Topic 8

Soot Chemistry

Why Does Condensed-Phase Matter Form?

$$\Delta G = \Delta H - T\Delta S$$

Progress variable
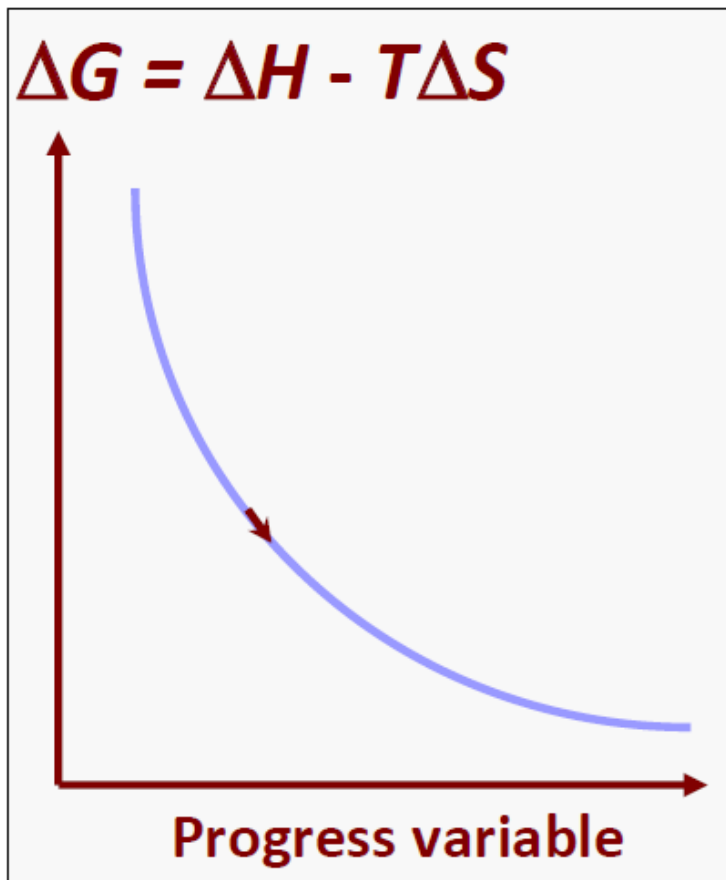
Gas-to-Solid Transformation

- **Type 1: enthalpy driven (heat release)**

    metal oxides
    carbides, nitrides

- **Type 2: entropy driven**

    soot

    $C_3H_8 \rightarrow$ solid carbon + $4H_2$
    ($\Delta H > 0$, but $\Delta S > 0$)

Driving Force – Soot
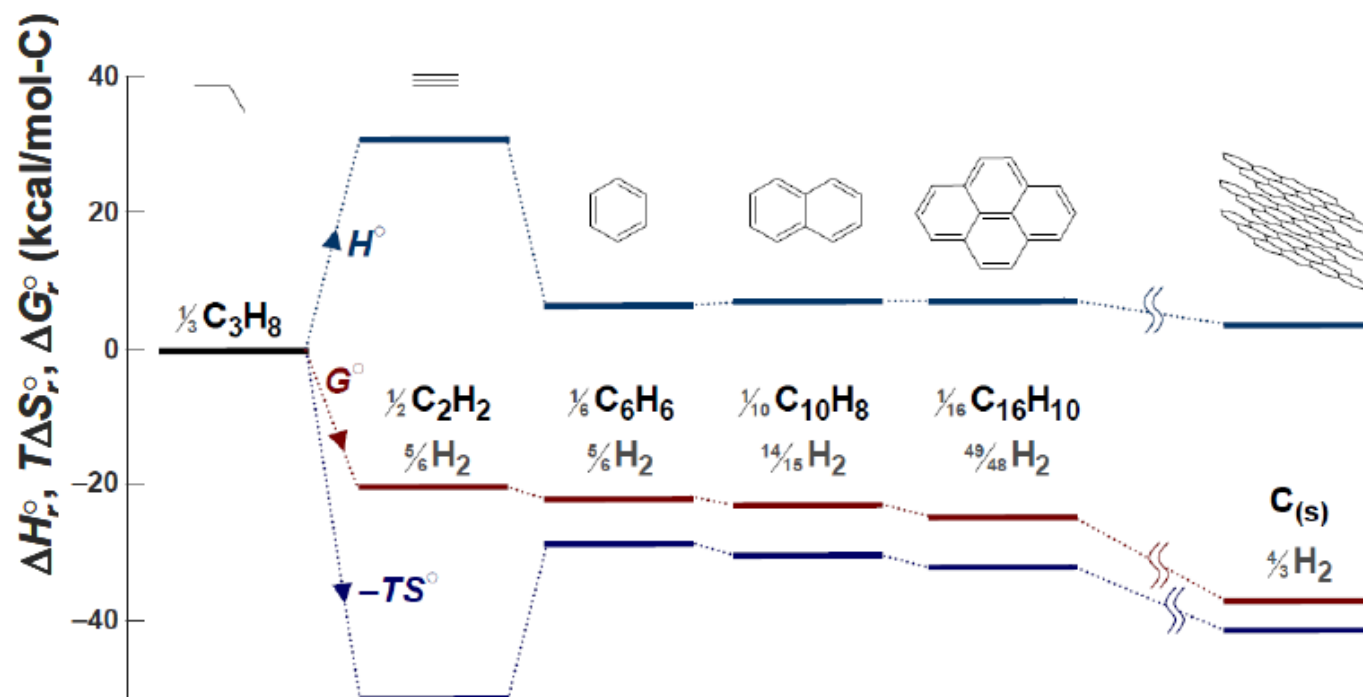
- Soot formation is entropy driven (H_2 goes free).
- Condensed-phase carbon forms as an aerosol (kinetics driven).

Soot as Particulate Air Pollutants

http://farm1.static.flickr.com/216/499969453_44089c6c1d.jpg

http://www.spacemart.com/images/cruis
e-ship-smoke-stack-emission-bg.jpg]

http://www.parks.ca.gov/pages/491/images/sierra_3
_steam_locomotive.jpg

http://www.sfgate.com/blogs/ima
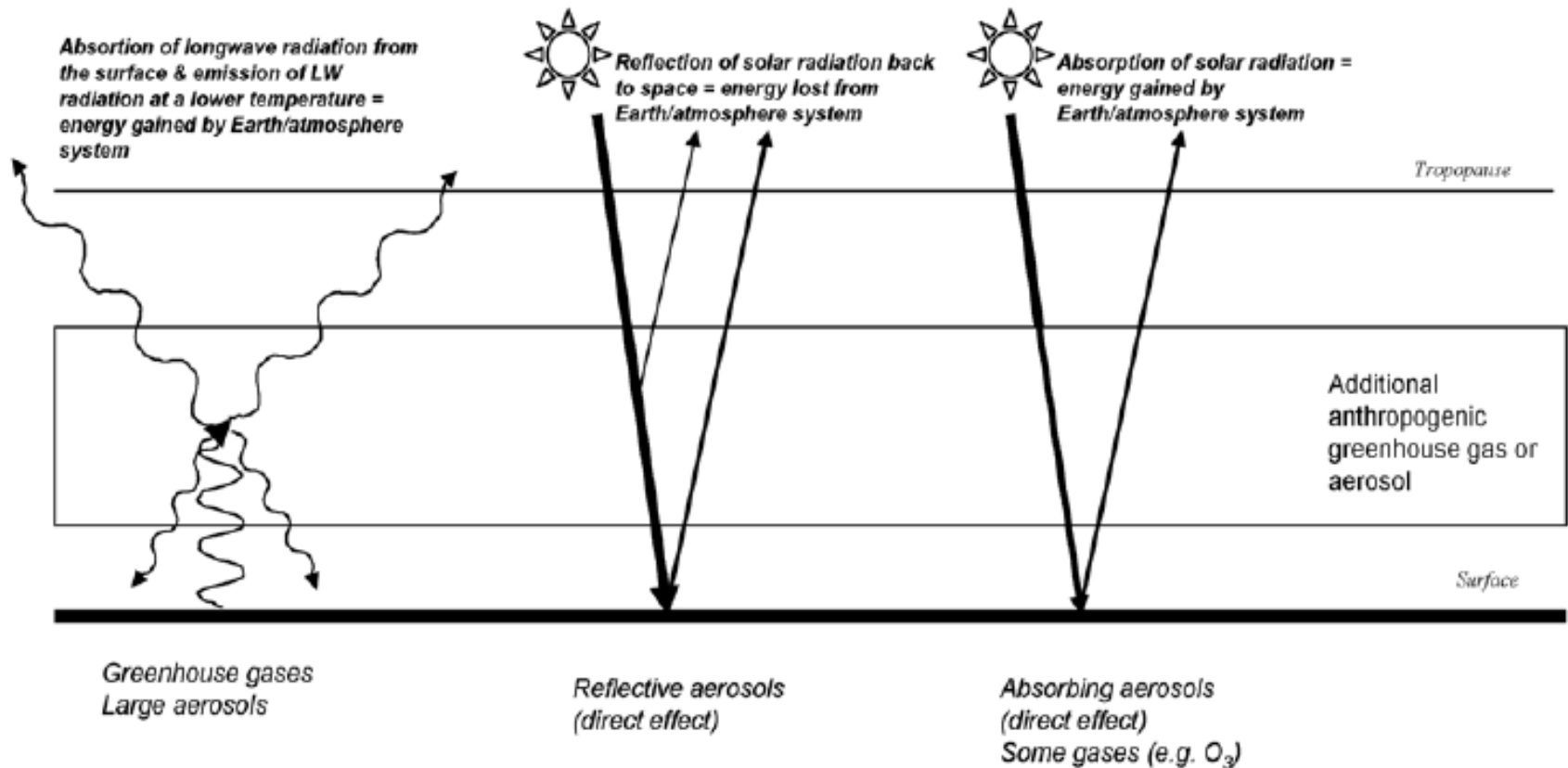ges/sfgate/green/2009/06/03/dies
el-smoke.jpg
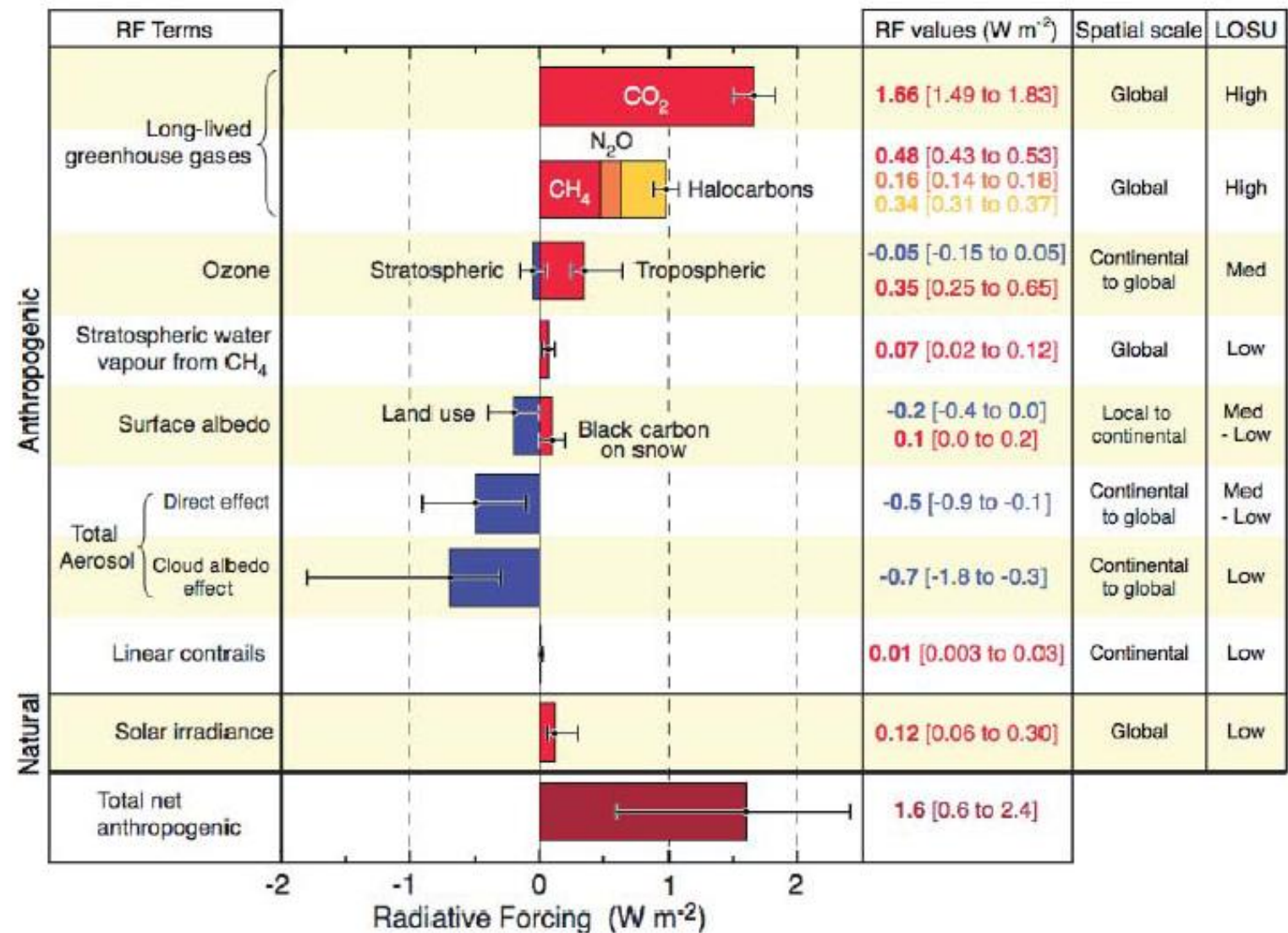

http://www.soot.biz/images/soot/soot
_250x251.jpg

Radiative Forcing

- Radiative forcing: the change in the net radiation balance at the tropopause caused by a particular external factor in the absence of any climate feedbacks.

- These forcing mechanisms can be caused by:
  - change in the atmospheric constituents such as the increase in greenhouse gases (GHGs)
  - aerosols due to anthropogenic activity,
  - changes in other components of the Earth/atmosphere system such as changes in the surface albedo (the fraction of incoming radiation that is reflected). Albedo changes are caused, e.g., by changes in vegetation (e.g. burn scars or agriculture).

Mechanisms of the radiative forcing
due to greenhouse gases and of the direct radiative forcings due to aerosols

Absorption of longwave radiation from the surface & emission of LW radiation at a lower temperature = energy gained by Earth/atmosphere system

Reflection of solar radiation back to space = energy lost from Earth/atmosphere system

Absorption of solar radiation = energy gained by Earth/atmosphere system

Tropopause

Additional anthropogenic greenhouse gas or aerosol

Surface

Greenhouse gases
Large aerosols

Reflective aerosols
(direct effect)

Absorbing aerosols
(direct effect)
Some gases (e.g. O_3)

Global-average radiative forcing (RF) estimates and ranges in 2005 (relative to 1750) for anthropogenic GHGs and other important agents and mechanisms

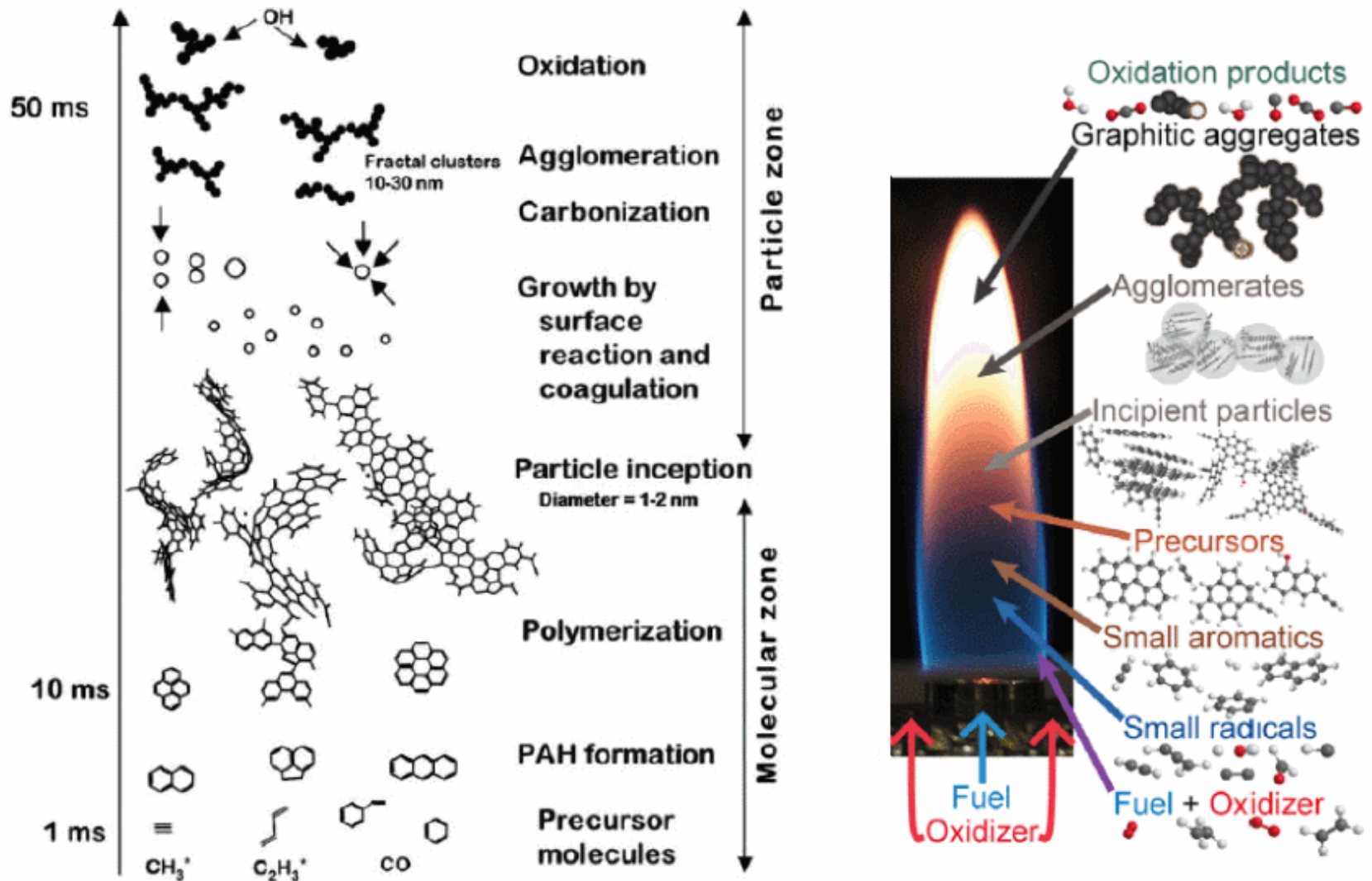| RF Terms		RF values (W m^{-2})	Spatial scale	LOSU
Anthropogenic				
Long-lived greenhouse gases	CO$_2$	1.66 [1.49 to 1.83]	Global	High
	N$_2$O / CH$_4$ / Halocarbons	0.48 [0.43 to 0.53] 0.16 [0.14 to 0.18] 0.34 [0.31 to 0.37]	Global	High
Ozone	Stratospheric / Tropospheric	-0.05 [-0.15 to 0.05] 0.35 [0.25 to 0.65]	Continental to global	Med
Stratospheric water vapour from CH$_4$		0.07 [0.02 to 0.12]	Global	Low
Surface albedo	Land use / Black carbon on snow	-0.2 [-0.4 to 0.0] 0.1 [0.0 to 0.2]	Local to continental	Med - Low
Total Aerosol	Direct effect	-0.5 [-0.9 to -0.1]	Continental to global	Med - Low
	Cloud albedo effect	-0.7 [-1.8 to -0.3]	Continental to global	Low
Linear contrails		0.01 [0.003 to 0.03]	Continental	Low
Natural				
Solar irradiance		0.12 [0.06 to 0.30]	Global	Low
Total net anthropogenic		1.6 [0.6 to 2.4]		

Radiative Forcing (W m^{-2})

Soot and the Climate

- Soot deposition responsible for 95% polar ice melting

- Dirty snow reduces ice albedo

- Brown clouds causes regional warming

- Contrail related cloud albedo

Emission of biomass smoke from Portugal in August 2003: effects on local albedo

Decrease in reflection over cloud = decrease in planetary albedo=local positive forcing

Increase in reflection over ocean = increase in planetary albedo=local negative forcing

Smoke

Fires

Soot Chemistry

H.A. Michelsen 2016
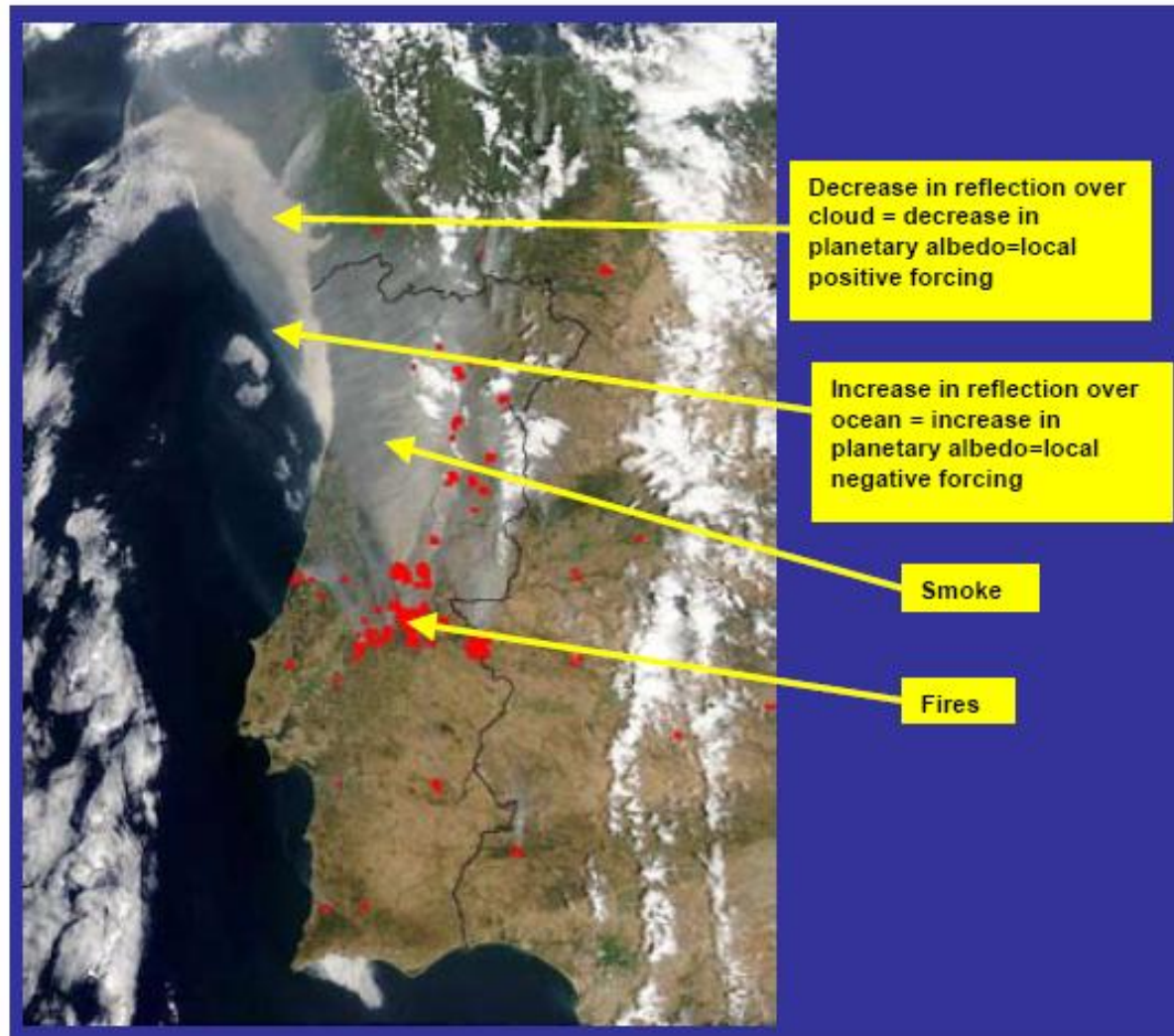
Driving Forces behind Soot Research (1)

The 80s' & 90s':

"A major break-through in understanding carbon formation will have been achieved when it becomes possible in at least one case to account for the entire course of nucleation and growth of carbon on the basis of a fundamental knowledge of reaction rates and mechanisms."

Palmer & Cullis, 1965

Frenklach, **Wang**, *Proc. Combust. Inst.* 23 (1990) 1559.

Frenklach, **Wang**, in: *Soot Formation in Combustion: Mechanisms and Models of Soot Formation*, Bockhorn, Ed. Springer-Verlag, Berlin, 1994, pp 162-190.

Colket, Hall, in *Soot Formation in Combustion: Mechanisms and Models of Soot Formation*, Bockhorn, Ed. Springer-Verlag, Berlin, 1994, pp 442-468.

Mauss, Schafer, and Bockhorn, *Combust. Flame* 99, 697-705 (1994)

Bockhorn, ed. *Soot Formation in Combustion: Mechanisms and Models of Soot Formation*, Springer-Verlag, Berlin, 1994.

Kennedy "Models of soot formation and oxidation," *Prog. Energy Combust. Sci.* 23 (1997) 95-132.
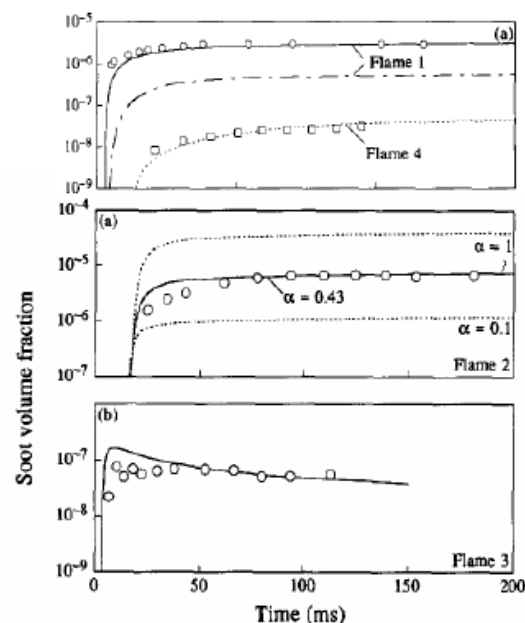
Data: Jander & Wagner, Simulation: Kazakov, Wang, Frenklach (1994)

Driving Forces behind Soot Research (2)

The most recent decade:

Predictive tools for combustion engine designs

Soot Mass w/Jet-A

Courtesy of Colket

Fuel injector/swirler

Fuel-rich front end — Quench Zone — Lean, Burn-Out Zone
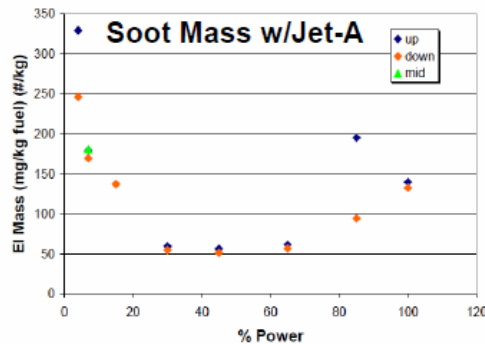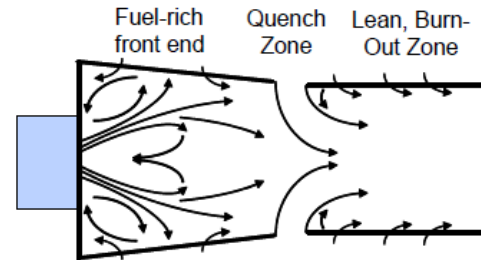
Network Reactor Simulation

Fuel-spray shear layer — Quench zones — Burn-out zones

Recirculation zones
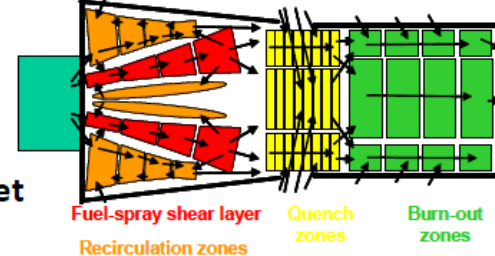
Bai, Balthasar, **Mauss**, Fuchs *Proc. Combust. Inst.* 27 (1998) 1623.

Pitsch, Riesmeier, **Peters** *Combust. Sci. Technol.* 158 (2000) 389.

Wen, Yun, **Thomson**, Lightstone *Combust. Flame* 135 (2003) 323.

Wang, **Modest**, **Haworth**, Turns *Combust. Theor. Model.* 9 (2005) 479.

Lignell, **Chen**, Smith, Lu, Law *Combust. Flame* 151 (2007) 2.

Mosback, Celnik, Raj, **Kraft**, Zhang, Kubo, Kim *Combust. Flame* 156 (2009) 1156.

Haworth *Prog. Energy Combust. Sci.* 36 (2010) 168-259.

Soot Chemistry
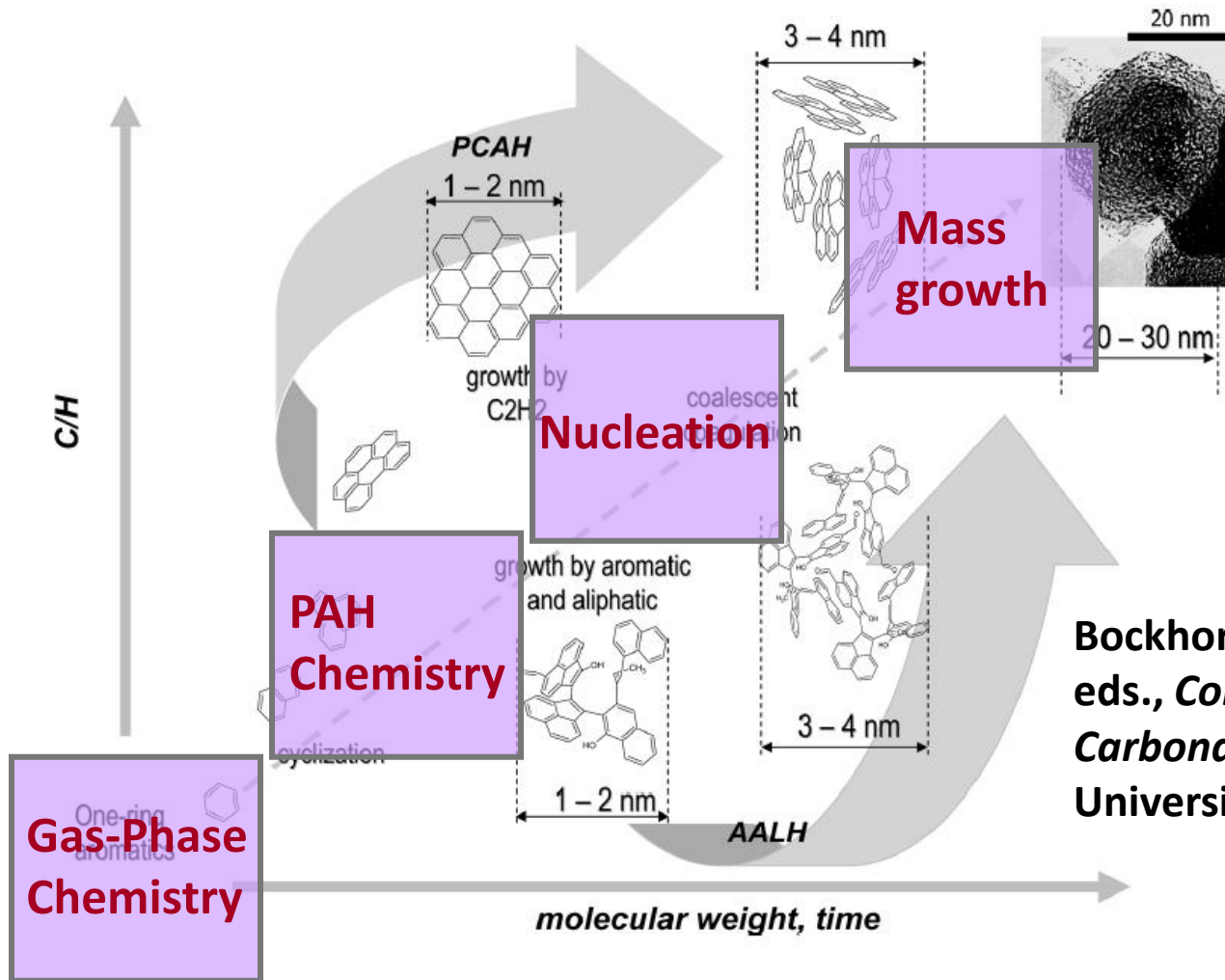
Bockhorn, D'Anna, Sarofim, Wang, eds., *Combustion Generated Fine Carbonaceous Particles*, Karlsruhe University Press, 2009.

Courtesy of D'Anna

13

Formation of the First Aromatic Ring
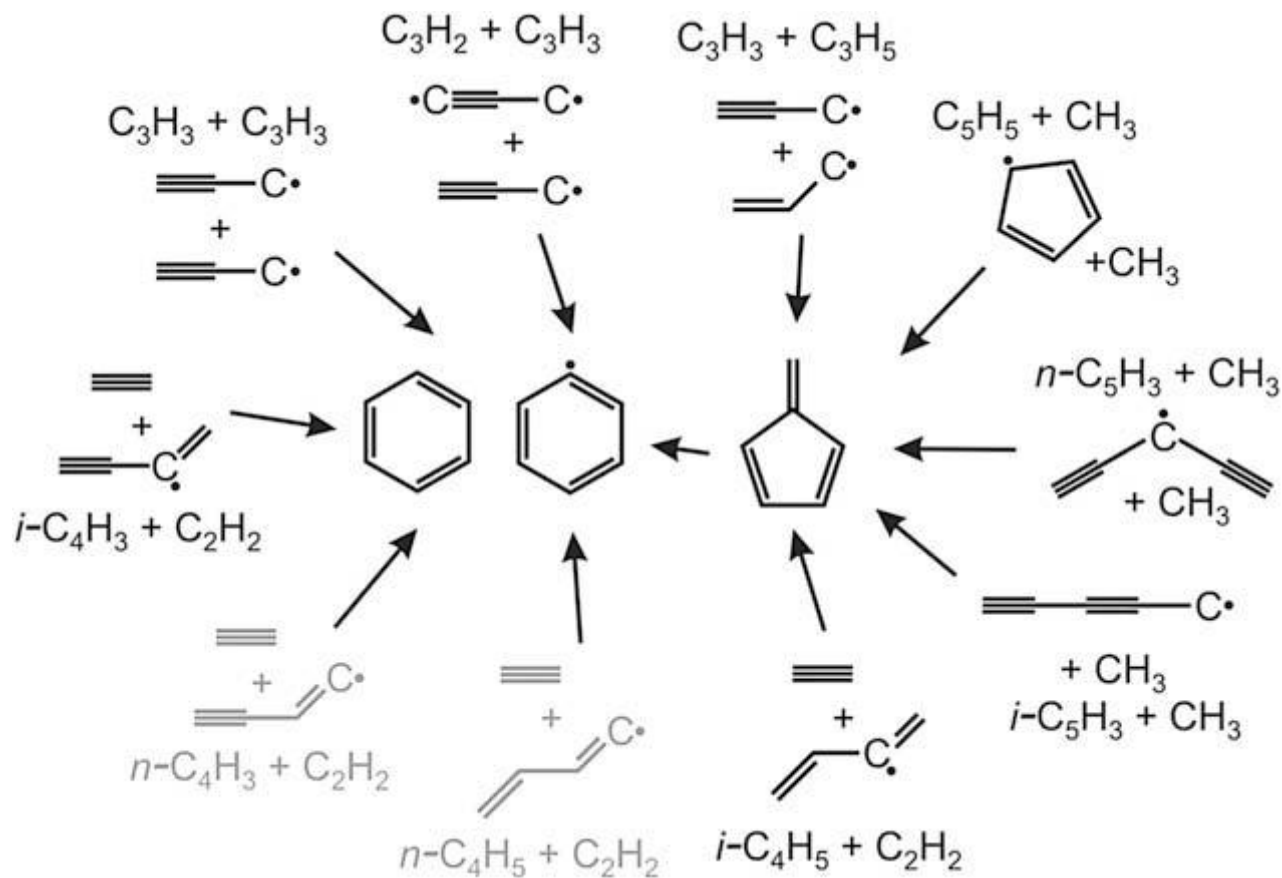
Various formation routes for forming aromatic species in flames

N. Hansen et al. 2009

Formation of the First Aromatic Ring
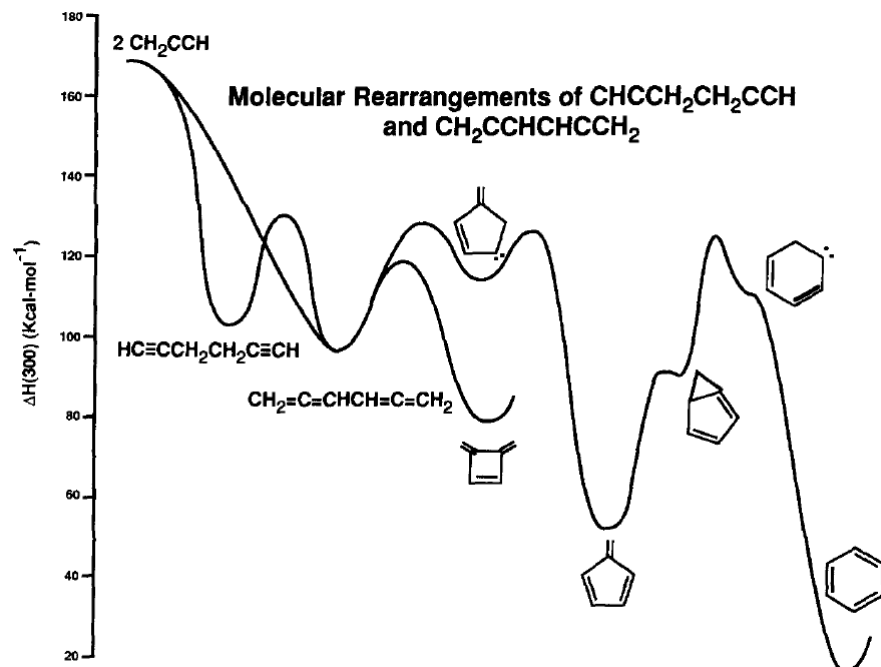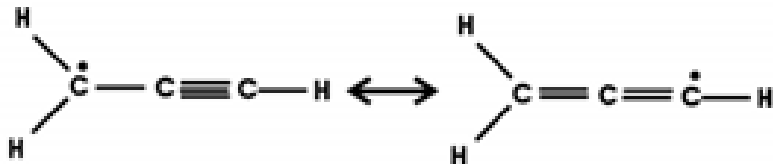
Fig. 10. Reaction coordinate diagram for head-to-head and tail-to-tail recombination of propargyl radicals (the CH₂ end of propargyl is called the head, the CH end the tail).
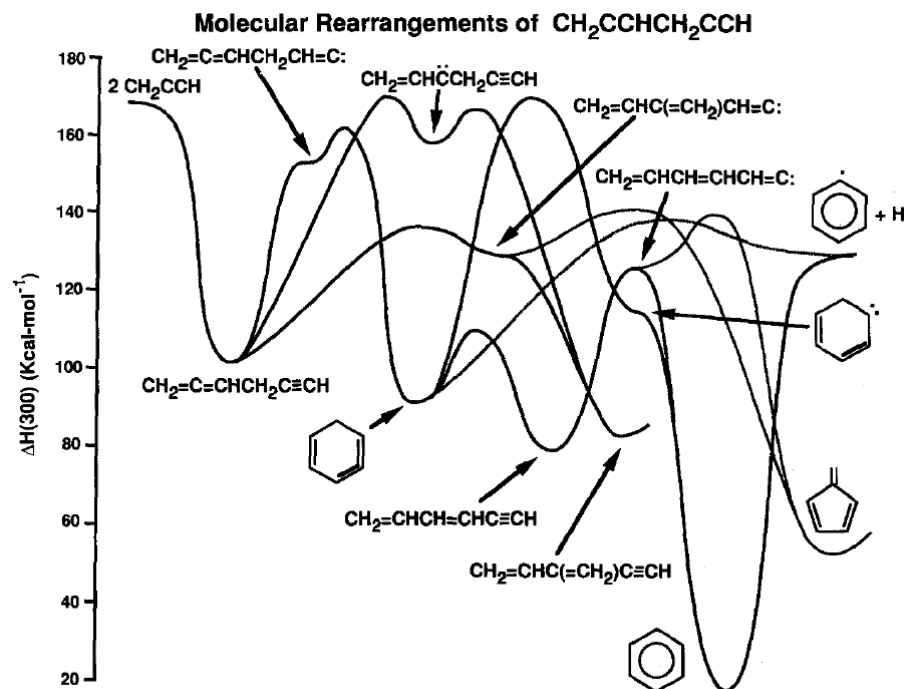
Fig. 11. Reaction coordinate diagram for head-to-tail recombination of propargyl radicals (the CH₂ end of propargyl is called the head, the CH end the tail).

J.A. Miller and C.F. Melius 1992

Formation of the First Aromatic Ring
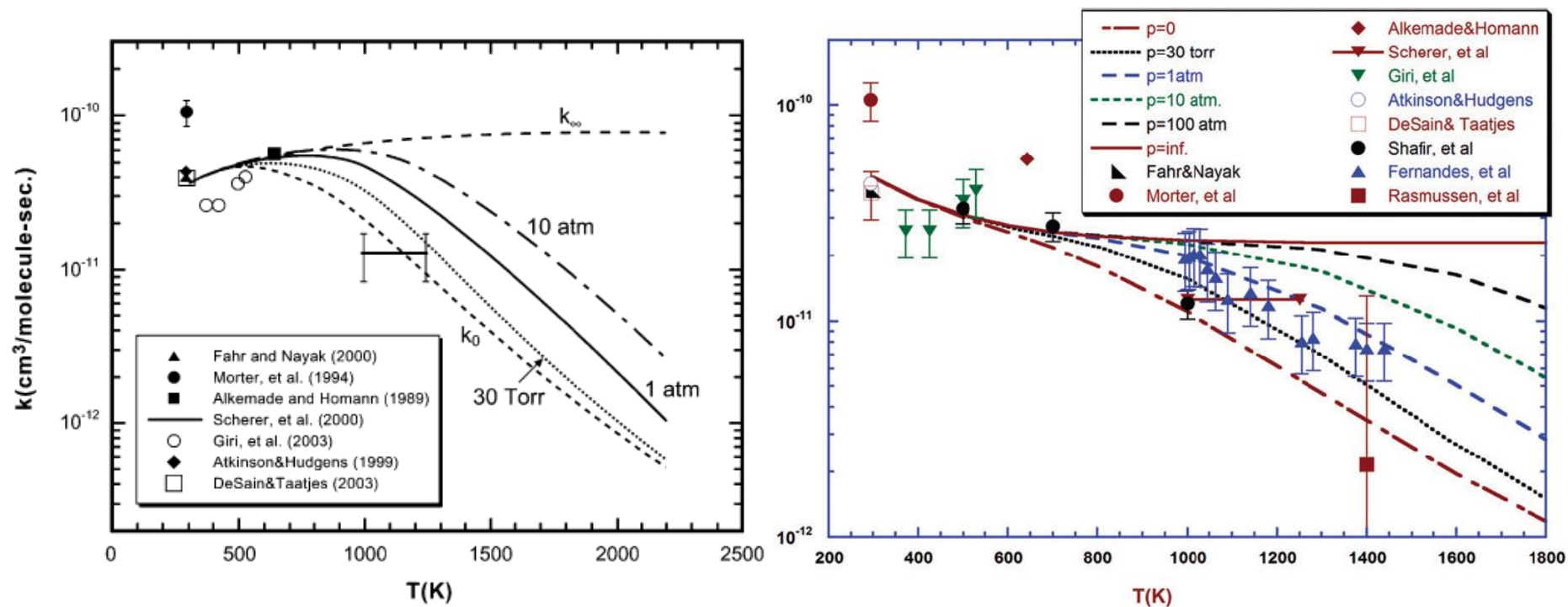
Figure 11. Total rate coefficient for the reaction $C_3H_3 + C_3H_3 \rightarrow$ products as a function of temperature and pressure.

J.A. Miller and S.J. Klippenstein 2003

Y. Georgievskii et al. 2007

Formation of the First Aromatic Ring

$n\text{-}C_4H_5$ $+ H - H$ $i\text{-}C_4H_5$
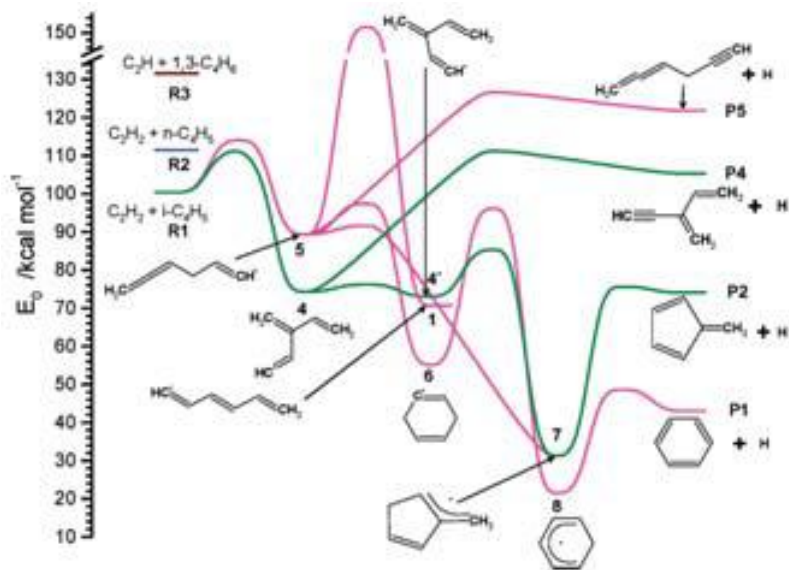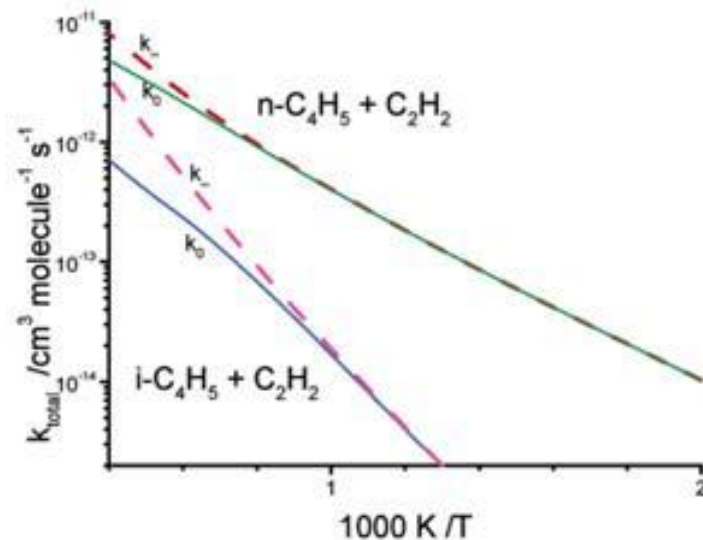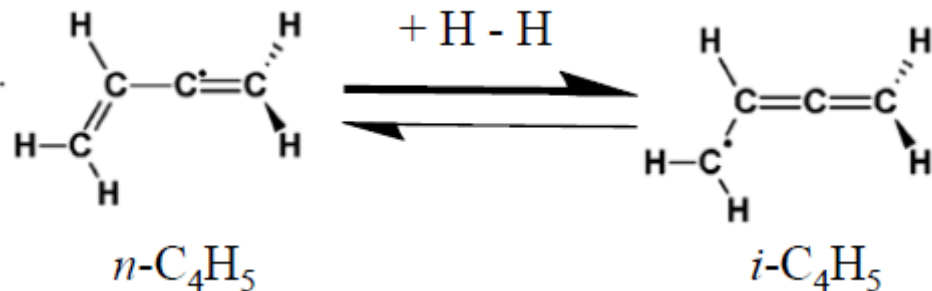
$i\text{-}C_4H_5 + C_2H_2$ J.P. Senosiain and J.A. Miller 2007 $n\text{-}C_4H_5 + C_2H_2$
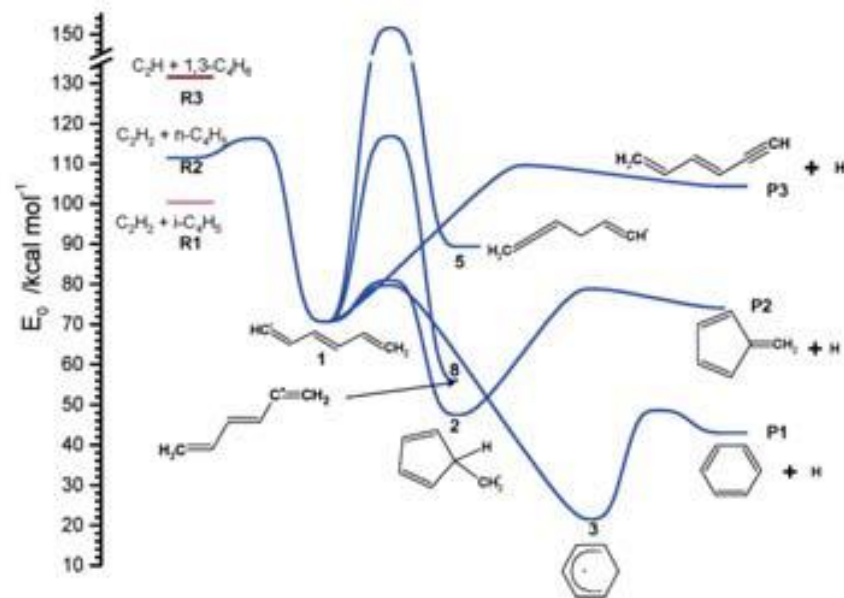
Formation of the First Aromatic Ring

C. F. Melius et al. 1996
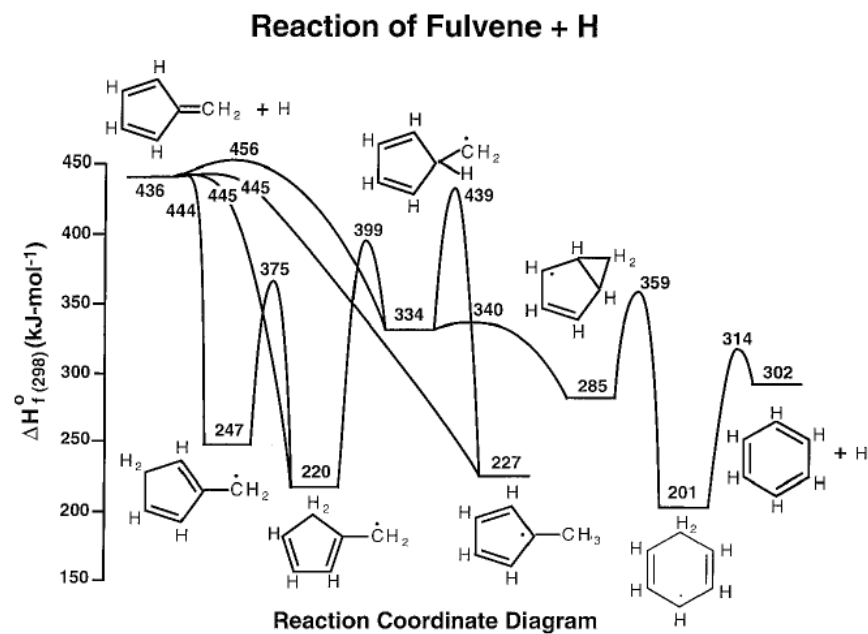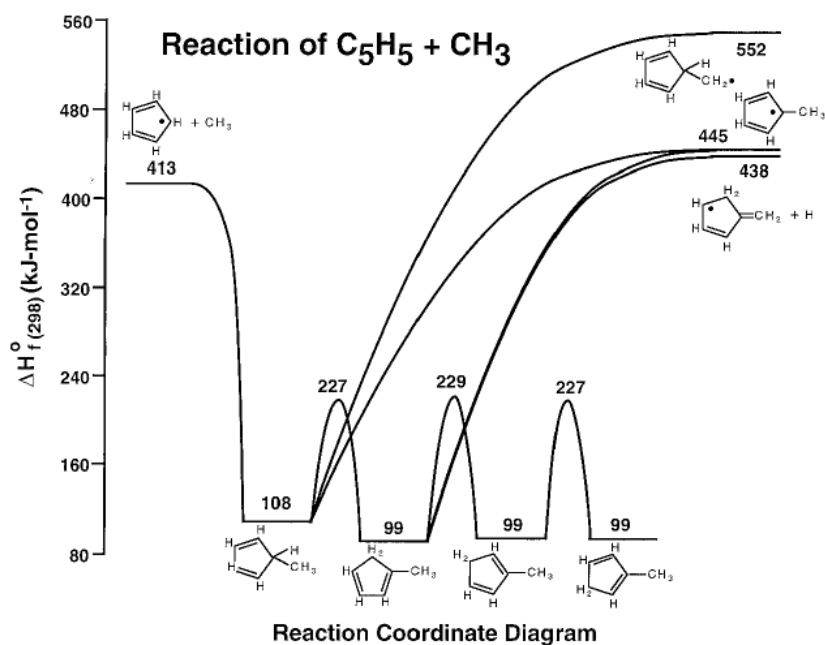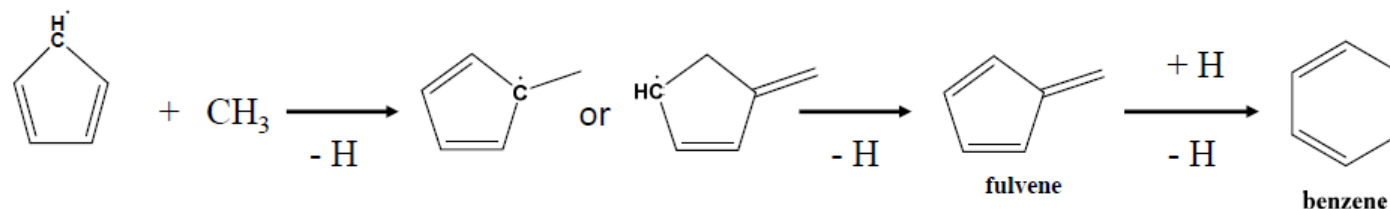
Formation of the First Aromatic Ring

H + fulvene→H + benzene and other products
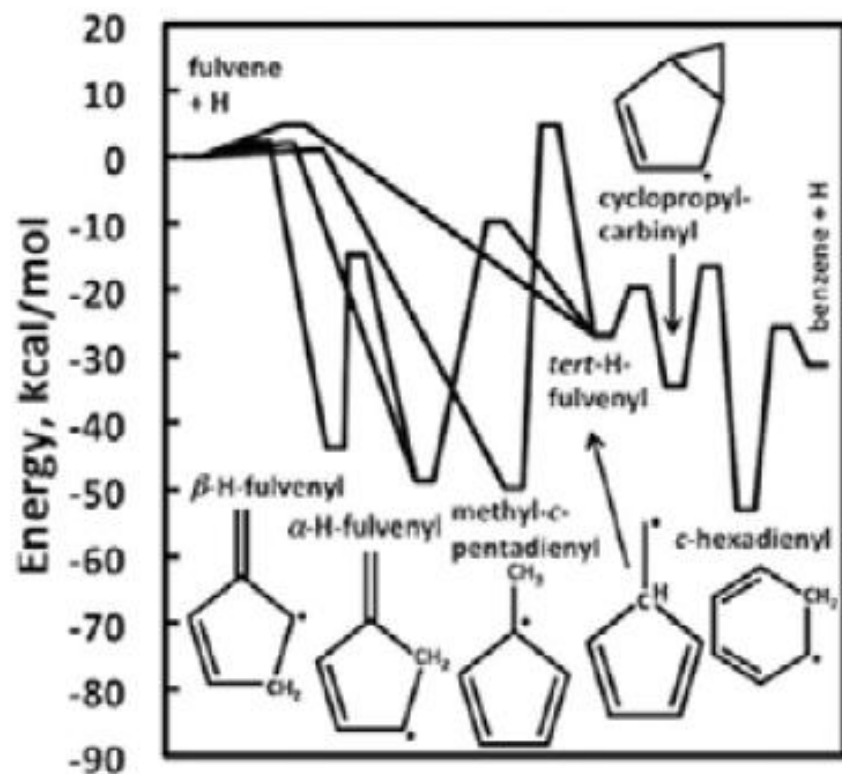
A.W. Jasper and N. Hansen 2013
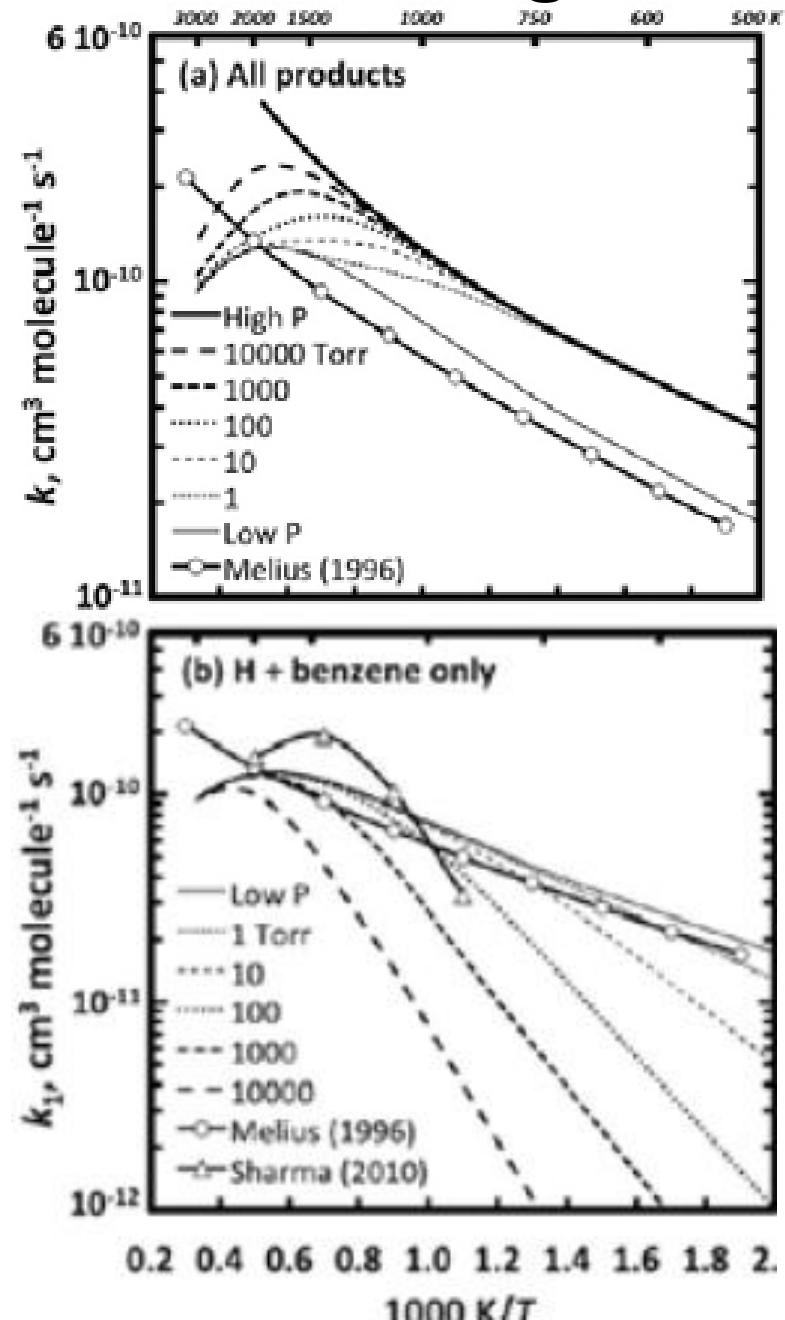
Formation of the First Aromatic Ring

Cascading dehydrogenation
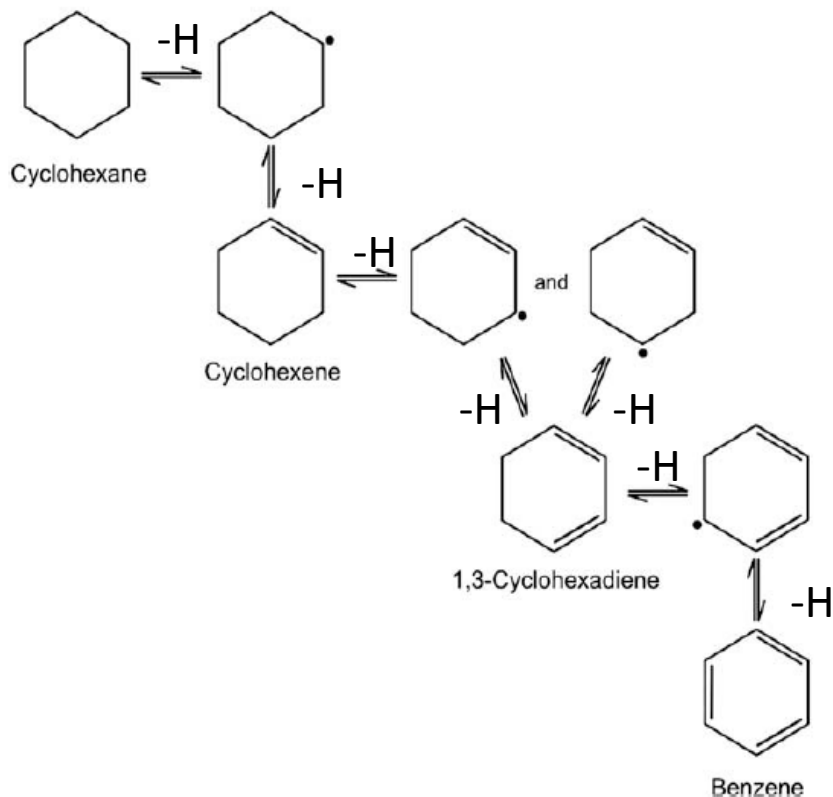
Benzene Formation is Fuel-structure Dependent

Cyclohexane

1,3-Cyclohexadiene

Benzene

N. Hansen et al. 2009

Cyclohexane

1-hexene
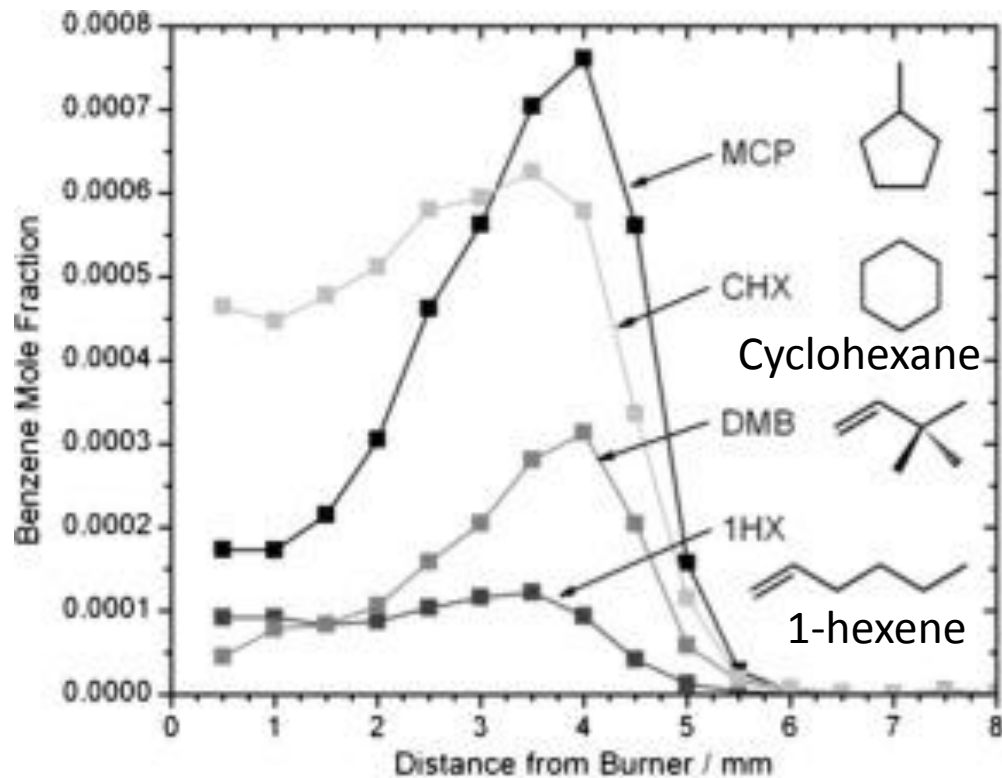
N. Hansen et al. 2011

Formation of Polycyclic Aromatic Hydrocarbons (PAHs)
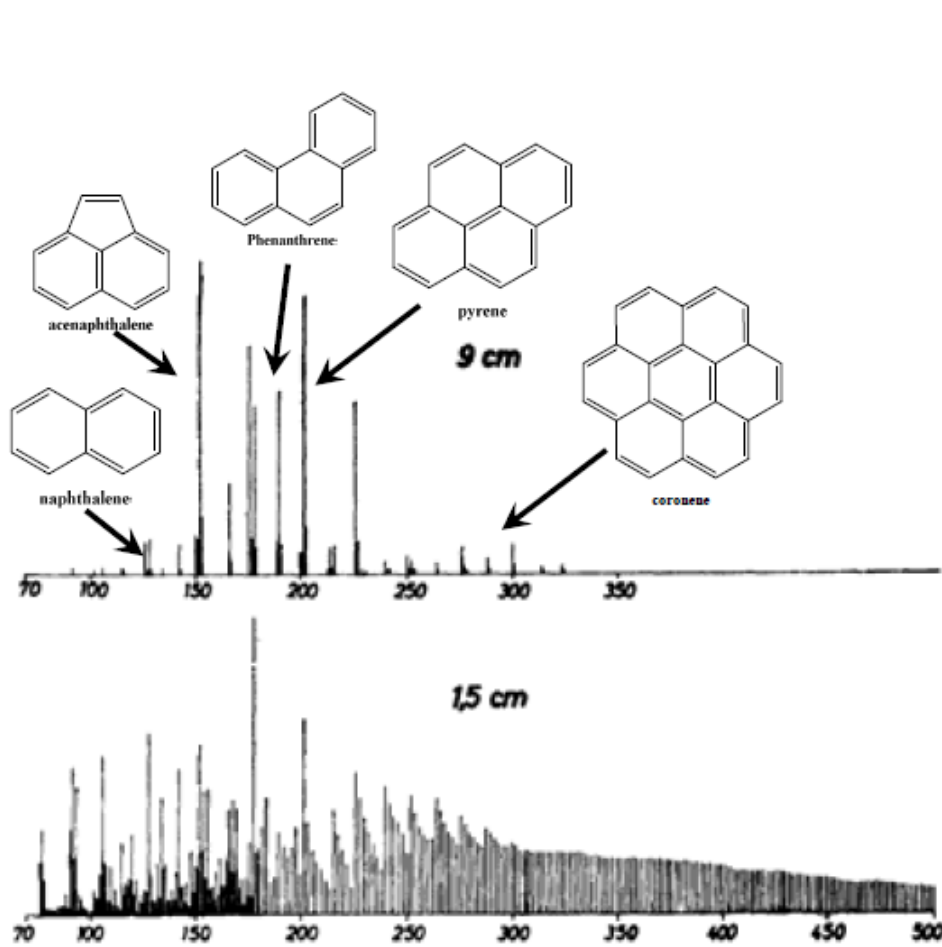
Molecular beam mass spectrum, C_2H_2/O_2 flame
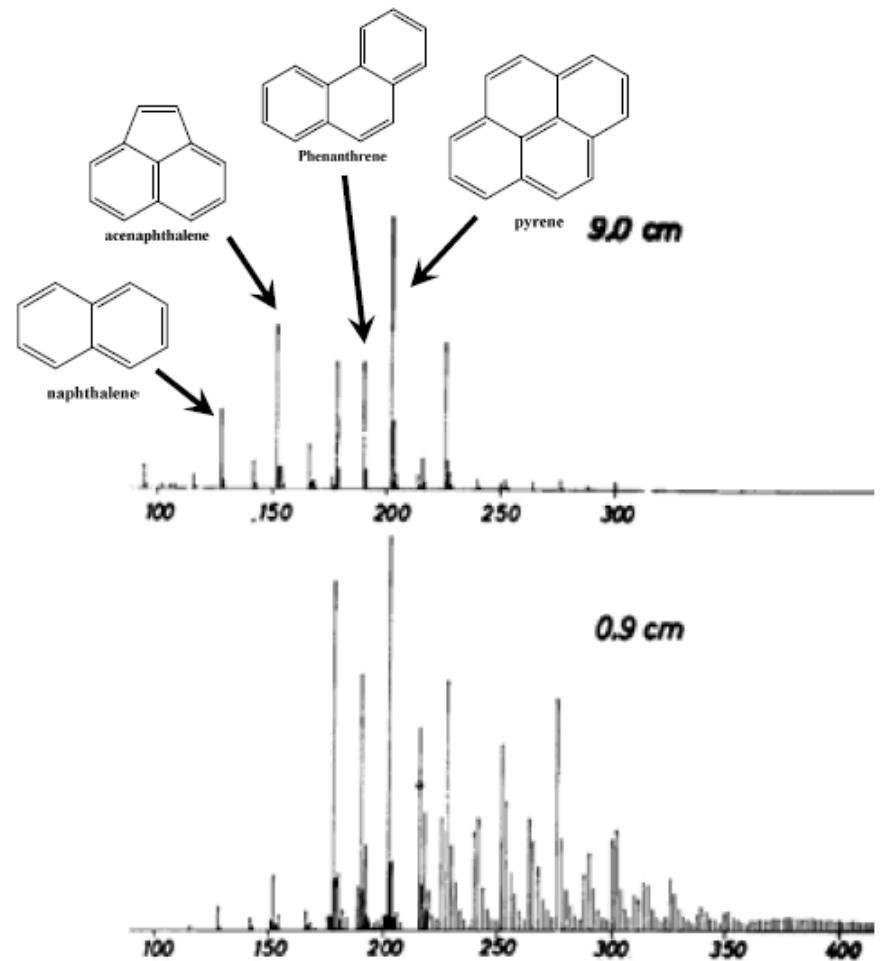
Molecular beam mass spectrum, C_6H_6/O_2 flame

K.H. Homann and H.G. Wagner 1967

Formation of Polycyclic Aromatic Hydrocarbons (PAHs)

Schematic diagram of the hydrogen-abstraction-carbon addition (HACA) reaction mechanism of PAH formation and growth.
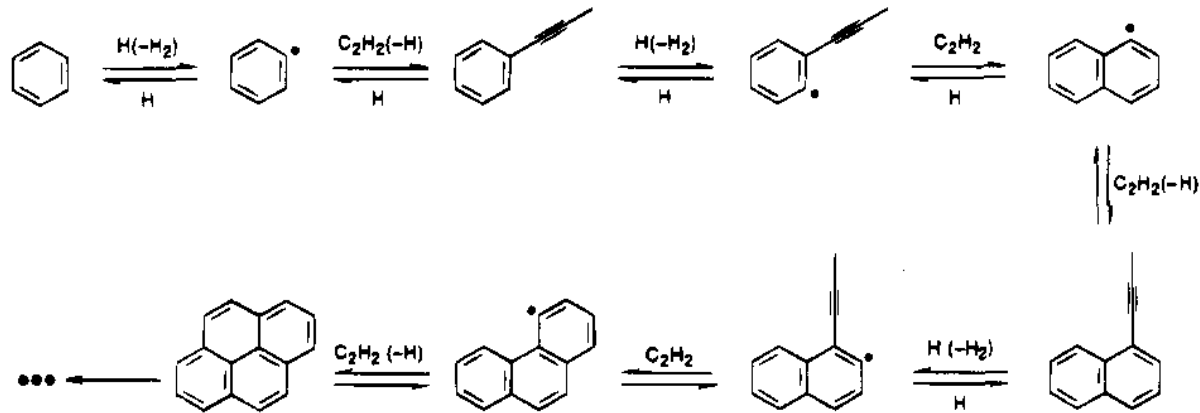
M. Frenklach et al. 1985
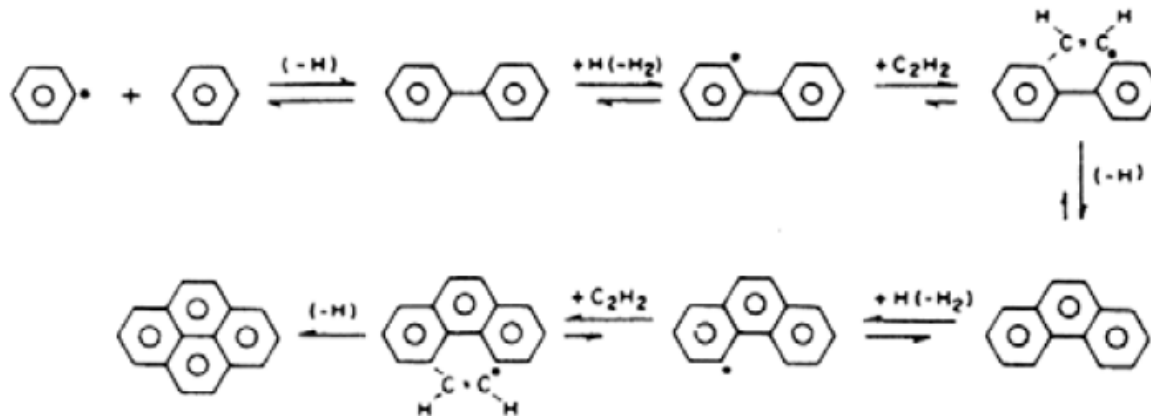
H atom – the driven force behind chain branching and flame propagation
C_2H_2 – the most abundant hydrocarbon intermediate in fuel-rich conditions

Formation of Polycyclic Aromatic Hydrocarbons (PAHs)

PAH formation is sensitive to a multitude of elementary reactions and local flame conditions.

H. Wang and M. Frenklach 1997

Formation of Polycyclic Aromatic Hydrocarbons (PAHs)

C$_2$H$_2$	5	5	4	4	3	2	2	1	0
H	1	0	1	0	0	1	0	0	1
H$_2$	0	1	1	2	2	2	3	3	3
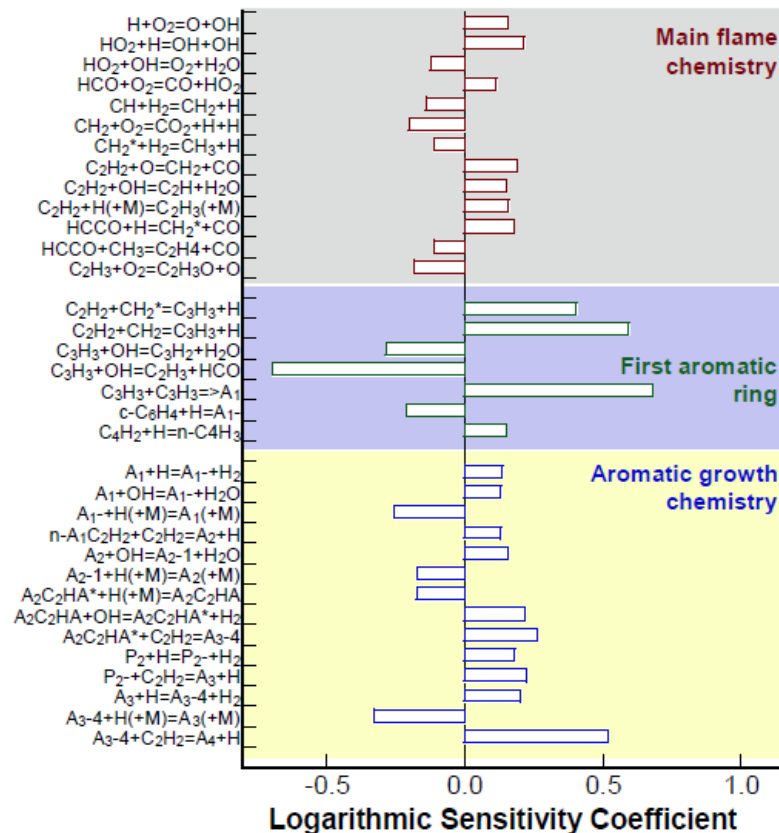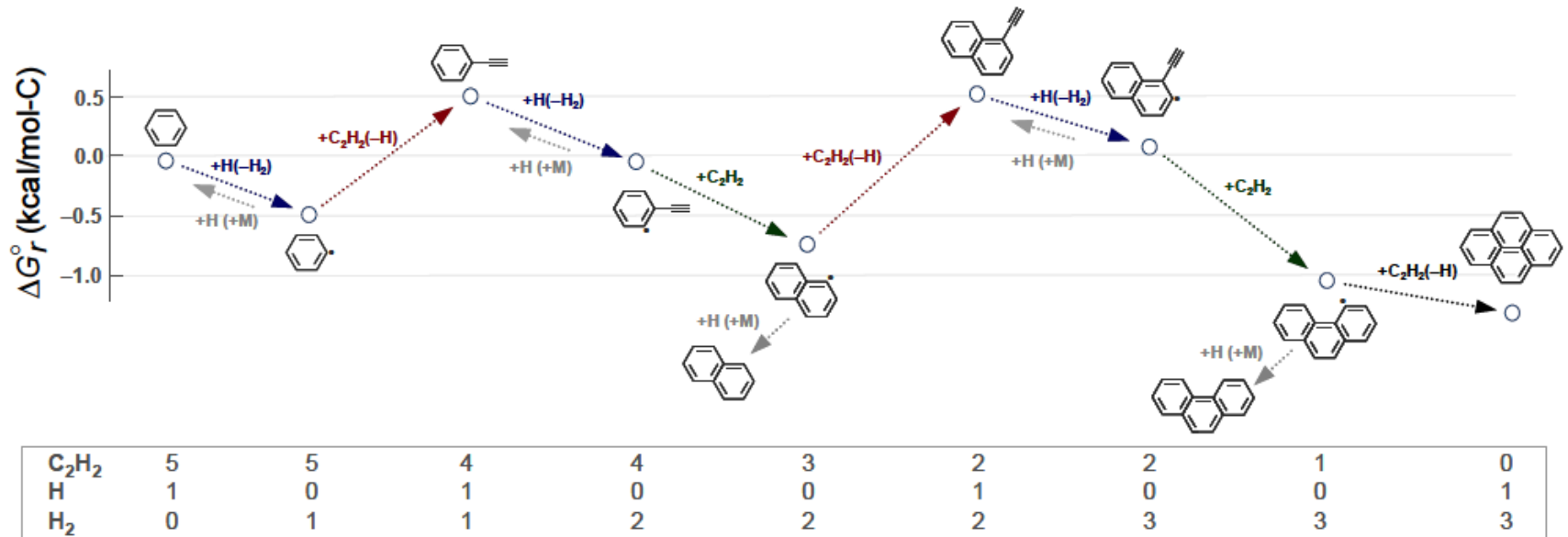
While HACA captures the thermo-kinetic requirements for PAH formation, its reversibility opens it to competitions from other pathways.

H. Wang 2011

Formation of Polycyclic Aromatic Hydrocarbons (PAHs)
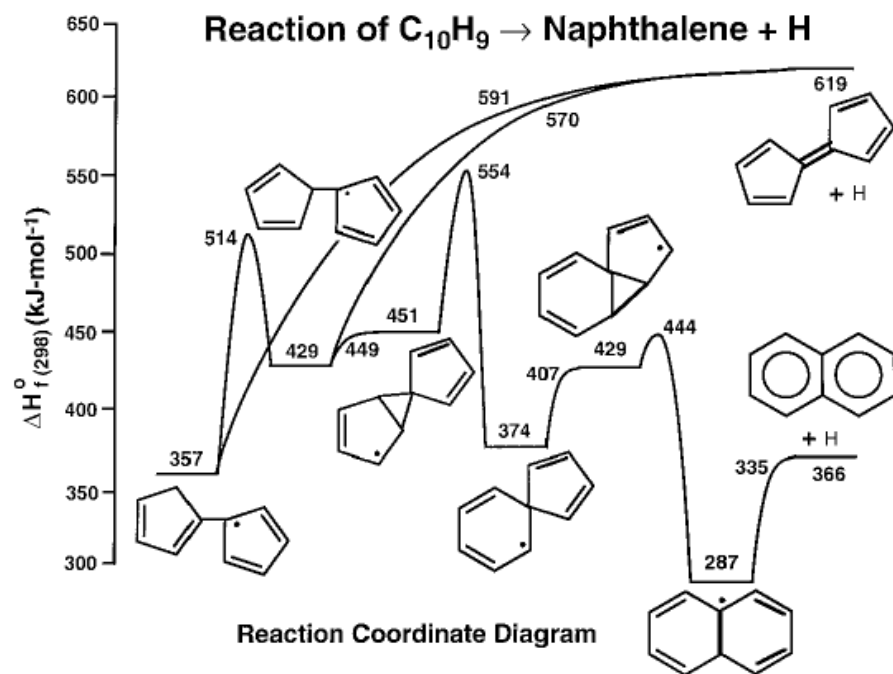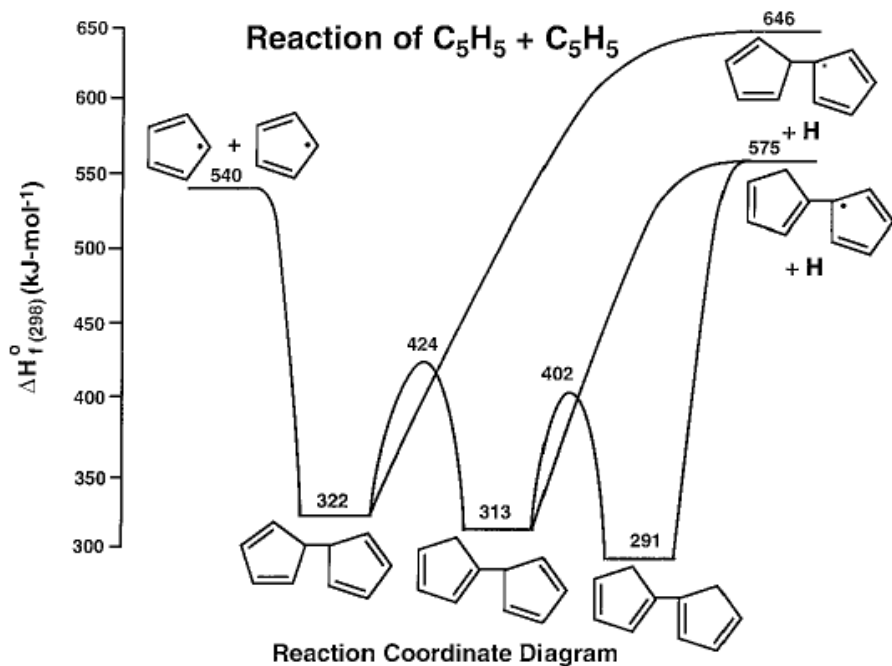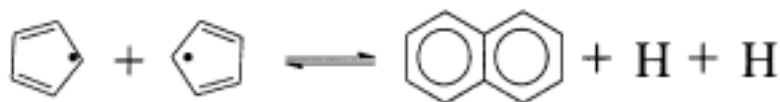
C. F. Melius et al. 1996
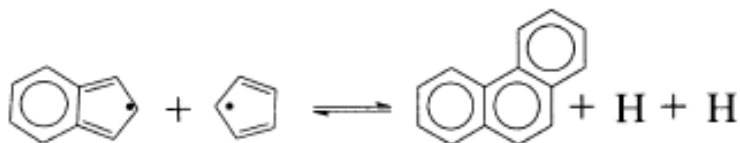
Formation of Polycyclic Aromatic Hydrocarbons (PAHs)

Phenyl Addition/Cyclization (PAC) mechanism
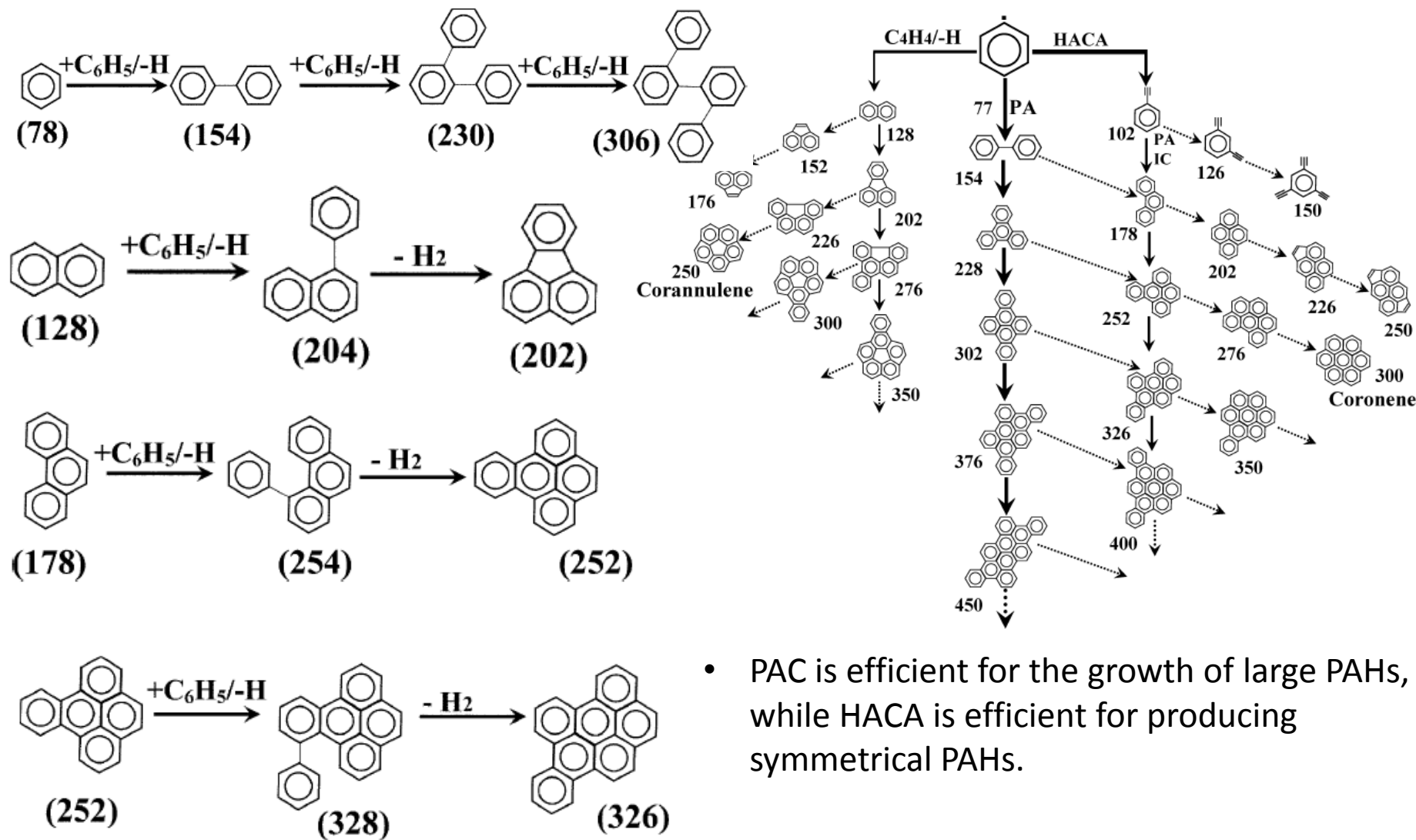
- PAC is efficient for the growth of large PAHs, while HACA is efficient for producing symmetrical PAHs.

B. Shukla and M. Koshi 2010

Nucleation
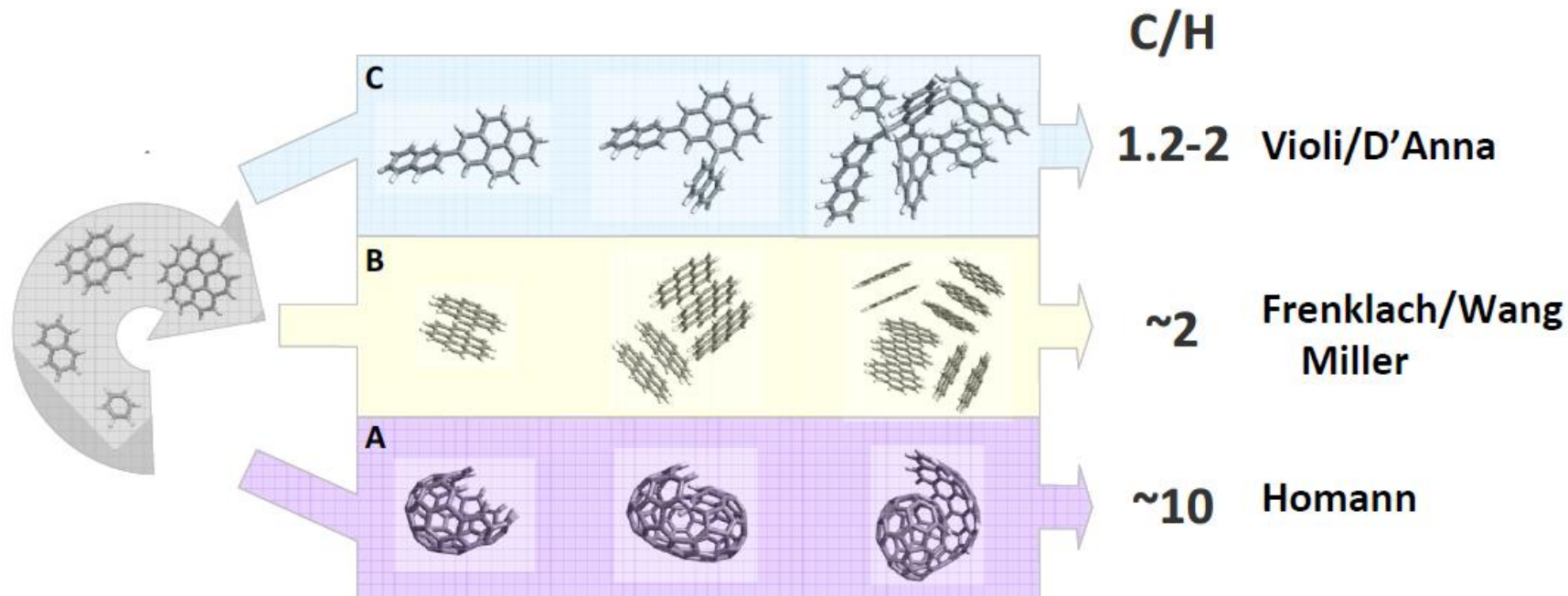
Path A: the growth of two-dimensional PAHs into curved, fullerene-like structures that are the nucleus of spherical particles. **Too slow** to explain the time scale of soot inception phenomena.

Path B: physical coalescence of moderate-sized PAHs into stacked clusters. **Unstable** at relatively high temperatures.

Path C: chemical coalescence of PAHs into crosslinked three-dimensional structures, forming aromatic-aliphatic-linked structures.
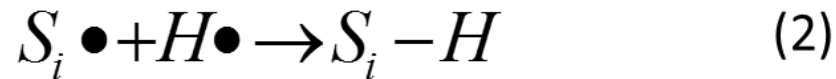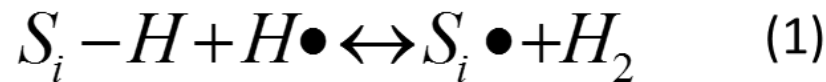
H. Wang 2011

Mass Growth

initial particles

agglomeration

coalescence

coagulation

agglomeration of two primary particles
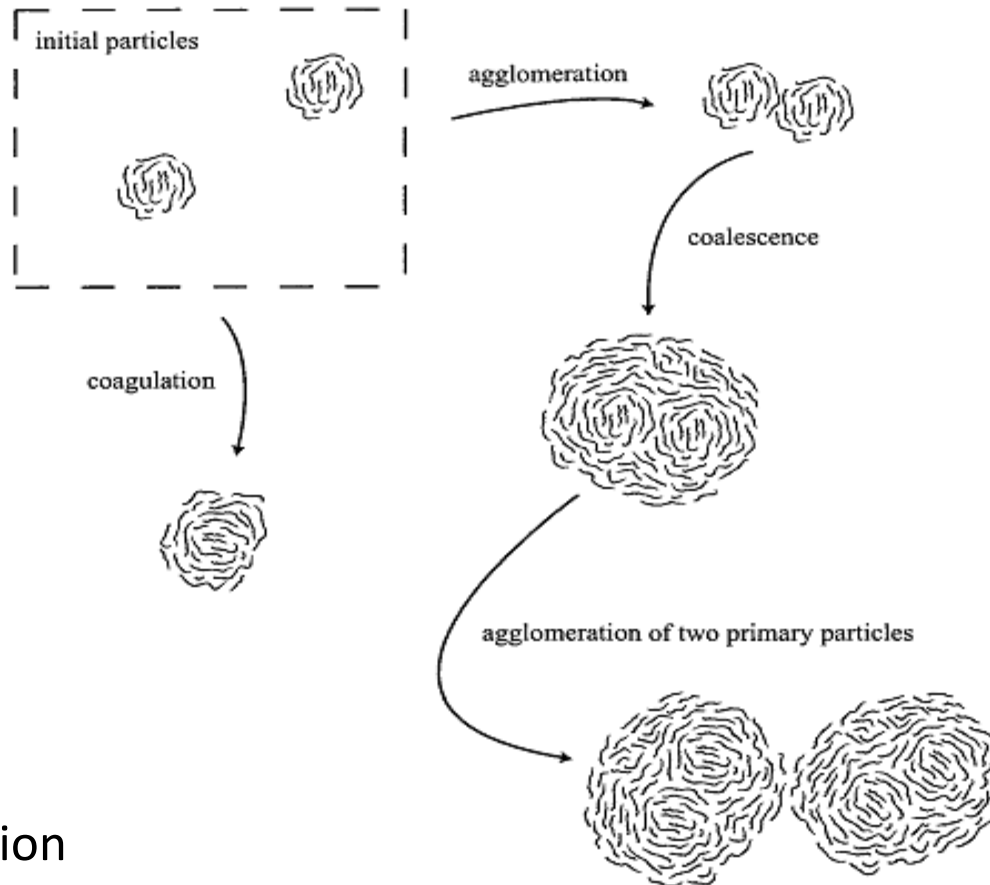
P.D. Teini 2011

- Coagulation
- Agglomeration
- Coalescence (Agglomeration + Surface growth)
- Surface growth (PAH condensation, Surface HACA etc.)
- Aggregation

Soot Surface Growth

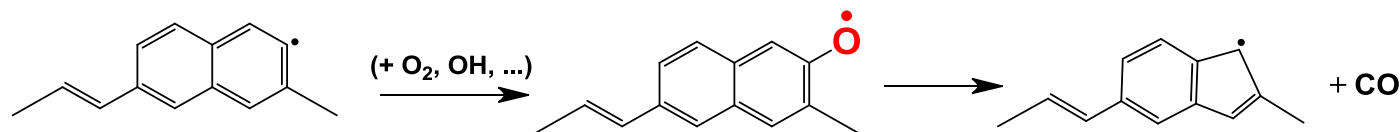Surface Hydrogen-Abstraction-Carbon-Addition （Frenklach and Wang, 1991 ）

$$S_i - H + H\bullet \leftrightarrow S_i\bullet + H_2 \qquad (1)$$

$$S_i\bullet + H\bullet \rightarrow S_i - H \qquad (2)$$

$$S_i\bullet + C_2H_2 \rightarrow S_{i+2} - H + H\bullet \qquad (3)$$
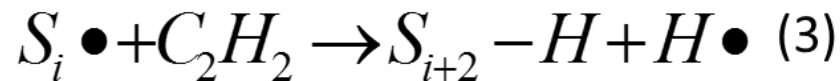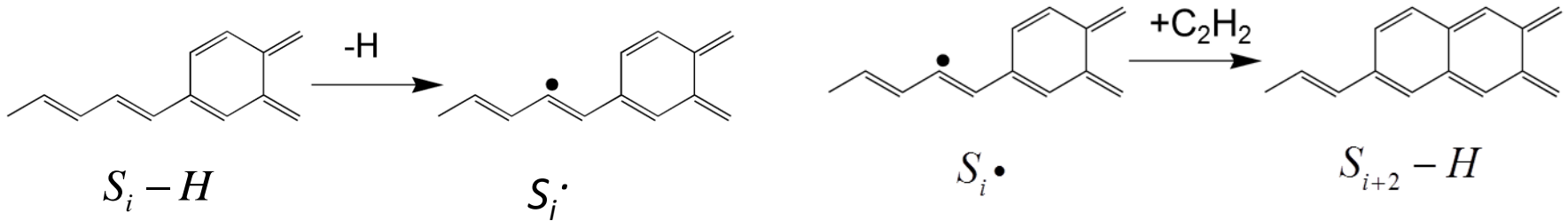
$$\omega_H = 2k_3 K^1_{eq} \frac{[H]}{[H_2]}[S_i - H][C_2H_2]$$

Soot Surface Growth

R. Whitesides and M. Frenklach 2010

Soot Surface Oxidation

Formation and decomposition of oxyradicals[1-3]

Migration of the five-membered ring[4]   **VS.**   Oxidation of an five-membered ring at the corner[5,6]
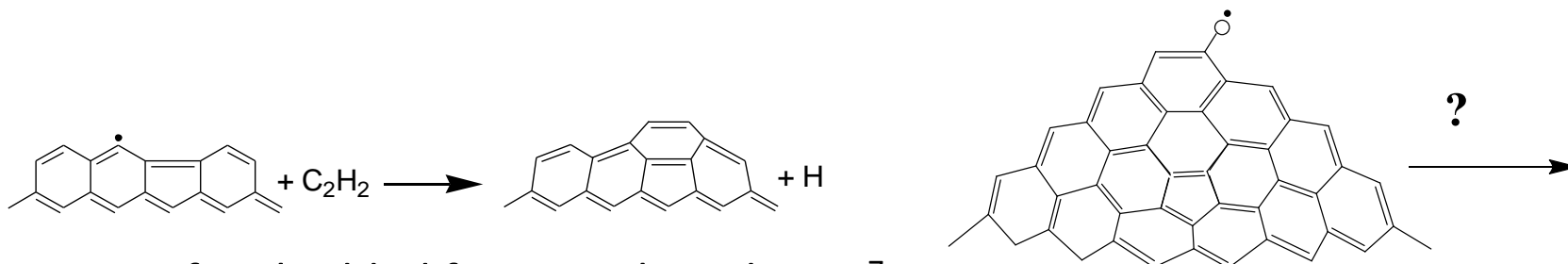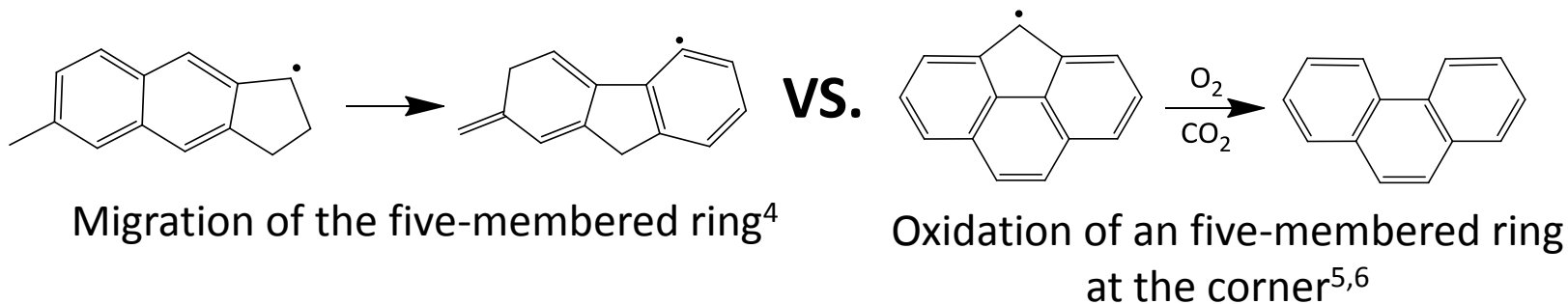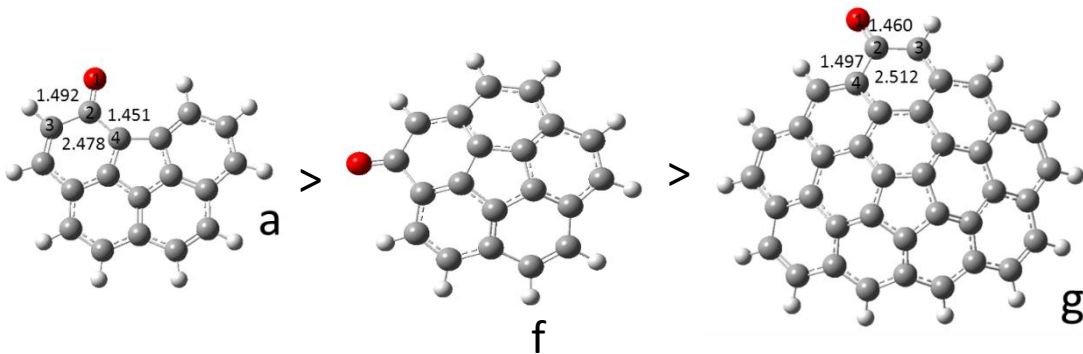
Formation of Embedded five-membered rings[7]

[1]Tokmakov et al. 2005, [2]You et al. 2011, [3]Edward et al. 2013, [4]Whitesides et al. 2009, [5]Raj et al. 2012, [6]Singh et al. 2015, [7]You et al. 2011
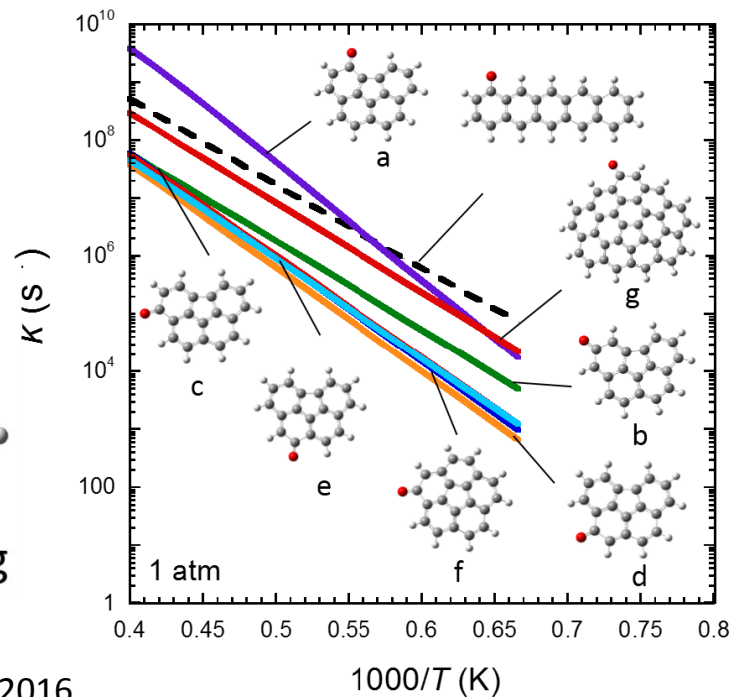
Soot Surface Oxidation

B3LPY/6-311g(d,p)
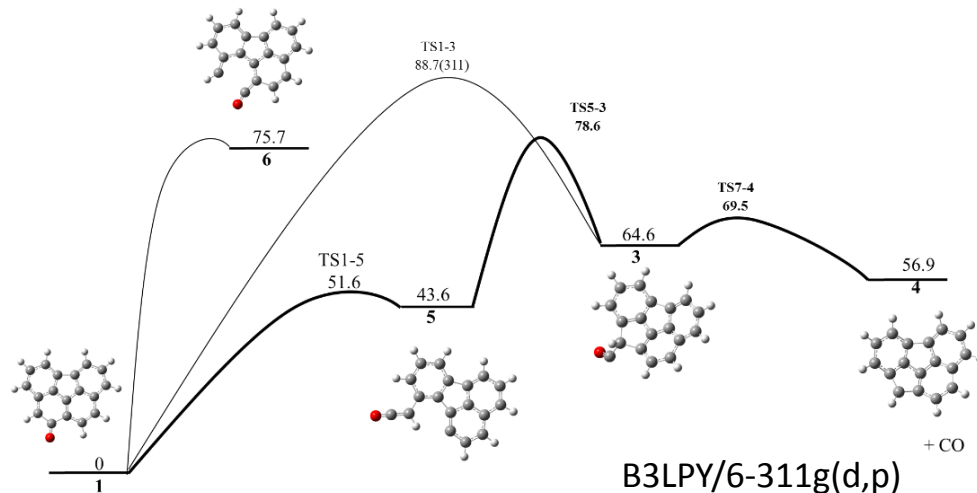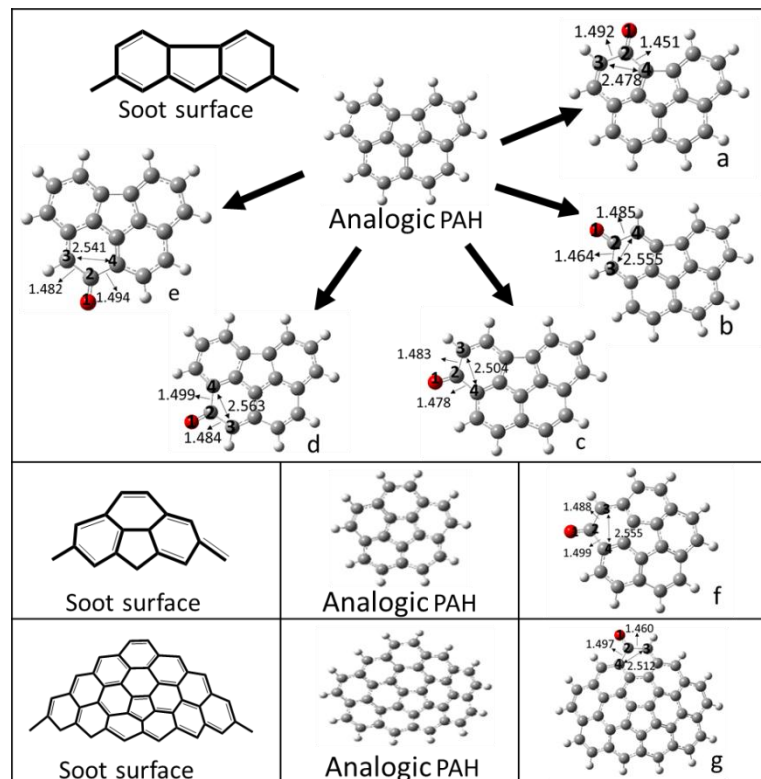
Oxyradicals with an embedded five-membered ring

Influence **diminishes**

X.Q. You et al. 2016
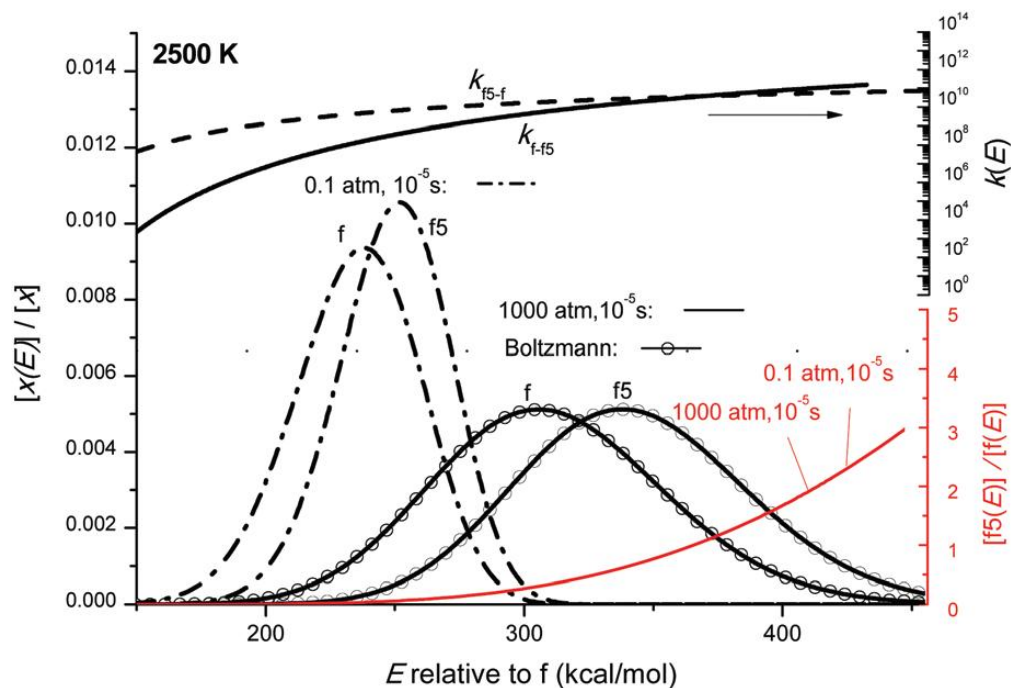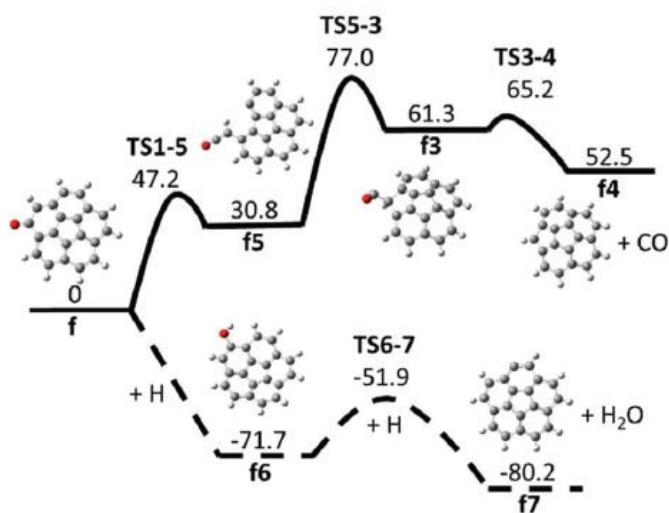
Unimolecular reactions of large molecules

- Large molecules have large densities of states and thermal distribution extends to high energies at high T;
- This distribution may peak well above the dissociation energy

Dissociation of corannulene oxy radical

Wang et al Physical Chemistry Chemical Physics, 2017, 19, 11064 - 11074

Implications for kinetics

➢ dissociation rate constants, k(E) can exceed the collision frequency
➢ This overlap of CSEs and IEREs mean that rate constants are not directly related to eigenvalues

Units: kcal/mol
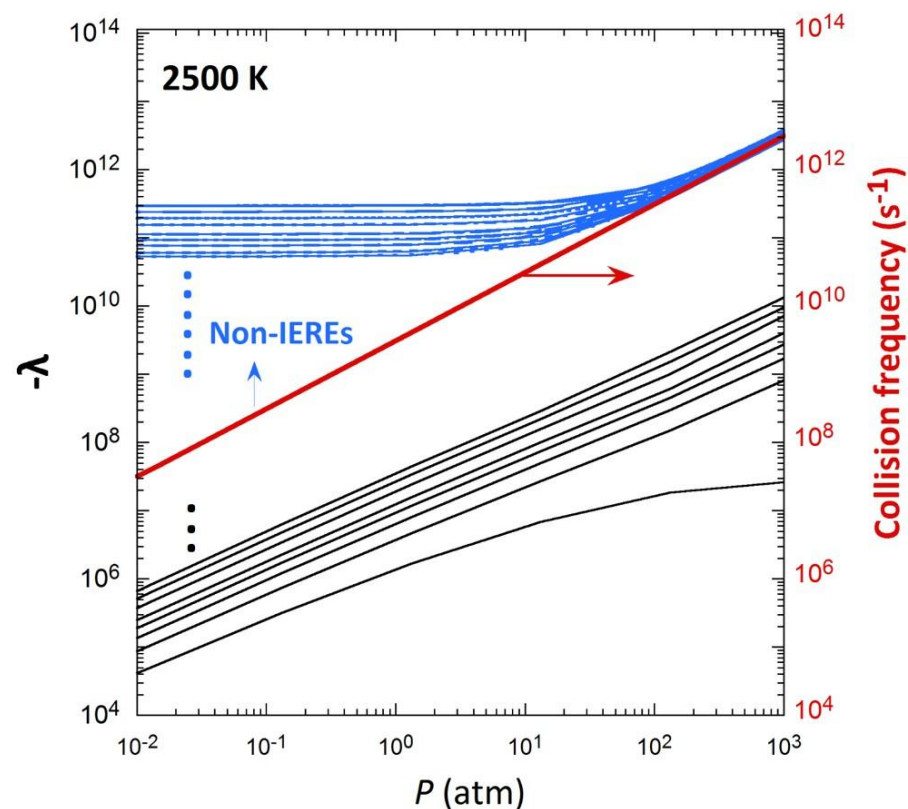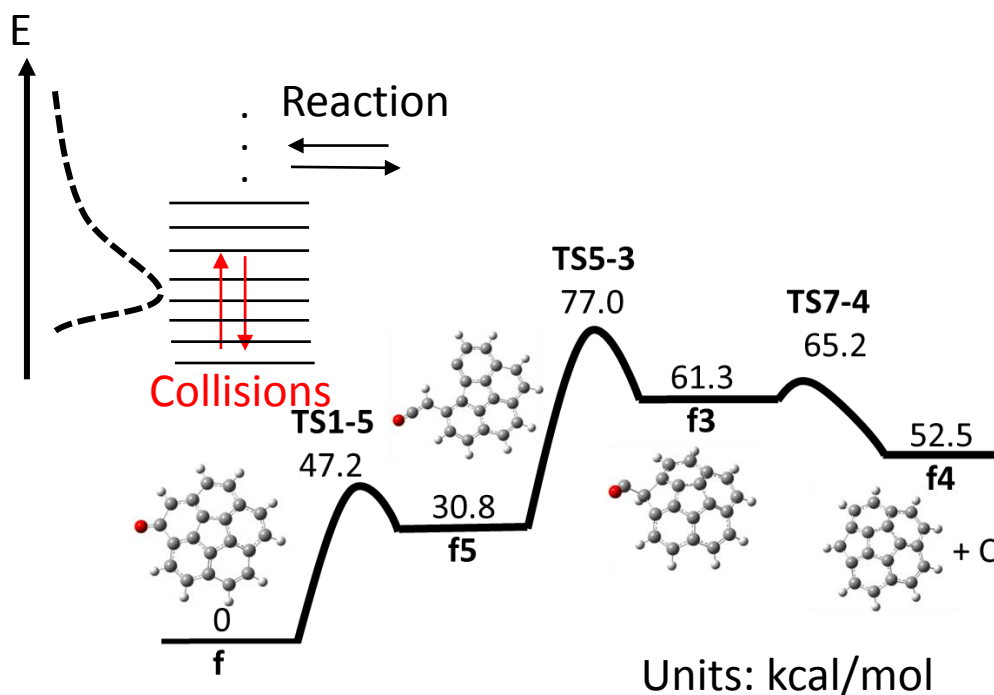
➢ How to obtain effective phenomenological rate coefficients?

Time dependence of the reactant and intermediates vs T
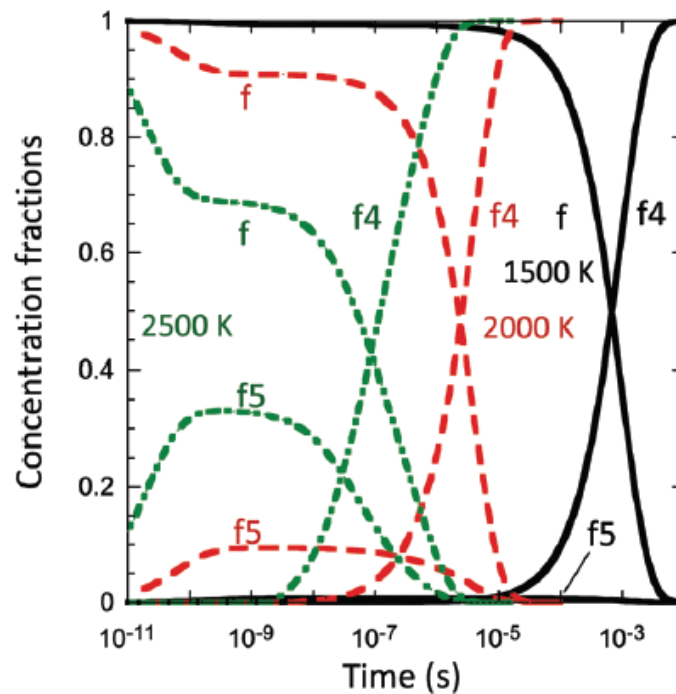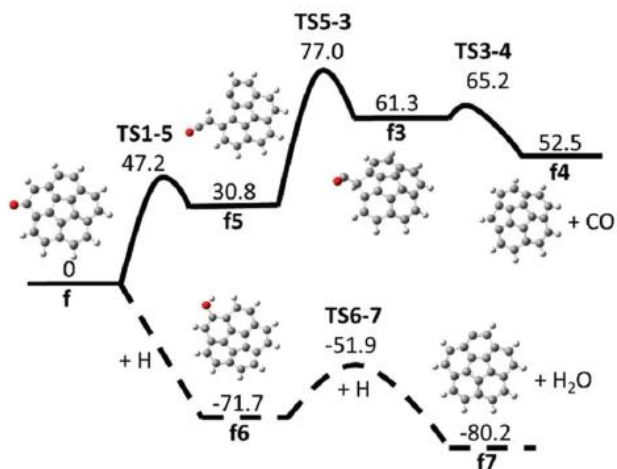
- The full curve in the PES diagram shows the dissociation of the corannulene oxyradical, f, via the intermediate isomer f5.
- The right hand figure shows the time dependence of f, f5 and the product f4. The isomerisation occurs on very short timescales and there is strong CSE/IERE overlap.
- Need strategy to determine rate constants

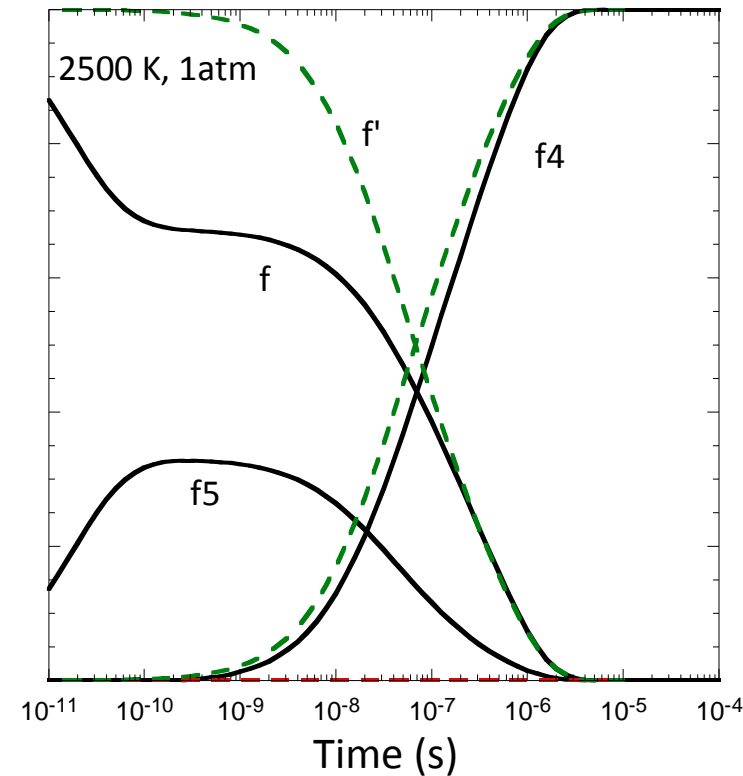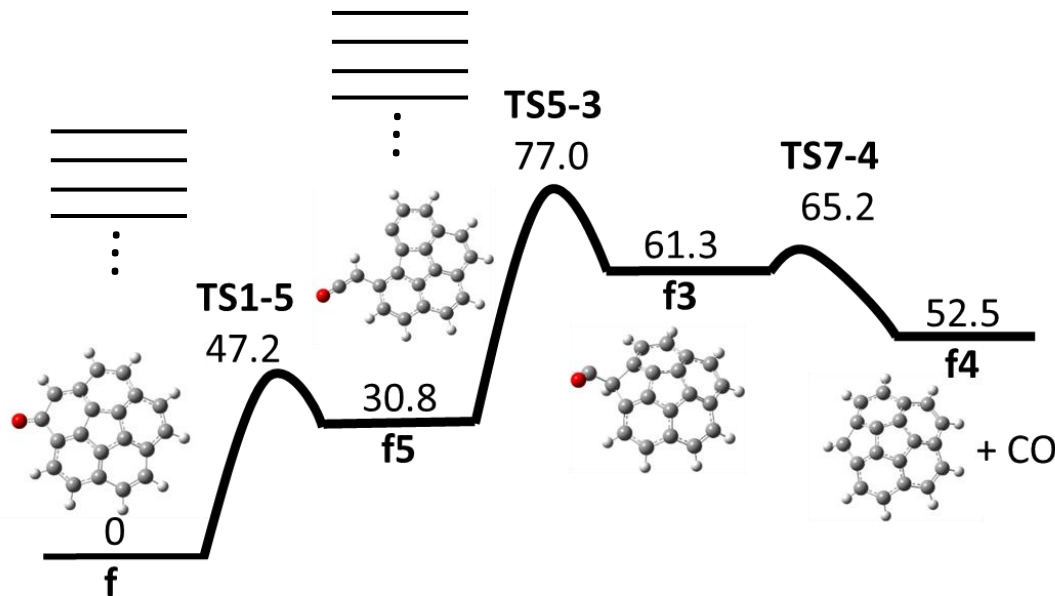# 1st step – how to deal with the fast isomerization

- **The early stage of f and f5 is too fast to be concerned in combustion modeling**
  - ➢ Apply the **micro-equilibrium** for f and f5
  - ➢ Create a combined species containing the sum of states of f and f5

$$\frac{x_f(E)}{\rho_f(E)} = \frac{x_{f5}(E)}{\rho_{f5}(E)} = \frac{x_{f'}(E)}{\rho_{f'}(E)}$$
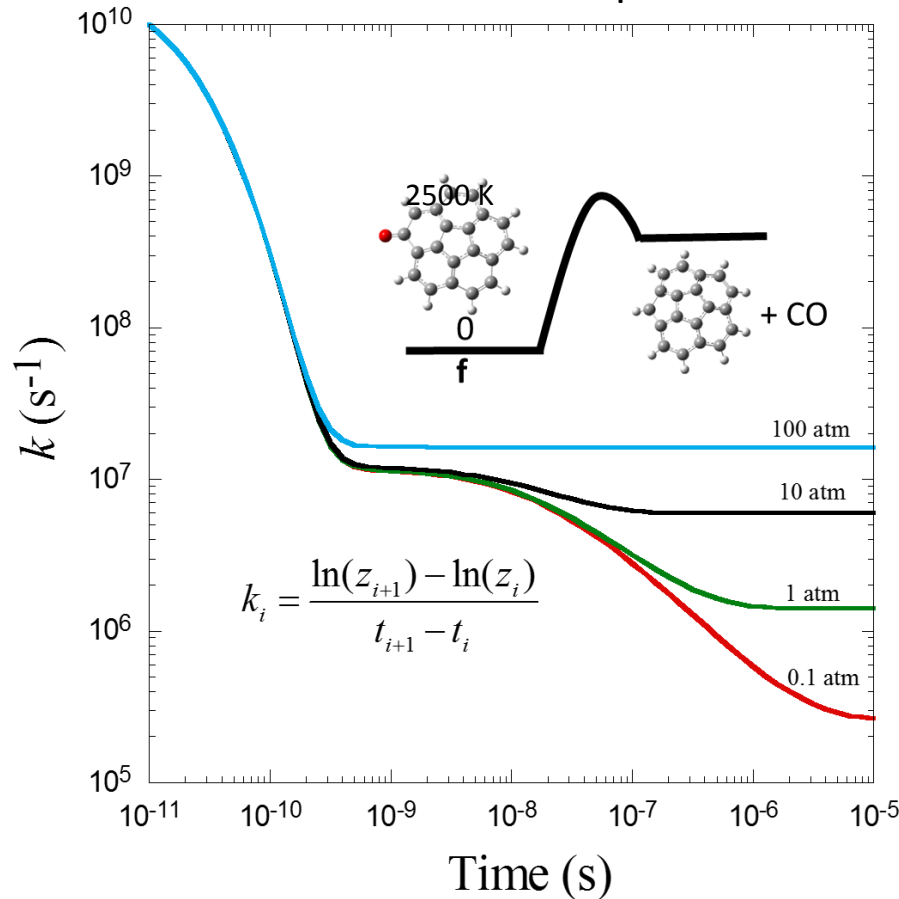
$$\rho_{f'}(E) = (\rho_f(E) + \rho_{f5}(E))$$

$$\frac{dx_{f'}(E)}{dt} = -\frac{W_{TSf5-f3}{}^{\dagger}(E)}{h(\rho_f(E)+\rho_{f5}(E))} x_{f'}(E)$$

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Second step – how to determine rate constants for the dissociation step

- Species reduction can be applied to both f5 and f3, and the reaction becomes f→f4+CO.

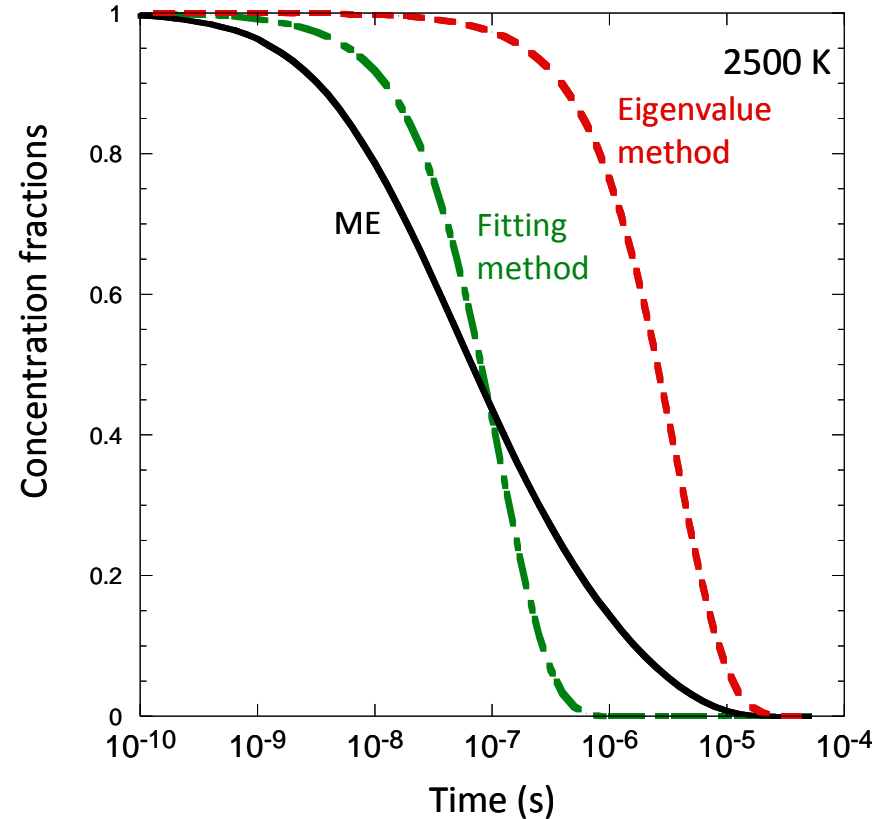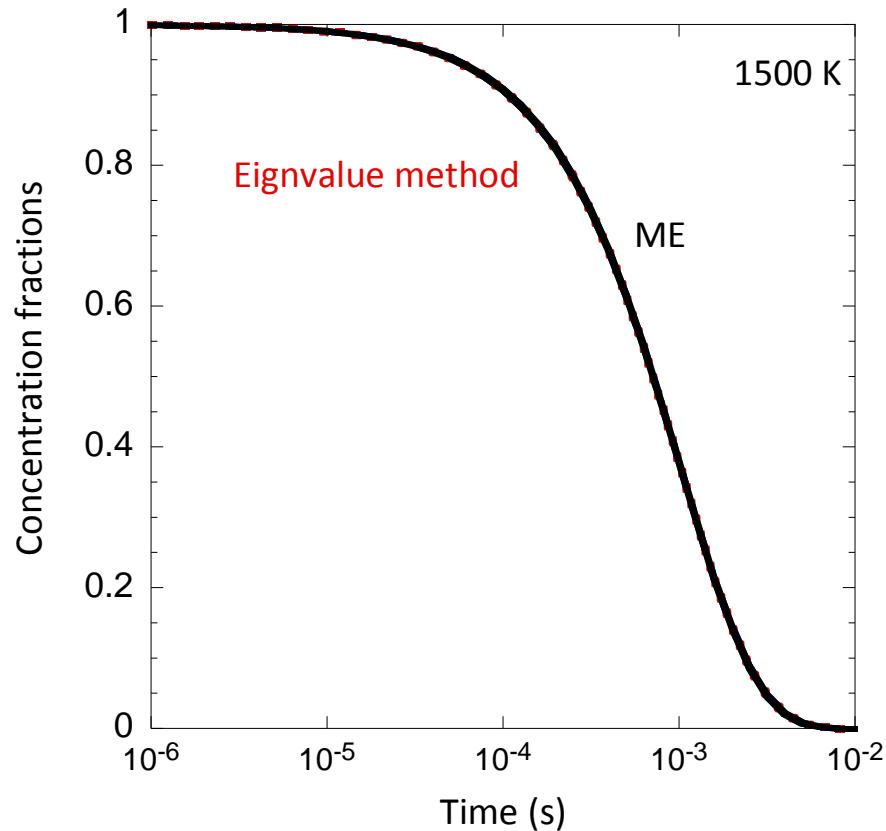- Decay of the reactant and the formation of the products are **highly non-exponential at high**

T.

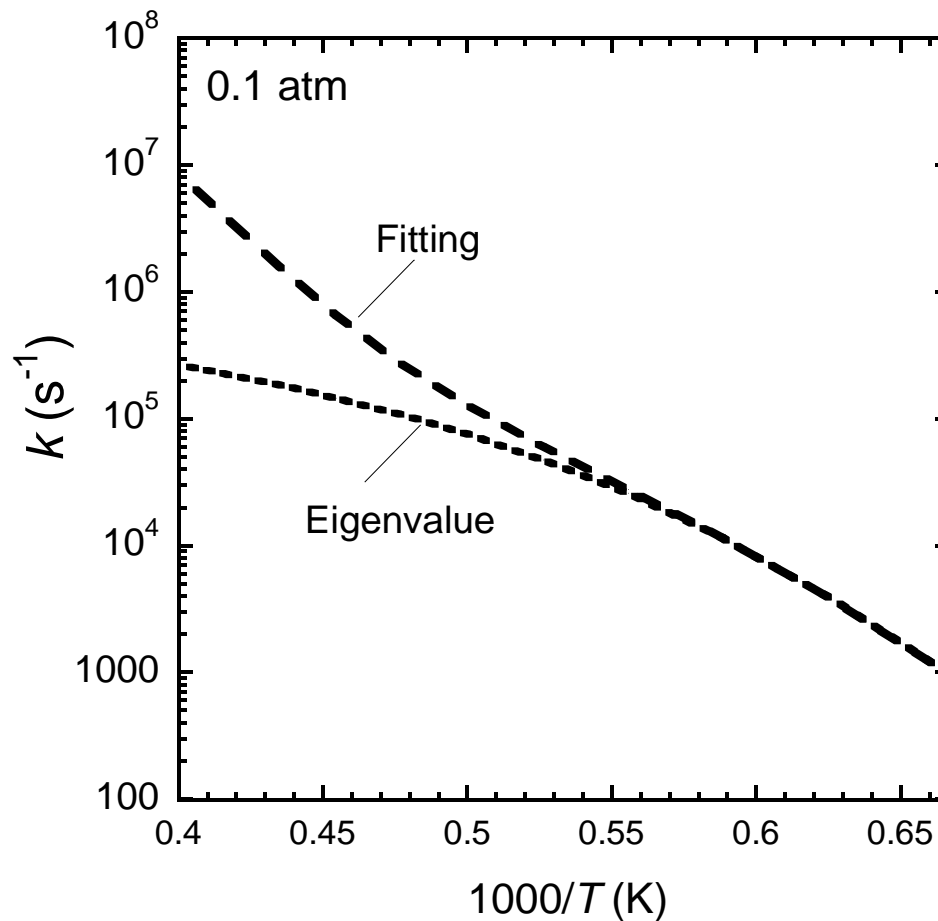$$\frac{d[f4]}{dt} = -\frac{d[f]}{dt} \approx k_{\text{eff}}(p, T)[f]$$

Effective Rate Coefficients

$exp(-k_{eff}t)$ vs. **ME solutions**

- Eigenvalue method: $k_{eff} = -\lambda_1$
- **Fitting method:** $k_{eff}: min \sum_{time}([f] - [f]_{fitted})^2$

Effective Rate Coefficients

- The effective rate coefficients determined by the optimal fitting method are much faster than those

  obtained by the eigenvalue method at high temperatures.