Dissociative recombination reactions

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Important electron-ion processes

- $A^+ + B^-$: Resonant ion pair formation (high energies)
- $AB + h\nu$: Radiative recombination (too slow)
- $AB^+_{(v=n)} + e^-$: Dissociative recombination
- $AB^+_{(v=m)} + e^-$: Elastic/inelastic/superelastic scattering

$A + B$
Mechanisms of dissociative recombination (DR)

- Direct process:
  - Rate governed by Coulomb interaction
  - Cross section $\propto E_{\text{collision}}^{-1}$
- Indirect process:
  - 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. CH₄)

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

★ Competing process for ion-molecule reactions

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

★ Sometimes unique destruction pathway for ions (c-C₃H₃⁺ 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. $\text{H}_2$ in dark clouds)

★ Reaction rate
   (R. Johnsen: “always about $3 \times 10^{-7} \text{ cm}^{-3}\text{s}^{-1}$ at 300 K”)
   → works fine with small ions $\text{HCO}^+$, $\text{N}_2\text{H}^+$
   → DR of larger ions tend to be much faster
   (often in the range of $2 \times 10^{-7} \text{ cm}^3\text{s}^{-1}$ at 300 K)
   → Exponential dependence not always $T^{-0.5}$

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

$$\text{CH}_5^+ + e^- \rightarrow \text{CH}_4 + \text{H}$$
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
$H_3^+ + CO \rightleftharpoons HCO^+ + H$

FA – Flowing Afterglow
100-700 K

He$^+$
He$^-$
e$^-$
He$_2^-$

H$_2$

H$_3^+$

CO

COH$^-$

HCO$^-$

H$_2$

QMS

Glosik et al. 2006

$\text{n}_{H_3^+} = (\text{n}_{H_3^+})_0 \exp(-kn_{\text{CO}}t)$

$t = \frac{L}{v}$

3D
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
- Intermediates can be deactivated by collisions
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
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
★ Ion current measurements difficult (until recently)
★ Full branching ratio analysis only for small ions
★ High set-up and running costs
General problems: Ion production

★ Mostly by discharge
★ Ring methods by hollow-cathode discharge
   → high energies involved (100-400 eV)
★ FA mostly by (e. g. by protonation through $H_3^+$ or charge transfer from e. g. $Ar^+$)
★ Precursors must be easily evaporated
   → but: electrospray ion source
★ Isomer ratio affected by precursor choice
General Problems: Different isomers

★ Many ions detected in cometary comae + planetary ionospheres (Cassini-Huygens mission) by mass spectrometers
★ Question of isomerism arises, e.g., in C$_3$H$_3^+$ (cyclic and linear form)
★ Linear form undergoes ion neutral reactions, cyclic only DR

\[ \text{INMS spectrum from the T5 flyby of Cassini-Huygens} \]

\[ 1-C_3H_3^+ + C_2H_4 \rightarrow C_5H_7^+ \]

Vuitton et al. 2006
**HCO⁺/HOC⁺**

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

- In FALP and hollow cathode ion sources both isomers formed:

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

  \[
  HOC^+ + H_2 \quad (2 \text{ %})
  \]

- Especially when CO is ionised

  \[
  H_2 + CO^+ \rightarrow HCO^+ + H \quad (~50 \text{ %})
  \]

  \[
  HOC^+ + H \quad (~50 \text{ %})
  \]

- DR of HCO⁺ and HOC⁺ have 3 different pathways:

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

  \[
  HOC^+ + e^- \rightarrow H + CO \quad \Delta H = - 7.79 \text{ eV}
  \]
  \[
  \rightarrow HC + O \quad \Delta H = - 0.17 \text{ eV}
  \]
  \[
  \rightarrow HO + C \quad \Delta H = - 1.09 \text{ eV}
  \]
HCO⁺/HOC⁺

<table>
<thead>
<tr>
<th>HCO⁺ + e⁻</th>
<th>DCO⁺ + e⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction channel</td>
<td>Branching ratio</td>
</tr>
<tr>
<td>CO + H</td>
<td>0.92</td>
</tr>
<tr>
<td>CH + O</td>
<td>0.01</td>
</tr>
<tr>
<td>C + OH</td>
<td>0.07</td>
</tr>
</tbody>
</table>

- In DCO⁺ excited states with long lifetime ($v_3$), not in HCO⁺ (Heninger et al. 1999) → CD + O channel opens
- C + OH (C+ OD) channels maybe from HOC⁺ contaminations
General problem: Excitation in e.g. $H_2^+$

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

- Imaging allows to gauge $v(H_2^+)$
General problems: 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>Rate constants $\times 10^{-7}$cm$^3$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Normal H$_2$</td>
</tr>
<tr>
<td>0</td>
<td>1.4</td>
</tr>
<tr>
<td>1</td>
<td>11</td>
</tr>
<tr>
<td>2</td>
<td>14</td>
</tr>
<tr>
<td>3</td>
<td>1.6</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
**HCNH**

- Major ion in Titan’s atmosphere
- DR of HCNH\(^+\) could be responsible for HNC/HCN ratio
- Rates:
  - FA: \(3.5 \times 10^{-7}\)
  - CRYRING: \(2.83 \times 10^{-7}(T/300)^{-0.65}\)
- Branching ratios very different

### Afterglow

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Product</th>
<th>Rate (FA)</th>
<th>Rate (CRYRING)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{HCNH}^+ + e^- \rightarrow \text{HCN/HNC} + \text{H})</td>
<td>0.00</td>
<td>-0.68</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\rightarrow \text{CN} + 2\text{H})</td>
<td>0.00</td>
<td>-0.31</td>
</tr>
<tr>
<td></td>
<td>(\rightarrow \text{CN} + \text{H}_2)</td>
<td>0.37</td>
<td>-0.69</td>
</tr>
</tbody>
</table>

### Storage ring

<table>
<thead>
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<th>Rate (CRYRING)</th>
</tr>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\rightarrow \text{CN} + 2\text{H})</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\rightarrow \text{CN} + \text{H}_2)</td>
<td>0.00</td>
<td></td>
</tr>
</tbody>
</table>
Different production pathways:

Afterglow: \( H_3^+ + \text{HCN} \)

Storage ring: \( \text{CH}_3\text{NH}_2 + \text{e}^- \)

→ Different isomers (\( \text{H}_2\text{CN}^+ \) or \( \text{CNH}_2^+ \) could be produced)

Flowing afterglow measurements assume slow DR of \( H_3^+ \)
(probably no consequences since reaction

\( H_3^+ + \text{HCN} \rightarrow \text{HCNH}^+ + \text{H}_2 \) is fast)

Collisional desactivation of intermediate HCNH
→ Unlikely to lead to \( \text{CN} + \text{H}_2 \)
Excited states of HCNH\(^+\) in the ring should have same cross section than ground state.

Such discrepancies also seen in other ions, e.g. D\(_3\)S\(^+\).

Branching ratio HCN + H / HNC + H still unclear. **But:** theoretical investigations point to a 1:1 ratio.

**Recommended values:**

<table>
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<tr>
<td>HCNH(^+) + e(^-) → HCN/HNC + H</td>
<td>0.68</td>
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<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>→ CN + 2H</td>
<td>0.32</td>
</tr>
<tr>
<td>→ CN + H(_2)</td>
<td>0.00</td>
</tr>
</tbody>
</table>

**Rate constant:** \(2.83 \times 10^{-7}(T/300)^{-0.65}\) cm\(^3\)s\(^{-1}\)
\[ C_2H_4^+ \]

- Can easily transfer protons to other hydrocarbons in high density media (planet and satellite atmospheres)
- DR could outcompete proton transfer in lower-density objects
- So far only ring experiment (ion probably difficult to form in afterglow)

**Branching ratios:**

\[
\begin{align*}
C_2H_4^+ + e^- & \rightarrow C_2H_3 + H & 0.11 \\
& \rightarrow C_2H_2 + H_2 & 0.06 \\
& \rightarrow C_2H_2 + 2H & 0.66 \\
& \rightarrow C_2H + H + H_2 & 0.10 \\
& \rightarrow CH_4 + C & 0.01 \\
& \rightarrow CH_3 + CH & 0.02 \\
& \rightarrow CH_2 + CH_2 & 0.04
\end{align*}
\]

**Rate constant:** \(5.6 \times 10^{-7} (T/300)^{-0.76} \text{ cm}^3\text{s}^{-1}\)

Values seem reasonable!
HSiO\(^+\)/HOSi\(^+\)

★ No measurements available due to
- lack of suitable precursor
- existence of 2 isomers, HOSi\(^+\) more stable

★ Educated guess from isovalent ions difficult, HCO\(^+\) and HN\(_2^+\) lose H, HCS\(^+\) breaks C-S bond
→ Equal distribution between H + SiO and HO + Si seems good assumption (DR to HSi + O almost thermoneutral)

★ No real reason to defect from model values:

**Branching ratios:**
\[
\text{HSiO}^+ + e^- \rightarrow H + \text{SiO} \quad 0.50
\]
\[
\rightarrow \text{HO} + \text{Si} \quad 0.50
\]

**Rate constant:** \(3.0 \times 10^{-7}(T/300)^{-0.50} \text{ cm}^3\text{s}^{-1} = 1 \text{ Johnsen}\)
The DR of all CH\(_x\)O\(^+\) ions have been investigated. Why not CH\(_2\)O\(^+\)?

→ two isomers almost equal in energy

Possibility to guess?

HCO\(^+\) and H\(_3\)CO\(^+\) leave their CO-bond intact with DR.
With more hydrogenated ions (CH\(_3\)OH\(_2\)) the heavy atom bond is preferentially broken

Assuming 90% CO bond retention in CH\(_2\)O we consider ejection of two hydrogen atoms to be a major process

No conclusions about the behaviour of two different isomers possible; for the guesses we consider H\(_2\)CO\(^+\)
Recommended values:

Branching ratios:
\[ CH_2O^+ + e^- \rightarrow HCO + H \quad 0.25 \]
\[ \rightarrow HOC + H \quad 0.05 \text{ (rearrangement)} \]
\[ \rightarrow CO + 2H \quad 0.50 \text{ (3-body !)} \]
\[ \rightarrow CO + H_2 \quad 0.15 \text{ (very exoergic)} \]
\[ \rightarrow CH + OH \quad 0.00 \text{ (C-O rupture)} \]
\[ \rightarrow C + H_2O \quad 0.00 \text{ (rearrangement)} \]
\[ \rightarrow CH_2 + O \quad 0.05 \text{ (C-O breakage)} \]

Rate constant: \( 5.0 \times 10^{-7}(T/300)^{-0.70} \text{ cm}^3\text{s}^{-1} \)

→ more in line with other \( CH_xO^+ \) ions
Several isomers available, discussion restricted to linear $\text{HCCCCC}NH^+$

No measurements, but following conclusions from $\text{HC}_3\text{NH}^+$:

- around 50% retention of carbon-nitrogen chain
- no breakage of multiple bonds
- 50% break-up into 2 fragments with 2 resp. 4 heavy atoms

No three-body channels energetically available
Recommended values:

Branching ratios:
\[ \text{HC}_5\text{NH}^+ + \text{e}^- \rightarrow \text{C}_5\text{N} + \text{H}_2 \quad 0.04 \text{ (heavy rearrangement)} \]
\[ \rightarrow \text{HC}_5\text{N} + \text{H} \quad 0.23 \]
\[ \rightarrow \text{C}_5\text{NH} + \text{H} \quad 0.23 \]
\[ \rightarrow \text{HCN} + \text{HC}_4 \quad 0.22 \]
\[ \rightarrow \text{HNC} + \text{HC}_4 \quad 0.22 \]
\[ \rightarrow \text{HC}_4\text{N} + \text{HC} \quad 0.00 \text{ (triple bond break)} \]
\[ \rightarrow \text{HC}_3\text{N} + \text{HC}_2 \quad 0.06 \text{ (rearrangement)} \]
\[ \rightarrow \text{HC}_2\text{N} + \text{HC}_3 \quad 0.00 \text{ (triple bond break)} \]
\[ \rightarrow \text{H}_2\text{C}_5 + \text{N} \quad 0.00 \text{ (triple bond break)} \]

Rate constant: \[ 2.0 \times 10^{-6}(T/300)^{-0.70} \text{ cm}^3\text{s}^{-1} \]
**CNC**

- No experimental studies available
- No kicking out of central atom in $\text{CO}_2^+$, $\text{SO}_2^+$ and $\text{OCS}^+$
- No three-body channels energetically available
- Rate constants of somewhat alike three-atomic ions around $4.0 \times 10^{-7} \text{ cm}^3\text{s}^{-1}$

**Recommended values:**

**Branching ratios:**

\[
\text{CNC}^+ + e^- \rightarrow \begin{array}{c}
\text{CN} + \text{C} \\
\rightarrow \text{C}_2 + \text{N}
\end{array} \quad \begin{array}{c}
0.95 \\
0.05
\end{array}
\]

**Rate constant:** $4.0 \times 10^{-7}(T/300)^{-0.60} \text{ cm}^3\text{s}^{-1}$
**C_4SH^+**

⭐ Neither experimental studies nor guesses available

⭐ Data situation too poor to make any guesses

**HC_3S^+**

⭐ Information available very poor

⭐ No reason to change the guesses in the models (any will do)
Theoretical studies show existence of 5 isomers

No similar ions studied, guesses very difficult

No changes from model values suggested

Elusive ion, only one ab initio study (published in Mandarin)

No founded guesses possible
Future chances in DR measurements

- Improvement of ion sources to 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 using a ring with higher rigidity (Lanzhou, China)
- Use of electrospray ion Sources to create ions from badly evaporable precursors

Dopfer and co-workers