Chapter 13

Chemical Reactivity in Interstellar Space

Gaston Berthier

Laboratoire d'Etude Théorique des Milieux Extrémes

École Normale Supérieure

24, rue Lhomond, F-75005 Paris˙

> Always pull a peach
> When it is in your reach
> (Swift, reported by Walter Scott)

13.1 Rudiments of Interstellar Physical Chemistry

13.1.2 Observational Background

The presence of molecular species in the space surrounding stars in our Galaxy is documented for more than half a century through investigations using spectroscopy methods: Three very simple diatomics, CH , CH^+, CN (an embryo of cyanide!) were detected between 1937 and 1941 by astrophysical observations of characteristic absorption lines at the border of the ultra-violet and

visible spectra (1). Given the rather special electronic structure of these interstellar objects, namely two radicals with pending valencies and a cation, it was difficult to consider them as ordinary chemical products; less "exotic" species, as water, ammonia, formaldehyde etc. were observed only towards the end of the sixties (2), due to progress in recording emission lines at millimetre wavelengths (1 mm = 30 GHz).

At the present time, about hundred compounds has been classified as interstellar molecules, without taking their isotopomers into consideration, for instance many deuterated species, but also rare compounds resulting from carbon ^{13}C and nitrogen ^{15}N substitutions. The deviation of the D/H ratio with respect to the value accepted for the elemental abundance of deuterium (0.000016) is an important parameter to be known for the processing of the interstellar matter. The list of Table 1 is expected to be complete up to the end of 1997. It includes species detected in the interstellar medium as well around some giant stars, in so far as they have been identified as single molecules. The only exception to this rule is the so-called PAH's (*i.e.*, polycyclic aromatic hydrocarbons) for reasons explained below. The molecule-ion H_3^+ predicted as being everywhere in space on the basis of theoretical schemes for proton-exchange reactions $X + H_3^+ \rightarrow XH^+ + H_2$, but never observed up to 1996, has been finally detected in infrared by its rotation-vibration band ν_2 at 3.7 mm (2726 cm^{-1}). This was a major achievement of the year 1996 (3) for astrochemists.

Table 1. Interstellar molecules identified between 1937 and 1997

Neutral Molecules				
H_2	NH NH$_3$	H_2O	H_2S	SiH_4
CH_2	NO	CO	CS	SiC
CH_4	N_2O	C_2O	C_2S	*cyc*-SiC$_2$
C_2	HCN	C_3O	C_3S	SiC$_4$
C_2H_2	HNC	C_5O	C_5S	SiN
C_2H_4	HNO	HCO	H_2CS	SiO
C_3	HNCO	H_2CO	CH_3SH	SiS
cyc-C$_3$H$_2$	HNCH$_2$	*cyc*- C$_2$H$_4$O	SO	PN
CH$_3$C≡CH	H$_2$NCHO	HCOOH	SO$_2$	HCl
C_4H_2	CH$_3$CN	CH$_3$OH	OCS	NaCl
C_5	CH$_3$NC	CH$_2$CO	HNCS	AlCl
CH$_3$(C≡C)$_2$-H	HC$_3$N	CH$_3$CHO		KCl
	CH2CHCN	(CH$_3$)$_2$CO		NaCN
	CH3CCCN	CH$_3$CH$_2$OH		
	HC$_5$N	CH$_3$OCH$_3$		HF
	HC$_7$N	CH$_3$OCHO		AlF
	HC$_9$N	CH≡C-CHO		

Table 1 (cont.). Interstellar molecules identified between 1937 and 1997

Free Radicals				
CH	NH_2	OH	NS	PC
C_2H	CN			MgCN
C_3H	H_2CN			MgNC
cyc-C_3H				
C_4H	H_2CCN			
C_5H	C_3N			
C_6H	C_4N			
C_7H				
C_8H				

Molecular Cations			
H_3^+	N_2H^+	CO^+	HCS^+
CH^+	$HCNH^+$	H_3O^+	SO^+
(PAH^+)	HC_3NH^+	HCO^+	
		HOC^+	
		$HOCO^+$	
		H_2COH^+	

The number and the variety of molecules in certain parts of space give us the astrophysical background of Interstellar Chemistry. Well-defined compounds are found in the so-called interstellar clouds and circumstellar envelopes, the former because they seem to mask stars behind them and the latter because they are issued from dying red stars. Chemistry problems will be discussed in the same time for both types of regions.

The most recent developments in Astrochemistry come from progress:

− concerning observational techniques, which include telescopes embarked on spacecrafts. Let us quote the only name of ISO (Infrared Space Observatory) launched in November 1995 in order to detect infrared signatures hidden by air on Earth.
− in modelling techniques necessary for interpreting astrophysical data in terms of reaction rates. The results of quantum-chemical calculations are now included in dynamic treatments based on potential energy surfaces, as it will be shown in Part 3 for the case of the puzzling problem of the abundance ratios of HCN / HNC isomers.

Finally, a close connection may be made between the chemical constitution of the matter investigated by astrophysicists and by planetarists, as the atmosphere of Titan, the big satellite of Saturn visited in November 1980 by Voyager, or the tails of the Hyakutake and Hall-Bopp comets appeared in our sky during the springs of 1996 and 1997.

Table 2. Comparison of molecular compositions in Titan atmosphere (●) and the Hall-Bopp comet (*)

H_2 ●	NH_3 *	H_2O *	H_2S *
CH_4 ● *	N_2 ●	CO ● *	CS *
C_2H_2 ● *	HCN ● *	CO_2 ● *	H_2CS *
C_2H_4 ● *	HNC *	H_2CO *	SO *
C_2H_6 ● *	$HNCO$ *	CH_3OH *	SO_2 *
Others ● (Hydro-carbons)	H_2NCHO *	$HCOOH$ *	OCS *
	CH_3CN ● *		S_2 *
	H_3CN ●		
	C_2N_2 ●		
		H_2O^+ H_3O^+ *	
		CO^+ HCO^+ *	

For instance, we can point out the ubiquitous presence of cyanides. At the other end of Universe, the pair of isomers HNC / HCN has been also detected, namely in the millimetric absorption spectrum from cold clouds illuminated by quasars of remote galaxies (4). This fact is fascinating for those who are interested by the life-origin problem, because cyanides are also involved in the composition of the famous "prebiotic soup" of Urey.

13.1.2 Physical Parameters of the Interstellar Medium

First of all, let us emphasize an essential difference between the work of a chemist in a terrestrial laboratory and the one of an astrochemist. The former is, in principle, free with the experiments he has planned. The second has nothing to his disposal, except effects of electromagnetic radiations in observational data, so that a great part of his activity is devoted, so to say, to molecular modelling. Two physical parameters are of paramount importance in interstellar space, temperature and density (*i.e.*, concentration of matter in definite chemical species); they are obtained by studying the intensity of emission and absorption bands in the line of sight of a telescope. In brief, the procedure can be described as follows ; When a compound excited by a radiation of intensity $I_0(v)$ towards a higher energy level yields a transmitted light of intensity $I(v)$,

the corresponding absorption coefficient $K(\nu)$ gives the number n of particles per volume unit through a specific proportionality factor, the molecular cross-section of the transition in question. If now there are n_1 and n_2 particles excited from two levels 1 and 2 separated by an energy gap $E_2 - E_1 = h\nu$, we can derive a value for the excitation temperature of the transition $1 \rightarrow 2$ by assuming a Boltzmann distribution of n_1 and n_2, namely $n_1/n_2 = exp\ (-h\nu/kT_{exc})$ (being h, k Planck and Boltzmann universal constants). The excitation temperature T_{exc} is expected to lie between the kinetic temperature of the medium and the black-body temperature of Universe at 2.7 K.

Table 3. Characteristics of the various interstellar regions

	Temperatures (K)	Number of particules per cm^3	Typical components
H II Region	10 000	100 - 1000	H$^+$ atomic ions
Diffuse nebulae	5 000 - 10 000	100 - 1000	H atomic ions
Diffuse clouds	100	100	H H$_2$ molecules
Translucent clouds	50	500 - 5000	H H$_2$ molecules
Dense clouds	10 - 20	1 000 - 100 000	molecules
Circumstellar envelopes	10 - 1500	10^{11}	molecules
Planetary nebulae	10 000 (and more)		atomic ions
Terrestrial laboratory (*pro memoria*)	300	10^{19}	

Far from being empty, the interstellar space is not even a homogeneous medium with respect to density and temperature. In Astronomy, it is customary to classify the galactic objects containing matter in different regions according to the latter criteria. They are:

- very hot regions at very low density with ionized hydrogen H$^+$ (the so-called H$_{II}$ regions) or with ionized and neutral hydrogen H$^+$ and H$^{\bullet}$ (the diffuse nebulae)
- very cold regions at low densities with atoms and molecules, namely the interstellar clouds which are known by the names of clear, translucent or dark clouds, or also of diffuse and dark clouds, according to their transparency to light
- rather warm and dense regions, the circumstellar envelopes above-mentioned whose matter comes from embedded red stars.

As examples of galactic regions well-known for their chemical content, let us mention the diffuse cloud in the direction of ζ Ophiuchus, various clouds in Orion (OMC1), in Sagittarius (Sgr B2) and in Taurus (TMC1), the circumstellar envelope (IRC+10216) around a matter-ejecting

red star in Leo etc ... In spite of their weak mean density, they are huge astronomical objects by their size (several parsecs, 1 parsec $=3.086 \ 10^{18}$ cm) and mass (several times the mass of the Sun: 1 M$_\Theta$ = 1.989 10^{33} g). (See Table 3)

13.1.3 Chemical Products in Space

The molecules present in space are detected by their spectroscopic signatures, in absorption if there are stars emitting light behind the region studied as in the case of diffuse clouds, and/or in emission if there are stars exciting them in the region itself as in the case of dense clouds and circumstellar envelopes. The possible carrier of a given spectrum is identified through the changes of molecular structure he undergoes, which vary according the nature of the radiation. The ultraviolet up to 400 nm and the visible spectra are produced by electron jumps with energies of say 1 eV or more, the infrared spectra by small vibration motions around their equilibrium positions with energies of about 0.1 eV, the microwave spectra by large rotation motions of the molecular skeleton, wholly or partly, with energies of 0.01 eV or less. In any case, selection rules determine line or band intensities as usual in spectroscopy (5).

At variance with other classifications, for instance based on the number of atoms forming interstellar molecules (2), the present one uses quantum-chemical criteria, namely neutral closed-shell systems, open-shell neutral radicals and positively charged systems. The first category includes uncommon molecules which are often called "radicals" by spectroscopists, *e.g.* PN, and for convenience's sake neutral carbenes, *e.g.* CH$_2$, which have two unpaired electrons. Amongst a hundred odd of compounds listed in Table 1, there are 12% of cations, 19% of free radicals, 28% of compounds without any carbon atom, 71% of compounds formed by hydrogen and/or first-row atoms from carbon to fluor, 25% of compounds including second-row atoms from sodium to chlorine. Up to now, no anion has been detected, perhaps because negative species could be hidden in the form of ion pairs with opposite charges (6), nor compounds of transition metals in spite of investigations concerning iron whose isotope [56]Fe has an especially stable nucleus.

Generally speaking, the distribution of elements in the interstellar space reflects the elemental composition of Universe: Taking apart the absolute predominance of hydrogen (91% of the total matter) and helium (9%), we can note that the abundance of about $10^{-3} \ 10^{-4}$ with respect to hydrogen for the first three atoms C, N, O is ten times greater or more than the abundance of their homologues of the second-row Si, P, S or the first metals Na, Mg. The so-called "depletion" in a given atom is most often explained by the fact it is incorporated in the dust of the galactic medium and, consequently, not easily detected by gas-phase spectroscopic investigations. This could be the case of the FeCO molecule, the detection of which was unsuccessful (7).

As appears from Table 1, the interstellar organic matter seems to be distributed amongst two categories, the oxygen-bearing molecules which have various chemical functional groups, *i.e.*, aldehydes, ketones, alcohols, acids, esters, and the carbon chains which may include a nitrogen

atom, *i.e.*, cyanides and isocyanides. The two types of compounds are generally detected in different places, so that astrophysicists are speaking of oxygen- and carbon-rich regions; for instance OH231.8+4.2 and IRC+10216 are envelopes originating from O- and C-stars respectively (8). However, chemistry in space should not be imagined as a kind of Organic Chemistry, for most of interstellar molecules have not very typical structures with only one chemical function and no branching or ring, except four triangular systems. Of course, the number of cyclic molecules shall be increased if the hypothesis of the PAH's (9) considered as possible carriers for various types of CH vibration modes at 3.3 , 6.2 , 7.7 , 8.6 and 11.3 μm (3040, 1615, 1310, 1150 and 885 cm^{-1}) will be confirmed by assignments to single compounds. Likewise, fullerene C_6O has not been detected and the assignment of the two bands at 960 nm to the C_6O^+ ion through rotational contours of the neutral species (10) is tentative.

In addition to carbon monoxide CO, the most abundant interstellar molecule after H_2, the interstellar medium also contains some carbene compounds with "divalent carbons". Space is like a "galactic park" for "exotic species": non-neutralized ions, non-dimerized free radicals, metastable isomers beside stable forms as the cyanide pair HNC / HCN etc... (11). At variance with the terrestrial environment, these compounds seem to be protected from a rapid destruction by the physical conditions of the medium.

13.2 Interstellar Chemical Reactivity

13.2.1 Chemical Constraints in Space

First of all, the theory of the chemical reactivity in space has to take into account the specific parameters of the medium with its population in electrons and photons. The more or less greater permeability of space to ionizing radiations explains the role of ions in the various interstellar processes. In diffuse nebulae containing atomic hydrogen mainly, the other atoms are transformed into ions as soon as their ionization potentials are lower than that of hydrogen (13.6 eV). In genuine interstellar clouds, there are both neutral species and ions, in atomic and molecular forms, but the ion-molecule reactions are generally easier than the reactions between uncharged species. It seems, however, that the importance of the latter has been somewhat underestimated in the past, as it will be seen in connection with the HNC / HCN equilibrium studied in part 3.

The chemical processes occurring in space are governed by its very special conditions of temperature and density, much lower than on Earth. From that two consequences follow:

- apart some photochemical reactions due to ambient radiations, no outer energy contribution can take place, so that endothermic reactions are precluded.
- no third body is available to carry away the energy Q released by exothermic reactions X + Y → XY + Q resulting from collisions between species X and Y. Except if there is a direct

emission of photons hv, the energy gain Q must be consumed in a subsequent transformation which brings back to the initial products or yields others X' and Y'.

The preceding constraints are essentially valid for interstellar gas-phase reactions, but they have to be somewhat relaxed for other chemical processes invoked by astrophysicists. One is the formation of molecules on the dust grains ejected in space by cold stars (12): The interstellar dust chemistry has some relationship to heterogeneous catalysis, the first step of which can be depicted as a chemisorption process. Another is the formation of molecules behind the front of shock waves produced by star bursts, with conditions of temperature and density very different from those of quiet galactic regions: The shock wave chemistry would require molecular modelling studies in turbulent regimes which are at their very beginning (13).

13.2.2 The Various Types of Interstellar Reactions

The chemical reactions of interstellar space are usually classified according to the nature of radiative and collisional processes concerning gas phase mainly. The meantime for a collision between two particles in the interstellar medium depends on the density of matter in the region considered, *i.e.* about 100 years for electron-molecule shocks and more than 1000 years for molecule-molecule shocks. Anticipating our picture of Section 2.3, we give a sketch of the most often quoted interstellar reactions in Table 4.

From the molecular point of view, rearrangements are certainly the most interesting chemical transformations. At the first place, we have charge-exchange reactions in diffuse clouds and proton -transfer reactions in dense clouds, provided of course that the processes in question are exothermic. For instance, it has been always admitted that the molecular ion H_3^+ acts as a proton donor in dense clouds if its dissociation energy ($D_{H_3^+}$ = 4.60 eV) is not opposed, even in the days when its presence in space was not yet established.

Next, we will mention ion-molecule reactions involving an X^+ ionized atom and an XY neutral diatomics, as the oxygen cation O^+ and the hydrogen molecule H_2. The case of carbon cation C^+ has not to be considered because H_2 is more stable than CH^+:

$$D(H_2) = 4.48 \text{ eV } \textit{versus } D(CH^+) = 4.09 \text{ eV, } \textit{but } D(OH^+) = 5.01 \text{ eV .}$$

The occurrence of such reactions in space is connected to the dominance of the long-distance attraction term between the X^+ cation and the dipole moment (if any) and/or the electric polarizability of the XYZ molecule: This term ensures the lack of any potential barrier along the reaction path leading to the $(XYZ)^+$ complex. According to the Collision Theory, the ion-molecule reaction rates are independent of temperature T if YZ is a homopolar diatomic molecule (therefore, possibility of laboratory experiments at ordinary temperatures) and increases if T decreases for heteropolar species (5).

Table 4. Sketch of an Astrochemical Scenario

Prologue: Bond formation				
Radiative association	$X + Y$		$\rightarrow$	$XY + h\nu$
Formation on grains	$X + Y$ (on grain)		$\rightarrow$	$XY +$ grain
Action: Molecular transformations				
Charge transfer	$X^+ + Y$		$\rightarrow$	$X + Y^+$
Proton exchange	$XH^+ + Y$		$\rightarrow$	$X + YH^+$
Ion molecule reactions	$X^+ + YZ$	$\rightarrow$ $(XYZ)^+_{ts}$	$\rightarrow$	$XY^+ + Z$
Neutral-neutral reactions	$X + YZ$	$\rightarrow$ $(XYZ)_{ts}$	$\rightarrow$	$XY + Z$
Epilogue: Bond breaking				
Photodissociation	$XY + h\nu$		$\rightarrow$	$X + Y$
Dissociative recombination	$XY^+ + e^-$		$\rightarrow$	$X + Y$
Shock-induced dissociation	$XY + M$ (shock)		$\rightarrow$	$X + Y + M$

On the other hand, it is more difficult to speculate on neutral-neutral reactions, as the globally exothermic exchange of an H atom between a CH radical and an O atom:

$$O + CH \rightarrow CO + H \; where \; D(CH) = 3.5 \; eV \; and \; D(CO) = 11.1 \; eV \; ;$$
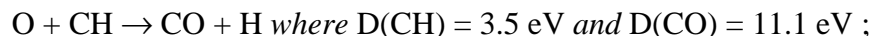
for the van der Waals-type attraction between neutral species is not sufficient to preclude the presence of potential barriers. The role of neutral-neutral reactions has been long neglected; explicit calculations are needed for having an idea on their possible potential barriers and the variations of their reaction rates with temperature.

The neutralization of ions present in interstellar clouds involves a molecular destruction process very specific of this medium, the so-called dissociative recombination (5). The XY^+ ion is broken into two fragments because the $(XY^+ + e)$ system resulting from the capture of an electron forms a neutral species of Rydberg type XY^*, which may be dissociative itself or, if not, turns dissociative by internal conversion into another excited state of XY. The understanding of dissociative recombination reactions requires quantum-mechanical detailed calculations, first

limited to diatomic hydrides (14) and extended later to two triatomic species HCO^+ and HCS^+ whose neutralization reaction rates have been successfully computed (15). This process has a major importance in the study of the HNC / HCN problem presented in Part 3.

Let us briefly mention the radiative association of atomic or diatomic species leaving an excess of energy Q released in the form of a photon emission (5). As these processes have low reaction rates, astrophysicists consider that the formation of simple molecules takes place rather on dust grains. Similarly, the formation of molecular "primordial" matter in this way, *e.g.* LiH^+ in the post big-bang period (16), is apparently improbable.

13.2.3 Astrochemical Scenarios

To assess the validity of the various chemical scenarios suggested by the presence of so many molecules in space, an ordinary practice in Astrophysics consists in modelling the formation and the destruction of the different species by a "network of reactions" and putting a set of *ad hoc* kinetic equations. These reaction schemes are connecting the molecules X observed or expected in a given cloud or envelope with their atomic components A_X through other existing chemical species Y or, possibly, through physical effects, for instance ionization and dissociation processes due to UV photons induced by cosmic rays in dense medium. Computer solutions of astrochemical networks may be considered as more or less equivalent to laboratory total syntheses. For instance, Figure 1 shows the formation of water H_2O in dark clouds by starting from atomic oxygen O and dihydrogen H_2 via the molecular ion H_3^+ . Many pictures of this kind are found in current literature
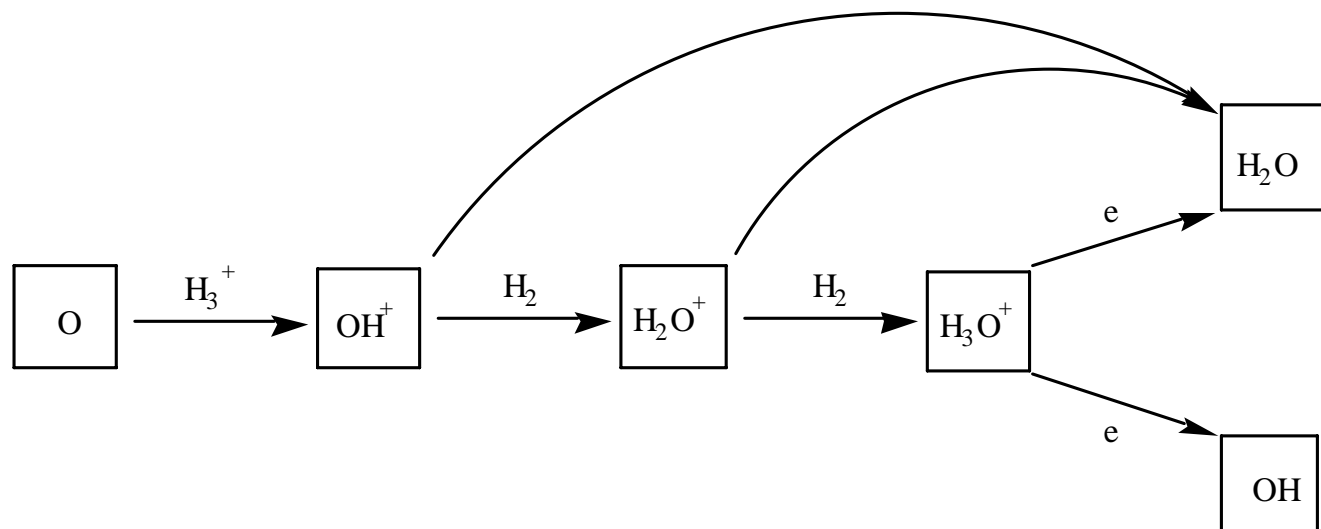

Fig. 1 Interstellar synthesis of water, adapted from ref (17)

For each species X_i of unknown concentration n_i, expressed in terms of number of particles per volume unit, we have the equation

$$dn_i / dt + \nabla(n_i\mathbf{v}) + (P_i - Q_i) = 0$$

where the sum of the first two terms is a continuity condition for a medium in expansion with a velocity $\mathbf{v}$ (about 10 km sec^{-1}, or more) and the last term includes all the processes of formation P_i and destruction Q_i concerning X_i; P_i and Q_i themselves are proportional to the concentrations of the various species involved in the kinetics of X_i, and the proportionality factors are the corresponding reaction rates k. For chemical formation and destruction processes described by equations of the form:

$$X_j + X_k \quad —(k_{jk})\rightarrow \quad X_i + A$$

$$X_i + A \quad —(k_{ia})\rightarrow \quad B + C$$
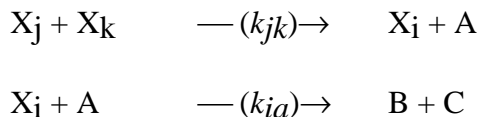
we have

$$P_i = \sum_j \sum_k k_{jk} n_j n_k$$
$$Q_i = \sum_a k_{ia} n_i n_a$$

The values of k are taken from terrestrial laboratory experiments (about 10^{-9} cm^3 sec^{-1} for typical ion-molecule reactions (18)) or computed theoretically.

There are as many coupled equations of this type as reactive species X_i in the interstellar region investigated, usually more than 100 equations in actual modelling studies (18). Most of the computer programs use the hypothesis of the so-called chemical equilibrium by putting

$$dn_i /dt + \nabla(n_i\mathbf{v}) = 0 \text{ valid for } t > 10^7 \text{ years.}$$

For shorter times, it is necessary to evaluate this quantity by giving simple geometrical shapes to the interstellar region considered, as a slab for a cloud or a sphere for an envelope with a definite size (19).

In Chemical Kinetics, theoreticians have presented model systems whose coupled equations have multiple solutions originating from their non-linear character as soon as the same compound X_i is present in several equations (20). The Brussellator model describing the oscillatory behaviour of the Belusov-Zhabotinsky reaction is an example. Recently, astrophysicists of the Meudon Observatory have reported bistabilities of that kind in chemical networks dominated by ion-molecule reactions in dark clouds (21): One solution corresponds to proton-transfer reactions prevailing in a low ionization region, another to charge exchange reactions in a high ionization, and between the two an instability region. Clearly, the standard scenario of the steady state has to be seriously amended.

13.3 Sample Calculations

13.3.1 A Test-Case : The Problem of Cyanides

The coexistence of cyanic and isocyanic compounds in the interstellar medium and even in planets, illustrated by the detection of the HNC / HCN pair of isomers towards 1975 and much more recently by that of the MgNC / MgCN pair (22), put a problem both of Quantum Chemistry and of Chemical Kinetics. In space, it is easy to distinguish the cyanic and isocyanic hydrides simply because they have rather different geometries and, consequently, inertia moments leading to well-separated rotation spectra in the millimetric domain:

HCN:

d_{CN} = 1.150 Å d_{CH} = 1.066 Å

B_0 = 44.323 GHz J_{1-0} = 88.631602 GHz

HNC:

d_{NC} = 1.168 Å d_{NH} = 0.996 Å

B_0 = 45.331 GHz J_{1-0} = 90.663593 GHz

for the ^{12}C and ^{14}N isotopomers.

In terrestrial environment, HCN is a dangerous stable compound and HNC a metastable fleeting compound, higher in energy by 15 kcal mol^{-1}. The isocyanide-cyanide direct isomerisation, ineffective at low temperature because of a rather high potential barrier of 29 kcal mol^{-1}, becomes possible at high temperature: It is a good example of unimolecular reaction explained by the RRKM theory (23). The theoretical abundance ratio n_{HNC} / n_{HCN} computed at 100 K, a temperature not too low with respect to a cold dense cloud, is found to be equal to 10^{-30}, at variance with any astronomical observation. This excludes the direct isomerisation as an interstellar mechanism.

Originally, astrophysicists tried to explain the more or less similar abundance of the two hydrides related to the cyano radical CN$^{\bullet}$ by assuming that both are issued from the same precursor, the HCNH^{+} ion they had detected in the interstellar space. A mechanism of dissociative recombination

$$HCNH^{+} + e^{-} \rightarrow HCN \text{ or } HNC$$
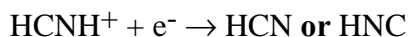
could be responsible for an equal abundance of both compounds, because the neutralization of $HCNH^+$ yields an intermediate $HCNH^*$ in a Rydberg state close, according to potential surface calculations, to two dissociative valence states $^2\Sigma$: One gives HCN by breaking of the N-H bond and the other gives HNC by breaking of the C-H bond.

Unfortunately, a so naive picture does not account for the large variation, from 10^2 to 10^{-2} of the observed abundances in terms of temperature and position: the n_{HNC}/n_{HCN} ratio is 1.55 in the cold molecular cloud of Taurus and 0.012 in the hot core of Orion K-L on its edges (24).

13.3.2 A Quantum-Chemical Analysis

To go further on the HCN / HNC problem, the conditions of formation and destruction of the $HCNH^+$ precursor have to be investigated, taking into account additional reactions changing or not the balance between the two isomers. They are summarized in Table 4.

The quantum-mechanical calculations of D. Talbi at the École Normale Supérieure de Paris, continued by calculations of statistical collisional Dynamics of E. Herbst at the Ohio State University, offer the possibility of testing the various assumptions made by astrophysicists on realistic potential energy surfaces (25). Generally, the Quantum Chemistry study was made in two steps: First, a draft of the energy profiles of the different reaction paths, using *ab initio* computations at the MP2 or limited CI levels with basis sets of medium size as 6-31G**. Second, a more accurate determination of the characteristic points of these curves (minima, saddle points or maxima) by means of better correlated MP3 or CI wave functions resulting from triple-zeta enlarged sets, like 6-311++G(3df,3dp), and specific CN bond functions for Rydberg state investigations. Standard projected energies (if given by UHF treatments) have been used and zero-point vibration energies have been added throughout.

From these computations, we can make the following statements:

− Concerning the dissociative recombination of the $HCNH^+$ ion, it is possible to use its CI natural orbitals to build a nearly localized molecular basis for having reliable quasi-diabatic Rydberg and dissociative states of its neutral parent HCNH. We observe a perfect similarity of these surfaces in their crossing regions, according as we look on the side of the CH bond or on the side of the NH bond. Therefore, no difference has to be expected between HCN yield and HNC yield from the dissociative recombination of the $HCNH^+$ ion. (Fig.2).
− Concerning the ion-molecule process from $C^+(^2P)$ and NH_3, the "singlet" reaction path of A' symmetry in the C_s subgroup of the CNH_3^+ intermediate (Fig.3) exhibits two minima separated by potential energy barriers before coming to its end, the final product $HCNH^+$. The last one is the Y-shaped isomer, but it can isomerise into the $HCNH^+$ linear form, more stable by 53 kcal mol^{-1}. The RRKM dynamics of this reaction gives a yield of 98% in favour of $HCNH^+$, so that the CNH_2^+ form does not increase the HNC abundance significantly by dis-

sociating. The "triplet" channel using the reaction path of A" symmetry is equally inefficient because it passes over a CNH_3^+ intermediate stabilized by a too large energy barrier, 120 kcal mol^{-1}, with respect to its expected dissociation product.

− Concerning the ion-molecule process from $N^+(^4S)$ and CH_3, the reaction path has only one intermediate minimum, NCH_3^+; it goes down continuously from the corresponding transition state, located at 44 kcal mol^{-1} higher, to the final product $HCNH^+$. This does not lead to any change on the HNC / HCN ratio.

− Concerning the neutral-neutral reactions invoked for destroying the isocyanide form, no definite conclusion can be drawn. The HNC / HCN interconversion by exchanging an hydrogen atom (Fig. 4) involve potential energy barriers much smaller than the direct isomerisation, but its reaction rate is low and works significantly in favour of HCN only beyond 300 K (26). Regarding the destruction reaction paths involving the approach of an oxygen atom along the CN bond or perpendicularly to its, they are repulsive, thus excluded
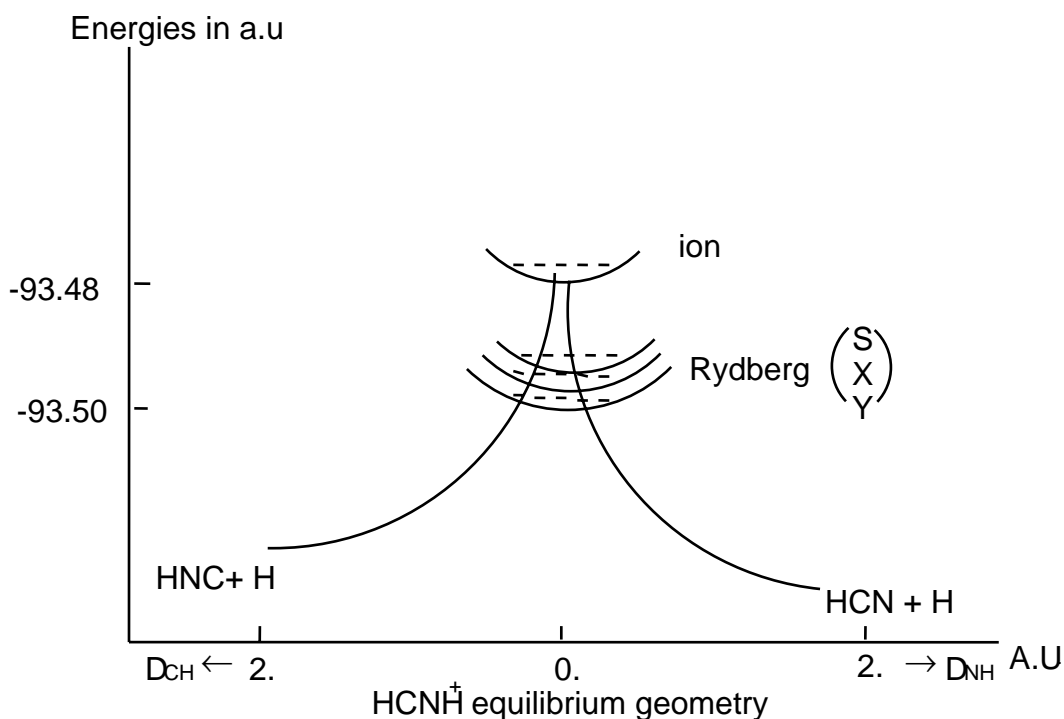

Figure 2. Outline of the HCNH$^+$ dissociative recombination curves

Table 4. Formation and Destruction Reactions for the HCN / HNC Pair

		$HCNH^+(^1\Sigma^+) + H$	a^+-m (1)
$C^+(^2P)$	$+ NH3 \rightarrow$	$CNH_2^+(^1A_1) + H$	a^+-m (2)
		$CNH_2^+(^3B_2) + H$	a^+-m (3)
$N^+(^1S)$	$+ CH3 \rightarrow$	$HCNH^+(^1\Sigma^+) + H$	a^+-m' (4)
		$NCH_2^+(^1A_1) + H$	a^+-m' (5)
$HCNH^+(^1\Sigma^+)$	$+ e^- \rightarrow$	$HCN + H$	r-d (1)
CNH_2^+	$+ e^- \rightarrow$	$HNC + H$	r-d (2)
		$HNC + H$	r-d (3)
HNC	$+ H \rightarrow$	$HCN + H$	n-n (1)
HNC	$+ O \rightarrow$	$NH + CO$	n-n (2)

a^+-m, a^+-m' : ion-molecule reactions ($a^+ = C^+$ or N^+)

r-d : dissociative recombinations

n-n : neutral-neutral reactions

Clearly, the problem of cyanides in space is not yet exhausted: To solve it, other mechanisms are wanted. We are presently thinking about the $C + NH_2$ and $N + CH_2$ reactions.
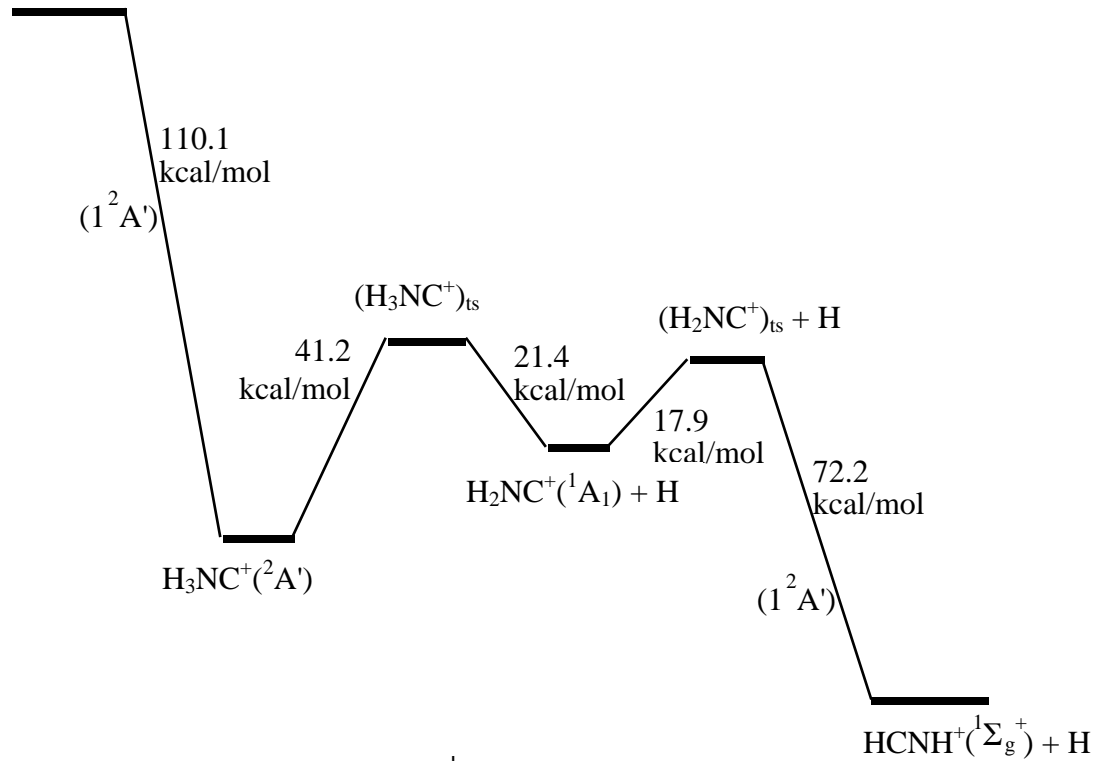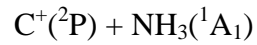
$C^+(^2P) + NH_3(^1A_1)$

110.1
kcal/mol

$(1\,^2A')$

$(H_3NC^+)_{ts}$

41.2
kcal/mol

21.4
kcal/mol

$(H_2NC^+)_{ts} + H$

17.9
kcal/mol

72.2
kcal/mol

$H_2NC^+(^1A_1) + H$

$H_3NC^+(^2A')$

$(1\,^2A')$

$HCNH^+(^1\Sigma_g^+) + H$

Figure 3. Energy profile of the $C^+ + NH_3$ reaction.

4.2 kcal/mol

$(H\text{-}CNH)_{ts}$

$H + CNH$

$(HCN\text{-}H)_{ts}$

17.8
kcal/mol

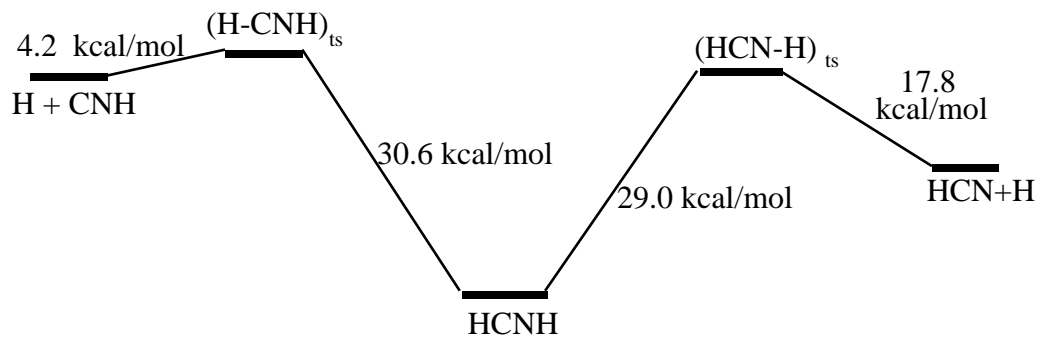30.6 kcal/mol

29.0 kcal/mol

$HCN+H$

$HCNH$

Figure 4. Energy profile of the HCN-HNC pair of isomers.

13.3.3 Towards Exobiology-Oriented Calculations

Up to now, there is no proof for a non-terrestrial origin of life, as suggested by the chemist Arrhenius at the beginning of this century, nor even for the presence of life on another planet than Earth in spite of recent promising statements of newspapers. This possibility, however, is attractive for astrochemists because the experimental findings concerning the so-called "prebiotic" synthesis on primitive Earth bring back to Interstellar Chemistry. The famous experiment of Miller in 1953 (27) showed that electric discharges in a mixture of hydrogen, water, ammonia and methane, mimicking the probably reduced conditions of early atmosphere, produce α-amino acids (glycine, alanine, α-amino-*n* butyric acid etc...), that is to say precursors of peptides and nucleosides. The point interesting for us is that the Miller synthesis involves cyanic intermediates connected to those identified in space (*i.e.*, HCN, $H_2C=CH-C\equiv N$ etc...). Note also that the purine basis included in DNA and RNA is adenine, that is to say the polymer $(HCN)_5$ of cyanide hydride.

Two main difficulties are remaining: First, no amino acid has been detected in the interstellar medium, in spite of several attempts for the simplest of them, glycine NH_2-CH_2-COOH (29). Second, *in vitro* syntheses of biomolecules always give racemic mixtures of enantiomers, whereas natural compounds have a definite chirality, for instance *l-* amino acids as alanine NH_2-CHCH_3-COOH or *d*-sugars ; consequently, an amplifying selection mechanism by chance or by physical necessity is added in order to explain the predominance of a single form (28).

Quantum Mechanics, however, suggests that a pair of *d* and *l* enantiomers does not form a pair of genuine degenerate states either from Physics and the Solid-State Chemistry points of view, but that the most stable form is just the one found on Earth. It is, indeed, possible to separate the energies of the two enantiomers using a molecular Hamiltonian with parity-violating terms due to weak neutral currents well-known in Nuclear Physics. Recent *ab initio* calculations in the frame of the coupled Hartree-Fock theory by Lazzeretti and Zanasi (29) show that the energy difference, formely evaluated to about 10^{-20} a.u. for a pair of enantiomers has been underestimated by at least one order of magnitude (*i.e.*, $12.3 \ 10^{-20}$ for alanine).

On the other hand, the study of the prebiotic chirality problem should not neglect the formation conditions of products themselves, which probably used mineral supports, as natural clays. Now, simple SCF calculations by Julg (30) indicate that α-amino propionitrile, the precursor of alanine resulting from the addition of CN^- to ethyl iminium cation $^+NH_2=CHCH_3$, has an adsorption energy on a kaolinite crystal stronger in the *l* form, by 0.36 kcal mol^{-1} than in the *d* form; in other words, an energy difference in favour of the biological *l* enantiomer much greater than any purely physical effect. This last conclusion is in line with the interests of many astro-

chemists, for it establishes a link between the problems of life origin and interstellar solid-state reactivity.

Bibliography

1. P. Swings , L. Rosenfeld (1937) Astrophys. J. 86, 483; W.S. Adams (1941) Astrophys. J. 91, 11
2. See A.P.C. Mann, D.A. Williams (1980) Nature 283, 721
3. T.R. Geballe, T. Oka (1996) Nature 384, 334
4. T. Wiklind, F. Combes (1996) Nature 379, 139
5. See J. Lequeux, E. Roueff (1991) Phys. Rep. 200, 241
6. D. Talbi, R.P. Saxon (1989) J. Chem. Phys. 91, 2376
7. E. Kagi, Y. Kasai, H. Ungerechts, K. Kawaguchi (1997) in press
8. A. Omont (1989) Nato Asi Series C 323, 171
9. A. Leger, J.L. Puget (1984) Astronom. Astrophys. 137, L5; L.J. Allamandola, A.G. Tielends, A.G. Baker (1985) Astrophys. J. 290, L25
10. B.H. Foing, P. Ehrenfreund (1997) Astronom. Astrophys. 317, L 59
11. P.F. Goldschmidt, N.D. Langer, J. Ellder, W. Irvine, E. Kollberg (1981) Astrophys. J. 249, 524
12. See D.A. Williams, in "Dust and Chemistry in Astronomy" (1993). T.J. Millar and D.A. William Eds, Chap. 7, Inst. Phys. Publ. Bristol
13. See J.E. Dyson, D.A. Williams "The Physics of the Interstellar Medium (1980) Chap. 6, Manchester Univ. Press
14. A. Giusti-Suzor, H. Lefebvre-Brion (1977) Astrophys. J. 214, L 101
15. D. Talbi, A.P. Hickman, F. Pauzat, Y. Ellinger, G. Berthier (1989) Astrophys. J. 339, 231
16. S. Lepp, J.M. Shull (1984) Astrophys. J. 458, 397
17. A. Sternberg, A. Dalgarno, S. Lepp (1987) Astrophys J. 320, 676
18. See W.W. Duley, D.A. Williams (1984 Interstellar Chemistry Acad. Press, London
19. J.J. Benayoun, Y. Viala, S. Warin (1993) C.O.S.M.M.I.C. Computer Program, Observatoire de Grenoble
20. See P. Gray, S.K. Scott (1990) Chemical Oscillations and Instabilities, Non-Linear Chemical Kinetics, Clarendon Press, Oxford
21. J. Le Bourlot, G. Pineau des Forets, E. Roueff (1993) Astrophys. J. 416, L 87
22. K. Kawaguchi, E. Kagi, T. Hirano, S. Takano, S. Saito (1993) Astrophys. J. 406, L 39 ; L.M. Ziurys, A.J. Apponi, M. Guelin, J. Cernicharo (1995) Astrophys. J. 445, L 47
23. P.K. Pearson, H.F. Schaefer III, U. Wahlgren (1975) J. Chem. Phys. 62, 350
24. W.M. Irvine, F.P. Schloerb (1984) Astrophys J. 282, 516; P. Schilke, M.C. Walmsley, G. Pineau des Forets, E. Roueff, D.R. Flower, S. Guilloteau Astronom. Astrophys. 256, 595
25. D. Talbi, Y. Ellinger (1998) Astronom. Astrophys. (in press) ; D. Talbi, Y. Ellinger, E. Herbst (1996) Astronom. Astrophys. 314, 688
26. D. Talbi, Y. Ellinger (1996) Chem. Phys. Lett. 263, 385
27. S.L. Miller (1953) Science 117, 528 ; S.L. Miller (1955) J. Amer. Chem. Soc. 77, 2351

28. See A. Brack, F. Raulin (1991) L'Evolution Chimique et les Origines de la Vie, Masson, Paris
29. P. Lazzeretti, R. Zanasi,(1997), private communication
30. A. Julg (1987) C.R. Acad. Sci. Paris, 305, II, 563