化学反応論と燃焼

Chemical Kinetics and Combustion

広島大学 大学院工学研究科 機械物理工学専攻
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JSSW2018 (Symposium on Shock Waves in Japan; Yokohama, Japan) Mar. 5–7, 2019

衝撃波管と化学物理

Shock Tube & Chemical Physics

衝撃波管と化学反応

Shock Tube & Chemical Reactions

衝撃波管-気相反応の最先端装置 (~20世紀半ば)

shock tube - state-of-the-art apparatus for gas-phase reactions (~mid-20th century)

均一瞬時並進加熱 - 振動緩和 (CO_2 etc.), 二原子分子の熱解離
homogeneous prompt translational heating - vibrational relaxation (of CO_2 etc.), thermal decomposition of diatomic molecules

- E. F. Greene & J. P. Toennies, Chemical Reactions in Shock Waves, Edward Arnold, 1964 (German ed. Springer, 1959).
- 倉谷健治・土屋荘次 "衝撃波の化学物理," 裳華房, 東京, 1968.
- A. Lifshitz, ed., "Shock Waves in Chemistry," Marcel Dekker, New York, 1981.

cf. 閃光分解, 放電流通発光
cf. flash photolysis, discharge flow afterglow

状態選別化学 (~20世紀末)

state-to-state chemistry (~late 20th century)

レーザ励起 / 分子線 - レーザ分光
laser excitation / molecular beam - laser spectroscopy

衝撃波管-理想的な着火遅れ計測装置 (20世紀末~)

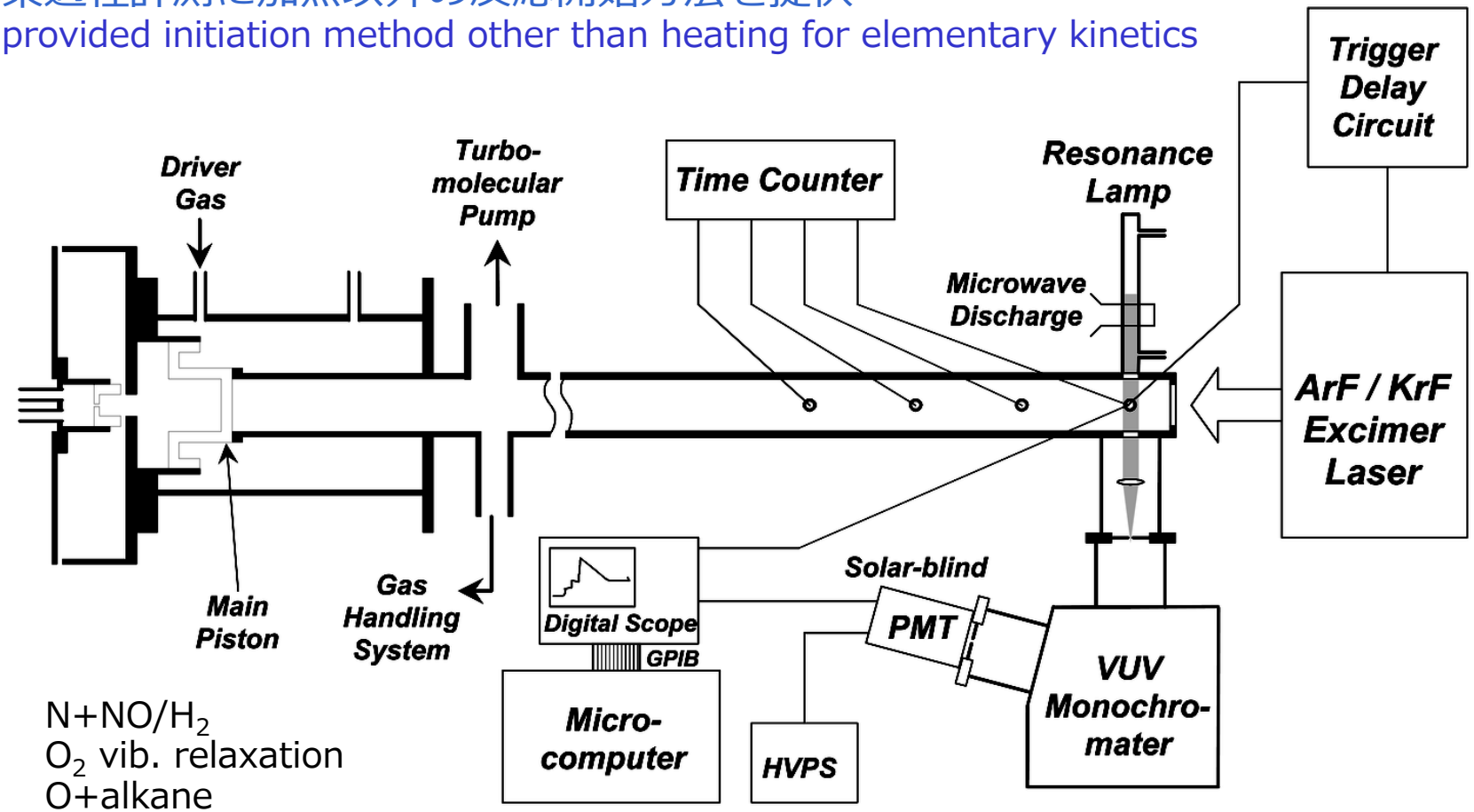
shock tube - ideal apparatus for ignition delay measurement (late 20th century~)

レーザ光分解-衝撃波管

Laser Photolysis - Shock Tube

1988~ D. F. Davidson, A. Y. Chang and R. K. Hanson, Proc. Combust. Inst. 22, 1877–1885 (1988).
M. Koshi, M. Yoshimura, K. Fukuda, **H. Matsui**, K. Saito, M. Watanabe, A. Imamura and C. Chen, J. Chern. Phys. 93, 8703–8707 (1990).
J. V. Michael, Prog. Energy Combust. Sci. 18, 327–347 (1992).

素過程計測に加熱以外の反応開始方法を提供
provided initiation method other than heating for elementary kinetics



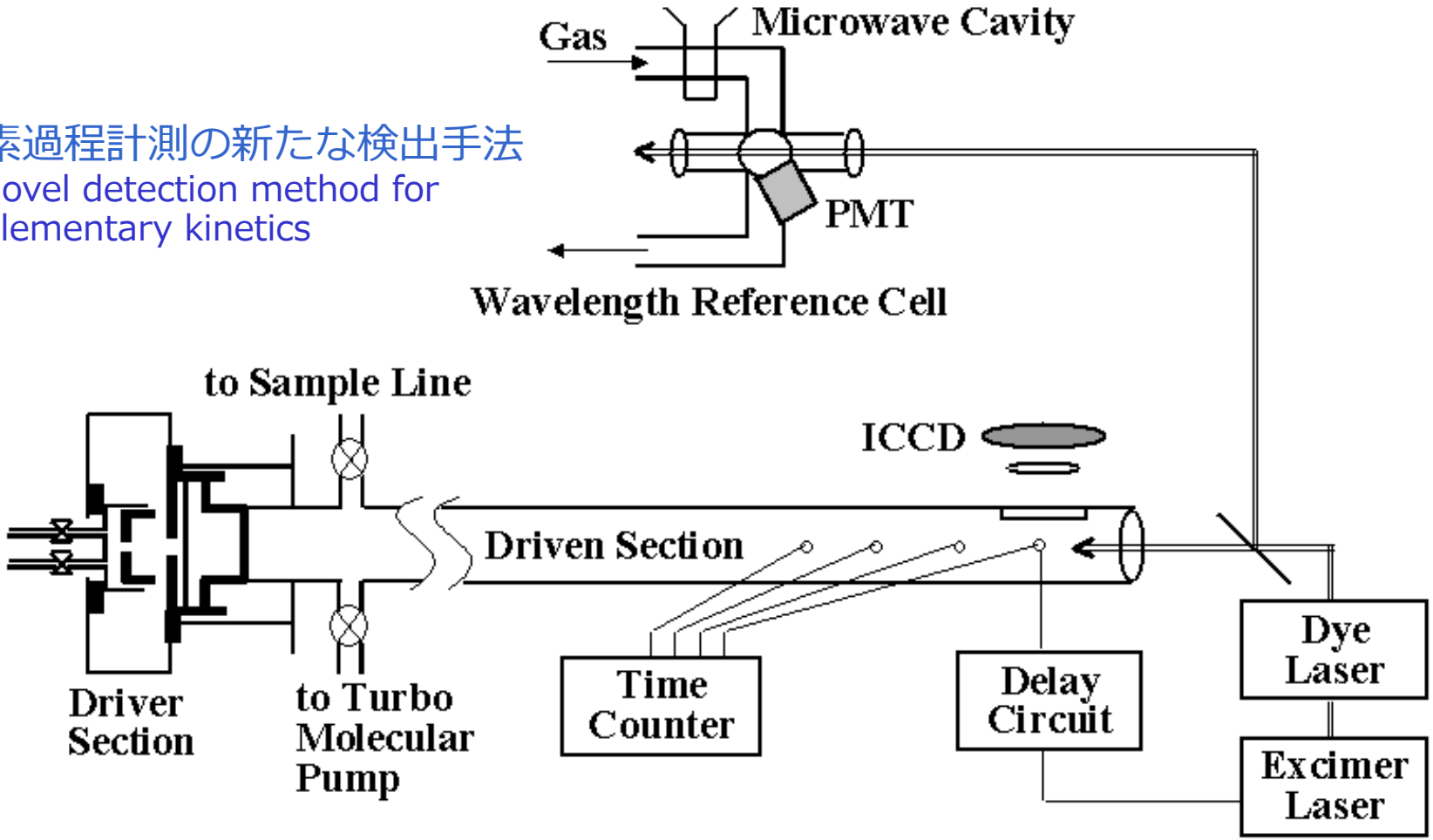
$N+NO/H_2$
O_2 vib. relaxation
O+alkane

衝撃波管と LIF

Shock Tube with LIF

2005~ T. Seta, M. Nakajima and A. Miyoshi, "Development of a technique for high-temperature chemical kinetics: Shock tube/pulsed laser-induced fluorescence imaging method," Rev. Sci. Instrum., 76, 064103 (2005).

素過程計測の新たな検出手法
novel detection method for elementary kinetics



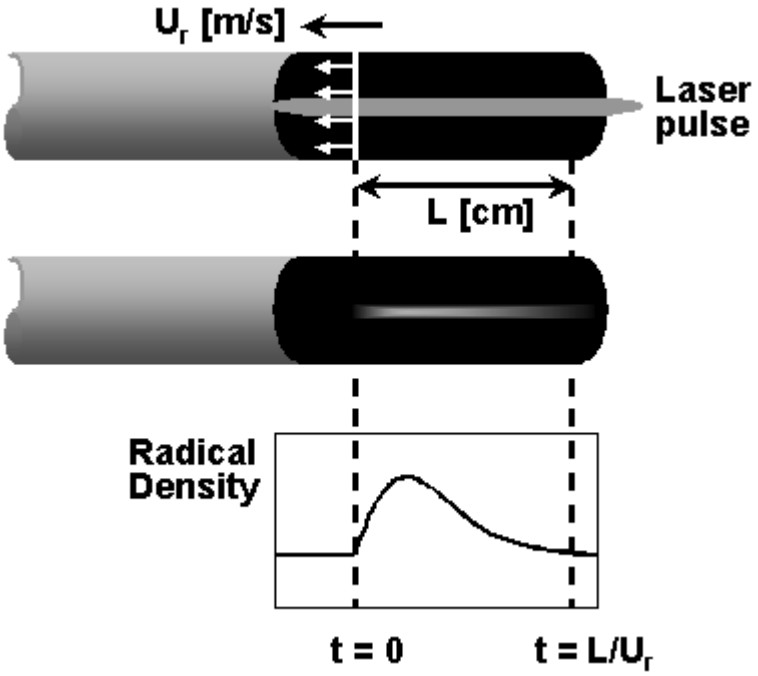
パルスレーザ蛍光画像

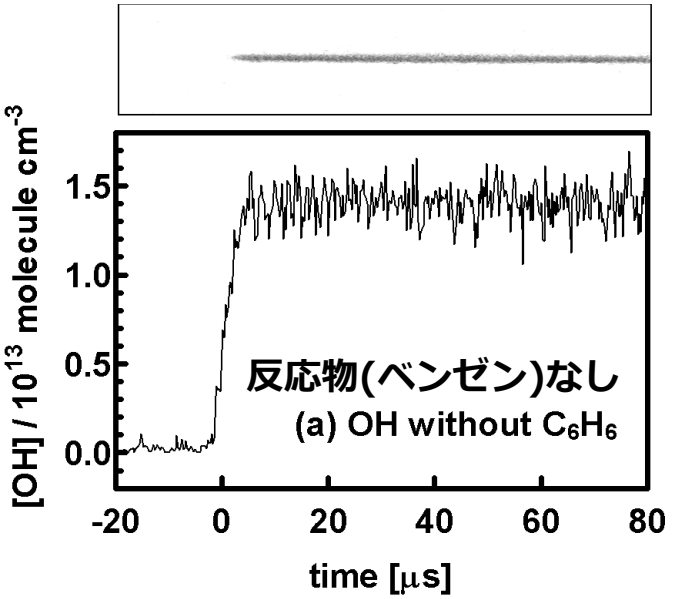
Pulsed Laser Fluorescence Imaging

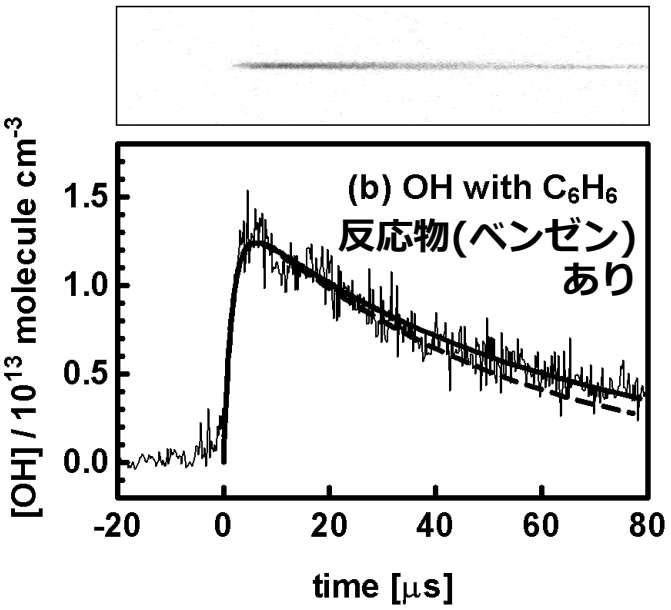
2005~ T. Seta, M. Nakajima and A. Miyoshi, Rev. Sci. Instrum., 76, 064103 (2005).

反射衝撃波背後には加熱履歴の異なる気体が空間的に分布

gases with different heating time exist behind the reflected shock wave





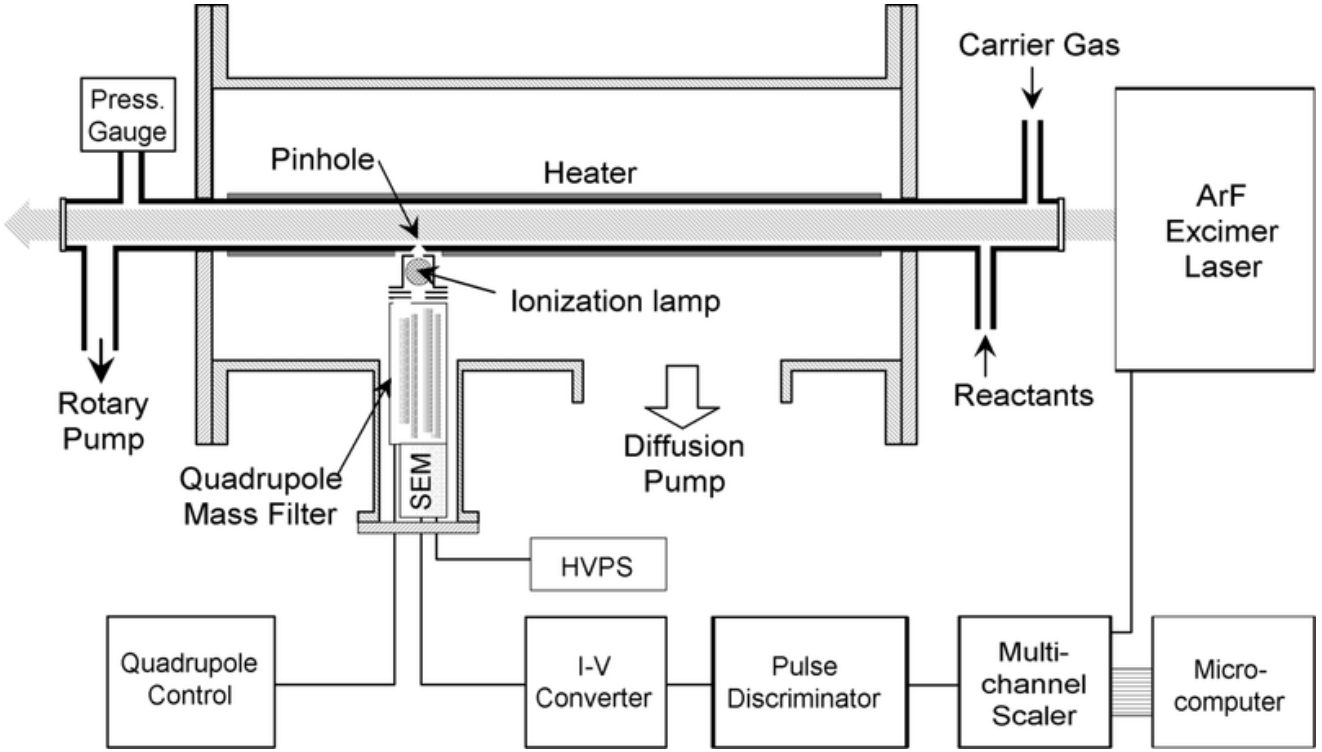


レーザ光分解-PIMS

Laser Photolysis - PIMS

1980~ T. M. Lenhardt, C. E. McDade and K. D. Bayes, J. Chem. Phys. 72, 304–310 (1980).
I. R. Slagle, F. Yamada and D. Gutman, J. Am. Chem. Soc. 103, 149-153 (1981).
A. Miyoshi, H. Matsui and **N. Washida**, Chem. Phys. Lett., 160 (3), 291–294 (1989).

低エネルギー単色光でのイオン化-ラジカルの検出
ionization by low energy monochromatic light - detection of radicals



alkyl+O_2

A. Miyoshi, N. Yamauchi and H. Matsui, "Site-Specific Branching Fractions for the O(^{3}P) and OH + C_3H_8 Reactions," J. Phys. Chem., 100, 4893–4899 (1996).

着火遅れ時間

Ignition Delay Times

1997~ K. Fiweger, R. Blumenthal and G. Adomeit, "Self-ignition of S.I. engine model fuels: a shock tube investigation at high pressure," Combust. Flame 109, 599–619 (1997).

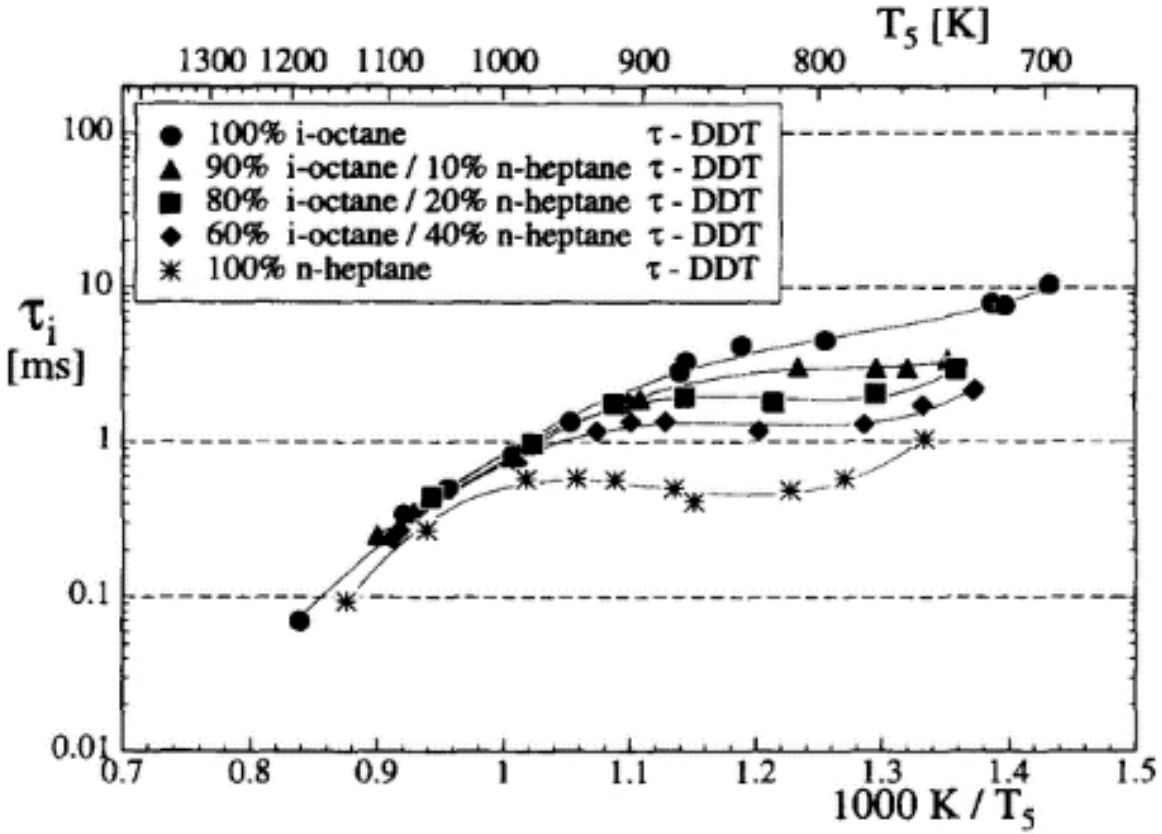


Fig. 17. Ignition delay time, τ_{DDT}, of *iso*-octane, *n*-heptane and different mixtures of both fuels, $\Phi = 1.0$, $p = 40 \pm 2$ bar.

ガソリンエンジン筒内条件における初の実験

first experiment under in-cylinder condition of gasoline engines

燃焼化学研究

Studies on Combustion Chemistry

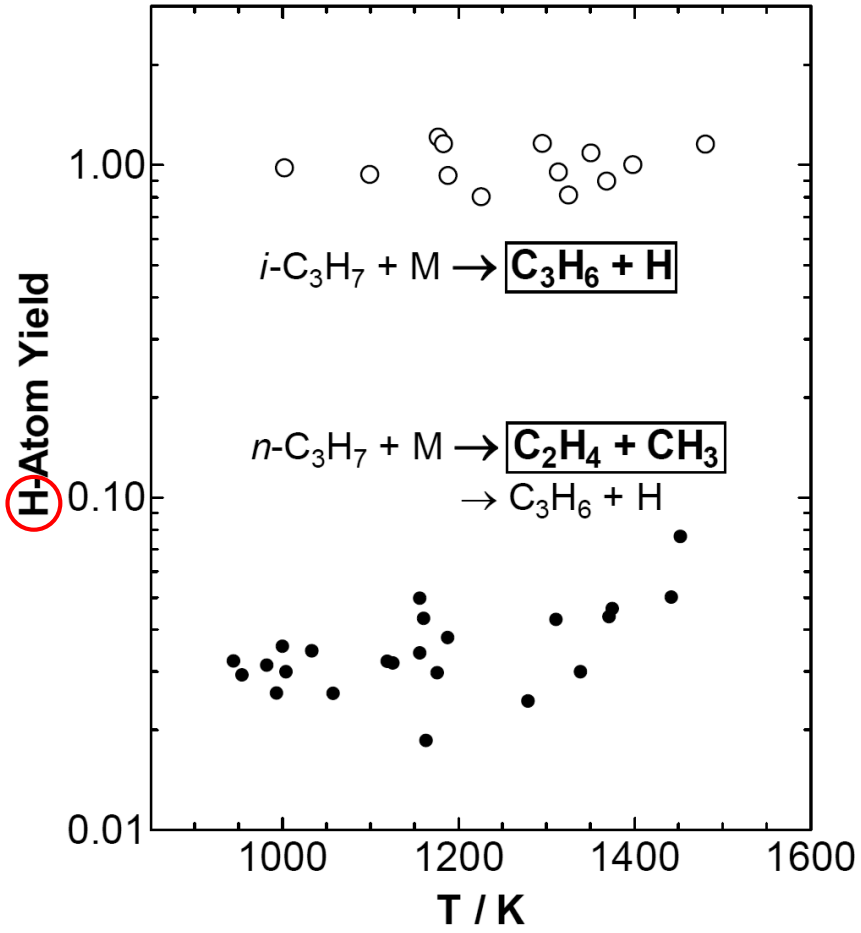
C_3H_7 異性体の観測 (ST)

Detection of C_3H_7 Isomers (ST)

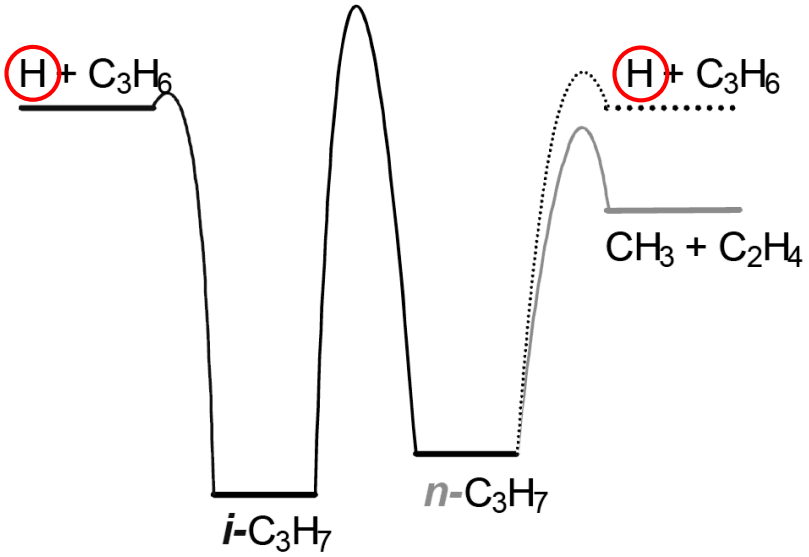
1996

A. Miyoshi, N. Yamauchi and H. Matsui, "Site-Specific Branching Fractions for the O(^{3}P) and OH + C_3H_8 Reactions," J. Phys. Chem., 100, 4893–4899 (1996).

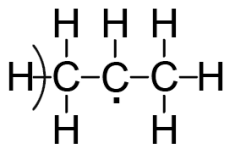
イソプロピルのみHを生成
only isopropyl produces H



衝撃波管: 水素原子の観測
shock tube: observation of H-atoms

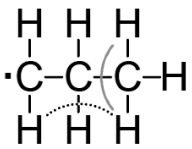


イソプロピル



isopropyl

n-プロピル



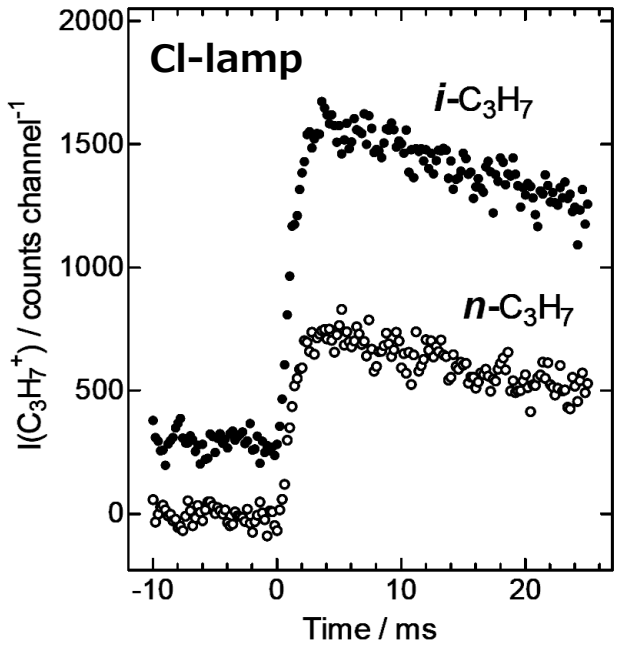
n-propyl

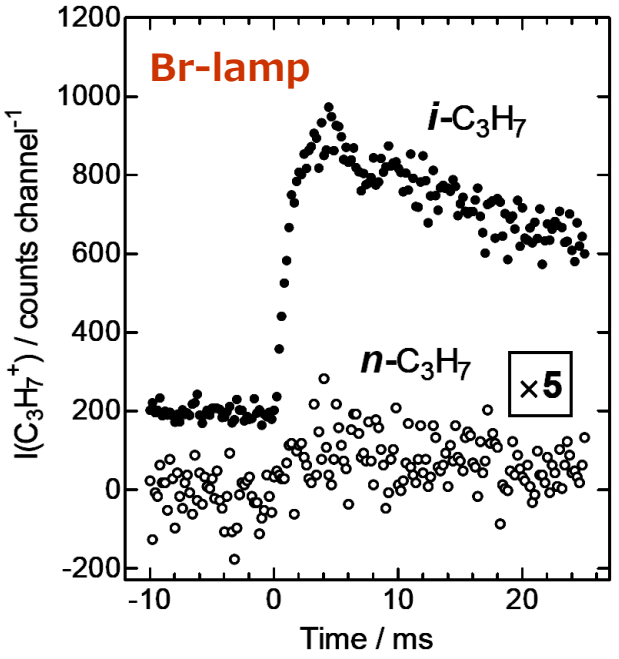
C_3H_7 異性体の観測 (PIMS)

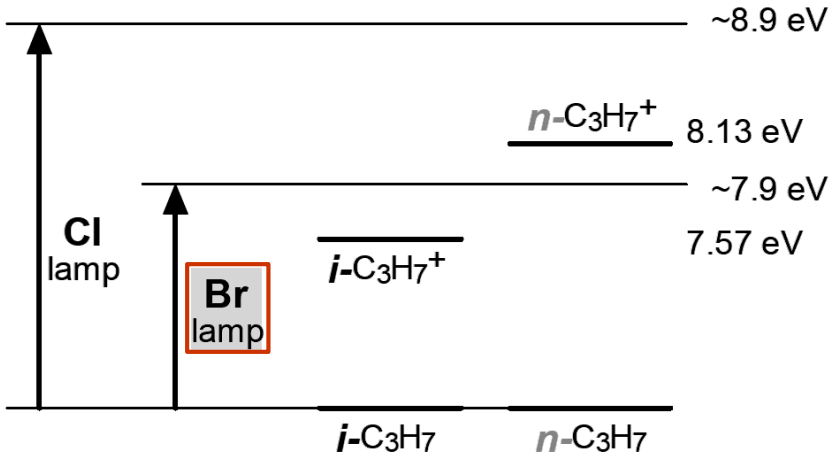
Detection of C_3H_7 Isomers (PIMS)

1996

A. Miyoshi, N. Yamauchi and H. Matsui, J. Phys. Chem., 100, 4893–4899 (1996).







Br光源-イソプロピルのみ検出
only isopropyl detected by Br-lamp

PIMS: IP による異性体選別
PIMS: Isomer selection by IP

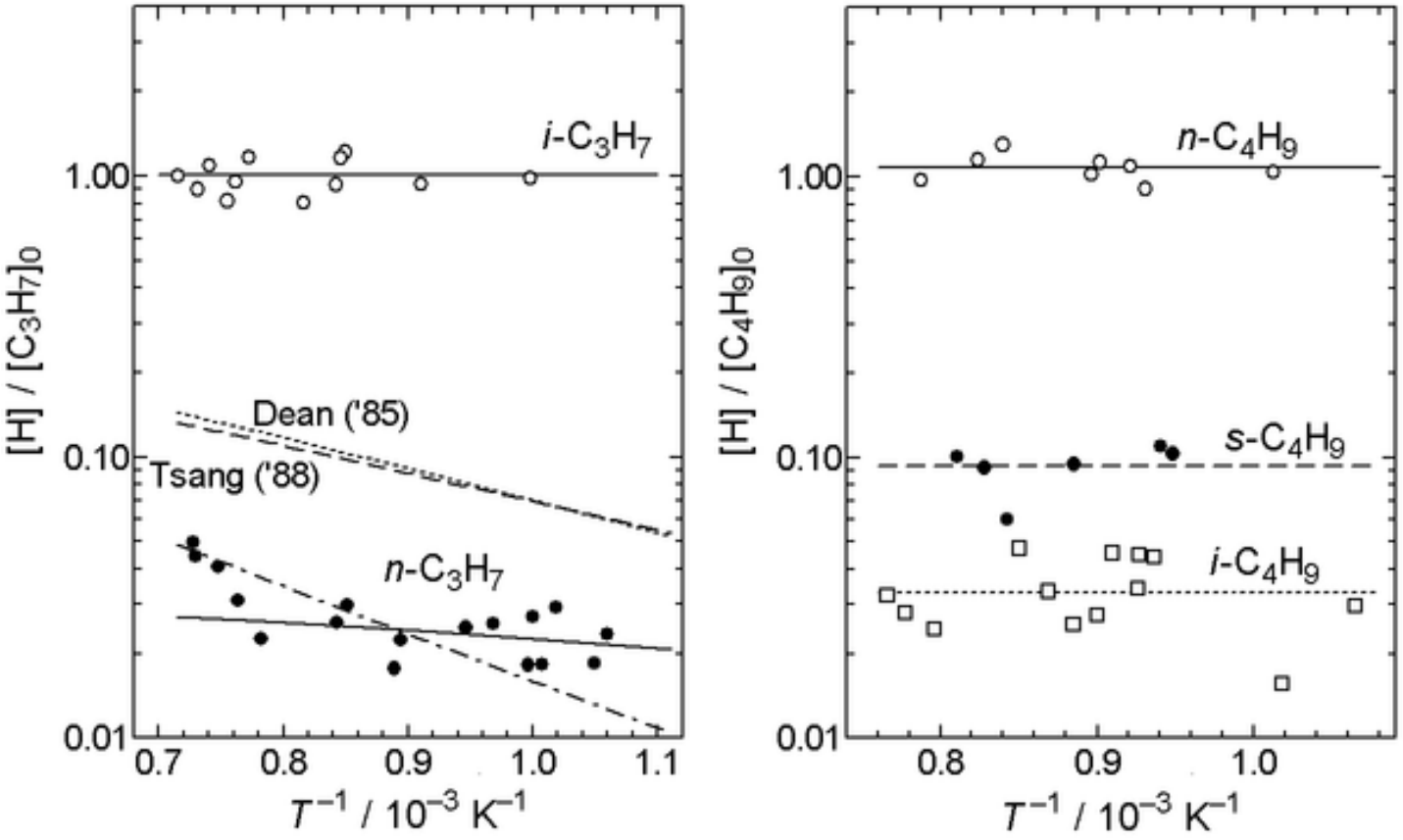
アルキルラジカルの熱分解 Decomposition of Alkyl Radicals

1999

N. Yamauchi, A. Miyoshi, K. Kosaka, M. Koshi and H. Matsui, "Thermal Decomposition and Isomerization Processes of Alkyl Radicals," J. Phys. Chem. A, 103 (15), 2723–2733 (1999).

衝撃波管: 水素原子の観測
shock tube: H-atom observation

C_3/C_4 ラジカルは予想通り
C_3/C_4 radicals were as expected

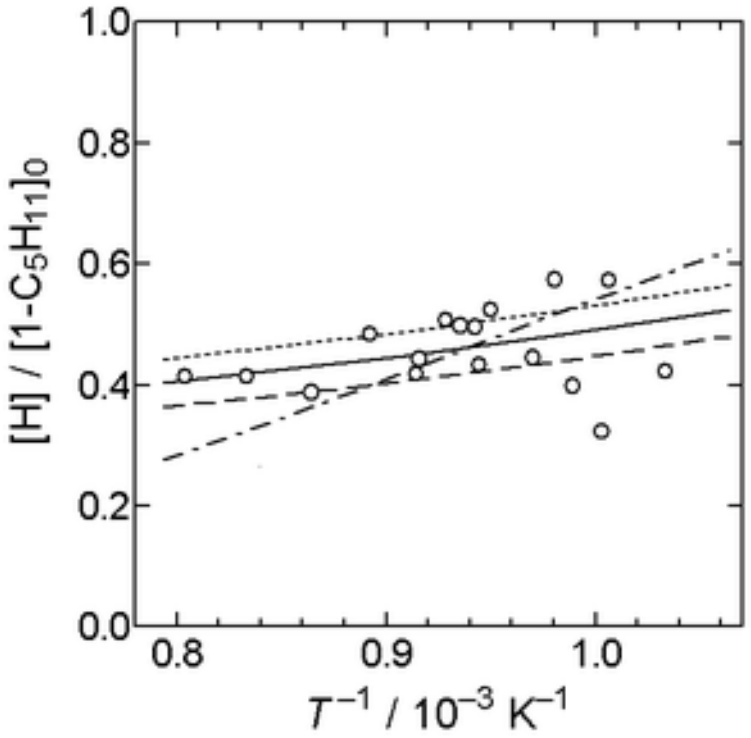


アルキルラジカルの熱分解 Decomposition of Alkyl Radicals

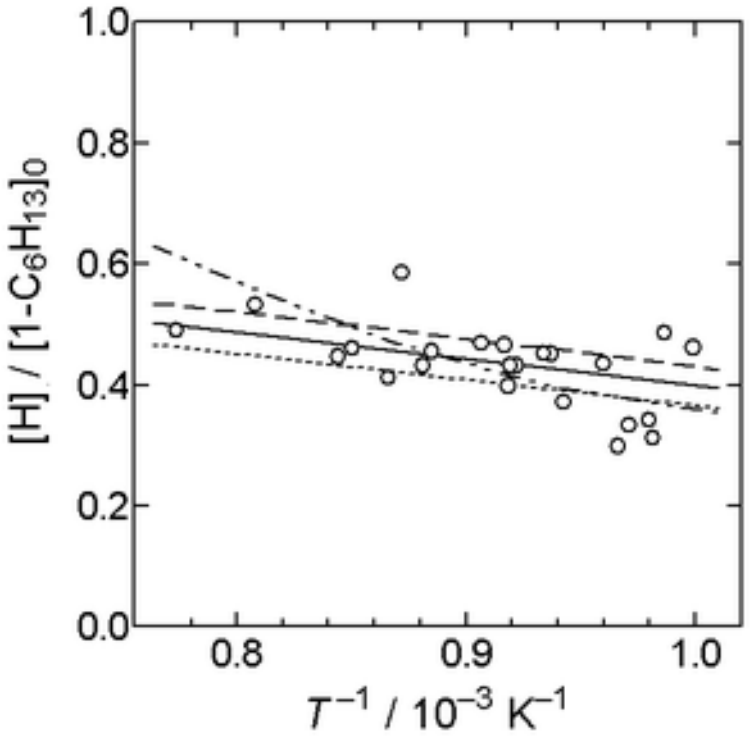
1999

N. Yamauchi, A. Miyoshi, K. Kosaka, M. Koshi and H. Matsui, J. Phys. Chem. A, 103 (15), 2723–2733 (1999).

1-ペンチル C_5H_{11}
1-pentyl C_5H_{11}



1-ヘキシル C_6H_{13}
1-hexyl C_6H_{13}



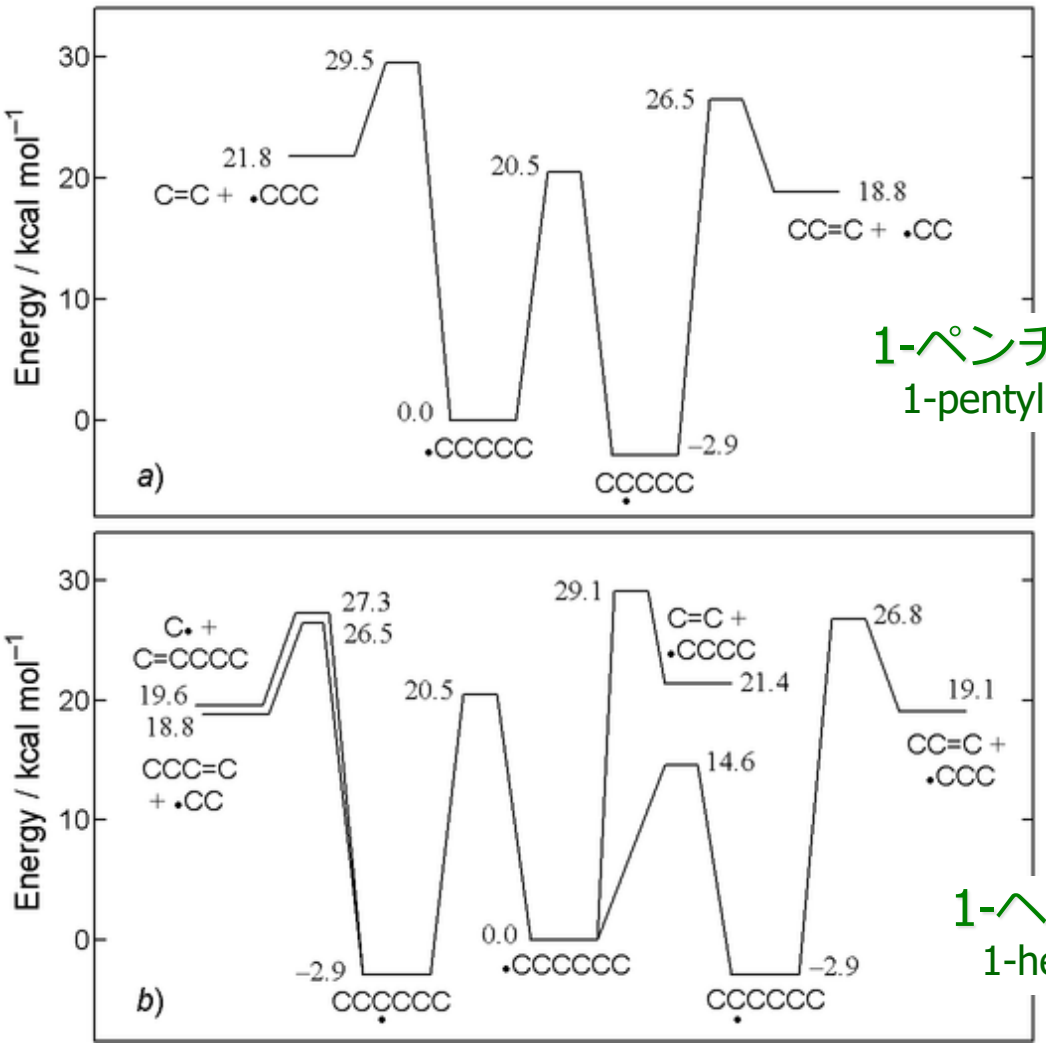
C_5 以上のラジカルでは予想に反する結果
unexpected results for C5 and larger radicals

アルキルラジカルの異性化

Isomerization of Alkyl Radicals

1999

N. Yamauchi, A. Miyoshi, K. Kosaka, M. Koshi and H. Matsui, J. Phys. Chem. A, 103 (15), 2723–2733 (1999).



1-ペンチル C_5H_{11}

1-pentyl C_5H_{11}

1-ヘキシル C_6H_{13}

1-hexyl C_6H_{13}

分解と異性化

Decomposition & Isomerization

1999 N. Yamauchi, A. Miyoshi, K. Kosaka, M. Koshi and H. Matsui, J. Phys. Chem. A, 103 (15), 2723–2733 (1999).

1-ペンチルラジカル C_5H_{11}

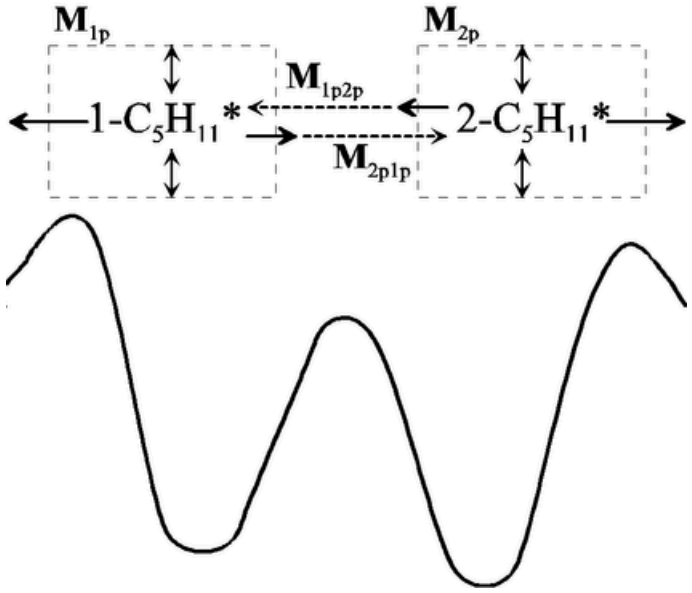
1-pentyl radical C_5H_{11}

$$\begin{pmatrix} \mathbf{M}_{1p} & \mathbf{M}_{1p2p} \\ \mathbf{M}_{2p1p} & \mathbf{M}_{2p} \end{pmatrix} \begin{pmatrix} \mathbf{g}_{1p} \\ \mathbf{g}_{2p} \end{pmatrix} = -k_{1p} \begin{pmatrix} \mathbf{g}_{1p} \\ \mathbf{0} \end{pmatrix}$$

1-ヘキシルラジカル C_6H_{13}

1-hexyl radical C_6H_{13}

$$\begin{pmatrix} \mathbf{M}_{1h} & \mathbf{M}_{1h2h} & \mathbf{M}_{1h3h} \\ \mathbf{M}_{2h1h} & \mathbf{M}_{2h} & \mathbf{0} \\ \mathbf{M}_{3h1h} & \mathbf{0} & \mathbf{M}_{3h} \end{pmatrix} \begin{pmatrix} \mathbf{g}_{1h} \\ \mathbf{g}_{2h} \\ \mathbf{g}_{3h} \end{pmatrix} = -k_{1h} \begin{pmatrix} \mathbf{g}_{1h} \\ \mathbf{0} \\ \mathbf{0} \end{pmatrix}$$



単分子反応論の課題

problem in theory of unimolecular reactions

非定常マスター方程式のソルバー solver for non-steady-state master equations

J. R. Barker, "Multiple-well, multiple-path unimolecular reactions systems. I. MultiWell computer program suite," Int. J. Chem. Kinet., 33, 232–245 (2001).

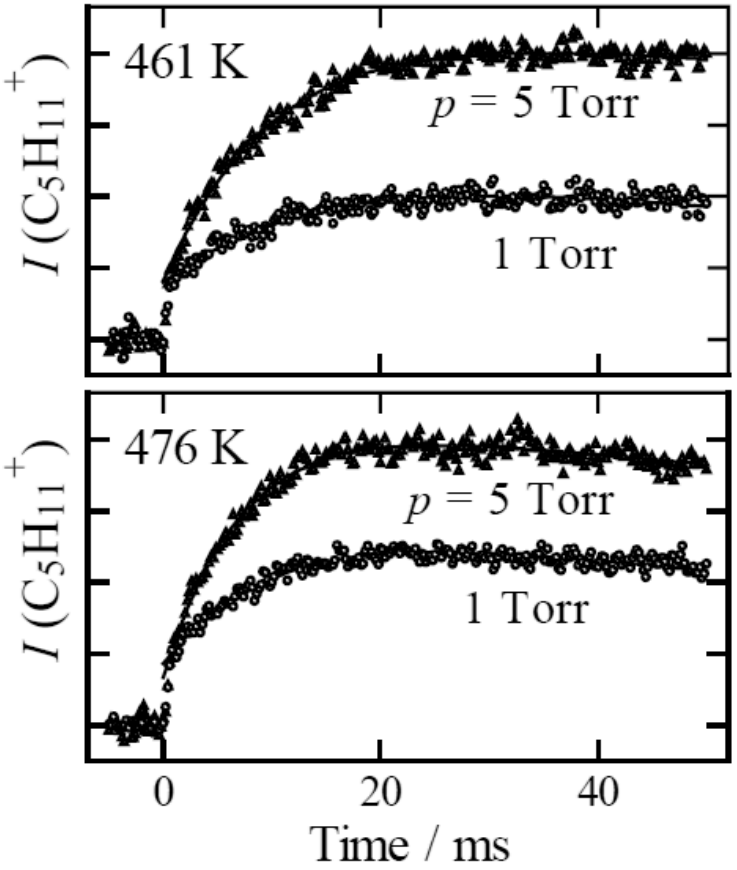
J. R. Barker and N. F. Ortiz, "Multiple-well, multiple-path unimolecular reactions systems. II, 2-Methylhexyl free radicals," Int. J. Chem. Kinet., 33, 246–261 (2001).

1-ペンチルの異性化反応

Isomerization of 1-Pentyl

2002

A. Miyoshi, J. Widjaja, N. Yamauchi, M. Kosh, and H. Matsui, "Direct Investigations on the Thermal Unimolecular Isomerization Reaction of 1-Pentyl Radicals," Proc. Combust. Inst., 29, 1285–1293 (2002).



Br 光源は 2-ペンチルを選択的にイオン化

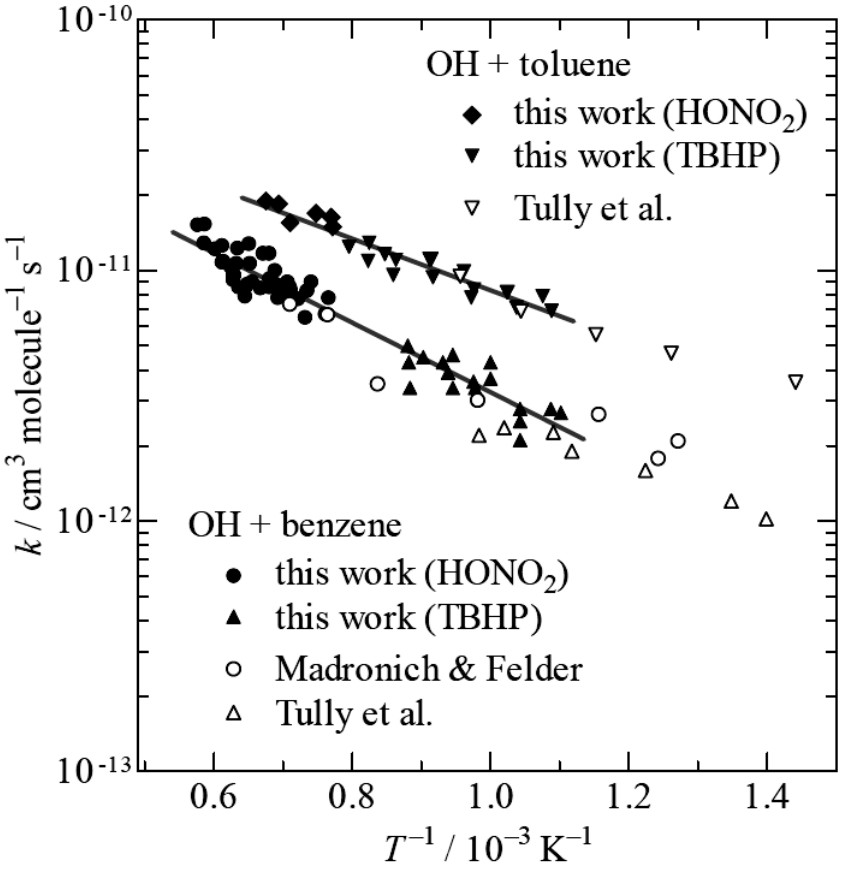
Br-lamp ionizes 2-pentyl selectively

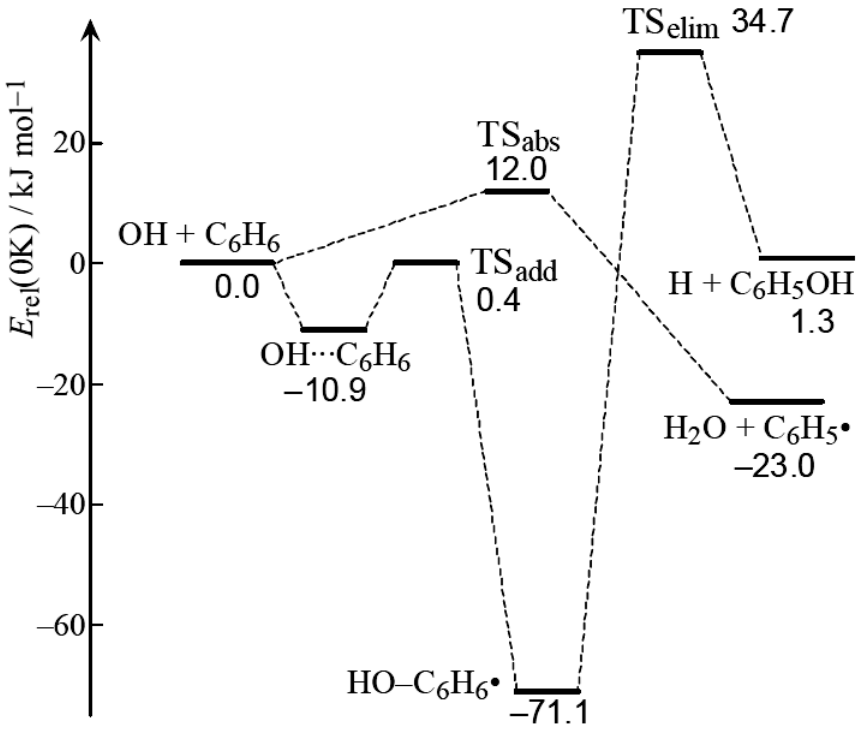
OH+ベンゼン/トルエン

OH+Benzene/Toluene

2006

T. Seta, M. Nakajima and A. Miyoshi, "High-temperature reactions of OH radicals with benzene and toluene," J. Phys. Chem. A 110, 5081–5090 (2006).





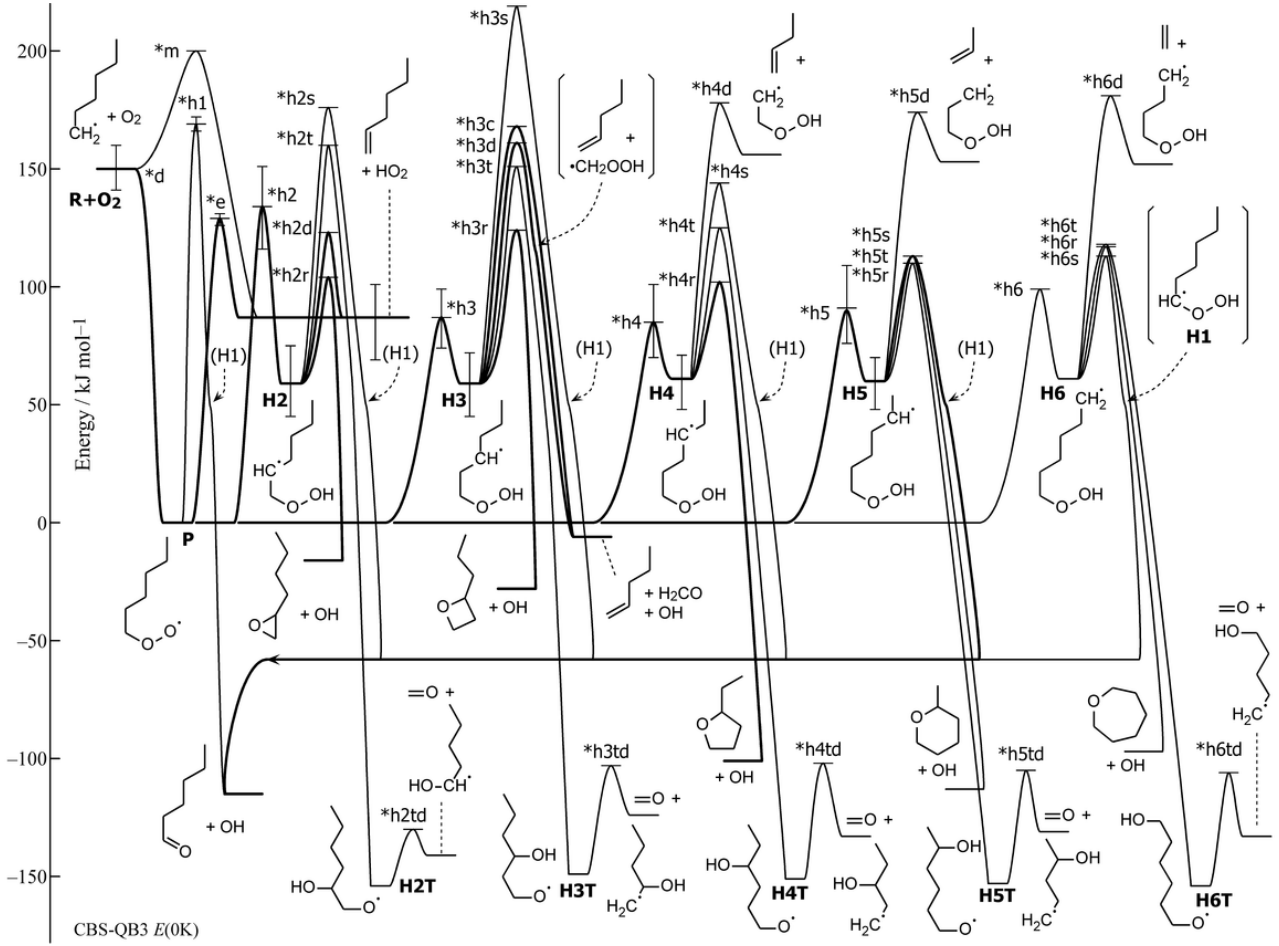
量子化学計算は速度定数を予測可能

quantum chemical calculations can predict the rate constants

量子化学

2011

A. Miyoshi, "Systematic computational study on the unimolecular reactions of alkylperoxy (RO_2), hydroperoxyalkyl (QOOH), and hydroperoxyalkylperoxy (O_2QOOH) radicals," J. Phys. Chem. A., 115, 3301–3325 (2011).

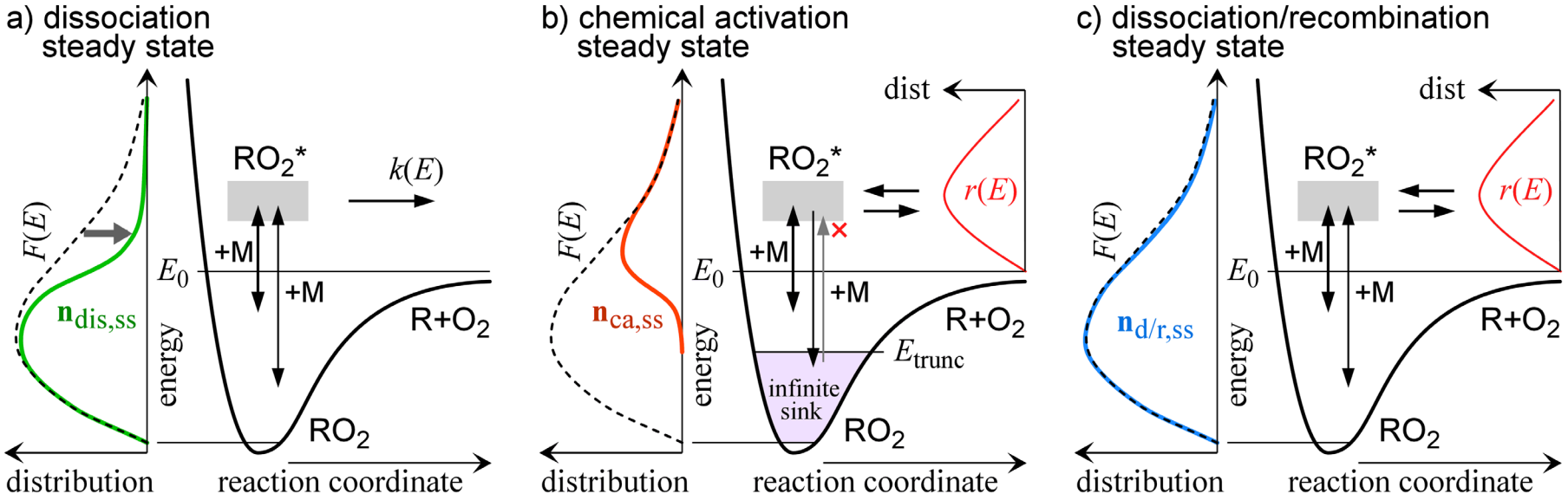


速度則の構築　construction of rate rules

単分子反応論 Theory of Unimolecular Reactions

2012

A. Miyoshi, "Molecular size dependent falloff rate constants for the recombination reactions of alkyl radicals with O_2 and implications for simplified kinetics of alkylperoxy radicals," Int. J. Chem. Kinet., 44 (1), 59–74 (2012).



単分子反応の圧力依存性の課題

problem in pressure dependence of unimolecular reactions

まとめ

Summary

衝撃波管と化学物理　shock tube & chemical physics

唯一の均一高温の発生装置
only one apparatus that generates homogeneous high-temperatures

化学反応素過程の測定　measurement of elementary reaction processes

繰返し速度と測定法の課題
challenges in repetition rate and detection methods

着火遅れ時間の測定による燃焼反応機構の検証装置

validation apparatus of combustion kinetic mechanisms via ignition delay measurements

エンジン筒内条件の実験は比較的最近 (20世紀末~)
in-cylinder condition experiments started only recently (end of 20th century~)

単分子反応論の課題の検証

validation of problems in unimolecular reaction theory

圧力依存は小分子のみに特異な課題ではない
pressure dependence is not a problem specific to small molecules