RECENT PROGRESS IN INTERSTELLAR CHEMISTRY

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ABSTRACT

In this article I shall summarise recent applications of interstellar chemistry to a variety of astronomical scenarios. I shall look in detail at some of these, in particular at the chemistry of the polycyclic aromatic hydrocarbons (PAHs) and of the fullerenes (C_{60} and C_{70}). I shall also consider the chemistry that occurs in hot molecular cores and show how observations of these regions can be used to probe the chemical history of the material. Finally I shall make some remarks about the possible presence of H_2CO and SO^+ in oxygen-rich circumstellar envelopes.

1. INTRODUCTION

Our understanding of the chemical processes which occur in astronomy has greatly increased in the last few years. In part this has to with the great amount of data which has emanated from chemical kinetic laboratories,(1),(2) in part to the detailed molecular identifications and maps available from observers and in part to the application of astrochemical models to a wide range of astronomical objects including diffuse and dense interstellar clouds, carbon-rich and oxygen-rich circumstellar shells, shocked gas, photon-dominated regions, protostellar outflows, external galaxies and the early universe(3),(4),(5).

To date, almost 100 molecules have been detected in interstellar and circumstellar clouds, comprising the elements H, C, N, O, Si, P, S, Cl and, most recently, Mg, although P and Mg are each detected in only one molecule and the identification of the only Cl-bearing molecule, HCl, remains insecure. The chemistries of most elements appear to be driven by ion-neutral reactions although neutral-neutral reactions make important contributions to the synthesis of molecules containing nitrogen and sulfur and the H_2 molecule, which is crucial to efficient molecular synthesis, is formed on grain surfaces. Ion-chemistry must be driven by ionisation; in diffuse clouds this is provided by the general interstellar ultraviolet radiation field, whilst in dense clouds it is provided by cosmic ray particles. In some regions, ionisation driven by X-rays might be important and lead to significantly different routes to molecule formation. In dense clouds, cosmic ray collisions with H_2 produce H_2^+ ions which, within about one day, are converted into H_3^+ ions. Because the proton affinity of H_2 is rather low, these ions transfer their protons to atoms such as C and O (but not N for which the proton transfer is slightly endothermic) to form ions such as OH^+ and CH^+. These ions react rapidly in a series of reactions with molecular hydrogen to form the terminating ions H_3O^+ and CH_5^+, respectively. These terminal ions then undergo dissociative recombination with electrons to form OH, H_2O and CH_4 among other possibilities. The H_3^+ ion is also crucial in the deuteration of interstellar molecules through its reaction with HD which, at low temperatures, is exothermic by about 220 K. The resulting H_2D^+ ion then transfers D through deuteron transfer reaction with neutrals such as CO, N_2, and H_2O, producing DCO^+, N_2D^+ and HDO. Once simple molecules are formed, reactive ions and radicals are produced through reaction with He^+ ions, which are formed by cosmic ray ionisation of He atoms, for example

$$He^+ + CO \rightarrow C^+ + O + He.$$

The C^+ ion can then react with methane to produce more complex hydrocarbon ions,

$$C^+ + CH_4 \rightarrow C_2H_2^+ + H_2$$

$$C^+ + CH_4 \rightarrow C_2H_3^+ + H.$$

Dissociative recombination of these ions with electrons can produce the observed interstellar molecules C_2, C_2H and C_2H_2.

Nitrogen bonds are formed through the reaction of N atoms with OH to produce NO which reacts with N atoms to form the N_2 molecule. N_2 takes a proton from H_3^+ to form the observed N_2H^+ ion and also reacts with He^+ to give kinetically excited N^+ ions. The reaction of N^+ with H_2 is slightly endothermic but the excess energy in the N^+ ions is sufficient to drive the reaction. The resulting NH^+ ion quickly undergoes a series of H-atom abstraction reactions with H_2 to form the terminating ion NH_4^+ which undergoes dissociative recombination to give NH_3. Reactions of this type are believed to form the bulk of interstellar molecules in dark clouds, although there is still a certain amount of doubt over the formation processes of some of the larger species, such as the cyanopolyynes - much of this is related to the lack of accurate laboratory studies on the reactivities of these species.

2. PAH/FULLERENE CHEMISTRY

In recent years, it has been suggested that a significant fraction of carbon is tied up in the form of small polycyclic aromatic hydrocarbon molecules. Such species appear to be required if a variety of observations, particularly those of the emission bands in the infrared are to be understood (see 6) for an up-to-date review of the subject). The influence of PAH, and fullerene, species on the chemistry of interstellar clouds has been discussed[7),8)]. It has been suggested that the majority of PAH molecules will be negatively charged even in diffuse clouds and that, since they will therefore carry the negative charge in these clouds, chemical models which incorporate dissociative recombination by free electrons in the gas phase may be seriously in error. In addition, PAH$^+$ ions have been suggested as the source of the diffuse interstellar absorption bands[9)]. The abundance of such molecules in the interstellar medium is uncertain. Although they are probably formed in the envelopes around late-type, carbon-rich stars,[10)] the mechanisms by which they are destroyed are unclear. It has been suggested that they are destroyed through being engulfed by supernova remnants[10)] on a time-scale of 10^8 years, while others[11)] have argued that they can be destroyed by oxygen atoms, although such a process may involve an appreciable activation energy barrier[12)].

More recently, there have been a number of experimental studies performed on the ion-neutral reactions of PAH and fullerene molecules, including C_{60} and C_{70} (see the review article [13)]). From these studies it is clear that doubly-charged PAH/fullerene cations are readily produced in the reaction of the neutrals with He$^+$ ions. The presence of such cations in interstellar clouds raises the possibility that their recombination with electrons may be dissociative rather than radiative, as is normally assumed for the singly-charged cations. The second ionisation potential of these neutrals is about 19 eV[14)] and the difference in energies between the first and second ionisation potentials - the energy released upon recombination - is about 12 eV. It is this large energy release which suggests that the recombination is dissociative rather than radiative. Note that since the energy difference is less than 13.6 eV, the general interstellar radiation field can produce doubly-charged PAH and fullerene cations in diffuse clouds[15)].

The influence of these new laboratory data on chemical models of diffuse and dense clouds has been investigated[16)]. In the particular case of dense clouds, if recombination is dissociative, and the molecules are not able to reform, a reasonable assumption,then all PAH/fullerene molecules are destroyed on a time-scale of $< 10^7$

years, while the time-scale in diffuse clouds is about 10^4 years because of the much larger electron abundance. This would suggest that PAH/fullerene species are not widespread in the interstellar medium. Although the thermodynamic properties of many PAH and fullerene molecules are remarkably similar, it is possible that the stability of the C_{60} sphere might ensure that the $C_{60}{}^{++}$ + e reaction is radiative rather than dissociative. Thus C_{60} may be long-lived while PAHs, and particularly the smaller ones, are not. Laboratory studies are required to confirm this conjecture.

3. HOT MOLECULAR CORES

It has been become clear that an important component of molecular clouds in regions of star formation is contained in the so-called hot molecular cores (HMCs). These are small (0.01-0.1 pc), warm (100-300 K), dense (10^6-10^8 particles cm^{-3}) and opaque (N ~ 10^{23}-10^{24} cm^{-2}, A_V = 100-1000 mag) clumps of gas which contain unusual abundances of various types of molecule. In particular, small, saturated molecules such as NH_3, H_2S, CH_4 and CH_3OH are detected with fractional abundances enhanced over those in dark, dense clouds by factors of 100-1000; molecules containing deuterium, e.g. HDO, NH_2D, CH_3OD, and even a doubly-deuterated species, D_2CO,$^{17)}$ are readily detected and show deuterium enhancements of 100-1000 times the cosmic D/H ratio; and large, complex and relatively saturated molecules such as ethyl cyanide, CH_3CH_2CN, dimethyl ether, CH_3OCH_3, and methyl formate, $HCOOCH_3$, are detected$^{18)}$. Since these observational facts are difficult to understand using conventional gas-phase chemistry,$^{19)}$ a consensus has emerged that the chemical composition of the hot gas is due to the evaporation of the icy mantles of dust grains due to the heating effects of nearby, newly-formed stars. In this type of picture there is an evolutionary sequence from cold, dark clouds with no embedded sources, such as TMC-1, in which molecules are observed in the gas phase, to cold regions, such as AFGL 2136, seen through infrared absorption toward protostars to contain dust having a rich molecular ice, to HMCs, such as the Hot Core and Compact Ridge regions in Orion, which have on-going star formation and anomalous gas-phase abundances. The chemistry of this type of sequence has been modelled[20),21),22)]. In this picture the hot core gas is chemically inert since it is largely composed of saturated, stable neutral molecules. For times up to 10^4 years after the mantle evaporation, little chemistry takes place because there is no ionisation from UV photons, and cosmic-ray ionisation is inefficient since the fractional ionisation produced by this means is inversely proportional to density. Radio observations of gas-phase species in hot cores may thus give important information on the physical and chemical processes occurring on the surfaces of cold dust particles; if this is so, radio observations are better able to detect the trace components of the mantles than direct IR measurements of the absorption bands due to the mantles themselves. As mentioned above, simple models appear to account reasonably successfully for the presence and amount of the smaller molecules and the degree of deuterium fractionation observed, providing that some molecular processing occurs in the grain mantle once material has been frozen out from the gas phase. However, these models are not able to account for the abundances of the larger molecules nor for the chemical differentiation observed between HMCs, including those which appear nearby in the sky. As examples of this, the Orion Hot Core, which has a density of 10^7 cm^{-3} and a temperature of 200 K is rich in nitrogen-bearing molecules, whilst the nearby Orion Compact Ridge, which has a density of 10^6 cm^{-3} and a temperature of 100 K, is rich in large, oxygen-bearing organic molecules. The chemistry of the Compact Ridge cloud has been modelled[19)] as due to the interaction of a wind containing H_2O and an ambient molecular cloud, following a previous suggestion,[23)] but the injected water is processed away from forming large oxygen-containing molecules. The evaporation of mantles rich in water ice was then studied[19)] but again poor agreement was found between calculated abundances and those observed. Finally, a model in which a methanol-rich mantle was evaporated was considered. In this case, good agreement between theory and observations was found, although there was no discussion as how different mantle compositions can arise in nearby regions - the Hot Core chemistry appears to be the result of the evaporation of ammonia-rich mantles[20]. Recent interferometric maps[24] of thermal CH_3OH, $HCOOCH_3$ and CH_3OCH_3 in Orion have shown that the spatial distribution of these molecules is consistent with the picture proposed in [19].

The hot gas-phase chemistry which occurs when simple molecules are released from the grain surfaces in hot core regions has been investigated in more detail[25] in an effort to see whether large complex molecules could be synthesised in the gas phase rather than on the grain mantles. It was shown that the evaporation of mantles which differed only in their NH_3/CH_3OH abundance ratio could account for the chemical differentiation observed in the Orion hot cores. In the Compact Ridge, release of CH_3OH drives the formation of methyl formate and dimethyl ether in the manner suggested by [19], namely that the released methanol takes a proton from H_3^+ and subsequently reacts with CH_3OH, to form CH_3OCH_3, or H_2CO, to form $HCOOCH_3$. The formation of other O-bearing molecules such as ketene, CH_2CO, and acetaldehyde, CH_3CHO, can be driven by the release of simple hydrocarbons such as ethene and ethane followed by protonation and reaction with oxygen atoms. Ethanol, CH_3CH_2OH, formation is slow in this model and gives a fractional abundance around 10^{-11}, in agreement with the upper limit of $5\ 10^{-10}$ derived by [23], but much less than the value of 10^{-6} derived by [18]. If correct, such an abundance would undoubtably imply a grain surface formation for ethanol. In any case, the gas-phase chemistry is unable to reproduce the fractional abundances of ethanol, $\sim 10^{-8}$, detected in other HMCs [26].

In the Orion Hot Core, which is denser and warmer, ion-molecule reactions play a less important role in driving the hot chemistry. NH_3 released from the grains is rapidly converted to the reactive CN radical which combines with the simple hydrocabons released to form complex, nitrogen-bearing species such as cyanoacetylene, HC_3N, and vinyl cyanide, CH_2CHCN. Ethyl cyanide, CH_3CH_2CN, is more difficult to form since the reaction of CN with C_2H_6 produces HCN and not ethyl cyanide[27]. A plausible scenario for the chemical differentiation between HMCs, involving both gas-phase and surface chemistry in a collapsing protostar, has been proposed28). The chemistry of two separated shells was followed for 10^5 years, at which time they are assumed to be impacted by a stellar wind from the protostar. The inner shell, which is dense, warm and molecular initially, was taken to represent the Orion Hot Core and the outer shell, less dense, colder and atomic initially, was taken to represent the Orion Compact Ridge. During the collapse phase, the surface chemistry of the two shells is different, molecules such as NH_3 and HC_3N dominating in the Hot Core and H_2O, CH_3OH and H_2CO dominating in the Compact Ridge. Important differences in the surface chemistry are related to the different grain temperatures which affect the evaporation rates of accreted material.

More recently, the hot gas-phase chemistry which results if alcohols more complex than methanol are evaporated from grains has been discussed29). Species such as methyl ethyl ether, $CH_3OC_2H_5$, and diethyl ether, $(C_2H_5)_2O$ can be formed with fractional abundances approaching 10^{-8} for an injected ethanol abundance of 10^{-6}. The abundances of these species scale with the adopted ethanol abundance.

4. OXYGEN-RICH CIRCUMSTELLAR SHELLS

Over the last few years, an increasing number of molecules containing carbon atoms have been detected in the circumstellar envelopes (CSEs) around late-type oxygen-rich stars. Since carbon should be entirely tied up in the stable CO molecule, the origin of the carbon in other molecules has been a matter of investigation. It has been suggested30),31) that the photodissociation of methane, CH_4, provided the carbon even though there is no evidence for its presence from either observation or theory. Recently, the hypothesis that methane is the primary source of the reactive carbon has been tested by investigating its chemistry in more detail32). In particular it has been shown that H_2CO is a detectable molecule, since it is formed in the $CH_3 + O$ reaction, in which CH_3 and O are the photodissociation products of CH_4 and H_2O, respectively. Radial column densities and predicted antenna temperatures for a number of millimeter transitions have been tabulated for a number of likely sources32). The column densities of other molecules formed by the reactions of CH_3, namely H_2CN

and H_2CS, are at least an order of magnitude smaller than that of H_2CO and are therefore undetectable with current instruments. As a by-product of these calculations, column densities for the ion SO^+ have also been estimated. SO^+ has recently been detected toward the supernova remnant IC 443[33)] suggesting that it arises in chemistry driven by the interaction between the remnant and small clumps of molecular gas, although it is more likely a result of chemistry in a photon-dominated region[34)]. In O-rich CSEs, the SO^+ ion is formed readily by the reaction of S^+ and OH and lost by photodissociation and by dissociative recombination with electrons. Column densities fall in the range 2 10^{12} - 2 10^{13} cm^{-2} for mass-loss rates in the range 2 10^{-7} - 2 10^{-5} solar masses per year (see Figure 1). Although the dipole moment of SO^+ is relatively large, 2.2 Debye, the lines are expected to be weak but may be detectable with a large telescope.

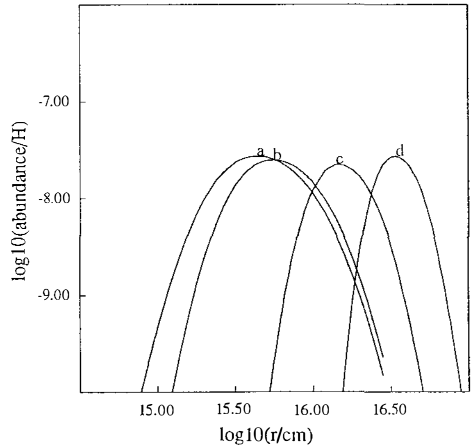

Figure1: The radial distribution of SO^+ is shown as a function of mass-loss rate: (a) 2 10^{-7}, (b) 5 10^{-7}, (c)5 10^{-6}, (d) 2 10^{-5} solar masses per year.

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