

Supplementary Material

Fragmentation vs. Functionalization: Chemical Aging and Organic Aerosol Formation

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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)
<i>n</i> -Tridecanal	~250 ppb	~1700	2	~1×10 ⁷
Pinonaldehyde	~300 ppb	~4000	0.8	~0.5×10 ⁷
<i>n</i> -Pentadecane Presto <i>et al.</i> , 2010	2 to 9 ppb	-	0.03-0.1	-
2-Tridecanone	~40 ppb	~3500	0.15	~0.5×10 ⁷
7-Tridecanone	~35 ppb	~3000	0.15	~0.5×10 ⁷
<i>n</i> -Nonadecane	~2 ppb	~1800	0.02	~0.5×10 ⁷
<i>n</i> -Heptadecanal	~3 ppb	~5000	0.01	~1×10 ⁷

Table A.*Supplementary Data*

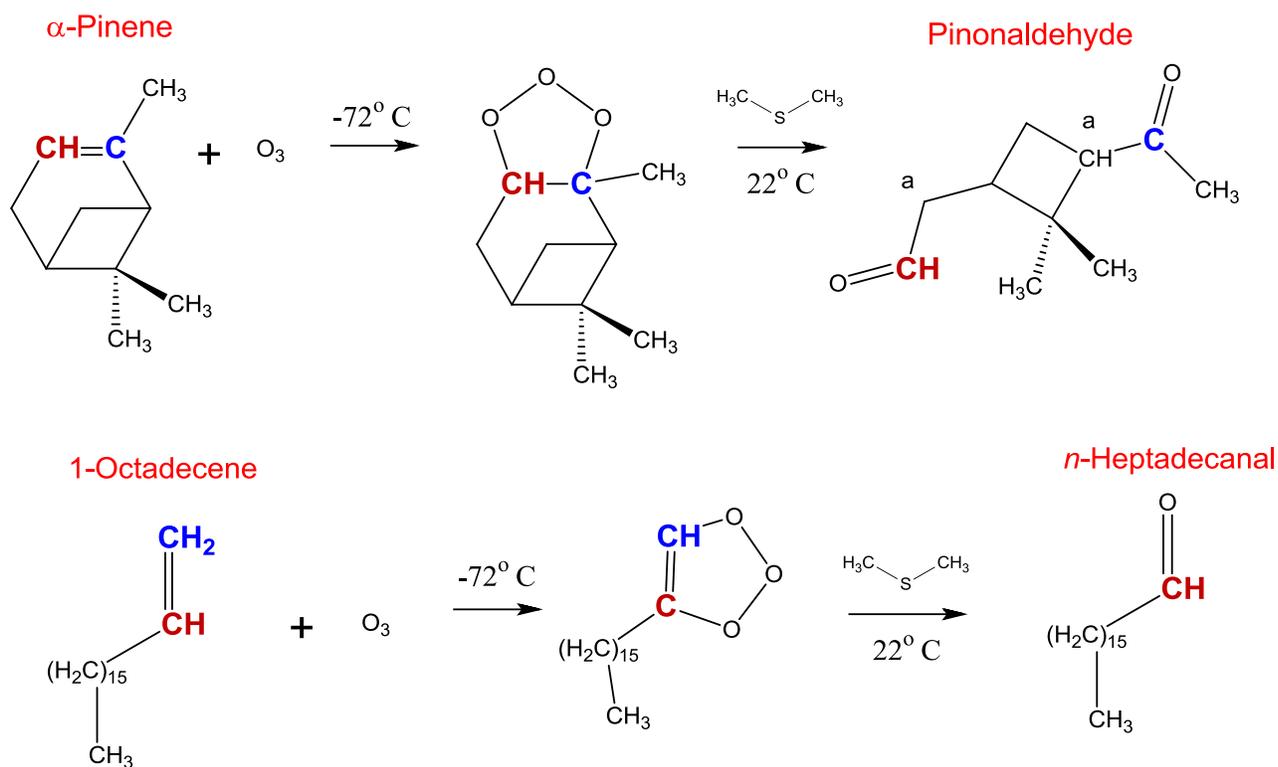


Figure A. α -Pinene and 1-octadecene were reacted (separately) with a flow of excess-ozone at $-72^\circ C$ to form the primary ozonide. Dimethylsulfide was used as a reducing agent to form the corresponding dicarbonyl. A bicarbonante solution was used to extract the carboxylic acids formed and other water soluble impurities. The procedure followed was the one by McMurry et al. (1987).

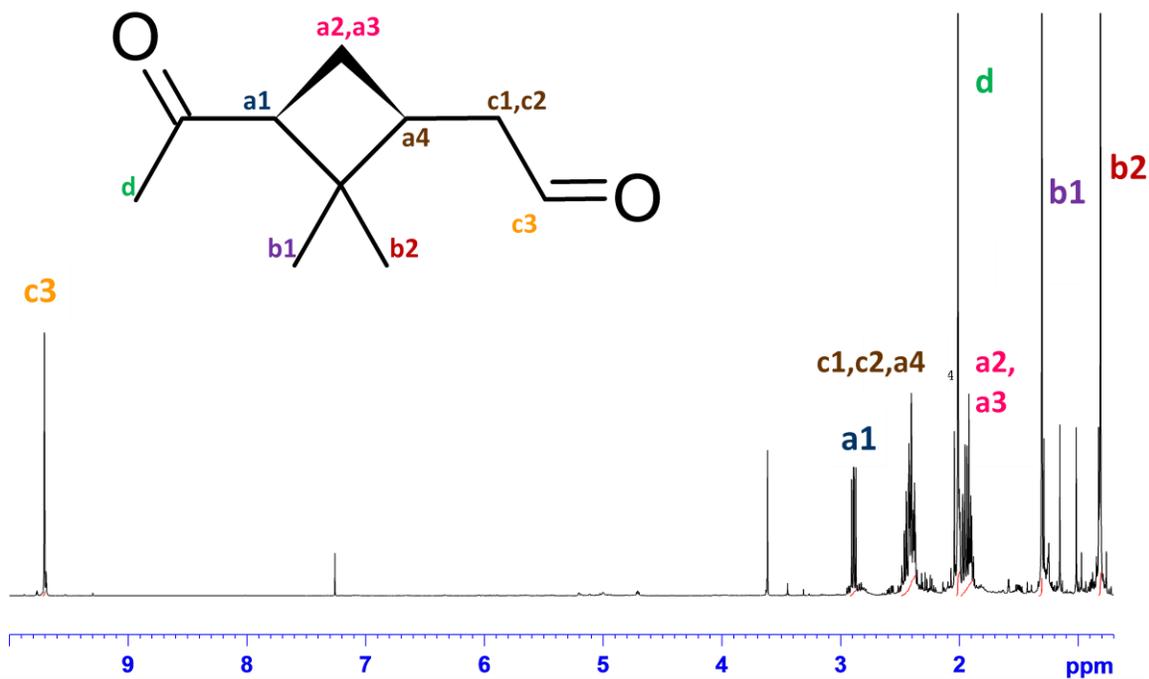


Figure B. ¹H NMR spectra were taken from the synthesized-pinonaldehyde sample in order to assess its purity level. Pinonaldehyde composed approximately ~85% of the sample, including the *cis*- and *trans*-isomers. Other minor species like peroxides were found. No acids were encountered. The biggest impurity was dimethyl sulfoxide (DMSO, at ~3.6 ppm). The signal at approximately 7.2 ppm corresponds to CDCl₃, which was the solvent used when the NMR spectra were taken.

Supplementary Data

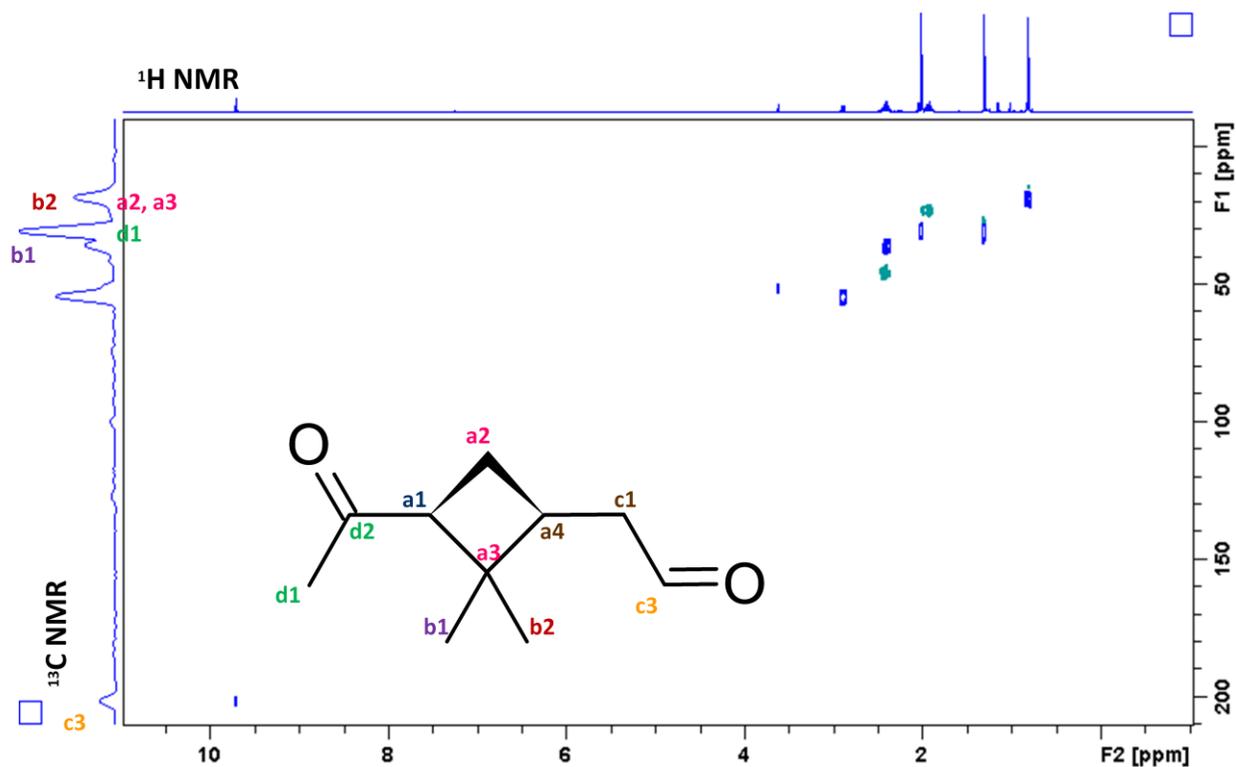


Figure C. This is a Heteronuclear Single Quantum Coherence (HSQC) spectra of the synthesized-pinonaldehyde sample that gives a strong suggestion of the abundance of the pinonaldehyde structure. There is an excellent connection between the ^{13}C NMR and the ^1H NMR which shows pinonaldehyde as the most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

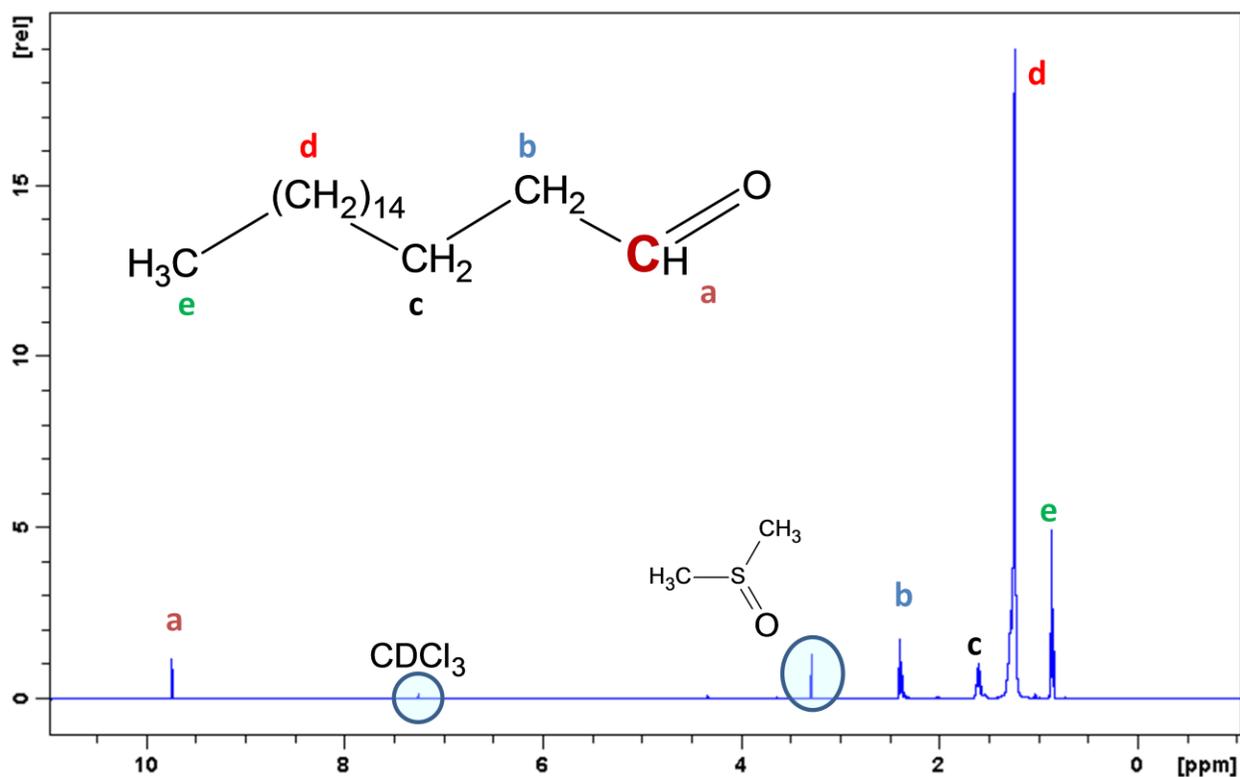


Figure D. This ^1H NMR spectra shows the presence of *n*-heptadecanal as the major product (>90%). The major contaminant is DMSO at ~ 3.3 ppm. CDCl_3 was the solvent used when the NMR spectra were taken, reason for a peak at ~ 7.2 ppm. Other than DMSO, contaminants such as peroxides are observed in minor concentrations.

Supplementary Data

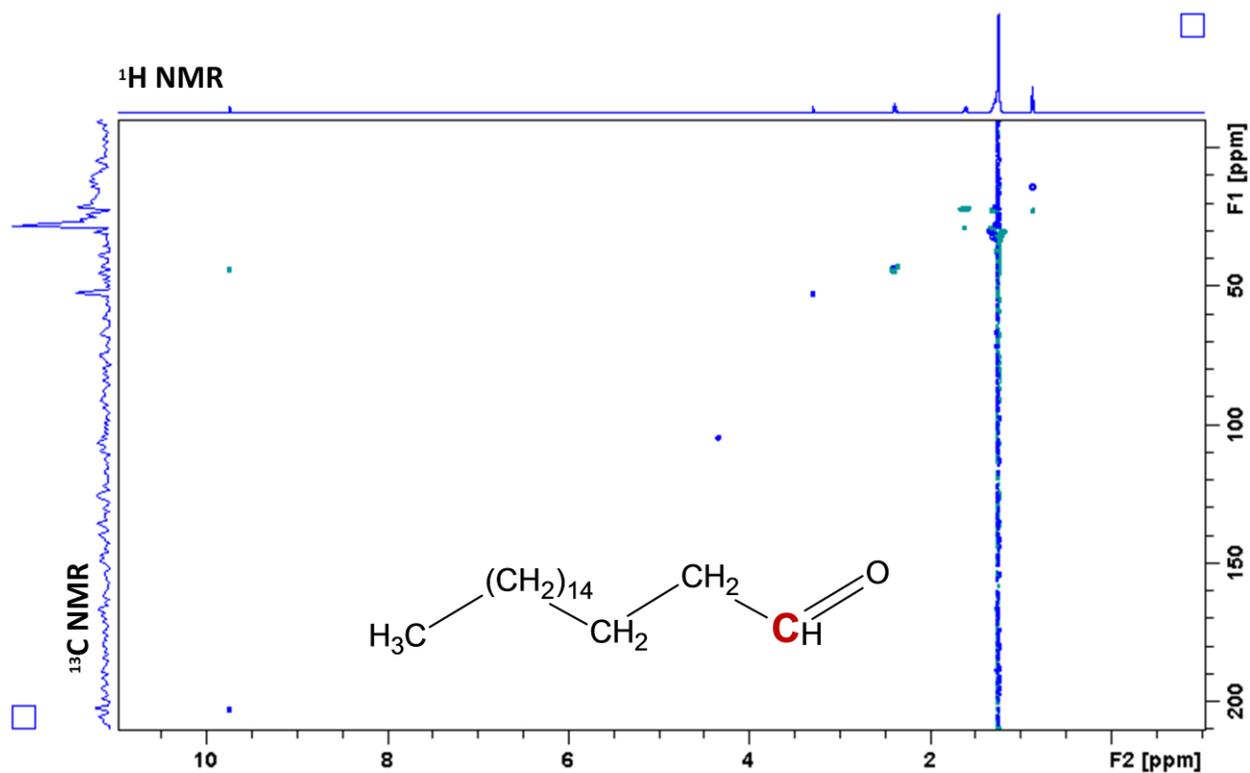


Figure E. This is an HSQC spectra of the synthesized-*n*-heptadecanal sample. This spectra strongly suggests abundance of *n*-heptadecanal in the sample. There is an excellent connection between the ^{13}C NMR and the ^1H NMR, describing *n*-heptadecanal as the most abundant species in the sample.

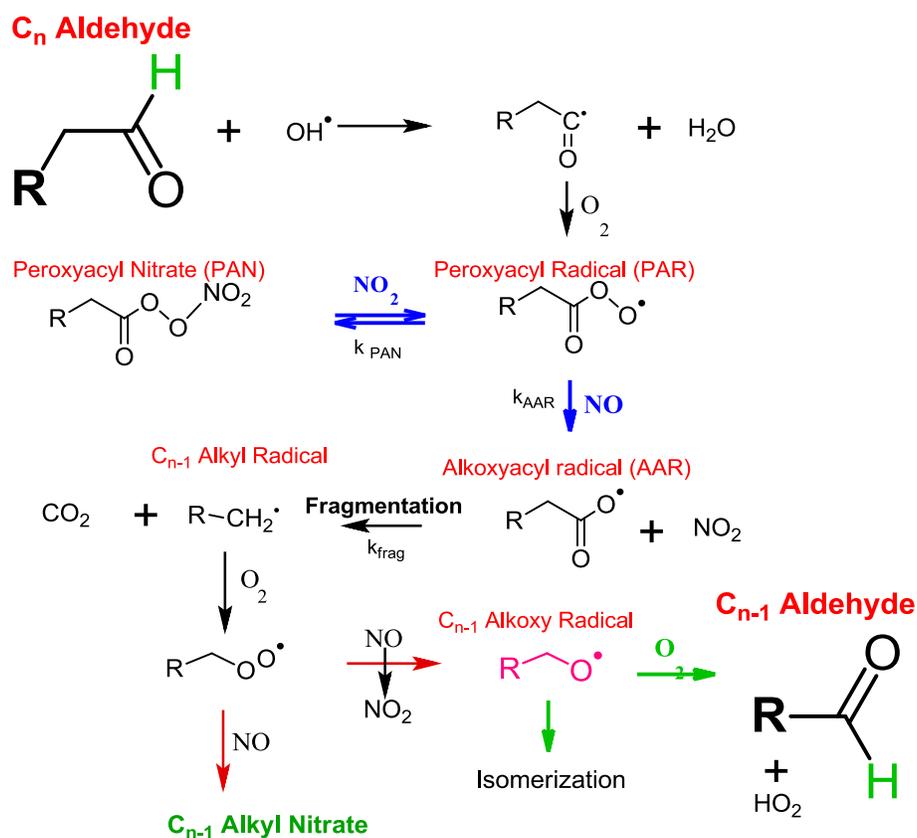


Figure F. Reaction mechanism of n -aldehyde + OH radical in the presence of high NO_x . The first branching point in the reaction mechanism (shown in blue) is the peroxyacyl radical (PAR) becoming either a peroxyacyl nitrate (PAN) or an alkoxyacyl radical (AAR). The alkoxyacyl radical will fragment and 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.

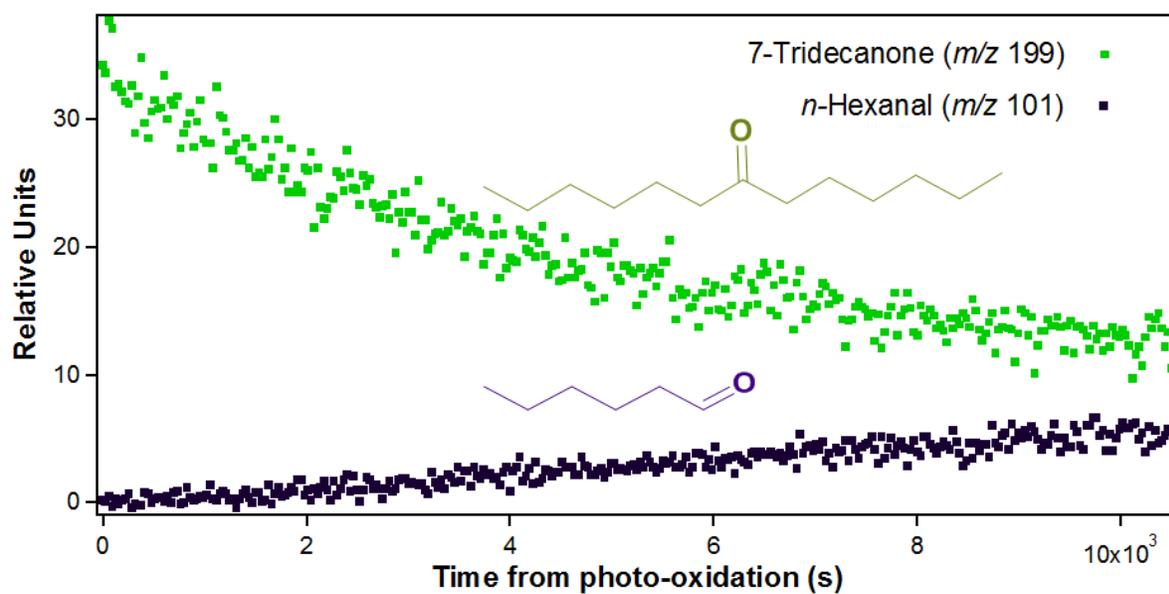


Figure G. Fragmentation of 7-tridecanone via OH radical oxidation in the presence of NO_x forms *n*-hexanal. The signals presented here have not been calibrated. *n*-Hexanal can be formed from attack on the α- and β-hydrogens of 7-tridecanone (refer to Figure 7, main manuscript). The reaction of 2-tridecanone with OH in the presence of NO_x does not show the formation of its respective aldehyde. That is because chemical fragmentation is a smaller path for 2-tridecanone versus 7-tridecanone.