

燃焼における化学反応解析

東京大学工学系研究科
総合研究機構 JAXA社会連携講座
越 光男

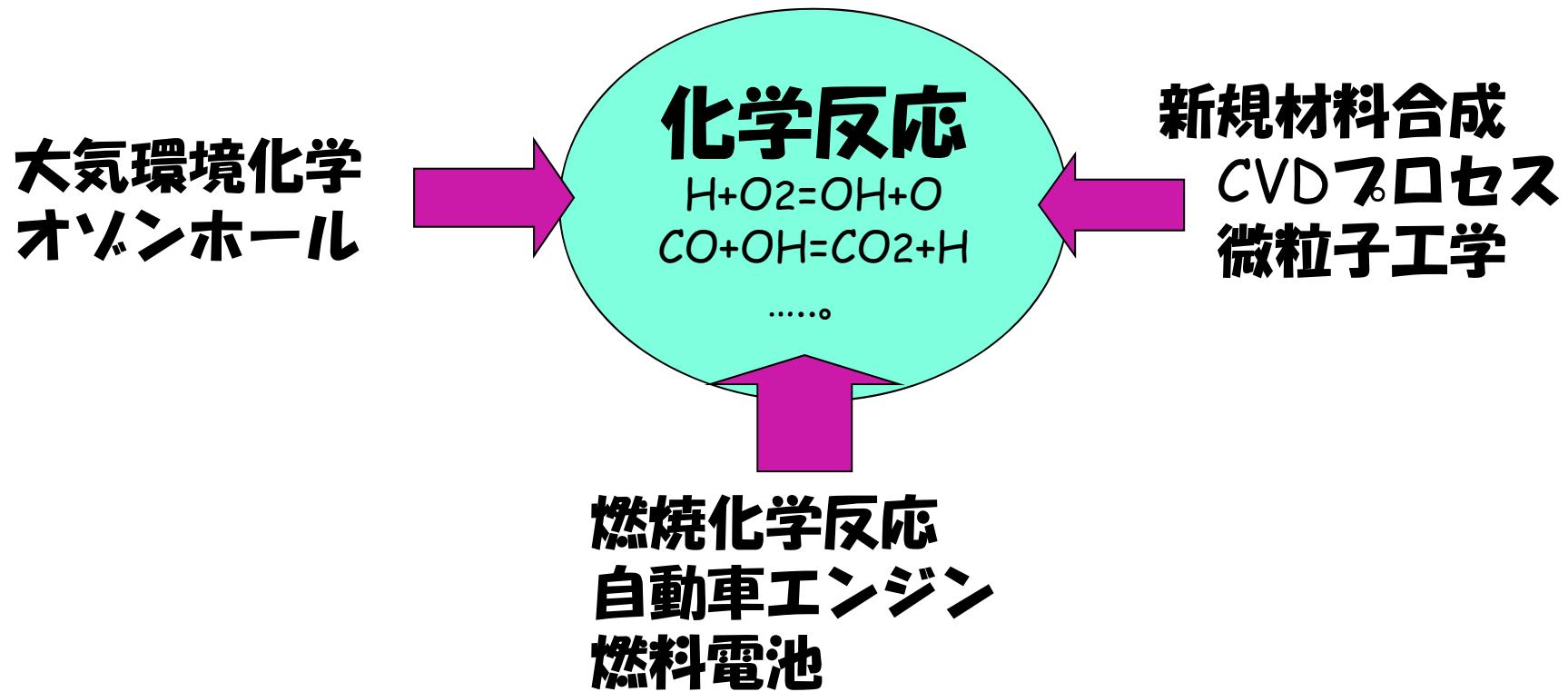
第48回 燃焼シンポジウム
2010.12.1 at 福岡

概要

1. はじめに
2. 素反応と反応速度定数
3. 燃焼反応機構
 - 水素の燃焼反応
 - 炭化水素(アルカン)の燃焼反応
4. 反応解析の応用
 - サロゲート燃料の反応機構
 - 反応機構の簡略化
5. おわりに

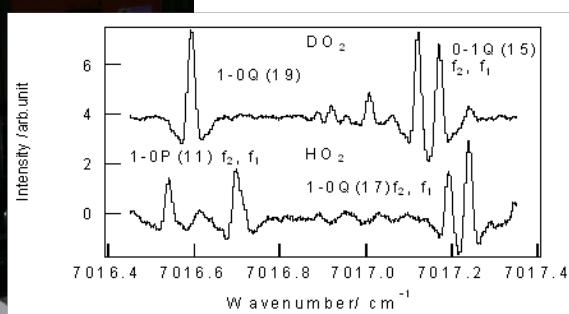
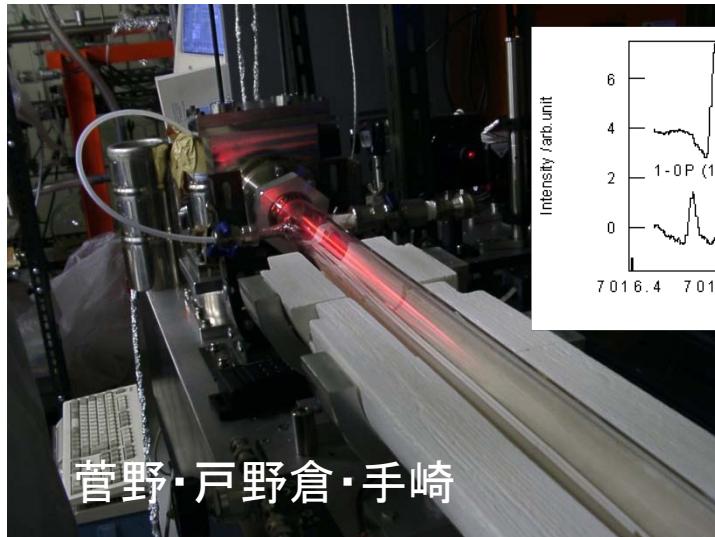
1. はじめに

化学反応の関与する現象=>反応解析

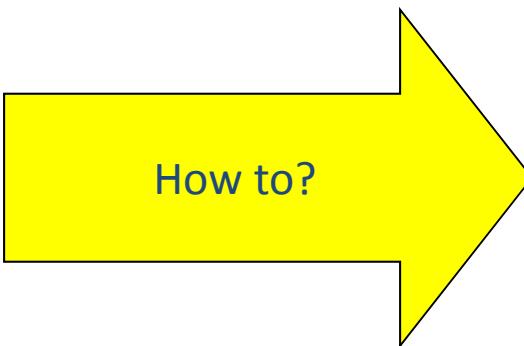
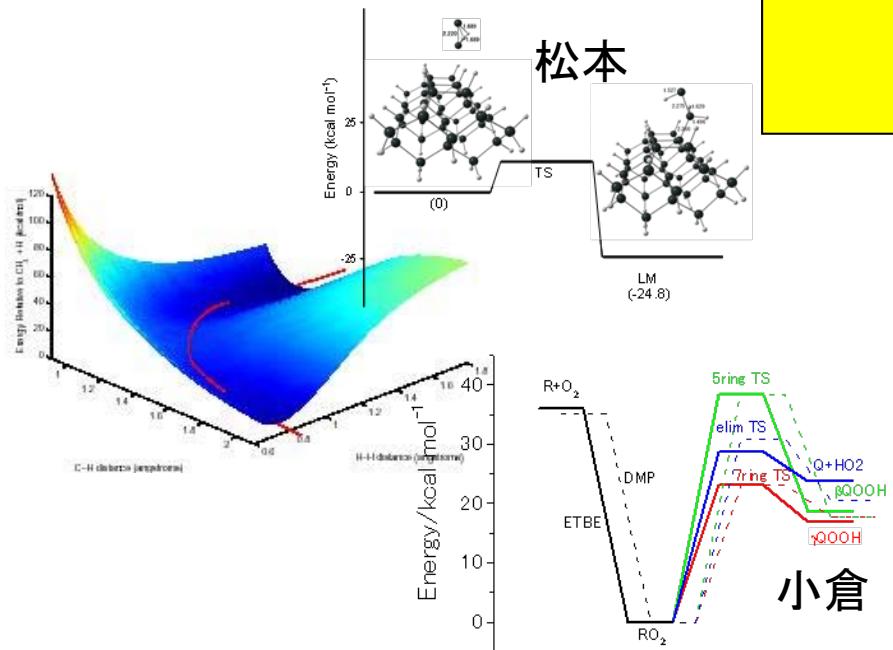


燃焼 = 流体力学 + 化学反応

反応素過程: 分子から実世界へ

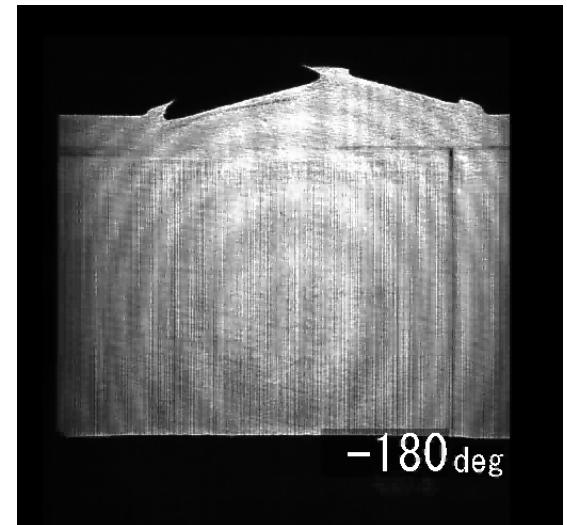


菅野・戸野倉・手崎



How to?

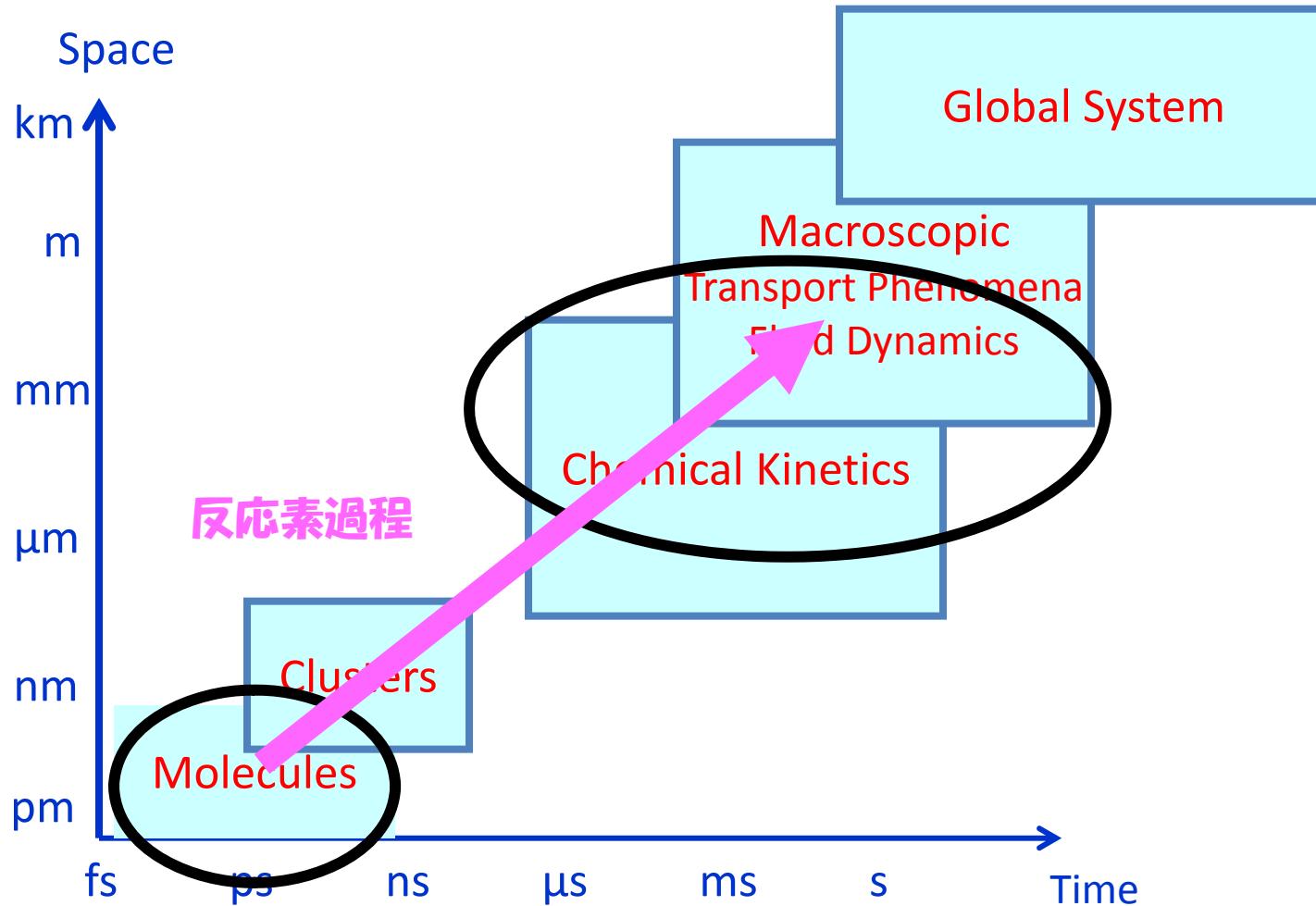
H-II Bロケット



HCCIエンジン
(提供:富士重工)

-180 deg

反応素過程: 分子から実世界へ



2. 素反応と反応速度定数

素反応と反応の“分子数”

- 素反応
分子が単一の過程で原子の組み換えを行う反応
- 反応の分子数
 - 单分子反応 $A = B + C$
 - 二分子反応 $A + B = C + D$
 - 三分子反応 $A + B + M = AB + M$
 M : Third Body(第三体)
- 反応機構
通常反応系は多数の素反応の集合からなる
素反応の集合 \Rightarrow 反応機構

(注 : 反応次数 $n = n_a + n_b - \frac{d[A]}{dt} = k[A]^{n_a} [B]^{n_B} \dots$)

素反応の反応速度定数

$$k_{uni} = \frac{\int_{E_0}^{\infty} k(E) g(E) dE}{\int_{E_0}^{\infty} g(E) dE}$$

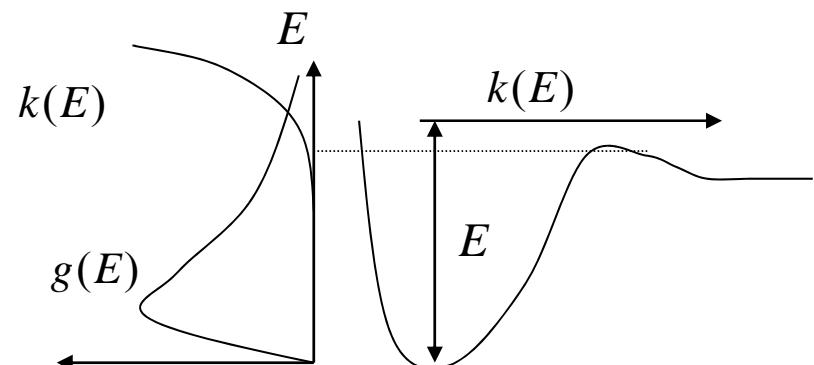
$$k(E) = \frac{\int_0^{E-E_0} \rho^+(E_+) dE_+}{h\rho(E)}$$

$k(E)$: microcanonical rate constant

$g(E)$: distribution function

$\rho(E)$: Density of states of reactants

$\rho^+(E_+)$: Density of states
of the activated complex



At thermal equilibrium:

Energy Transfer Rates $\gg k(E) \Rightarrow$ Boltzmann distribution

$$g(E) = \rho(E) \exp(-E/kT) \quad k_{uni}^\infty = \frac{kT}{h} \frac{Q^+}{Q} \exp(-E_0/kT)$$

\Rightarrow 高圧極限 = 遷移状態理論による速度定数

$g(E)$ がBoltzmann分布でないときは？

- Master equation analysis

$$\frac{\partial g(E,t)}{\partial t} = [M] \int_0^\infty [R(E,E')g(E',t) - R(E',E)g(E,t)]dE' - k(E)g(E,t)$$

at steady state

$R(E',E)$:エネルギー移動速度

$$-k_{uni}g(E) = [M] \int_0^\infty [R(E,E')g(E') - R(E',E)g(E)]dE' - k(E)g(E)$$

低圧では

$$R(E',E) \ll k(E)$$

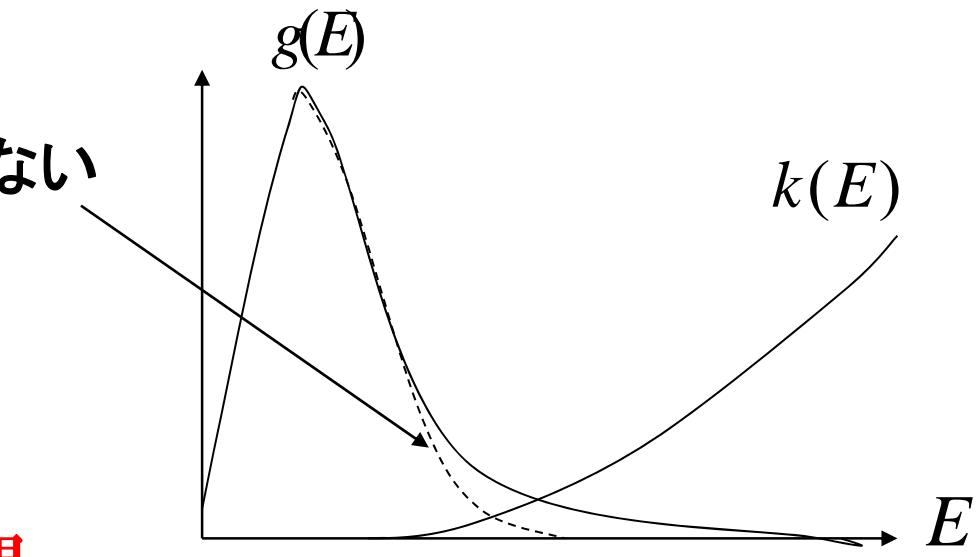
=> Boltzmann分布にならない

=> 速度の低下

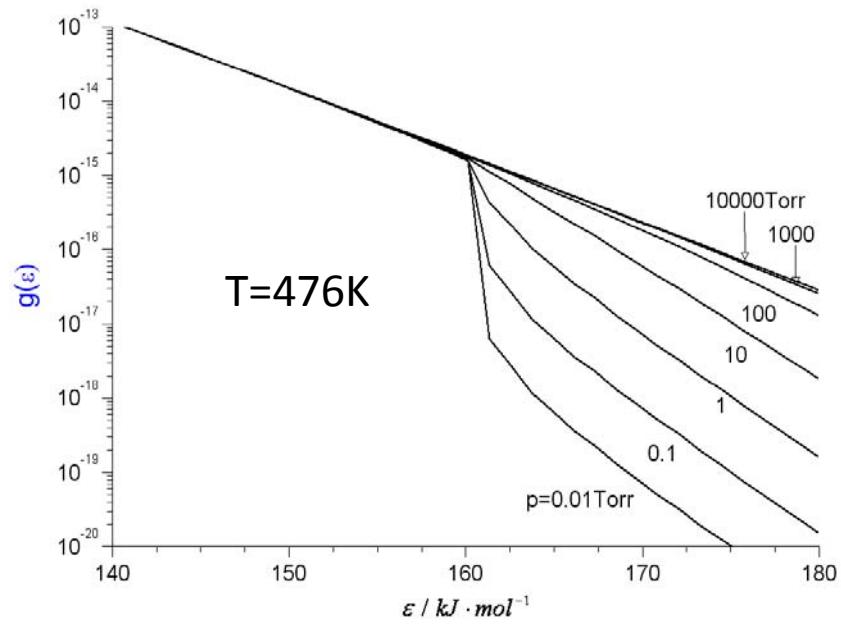
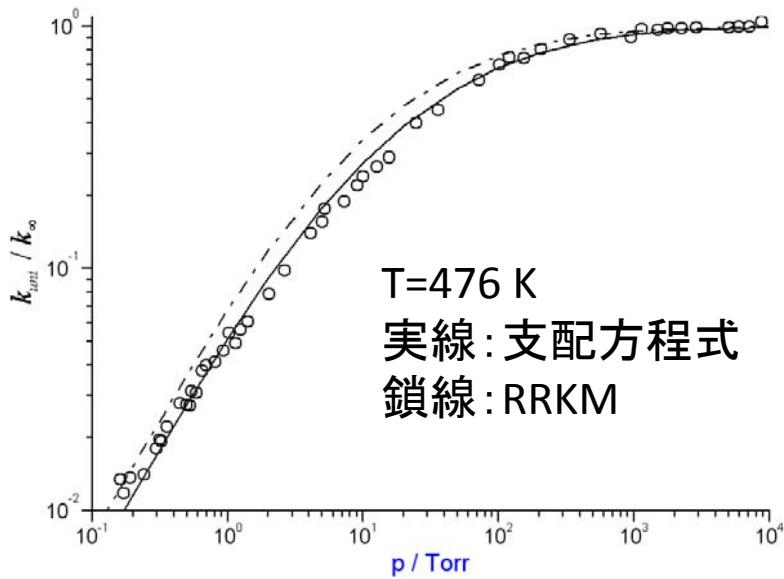
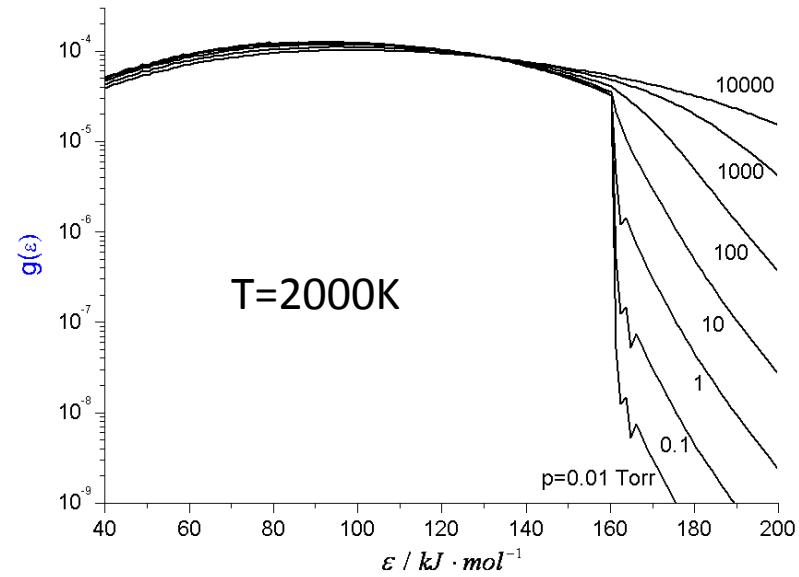
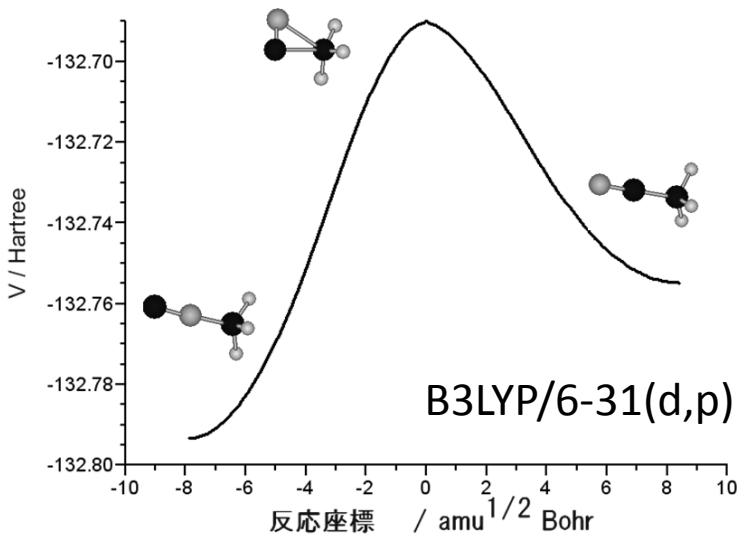
=> 低圧極限

$R(E',E) \leq M$ により異なる

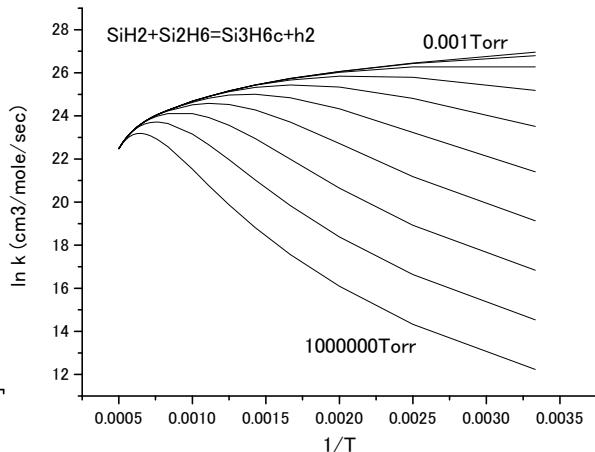
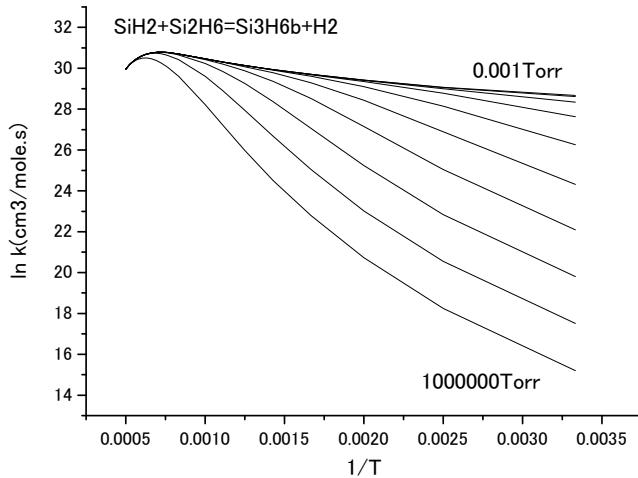
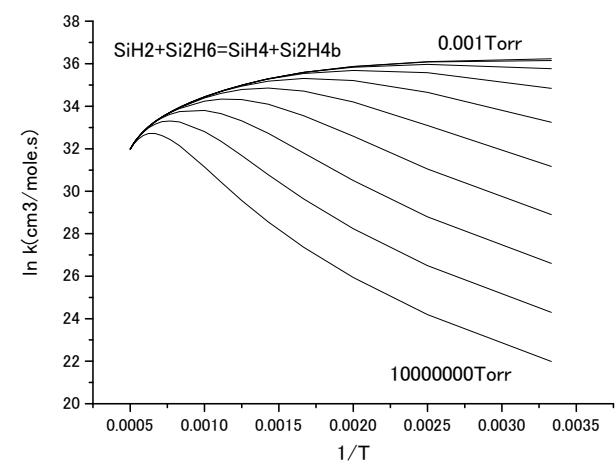
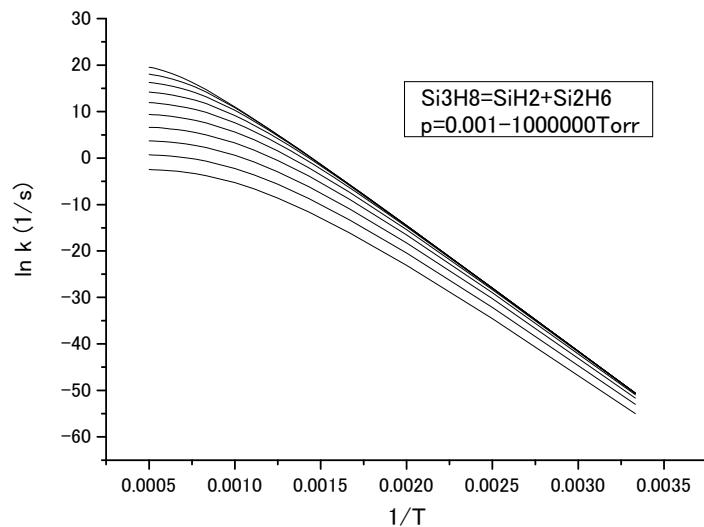
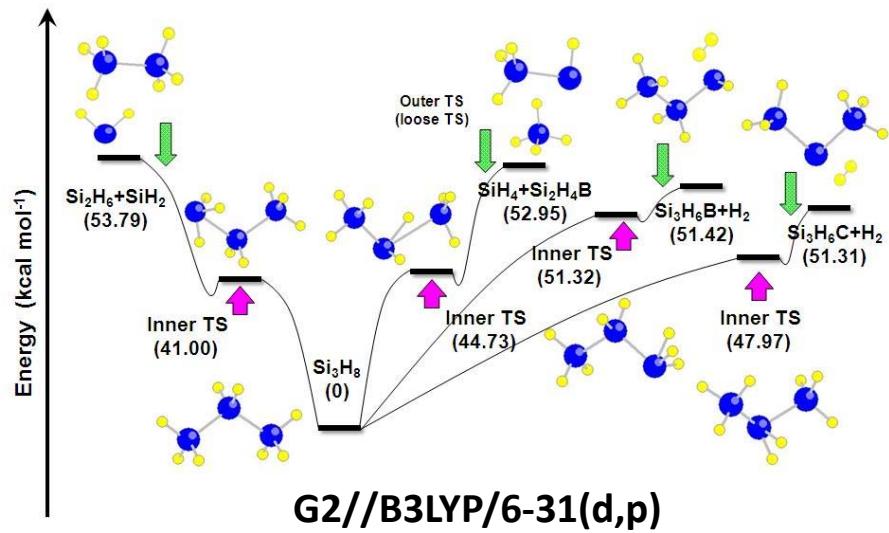
=> 第三体効果



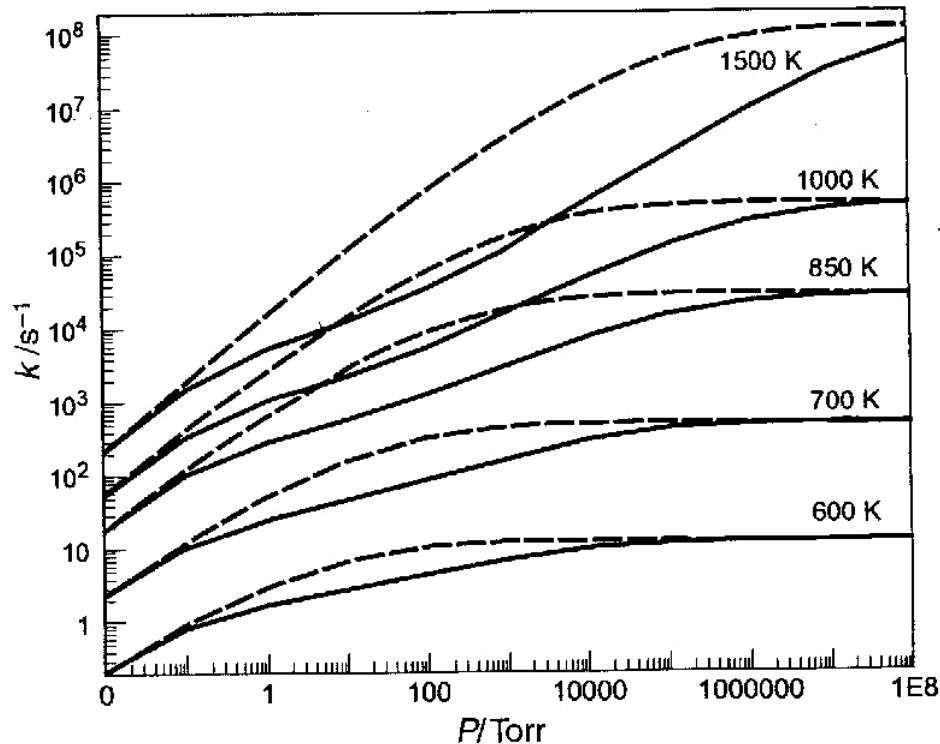
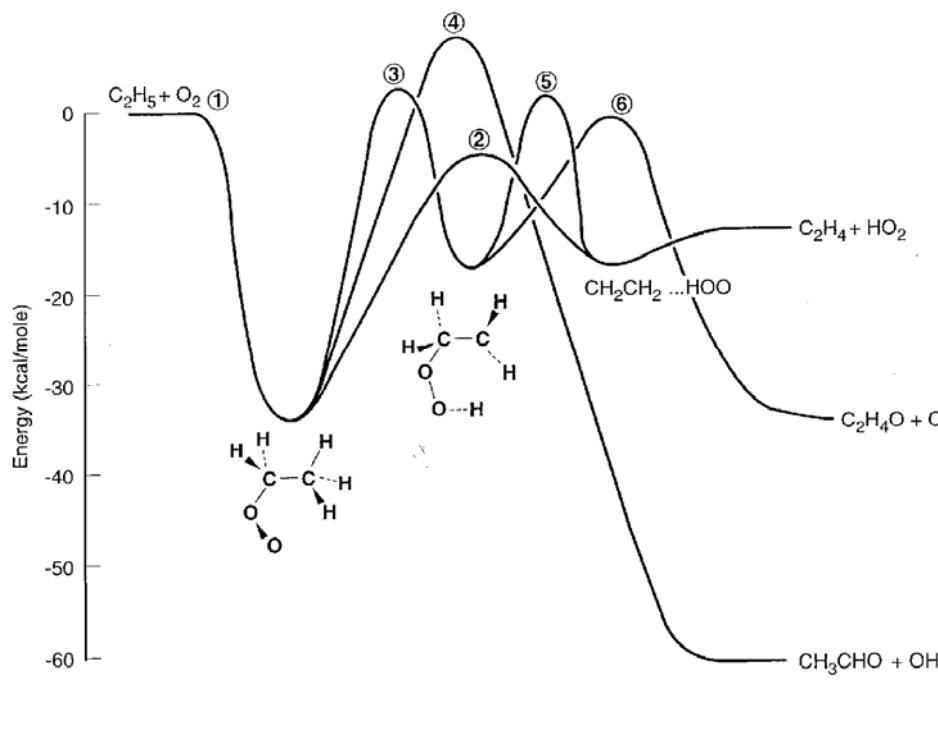
例1:異性化反応($\text{CH}_3\text{NC} \rightleftharpoons \text{CH}_3\text{CN}$)



例2: 化学活性化反応(Si_3H_8 の反応)

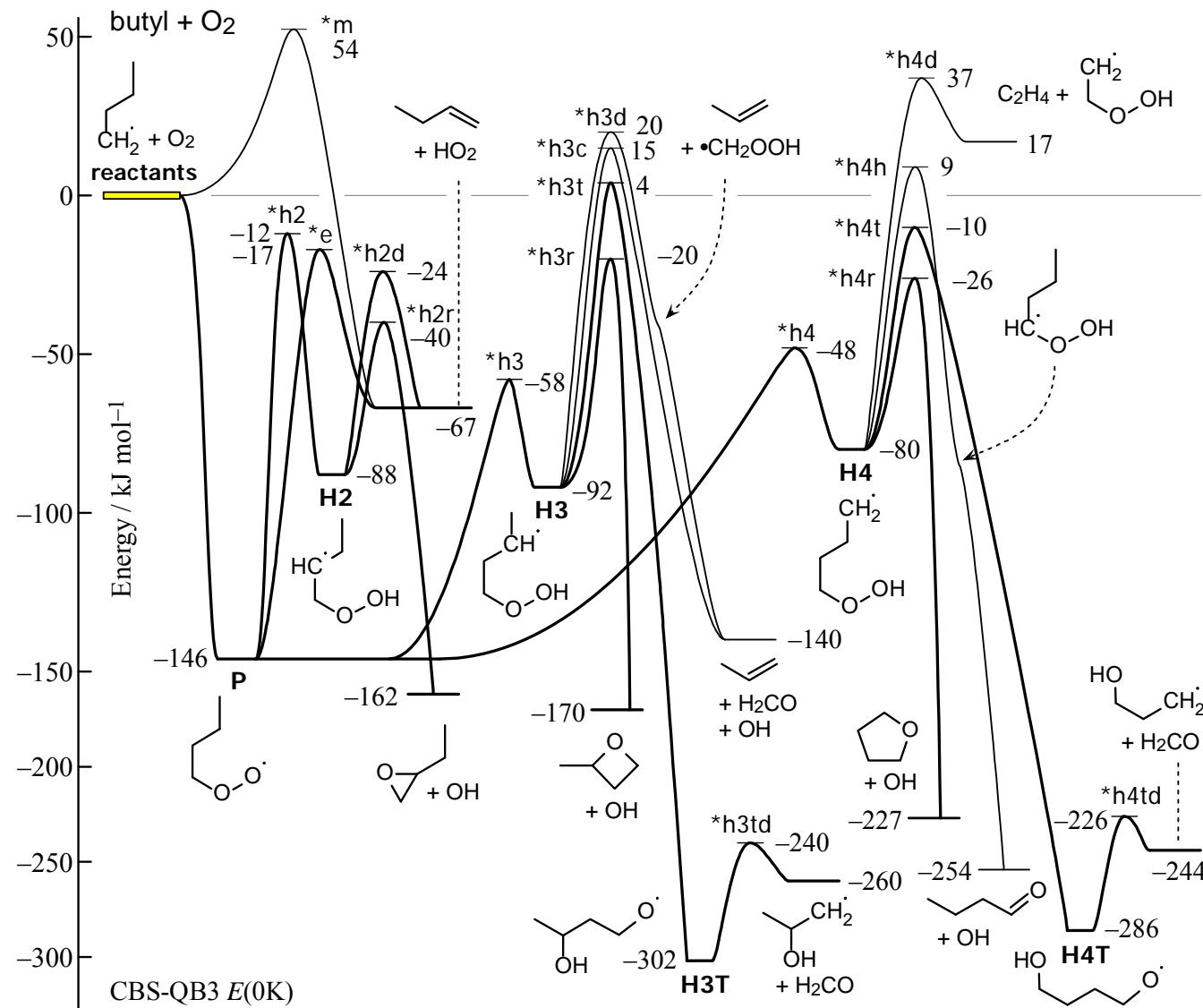


例3 $C_2H_5 + O_2$



$C_2H_5O_2 \rightarrow HO_2 + C_2H_4$ の速度定数の計算値。
 $C_2H_5O_2 \rightarrow C_2H_5 + O_2$ の反応経路を考慮しなかった場合

例4 $C_4H_9 + O_2$



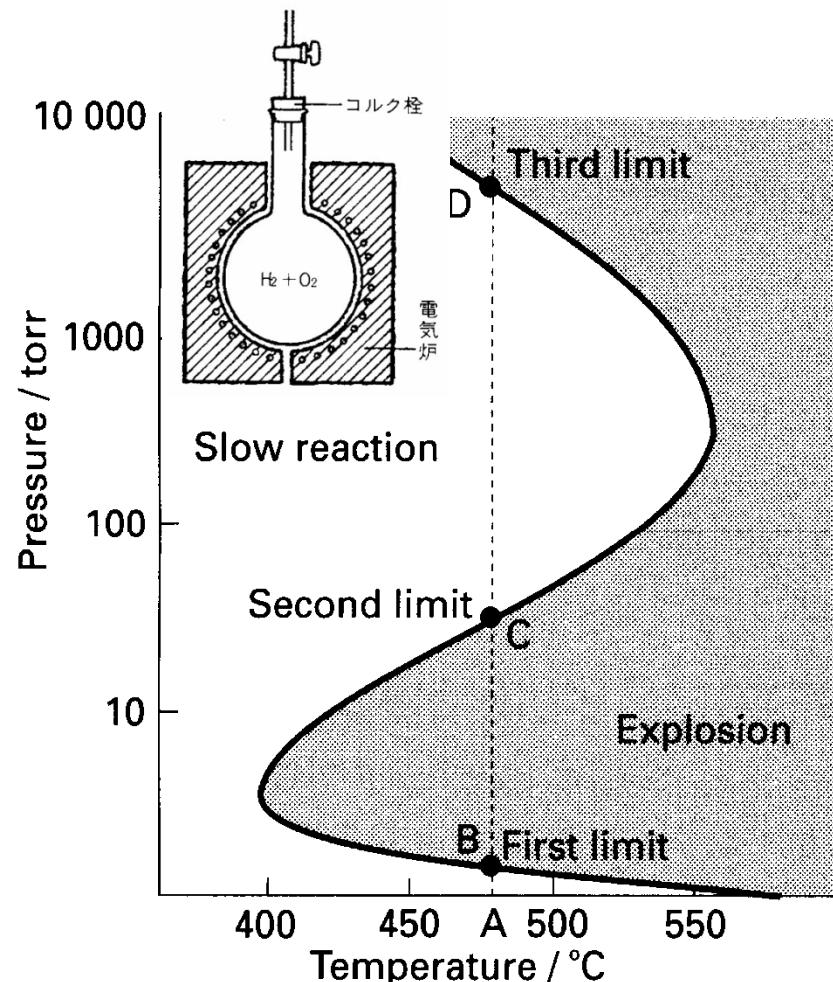
3. 燃燒反應機構

3.1 水素の燃焼反応機構

ポスター P118 清水・越 本日!!!
Please come!!!

水素の爆発限界と反応機構

- Initiation $H_2 + O_2 \rightarrow HO_2 + H$
- Chain reactions $H + O_2 \rightarrow OH + O$
 $O + H_2 \rightarrow OH + H$
 $OH + H_2 \rightarrow H_2O + H$
- Recombination $H + H + M \rightarrow H_2 + M$
 $O + O + M \rightarrow O_2 + M$
 $H + OH + M \rightarrow H_2O + M$
 $O + H_2 + M \rightarrow HO_2 + M$
 $OH + OH + M \rightarrow H_2O_2 + M$
- HO_2 reactions $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$
 $H + HO_2 \rightarrow OH + OH, H_2 + O_2$
 $O + HO_2 \rightarrow OH + O_2$
 $OH + HO_2 \rightarrow H_2O + O_2$
 $H + H_2O_2 \rightarrow H_2 + HO_2, OH + H_2O$
 $O + H_2O_2 \rightarrow OH + HO_2$



高圧水素の燃焼速度

M.P.Burke, M.Chaos, F.L.Dryer, and Y.Ju, AIAA 2009-990

M.P.Burke, F. L.Dryer, and Y.Ju, AIAA 2010-776

M.P.Burke, M.Chaos, F.L.Dryer, and Y.Ju, Combust. Flame, 157 (2010) 618-631

$$f^0 \equiv \rho_u S_u \approx \frac{\rho D}{l^0} \quad f^0 \approx \omega l^0 \Rightarrow (f^0)^2 = (\rho D) \omega$$

$$\omega \sim p^n \exp(-E_a/R^0 T_f)$$

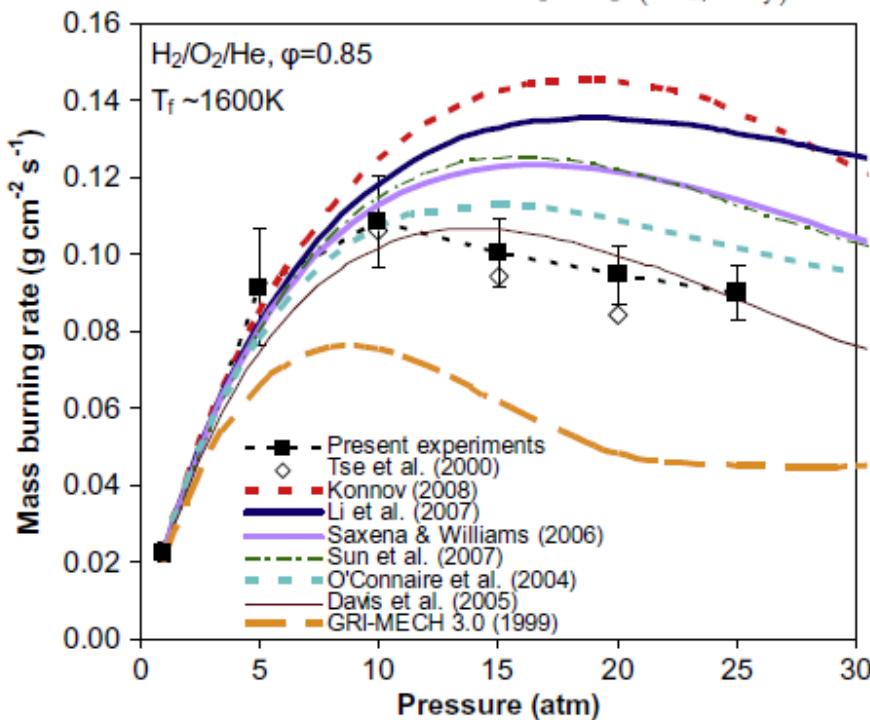


Fig. 4. Mass burning rate measurements from the present study and from Ref. [10] for various pressures for $\text{H}_2/\text{O}_2/\text{He}$ flames of equivalence ratio 0.85 and flame temperature of ~ 1600 K. Lines show predictions from the different models considered in this study [12,17–21,24].

$$f^0 \sim p^{n/2} \exp(-E_a/2R^0 T_f) \quad n = 2 \left\{ \frac{\partial \ln(f^0)}{\partial \ln(p)} \right\}_{T_f}$$

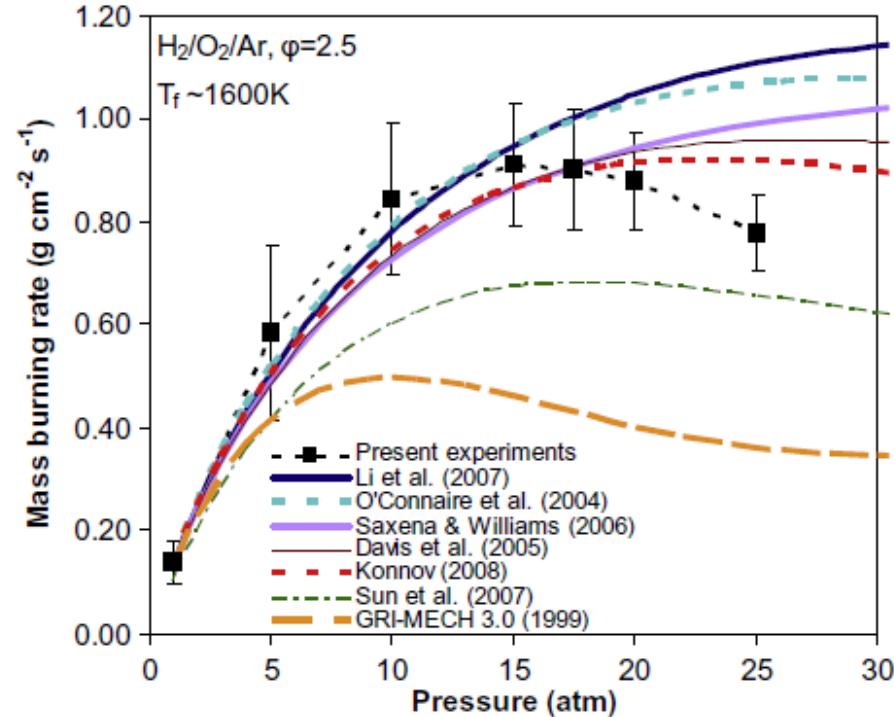


Fig. 5. Mass burning rate measurements for various pressures for $\text{H}_2/\text{O}_2/\text{Ar}$ flames of equivalence ratio 2.5 and flame temperature of ~ 1600 K. Lines show predictions from the different models considered in this study [12,17–21,24].

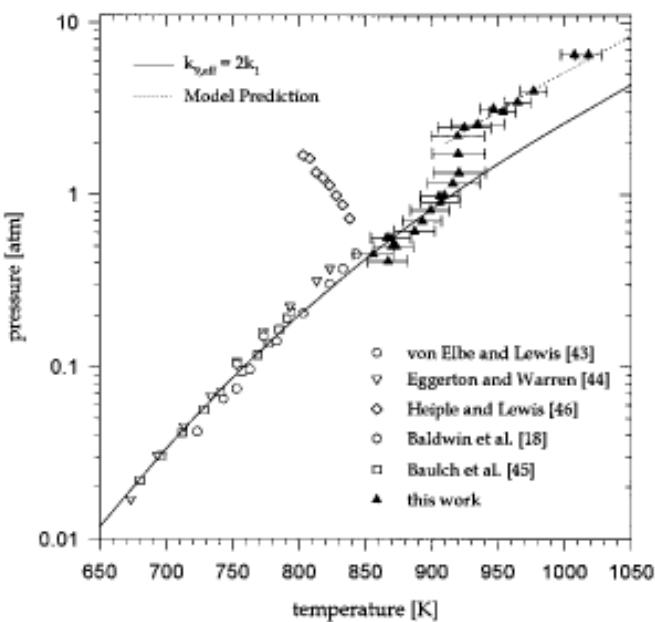
Revision of Rate Constants: an example

$\text{H}+\text{HO}_2=\text{H}_2+\text{O}_2$, $\text{OH}+\text{OH}$, $\text{H}_2\text{O}+\text{O}$

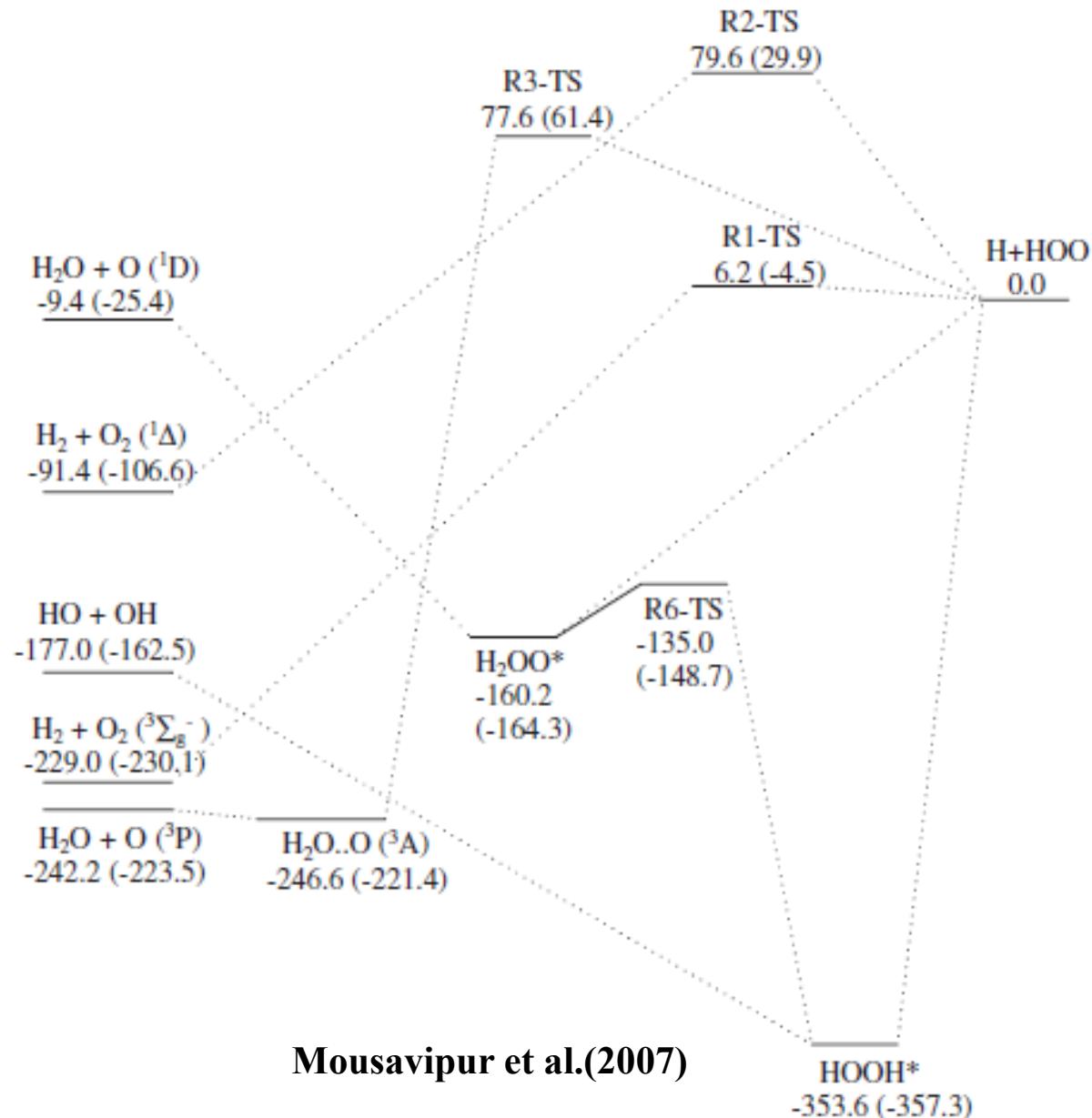
Extended 2nd explosion Limit

- (2) $\text{H}+\text{O}_2=\text{HOH}+\text{O}$
- (15) $\text{H}+\text{O}_2+\text{M}=\text{HO}_2+\text{M}$
- (5) $\text{H}+\text{HO}_2=\text{H}_2+\text{O}_2$
- (6) $\text{H}+\text{HO}_2=\text{OH}+\text{OH}$

$$\frac{k_5 + k_6}{2k_5} \frac{2k_2}{k_{15}[\text{M}]} = 1$$



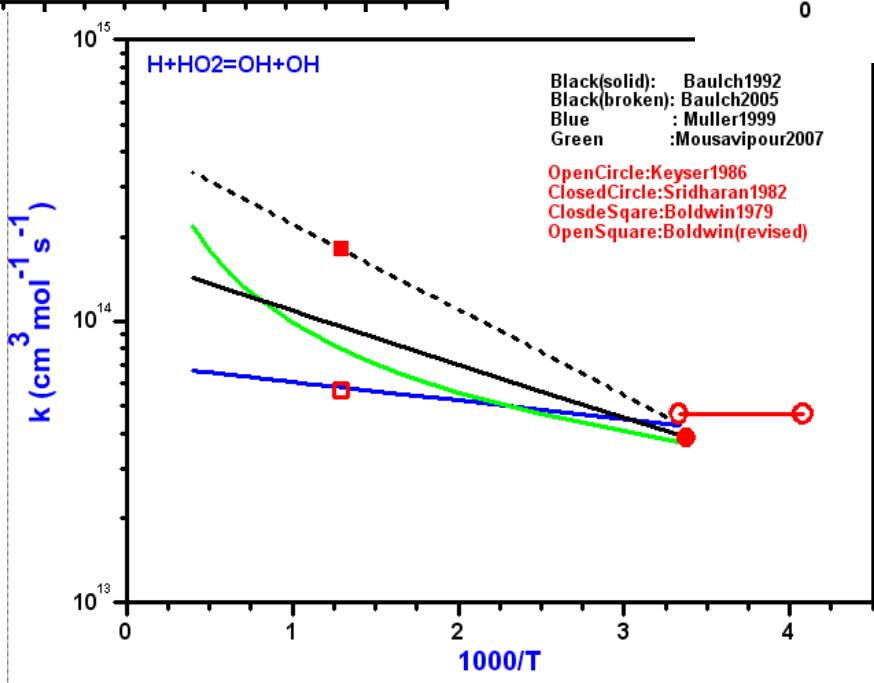
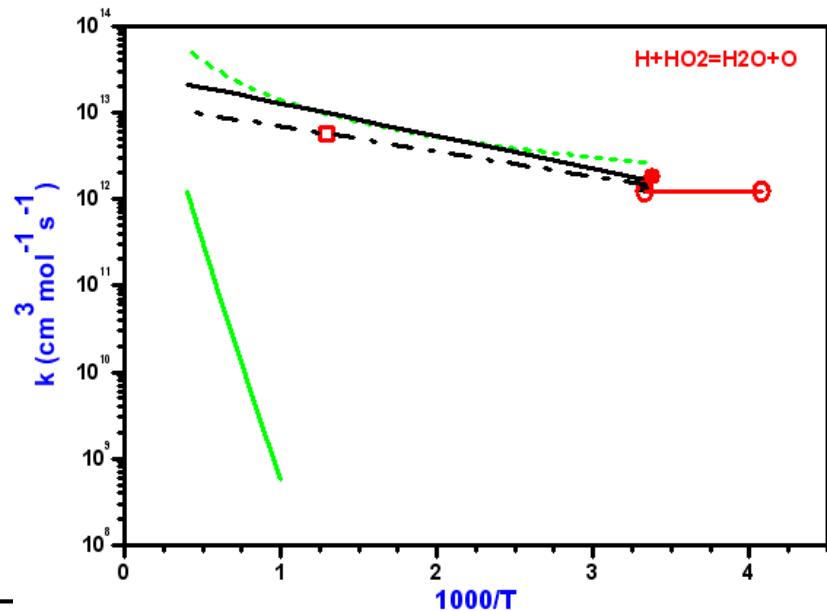
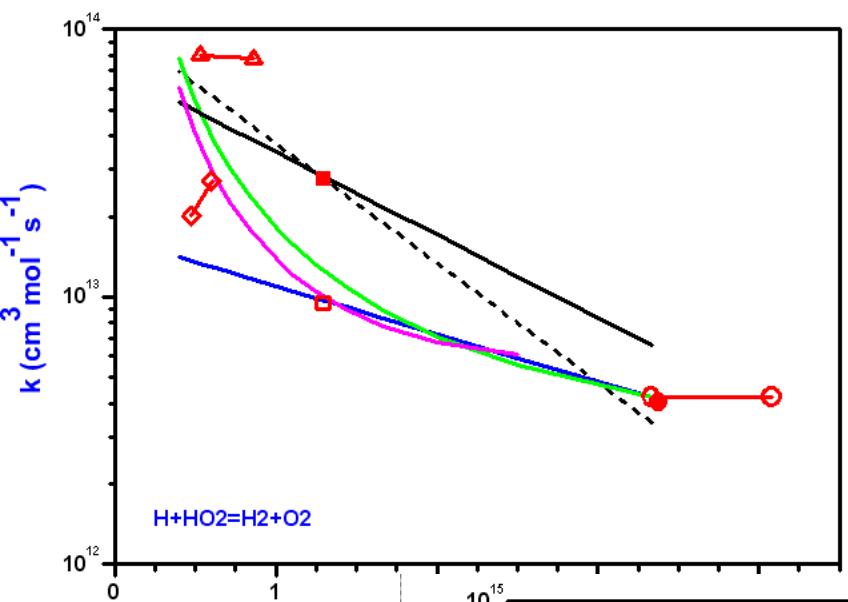
Muller et al. (1999)



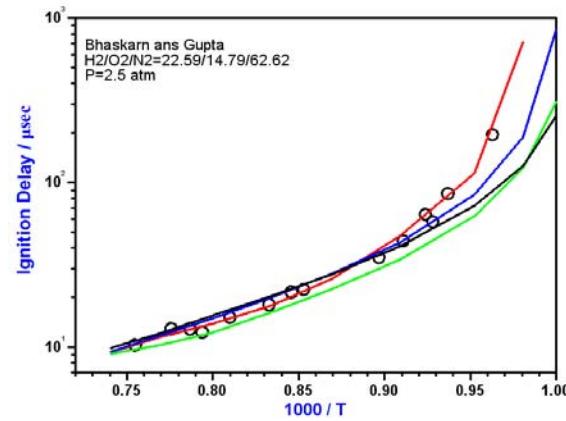
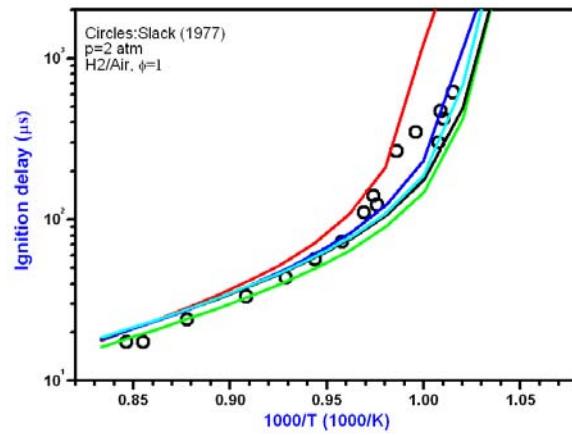
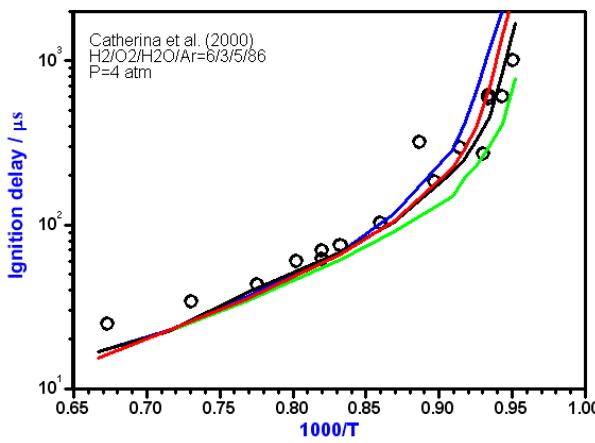
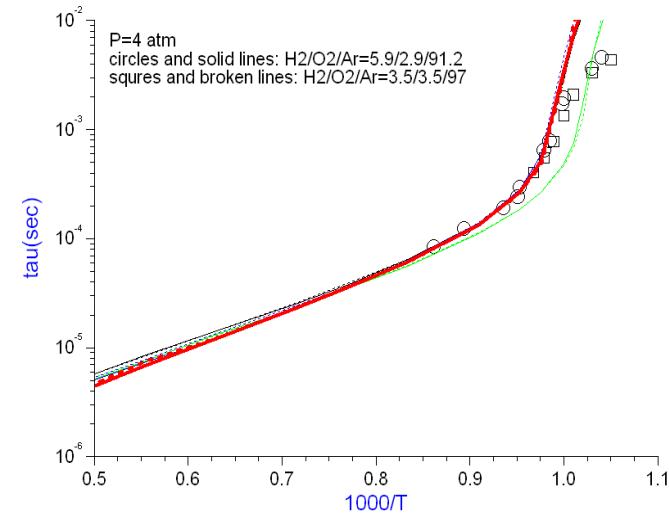
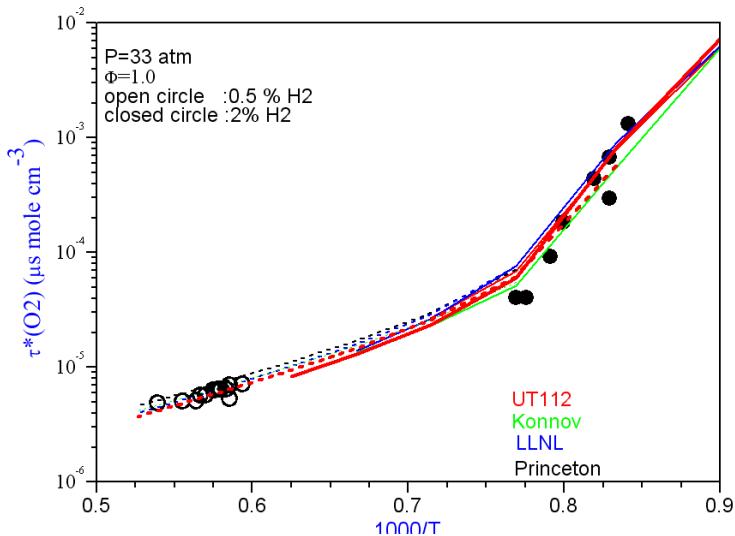
Mousavipur et al. (2007)

Revision of Rate Constants

$H + HO_2 = H_2 + O_2, OH + OH, H_2O + O$



Validation: Shock Tube Ignition delay



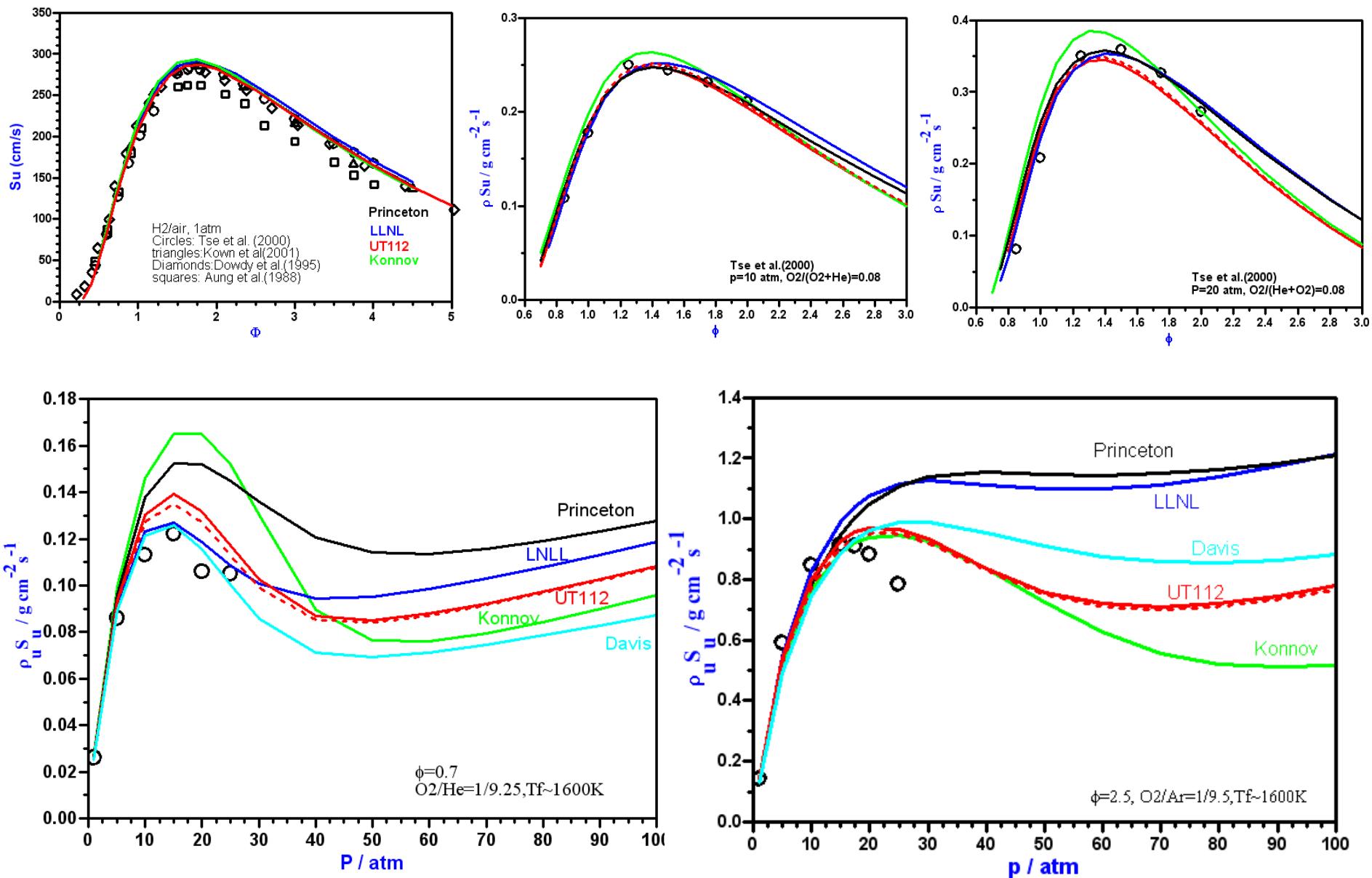
Princeton : J.Li, Z.Zhao, A.Kazakov, F.L. Dryer,
 Int.J.Chem.Kinet., 36 (2004) 566-575

LLNL : M.O'Conaire, H.J.Curran, J.M.Simmie, W.J.Pitz, .K.Westbrook,
 Int. J. Chem. Kinet., 36 (2004) 603-622

Brussel : A.A.Konnov, Combust. Flame, 152 (2008) 507-528

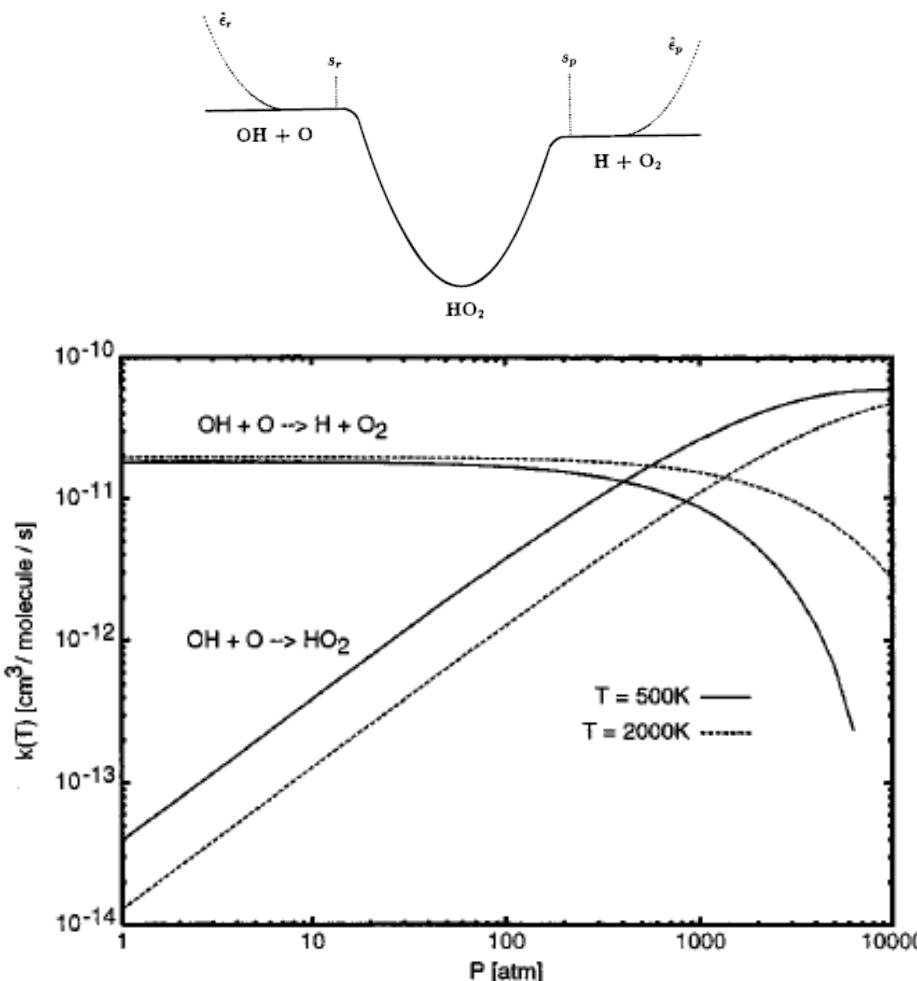
UT-JAXA ver 1.12a :still in progress

Validation: Flame Speed



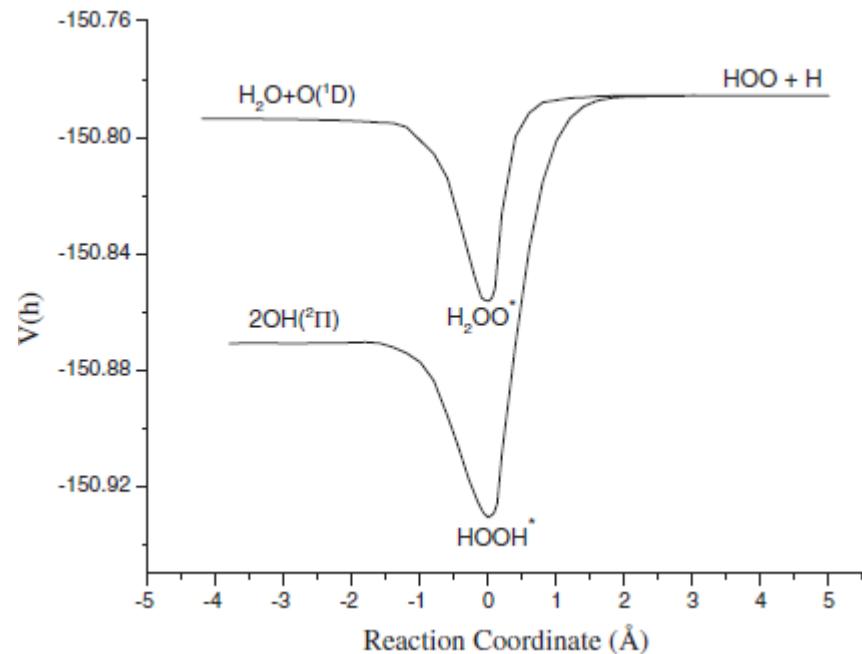
Missing Reactions?

No model includes $\text{O}+\text{OH}+\text{M}=\text{HO}_2+\text{M}$.
 (Burke et al. 2010)



Germann and Miller (1997)

Production of electronically excited species:
 $\text{H}+\text{HO}_2=\text{O}(\text{1D})+\text{H}_2\text{O}$



$\text{O}(\text{1D})+\text{M}=\text{O}(\text{3P})+\text{M}$
 $\text{M}=\text{Ar}, \text{He}, \text{H}_2$: slow (spin forbidden)
 $\text{M}=\text{O}_2, \text{H}_2\text{O}, \text{N}_2$: fast
 $\text{O}(\text{1D})+\text{H}_2=\text{OH}+\text{H}$
 $\text{O}(\text{1D})+\text{H}_2\text{O}=\text{OH}+\text{OH}$

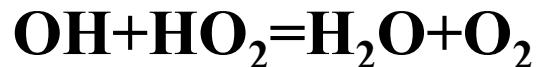
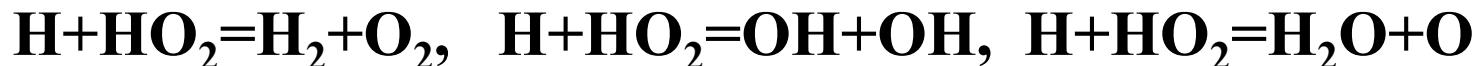
$\text{H}+\text{HO}_2+\text{M}=\text{H}_2\text{O}_2+\text{M}$?

Concluding Remarks

No model can predict high pressure mass burning rate at fuel rich conditions.

Differences in each model prediction are considerably large.

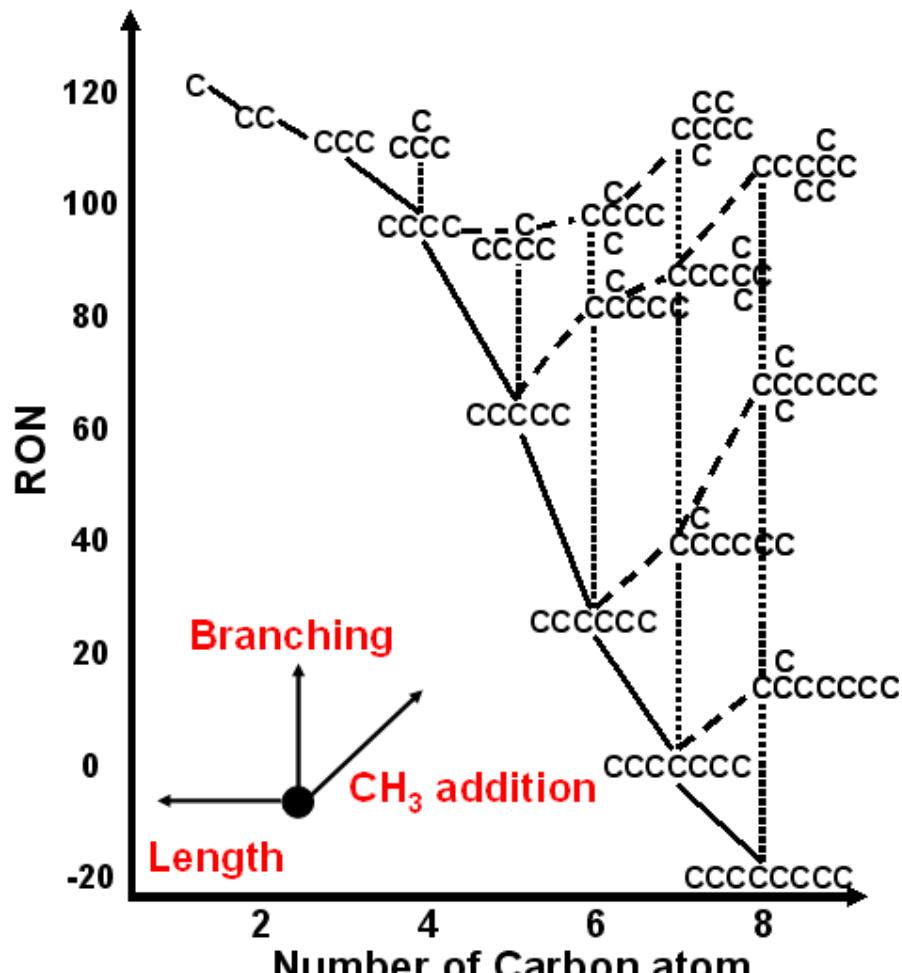
More precise values of rate constants for following reactions are required for the better understandings of high pressure H₂ combustion:



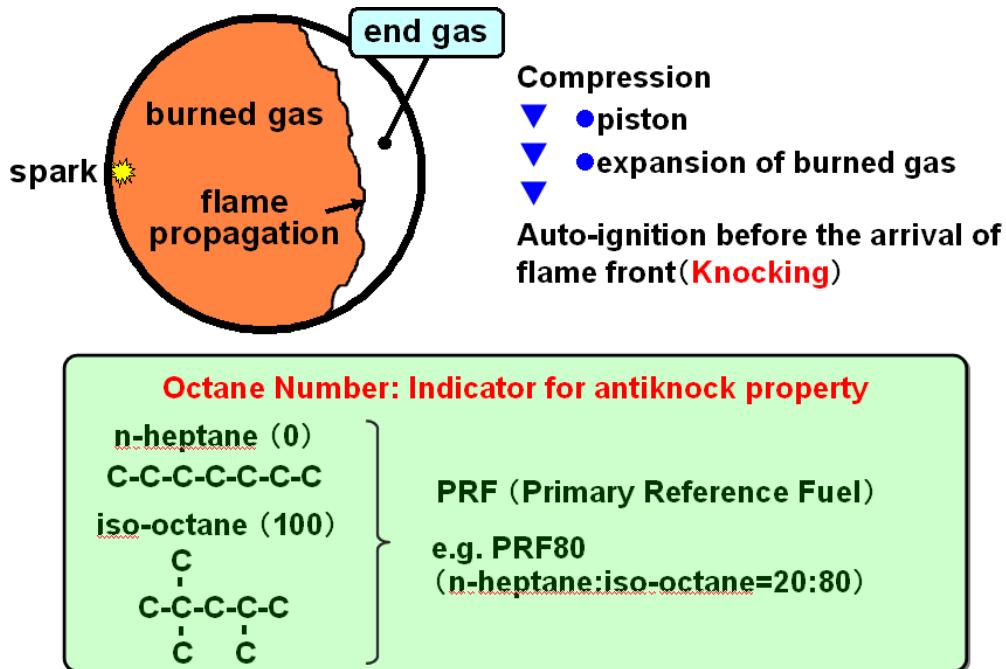
There is a possibility that some important reactions are not included in the kinetic model.

3. 2 炭化水素の燃焼反応機構 (アルカンの燃焼反応)

燃料の分子構造と着火特性

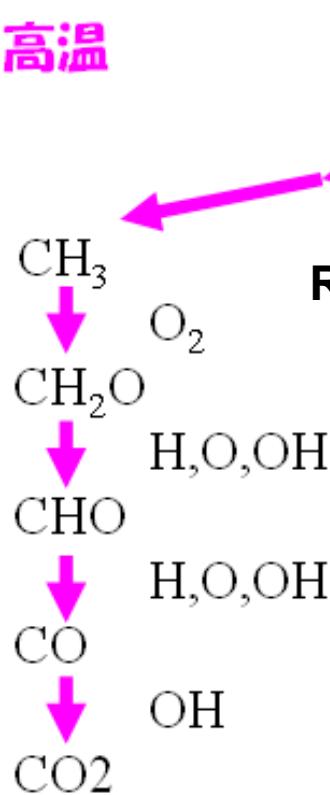


(Lovell et al. 1948)



炭化水素の燃焼反応機構: 高温と低温

高温

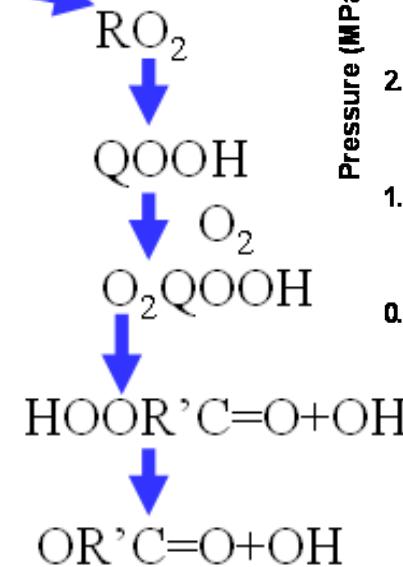


RH

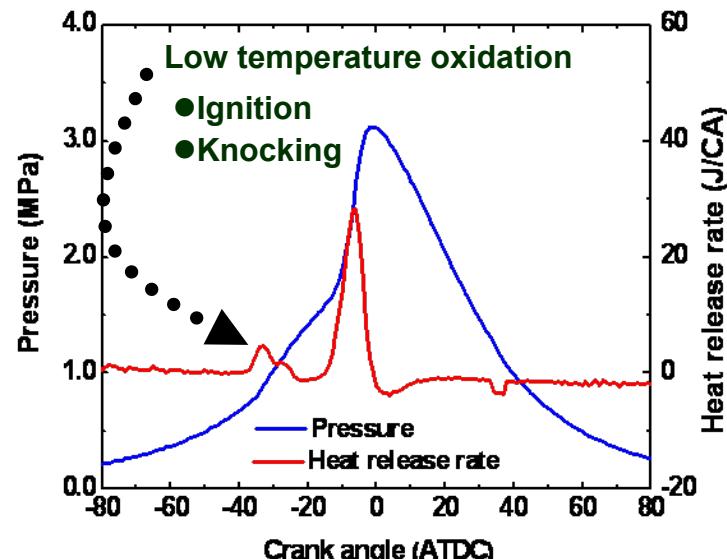
R

O₂

低温



R: アルキルラジカル



高温 > 天井温度 > 低温

天井温度: $\text{R} + \text{O}_2 = \text{RO}_2$ $[\text{R}] = [\text{RO}_2]$

高温 => Rが安定

低温 => RO₂が安定

高温域と低温域? What is the Criteria?

低温 < 天井温度 < 高温

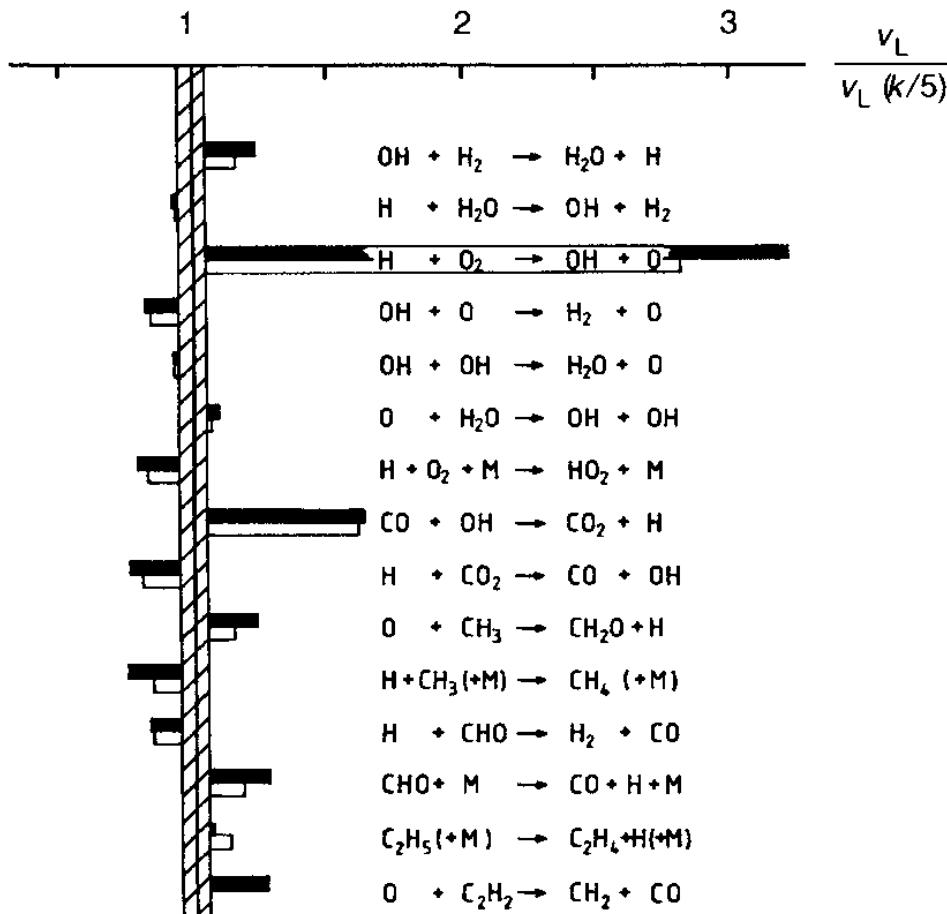


R	ΔH_{298}° kJ mol ⁻¹	log K/atm ⁻¹			Ceiling temp/K [R]=[RO ₂] at O ₂ =0.1 atm
		500 K	800 K	1200 K	
H[3]	208	16.8	8.6	4.1	1920
CH ₃ [3]	-135	7.4	2.1	-0.85	930
C ₂ H ₅ *	-147	7.6	1.9	-1.30	900
i-C ₃ H ₇ **	-155	7.7	1.6	-1.75	860
t-C ₄ H ₉ *	-153	7.1	1.1	-2.3	820
CH ₂ CHCH ₂ **	-75	1.6	-1.35	-3.0	550

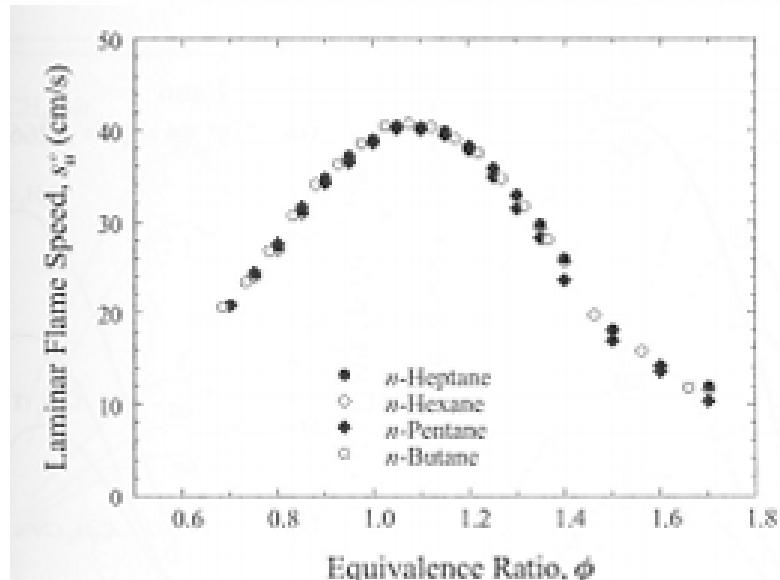
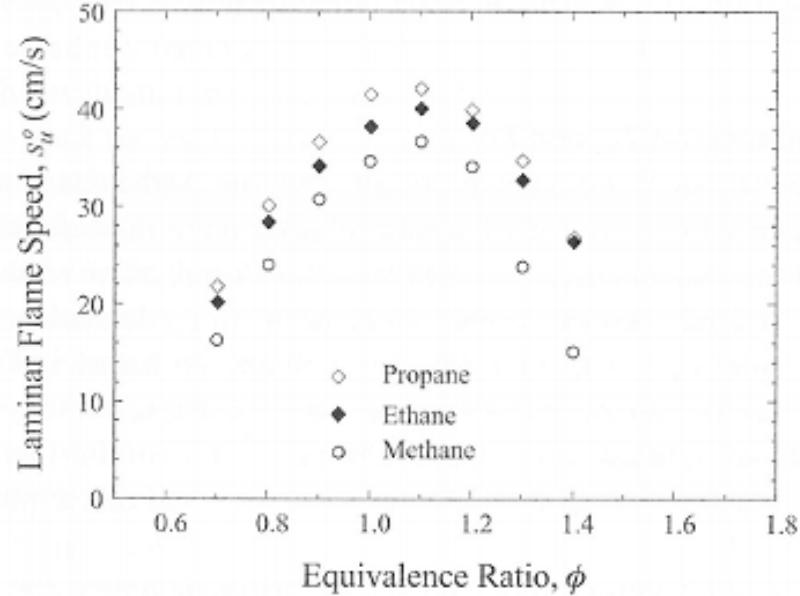
* I.R. Slagle, E. Ratajczak and D. Gutman, J. Phys. Chem., 90 (1986) 402

** I.R. Slagle, E. Ratajczak, M.C. Heaven, D. Gutman and A.F. Wagner, J. Am. Chem. Soc., 107 (1985) 1838.

炭化水素燃料の燃焼反応機構 一高温域



$H + O_2 = OH + O$ 最も重要
燃料の個性は現れない

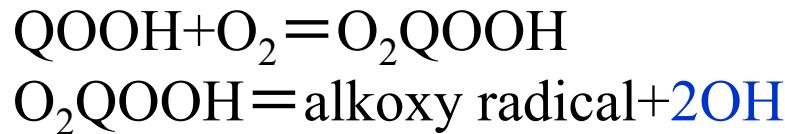


低温反応機構

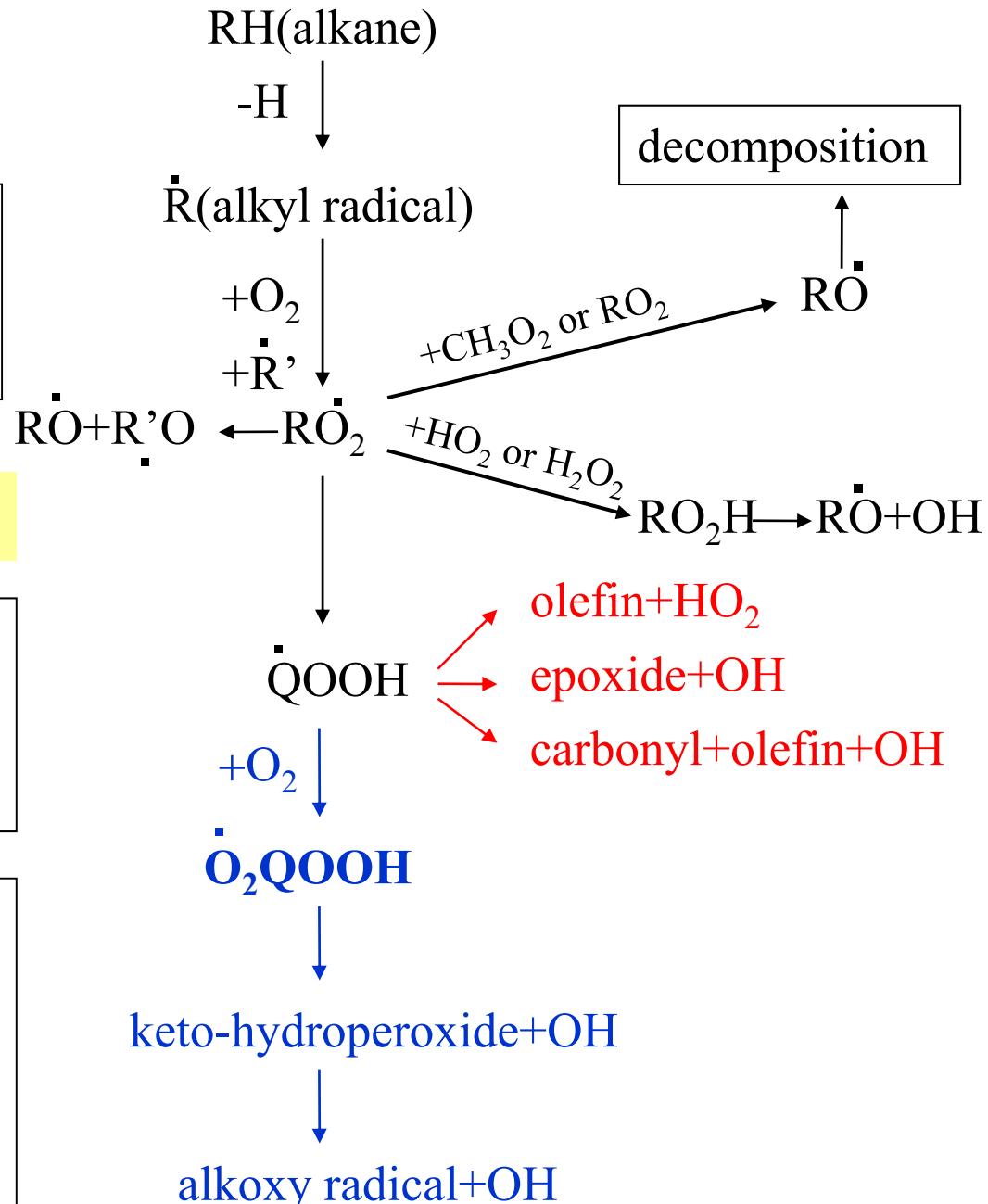
Engine ignition:
lower than 800 K
⇒ low temp. mechanism

OH: ignition promoter

chain branching

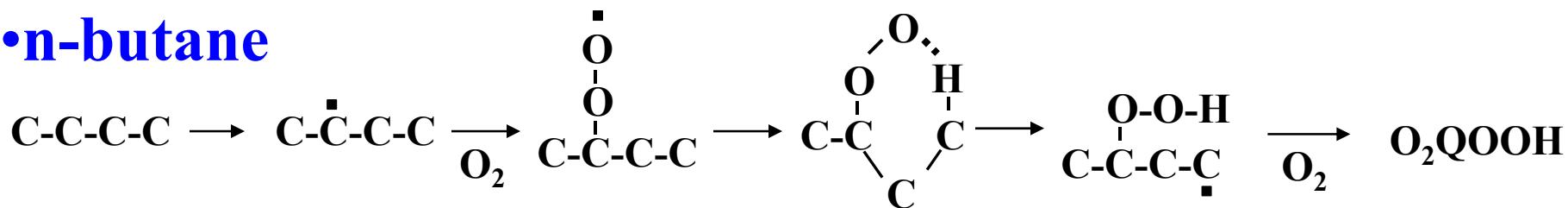


propagation



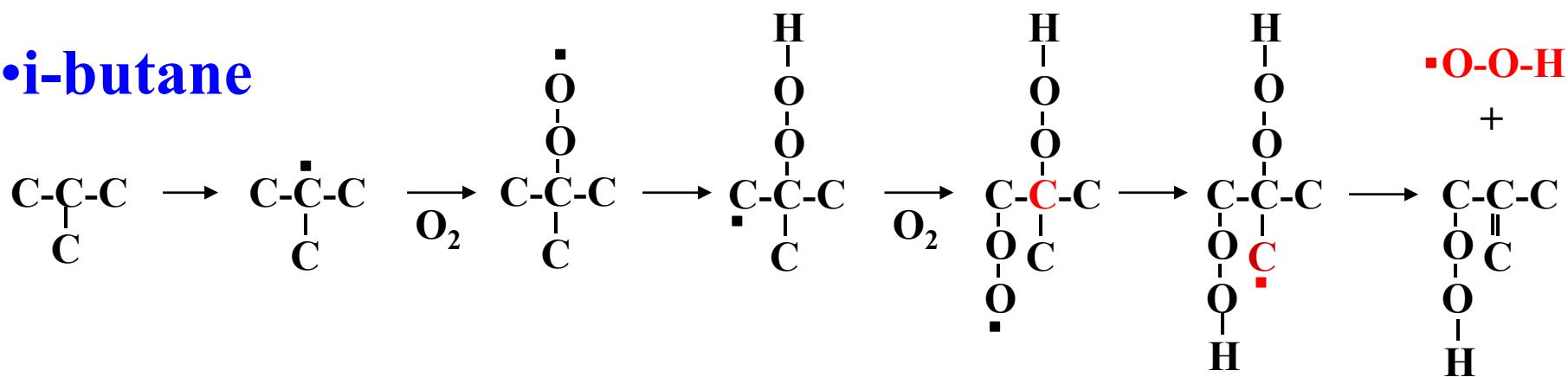
分子構造による着火性の差違

•n-butane



6員環構造を経て O_2QOOH を生成

•i-butane



6員環での分子内水素引き抜きが出来ない
OHラジカルを二つ出さない場合がある

- H原子の引き抜きやすさ: $-\text{C}_3\text{H}$ (三級炭素) $>-\text{C}_2\text{H}_2$ (二級) $>-\text{CH}_3$ (一級)
- 遷移構造は6員環構造が最も出来やすい←歪みエネルギーのため

KUCRS システム

KUCRS:

Knowledge-basing Utilities

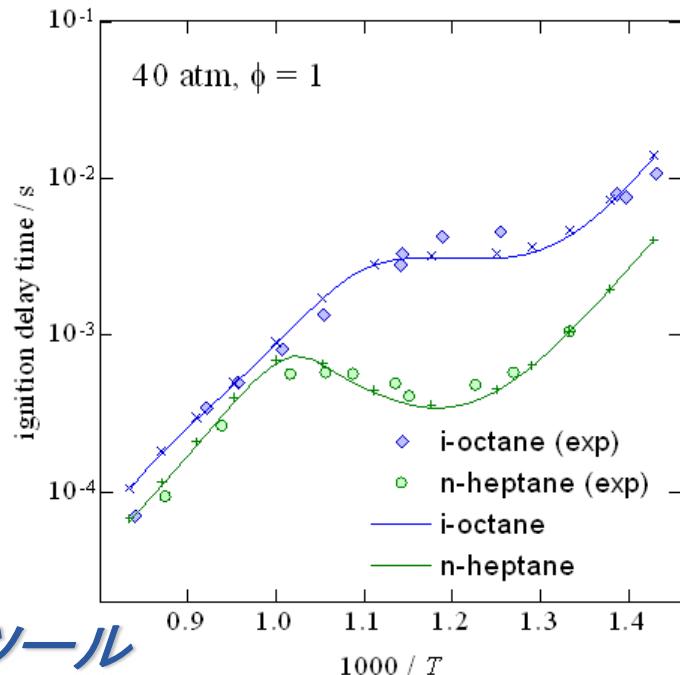
for Complex Reaction Systems

— ルールベース詳細反応機構構築支援ツール

- 反応機構生成のためのライブラリクラスの集積
 - molecule クラス (構造同定, 属性検出, 構造操作, etc.)
 - specAdmin クラス (化学種管理 - 名称, ステータス, etc.)
 - reaction クラス (反応記述支援 - 重複検出, 盲腸種検出, etc.)

— 完成された自動生成ソフトウェア? ... NO

- 反応速度定数マクロは外部ファイル記述 - ユーザが改訂・調整
- ユーザによる新たな反応の記述 - 公開ソース / GPL配布 *new: 2010.02.21
- 検証されているのは一部
 - 代表燃料 (n-heptane, i-octane) の自着火性の検証
 - RON との相関による燃料の系統的傾向の検証



4. 反応解析の応用

4.1 サロゲート燃料の反応機構

実燃料の反応機構を目指して: サロゲート燃料

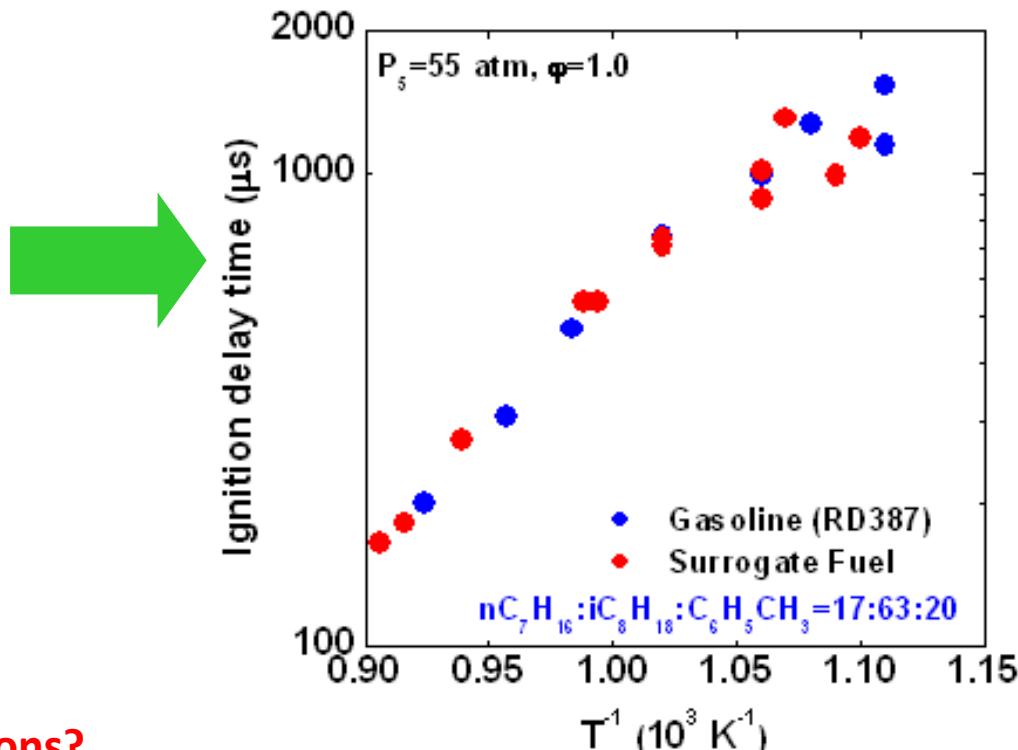
レギュラーガソリンの組成 (提供: PEC)

No.	Vol%	NAME
1	1.26E-03	ethane
2	5.07E-03	propylene
3	3.16E-02	propane
4	1.07E+00	iso-butane
5	3.00E-01	iso-buthylene
6	3.16E-01	1-butene
7	5.52E-03	1,3-butadiene
8	1.92E+00	n-butane
9	6.19E-01	t-2-butene
10	1.89E-02	2,2-dimethyl propane
11	5.08E-01	c-2-butene
12	1.26E-01	3-methyl-1-butene
13	9.57E+00	iso-pentane
14	2.61E-03	1,4-pentadiene
15	3.63E-01	1-pentene
16	6.96E-01	2-methyl-1-butene
17	5.39E+00	n-pentane
18	1.94E-02	2-methyl-1,3-butadiene

:

425 C₄-C₁₀ species, Millions of reactions?

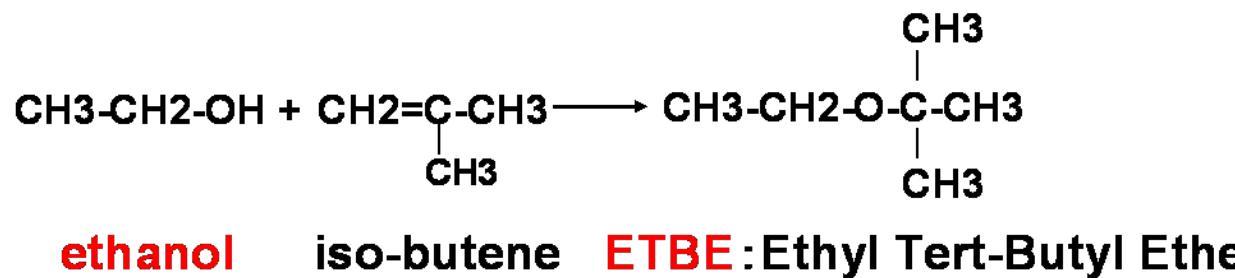
*Comparison of T_{ign} between gasoline and surrogate Fuel
(B. M. Gauthier et al., 2004)*



ガソリン・サロゲート燃料

Real Fuel Component	Surrogate Fuel Component
iso-paraffins	iso-octane
normal paraffins	n-heptane, n-hexadecane
cyclo-paraffins	methylcyclohexane
single ring aromatics	toluene
multi-ring aromatics	alpha methylnaphthalene
olefic species	1-pentene
ethers	ETBE

KUCRS



PRF + EtOH + ETBE の反応機構の構築(1)

PRFの反応機構 <= KUCRSによる自動生成

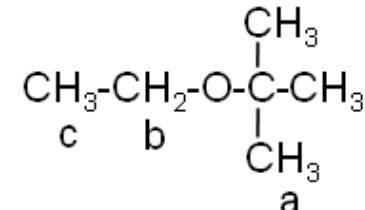
EtOHの反応機構 <= Marinovらの機構

ETBE <= 重要な反応について量子化学計算+速度理論により速度定数を評価

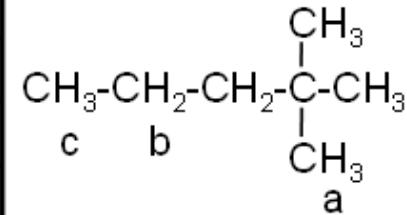


Abstracting radical	Site	Calculated E_a /kcal mol ⁻¹	
		ETBE	DMP
H	a (primary)	11.7	10.5
	b (secondary)	5.4	8.0
OH	c (primary)	11.9	10.7
	a (primary)	2.4	2.0
	b (secondary)	0.2	1.7
	c (primary)	3.2	2.6

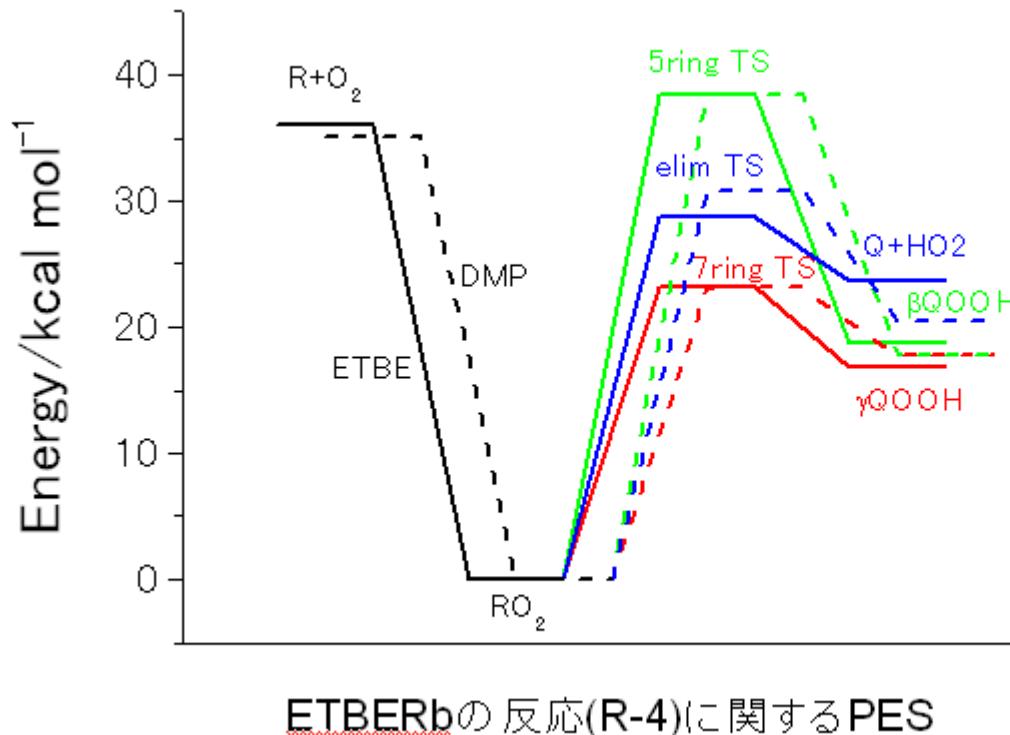
ETBE



DMP



PRF + EtOH + ETBEの反応機構の構築(2)



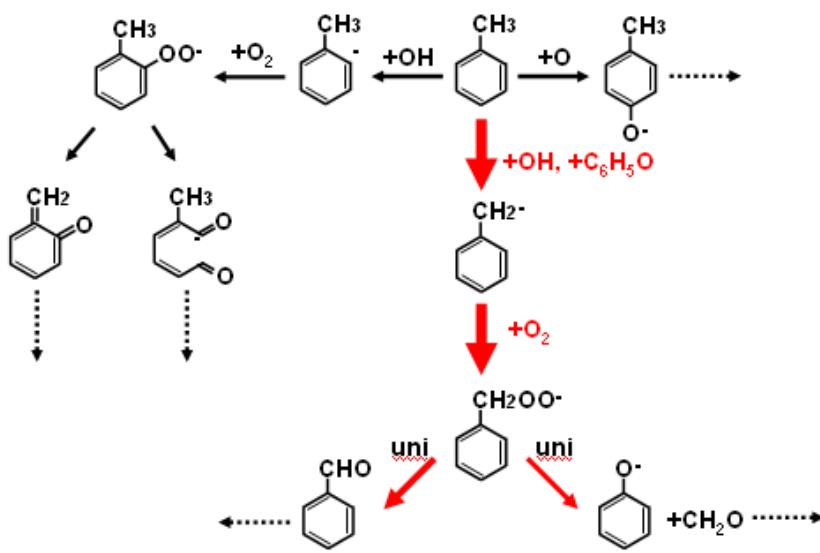
Reaction	$E_a / \text{kcal mol}^{-1}$	
	ETBE Rb	DMP Rb
R+O ₂	36.1	35.1
7ring TS	23.2	23.1
QOOH	16.9	17.7
5ring TS	38.4	38.3
QOOH	18.7	17.7
HO ₂ elimTS	28.8	30.8
Q+HO ₂	23.7	20.5

=>化学種数625、反応数2254の詳細反応モデルを作成

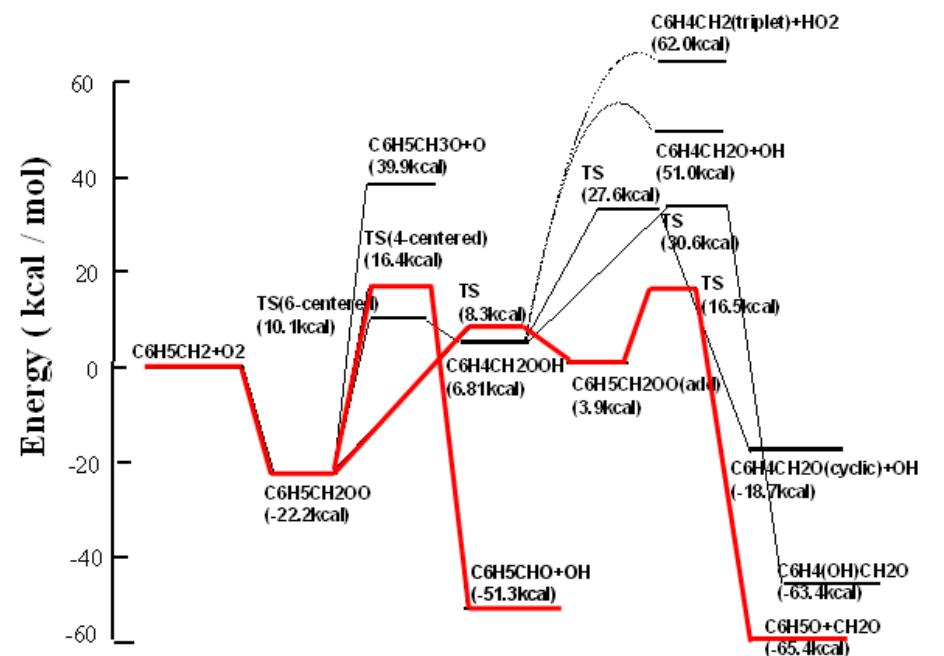
トルエンの燃焼反応機構の構築

(未完成: 繼続して改良がおこなわれている)

Main reaction path below 1000 K and 1 atm

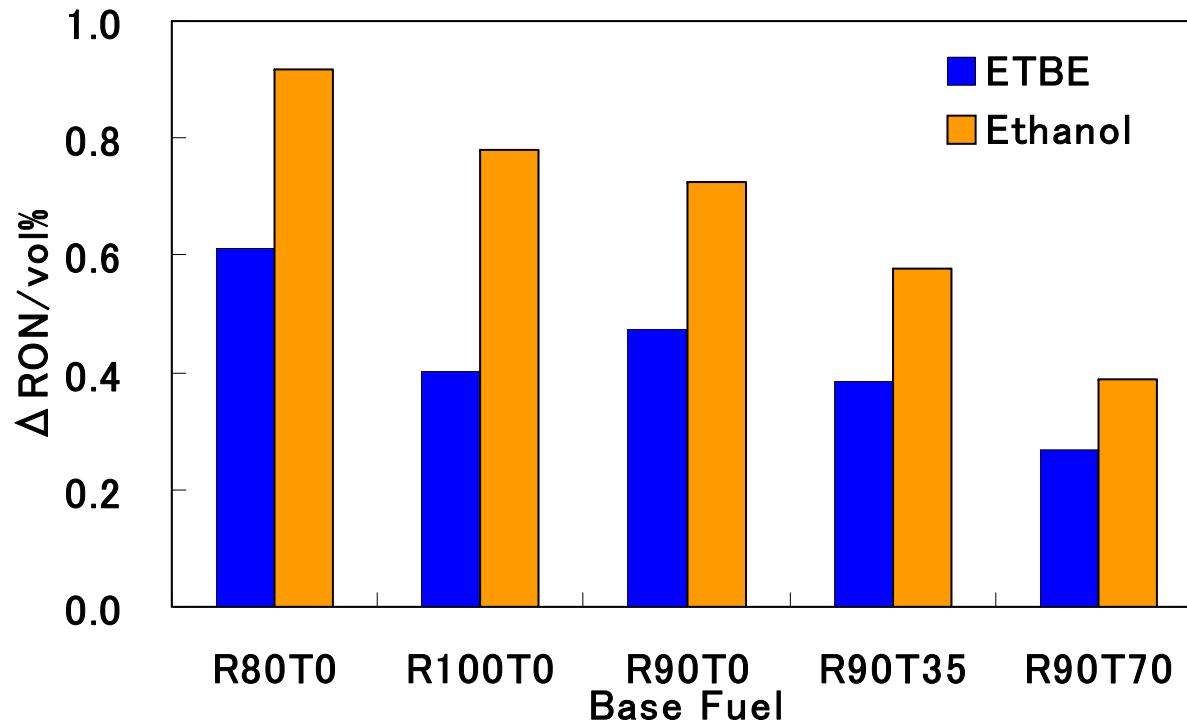


酒井: 2008



Murakami,Oguchi,Hashimoto,Nozaka, J.Phys.Chem.(2008)

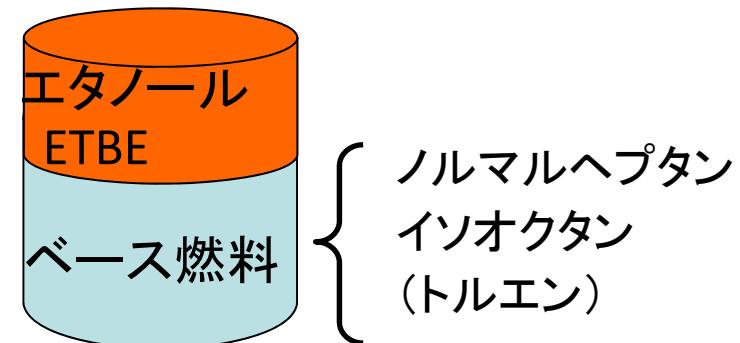
CFRエンジンによるRON測定結果



各ベース燃料のRON増加量(ETBE・エタノール1.0vol%当たり)

オクタン価向上効果は

- エタノール > ETBE
- R90T0 > R90T35 > R90T70

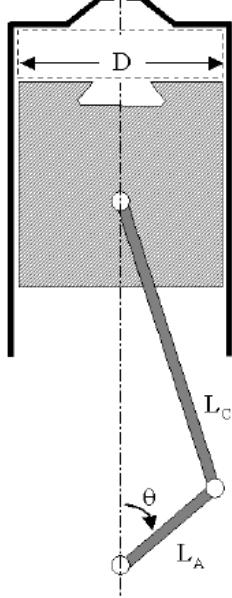


オクタン価の評価 <= CCRとRONの関係

PRFについて圧縮自着火の限界圧縮比(CCR)を計算し、RONとCCRの検量線を求める。

未知の燃料について、CCRを計算しRONを上記の検量線から決定する。

$$\frac{V(t)}{V_c} = 1 + \frac{C-1}{2} [R + 1 - \cos \theta - \sqrt{R^2 - \sin^2 \theta}]$$



Heat loss model

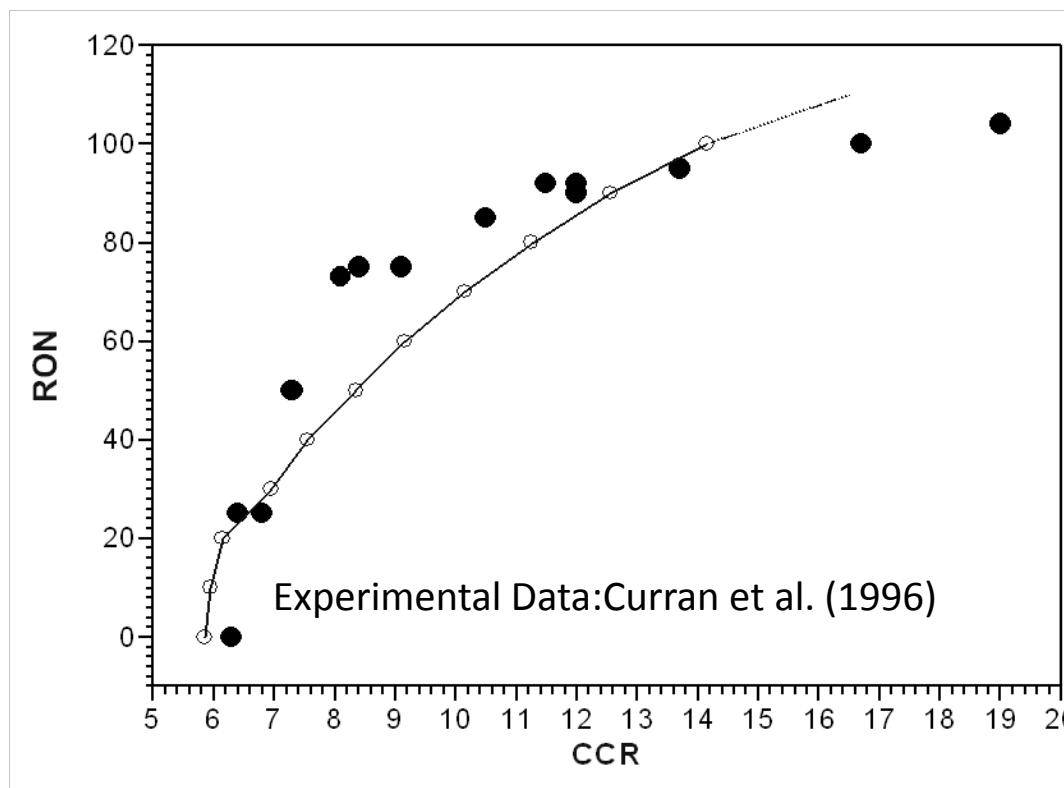
$$Q_{\text{wall}} = hA(T - T_{\text{wall}})$$

$$Nu_h \equiv \frac{hD}{\lambda}$$

$$Nu_h = aRe^b Pr^c$$

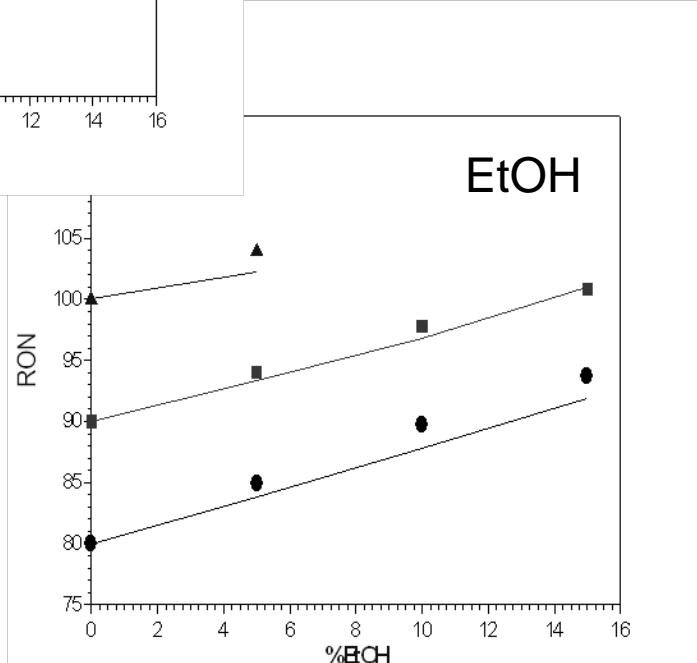
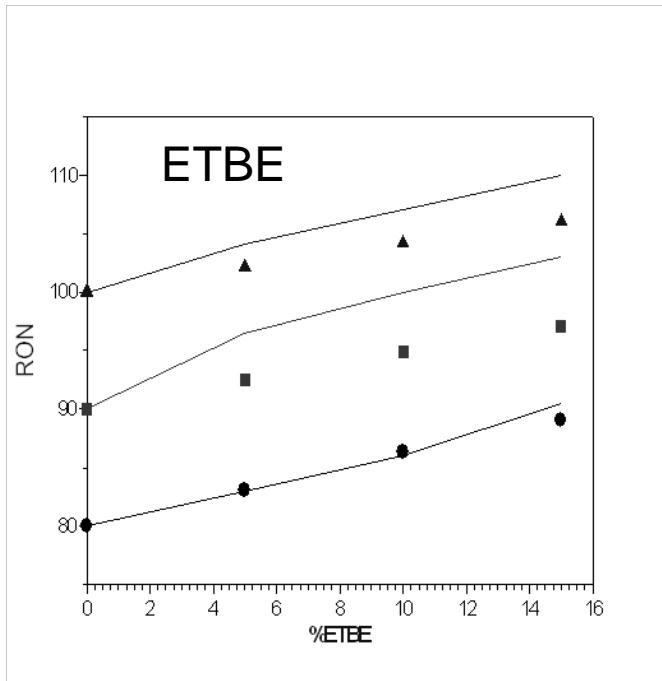
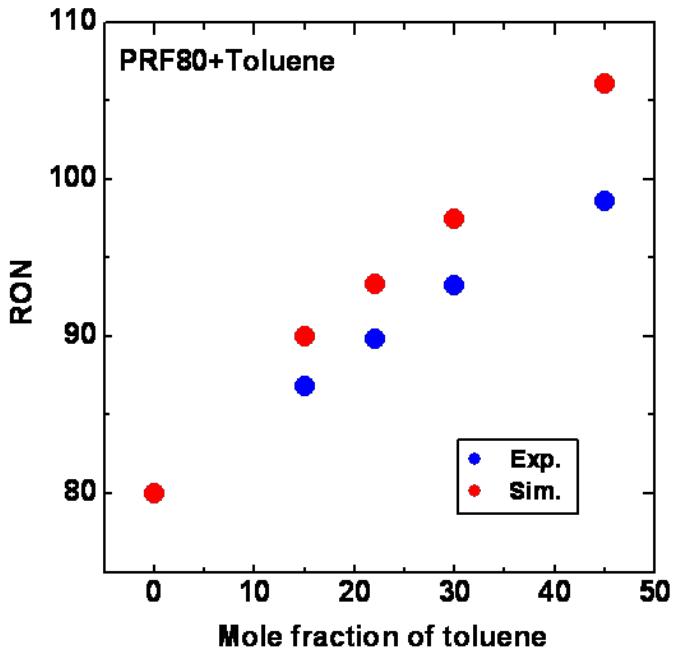
$$Re \equiv \frac{Dw\rho}{\mu}$$

$$w = \left[\left(C_{11} + C_{12} \frac{v_{\text{swirl}}}{S_p} \right) \right] \bar{S_p} + C_2 \frac{V_d T_i}{P_i V_i} (P - P_{\text{motored}})$$



オクタン価の評価

PRFに対するトルエン、EtOH、ETBEの添加効果



実験値はPECのCFRエンジンで取得

酒井、小倉:2008-2007

Model Fuels Consortium (MFC)

With engine and fuel design becoming increasingly coupled, the combined obstacles make the use of combustion simulation key to engine development.

The **MFC** engages industry luminaries in accelerating the development of **software tools** and **databases** to enable the design of cleaner burning, more efficient engines and fuels.



ConocoPhillips



GE Energy



VOLKSWAGEN
AKTIENGESELLSCHAFT

MFC Technical Advisory Team

- **Dr. Charles Westbrook – Chief Technical Advisor**
 - A pioneer in combustion modeling while at the Lawrence Livermore National Laboratory
- **Prof. Mitsuo Koshi, Tokyo University**
 - Expert in combustion kinetics and mechanism generation
- **Prof. Anthony Dean, Colorado School of Mines**
 - Expert kineticist; formerly lead scientist at Exxon
- **Prof. William Green, Massachusetts Inst. of Technology**
 - Expert in numerical methods for model reduction and mechanism generation techniques
- **Prof. Ulrich Maas, Universität Karlsruhe**
 - Expert in engine combustion simulation and numerical methods
- **Prof. Hiromitsu Ando, Fukui University**
 - Former deputy general manager of engine research at Mitsubishi Motors
- **Prof. Rolf D. Reitz, University of Wisconsin**
 - Soot formation kinetics
- **Prof. Angela Violi, University of Michigan**
 - Soot formation, experimentals

Surrogate Composition Optimizer

• Pure component data

- Existing surrogate mechanism with the required pure component fuel properties
- Newly merged mechanisms will need additional commented values for a new fuel added to the input

```
! [__ SMILES="CCCC-C" __]
! [__ INCHI="InChI-1/C5H10/c1-3-5-4-2/h3H,1,4-5H2,2H3" __]
! [__ CAS="109-67-1" __]
! [__ Class="n-Alkenes" __]
! [__ Boilingpoint="303" __]
! [__ LowerHeatingValue="44.981" __]
! [__ Cetane="24.4" __]
! [__ RON="91" __]
! [__ MON="77" __]
c5h10-1      -thermH 10C   5          G   300.00   500
  1.45851539e+1 2.24072471e-2 -7.63348025e-6 1.18188966e-9
  -1.00898205e+4 -5.23683936e+1 -1.06223481e+0 5.74218294e-2
  1.27364989e-8-1.79609789e-12 -4.46546666e+3 3.22739790e+1
```

- * Fuel Class
- * Octane Number
- * Cetane Number
- * Hydrogen Carbon Ratio
- * Oxygen Carbon Ratio
- * Lower Heating Value
- * D-2337 Distillation Curve

Output screen details the optimized properties

- Export of a composition array to an ASCII format
- Readable by CHEMKIN-MFC

Targeted Property	Targeted Value	Optimized Property
aromatic	.28	.285
n-Alkene	.05	.05
i-Alkane	0.4	0.4
n-Alkane	0.19	0.199
cycloalkane	0.08	0.084
RON	91	98
H/C Ratio	2.03	1.96
T10	324	321.1
T20	337	368.2
T30	351	371.7
T50	368	372.1
T70	378	374.0
LHV	44.5	44.51

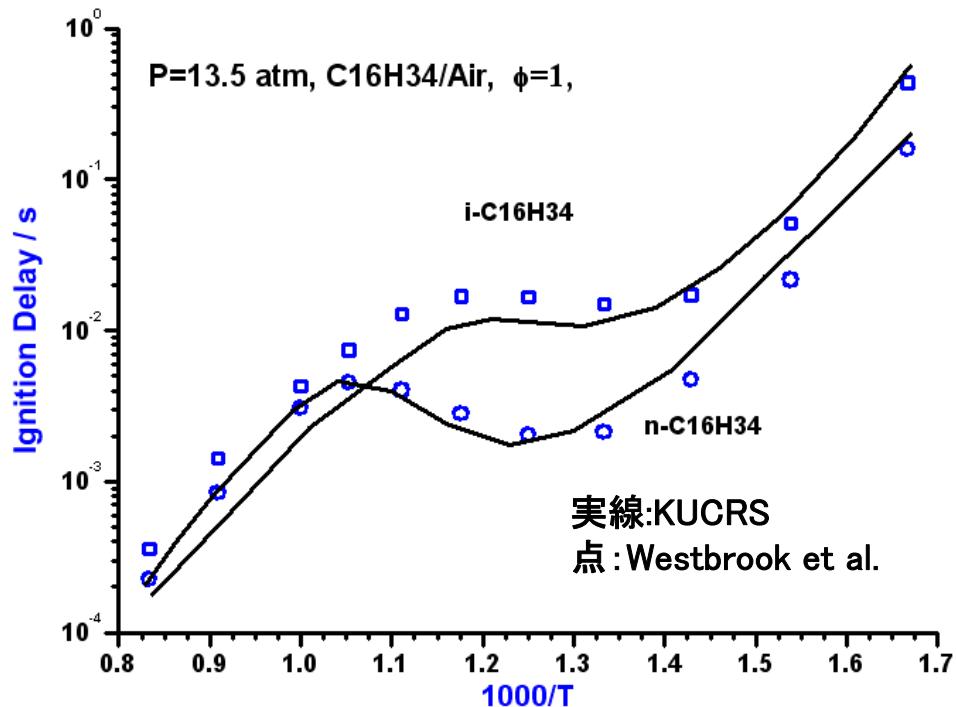
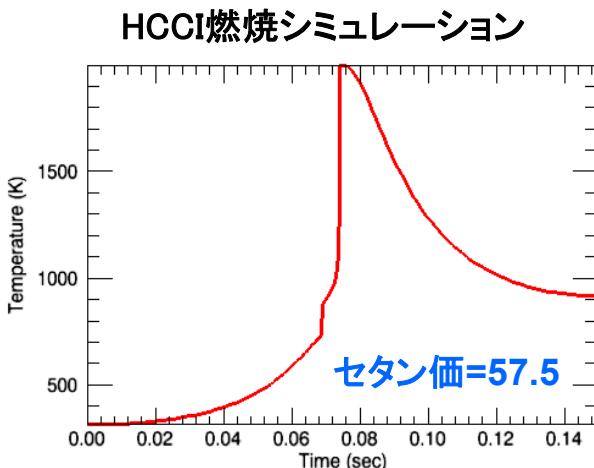
KUCRSによる Diesel+サロゲート燃料の反応機構構築

Diesel サロゲート:
ノルマルセタン+イソセタン

n-C16H34
1555 species, 4979 reactions

i-C16H34
2,2,4,4,6,8,8- heptamethylnonane(HMN)
 $\text{CC}(\text{C})(\text{C})\text{CC}(\text{C})(\text{C})\text{CC}(\text{C})(\text{C})\text{CC}(\text{C})(\text{C})\text{C}$
 5524 species, 17539 reactions

n-C16H34+HMN
6907 species, 27033 reactions



C.K.Westbrook, W.J.Pitz, M.Mehl, and H.J.curran,
Proc. Combust. Inst., 33, in press.
 C.K.Westbrook, W.J.Pitz, O.Herbinet, H.J.Curran, E.J.Silke,
Combust. Flame, 156, 181-199, (2009).

4.2 反応機構の簡略化

CFDへの組み込み<=反応機構の簡略化

ReductionとLumping

DRG: Directed Relation Graph

T.Lu, C.K.Law, Proc. Combust. Inst., 30 (2005) 1333

PCA: Principal Component Analysis

S.Vajda, P.Valko, T.Turnyi, Int. J. Chem. Kinet., 17(1985) 55

CSP: Computational Singular Perturbation

S.H.Lam, D.A.Goussls, Int. J. Chem. Kinet., 26(1994) 461

ILDM: Intrinsic Low-Dimensional Manifolds

U.Maas, S.B.Pope, Combust. Flame, 88 (1992) 239

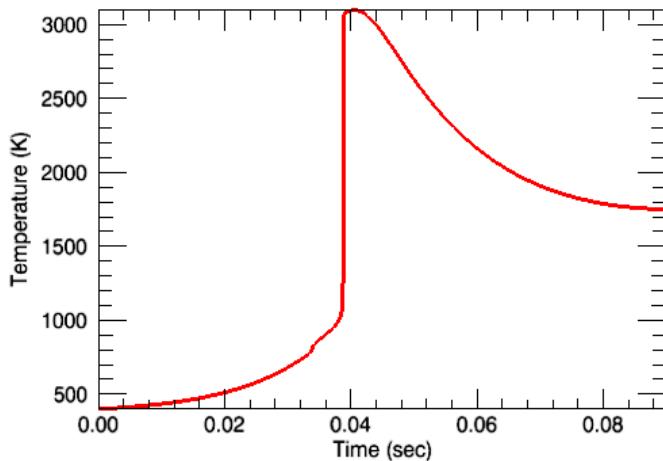
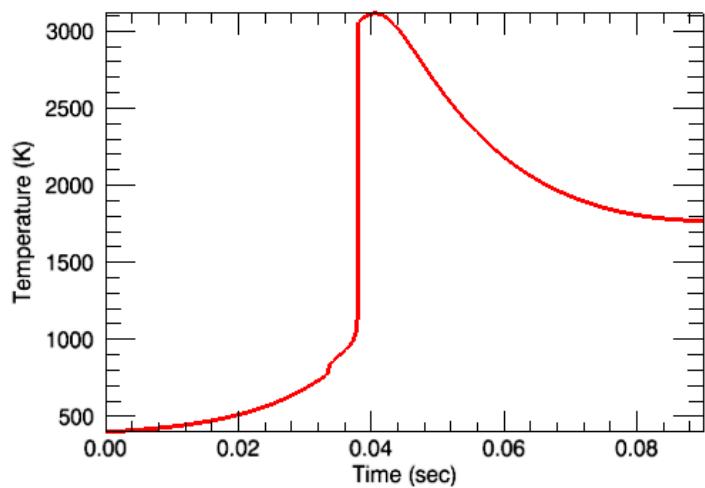
RCCE : Rate-Controlled Constrained Equilibrium

J.C.Keck, D.Gillespie, Combust. Flame, 17,237(1971)

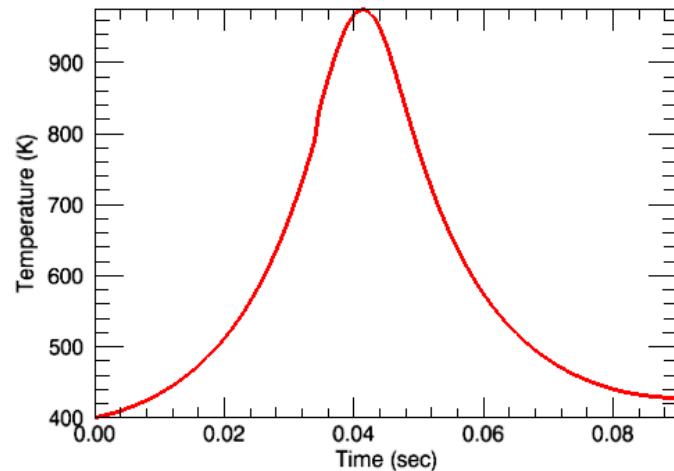
変数の減少とStiffnessの緩和

DRGによる簡略化の例: TRF

HCCI燃焼シミュレーション、
CR=17, 600RPM



$\epsilon=0.2$, 280 species, 1183 reactions

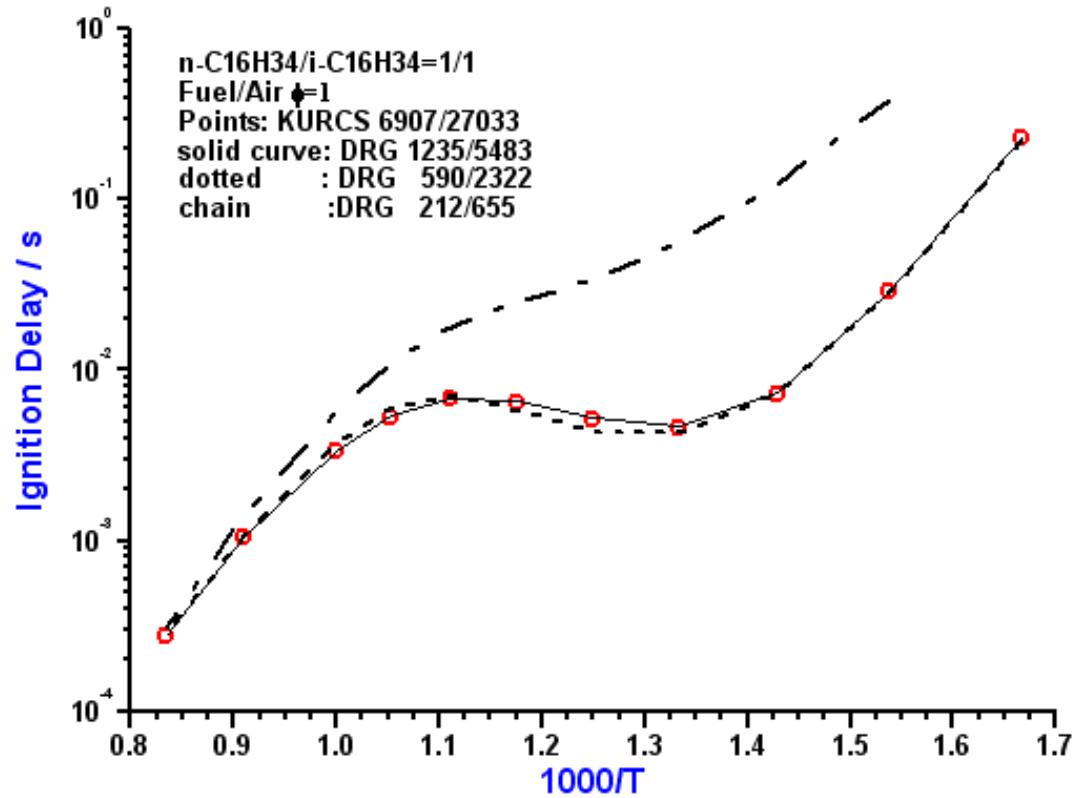
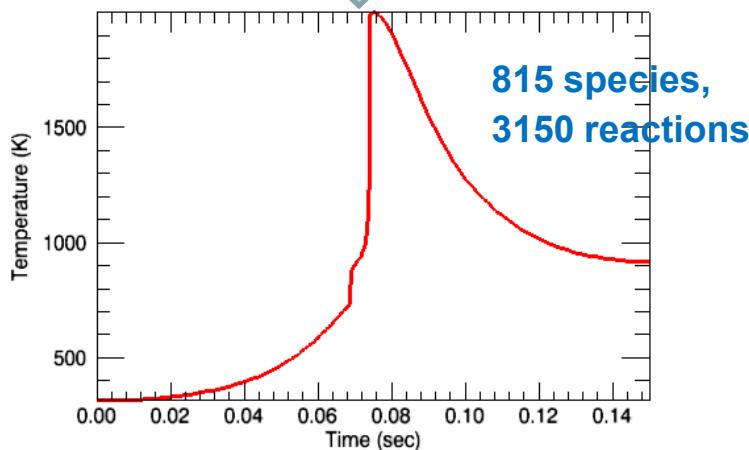
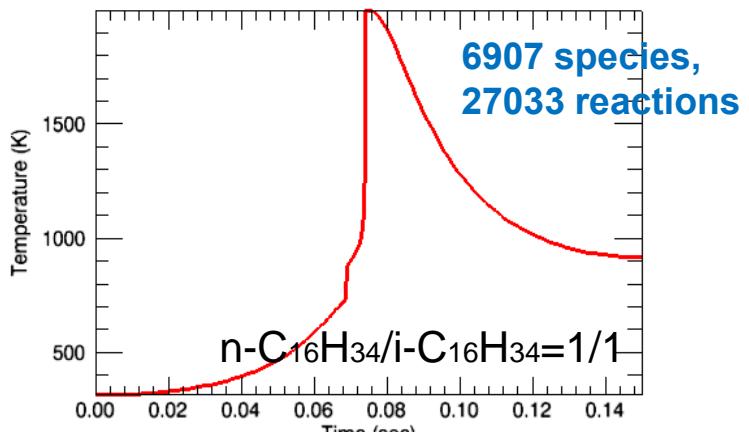


$\epsilon=0.3$, 180 species, 720 reactions

Full Mechanism:
758 species, 2877 reactions

DRGによるDieselサロゲート機構の簡略化

HCCI燃焼シミュレーション
CR=17, 600RPM



CFDに組み込むためにはさらなる簡略化が必要?
=> RCCE法の可能性?

RCCE (Rate-Controlled Constraint-Equilibrium)

Jones and Rigopoulos, Combust. Theory Modelling, 11, 755 (2007)

Gibbs Free energy and chemical potential

$$g = \sum_{j=1}^N \mu_j n_j \quad (1) \quad N: \text{number of chemical species}, \quad n_j: \text{mol/g}$$

$$\mu_j = \mu_j^0 + RT \ln p_j / p^0 = \overline{\mu_j^0} + RT \ln n_j / n \quad (2) \quad p^0: 1 \text{ bar}$$

$$\overline{\mu_j^0} = \mu_j^0 + RT \ln p / p^0 = H_j^0 - TS_j^0 + RT \ln p / p^0 \quad (3)$$

$$n = \sum_j n_j \quad (4)$$

Constraints

$$b_i = \sum_{j=1}^N a_{ij} n_j \quad (i = 1, \dots, M_e) \quad (5) \quad \mathbf{M}_e = \text{number of elements}$$

$$d_k = \sum_{j=1}^N c_{kj} n_j \quad (k = 1, \dots, M_c) \quad (6) \quad \mathbf{M}_c = \text{number of constraints}$$

Lagrangean: L $L = g + \sum_i \overline{\lambda}_i b_i + \sum_k \overline{\beta}_k d_k$

$$\frac{\partial L}{\partial n_j} = 0 \Rightarrow n_j = n \exp\left(-\frac{\overline{\mu}_j^0}{RT}\right) \exp\left(\sum_i \lambda_i a_{ij}\right) \exp\left(\sum_k \beta_k c_{kj}\right) \quad (7)$$

$$\lambda_i = -\overline{\lambda}_i / RT, \quad \beta_k = -\overline{\beta}_k / RT$$

For $H, p = \text{constant}$ conditions

Thermodynamic constraints $h = \sum_j H_j n_j \quad (8)$

$$p = n\rho RT \quad (9)$$

Kinetic constraints $d(d_k) / dt = \sum_j c_{kj} (dn_j / dt) = \sum_j c_{kj} W_j \quad (10)$

$W_j \Leftarrow$ From detailed chemical kinetic mechanism

Index 1 Solution: Solve the algebraic Eqs.(5),(6),(8),(9) and differential eq. (10).

Index 0 Solution: (constraint potentials) formulation

Differential equations for $M_e + M_c + 2$ variables

$$\rho, T, \lambda_i (i = 1, \dots, M_e), \beta_k (k = 1, \dots, M_c)$$

From eq.(7)

$$\frac{\partial n_j}{\partial \lambda_i} = a_{ij} n_j \quad \frac{\partial n_j}{\partial \beta_k} = c_{kj} n_j \quad \frac{\partial n_j}{\partial T} = \frac{1}{T} \left(\frac{H_j^0}{RT} - 1 \right) n_j \quad \frac{\partial n_j}{\partial \rho} = -\frac{n_j}{\rho} \quad (11)$$

Solver of DAE used in the present study: **DASPK**

RCCEによる簡略化: CH₄/O₂

RCCE9C: CH₄, O₂, H₂, H₂O, CO₂, CO, OH, O, H

RCCE19C: CH₄, O₂,
H, O, OH, HO₂, H₂O₂
CH₃, HCO, CH₂O, CH₃OH, CH₃OO,
CH₃OOH, C₂H₅, C₂H₆
CO, CO₂, H₂O

DRG 17: RCCE19C – C₂H₅ – C₂H₆

RCCE 17 <= DRG 17 同じ化学種を束縛条件

RCCE9 : CH₄, O₂, H, CO

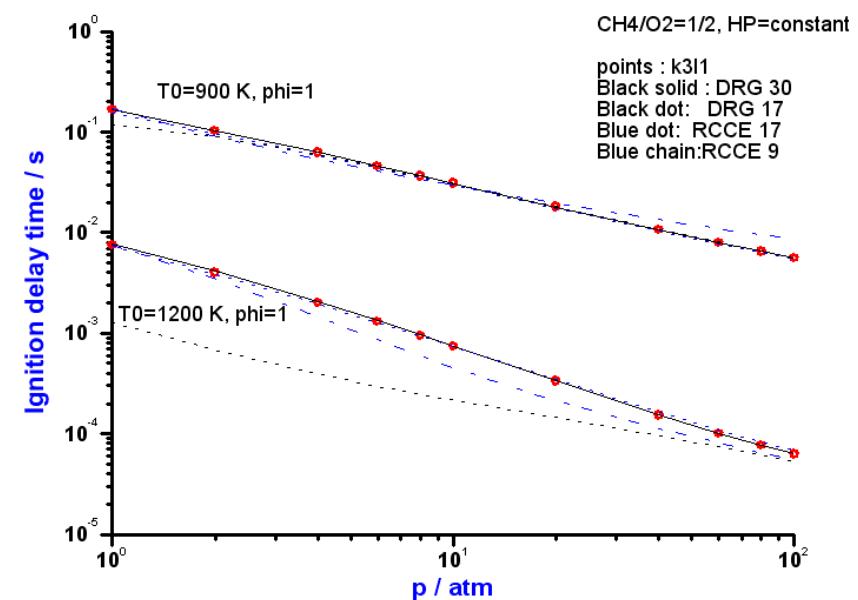
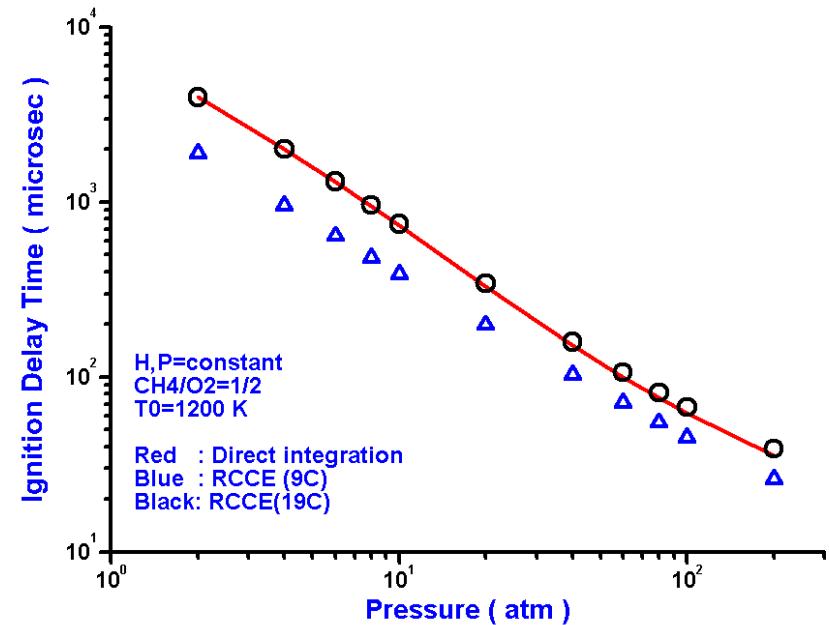
M

OH+O+HCO+CH₃O

HO₂+CH₃OO

H₂O₂+CH₃OOH

CH₂O+CH₃OH



RCCEによるn-C₇H₁₄燃焼反応機構の簡略化

Base mechanism: generated by KUCRS
(280 species, 903 reactions)

束縛条件

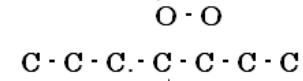
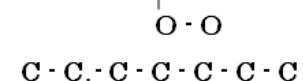
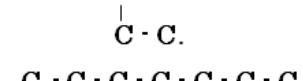
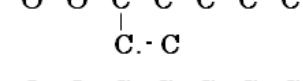
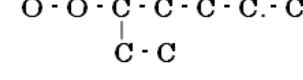
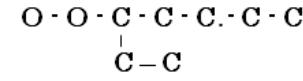
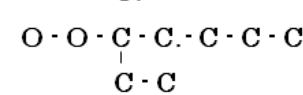
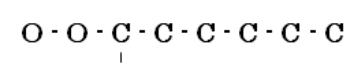
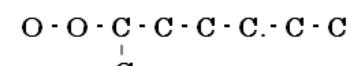
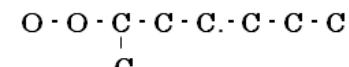
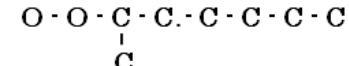
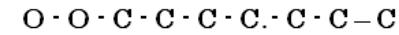
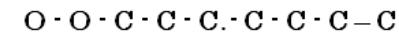
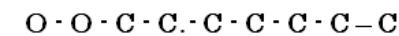
=> 分子構造にしたがって化学種を分類する
(KUCRSの出力を利用)

同じグループの化学種の線形結合を束縛条件とする。

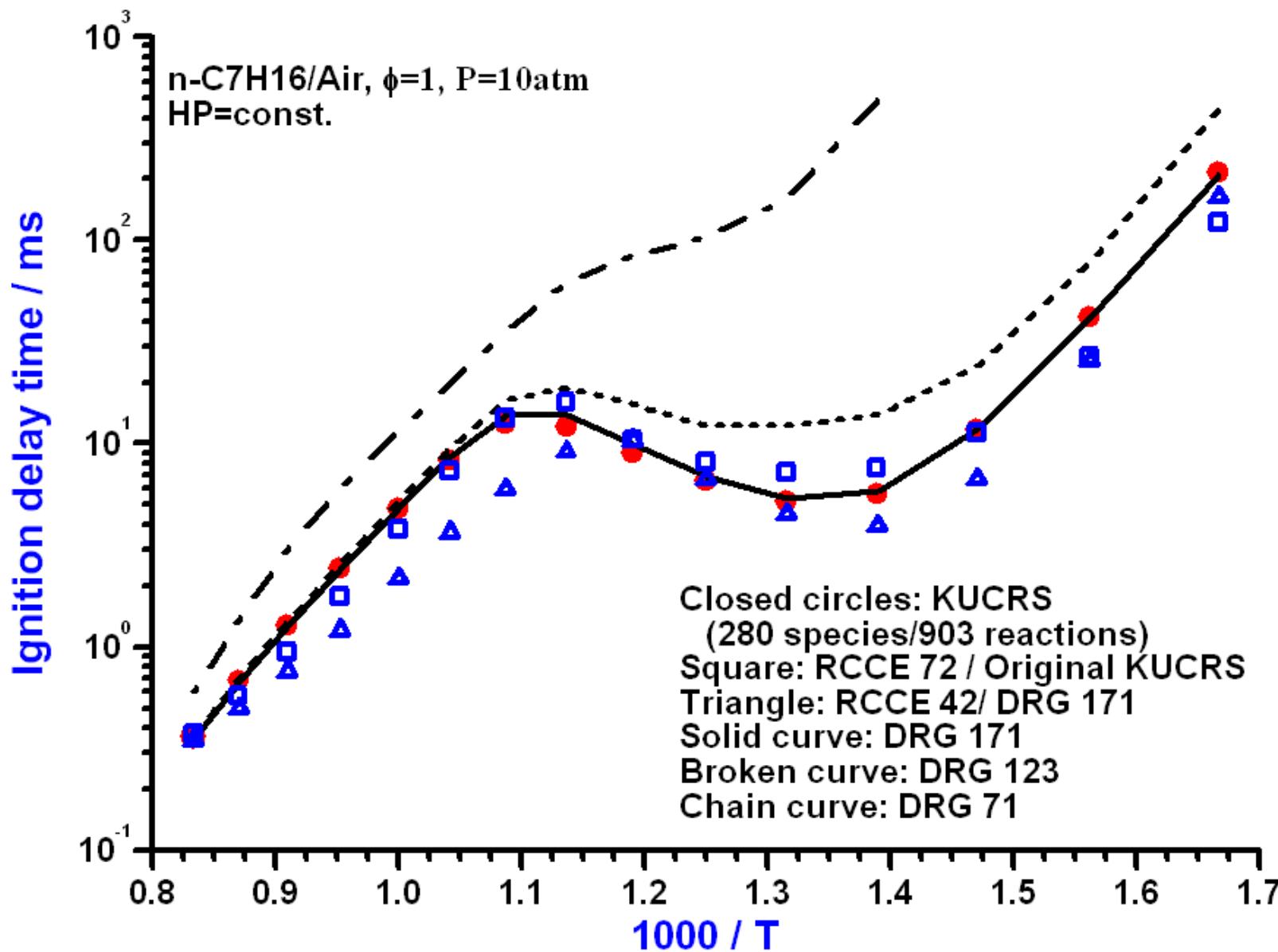
KUCRSの出力例

name: C7H14OOHa
formula: C7H15O2
SMILES: OOC[CH]CCCCC
struct:
O - O - C - C - C - C - C - C
groups: C7H14OOHa R C 7 H 15 O 2 \$ C/C/H2/O 1 C/C/H3 1 C/C2/H2 5 O/C/O 1 O/H/O 1 \$ S 8 3
code: a0008024 (QOOH)

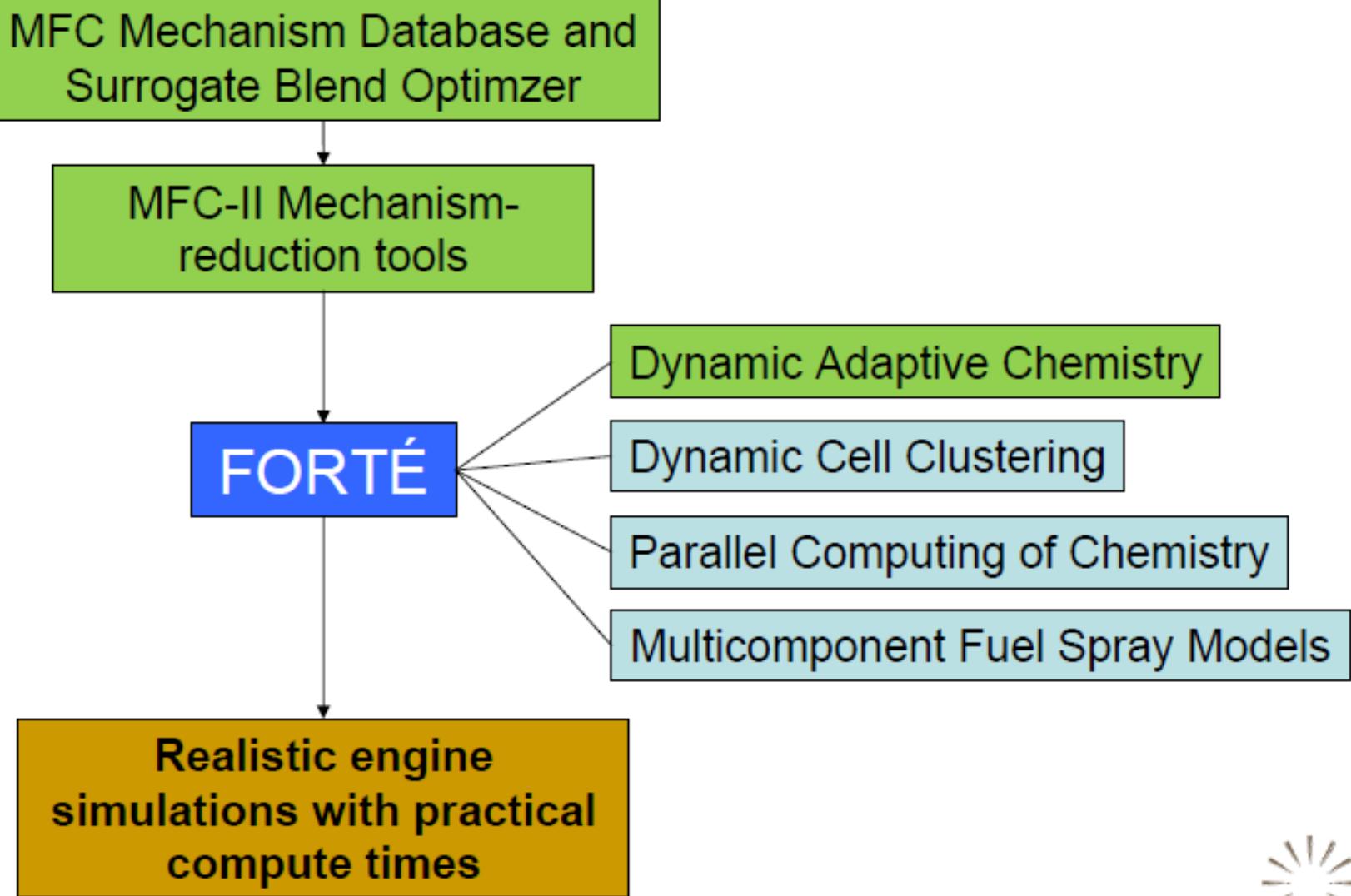
R	RO	ROO	ROOH	QOOH	OOQOOH	Cyclic ether
nC7H15a	C7H15Oa	C7H15OOa	C7H15OOHb	C7H14OOHa	HOOC7H14OOb	C7H14cyOa
nC7H15b	C7H15Ob	C7H15OOb	C7H15OOHa	C7H14OOHb	HOOC7H14OOc	C7H14cyOb
nC7H15c	C7H15Oc	C7H15OOc	O6H12OOHa	C7H14OOHc	HOOC7H14OOe	C7H14cyOc
nC7H15d	C7H15Od	C7H15OOd	C7H15OOHc	C7H14OOHd	HOOC7H14OOf	C7H14cyOd
		nC3H7OOH		C7H14OOHe	HOOC7H14OOh	C7H14cyOe
C6H13a	C6H11Oa	C6H13OOa	C2H5OOH	C7H14OOHf	HOOC7H14OOi	C7H14cyOf
C6H13b	C5H11Oa	C6H13OOb	CH3OOH	C7H14OOHg	HOOC7H14OOj	C7H14cyOg
C6H13c	nC4H9O	C5H11OOa	H2O2	C7H14OOHh	HOOC7H14OOk	C7H14cyOh
C5H11a	nC3H7O	C5H11OOb		C7H14OOHi	HOOC7H14OOl	C6H12cyOa
C5H11b	C2H5O	nC4H9OO		C7H14OOHj	HOOC7H14OOm	C6H12cyOb



RCCEによるn-C₇H₁₆の簡略化



Simulations with FORTÉ are one way to use of detailed kinetics directly



5. おわりに

- 実用燃料の詳細反応機構構築

自動生成がかなりできるようになりつつある。

○アルカン、○アルケン、△ナフテン、×芳香族

自動生成プログラム

○KUCRS ?EX-GAS ?RGM

- 詳細反応機構を有効に用いるために 簡略化手法の開発が必要

DRG :簡便で強力であるがサイズに限界あり。

RCCE:有望である。発展途上。

謝辞

疋田 強 先生
浅羽 哲郎先生
藤井 信行先生
松為 宏幸先生
幸田 清一郎先生

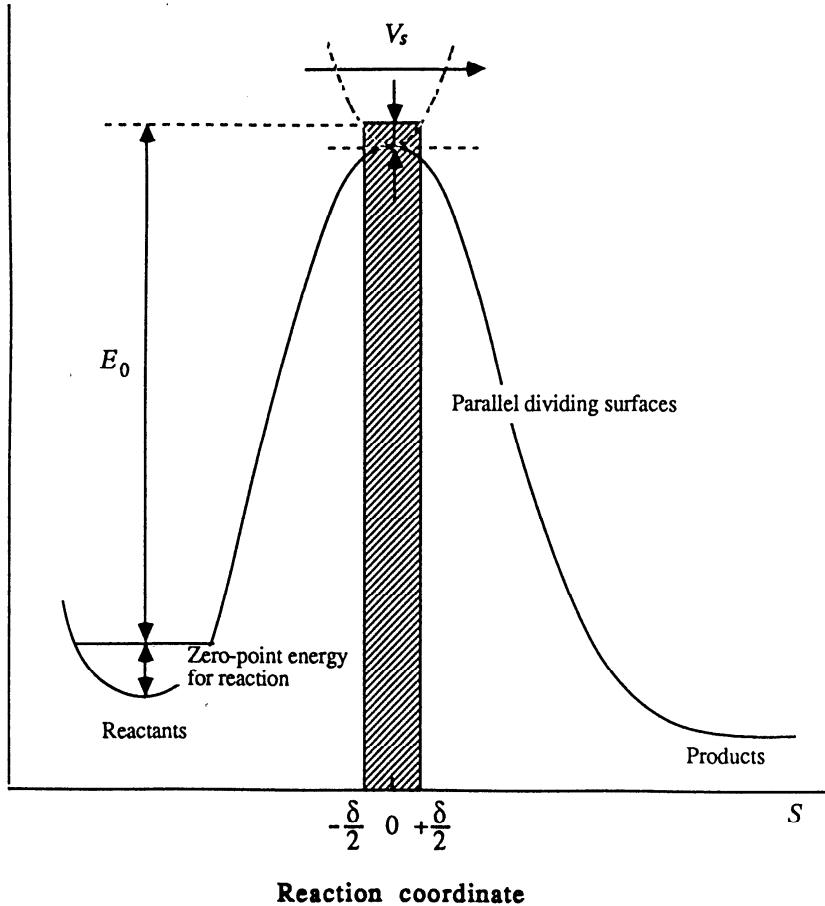
安東 弘光先生

手崎 衆 先生
三好 明 先生
戸野倉 賢一先生
村上 能規 先生
小口 達夫 先生
須佐 秋夫 先生
小倉 鉄平 先生
酒井 康行 先生
清水 和弥 先生

Buck up

速度定数の評価：遷移状態理論

Potential energy



$$\frac{dN}{dt} = \frac{N^\ddagger}{2} \frac{\bar{v}_s}{\delta}$$

$$\frac{dN}{dt} = \frac{N^\ddagger}{2} \left(\frac{2k_B T}{\pi \mu_s} \right)^{1/2} \frac{1}{\delta}$$

$$K_c^\ddagger = \frac{N^\ddagger}{[A][B]} = \frac{Q_{\text{tot}}^\ddagger}{Q_A Q_B} e^{-E_0/k_B T}$$

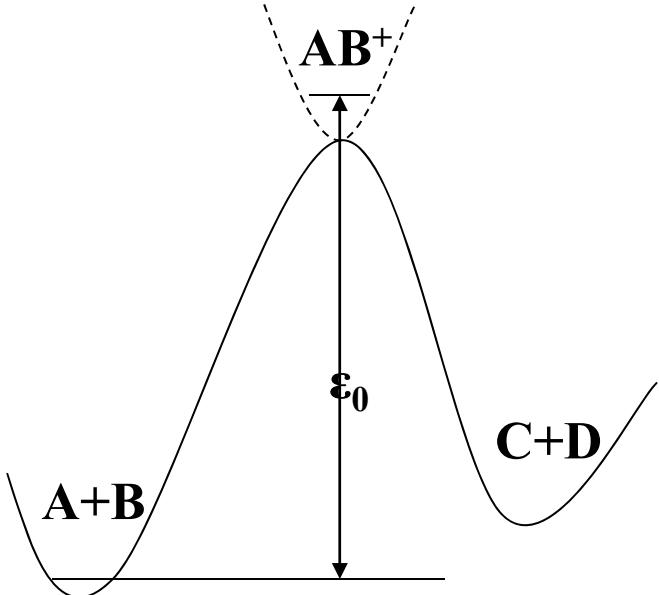
$$\frac{dN}{dt} = \left(\frac{2k_B T}{\pi \mu_s} \right)^{1/2} \frac{1}{2\delta} \frac{Q_{\text{tot}}^\ddagger}{Q_A Q_B} e^{-E_0/k_B T} [A][B]$$

$$Q_{\text{tot}}^\ddagger = Q_s Q^\ddagger$$

$$Q_s = (2\pi \mu_s k_B T)^{1/2} \delta / h$$

$$k = k_{\text{abs}} = \frac{k_B T}{h} \frac{Q^\ddagger}{Q_A Q_B} e^{-E_0/k_B T}$$

素反応：二分子反応



分子Aと分子Bが衝突し反応する。

$$-\frac{d[A]}{dt} = k[A][B]$$

k :速度定数

反応するためには ε_0 以上の
衝突エネルギーが必要。

速度定数

= (衝突数)

× (エネルギーが ε_0 以上の割合)

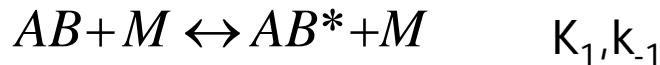
$$\varepsilon = \frac{1}{2} \mu v^2 > \varepsilon_0 \quad \text{ならばすべて反応するとすれば (cf. アレーニウス式)}$$

$$k(T) = \pi b_{\max}^2 \left(\frac{8kT}{\pi\mu} \right)^{1/2} \left(1 + \frac{\varepsilon_0}{kT} \right) \exp\left(-\frac{\varepsilon_0}{kT}\right)$$

单分子 (一分子) 反应

Lindeman mechanism

- $AB = A + B$

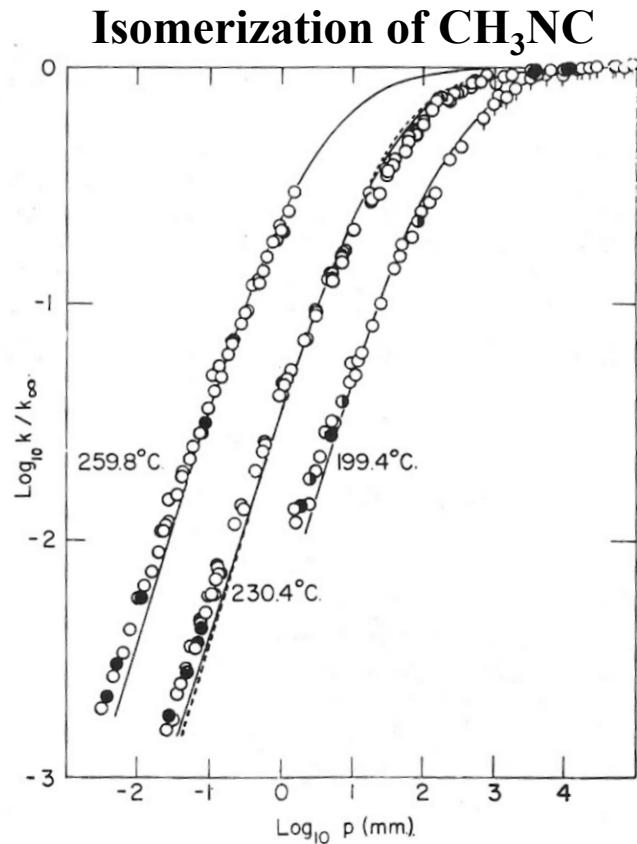


$$\frac{d(AB^*)}{dt} = k_1(AB)(M) - k_{-1}(AB^*)(M) - k_2(AB^*) = 0$$

$$(AB^*) = \frac{k_1(AB)(M)}{k_{-1}(M) + k_2}$$

$$R = k(AB) = \frac{k_1 k_2 (AB)(M)}{k_{-1}(M) + k_2}$$

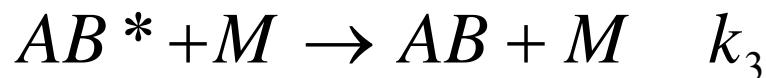
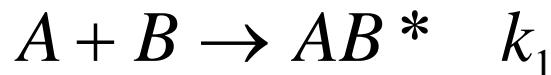
$$k_{uni} = \frac{k_1 k_2 (M)}{k_{-1}(M) + k_2} \quad k_\infty = \frac{k_1}{k_{-1}} k_2, k_0 = k_1(M), k_{uni} = \frac{k_\infty}{1 + k_\infty / k_1(M)}$$



三分子反應

Reverse of unimolecular reaction

- A+B+M = AB+M



$$\frac{d(AB^*)}{dt} = k_1(A)(B) - k_2(AB^*) - k_3(AB^*)(M)$$

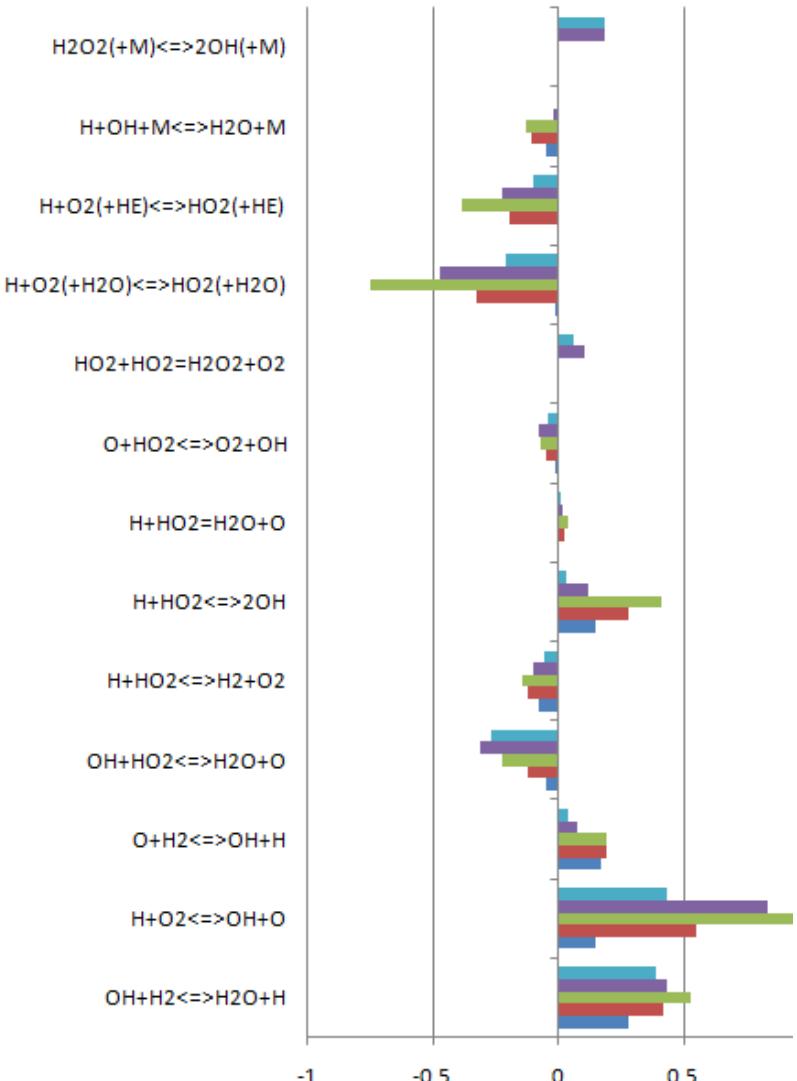
$$R = \frac{d(AB)}{dt} = \frac{k_1 k_3}{k_2 + k_3(M)} (A)(B)(M)$$

$$k_3(M) \gg k_2 \quad \Rightarrow \quad R \approx k_1(A)(B)$$

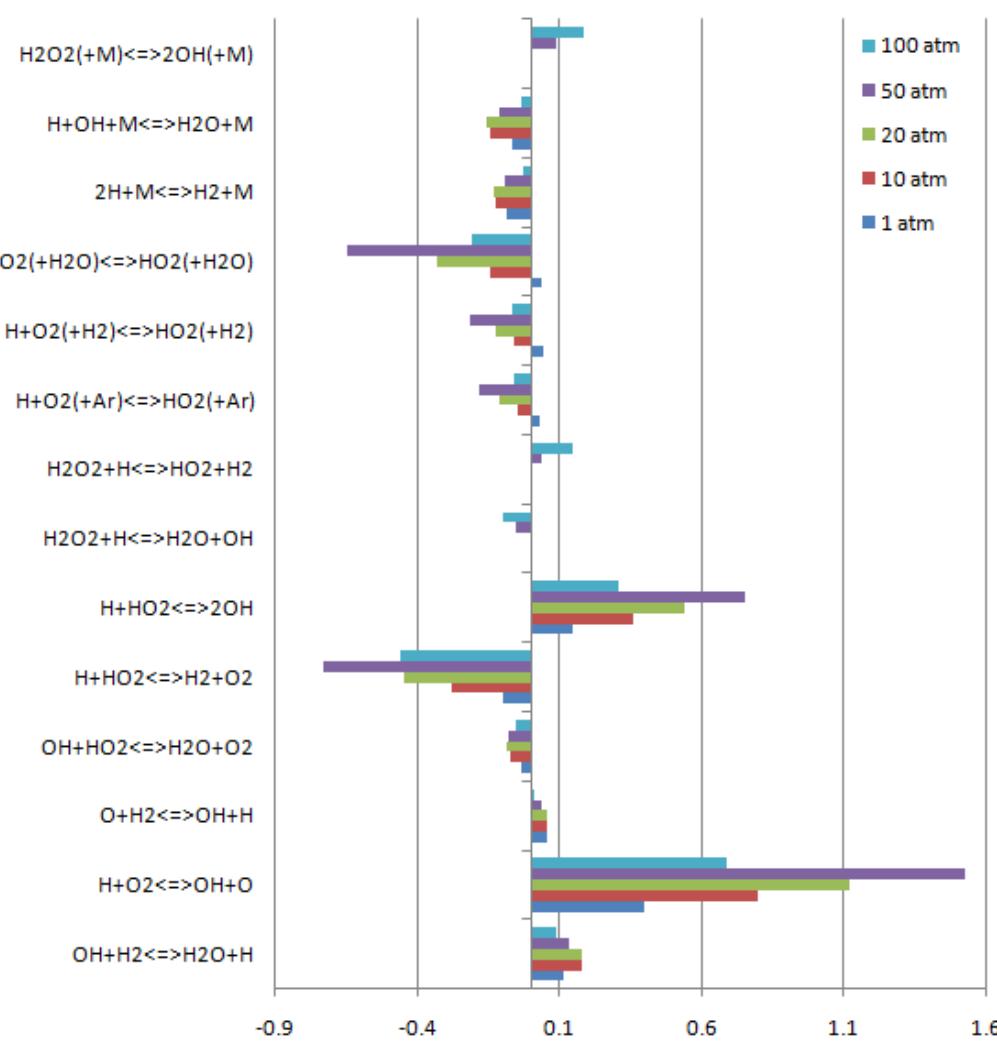
$$k_3(M) \ll k_2 \quad \Rightarrow \quad R \approx \frac{k_1 k_3}{k_2} (A)(B)(M)$$

Sensitivity for Flame Speed

$\phi=0.7, \text{H}_2/\text{O}_2/\text{He}$



$\phi=2.5, \text{H}_2/\text{O}_2/\text{Ar}$



PRF+EtOH+ETBE機構の検証

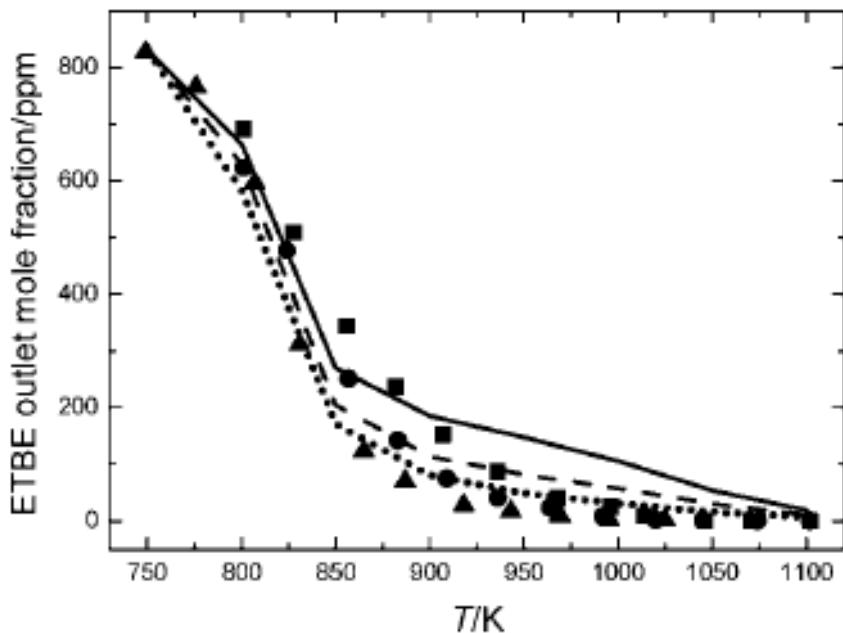


Figure 4. Experimental (symbols) and simulated (curves) outlet mole fractions of ETBE in a jet-stirred reactor at 10 atm and $\tau = 0.5$ s. Experimental results were taken from Glaude et al.¹² Squares and solid curve, $\phi = 2.0$ (ETBE/O₂/N₂ = 0.1/0.45/99.45); circles and dashed curve, $\phi = 1.0$ (ETBE/O₂/N₂ = 0.1/0.9/99.0); triangles and dotted curve, $\phi = 0.5$ (ETBE/O₂/N₂ = 0.1/0.018/98.1).

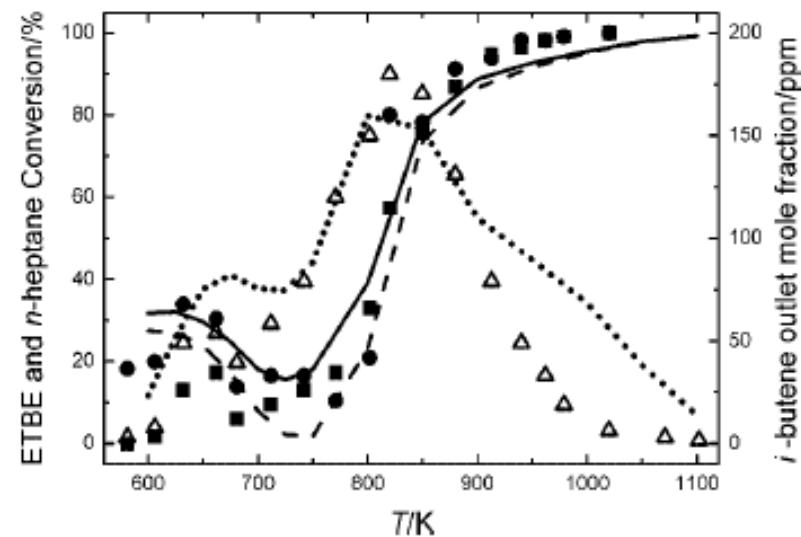
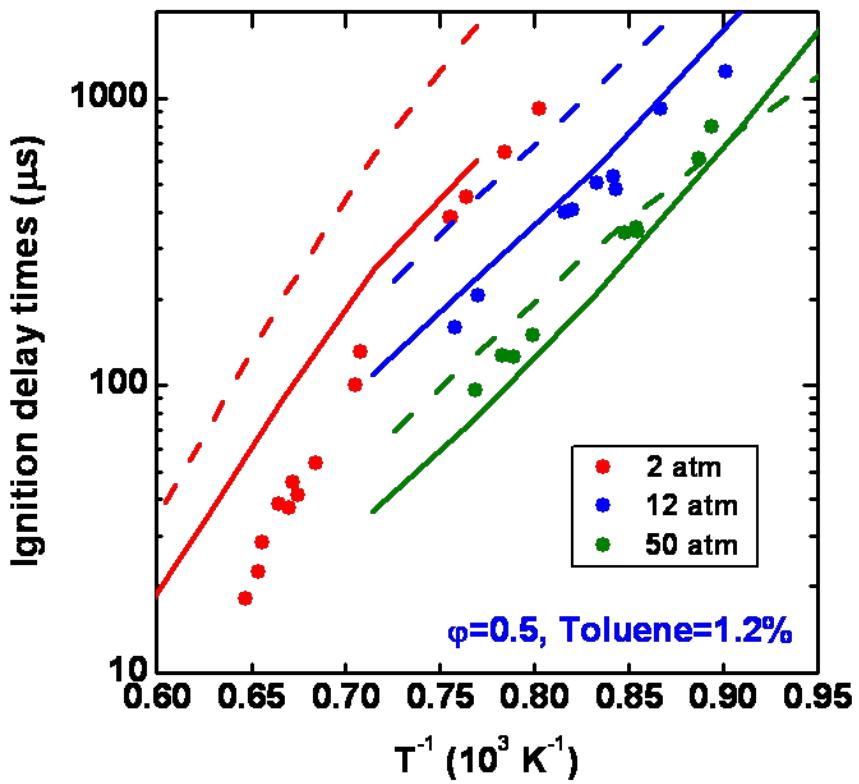


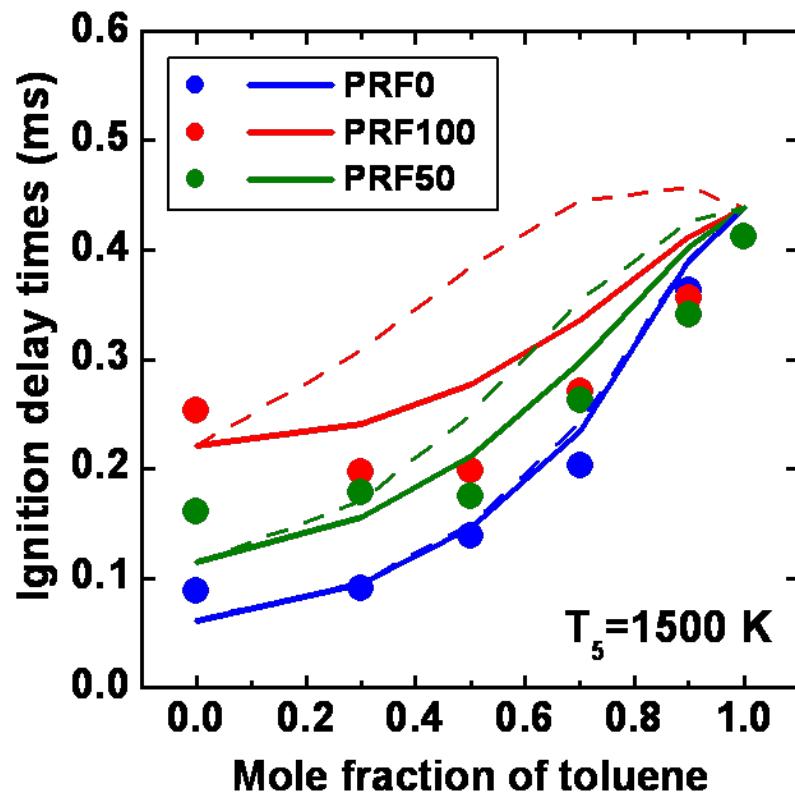
Figure 6. Experimental (symbols) and simulated (curves) fuel conversions and outlet mole fractions of *i*-butene for the oxidation of ETBE/*n*-heptane mixtures in a jet-stirred reactor at 10 atm, $\phi = 0.5$ (ETBE/*n*-C₇H₁₆/O₂/N₂ = 0.05/0.05/1.0/98.9), and $\tau = 0.5$ s. Experimental results were taken from Dagaut et al.¹⁰ Squares and solid curve, ETBE; circles and dashed curve, *n*-heptane; open triangles and dotted curve, *i*-butene.

T.Ogura, Y.Sakai, A.Miyoshi, M.Koshi, P.Dagaut
Energy and Fuel 21, 3233(2007)

トルエンの燃焼反応機構の検証



12 and 50 atm: Oehlslaeger et al, 2008
 2 atm: Sakai et al., 2007
 solid line: this model, dashed line: Pitz model

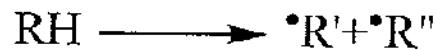


トルエン/PRF混合燃料
 => Effects of Cross Reactions?

Empirical estimation of the rate constants

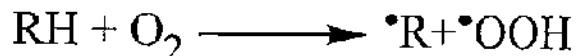
2.5 - Initiations

a) Unimolecular initiations



Broken bond	log A	E
C _p -C _s	17.00	369
C _s -C _s	16.35	358
C _s -C _t	16.80	347
C _t -C _t	16.80	340
RO-OH	14.85	176
RO-OR'	14.85	176

b) Bimolecular initiations



Nature of H atom	log A	E
H _p	12.60	205
H _s	12.00	201
H _t	12.30	192
H _a	13.30	199
H _v	13.00	241
H _a : H allylic		
H _v : H vinylic		

Guy-Marie Come, "Gas-Phase Thermal Reactions" Kluwer (2001)

Ex.



Directed Relation Graph

$$r_{AB} \equiv \frac{\sum_{i=1,I} |v_{A,i} \omega_i \delta_{Bi}|}{\sum_{i=1,I} |v_{A,i} \omega_i|},$$

$$\delta_{Bi} = \begin{cases} 1, & \text{if the } i\text{th reaction involves} \\ & \text{species B,} \\ 0, & \text{otherwise,} \end{cases}$$

- (1) Each vertex in DRG is uniquely mapped to a species in the detailed mechanism.
- (2) There exists a directed edge $A \rightarrow B$ if and only if $r_{AB} \geq \varepsilon$.
- (3) The starting vertices of DRG correspond to the major species in the mechanism.

T.Lu, C.K.Law,
Proc. Combust. Inst., 30 (2005) 1333

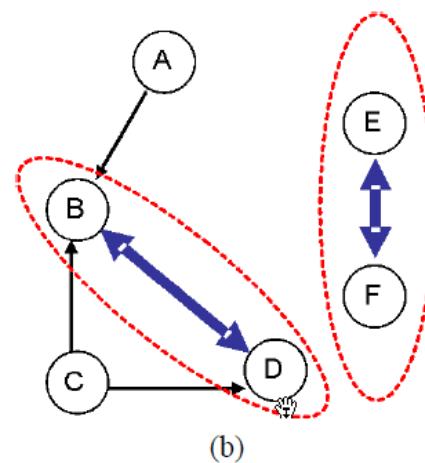
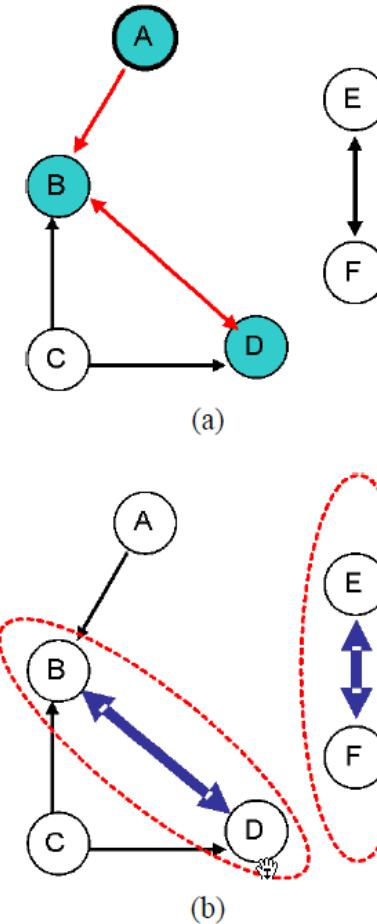


Fig. 1. Schematics showing typical configuration of the directed relation graph (DRG); the vertices correspond to the species and the directed edges correspond to the immediate requirement of one species to another. (a) Basic configuration and identification of skeletal species. (b) Demonstration of strongly coupled species groups.

Constraint potential formulation

Differential equations of Index Zero.

$$\begin{aligned} \frac{d(d_k)}{dt} &= \sum_j c_{kj} W_j = \frac{\partial d_k}{\partial \rho} \frac{d\rho}{dt} + \frac{\partial d_k}{\partial T} \frac{dT}{dt} + \sum_{i=1}^{M_e} \frac{\partial d_k}{\partial \lambda_i} \frac{d\lambda_i}{dt} + \sum_{l=1}^{M_c} \frac{\partial d_k}{\partial \beta_l} \frac{d\beta_l}{dt} \\ &= -\sum_j c_{kj} n_j \frac{1}{\rho} \frac{d\rho}{dt} + \sum_j c_{kj} n_j \frac{1}{T} \left(\frac{H_j^0}{RT} - 1 \right) \frac{dT}{dt} + \sum_i \sum_j a_{ij} c_{kj} n_j \frac{d\lambda_i}{dt} + \sum_l \sum_j c_{kj} c_{lj} n_j \frac{d\beta_l}{dt} \\ &\quad (k = 1, \dots, M_c) \end{aligned}$$

$$\begin{aligned} \frac{db_i}{dt} &= -\sum_j a_{ij} n_j \frac{1}{\rho} \frac{d\rho}{dt} + \sum_j a_{ij} n_j \frac{1}{T} \left(\frac{H_j^0}{RT} - 1 \right) \frac{dT}{dt} + \sum_{l=1}^{M_e} \sum_j a_{ij} a_{lj} n_j \frac{d\lambda_l}{dt} + \sum_{k=1}^{M_c} \sum_j a_{ij} c_{kj} n_j \frac{d\beta_k}{dt} \\ &= 0 \quad (i = 1, \dots, M_e) \end{aligned}$$

$$\begin{aligned} \frac{dh}{dt} &= -\sum_j H_j^0 n_j \frac{1}{\rho} \frac{d\rho}{dt} + \sum_j n_j \left[\frac{\partial H_j^0}{\partial T} + \frac{H_j^0}{T} \left(\frac{H_j^0}{RT} - 1 \right) \right] \frac{dT}{dt} + \sum_{i=1}^{M_e} \sum_j H_j^0 a_{ij} n_j \frac{d\lambda_i}{dt} + \sum_{k=1}^{M_c} \sum_j H_j^0 c_{kj} n_j \frac{d\beta_k}{dt} \\ &= 0 \end{aligned}$$

$$\begin{aligned} \frac{dp}{dt} &= \left[\frac{p}{T} + \frac{p}{n} \sum_j \frac{n_j}{T} \left(\frac{H_j^0}{RT} - 1 \right) \right] \frac{dT}{dt} + \frac{p}{n} \sum_{i=1}^{M_e} \sum_j a_{ij} n_j \frac{d\lambda_i}{dt} + \frac{p}{n} \sum_{k=1}^{M_c} \sum_j c_{kj} n_j \frac{d\beta_k}{dt} \\ &= 0 \end{aligned}$$