Use of detailed kinetic mechanism for the prediction of autoignitions

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PHENOMENA OBSERVED DURING THE REACTION BETWEEN HYDROCARBON AND OXYGEN

Pressure-temperature diagram in the case of 1,3-dioxan

Static reactor

Cool flame

Autoignition

Slow reaction
COOL FLAMES

SINGLE

Measurement of pressure by a pressure transducer

DOUBLE

Measurement of temperature by a small thermocouple
Rise below 100 °C

Formation of intermediate products (hydroperoxides)

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PHENOMENA OBSERVED DURING THE REACTION BETWEEN HYDROCARBON AND OXYGEN

Pressure-temperature diagram in the case of 1,3-dioxan

Static reactor

![Static reactor](image)

![Pressure-temperature diagram](image)

- Cool flame
- Autoignition
- Slow reaction
AUTOIGNITION

Starts like a cool flame, but does not stop

Rise of temperature over 500°C

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Prevention of explosions during oxidation processes

Prediction of the phenomena observed during the oxidation of hydrocarbons

Development of detailed chemical mechanisms for the oxidation and autoignition of hydrocarbons by using an automatic generator
AUTOMATIC GENERATOR OF DETAILED MECHANISMS OF COMBUSTION

EXGAS
Reaction Bases
Free Radicals
Primary Mechanism Generator
C2 Molecules and Free Radicals
Secondary Mechanism Generator

KINGAS
Thermochemical Data
Kinetic Data
THERGAS
Thermochemical Data

Reactants

Reaction Model in a CHEMKIN II Format

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GENERIC ELEMENTARY REACTIONS
IN THE PRIMARY MECHANISM OF AKKANES

1- Initiation reactions
- unimolecular initiations (ui) : ch3/ch2/ch2/ch3 $\rightarrow$ 2 $\cdot$ch2/ch3
- bimolecular initiations (bi) : ch3/ch2/ch2/ch3 + //o2 $\rightarrow$ $\cdot$o/oh + $\cdot$ch(/ch3)/ch2/ch3

2- Propagation reactions
- addition of free radicals on oxygen (adox) :
  •ch(/ch3)/ch2/ch3 + //o2 $\rightarrow$ $\cdot$o/o/ch(/ch3)/ch2/ch3
- isomerization of free radicals (is) :
  $\cdot$o/o/ch(/ch3)/ch2/ch3 $\leftrightarrow$ $\cdot$ch2/ch(/o/oh)/ch2/ch3
- decomposition of free radicals by beta-scission (bs) :
  •ch(/ch3)/ch2/ch3 $\rightarrow$ •ch3 + ch3/ch//ch2
- decomposition of free radicals to cycloethers (or) :
  •ch2/ch(/o/oh)/ch2/ch3 $\rightarrow$ c(#1)h(/ch2/ch3)/ch2/o/1 + $\cdot$oh
- oxidation of free radicals (ox) : $\cdot$ch(/ch3)/ch2/ch3 + //o2 $\rightarrow$ ch3/ch2/ch//ch2 + $\cdot$o/oh
- metathesis reactions (me) : ch3/ch2/ch2/ch3 + $\cdot$oh $\rightarrow$ oh2 + $\cdot$ch2/ch2/ch2/ch3

3- Termination reactions
- combination of free radicals (co) : $\cdot$ch2/oh + $\cdot$ch(/ch3)2 $\rightarrow$ ch(/ch3)2/ch2/oh
- disproportionation of free radicals (dis) :
  •o/o/ch(/ch3)2 + •o/oh $\rightarrow$ ch3/ch(/o/oh)/ch3 + //o2
STRUCTURE OF THE PRIMARY MECHANISM FOR ALKANES

Initial reactant

- \( \cdot R' \)
- \( \cdot R \)
- \( O_2 \)
- \( \cdot OOH \)
- \( \cdot OH \)
- \( \cdot R \)
- \( \cdot R' \)
- \( \cdot OOR \)
- \( \cdot QOOH \)
- \( \cdot OOQOOH \)
- \( \cdot U(OOH)2 \)

Reactions:
1. \( \text{hydroperoxyalkane} + \cdot R' \rightarrow \text{hydroperoxyalkene} + \cdot OH \)
2. \( \text{cyclic ether} + \cdot OH \rightarrow \text{aldehyde / ketone} + \cdot OH \)
3. \( \text{hydroperoxyalkane} + \cdot R' \rightarrow \text{conjugated olefin} + \cdot OOH \)
4. \( \text{hydroperoxyalkene} + \cdot OOH \rightarrow \text{hydroperoxyalkene} + \cdot R' \)
5. \( \text{di-hydroperoxyalkane} + \cdot R' \rightarrow \text{hydroperoxyalkene} + \cdot R' \)
6. \( \text{hydroperoxy-cycloether} + \cdot OH \rightarrow \text{oxo - hydroperoxyalkane} + \cdot OH \)
7. \( \text{di-hydroperoxyalkene} + \cdot OOH \rightarrow \text{hydroperoxyalkene} + \cdot R' \)
KINETIC DATA OF THE PRIMARY MECHANISM OF LINEAR ALKANES AT HIGH TEMPERATURE


\( k = A \times T^b \times \exp\left(- \frac{E}{RT}\right) \), Units: cm\(^3\), mol, s, kJ

<table>
<thead>
<tr>
<th>H-abstraction (per H atom)</th>
<th>Primary H (i.e. R-CH(_3))</th>
<th>Secondary H (i.e. R(_1)-CH(_2)-R(_2))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>lg A</td>
<td>b</td>
</tr>
<tr>
<td>Initiation with O(_2)</td>
<td>112.6</td>
<td>0</td>
</tr>
<tr>
<td>Oxidation</td>
<td>11.37</td>
<td>0</td>
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<tr>
<td>H-atom abstraction by</td>
<td></td>
<td></td>
</tr>
<tr>
<td>•O</td>
<td>13.23</td>
<td>0</td>
</tr>
<tr>
<td>•H</td>
<td>6.98</td>
<td>2</td>
</tr>
<tr>
<td>•OH</td>
<td>5.95</td>
<td>2</td>
</tr>
<tr>
<td>•CH(_3)</td>
<td>-1</td>
<td>4</td>
</tr>
<tr>
<td>•OOH</td>
<td>11.30</td>
<td>0</td>
</tr>
<tr>
<td>Other reactions</td>
<td>lg A</td>
<td>b</td>
</tr>
<tr>
<td>Addition of a free radical on O(_2)</td>
<td>19.34</td>
<td>-2.5</td>
</tr>
<tr>
<td>to •CH(_3) + molecule</td>
<td>13.30</td>
<td>0</td>
</tr>
<tr>
<td>Beta-scission of a free radical</td>
<td></td>
<td></td>
</tr>
<tr>
<td>to •R + molecule</td>
<td>13.30</td>
<td>0</td>
</tr>
<tr>
<td>to •OOH + molecule</td>
<td>12.92</td>
<td>0</td>
</tr>
<tr>
<td>to •OH + molecule</td>
<td>9.00</td>
<td>0</td>
</tr>
<tr>
<td>Cyclic ether formation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 members ring</td>
<td>12.00</td>
<td>0</td>
</tr>
<tr>
<td>4 members ring</td>
<td>11.30</td>
<td>0</td>
</tr>
<tr>
<td>5 members ring</td>
<td>10.77</td>
<td>0</td>
</tr>
<tr>
<td>6 members ring</td>
<td>10.00</td>
<td>0</td>
</tr>
<tr>
<td>Disproportionation of •OOR and •OOH</td>
<td>11.30</td>
<td>0</td>
</tr>
<tr>
<td>Isomerizations and unimolecular initiations</td>
<td>Calculated according to the methods proposed by S.W. Benson</td>
<td></td>
</tr>
</tbody>
</table>
Examples of predictions using detailed kinetic mechanisms generated by EXGAS
N-butane

Prediction of a composition – temperature ignition diagram mixture in air, at 0.2 MPa in a closed vessel 0.5 dm3


Black lines : Simulations performed in Leeds with a mechanism generated in Nancy

![Diagram showing ignition temperatures and compositions for N-butane]
N-butane
Simulated two-stage ignition profile
1.45 % in air, at 0.2 MPa and 600 K
N-heptane

Modeling of the reaction in a rapid compression machine

T\text{after compression} = 706\, \text{K}, \ P\text{after compression} = 3.2\, \text{bar}, \ \Phi = 1

Rapid compression machine of Lille
(R. Minetti and M. Ribaucour)
N-heptane
Modeling the autoignition delay times in a shock tube (ST) and in a rapid compression machine (RCM)


Points are experiments, lines simulations, $\Phi = 1$

Negative temperature coefficient (NTC) region
**N-decane**

**Modeling the autoignition in a shock tube**


*Points are experiments, lines simulations, $\Phi = 1$*

![Graph showing ignition delay times vs. 1000/T (K) for different pressures. The NTC region is displaced towards higher temperatures as pressure increases.](graph.png)

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Detailed chemical mechanisms for the oxidation and autoignition of alkanes automatically generated

- Semi quantitative prediction of the experimental conditions of the different oxidation phenomena (cool flame, ignition)
- Quantitative modeling of autoignition delay times in given conditions
- Prediction of the formation of intermediate products