State-of-the-art laboratory experiments combined with quantum chemistry to study reactive ion-molecule collisions under interstellar conditions

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Motivation

- Molecular ions are important ingredients of interstellar molecular clouds, despite their low fractional abundances relative to $\text{H}_2$ [1-3].

- Ion-molecule reactions often do not possess activation-energy barriers (unlike most neutral-neutral reactions) [3].

- Ion-molecule reactions synthesize complex ions that often undergo dissociative recombination reactions to form somewhat smaller neutral species. [3].

- One of the most important classes of ion-molecule reactions are carbon insertion [3].

Experimental method for ion-molecule reactions

Uniform supersonic flow reactors can provide reaction rates under well-controlled thermalized conditions.

The CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme) reactor is combined with a mass-selective ion source (SIS) [Joalland et al 2019], which allows one to measure absolute reaction rate coefficients and product branching ratios at low temperatures.

Our instrument is capable to produce stable ionic species at thermal energies (down to about 10 K)

FIG. 1. The CRESU reaction chamber incorporating the new mass-selective ion transfer line. A movable quadrupole mass spectrometer updated with a skimmer/hexapole ion guide combination is used for monitoring ions in the de Laval expansion. High-capacity Roots pumps maintain the desired pressure (0.1–2.0 mbar) in the reaction chamber.
The $\text{N}_2^+$ – $\text{C}_3\text{H}_4$ reaction

Propyne or methyl acetylene ($\text{CH}_3\text{CCH}$) has been first uncovered in the Voyager IR spectrum of Titan in the 80’s [1].

Another $\text{C}_3\text{H}_4$ isomer, propadiene or allene ($\text{CH}_2\text{CCH}_2$), was observed in Titan’s atmosphere by TEXES observations on the NASA Infrared Telescope Facility [2].

Propyne and allene is the first hydrocarbon isomer pair detected on Titan with a $\text{CH}_3\text{CCH}/\text{CH}_2\text{CCH}_2$ abundance ratio of 8.2 [3].

The dense atmosphere of Titan dominated by $\text{N}_2$ and $\text{CH}_4$. $\text{N}_2^+$ is generated by photo-ionization.

Propyne ($\text{CH}_3\text{CCH}$) was widely detected in different ISM regions [4-6].

The non-polar allene is obviously not detected, but the $\text{CH}_2\text{CCH}$ radical was recently reported by Agúndez et al. (2021) [7].

**N₂⁺ - C₃H₄ : mass spectra**

For both reactions, the **main ion product** detected is C₃H₃⁺, followed by C₃H₂⁺ and C₃H₄⁺.

- N₂H⁺, NO⁺, O₂⁺, H₂O⁺ and H₃O⁺ cations are the products of the **reaction of N₂⁺ with impurities**

**Mass spectra recorded at 49 K for propyne (left) and allene (right).**

\[ \text{Experimental measurements:} \]

- \( \text{N}_2^+ + \text{CH}_2\text{CCH} \) (red filled circles)
- \( \text{N}_2^+ + \text{CH}_3\text{CCH} \) (blue filled circles)

\[ \text{Capture models:} \]

- \( \text{Su} \& \text{Chesnavich} \)
- \( \text{Langevin} \)

**For allene reaction** the reaction rate shows a quasi-independence with temperature, which is in good agreement with the **Langevin** value:

\[ k_L = 2\pi e \sqrt{\alpha/\mu} = 1.38 \times 10^{-9} \text{ cm}^3 \text{ mol.}^{-1} \text{ s}^{-1} \]

**For the reaction with propyne** the Langevin model is not suitable. For this polar reactant the model of **Su and Chesnavich** [1] gives a rate coefficient:

\[ k_{SC} = K_{\text{cap}} \times k_L \]

\[ K_{\text{cap}} = 0.4767x + 0.62 \]

where \( x = \mu D l / \sqrt{2\alpha Tk_B} \).


**Measured reaction rates as a function of temperature** for the reaction of \( \text{N}_2^+ \) with \( \text{CH}_3\text{CCH} \) (red filled circles) and \( \text{CH}_2\text{CCH}_2 \) (blue filled circles) along with the reaction rates calculated with capture models.

**N$_2^+$ – C$_3$H$_4$ : branching ratios**

The **temperature dependence of the branching ratios** between the primary products of N$_2^+/CH_3CCH$ (left) and N$_2^+/CH_2CCH_2$ (right) reactions.

- For both reactions the **branching ratio of the dominant exit channel (C$_3$H$_3^+$) increases** with temperature.
- The C$_3$H$_2^+$ **slightly decreases** *(propyne)* or remains quasi-constant *(allene).*
- The route of **pure charge transfer** *(C$_3$H$_4^+$)* **significantly decreases.**

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*Sándor Demes, PCMI, Paris, 24 Oct 2022*  
The unimolecular decomposition of CH$_2$CCH$_2^+$

- Once supposing that the reactions proceed with an initial formation of C$_3$H$_4^+$ parent ion first, a unimolecular decomposition scheme can be proposed then.

- Based on the study of Mebel and Bandrauk [1] for the photodissociation of CH$_2$CCH$_2^+$ (CCSD(T)/cc-pVTZ // B3LYP/6-311G** theory), we provide a new, quantitative explanation for the branching ratios for propyne and allene reaction with N$_2^+$.

- What about the temperature dependence of the reaction rates then?


Interstellar noble gas chemistry

Before 2013, noble gas molecules have not been detected in space.

The first detection of argonium cation (ArH\(^+\)) was published by Barlow et al (2013) [1]. It is also actively studied recently [2]

Later another important detection was reported: HeH\(^+\) in nearby interstellar space [3]. Our understanding of the chemical networks that control the formation of this molecular ion, including the rates of radiative association and dissociative recombination are still very limited [3]

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The reactivity of $\text{Ar}^+$ ions with hydrocarbons has been the subject of numerous investigations including saturated ($\text{CH}_4$, $\text{C}_2\text{H}_6$, ...) and unsaturated species ($\text{C}_2\text{H}_2$, $\text{C}_2\text{H}_4$, c-$\text{C}_6\text{H}_6$, ...) [1], with some potential interest for astrophysical environments.

Most of the studies have been performed at room temperature and show multiple fragmentation pathways. E.g., the rate coefficient and the branching ratios of the $\text{Ar}^+$ + $\text{C}_2\text{H}_4$ / $\text{CH}_4$ reactions were measured at room temperature by Tsuji et al. (1993) [2]

The temperature dependence of some of these reactions has been explored, but mainly above room temperature.

Temperature dependence of the branching ratios for the primary products of the Ar\(^+\) – C\(_2\)H\(_4\) reaction

<table>
<thead>
<tr>
<th>Primary products of the Ar(^+) + C(_2)H(_4) reaction</th>
<th>(T) (K)</th>
<th>(C(_2)H(_4)^+) (m/z= 28 u)</th>
<th>(C(_2)H(_3)^+) (m/z= 27 u)</th>
<th>(C(_2)H(_2)^+) (m/z= 26 u)</th>
<th>(ArH^+) (m/z= 41 u)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CRESU-SIS</td>
<td>18.7</td>
<td>0.22 ± 0.03</td>
<td>0.58 ± 0.05</td>
<td>0.16 ± 0.02</td>
<td>0.04 ± 0.02</td>
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<tr>
<td></td>
<td>71.6</td>
<td>0.10 ± 0.02</td>
<td>0.68 ± 0.05</td>
<td>0.19 ± 0.03</td>
<td>0.03 ± 0.02</td>
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<tr>
<td>Previous</td>
<td></td>
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<tr>
<td>measurements</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Tsuji et al. (1993)</td>
<td>298</td>
<td>0.04</td>
<td>0.76</td>
<td>0.20</td>
<td>-</td>
</tr>
<tr>
<td>Franklin et al. (1961)</td>
<td>298</td>
<td>-</td>
<td>0.87</td>
<td>0.13</td>
<td>-</td>
</tr>
</tbody>
</table>
Ar\(^+\) – C\(_2\)H\(_4\) : measured branching ratios

**Temperature dependence of the branching ratios** for the primary products of the Ar\(^+\) – C\(_2\)H\(_4\) reaction

- The branching ratio of the dominant exit channel (C\(_2\)H\(_3\)\(^+\)) increases with temperature, while the C\(_2\)H\(_2\)\(^+\) channel slightly decreases.

- The strength of the charge transfer channel (C\(_2\)H\(_4\)\(^+\)) significantly decreases.

- ArH\(^+\) is formed only at lower temperatures.
The most exothermic channel is the charge-exchange process, but it is not likely to proceed, since the large excess energy cannot be distributed by its vibrational modes, which will always favor a dissociation.

The two only possible reaction channels lead to CH$_3^+$ (the dominant) and CH$_2^+$ production.

ArH$^+$ cannot be formed due to a large barrier.

Energy diagram for the Ar$^+ –$ CH$_4$ reaction, calculated at the M06-2X / 6-31G(2df,p) level of theory.
**Ar⁺ – C₂H₄ : energy landscape**

Energy diagram for the **Ar⁺ – C₂H₄ reaction**, calculated at the M06-2X / 6-31G(2df,p) level of theory

- The most exothermic channel is again the pure charge-exchange process. **C₂H₄⁺** is formed, but is **not a strong channel**.
- The **most dominant** product formation channel is **C₂H₃⁺**
- **C₂H₂⁺** is also efficiently formed
- **ArH⁺** can be formed effectively, but in tiny amount only.

Sándor Demes, PCMI, Paris, 24 Oct 2022
Calculated branching ratios \((RRKM)\) as a function of the internal energy for the \(\text{Ar}^+ + \text{CH}_4\) (a) and \(\text{Ar}^+ + \text{C}_2\text{H}_4\) (b) reactions. In case of (b) a direct dissociation pathway of the \([\text{Ar} \ldots \text{C}_2\text{H}_4]^+\) complex is considered instead of the dissociation following the minimum energy path.
Perspectives: the growth of molecular complexity

- \(\text{CH}_3^+ + \text{C}_2\text{H}_4\) highlights the evolution of branching ratios at low temperatures from 51 to 69%.

- All heavy atoms are conserved in the dominant product, leading to the formation of \(\text{C}_3\text{H}_5^+\) reaction promoting rapid growth.

What is the role of ions in the growth schemes of molecular complexity?

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CRESU experiments for \(\text{CH}_3^+ + \text{CH}_4 / \text{C}_2\text{H}_4\)

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The synthesis of large interstellar molecules

Eric Herbst
Take home message

- **State-of-the-art laboratory experiments combined with quantum chemistry** are powerful and perspective tools to study ion-molecule reactions at thermal energies to explore interstellar chemistry.

- **Temperature-dependent reaction rates and branching ratios** could be measured and calculated, which is a double validation of the results.

- **Different structural isomers and isotopologues can be studied separately** with this combined laboratory method.

- **Our future work will focus on the reactivity of key molecular species** to extend and enhance the interstellar chemical networks, which involve ionic species.
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