An experimental and theoretical study of cyclopentadiene-ethene co-pyrolysis: Growth of polycyclic aromatic hydrocarbons


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Introduction

- Polycyclic aromatic hydrocarbons (PAHs) are a group of more than 100 chemicals that can be produced from various anthropogenic sources, such as the incomplete combustion of heating fuels, oil refining processes and the combustion of diesel fuels.
- Many PAHs are known to be carcinogenic or mutagenic and important precursors to soot, which has been linked to human morbidity and global warming.
- Among many potential soot precursors’ reactions those involving the cyclopentadiene (CPD) and its corresponding cyclopentadienyl (CPDy) radical are considered to be one of the most important contributors to PAHs and soot formation.

Role of CPD and CPDy

- The CPDy radical is a resonance-stabilized, ambident, i.e. containing multiple reactive centers, radical that may undergo self-recombination reactions.
- Due to its importance significant amount of experimental and theoretical data has been published on the gas phase chemistry involving CPDy and CPD in the growth of PAHs.
- This work deals both experimentally and theoretically with the growth of PAHs starting from CPD and CPDy.

Experimental and Kinetic Modeling Results

- A single-event microkinetic model was generated using an automated reaction network generator, RMG.
- Parameters requiring refinement are identified through sensitivity analysis.
- No fitting of the parameters to the experimental data.
- Individual reactions are subjected to an increased level of theoretical analysis.
- Thermodynamics and kinetic data of sensitive species and reactions were calculated using quantum chemistry calculations at the CBS-QB3 level using Gaussian 03.

Kinetic Modeling

- Dedicated CGCGC setup combining FID and TOF-MS.
- Implemented in an on-line analysis section of a bench scale set-up for (steam) co-pyrolysis of CPD/\textit{C}_4\textit{H}_4.
- Detection of PAHs up to carbon number \textit{C}_{30}.
- Excellent agreement between experiments and theory.

Conclusions

- The work at the LCT was supported by the ‘Long Term Structural Methusalem Funding by the Flemish Government’.
- The work at the MIT was supported by the Combustion Energy Frontier Research Center, funded by the U.S. Department of Energy, Office of Basic Energy Sciences under award number DE-SC0001198.

Acknowledgment

- Bench scale set-up for (steam) pyrolysis
- GCxGC-FID/TOF-MS
- Identification and quantification of PAHs

Experimental conditions:

- A co-pyrolysis of CPD-ethene mixture
  - A tubular continuous flow reactor (Isolox 800HT; 1.5 m L, 6 mm I.D.)
  - \textit{T}_{inlet}= 873 - 1163 K, nearly isothermal, COP=1.7 bara.
- Nitrogen was used as a diluent and primary \textit{Internal standard}.
  - Dilution of 1 mol CPD/1 mol \textit{C}_4\textit{H}_4/10 mol \textit{N}_2; \textit{F}_{\text{N}_2}=3.6 ng/l.
- Argon was used as additional (as a double-check) \textit{Internal standard}.
  - On-line sampling of the effluent using heated transfer lines (573 K).
- Dedicated analysis section: GCxGC-FID/TOF-MS + RGA/FID, TCD.

Summary of the measured product yields at the reactor outlet:

<table>
<thead>
<tr>
<th>Component</th>
<th>Carbon number (C)</th>
<th>yield (% of total)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPD</td>
<td>2</td>
<td>95.0</td>
</tr>
<tr>
<td>Ethene</td>
<td>2</td>
<td>5.0</td>
</tr>
</tbody>
</table>

Current state prediction (full lines) of the main reaction products.