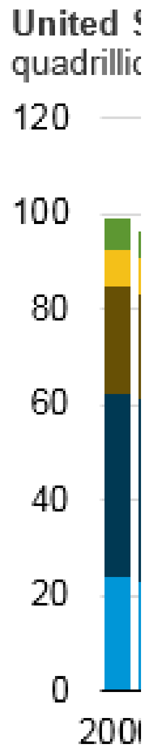
SAND2017-5236C

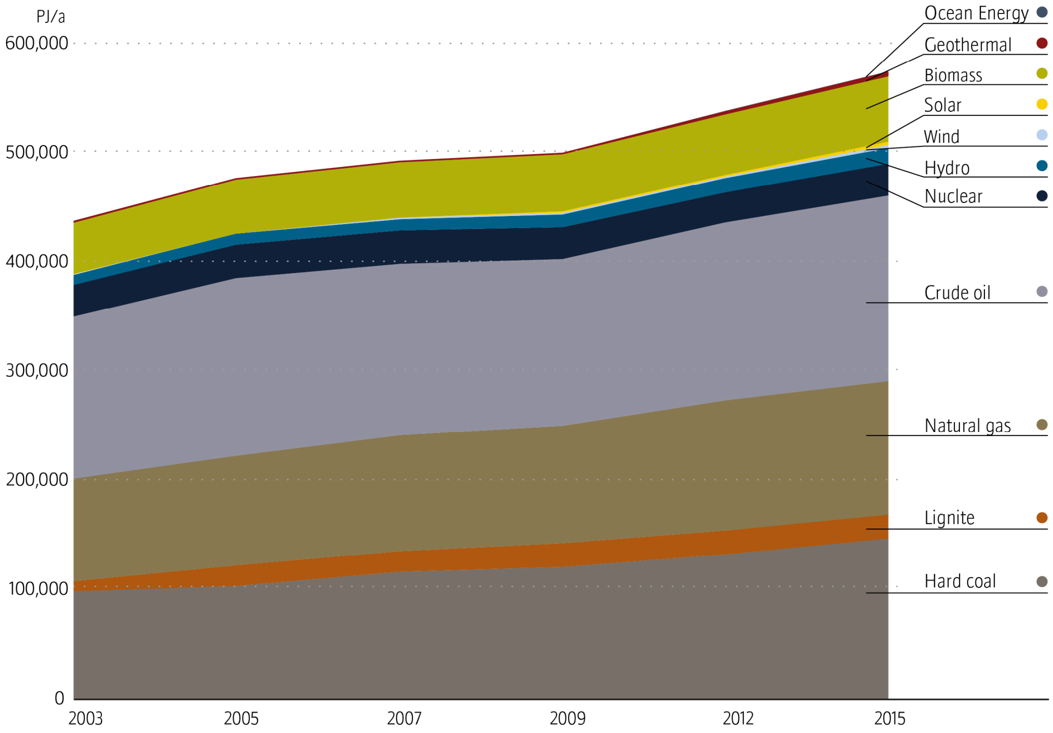
Direct Measurement of OH and HO_2 Formation in R + O_2 Reactions of Cyclohexane and Tetrahydropyran: Influence of Oxygenation in Cyclic Hydrocarbons

Ming-Wei Chen, Brandon Rotavera, Wen Chao, Jim Jr-Min Lin, Judit Zádor
and Craig A. Taatjes

The 10th International Conference on Chemical Kinetics, Chicago, 23 May 2017

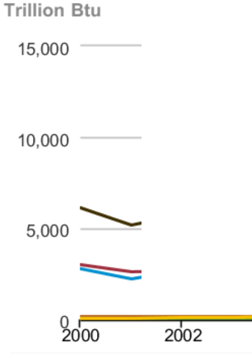


Global primary energy supply, 2003 – 2015

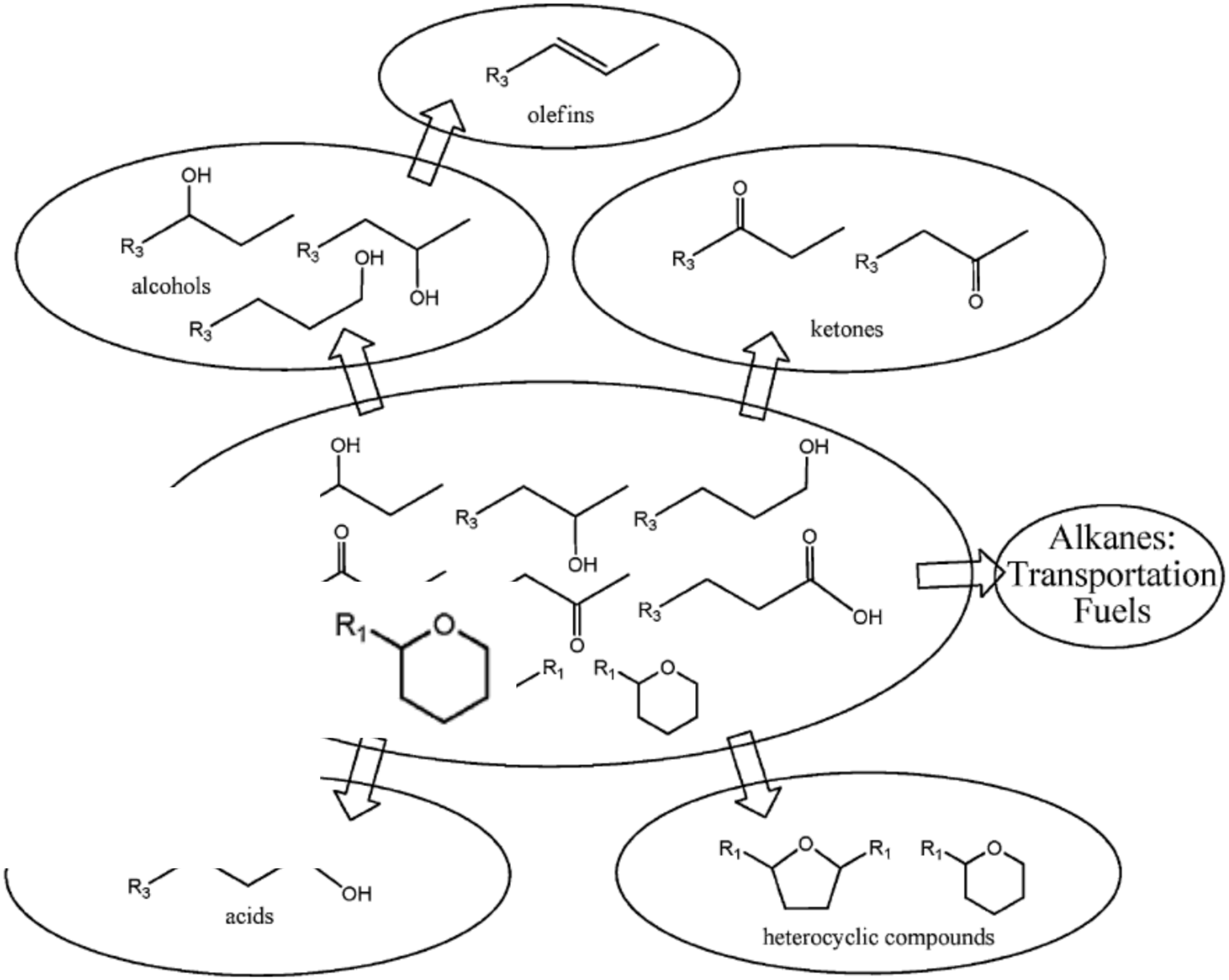


Renewables Global Futures Report Great debates towards 100 % renewable energy

Source: International Energy Agency, Paris/France, Data compilation: Dr. Sven Teske, UTS/ISF, Australia



Data source:
Renewable Energy Policy Network for 21st centry (REN21)
U.S. Energy Information Administration



R. M. West, *et al.*, *Catalysis Today*, **147**, 115 (2009)

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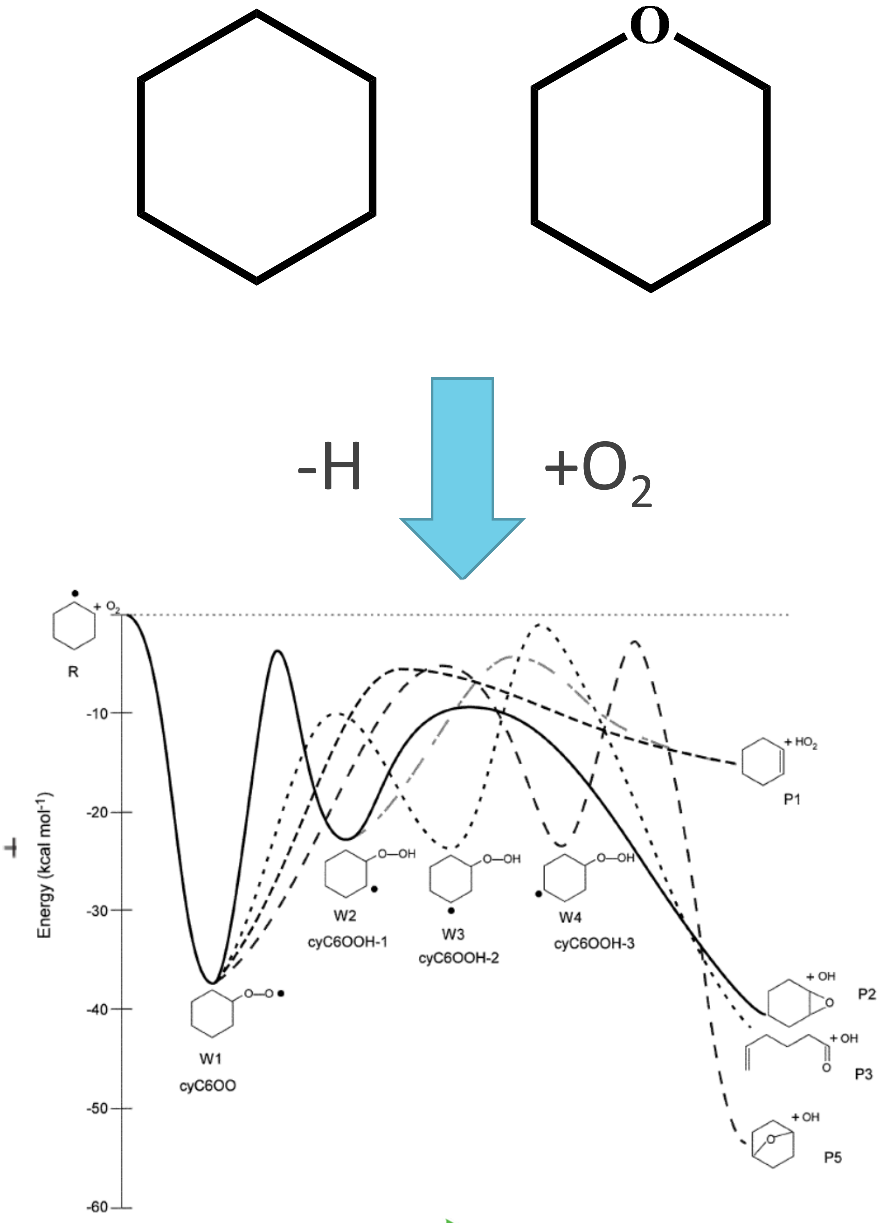


- Monoether analog of cyclohexane and core structure of sugars and polysaccharides.
- Cyclohexane oxidation was studied previously combining OH / HO_2 measurements and theory.
- Tetrahydropyran (THP) oxidation was studied recently by monitoring the alkene production.
- Quantitative, direct laser diagnostic method to explore the key intermediates formation in the low temperature combustion regime
- How oxygenation affect oxidation chemistry (and why)?

A. M. Knepp *et al.*, *Phys. Chem. Chem. Phys.*, **9**, 4315 (2007)
R. X. Fernandes *et al.*, *Phys. Chem. Chem. Phys.*, **11**, 1320 (2009)
B. Rotavera, *et al.*, *Proc. Combust. Inst.*, **36**, 597 (2017)

IR Absorption Experiment

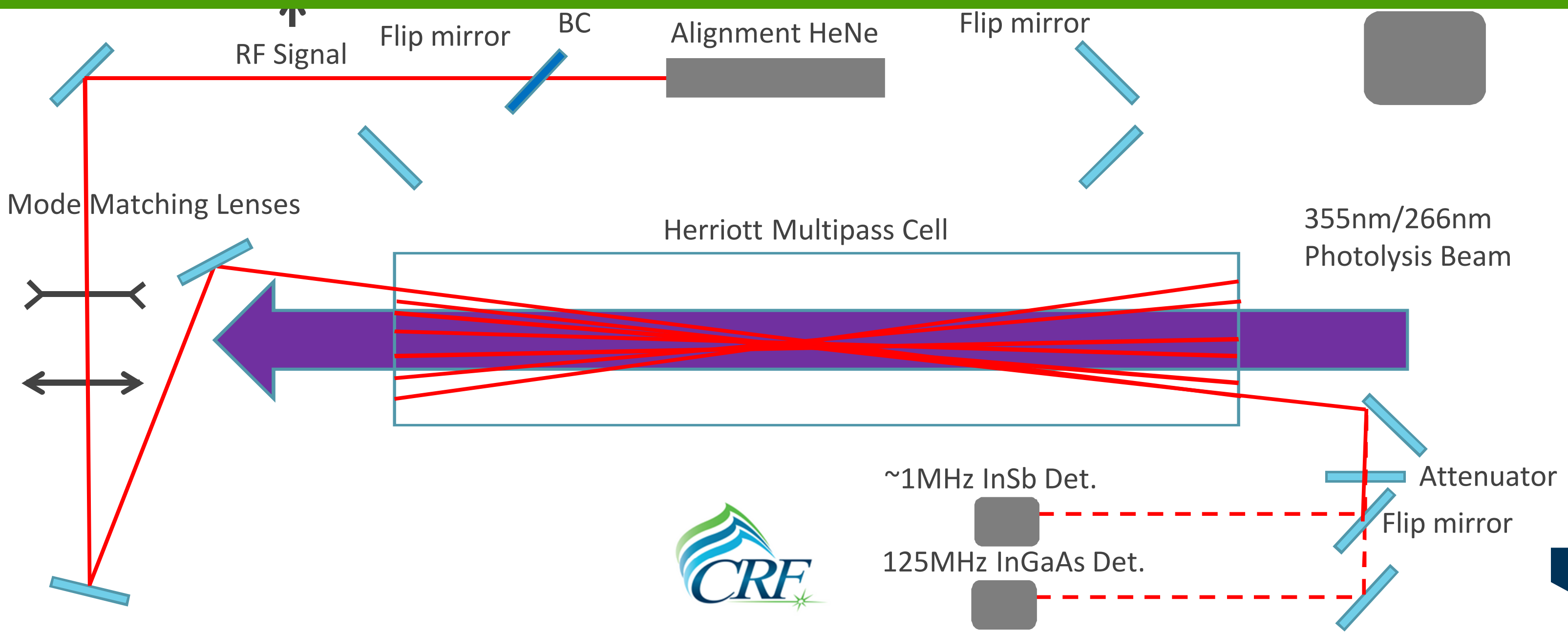
Total density of molecules = 2.6-3.9×10^{17} molecules/cm^3

Temperature = 500-750K

[Fuel] ≈ 1×10^{15} molecules/cm^3

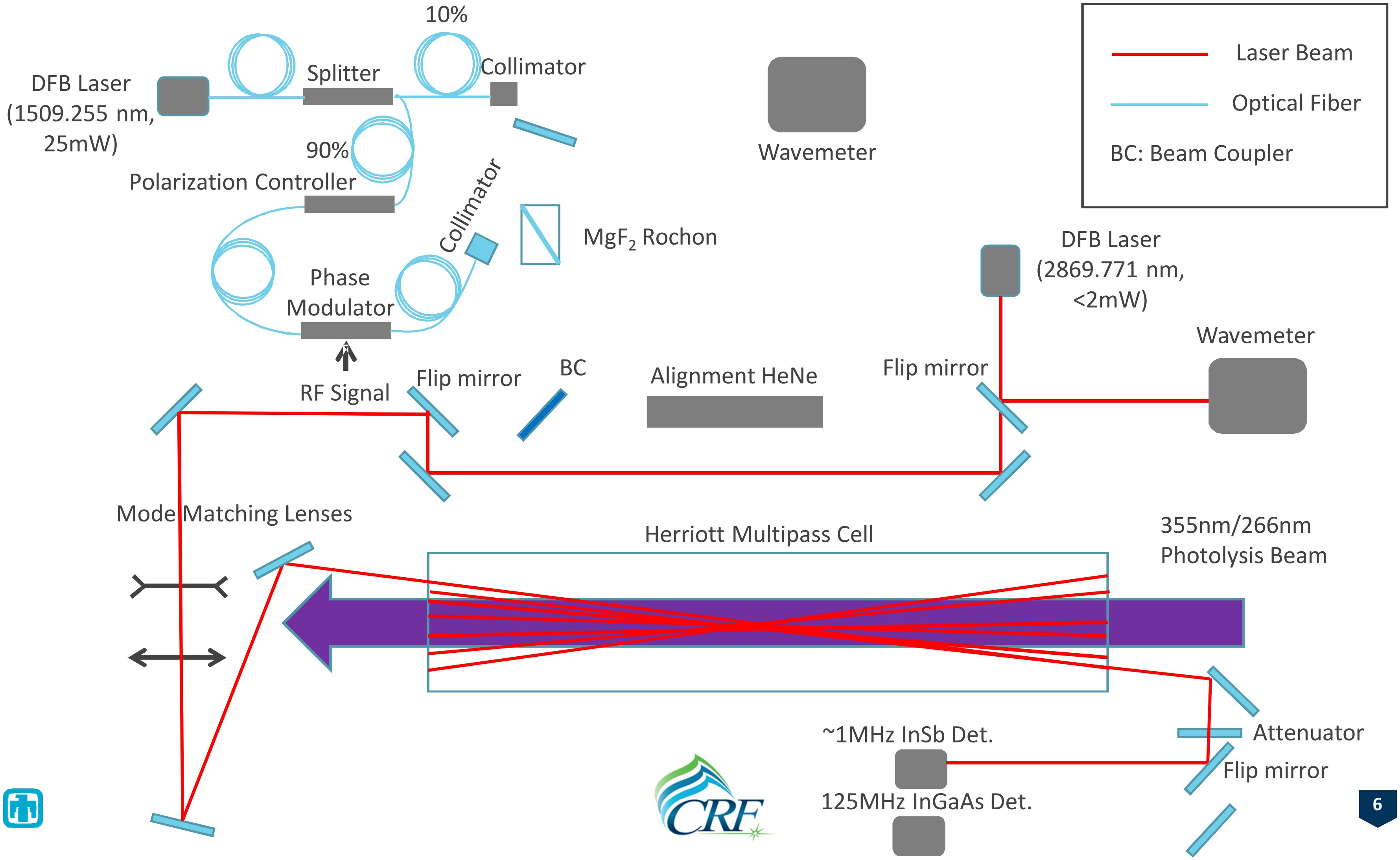
$[Cl]_0$ ≈ 8×10^{13} molecules/cm^3 (From OxCl or Cl_2 photolysis)

$[O_2]$ ≈ 4×10^{16} molecules/cm^3



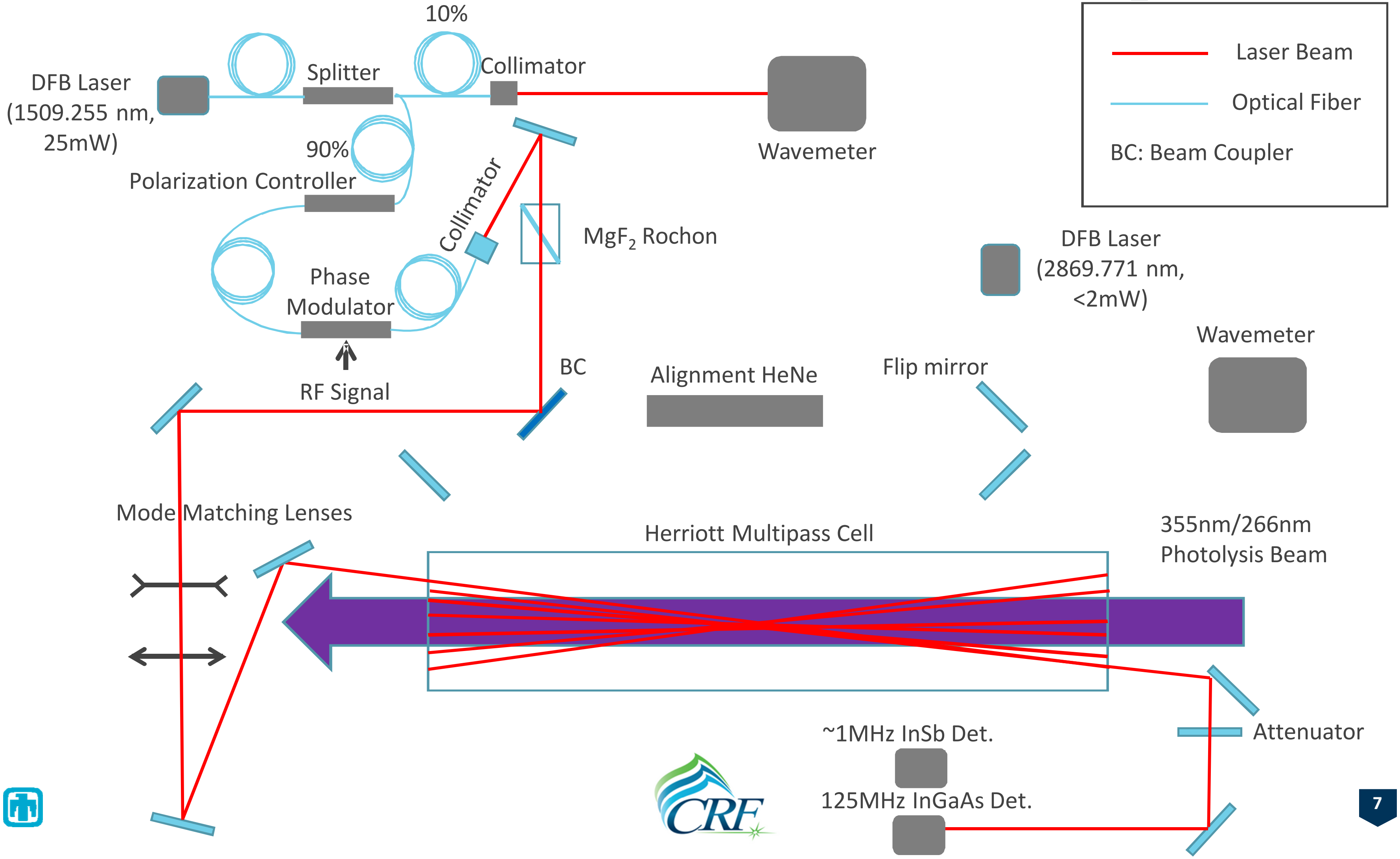
C. A. Taatjes and D. B. Oh, *Applied Optics*, **24**, 5817 (1997)

IR Absorption Experiment – Direct Absorption Measuring OH



C. A. Taatjes and D. B. Oh, *Applied Optics*, **24**, 5817 (1997)

IR Absorption Experiment – Two-Tone Frequency Modulation Measuring HO_2



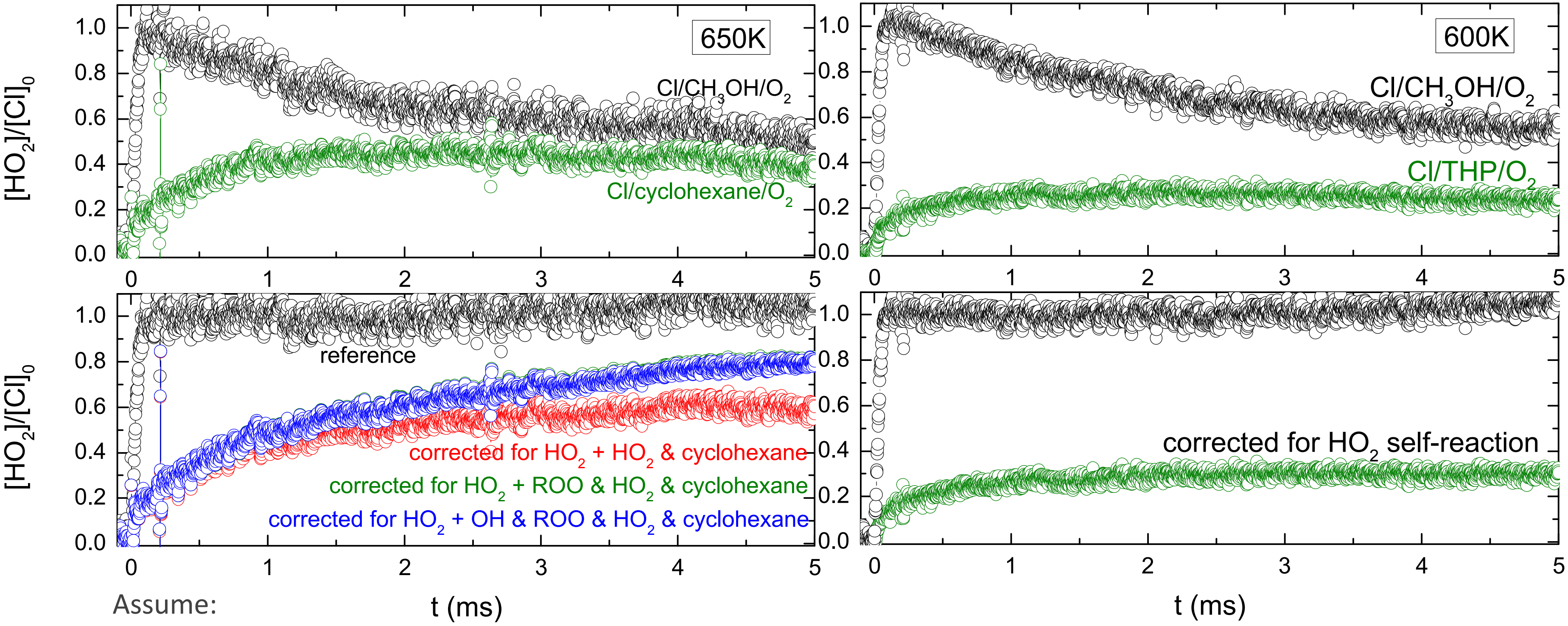
C. A. Taatjes and D. B. Oh, *Applied Optics*, **24**, 5817 (1997)

Integral Profile Correction – HO_2

$$\alpha \int_0^t R_{production}(t')dt' = I(t) + 2\alpha k_{self} \int_0^t [HO_2]_t^2 dt' + \alpha \int_0^t R_{removal}(t')[HO_2]_t dt' \, {}^{*}$$

cyclohexane & methanol

tetrahydropyran (THP) & methanol



Assume:

$^{*}[ROO] = [R]_0 - [HO_2] \approx [Cl]_0 - [HO_2]$

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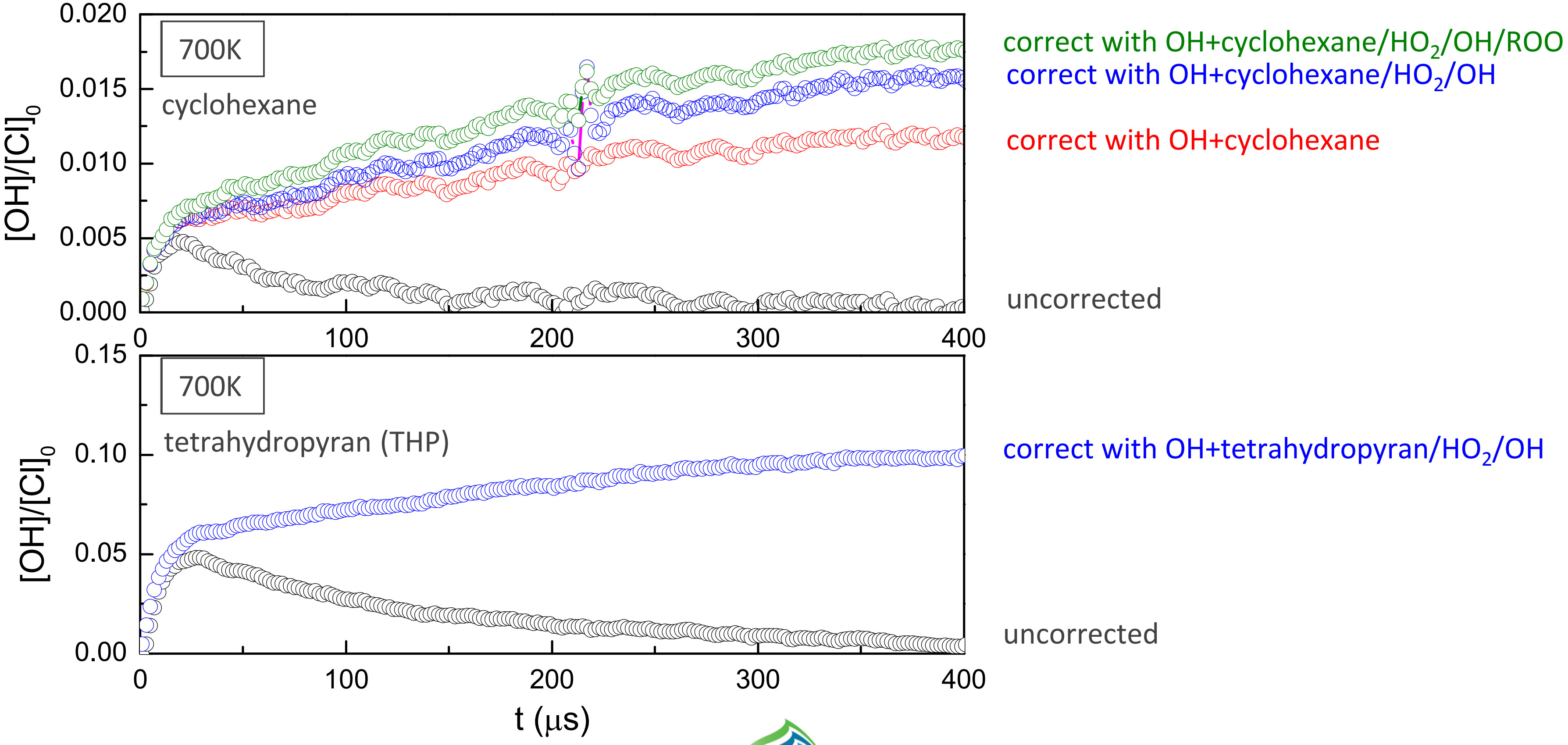
*J. D. DeSain, E. P. Clifford, and C. A. Taatjes, *J. Phys. Chem. A*, **105**, 3205 (2001)

Integral Profile Correction – OH

$$\alpha \int_0^t R_{production}(t')dt' = I(t) + 2\alpha k_{self} \int_0^t [OH]_t^2 dt' + \alpha \int_0^t R_{removal}(t')[OH]_t dt'$$

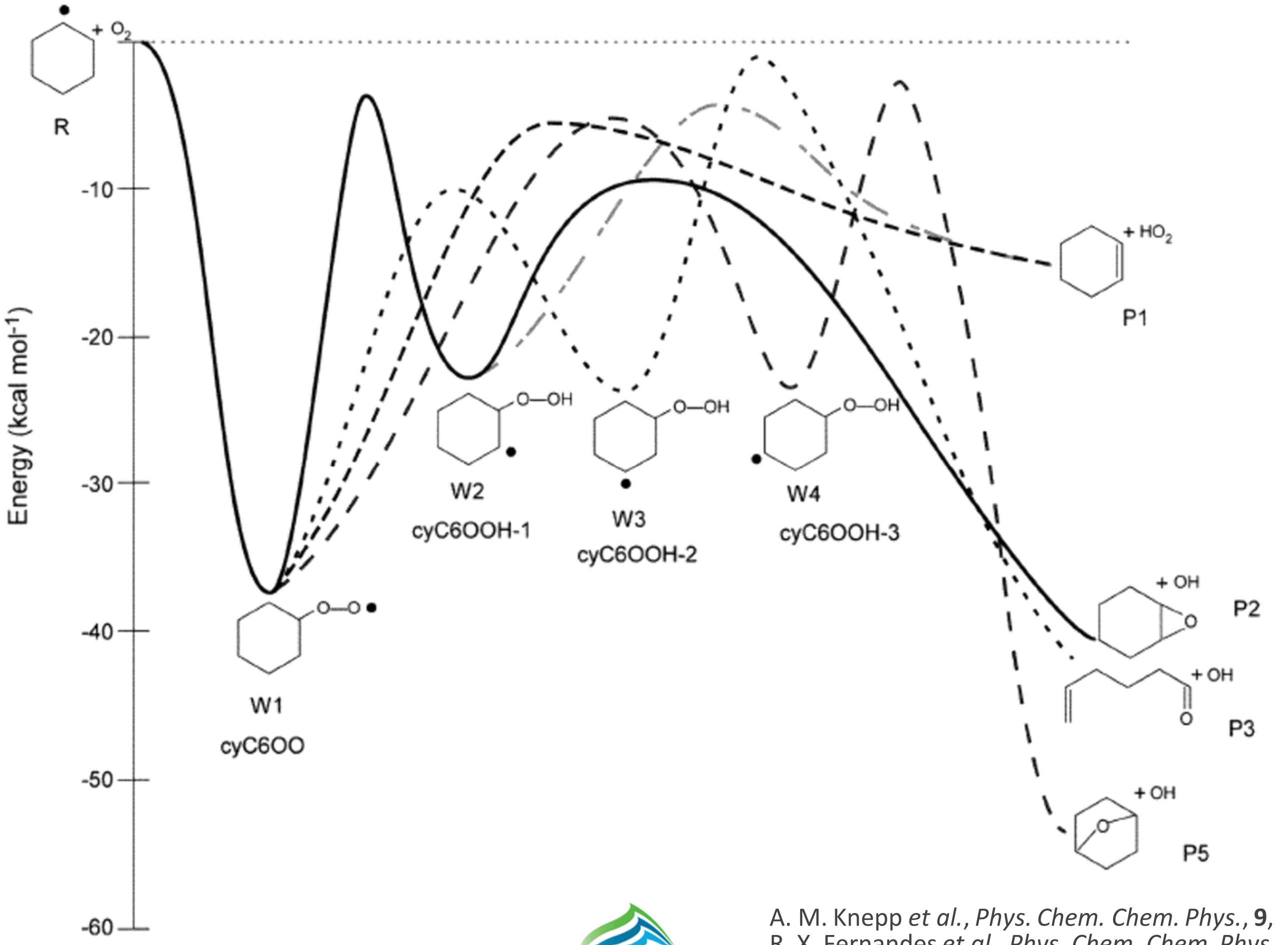


List of Rate Coefficients

Reaction	Rate coefficient (cm^3/molecule/s)	Ref.
$HO_2 + HO_2 \rightarrow O_2 + H_2O_2$	$2.2 \times 10^{-13} \times e^{\frac{820}{T}} + 7.0 \times 10^{-10} \times e^{\frac{-6030}{T}}$	(1)
$HO_2 + C_6H_{11}OO \rightarrow C_6H_{11}OOH + O_2$	$2.61 \times 10^{-13} \times e^{\frac{1240}{T}}$	(1)
$HO_2 + OH \rightarrow O + H_2O$	$4.8 \times 10^{-11} \times e^{\frac{250}{T}}$	(1)
$OH + OH \rightarrow O + H_2O$	$1.65 \times 10^{-12} \times \left(\frac{T}{298}\right)^{1.14} \times e^{\frac{-50}{T}}$	(1)
$OH + C_6H_{12} \rightarrow C_6H_{11} + H_2O$	$3.97 \times 10^{-12} \times \left(\frac{T}{298}\right)^{1.64} \times e^{\frac{80}{T}}$	(1)
$OH + C_5H_{10}O \rightarrow C_5H_9O + H_2O$	$7.8 \times 10^{-12} \times e^{\frac{130}{T}}$	(2)

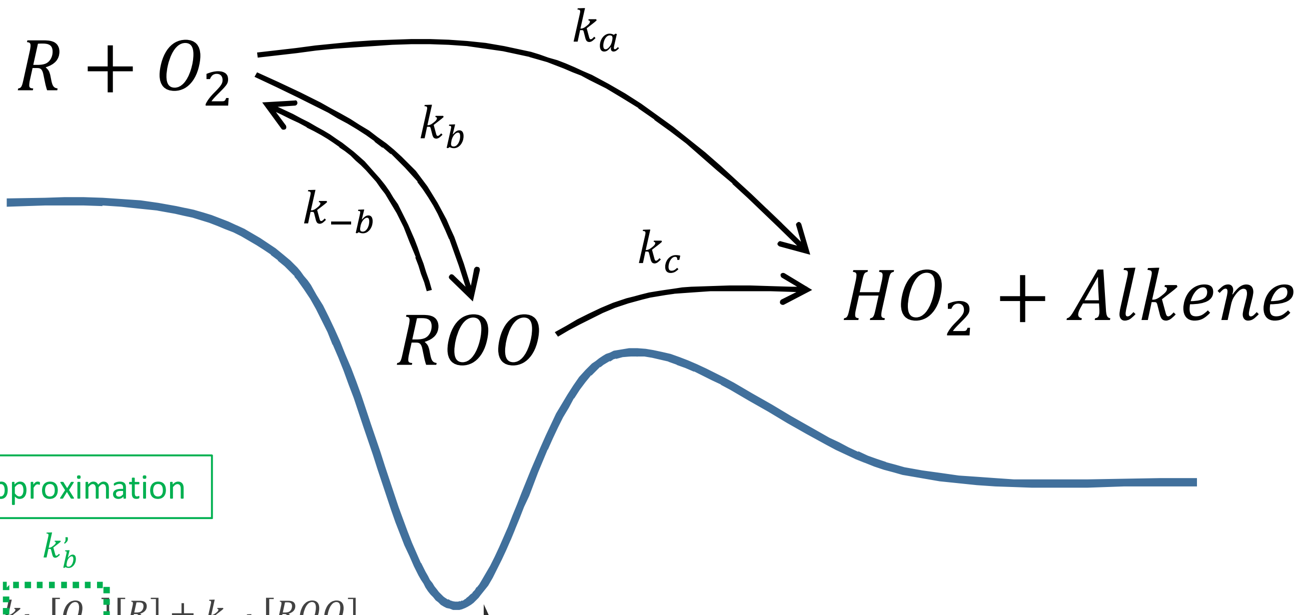
(1) A. M. Knepp *et al.*, *Phys. Chem. Chem. Phys*, **9**, 4315 (2007)
(2) J. Moriarty *et al.*, J. *Phys. Chem. A*, **107**, 1499 (2003)

Cyclohexyl + O_2 Reaction PES



A. M. Knepp *et al.*, *Phys. Chem. Chem. Phys.*, **9**, 4315 (2007)
R. X. Fernandes *et al.*, *Phys. Chem. Chem. Phys.*, **11**, 1320 (2009)

Reduced Model – HO_2



Pseudo-first-order approximation

$$\frac{d}{dt}[R] = -\overset{k'_a}{\boxed{k_a[O_2]}}[R] - \overset{k'_b}{\boxed{k_b\,[O_2]}}[R] + k_{-b}[ROO]$$

$$\frac{d}{dt}[ROO] = \overset{k'_b}{\boxed{k_b[O_2]}}[R] - k_{-b}[ROO] - k_c[ROO]$$

$$\frac{d}{dt}[HO_2] = \overset{k'_a}{\boxed{k_a[O_2]}}[R] + k_c[ROO] - k_d[HO_2]^2$$

By integral profile correction

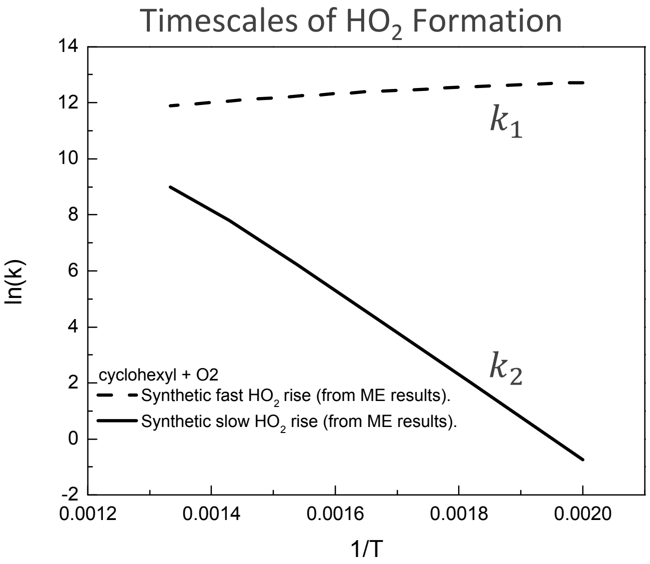
- Alkylperoxy-chemistry-centered reduced model.
- Solvable differential equations

Solution of Differential Equations

$$\boxed{[HO_2]_t = A_1\left(1 - e^{-k_1 t}\right) + A_2\left(1 - e^{-k_2 t}\right)}$$

$$k_1 = \frac{k_a{}' + k_b{}' + k_{-b} + k_c + \sqrt{\left(k_a{}' + k_b{}' + k_{-b} + k_c\right)^2 - 4\left(k_b{}'k_c + k_a{}'k_{-b} + k_a{}'k_c\right)}}{2}$$

$$k_2 = \frac{k_a{}' + k_b{}' + k_{-b} + k_c - \sqrt{\left(k_a{}' + k_b{}' + k_{-b} + k_c\right)^2 - 4\left(k_b{}'k_c + k_a{}'k_{-b} + k_a{}'k_c\right)}}{2}$$


Timescales of HO_2 Formation

$$A_1 = -\frac{A_0\left(k_a{}' + k_b{}' + k_{-b} + k_c - \sqrt{\left(k_a{}' + k_b{}' + k_{-b} + k_c\right)^2 - 4\left(k_b{}'k_c + k_a{}'k_{-b} + k_a{}'k_c\right)}\right)\left(k_b{}'\left(2k_c - k_a{}'\right) + k_a{}'\left(k_{-b} + k_c - k_a{}' - \sqrt{k_b{}'^2 + \left(k_{-b} + k_c - k_a{}'\right)^2 + 2k_b{}'\left(k_{-b} - k_c + k_a{}'\right)}\right)\right)}{4\left(k_b{}'k_c + k_a{}'k_{-b} + k_a{}'k_c\right)\sqrt{\left(k_a{}' + k_b{}' + k_{-b} + k_c\right)^2 - 4\left(k_b{}'k_c + k_a{}'k_{-b} + k_a{}'k_c\right)}}$$

$$A_2 = \frac{A_0\left(k_a{}' + k_b{}' + k_{-b} + k_c - \sqrt{\left(k_a{}' + k_b{}' + k_{-b} + k_c\right)^2 - 4\left(k_b{}'k_c + k_a{}'k_{-b} + k_a{}'k_c\right)}\right)\left(k_b{}'\left(2k_c - k_a{}'\right) + k_a{}'\left(k_{-b} + k_c - k_a{}' + \sqrt{k_b{}'^2 + \left(k_{-b} + k_c - k_a{}'\right)^2 + 2k_b{}'\left(k_{-b} - k_c + k_a{}'\right)}\right)\right)}{4\left(k_b{}'k_c + k_a{}'k_{-b} + k_a{}'k_c\right)\sqrt{\left(k_a{}' + k_b{}' + k_{-b} + k_c\right)^2 - 4\left(k_b{}'k_c + k_a{}'k_{-b} + k_a{}'k_c\right)}}$$

Reduced Model – OH

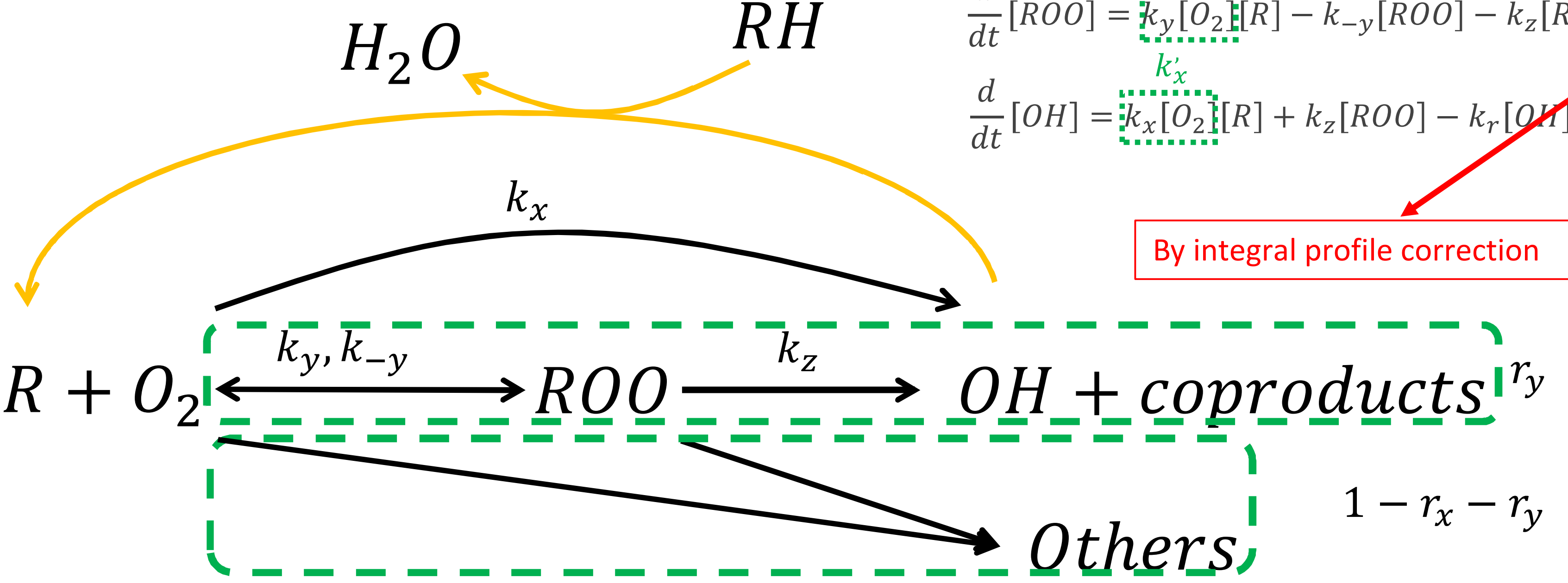
Pseudo-first-order approximation

$$\frac{d}{dt}[R] = -\overset{k'_x}{\boxed{k_x[O_2]}}[R] - \overset{k'_y}{\boxed{k_y[O_2]}}[R] + k_{-y}[ROO]$$

$$\frac{d}{dt}[ROO] = \overset{k'_y}{\boxed{k_y[O_2]}}[R] - k_{-y}[ROO] - k_z[ROO]$$

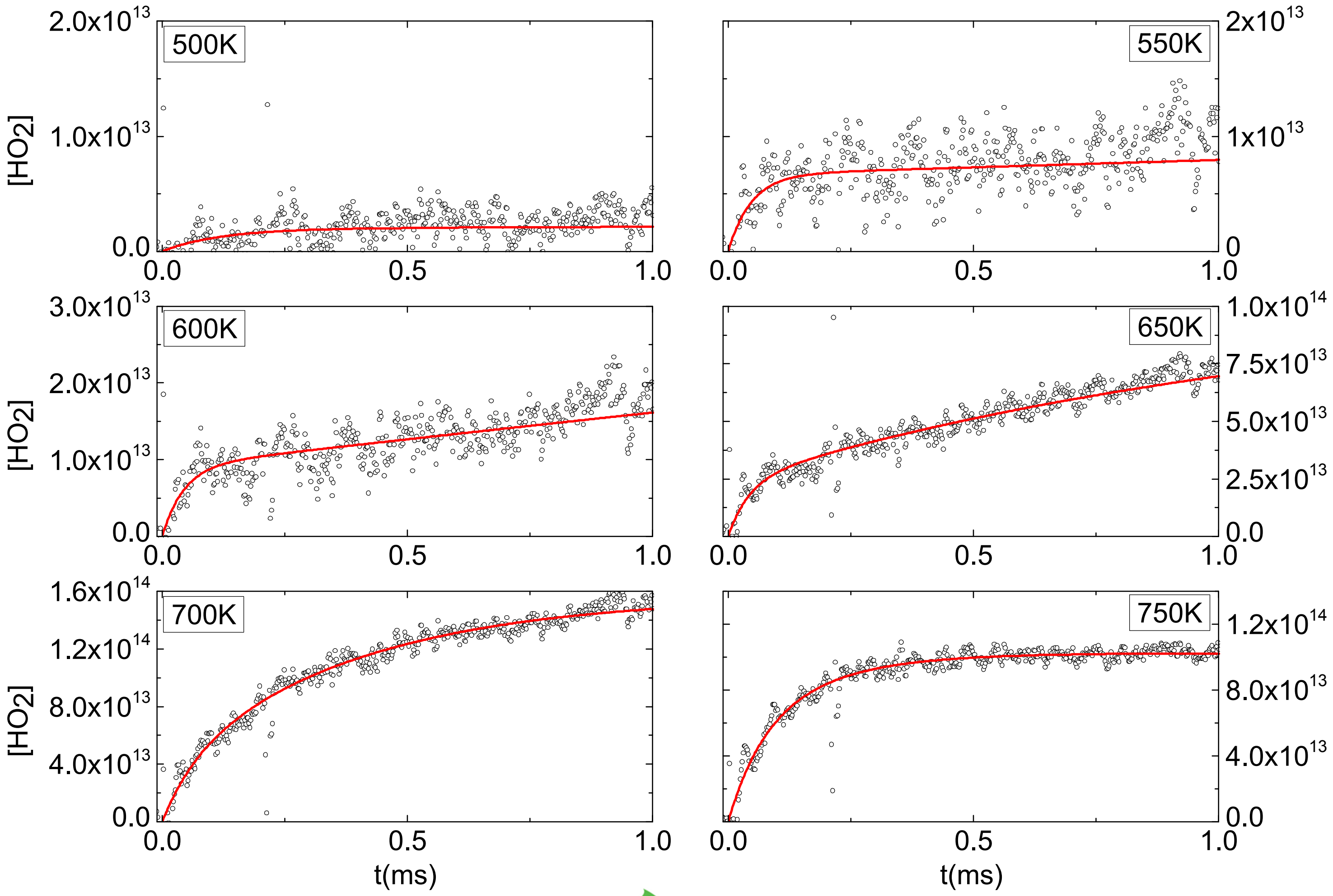
$$\frac{d}{dt}[OH] = \overset{k'_x}{\boxed{k_x[O_2]}}[R] + k_z[ROO] - \cancel{k_r[OH]^2}$$

By integral profile correction



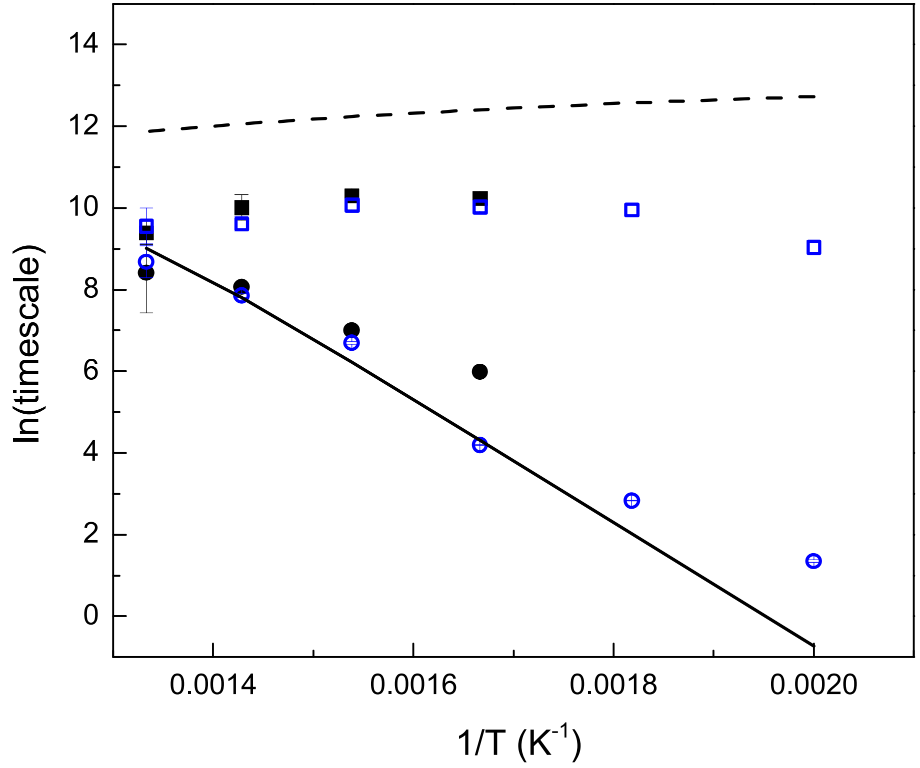
$$OH\ yield = \sum_{i=1}^{\infty} r^i = -\frac{r}{r-1}$$

Fitting Examples (Cyclohexane Oxidation)



Cyclohexyl + O_2: HO_2 Formation Timescales

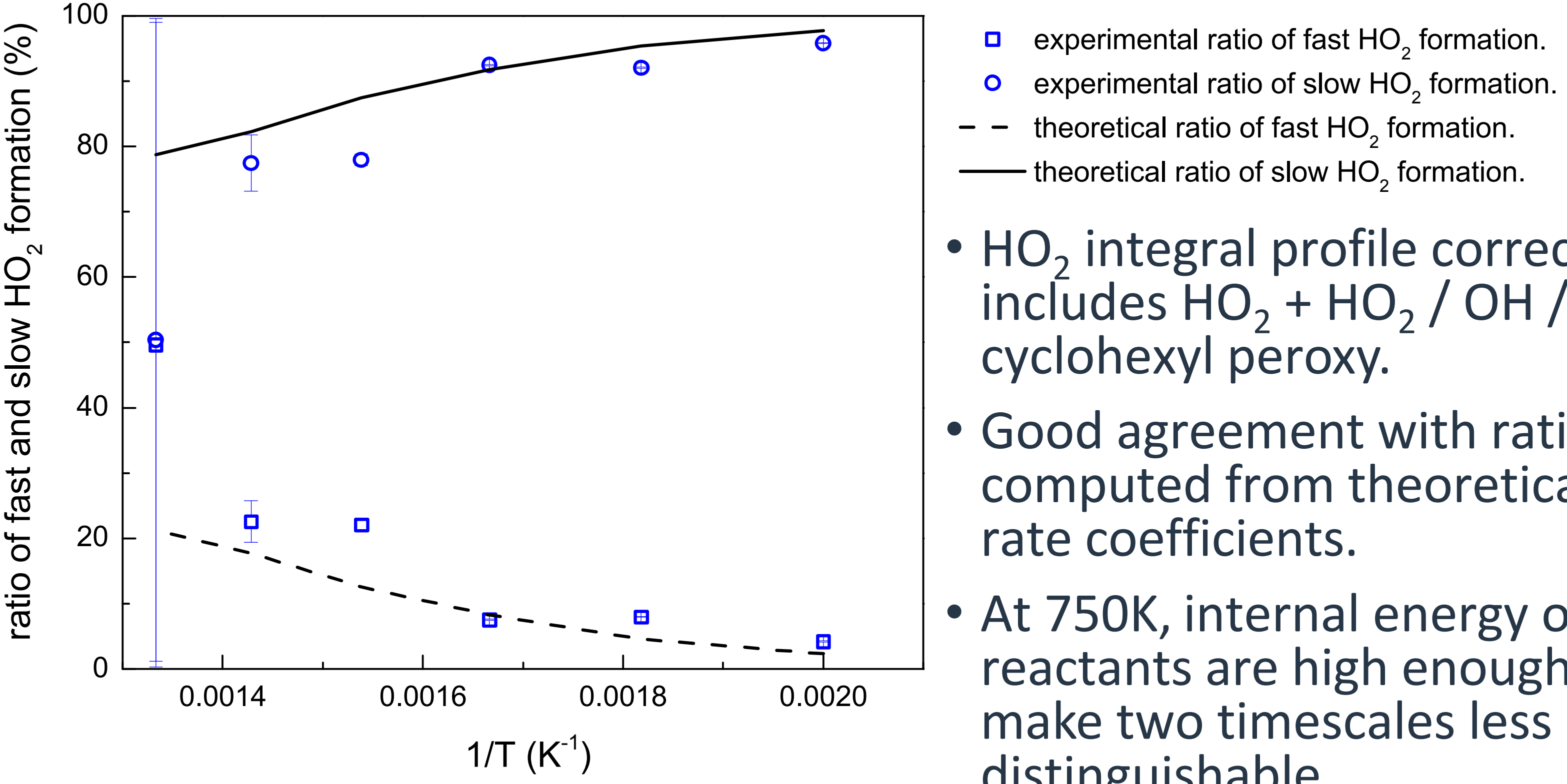
$$[HO_2]_t = A_1\left(1 - e^{-\boldsymbol{k_1} t}\right) + A_2\left(1 - e^{-\boldsymbol{k_2} t}\right)$$



- Temperature-sensitive slow HO_2 formation timescales. Mainly governed by sequential HO_2 formation.

Cyclohexyl + O_2: Fast/Slow HO_2 Formation Ratio

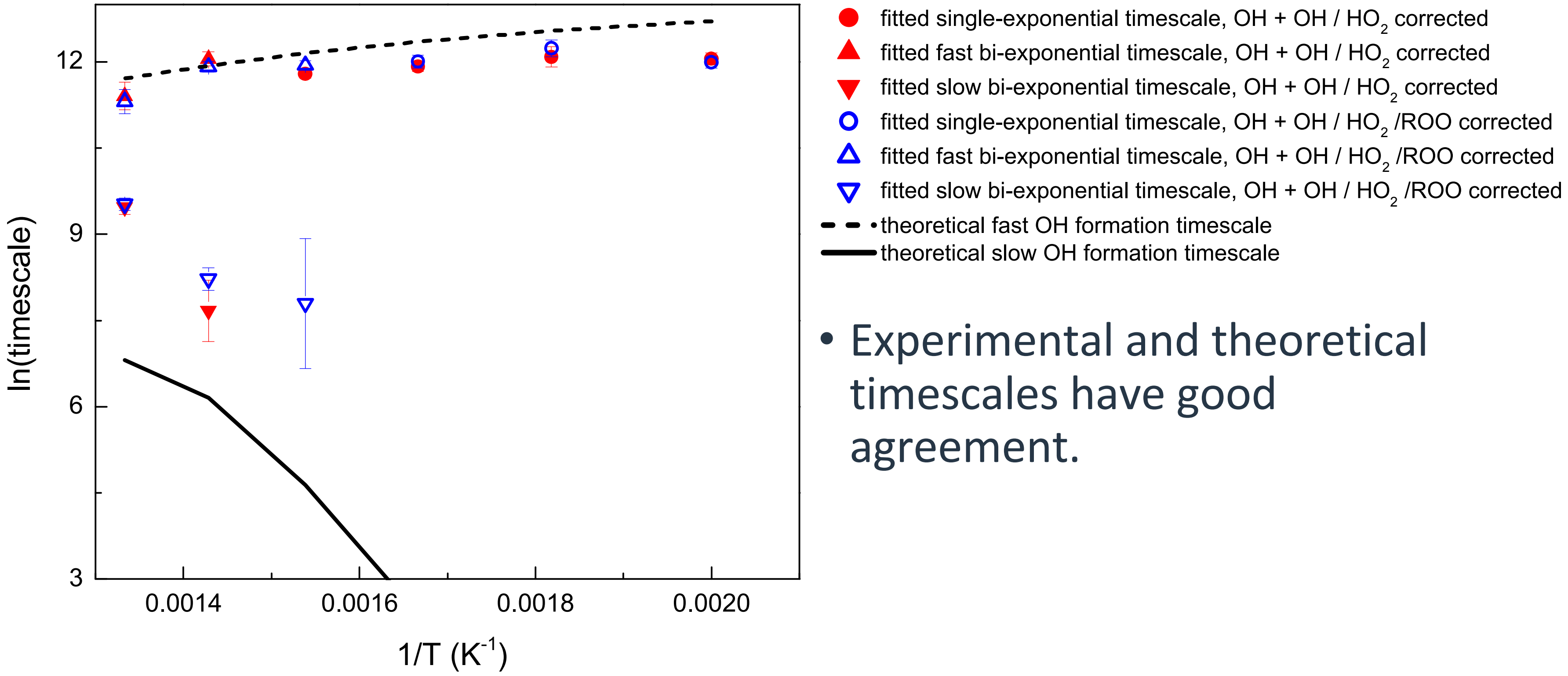
$$[HO_2]_t = \boldsymbol{A_1}\left(1 - e^{-k_1 t}\right) + \boldsymbol{A_2}\left(1 - e^{-k_2 t}\right)$$



- HO_2 integral profile correction includes HO_2 + HO_2 / OH / cyclohexyl peroxy.
- Good agreement with ratios computed from theoretical rate coefficients.
- At 750K, internal energy of reactants are high enough to make two timescales less distinguishable.

Cyclohexyl + O_2: OH Formation Timescales

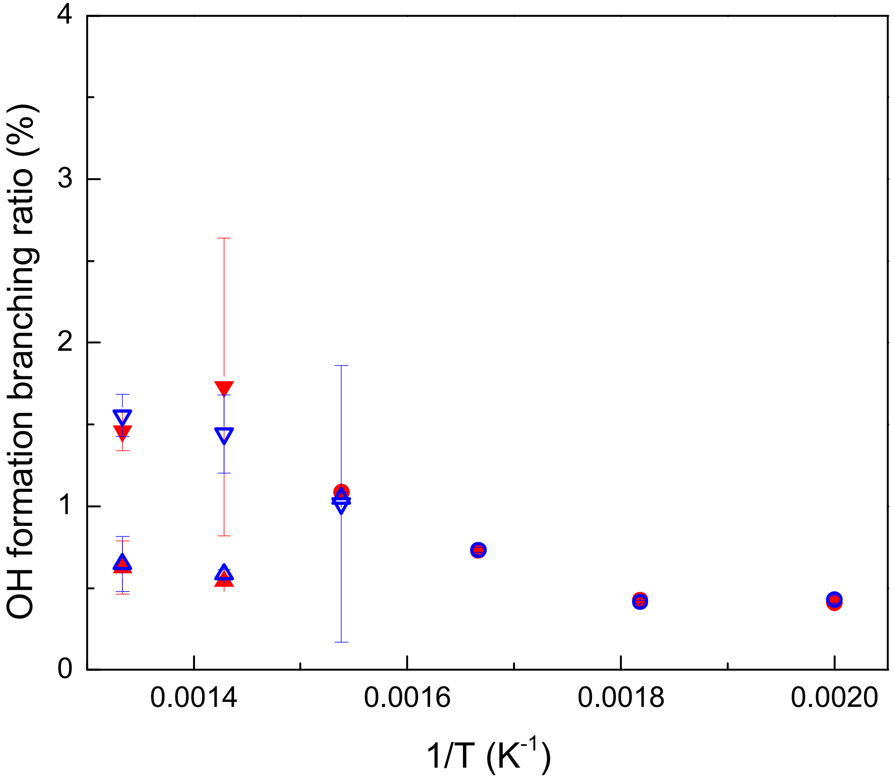
$$[OH]_t = A_1\left(1-e^{-\mathbf{k_1}t}\right) + A_2\left(1-e^{-\mathbf{k_2}t}\right)$$



- Experimental and theoretical timescales have good agreement.

Cyclohexyl + O_2: OH Formation Yield

$$[OH]_t = \boldsymbol{A_1}\left(1 - e^{-k_1 t}\right) + \boldsymbol{A_2}\left(1 - e^{-k_2 t}\right)$$

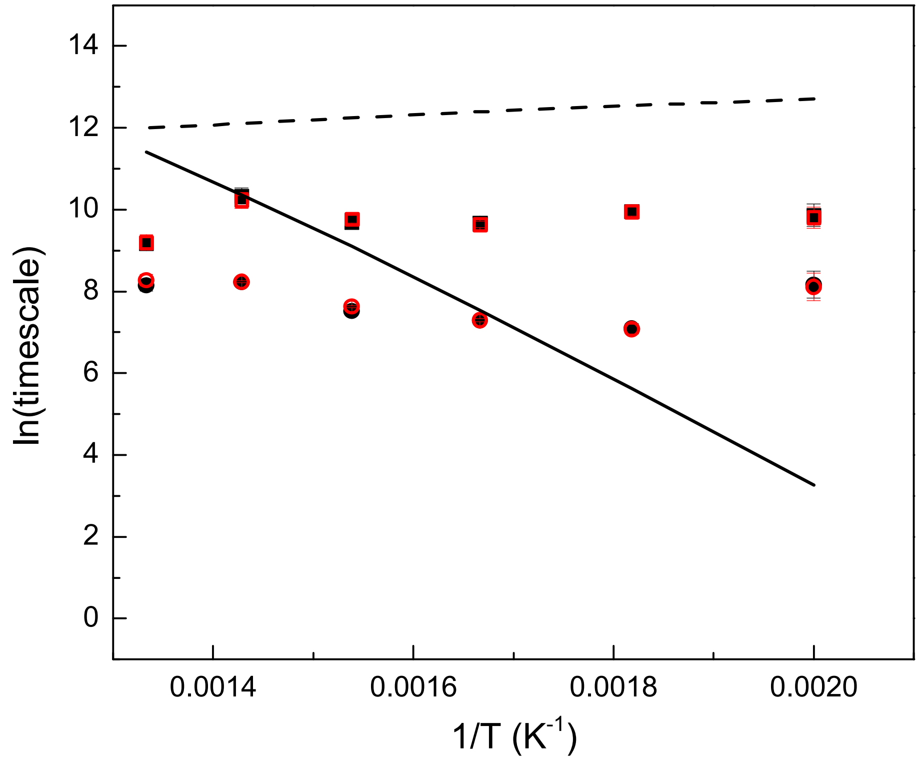


- Two distinct OH formation timescales started to appear at 650K and above.
- Sequential OH formation becomes major OH source at high temperature.
- Total OH yield doesn't exceed 3%.

$$OH\ yield = \frac{A_1\ or\ A_2}{[Cl]_0} = \sum_{i=1}^{\infty} r^i = -\frac{r}{r-1}$$

THP-yl + O_2: HO_2 Formation Timescales

$$[HO_2]_t = A_1\left(1 - e^{-\mathbf{k_1} t}\right) + A_2\left(1 - e^{-\mathbf{k_2} t}\right)$$

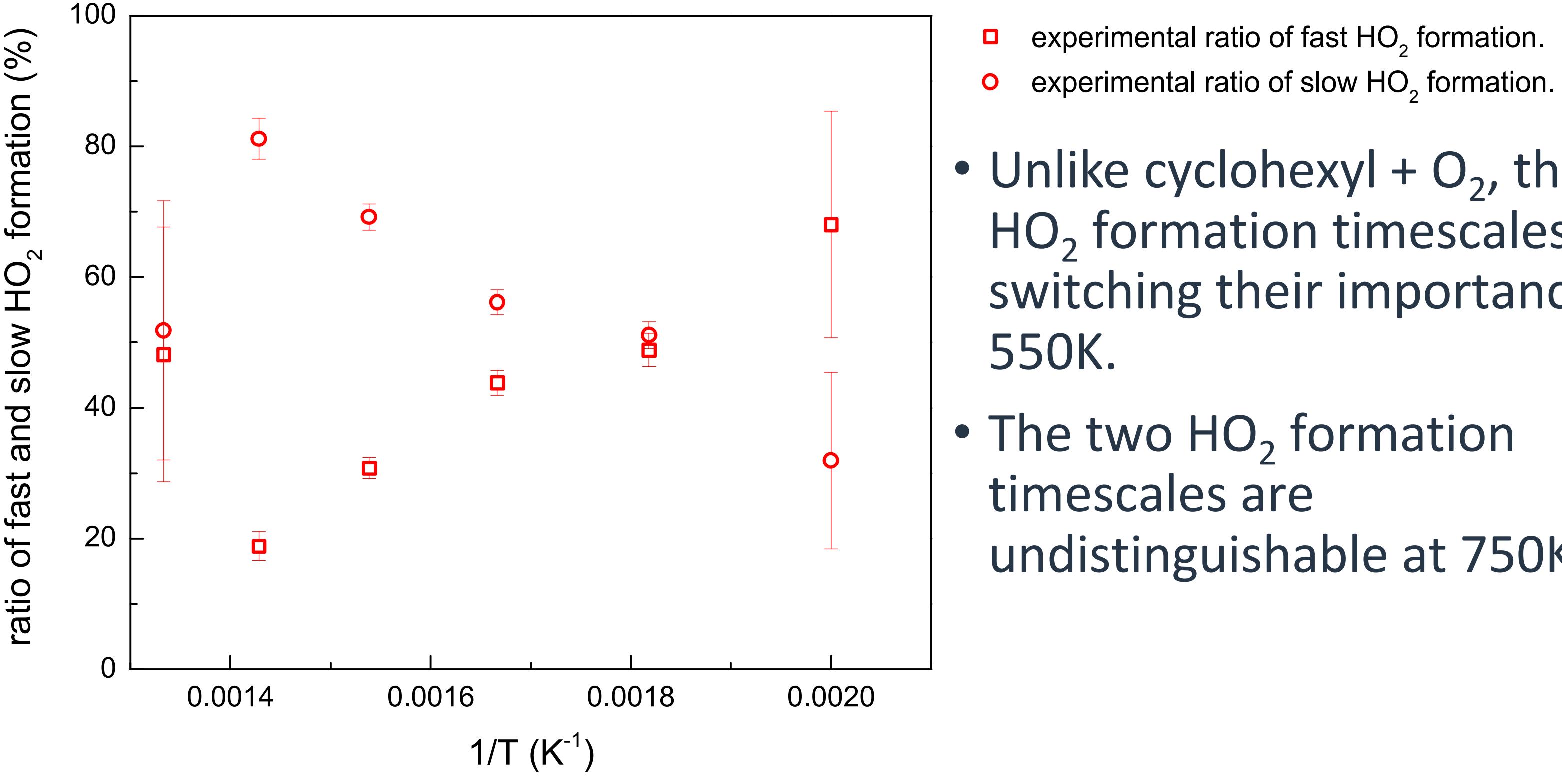


- Both fast and slow HO_2 formation timescales are temperature in-sensitive.
- Ineffective PES adjustment* based on cyclohexyl + O_2 or insufficient pathways involved in reduced model.

*PES adjusted from cyclohexyl + O_2 model by +2kcal/mol for ROO and -2kcal/model for TS.

THP-yl + O_2: Fast/Slow HO_2 Formation Ratio

$$[HO_2]_t = \boldsymbol{A_1}\left(1 - e^{-k_1 t}\right) + \boldsymbol{A_2}\left(1 - e^{-k_2 t}\right)$$

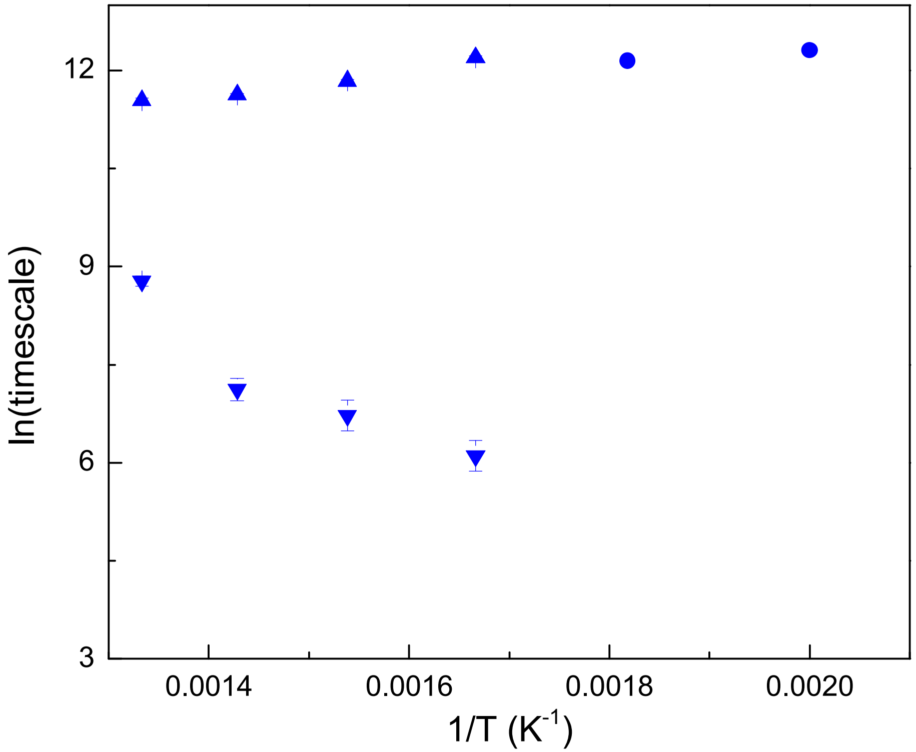


- Unlike cyclohexyl + O_2, the two HO_2 formation timescales are switching their importance at 550K.
- The two HO_2 formation timescales are undistinguishable at 750K.

*PES adjusted from cyclohexyl + O_2 model by +2kcal/mol for ROO and -2kcal/model for TS.

THP-yl + O_2: OH Formation Timescales

$$[OH]_t = A_1\left(1 - e^{-\mathbf{k_1} t}\right) + A_2\left(1 - e^{-\mathbf{k_2} t}\right)$$

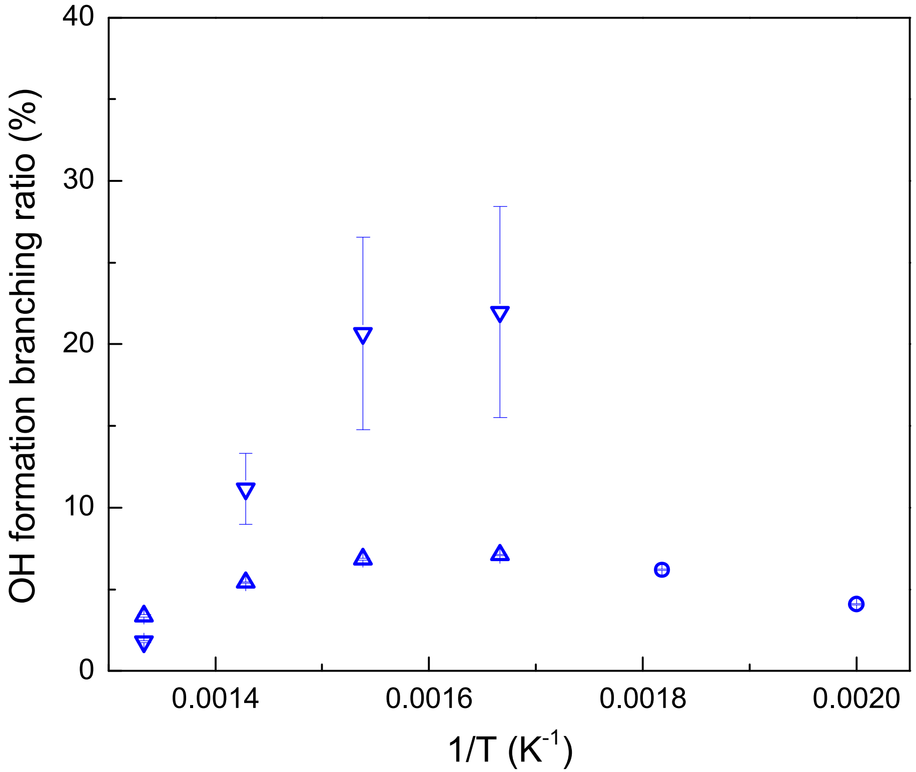


- OH formation shows two distinct timescales at 600K and above.
- The slow OH formation timescale has positive temperature dependence.

*PES adjusted from cyclohexyl + O_2 model by +2kcal/mol for ROO and -2kcal/model for TS.

THP-yl + O_2: OH Formation Yield

$$[OH]_t = \boldsymbol{A_1}\left(1 - e^{-k_1 t}\right) + \boldsymbol{A_2}\left(1 - e^{-k_2 t}\right)$$



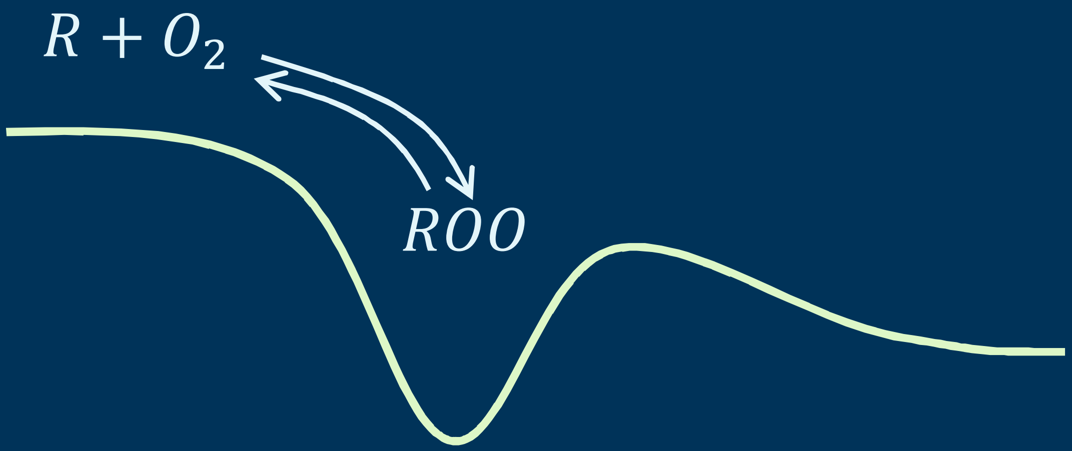
- The slow OH formation reaches peak at 600K when the OH time trace shows two distinct formation timescales, but becomes lower as temperature increased.
- The max OH yield is ~30% among all temperatures, roughly 10 times higher than the OH production yield from cyclohexyl + O_2.

$$OH\ yield = \frac{A_1\ or\ A_2}{[Cl]_0} = \sum_{i=1}^{\infty} r^i = -\frac{r}{r-1}$$

Conclusions

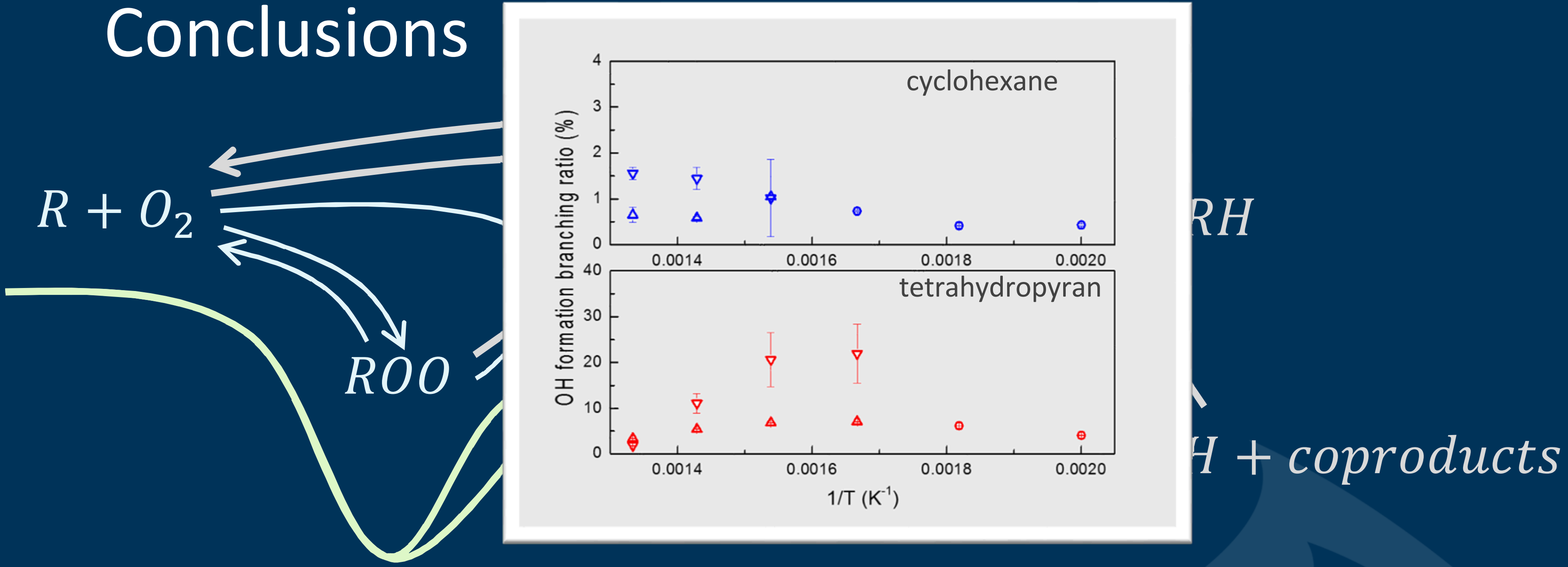
- Quantitative HO_2 and OH formation timescales from Cl-initiated cyclohexane and tetrahydropyran oxidation have been measured by our IR absorption flow system.

Conclusions



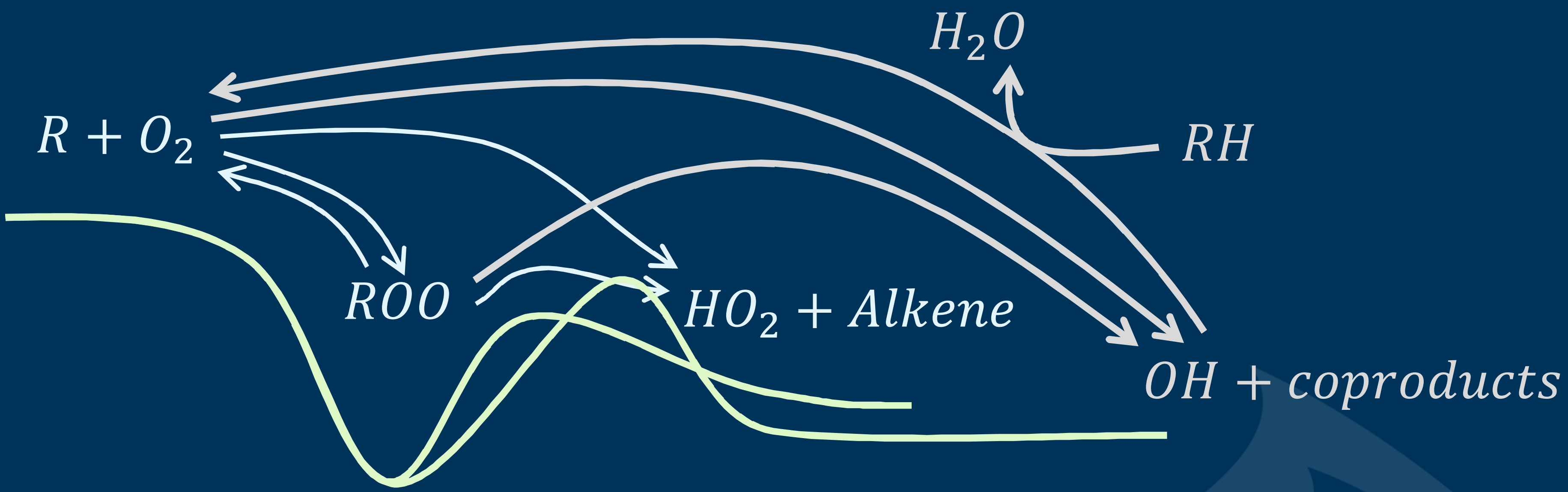
- Alkylperoxy-centered chemistry is proposed for a reduced model, and applied to analyze the experimental results.

Conclusions



- Major differences of THP oxidation have been observed by measuring key intermediates, and compared with cyclohexane oxidation:
  - Slow (sequential?) HO_2 formation timescales is temperature-insensitive.
  - Contribution of slow (sequential?) HO_2 production is high at lower temperatures and suppressed at higher temperatures.
  - Slow (sequential) OH formation branching ratio has negative temperature dependence, after reaching the peak OH yield at 600K.

Conclusions



H_2O

$R + O_2$

RH

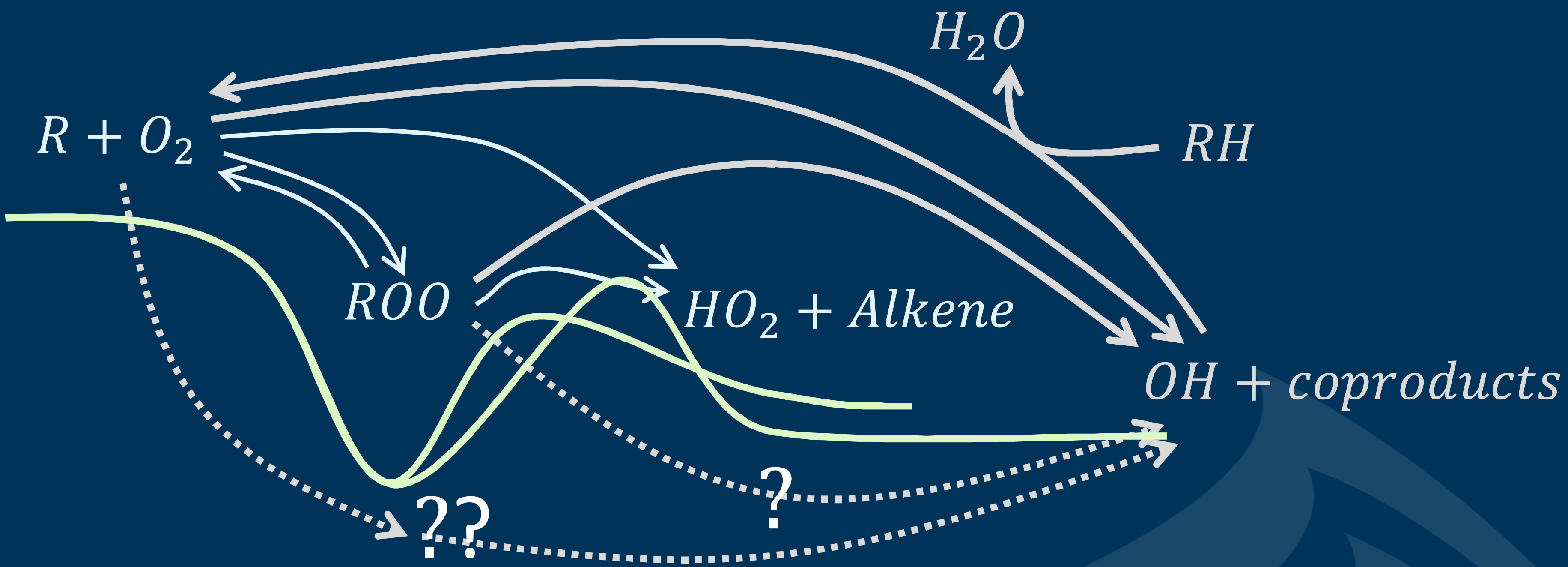
ROO

$HO_2 + Alkene$

$OH + coproducts$

- The OH formation kinetics seems to influence the HO_2 formation kinetics. – But the temperature-dependent OH formation doesn’t explain the temperature-independent sequential HO_2 formation.

Current and Future Works



- Some theoretical calculations may help to narrow down the possible pathways opened in the tetrahydropyran oxidation.
- Experimentally, we can test the change of HO_2/OH quantity from excess O_2 reacting with reactive intermediates. (Second O_2 addition)
- Insights from combination of laser & mass spectrometer experiments.

Acknowledgement

- Laser Chemistry Laboratory, Combustion Research Facility, Sandia National Laboratories.
- Dr. Craig A. Taatjes (supervisor, manager)
- Mr. Kendrew Au (technical support)

- Funding support:
- Division of Chemical Sciences, Geosciences and Biosciences, Office of Basic Energy Sciences (BES), U.S. Department of Energy (USDOE). (DE-NA0003525)

Your attention!!!

COMBUSTION RESEARCH FACILITY

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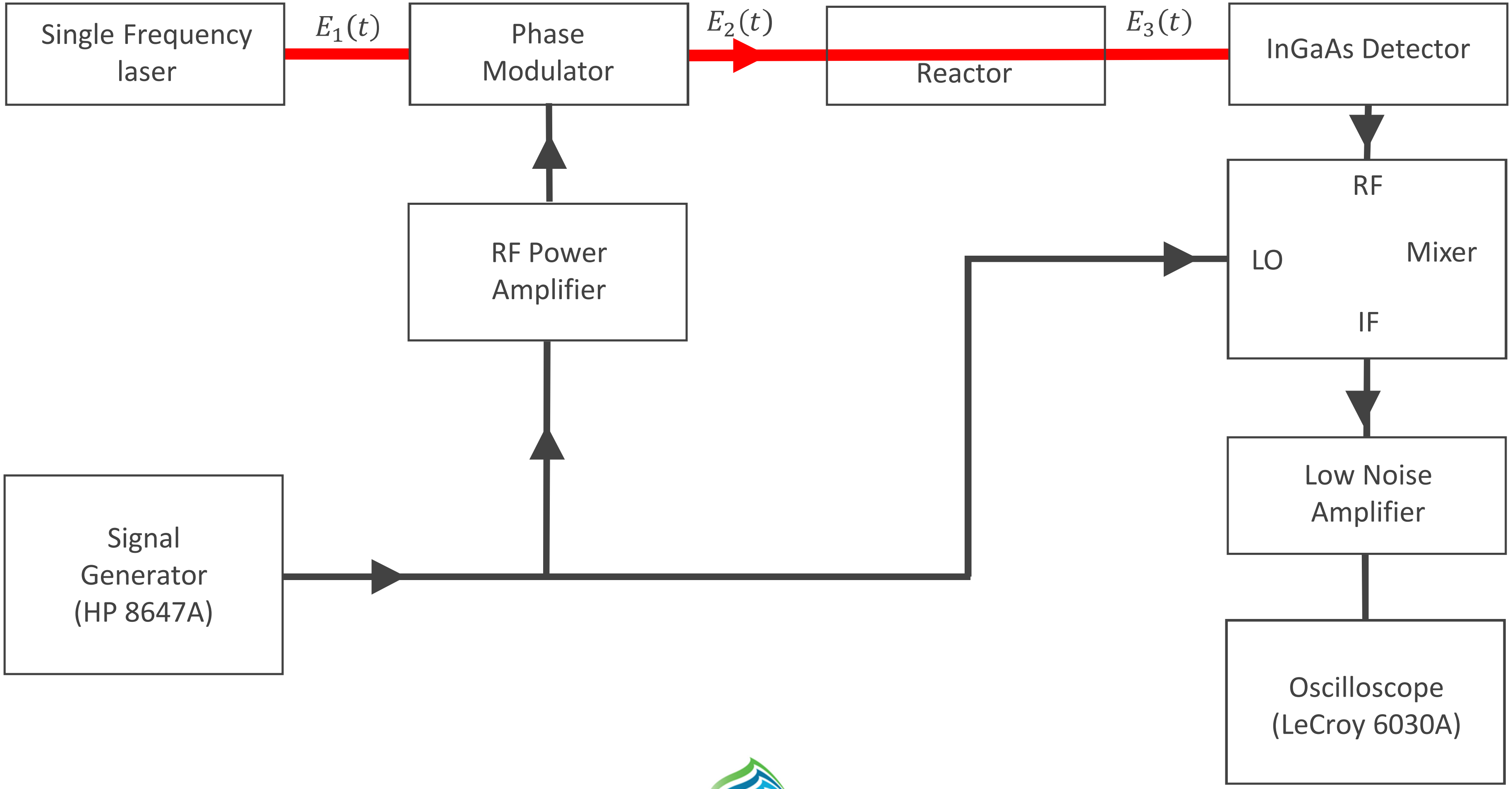
Frequency Modulation – Basic Layout



Single Frequency laser

$E_1(t)$

Phase Modulator

$E_2(t)$

Reactor

$E_3(t)$

InGaAs Detector

RF Power Amplifier

RF

LO

Mixer

IF

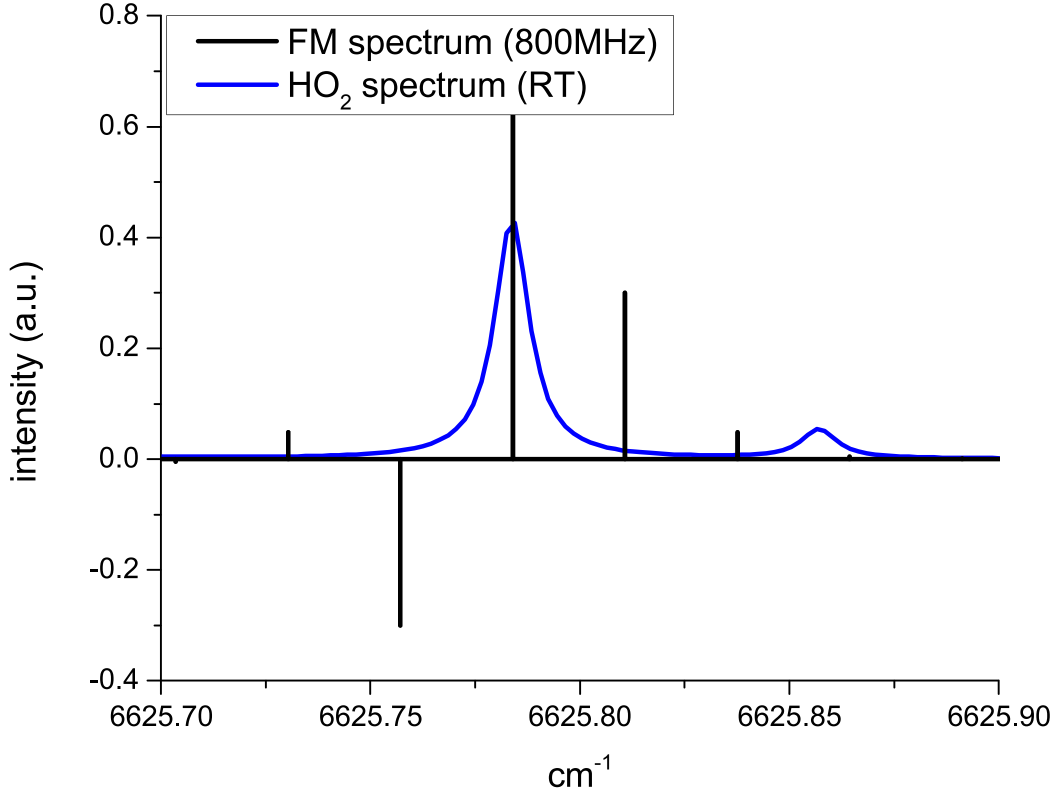
Signal Generator (HP 8647A)

Low Noise Amplifier

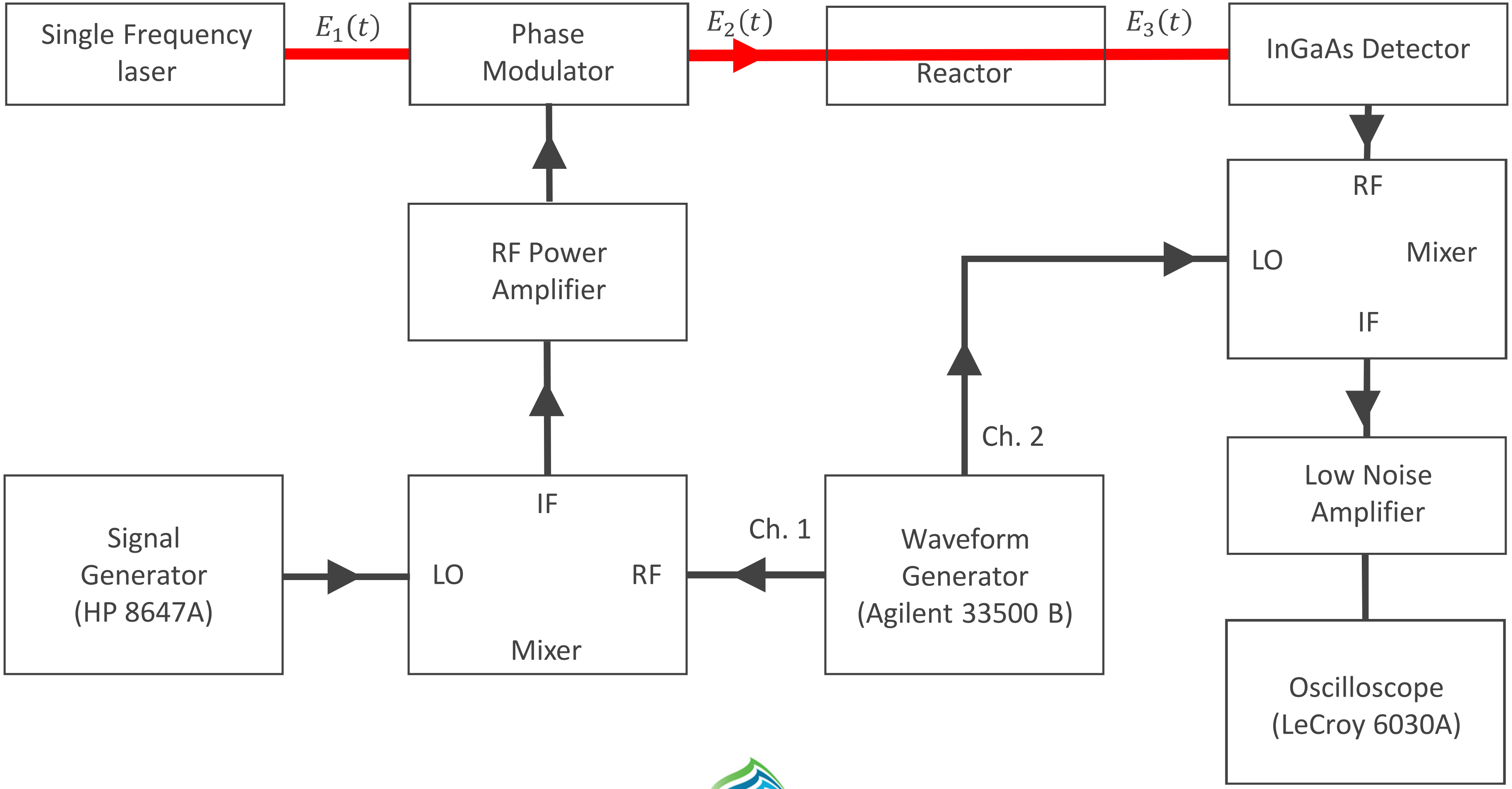
Oscilloscope (LeCroy 6030A)

Frequency Modulation - Spectroscopy

$$E_2(t) = E_0 e^{i\omega_0 t} \sum_{n=-\infty}^{\infty} J_n(\beta) e^{in\omega_1 t} + c.c.$$



Two-Tone Frequency Modulation – Basic Layout



Two-Tone Frequency Modulation – Spectroscopy

$$E_2(t) = E_0 e^{i\omega_0 t} \sum_{n=-\infty}^{\infty} J_n(\beta_1) e^{in\omega_1 t} \sum_{m=-\infty}^{\infty} J_m(\beta_2) e^{im\omega_2 t} + c.c.$$