Supporting Information: OH-initiated oxidation of sub-micron unsaturated fatty acid particles

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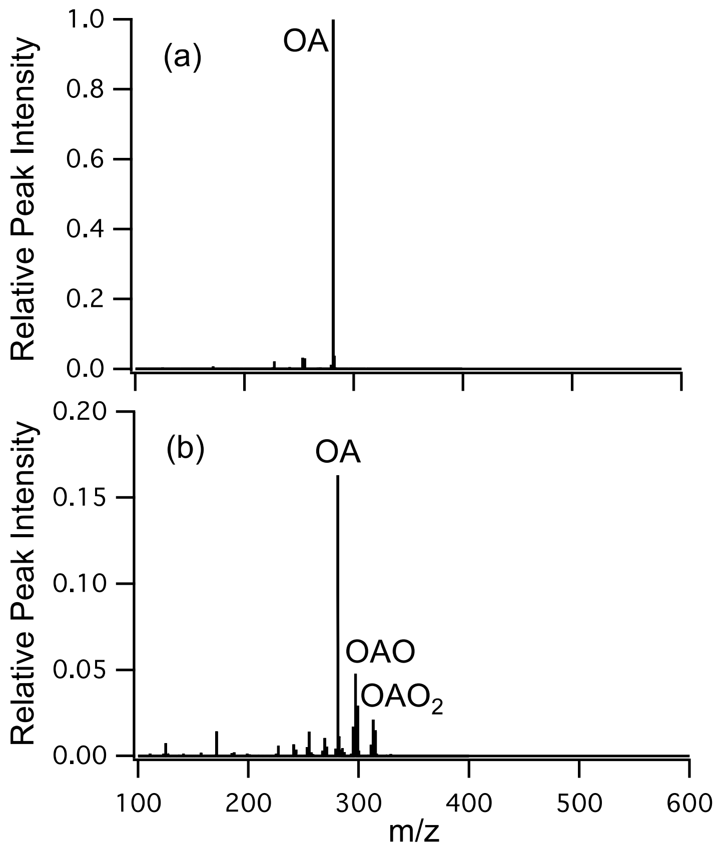

Figure S-1 The negative-ion APCI mass spectrum of oleic acid (OA) particles from m/z 100 to 600. No peaks are observed above the background at masses lower than m/z 100. (a) Before reaction, the main peak observed in the spectrum is the oleic acid parent ion ($[M-H]^-$, m/z 281). (b) After reaction with OH radicals (~ 2.4 x 10^{11} molecule cm^{-3} s) at $[H_2O_2]$ = 20.7 ppm and $[O_2]$ = 10 %, the oleic acid peak intensity decreases and higher molecular weight oxygenated reaction products are formed. The groups of higher molecular weight oxygenated reaction products are denoted as OAO, OAO_2 and OAO_3

respectively to denote the number of oxygen atoms added to the oleic acid molecule. The mass spectra are normalized to the initial oleic acid peak intensity before reaction.

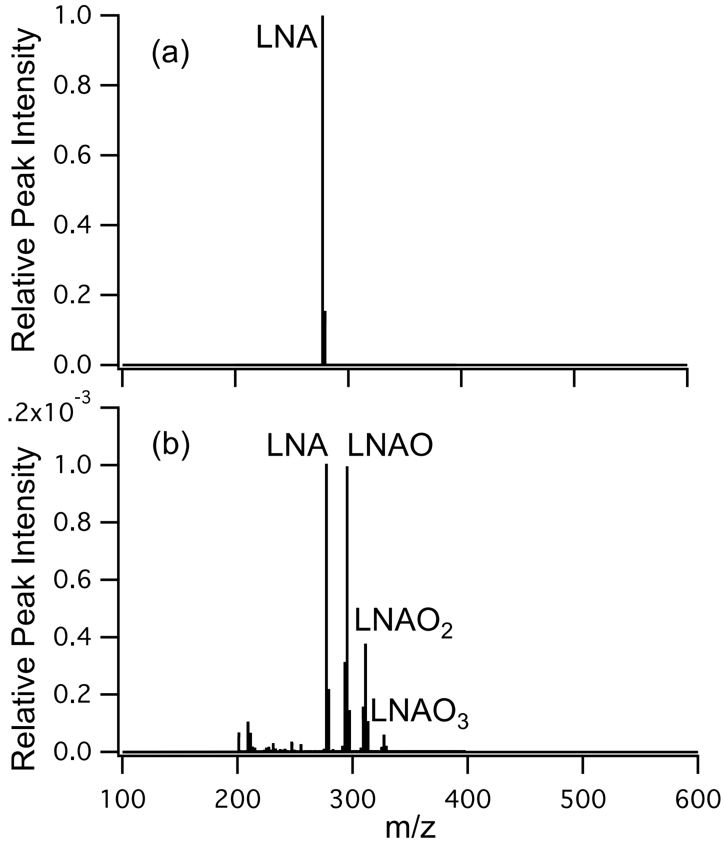

Figure S-2 The negative-ion APCI mass spectrum of linolenic acid (LNA) particles from m/z 100 to 600. No peaks are observed above the background at masses lower than m/z 100. (a) Before reaction, the main peak observed in the spectrum is the linolenic acid parent ion ($[M-H]^-$, m/z 277). (b) After reaction with OH radicals (~ 2.6×10^{11} molecule cm^{-3} s) at $[H_2O_2]$ = 20.7 ppm and $[O_2]$ = 10 %, the linolenic acid peak intensity decreases and higher molecular weight oxygenated reaction products are formed. The groups of higher molecular weight oxygenated reaction products are denoted as LNAO, $LNAO_2$ and $LNAO_3$ respectively to denote the number of oxygen atoms added to the linolenic acid molecule. The mass spectra are normalized to the initial linolenic acid peak intensity before reaction.

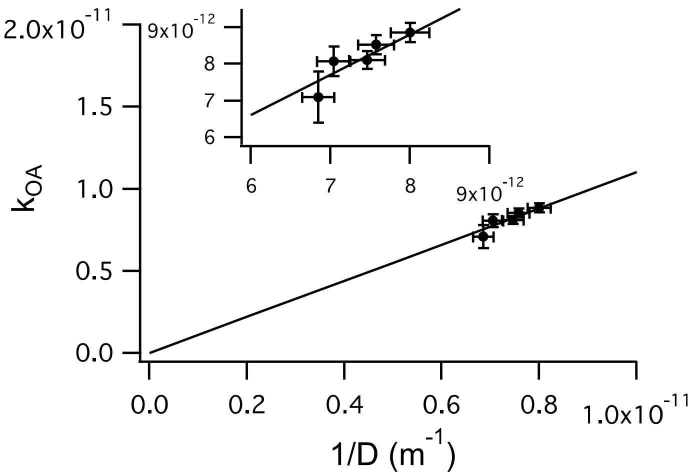

Figure S-3 Rate constants for oleic acid (k_{OA}) as a function of inverse particle diameter (1/D), measured at 2 ppm [H_2O_2] and 5 % [O_2]. The uncertainties represent the standard deviations of each individual measurement. The linear fit to the data set indicates that k_{OA} is inversely dependent on the particle diameter. The figure inset shows the magnified view of k_{OA} *vs.* 1/D.

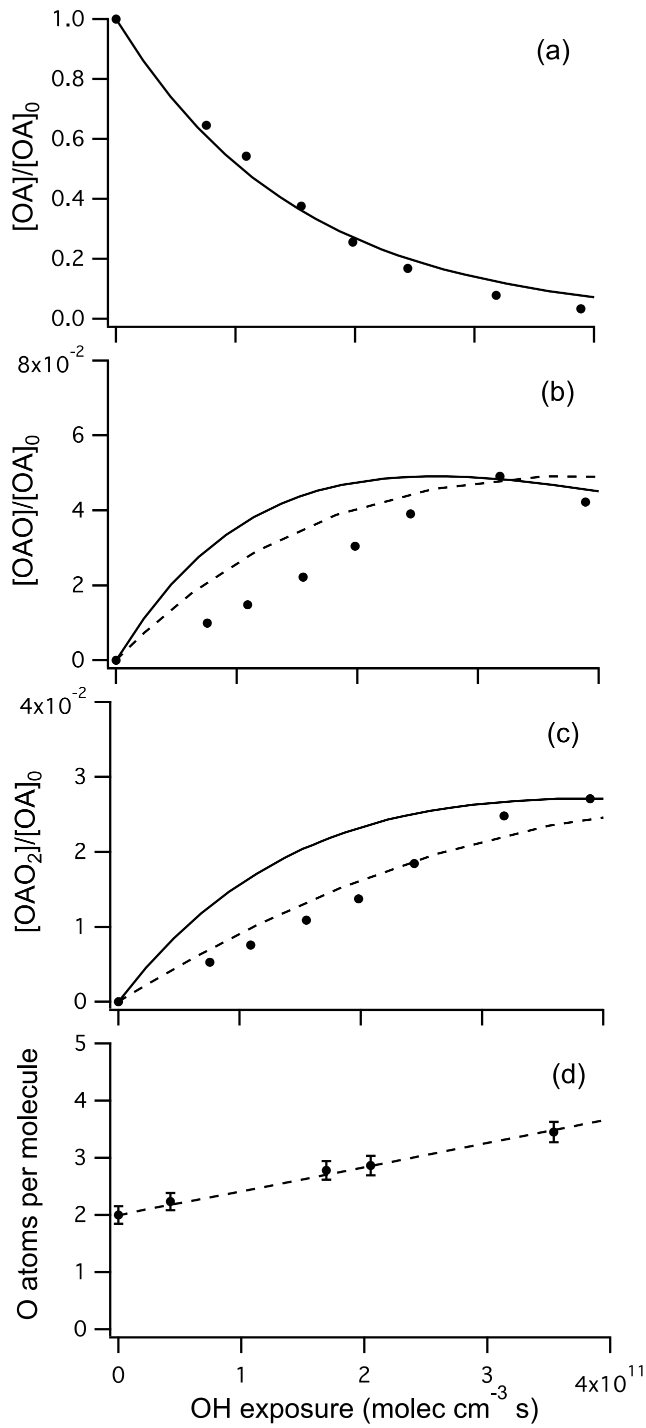

Figure S-4 (a) to (c) The kinetic evolution of oleic acid, OAO and OAO_2 as a function of OH exposure at $[H_2O_2]$ = 20.7 ppm for $[O_2]$ = 10 %. In panel (a), the decay of oleic acid is fit using Eq. (3) to obtain k_{OA} (solid line). In panels (b) and (c), the OAO and OAO_2 data sets are fit (dashed lines) using k_{OA}' (*i.e.* $k_{OA}' = 0.38 \times k_{OA}$) as described in the text. The solid lines in panels (b) and (c) are model predictions calculated using SAR, which serve as a comparison to the measured product evolutions. (d) Average number of oxygen atoms per oleic acid molecule as a function of OH exposure at $[H_2O_2]$ = 20.7 ppm for $[O_2]$ = 10 %. The uncertainties represent the standard deviations of individual measurements made at each OH exposure. The measured data are compared with predictions (dashed line) using k_{OA}' and the assumption that first generation higher molecular weight oxygenated reaction products with one and two added oxygenated functional groups are formed with equal probability.

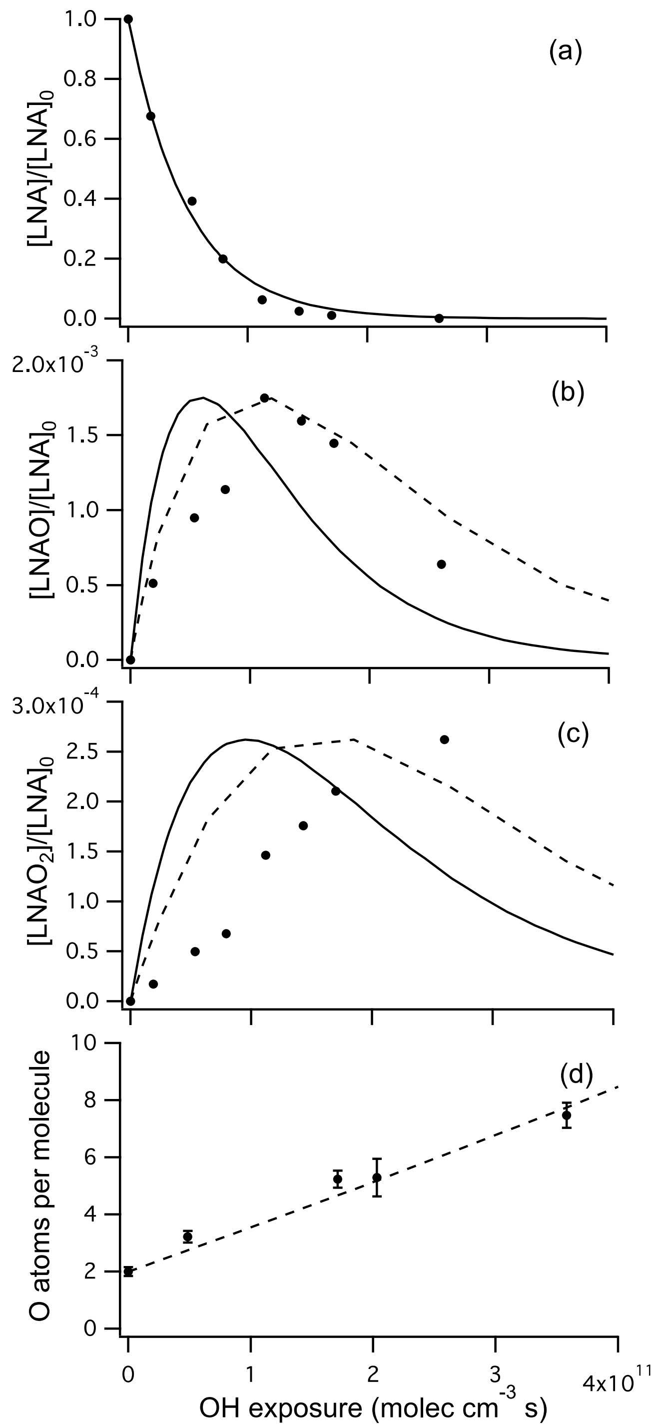

Figure S-5 (a) to (c) The kinetic evolution of linolenic acid, LNAO and $LNAO_2$ as a function of OH exposure at $[H_2O_2]$ = 20.7 ppm for $[O_2]$ = 10 %. In panel (a), the decay of linolenic acid is fit using Eq. (3) to obtain k_{LNA} (solid line). In panels (b) and (c), the LNAO and $LNAO_2$ data sets are fit (dashed lines) using k_{LNA}' (*i.e.* $k_{LNA}' = 0.46 \times k_{LNA}$) as described in the text. The solid lines in panels (b) and (c) are model predictions calculated using SAR, which serve as a comparison to the measured product evolutions. (d) Average number of oxygen atoms per linolenic acid molecule as a function of OH exposure at $[H_2O_2]$ = 20.7 ppm for $[O_2]$ = 10 %. The uncertainties represent the standard deviations of individual measurements made at each OH exposure. The measured data are compared with predictions (dashed line) using k_{LNA}' and the assumption that first generation higher molecular weight oxygenated reaction products with one and two added oxygenated functional groups are formed with equal probability.