Dissociative recombination reactions

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Important electron-ion processes

- \( \text{A}^+ + \text{B}^- \)
  Resonant ion pair formation (high energies)

- \( \text{AB} + h\nu \)
  Radiative recombination (too slow)

- \( \text{AB}^+_{(\nu=m)} + \text{e}^- \)
  Elastic/inelastic/superelastic scattering

- \( \text{AB}^+_{(\nu=n)} + \text{e}^- \)
  Dissociative recombination
Mechanisms of dissociative recombination (DR)

- Rate governed by Coulomb interaction
- Cross section $\propto E_{\text{collision}}^{-1}$
- Interim Rydberg state with certain lifetime
- Resonances in $\sigma/E$ plot possible
Importance of dissociative recombination (DR) in space

★ **Major process** in molecular clouds, planetary ionospheres and cometary comae

★ **final step** in synthesis of neutrals (e.g. CH$_4$)

\[
\begin{align*}
H_3^+ + C & \rightarrow CH^+ + H_2 \\
CH^+ + H_2 & \rightarrow CH_2^+ + H \\
CH_2^+ + H_2 & \rightarrow CH_3^+ + H \\
CH_3^+ + H_2 & \rightarrow CH_5^+ + hv \\
CH_5^+ + e^- & \rightarrow CH_4 + H
\end{align*}
\]

★ **Competing process** for ion-molecule reactions

\[
CH^+ + e^- \rightarrow C + H
\]

★ **Sometimes unique destruction pathway** for ions (c-C$_3$H$_3^+$ in Titan’s ionosphere)
What information is required about DR reactions?

★ Feasability in the ISM (absence of barrier, two-body process)
  → generally no problem, but: competition with ion-molecule reactions with abundant species (e.g. H₂ in dark clouds)

★ Reaction rate
  (R. Johnsen: “always about 2×10⁻⁷ cm⁻³ at 300 K”)
  → works fine with small ions HCO⁺, N₂H⁺ DR of larger ions much faster

★ Branching ratios
  Big problem: unpredictable, counter-intuitive, results from different methods disagree:

\[
\text{CH}_5^+ + \text{e}^- \rightarrow \text{CH}_4 + \text{H}
\]
only 5 % in ring (Semaniak et al.), dominant in afterglow (Adams et al.)
Methods for investigating DR reactions

Two groups:

Flowing afterglow methods

★ Production of He\(^+\) by microwave discharge
★ Ion production by consecutive reactions
★ Measurements of ion and electron (Langmuir probe) decay

Storage ring methods

★ Ions stored in magnetic or electrostatic ring
★ Merged with electron beam
**FA** - Flowing Afterglow

100-700 K

\[ H_3^+ + CO \rightleftharpoons HCO^+ + H \]

Glosik et al. 2006

**FALP**

QMS

**Formation region**

**Reaction region**

n_{H3^+} = (n_{H3^+})_0 \exp(-k_{nCO}t)

\[ t = L/v \]
FA methods - advantages and disadvantages

**Advantages**

- Thermic equilibrium by frequent collisions
- Low running costs

**Disadvantages**

- Restricted to ions that are easily produced (e.g. by protonation through $\text{H}_3^+$)
- No pure ion beam
- No interstellar conditions ($T=100-700\text{K}$, collisions of intermediates with gas molecules possible)
- Detection of all products difficult
The CRYRING storage ring

Schematic view of CRYRING

Steps during the experiment

1. Formation of ions in source
2. Mass selection by bending magnet
3. Injection via RFQ and acceleration
4. Merging with electron beam
5. Detection of the neutral products
Bending magnets

Cooled cathode

Anode

Neutral fragments

Electron cooler
**Grid technique**

- **without grid**
  - Surface barrier detector
  - Signal without grid (all events lead to full mass signal)
  - Particle loss

- **with grid**
  - Grid $T=0.3$
  - Probability $T(1-T)$
  - Signal with grid (mass spectrum dependent on branching ratio and $T$)
  - Branching ratio
Branching ratio of \( CH_5^+ \)

\[ \text{Disagreement with flowing afterglow (Adams et al.)} \]
Imaging analysis

Yields information about displacement of products (kinetic energy release of products)

→ but not only that!
Synchronous or sequential break-up

**Fluxional ion!**

- **Synchronous concerted**
- **Asynchronous concerted**

**Sequential**

- \( \tau > \tau_{\text{rot}} \)

**Isotropic angular distribution**

- \( \tau < \tau_{\text{rot}} \)

**Anisotropic angular distribution**

- Fixed angle, equal kinetic energy

**+ e**
Imaging results from DR of CH$_5^+$

★ Preliminary results suggest a sequential break-up of the CH$_5$ intermediate:

\[
\begin{align*}
\text{CH}_5^+ + \text{e}^- & \rightarrow \text{CH}_4^* + \text{H} \\
\text{CH}_4^* & \rightarrow \text{CH}_3 + \text{H}
\end{align*}
\]

In presence of buffer gas (FALP):

\[
\begin{align*}
\text{CH}_4^* + [\text{M}] & \rightarrow \text{CH}_4 + [\text{M}]
\end{align*}
\]

Desactivation of excited CH$_4^*$ → higher yield of CH$_4$
Three-body processes in DR: $H_3^+$

$H_3^+ + e^- + He \rightarrow H_2 + H$
$\rightarrow 3H$
$\rightarrow H_3^*$ (long-lived Rydberg)

With high He concentrations $H_3^*$ formation important:

at low $H_2$ abundance: $H_3^*$ formation competes with DR

at high $H_2$ abundance: Collisions with $H_2$ lead to less stable $H_3^{**}$

$H_2 + H_3^* \rightarrow H_2 + H_3^{**}$
$H_3^{**} \rightarrow 3H, H_2 + H, H_3^+$
$\rightarrow$ DR rate constant dependent on $[H_2]$

Dependence of DR rate on $[He]$ and $[H_2]$
Vibrational excitation and DR: $H_2^+$

- DR faster for vibrationally excited states of $H_2^+$
- Opening of direct channel(s) at $v>1$
- Cooling of ions in supersonic ion source
- Cooling in ring by superelastic collisions
  $$H_2^+(v=n) + e^- \rightarrow H_2^+(v<n) + e^-$$
- Imaging allows to gauge $v(H_2^+)$
Nuclear spin and DR

★ Different rates of DR in ortho/para H$_2^+$
★ Resonances in ortho and para H$_2^+$
★ DR of hot H$_2^+$ faster
★ Resonances different and broader in H$_2^+$
★ Differences observed in H$_3^+$ (I=1/2, 3/2) also

<table>
<thead>
<tr>
<th>$v$</th>
<th>Normal H$_2$</th>
<th>Para H$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.4</td>
<td>2.7</td>
</tr>
<tr>
<td>1</td>
<td>11</td>
<td>6.0</td>
</tr>
<tr>
<td>2</td>
<td>14</td>
<td>13.6</td>
</tr>
<tr>
<td>3</td>
<td>1.6</td>
<td>3.7</td>
</tr>
</tbody>
</table>

DR rate constants of normal and para H$_2^+$ at different vibrational excitation levels

Rate constants of the DR of hot and cold normal (solid) and para (dashed) H$_2^+$
(Not to scale)

Zhaunerchyk et al. 2007
Influence of isomers

★ Many ions detected in cometary comae + planetary ionospheres (Cassini-Huygens mission) by mass spectrometers

★ Question of isomerism arises, e.g. in $C_3H_3^+$ (cyclic and linear form)

★ Linear form undergoes ion neutral reactions, cyclic only DR

\[ l-C_3H_3^+ + C_2H_4 \rightarrow C_5H_7^+ \]

INMS spectrum from the T5 flyby of Cassini-Huygens
Both isomers detected in the interstellar medium

HCO\(^+\)/HOC\(^+\) ratio about 360-6000 in dense clouds (Apponi & Ziurys 1997)

In FALP and hollow cathode ion sources both isomers formed:

\[ H_3^+ + CO \rightarrow HCO^+ + H_2 \text{ (98\%)} \]
\[ HOC^+ + H_2 \text{ (2\%)} \]

DR of HCO\(^+\) and HOC\(^+\) have 3 different pathways:

\[
\begin{align*}
\text{HCO}^+ + e^- & \rightarrow H + CO \quad \Delta H = -7.45 \text{ eV} \\
& \rightarrow HC + O \quad \Delta H = +0.17 \text{ eV} \\
& \rightarrow HO + C \quad \Delta H = -0.75 \text{ eV}
\end{align*}
\]

\[
\begin{align*}
\text{HOC}^+ + e^- & \rightarrow H + CO \quad \Delta H = -7.79 \text{ eV} \\
& \rightarrow HC + O \quad \Delta H = -0.17 \text{ eV} \\
& \rightarrow HO + C \quad \Delta H = -1.09 \text{ eV}
\end{align*}
\]
In DCO$^+$ excited states with long lifetime (v3), not in HCO$^+$ (Heninger et al. 1999) → CD + O channel opens

C + OH (C+ OD) channels maybe from HOC$^+$ contaminations
Heavier systems: Protonated nitriles

★ Detected in greater abundances in Titan’s ionosphere than thought
★ can polymerise (With HCN) to tholines (haze formation)

\[
nRCN + nHCN \rightarrow \left[ \begin{array}{c}
\text{NH} \\
\| \\
\text{C} \end{array} \right] \begin{array}{c}
\| \\
\text{N} \end{array} \begin{array}{c}
\| \\
\text{C} \\
\end{array} \text{Tholins}
\]

★ very little about ion chemistry of protonated nitriles and other nitrogen-containing ions known
★ models still flawed
★ identification of ions not unambiguous

→ more molecular data is needed

Titan’s haze seen by Voyager
Protonated acetonitrile ($\text{CH}_3\text{CNH}^+$)

- 20 different channels
- Inadequate resolution of peaks separated by single hydrogen (D) mass
- Ring with higher rigidity ($B \times r$) necessary
- In 65% of cases $\text{CCC}N$ chain retained.
- Reaction rate constant $8.1 \times 10^{-7} (T/300)^{-0.69}$
- Reaction rate constant $8.1 \times 10^{-7} (T/300)^{-0.69}$ (2.5 times higher than in FALP)

DR fragment energy spectrum of $\text{CD}_3\text{CND}^+$
Statistical errors in reaction rate

Constants measured by ring methods

★ Ion current measurement ~10%

★ Background from rest gas collisions (few % at low collision energies)

★ Electron energy spread

★ Contribution from toroidal regions

★ Errors totally around 30%
Ring methods - advantages and disadvantages

Advantages

★ Mass selection of ions - enables study of more “exotic” species
★ Ultrahigh vacuum (10^{-11} mbar), excludes 3-body processes
★ Stepless variation of collision energy down to ~2meV
★ Identification of all possible reaction pathways (for lighter ions)

Disadvantages

★ Restricted to lighter ions (Cryring: M < 100 Dalton)
★ Isomers and isobars cannot be separated
★ Contributions of long-lived excited states possible
★ High set-up and running costs
Future challenges in DR measurements

- Perform experiments with rovibrationally cold ions
- Create pure on beams of isomeric species (e.g. through cluster dissociation)
- Extend measurements to heavier and more “difficult” ions
- Develop strategies for identifying new ions
- Is DR the only important neutralisation process in the ISM and planet atmospheres?

Dopfer and co-workers
Cold storage ring (MPIK, Heidelberg)

- Electrostatic storage ring
- Cooling down to 2K possible
- Ion energy 20-300 keV/charge (CRYRING 2-96 MeV/charge)
- Electron target with high resolution (500 μeV)
- Detection of products by microcalorimeters
- Commissioning planned 2008
★ Negative charge thought mostly to be present in the form of electrons.

★ Anions first predicted by Herbst (1981), but detection hampered (lack of spectral, data, receivers, air absorption)

★ Tentative detection of HS\(^-\) by ODIN in the Orion Molecular Cloud (OMC)
Detection of $\text{HC}_6^-$ (Thaddeus & co-workers)

★ Detected in IRC+10216 (envelope of high-mass-loss carbon star)
★ Also observed in dark cloud TMC-1
★ Ratio of $\text{HC}_6^-/\text{HC}_6$ $\sim 10\%$
★ Further detected anions: $\text{HC}_4^-,(\text{L1527}), \text{HC}_8^-$(IRC+10216)
Possible other anion sources: Photon-dominated regions (PDRs)

= strongly irradiated edges of dark clouds

★ Strategy to look at diffuse clouds (high electron abundance) might be wrong

Model by Millar et al. 2007
Anion reactions in space

**Associative detachment**

\[ C_6H^- + H \rightarrow C_6H_2 + e^- \]

probably important in diffuse clouds

**Photodetachment**

\[ C_6H^- + h\nu \rightarrow C_6H + e^- \]

**Ion-ion reactions** (e. g. mutual neutralisation)

\[ C_6H^- + C_2H_2^+ \rightarrow \text{neutral products} \]

Experimental data often lacking!
Relative importance of anion reactions

- Often dependent on different parameters (density, photon flux) e.g. in photon-dominated regions.
- In hot H\(^+\) (HII) zones UV photo-dissociation dominant.
- In H region reaction with H.
- In darker regions mutual neutralisation.
Can we elucidate these processes?

**Associative detachment:** Ion traps with H sources (e.g. Chemnitz)

**Mutual neutralisation + photodetachment:** DESIREE
Conclusions

★ Uncertainties in DR reaction not statistic, but systematic

★ Main problems:
  - Involvement of excited states
  - Isomerism
  - Influence of nuclear spin

★ Many reaction pathways with larger ions

★ Anion reactions might play larger role than estimated

★ Reliable, up-to date and exhaustive database lacking
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Requirements for a new on-line database on astrochemical reactions

- Exhaustive (not only referring to reactions going into standard models)
- Critical (not only recommending values, reporting state of discussions, identifying crucial processes)
- Interactive (allowing discussions)
- Run by international advisory board
- Up to date
- Funded securely (COST)