Supplementary Data
Photo-oxidation of pinonaldehyde under low NO_x: from chemistry to organic aerosol formation

Heber J. Chacon-Madrid,
Kaytlin Henry and
Neil M. Donahue

Species oxidized	**Initial Concentration in the Smog Chamber**	**Initial NO_x (ppb)**	**Initial VOC_0/NO_x (ppbC/ppb)**	**Initial OH concentration (molecule cm^{-3})**
***n*-Tridecanal high NO_x**	~250 ppb	~1700	~2	$\sim 1\times10^7$
Pinonaldehyde high NO_x	~300 ppb	~4000	~0.8	$\sim 0.5\times10^7$
***n*-Pentadecane Presto *et al.*, 2010**	2 to 9 ppb	-	0.03-0.1	-
***n*-Tridecanal low NO_x**	~69 ppb	~2000	~0.46	$\sim 0.3\times10^7$
Pinonaldehyde low NO_x	~70 ppb	~2000	~0.47	$\sim 0.3\times10^7$
Pinonaldehyde low NO_x Dark Experiment	~93 ppb	~2000	~0.35	$\sim 0.3\times10^7$

Table A. Conditions of all experiments performed.

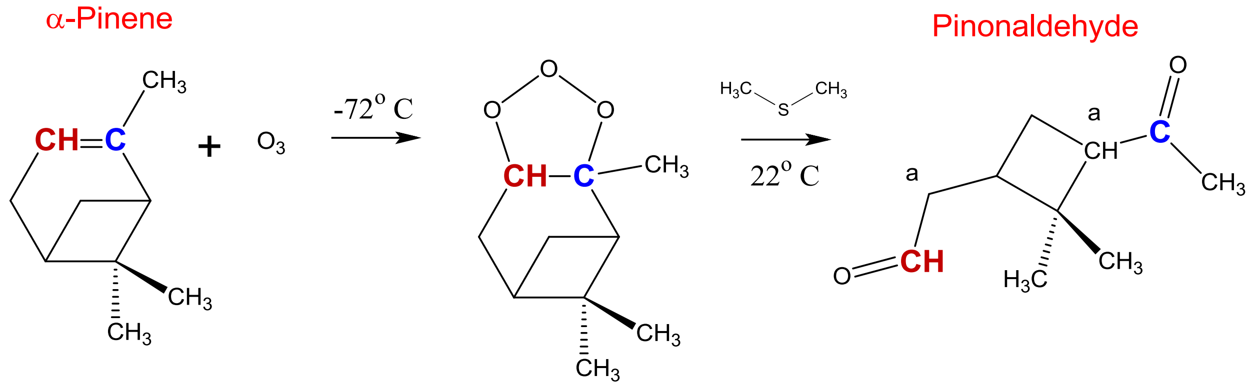

Figure A. α-Pinene is reacted with a flow of excess ozone at -72° C to form a primary ozonide. Dimethylsufide was used as a reducing agent to form the corresponding dicarbonyl (pinonaldehyde). A bicarbonante solution was used to extract carboxylic acids formed and other water soluble impurities. The procedure followed was the one by McMurry et al. (1987).

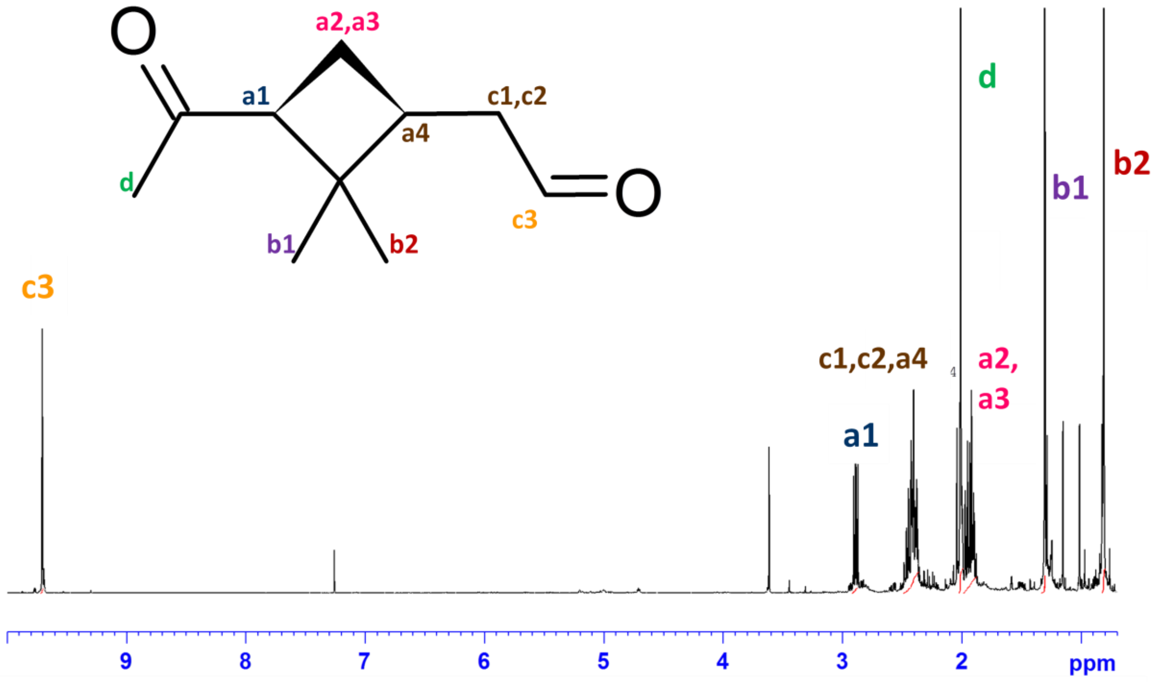

Figure B. ^{1}H NMR spectra are taken from the synthesized pinonaldehyde sample in order to assess its purity level. Pinonaldehyde composes approximately ~85% of the sample, including the *cis*- and *trans*-isomers. Other minor species like peroxides are found. No acids are encountered. The biggest impurity was dimethyl sulfoxide (DMSO, at ~3.6 ppm). The signal at approximately 7.2 ppm corresponds to $CDCl_3$, wich was the solvent used when the NMR spectra were taken. $CDCl_3$ is not part of the original synthesis.

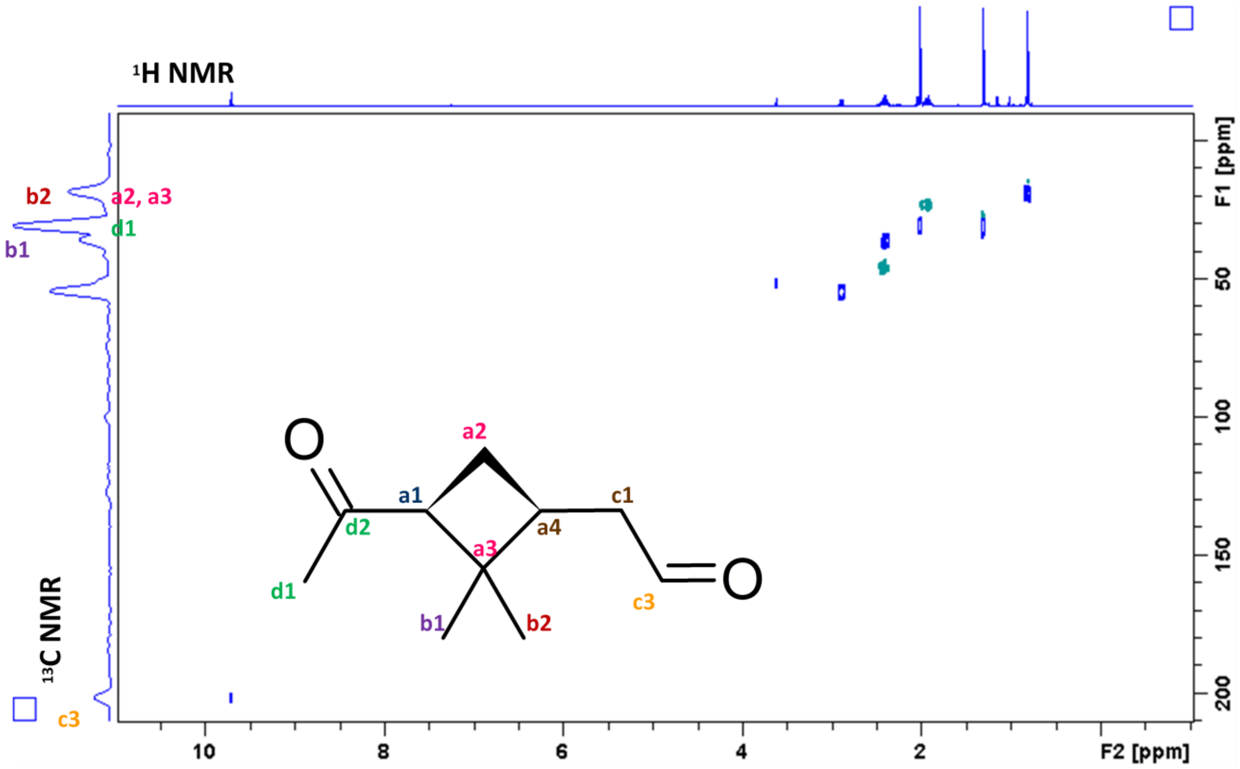

Figure C. This is a Heteronuclear Single Quantum Coherence (HSQC) spectra of the synthesized pinonaldehyde sample that gives a strong suggestion of the abundance of the pinonadehyde structure. There is an excellent connection between the ^{13}C NMR and the ^{1}H NMR which shows pinonaldehyde as the most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

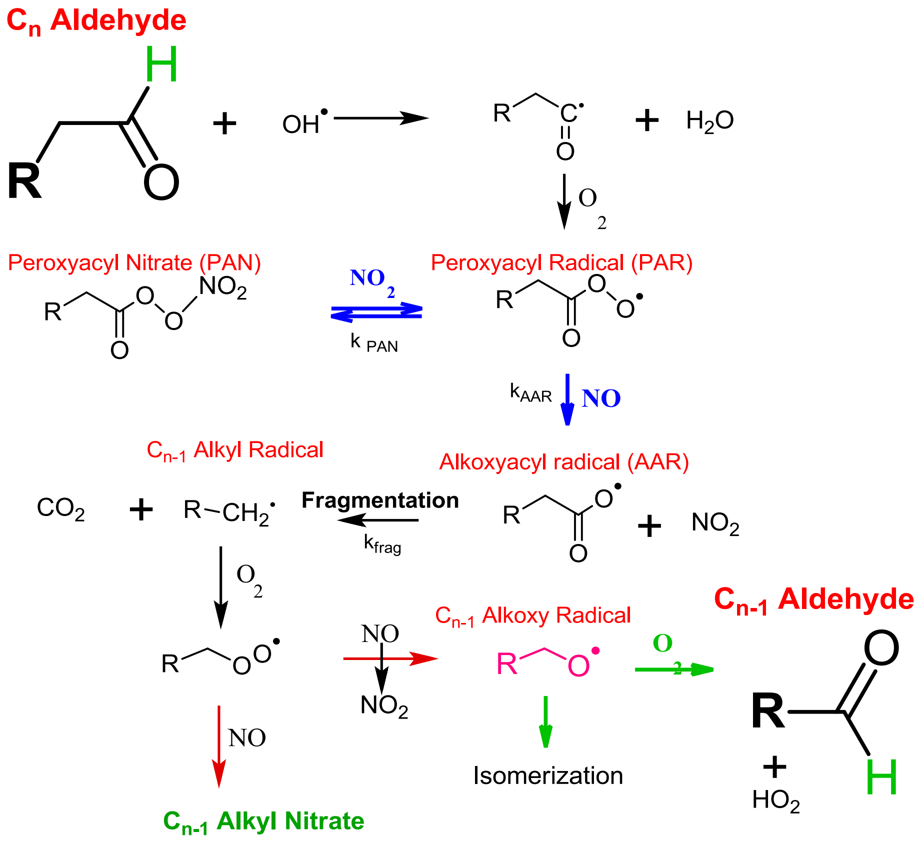

Figure D. Reaction mechanism of *n*-aldehyde + OH radical in the presence of high NO$_x$. The first branching point in the reaction mechanism (shown in blue) is the peroxyacyl radical (PAR) becoming either a peroxyacyl nitrate (PAN) or an alkoxyacyl radical (AAR). The alkoxyacyl radical will fragment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