Kinetics of Autoignition

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Kinetics of Autoignition

A. Miyoshi, "Kinetics of Autoignition: Simple Intuitive Interpretation and Its Relation to the Livengood-Wu Integral," *Phys. Chem. Chem. Phys.*, <u>20</u>, 10762–10769 (2018).

Straight Chain Reactions

Cl_2-H_2 — typical chain reactions (and thermal explosion)

$Cl + H_2 \rightarrow H + HCl$
$H + Cl_2 \rightarrow Cl + HCl$

net: **$H_2 + Cl_2 \rightarrow 2\,HCl$**

└ Chain carriers are cancelled out

- Formation of chain carrier
  → reactions continue
  → explosion (thermal feedback)

by using $r_1 = k_1[H_2]$ and $r_2 = k_2[Cl_2]$

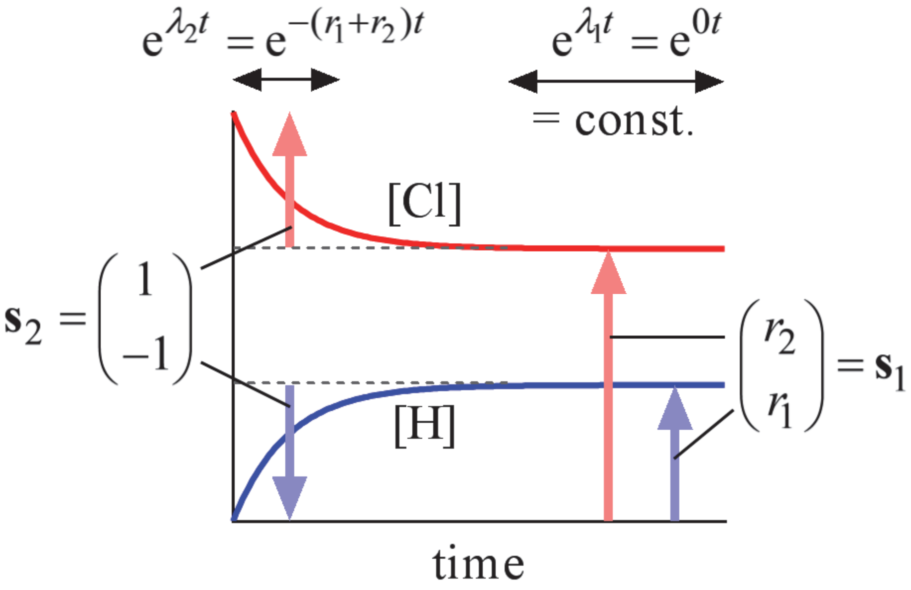
rate equation $\dot{\mathbf{x}} = \mathbf{A}\mathbf{x}$

where $\mathbf{x} = \begin{pmatrix} [Cl] \\ [H] \end{pmatrix}$ and $\mathbf{A} = \begin{pmatrix} -r_1 & r_2 \\ r_1 & -r_2 \end{pmatrix}$

solution $\mathbf{x} = \sum_i a_i \mathbf{s}_i \, e^{\lambda_i t}$

λ_i : eigenvalues, $\mathbf{s}_i$: eigenvectors

building up steady state



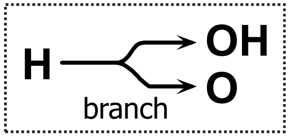
$\lambda_i < 0$ … converging term
$\lambda_i = 0$ … constant term

Branched Chain Reactions

at high temperature & low pressure

H_2-O_2 — typical branched chain reactions (and chain explosion)

$$H + O_2 \rightarrow OH + O$$
$$O + H_2 \rightarrow OH + H$$
$$OH + H_2 \rightarrow H_2O + H$$



net: $2\,H_2 + O_2 \rightarrow OH + H + H_2O$

└ Chain carriers CANNOT be cancelled out

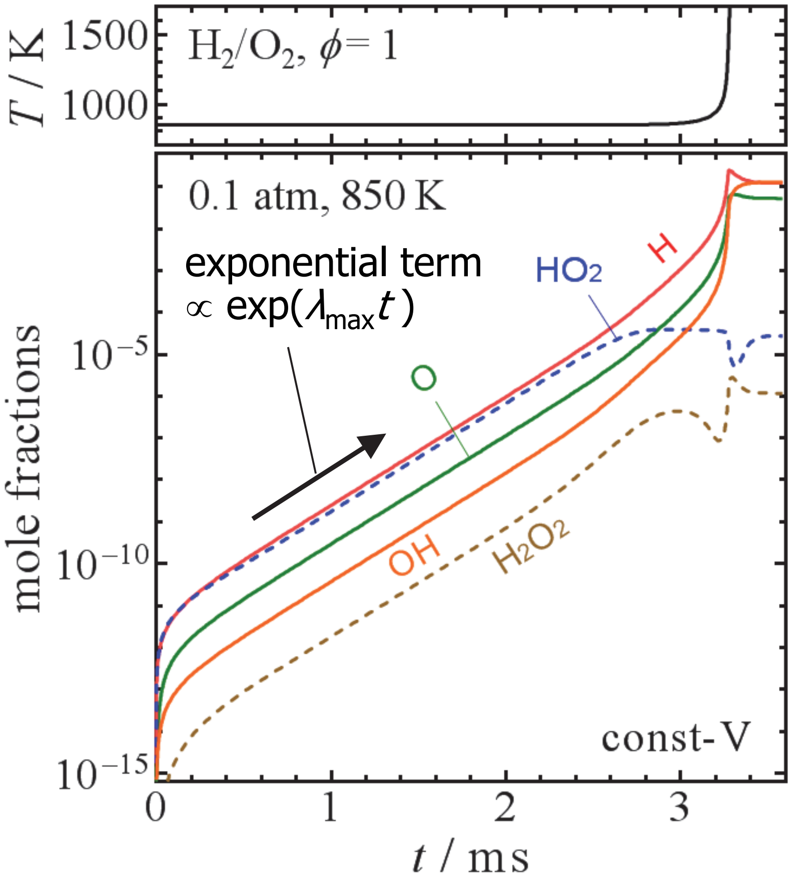
- Selfmultiplication of chain carriers → autoacceleration → explosion

by using $r_1 = k_1[O_2]$, $r_2 = k_2[H_2]$,
and $r_3 = k_3[H_2]$

rate equation $\dot{\mathbf{x}} = \mathbf{A}\mathbf{x}$ where

$$\mathbf{x} = \begin{pmatrix} [H] \\ [O] \\ [OH] \end{pmatrix} \text{ and } \mathbf{A} = \begin{pmatrix} -r_1 & r_2 & r_3 \\ r_1 & -r_2 & 0 \\ r_1 & r_2 & -r_3 \end{pmatrix}$$

solution $\mathbf{x} = \sum_i a_i \mathbf{s}_i \, e^{\lambda_i t}$



exponential term $\propto \exp(\lambda_{max} t)$

$\lambda_{max} > 0$ … diverging solution

Explosion Limits as $\lambda_{max} = 0$

$$H + O_2 \rightarrow OH + O$$
$$O + H_2 \rightarrow OH + H$$
$$OH + H_2 \rightarrow H_2O + H$$
$$\boxed{H + O_2 + M \rightarrow HO_2 + M}$$

added

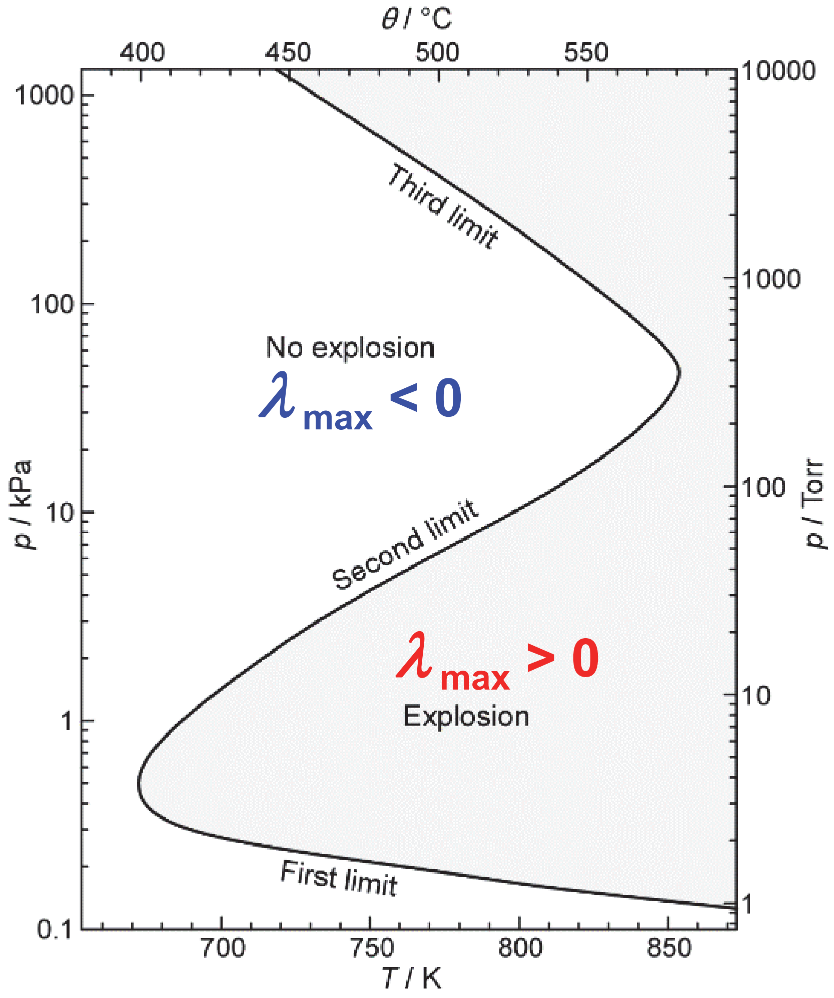
- Sign of λ_{max} varies with condition
  → 2nd explosion limit

by using $r_1 = k_1[O_2]$, $r_2 = k_2[H_2]$, $r_3 = k_3[H_2]$, and $r_4 = k_4[O_2][M]$

rate equation $\dot{\mathbf{x}} = \mathbf{A}\mathbf{x}$ where

$$\mathbf{x} = \begin{pmatrix} [H] \\ [O] \\ [OH] \end{pmatrix} \text{ and } \mathbf{A} = \begin{pmatrix} -r_1 - r_4 & r_2 & r_3 \\ r_1 & -r_2 & 0 \\ r_1 & r_2 & -r_3 \end{pmatrix}$$

solution $\mathbf{x} = \sum_i a_i \mathbf{s}_i \, e^{\lambda_i t}$



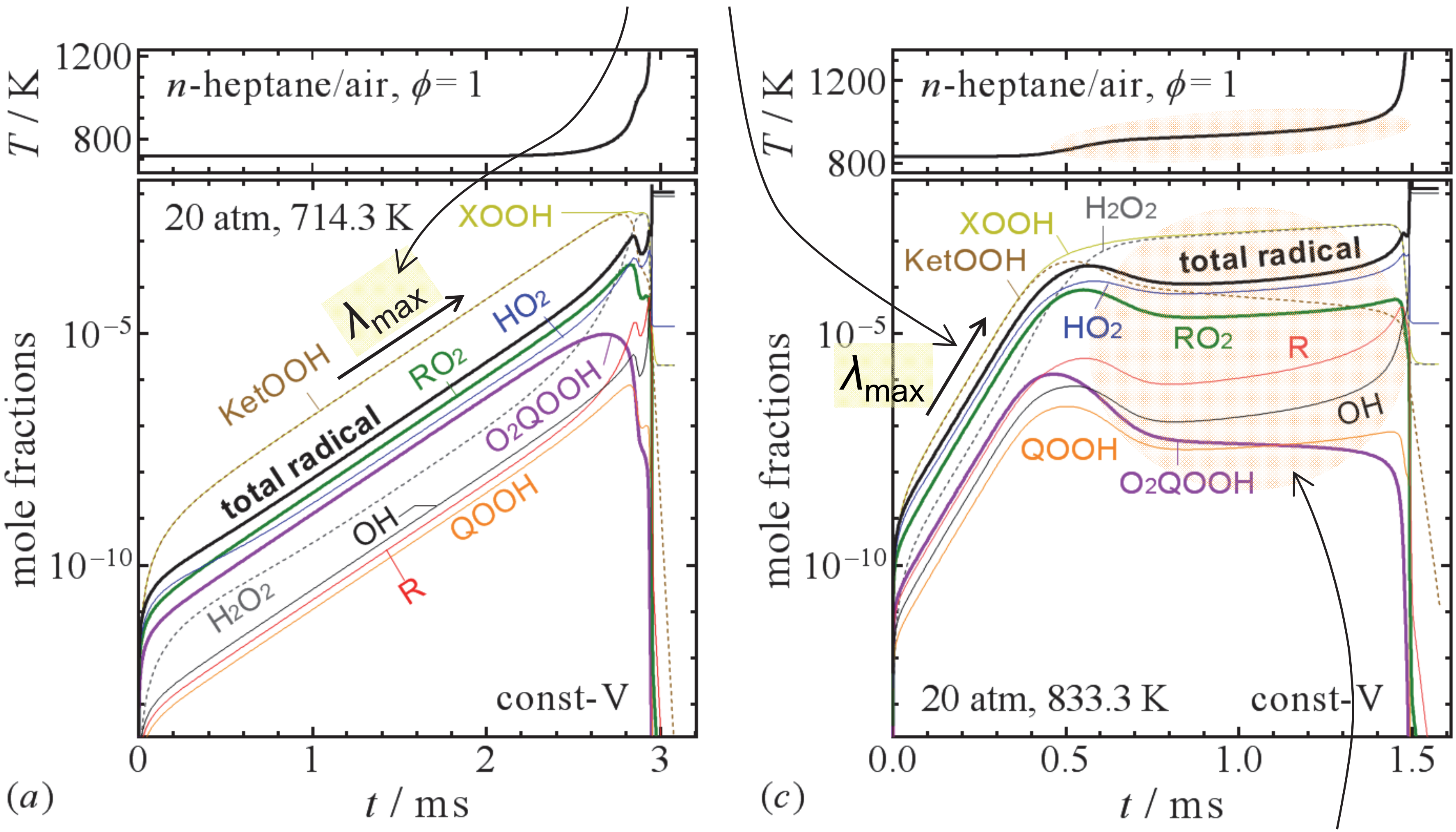
λ_{max} = 0 … explosion limit

K. K. Foo and C. H. Yang, *Combust. Flame*, 17, 223–235 (1971).
W. Kordylewski and S. K. Scott, *Combust. Flame*, 57, 127–139 (1984).

Autoignition of Alkanes

Ignition mechanism varies with condition

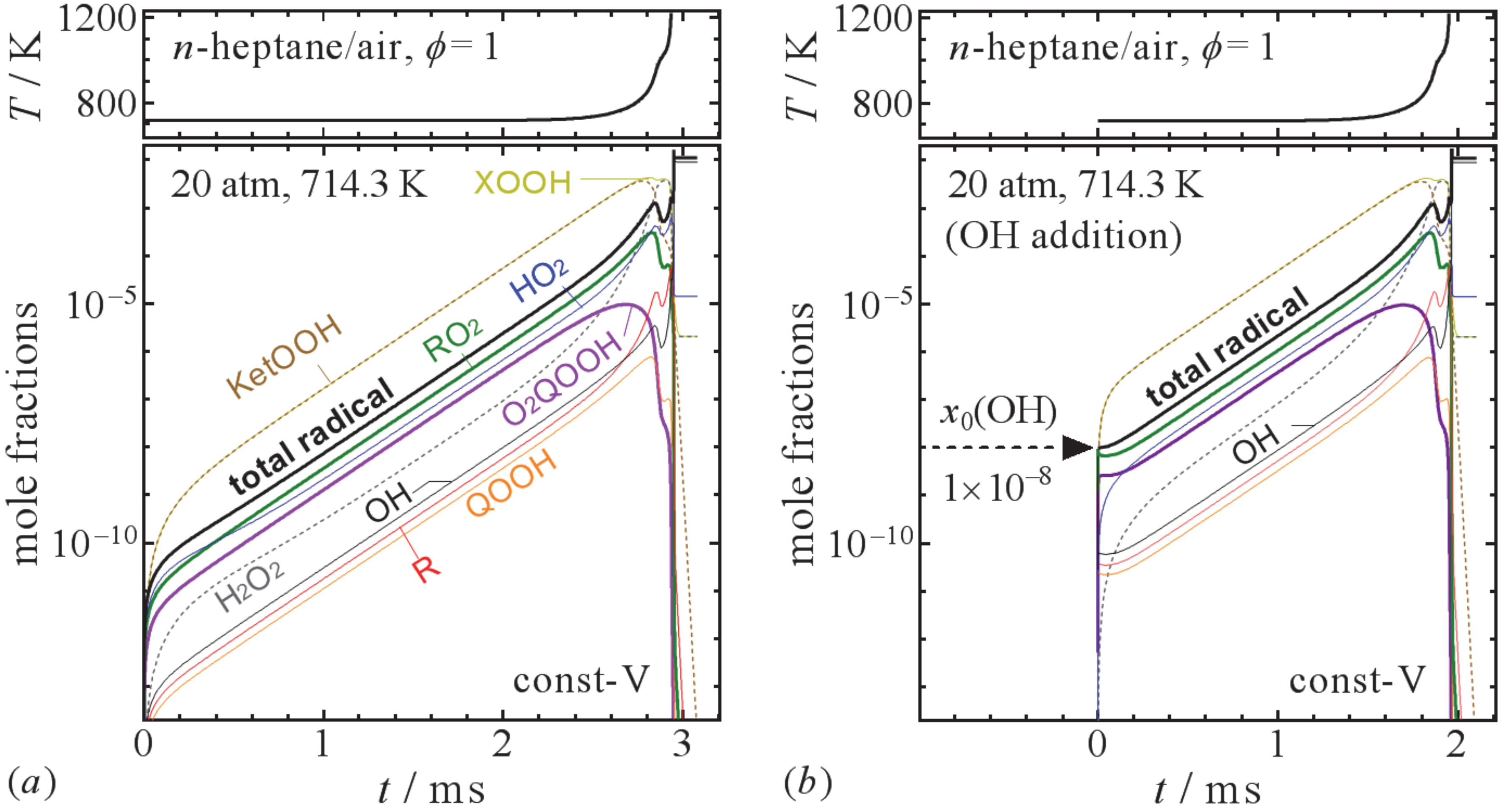
Before Cool Flame: **Chain-Reaction** Controlled (chain explosion)



After Cool Flame: **Thermally** Controlled (thermal explosion)

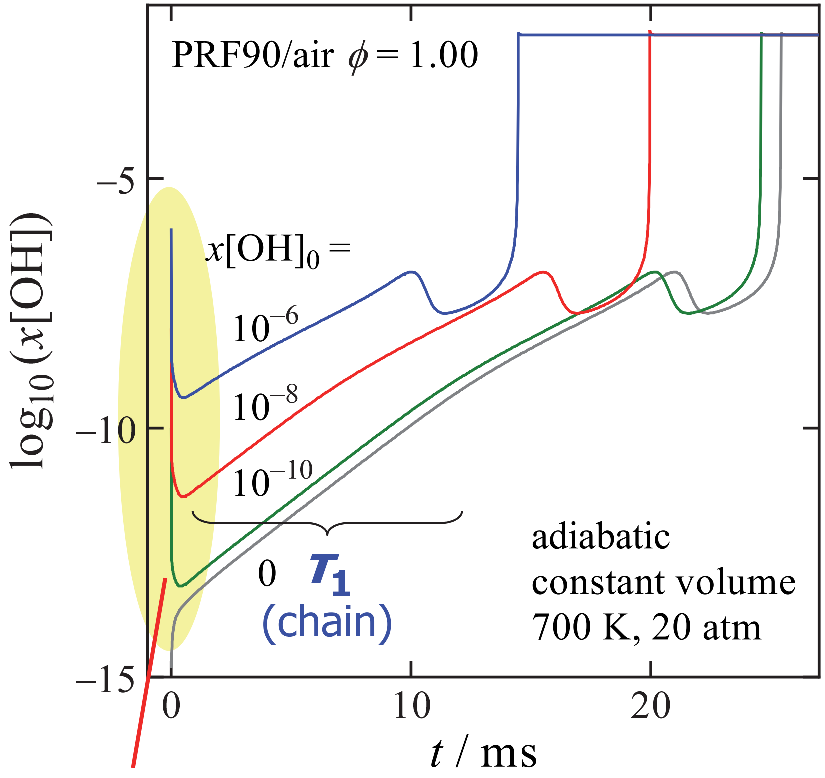
Active Species Addition (chain-controlled region)

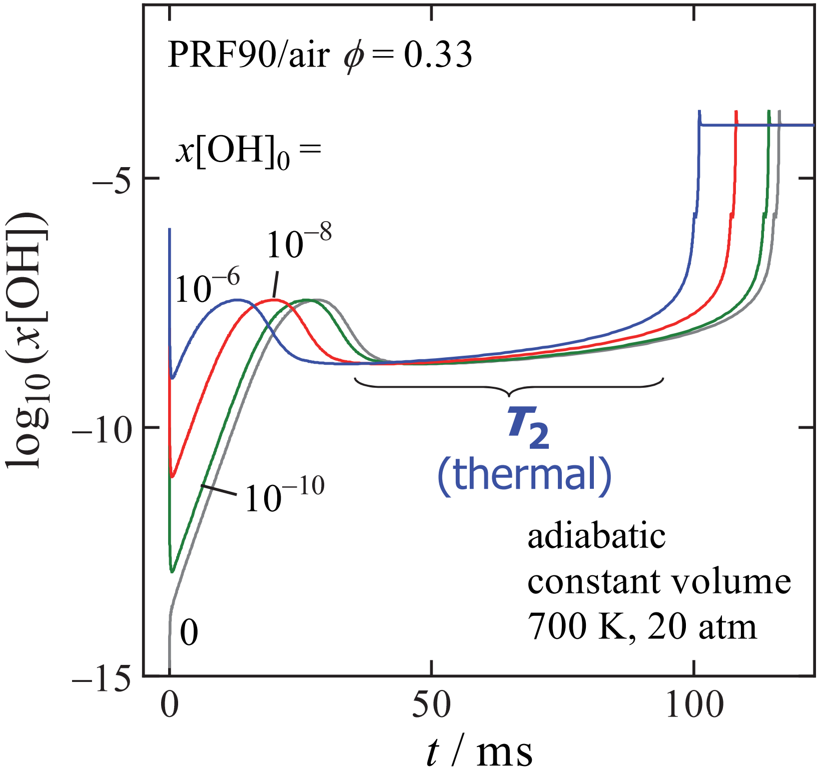
- **x(OH) ≈ x(total radical)** → **independent** of species added
- x(OH) promptly decays to steady state → robust steady state of radicals
- Additive effect diminishes exponentially with time



Logarithmic Effect of Active Species Addition

- OH addition increases starting point of exponential growth (Effect is **logarithmic**)
- Affects **only** τ_1 (chain ignition)
- **Not effective** where τ_2 dominate (e.g. at low equivalence ratio)

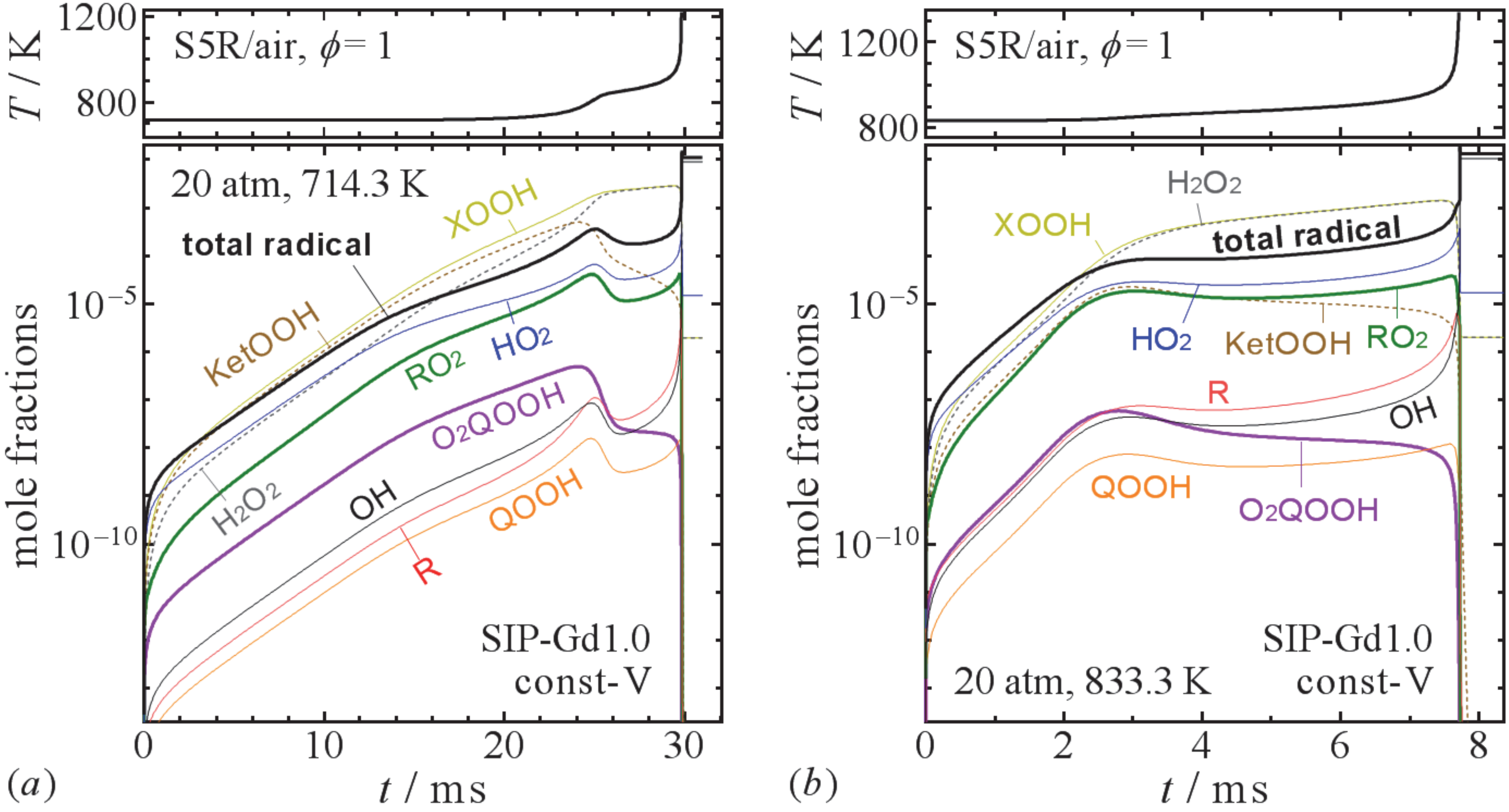




$[OH]_{ss} \approx 10^{-3}\ [OH]_{added}$

Autoignition of Gasoline Surrogate

- 5-component surrogate (alkane, cycloalkane, alkene, aromatics) shows **essentially the same behavior**



Livengood-Wu Integral

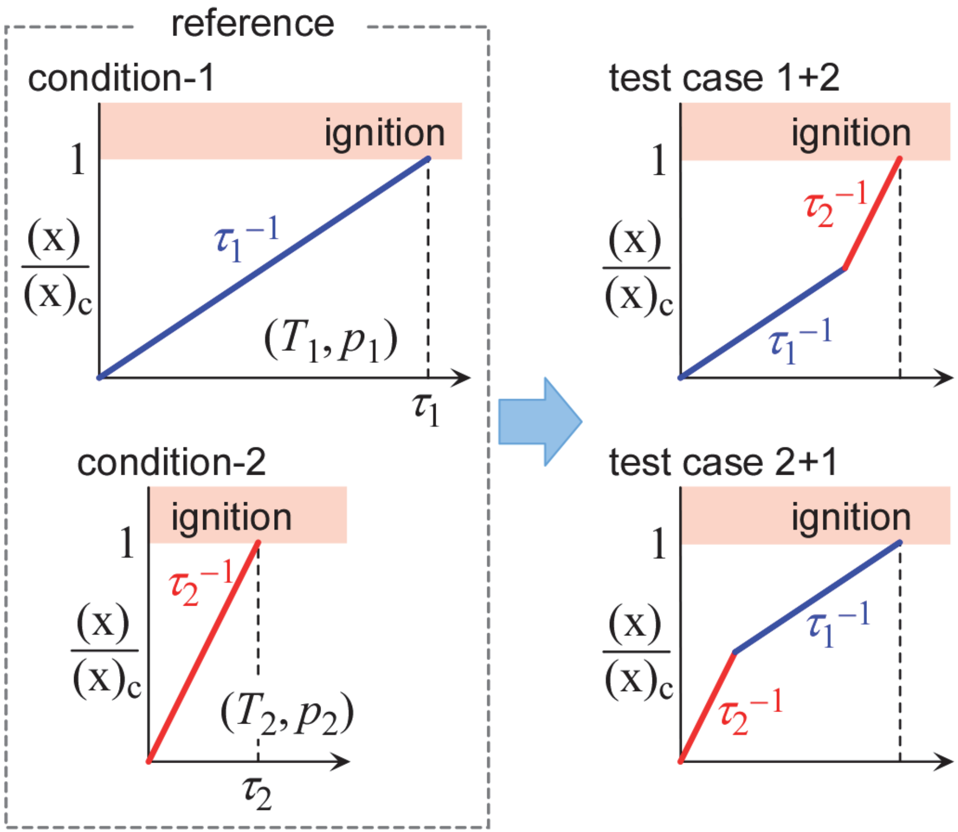
Livengood-Wu (L-W) Integral

J. C. Livengood and P. C. Wu, *Proc. Combust. Inst.*, 5, 347–356 (1955).

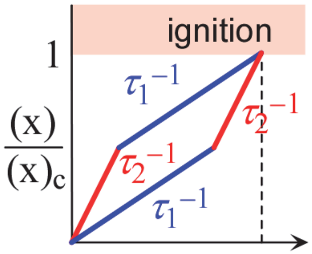
Assumptions:

- Autoignition occurs when the concentration of "pertinent reaction product *x*" reaches the critical value $(x)_c$.
- The rate of increase of $(x)/(x)_c$ is a function of T and p and equal to $\tau^{-1}(T, p)$, reciprocal of the ignition delay time, $\tau(T, p)$, at this condition.
- This relation holds for all T and p during the piston compression and expansion

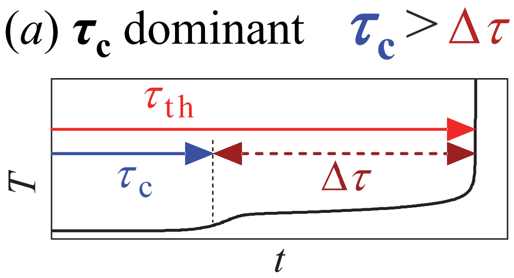
$$1 = \int_0^{t_{\mathrm{ign}}} \frac{\mathrm{d}t}{\tau(T, p)}$$

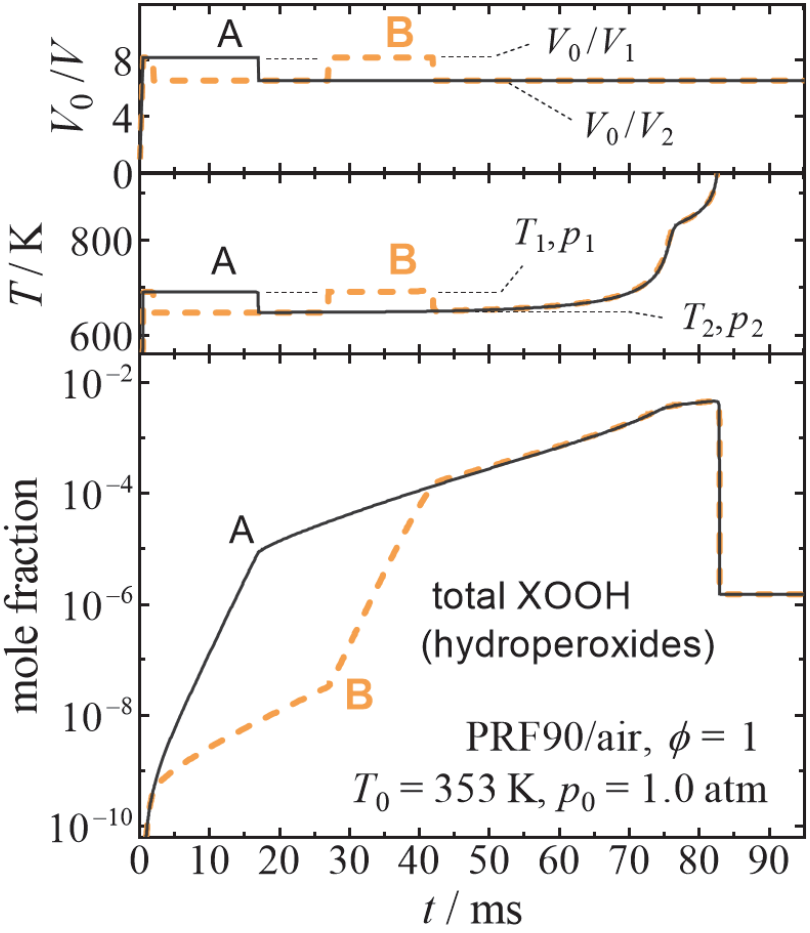


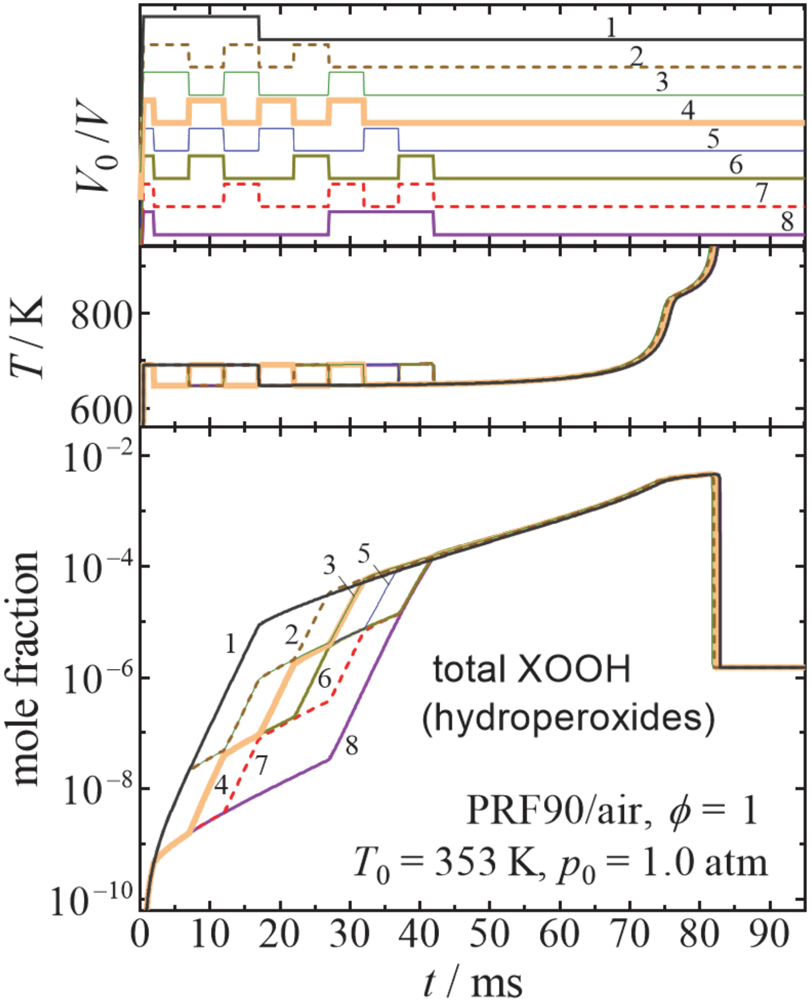
Volume Change (80 °C, 1.0 atm)



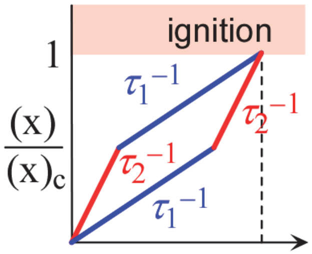
- *V*-change only before cool flame
  → Same ignition delay time





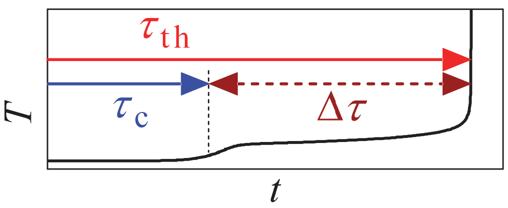


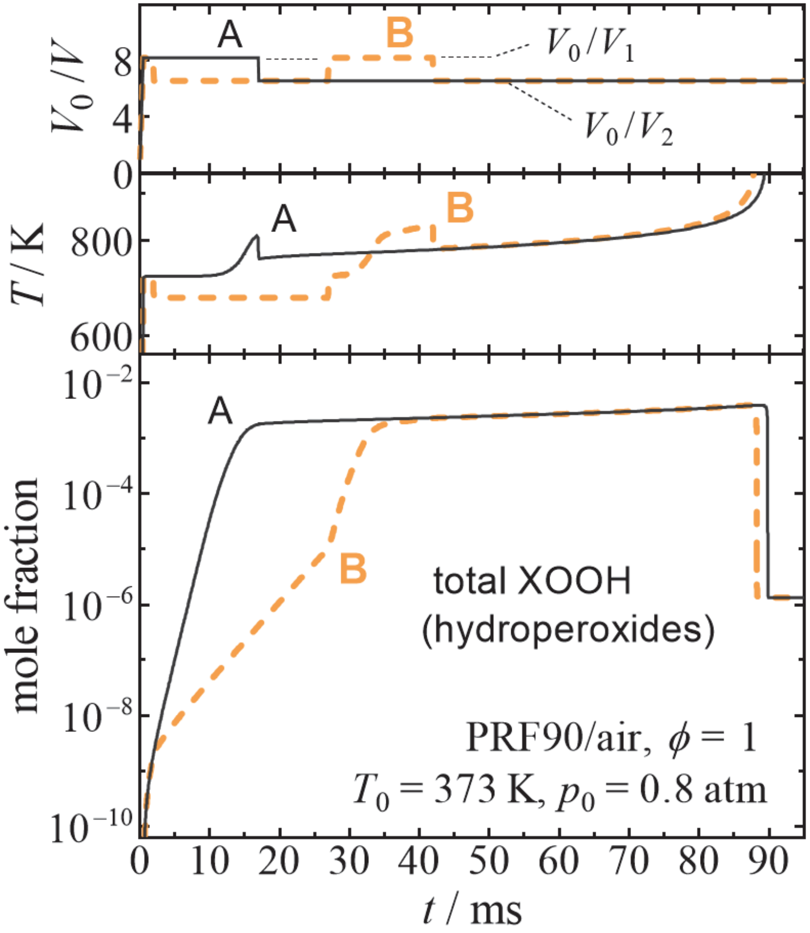
Volume Change (100 °C, 0.8 atm)

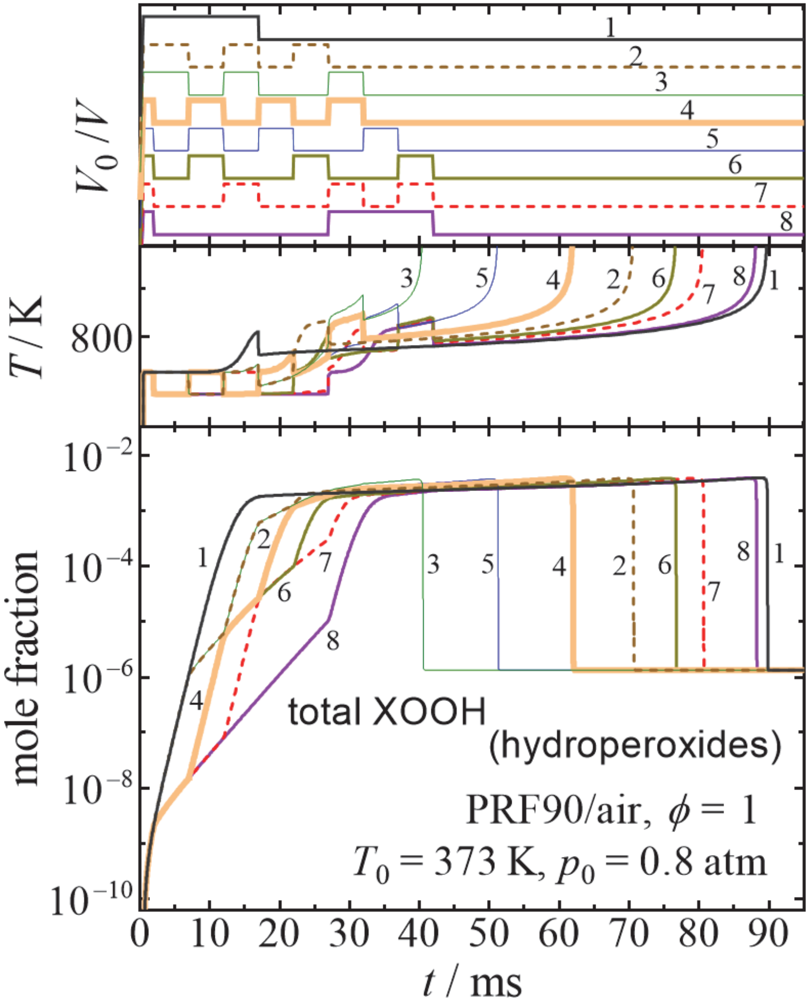


- *V*-change both before and after cool flame → Large non-ordered variation

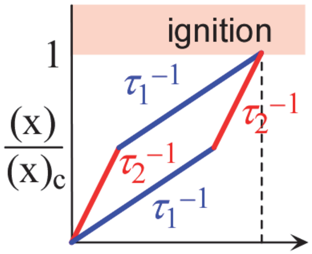
(*b*) $\boldsymbol{\tau_c}$ & $\boldsymbol{\Delta\tau}$ $\tau_c \sim \Delta\tau$





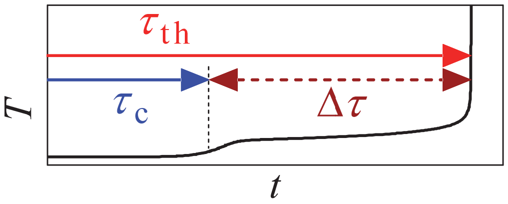


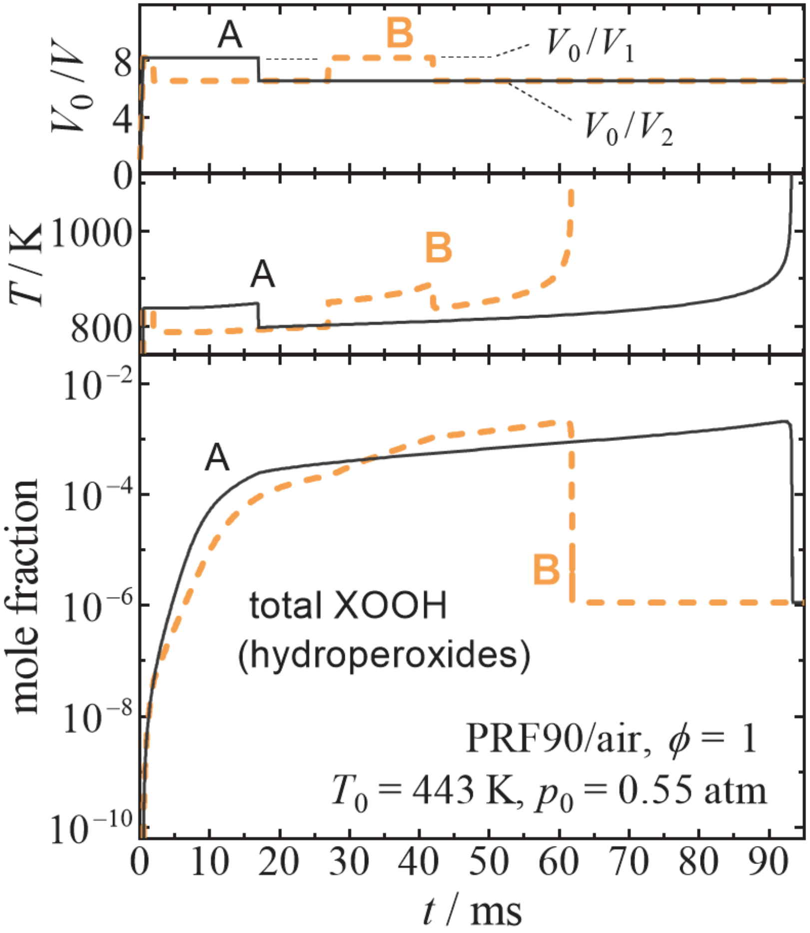
Volume Change (170 °C, 0.55 atm)

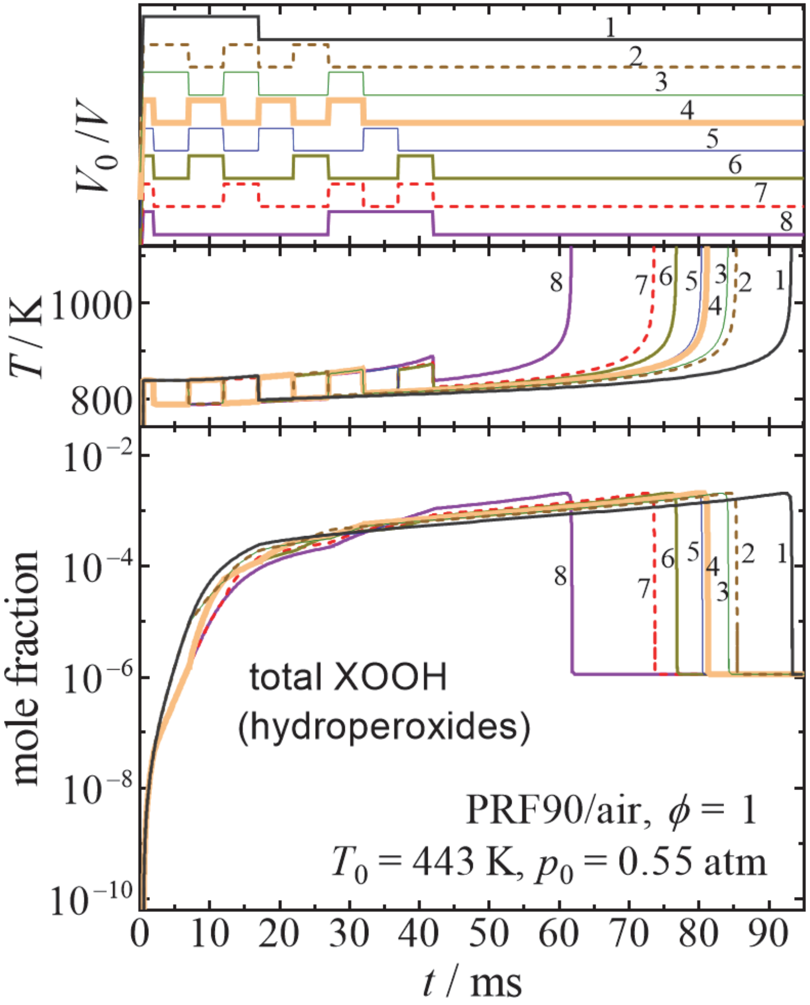


- *V*-change mostly after cool flame
  → Small but ordered variation

(*c*) **Δτ** dominant $\tau_c < \Delta\tau$







Zero-Dimensional SI Knock Modeling

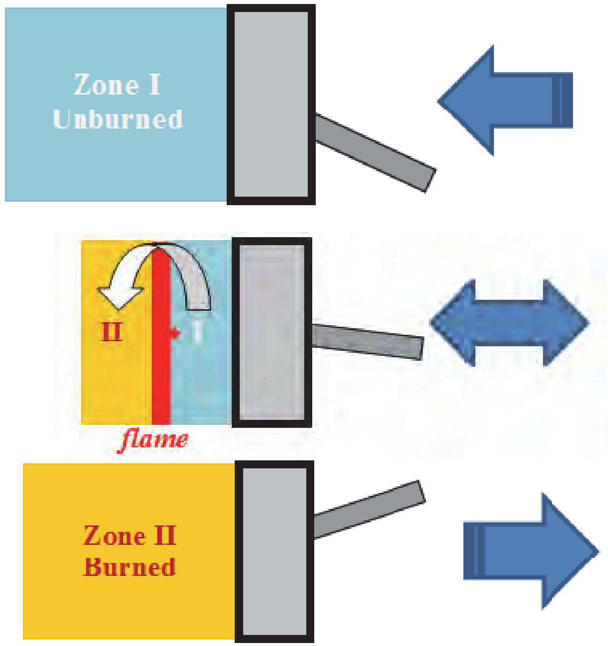
A. Miyoshi, "Chemical Kinetic Analysis on the Effect of the Occurrence of Cool Flame on SI Knock," *Int. J. Automotive Engineering*, 8 (3) 130–136 (2017) #20174103.

Zero-Dimensional Knock Modeling

— SI Engine Zonal Model

in Chemkin-Pro 15141 and later
(15151, ANSYS 17.X/18.0)

- Reciprocating engine with Woschni heat loss
- Mass fraction of burnt zone: Vibe (Wiebe) function (function of crank angle)
- Pressure equilibrium between zones



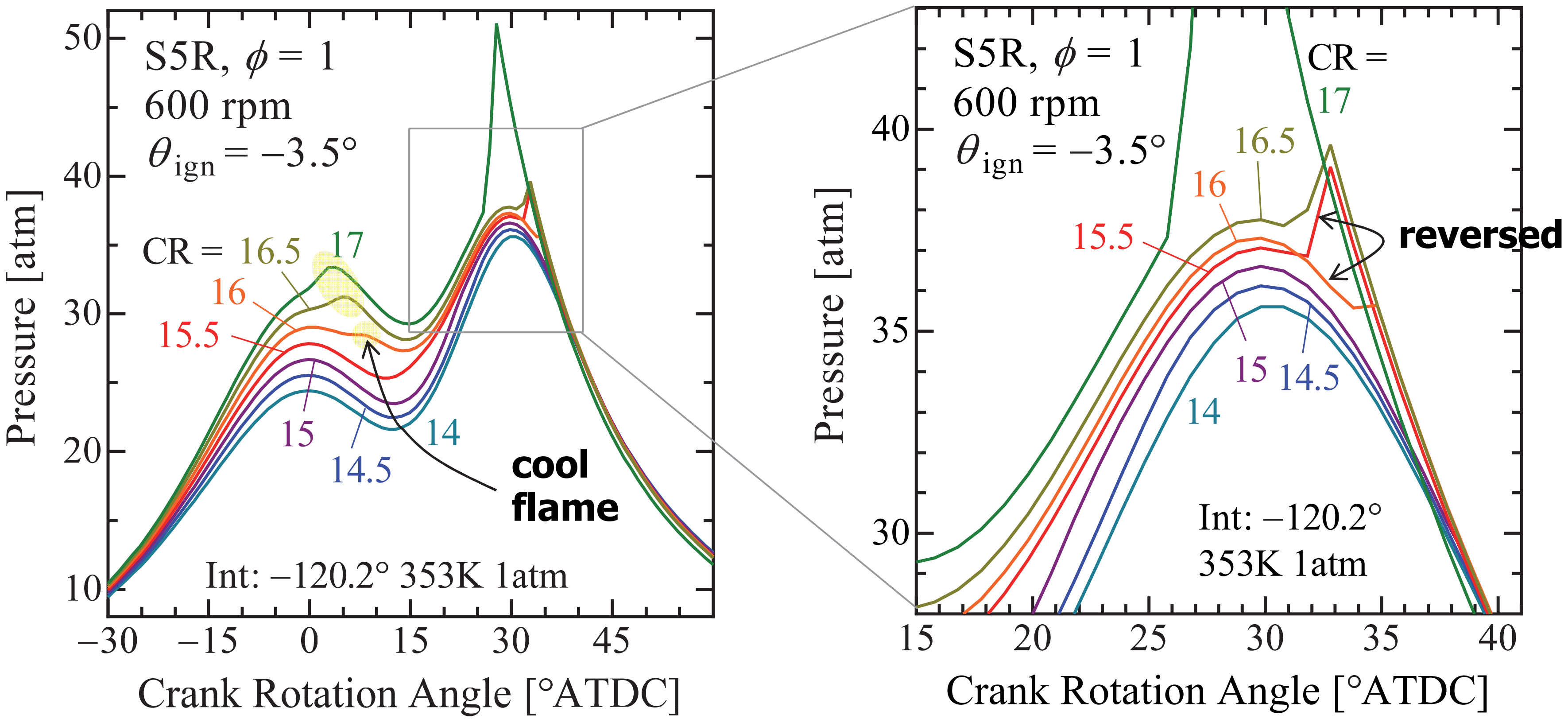
Model based on: T. Noda, K. Hasegawa, M. Kubo and T. Itoh, "Development of Transient Knock Prediction Technique by Using a Zero-Dimensional Knocking Simulation with Chemical Kinetics," SAE Technical Paper 2004-01-0618 (2004).

Illustration from: Chemkin-Pro Theory Manual (15141)

Pressure Profiles around Knock Limit

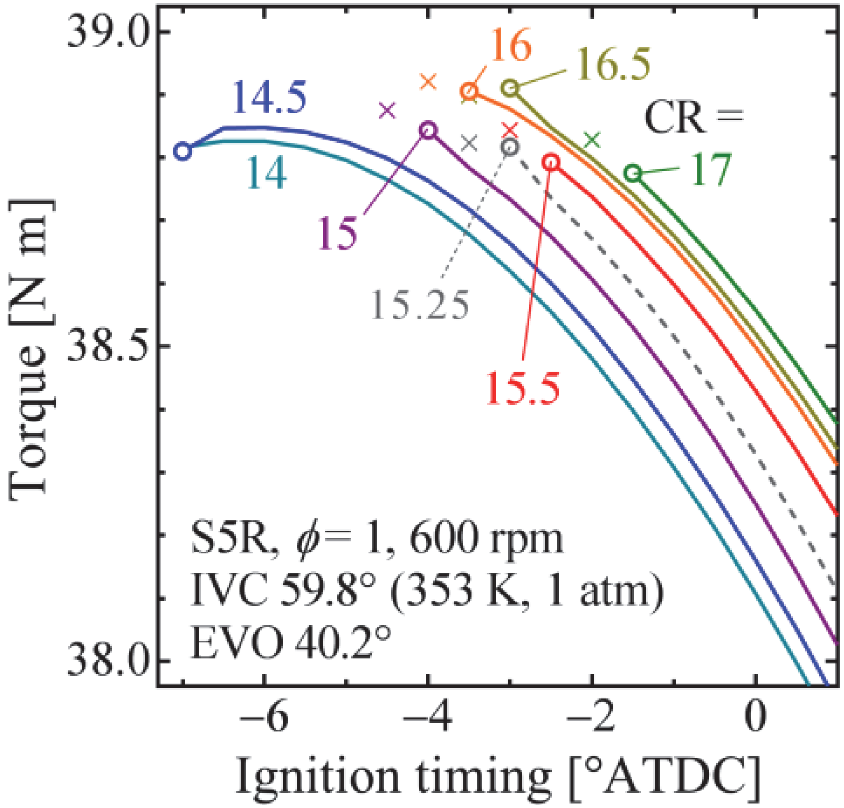
— Pressure profiles at IGT=3.5 BTDC (near knock limit)

- Appearance of cool flame seems to be inhibiting (?) knock
- IMEP increases by the occurrence of cool flame



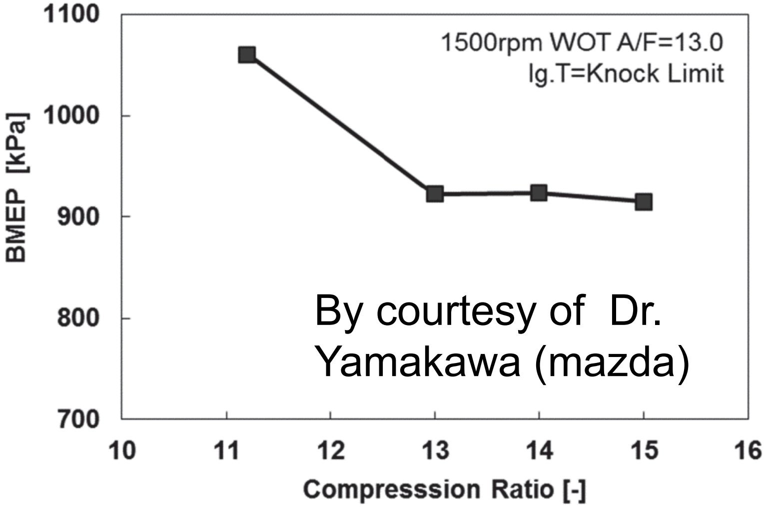
SKYACTIV-G

- Knock limit advances as CR ↑: CR15.5(−2.5°) → CR16(**−3.5°**)



Resembles SKYACTIV-G engine combustion

(High compression ratio gasoline engine)

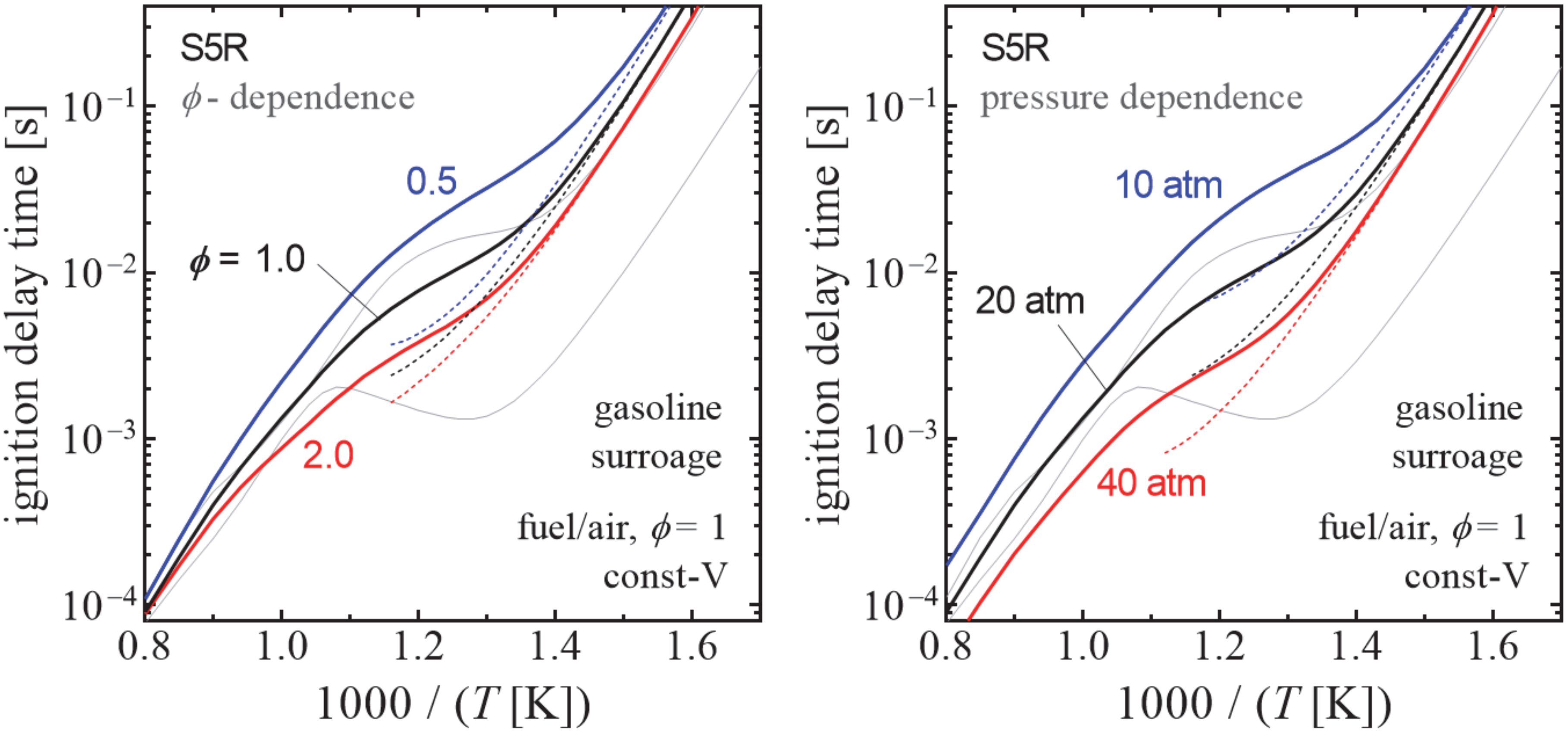


By courtesy of Dr. Yamakawa (mazda)

Yamakawa, M., Youso, T., Fujikawa, T., Nishimoto, T., Wada, Y., Sato, K., and Yokohata, H., SAE Int. J. Fuels Lubr. 5: 98−105 (2012).

Surrogate Shows No NTC Behavior

- Not because of NTC!



Summary

— Kinetics of Autoignition (chain explosion)

- Total concentration of radical (or XOOH) increases exponentially with time before cool flame

→ log x(radical) increases LINEARLY with time

— Livengood-Wu Integral

- Integrand supposed to be the log(radical) or log(XOOH)
- Good predictability for tau-cool, but moderate for tau-thermal

— Knock Modeling (SKYACTIV-G)

- Increase of compression ratio results in advance of TGT
- Similar phenomenon has been recognized during the development of SKYACTIV-G