Dissociative Recombination in \( \text{N}_2/\text{CH}_4 \) plasmas: impact on molecular growth

P. Pernot\(^1\), Z. Peng\(^1\), S. Plessis\(^1\) and N. Carrasco\(^2\)

\(^1\)LCP, UMR8000 CNRS/Univ. Paris-Sud, Orsay

\(^2\)LATMOS, UMR8190 CNRS/UVSQ, UPMC, Guyancourt

DR2013, Jul. 7-12
1. DR in detailed N₂/CH₄ plasma photochemical models: problems and solutions

2. Probabilistic representation of (DR) branching ratios

3. Application to N₂/CH₄ photochemical plasmas

4. Conclusions & Wish List
Molecular growth in N2/CH4 VUV plasmas

Ions

Neutrals

mass

mass

0

1

2

3

4

5 Generations

CH4

N2

P. Pernot et al. (LCP@Orsay) Dissoc. recomb. in N2/CH4 plasmas DR2013, Jul. 7-12
Molecular growth in N2/CH4 VUV plasmas

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Molecular growth in N2/CH4 VUV plasmas

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Dissoc. recomb. in N2/CH4 plasmas

DR2013, Jul. 7-12
How modelers see DR

Main corpus of models is for Titan’s ionosphere
(natural N₂/CH₄ plasma)

- the main/only DR pathway for CₓHᵧNₚ⁺ ions is “H-loss”

  - advantage: “DR is useful to produce large neutral species”

- H-loss sometimes abandoned to use DR branching ratios as adjustable variables to improve model fit to observations !!!
How modelers use DR

Examples from a recent model of Titan’s ionospheric chemistry

[Krasnopolsky 2009]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Channel</th>
<th>((b_i))</th>
<th>Exoergic channels</th>
<th>Measured contribution of chosen channels</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCNH(^+) + e(^-)</td>
<td>HCN + H</td>
<td>((1.0))</td>
<td>4</td>
<td>0.26 – 0.41 [1]</td>
</tr>
<tr>
<td>CH(_4)(^+) + e(^-)</td>
<td>CH(_3) + H</td>
<td>((1.0))</td>
<td>8</td>
<td>0.15 – 0.21 [3]</td>
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<tr>
<td>C(_4)H(_3)(^+) + e(^-)</td>
<td>C(_3)H(_2) + CH</td>
<td>((1.0))</td>
<td>14</td>
<td>0.00 – 0.07 [2]</td>
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<tr>
<td>C(_4)H(_5)(^+) + e(^-)</td>
<td>C(_3)H(_4) + CH</td>
<td>((0.7))</td>
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<td>0.00 – 0.11 [2]</td>
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Why ?
What experimentalists tell us about branching ratios

DR branching ratios measurements provide complex results, not directly transferable to conventional models


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$x + y + z + 2w = 4 \ / \text{exoergicity}$

$\text{C}_2\text{H}_x$ is NOT a chemical species!
Experimentalists take modelers by the hand

The measurement results are translated into the “one line per reaction” format for databases (UMIST, KIDA...)

<table>
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- what happened to the 19 other channels? (might be important pathways for minor products)
- why equipartition scenario amongst channels 2 and 3?
- what about isomers (e.g. HNC)?
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- what happened to the 19 other channels? (might be important pathways for minor products)
- why equipartition scenario amongst channels 2 and 3?
- what about isomers (e.g. HNC)?
A change of paradigm is needed!

The bottom line

- a single-valued/nominal/deterministic representation is too poor to embrace the complexity of partial BR measurements

The proposed solution

- probabilistic representations of branching ratios (and rate coefficients) based on available knowledge

- Monte Carlo Uncertainty Propagation (MCUP): stochastic modeling
First step: separation of reaction rate and branching ratios

- Reaction rates ($k$) and branching ratios ($b_i$) are typically measured by different experiments/techniques.

- Golden rule of Uncertainty Management/Analysis: "Keep an explicit separation of uncertainty sources"
  - It is vital to implement the sum-to-one rule of BR
    - More pertinent uncertainty and sensitivity analysis.
Introduction to probabilistic BR trees

Basic example

- one experiment measured the probabilities of \( \{M_1, M_2\} (B_1) \) and \( M_3 (B_3 = 1 - B_1) \);
- and another experiment measured the probabilities of \( M_1 (B_{11}) \) and \( M_2 (B_{12} = 1 - B_{11}) \) (or they are unknown...)

\[
\begin{align*}
\text{I}^+ + \text{e}^- & \rightarrow \begin{cases} 
B_1 \pm \Delta B_1 & \rightarrow B_{11} \pm \Delta B_{11} \\
B_3 \pm \Delta B_3 & \rightarrow M_3
\end{cases} \rightarrow M_1 (b_1) \\
& \rightarrow B_{12} \pm \Delta B_{12} \rightarrow M_2 (b_2)
\end{align*}
\]

and

\[
\begin{align*}
\mu_1 &= B_1 \times B_{11} \\
\mu_2 &= B_1 \times B_{12} \\
\mu_3 &= B_3
\end{align*}
\]
One could envision to use instead a 1-level representation

\[ I^+ + e^- \rightarrow \nu_1 \pm u_1 \rightarrow M_1 (b_1) \]

\[ \nu_2 \pm u_2 \rightarrow M_2 (b_2) \]

\[ \nu_3 \pm u_3 \rightarrow M_3 (b_3) \]

with \( u_i \) obtained by combination of variances

\[ \frac{u_i}{\mu_i} = \sqrt{\left( \frac{\Delta B_1}{B_1} \right)^2 + \left( \frac{\Delta B_{1i}}{B_{1i}} \right)^2} ; \quad i = 1, 2 \]
On the importance of nesting

Ex.: $B_1 = 0.6 \pm 0.1$, $B_3 = 0.40 \pm 0.05$, $B_{11} \in [0, 1]$, and $B_{12} \in [0, 1]$

Nested representation

Flat representation

\{b_1, b_2, b_3\} \sim \text{Dirg}(0.6 \otimes \text{Diun}(2), 0.4 ; 0.1, 0.05)

\{b_1, b_2, b_3\} \sim \text{Dirg}(0.30, 0.30, 0.40 ; 0.18, 0.18, 0.05)
From experimental data...

\[ \text{CH}_2\text{CHC}N\text{H}^+ + e^- \quad [\text{Vigren et al. (2009) ApJ 695:317-324}] \]

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...to probabilistic tree

\[ \text{CH}_2\text{CHCNH}^+ + e^- \rightarrow \]

\[ \begin{align*}
B_1 &= 0.50 \pm 0.04 \\
B_2 &= 0.49 \pm 0.04 \\
B_3 &= 0.01 \pm 0.01
\end{align*} \]

\[ \begin{align*}
B_{11} &\in [0,1] \quad \rightarrow \quad \text{C}_3\text{H}_3\text{N} + \text{H} \\
B_{12} &\in [0,1] \quad \rightarrow \quad \text{C}_3\text{H}_2\text{N} + 2\text{H} \\
B_{13} &\in [0,1] \quad \rightarrow \quad \text{C}_3\text{H}_2\text{N} + \text{H}_2 \\
B_{14} &\in [0,1] \quad \rightarrow \quad \text{C}_3\text{HN} + \text{H}_2 + \text{H} \\
B_{15} &\in [0,1] \quad \rightarrow \quad \text{C}_3\text{N} + \text{H}_2 + 2\text{H} \\
B_{16} &\in [0,1] \quad \rightarrow \quad \text{C}_3\text{N} + 2\text{H}_2 \\
B_{21} &\in [0,1] \quad \rightarrow \quad \text{CNH}_3 + \text{C}_2\text{H} \\
B_{22} &\in [0,1] \quad \rightarrow \quad \text{CNH}_2 + \text{C}_2\text{H}_2 \\
B_{23} &\in [0,1] \quad \rightarrow \quad \text{HCN} + \text{C}_2\text{H}_3 \\
B_{24} &\in [0,1] \quad \rightarrow \quad \text{HCN} + \text{C}_2\text{H}_2 + \text{H} \\
B_{25} &\in [0,1] \quad \rightarrow \quad \text{HCN} + \text{C}_2\text{H} + \text{H}_2 \\
B_{26} &\in [0,1] \quad \rightarrow \quad \text{CN} + \text{C}_2\text{H}_4 \\
B_{27} &\in [0,1] \quad \rightarrow \quad \text{CN} + \text{C}_2\text{H}_2 + \text{H}_2
\end{align*} \]

9 minor channels
Accounting for isomers

The case of $\text{HCCCNH}^+$

  - $B_1 = 0.52 \pm 0.05$ for $\{\text{DC}_3\text{N} + \text{D}, \text{C}_3\text{N} + \text{D}_2\}$
  - $B_2 = 0.48 \pm 0.05$ for $\{\text{DCN} + \text{CD}_2, \text{CN} + \text{C}_2\text{D}_2\}$

- Isotope effects expected to be small: we can transpose information to $\text{HCCCNH}^+$

  - Interconversion barriers low enough for isomerisation of $\text{HC}_3\text{N}$
  - Formation of $\text{HC}_3\text{N}$ more likely than $\text{HC}_2\text{NC}$

$\text{HCN} / \text{HNC}$
Accounting for isomers

The case of HCCCNH⁺

  - $B_1 = 0.52 \pm 0.05$ for \{DC₃N + D, C₃N + D₂\}
  - $B_2 = 0.48 \pm 0.05$ for \{DCN + CD₂, CN + C₂D₂\}
- Isotope effects expected to be small: we can transpose information to HCCCNH⁺

  - Interconversion barriers low enough for isomerisation of HC₃N
  - Formation of HC₃N more likely than HC₂NC

HCN / HNC
The case of HCCCNH$^+$

  - $B_1 = 0.52 \pm 0.05$ for \{DC$_3$N + D, C$_3$N + D$_2$\}
  - $B_2 = 0.48 \pm 0.05$ for \{DCN + CD$_2$, CN + C$_2$D$_2$\}

- Isotope effects expected to be small: we can transpose information to HCCCNH$^+$

  - Interconversion barriers low enough for isomerisation of HC$_3$N
  - Formation of HC$_3$N more likely than HC$_2$NC

- HCN / HNC
Accounting for isomers

The case of $\text{HCCCNH}^+$

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- $\text{HCN} / \text{HNC}$
Accounting for isomers

The resulting tree is

\[ \text{HCCCNH}^+ + \text{e}^- \]

\[ \begin{align*}
B_1 &= 0.52 \pm 0.05 \\
B_2 &= 0.48 \pm 0.05
\end{align*} \]

\[ \begin{align*}
B_1 &\in [0,1] \\
B_2 &\in [0,1] \\
B_{11} &\in [0,1] \\
B_{12} &\in [0,1] \\
B_{21} &\in [0,1] \\
B_{22} &\in [0,1]
\end{align*} \]

\[ \begin{align*}
\text{C}_3\text{N} + \text{H}_2 &\rightarrow \text{HC}_3\text{N} + \text{H} \\
\text{HC}_3\text{N} + \text{H} &\rightarrow \text{C}_3\text{NH} + \text{H} \\
\text{C}_3\text{NH} + \text{H} &\rightarrow \text{C}_2\text{NCH} + \text{H} \\
\text{C}_2\text{NCH} + \text{H} &\rightarrow \text{HC}_2\text{NC} + \text{H}
\end{align*} \]

\[ \begin{align*}
\text{HCN} + \text{C}_2\text{H} &\rightarrow \text{HC}_3\text{N} + \text{H} \\
\text{HNC} + \text{C}_2\text{H} &\rightarrow \text{C}_3\text{NH} + \text{H} \\
\text{H}_2 &\rightarrow \text{C}_3\text{N} + \text{H}_2
\end{align*} \]
Sampling in the simplex

A toolbox of knowledge-adapted Dirichlet-based distributions

Preferred values and uncertainties \( (b_i = \mu_i \pm u_i) \)

\[
\{b_1, b_2, b_3\} \sim \text{Dirg} (\mu_1, \mu_2, \mu_3 ; u_1, u_2, u_3)
\]

Sampling in the simplex

**A toolbox of knowledge-adapted Dirichlet-based distributions**

**No preference: total uncertainty**

\[
\{b_1, b_2, b_3\} \sim \text{Diun} (3)
\]


Sampling in the simplex

A toolbox of knowledge-adapted Dirichlet-based distributions

Ordering rule $b_1 \geq b_2 \geq b_3$

\[ \{b_1, b_2, b_3\} \sim \text{Dior (3)} \]


Sampling in the simplex

A toolbox of knowledge-adapted Dirichlet-based distributions

Partial/Heterogeneous data

\{b_1, b_2, b_3\} \sim \text{Dirg} (\mu_1 \otimes \text{Diun} (2), \mu_2; u_1, u_2)

What we learned up to now...

- the complexity of DR branching ratios measurements can be captured by a representation in probabilistic trees
  - in most cases, the design of probabilistic tree is straightforward
  - we have the tools to generate representative samples of probabilistic trees (available upon request to author)
- let’s go!
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DR data for observed ions in Titan’s ionosphere

**Ions MS@1100 km \( (T \sim 150 \text{ K}, T_i \sim 300 \text{ K}, T_e \sim 600 \text{ K}) \)**

\[ C_x = C_{x-y}N_yH_z^+ \]

Graph showing ionic densities as a function of mass-to-charge ratio (m/z) with ions labeled and categorized by their mass and charge state.
Major breakup patterns

Summary for Titan’s ionosphere $C_xN_yH_z^+$ ions

Two DR models

Our full N$_2$/CH$_4$-based chemical network contains $\sim$1700 réactions (photolysis, bi- and ter-molecular, ion-molecule and dissoc. recomb.) and 237 species (neutrals and positive ions).

- “full scheme” **implementing all available data:** FullDR
  - probabilistic trees for 58 ions (over 116)
  - 448 partial reactions
  - 62 neutral products

- from this, we derive a “H-loss” scheme: Hloss
  - 63 partial reactions
  - 48 neutral products

---

Plessis et al., *JCP* (2010)
Two “reactor” models

- **“Upper Titan-like” conditions**
  \[ P = 7 \times 10^{-4} \text{ Pa}; \quad T = 150 \text{ K}; \quad t_{res} = 2.8 \times 10^6 \text{ s}; \text{ Solar irradiation} \]

- **APSIS**
  \[ P = 7 \times 10^2 \text{ Pa}; \quad T = 300 \text{ K}; \quad t_{res} = 2.8 \times 10^2 \text{ s}; \text{ DISCO@SOLEIL irradiation} \]
Mean stationary concentrations: FullDR / Hloss

Empirical Cumulative Density

log10(yFullDR/yHloss)

Titan
APSIS

Z. Peng PhD Thesis (Sept 2013)
DR in APSIS: H-loss vs. full model

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- **due to** partial measurement of products distributions, we have to use an *adapted representation of branching ratios* and to adopt stochastic modeling (MCUP).

- **explicit enforcement of conservation equations** is a necessity for reliable Uncertainty Propagation and Sensitivity Analysis.

- The probabilistic tree representation of branching ratios is a powerful tool to deal with partial measurements (and to implement empirical rules).

- It can be applied to other processes (photolysis, reactions...) [Gans et al. (2013) *Icarus* 223:330-343].
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- DR can be an efficient promotor of radical chemistry with strong effects on minor species

- the global impact of DR is strongly modulated by pressure (radicals recombination reactions)
Wish list

To improve the modeling of complex ions DR, we need

- dissociation of ions into smaller neutrals results in a cascade effect: we need the breakup patterns, if any, of $C_{x-y}N_yH_z^+$ ($x \geq 5$)

- empirical rules to increase prediction precision!

- kinetics databases with adapted data models (implementation into KIDA awaits funding...)

- $T_e$, $T_i$ temperature effects (for rates AND branching ratios)
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Open questions: Temperature effects

Basically, no data for $T$ effects on branching ratios but for the rate constant, we have the $T_e T_i$ model

$[\text{McLain \\& Adams (2009); Mikus et al. (2009); Lukac et al. (2012)…}]$

\[ \alpha(T_e, T_i) = \alpha(T_{e0}, T_{i0}) \times \left( \frac{T_e}{T_{e0}} \right)^{-\beta_e} \times \left( \frac{T_i}{T_{i0}} \right)^{-\beta_i} \]

Open questions: Temperature effects

in Flowing Afterglow experiments, this becomes

\[ \alpha_{FALP}(T_e) = \alpha(T_{e0}, T_{i0}) \times \left( \frac{T_e}{T_{e0}} \right)^{-\beta_e} \times \left( \frac{T_i = T_e}{T_{i0}} \right)^{-\beta_i} \]

\[ = \alpha(T_{e0}, T_{i0}) \times \left( \frac{T_e}{T_{e0}} \right)^{-(\beta_e + \beta_i)} \]

Plessis et al. (2012) Icarus 219:254
Open questions: Temperature effects

whereas for storage rings, one has

\[ \alpha_{SR}(T_e) = \alpha(T_{e0}, T_{i0}) \times \left( \frac{T_e}{T_{e0}} \right)^{-\beta_e} \times \left( \frac{T_i = T_{i0}}{T_{i0}} \right)^{-\beta_i} \]

\[ = \alpha(T_{e0}, T_{i0}) \times \left( \frac{T_e}{T_{e0}} \right)^{-\beta_e} \]

Open questions: Temperature effects

Which one is best for Titan’s atmosphere?

Open questions: Temperature effects


Plessis et al. (2012) Icarus 219:25
Thank you!

- **The workforce**
  - S. Plessis - PhD thesis (LCP, Orsay)
  - Z. Peng - PhD thesis (LCP, Orsay)
  - N. Carrasco (LATMOS, Versailles-Saint-Quentin)
  - M. Dobrijevic (LAB, Bordeaux)

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  - K. Béroff and M. Chabot (Orsay)

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