Gas-phase formation routes of simple prebiotic molecules in the interstellar medium

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### Basic steps in the origin of life

<table>
<thead>
<tr>
<th>Event</th>
<th>Time (billion years ago)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formation of Earth</td>
<td>4.5</td>
</tr>
<tr>
<td>Stable hydrosphere</td>
<td>4.2</td>
</tr>
<tr>
<td>Prebiotic chemistry</td>
<td>4.2–4.0</td>
</tr>
<tr>
<td>Pre-RNA world</td>
<td>4.0</td>
</tr>
<tr>
<td>RNA world</td>
<td>~3.8</td>
</tr>
<tr>
<td>First DNA/protein life</td>
<td>~3.6</td>
</tr>
<tr>
<td>Diversification of life</td>
<td>3.6–present</td>
</tr>
</tbody>
</table>

*Gerald F. Joyce, Nature (2002)*

This contribution is focused on the chemical evolution which has taken place during the early steps along this sequence of events.
Very first steps in the origin of life: exogenous delivery or local formation of prebiotic molecules?

- **Formation of Earth**
- **Stable hydrosphere**
- **Prebiotic chemistry**

Exogenous delivery:
- Carriers: IDPs, meteorites, asteroids, comets

Endogenous synthesis of complex organic molecules from simple parent species

Interstellar clouds
### Chemical composition: Universe vs human body

#### Universe Mole Fractions

<table>
<thead>
<tr>
<th>Element</th>
<th>Mole Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0.63</td>
</tr>
<tr>
<td>He</td>
<td>-</td>
</tr>
<tr>
<td>O</td>
<td>0.24</td>
</tr>
<tr>
<td>C</td>
<td>0.12</td>
</tr>
<tr>
<td>N</td>
<td>0.01</td>
</tr>
<tr>
<td>S</td>
<td>0.12</td>
</tr>
<tr>
<td>Si</td>
<td>0.01</td>
</tr>
<tr>
<td>Mg</td>
<td>0.01</td>
</tr>
<tr>
<td>Fe</td>
<td>0.01</td>
</tr>
<tr>
<td>Others</td>
<td>~6x10^{-3}</td>
</tr>
</tbody>
</table>

#### Human Body Mole Fractions

<table>
<thead>
<tr>
<th>Element</th>
<th>Mole Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0.91</td>
</tr>
<tr>
<td>He</td>
<td>0.09</td>
</tr>
<tr>
<td>O</td>
<td>2.7x10^{-4}</td>
</tr>
<tr>
<td>C</td>
<td>1.3x10^{-4}</td>
</tr>
<tr>
<td>N</td>
<td>7.3x10^{-5}</td>
</tr>
<tr>
<td>S</td>
<td>2.7x10^{-5}</td>
</tr>
<tr>
<td>Si</td>
<td>1.8x10^{-6}</td>
</tr>
<tr>
<td>Mg</td>
<td>9x10^{-7}</td>
</tr>
<tr>
<td>Fe</td>
<td>1.8x10^{-7}</td>
</tr>
<tr>
<td>Others</td>
<td>~10^{-12}</td>
</tr>
</tbody>
</table>

atomic species or simple molecules

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[Diagram showing chemical composition contrasts between the universe and the human body]
Identified interstellar and circumstellar molecules/ions

2 atoms
AIF AlCl C₂ CH CH⁺ CN CO CO⁺ CP CS CSi HCl H₂ KCl NH NO NS NaCl OH PN SO SO⁺ SiN SiO SiS HF SH FeO S₂ CF+ O₂ PO SH⁺ AlO ArH⁺ NO⁺ TiO HCl⁺

3 atoms
C₃ C₂H C₂O C₂S CH₂ HCN HCO HCO⁺ HCS⁺ HOC⁺ H₂O H₂S HNC HNO MgCN MgNC N₂H⁺ N₂O NaCN OCS SO₂ c-SiC₂ CO₂ NH₂ H₃⁺ AlNC FeCN KCN SiNC HCP CCP SiCSi CCN TiO₂ HO₂

4 atoms
c-C₃H₁ l-C₃H₂ C₃N C₃O C₃S C₂H₂ CH₂D⁺ HCCN HCNH⁺ HNCO HNCS HOCO⁺ H₂CO H₂CN H₂CS H₃O⁺ NH₃ SiC₃ C₃N⁺ PH₃ HCNO HOCN HCCO NCCP MgCCH HMgNC l-C₃H⁺ H₂O₂

5 atoms
C₅ C₄H C₄Si l-C₃H₂ C-C₃H₂ CH₂CN CH₄ HC₃N HC₂NC HCOOH CH₂NH H₂C₂O H₂NCN HNCNH

6 atoms
C₅H C₅O C₂H₄ CH₃CN CH₃NC CH₃OH CH₃SH HC₃NH⁺ HC₂CHO HCONH₂⁺ H₂C₄ C₅N⁺ HC₄N c-H₂C₃O CH₂CNH C₅N⁻ C₅S⁻ CNCHNH

7 atoms
C₆H CH₂CHCN CH₃C₂H HC₅N HCOCH₃ NH₂CH₃ C-C₂H₄ O CH₂CHOH C₆H⁺

8 atoms
CH₃C₃N HCOOCH₃ CH₃COOH C₇H₂C₆ CH₂OHCHO CH₂CHCHO C₄H₆ CH₂CCHCN NH₂CH₂CN (NH₂)₂CO CH₃CHNH

9 atoms
CH₃C₄H CH₃CH₂CN (CH₃)₂O CH₃CH₂OH HC₇N C₈H CH₃CONH₂ C₈H⁺ CH₂CHCH₃ CH₃CH₂SH

10 atoms
CH₃C₅N (CH₃)₂CO NH₂CH₂COOH CH₃CH₂CHO CH₂OHCH₂OH

≥ 11 atoms
HC₉N CH₃C₆H C₆H₆ HC₁₁N CO(CH₂OH)₂ HCOOC₂H₅ CH₃COOCH₃ C₃H₇CN C₁₄H₁₀⁺ C₆₀ C₆₀⁺

Only 37 species do not contain carbon !!

+ PAHs family
Simple organic molecules: are they the link between matter in the Universe and matter in living entities?

<table>
<thead>
<tr>
<th>gas-phase molecules</th>
<th>potential precursor of</th>
</tr>
</thead>
<tbody>
<tr>
<td>with C-N bonds (e.g. HCN, CH₃CN, C₂N₂, HCCCN, CH₂NH, C₂H₃CN)</td>
<td>aminoacids &amp; nucleic bases</td>
</tr>
<tr>
<td>with C-O bonds (e.g. H₂CO, CH₃OH, CH₃COH, CH₃CHO, (CH₂OH)₂, CH₂OHCHO)</td>
<td>sugars &amp; aminoacids</td>
</tr>
<tr>
<td>with C-C multiple bonds (e.g. from C₂H₂ up to long carbon chain molecules, PAHs)</td>
<td></td>
</tr>
</tbody>
</table>

If we agree that the answer is yes, we need to face another question: how were they formed to begin with?
Laboratory experiments

modelling

observations

Hundreds or thousands of elementary reactions including:
- dissociation, excitation & ionization processes
- neutral-neutral reactions
- ion-molecule reactions
- heterogeneous processes

a large fraction of these processes need to be characterized in lab experiments yet
Successes for quiescent cores:

1. Reproduces 80% of abundances including ions, radicals, isomers
2. Predicts strong deuterium fractionation

GAS-PHASE MODEL NETWORKS

4,400 reactions; 10-20% "studied";
450 species through 13 atoms in size

- Elements: H, He, N, O, C, S, Si, Fe, Na
- Elemental abundances: “low metal”
- Photodestruction: external, internal (via collisions)

In 9 years this percentage has not changed much; more recent models: 8000 reactions involving also negative ions
Dust particles and icy mantles: preferential sites to induce chemical reactivity?

Problems:
- mobility of frozen species at 10 K;
- desorption mechanisms

by Wendy Brown (PCCP 2014)
The ISM ice composition

either hydrides or fully hydrogenated species
Different formation routes?

Degrees of saturation: in the ISM there are completely saturated (e.g. CH₄, CH₃NH₂, CH₃OH), partially saturated (e.g. CH₃CH=CH₂, CH₂=NH, H₂CO) and strongly unsaturated molecules (e.g. C₂H₂ and cyanopolyynes, HCN, PAHs) in the presence of abundant hydrogen atoms/molecules.

many gas-phase routes have actually been overlooked and not considered in the astrochemical models, while their inclusion with the parameters determined in laboratory experiments or via accurate theoretical calculations could be decisive in reproducing the observed abundances of complex molecules.
Following the observation of relatively complex molecules also in very cold interstellar objects (no mobility, no easy desorption), in Grenoble we have started a systematic search for new formation routes in the gas phase by:
Following the observation of relatively complex molecules also in very cold interstellar objects (no mobility, no easy desorption), in Grenoble we have started a systematic search for new formation routes in the gas phase by:

1) extensively searching the literature for previously overlooked bimolecular reactions in the gas phase;

2) making use of recent experimental results where the reactions of interest have been investigated under the appropriate experimental conditions (low T and P);

3) guiding theoretical chemists in the choice of reactions for which laboratory experiments are extremely difficult (if not impossible);

4) testing the new formation routes in astrochemical models.
1) extensively searching the literature for previously overlooked bimolecular reactions in the gas phase:

- methyl formate formation: unsolved puzzle
- grain surface chemistry invoked
1) extensively searching the literature for previously overlooked bimolecular reactions in the gas phase

**Gas phase reactions leading from dimethylether to methyl formate**

\[
\text{Cl/F + CH}_3\text{OCH}_3 \rightarrow \text{CH}_3\text{OCH}_2 + \text{HCl/HF}
\]

\[
\text{O + CH}_3\text{OCH}_2 \rightarrow \text{HCOOCH}_3 + \text{OH}
\]


Formation of complex organic molecules in cold objects: the role of gas-phase reactions

Nadia Balucani,1,2,3 Cecilia Ceccarelli2,3* and Vianney Taquet4

a purely gas phase route to methyl formate

CH$_3$OCH$_3$ is the parent molecule of HCOOCH$_3$
Abundance of dimethyl ether as a function of the abundance of methyl formate in different ISM sources

$r = \text{correlation coefficient} + \text{power-law index}$

Jaber, Ceccarelli, Kahane, Caux
2) making use of recent experimental results where the reactions of interest have been investigated under the appropriate experimental conditions (low T and P)

\[ \text{OH} + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O} / \text{CH}_2\text{OH} + \text{H}_2\text{O} \]

\[ k \ (300 \text{ K}) = 9 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \]

\[ E_a = 3 \text{ kJ/mol} \ (\text{CH}_2\text{OH}+\text{H}_2\text{O}) \]

\[ 15 \text{ kJ/mol} \ (\text{CH}_3\text{O}+\text{H}_2\text{O}) \]
Despite the presence of an entrance barrier, the rate coefficient at 63 K was found to be larger than that at 200 K. Deviations from Arrhenius behavior are quite common. In some cases they are associated to the tunnelling effect...
According to master equation calculations explicitly considering the tunnelling effects, at temperatures lower than 200 K the lifetime of the van der Waals complex is very long and tunnelling towards $\text{CH}_3\text{O}+\text{H}$ becomes the dominant channel (99%)
Not only is the reaction several orders of magnitude faster than suggested by room temperature experiments, but the dominant products are $CH_3O+H$ and not $CH_2OH+H$.

$CH_3O$ (methoxy radical) has been recently observed by Cernicharo.

This $CH_3O$ formation route in the gas-phase is very efficient also in cold clouds and can account for the observed amount.
The conversion of $\text{CH}_3\text{OH}$ to $\text{CH}_3\text{O}$ is pivotal to achieve the formation of $\text{CH}_3\text{OCH}_3$. 

Formation of complex organic molecules in cold objects: the role of gas-phase reactions

Nadia Balucani, Cecilia Ceccarelli and Vianney Taquet

a) Standard model
- Without new reactions
- With new reactions

b) Chemical de...
3) guiding theoretical chemists in the choice of reactions for which laboratory experiments are difficult (if not impossible)

**Formamide formation in the gas phase**

\[ \text{NH}_2 + \text{H}_2\text{CO} \rightarrow \text{HCONH}_2 + \text{H} \]

- both NH\(_2\) and H\(_2\)CO are abundant species in cold clouds

- previously disregarded because the similar reaction OH + H\(_2\)CO is slow and characterized by a significant energy barrier
3) guiding theoretical chemists in the choice of reactions for which laboratory experiments are difficult (if not impossible)

Barone, Latouche, Skouteris, Vazart, Balucani, Ceccarelli, Lefloch
MNRAS 2015, in press
Rate coefficient as a function of $T$ (10-300 K):
\[ \alpha = 2.6 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}, \beta = -2.1, \gamma = 26.9 \]
the proposed mechanism can well reproduce the abundances of formamide observed in two very different interstellar objects: the cold envelope of the Sun-like protostar IRAS16293-2422 and the molecular shock L1151-B2. There is no need to invoke grain-surface chemistry to explain the presence of formamide provided that its precursors, NH$_2$ and H$_2$CO, are available in the gas-phase.
Summary

1) Gas phase reactions are major actors in the formation of relatively complex organic molecules in the cold objects of the interstellar medium (methoxy radical, dimethylether, methyl formate, formamide)

   This challenges the exclusive role of grain surface chemistry and favours a combined grain-gas chemistry

2) Hydrogenation of simple molecules (CO, C₂, HCN ↔ CH₃OH, C₂H₆, CH₃NH₂) is still the realm of grain surface chemistry, but molecular complexity can be achieved also in gas phase reactions leading to or involving unsaturated species

3) More work in progress. Other examples: cyanomethanimimine formation or methanimimine dimerization (see the oral contributions by Fanny Vazart and Marzio Rosi)
Gas-phase prebiotic chemistry: the first chemical step in abiogenesis?

physics

biology

chemistry of increasing complexity
The aggregation of H, O, N, C (and other elements) atoms into molecules and the subsequent chemical evolution are all occurring now in the Universe, as witnessed by the identification of more than a hundred molecular species in the harsh chemical environments of interstellar clouds and by the gas-phase chemical evolution of the atmospheres of several solar objects like Titan.

Simple as they might seem compared to other processes of relevance in the study of the origin of life, the formation mechanisms of many of the observed molecules and radicals are far from being understood, while a comprehension of those processes can help to set the stage for the emergence of life to occur.

THANK YOU FOR YOUR ATTENTION
The 50 molecules/ions detected in comets

Organic molecules & meteorites

Table 1. Soluble Organic Compounds in the Murchison Meteorite

<table>
<thead>
<tr>
<th>Class of Compounds</th>
<th>ppm</th>
<th>n^a</th>
</tr>
</thead>
<tbody>
<tr>
<td>aliphatic hydrocarbons</td>
<td>&gt; 35</td>
<td>140</td>
</tr>
<tr>
<td>aromatic hydrocarbons</td>
<td>15–28</td>
<td>87</td>
</tr>
<tr>
<td>polar hydrocarbons</td>
<td>&lt;120</td>
<td>10^c</td>
</tr>
<tr>
<td>carboxylic acids</td>
<td>&gt;300</td>
<td>48^c</td>
</tr>
<tr>
<td>amino acids</td>
<td>60</td>
<td>75^c</td>
</tr>
<tr>
<td>imino acids^d^</td>
<td>nd^b</td>
<td>10</td>
</tr>
<tr>
<td>hydroxy acids</td>
<td>15</td>
<td>7</td>
</tr>
<tr>
<td>dicarboxylic acids</td>
<td>&gt;30</td>
<td>17^e</td>
</tr>
<tr>
<td>dicarboximides</td>
<td>&gt;50</td>
<td>2</td>
</tr>
<tr>
<td>pyridine carboxylic acids</td>
<td>&gt;7</td>
<td>7</td>
</tr>
<tr>
<td>sulfonic acids</td>
<td>67</td>
<td>4</td>
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<tr>
<td>phosphonic acids</td>
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<td>4</td>
</tr>
<tr>
<td>N-heterocycles</td>
<td>7</td>
<td>31</td>
</tr>
<tr>
<td>amines</td>
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<td>20^e</td>
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<tr>
<td>amides</td>
<td>nd^b</td>
<td>27</td>
</tr>
<tr>
<td>polyols</td>
<td>30</td>
<td>19</td>
</tr>
</tbody>
</table>

from Pizzarello, Acc. Chem. Res. 2006

from www.astrochymist.org