

## **Supplementary Information**

### **Kinetics of Oligomer-Forming Reactions Involving the Major Functional Groups Present in Atmospheric Secondary Organic Aerosol Particles**

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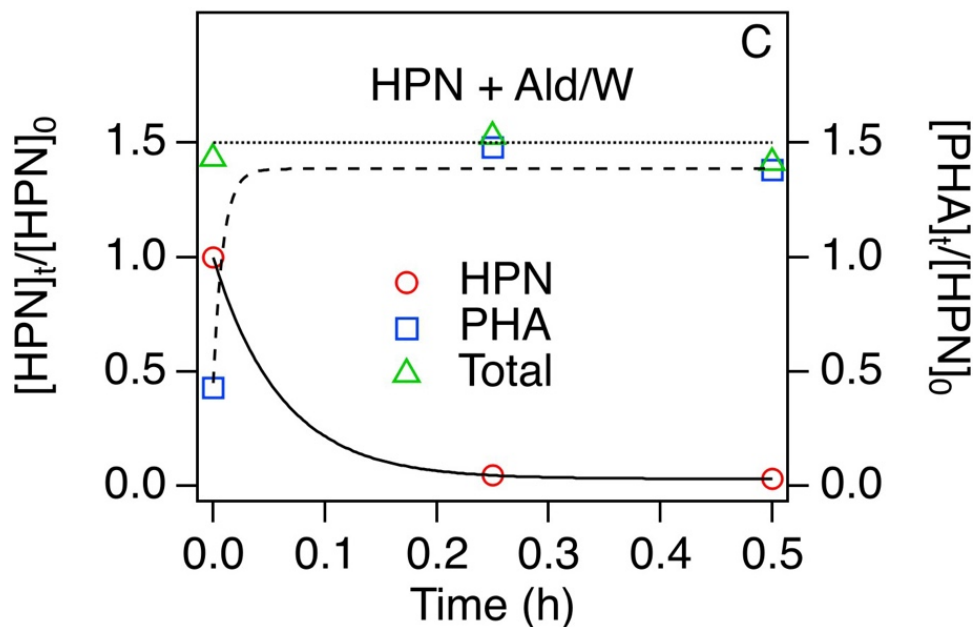


Figure S1. Time profile of the ratio  $[HPN]_t/[HPN]_0$ , the ratio of the PHA product  $[PHA]_t/[HPN]_0$ , and the sum of the ratios, for reaction of HPN with nonanal (Ald) in a phase-separated organic/aqueous mixture with the aqueous phase being water (W). The time period has to narrowed to 0 to 0.5 h from the 0 to 24 h time period shown in Figure 4B.

Table S1. Summary of results from all experiments with the four different probe molecules.

Probe	Excess reactant	Catalyst	Major product	Equilibrium constant (K <sub>eq</sub> )	Forward rate constant (k <sub>f</sub> )	Reverse rate constant (k <sub>r</sub> )
HPN	3-decanone	none	peroxyhemiketal	no reaction	no reaction	no reaction
HPN	3-decanone	3.0 M H <sub>2</sub> SO <sub>4</sub>	peroxyhemiketal	no reaction	no reaction	no reaction
HPN	nonanal	none	peroxyhemiacetal	4 M <sup>-1</sup>	>1.5 M <sup>-1</sup> h <sup>-1</sup>	>0.24 M <sup>-1</sup> h <sup>-1</sup>
CN	1-octanol	none	ester	no reaction	no reaction	no reaction
CN	1-octanol	0.005 M H <sub>2</sub> SO <sub>4</sub>	ester	n/a	5.9 M <sup>-2</sup> h <sup>-1</sup>	no reaction
CN	1-octanol	3.0 M H <sub>2</sub> SO <sub>4</sub>	ester	2.9	0.068 M <sup>-2</sup> h <sup>-1</sup>	0.023 M <sup>-2</sup> h <sup>-1</sup>
HN	5-hydroxy-2-pentanone	none	acetal	no reaction	no reaction	no reaction
HN	5-hydroxy-2-pentanone	3.0 M H <sub>2</sub> SO <sub>4</sub>	acetal	no reaction	no reaction	no reaction
HN	6-hydroxy-5-decanone	none	hemiketal	no reaction	no reaction	no reaction
HN	6-hydroxy-5-decanone	3.0 M H <sub>2</sub> SO <sub>4</sub>	hemiketal	no reaction	no reaction	no reaction
HN	1-octanol	3.0 M H <sub>2</sub> SO <sub>4</sub>	ether	no reaction	no reaction	no reaction
HN	HN	3.0 M H <sub>2</sub> SO <sub>4</sub>	ether	no reaction	no reaction	no reaction
βHN	βCN	none	hemiketal	no reaction	no reaction	no reaction
βHN	βCN	3.0 M H <sub>2</sub> SO <sub>4</sub>	hemiketal	no reaction	no reaction	no reaction
βCN	1,2-octanediol	none	hemiketal	no reaction	no reaction	no reaction
βCN	1,2-octanediol	3.0 M H <sub>2</sub> SO <sub>4</sub>	hemiketal	no reaction	no reaction	no reaction
βCN	1-octanol	none	hemiketal	no reaction	no reaction	no reaction
βCN	1-octanol	3.0 M H <sub>2</sub> SO <sub>4</sub>	hemiketal	no reaction	no reaction	no reaction
βCN	α-pinene SOA	none	hemiketal	no reaction	no reaction	no reaction
βCN	α-pinene SOA	3.0 M H <sub>2</sub> SO <sub>4</sub>	hemiketal	no reaction	no reaction	no reaction
CN	α-pinene SOA	none	Ester	no reaction	no reaction	no reaction
CN	α-pinene SOA	3.0 M H <sub>2</sub> SO <sub>4</sub>	Ester	no reaction	no reaction	no reaction