Chemical Kinetic Reaction Mechanisms

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J. Warnatz Memorial Colloquium

How do we measure a career?

- In scientific careers, we look for “impact”
- How would their field have been different?
- How much did this person advance their field?
- What kind of people did they train?
- What kind of a scientist did they become?

Reaction mechanisms

- JW first publications, c. 1978
- Pioneering contributions over many years
- Technical and personal leadership
- Reaction mechanisms are a current topic of significant and growing interest in industry and basic research

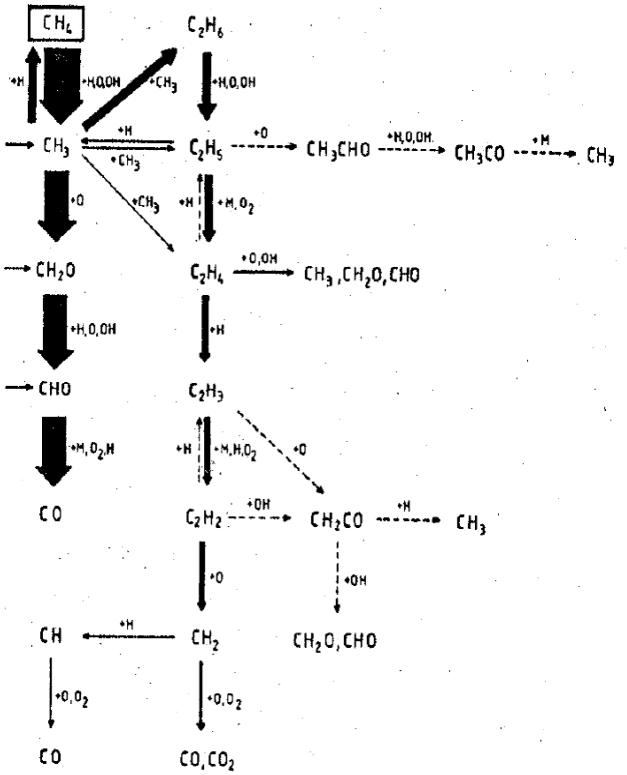
Early impacts

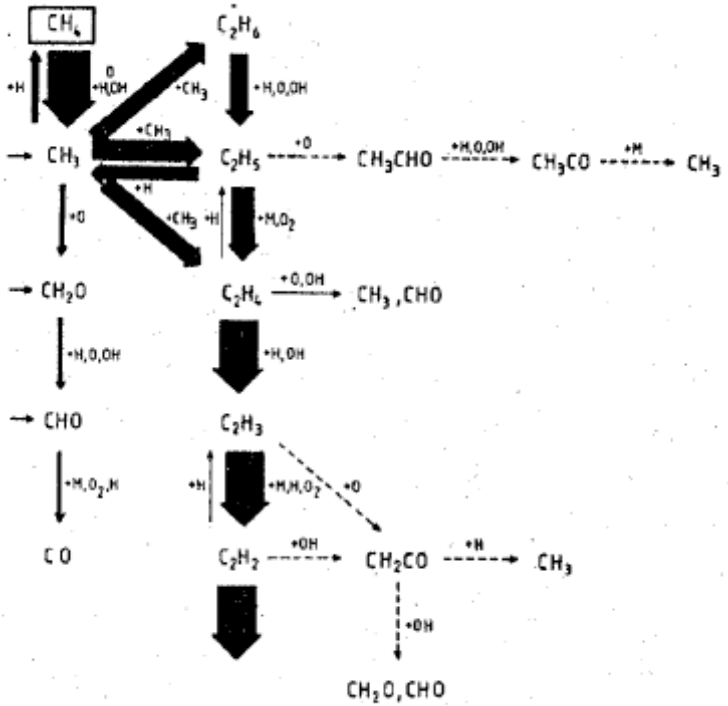
- Silver medal paper at Haifa symposium
  - “The structure of laminar alkane-, alkene- and acetylene flames”
  - First chemical kinetic modeling Silver Medal award 1982
  - Followed in 1990 by awards to Kee, Miller, Evans and Dixon-Lewis (noted collaborators of Jürgen Warnatz), and to Zhu, Egolfopoulos and Law.

In the early days, methane oxidation kinetics was a major subject

- small computers
- methane reaction diagram
- importance of $CH_3 + CH_3$
- practical applications to natural gas, LNG
- difficulty of methane ignition
- methane combustion is unique
  - implications for benzene, others

One of the most significant reaction flux diagrams in all of combustion chemistry





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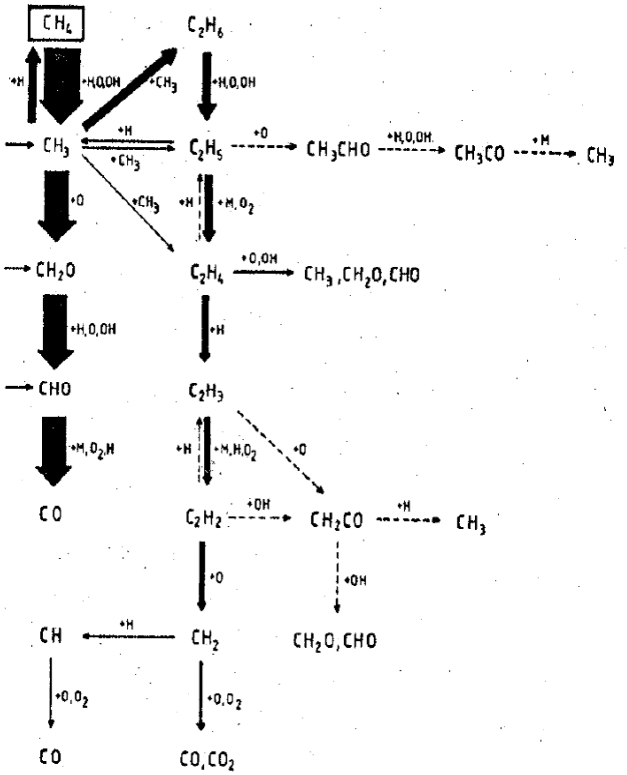
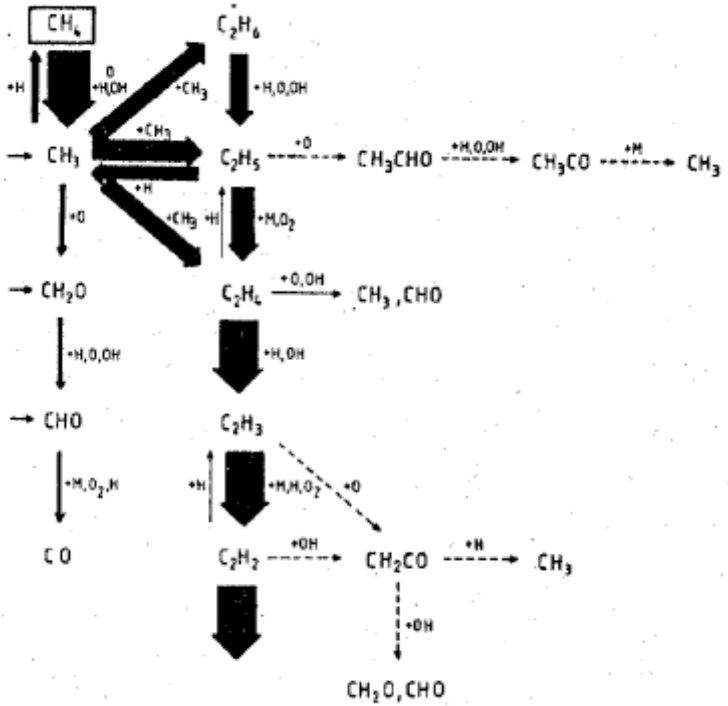




Solving this “puzzle” unlocked the problem of hydrocarbon kinetics

This work guided subsequent research for the next 20 years

- Central role of methane combustion
  - Hierarchical mechanisms
- Importance of detailed analysis of reaction pathways
- Emerging role of kinetic modeling

Two important uses of chemical kinetic mechanisms

1. Detailed descriptions of fuel combustion
   - Theory of fuel oxidation, Reaction rate theory, Benson, Gaussian, etc., experiments
   - Software for flame solution was an essential tool

2. Applications to practical systems
   - Use of mechanisms to describe real systems

Much of Jürgen's career was focused on finding ways to insert reaction mechanisms into practical problems

Development of mechanisms by Jürgen

- ozone, 1978
- h2, 1978
- h2-co, 1979
- ch4, c2h6, ch3oh, 1983
- c3h8, c4h10, 1983
- c8h18, 1985
- c2h2 and PAH, 1987
- almost all in laminar flames

This was a period of rapid growth in computer capacity

Mechanism growth followed computing capacity

year	fuel	# of species
1970	H2	10
1975	CH4	25
1980	CH3OH	30
1980	C2H2, C2H4, C2H6	35
1985	C3H8, nC4H10	41
1986	C8H18	65
….		
1998	C7H16	800

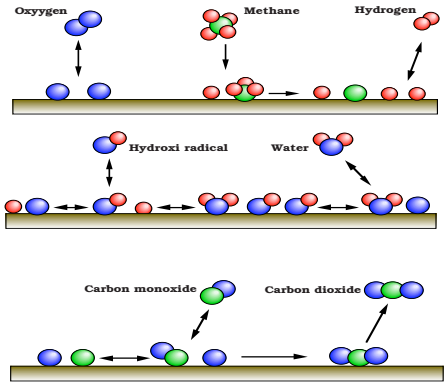
Applications of kinetic mechanisms

- Kinetic models of counterflow diffusion flames – 1984
- Turbulent non-premixed flames – 1986
- Laser-induced ignition – 1986
- Other ignition – 1988
- Development/application of laser diagnostics, CARS - 1986
- Engines and engine knock - 1988

Applications of kinetic mechanisms - 2

- Heterogeneous and surface chemistry and catalysis kinetic modeling
  - 1992 invited paper at symposium
  - other work with Kee, Deutschmann, Behrendt, Riedel, Maas, Chatterjee, Coltrin
  - CVD
  - Catalyzed partial oxidation
  - Solid oxide partial oxidation

Phenomenology of reaction is used to develop a detailed vapor/surface reaction mechanism



				A (mol,cm,s)	E (kJ/mol)
H_2	+ 2 Pt(s)	→ 2 H(s)		$4.60 \cdot 10^{-02}$	sticking coeff.
2 H(s)		→ 2 Pt(s)	+ H_2	$3.70 \cdot 10^{+21}$	67.4 - 6 $\Theta_{H(s)}$
H	+ Pt(s)	→ H(s)		$1.00 \cdot 10^{-00}$	sticking coeff.
O_2	+ 2 Pt(s)	→ 2 O(s)		$7.00 \cdot 10^{-02}$	sticking coeff.
2 O(s)		→ 2 Pt(s)	+ O_2	$3.70 \cdot 10^{+21}$	213.2 - 60 $\Theta_{O(s)}$
O	+ Pt(s)	→ O(s)		$1.00 \cdot 10^{-00}$	sticking coeff.
H_2O	+ Pt(s)	→ H_2O(s)		$0.75 \cdot 10^{-00}$	sticking coeff.
H_2O(s)		→ H_2O	+ Pt(s)	$1.00 \cdot 10^{+13}$	40.3
OH	+ Pt(s)	→ OH(s)		$1.00 \cdot 10^{-00}$	sticking coeff.
OH(s)		→ OH	+ Pt(s)	$1.00 \cdot 10^{+13}$	192.8
O(s)	+ H(s)	⇔OH(s)	+ Pt(s)	$3.70 \cdot 10^{+21}$	11.5
H(s)	+ OH(s)	⇔H_2O(s)	+ Pt(s)	$3.70 \cdot 10^{+21}$	17.4
OH(s)	+ OH(s)	⇔H_2O(s)	+ O(s)	$3.70 \cdot 10^{+21}$	48.2
CO	+ Pt(s)	→ CO(s)		$8.40 \cdot 10^{-01}$	sticking coeff.
CO(s)		→ CO	+ Pt(s)	$1.00 \cdot 10^{+13}$	125.5
CO_2(s)		→ CO_2	+ Pt(s)	$1.00 \cdot 10^{+13}$	20.5
CO(s)	+ O(s)	→ CO_2(s)	+ Pt(s)	$3.70 \cdot 10^{+21}$	105.0
CH_4(s)	+ 2 Pt(s)	→ CH_3(s)	+ H(s)	$1.00 \cdot 10^{-02}$	sticking coeff.
CH_3(s)	+ Pt(s)	→ CH_2(s)	+ H(s)	$1.00 \cdot 10^{+21}$	20.0
CH_2(s)	+ Pt(s)	→ CH(s)	+ H(s)	$1.00 \cdot 10^{+21}$	20.0
CH(s)	+ Pt(s)	→ C(s)	+ H(s)	$1.00 \cdot 10^{+21}$	20.0
C(s)	+ O(s)	→ CO(s)	+ Pt(s)	$3.70 \cdot 10^{+21}$	62.8
CO(s)	+ Pt(s)	→ C(s)	+ O(s)	$1.00 \cdot 10^{+18}$	184.0

Example based on “Detailed Surface Reaction Mechanism in a Three-Way Catalyst”, D. Chatterjee, O. Deutschmann and J. Warnatz, Faraday Discussions, 2001

Modeling the Surface Reactions

Reaction rate:

$$\dot{s}_i = \sum_{k=1}^{K_s} \nu_{ik} k_{f_k} \prod_{j=1}^{N_g+N_s} [X_j]^{\nu'_{ik}} \quad (i = 1, N_g + N_s)$$

Rate coefficient:

$$k_{f_k} = A_k T^{\beta_k} \exp\left[\frac{-E_{a_k}}{RT}\right] \prod_{i=1}^{N_s} \Theta_i^{\mu_{i_k}} \exp\left[\frac{\epsilon_{i_k}\Theta_i}{RT}\right]$$

Sticking coefficient:

$$k_{f_k}^{ads} = S_i^0 \frac{1}{\Gamma^\tau} \sqrt{\frac{RT}{2\pi M_i}}$$

Surface Coverages:

$$\frac{\partial \Theta_i}{\partial t} = \frac{\dot{s}_i \sigma_i}{\Gamma} \quad (i = N_g + 1, N_g + N_s)$$

Example: H_2O sub-mechanism

			A (mol,cm,s)	E (kJ/mol)
H_2 + 2 Pt(s)	→ 2 H(s)		$4.60 \cdot 10^{-02}$	sticking
2 H(s)	→ 2 Pt(s)	+ H_2	$3.70 \cdot 10^{+21}$	$67.4-6\Theta_{H(s)}$
H + Pt(s)	→ H(s)		$1.00 \cdot 10^{-00}$	sticking
O_2 + 2 Pt(s)	→ 2 O(s)		$7.00 \cdot 10^{-02}$	sticking
2 O(s)	→ 2 Pt(s)	+ O_2	$3.70 \cdot 10^{+21}$	$213.2-70\Theta_{O(s)}$
O + Pt(s)	→ O(s)		$1.00 \cdot 10^{-00}$	sticking
H_2O + Pt(s)	→ H_2O(s)		$0.75 \cdot 10^{-00}$	sticking
H_2O(s)	→ H_2O	+ Pt(s)	$1.00 \cdot 10^{+13}$	40.3
OH + Pt(s)	→ OH(s)		$1.00 \cdot 10^{-00}$	sticking
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O(s) + H(s)	= OH(s)	+ Pt(s)	$3.70 \cdot 10^{+21}$	11.5
H(s) + OH(s)	= H_2O(s)	+ Pt(s)	$3.70 \cdot 10^{+21}$	17.4
OH(s)+ OH(s)	= H_2O(s)	+ O(s)	$3.70 \cdot 10^{+21}$	48.2

Other applications

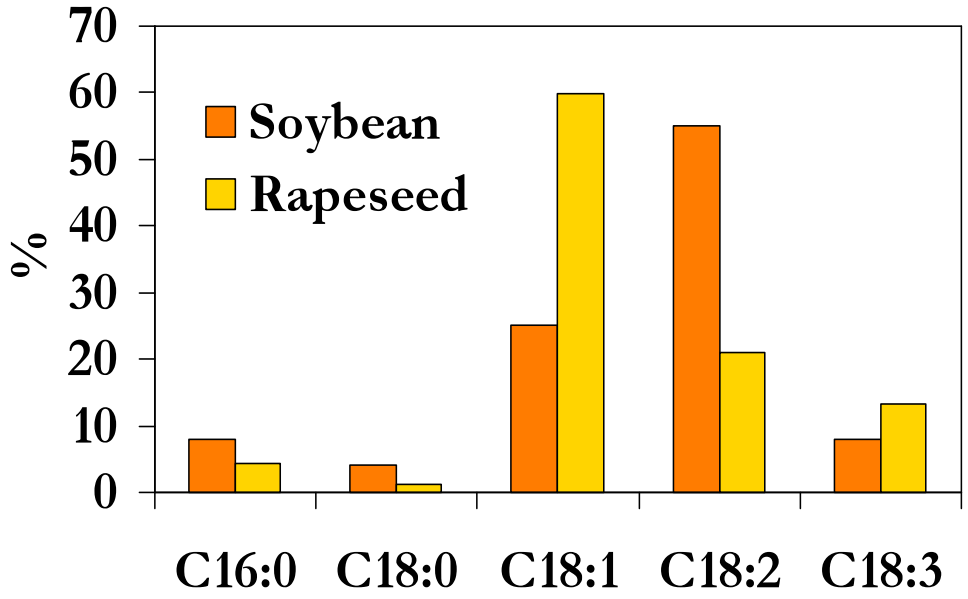
- Energetic materials – 2006
  - RDX, TNT, etc
- Hypersonic flames – 1993
- Ionized species, plasma etching – 1996
- Supercomputing issues – 1995, 2007

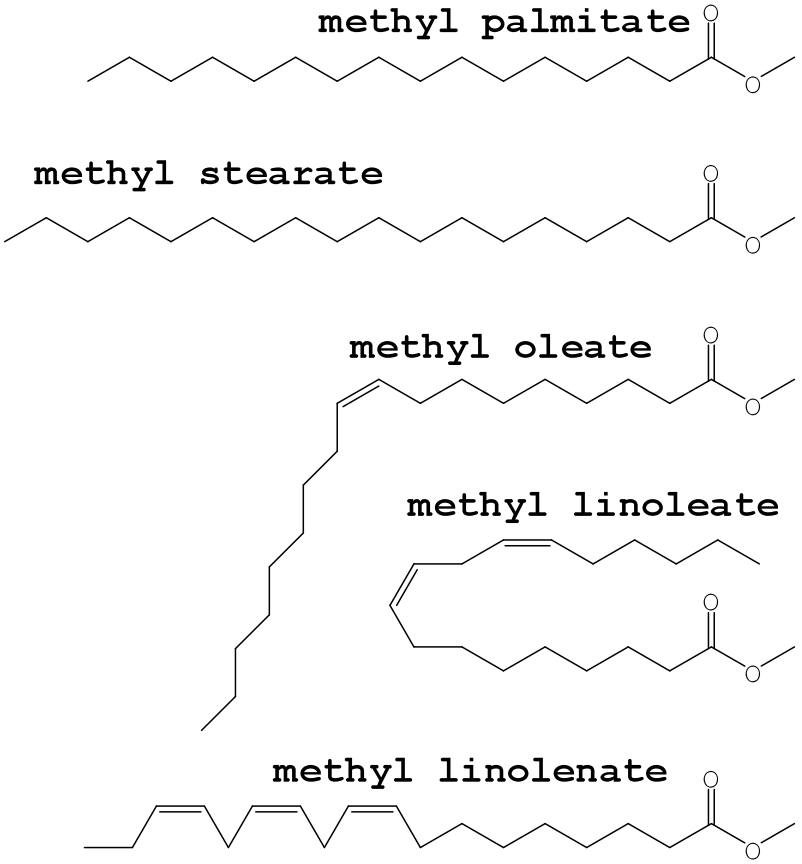
Jürgen Warnatz identified an astonishing range of important problems where detailed chemical kinetic mechanisms could provide unique insights

How far have we come?

- Detailed reaction mechanisms can be generated and reduced in software
- Fuels of nearly limitless size and complexity can be modeled
- Mechanisms for realistic practical fuels with many components can be produced
- Non-experts are now routinely using detailed kinetic reaction mechanisms
- A couple of examples:

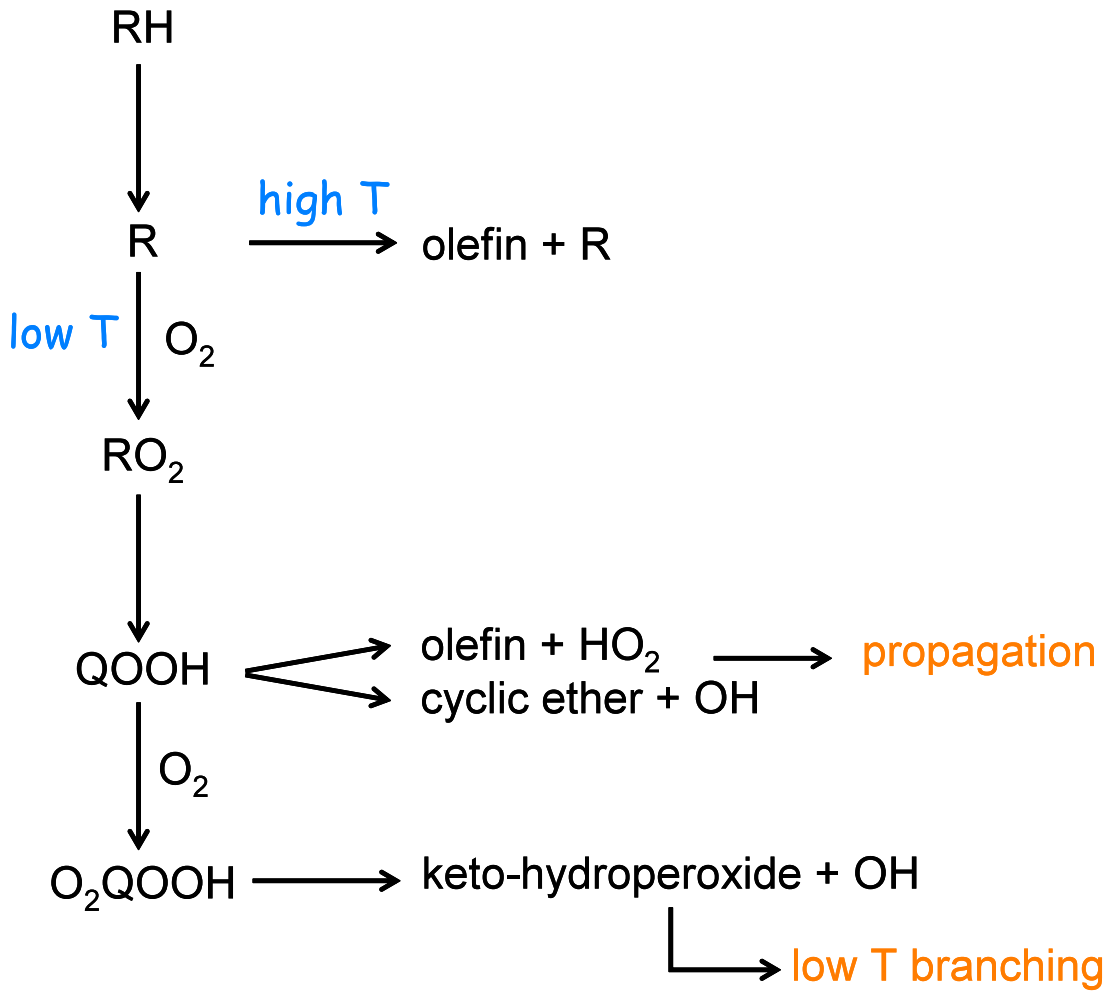
Composition of Biodiesels





Mechanism Structure

- Written in a systematic way (reaction rate rules)
- High and low T chemistry



→ 8580 reactions

→ 3034 species

Surrogate Fuel Component Selection

We have greatly extended the components in the palette that can be modeled in the high molecular weight range:

- n-octane (n-C8H18)
- n-nonane (n-C9H20)
- n-decane (n-C10H22)
- n-undecane (n-C11H24)
- n-dodecane (n-C12H26)
- n-tridecane (n-C13H28)
- n-tetradecane (n-C14H30)
- n-pentadecane (n-C15H32)
- n-hexadecane (n-C16H34)

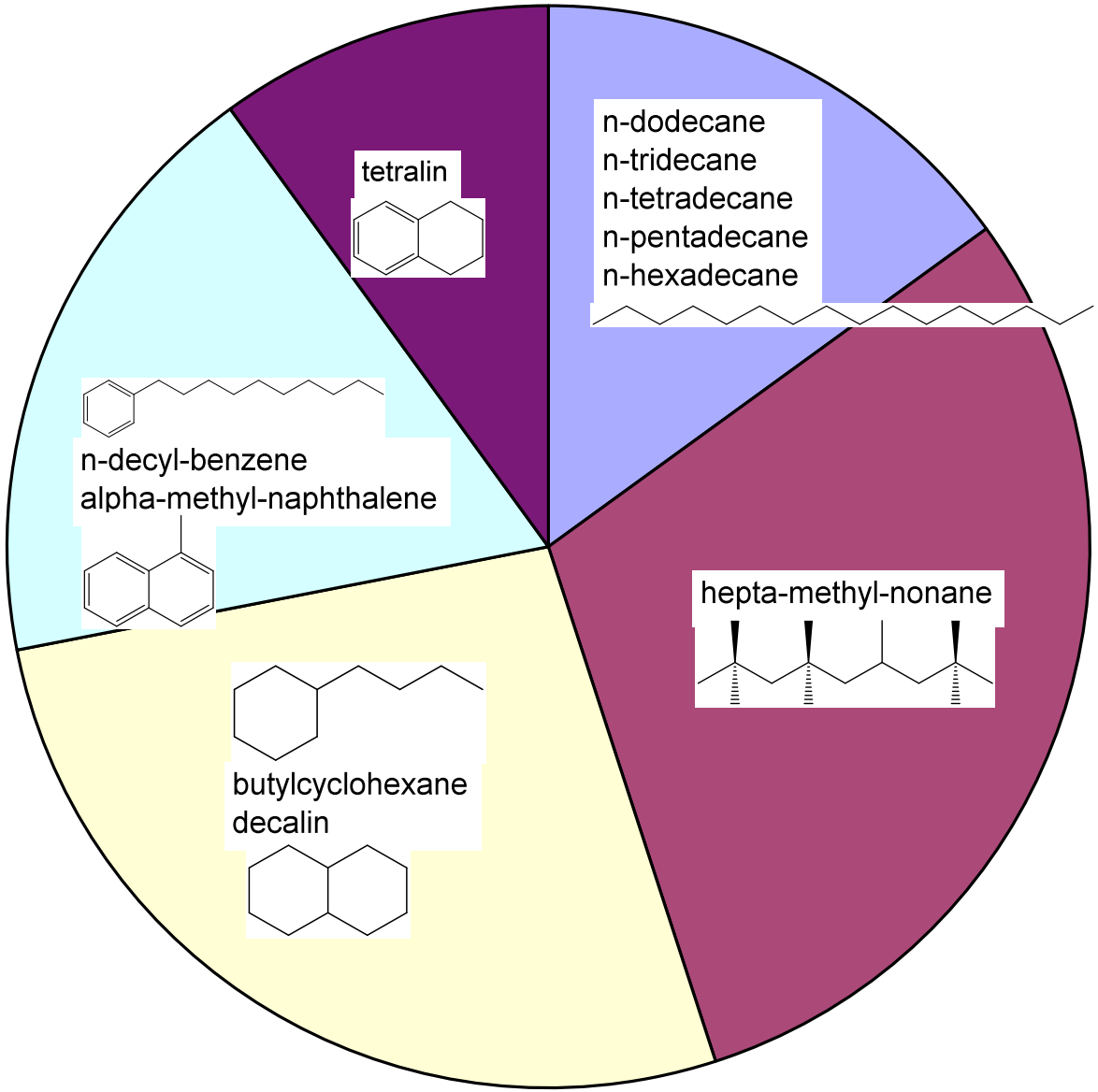
Detailed Chemical Kinetics for Components

Chemical kinetic mechanism for nC8-nC16 surrogate components:

- 2116 species
- 8130 reactions
- Low and high temperature chemistry => can use to investigate low temperature combustion strategies
- Same reaction rate rules as highly validated n-heptane mechanism
- Tailor the mechanism to fit specific fuels for computational efficiency

	$C_{16}H_{34}$	$C_{14}H_{30}$	$C_{12}H_{26}$	$C_{10}H_{22}$
Reactions	8130	6449	5030	3878
Species	2116	1668	1282	940

Fuel Surrogate Palette for Diesel



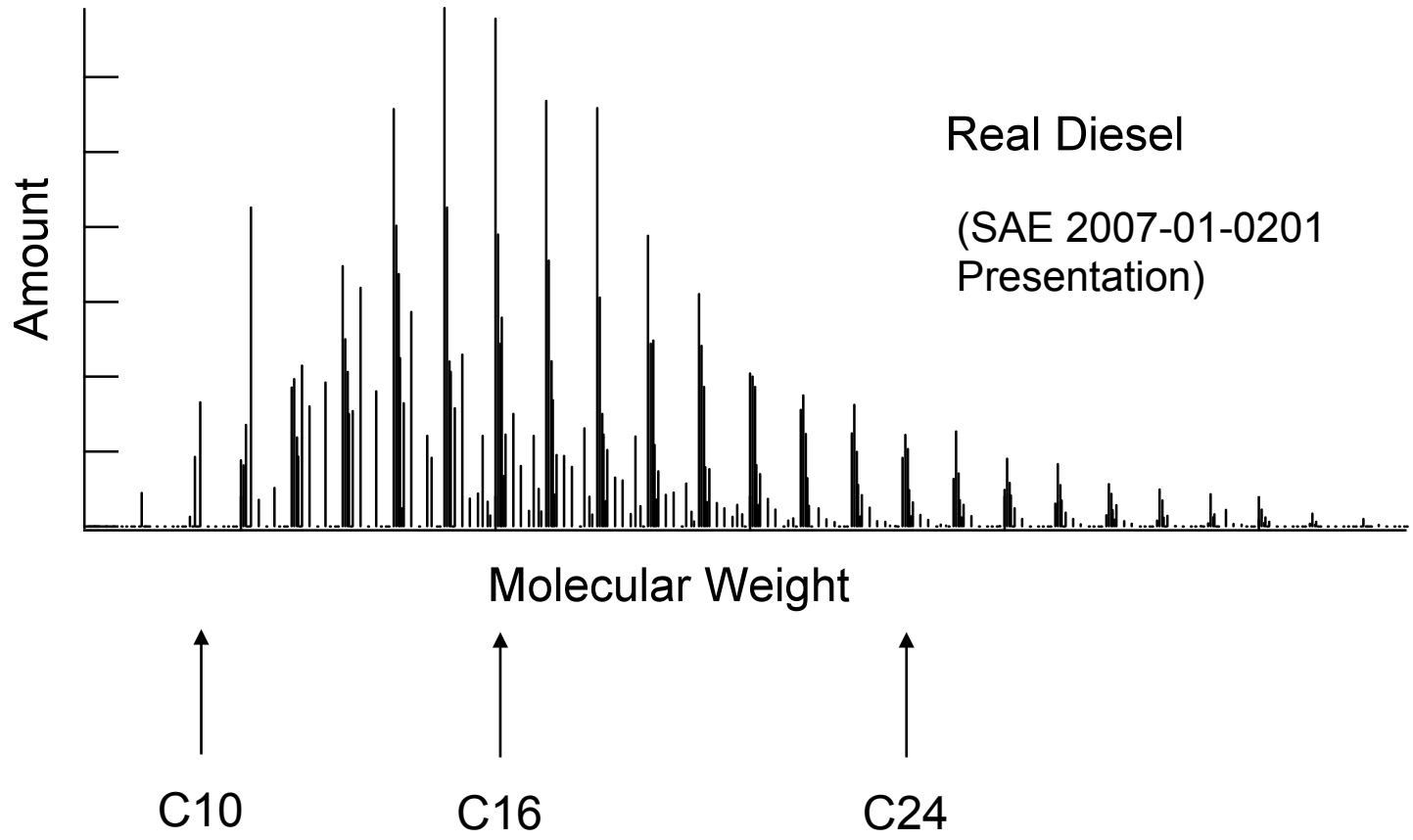
Surrogate Fuel Component Selection

- n-alkane
- branched alkane
- cycloalkanes
- aromatics
- others

Fuel components that have higher molecular weights are needed

Surrogate Fuel Component Selection

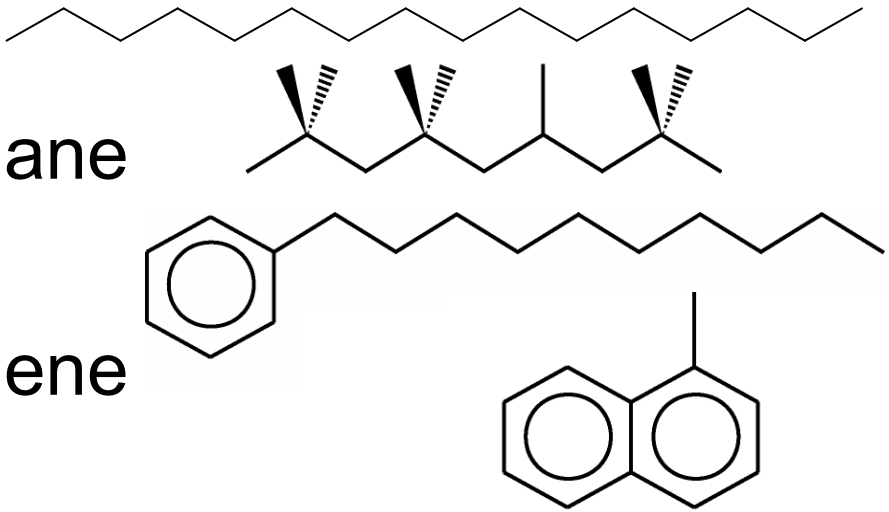
- Diesel fuel has mostly C14 to C24 components centered around C16



Surrogate Fuel Formulation

To span the cetane number scale, easily ignitable components (e.g. n-hexadecane) and less-ignitable components (aromatics, iso-alkanes) are needed

- Recommended components from Diesel Surrogate Fuel Working Group (SAE 2007-01-0201):
  - n-hexadecane
  - heptamethylnonane
  - n-decylbenzene
  - 1-methylnapthalene



Surrogate fuels

- past use of n-heptane surrogate for diesel
- many similarities between all large n-alkanes
- n-decane surrogate for kerosene
- n-hexadecane surrogate for biodiesel
- n-decane and methyl decanoate similarities
- role of methyl ester group
- potential of n-cetane + methyl decanoate or smaller methyl ester for biodiesel surrogate

The science of kinetic modeling and mechanism development

- In 1980, there were only a few groups building kinetic mechanisms, and even fewer producing mechanisms for large hydrocarbon molecules
- Today, there are dozens of groups worldwide in the same business
- There are important automatic mechanism generation algorithms
- Many varieties of mechanism reduction algorithms and software
- Many high quality experiments generate data for kinetic mechanism validation for large and practical fuels
- Experimental papers often cannot publish without kinetic modeling component and insights
- Many non-specialists now use kinetic mechanisms routinely

We have come a long way

- Kinetic modeling is an established science
- Kinetic modeling supports many other technical fields
  - Engines, industrial burners, CVD, catalytic processes, material synthesis, molecular biology, explosives, many others
- This field has grown dramatically and rapidly
- Jürgen Warnatz has been a pioneer in this field since its beginning, and his impact will be felt for a long time