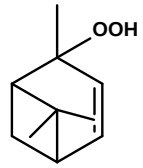
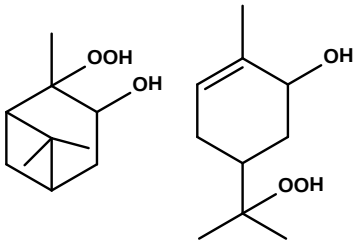
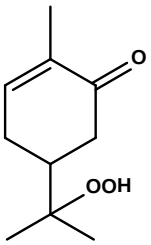
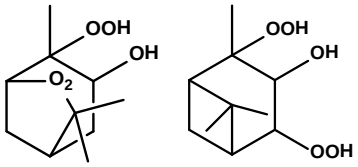
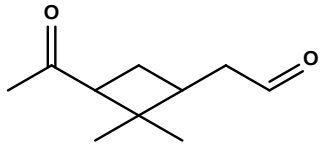
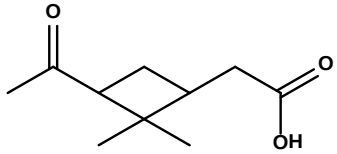
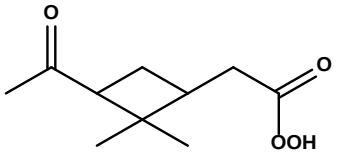
Table S1 – Photooxidation products from low-NO_x

Structure	Name Abbreviation	Molecular Weight	Detected at By CIMS
	α-pinene hydroperoxide APINENEOOH	168.228	253
	α-pinene hydroxyl hydroperoxide APINENEOHOOH	186.244	271
	α-pinene hydroperoxy carbonyl APINENEOOHO	184.228	269
	a-pinene hydroxyl dihydroperxide APINENEOHOOHOOH	218.244	303
	Pinonaldehyde PINON	168.288	(+) 169
	Pinonic acid PINON ACID	184.228	203, 269 Ratio of 9:1 for 203:269
	Pinonic peracid PINON PERACID	200.228	219, 285 Ratio 1:4 for 219:285

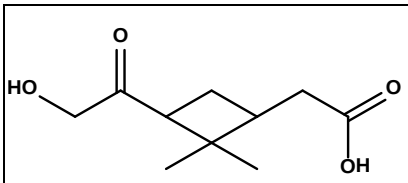
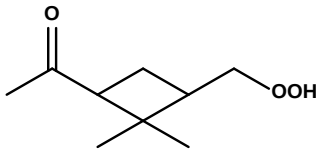
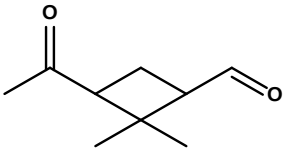
	10-hydroxy pinonic acid 10-OH PINON ACID	200.228	219, 285
	C9OOH	172.218	257
	Norpinonaldehyde NORPINON	154.202	(+) 155

Table S2 – Kinetic model of low-NO_x α-pinene photooxidation

Reaction	Rate constant / photolysis rate[a,b]	Reference[c]
$H_2O_2 \xrightarrow{h\nu} 2\ OH$	$j_1 = 2.25x10^{-6}$	Sander, 2006
$OH + H_2O_2 \rightarrow HO_2 + H_2O$	$k_1 = 1.8x10^{-12}$	Sander, 2006
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$k_2 = 1.5x10^{-12}$	Sander, 2006
$OH + OH \rightarrow H_2O_2$	$k_3 = 6.28x10^{-12}$	Sander, 2006
$OH + HO_2 \rightarrow O_2 + H_2O$	$k_4 = 1.1x10^{-10}$	Sander, 2006
$APINENE + OH \rightarrow APINENEOH^{\bullet}$	$k_5 = 4.8x10^{-11}$ [d]	Atkinson, 2006
$\rightarrow APINENE^{\bullet} + H_2O$	$k_6 = 5.4x10^{-12}$ [d]	Atkinson, 2006
	$k_{total} = 5.34x10^{-11}$	
$APINENE^{\bullet} + O_2 \rightarrow APINENEOO^{\bullet}$	*Instantaneous*	
$APINENEOO^{\bullet} + HO_2 \rightarrow APINENEOOH + O_2$	$k_7 = 1.2x10^{-11}$	
$\rightarrow$ Products	$k_8 = 8.0x10^{-12}$	
	$k_{total} = 2.0x10^{-11}$	
$APINENEOH^{\bullet} + O_2 \rightarrow APINENEOHOO^{\bullet}$	*Instantaneous*	

APINENEOHOO$^{\bullet}$ + HO_2 $\rightarrow$ APINENEOHOOH	$k_9 = 5.1x10^{-12}$	
$\rightarrow$ PINON + O_2 + OH	$k_{10} = 4.0x10^{-12}$	
$\rightarrow$ APINENEOHOOHOOH	$k_{11} = 4.2x10^{-13}$	
$\rightarrow$ APINENEOH other products	$k_{12} = 1.05x10^{-11}$	
	$k_{total} = 2.0x10^{-11}$	
APINENEOHOO$^{\bullet}$ + APINENEOHOO$^{\bullet}$ $\rightarrow$ Products	$k_{13} = 2.0x10^{-12}$	
APINENEOHOOH $\xrightarrow{h\nu}$ PINON + OH	$j_2 = 1.46x10^{-6}$	
APINENEOHOOH + OH $\rightarrow$ PINON	$k_{14} = 1.2x10^{-11}$	
$\rightarrow$ APINENEOHOO$^{\bullet}$ + H_2O	$k_{15} = 1.1x10^{-11}$	
$\rightarrow$ APINENEOHOOH$^{\bullet}$	$k_{16} = 2.4x10^{-12}$	
	$k_{total} = 2.54x10^{-11}$	
APINENEOHOOH$^{\bullet}$ + O_2 $\rightarrow$ APINENEOHOOHOO$^{\bullet}$	*Instantaneous*	
PINON $\xrightarrow{h\nu}$ Products	$j_3 = 7.26x10^{-6}$	Atkinson, 2006
PINON + OH $\rightarrow$ PINON$^{\bullet}$ + H_2O	$k_{17} = 3.7x10^{-11}$	Atkinson, 2006 Davis, 2007
PINON$^{\bullet}$ + O_2 $\rightarrow$ PINONOO$^{\bullet}$	*Instantaneous*	
PINONOO$^{\bullet}$ + HO_2 $\rightarrow$ PINON ACID + O_3	$k_{18} = 5.0x10^{-12}$	
$\rightarrow$ PINON PERACID + O_2	$k_{19} = 5.0x10^{-12}$	
$\rightarrow$ C9OOH + CO_2	$k_{20} = 2.8x10^{-12}$	
$\rightarrow$ NORPINON	$k_{21} = 2.2x10^{-12}$	
$\rightarrow$ Products	$k_{22} = 5.0x10^{-12}$	
	$k_{total} = 2.0x10^{-11}$	
APINENEOOH + OH $\rightarrow$ APINENEOOHOH$^{\bullet}$	$k_{23} = 4.0x10^{-11}$	
APINENEOOHOH$^{\bullet}$ + O_2 $\rightarrow$ APINENEOHOOHOO$^{\bullet}$	*Instantaneous*	
APINENEOHOOHOO$^{\bullet}$ + HO_2 $\rightarrow$ APINENEOHOOHOOH + O_2	$k_{24} = 1.1x10^{-11}$	
$\rightarrow$ Products	$k_{25} = 9.0x10^{-12}$	
	$k_{total} = 2.0x10^{-11}$	

APINENEOOHOHOOH + OH $\rightarrow$ Products $k_{26} = 4.0x10^{-11}$

[a] Units: Rate constants cm^3 $molecule^{-1}$ s^{-1}, photolysis rates s^{-1}

[b] Photolysis rates calculated from absorption cross sections and the spectral radiance of the chamber lights

[c] Reactions without a reference listed were determined here, see text for details

[d] Total Rate constant for α-pinene + OH ($k_5 + K_6$) is from the Atkinson, 2006. Each individual rate constant represents the branching ratio of the reaction between OH addition to the double bond and H-abstraction by OH.

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II - gas phase reactions of organic species, Atmos. Chem. Phys., 6, 3625-4055, 2006.

Davis, M. E., Talukdar, R. K., Notte, G., Ellison, G. B., and Burkholder, J. B.: Rate coefficients for the OH plus pinonaldehyde ($C_{10}H_{16}O_2$) reaction between 297 and 374 K, Environ. Sci. Technol., 41, 3959-3965, 2007.

Sander, S. P., Finlayson-Pitts, B. J., Friedl, R. R., Golden, D. M., Huie, R. E., Kolb, C. E., Kurylo, M. J., Molina, M. J., Moortgat, G. K., Orkin, V. L., and Ravishankara, A. R.: Chemical kinetics and photochemical data for use in atmospheric studies, evaluation number 15, Jet Propulsion Laboratory, Pasadena, CA, 2006.

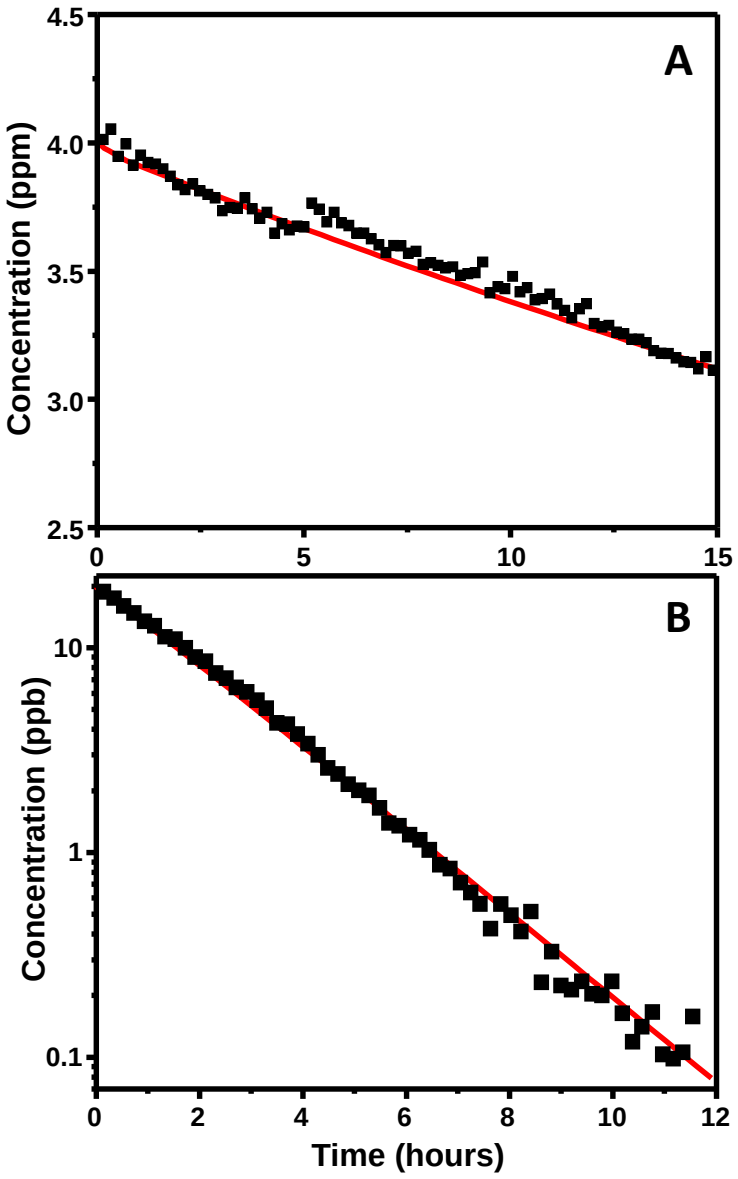


Figure S1 – Photolysis of H_2O_2 (A) by black lights in the Caltech environmental chamber and Consumption of α-pinene by OH (B) during the same experiment. In each case the black squares are the data and the red line is the simulation from the kinetic model from Table S2. The concentration of α-pinene is plotted on a log scale to show the first order kinetics.

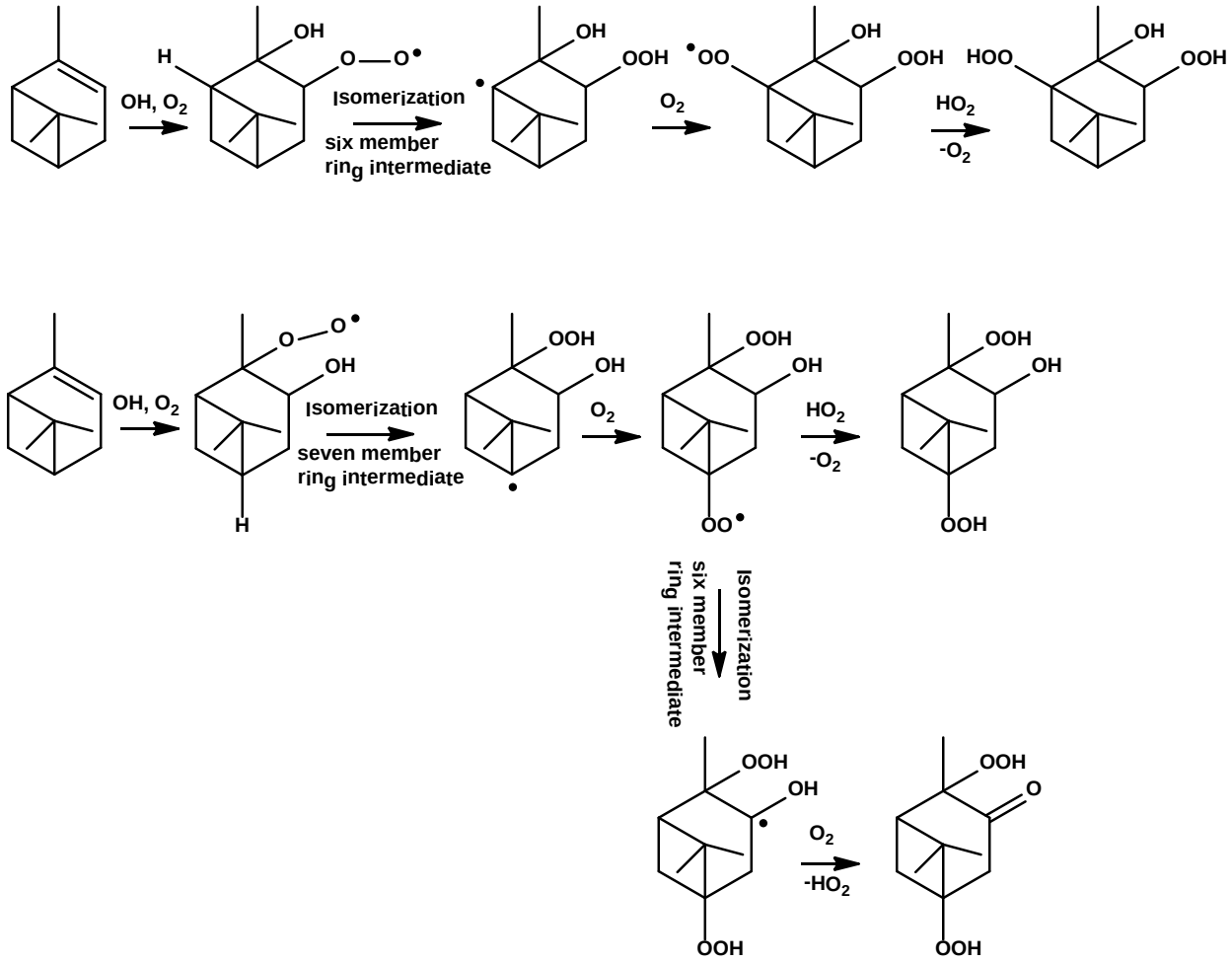


Figure S2 – Proposed mechanism of peroxy radical isomerization from addition of OH to either the tertiary or secondary carbon of the double bond of α-pinene.

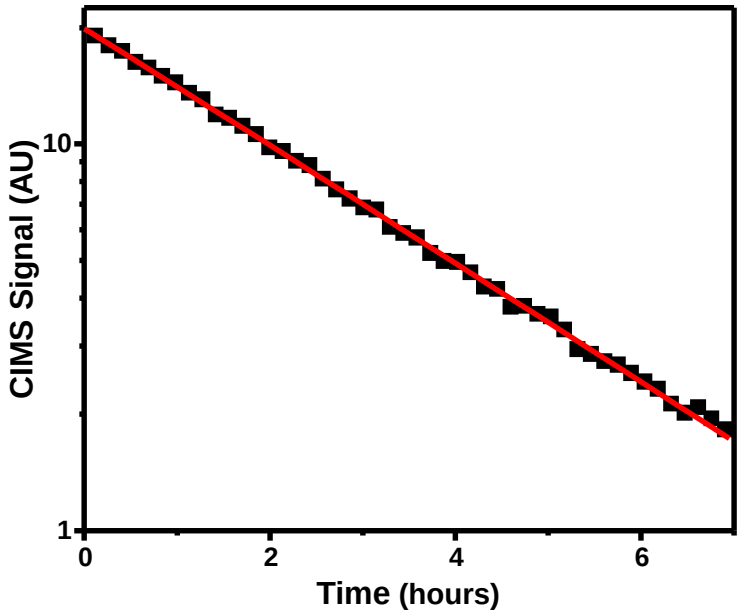


Figure S3 – Signal of pinonaldehyde from direct injection in the presence of 4 ppm H_2O_2 photolyzed by black lights. The simulation (red line) incorporates both reaction with OH (k_{OH} = 3.7 x 10^{-11} cm^3 $molecules^{-1}$ s^{-1}) and photolysis (j = 7.26 x 10^{-6} s^{-1}).