Supporting Information

Enami et al. 10.1073/pnas.0710791105

SI Text

Aqueous solutions are pumped (50 μl min⁻¹; Harvard Apparatus) into the spraying chamber of a commercial ESMS instrument (HP-1100 MSD; Agilent) through a grounded stainless steel needle injector (100-μm internal diameter, 150-μm external diameter) and pneumatically nebulized by means of N₂ gas flowing through a coaxial sheath (1). The difference between the exit velocities of the liquid jet (10.6 cm s⁻¹) and nebulizer gas (2.65 × 10⁻³ cm s⁻¹) is so large that the drag imposed on the liquid breaks it apart into submicron-size droplets. The terminal velocities of the microdroplets thus produced exceed ~10⁻³ cm s⁻¹ (2) that lead to transit times shorter than τ = 1 ms across the ~0.5-cm-wide O₃(g) plume. These droplets, which are produced by fragmentation of electrically neutral solutions from a grounded injector, are charged via statistical fluctuations that scale with (drop size)⁻¹/² (3). The ensemble of spray droplets is, on average, neutral, but individual droplets actually carry charges that follow a Gaussian distribution, as expected for a random process. This phenomenon is the basis of the classical oil drop experiment performed by Millikan (4) to determine the magnitude of the elementary charge. It should be emphasized that spontaneous, asymmetrical charge separation during pneumatic nebulization of liquids does not produce highly charged droplets, and, therefore, it is unrelated to electrospray ionization of droplets issuing from high-field nozzles. Sprayed droplets eventually contract via solvent evaporation, a process regulated by ambient temperature and relative humidity, thereby increasing electrostatic repulsion among excess surface charges. Coulomb explosions ensue in which drops shed interfacial charge and mass into smaller droplets. In the final stage, ions are ejected from nanodroplets into the gas phase (5–7). It is apparent that, by its very nature, this technique effectively samples the interfacial layers of nano-droplets. Product identities were confirmed via MS–MS analyses performed in an Agilent MSD-Trap mass spectrometer.

Ozone is generated by flowing ultrapure O₂(g) (Air Liquid America Co.) through a commercial ozonizer (Ozone Solutions), diluted tenfold with ultrapure N₂(g), and quantified by UV absorption spectrophotometry (HP 8452) at 250 and 300 nm before entering the spraying chamber, where it contacts the aqueous AH₂ droplets for ~1 ms. This arrangement has been described and illustrated in detail in ref. 1. Throughout the reported [O₃(g)] values, which correspond to the concentrations actually sensed by microdroplets in the reaction chamber, are estimated to be ~10 times smaller than the values determined from UV absorbances because of further dilution by the N₂ drying gas. Gas flows were regulated by calibrated mass flow controllers (MKS). Typical instrumental parameters were as follows: drying gas temperature, 250°C; nebulizer pressure, 2 atm; collector capillary voltage, +3.5 kV; fragmentor voltage, 17 V. We have evidence that droplets are weakly charged under present conditions. Solutions were prepared in MilliQ water, or in D₂O (D > 99.9%; Cambridge Isotope Laboratories) that had been previously purged with ultrapure N₂(g) longer than 30 min. L-[¹³C]AH₂ (> 99%; Sigma–Aldrich), L-[¹-¹³C], L-[²-¹³C], and L-[³-¹³C] AH₂ (Omicon), calcium threonate (Sigma–Aldrich), DHA (Sigma–Aldrich), and tert-butanol (Fisher) were used as received. Solutions pH was measured with a calibrated pH meter (VWR).

Appendix 1. Reactant diffusion from the droplets core may account for the leveling off, i.e., the weaker than exponential decay of [AH⁻][AH⁺]₀ vs. [AH⁺]₀ (Fig. S5 Upper). If the concentration of X = AH⁻ in the interfacial layers is determined by its reaction with O₃(aq) = O₃(g), and by diffusion from the droplets core, then:

\[ \frac{\partial [X]}{\partial t} = \frac{D[X]_0 - [X]}{\delta} - kO_3[X]; D' = \frac{D}{\delta \Delta} \]  
\[ [X] = \frac{D'[X]_0 - kO_3[X] \exp{(-D'[kO_3]t)}}{D' + kO_3} \]  
\[ \frac{[X]_{ss}}{[X]_0} = \frac{D'}{D' + kO_3} \]  
\[ \frac{\partial ([X]_0/[X]_0)}{\partial [O_3]} \to -k \]  

where D is the diffusion coefficient of X in water, δ is the thickness of the interfacial shell, and Δ is the length over which its intradroplet concentration gradient is established. k is the local (X + O₃) reaction rate constant in the interfacial layers. The solution of Eq. 1 is given by Eq. 2. In the absence of diffusion, i.e., D' = 0, [X] decays exponentially with time, at constant [O₃]. However, since X can diffuse (with D' = 2 × 10⁻³ cm² s⁻¹) in tens of nanoseconds through, say, a Δ = 10-nm layer, a stationary state should be rapidly established within the ~1-ms timeframe of our experiments. This condition is encoded by equation Eq. 3, the limiting form of Eq. 2 at t → ∞. By assuming, as a first approximation, that D' is constant, the [X]₀/[X]₀ ratio becomes an inverse rational function of [O₃] at constant contact time. The initial slope, given by Eq. 4, is therefore proportional to the reaction rate constant k. Plots calculated from Eq. 3 for various parameter combinations (Fig. S3) show that [X]₀/[X]₀ indeed “levels off” at large [O₃(g)], supporting our interpretation of this phenomenon. A more realistic analysis should deal with the development of intradroplet concentration gradients as functions of time, radius, and [O₃(g)] (8), but it is doubtful that classical continuum diffusion models will be adequate for this task. The leveling off of experimental [AH⁻][AH⁺]₀ vs. [O₃(g)] curves cannot be due to diffusional limitations in the gas-phase because this event is not replicated in the ozonolysis of other anions, such as S₂O₅⁻ or I⁻, over the same [O₃(g)] range in 1 atm N₂(g) (1). Note that, since intradroplet diffusion contributes significantly to monitored interfacial [X] concentrations, interfacial layers behave as open reactors in which formal product P yields calculated as: Yₚ = ([P]₀ - [P]₀)/([X]₀ - [X]₀) may exceed unity (1, 9). Conventional integrated kinetic equations for closed, well mixed chemical reactors are, of course, inapplicable to interfacial layers.

Appendix 2. In Appendix 1, it was shown that the slopes of [AH⁻][AH⁺]₀ vs. [O₃(g)] curves at [O₃(g)] = 0 are proportional to reaction rate constants k (Eq. 4). To obtain limiting slopes, γ, Eq. 7, from experimental data, [AH⁻][AH⁺]₀ curves were fitted over the full [O₃(g)] range (Fig. S5 Upper) using the four-parameter expression Eq. 5:

\[ y = y_0 + a \exp(-bx) + cx \]  
\[ y = [AH^{-}][AH^{+}]_0; x = [O_3(g)] \]  
\[ \gamma = \left[ \frac{\partial y}{\partial x} \right]_{x=0} = -ab + c \]
Regression results are shown in Table S1. Notice that c values make negligible contributions to γ. γ is in [ppm⁻¹]. A γ vs. pH plot is shown in Fig. S4.

\[
\gamma = \gamma_0 + \frac{A}{1 + \exp \left( \frac{\text{pH} - \text{pH}_{0.5}}{B} \right)}
\]

\[
\gamma_0 = 0.41; A = -0.26; B = 0.21; \text{pH}_{0.5} = 3.98
\]

**Appendix 3. Initial slopes in Fig. 3:**

\[
\gamma_P = \left[ \frac{\partial [P]}{\partial [O_3]} \right]_{[O_3]=0}
\]

were calculated from best-fit numerical regressions to experimental data. Second-order polynomials \([P] = A_0 + A_1 [O_3(g)] + A_2 [O_3(g)]^2; \gamma_P = A_1\) were used in the case of \(P \equiv \text{THR and AOZ}\), and exponential growth curves \([P] = B_0 + B_1 \times (1 - \exp(-B_2 [O_3(g)])); \gamma_P = B_1 \times B_2\) for \(P \equiv \text{DHA, }<20 \text{ ppm [O}_3(g)\text{]}.\) Concentrations are directly proportional to signal intensities in these ranges. The results are shown in Table S2. \(\gamma_P\) is in [signal intensity/μu. ppm⁻¹]. The \((\gamma_{\text{THR}}/\gamma_{\text{DHA}})\) and \((\gamma_{\text{AOZ}}/\gamma_{\text{DHA}})\) ratios are plotted as function of pH in Fig. 4a. The ratios of the corresponding signal intensities measured at 800 ppm [O₃(g)] as functions of pH, which are more representative of net product formation after the complete decomposition of the primary ozonide intermediate POZ, are shown in Fig. 4b.

**Appendix 4.** The dissimilar evolution of AH₂ and DHA versus THR and AOZ with [O₃(g)] indicate that DHA is a primary product, whereas THR and AOZ ensue from the decomposition of an unstable intermediate, probably the primary ozonide POZ (Scheme 1). \(A \equiv [\text{AH}_2], B \equiv [\text{DHA}], C \equiv [\text{POZ}]\) and \(D \equiv [\text{AOZ}]; [\text{AH}^+] = [\alpha [\text{AH}_2]]\) throughout. The following simplified mechanism should describe our system at small conversions, i.e., barring extensive diffusion (see Appendix 1):

\[
A + O_3 \rightarrow B; \, a k_1 = k'_1
\]

\[
A + O_3 \rightarrow C; \, (1 - a) k_2 = k'_2
\]

\[
C \rightarrow D; \, k_3
\]

\[
C + O_3 \rightarrow D; \, k_4
\]

\[
f = \exp(-(k'_1 + k'_2)[O_3]^3)
\]

\[
g = \exp(-(k_3 + k_4)[O_3]^3)
\]

\[
h = k_3 [O_3]^3 [k_3 + (k_4 - k_1 - k_2)] [O_3]^3]
\]

\[
m = k_3 [O_3]^3 [k_3 + (k_4 - k_1 - k_2)] [O_3]^3]
\]

\[
A_0 = 1; B_0 = C_0 = D_0 = 0
\]

\[
D = m (1 - f); \, C = h (f - g); \, D = 1 - f - m (1 - f) - h (f - g)
\]

Fig. S7 shows experimental data for DHA and AOZ vs. [O₃(g)] at pH 5.8 (from Fig. 3) and the results of evaluating B and D using \(\tau = 0.001 \text{ s}, k'_1 = 600, k'_2 = 200, k_4 = 12 \text{ (in ppm}^{-1} \text{s}^{-1} \text{units)}\) and \(k_3 = 50 \text{ s}^{-1}\), in the equations above. The dashed line corresponds to the curve calculated by substituting \((k_3 = 0; k_4 = 16 \text{ ppm}^{-1} \text{s}^{-1})\) for \((k_3 = 50 \text{ s}^{-1}; k_4 = 12 \text{ ppm}^{-1} \text{s}^{-1})\) in the previous set of parameters. It is apparent that the decomposition of POZ involves unimolecular (step 3) and ozone-catalyzed (step 4) pathways (10). Neither pathway alone is able to account for a nonvanishing initial slope \(\gamma_{\text{AOZ}}\) and increased AOZ production at larger [O₃(g)]. At the [O₃(g)] <0.5 ppm concentrations prevalent in polluted atmospheres, the decomposition of POZ will largely proceed unimolecularly via step 3 in less than \(\approx 1\) s.

Fig. S1. Lack of initial AH2 concentration effects on its reactivity toward O3(g) at pH 3.8.
Fig. S2A. Continuous flow T-mixer setup used to study the reaction between AH$_2$ and O$_3$ in bulk water. Aqueous AH$_2$ solutions (1 mM) at pH 3.8 and O$_3$-sparged water were pumped through the T-mixer into the ESMS for analysis after ~4-s contact time.
Fig. S2B. ESMS of AH2 in the absence of O3(aq). ESMS of AH2 mixed with O3(aq). Note the formation of THR (m/z = 135), DHA·H2O⁻ (m/z = 191) and DHA·(H2O)₂⁻ (m/z = 209), and the absence of AOZ⁻ (m/z = 223).
Fig. S3: \([\text{AH}^-]/[\text{AH}^-]_0\) vs. \([\text{O}_3(g)]\) plots calculated from Eq. 3 using the reported parameters. (Upper) Log \([\text{AH}^-]/[\text{AH}^-]_0\) vs. \([\text{O}_3(g)]\). (Lower) \([\text{AH}^-]/[\text{AH}^-]_0\) vs. \([\text{O}_3(g)]\).
Fig. S4. Symbols indicate initial slopes $\gamma$ (Eq. 7 and Table S1) vs. bulk pH for the decay of AH$^+$ in the ozonolysis of AH$_2$. The curve is a best fit to the experimental slopes from Table S1 using the sigmoidal function Eq. 8. Best-fit parameters lead to $\gamma_{pH=3}/\gamma_{pH=0} = 2.73$. Note that pH$_{0.5} = 3.98 \pm 0.18 = pK_a(AH_2) = 4.10$. 
Fig. S5. Ascorbate and reaction products as functions of $[O_3(g)]$ in the range of 0–880 ppm. Red, pH 3.8; light blue, pH 4.7; green, pH 5.8; dark blue, pH 8.1.
Fig. S6. Decay of OD-substituted AH\(^+\) isotopologues as a function of \([\text{O}_3(\text{g})]\) in the ozonolysis of 1 mM AH\(_2\) in 50/50 H\(_2\)O/D\(_2\)O (vol/vol) at pH 6.7. The virtually indistinguishable decays of the various isotopologues exclude significant H-transfer control in the rate-controlling steps of AH\(_2\) ozonolysis.
Fig. S7. Results of calculations based on the mechanism and parameters given in Appendix 4.
Fig. S8. Symbols indicate experimental data at pH 5.8 from Fig. 3. Solid lines, calculated with the mechanism and parameters given in Appendix 4; dashed line, calculated by assuming that the primary ozonide is stable ($k_3 = 0$) but decomposes when assisted by O$_3$ (9). (Lower) Expanded view of the fit to AOZ near the origin in a linear ordinate scale.
Table S1. Parameters obtained by fitting Eq. 5 to the data of Fig. S3 Upper

<table>
<thead>
<tr>
<th>pH</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>$R^*$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2</td>
<td>0.24 ± 0.00</td>
<td>0.66 ± 0.02</td>
<td>−0.001</td>
<td>0.992</td>
<td>−0.159 ± 0.005</td>
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<tr>
<td>3.8</td>
<td>0.35 ± 0.00</td>
<td>0.53 ± 0.02</td>
<td>−0.0045</td>
<td>0.998</td>
<td>−0.190 ± 0.007</td>
</tr>
<tr>
<td>3.8</td>
<td>0.28 ± 0.01</td>
<td>1.18 ± 0.09</td>
<td>−0.0139</td>
<td>0.976</td>
<td>−0.270 ± 0.021</td>
</tr>
<tr>
<td>4.5</td>
<td>0.48 ± 0.01</td>
<td>0.76 ± 0.03</td>
<td>−0.0106</td>
<td>0.988</td>
<td>−0.375 ± 0.015</td>
</tr>
<tr>
<td>4.7</td>
<td>0.67 ± 0.01</td>
<td>0.63 ± 0.02</td>
<td>−0.009</td>
<td>0.998</td>
<td>−0.431 ± 0.014</td>
</tr>
<tr>
<td>5.8</td>
<td>0.70 ± 0.00</td>
<td>0.57 ± 0.01</td>
<td>−0.007</td>
<td>0.999</td>
<td>−0.406 ± 0.007</td>
</tr>
<tr>
<td>7.7</td>
<td>0.74 ± 0.01</td>
<td>0.53 ± 0.01</td>
<td>−0.008</td>
<td>0.999</td>
<td>−0.400 ± 0.008</td>
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</tbody>
</table>

*Correlation coefficient.
Table S2. Initial slopes, $\gamma_p$, for the DHA, THR, and AOZ curves of Fig. 3

<table>
<thead>
<tr>
<th>pH</th>
<th>$\gamma_{DHA}$</th>
<th>$\gamma_{THR}$</th>
<th>$\gamma_{AOZ}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.8</td>
<td>755 ± 30</td>
<td>470 ± 2</td>
<td>100.0 ± 0.4</td>
</tr>
<tr>
<td>4.7</td>
<td>1896 ± 81</td>
<td>369 ± 5</td>
<td>45.7 ± 0.6</td>
</tr>
<tr>
<td>5.8</td>
<td>1572 ± 72</td>
<td>260 ± 3</td>
<td>28.6 ± 0.8</td>
</tr>
<tr>
<td>8.1</td>
<td>2577 ± 95</td>
<td>349 ± 5</td>
<td>32.5 ± 1.4</td>
</tr>
</tbody>
</table>