Acetonylperoxy and hydroperoxy kinetics from the perspective from the product hydroxyl radical

Kristen Zuraski, Frank A. F. Winiberg, Carl J. Percival, Aileen Hui, Fred J. Grieman, and Stanley P. Sander

NASA POSTDOCTORAL PROGRAM

Jet Propulsion Laboratory
California Institute of Technology

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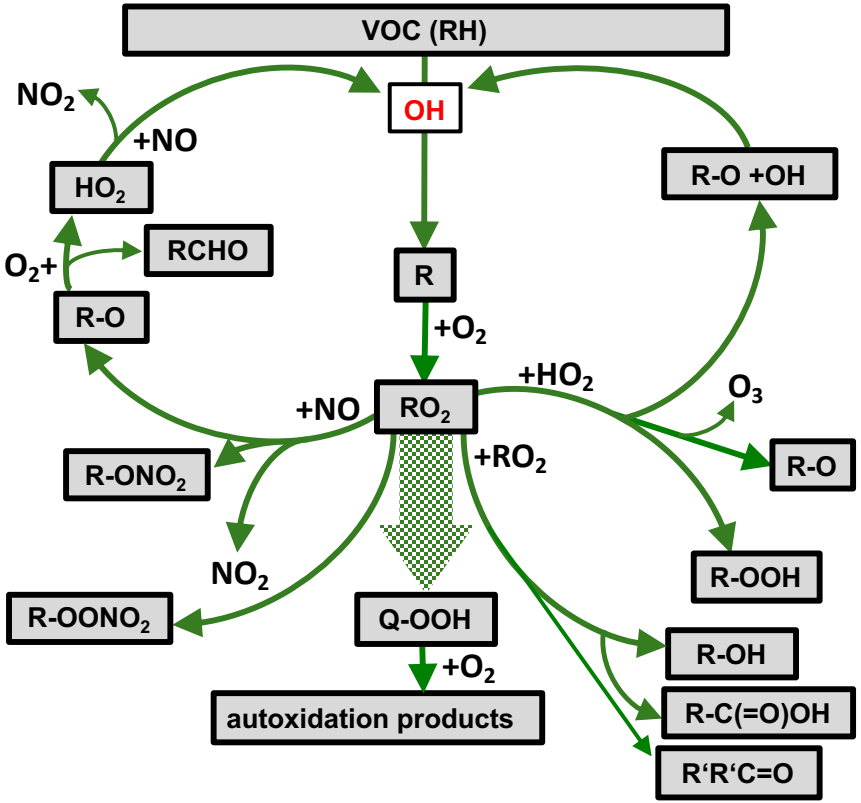
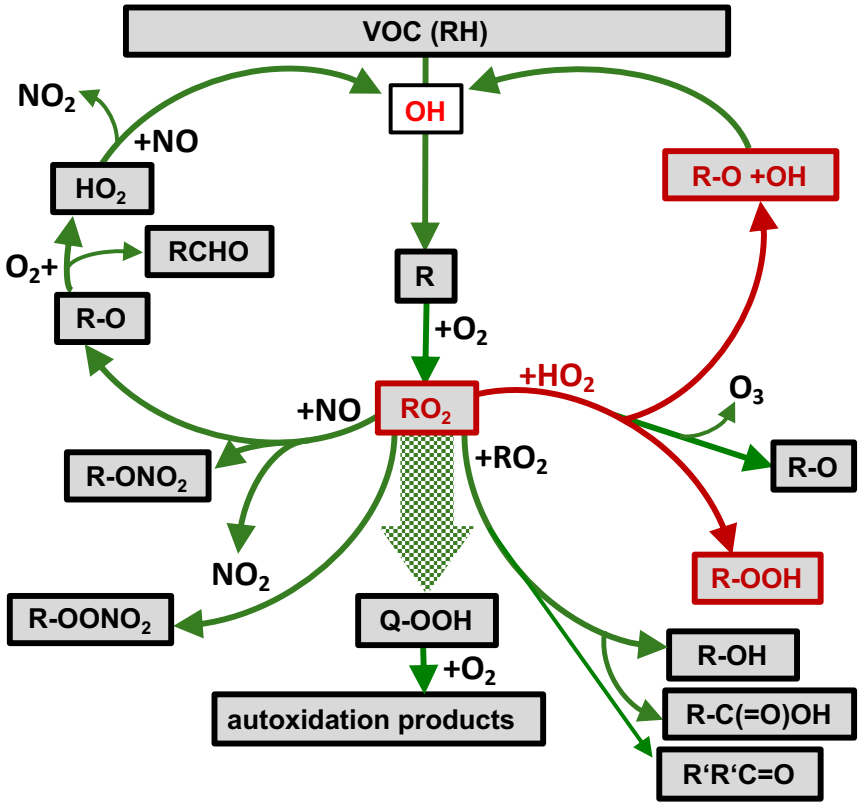
Peroxy Radicals in the Troposphere

High NO_x



Low NO_x

Peroxy Radicals in the Troposphere

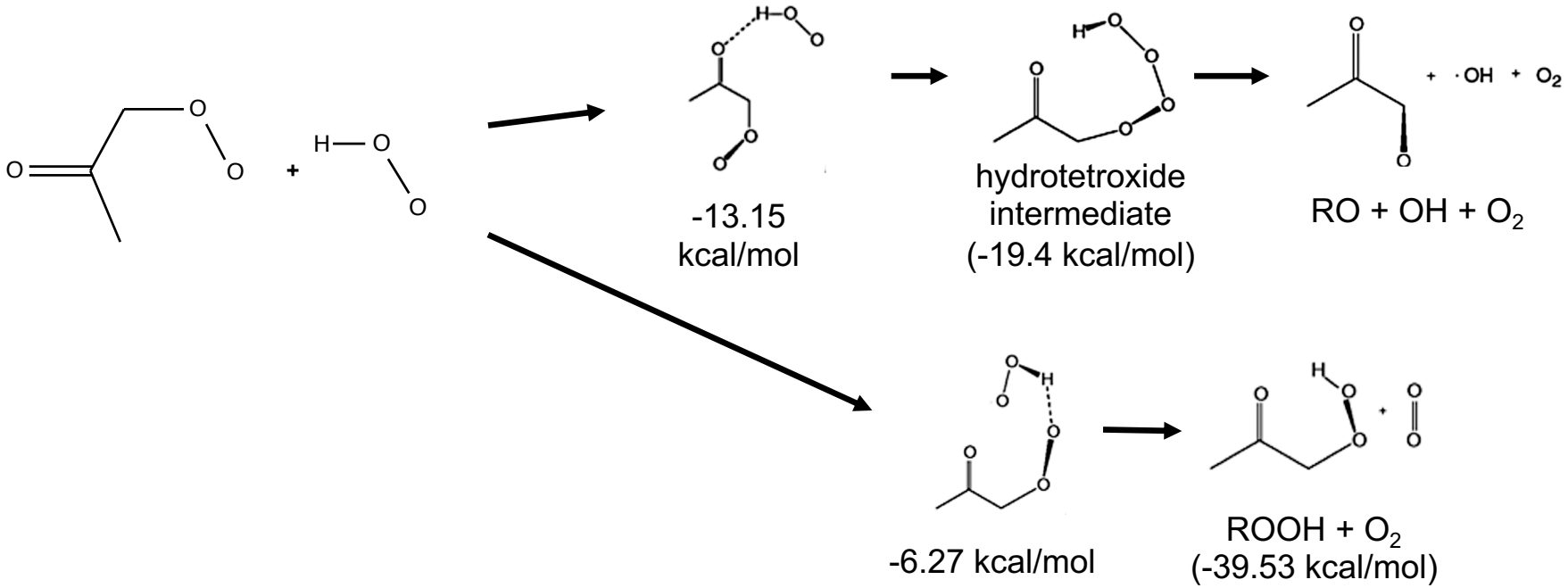


Low NO_x

RH = Acetone, $CH_3C(O)CH_3$

RO_2 = acetonylperoxy $CH_3C(O)CH_2O_2$

Reaction Between Acetonylperoxy and HO_2 - Theory



Level of theory: CBS-QB3 and Master equation calculations

A. S. Hasson et al, *J. Photochem. Photobio. A: Chemistry* 176 (2005) 218.

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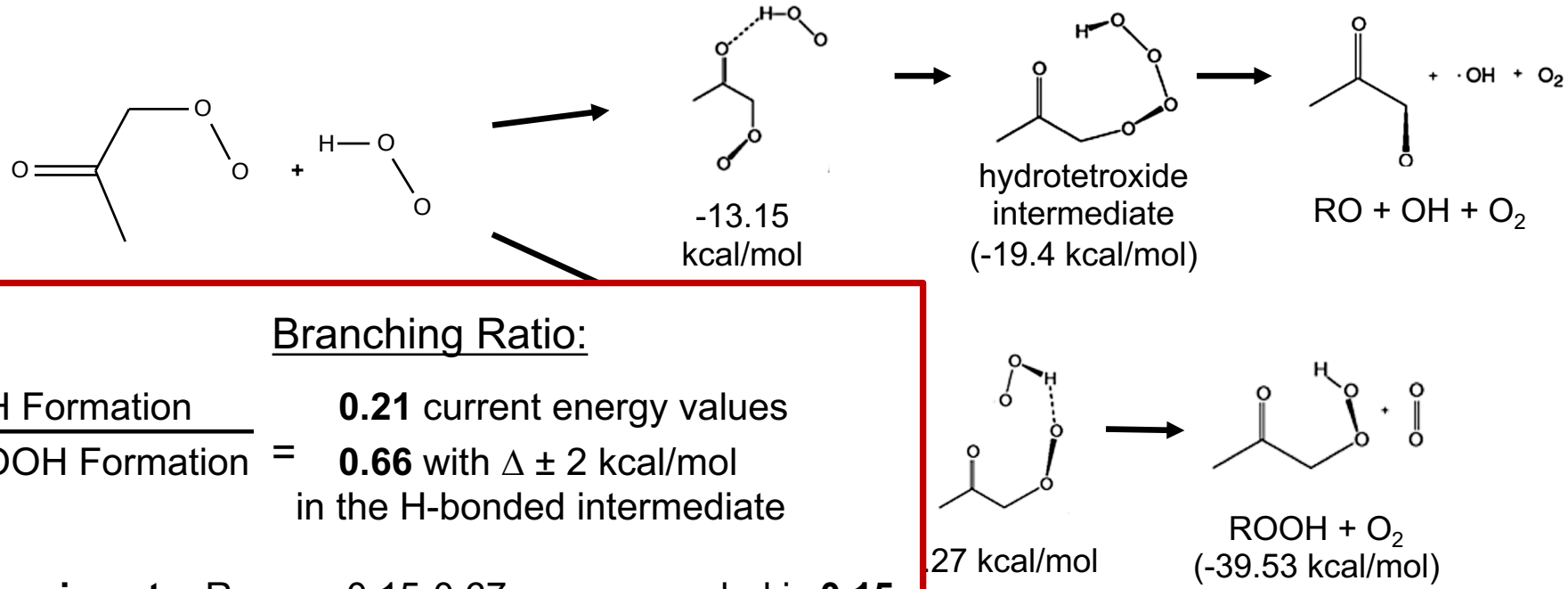


Branching Ratio:

$$\frac{\text{OH Formation}}{\text{ROOH Formation}} = \begin{array}{l} \textbf{0.21} \text{ current energy values} \\ \textbf{0.66} \text{ with } \Delta \pm 2 \text{ kcal/mol} \\ \text{in the H-bonded intermediate} \end{array}$$

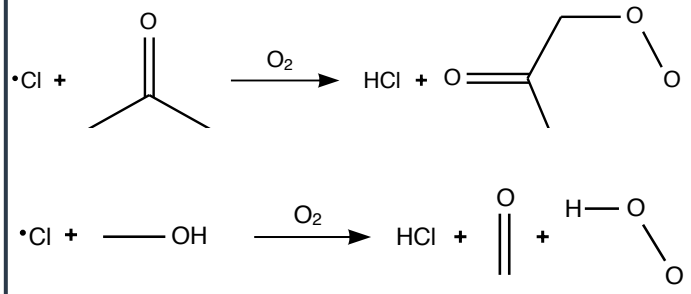
Experiments: Ranges 0.15-0.67, recommended is **0.15**

Level of theory: CBS-QB3 and Master equation calculations

A. S. Hasson et al, *J. Photochem. Photobio. A: Chemistry* 176 (2005) 218.

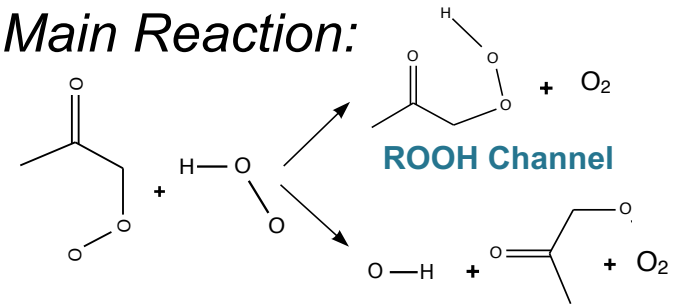
Experiments with the Infrared Kinetics Spectroscopy Instrument

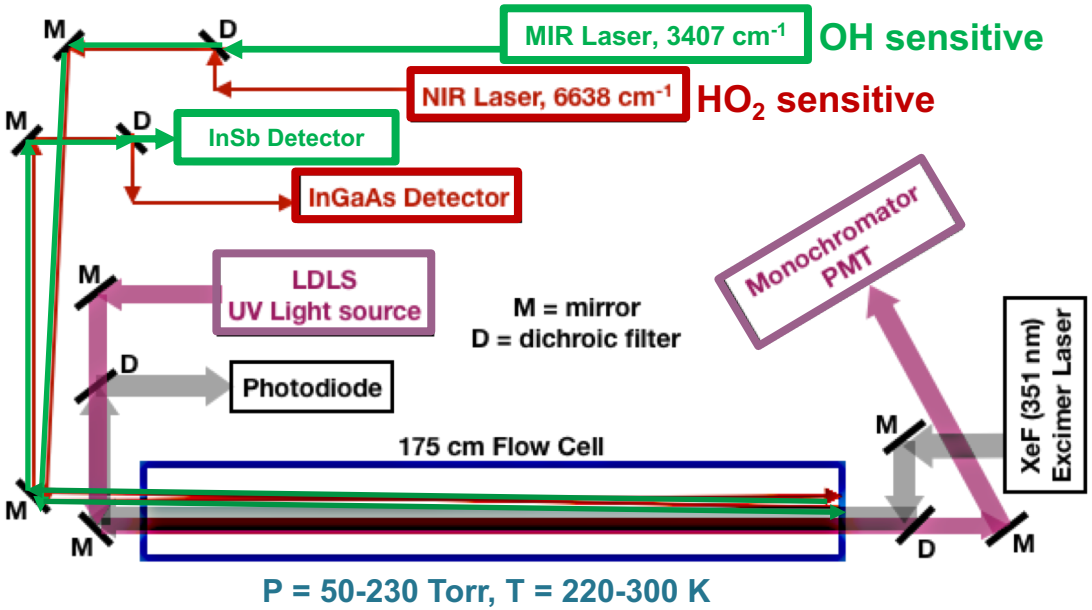
Radical Generation:



$[HO_2]_0$ > [Acetonylperoxy]$_0$

Main Reaction:





Experiments with the Infrared Kinetics Spectroscopy Instrument

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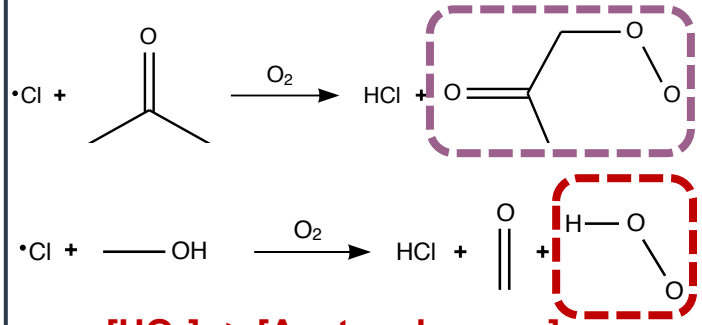

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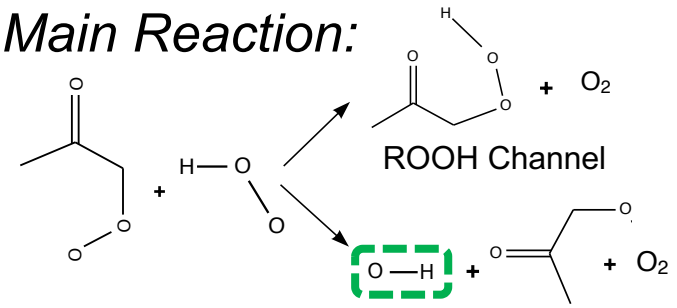
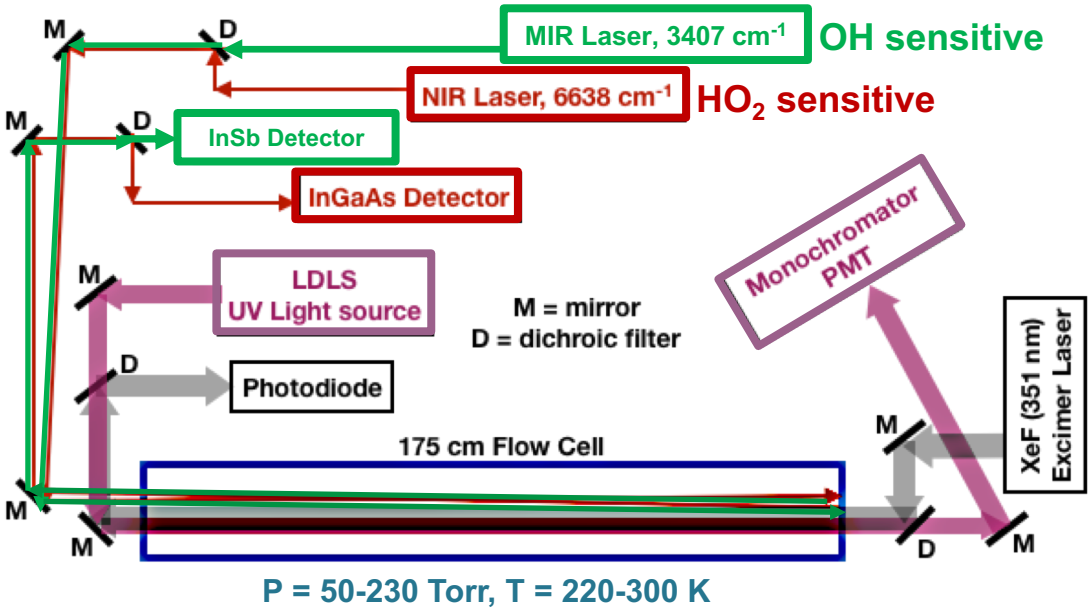




Simultaneous detection of three species

Model Mechanism – *35 total reactions*

$$CH_3C(O)CH_2O_2 + HO_2 \rightarrow CH_3C(O)CH_2O + OH + O_2$$

$$\rightarrow CH_3C(O)CH_2OOH + O_2$$

$$2CH_3C(O)CH_2O_2 \rightarrow CH_3COCH_3OH + CH_3COCHO + O_2$$

$$\rightarrow 2CH_3C(O)CH_2O + O_2 \rightarrow\rightarrow\rightarrow R'O_2$$

$$2HO_2 \rightarrow H_2O_2 + O_2$$

Model Mechanism – *35 total reactions*

$CH_3C(O)CH_2O_2 + HO_2 \rightarrow CH_3C(O)CH_2O + OH + O_2$ k_1 x BR

$\rightarrow CH_3C(O)CH_2OOH + O_2$ k_1 x (1-BR)

$2CH_3C(O)CH_2O_2 \rightarrow CH_3COCH_3OH + CH_3COCHO + O_2$

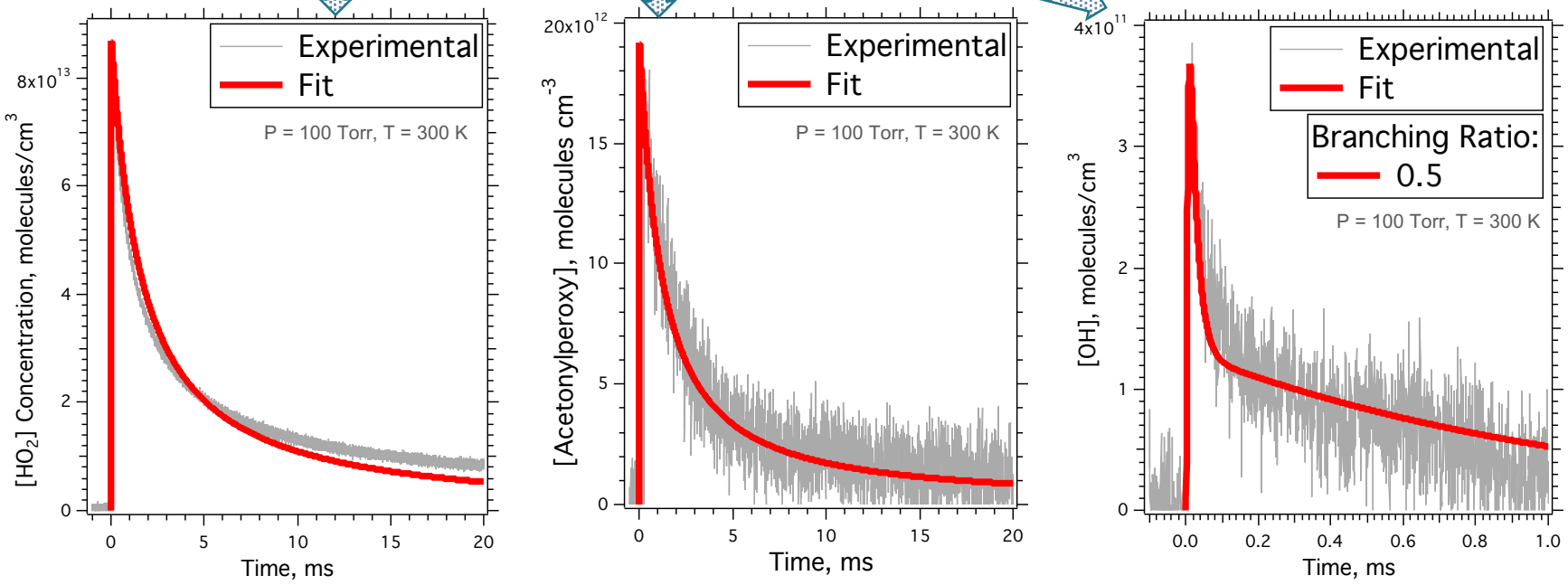
$\rightarrow 2CH_3C(O)CH_2O + O_2 \rightarrow\rightarrow\rightarrow R'O_2$

$2HO_2 \rightarrow H_2O_2 + O_2$

Fitting for k_1 and branching ratio (BR) for k_1

Signal From Three Species

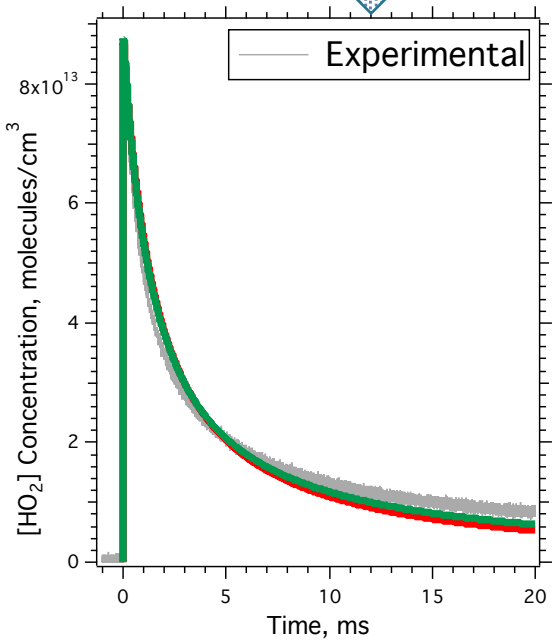
HO_2 + Acetonylperoxy → OH + coproduct, ROOH + O_2

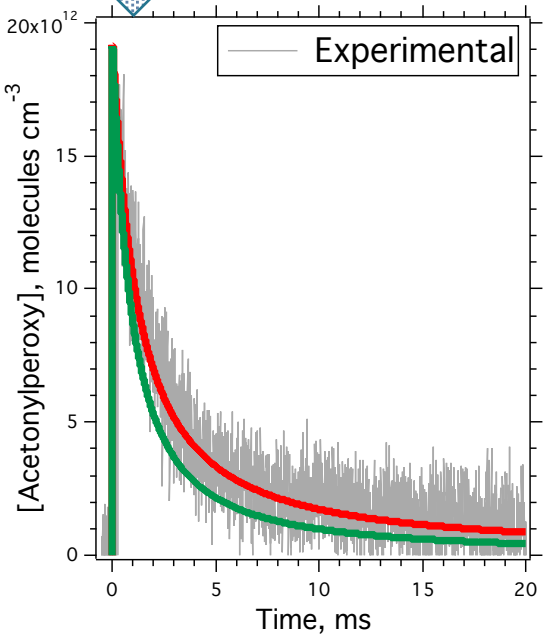


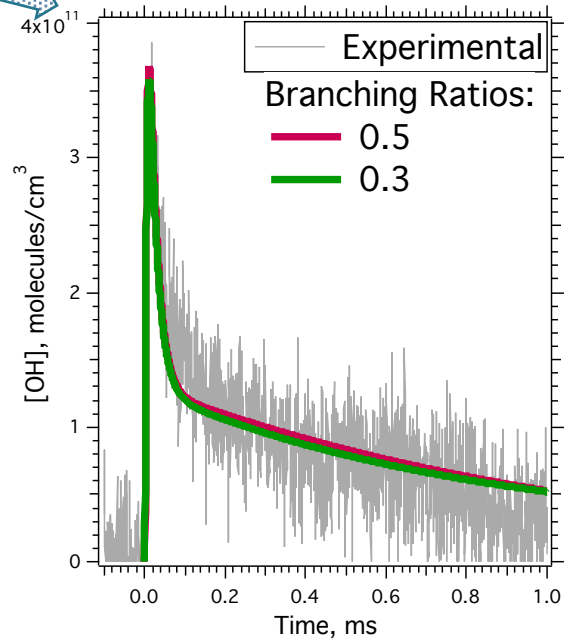
Rate = 6.3 x 10^{-12} cm^3 $molecule^{-1}$ s^{-1}, OH Channel Branching Ratio = 0.5

Sensitivity of Fits to the Rate of HO_2 + Acetonylperoxy

HO_2 + Acetonylperoxy ⟶ OH + coproduct, ROOH + O_2

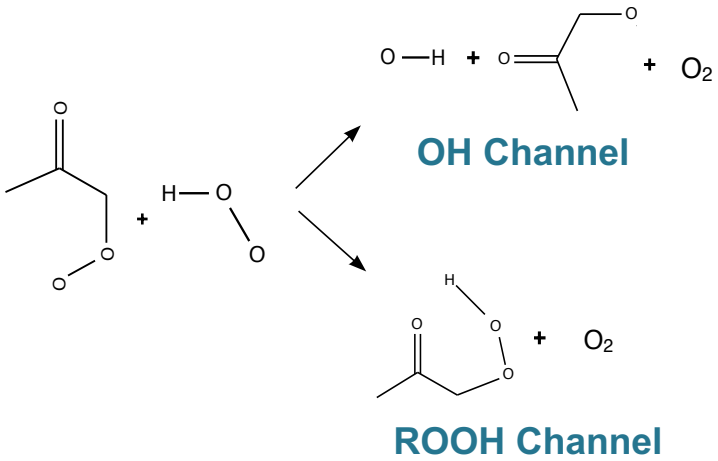


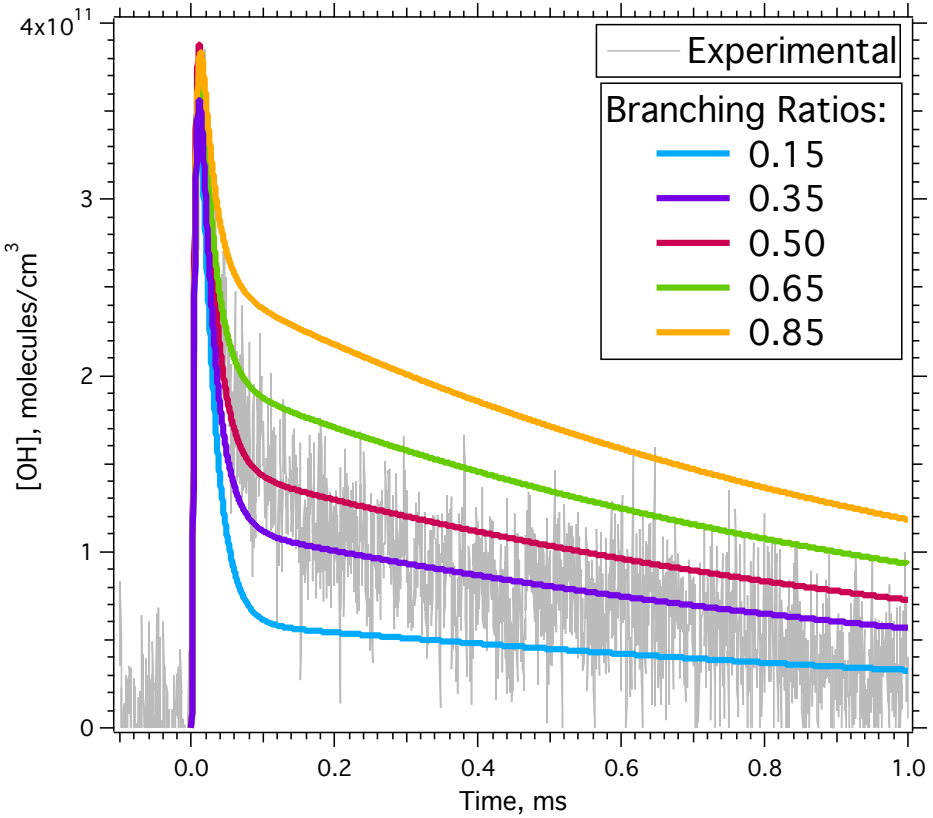




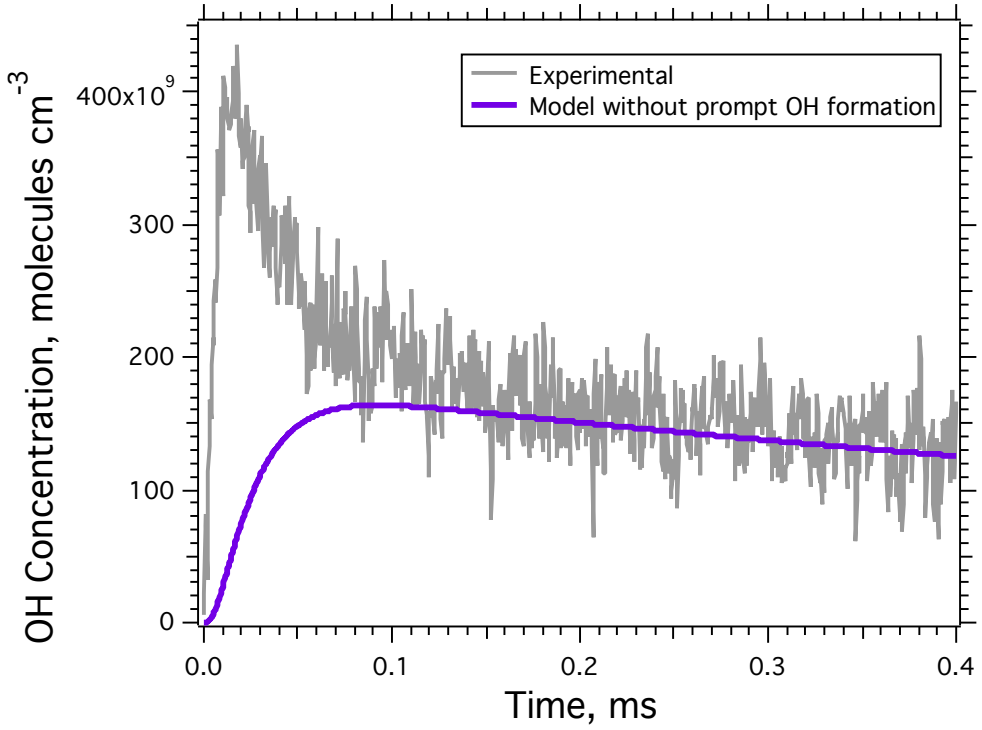
Rate, cm^3 $molecule^{-1}$ s^{-1} = 6.3 x 10^{-12} 9.0 x 10^{-12}

Sensitivity of Fits to the Branching Ratio





Additional Chemistry – First Observation of OH Formation from Alkyl + O_2?



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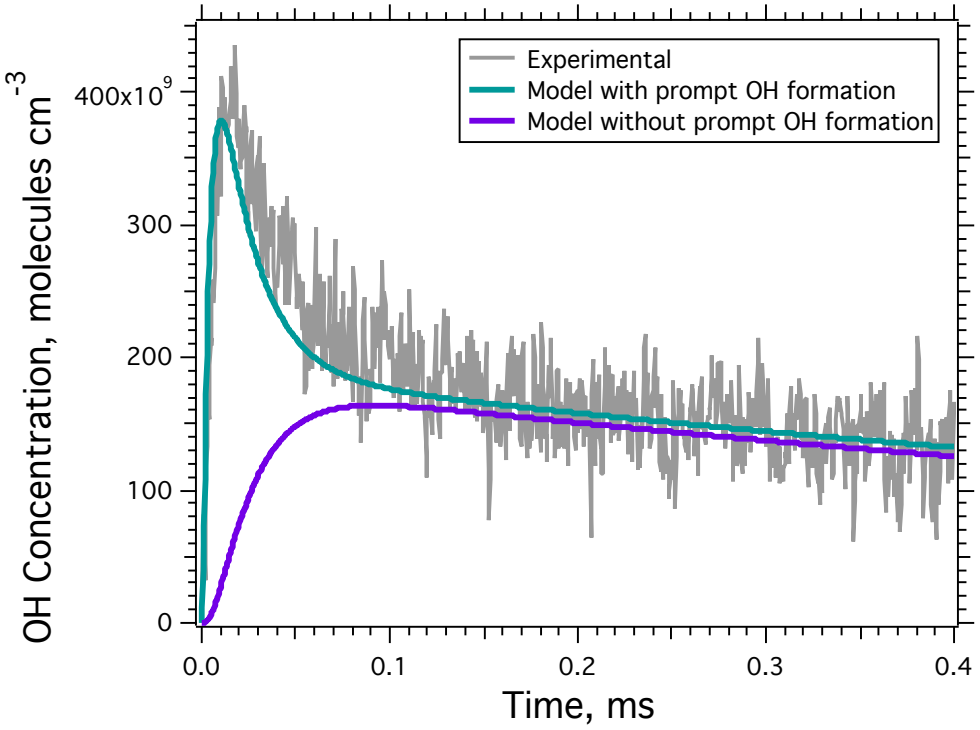


Sources?

$$Cl + HO_2 \rightarrow OH + ClO$$

$$CH_3C(O)CH_2\bullet + O_2 \rightarrow CH_3C(O)CH_2O_2\bullet$$
$$\rightarrow OH + \text{coproducts}$$

1-2%

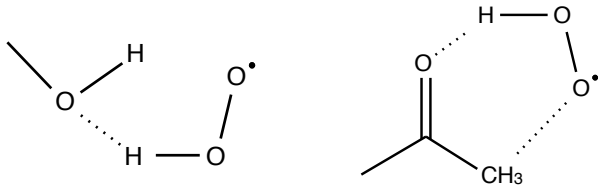
G Kovács et al, *Phys. Chem. Chem. Phys.,* 9 (**2007**) 4154.
Currently working with H. Kjaergaard on mechanism and kinetics.

Details in Early Analysis – HO_2 Decay and the Chaperone Effect

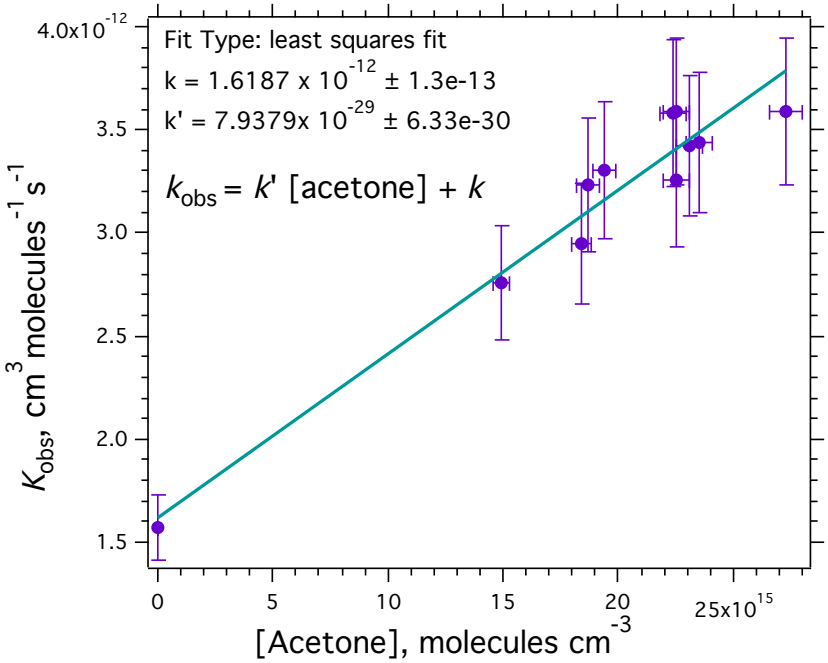
Component of the HO_2 decay from

$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2$$

This rate can be enhanced from hydrogen bond complexation of HO_2 with acetone and/or methanol



Experiments to isolate this effect:
Keep all concentrations constant except [acetone]



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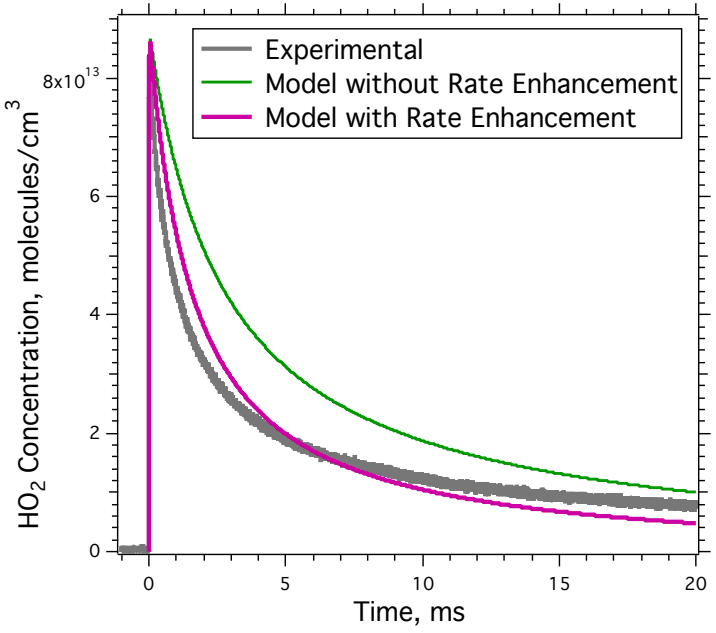

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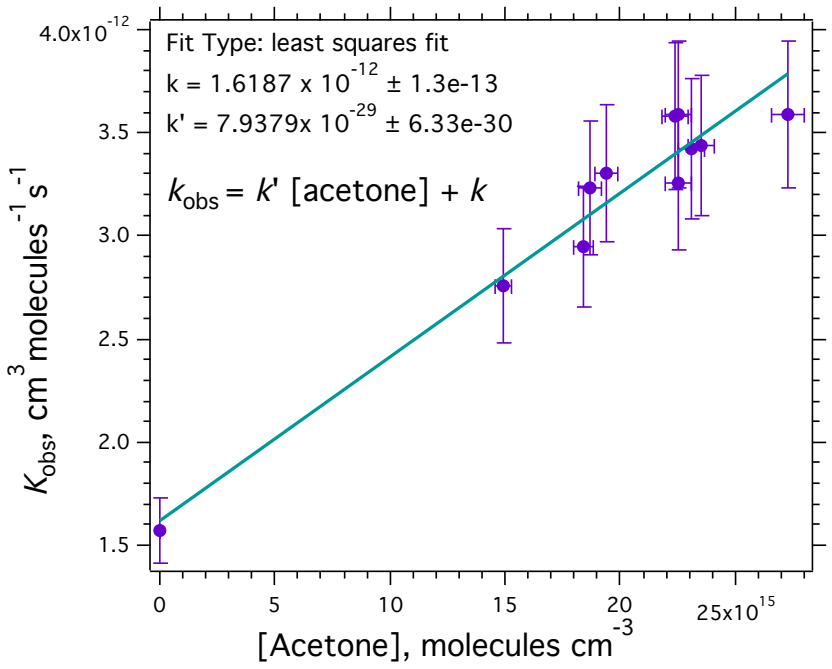
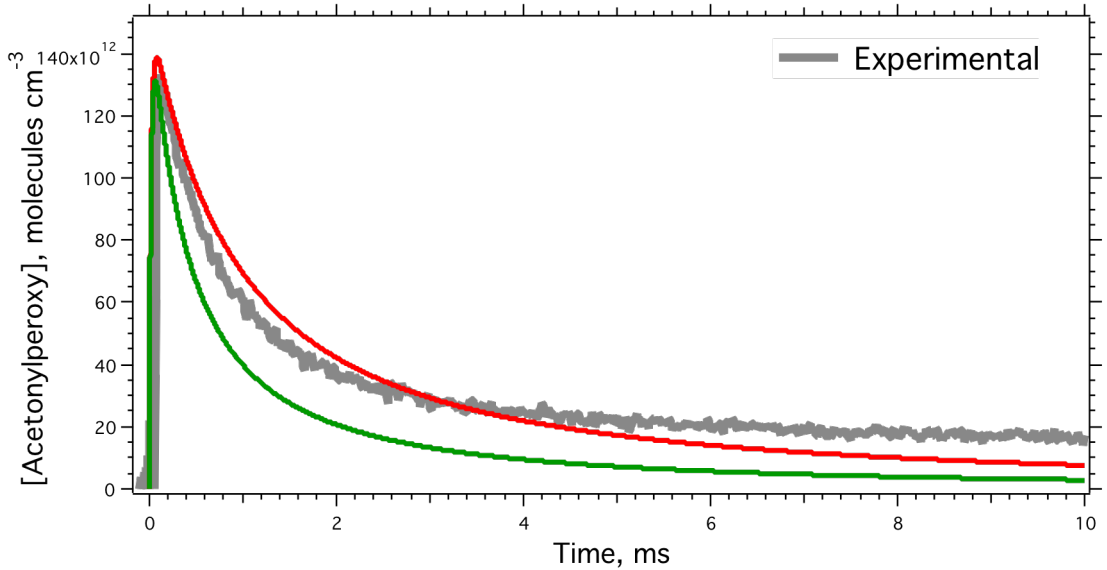


A Look at Acetonylperoxy Self-Reaction

$$2\ CH_3C(O)CH_2O_2 \rightarrow CH_3COCH_3OH + CH_3COCHO + O_2$$

$$\rightarrow 2\ CH_3C(O)CH_2O + O_2$$

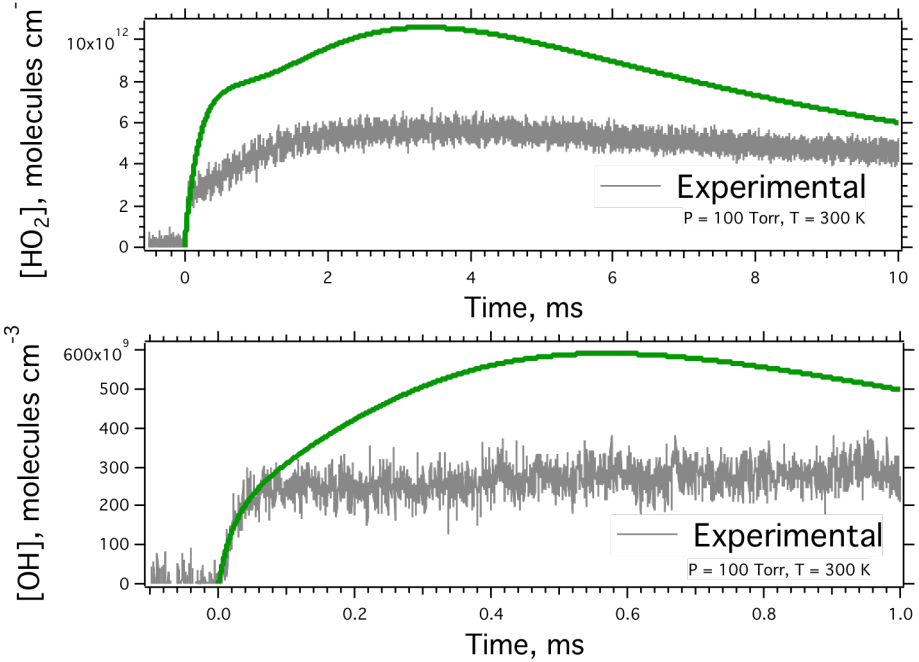


Rate, $cm^3\ molecule^{-1}\ s^{-1}$ = 4.0 x 10^{-12} 8.0 x 10^{-12}

Side Chemistry from Acetonylperoxy Self-Reaction

$$2CH_3C(O)CH_2O_2 \rightarrow CH_3COCH_3OH + CH_3COCHO + O_2$$

$$\rightarrow 2CH_3C(O)CH_2O + O_2$$



Side Chemistry from Acetonylperoxy Self-Reaction

$$2CH_3C(O)CH_2O_2 \rightarrow CH_3COCH_3OH + CH_3COCHO + O_2 \quad \textbf{(BR)}$$

$$\rightarrow 2CH_3C(O)CH_2O + O_2 \quad \textbf{(1-BR)}$$

rapid

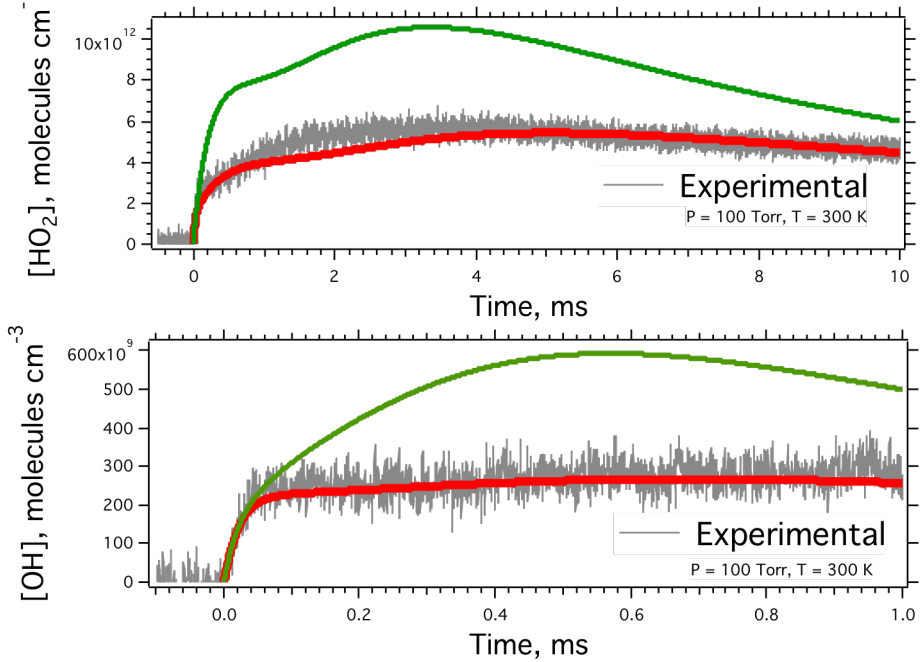
$$CH_3CO + CH_2O$$

$$+ O_2$$

$$CH_3C(O)O_2 \ (+M)$$

$$OH + \text{products}$$

$$HO_2 + \text{products}$$



Recommended Branching Ratio:

0.37

Branching ratio from fits:

0.67

Atkinson *et al*, Atmos. Chem. Phys., 6, 3625, **2006**
A.O. Hui *et al*, J Phys. Chem. A 123, 3655, **2019**

Summary of Preliminary Results from Fitting

RO_2 = Acetonylperoxy, RT	Literature	This work (in progress)
Rate $RO_2 + RO_2$, cm^3 $molecule^{-1}$ s^{-1}	[a](8.0 ± 0.2) x 10^{-12}	~ 4.0 x 10^{-12}
Branching Ratio for RO formation	[a](0.37)	average of 0.67
Rate $RO_2 + HO_2$, cm^3 $molecule^{-1}$ s^{-1}	[b](9.0 ± 1.0) x 10^{-12}	~ 6.3 x 10^{-12}
Branching Ratio for OH formation	[d](0.15 ± 0.1)	average of 0.50

Comparison to similar reactions

Reaction	Branching Ratio for OH formation
$HO_2 + CH_3C(O)O_2$	0.51 (±0.12)[c]
$HO_2 + C_2H_5(O)O_2$	0.40 (±0.1)[d]
$HO_2 + C_3H_7(O)O_2$	0.47 (±0.15)[d]
$HO_2 + CH_3C(O)CH_2O_2$ (this work)	average of 50%

[a] Atkinson *et al*, Atmos. Chem. Phys., 6, 3625, **2006**
[b] Burkholder *et al*, JPL Publication No. 15-10, **2015**
[c] Winiberg *et al*, Atmos. Chem. Phys., *16*, 4023, **2016**
[d] Orlando *et al,* Chem. Soc. Rev., *41*, 6294, **2012**

Acknowledements

Group at JPL:

Frank A. F. Winiberg

Rebecca Caravan

Carl Percival

Stan Sander

Xu Zhang

Aileen Hui

Fred J. Grieman

Mathieu Fradet

Ken Manatt

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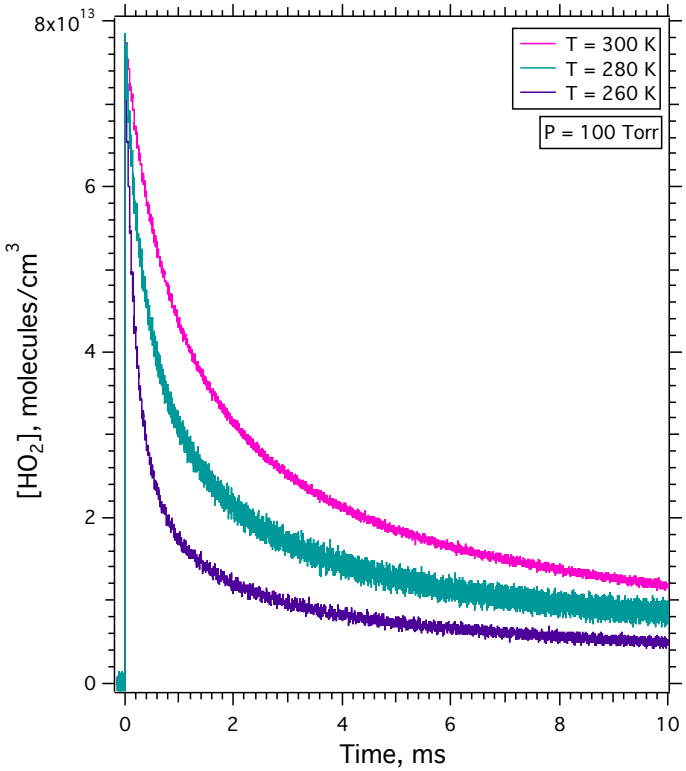
NASA Postdoctoral Program

Jet Propulsion Laboratory
California Institute of Technology

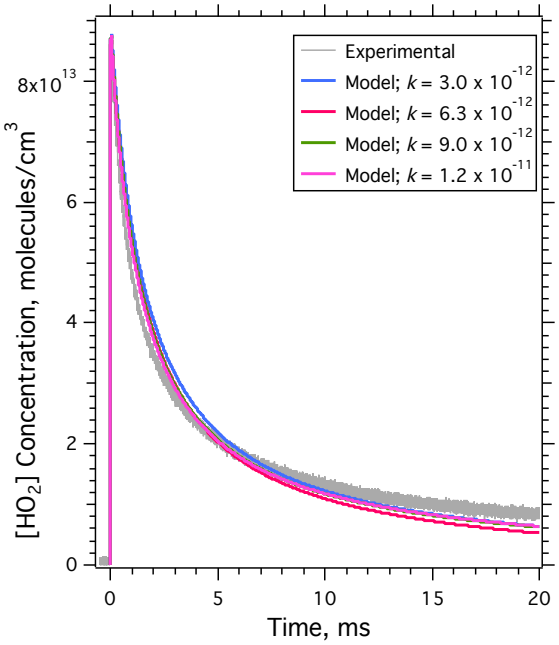
Continuation of This Work

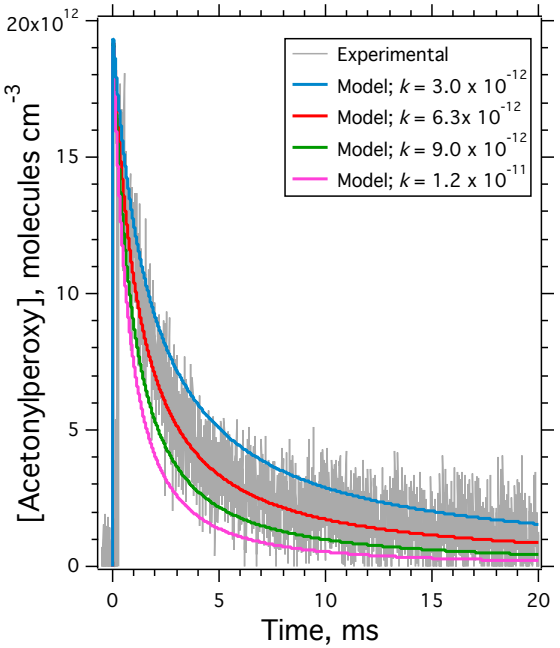
Experiments to look at the reaction rate and branching ratio as function of temperature and relative humidity.

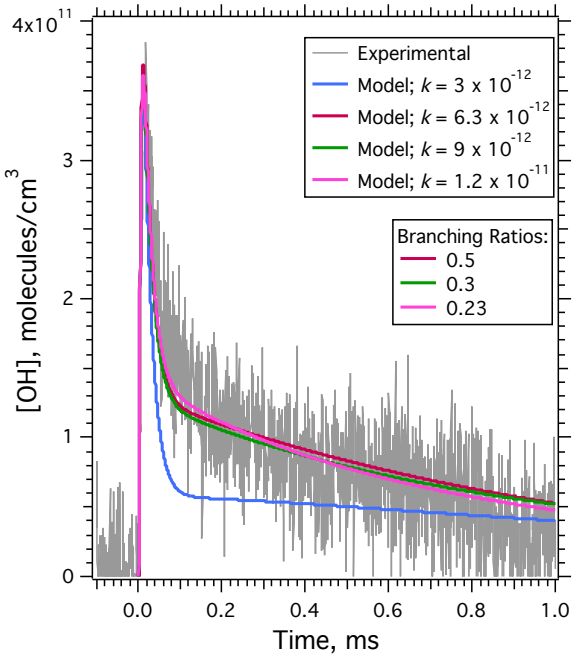


Sensitivity of Fits to the Rate of HO_2 + Acetonylperoxy

HO_2 + Acetonylperoxy ⟶ OH + coproduct, ROOH + O_2



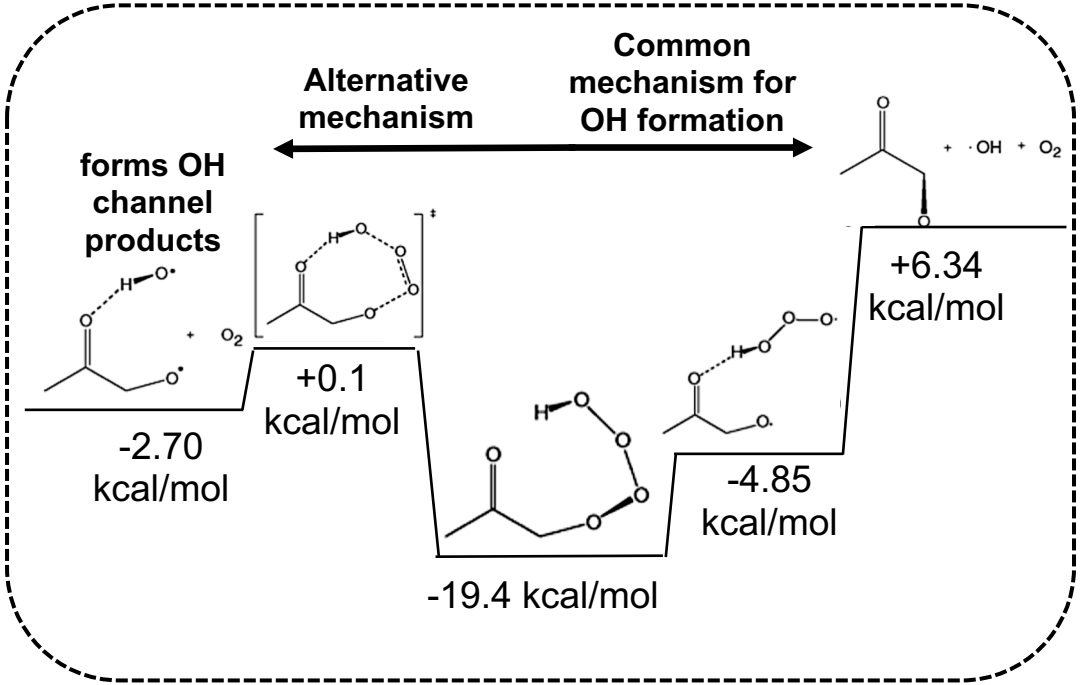




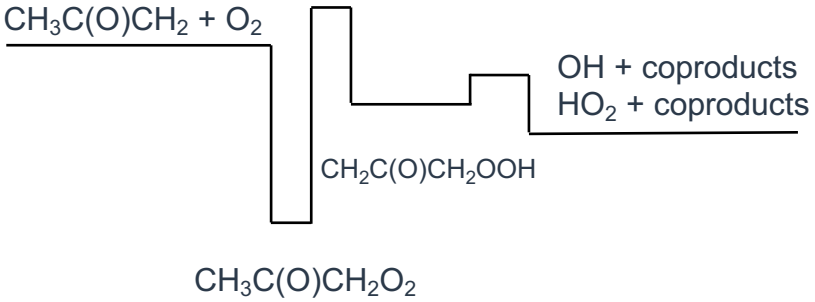
typical concentrations for experiments

Species	Molecules cm^{-3}
Cl	$1\ (\pm 2) \times 10^{14}$
CH_3OH	$4\ (\pm 1) \times 10^{15}$
$(CH_3)_2CO$	$2\ (\pm 1) \times 10^{16}$
O_2	$2\ (\pm 1) \times 10^{18}$

Mechanism for OH Formation Channel:



Possible mechanism for alkyl + O_2

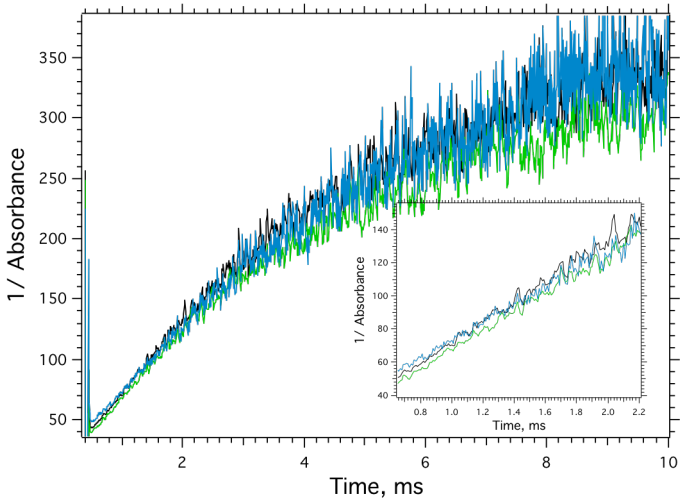


G Kovács et al, *Phys. Chem. Chem. Phys.,* 9 (**2007**) 4154.
El-Nahas et al, *Phys. Chem. Chem. Phys.,* 10 (**2008**) 7139.

Cross-Section Determination

Method 1 : Extrapolating the UV data to t = 0 using pseudo-second order kinetics for early times

Method 2 : Floating the cross-section while fitting the self-reaction kinetics



$$\frac{1}{[CH_3C(O)CH_2O_2]} = 2kt + \frac{1}{[CH_3C(O)CH_2O_2]_0}$$

$$\frac{1}{A} = \frac{2kt}{\sigma_{CH_3C(O)CH_2O_2} * l} + \frac{1}{[CH_3C(O)CH_2O_2]_0 \sigma_{CH_3C(O)CH_2O_2} * l}$$