Supplementary material

Glyoxal SOA chemistry: effects of dilute nitrate and ammonium and support for organic radical-radical oligomer formation

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**Fig. S1.** Measured and modelled H$_2$O$_2$ concentration in H$_2$O$_2$ + UV control experiment. The concentration of H$_2$O$_2$ as a function of time in the H$_2$O$_2$ + UV control experiments was modelled (FACSIMILE for Windows Version 4.1.45) using the following reactions and rate constants provided by Lim et al.\[1\] with the exception of $k_1$.

- H$_2$O$_2$ + UV $\rightarrow$ OH$^-$ + OH$^-$ ($k_1$)
- OH$^-$ + H$_2$O$_2$ $\rightarrow$ HO$_2$ + H$_2$O
- HO$_2$ + H$_2$O$_2$ $\rightarrow$ OH$^-$ + H$_2$O + O$_2$
- HO$_2$ + HO$_2$ $\rightarrow$ H$_2$O$_2$ + O$_2$
- OH$^-$ + HO$_2$ $\rightarrow$ H$_2$O + O$_2$
- OH$^-$ + OH$^-$ $\rightarrow$ H$_2$O$_2$

The H$_2$O$_2$ photolysis rate constant, $k_1 = 1.0 \times 10^{-4}$ was determined by fitting the model to measured H$_2$O$_2$ concentrations. This value of $k_1$ was then used in the FACSIMILE model for glyoxal to estimate the concentration of OH$^-$ ([OH$^-$]$_{initial} = 7.8 \times 10^{-13}$, [OH$^-$]$_{final} = 6.0 \times 10^{-12}$, [OH$^-$]$_{average} = (1 \pm 2) \times 10^{-12}$) during glyoxal experiments from initial precursor concentrations (e.g., 5 mM H$_2$O$_2$, 1 mM GLY).\[1\]
Fig. S2. Modelled OH$^-$ concentration in GLY + OH$^-$ in the presence and absence of HNO$_3$. Note OH$^-$ is formed from H$_2$O$_2$ photolysis and reacts with GLY and its reaction products. Inclusion of HNO$_3$ reactions discussed in the methods does not change [OH$^-$] prediction.

Fig. S3. Modelled oxalate concentrations from GLY + OH$^-$ with and without HNO$_3$. 
Fig. S4.  Modelled nitrate concentration in GLY + OH\(^{-}\) + HNO\(_3\) experiment.

Fig. S5.  Modelled pH in GLY + OH\(^{-}\) experiments conducted in the presence and absence of HNO\(_3\).
**Fig. S6.** Oxalate concentration measured by IC in GLY + HNO₃ + UV control experiment. Some oxalate formation is seen, but concentrations are much lower and formation is much slower than in GLY + OH⁻ + HNO₃ experiments. OH⁻ production from HNO₃ + UV is modest.

**Fig. S7.** Nitrate concentration measured by IC in GLY + HNO₃ + UV control experiment.
Fig. S8. Nitrate concentration measured by IC in GLY + OH’ + HNO₃ experiment. Error bars represent the coefficient of variation (<1 %) across three experiments.

References