# Interstellar Chemistry

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Although the discovery of the first interstellar molecular species comes from the early '40's with the detection by optical means of CH, $CH^+$, and CN (*1–3*), the true birth of interstellar chemistry can be placed in 1963 when the OH radical was identified using radiotelescope techniques (*4*). The enormous technological development experienced by radioastronomy during the past 20 years has been reflected in more than 90 new molecular species (including isotopic varieties) unequivocally identified in the interstellar medium (Table 1), and this number increases every year. Parallel to the experimental radioastronomic research, a considerable amount of theoretical work has been done, and at the present time astrochemistry can be thus properly considered as a new branch of chemistry with its own status as an independent discipline.

In spite of its youth, interstellar chemistry has made substantial contributions to the better understanding of different phenomena of both chemistry and astronomy. Its importance can be evaluated by considering the relevance of some of the questions with which it is concerned: the distribution of matter in the Galaxy, the origin of stars and the solar system itself (interstellar molecular clouds are thought to be sites of star birth), the determination of the cosmic isotopic ratios of the diverse elements and their direct relation to the origin of the universe, the implication of interstellar molecules in the origin of life, etc. are several of the problems in which interstellar chemistry is directly involved.

Although the subject of the present paper has been extensively reviewed by several authors (*5–19*), we have found no references to the topic in THIS JOURNAL. Our aim is thus to expose in a concise way some of the features which characterize the present status of interstellar chemistry. As the field is too broad to be covered within the space limitations of this article, we have focused our attention to those aspects more strictly related to formation and destruction of molecules, which we feel are more relevant to the chemistry community.

### The Interstellar Medium

The matter of our Galaxy—the Milky Way—is distributed between stars (~90%) and the so-called interstellar medium (~10%). The interstellar material, mainly hydrogen, the most abundant element of the universe (see Table 2), comes from either original (nonprocessed) material or the residues of the nuclear burning of former stars. The chemical elemental composition of the intersellar medium is currently supposed to be similar to that of the entire cosmos (see Table 2).

As can be inferred from observational data, the distribution of interstellar mass is not uniform; instead, most of space is almost empty, with a typical density of ~0.1 particles/$cm^3$, and matter accumulates in "clouds." The cloud material is not homogeneous, and it is composed of a solid fraction or "cosmic dust" of uncertain (and controversial) (*20, 21*) composition (~1%) and gas (~99%).

Traditionally two kinds of interstellar clouds are distinguished, according to their physical properties and chemical constitution. The first type is the "diffuse" cloud characterized by low density and high temperature (see Table 3), which is easily penetrated by the starlight, and this precludes the formation of complex molecules. Consequently, these clouds' chemistry is reduced to that involving atomic or simple

**Table 1. Interstellar Molecules (*14, 36, 37*)**

| Molecule | Detection[a] | Molecule | Detection[a] |
|---|---|---|---|
| $H_2$ | UV,IR | HNCO | radio |
| $CH^+$ | VIS | $H_2CS$ | radio |
| CH | VIS,radio | $C_3N$ | radio |
| OH | radio | HNCS | radio |
| $C_2$ | UV,IR | $CH_4$[b] | radio |
| CN | VIS,radio | $CH_2NH$ | radio |
| CO | UV,IR,radio | $CH_2CO$ | radio |
| NO | radio | $NH_2CN$ | radio |
| CS | radio | HCOOH | radio |
| SiO | radio | $C_4H$ | radio |
| SO | radio | $HC_3N$ | radio |
| NS | radio | $CH_3OH$ | radio |
| SiS | radio | $CH_3CN$ | radio |
| $H_2O$ | radio | $NH_2CHO$ | radio |
| $C_2H$ | radio | $CH_3SH$ | radio |
| HCN | radio | $CH_3NH_2$ | radio |
| HNC | radio | $CH_3C_2H$ | radio |
| HCO | radio | $CH_3CHO$ | radio |
| $HCO^+$ | radio | $C_2H_3CN$ | radio |
| $N_2H^+$ | radio | $HC_5N$ | radio |
| $H_2S$ | radio | $HCOOCH_3$ | radio |
| OCS | radio | $CH_3C_2CN$ | radio |
| $SO_2$ | radio | $C_2H_5OH$ | radio |
| HNO | radio | $CH_3OCH_3$ | radio |
| $HCS^+$ | radio | $C_2H_5CN$ | radio |
| $NH_3$ | radio | $HC_7N$ | radio |
| $C_2H_2$ | IR | $HC_9N$ | radio |
| $H_2CO$ | radio | | |

[a] UV: ultraviolet; VIS: visible; IR: infrared; radio: microwave or radiofrequency.
[b] This identification remains controversial.

**Table 2. Cosmic Abundances of Elements, Relative to Hydrogen (*7*)**

| Element | Abundance | Element | Abundance |
|---|---|---|---|
| H | 1.00 | S | $2 \times 10^{-5}$ |
| He | 0.09 | Ar | $6 \times 10^{-6}$ |
| O | $7 \times 10^{-4}$ | Al | $2 \times 10^{-6}$ |
| C | $3 \times 10^{-4}$ | Ca | $2 \times 10^{-6}$ |
| N | $9 \times 10^{-5}$ | Ni | $2 \times 10^{-6}$ |
| Ne | $8 \times 10^{-5}$ | Na | $2 \times 10^{-6}$ |
| Fe | $4 \times 10^{-5}$ | Cr | $7 \times 10^{-7}$ |
| Si | $3 \times 10^{-5}$ | Cl | $4 \times 10^{-7}$ |
| Mg | $3 \times 10^{-5}$ | P | $3 \times 10^{-7}$ |

**Table 3. Interstellar Matter: Distribution and General Properties[a]**

Total mass of interstellar matter: $5 \times 10^9$ M⊙[b]
Gas: ~99%
Dust: ~1%

| Region | Temperature (°K) | Density (particle $cm^{-3}$) | Fraction by Mass (%) | Fraction by Volume (%) |
|---|---|---|---|---|
| Intercloud | ⩾7000 | ⩽0.2 | 20 | 90 |
| Diffuse clouds | 100 | $1 - 10^2$ | 40 | ~10 |
| Dark clouds | 10 | $10^2 - 10^7$ | 40 | ~0.5 |

[a] Adapted from refs. (*8*) and (*12*).
[b] 1 M⊙ (solar mass) = $1.989 \times 10^{33}$ g.

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species. On the other hand, the second type is the "dark" cloud which is denser, colder, and opaque to starlight, circumstances that allow the existence of more complex chemical species. In fact, dark or dense clouds have been the main source of the majority of the interstellar molecules discovered.

The physical conditions of the interstellar medium are so unusual, if compared to those available at present in the terrestrial laboratories, that they permit the on-going existence of some unstable and reactive (from our "terrestrial" point of view) species such as molecular ions ($CH^+$, $HCO^+$, $N_2H^+$, etc.) or radicals (OH, $HC_4$, etc.). In this sense, the interstellar medium must be regarded as a unique laboratory.

### Interstellar Chemistry

#### *General*

The growing catalog of interstellar chemicals has caused astrochemists to look for qualitative and quantitative models which would enable them to explain how molecules are formed and destroyed in the interstellar environment. The drastically different physical conditions found in this medium contrast severely with those available on the Earth, and, accordingly, a substantially different chemistry must be expected.

Since the first studies undertaken by Spitzer and Bates (*22*) concerning CH and $CH^+$, much work has been done and some of the questions clarified. Speaking in general terms, it can be said that the qualitative picture of interstellar chemistry is reasonably clear, while its quantitative aspects remain uncertain.

Due to the very low temperatures and densities prevailing in the interstellar medium, its chemistry becomes restricted to the following process: (a) exothermic reactions; (b) bimolecular reactions (three-body collisions are very improbable) (*9*)

$$t_{\text{two-body collision}} \simeq 3 \times 10^2/n \text{ y}$$
$$t_{\text{three-body collision}} \simeq 3 \times 10^{23}/n^2 \text{ y}$$
$$n = \text{density in molecules per cm}^3$$

In addition, exothermic reactions are likely only if they have a reasonably high rate constant $r$, which results if the activation energy $E_a$ of the Arrhenius equation is comparable to the thermic energy $kT$

$$r = A \cdot e^{-Ea/kT}$$

Two types of mechanisms seem to fit the previous requirements: gas-phase chemistry based upon positive ion-molecule reactions and formation of molecules on the surface of cosmic dust grains. We will consider both schemes separately. Some other alternative processes such as synthesis in stellar atmospheres followed by ejection of molecules during stellar evolution or synthesis in shocked clouds, which sometimes are invoked, will be omitted in the present discussion. The reader is referred to the original papers such as (*23*).

#### *Grain-Catalyzed Chemistry*

Due to the large uncertainties that still remain about the physical and chemical constitution of cosmic dust, it is difficult to make a realistic evaluation of the importance of grain-catalyzed surface reactions to the synthesis of interstellar molecules.

Nevertheless, it seems necessary to consider such a process to account for the observed abundances of molecular hydrogen, which cannot be explained exclusively by gas-phase chemistry.

$$H + H + \text{grain} \rightarrow H_2 + \text{grain} \tag{1}$$

The sequence of steps needed to produce a molecule by surface chemistry are the following: (1) adsorption of atoms on the dust grain surface, (2) an encounter between the atoms involved in the reaction, and (3) ejection of the molecule formed to the gas phase. While steps (1) and (2) are supposed to occur with reasonable efficiency (i.e., hydrogen atoms are expected to collide with interstellar grains with a 30–100% extent of reaction), the desorption step by means of the energy liberated during the exothermic reaction seems possible only for molecular hydrogen. For other, heavier molecules, additional desorption mechanisms must be invoked; photodesorption, thermal evaporation, and collisional ejection are some of them.

In summary, model building and numerical predictions based upon grain-catalyzed chemistry are at the moment tentative (with the probable exception of molecular hydrogen) and subject to uncertainty. For that reason, much more attention has been directed to gas-phase chemistry.

#### *Gas-Phase Chemistry*

A qualitative list of the reaction types that are supposed to be involved in the gas-phase chemistry of the interstellar medium is given in Table 4. Reactions between positive ions and neutral species are currently thought to be the most likely processes; their superior efficacy if compared to neutral-neutral reactions arises because of their lower activation energies.

In order to discuss more properly the gas-phase chemistry of interstellar molecules it is convenient to treat separately diffuse and dark clouds, as their chemistry is controlled by entirely different processes.

#### *Diffuse Clouds*

Diffuse clouds are more or less penetrated by the galactic diffuse starlight, which is predominately in the 1000–2000 Å wavelength range. Such ultraviolet photons are the principal

**Table 4. Gas-Phase Reaction Types of Importance in Interstellar Chemistry**

| | |
|---|---|
| I. Ion-molecule reactions | |
| a) Charge transfer | |
| | $A^+ + B \rightarrow B^+ + A$ |
| b) Radiative association | |
| | $A^+ + B \rightarrow AB^+ + h\nu$ |
| c) Atom transfer | |
| | $A^+ + BC \rightarrow AB^+ + C$ |
| | $AB^+ + C \rightarrow A^+ + BC$ |
| II. Electron recombination reactions | |
| a) Radiative | |
| | $A^+ + e^- \rightarrow A + h\nu$ |
| b) Dissociative | |
| | $AB^+ + e^- \rightarrow A + B$ |
| III. Photochemical reactions | |
| a) Photodissociation | |
| | $AB^+ + h\nu \rightarrow A^+ + B$ |
| b) Photoionization | |
| | $A + h\nu \rightarrow A^+ + e^-$ |
| IV. Neutral-neutral reactions | |
| a) Atom (or atom group) transfer | |
| | $A + BC \rightarrow AB + C$ |
| b) Radiative association | |
| | $A + B \rightarrow AB + h\nu$ |
| c) Chemionization | |
| | $A + B \rightarrow AB^+ + e^-$ |
| V. Other reactions | |
| a) Ion-ion neutralization | |
| | $A^+ + B^- \rightarrow AB$ |
| b) Negative ion-neutral | |
| | $A^- + B \rightarrow AB + e^-$ |
| | $A^- + BC \rightarrow AB^- + C$ |

external energy source, and they govern the ionization and destruction processes of atoms and molecules within the cloud. The absorption of atomic hydrogen cuts off the spectrum of the light to photons with wavelengths greater than 912 Å (13.6 eV), which corresponds to hydrogen's ionization potential. This energetic barrier divides the elements in two groups: those whose ionization potential is lower than 13.6 eV (such as C) exist mainly as ions, while those with ionization potentials greater than this value remain in neutral form (i.e., O, N). The chemical composition of diffuse clouds is thus very simple and the only available molecules are mostly diatomics such as $H_2$, HD, OH, CO, CH, $CH^+$, $N_2$, NO, CN, $O_2$, etc.

The accepted formation mechanisms for some of these species are given in Table 5. It must be noticed that the CH and $CH^+$ chemistry, whose study began more than 30 years ago, still remains controversial and one of the unsolved problems of interstellar chemistry.

*Dense Clouds*

In these clouds, opaque to ultraviolet starlight, photodissociation and photoionization are negligible, and they have a unique external energetic source—the cosmic rays (i.e., highly energetic nuclei of 1–100 MeV/nucleon), which are present throughout the whole Galaxy. Cosmic rays are responsible of the initial ionization step of hydrogen and helium, the two preponderant elements

$$\begin{aligned} &\text{Cosmic ray} + H_2 \rightarrow H_2^+ + e^- \\ &\text{Cosmic ray} + He \rightarrow He^+ + e^- \end{aligned} \qquad (2)$$

The next step is the reaction between these ions and other species to produce highly reactive ions, the most important being $H_3^+$, formed by reaction of $H_2^+$ with molecular hydrogen

$$H_2^+ + H_2 \rightarrow H_3^+ + H \qquad (3)$$

The $H_3^+$ ion tends to react with molecules through reactions of the type shown in eqn. (4), yielding hydrogenated molecular ions

$$\begin{aligned} &H_3^+ + A \rightarrow AH^+ + H_2 \\ &A = CO, N_2, O, N, C_2 \\ &AH^+ = HCO^+, N_2H^+, NH^+, C_2H^+, OH^+ \end{aligned} \qquad (4)$$

The detection of $HCO^+$ and $N_2H^+$ provides good support for these mechanisms.

In turn, helium ions can dissociate molecules producing atomic ions according to the following reaction

$$\begin{aligned} &AB + He^+ \rightarrow A^+ + B + He \\ &AB = CO, N_2, O_2, C_2 \\ &A^+ = C^+, N^+, N_2^+, O^+, C^+ \end{aligned} \qquad (5)$$

Reaction (5) is the main source of atomic ions, as other processes, such as photoionization, are unimportant in dense clouds.

Ionic molecular species may react with molecular hydrogen (the most abundant chemical in dark clouds), giving rise to ions increasingly hydrogenated

$$\begin{aligned} &A^+ + H_2 \rightarrow AH^+ + H \\ &A^+ = OH^+, H_2O^+, NH^+, NH_2^+, O^+, N^+, CH^+, CH_2^+ \\ &AH^+ = H_2O^+, H_3O^+, NH_2^+, NH_4^+, \\ &\quad OH^+, NH^+, CH^+, CH_2^+, CH_3^+ \end{aligned} \qquad (6)$$

Those ions that do not react further with molecular hydrogen are destroyed by dissociative electron recombination. Some of the known interstellar species (i.e., OH, $H_2O$, CH) are produced in this way

$$\begin{aligned} AH_n^+ + e^- &\rightarrow AH_{n-1} + H \\ &\rightarrow AH_{n-2} + 2H \\ &\rightarrow AH_{n-2} + H_2 \end{aligned} \qquad (7)$$

Ammonia is formed by charge exchange between $NH_3^+$ and

**Table 5. Proposed Formation Mechanisms for Some Selected Species in Diffuse Interstellar Clouds**

| | | |
|---|---|---|
| HD | | |
| | $H^+ + D$ | $\rightarrow H + D^+$ |
| | $D^+ + H_2$ | $\rightarrow HD + H^+$ |
| $H_2O$,OH | | |
| | $H^+ + O$ | $\rightarrow O^+ + H$ |
| | $O^+ + H_2$ | $\rightarrow OH^+ + H$ |
| | $OH^+ + H_2$ | $\rightarrow H_2O^+ + H$ |
| | $H_2O^+ + H_2$ | $\rightarrow H_3O^+ + H$ |
| | $H_3O^+ + e^-$ | $\rightarrow H_2O + H$ |
| | | $\rightarrow OH + H + H$ |
| | | $\rightarrow OH + H_2$ |
| | $H_2O + h\nu$ | $\rightarrow OH + H$ |
| CH,$CH^+$ | | |
| | a) $C^+ + H$ | $\rightarrow CH^+ + h\nu$ |
| | $C + H$ | $\rightarrow CH + h\nu$ |
| | $CH^+ + e^-$ | $\rightarrow CH + h\nu$ |
| | | $\rightarrow C + H$ |
| | b) $C^+ + H_2$ | $\rightarrow CH_2^+ + h\nu$ |
| | $CH^+ + H_2$ | $\rightarrow CH_2^+ + H$ |
| | $CH_2^+ + H_2$ | $\rightarrow CH_3^+ + H$ |
| | $CH_2^+ + e^-$ | $\rightarrow CH + H$ |
| | $CH_3^+ + e^-$ | $\rightarrow CH_2 + H$ |
| | | $\rightarrow CH + H_2$ |
| CO,CN,$C_2$ | | |
| | a) $CH^+ + O,N,C$ | $\rightarrow CO,CN,C_2 + H^+$ |
| | b) $OH + C^+$ | $\rightarrow CO + H^+$ |

**Table 6. Proposed Formation Mechanisms for Some Intermediate Complex Molecules in Dense Interstellar Clouds**

| | | |
|---|---|---|
| CN,HCN,HNC | | |
| | $NH_3 + C^+$ | $\rightarrow H_2CN^+ + H$ |
| | | $\rightarrow HCN^+ + H_2$ |
| | $H_2CN^+ + e^-$ | $\rightarrow HCN + H$ |
| | | $\rightarrow HNC + H$ |
| | | $\rightarrow CN + H_2$ |
| | $HCN + C^+$ | $\rightarrow C_2N^+ + H$ |
| | $C_2N^+ + e^-$ | $\rightarrow CN + C$ |
| $H_2CO$ | | |
| | a) $CH_3 + O$ | $\rightarrow H_2CO + H$ |
| | b) $HCO^+ + H_2$ | $\rightarrow H_3CO^+ + h\nu$ |
| | | $\rightarrow H_2CO^+ + H$ |
| | $H_3CO^+ + e^-$ | $\rightarrow H_2CO + H$ |
| | c) $CH_3^+ + O$ | $\rightarrow H_2CO^+ + H$ |
| | $H_2CO^+ + M$ | $\rightarrow M^+ + H_2CO$ |
| | M: Fe,Mg,Na . . . etc. | |
| $HC_2$,$H_2C_2$ | | |
| | a) $C^+ + CH$ | $\rightarrow C_2^+ + H$ |
| | $C_2^+ + H_2$ | $\rightarrow C_2H^+ + H$ |
| | $C_2H^+ + H_2$ | $\rightarrow C_2H_2^+ + H$ |
| | $C_2H_2^+ + e^-$ | $\rightarrow C_2H + H$ |
| | b) $CH_4 + CH_3^+$ | $\rightarrow C_2H_5^+ + H_2$ |
| | $C_2H_5^+ + e^-$ | $\rightarrow C_2H_2 + H_2 + H$ |
| | | $\rightarrow C_2H_4 + H$ |

metals of low ionization potential (i.e., Na, Mg, Ca, Fe) or by dissociative electron recombination of $NH_5^+$.

The synthetic schemes for some molecules of intermediate complexity such as HCN, HNC, $H_2CO$, and CN are recorded in Table 6.

The key problem of interstellar chemistry is how the more complex organic molecules are formed. Much effort has been spent in the field, including both the experimental determination of many rate constants of gas-phase reactions and theoretical calculations; nevertheless, many questions remain unsolved.

An exhaustive exposition of all the work in this area is beyond the scope of this review, but some indications about the most promising trends of gas-phase chemistry of complex molecules can be outlined.

*Chemistry of Cyanopolyynes.* According to Winnewisser et al. (*24*), the carbon chain of cyanopolyynes can be built by a successive incorporation of acetylene units through the following reaction

$$C_2H_x^+ + C_2H_2 \rightarrow C_4H_y^+ + C_2H_2 \rightarrow C_6H_z^+ \ldots \quad (8)$$

The terminal cyano group is incorporated either by reaction with CN or HCN, which are both common interstellar species

$$H_2C_n^+ + CN \rightarrow HC_{n+1}N^+ + H \quad (9)$$
$$H_2C_n^+ + HCN \rightarrow H_2C_{n+1}N^+ + H \quad (10)$$
$$H_3C_n^+ + CN \rightarrow H_2C_{n+1}N^+ + H \quad (11)$$
$$H_3C_n^+ + HCN \rightarrow H_2C_{n+1}N^+ + H_2 \quad (12)$$

followed by electron recombination

$$H_2C_{n+1}N^+ + e^- \rightarrow HC_{n+1}N + H \quad (13)$$
$$n = 2,4,6,\ldots$$

If such a mechanism is correct, substituted polyynes with groups different from cyano (i.e., —CHO, —$NH_2$, —OH) should be abundant too. These molecules have not yet been detected, probably because they are asymmetric rotors instead of simple linear molecules, a circumstance that makes difficult their radioastronomical detection.

*Synthesis of Complex Molecules by Radiative Association Reactions.* Radiative associations of the type

$$A^+ + B \rightarrow AB^+ + h\nu \quad (14)$$

followed by electron recombination (usually with abstraction of an hydrogen atom) have been recently reexamined by several authors (*25–28*), and it seems that they can account for the formation of many of the more complex molecules. As an example, the proposed interstellar synthesis of methanol is given

$$\begin{aligned} CH_3^+ + H_2O &\rightarrow CH_3OH_2^+ + h\nu \\ CH_3OH_2^+ + e^- &\rightarrow CH_3OH + H \end{aligned} \quad (15)$$

By appropriate variation of the parent ions and the neutral molecules (see Table 7) the majority of the interstellar species can be explained.

Radiative association reactions have been experimentally studied by comparison with analogous three-body association reactions

$$A + B + M \rightarrow AB + M \quad (16)$$

or

$$\begin{aligned} A + B &\rightleftharpoons AB^* \\ AB^* + M &\rightarrow AB + M \end{aligned} \quad (17)$$

The last step is substituted in a low-density medium, such as interstellar clouds, by radiative stabilization

$$AB^* \rightarrow AB + h\nu \quad (18)$$

Finally, surface reactions cannot be ignored, although their relative importance in the synthesis of complex organic molecules is a poorly understood matter.

**Table 7. Radiative Association Formation Mechanisms Proposed for Some Complex Molecules in Dense Interstellar Clouds, according to ref. (*25*)**

General mechanism: $A^+ + X \rightarrow AX^+ + h\nu$
$AX^+ + e^- \rightarrow B + H$ or $H_2$
$AX^+$: hydrogenated ion

| Parent Ion ($A^+$) | Neutral (X) | Final Molecule (B) |
|---|---|---|
| $CH_3^+$ | $H_2$ | $CH_4$,$CH_3$ |
| | $H_2O$ | $CH_3OH$ |
| | CO | $CH_2CO$ |
| | $H_2CO$ | $CH_3CHO$ [a] |
| | $CH_3OH$ | $CH_3OCH_3$ [a] |
| | $NH_3$ | $CH_3NH_2$ |
| | HCN | $CH_3CN$ |
| $CH_5^+$ | CO | $CH_3CHO$ [a] |
| ($CH_3^+ + H_2 \rightarrow CH_5^+ + h\nu$) | $H_2CO$ | $CH_3CH_2OH$ [a], $CH_3OCH_3$ [a] |
| $CH_3O^+$ | $H_2CO$ | $HCOOCH_3$ |
| ($CH_5^+ + O \rightarrow CH_3O^+ + H_2$) | | |
| $HCO^+$ | $H_2$ | $H_2CO$ [a] |
| | $H_2O$ | HCOOH |
| $C_2H_5^+$ | $H_2O$ | $CH_3CH_2OH$ [a] |
| $NH_3^+$ | O | HNO [a] |
| | CO | HNCO |
| | HCN | $NH_2CN$ [a] |
| | $H_2CO$ | $NH_2CHO$ |
| $NO^+$ | $H_2$ | HNO [a] |

[a] Alternative processes have been postulated

### Quantitative Models

The general purpose of quantitative models of interstellar chemistry is to make predictions of the densities of the various chemical species that agree well with those inferred from observational radioastronomic data, in order to validate the supporting reaction schemes.

Actually, several quantitative models appeared in the current literature (*29–35*, *38*), with variable degrees of sophistication. However, all of them show some features in common

1) A set of starting conditions of total density, temperature, optical depth, and element abundances is assumed for the model cloud. Temperature controls many rate constants, while optical depth (which is interdependent with total density and cloud mass) is mainly concerned with photochemical processes. Element abundances are usually taken equal to the cosmic ones, and they act as additional constraints.
2) A series of chemical reactions (each one characterized by their respective rate constant) is set up, and the subsequent system of kinetic equations solved.

The main differences lay in the following aspects:

1) The number of chemical species considered.
2) The number of reactions considered.
3) The estimates for the values of the rate constants.
4) The mathematical resolution procedure of the kinetic equation system.

Information relative to points (1), (2), and (4) is summarized in Table 8 for the most important published computations, and they need no further comment, except for the last point (4): two mathematical approaches have been used. On the one

Table 8. A Comparison of Quantitative Models of Interstellar Chemistry

| Model (Ref.) | Number of Species | Number of Reactions | Calculation Type | Other Remarks |
|---|---|---|---|---|
| Mitchell-Ginsburg-Kuntz (*29*) | 100 | 455 | steady-state | ... |
| Prasad-Huntress (*30, 31*) | 137 | 1423 | time-dependent | ... |
| Graendel-Langer-Frerking (*32*) | 126 | 1067 | time-dependent | 12 Grain-surface reactions included. Isotopic substituted varieties of C and O included. |
| Tielens-Hagen (*33*) | 139 | 1520 | steady-state | Grain-surface chemistry included. |
| Pickles-Williams (*34*) | ... | ... | steady-state | Grain-surface chemistry included. Some reactions treated as parameters. |
| Millar (*35*) | 95 | 211 | steady-state | 20 Grain-surface reactions included. |
| Watt (*38*) | 89 | 1427 | time-dependent | ... |

hand, there are some models which make use of the steady-state assumption; i.e., if we represent the rate of formation/destruction for each chemical species $x_i$ by $\dot{\mathbf{x}}_i$, it will be expressed as a nonlinear function of all the concentrations $\mathbf{x} = \{x_1 \ldots x_n\}$ ($n$ being the number of species considered): $f_i(\mathbf{x})$

We can express the system in a vectorial form as

$$\dot{\mathbf{x}} = \boldsymbol{f}$$

where

$$\dot{\mathbf{x}} = \left\{\dot{x}_i = \frac{dx_i}{dt}\right\} \quad \text{and } \boldsymbol{f} = \{f_i(\mathbf{x})\}$$

The steady-state method computes the stationary concentrations solving the set of equations $\boldsymbol{f} = 0$. In other words, an equilibrium situation is assumed.

On the other hand, there are models that integrate the differential nonlinear system of equations, computing a time-dependent solution for every species.

The appropriate question is whether the lifetime of the cloud is long enough to allow the steady-state to be reached or not. It seems that at $t = 10^6$–$10^7$ y the equilibrium is accomplished for the majority of the species. This is roughly a value of the same order (or perhaps one order less) of that estimated for the cloud lifetime.

A second differentiating aspect to be mentioned is grain-surface chemistry, which has been employed to variable extent on some of the models already published (*32–35*) (the exception is, of course, the grain formation of $H_2$, which has been considered throughout all the models).

Although many of the quantitative models agree with remarkable coincidence with the experimental measurements, the principal criticism to be made is the omission of the more complex molecules in these calculations. There is no doubt that increasing computing facilities, together with the experimental determination of more kinetic constants, will help to improve the results.

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## Note Added in Proof

After submitting this paper for publication the following new interstellar molecules have been discovered: $CH_3C_4H$, $C_3O$, $HC_{11}N$, $SiC_2$, and probably $COH^+$; and the following calculations on kinetic quantitative models published:

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