Outline

Astrochemical processes:

The formation of H2

H3+ formation

The chemistry initiated by H3+

Formation and destruction of CO

Surface chemistry

Examples: pre-stellar cores, protostellar envelopes, outflows, hot cores, protoplanetary disks...
Interstellar Molecules

Known Interstellar Molecules (Total: 151 as of 2009)

<table>
<thead>
<tr>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>Number of Atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>H₂O</td>
<td>NH₃</td>
<td>SH₂</td>
<td>CH₃OH</td>
<td>CH₃OH₂</td>
</tr>
<tr>
<td>OH</td>
<td>H₂S</td>
<td>HCN</td>
<td>H₂S</td>
<td>CH₂OH</td>
<td>CH₃CHO</td>
</tr>
<tr>
<td>SO</td>
<td>SO₂</td>
<td>NSH</td>
<td>SO₂</td>
<td>CH₂OH</td>
<td>CH₃CHO</td>
</tr>
<tr>
<td>NO</td>
<td>NO₂</td>
<td>HNO</td>
<td>HNO</td>
<td>CH₂OH</td>
<td>CH₃CHO</td>
</tr>
<tr>
<td>H₂O</td>
<td>H₂SO</td>
<td>H₂SO₂</td>
<td>H₂SO₃</td>
<td>CH₂OH</td>
<td>CH₃CHO</td>
</tr>
</tbody>
</table>

Amino acetonitrile in SgrB2(N) (Belloche et al. 2008)

Glycine - the simplest amino acid

How do molecules form in the interstellar medium?

The most elementary chemical reaction is the association of A and B to form a molecule AB with internal energy:

\[
A + B \rightarrow AB
\]

The molecule AB* must lose the internal energy. In the Earth atmosphere, where the number of particles per cubic centimeter (cc) is very large (~10^{19}), the molecule loses its energy via three-body reactions:

\[
AB^* + M \rightarrow AB
\]

But this is not an efficient process in interstellar clouds (F_{AB} \sim 10^{-36} n^3 cm^{-3} s^{-1}), where the number of particles per cc ranges between a few hundred and 10^7.
1. **The formation of H$_2$**

The reaction that starts the chemistry in the interstellar medium is the one between two hydrogen atoms to form molecular hydrogen:

$$\text{H} + \text{H} \rightarrow \text{H}_2$$

This reaction happens on the surface of dust grains.

The H$_2$ formation rate (cm$^{-3}$ s$^{-1}$) is given by (Gould & Salpeter 1963; Hollenbach & Salpeter 1970; Jura 1974; Pirronello et al. 1999; Cazaux & Tielens 2002; Habart et al. 2003; Bergin et al. 2004; Cuppen & Herbst 2005):

$$R_{\text{H}_2} = \frac{1}{2} n_H v_H A n_g S_{\text{H}} \gamma \approx 10^{-17} \text{ cm}^3 \text{s}^{-1}$$

$n_H$ = gas number density

$v_H$ = H atoms speed in gas-phase

$A$ = grain cross sectional area

$n_g$ = dust grain number density

$S_{\text{H}}$ = sticking probability

$\gamma$ = surface reaction probability
Ingredients of gas phase chemistry

Table 1. Measured elemental abundances (with respect to total hydrogen) and those adopted in chemical models.

<table>
<thead>
<tr>
<th>Element</th>
<th>MEASURED</th>
<th>ADOPTED</th>
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<tbody>
<tr>
<td></td>
<td>Solar</td>
<td>Cosmic</td>
</tr>
<tr>
<td>C</td>
<td>3.6(-4)</td>
<td>2.1(-4)</td>
</tr>
<tr>
<td>N</td>
<td>9.3(-5)</td>
<td>6.6(-5)</td>
</tr>
<tr>
<td>O</td>
<td>7.4(-4)</td>
<td>4.6(-4)</td>
</tr>
<tr>
<td>S</td>
<td>1.9(-5)</td>
<td>1.2(-5)</td>
</tr>
<tr>
<td>Si</td>
<td>3.6(-5)</td>
<td>1.9(-5)</td>
</tr>
<tr>
<td>Fe</td>
<td>3.2(-5)</td>
<td>2.7(-5)</td>
</tr>
<tr>
<td>Na</td>
<td>1.9(-6)</td>
<td>...</td>
</tr>
<tr>
<td>Mg</td>
<td>3.8(-5)</td>
<td>2.5(-5)</td>
</tr>
</tbody>
</table>

Note: a(b) ≡ a×10^b.


+ electrons, dust grains, cosmic-rays, UV photons, X-rays

Neutral-neutral reactions

- Generally very slow and inefficient, because of:
  - small cross section
  - activation energy barriers (especially in cold, molecular clouds)
  - the need to carry away energy and momentum in a 3rd species
Ion-neutral reactions

• Occur much more easily: as ion approaches a neutral it induces an electric dipole moment, leading to enhanced electrostatic attraction.

\[ \text{I}^+ + \text{AB} \rightarrow \text{I} + \text{AB}^+ \]

Need source of ionization

Two main sources: (1) Cosmic Ray (CR) ionization; (2) Photoelectric effect on dust grains by FUV photons. But in molecular cores that are heavily shielded by dust, CR ionization is most important.

**Cosmic-ray ionization rate (Dalgarno 2006, PNAS)**

\[ \zeta \geq 10^{-18} \text{ s}^{-1} \text{ from the known spectrum of high energy cosmic rays.} \]

\[ \zeta < 10^{-14} \text{ s}^{-1} \text{ from thermal equilibrium in diffuse clouds.} \]

\[ \zeta \leq 6 \times 10^{-17} \text{ s}^{-1} \text{ molecule in some dark clouds, from thermal equilibrium.} \]

\[ \text{H}_2 + \text{c.r.} \rightarrow \text{H}_2^+ + \text{e} + \text{c.r.} \]
Cosmic-ray ionization of $\text{H}_2$

After the formation of molecular hydrogen, cosmic rays ionize $\text{H}_2$ initiating fast routes towards the formation of complex molecules in dark clouds:

$$\text{H}_2 + \text{c.r.} \rightarrow \text{H}_2^+ + \text{e}^- + \text{c.r.}$$

Once $\text{H}_2^+$ is formed (in small percentages), it very quickly reacts with the abundant $\text{H}_2$ molecules to form $\text{H}_3^+$, the most important molecular ion in interstellar chemistry:

$$\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$$

The chemistry initiated by $\text{H}_3^+$

Once $\text{H}_3^+$ is formed, a cascade of reactions greatly enhance the chemical complexity of the ISM.

In fact, $\text{H}_3^+$ can easily donate a proton and allow larger molecules to build.

Example ➔ OXYGEN CHEMISTRY (the formation of water in the ISM)
The chemistry initiated by $H_3^+$

CARBON CHEMISTRY (the formation of hydrocarbons)

The formation of more complicated species from neutral atomic carbon begins with a sequence very similar to that which starts the oxygen chemistry:

\[
\begin{align*}
C & \quad H_3^+ & \quad H_2 & \quad CH_2^+ & \quad H_2 & \quad CH_3^+ & \quad e & \quad CH_2 \\
& & & & & & & \\
& & & & & & & \\
\end{align*}
\]

A. Proton transfer from $H_3^+$ to a neutral atom;
B. Hydrogen abstraction reactions terminating in a molecular ion that does not react with H2;
C. Dissociative recombination with electrons.

Formation and destruction of CO

- [a] $C + H_3O^+ \rightarrow HCO^+ + H_2$
- [b] $O + CH_3^+ \rightarrow HCO^+ + H_2$
- [c] $HCO^+ + e \rightarrow CO + H$ is the most important source of CO.

CO is very stable and difficult to remove. It reacts with $H_3^+$:
- [d] $H_3^+ + CO \rightarrow HCO^+ + H_2$
but reaction [c] immediately reform CO.

The main mechanisms for removing CO are:
- [e] $He^+ + CO \rightarrow He + C^+ + O$
- [f] $hv + CO \rightarrow C + O$

Some of $C^+$ react with OH and $H_2O$ (but not with $H_2$):
- [g] $C^+ + OH \rightarrow CO^+ + H$
- [h] $CO^+ + H_2 \rightarrow HCO^+ + H$
- [i] $C^+ + H_2O \rightarrow HCO^+ + H$

The timescale to form CO

Assume: dark region where all H is in H₂ and all atoms more massive than He are in neutral atomic form.

The timescale on which almost all carbon becomes contained in CO ($n_0 > n_C$) is at least equal to the timescale for one hydrogen molecule to be ionized for every C:

$$n_C / [\zeta n(H_2)] = 2 n_C / [\zeta n_H]$$

For $\zeta = 6 \times 10^{-17}$ s⁻¹ and $n_C/n_H = 10^{-4}$, the above expression gives a value of $10^5$ yr.

Chemical Evolution?

Suzuki et al. 1992
**Chemical Evolution?**

Dust has to be taken into account!

**Freeze-out vs. free-fall:**

\[ t_{\text{dep}} = \frac{1}{\alpha n_d \pi a_d^2 v_t} \approx 10^9 \sqrt{m_X/T(n_H \alpha)^{-1}} \text{ yr} \]

\[ t_{ff} = \left( \frac{3\pi}{32G\rho} \right)^{-1/2} = 4 \times 10^7 (n_H)^{-1/2} \text{ yr} \]

Walmsley 1991
van Dishoeck et al. 1993

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**Evidences of freeze-out: solid features**

from van Dishoeck et al. 2003

Pontoppidan et al. 2007