Molecular insights into carbonaceous nanoparticle formation in flames

Jacob Martin, Gustavo Leon, Kimberly Bowal, Angiras Menon, Laura Pascazio, Maurin Salamanca and Markus Kraft

...with contributions from members of the Computational Modelling Group and others

Flame Chemistry Workshop | Nov – Dec 2020
Internal combustion engines and furnaces produce soot (black carbon) contributing to climate change.

1 μg/m³ in PM$_{2.5}$ is associated with an 11% increase in COVID-19 death rate in the USA?


How can we stop the emission of industrial sources of soot?
Useful materials - carbon blacks, nanodots

- Carbon blacks and hydrogen production.


We need to understand how to improve the conversion of fossil fuels into hydrogen and carbon materials with tuneable properties.
Overview

Precursor formation

- Pericondensed aromatic hydrocarbons (PCAH)
  - Size <250 Da
  - 1 – 10 aromatic rings.
  - Growth via HACA

- Aromatic oligomers (aromers)
  - Size ~450 – 550 Da
  - 10 – 20 aromatic rings
  - Growth via HACA and crosslinks

- Clustering PAH
  - PAH clustering with periodicity 450-550 Da. (Grotheer 2011, Carbone 2018)

Nanoparticle formation

- Physical nucleation
  - Flat PAH clustering
  - Curved PAH clustering (with ions)

- Chemical inception
  - Comparing reactive crosslinks

- Physically stabilised chemical inception
  - Diradicaloids
  - Pancake bonds
  - Rim bonds
High resolution atomic force microscopy

1. C₃H₄/air, PMX, φ = 2.03, p = 101.3 kPa (1 atm) (Commodo, D’Anna et al. 2019)
2. CH₃/O₂/N₂, PMX φ = 1.95, p = 26.7 kPa (Irimiea, Fosca et al. 2018)
4. CH₃/O₂/N₂, φ = 2.32, p = 26.66 kPa (Faccinetto, Fosca et al. 2011)
5. C₃H₄/air, PMX, φ = 2.07, p = 101.3 kPa (1 atm) (Carbone, Gomez et al. 2019)
6. CH₃/O₂/N₂, PMX φ = 2.32, p = 26.7 kPa (Irimiea, Fosca et al. 2018)
7. CH₄/air/Ar, DF & QDF, p = 101.3 kPa (1 atm) (Irimiea, Fosca et al. 2018)
8. C₅H₅N₂/O₂, PMX φ = 6.0, p = 2.66 kPa (Keller, Homann et al. 2000)
9. C₅H₅N₂/O₂, PMX φ = 2.0, p = 2.67 kPa (Weilmünster, Homann et al. 1999)
10. C₅H₅N₂/O₂, PMX φ = 2.5, p = 2.67 kPa (Weilmünster, Homann et al. 1999)
11. C₅H₅N₂/O₂, PMX φ = 3.0, p = 12.0 kPa (Grotheer et al. 2007)
12. C₅H₅N₂/O₂, PMX φ = 2.8, p = 2.68 kPa (Baum, Homann et al. 1992)
13. C₃H₄/air, PMX φ = 2.01, p = 101.3 kPa (Stirm, Grotheer, Aigner et al. 2009)

Size exclusion chromatography

14. C₃H₄/air, IDF, p = 101.3 kPa (1 atm) (Russo, Tregrossia et al. 2017)
Precursor formation

Nanoparticle formation

Key Question:
What allows molecular species to cluster past 1000 Da and form nanoparticles?

High resolution atomic force microscopy
1. C$_2$H$_4$/air, PMX, $\phi = 2.03$, $p = 101.3$ kPa (1 atm) (Commodo, D’Anna et al. 2019)

Mass spectrometry
2. CH$_4$/O$_2$/N$_2$, PMX $\phi = 1.95$, $p = 26.7$ kPa (Irimiea, Fosca et al. 2018)
4. CH$_4$/O$_2$/N$_2$, $\phi = 2.32$, $p = 26.7$ kPa (Faccineto, Fosca et al. 2011)
5. C$_2$H$_4$/air, PMX, $\phi = 2.07$, $p = 101.3$ kPa (1 atm) (Carbone, Gomeza et al. 2019)
6. CH$_4$/O$_2$/N$_2$, PMX $\phi = 2.32$, $p = 26.7$ kPa (Irimiea, Fosca et al. 2018)
7. CH$_4$/air/Ar, DF & QDF, $p = 101.3$ kPa (1 atm) (Irimiea, Fosca et al. 2018)
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Size exclusion chromatography
14. C$_2$H$_4$/air, ID, $p = 101.3$ kPa (1 atm) (Russo, Tregrossia et al. 2017)
Physical nucleation – flat PAH

- Wang in 2011 developed full statistical mechanical description for flat PAH dimerization.

- Totton 2012 extended using isoPAHAP forcefield (developed with high accuracy calculations) to determine frequencies, energies and full thermodynamics.

\[
\Delta H = \sum_{i=1}^{6} \left( \frac{1}{2} + \frac{1}{\exp(hv_i/k_BT) - 1} \right) hv_i - 4k_BT - E_{int},
\]

\[
\frac{\Delta S}{k_B} = \ln \left[ \frac{h^6 \rho}{\pi^4 (8M)^{3/2} (e k_BT)^4 \sigma_d} \right] \frac{\sigma_m}{I_{A,m} I_{B,m} I_{C,m}}^{1/2} + \sum_{i=1}^{6} \left[ \frac{hv_i/k_BT}{\exp(hv_i/k_BT) - 1} - \ln(1 - \exp(-hv_i/k_BT)) \right],
\]

\[
K = \exp \left( -\frac{\Delta H - T \Delta S}{k_BT} \right),
\]

Binding energies greater in magnitude than 40 kcal/mol required.

A quantitative study of the clustering of polycyclic aromatic hydrocarbons at high temperatures
Early soot particle possess tortuous fringes indicating curved aromatics are present.

HACA and curvature

PAH with 5-member rings observed by the HR-AFM [Commodo et al. 2019]


Crosslinking and curvature integration

Hypothesis: Curvature integrated from HACA combined with crosslinking reactions.

Homann 1998


i) aryl crosslinking

fPAH + fPAH → a-mer1

iv) cyclodehydrogenation

fjord site → a-mer2 → a-mer3

bay site → a-mer4

cove site → a-mer5 → a-mer6 → a-mer7

Curved PAH do not have sufficient binding energies to physically nucleate at flame temperatures.

Physical nucleation – curved PAH

Physical nucleation – curved PAH, ions

Molecular dynamics

- corannulene without ions
- corannulene with ions
- coronene without ions
- coronene with ions

Electrical interactions between curved PAH and ions can only stabilise a few curved PAH and cannot explain molecular growth to nanoparticles

Ion-Induced Soot Nucleation Using a New Potential for Curved Aromatics
Kimberly L. Bowal, Jacob W. Martin, Alston J. Misquitta, and Markus Kraft,
Aryl-linked species form many thermally stable configurations.


Chemical mechanism comparison

Reactions with barriers

Frenklach and Mebel in 2020 showed acepyrene-pyrenyl (A2 + E) reaction required using collision frequency factor of $10^{12} - 10^{13}$ to provide sufficient nucleation flux.

No aryl-linked reactions between small PAH studied provides sufficient nucleation flux.

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Reactive forcefields gave values of $C_E = 0.001$ [Mao et al. 2018]. $C_E = 0.01 - 1.0$ required in simulations to provide sufficient nucleation flux.


Reaction rate

Kinetic and equilibrium conditions.

Rate constant $k_{for} \approx 10^{12} \frac{cm^3}{mol \cdot s} \rightarrow C_E \approx 0.003 (1500 K)$

Barrierless reactions (not shown)
“Once coagulated they will quickly become chemically knit together since a significant fraction of the aromatic species are radicals”

*Harris and Weiner, 1989*

“..if individual PAH or their dimers undergo rapid, irreversible reactions, the net rate of production of the soot nuclei may be sufficiently high so that the concentration of the nuclei far exceeds the concentrations of the reacting, intermediate species.”

*Miller, 1991*

“…the mass flux is likely to be driven by an irreversible process following the dimer formation...It is also possible that a PAH dimer is stabilized by a reaction with an aliphatic, forming a covalently bonded link between the PAH layers... the van der Waals enhancement should be larger than the factor of 2.2 assumed in the present study.”

*Frenklach and Wang, 1991*
Diradicaloids

Wang in 2011 highlighted localization of π-radicals on zig zag edges


Diradicaloids dimerise with moderate strength (<40 kcal/mol) but require long zig-zag edges (>3).
π-dimers (pancake bonds) and σ-dimers

 Derived from X-ray structures

 **σ-dimer**

 Pancake bond

 **π-dimer**


 Delocalised π-radicals on hexagonal rings form weak single or multicentre bonds (<20 kcal/mol)

 UM052X/6-31G(d)

 **E_{int} (kcal/mol)**

### Chemical mechanism comparison

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<thead>
<tr>
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<tbody>
<tr>
<td>Classes</td>
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<td>-130.4</td>
<td>-120.8</td>
<td>-61.9</td>
<td>-17.0</td>
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<td>-125.3</td>
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<td>cPAH</td>
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<td>-97.3</td>
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<td>rim-based pentagon</td>
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<td>-73.6</td>
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<tr>
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<td>-36.2</td>
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Some π-radicals provide thermally stable bonds

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### Delocalised vs. Localised π-radicals

Spin density analysis shows localised π-radicals can be stabilised on non-hexagonal rings.

<table>
<thead>
<tr>
<th>Delocalised π-radicals</th>
<th>Localised π-radicals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenalenyl-type</td>
<td>Fluorenyl-type</td>
</tr>
<tr>
<td></td>
<td>Indenyl-type</td>
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<tr>
<td></td>
<td>Benzyl-type</td>
</tr>
<tr>
<td></td>
<td>Part. sat. PCAH-type</td>
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<tr>
<td></td>
<td>Part. sat. diradicaloid-type</td>
</tr>
<tr>
<td></td>
<td>Part. sat. rim pent.-type</td>
</tr>
<tr>
<td></td>
<td>Part. sat. phenalenyl-type</td>
</tr>
<tr>
<td></td>
<td>Part. sat. indenyl-type</td>
</tr>
</tbody>
</table>

| 0.30 | 0.62 | 0.52 | 0.79 | 0.67 | 0.62 | 0.65 | 0.66 | 0.73 |
| 0.41 | 0.62 | 0.53 | 0.80 | 0.67 | 0.59 | 0.63 | 0.63 | 0.63 |
| 0.31 | 0.26 | 0.50 | 0.72 | 0.58 | 0.57 | 0.67 | 0.66 | 0.66 |

Reactive localized π-radicals on rim-based pentagonal rings: properties and concentration in flames

Angiras Menon, Jacob W. Martin, Gustavo Leon, Dingyu Hou, Laura Pascazio, Xiaoqing You, and Markus Kraft,
Proceedings of the Combustion Institute, 2020, In Press

Physical + Chemical

Jacob W. MARTIN
Rim bonds: localised \( \pi \)-radicals

<table>
<thead>
<tr>
<th></th>
<th>( \sigma )-dimer</th>
<th>( \pi )-dimer</th>
<th>spin density</th>
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<tr>
<td>Delocalised ( \pi )-radical</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td>0.29</td>
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<tr>
<td>Localised ( \pi )-radical</td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
<td>0.63</td>
</tr>
<tr>
<td></td>
<td>Rim bond (stacked ( \sigma )-dimer)</td>
<td>Pancake bond (stacked ( \pi )-dimer)</td>
<td>None</td>
</tr>
</tbody>
</table>

Rim-bonding allows for strong single-centre \( \sigma \)-bonding and physical interactions.
Potential role in soot formation

- Physical interactions do enhance equilibrium and could enhance reaction rate.
- Localised π-radicals allow for multiradicals that could lead to a chain reaction.


Reactive localized π-radicals on rim-based pentagonal rings: properties and concentration in flames


Bonding is possible in the stacked configuration as well as chain polymerisation with rim-bonded species.
The Middle Way
Physical/Electrical + Chemical

Physical + Chemical

Physical + Chemical

Physical

Chemical

Molecular weight

C/H

ion, cPCAH

cPCAH

fPCAH

APLH

AMLH

AZLH

ARLH

CHCR

AALH
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