

## Supplementary Data

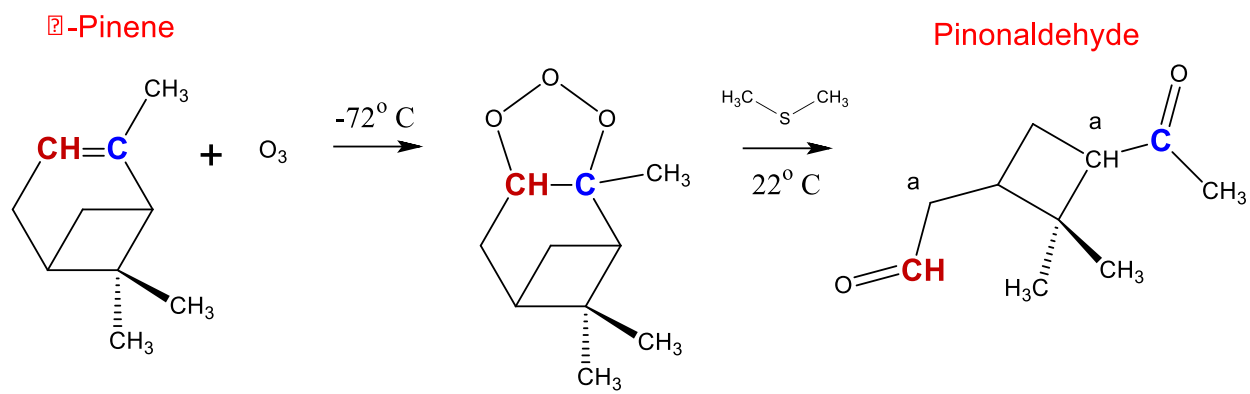
### Simulations of smog-chamber experiments using the two-dimensional-volatility basis set: linear oxygenated precursors

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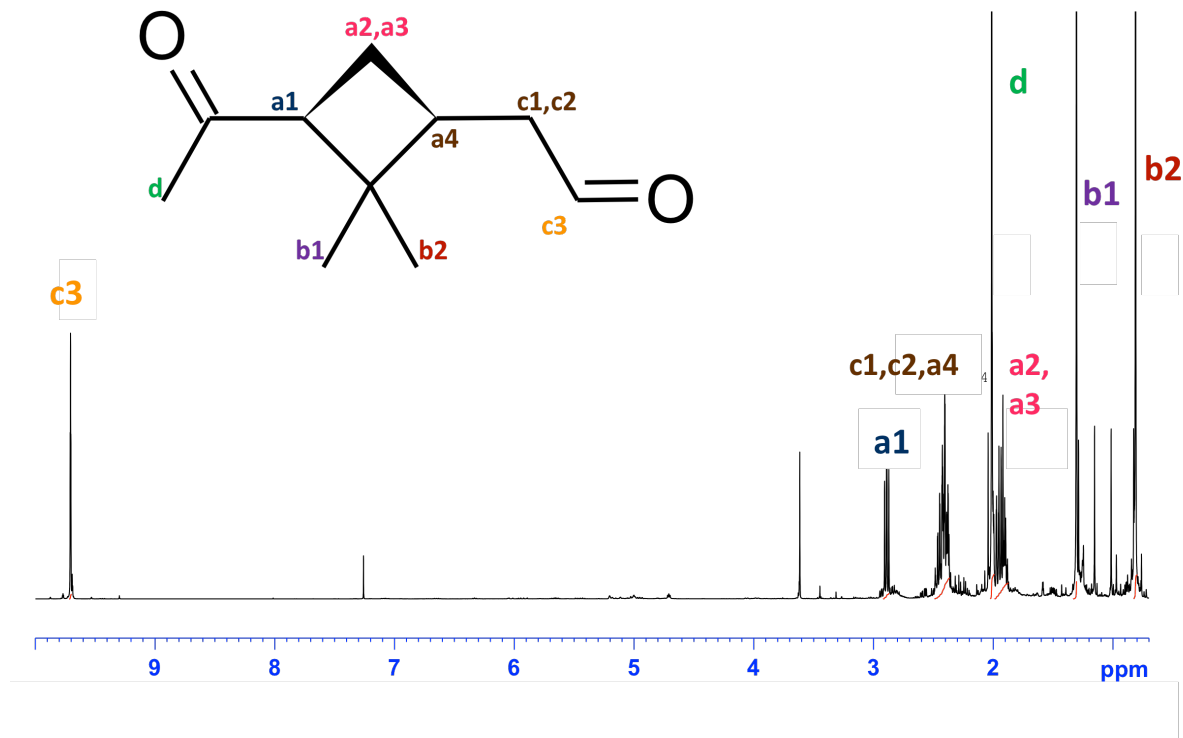
Species oxidized	Initial Concentration in the Smog Chamber	Initial NO <sub>x</sub> (ppb)	Initial VOC <sub>0</sub> /NO <sub>x</sub> (ppbC/ppb)	Initial OH concentration (molecule cm <sup>-3</sup> )
<i>n</i> -Tridecanal high NO <sub>x</sub>	~250 ppb	~1700	~2	~1×10 <sup>7</sup>
Pinonaldehyde high NO <sub>x</sub>	~250 ppb	~1700	~2	~1×10 <sup>7</sup>
<i>n</i> -Pentadecane Presto <i>et al.</i> , 2010	2 to 9 ppb	-	0.03-0.1	-
<i>n</i> -Tridecanal low NO <sub>x</sub>	~69 ppb	~2000	~0.46	~0.3×10 <sup>7</sup>
Pinonaldehyde low NO <sub>x</sub>	~70 ppb	~2000	~0.47	~0.3×10 <sup>7</sup>
Pinonaldehyde low NO <sub>x</sub> Dark Experiment	~93 ppb	~2000	~0.35	~0.3×10 <sup>7</sup>

**Table A.** Conditions of all experiments performed.

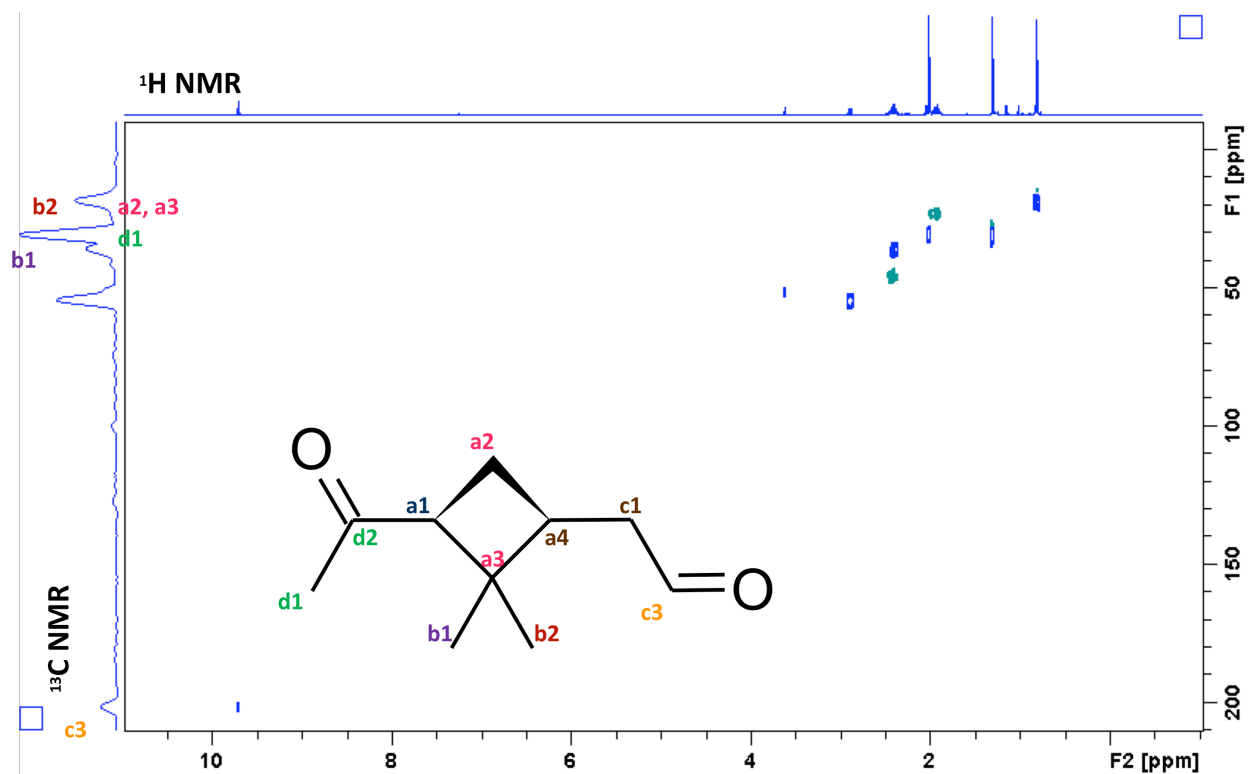
*Supplementary Data*



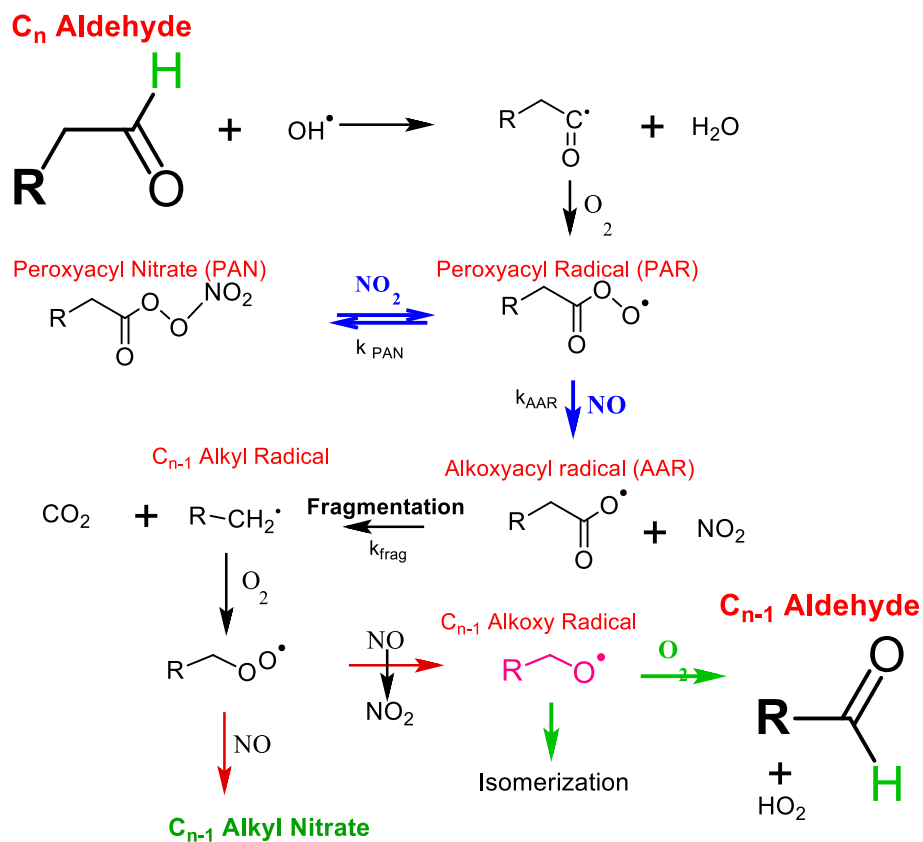
**Figure A.**  $\alpha$ -Pinene is reacted with a flow of excess ozone at  $-72^{\circ}\text{C}$  to form a primary ozonide. Dimethylsulfide was used as a reducing agent to form the corresponding dicarbonyl (pinonaldehyde). A bicarbonate solution was used to extract carboxylic acids formed and other water soluble impurities. The procedure followed was the one by McMurry et al. (1987).



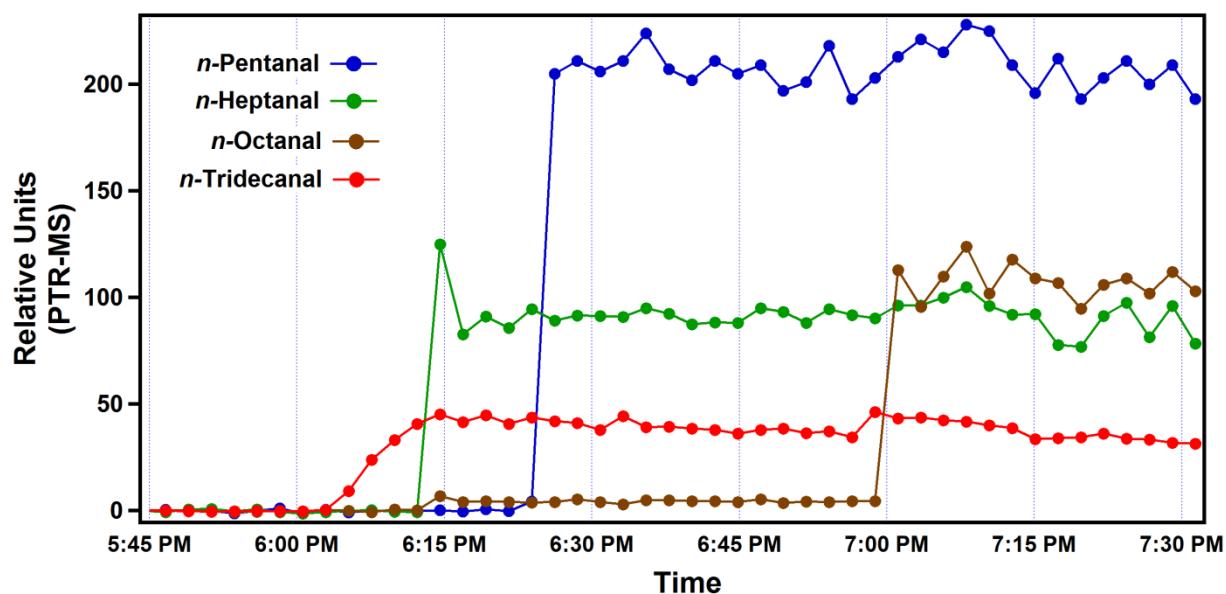
**Figure B.** <sup>1</sup>H NMR spectra are taken from the synthesized pinonaldehyde sample in order to assess its purity level. Pinonaldehyde composes approximately ~85% of the sample, including the *cis*- and *trans*-isomers. Other minor species like peroxides are found. No acids are encountered. The biggest impurity was dimethyl sulfoxide (DMSO, at ~3.6 ppm). The signal at approximately 7.2 ppm corresponds to CDCl<sub>3</sub>, which was the solvent used when the NMR spectra were taken. CDCl<sub>3</sub> is not part of the original synthesis.



**Figure C.** This is a Heteronuclear Single Quantum Coherence (HSQC) spectra of the synthesized pinonaldehyde sample that gives a strong suggestion of the abundance of the pinonaldehyde structure. There is an excellent connection between the  $^{13}\text{C}$  NMR and the  $^1\text{H}$  NMR which shows pinonaldehyde as the most abundant species in the sample.



**Figure D.** Reaction mechanism of  $n$ -aldehyde + OH radical in the presence of high  $\text{NO}_x$ . Larger fonts indicate major products. The first branching point in the reaction mechanism (shown in blue) is the peroxyacyl radical (PAR) becoming either a peroxyacyl nitrate (PAN) or an alkoxyacyl radical (AAR). The alkoxyacyl radical will fragment and form a  $\text{C}_{n-1}$  alkyl radical that will eventually branch between a  $\text{C}_{n-1}$  alkyl nitrate and a  $\text{C}_{n-1}$  alkoxy radical. This alkoxy radical branches (arrows in green) between the  $\text{C}_{n-1}$  aldehyde and an isomerization structure. Long straight-chain aldehydes have a preference towards isomerization in this last step.



**Figure E.** A series on *n*-aldehydes were injected into the Carnegie Mellon smog chamber. They were not exposed to UV light or any oxidizer. The objective of the experiment is check for the possibility of vapors being lost to the Teflon walls in the chamber. All species were relatively constant in concentration throughout this experiment, so we conclude that vapor losses to chamber walls are not significant. All species were in concentration of  $\sim 100 \mu\text{g m}^{-3}$  or less.