Organic Aerosol and Solar Radiation

W. Sean McGivern

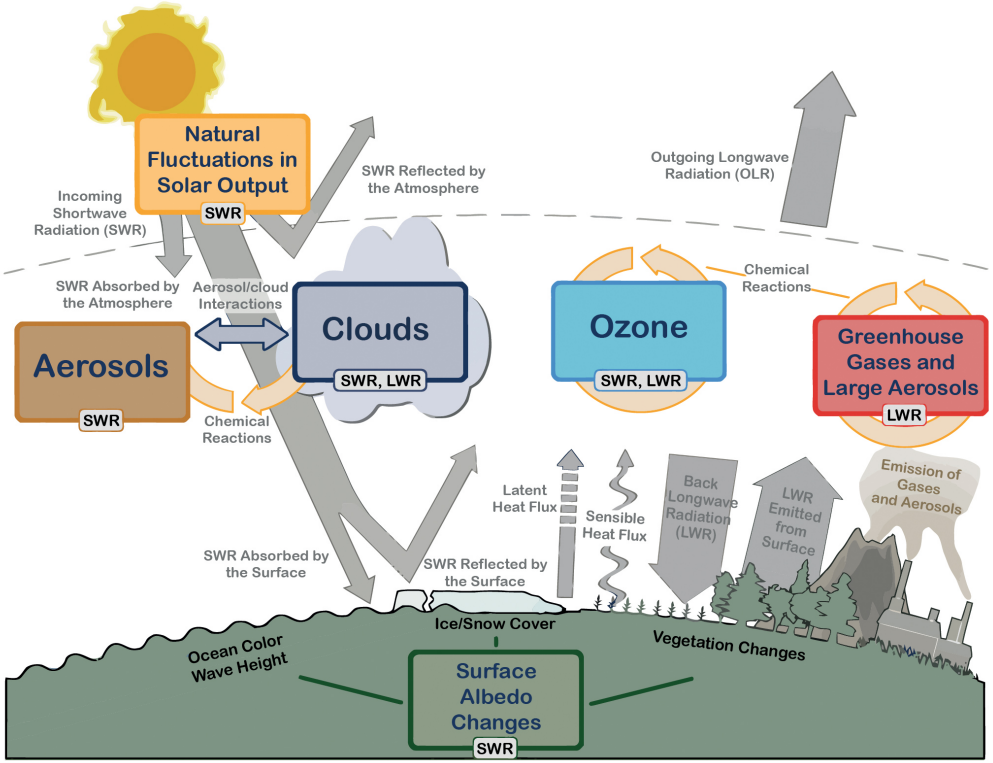
2014 Greenhouse Gas and Climate Science Measurements Program Review

Outline

1. Chemistry and Climate
2. Radiative Forcing
   - Direct Effect
   - Cloud Condensation Nuclei
   - Droplet Formation
3. Photochemistry
   - New Chemistry
   - Impacts of Photochemical Pathways

Aerosols Affect Climate

Direct and indirect effects



IPCC 2013

- Indirect Effect
  - Cloud albedo major input into climate models
  - Mostly scattering from transparent particles.
  - Major research emphasis
- Direct Effect
  - Colorless particles lead to scattering.
  - Smaller effect due to typical particle sizes.

Secondary Organic Aerosol

Organic aerosols: particles of organic compounds in air.

Some sources:

- Combustion (cooking, diesel, wood)
- Abrasion (leaf abrasion, tire dust)
- **VOC oxidation and condensation (Secondary Organic Aerosol)**

Major Sources of Short-Lived VOC

- Biogenic
  - Vegetation (largest source)
  - Wildfires/Forest Fires
- Anthropogenic
  - Solvents
  - Petroleum and Related Industries
  - Highway Vehicles
  - Storage/Transport

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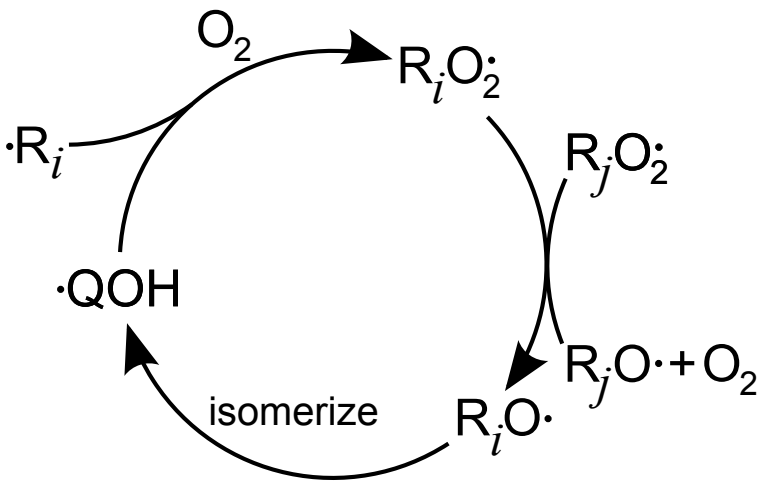
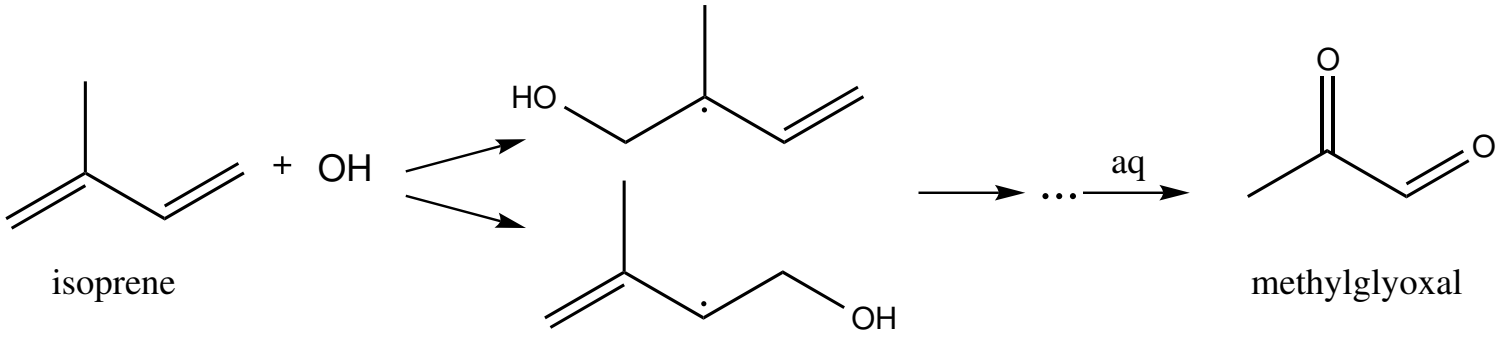
Driven by Oxidation Processes



- Free radical formed via OH reaction
- Rapid O_2 addition
- Decomposition (from RO·, not shown) and isomerization.
- Cycle continues

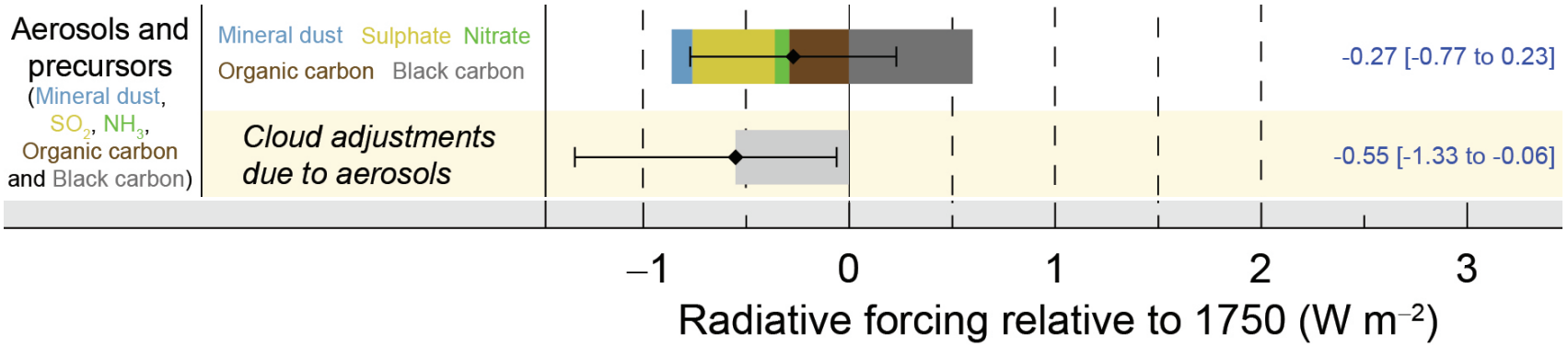
First step for isoprene:



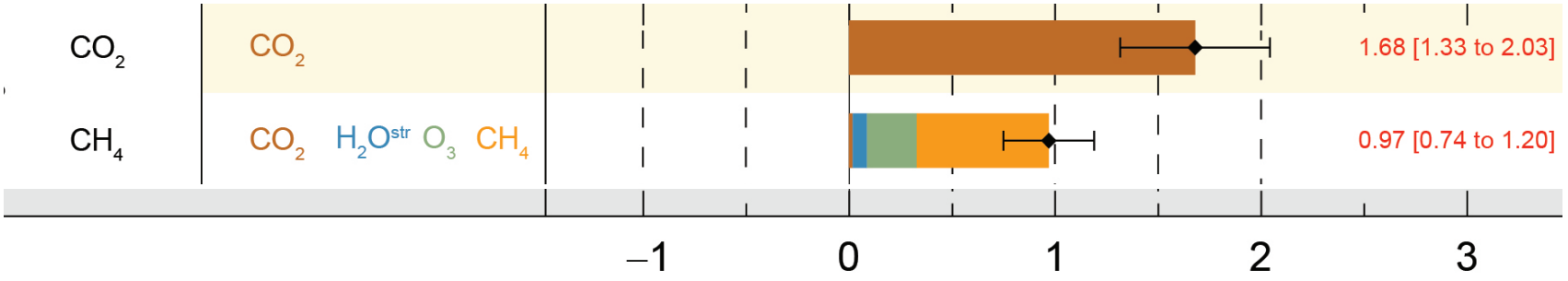
Uncertainties Due to Organic Aerosol

O_2 giveth; O_2 taketh away.

From the IPCC:



Comparing it to gases:



Chemical Impacts on Climate

- Climate change is inherently a physics problem.

$$\iiint \frac{2h\nu^3}{c^2}(\exp(h\nu/kT)-1)^{-1}\,d\Omega\,d\nu$$

Chemistry affects inputs.

Direct Effects: Browning of Organic Carbon

$$I = I_0 \exp\left(-l(\boldsymbol{\epsilon}_{\mathbf{a}[\mathbf{a}]} + \epsilon_g[g] + \cdots)\right)$$

Indirect Effects: Cloud Condensation Nuclei

$$\ln\left(\frac{p_w(D_p)}{p^0}\right) = \frac{4M_w\boldsymbol{\sigma}_{\mathbf{w}}}{RT\rho_w D_p} - \frac{6\mathbf{n_s}M_w}{\pi\rho_w D_p^3}$$

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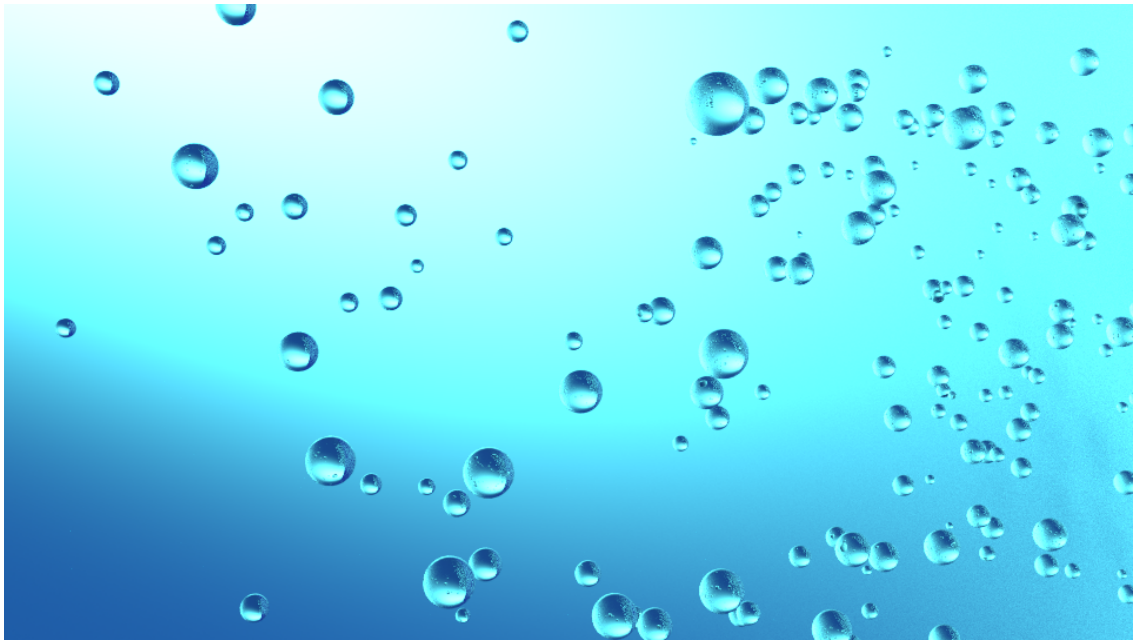
Absorption of Water-Soluble Compounds

Colorless organic compounds only scattering incoming visible radiation.

Browning reactions cause absorption of visible radiation.



↑ Forcing; ↑ Temperature

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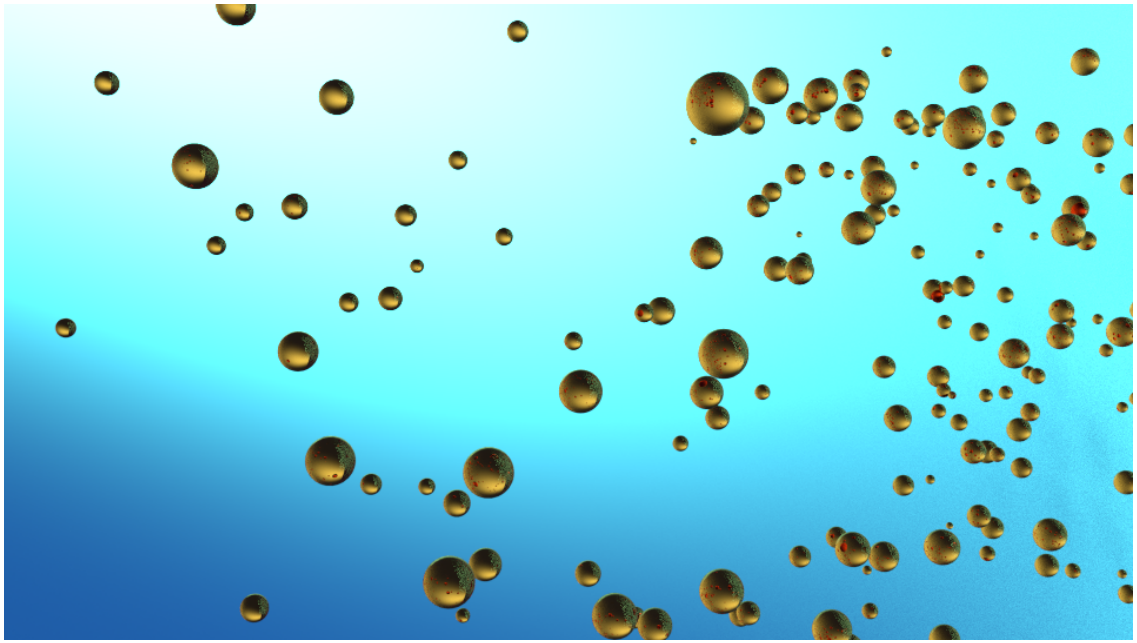

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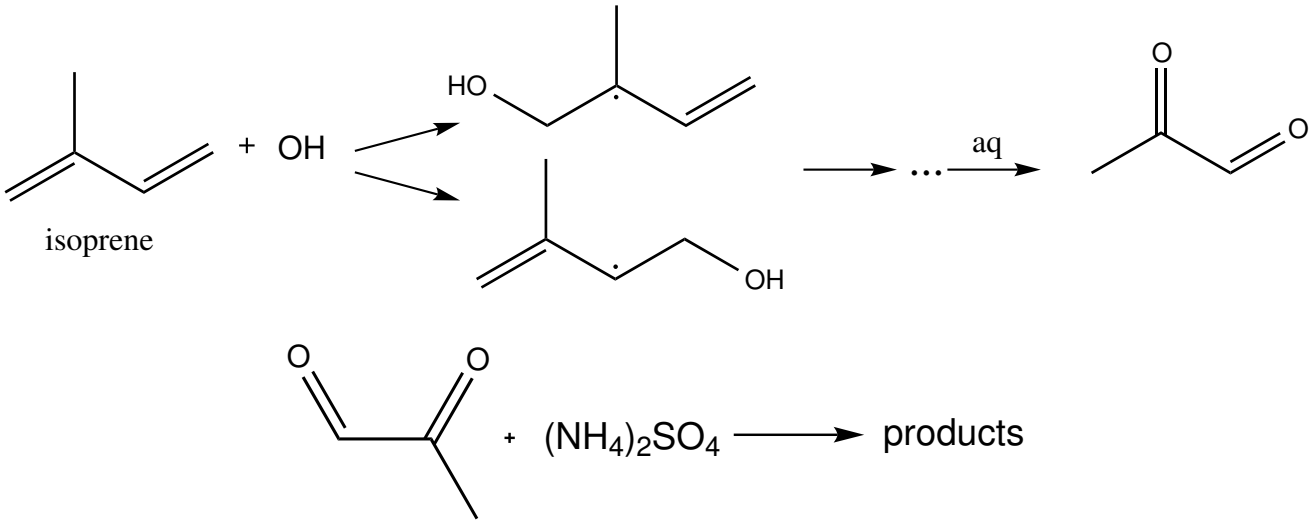
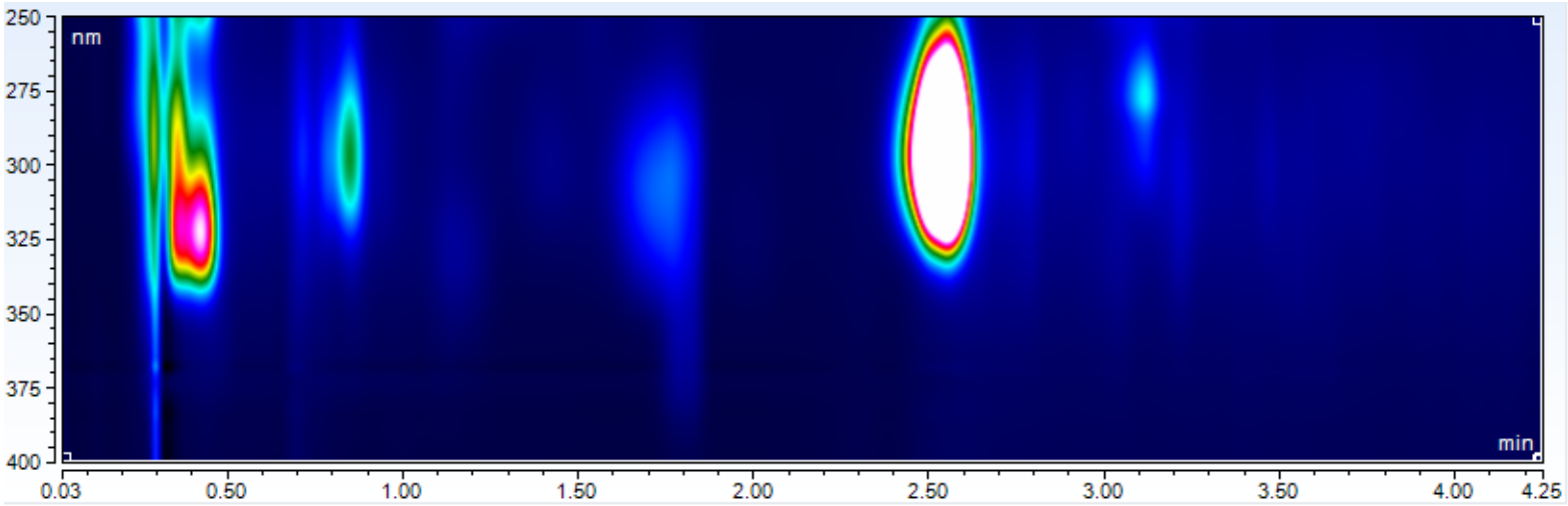
Browning of Colorless Organics

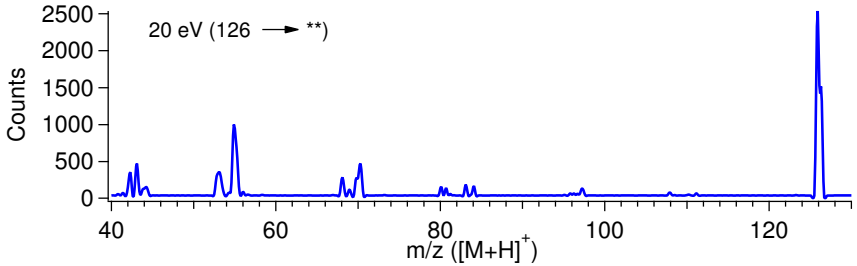


- Methylglyoxal + $(NH_4)_2SO_4$ gives complex series of products.
- Chromatography revealed fortunate simplicity.

Visible Methylglyoxal-NH_3 Products



- Large number of compounds.
- Very small number that absorb in the visible.
- Identified by tandem mass spectrometry



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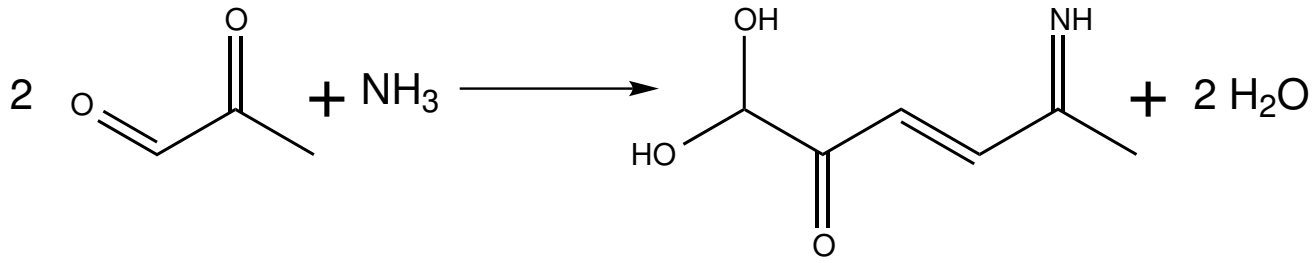
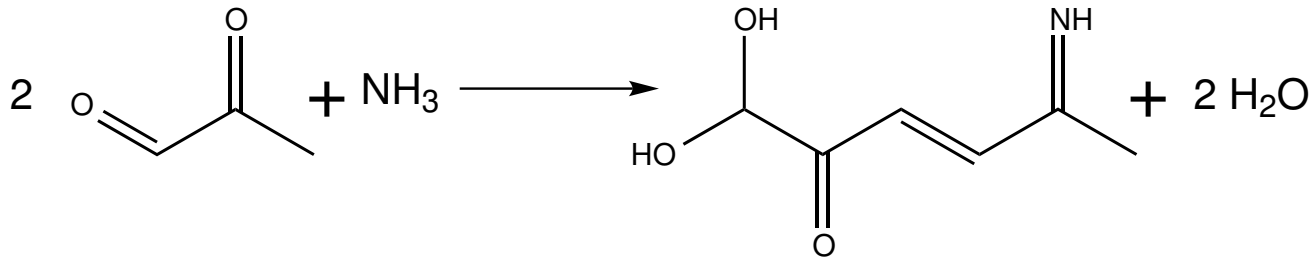


- Colorless VOC
  - Reacts with atmospheric $(NH_4)_2SO_4$
  - Produces deep brown particle
  - **Pathway to decrease overall scattering.**
- Sources of nitrogen and sulfur
  - N: ammonia (65 % from agriculture)
  - S: sulfur dioxide (91 % from fossil fuels)
  - **Another anthropogenic source for global warming.**

Browning of Colorless Organics



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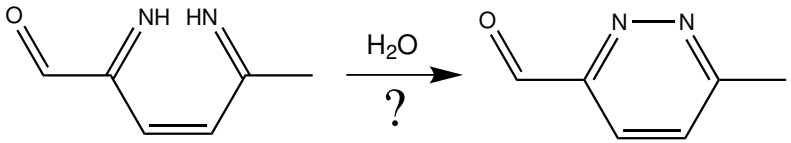
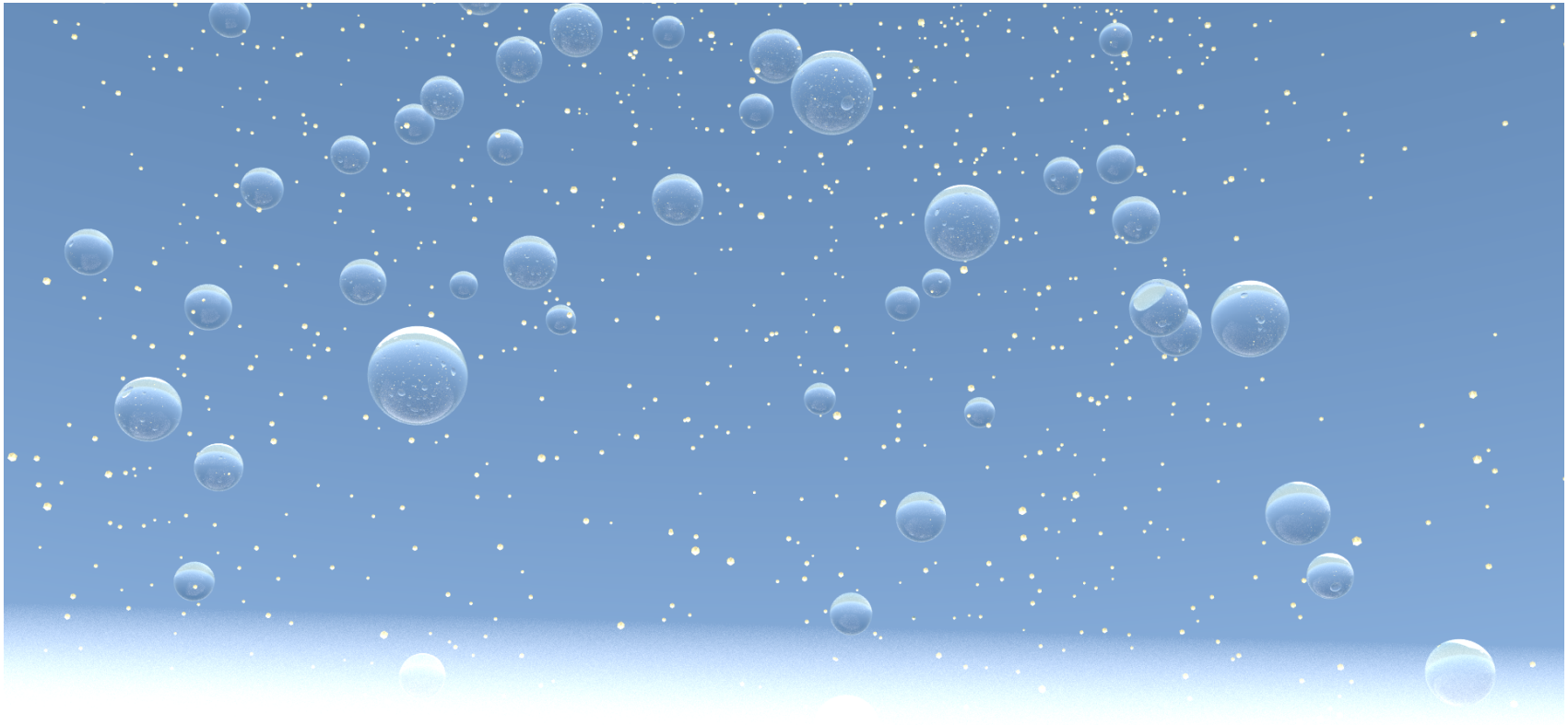
Future Studies in Direct Climate Effect

- Isolation/synthesis of imine – Possible "brown carbon" standard?
- pH – affects reaction rates and possible new products.



- Imine calculations anomalous – experiment/theory solvation study

Cloud Condensation: Climate Effects



Studying indirect effect requires work in two areas:

- Seed Particles
- Droplet Formation

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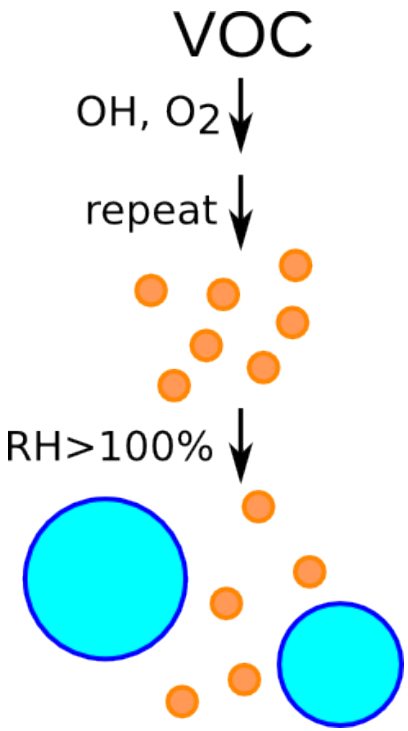
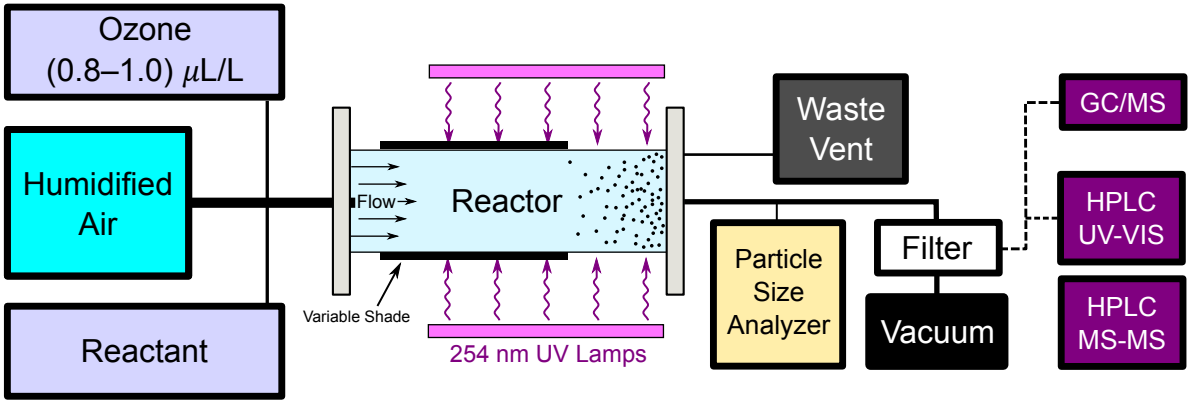
Seed Particles: Gas-to-Particle Conversion

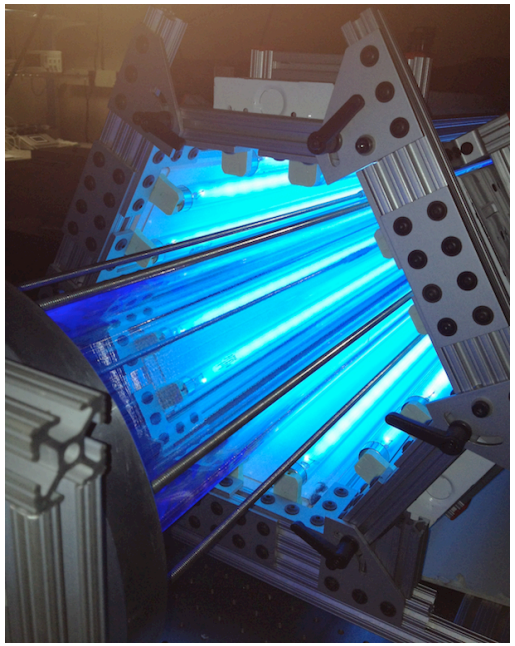
Conversion of volatile gases to particles via condensation



- Oxidation:
  - Initiated by OH radicals in atmosphere
  - Oxygen primarily from atmospheric O_2
  - Increases water solubility
  - Decreases volatility
- CCN propensity depends on the parent
  - Functional groups in the molecule change properties
  - Vapor pressure affects nucleation

Seed Particles: NIST Photochemical Flow Reactor





Choose radical initiation strategy

- Probe specific chemistry: use direct photolysis
  $RI \xrightarrow{h\nu} R\cdot + I\cdot$
- Simulate atmospheric oxidation: generate massive OH concentrations
  $O_3 \xrightarrow{h\nu} O_2 + O(^1D)$
  $H_2O + O(^1D) \longrightarrow OH + OH$

Seed Particles: Oxidation Measurements

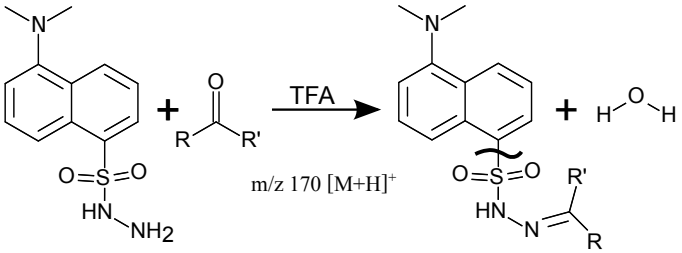
- Organic aerosol mixtures highly complex.
- Intractable to observe every product
- **Functional Group Distribution**
- Relative quantities of oxygen-containing moieties

Name	Group	Vapor P Factor
hydroxy	OH	10×
carbonyl	C=O	3×
acid	COOH	30×

- Chemical derivatization to differentiate using UV and mass spec.

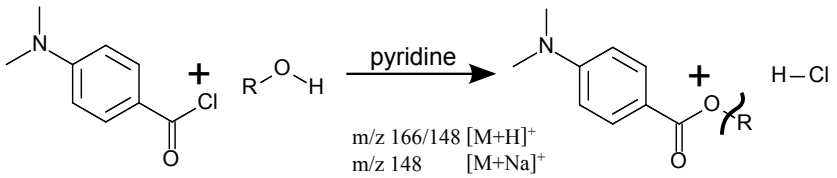
Seed Particles: Derivatization

Dansyl Hydrazine
DnsHz



- Sensitive to aldehydes and ketones

4-(dimethylamino) benzoyl chloride
DMABC



- Sensitive to alcohols, mildly to carboxylic acid

- UV absorption linear and quantitative at longer wavelengths ($>$ 250 nm).
- Tandem MS (triple quad) to selectively identify masses and functional groups.

Seed Particles: Derivatization

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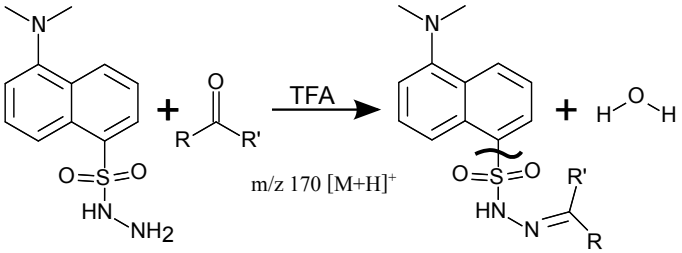

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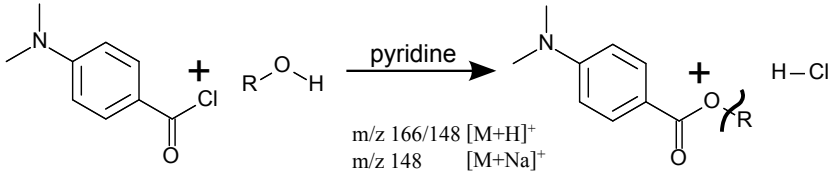

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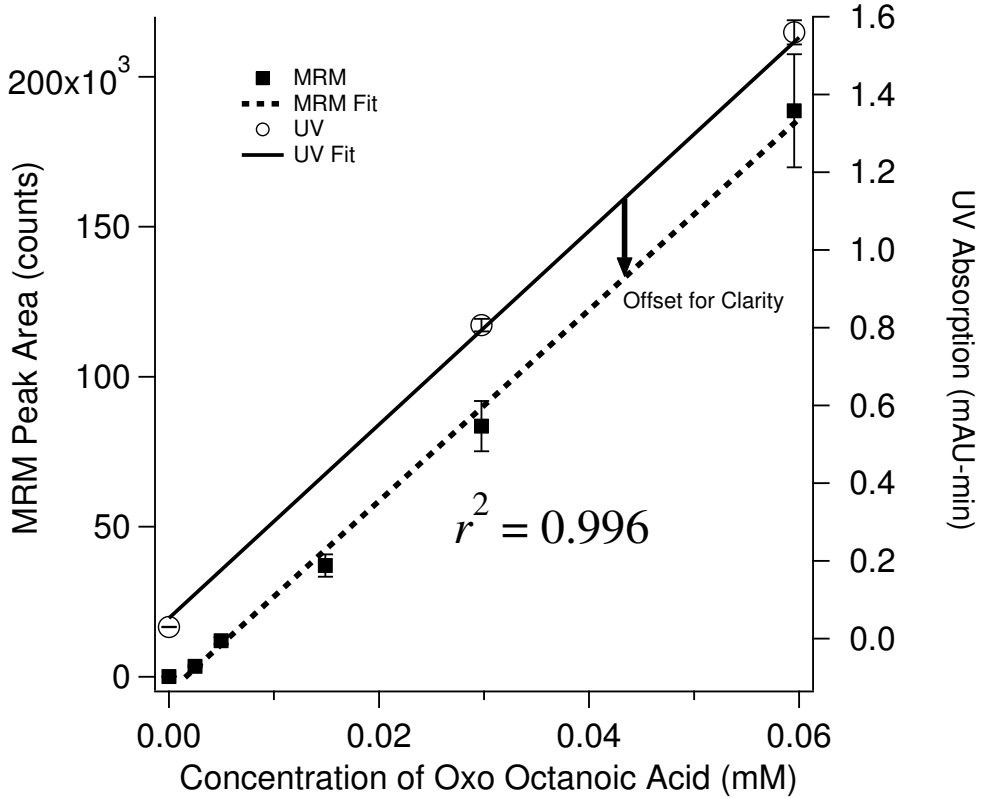
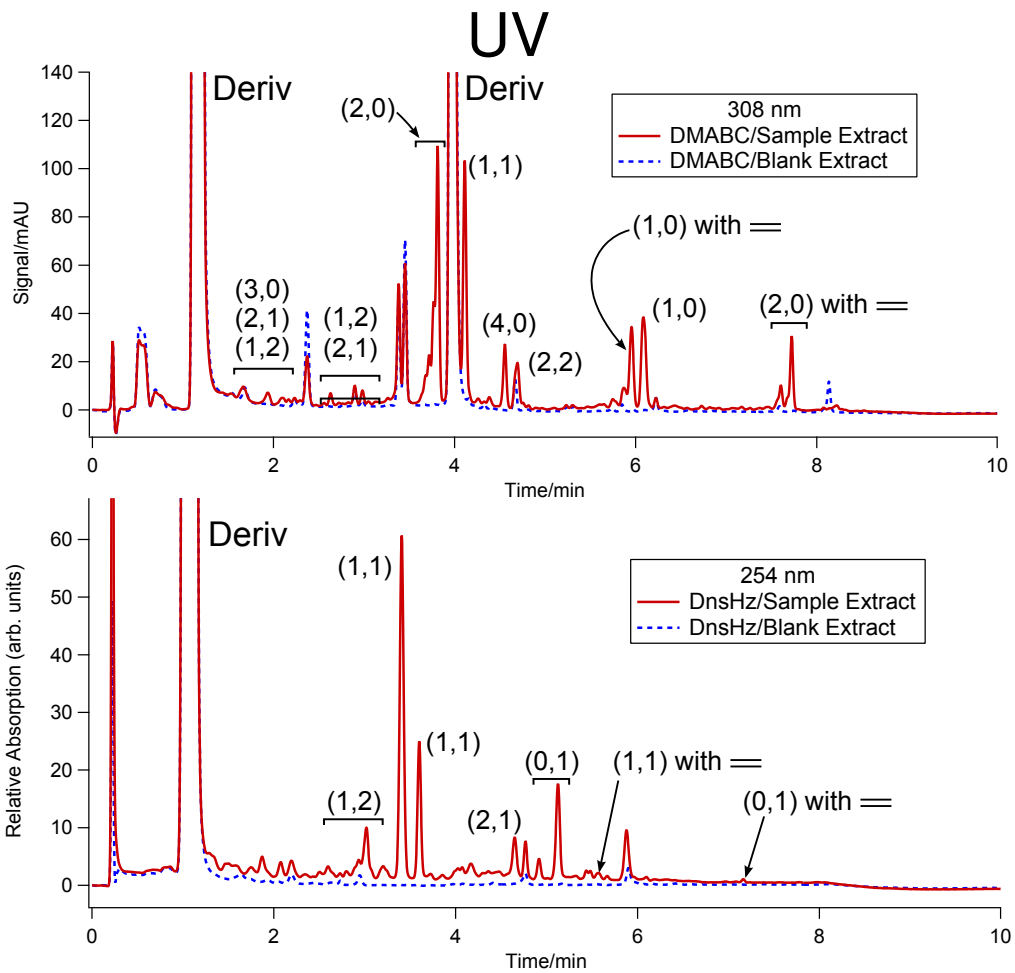
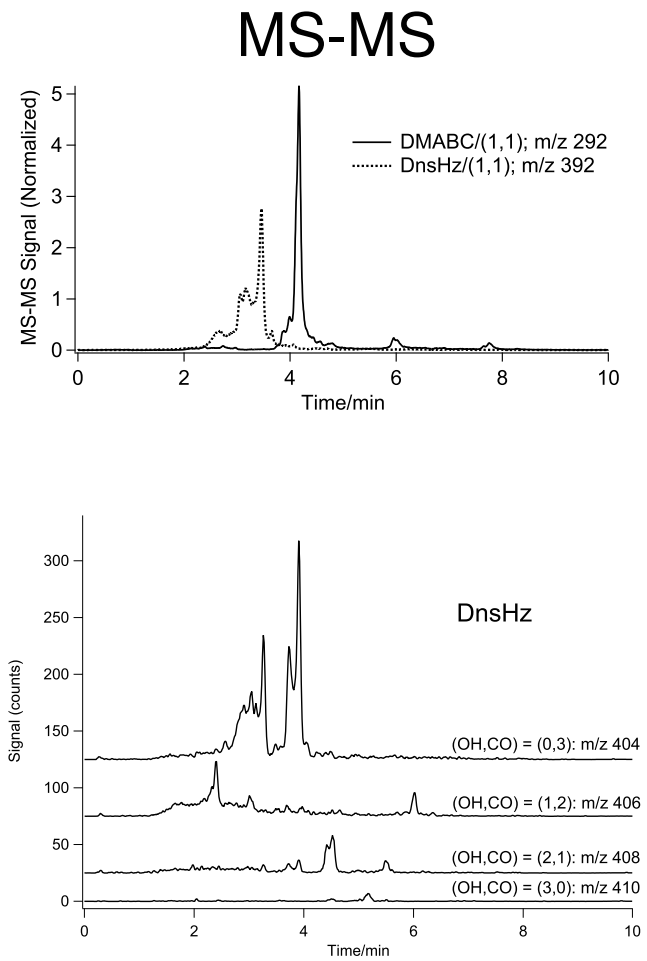
Seed Particles: Calibration



- Tandem MS generally nonquantitative
- Derivatization allows UV to be quantitative and selective
- Closed circles MS-MS data for 2-oxooctanoic standard
- Open circles UV data

Seed Particles: Chromatograms

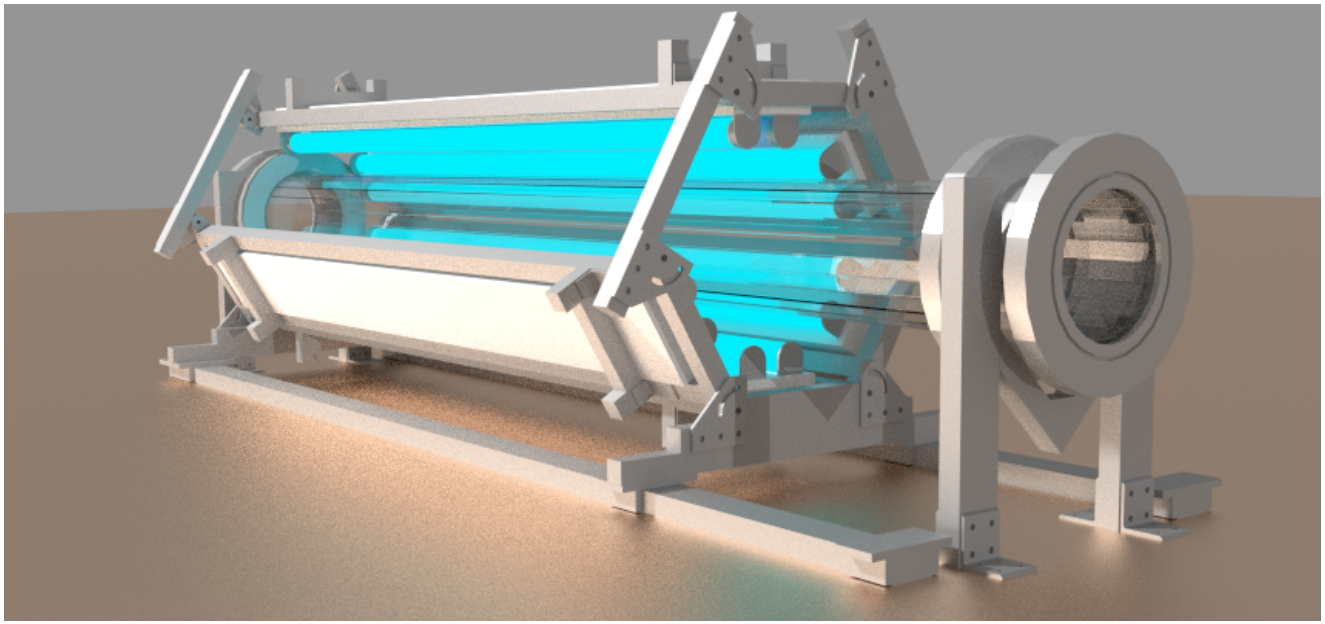




Compounds: $(n_{\mathrm{OH}}, n_{\mathrm{C=O}})$

Seed Particles

Controllably generate well-characterized organic aerosol



Seed Particles: Future Studies

Controllably generate well-characterized organic aerosol

- Better functional group analytical methods
  - New derivatization reagents
  - Aqueous analyses
  - Post column techniques; single-peak functional group dists.
- Multiple parent molecules to tune properties
- Novel photochemical pathways (More later)

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Droplet Formation: State-of-the-art

Cloud Condensation Nucleus Counter

- Optical size spectrometry of droplets
- Single supersaturation
- Applied to environment via Köhler theory.

- *Solute identities?*
- *Local relative humidity?*
- *Cloud = nonequilibrium growth*

Adiabatic Expansion Cloud Chamber

- Full range of aerosol analyses possible
- Clouds formed from adiabatic expansion via piston
- Simulate cumulus cloud

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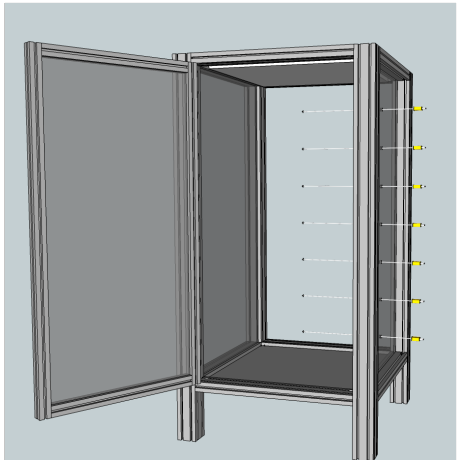
Droplet Formation: Cloud Condensation Chamber



Experiment:

- Infrared heating of humid air/analyte.
- Dew points: $T_{dp}^{\text{inside}} > T^{\text{outside}}$
- Heater off: radiative cooling to supersaturation

- Simultaneously measure small (<200 nm) and large (>500 nm) size distributions.
- Simulate stratus cloud mechanism

Future Studies in Indirect Climate Effects

- Expanding cloud chamber in two directions:
  - Make larger to minimize wall effects
    - Minimize convective heating from cooling walls
    - Larger homogeneous region to permit multiple simultaneous analyses of size, scattering and absorption.
  - Perform experiments in cold environments ($<5\,^{\circ}$C) — don't forget your parka!
    - Operating instruments under harsh conditions.
    - Limited water concentration for relatively cold inputs.

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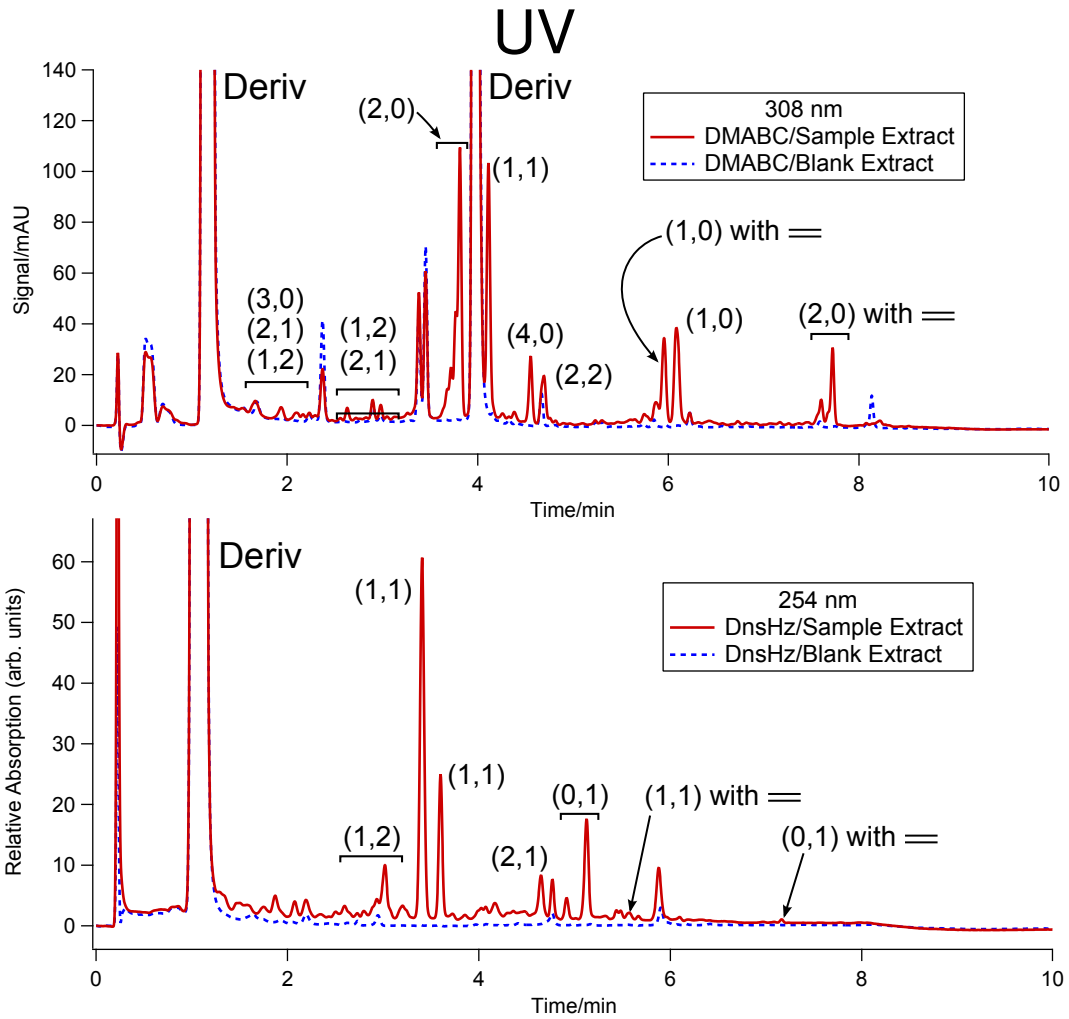
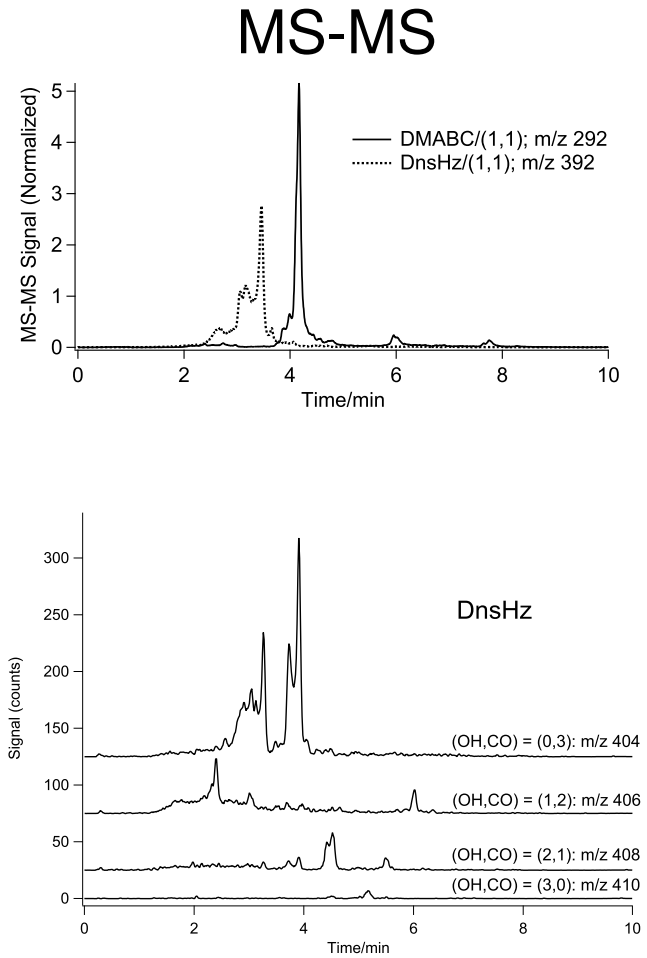
Complexity of Observed Product Spectrum





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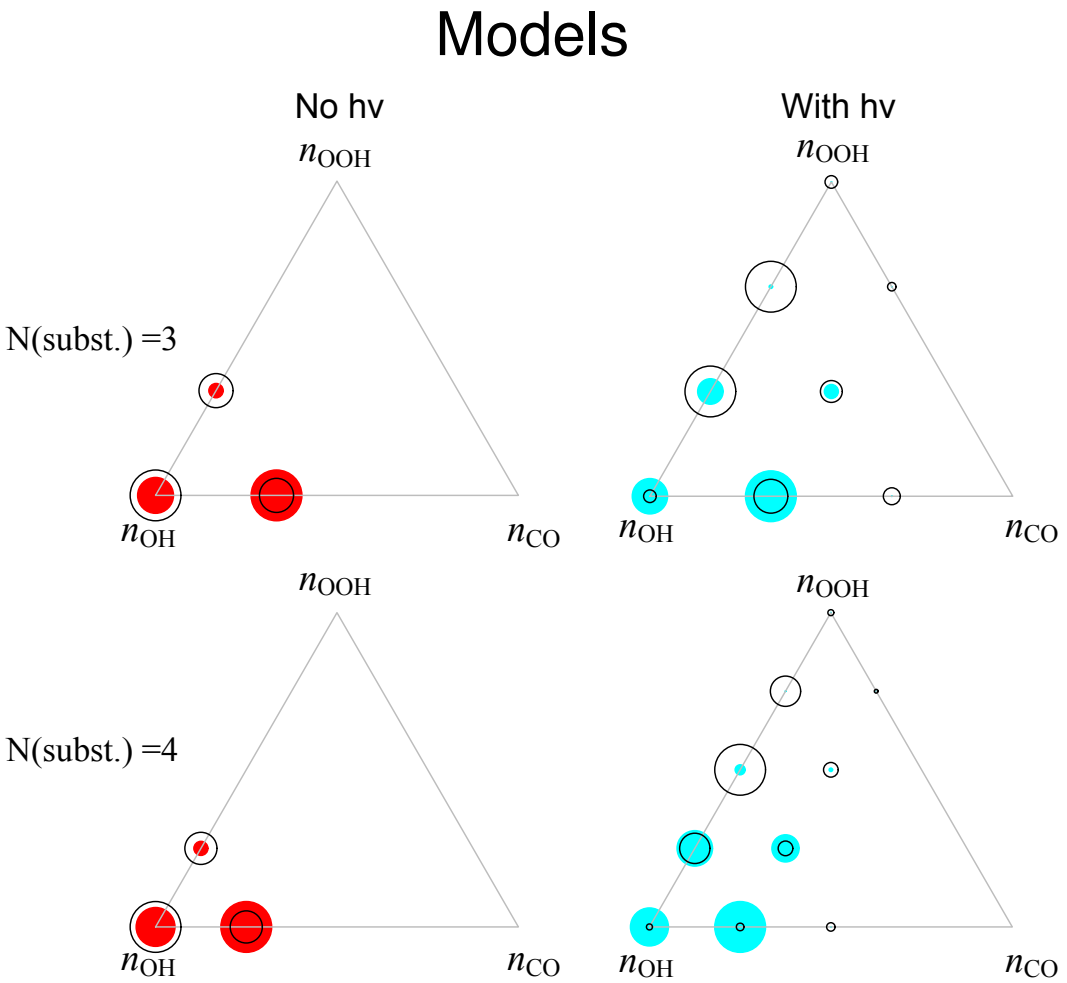
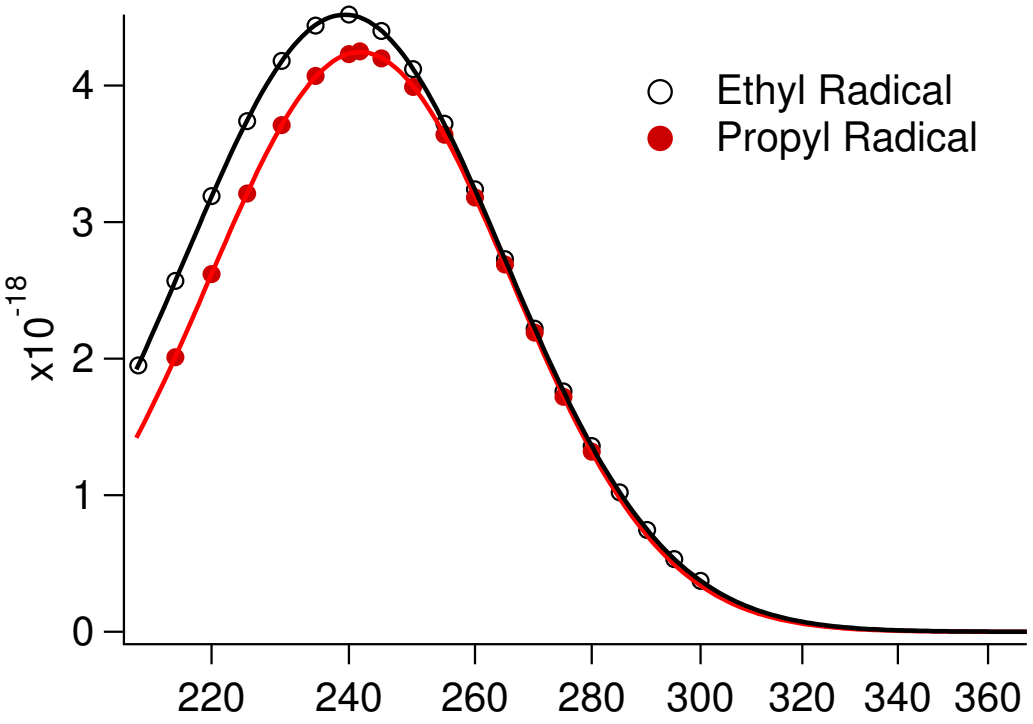
Complex Mixtures Require New Chemistry



- Complexity of observed composition not explained by simple mechanism
- Peroxy radicals absorb strongly at experimental wavelengths.

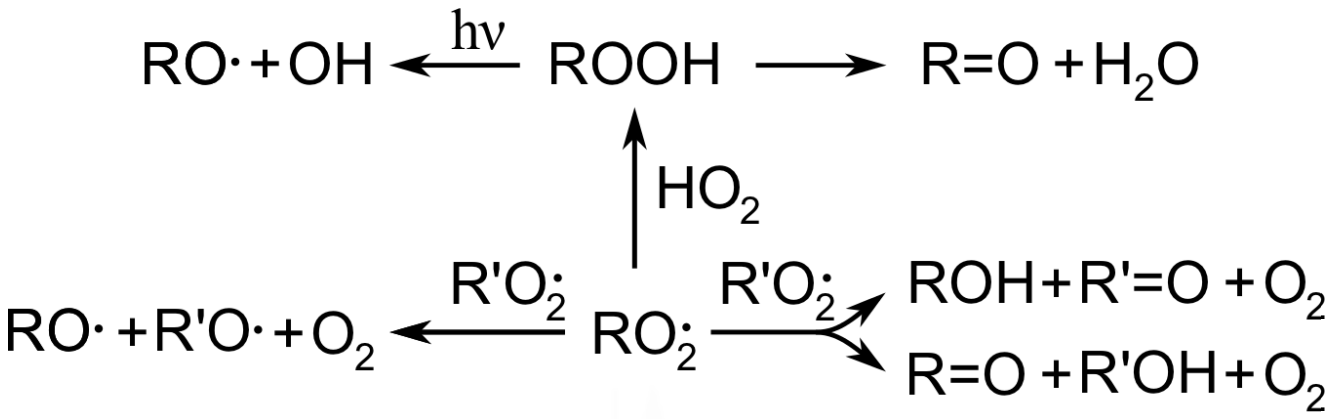
Peroxy Radicals Undergo Photochemistry



- Available data show significant σ at UV wavelengths.
- Photon energy permits reaction prior to collisional cooling.
- Not previously considered as significant channel.

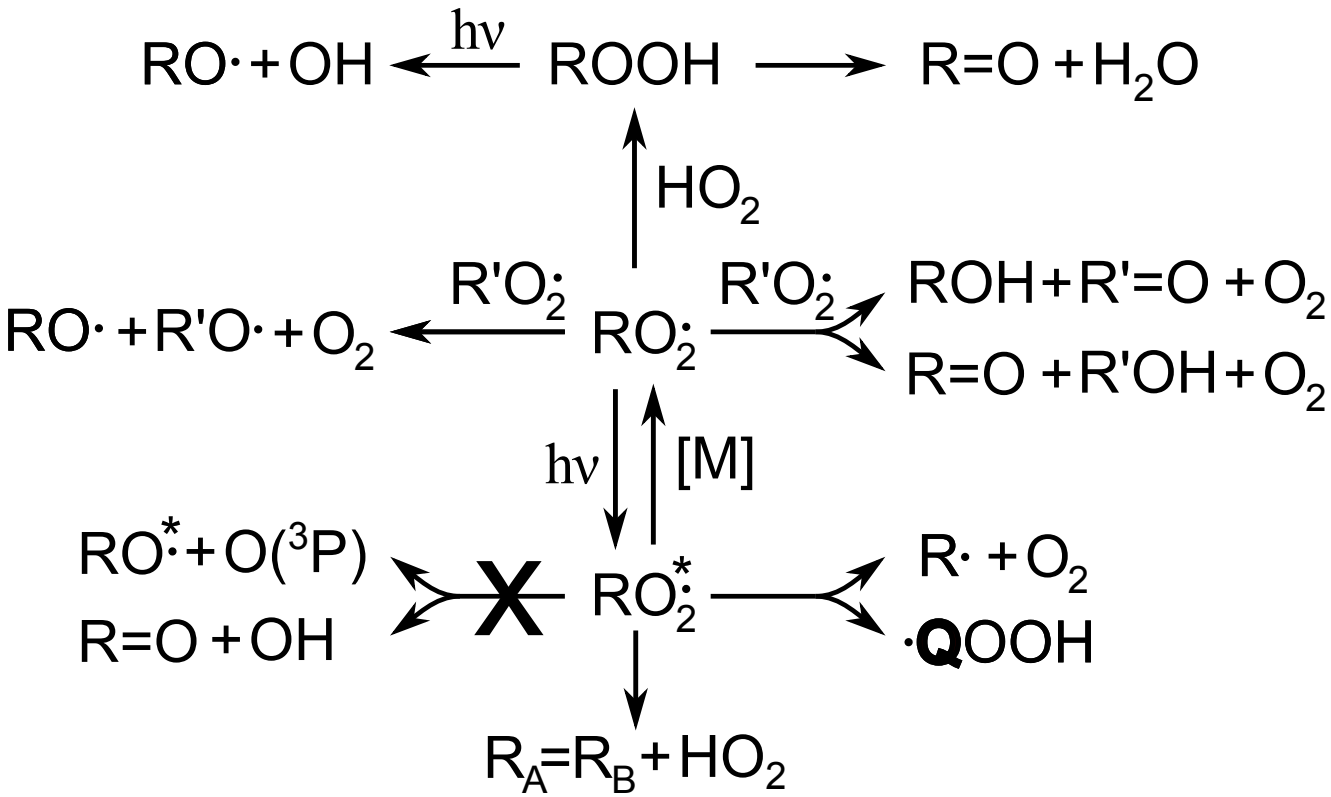
NASA-JPL Evaluation, 2012

Mechanism



Nascent $RO_2{}^{*}\cdot$ temperature $\sim$1500 K – **Combustion**

Mechanism



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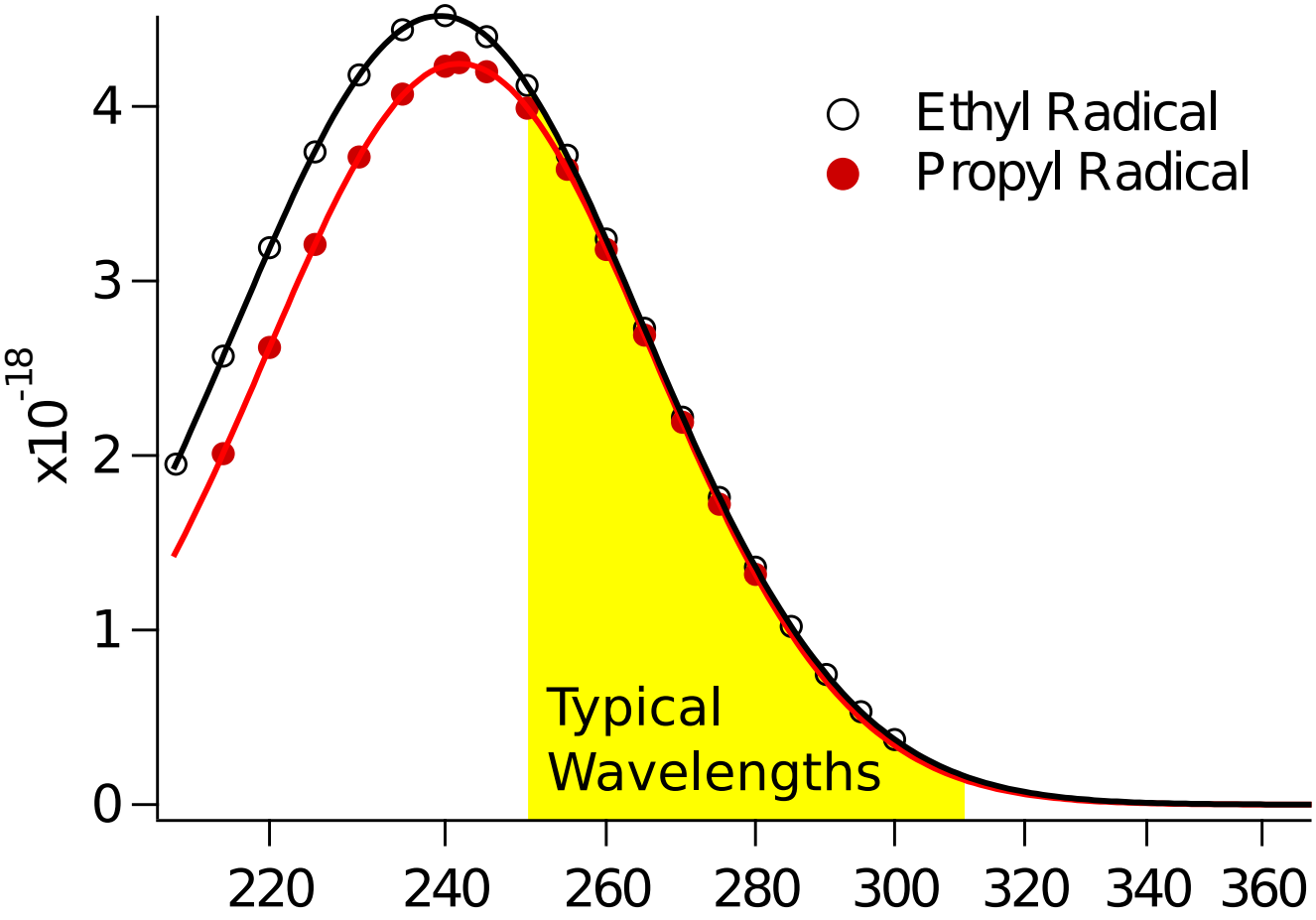
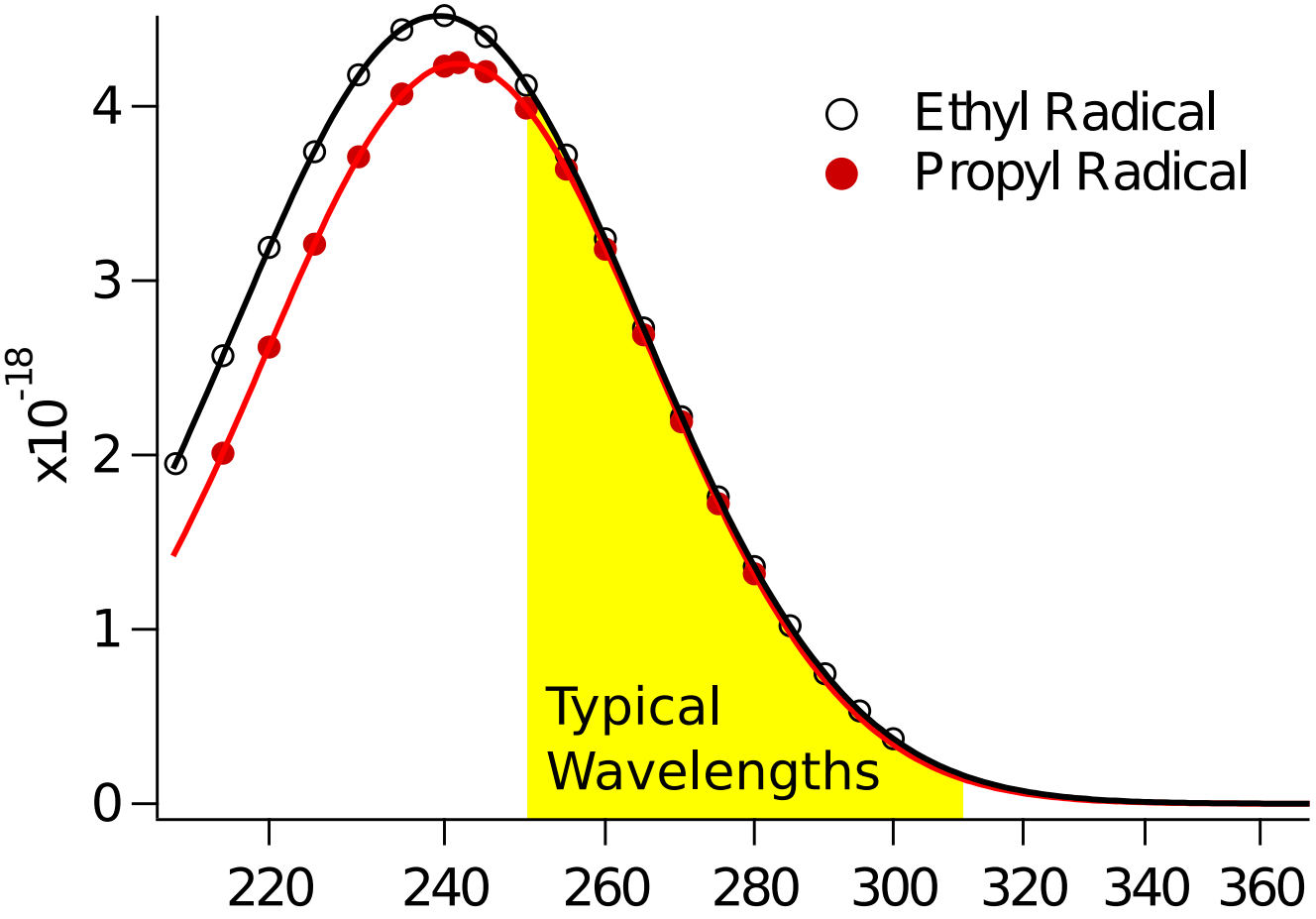
Laboratory Experiments



NASA-JPL Evaluation, 2012

- Flow Tubes
- Smog Chambers
- Chambers are known to "lose" up to 50 % of their mass.
- Is this a source?

Laboratory Experiments



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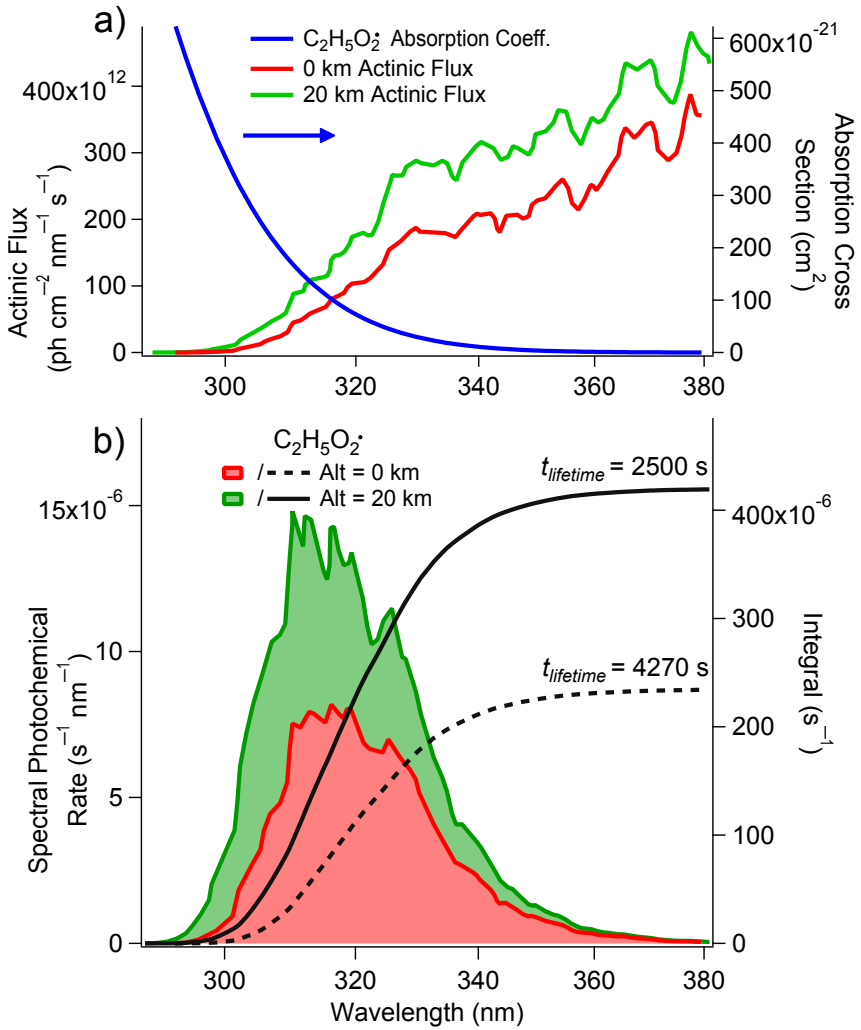
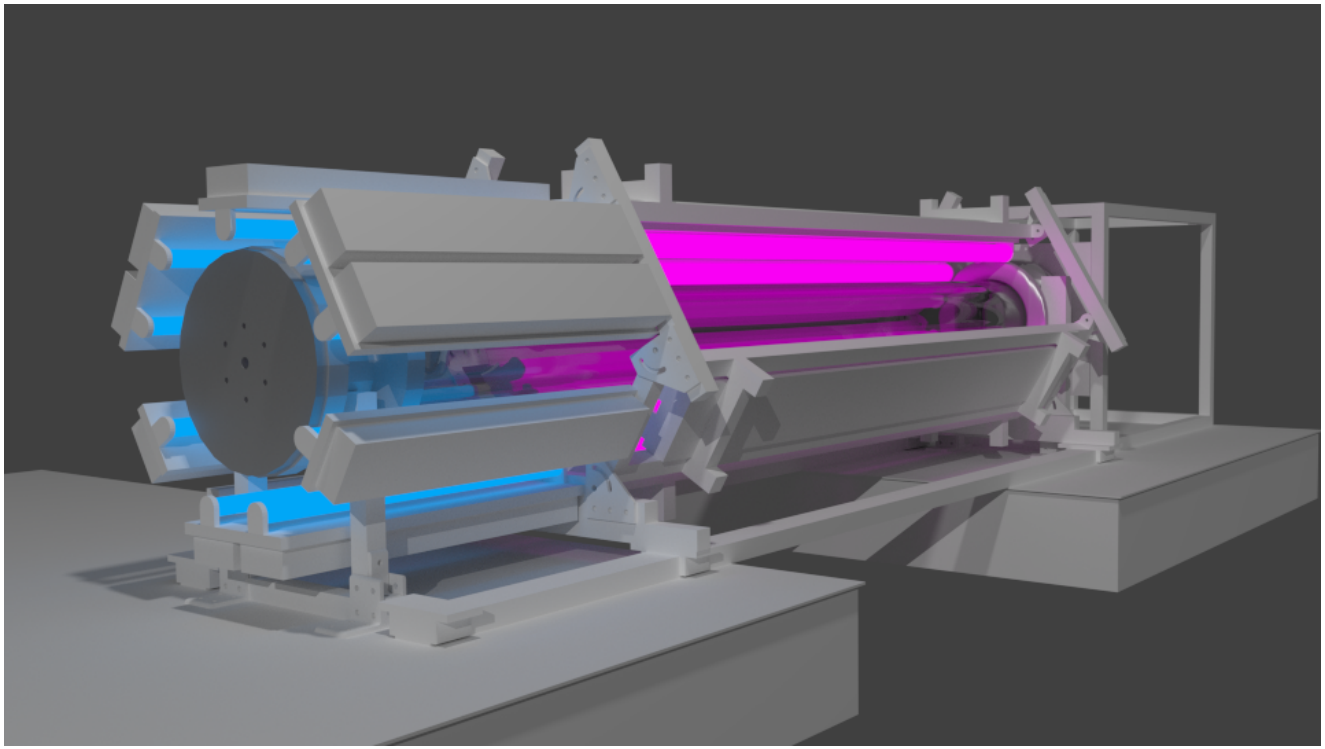
Atmosphere



- Lifetime in clean areas of alkyl peroxy radicals: order of 10 min.
- Possibly significant fraction in atmosphere.
- Based on best-fit extrapolation of spectrum.

Future Photochemistry

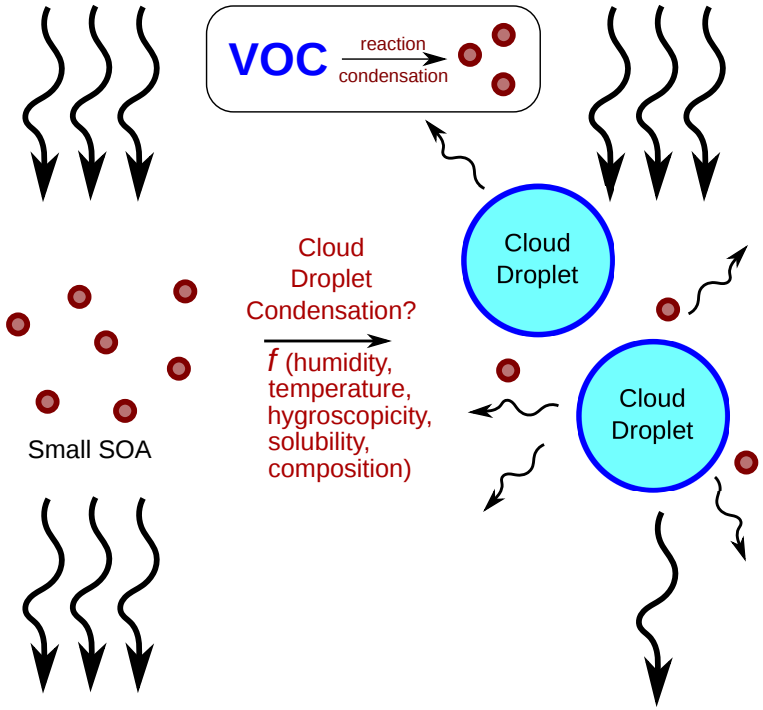
Multiple wavelength: Photolysis and propagation



How does $-$OH or C$=$O substitution affect peroxy photochemistry?
[Experiment and Theory]

Conclusions

Chemistry crucial for reducing RF uncertainty from aerosols.



Ongoing Programs:

- Direct: Brown C chemistry
- Indirect (Seed): Photochemical Flow Cell
- Indirect (CCN): Radiative Cooling CCN Chamber

Future Directions:

- Direct: Brown C Imine Standard
- Indirect (Seed): Realistic CCN Generator
- Indirect (CCN): Non-equilibrium Cloud Chamber

Participants and Acknowledgments

Primary Researchers:

- W. Sean McGivern
- Alicia J. Kalafut-Pettibone (NRC Postdoc, now at Schafer Corp., Washington, DC)
- Joseph P. Klems (NRC Postdoc, now at DuPont, Newark, DE)
- Iftikhar Awan (begins October 2014)

Collaborators:

- Thomas Allison
- Donald Burgess
- James Radney
- Christopher Zangmeister

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National Institute of Standards and Technology
U.S. Department of Commerce

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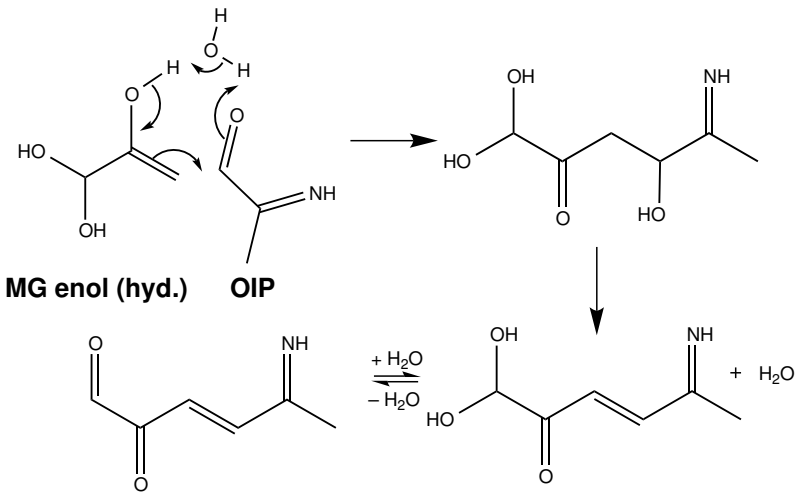
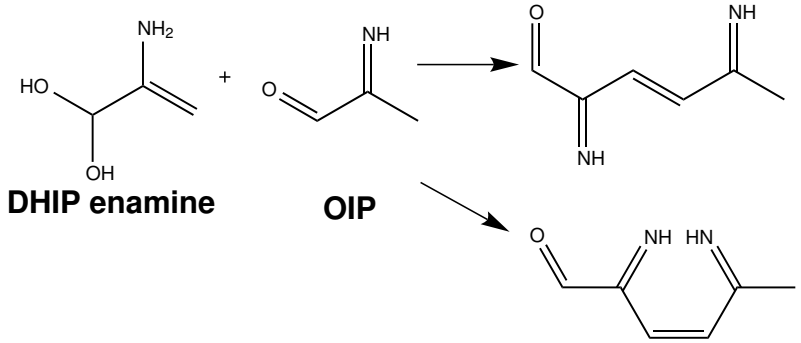
Simplicity

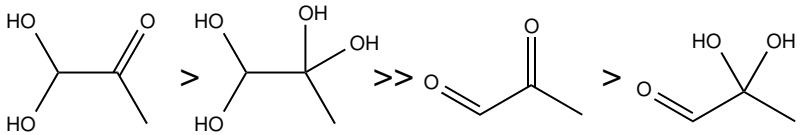
- Simplicity due to formation of conjugated imine-substituted enones that absorb at longer λ.



- Analogous imine condensation.



- Both the nearly exclusive formation of ketimine and the extremely slow rate due to the hydration of the carbonyls.



Source of Unknown Mass

Gas-phase products of 248 nm photolysis of iodopentane in air by Warneck and coworkers.

- 28 % of observed products unknown.
- Hydroperoxides predicted but not observed.

$$RO_2\cdot + HO_2\cdot \longrightarrow ROOH + O_2$$

- **Lifetime of $RO_2\cdot$ too short due to photochemistry.**

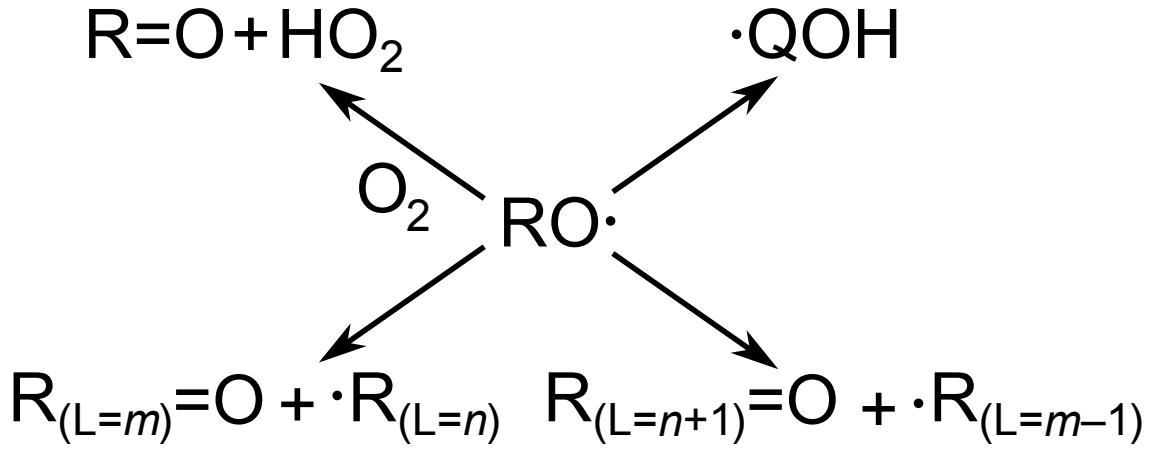
Table III Photooxidation of 1-Iodopentane: Observed and Calculated Relative Product Distribution

	Relative Yield		
		Calculated[a]	
Product	Experimental	Case (a)	Case (b)
Pentanol	1.0 ± 0.09	1.0	1.0
Pentanal	1.14 ± 0.06	1.14	1.16
Butanal	0.102 ± 0.008	0.100	0.104
Butanol	0.034 ± 0.003	0.033	0.035
Pentan-1,4-diol	0.080 ± 0.025	0.194	0.077
1-Hydroxypentan-4-one	≤0.02	0.195	0.080
Acetaldehyde	≤0.02	0.008	0.001
Unidentified products[c]	0.91 ± 0.07	–	–
4-Hydroxypentanal	nd[b]	0.375	0.559
Propan-1,3-diol	nd	0.002	0.003
3-Hydroxypropanal	nd	0.006	0.009
Formaldehyde	nd	0.141	0.151
Hydroperoxides[d]	nd	0.152	0.214
Hydroxy-hydroperoxides[d]	nd	0.439	0.580

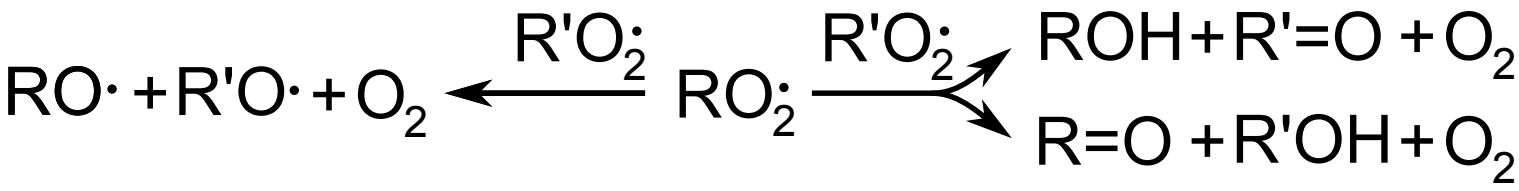
*Heimann, et al. IJCK, **34**, 126–138 (2002).*

Cannot Be From Only RO·

RO· reactivity:



In low NOx, RO· generated from peroxy-peroxy radical reactions



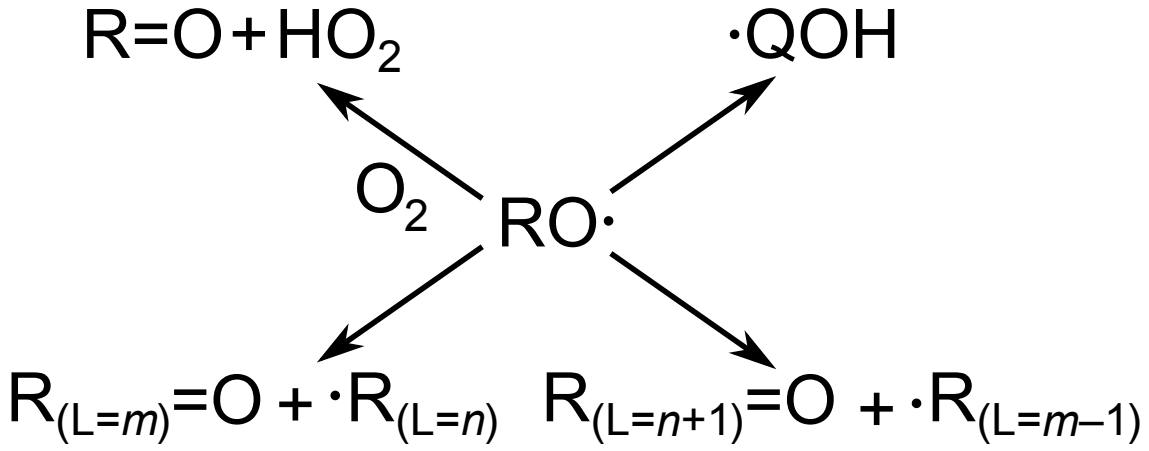
Rate constants:

- $1^\circ \rightarrow 1^\circ$: $k = 1 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}
- $2^\circ \rightarrow 2^\circ$: $k = 5 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}

Ziemann and Atkinson, Chem. Soc. Rev. 2012.

Cannot Be From Only RO·

RO· reactivity:



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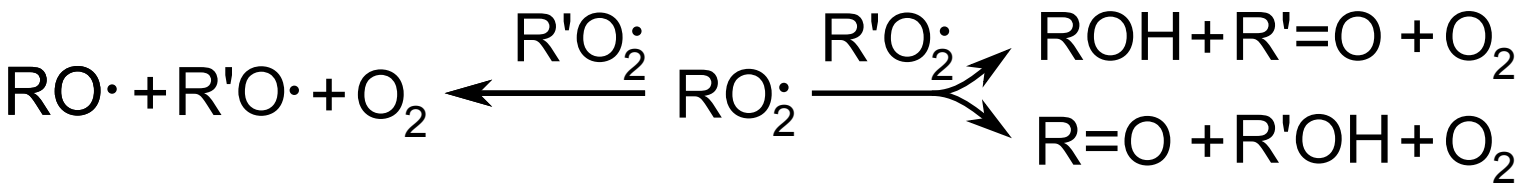

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Ziemann and Atkinson, Chem. Soc. Rev. 2012.

Estimating the Branching Ratio

Large molecule

- Fast intramolecular vibrational redistribution
- Nonthermal distributions (as from photon) can be treated as Boltzmann with elevated temp.
- Good for systems with more than 25 oscillators

$$E_{h\nu} - E_b = kT^* + \frac{r}{2}kT^* + \sum_{\mathrm{p}\in\mathrm{products}} \sum_{i=1}^{N} \frac{\epsilon_{p,i}}{\exp(\epsilon_{p,i}/kT^*)},$$

$E_{h\nu}$: Photon energy
E_b: Bond energy
k: Boltzmann const.
r: Num rot. dof
N: Num. vibrations
$\epsilon_{p,i}$: vib. freq.

Iteratively solve for T^* for given $E_{h\nu} - E_b$.

Georgiou and Wight, JCP, 1988;
Baer and Hase, Unimolecular Reaction Dynamics, 1996

Boltzmann Temperature

- Large photoexcited molecules can be treated as thermal at elevated T^*

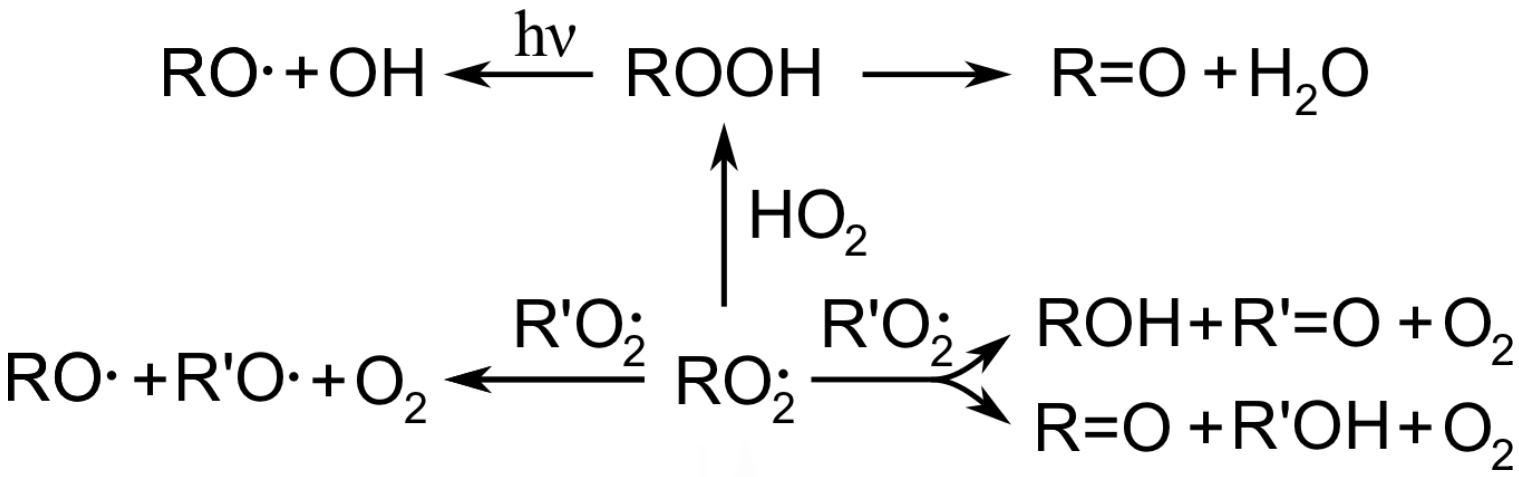
$$E_{h\nu} - E_b = kT^* + \frac{r}{2}kT^* + \sum_{\mathrm{p}\in\mathrm{products}} \sum_{i=1}^{N} \frac{\epsilon_{p,i}}{\exp(\epsilon_{p,i}/kT^*)},$$

$E_{h\nu}$: Photon energy
E_b: Bond energy
k: Boltzmann const.
r: Num rot. dof
N: Num. vibrations
$\epsilon_{p,i}$: vib. freq.

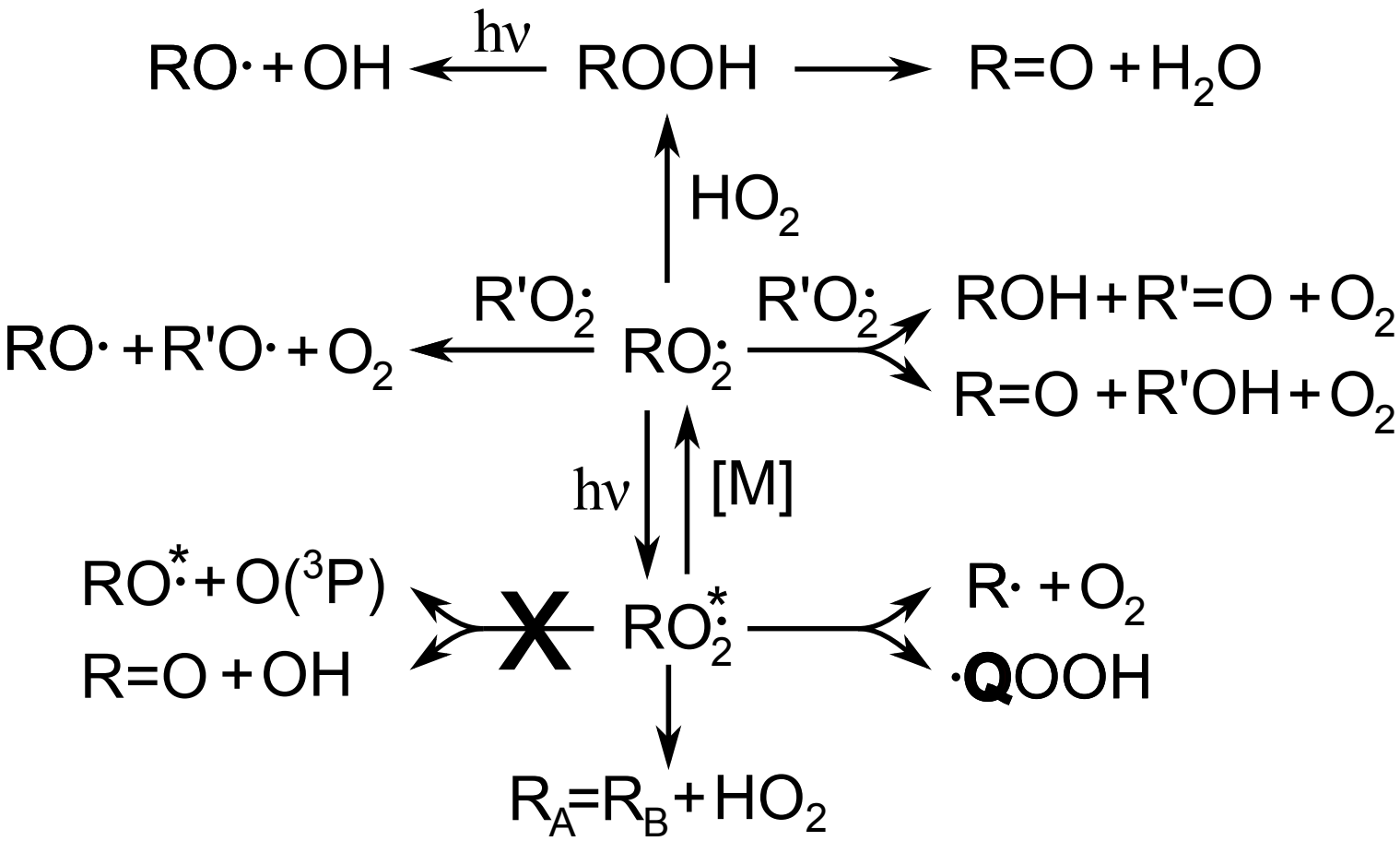
- $\mathrm{DDAO_2}\cdot \xrightarrow{h\nu} \mathrm{DDAO_2}\cdot^*$; nascent $T^*(\mathrm{DDA{-}O_2}\cdot^*) = 1440\,\mathrm{K}$
- $\mathrm{DDAO_2}\cdot^* \longrightarrow \cdot\mathrm{DDAOOH}$; nascent $T^*(\cdot\mathrm{DDA{-}OOH}) = 1520\,\mathrm{K}$
- $\mathrm{DDAO_2}\cdot^* \longrightarrow \mathrm{DDA}\cdot + \mathrm{O_2}$; nascent $T^*(\mathrm{DDA}\cdot) = 1047\,\mathrm{K}$

"Combustion" for first few nanoseconds.

Peroxy Radical Channels



Peroxy Radical Channels



Computationally Intractable

- Ideally, model all possible isomers
- Computationally Intractable (cross reactions of $8!$ species per moiety added)
- Lump by considering only order in which moieties add:
  - $C_8I \xrightarrow{h\nu} C_8\cdot + \cdot I$
  - C_8OH = any octanol isomer
  - $C_8{=}O$ = any octanone isomer (or octanal)
  - e.g. $C_8OH{=}O$ = hydroxyketone formed from $C_8O\cdot$ isomerization
  - e.g. $C_8OOH{=}O$ = hydroperoxyketone formed two separate radical formation steps:
    - $C_8O_2\cdot + HO_2\cdot \longrightarrow C_8OOH + O_2$
    - $H{-}C_8OOH + OH \longrightarrow \cdot C_8OOH + H_2O$
    - $\cdot C_8OOH + O_2 \longrightarrow C_8OOHO_2\cdot$
    - ...

The Generative Model

- Generate a list of species:
  - All possible permutations of OH, C=O, and OOH
  - Up to four possible substituents
- Substitute into generative model reactions
  - Model includes peroxy formation: $R_i\cdot + O_2 \longrightarrow R_iO_2\cdot$
  - Also includes alkoxy reactions
  - All peroxy-peroxy cross reactions ($R_iO_2\cdot + R_jO_2\cdot$) where the R_j iterates over entire list.
  - Necessary to ensure all peroxy radical load properly considered.
  - Alkoxy and peroxy radical termination with O_2 and HO_2
  - 904 species and 23 148 reactions
- Integrate with and without peroxy photochemistry