

## **Supplemental Information**

Chemistry of Hydroperoxycarbonyls in Secondary Organic Aerosol

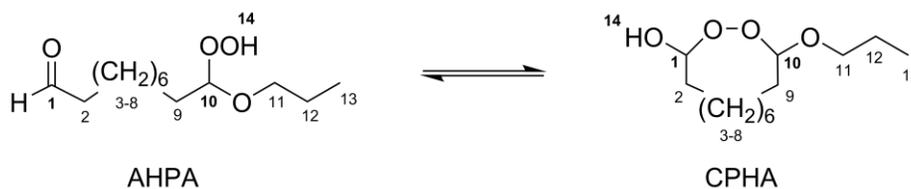
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## NMR Determination of AHPA Cyclization Equilibrium Constant.

The equilibrium constant for cyclization of AHPA to a CPHA was measured using proton nuclear magnetic resonance spectroscopy ( $^1\text{H-NMR}$ ). Preparation of AHPA is described in the body of the text. Peak shifts, areas, and assignments are presented below in Table S1. We normalize all peaks using the methyl triplet at 0.87 ppm, since the peak is large, isolated, and straightforward to assign. All peak splitting is consistent with assignments in Table S1, with long-range splitting observed across the alcohol and propoxy oxygens, giving rise to a doublet of multiplets, a doublet of triplets, and a quintet for assignments 11, CPHA 1, and CPHA 10, respectively. The methylene hydrogens (2-9, 11-12) and the methyl hydrogens (13) do not undergo any significant change in chemical environment upon cyclization, and so they each give an integrated area of  $\sim 1$ . We observe that three peaks in AHPA undergo a change in chemical environment upon cyclization to CPHA: the aldehydic hydrogen (1), the hydroperoxide hydrogen (14), and the hydrogen bonded to the hydroperoxide carbon (10). Since  $^1\text{H-NMR}$  peak areas are quantitative, we can use the average integrated areas of the peaks assigned to AHPA and CPHA to determine the relative concentration of each species and calculate the equilibrium constant for cyclization as outlined in the text, Equation 2.

Table S1. Peak shifts and assignments for  $^1\text{H-NMR}$  spectrum of AHPA-CPHA equilibrium. Molecular structures with assignment labels are included to show which protons undergo a change in chemical environment following the cyclization reaction (depicted in bold).

$\delta$ (ppm)	Area	Multiplicity	Assignment
0.87	3.00 <sup>a</sup>	3	CH <sub>3</sub> : 13
1.24	11.71	m	CH <sub>2</sub> : 3-8
1.50	6.18	m	CH <sub>2</sub> : 2, 9, 12
3.57	1.96	$2 \times m^b$	CH <sub>2</sub> -OR: 11
4.69	0.26	3	HOO-CH-OR: AHPA 10
4.88	0.69	$2 \times 3$	ROO-CH-OH: CPHA 1
5.02	0.66	5	ROO-CH-OR: CPHA 10
6.43	0.65	2	ROH: CPHA 14
9.66	0.22	3	C(O)H: AHPA 1
11.44	0.24	1	ROOH: AHPA 14



<sup>a</sup> Used for area normalization.

<sup>b</sup> Doublet of multiplets.

## Reference Spectra.

Reference EI spectra from NIST and AIST described in the text are presented below in Figure S1 (Stein, 2016; SDBSWeb, 2017). Dipropoxyacetals give a characteristic pair of fragments at  $m/z$  131 and 89, corresponding to  $\alpha$ -cleavage at the acetal carbon and the subsequent loss of propene, respectively. This fragmentation pattern is observed for 1,1-dipropoxyheptane, 1,1-dipropoxypropane, and 1,1-dipropoxytrimethylamine, all shown in Figure S1 (Stein 2016; SDBSWeb 2017).

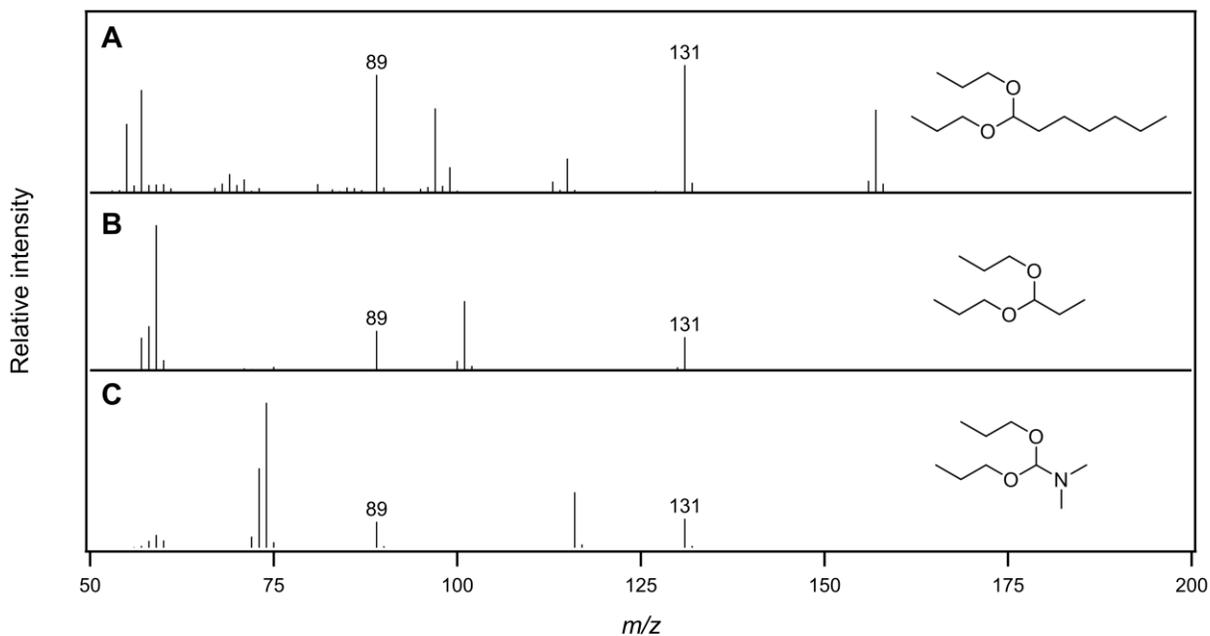


Figure S1. Reference EI spectra of dipropoxy acetals: 1,1-dipropoxyheptane (A), 1,1-dipropoxypropane (B), and 1,1-dipropoxytrimethylamine (C) (Stein 2016; SDBSWeb, 2017). The characteristic fragmentation pattern is  $\alpha$ -cleavage at the acetal carbon ( $m/z$  131) followed by neutral loss of propene ( $m/z$  89).

### Identification of Sebaccic Acid as an AHPA Co-Product in SOA.

The EI-TDPBMS spectrum of SOA produced from the ozonolysis of cyclodecene in the presence of a large excess of carbon monoxide is presented below in Figure S2A. The peaks at  $m/z$  166, 138, and 98 are all characteristic of sebaccic acid, as can be seen in the NIST reference spectrum in Figure S2B (Stein 2016). We note that dioctyl sebaccate (DOS) seed aerosol was not used in this experiment, so the sebaccic acid fragments in Figure S1A are not from the DOS seed. Offline functional group analysis indicates that the SOA produced in this experiment has 0.9 acid groups per molecule (assuming an average molecular weight of  $250 \text{ g mol}^{-1}$ ). Based on the EI-TDPBMS mass spectrum and the functional group analysis indicating high acid content of the SOA we identify sebaccic acid as a product of the excited Criegee intermediate pathway of the cyclodecene ozonolysis reaction. Since this pathway is unaffected by the SCI scavenger used, sebaccic acid is expected to be a co-product of AHPA when propanol is used as an SCI scavenger.

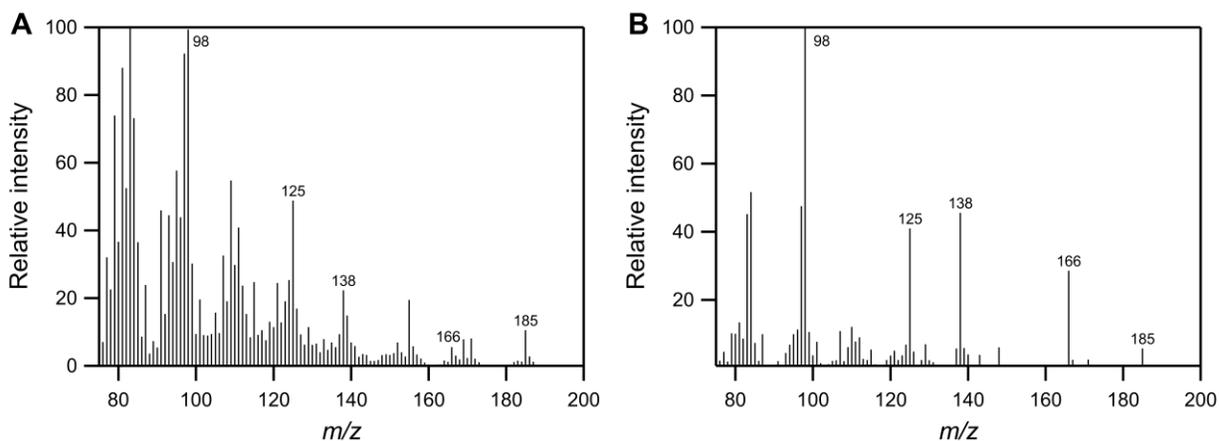


Figure S2. EI-TDPBMS spectrum of SOA produced from ozonolysis of cyclodecene in the presence of a large excess of carbon monoxide (A). NIST reference spectrum of sebaccic acid (B) (Stein, 2016).

## Potential Reactions of Hydroperoxyaldehydes.

The reaction scheme presented in in the text has been adapted in Figure S3 to show the potential reactions of a hydroperoxyaldehyde analogous to AHPA, but with an alkyl substituent in place of a propoxy substituent.

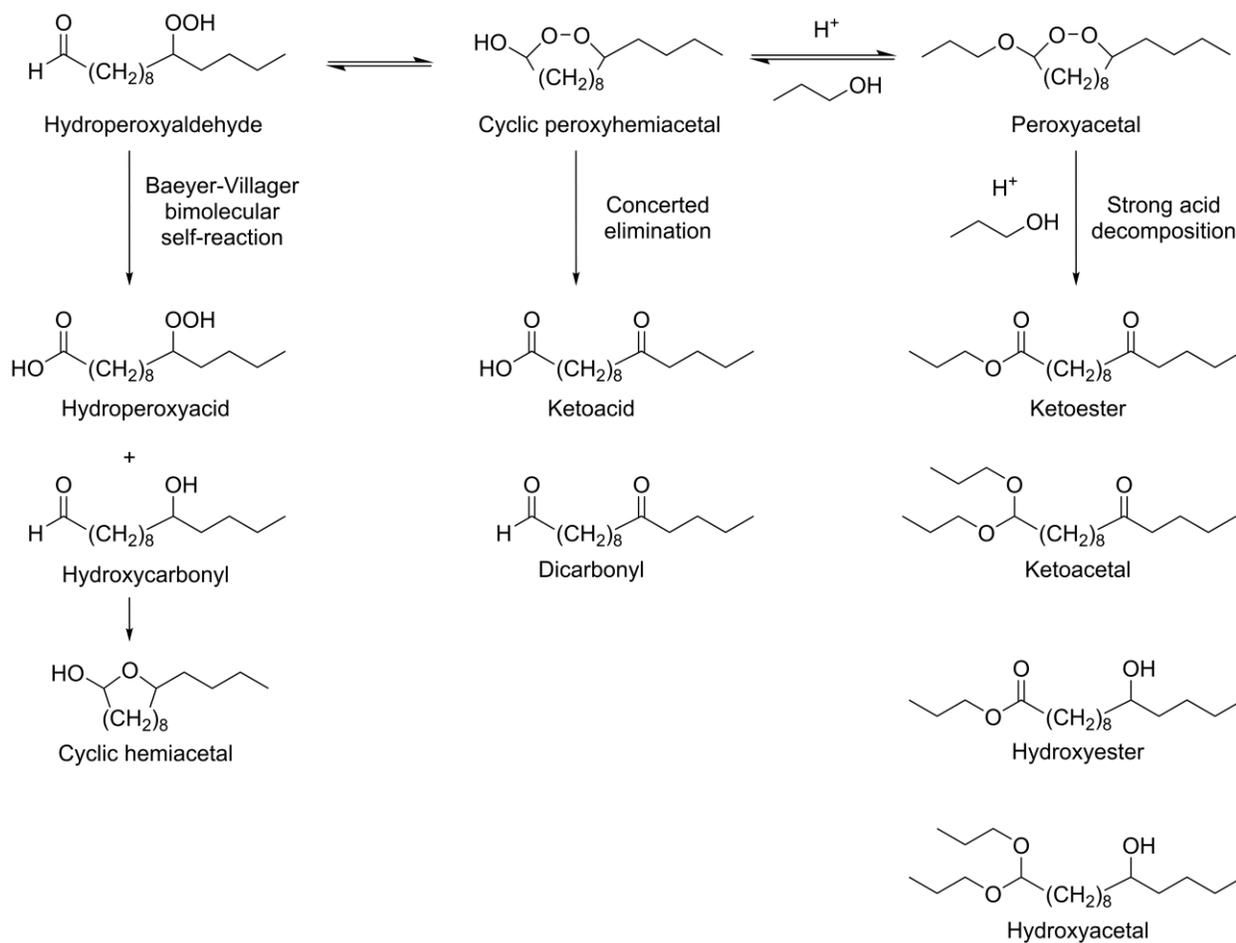


Figure S3. Potential reactions of hydroperoxyaldehydes in SOA. In the concerted elimination and strong acid decomposition pathways coproducts of hydrogen and water are not shown.

## References

McLafferty, F. W. and Tureček, F. (1993). Interpretation of Mass Spectra, 4<sup>th</sup> Ed. University Science Books, Sausalito, CA, USA.

SDBSWeb : <http://sdbb.db.aist.go.jp> National Institute of Advanced Industrial Science and Technology. Accessed December 2017.

Stein, S.E. (2016). Mass Spectra., in NIST Chemistry WebBook, NIST Standard Reference Database Number 69, Eds. Linstrom, P. J. and Mallard, W. G., National Institute of Standards and Technology, Gaithersburg, MD 20899.