The Role of Surface Chemistry in the Synthesis of Interstellar Molecules

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Gaseous interstellar molecules (151)

<table>
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N = 11

N = 12

C\textsubscript{6}H\textsubscript{6}

N = 13

HC\textsubscript{10}CN
Chemical Simulations

- Gas-phase reactions
- Grain-surface reactions

Abundances, columns, spectra, uncertainties

Observations

Limited by chemical knowledge

Physical conditions, history
Sources Modeled

- Diffuse clouds
- Cold cores (10 K)
- Pre-stellar cores
- Hot Cores (100 K)
- Outflows
- Shocks
- Protoplanetary disks
- PDR’s; XDR’s
- IRDC’s
- Circumstellar envelopes
- Protoplanetary nebulae
- Planetary nebulae
- AGN disks
- Earliest clouds
- Exo-planetary atmospheres
Strengths/Failures of Gas-Phase Networks

• Exotic and unsaturated gaseous species (carbon chains, ions, radicals, isomers) in cold dense cores (ion-molecule chemistry; no barriers)
• Carbon-rich stellar envelopes
• Early universe chemistry (H and He)
• Formation of molecular hydrogen in the ISM
• Explanation of ices in cold cores
• Existence of saturated species in gas of cold cores (methanol, propylene)
• High abundances of complex organic molecules in hot cores
An Interplanetary Dust Particle

Size of interstellar dust ranges from 1-1000 nm; Mainly silicates and carbonaceous material
IR Absorption Spectroscopy

IR absorption showing a silicate core and ice mantle, mainly water. Not sensitive enough to find larger species.
Granular Processes

1. Bare surface chemistry (silicates, carbon)
2. Thermal chemistry on and possibly in ices
3. Photochemistry
4. Other non-thermal mechanisms (hot atoms, cosmic rays, X-rays, energetic electrons)
5. Thermal desorption
6. Non-thermal desorption (photodesorption; reactive desorption)
Reactive Mechanisms

accretion

desorption

hopping

tunnelling

Eley-Rideal

Langmuir-Hinshelwood

“flat” corrugated surface in 1D
Mathematical Methods for Model Including Surface Chemistry

- Rate equations: used for most calculations.
- Stochastic methods (master equation, method of moments, Monte Carlo).
- Monte Carlo: Random numbers determine process in time interval based on relative rates.
  - Macroscopic MC: Vasyunin et al.
  - Microscopic MC (CTRW, KMC): soon!
Coupled Rate Equations: gas or grain

\[ A + B \rightarrow C + D \]

\[ C + E \rightarrow F + G \]

\[ \frac{d[C]}{dt} = k_1[A][B] - k_2[C][E] \]

Master Equation: \( dP_n(C)/dt = \ldots, n = 0, 1, 2, 3\ldots \)

Solve coupled differential equations vs time: terms include accretion and desorption
A Monte Carlo approach in which the actual positions of individual species on a lattice are followed with time. Can use to follow reactions (LH, ER) and mantle build-up.
Desorption Processes: Coupling Gas & Dust Chemistries

- Thermal desorption: ice mixtures very complex, as measured in TPD experiments. Trapping and volcanic effects for binary mixtures.
- Non-thermal desorption:
  - Photodesorption (appears to follow electronic spectrum; more experiments, theory needed) competes with photodissociation
  - Reactive Desorption: uses energy of exothermic surface reactions to blow product off surface (simple theory only)
  - Cosmic ray desorption: thermal and sputtering, rates uncertain
Formation of Hydrogen

Physisorption mechanism
Vidali and co-workers

$T = 10-20 \text{ K}$

Ejection or desorption association

dust particle
H2 - More Recent Work

- Experiments
  - Rough surfaces
  - Chemisorption on graphite, PAHs

- Theory
  - Stochastic heating
  - Physisorption & chemisorption – T range
  - Molecular dynamics
Surface/ice processes in gas-grain networks

Cold core (10 K); build up of ice mantles including water, CO, CO2, CH4, methanol

Many studies

Photons

Radical-radical reactions

40-100 K reactions produce terrestrial organics

HCO + CH3O → HCOOCH3
Cold Core Chemistry

Rate equations

Macroscopic MC

Moment equations

Modified rate method

Microscopic MC - almost
Hot Core Chemistry: gas-grain model

Desorption after reaction

Terrestrial organics

200 K

Rate equations only, so far….

WCCC

10 K

Ion-mol. rx + accretion + surface chemistry (H-rich) leads to saturated ices

Surface chemistry involving radicals (formed by photolysis)

Garrod et al. (2008); Hassel et al. (2011)
Recent Laboratory Success: Warm-up chemistry

- Photochemistry in warming regions: indicates that basic model of complex molecular formation OK (Oberg et al. 2009), BUT..........

- Severe problems with transferring laboratory results for multi-reaction system into space.

- Solution: Try to simulate complex chemistry occurring in the laboratory; obtain rate parameters for use in interstellar codes (Garrod, Oberg, in progress).
SUMMARY

• Current standard gas-grain model: rate equations, homogeneous ice
• Improvements on the way for surface/ice chemistry: improved laboratory simulations and more use of stochastic approaches, including microscopic ones.
• More realistic, time-dependent physical conditions.
The Real Future

As we know,
There are known knowns.
There are things we know we know.
We also know
There are known unknowns.
That is to say,
We know there are some things
We do not know.
But there are also unknown unknowns,
The ones we don’t know
We don’t know.
Homogeneous Warm-up Model

Garrod et al.
Problem: lab to space conversion

- LABORATORY
  - High density/flux
  - Large surface
  - High radiation field
  - Pure ice

- SPACE
  - Low density/flux
  - Nanoparticle
  - Low radiation field
  - Dirty ice
Irregularities on rough surface
Predictions for the Future

1. Better simulations of laboratory experiments leading to more accurate rate coefficients under interstellar conditions.

2. Inclusion of 3-D hydrodynamics into gas-grain codes for protostar formation (Aikawa)

3. Greater use of stochastic approaches for surface chemistry.

4. More detailed studies of the chemistry occurring as protoplanetary disks and planets form.

5. Greater use of high-speed computing in models
Hydrogenation of CO into methanol at temperatures of (top to bottom) 12.0 K, 13.5 K, 15.0 K, and 16.5 K

Cuppen et al. 2009

2 x 10^5 yr cold core