



Does water complexation affect the reaction of β -hydroxyethylperoxy with NO?

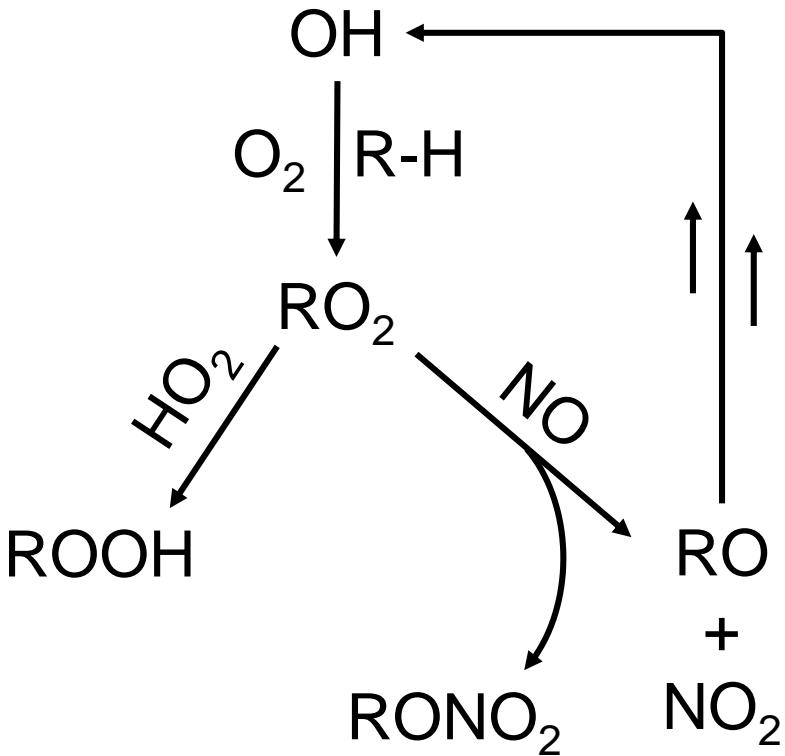
Frank A. F. Winiberg, Aileen Hui, Kristen Zuraski,
Matthew D. Smarte, Rebecca L. Caravan, Greg Jones,
Joseph Messinger, Mitchio Okumura, David Osborn,
Carl. J. Percival, Craig Taatjes and Stanley P. Sander



Jet Propulsion Laboratory
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Organic Nitrates – RONO₂



Important sink for nitrogen oxides (NO_x) and HO_x radicals (OH and HO₂)

Understanding important:

- Atmosphere Oxidative Capacity
- Tropospheric Ozone Prediction
- SOA formation

Isoprene-derived nitrates:

- Possibly 25 - 50% of total

β -hydroxyperoxy radicals

OH + unsaturated hydrocarbons

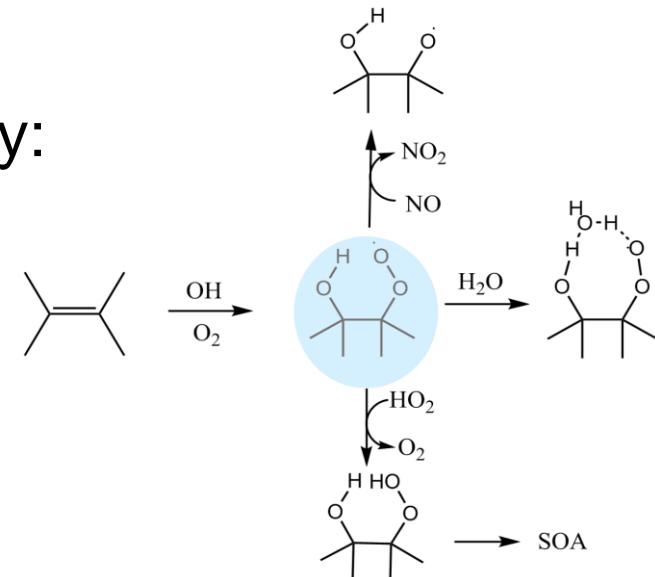
Experimental work - β -hydroxyethylperoxy:

- $\sim 6x k$ @ 50% RH between 298 and 270 K

Theoretical work:

- Expt supported by formation of $\text{RO}_2\text{-H}_2\text{O}$ complex

Possibility: $\sim 14\%$ RO_2 complexed with H_2O



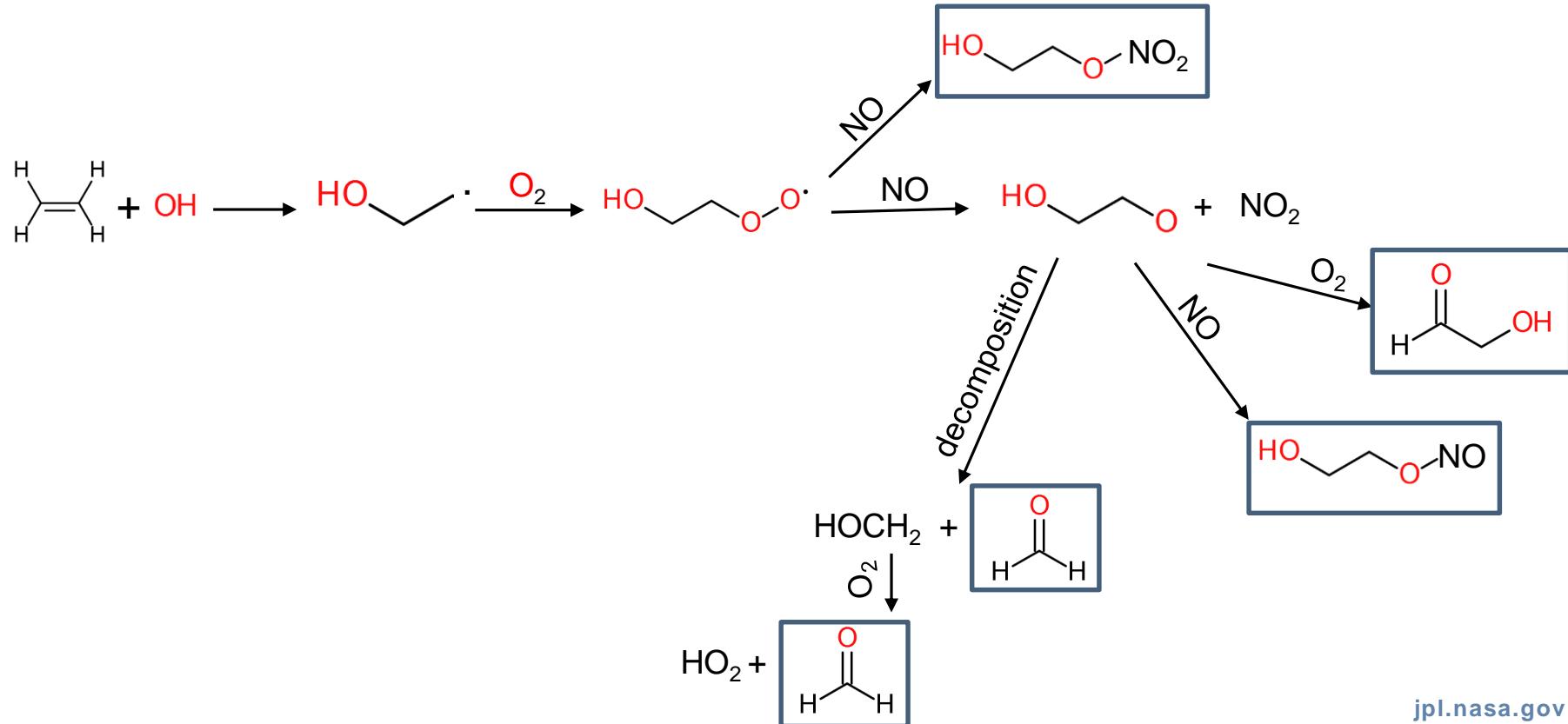
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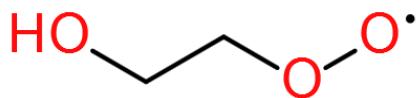
Shirts et al., *Theor. Chem. Acc.*, 2018, **137**, 96.

Khan et al., *Atmos. Environ.*, 2015, **106**, 278-287.

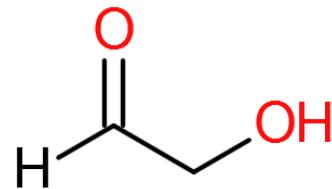
The Plan...



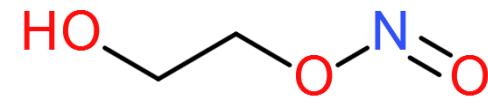
Key Species



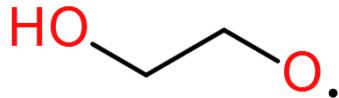
Hydroxyethyl peroxy



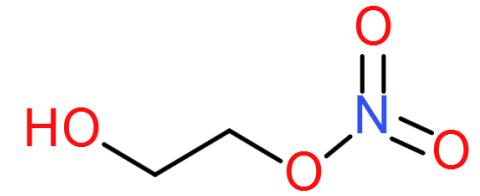
Glycolaldehyde



Hydroxyethyl nitrite



Hydroxyethyl alkoxy



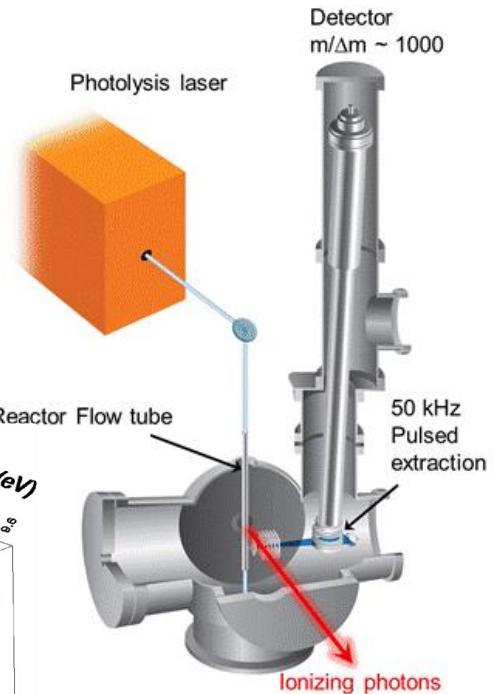
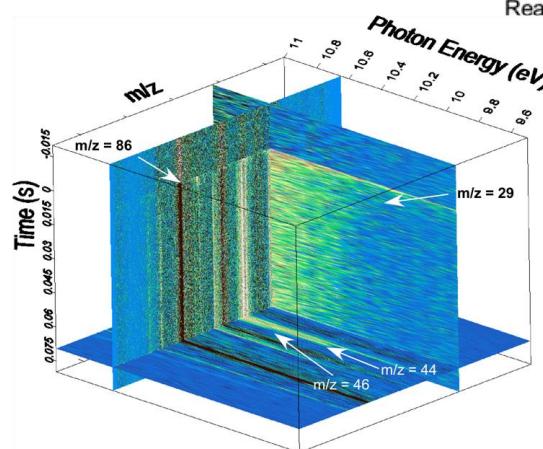
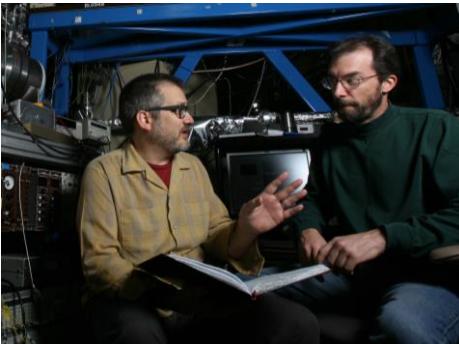
Hydroxyethyl nitrate

PIMS at the ALS

Photoionization Mass Spectrometry

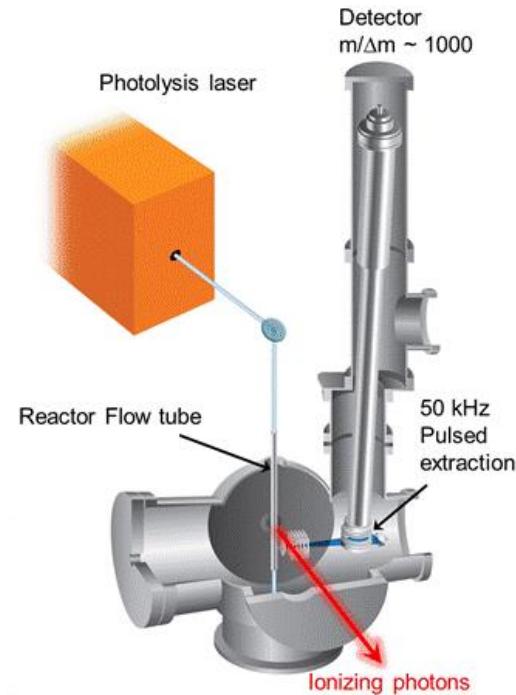
At the Advanced Light Source, Berkeley

Collaboration with Combustion Research Facility at Sandia National Labs



PIMS at the ALS

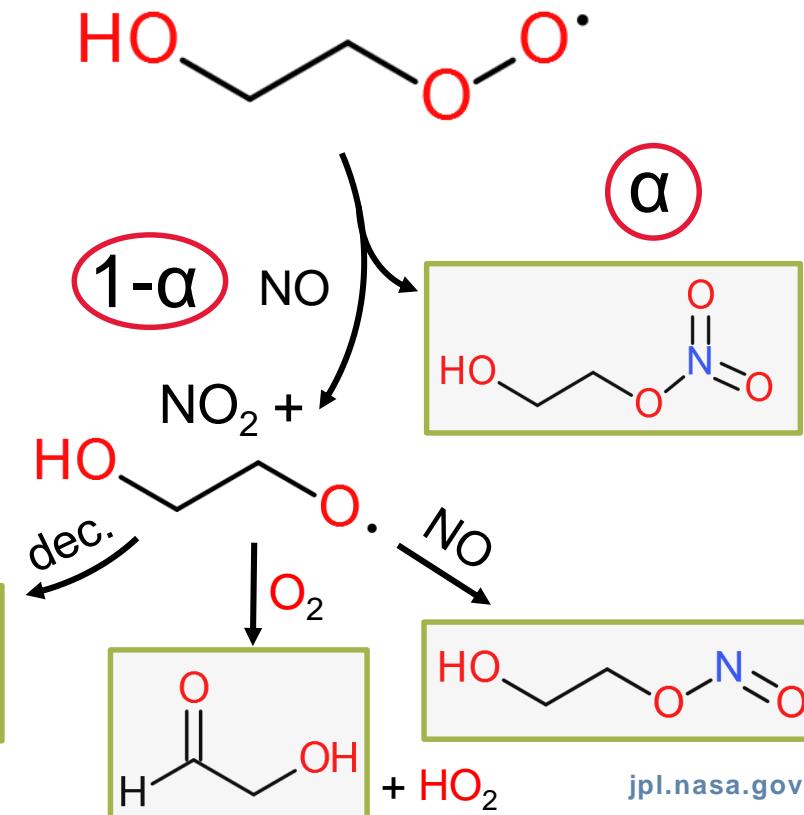
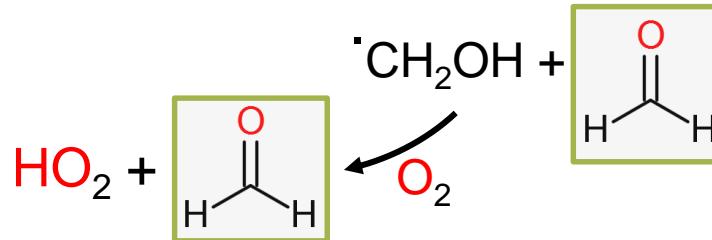
- 30 Torr He
- 280 and 300 K
- 10% O₂
- [H₂O] = 0 – 5 × 10¹⁶ cm⁻³
- H₂O₂ photolysis at 248 nm



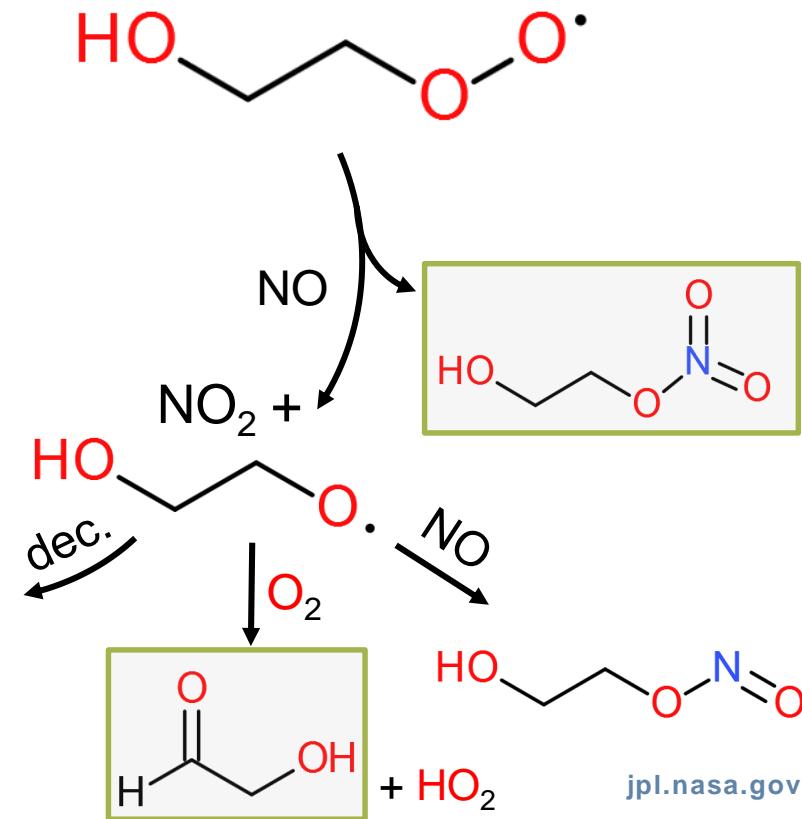
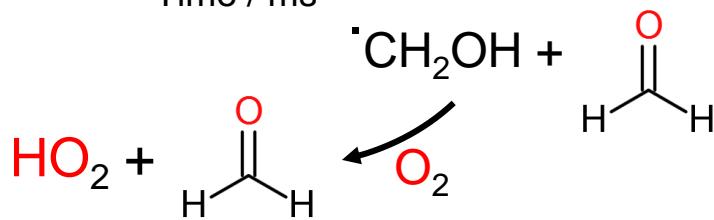
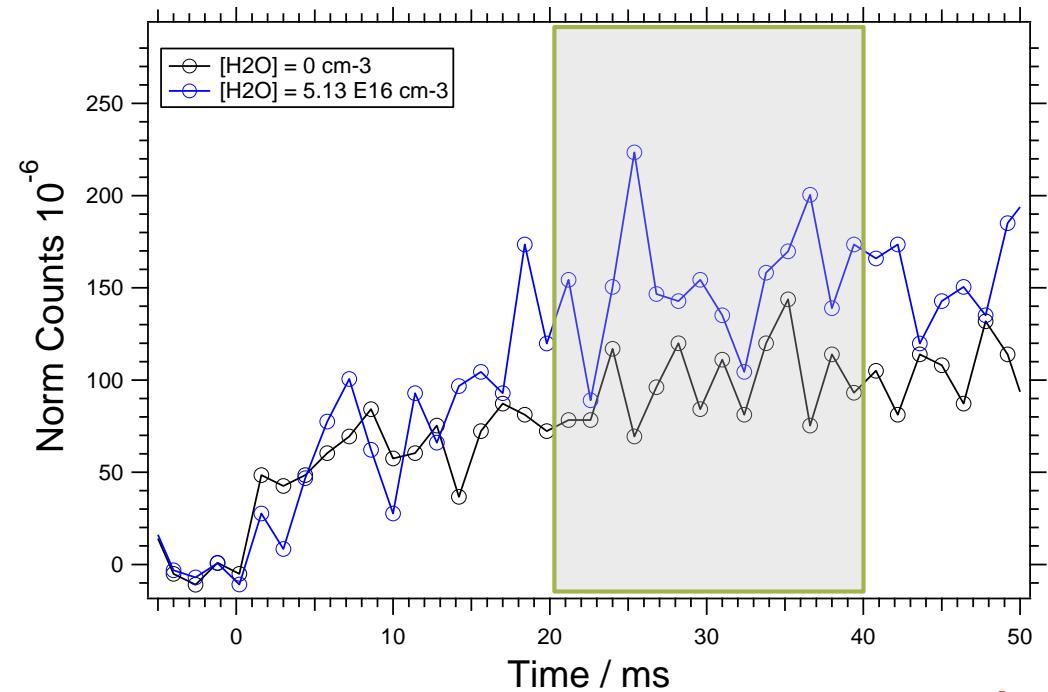
“Yield” Method

$$\alpha = \frac{[\text{Nitrate}]}{([\text{HCHO}] * 0.5) + [\text{GALD}] + [\text{Nitrite}]}$$

Relative change vs H_2O

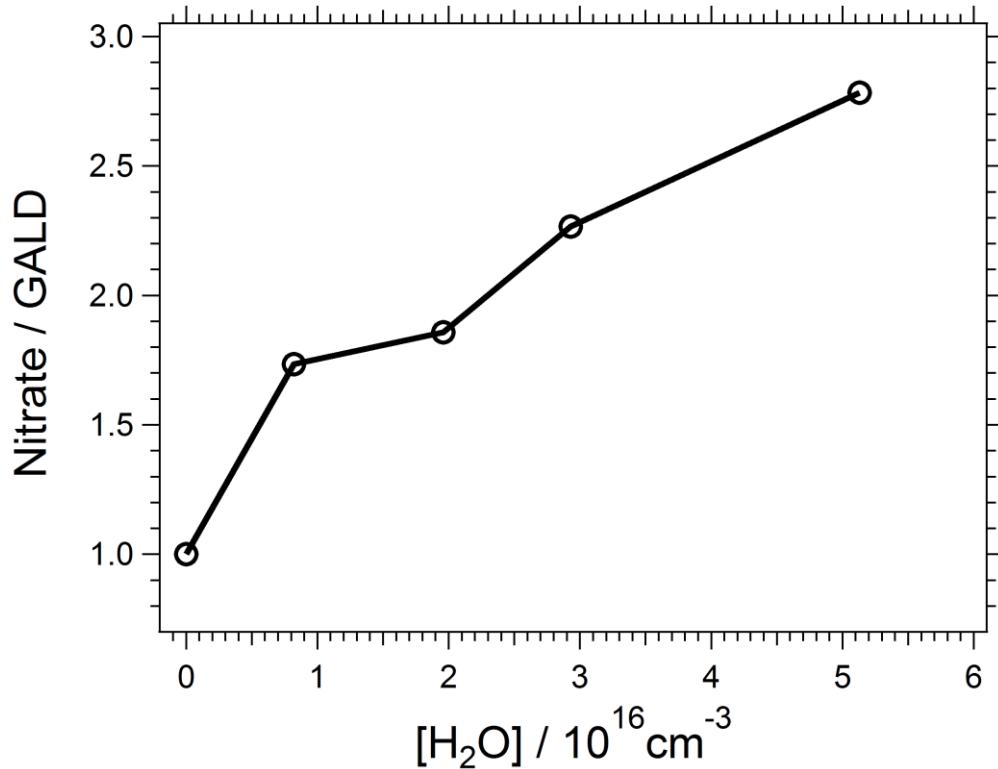


Nitrate Results



Results

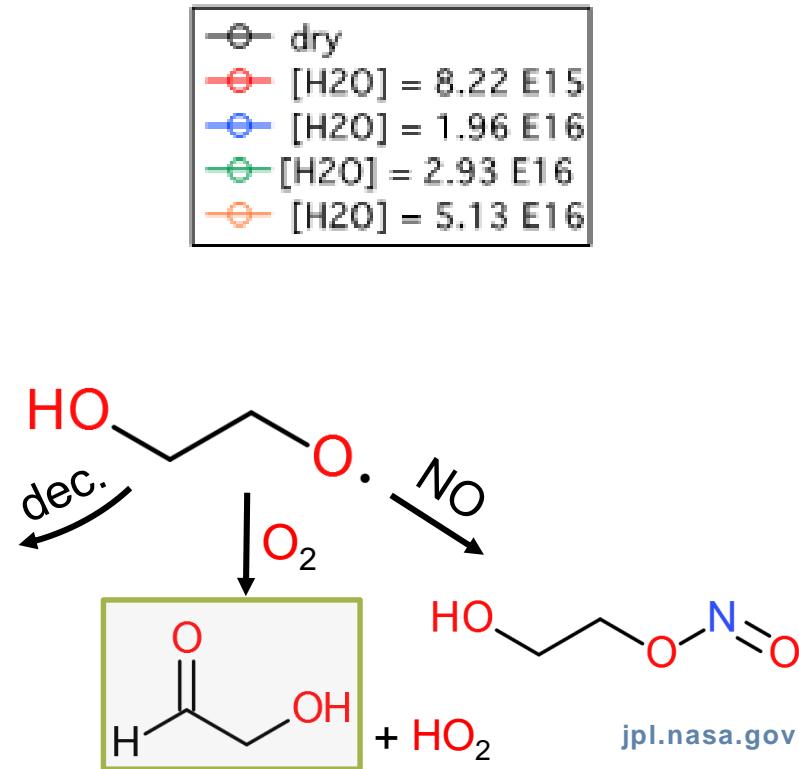
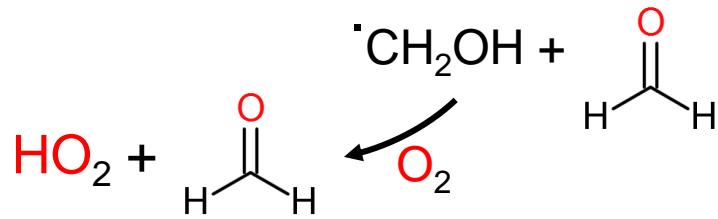
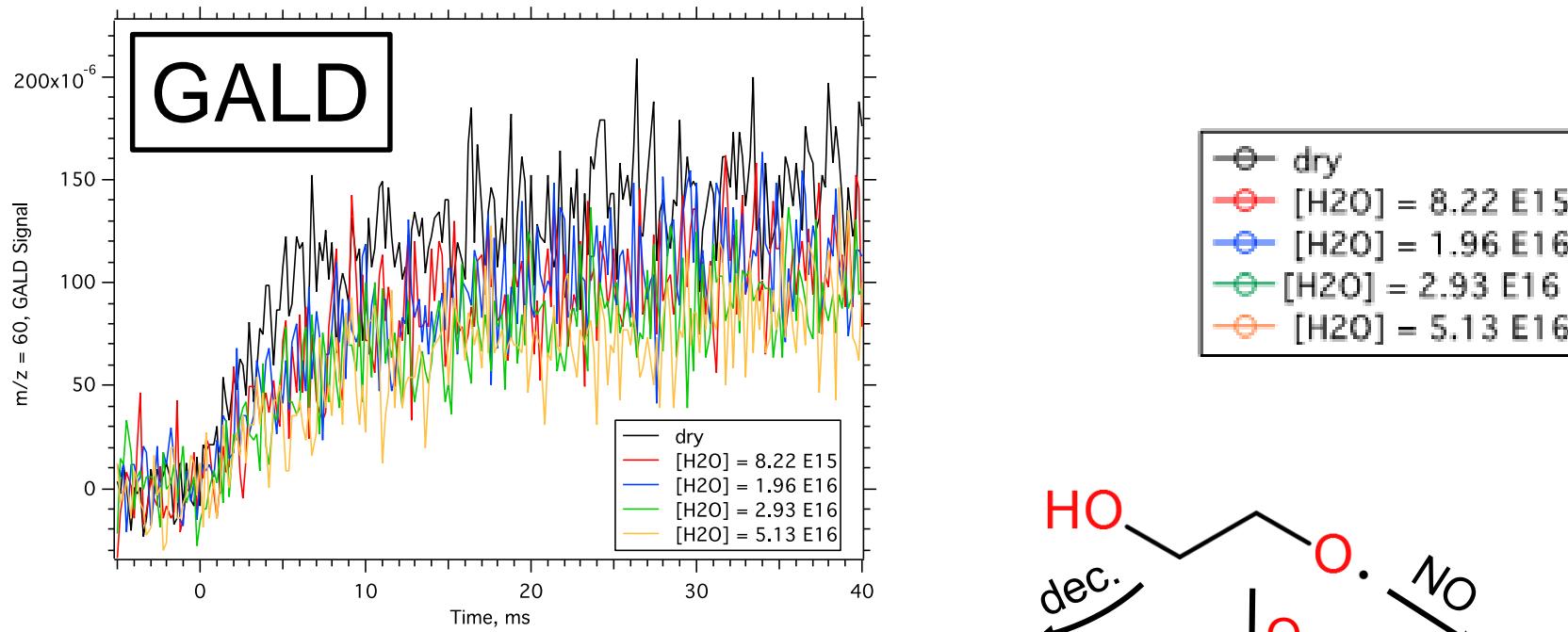
- Increase with H_2O !
- Larger nitrate yield at higher $[\text{H}_2\text{O}]$



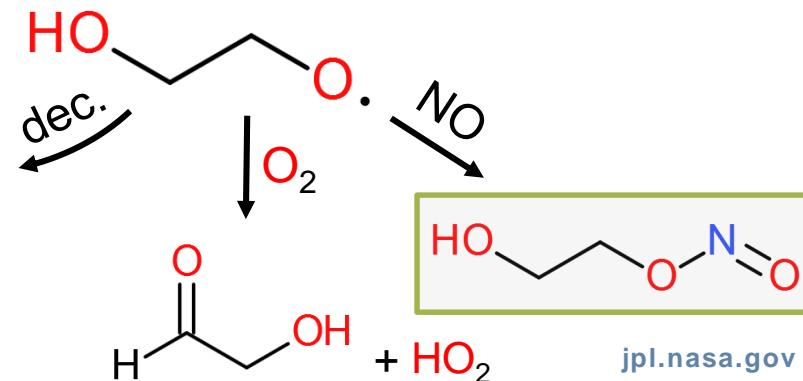
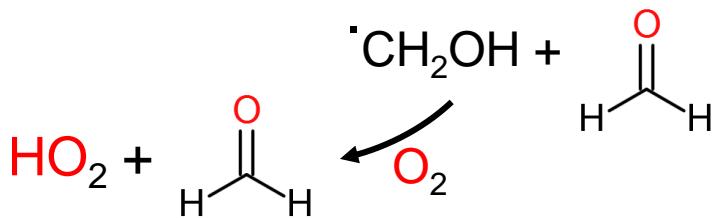
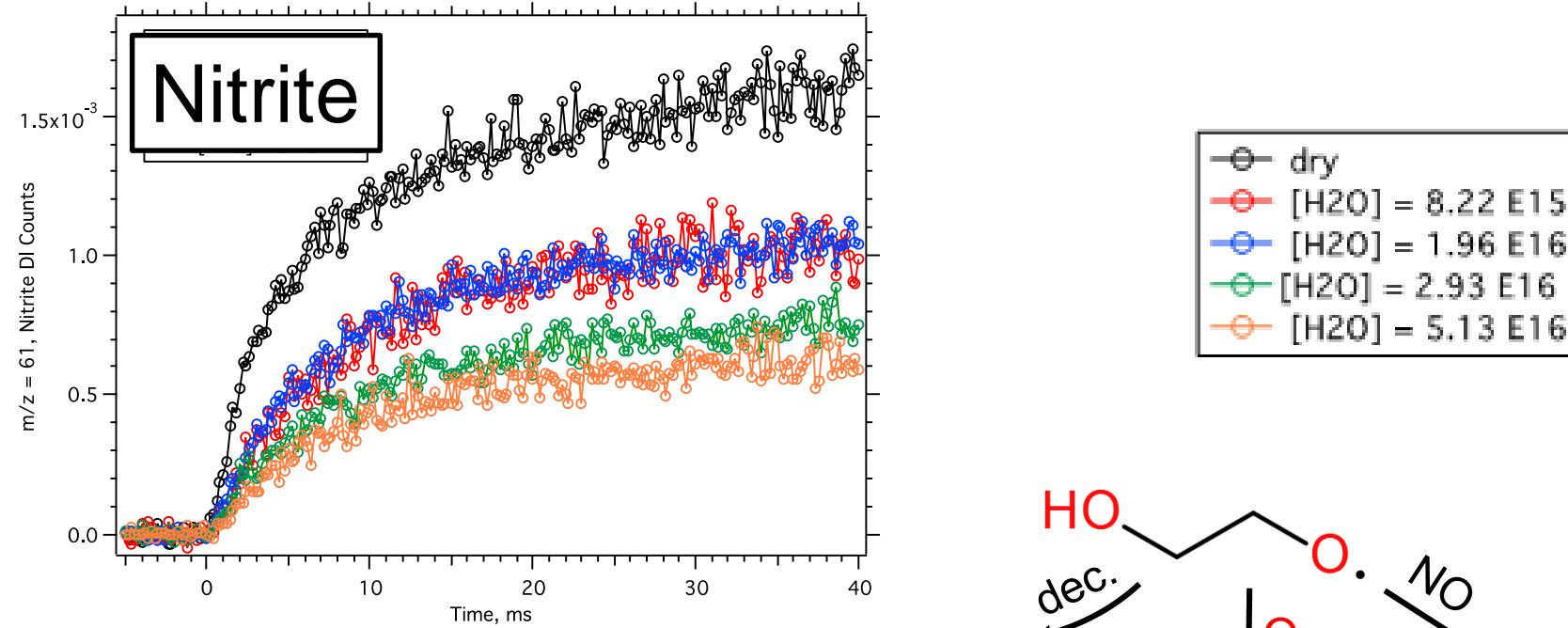
**Does water complexation affect the
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Maybe...?

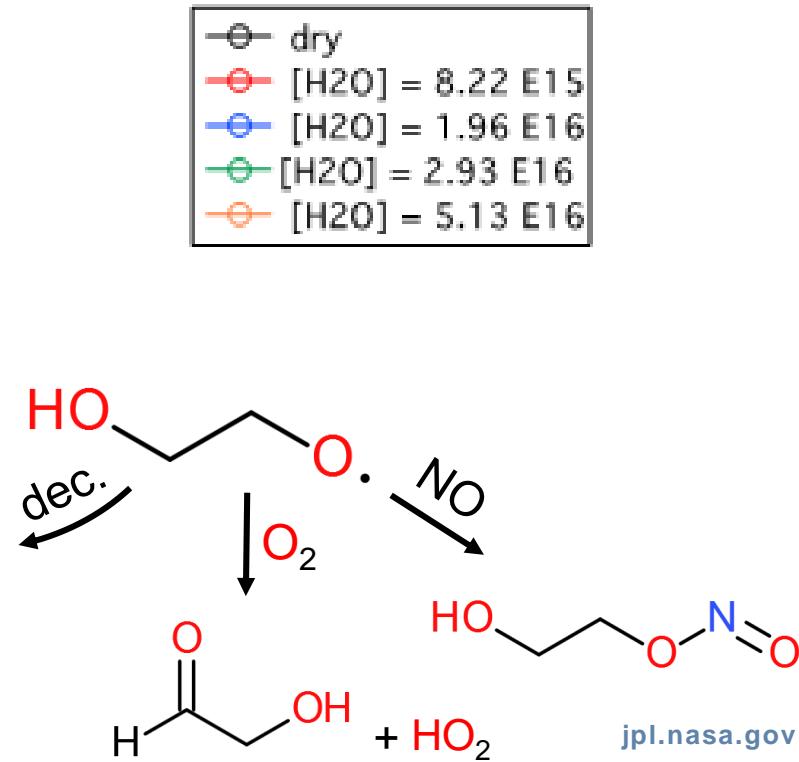
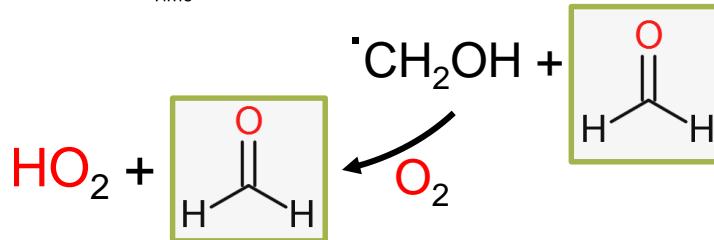
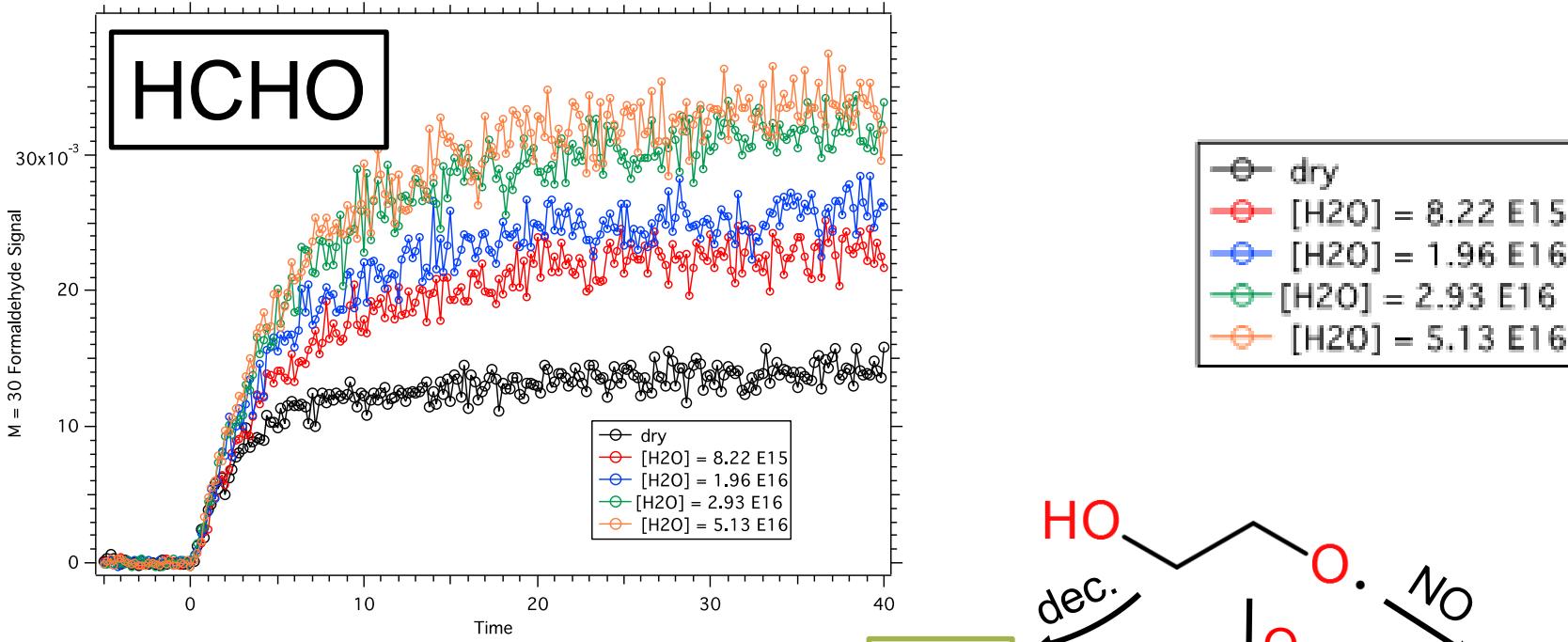
Alkoxy Chemistry



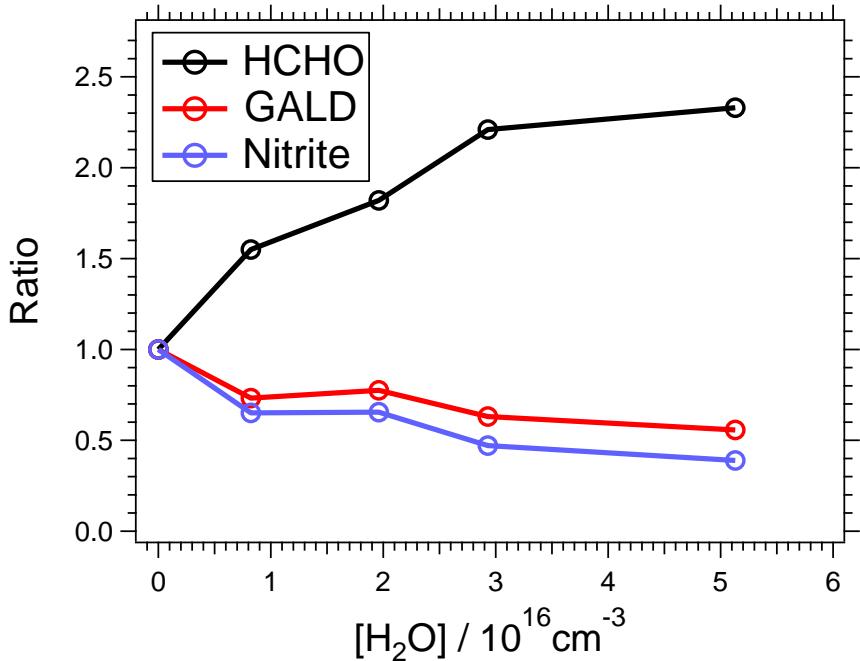
Alkoxy Chemistry



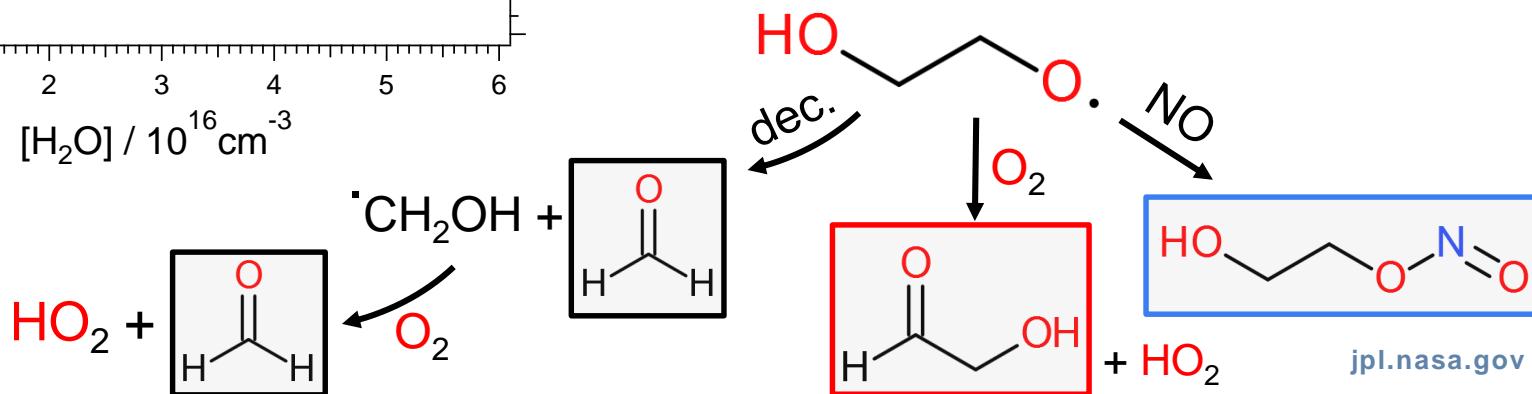
Alkoxy Chemistry



Alkoxy Chemistry



Anti-correlation of HCHO with Nitrite and Glycolaldehyde (GALD)



Discussion?

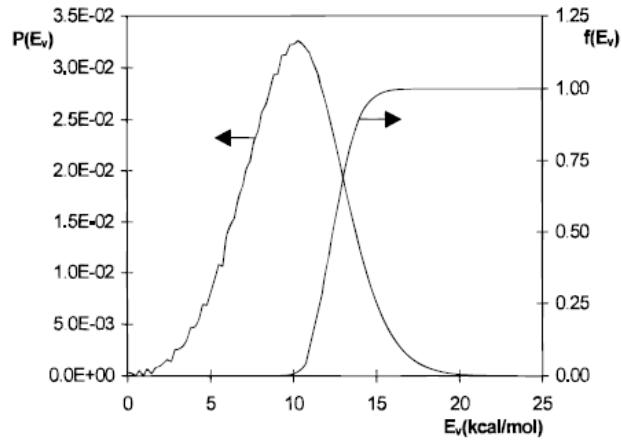
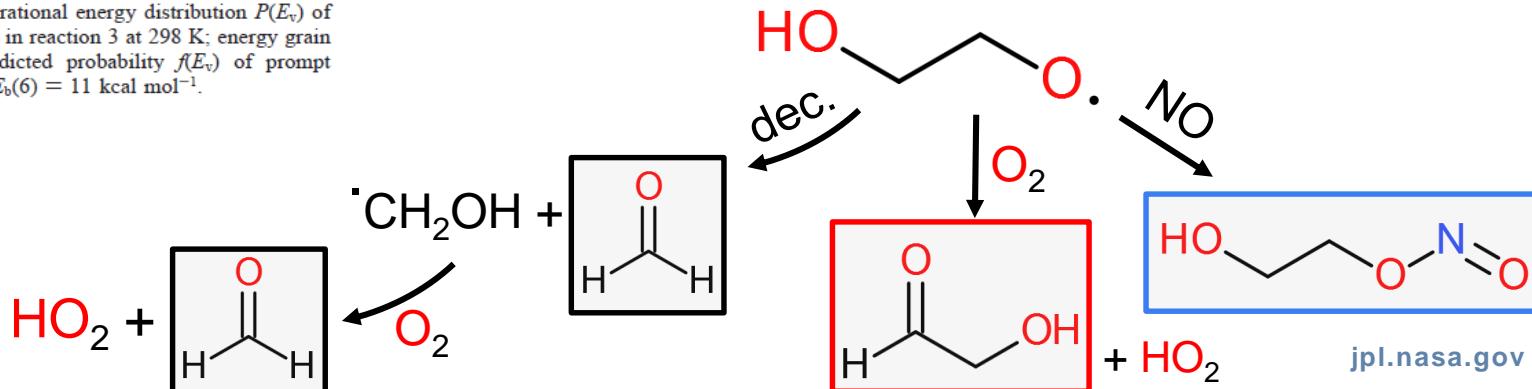
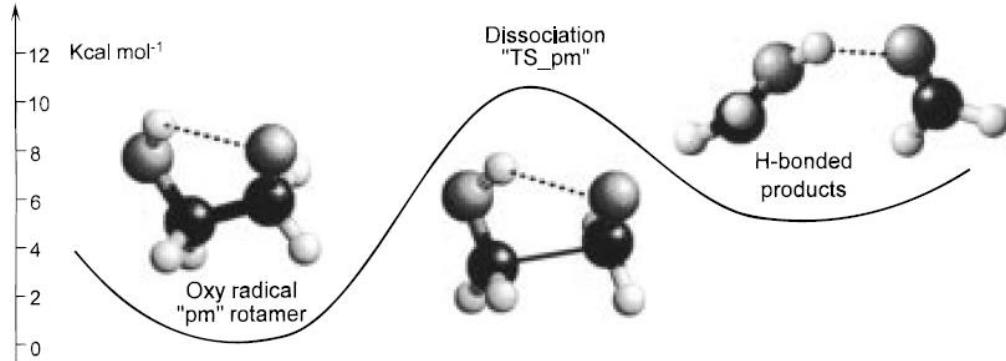


Figure 5. Predicted nascent vibrational energy distribution $P(E_v)$ of the $\text{HOCH}_2\text{CH}_2\text{O}$ radical formed in reaction 3 at 298 K; energy grain size = 0.239 kcal mol $^{-1}$. Predicted probability $f(E_v)$ of prompt dissociation at 760 Torr N $_2$ for $E_b(6) = 11$ kcal mol $^{-1}$.



Summary

β -hydroxyethylperoxy + NO reaction studied under varying H₂O conditions at 298 K

So far:

- Relative change in Hydroxy Ethyl Nitrate measured
- Hydroxy Ethyl Nitrate seen to increase with increased [H₂O]
- Could imply larger organic nitrate yields under humid conditions?

Bonus chemistry:

- Anti-correlation of alkoxy products (decomp vs bi-mol) implies effect on alkoxy fate as a function of water
- Anyone fancy some calculations?
- More to follow...

Acknowledgements

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Bruce Rude and Oleg Kostko

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NASA Postdoctoral Program

Advanced Light Source

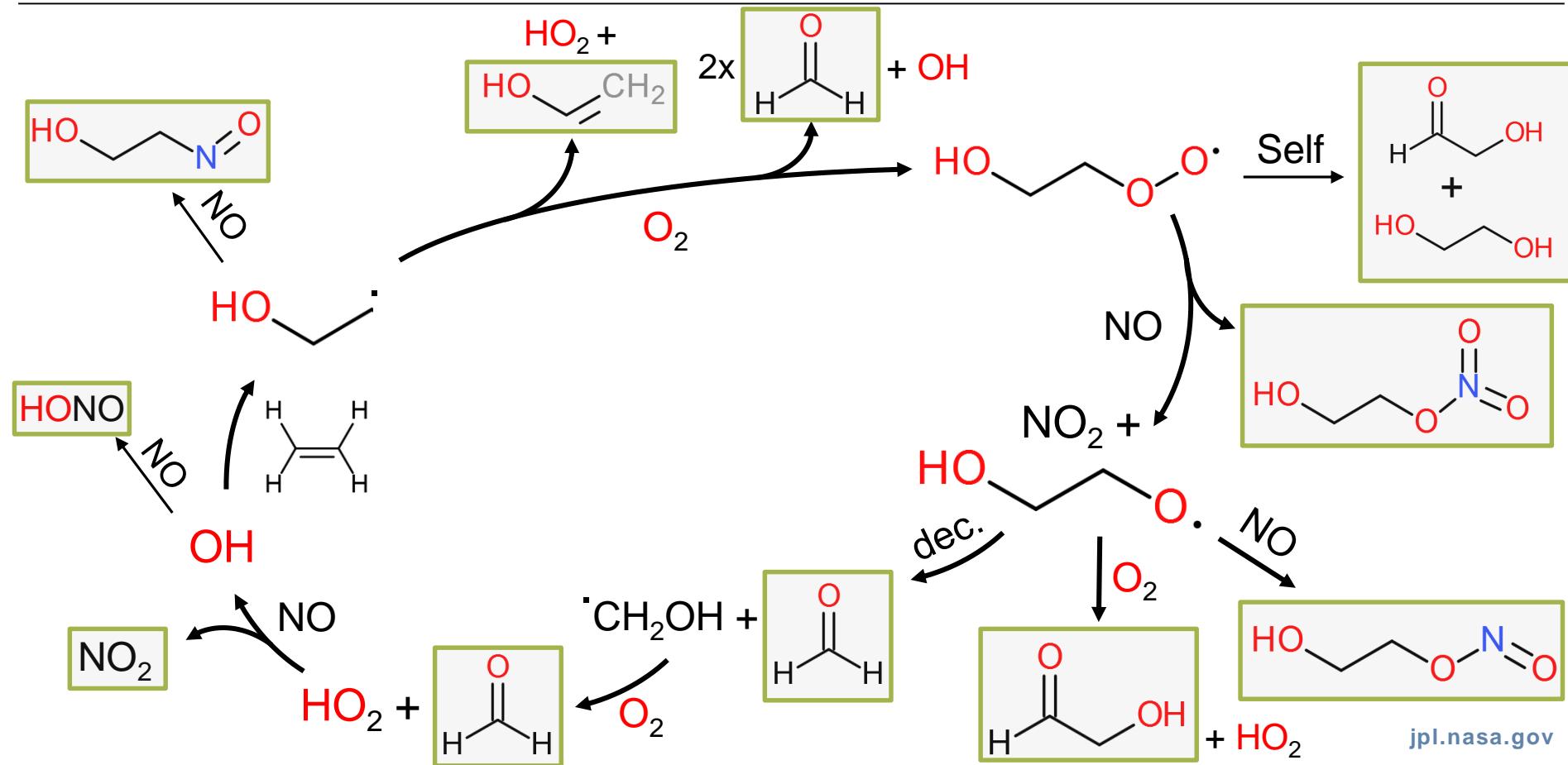




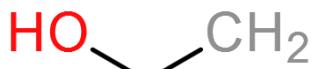
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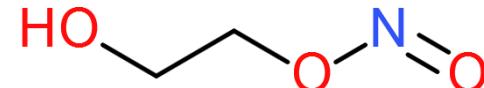
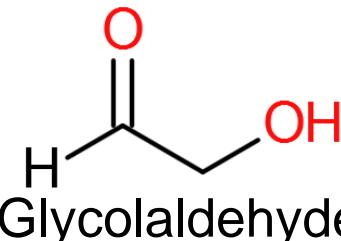
... the reality



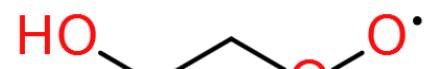
Key Species



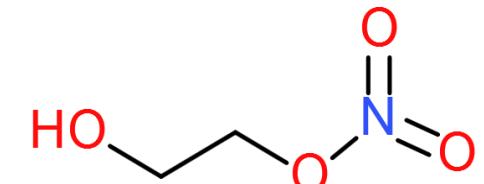
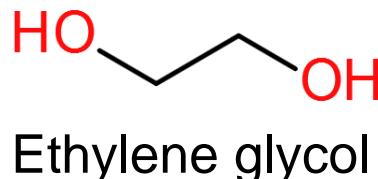
Vinyl alcohol



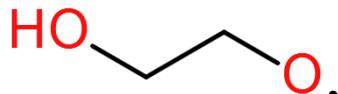
Hydroxyethyl nitrite



Hydroxyethyl peroxy



Hydroxyethyl nitrate



Hydroxyethyl alkoxy

