Experimental and modeling study of the pyrolysis and combustion of dimethoxymethane

Florence Vermeire, Hans-Heinrich Carstensen, Olivier Herbinet, Frédérique Battin-Leclerc, Guy B. Marin and Kevin M. Van Geem

Laboratory for Chemical Technology, Ghent University

http://www.lct.UGent.be

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Objectives: Acquire experimental dataset in an isothermal jet-stirred reactor
Develop a first principles based microkinetic model for the oxidation and pyrolysis of dimethoxymethane (DMM)
Outline of talk

Experimental setup
Kinetic modeling
Potential energy surface
Model performance
Rate of production analysis
Conclusion
Jet-stirred reactor set-up

Operating conditions

$x_{\text{fuel},0} = 0.01$

$\phi = 0.25, 1.0, 2.0, \infty$

$P = 0.107 \text{ MPa}$

$T = 500 - 1100 \text{ K}$

$F_{V,0} = 3.0 \times 10^{-5} \text{ m}^3/\text{s}$

Diluent: He

Calibration (relative error %)

1. Injection of known amount (5%)
2. Effective carbon number method (10%)

22 product species identified and quantified

Elemental C balance close within 5 % for most conditions

Product analysis

- $O_2, CO, CO_2$ GC TCD (carbosphere)
- $C_1-C_6$ GC FID (PLOT-Q) + methanizer
- $C_6+$ GC FID (HP-5MS)

Outline of talk

Experimental setup

**Kinetic modeling**
Potential energy surface
Model performance
Rate of production analysis
Conclusion
Kinetic model development

**Genesys**
Automatic kinetic model generation
- 351 species
- 2904 reactions

**Base mechanism**
AramcoMech 1.3.
- Smallest species and reactions during combustion

**Extensive databases** with quantum mechanical calculations at the **CBS-QB3** level of theory
- Thermodynamic databases
- Kinetic databases

Extended for **DMM pyrolysis and oxidation**

**Reactant input**
1. Inchi: InChI=1S/C3H8O2/c1-4-3-5-2/h3H2,1-2H3
2. SMILES: COCCOC

**Reaction family input**
1. Low temperature reactions
2. High temperature reactions

**Kinetic and thermodynamic databases**
1. CBS-QB3 species and reactions
2. Structure related rules
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Formaldehyde and methyl formate main product species

Note: difference in barrier height for β-scission reactions

\[ T = 700 \text{ K} \]

\[ k_{\beta-sc,1} = 1.6 \times 10^8 \text{ s}^{-1} \]

\[ k_{\beta-sc,2} = 3.5 \times 10^6 \text{ s}^{-1} \]

Life-time of secondary radical short because of fast \textbf{β-scission}, no addition of molecular oxygen
C$_3$H$_7$O$_4$ potential energy surface

3 isomerizations
Transition state can have 4-ring, 6-ring or 8-ring

Isomerization with aldehyde formation
Cyclic ether formation
β-scission
Subsequent chain branching

T = 700 K
k$_{\text{isom,4-ring}}$ = 1.6 $10^6$ s$^{-1}$
k$_{\text{isom,6-ring}}$ = 6.4 $10^4$ s$^{-1}$
k$_{\text{isom,3-ring}}$ = 2.1 $10^6$ s$^{-1}$

T = 700 K, alkanes
k$_{2,\text{Htr}}$ = 3.9 $10^6$ s$^{-1}$
k$_{2,\text{CE}}$ = 2.8 $10^7$ s$^{-1}$
k$_{2,\beta-sc}$ = 5.3 $10^8$ s$^{-1}$
k$_{1,\beta-sc2}$ = 1.5 $10^9$ s$^{-1}$

T = 700 K, alkanes
k$_{2,\text{CE}}$ = 6.8 $10^6$ s$^{-1}$
k$_{1,\beta-sc}$ = 3.0 $10^5$ s$^{-1}$

(Bugler et al. 2015)
2nd addition of molecular oxygen

Potential energy surfaces for:

- 4 isomerizations
- Transitions state can have 4-ring, 6-ring or 8-ring

\[ T = 700 \text{ K} \]
\[ k_{\text{isomKP3,4-ring}} = 9.4 \times 10^6 \text{ s}^{-1} \]
\[ k_{\text{isomKP1,6-ring}} = 1.8 \times 10^5 \text{ s}^{-1} \]
\[ k_{\text{isom6-ring}} = 1.5 \times 10^5 \text{ s}^{-1} \]
\[ k_{\text{isomOO,8-ring}} = 9.3 \times 10^5 \text{ s}^{-1} \]
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Model performance for DMM pyrolysis

Burke mechanism

Aramco 1.3 mechanism
Model performance for DMM oxidation (1)

- Simulations with CHEMKIN PRO using a CSTR
  - $\phi = 2.0$
  - $x_{\text{fuel},0} = 0.01$
  - $P = 0.107$ Mpa
  - $T = 500 - 1100$ K
  - $F_{V,0} = 3.0 \times 10^{-5}$ m³/s

- Model performance for low temperature oxidation can be improved, see formaldehyde mole fraction
  - $\phi = 1.0$
  - $\phi = 0.25$
Model performance for DMM oxidation (2)

- Simulations with CHEMKIN PRO using a CSTR

  \( \phi = 2.0 \)

- \( x_{\text{fuel},0} = 0.01 \)
  
  \( P = 0.107 \text{ Mpa} \)
  
  \( T = 500 - 1100 \text{ K} \)
  
  \( F_{V,0} = 3.0 \times 10^{-5} \text{ m}^3/\text{s} \)

  \( \phi = 1.0 \)

- Model performance for low temperature oxidation can be improved, see methyl formate mole fraction

  \( \phi = 0.25 \)

- Hydrocarbon mole fractions overpredicted by the micro kinetic model
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Pathways at low temperatures

• Rate of production analysis with CHEMKIN PRO. Rate of production relative to DMM

  • $x_{\text{fuel},0} = 0.01$
  • $P = 0.107$ Mpa
  • $T = 650\, K$ and $700\, K$
  • $F_{V,0} = 3.0 \times 10^{-5}$ m$^3$/s
  • $\phi = 1.0$

• Secondary radical only reacts through $\beta$-scission

• Primary radical competition between $\beta$-scission and oxygen addition

• 3 branching pathways
  $\text{CH}_3\cdot \rightarrow$ base mechanism
New **experimental dataset** acquired for the pyrolysis and oxidation of dimethoxymethane in an isothermal jet-stirred reactor

Development of a **first-principles based microkinetic model** for the pyrolysis and oxidation of dimethoxymethane with quantum mechanical calculations at the **CBS-QB3 level of theory**

Using kinetics developed for **alkanes** to describe the pyrolysis and oxidation of dimethoxymethane introduces large errors

**Aramco 1.3** mechanism selected as base mechanism, because of better performance for pyrolysis

**Good model performance obtained for most compounds**, prediction of low temperature reactivity and hydrocarbon mole fractions can be improved
This work was supported by the Institute for promotion of Innovation through Science and Technology in Flanders (IWT) through the SBO project “ARBOREF” and the SMARTCATS STSM COST Action CM1404.
Thank you
Back-up
### Genesys reaction families and kinetics

<table>
<thead>
<tr>
<th>Reaction family</th>
<th>Kinetic source*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen abstraction by H•, -C•, -O•</td>
<td>GAV (Paraskevas et al. 2014)(Paraskevas et al. 2015)</td>
</tr>
<tr>
<td>Hydrogen abstraction by HO₂•, HO•, O₂, O•</td>
<td>Similar to alkanes (Cai et al. 2016)(Sivaramakrishnan and Michael 2009)</td>
</tr>
<tr>
<td>β-scission &amp; CO α-scission</td>
<td>Well chosen similar reactions calculated at CBS-QB3 level of theory</td>
</tr>
<tr>
<td>Homolytic scissions</td>
<td>Similar to DME (Curran et al. 1998) and DEE (Yasunaga et al. 2010)</td>
</tr>
<tr>
<td>O₂ addition</td>
<td>Similar to alkanes (Cai et al. 2016)</td>
</tr>
<tr>
<td>Isomerization after 1st and 2nd addition</td>
<td>Similar to alkanes (Bugler et al. 2015)(Cai et al. 2016)(Sharma, Raman, and Green 2010)</td>
</tr>
<tr>
<td>Cyclic ether formation</td>
<td>Similar to alkanes (Bugler et al. 2015)(Cai et al. 2016)(Sharma, Raman, and Green 2010)</td>
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<tbody>
<tr>
<td>R + RO₂ → RO + RO</td>
</tr>
<tr>
<td>R + HO₂ → RO + HO</td>
</tr>
<tr>
<td>R + CH₃O₂ → RO + CH₃O</td>
</tr>
<tr>
<td>ROOH → RO + OH</td>
</tr>
<tr>
<td>RO₂ + HO₂ → ROOH + O₂</td>
</tr>
<tr>
<td>RO₂ + H₂O₂ → ROOH + HO₂</td>
</tr>
<tr>
<td>RO₂ + CH₃O₂ → RO + CH₃O + O₂</td>
</tr>
<tr>
<td>RO₂ + RO₂ → RO + RO + O₂</td>
</tr>
</tbody>
</table>

* Kinetics applied if no data at CBS-QB3 level of theory is available in extensive database
• Sensitivity analysis with CHEMKIN PRO. Normalized sensitivity coefficients

\[ x_{\text{fuel,0}} = 0.01 \]
\[ P = 0.107 \text{ Mpa} \]
\[ T = 900 \text{ K} \]
\[ F_{V,0} = 3.0 \times 10^{-5} \text{ m}^3/\text{s} \]
\[ \phi = 1.0 \]
• Sensitivity analysis with CHEMKIN PRO. Normalized sensitivity coefficients

• $x_{\text{fuel},0} = 0.01$
  $P = 0.107 \text{ Mpa}$
  $T = 700 \text{ K}$
  $F_{V,0} = 3.0 \times 10^{-5} \text{ m}^3/\text{s}$
  $\phi = 1.0$