



Chemical Kinetic Reaction Mechanisms

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May 31, 2008

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

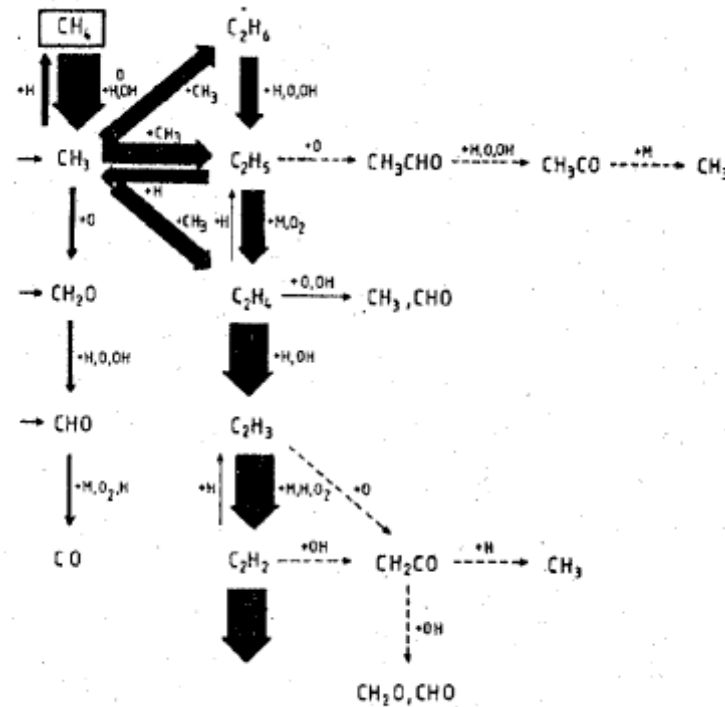
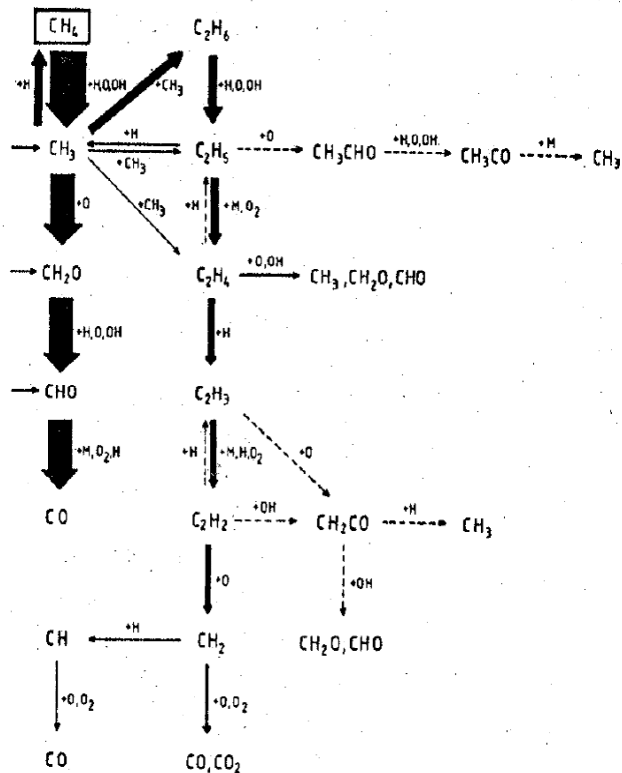
- Silver medal paper at Haifa symposium
 - “The structure of laminar alkane-, alkene- and acetylene flames”
 - First chemical kinetic modeling Silver Medal award 1982
 - Followed in 1990 by awards to Kee, Miller, Evans and Dixon-Lewis (noted collaborators of Jürgen Warnatz), and to Zhu, Egolfopoulos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



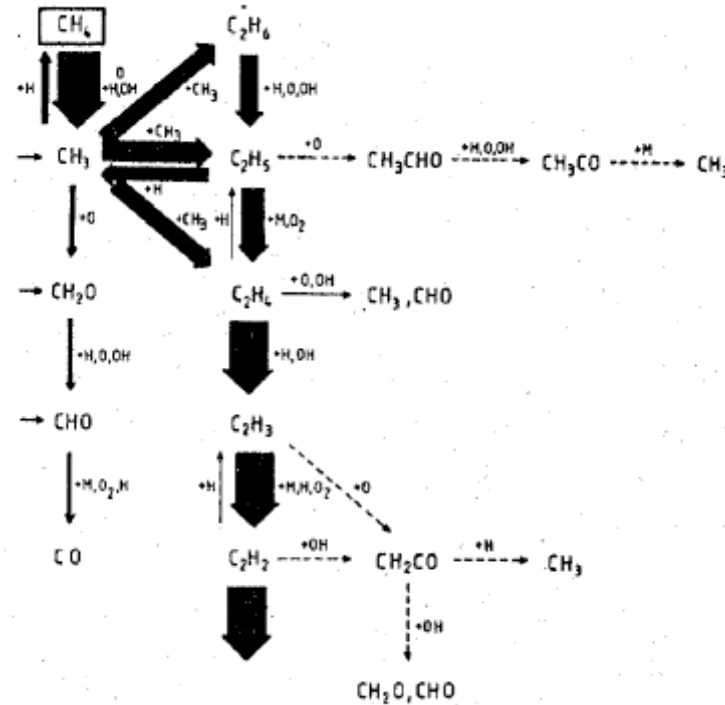
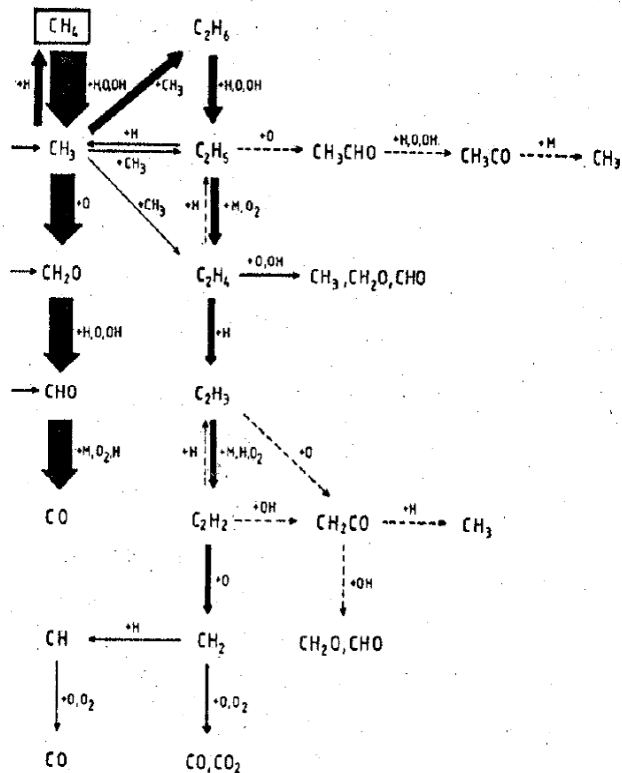
In the early days, methane oxidation kinetics was a major subject

- small computers
- methane reaction diagram
- importance of $\text{CH}_3 + \text{CH}_3$
- 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



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



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
- H_2 , 1978
- H_2 -CO, 1979
- CH_4 , C_2H_6 , CH_3OH , 1983
- C_3H_8 , C_4H_{10} , 1983
- C_8H_{18} , 1985
- C_2H_2 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	H ₂	10
1975	CH ₄	25
1980	CH ₃ OH	30
1980	C ₂ H ₂ , C ₂ H ₄ , C ₂ H ₆	35
1985	C ₃ H ₈ , nC ₄ H ₁₀	41
1986	C ₈ H ₁₈	65
....		
1998	C ₇ H ₁₆	800



Applications of kinetic mechanisms

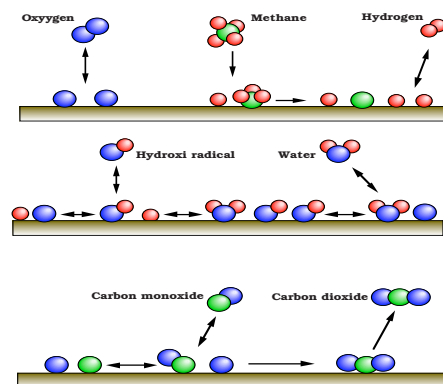
- Kinetic models of counterflow diffusion flames – 1984
- Turbulent non-premixed flames – 1986
- Laser-induced ignition – 1986
- Other ignition – 1988
- Development/application of laser diagnostics, CARS - 1986
- Engines and engine knock - 1988



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	$+ 2 Pt(s) \rightarrow 2 H(s)$	$4.60 \cdot 10^{-02}$	sticking coeff.
$2 H(s)$	$\rightarrow 2 Pt(s) + H_2$	$3.70 \cdot 10^{+21}$	$67.4 - 6 \theta_{H(s)}$
H	$+ Pt(s) \rightarrow H(s)$	$1.00 \cdot 10^{-00}$	sticking coeff.
O_2	$+ 2 Pt(s) \rightarrow 2 O(s)$	$7.00 \cdot 10^{-02}$	sticking coeff.
$2 O(s)$	$\rightarrow 2 Pt(s) + O_2$	$3.70 \cdot 10^{+21}$	$213.2 - 60 \theta_{O(s)}$
O	$+ Pt(s) \rightarrow O(s)$	$1.00 \cdot 10^{-00}$	sticking coeff.
H_2O	$+ Pt(s) \rightarrow H_2O(s)$	$0.75 \cdot 10^{-00}$	sticking coeff.
$H_2O(s)$	$\rightarrow H_2O + Pt(s)$	$1.00 \cdot 10^{+13}$	40.3
OH	$+ Pt(s) \rightarrow OH(s)$	$1.00 \cdot 10^{-00}$	sticking coeff.
$OH(s)$	$\rightarrow OH + Pt(s)$	$1.00 \cdot 10^{+13}$	192.8
$O(s)$	$+ H(s) \rightleftharpoons OH(s) + Pt(s)$	$3.70 \cdot 10^{+21}$	11.5
$H(s)$	$+ OH(s) \rightleftharpoons H_2O(s) + Pt(s)$	$3.70 \cdot 10^{+21}$	17.4
$OH(s)$	$+ OH(s) \rightleftharpoons H_2O(s) + O(s)$	$3.70 \cdot 10^{+21}$	48.2
CO	$+ Pt(s) \rightarrow CO(s)$	$8.40 \cdot 10^{-01}$	sticking coeff.
$CO(s)$	$\rightarrow CO + Pt(s)$	$1.00 \cdot 10^{+13}$	125.5
$CO_2(s)$	$\rightarrow CO_2 + Pt(s)$	$1.00 \cdot 10^{+13}$	20.5
$CO(s)$	$+ O(s) \rightarrow CO_2(s) + Pt(s)$	$3.70 \cdot 10^{+21}$	105.0
$CH_4(s)$	$+ 2 Pt(s) \rightarrow CH_3(s) + H(s)$	$1.00 \cdot 10^{-02}$	sticking coeff.
$CH_3(s)$	$+ Pt(s) \rightarrow CH_3(s) + H(s)$	$1.00 \cdot 10^{+21}$	20.0
$CH_2(s)$	$+ Pt(s) \rightarrow CH(s) + H(s)$	$1.00 \cdot 10^{+21}$	20.0
$CH(s)$	$+ Pt(s) \rightarrow C(s) + H(s)$	$1.00 \cdot 10^{+21}$	20.0
$C(s)$	$+ O(s) \rightarrow CO(s) + Pt(s)$	$3.70 \cdot 10^{+21}$	62.8
$CO(s)$	$+ Pt(s) \rightarrow C(s) + O(s)$	$1.00 \cdot 10^{+18}$	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:

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

Rate coefficient:

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

Sticking coefficient:

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

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: H₂O sub-mechanism

		A (mol,cm,s)	E (kJ/mol)
H ₂ + 2 Pt(s)	→ 2 H(s)	4.60 · 10 ⁻⁰²	sticking
2 H(s)	→ 2 Pt(s) + H ₂	3.70 · 10 ⁺²¹	67.4 - 6Θ _{H(s)}
H + Pt(s)	→ H(s)	1.00 · 10 ⁻⁰⁰	sticking
O ₂ + 2 Pt(s)	→ 2 O(s)	7.00 · 10 ⁻⁰²	sticking
2 O(s)	→ 2 Pt(s) + O ₂	3.70 · 10 ⁺²¹	213.2 - 70Θ _{O(s)}
O + Pt(s)	→ O(s)	1.00 · 10 ⁻⁰⁰	sticking
H ₂ O + Pt(s)	→ H ₂ O(s)	0.75 · 10 ⁻⁰⁰	sticking
H ₂ O(s)	→ H ₂ O + Pt(s)	1.00 · 10 ⁺¹³	40.3
OH + Pt(s)	→ OH(s)	1.00 · 10 ⁻⁰⁰	sticking
OH(s)	→ OH + Pt(s)	1.00 · 10 ⁺¹³	192.8
O(s) + H(s)	= OH(s) + Pt(s)	3.70 · 10 ⁺²¹	11.5
H(s) + OH(s)	= H ₂ O(s) + Pt(s)	3.70 · 10 ⁺²¹	17.4
OH(s) + OH(s)	= H ₂ O(s) + O(s)	3.70 · 10 ⁺²¹	48.2



Other applications

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

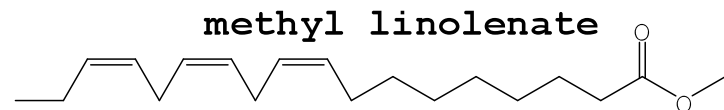
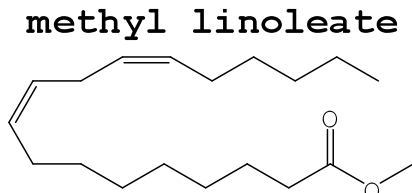
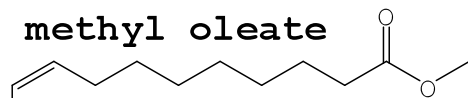
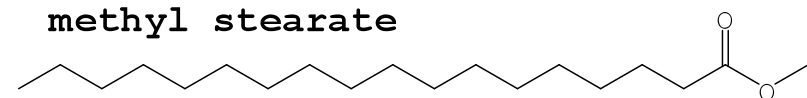
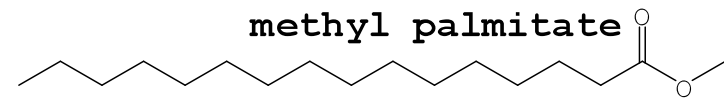
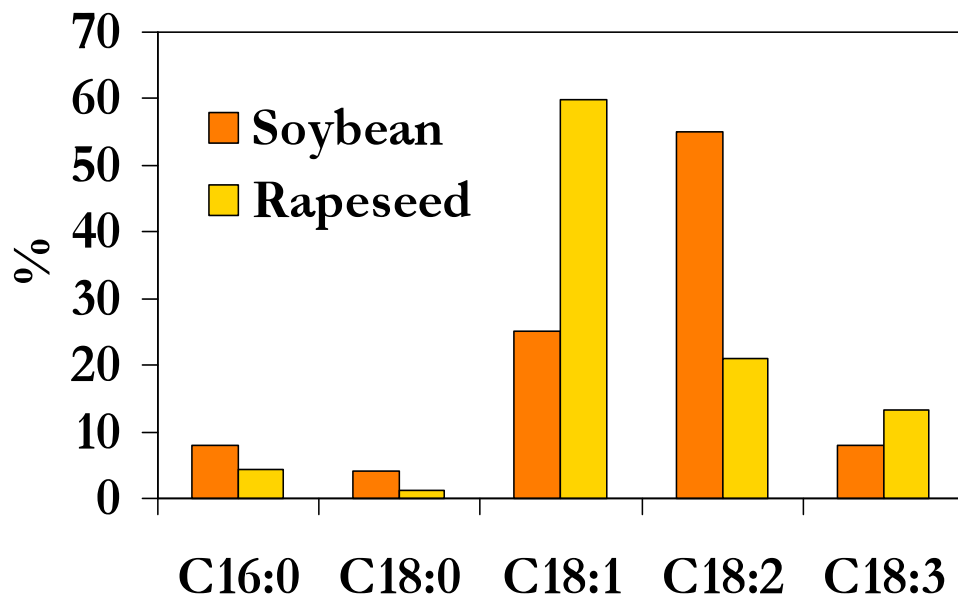
Jürgen Warnatz identified an astonishing range of important problems where detailed chemical kinetic mechanisms could provide unique insights



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



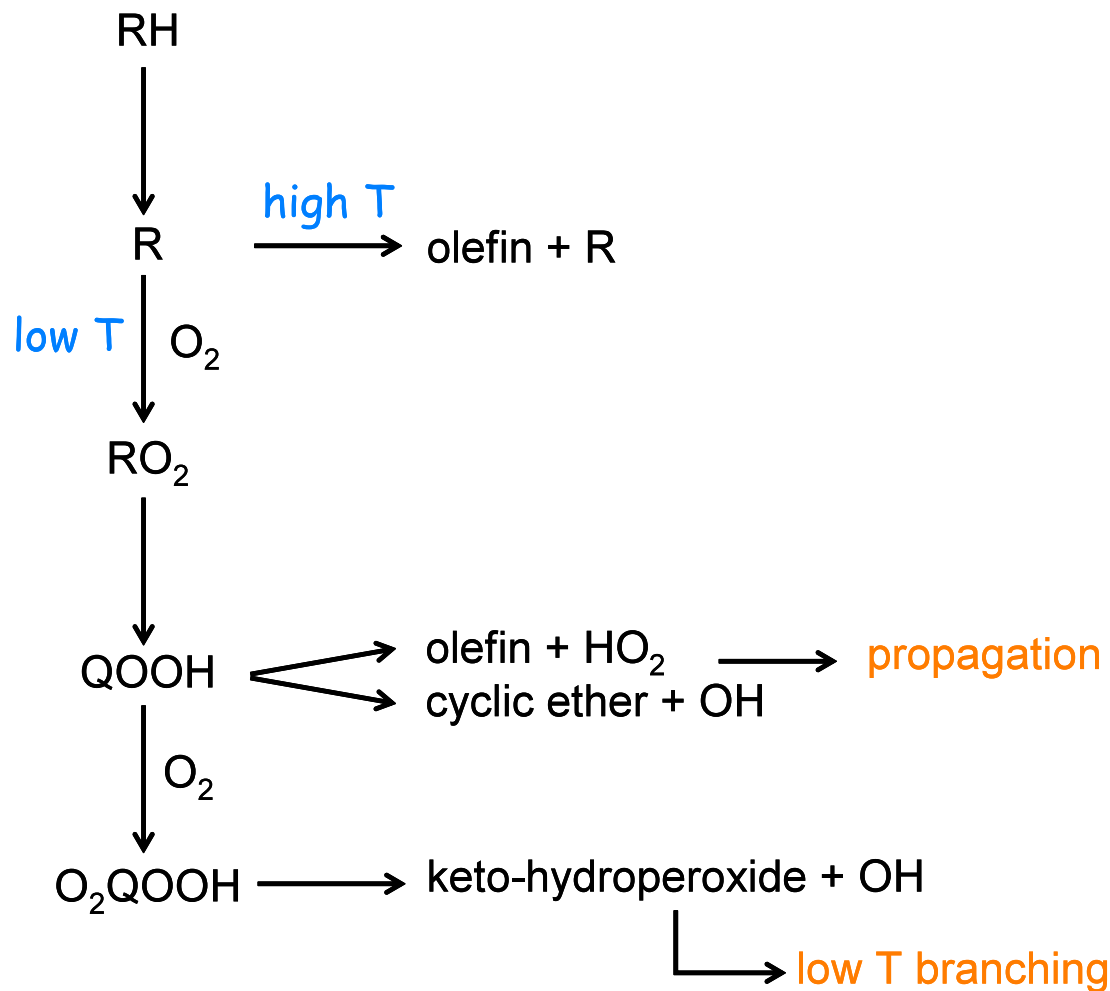
Mechanism Structure

- Written in a systematic way (reaction rate rules)

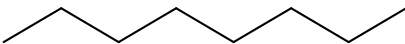
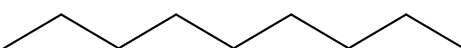
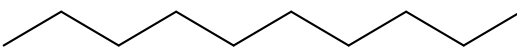
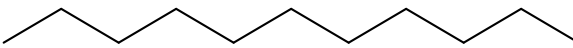
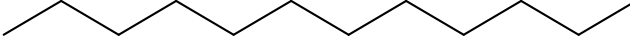
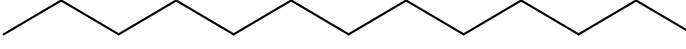
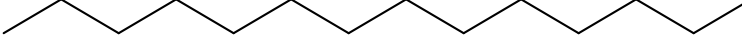
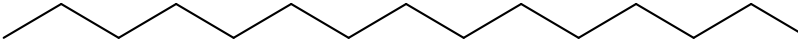
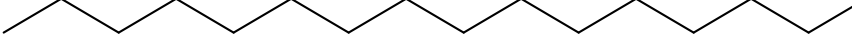
- High and low T chemistry

→ 8580 reactions

→ 3034 species



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

■ n-octane	(n-C ₈ H ₁₈)	
■ n-nonane	(n-C ₉ H ₂₀)	
■ n-decane	(n-C ₁₀ H ₂₂)	
■ n-undecane	(n-C ₁₁ H ₂₄)	
■ n-dodecane	(n-C ₁₂ H ₂₆)	
■ n-tridecane	(n-C ₁₃ H ₂₈)	
■ n-tetradecane	(n-C ₁₄ H ₃₀)	
■ n-pentadecane	(n-C ₁₅ H ₃₂)	
■ n-hexadecane	(n-C ₁₆ H ₃₄)	

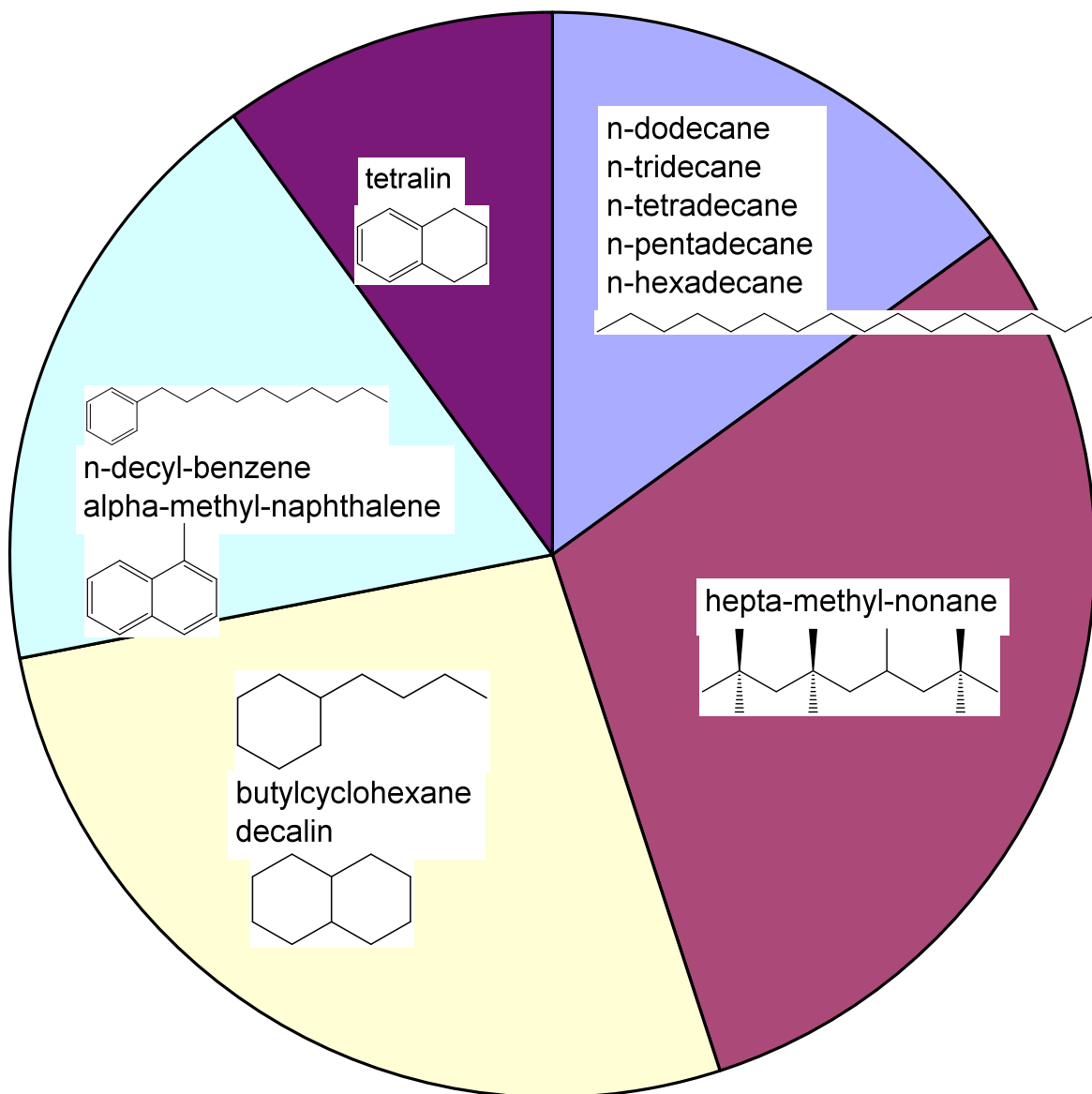
Chemical kinetic mechanism for nC8-nC16 surrogate components:

- 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



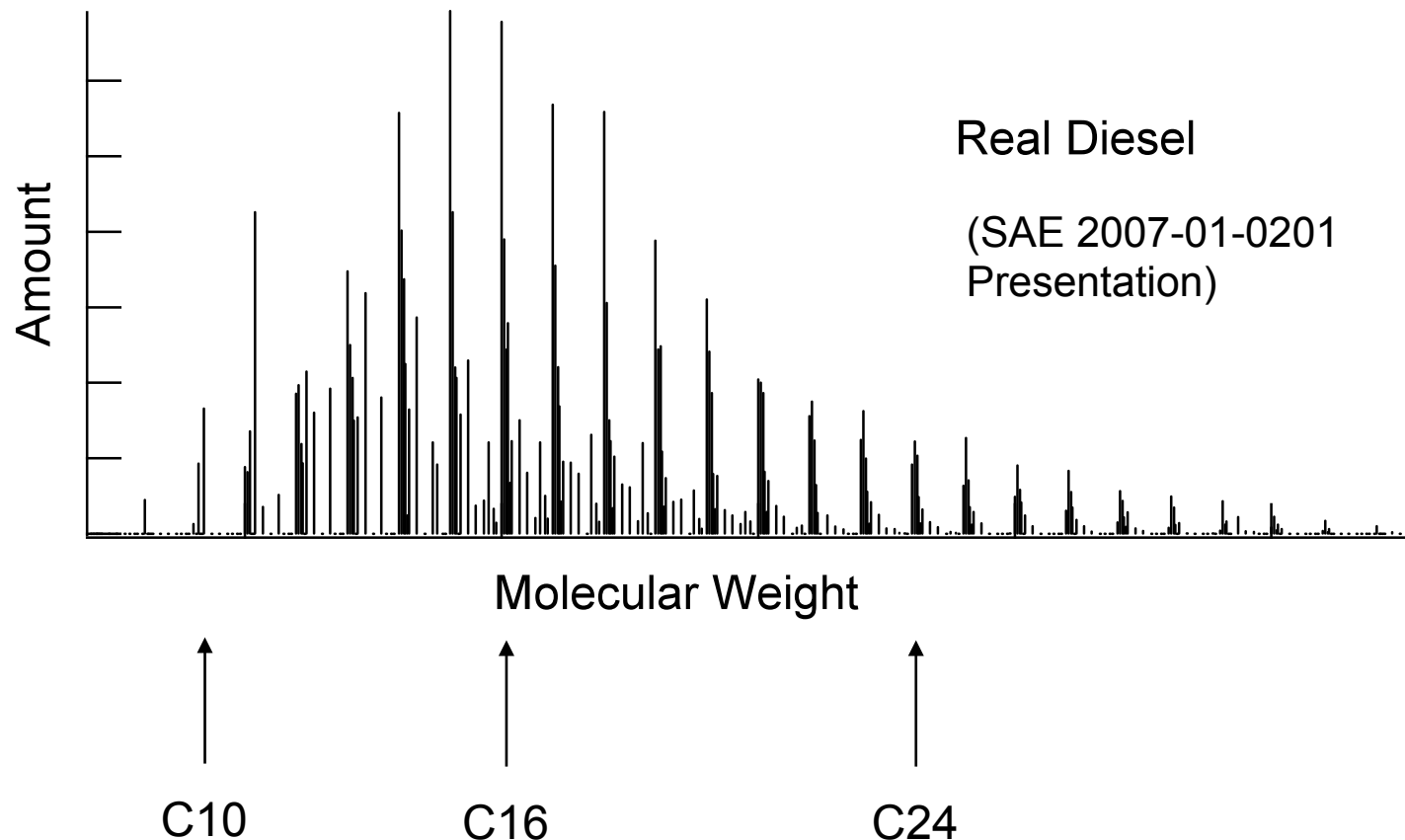
- n-alkane
- branched alkane
- cycloalkanes
- aromatics
- others



Fuel components that have higher molecular weights are needed

Surrogate Fuel
Component
Selection

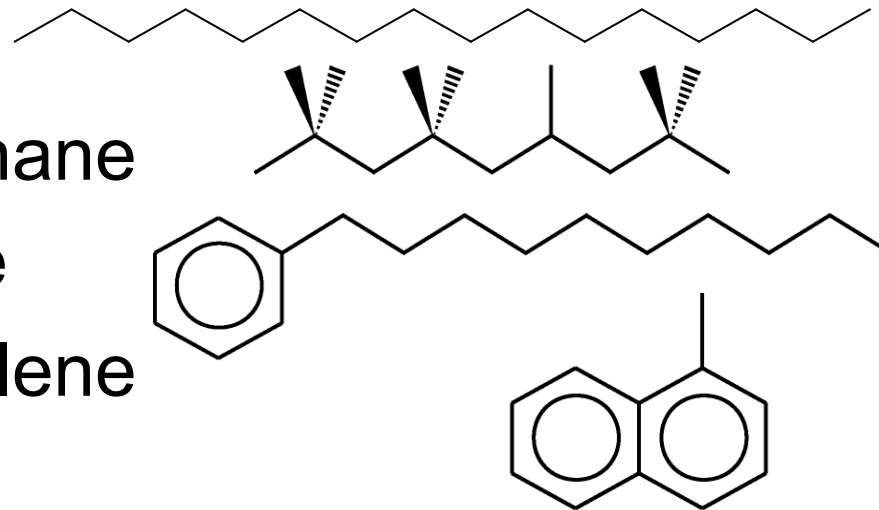
- Diesel fuel has mostly C14 to C24 components centered around C16



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-methylnaphthalene





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