Supplemental Information

Thermal Desorption Behavior of Hemiacetal, Acetal, Ether, and Ester Oligomers

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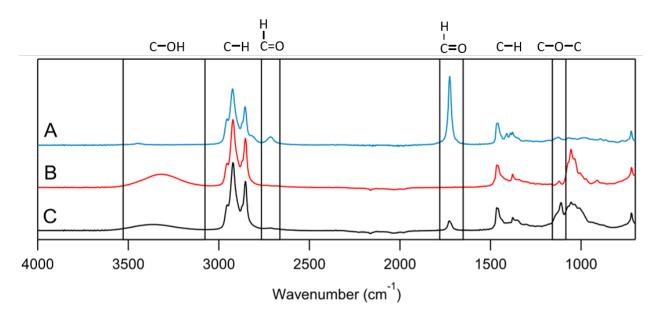


Figure S1. ATR-FTIR spectra of (A) decanal, (B) 1-nonanol, and the (C) reaction mixture containing hemiacetal oligomers and small amounts of unreacted decanal and 1-nonanol. Peaks at 1725 and 2715 cm $^{-1}$ are due to the C=O stretch and aldehydic C–H stretch in decanal, the broad peak centered at $\sim \! 3300 \; \text{cm}^{-1}$ is due to the O–H stretches in 1-nonanol and the hemiacetal oligomers, and the peak at 1110 cm $^{-1}$ is due to the C–O–C stretches in the hemiacetal oligomers.

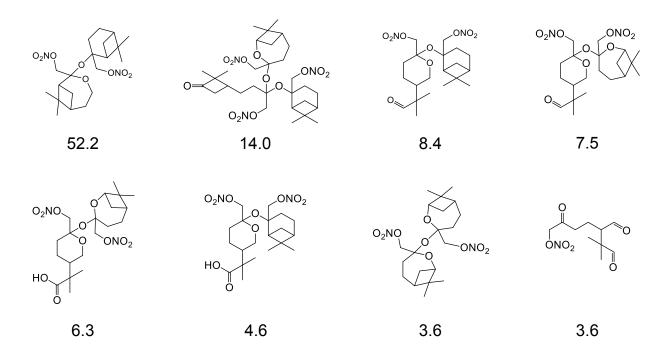


Figure S2. Acetal oligomers present in SOA formed from the reaction of β -pinene with NO₃ radicals. Values are the mass fraction (%) of oligomer in the SOA.

Figure S3. Structures of C_{10} diol, hydroxynitrate, and dinitrate monomers used for TPTD analysis.

Hemiacetal Oligomer (MW 300)

$$R \xrightarrow{OH} R \xrightarrow{e^{-}} R - CH_{2}^{\bullet} + {}^{\dagger}OH$$

$$R \xrightarrow{OH} R \longrightarrow R - CH_{2}^{\bullet} + {}^{\dagger}OH$$

$$R = C_8 H_{17}$$

Ether Oligomer (MW 456)

$$R = C_9H_{19}$$

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Figure S4. Fragmentation pathways for forming major ions observed in the TDPBMS mass spectrum of the hemiacetal and ether oligomers.

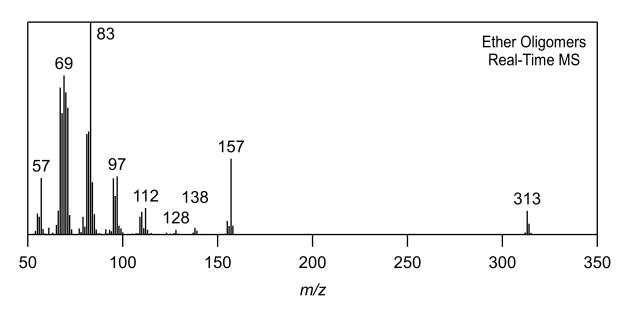


Figure S5. Real-time TDPBMS electron ionization mass spectrum of the ether oligomer formed from decanal.

Ester Oligomer (MW 426)
$$m/z$$
 R_1
 R_2
 R_3
 R_4
 R_5
 R_7
 R_7

Figure S6. Fragmentation pathways for forming major ions observed in the TDPBMS mass spectrum of the ester oligomer.