On the galactic scale the interstellar molecules are found in a large variety of astronomical objects with widely different physical parameters, ranging from the diffuse clouds and the cold dark clouds to the dense hot circumstellar environment. In the list of molecules detected to date, carbon based molecules dominate the larger molecules, due to the ability of carbon to form long chain molecules. Oxygen and nitrogen with similar cosmic abundance do not share this ability; at most they form hydrogenperoxide, HOOH, or hydrazin, HNNH, as chain molecules. Silicon, with lower cosmic abundance than C, N and O does form silicon chains (mainly a silicon-oxygen bond). However, its high affinity to oxygen rather forms silicon oxides than silicon hydrites and thus most of the silicon will be locked up as SiO in interstellar space. Even in a very reducing atmosphere SiH_4 is only formed as a high temperature species ($T \sim 1000$ K) and one does not therefore expect to find SiH in interstellar space in detectable quantities.

Carbon based chemistry (organic chemistry) has thus been established to be of fundamental importance in interstellar molecular clouds. Similarly the observed composition of comets is dominated by carbon bearing molecules, and in the reducing atmospheres of Jupiter and Saturn the carbon chain molecules C_2H_2, C_2H_6 have been detected.

Interstellar molecules are detected at the position where they are formed. Their formation mechanism is usually modelled for a steady-state situation, although their abundances are not in thermodynamic equilibrium. Cosmic rays and ultraviolet radiation prevent equilibrium from being reached. Cosmic ray ionization is seen as the driving force for a large number of chemical reactions.

Catalytic processes and gas-phase-reactions are required to explain molecule formation. The rate at which atoms stick to the surface of interstellar dust grains seems to be comparable to the reaction rates of various important gas phase reactions. Although there is general agreement that H_2 is formed on grain surfaces, HD is the strongest evidence for gas phase reaction mechanisms. In fact, gas-phase models have had the better of the arguments so far, at least for the explanation of the abundance of simple molecules, notably the ions HCO^+, N_2H^+ and HCN, HNC, CCH. For this simple class of gas phase reactions, the ion-molecule model produces predictable results. For ion-molecule reactions to be fast they must be exothermic and have no activation energy barrier. Already for intermediate sized molecules such as NH_3, H_2CO predictions based on the ion-molecule scheme become uncertain. The formation of complex molecules is presently a great challenge in interstellar chemistry. Although both mechanisms, grain-surface and ion-molecule reactions are thought to contribute, their main problems remain: uncertainties concerning the surface processes are mainly connected with the ejection mechanism on one hand, branching ratios and reaction rates on the other require considerably more detailed, but extremely interesting and rewarding laboratory investigations. In addition, the many unidentified lines detected to date in interstellar space are likely to be caused by short lived reaction intermediates or by complex molecules not yet synthesized in the laboratory. For their proper identification precise laboratory microwave frequencies are required. These studies have now being extended to high resolution infrared studies of molecules.

8 References

Aanestad, Per A., Purcell, E. M.: Ann. Rev. of Astron. Astrophys. *11*, 309 (1973).

Adams, N. G., Smith, D.: IAU No. 87, Interstellar Molecules (B. H. Andrew, ed.) p. 311 (1980).

Arnold, F.: Proc. XXI Liège Colloquium, 494 (1977).

Bates, D. R., Spitzer, L.: Astrophys. J. *113*, 441 (1951).

Black, J. H., Dalgarno, A.: Astrophys. (Letters), *15*, L79 (1973).

Black, J. H., Dalgarno, A.: Astrophys. J. Suppl. *34*, 405 (1977).

Black, J. H., Hartquist, T. W., Dalgarno, A.: Astrophys. J. *224*, 448 (1979).

Broton, N. W., Oka, T., Avery, L. W., MacLeod, J. M., Kroto, H. W.: Astrophys. J. *223*, L105 (1978).

Burt, J. A., Dunn, J. L., McEwan, J. M., Sutton, M. M., Roche, A. E., Schiff, H. I.: J. Chem. Phys. *52*, 6062 (1970).

Conrad, M. P., Schaefer, H. F.: Nature *274*, 456 (1978).

Dalgarno, A.: Atomic Processes and Applications (ed. P. G. Burke, B. L. Moiseiwitsch), p. 109, Amsterdam: North Holland (1976).

Dalgarno, A.: IAU No. 87, Interstellar Molecules (B. H. Andrew, ed.) 273 (1980).

Dalgarno, A., Black, J. H.: Rep. Prog. Phys. *39*, 573 (1976).

Dalgarno, A., McCray, R. A.: Astrophys. J. *181*, 95 (1973).

Douglas, A. E.: Nature *269*, 130 (1977).

Duley, W. W., Williams, D. A.: Nature *277*, 40 (1979).
Elitzur, M., de Jong, T.: Astrophys. J. (Letters) *222*, L141 (1978).
Fehsenfeld, F. C., Schmeltekopf, A. L., Dunkin, D. B., Ferguson, E. E.: ESSA tech. Rep. ERL 135-AL3 (U.S. Dep. Commerce) (1969).
Fehsenfeld, F. C., Dunkin, D. B., Ferguson, E. E., Albritton, D. L.: Astrophys. J. *183*, L25 (1973).
Green, S., Herbst, E.: Astrophys. J. *229*, 121 (1979).
Guélin, M., Langer, W. D., Snell, R. L., Wootten, H. A.: Astrophys. J. *217*, L165 (1977).
Hartquist, T. W., Black, J. H., Dalgarno, A.: Mon. Not. Roy. Astr. Soc. *185*, 643 (1978).
Hartquist, T. W., Oppenheimer, M., Dalgarno, A.: Astrophys. J. (in press) (1981).
Herbst, E., Klemperer, W.: Astrophys. J. *185*, 505 (1973).
Herbst, E., Klemperer, W.: Physics Today *29*, 32 (1976).
Herbst, E.: Astrophys. J. *222*, 508 (1978).
Herbst, E.: in Protostars and Planets, p. 88 (T. Gehrels ed.), Univ. of Arizona Press, Tucson (1978).
Hollenbach, D. J., Salpeter, E. E.: Astrophys. J. *163*, 155 (1971).
Hollenbach, D. J., Werner, M. W., Salpeter, E. E.: Astrophys. J. *163*, 165 (1971).
Hollenbach, D. J., McKee, C. F.: Astrophys. J. Suppl. (in press) (1980).
Hunter, D. A., Watson, W. D.: Astrophys. J. *226*, 447 (1978).
Huntress, W. T., Jr.: Astrophys. J. Suppl. *33*, 495 (1976).
Huntress, W. T., Jr., Prasad, S. S., Mitchell, G. F.: IAU No. 87, Interstellar Molecules (B. H. Andrew, ed.) p. 331 (1980).
Iglesias, E. R., Silk, J.: Astrophys. J. *226*, 851 (1978).
Johnsen, R., Biondi, M. A.: J. Chem. Phys. *61*, 2112 (1974).
Jura, A.: Astrophys. J. *197*, 581 and references therein (1975).
Langer, W. D., Frerking, M. A., Linke, R. A., Wilson, R. W.: Astrophys. J. *232*, L65 (1979).
McCabe, E. M., Smith, R. C., Clegg, R. E. S.: IAU Interstellar Molecules p. 497–502, (B. H. Andrew, ed.) (1980).
McDaniel, E. W., Cermak, V., Dalgarno, A., Ferguson, E. E., Friedman, L.: Ion-Molecule Reactions, Wiley-Interscience, New York (1970).
McEwan, M. J., Anicich, V. G., Huntress, W. T., Jr., Kemperer, P. R., Bowers, M. T.: in IAU No. 87, Interstellar Molecules, (B. H. Andrew, ed.), p. 305 (1980).
Prinn, R. G., Owen, T.: in Jupiter (T. Gehrels, ed.) p. 319 (1976).
Sagan, C., Khare, B. N.: Nature *277*, 102 (1979).
Sakata, A., Nakagawa, N., Iguchi, T., Isobe, S., Morimoto, M., Hoyle, F., Wickramasinghe, N. C.: Nature *266*, 241 (1977).
Sando, K. M., Cohen, R., Dalgarno, A.: Conf. Electronic and Atomic Collisions (T. R. Govers, F. J. de Heer eds.) North Holland, Amsterdam, p. 973 (1972).
Savage, B. D., Mathis, J. S.: Ann. Rev. Astron. Astrophys. *17*, 73–111 (1979).
Schmeltekopf, A. L., Fehsenfeld, F. C., Ferguson, E. E.: Astrophys. J. *148*, L155 (1967).
Smith, D., Adams, N. G.: Kinetics of Ion Molecule Reactions (P. Auloos, ed.), Plenum Press, New York, p. 345 (1978).
Snow, T. P., Jr.: IAU No. 87, Interstellar Molecules p. 247 (B. H. Andrew, ed.) (1980).
Thaddeus, P., Guélin, M., Linke, R. A.: Astrophys. J. (in press) (1981).
Vasile, M. J., Smolinsky, G.: Int. J. Mass Spect. Ion Phys. *24*, 11 (1977).
Watson, W. D.: Astrophys. J. *182*, L69 (1973).
Watson, W. D.: Astrophys. J. *183*, L17 (1973).
Watson, W. D.: Astrophys. J. *188*, 35 (1974).
Watson, W. D.: Rev. Mod. Phys. *48*, 513 (1976).
Watson, W. D.: Ann. Rev. Astron. Astrophys. *16*, 585 (1978).
Watson, W. D.: Proc. Liège Int. Astrophys. Symp. 21st, p. 526 (1978).
Watson, W. D., Christiensen, R. B., Deissler, R. J.: Astron. a. Astrophys. *69*, 159 (1978).
Watson, W. D.: in IAU No. 87. Interstellar Molecules (B. H. Andrew ed.) p. 341, (1980).
Whipple, F. L., Huebner, W. F.: Ann. Rev. Astron. Astrophys. *14*, 143 (1976).
Winnewisser, G., Churchwell, E., Walmsley, C. M.: in Modern Aspects of Microwave Spectroscopy, (G. W. Chantry ed.), 313-503 Academic Press, London (1979).
Winnewisser, G., Mezger, P. G., Breuer, H. D.: Topics in Current Chemistry, Vol. 44, Springer-Verlag, Berlin, Heidelberg, New York (1974).
Winnewisser, G., Walmsley, C. M.: Astrophys. a. Space Sci. *65*, 83 (1979)

Winnewisser, G., Toelle, F., Ungerechts, H., and Walmsley, C. M.: in IAU No. 87, in Interstellar Molecules (B. H. Andrew, ed.), p. 59 (1980).
Winnewisser, G., Winnewisser, M., Christiansen, J. J.: Astron. a. Astrophys. (in press) (1981).
York, D. G., Rogerson, J. B. Jr.: Astrophys. J. *203*, 378 (1976).
Zuckerman, B.: Ann. Rev. Astron.-Astrophys. *18*, 263 (1980).

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Note 1 Added in Proof

Johnsen et al. (1980) have measured the rate coefficient for $He^+ + H_2$ to be 10^{-13} cm³ sec⁻¹ down to 78 K. Thus this reaction cannot be neglected any longer compared to the ionization of C, N, O ... by He^+.

Johnsen, R., Chen, A., Biondi, M. A.: J. Chem. Phys. *72*, 3085 (1980).

Note 2 Added in Proof

The reaction of C^+ with NH_3 might lead preferentially to HNC via the isomer H_2NC^+ (Allen et al. (1980), Brown, (1977)) which lies ~2 eV above the linear isomer $HNCH^+$. The stable triplet configuration H_2NC^+ might radiatively decay into singlet H_2NC^+ rather than isomerize to the linear form.

In this connection it worthwhile to note that HCN and HNC can be converted into each other by reactions of the form

$$\left.\begin{matrix} HCO^+ \\ N_2H^+ \\ H_3^+ \end{matrix}\right\} + HCN, HNC \rightarrow HNCH^+ + \left\{\begin{matrix} CO \\ N_2 \\ H_2 \end{matrix}\right.$$

or by proton exchange

$$HNC + H^+ \rightarrow HCN + H^+$$

Local disturbances in the clouds might favour one or the other molecule. In the Orion ridge Goldsmith et al. (1981) find an overabundance of HCN which might be an indication of shock influence.

Allen, M., Goddard, J. D., Schaefer, H. F., III., J. Chem. Phys. *73*, 3266, (1980).
Brown, R. D., Nature *270*, 39 (1977).
Goldsmith, P. F., Langer, W. D., Ellder, J., Irvine, W., Kollberg, E., (1981), preprint.