



Direct Measurement of OH and HO₂ Formation in R + O₂ 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

120

Global primary energy supply, 2003 – 2015

100

PJ/a
600,000

80

500,000

60

400,000

40

300,000

30

200,000

20

100,000

10

2001

Trillion Btu

15,000

0

2003

2005

2007

2009

2012

2015

2006

2008

2010

2014

2016

Renewables Global Futures Report Great debates towards 100 % renewable energy

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

0 2000 5,000 10,000 15,000

0 2002 2004 2006 2008 2010 2012 2014 2016

0

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10,000

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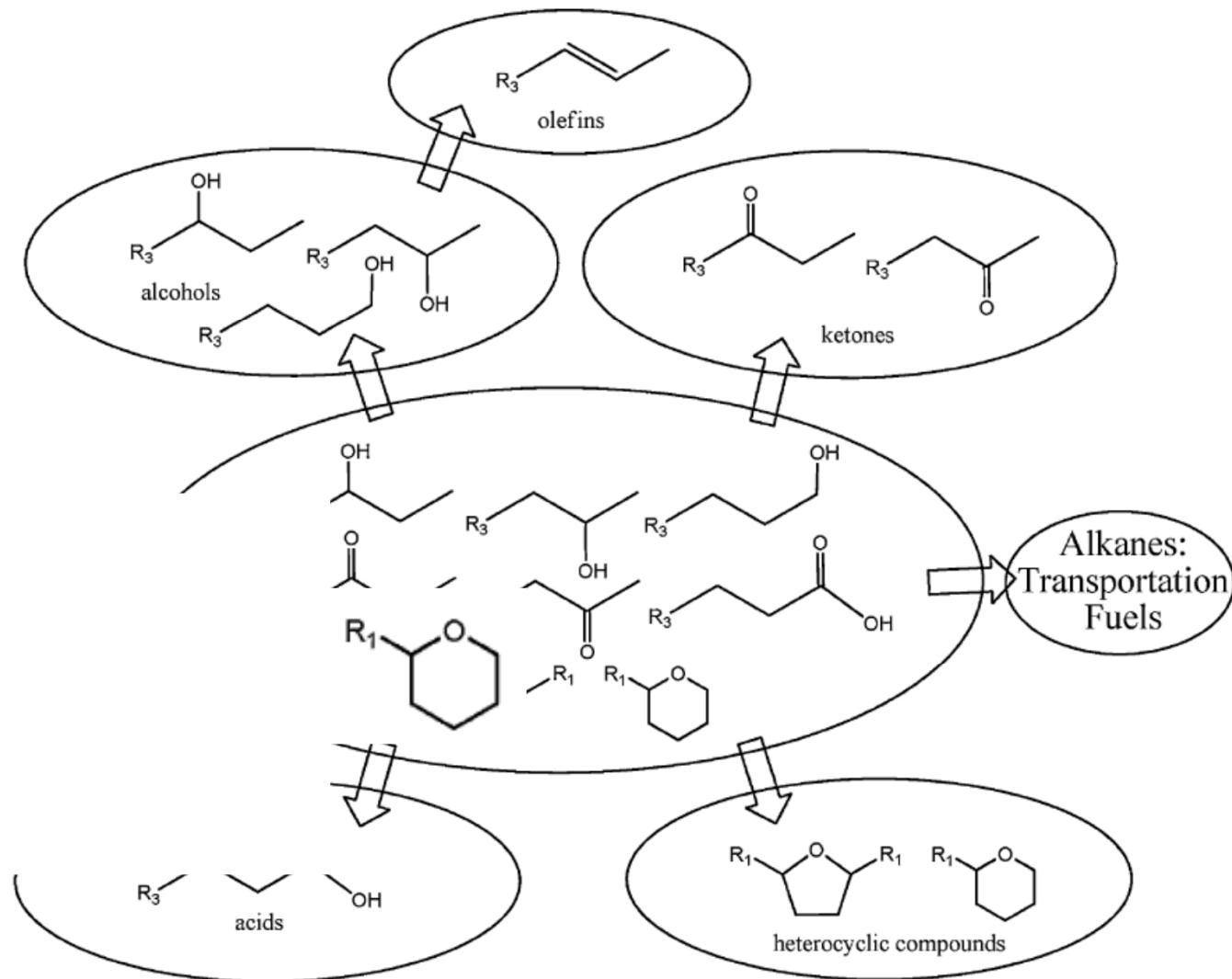
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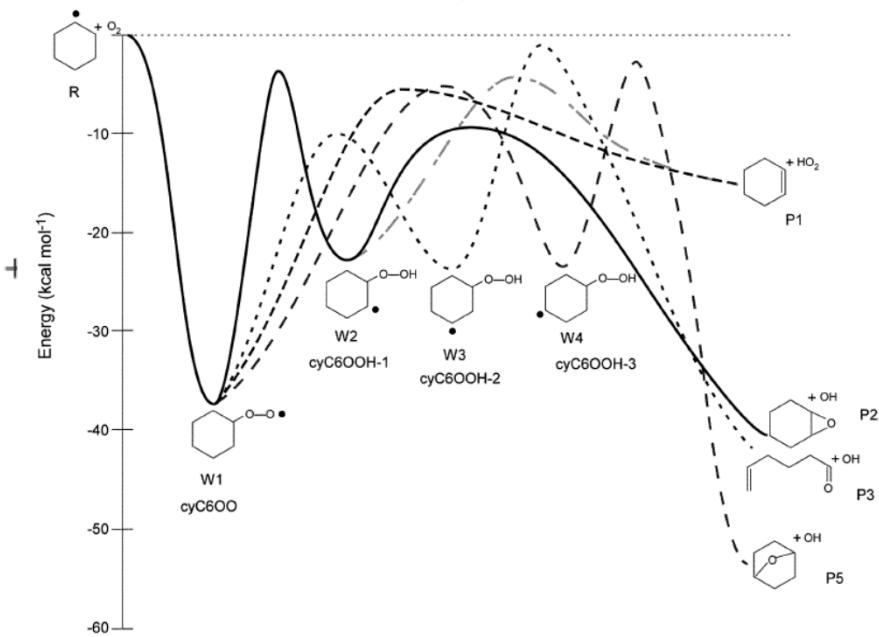
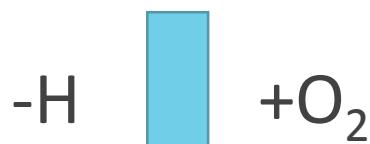
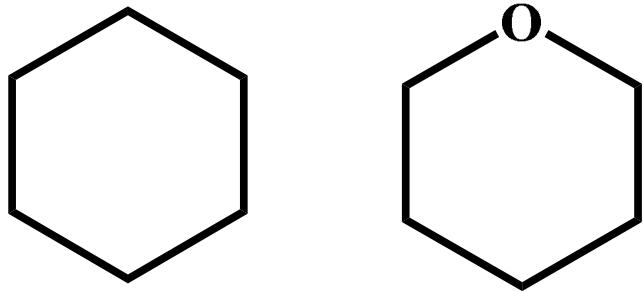
1,265,000

1,270,000

1



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



- Monoether analog of cyclohexane and core structure of sugars and polysaccharides.
- Cyclohexane oxidation was studied previously combining OH / HO₂ 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

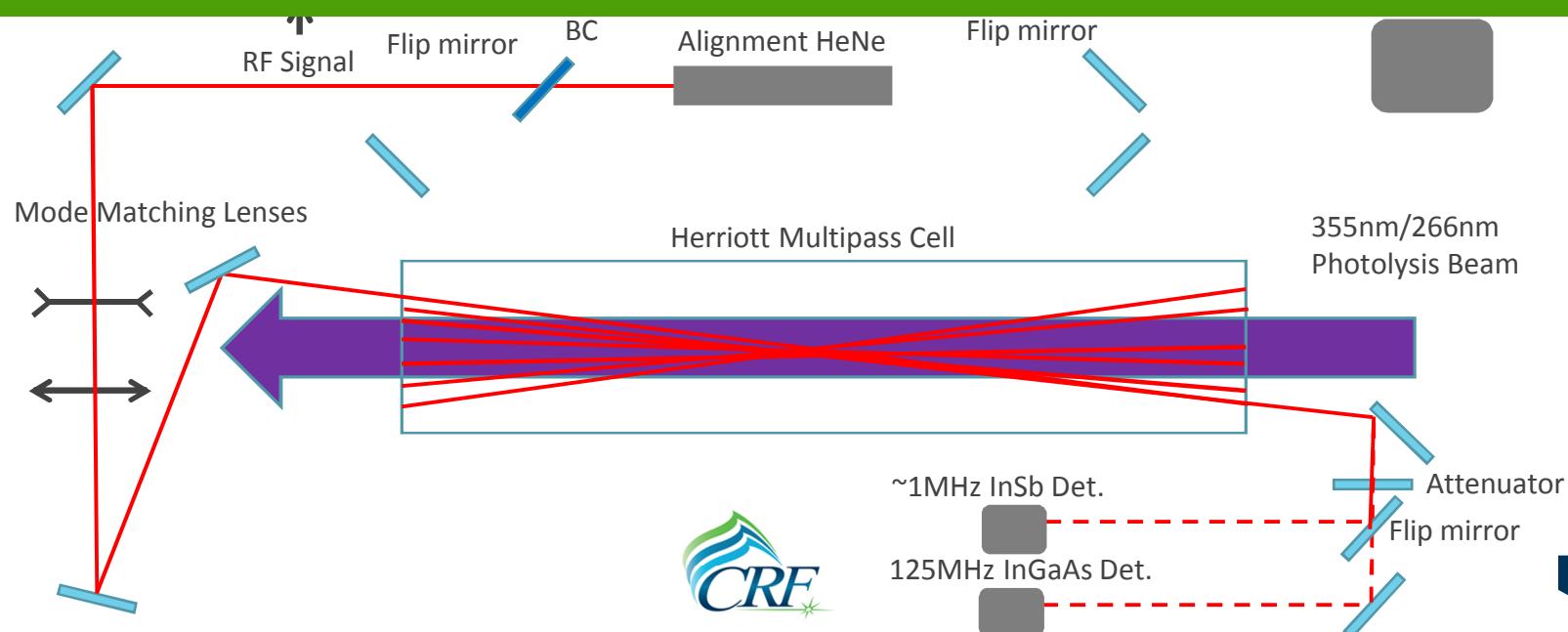
Total density of molecules = $2.6\text{-}3.9 \times 10^{17}$ molecules/cm³

Temperature = 500-750K

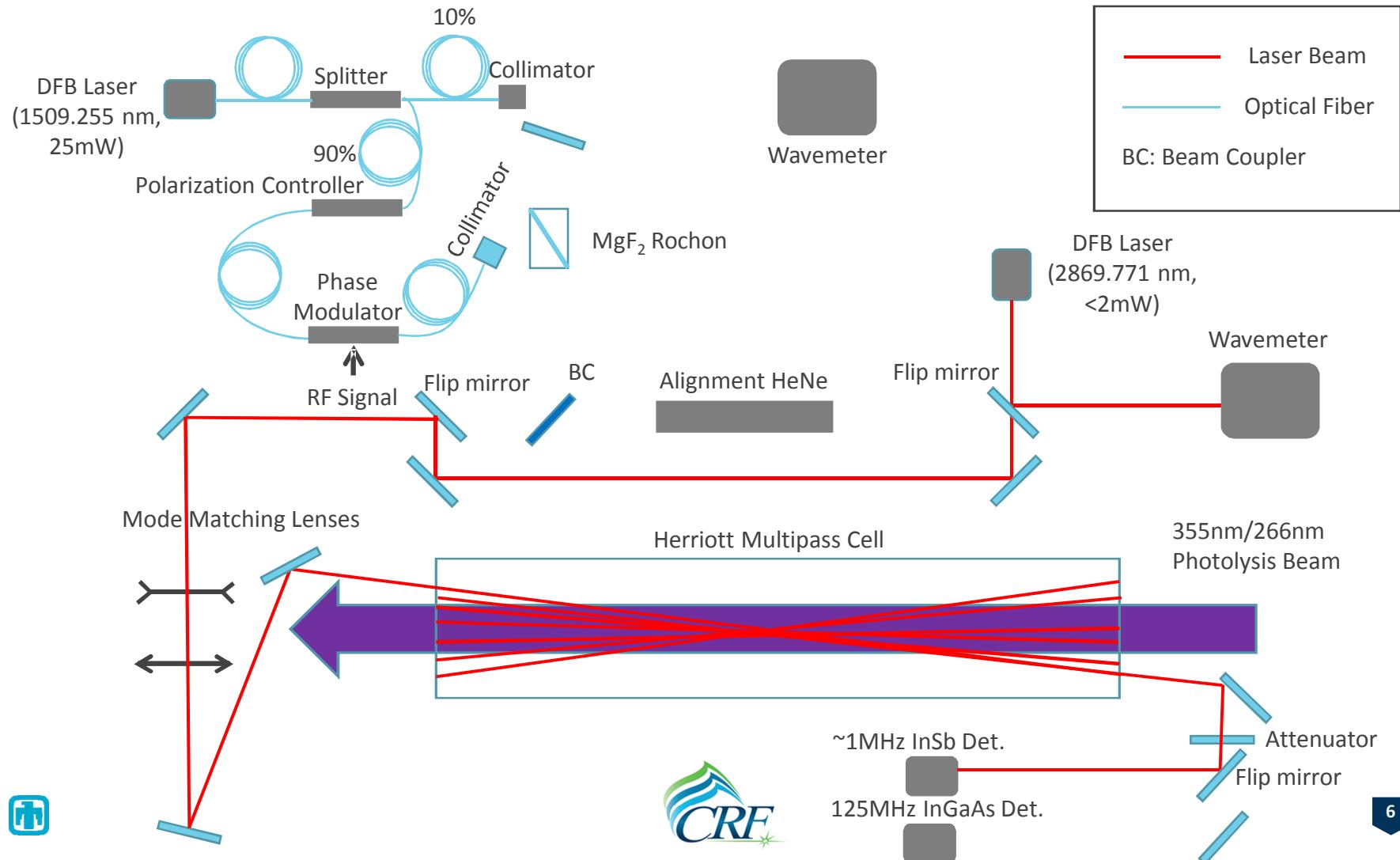
[Fuel] $\approx 1 \times 10^{15}$ molecules/cm³

[Cl]₀ $\approx 8 \times 10^{13}$ molecules/cm³ (From OxCl or Cl₂ photolysis)

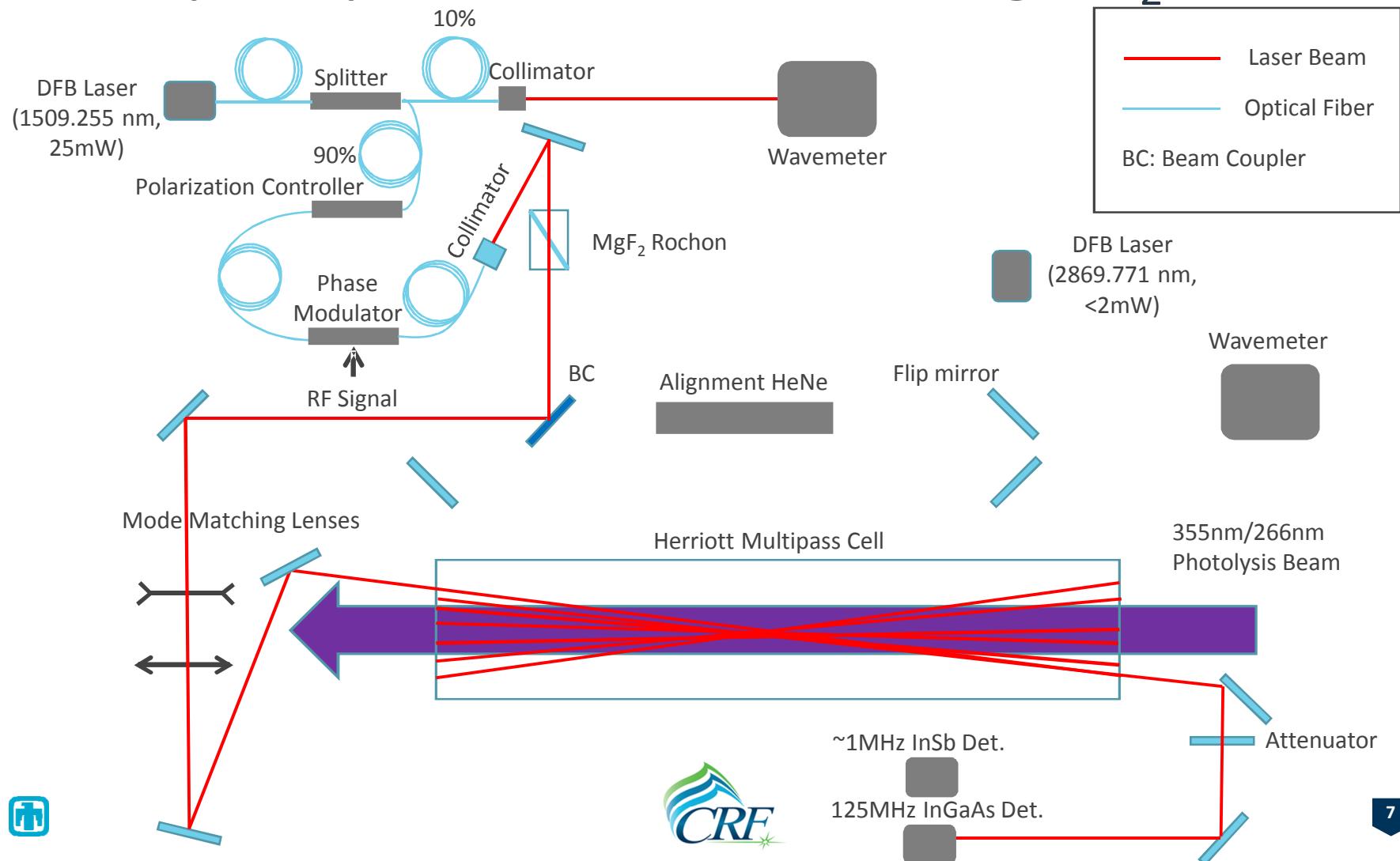
[O₂] $\approx 4 \times 10^{16}$ molecules/cm³



IR Absorption Experiment – Direct Absorption Measuring OH



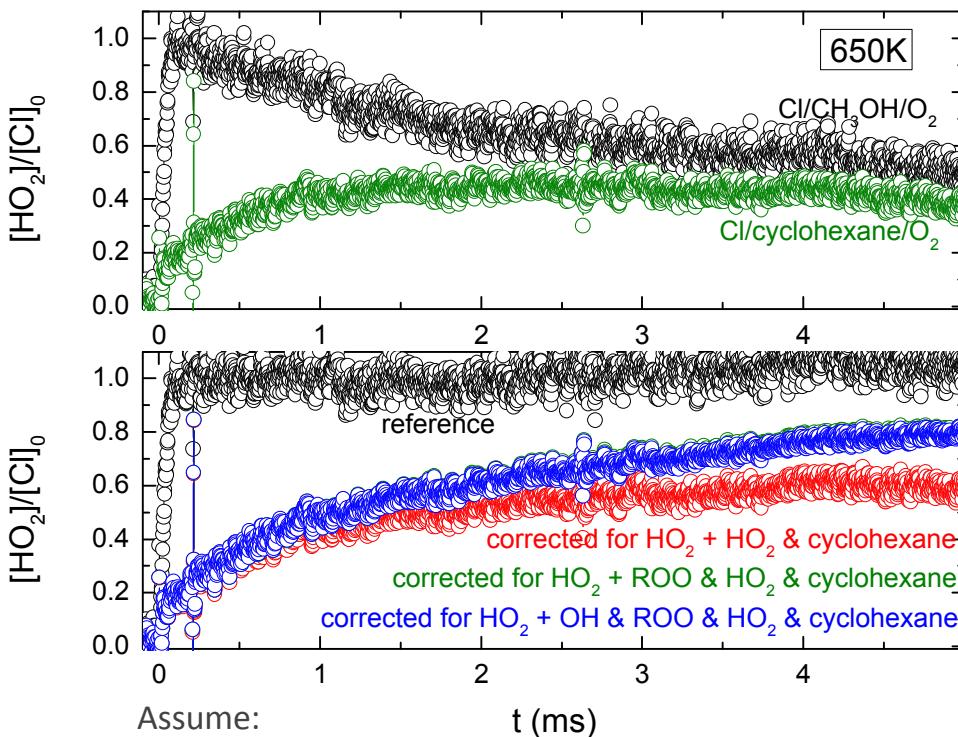
IR Absorption Experiment – Two-Tone Frequency Modulation Measuring HO₂



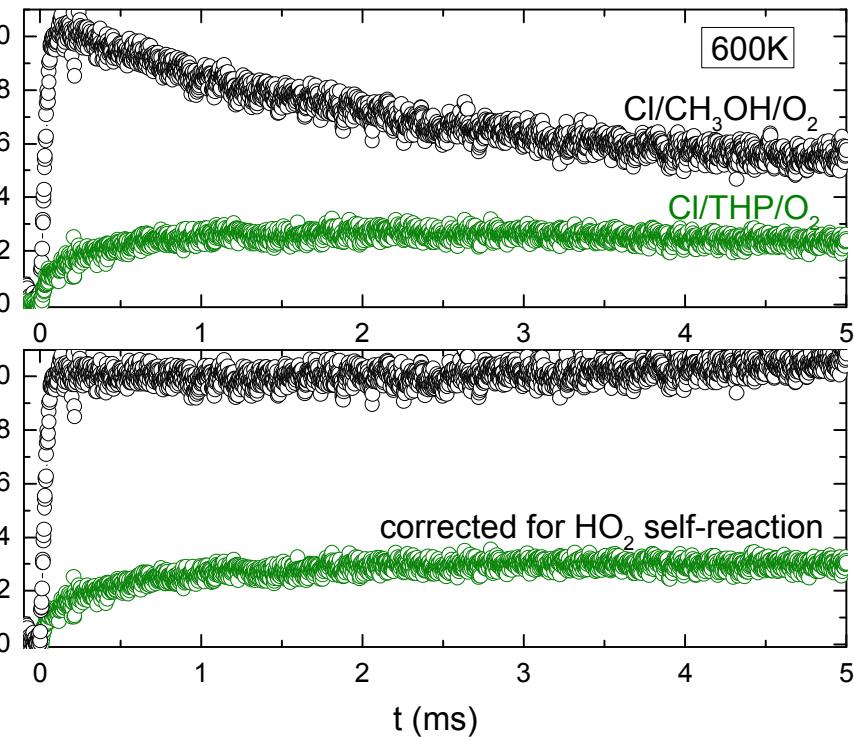
Integral Profile Correction – HO_2

$$\alpha \int_0^t R_{\text{production}}(t') dt' = I(t) + 2\alpha k_{\text{self}} \int_0^t [\text{HO}_2]_t^2 dt' + \alpha \int_0^t R_{\text{removal}}(t') [\text{HO}_2]_t dt' *$$

cyclohexane & methanol



tetrahydropyran (THP) & methanol



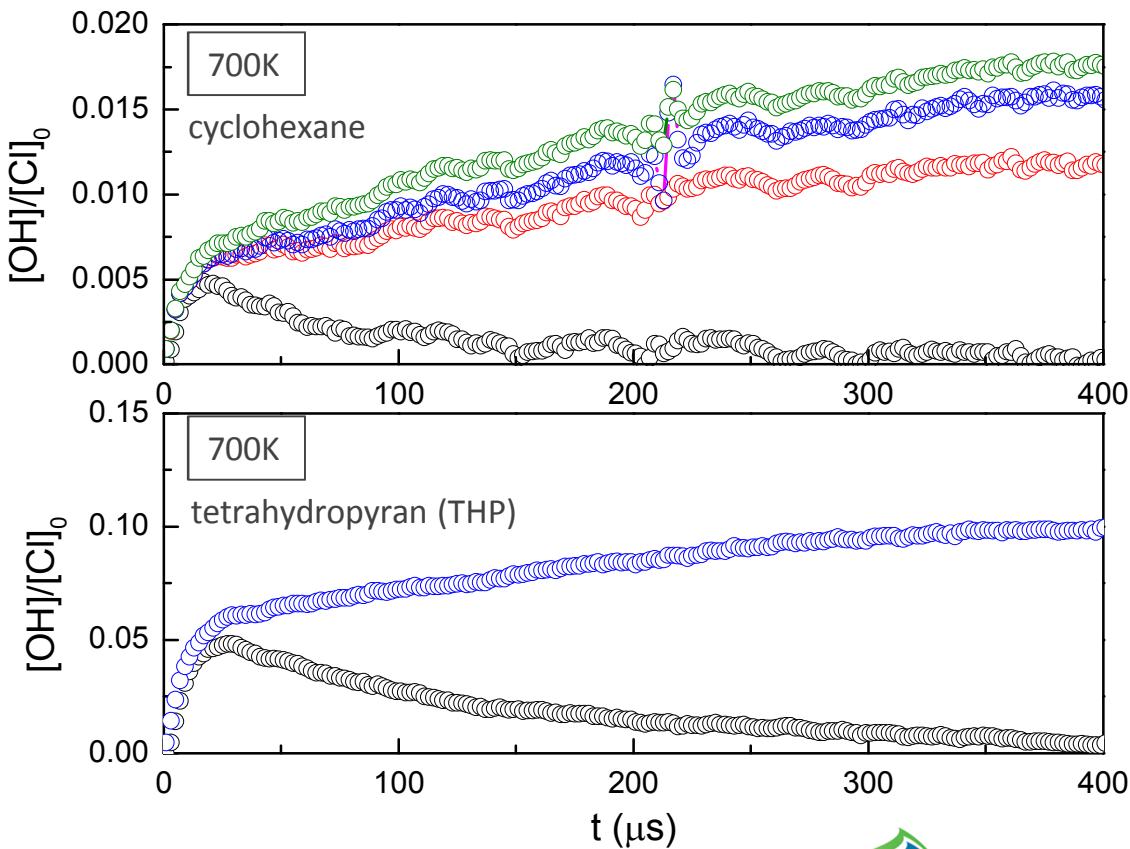
Assume:

$$*[R\text{OO}] = [R]_0 - [\text{HO}_2] \approx [\text{Cl}]_0 - [\text{HO}_2]$$



Integral Profile Correction – OH

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



correct with OH+cyclohexane/HO₂/OH/ROO
correct with OH+cyclohexane/HO₂/OH

correct with OH+cyclohexane

uncorrected

correct with OH+tetrahydropyran/HO₂/OH

uncorrected

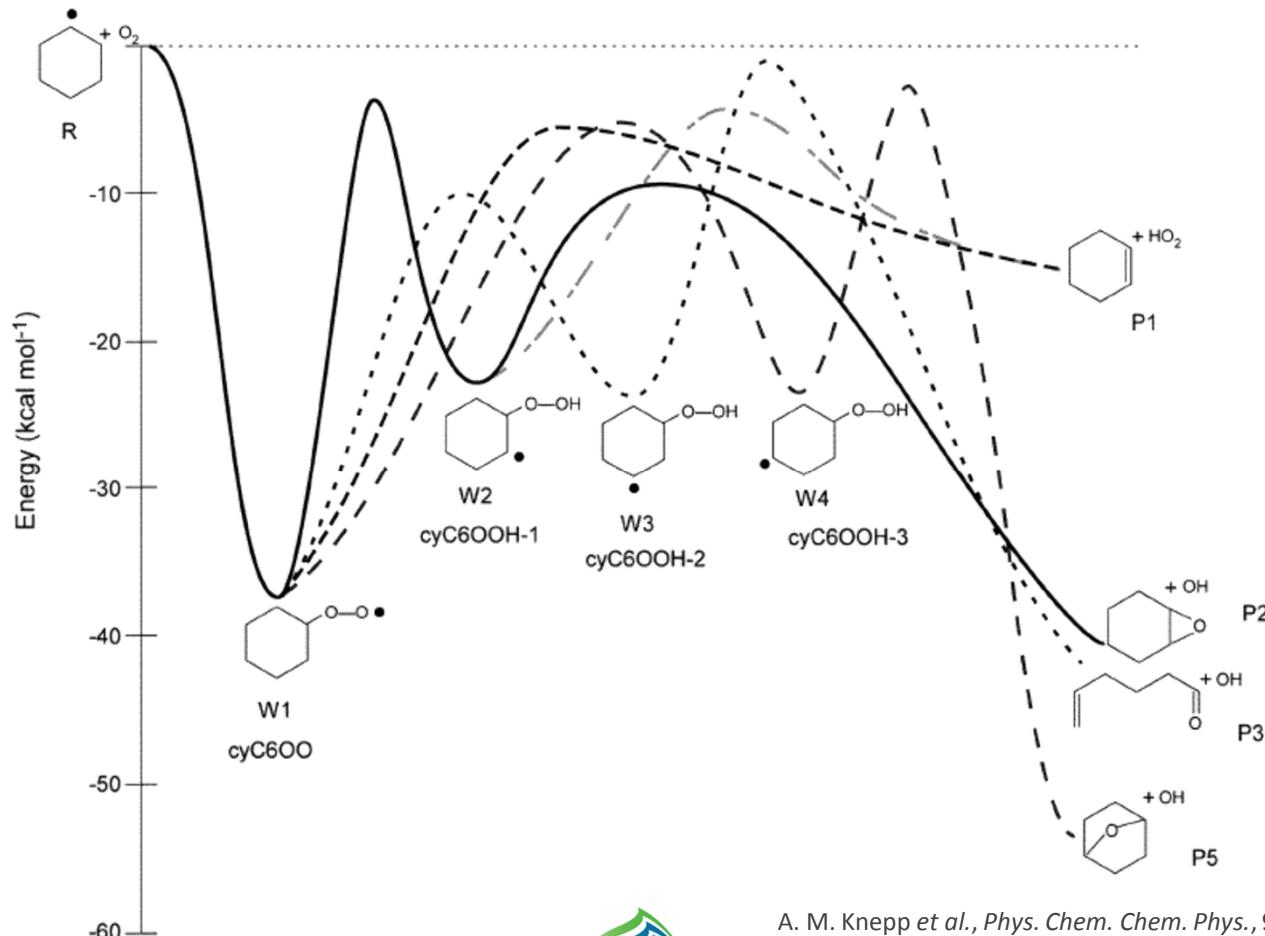
List of Rate Coefficients

Reaction	Rate coefficient (cm ³ /molecule/s)	Ref.
$\text{HO}_2 + \text{HO}_2 \rightarrow \text{O}_2 + \text{H}_2\text{O}_2$	$2.2 \times 10^{-13} \times e^{\frac{820}{T}} + 7.0 \times 10^{-10} \times e^{\frac{-6030}{T}}$	(1)
$\text{HO}_2 + \text{C}_6\text{H}_{11}\text{OO} \rightarrow \text{C}_6\text{H}_{11}\text{OOH} + \text{O}_2$	$2.61 \times 10^{-13} \times e^{\frac{1240}{T}}$	(1)
$\text{HO}_2 + \text{OH} \rightarrow \text{O} + \text{H}_2\text{O}$	$4.8 \times 10^{-11} \times e^{\frac{250}{T}}$	(1)
$\text{OH} + \text{OH} \rightarrow \text{O} + \text{H}_2\text{O}$	$1.65 \times 10^{-12} \times \left(\frac{T}{298}\right)^{1.14} \times e^{\frac{-50}{T}}$	(1)
$\text{OH} + \text{C}_6\text{H}_{12} \rightarrow \text{C}_6\text{H}_{11} + \text{H}_2\text{O}$	$3.97 \times 10^{-12} \times \left(\frac{T}{298}\right)^{1.64} \times e^{\frac{80}{T}}$	(1)
$\text{OH} + \text{C}_5\text{H}_{10}\text{O} \rightarrow \text{C}_5\text{H}_9\text{O} + \text{H}_2\text{O}$	$7.8 \times 10^{-12} \times e^{\frac{130}{T}}$	(2)

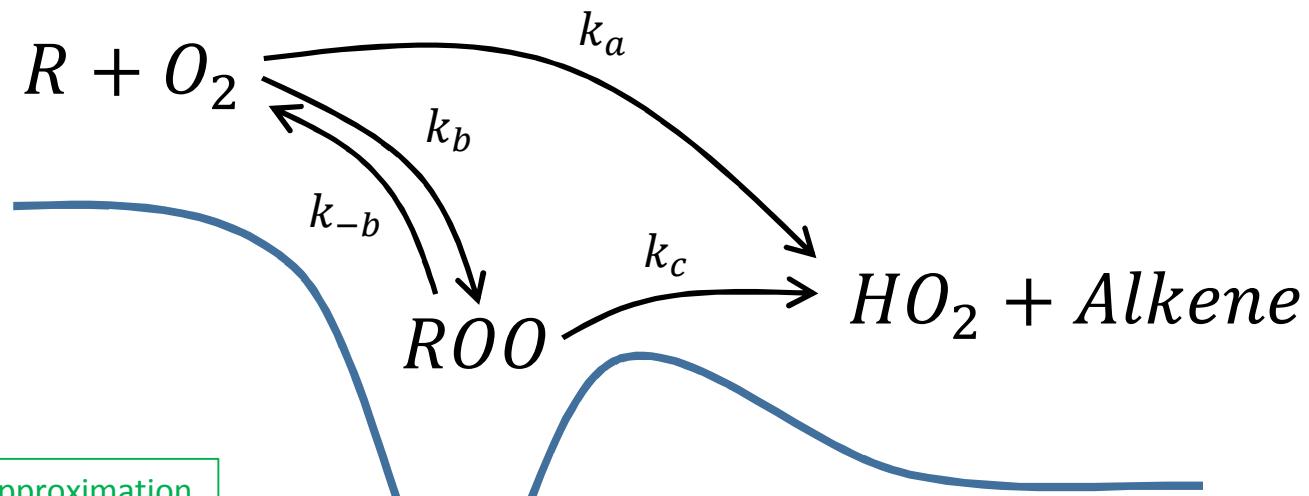
(1) A. M. Knepp *et al.*, *Phys. Chem. Chem. Phys.*, **9**, 4315 (2007)

(2) J. Moriarty *et al.*, *J. Phys. Chem. A*, **107**, 1499 (2003)

Cyclohexyl + O₂ Reaction PES



Reduced Model – HO₂



Pseudo-first-order approximation

$$\frac{d}{dt}[R] = -k_a [O_2][R] - k_b [O_2][R] + k_{-b}[ROO]$$

$$\frac{d}{dt}[ROO] = k_b [O_2][R] - k_{-b}[ROO] - k_c[ROO]$$

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

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

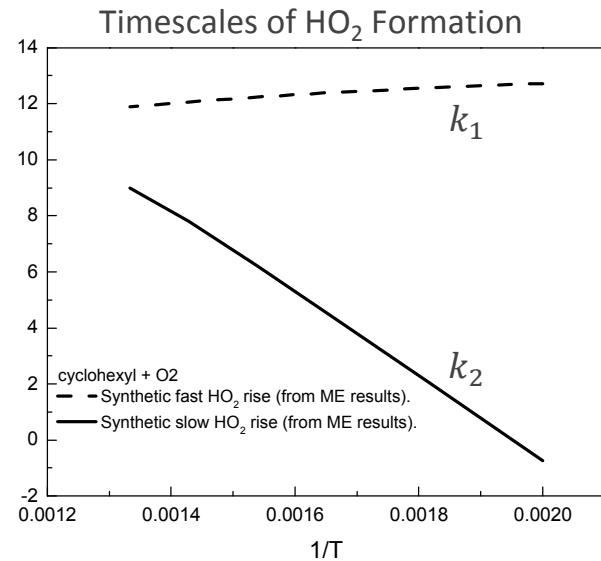
By integral profile correction

Solution of Differential Equations

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

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

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



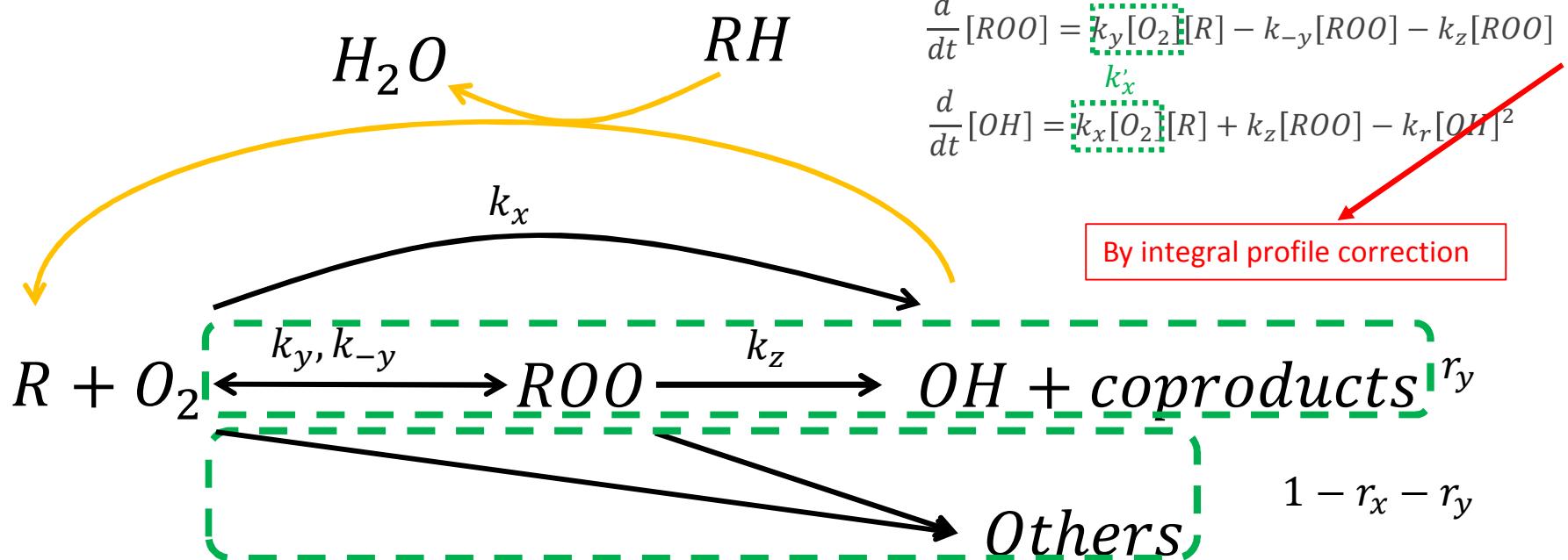
$$A_1$$

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

$$A_2$$

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

Reduced Model – OH



Pseudo-first-order approximation

$$\frac{d}{dt} [R] = -k_x [O_2] [R] - k_y [O_2] [R] + k_{-y} [ROO]$$

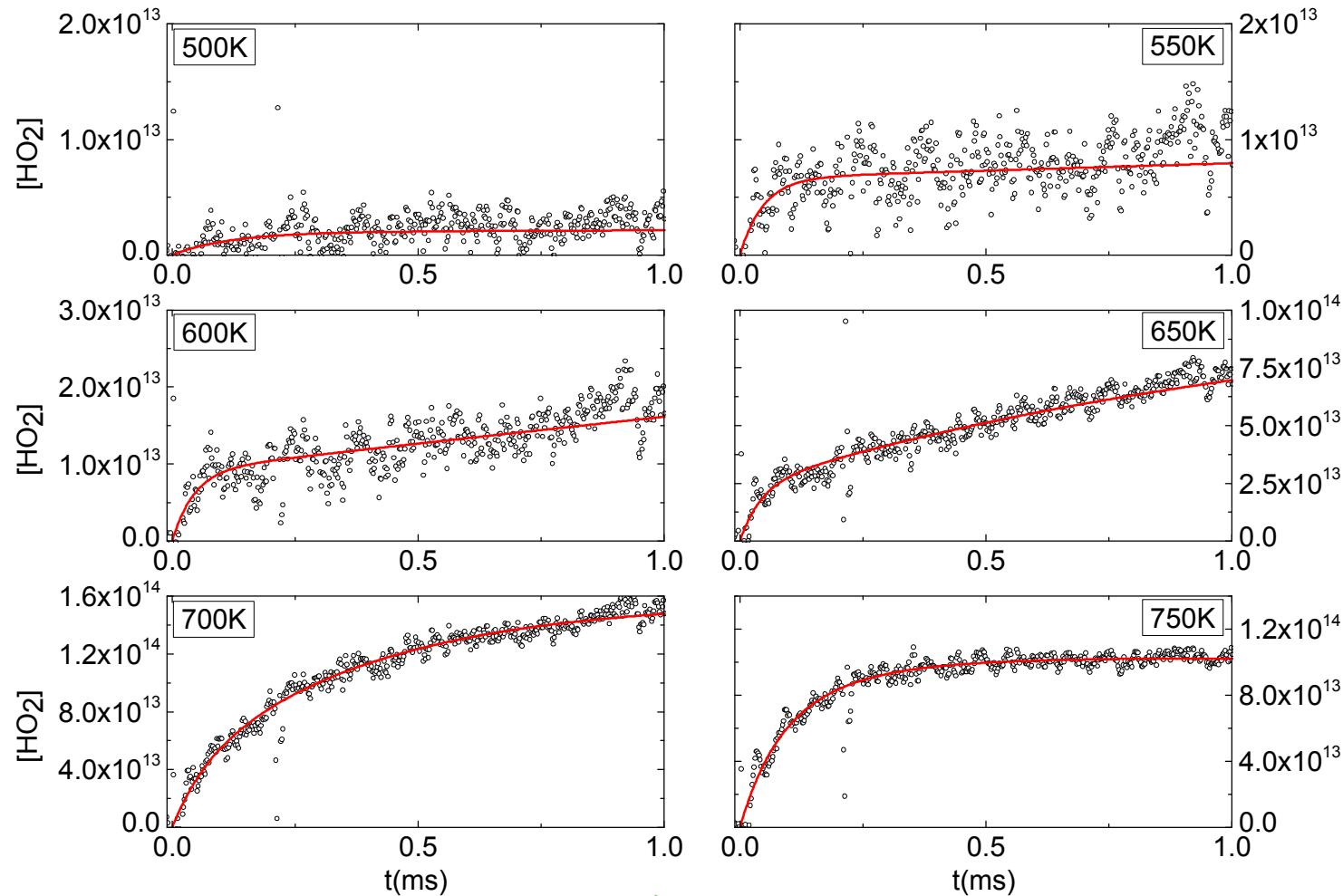
$$\frac{d}{dt} [ROO] = k_y [O_2] [R] - k_{-y} [ROO] - k_z [ROO]$$

$$\frac{d}{dt} [OH] = k_x [O_2] [R] + k_z [ROO] - k_r [OH]^2$$

By integral profile correction

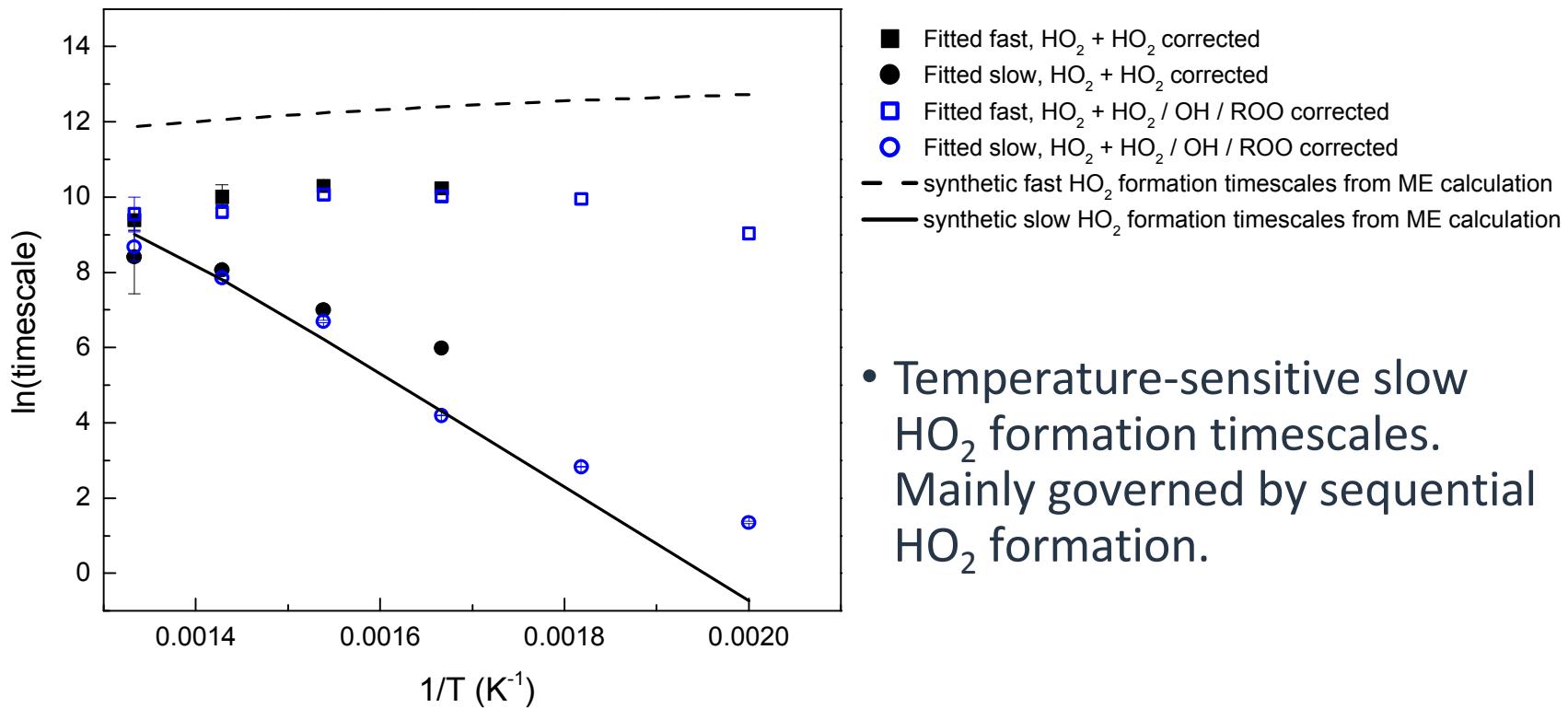
$$OH \text{ yield} = \sum_{i=1}^{\infty} r^i = -\frac{r}{r-1}$$

Fitting Examples (Cyclohexane Oxidation)



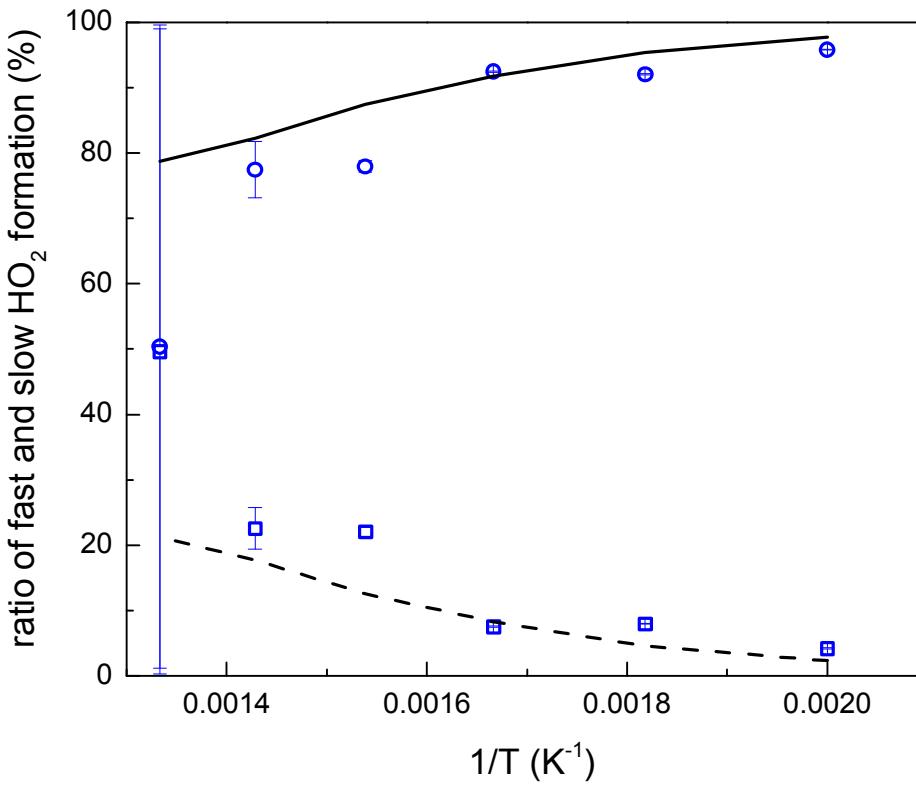
Cyclohexyl + O₂: HO₂ Formation Timescales

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



Cyclohexyl + O₂: Fast/Slow HO₂ Formation Ratio

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

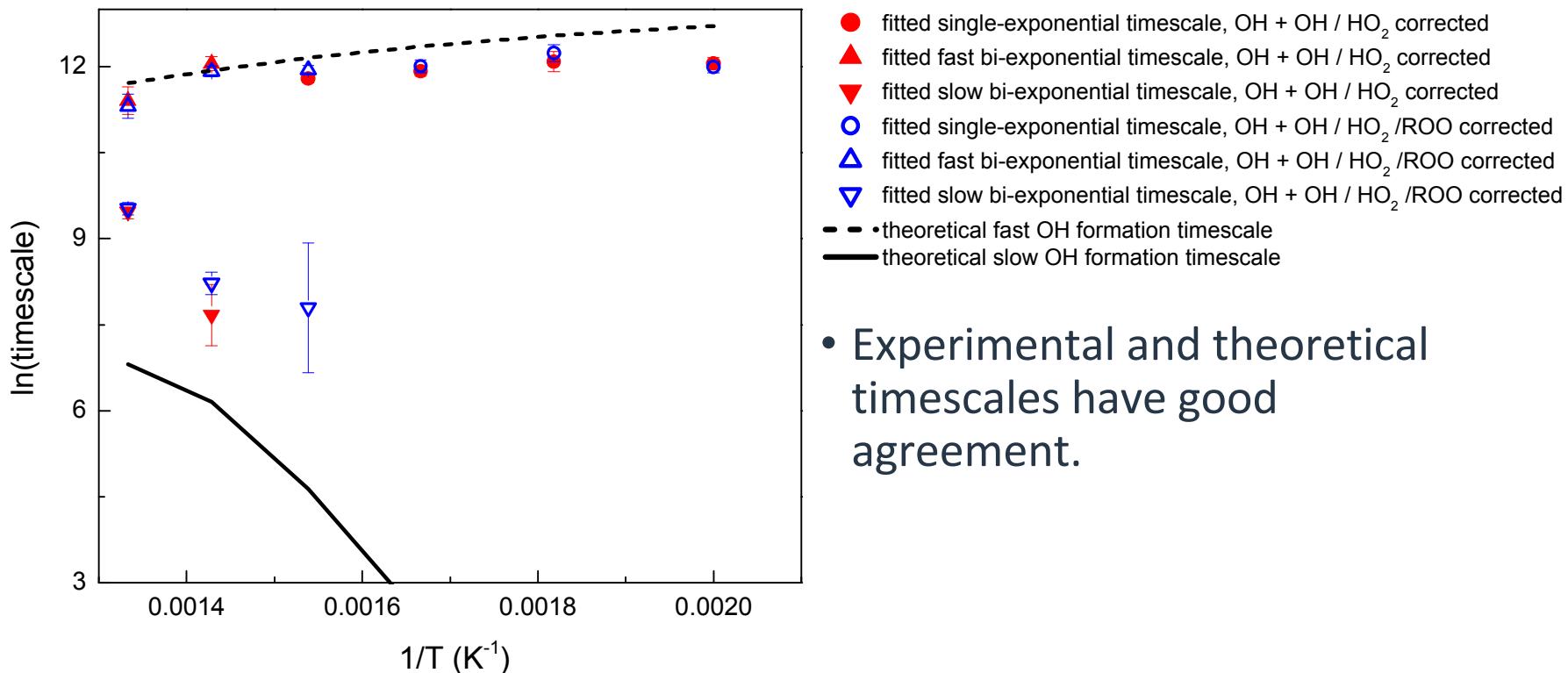


- experimental ratio of fast HO₂ formation.
- experimental ratio of slow HO₂ formation.
- theoretical ratio of fast HO₂ formation.
- theoretical ratio of slow HO₂ formation.

- HO₂ integral profile correction includes HO₂ + HO₂ / 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.

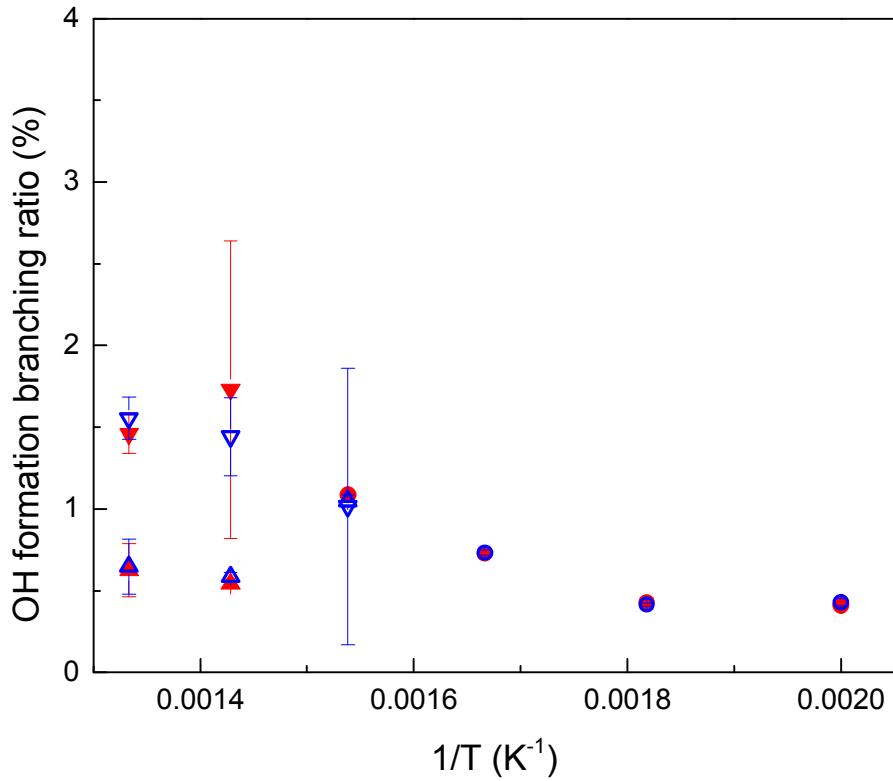
Cyclohexyl + O₂: OH Formation Timescales

$$[OH]_t = A_1(1 - e^{-\mathbf{k}_1 t}) + A_2(1 - e^{-\mathbf{k}_2 t})$$



Cyclohexyl + O₂: OH Formation Yield

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



OH + OH / HO₂ corrected

- experimental single-exponential OH formation branching ratio
- ▲ experimental fast OH formation branching ratio
- ▼ experimental slow OH formation branching ratio

OH + OH / HO₂ / ROO corrected

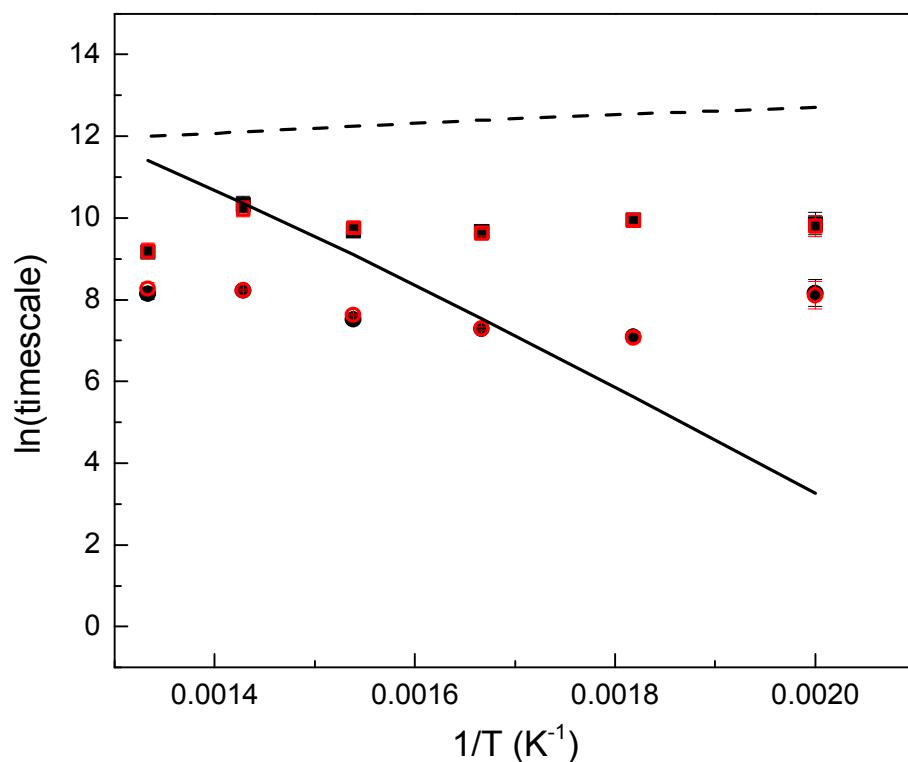
- experimental single-exponential OH formation branching ratio
- △ experimental fast OH formation branching ratio
- ▽ experimental slow OH formation branching ratio

- 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 + O₂: HO₂ Formation Timescales

$$[HO_2]_t = A_1(1 - e^{-\mathbf{k}_1 t}) + A_2(1 - e^{-\mathbf{k}_2 t})$$



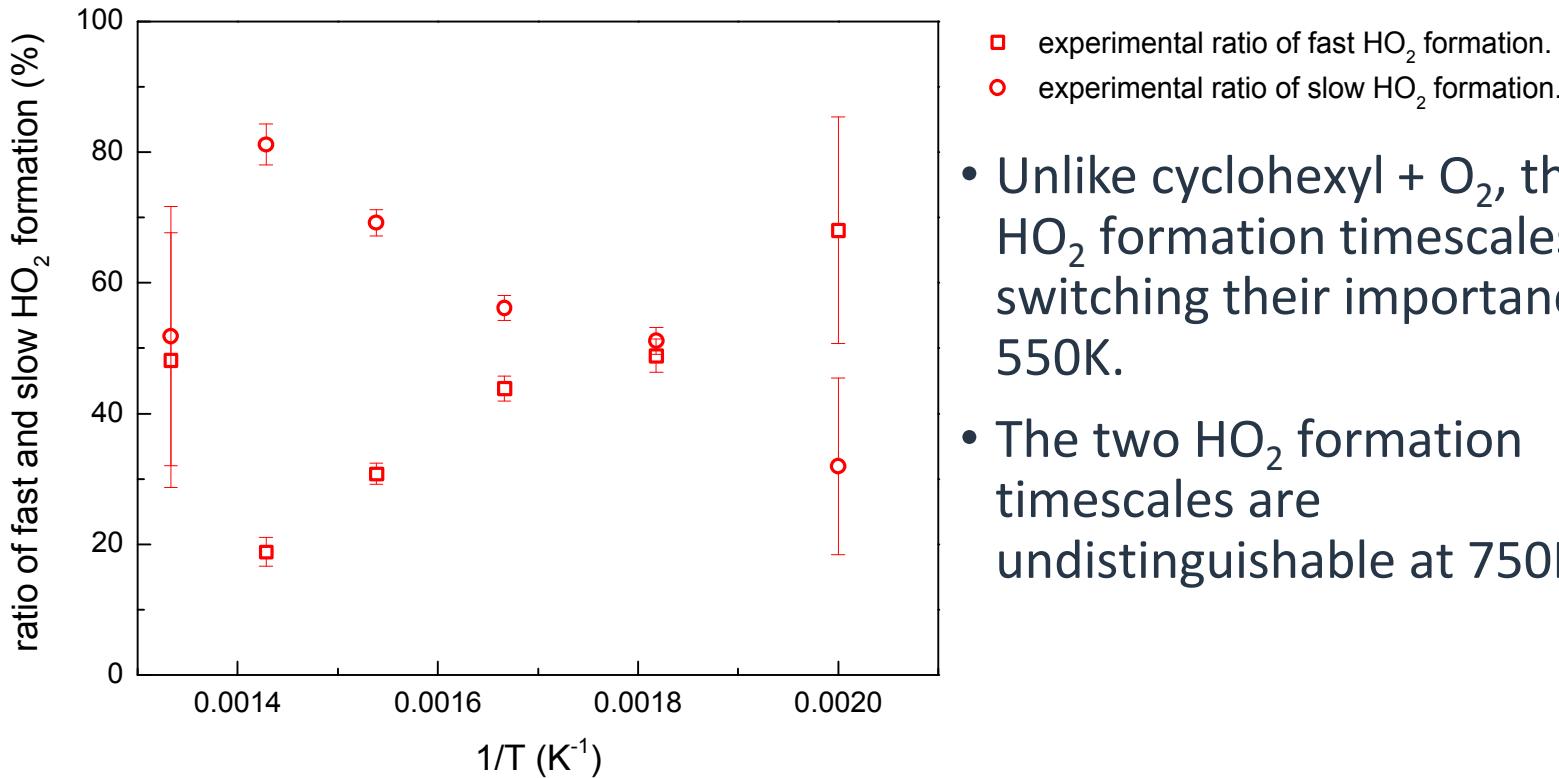
- Fitted fast, HO₂ + HO₂ corrected
- Fitted slow, HO₂ + HO₂ corrected
- Fitted fast, HO₂ + HO₂ / OH corrected
- Fitted slow, HO₂ + HO₂ / OH corrected
- - - synthetic fast HO₂ formation timescales from adjusted ME calculation
- - - synthetic slow HO₂ formation timescales from adjusted ME calculation

- Both fast and slow HO₂ formation timescales are temperature in-sensitive.
- Ineffective PES adjustment* based on cyclohexyl + O₂ or insufficient pathways involved in reduced model.

*PES adjusted from cyclohexyl + O₂ model by +2kcal/mol for ROO and -2kcal/mol for TS.

THP-yl + O₂: Fast/Slow HO₂ Formation Ratio

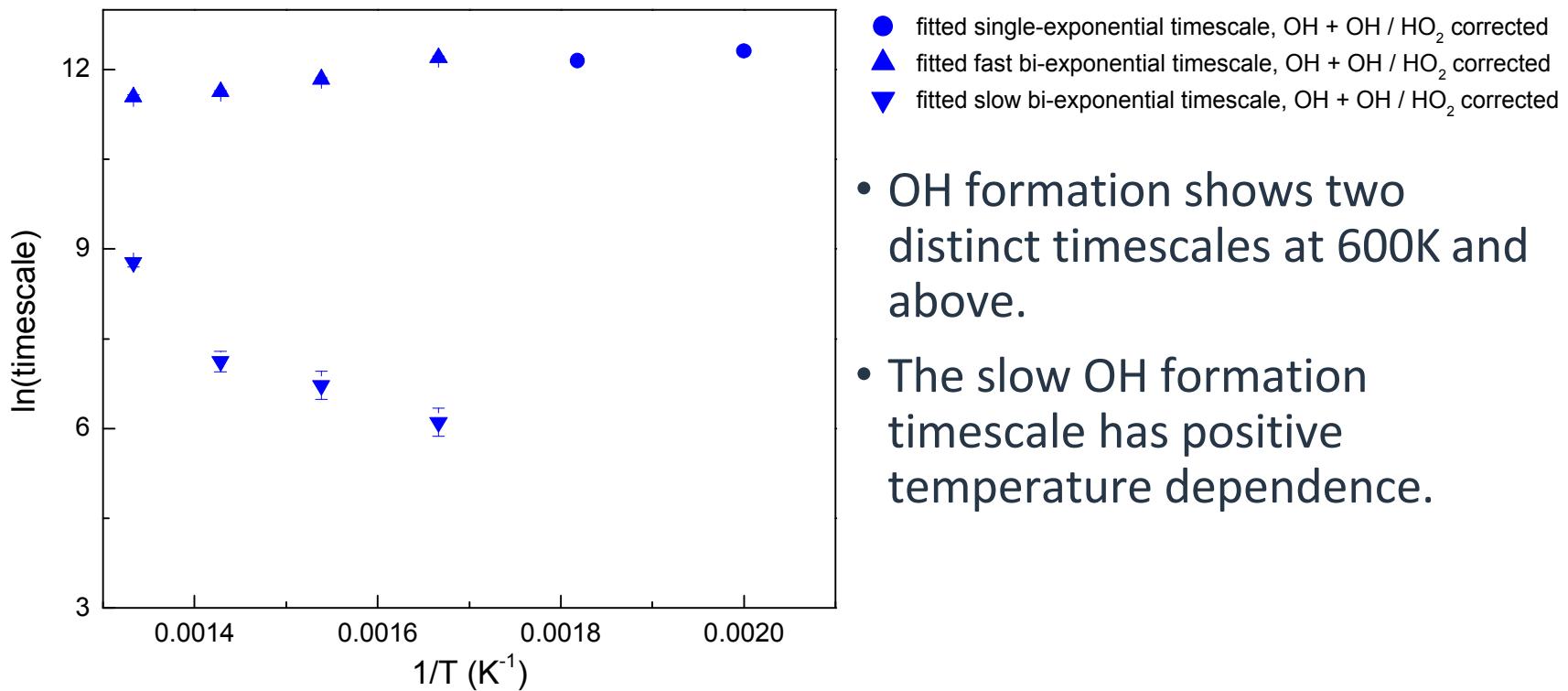
$$[HO_2]_t = \mathbf{A_1}(1 - e^{-k_1 t}) + \mathbf{A_2}(1 - e^{-k_2 t})$$



*PES adjusted from cyclohexyl + O₂ model by +2kcal/mol for ROO and -2kcal/mol for TS.

THP-yl + O₂: OH Formation Timescales

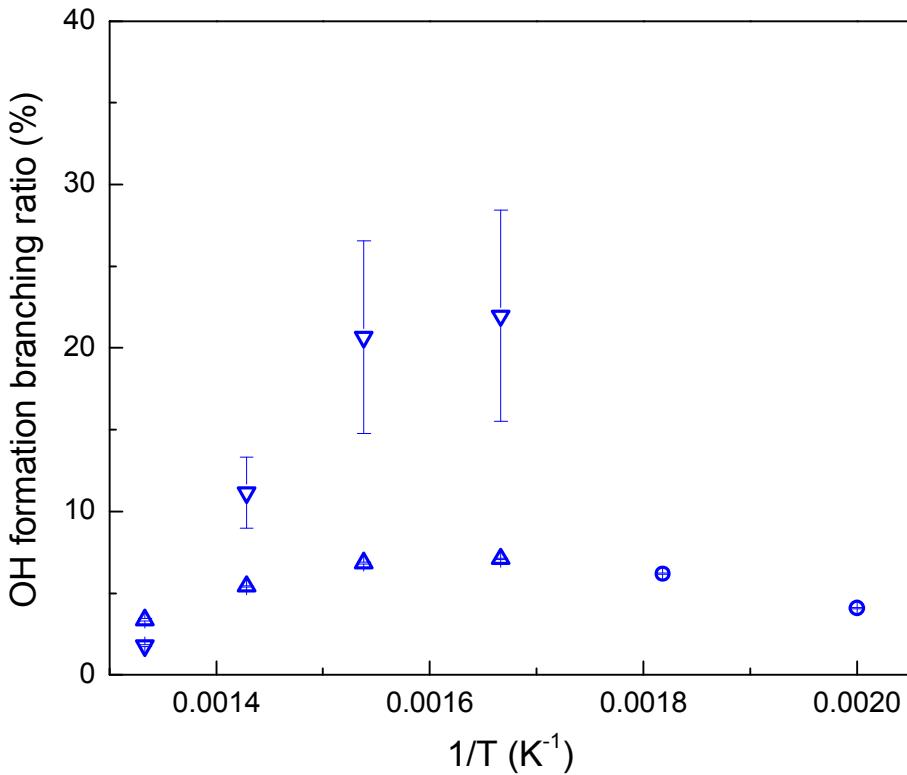
$$[OH]_t = A_1(1 - e^{-\mathbf{k}_1 t}) + A_2(1 - e^{-\mathbf{k}_2 t})$$



*PES adjusted from cyclohexyl + O₂ model by +2kcal/mol for ROO and -2kcal/model for TS.

THP-yl + O₂: OH Formation Yield

$$[OH]_t = \mathbf{A}_1(1 - e^{-k_1 t}) + \mathbf{A}_2(1 - e^{-k_2 t})$$



OH + OH / HO₂ corrected

- experimental single-exponential OH formation branching ratio
- experimental fast OH formation branching ratio
- experimental slow OH formation branching ratio

- 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 + O₂.

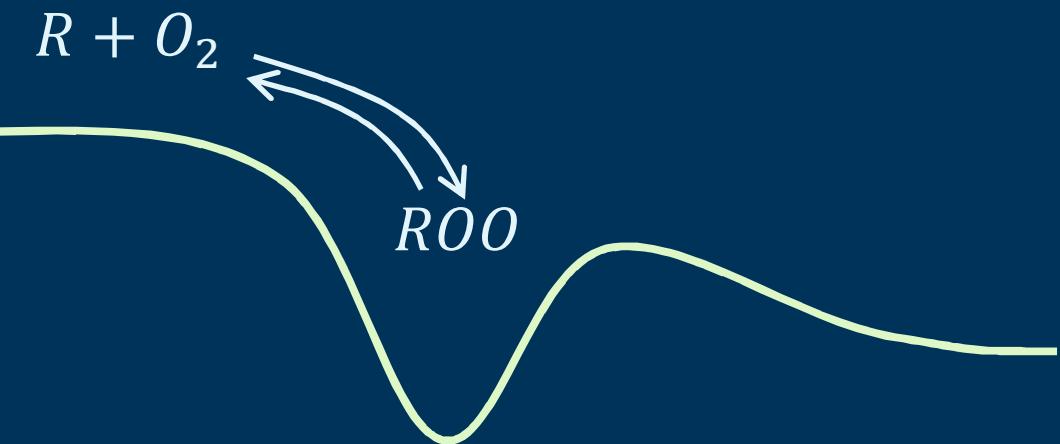
$$OH\ yield = \frac{A_1\ or\ A_2}{[Cl]_0} = \sum_{i=1}^{\infty} r^i = -\frac{r}{r-1}$$

Conclusions

- Quantitative HO₂ and OH formation timescales from Cl-initiated cyclohexane and tetrahydropyran oxidation have been measured by our IR absorption flow system.

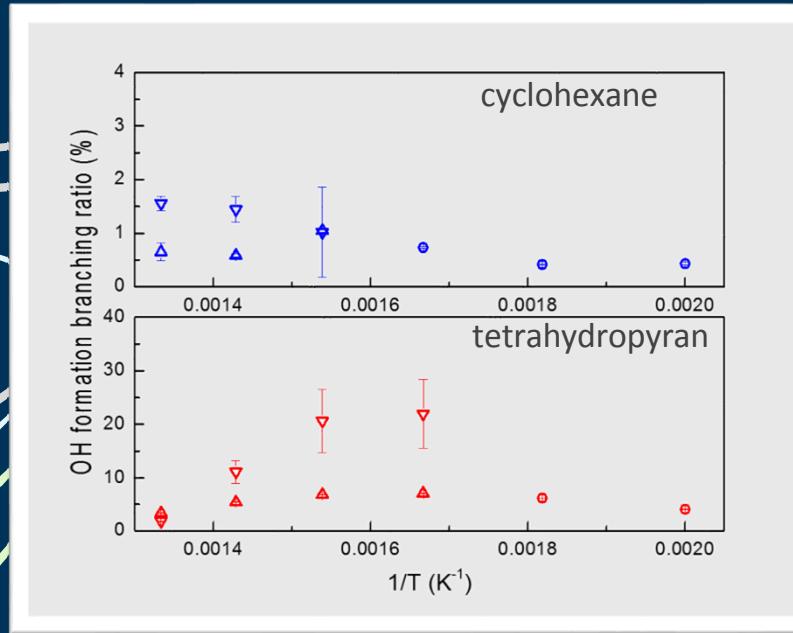
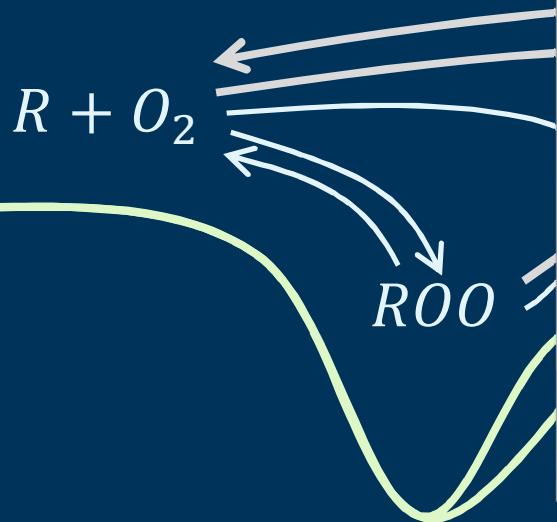


Conclusions



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

Conclusions

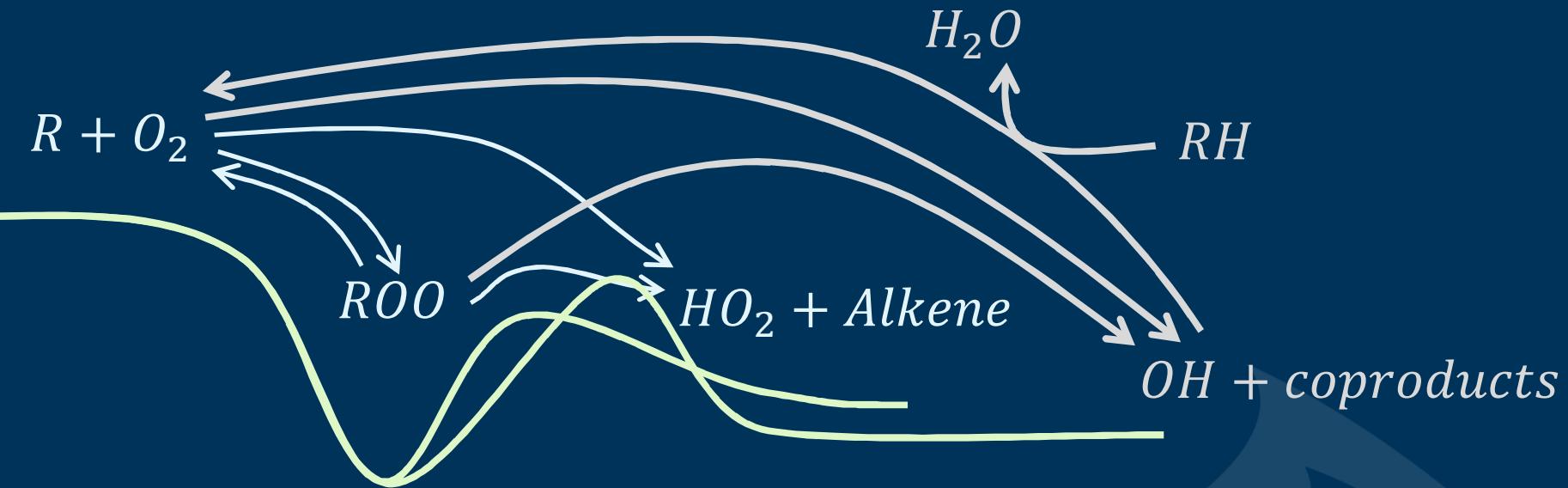


RH

$H + coproducts$

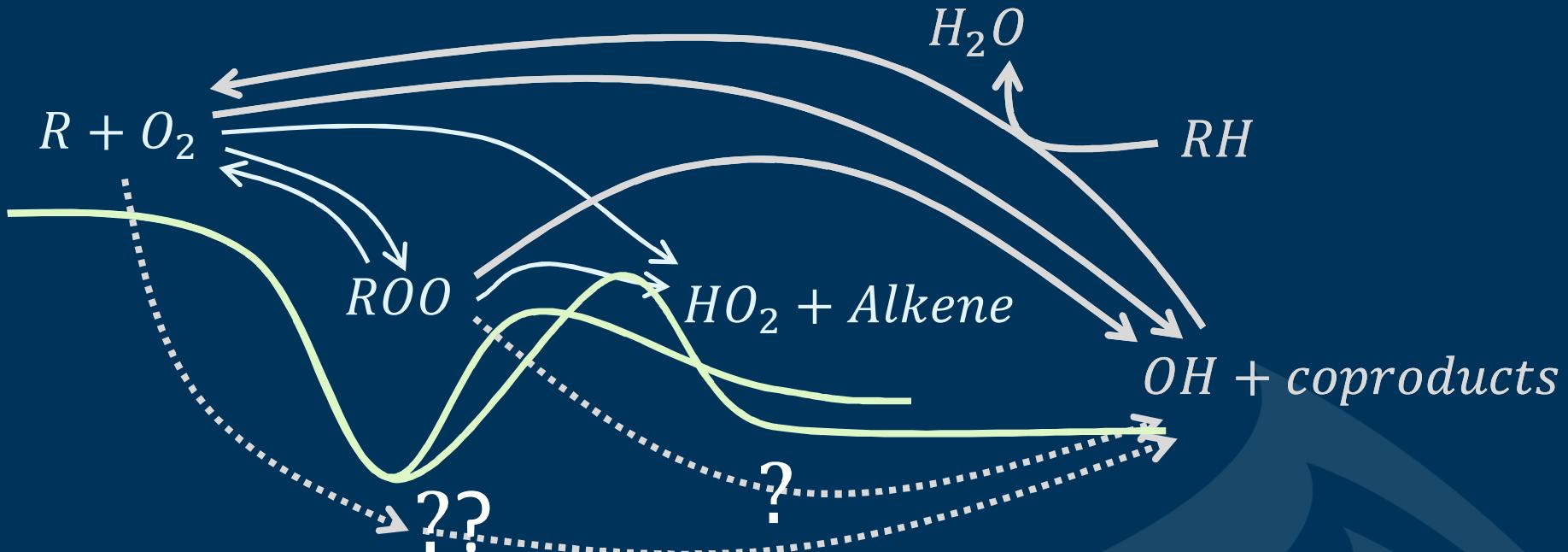
- Major differences of THP oxidation have been observed by measuring key intermediates, and compared with cyclohexane oxidation:
 - Slow (sequential?) HO_2 formation timescales is temperature-insensitive.
 - Contribution of slow (sequential?) HO_2 production is high at lower temperatures and suppressed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

Conclusions



- 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.

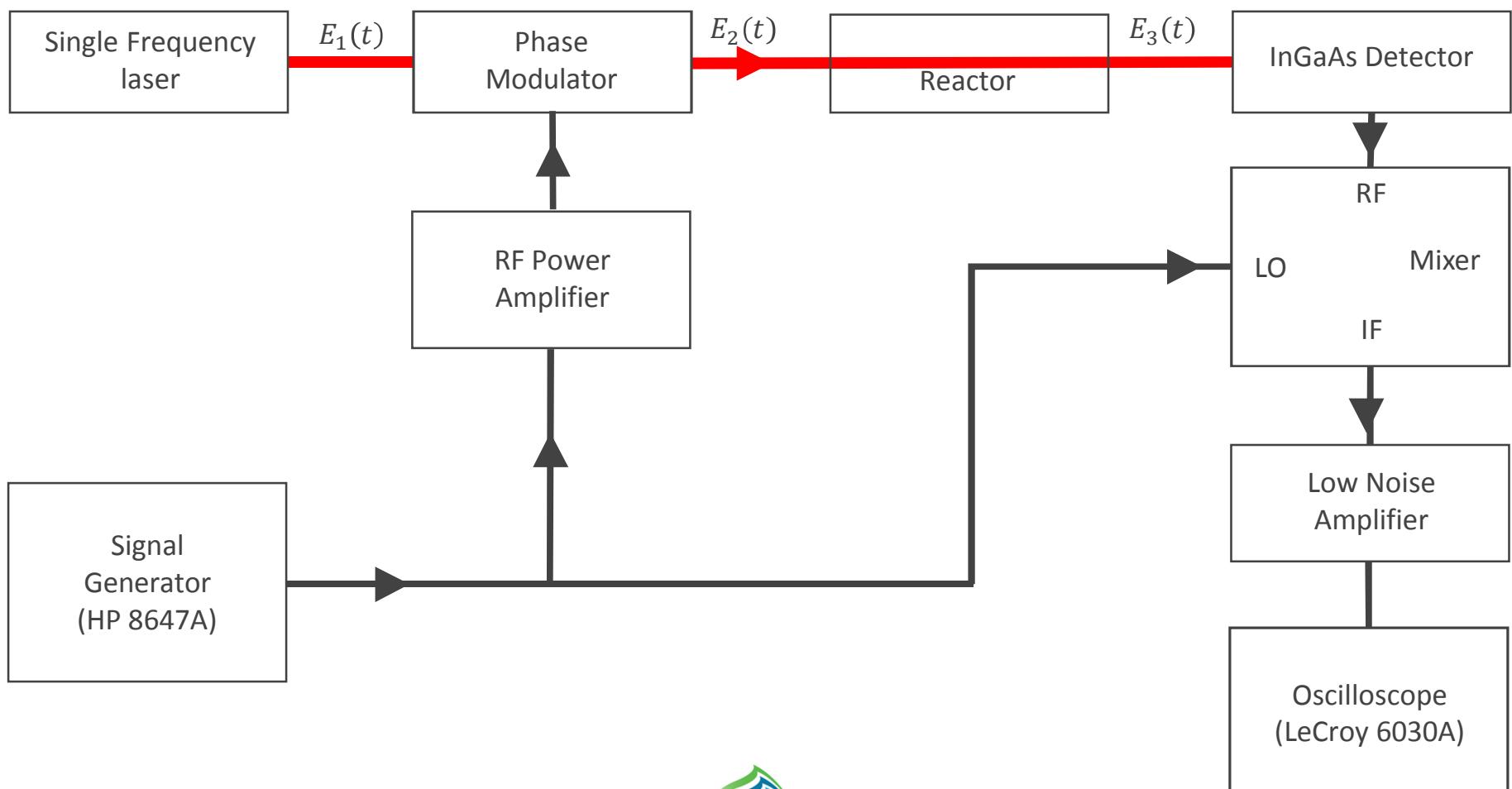
Acknowledgement

- 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!!!

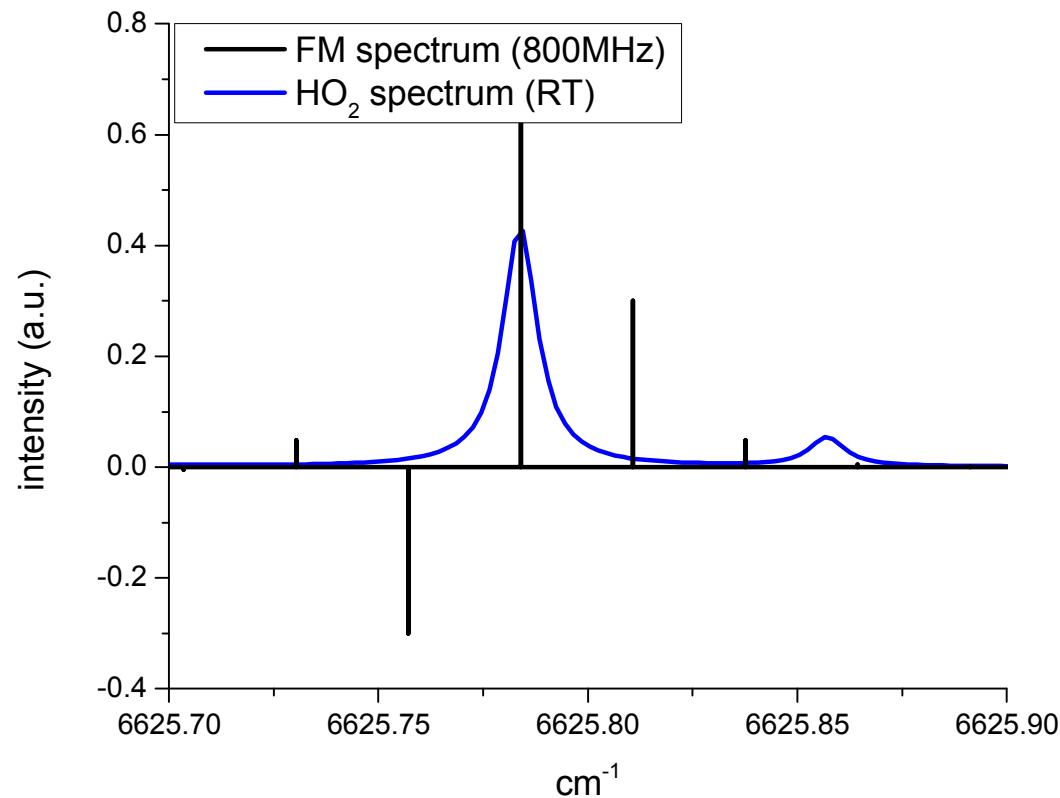


Frequency Modulation – Basic Layout

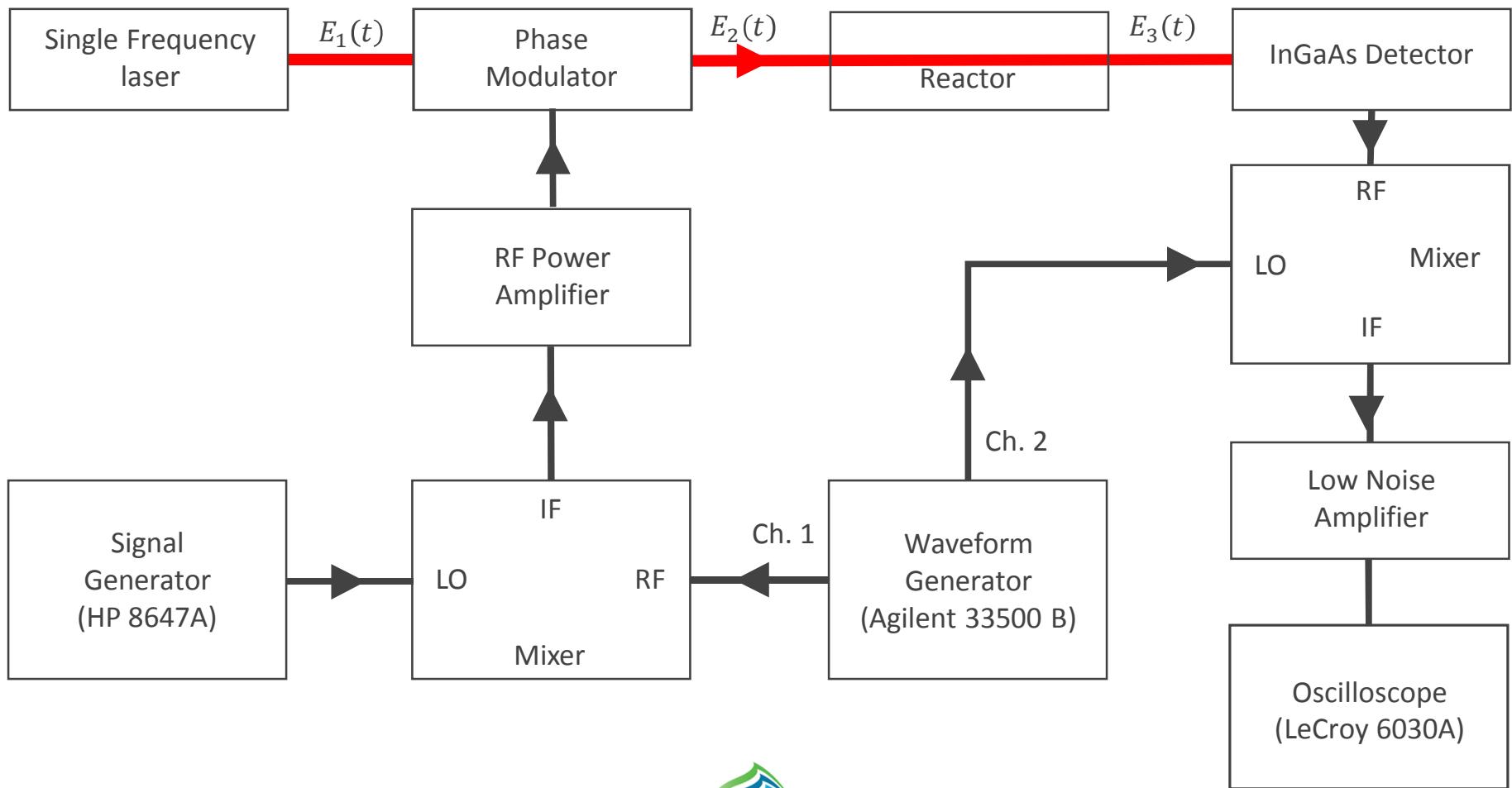


Frequency Modulation - Spectroscopy

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



Two-Tone Frequency Modulation – Basic Layout



Two-Tone Frequency Modulation – Spectroscopy

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

