Coupled interfacial and bulk kinetics govern the timescales of multiphase ozonolysis reactions

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Abstract

Chemical transformations in aerosol impact the lifetime of particle-phase species, the fate of atmospheric pollutants, and both climate and health-relevant aerosol properties. Timescales for multiphase reactions of ozone in atmospheric aqueous phases are governed by coupled kinetic processes between the gas-phase, the particle interface and its bulk, which respond dynamically to reactive consumption of O\(_3\). However, models of atmospheric aerosol reactivity often do not account for the coupled nature of multiphase processes. To examine these dynamics, we use new and prior experimental observations of aqueous droplet reaction kinetics, including three systems with a range of surface affinities and ozonolysis rate coefficients (trans-aconitic acid (C\(_6\)H\(_6\)O\(_6\)), maleic acid (C\(_4\)H\(_4\)O\(_4\)) and sodium nitrite (NaNO\(_2\))). Using literature rate coefficients and thermodynamic properties, we constrain a simple two-compartment stochastic kinetic model, which resolves the interface from the particle bulk and represents O\(_3\) partitioning, diffusion and reaction as a coupled kinetic system. Our kinetic model accurately predicts decay kinetics across all three systems, demonstrating that both the thermodynamic properties of O\(_3\) and the coupled kinetic and diffusion processes are key to making accurate predictions. An enhanced concentration of adsorbed O\(_3\), compared to gas and bulk phases, is rapidly maintained and remains constant even as O\(_3\) is consumed by reaction. Multiphase systems dynamically seek to achieve equilibrium in response to reactive O\(_3\) loss, but this is hampered at solute concentrations relevant to aqueous aerosol by the rate of O\(_3\) arrival in the bulk by diffusion. As a result, bulk-phase O\(_3\) becomes depleted from its Henry’s Law solubility. This bulk-phase O\(_3\) depletion limits reaction timescales for relatively slow-reacting organic solutes with low interfacial affinity (i.e., trans-aconitic and maleic acids, with k\(_{rxn}\) \(\sim\) 10\(^3\) - 10\(^4\) M\(^{-1}\) s\(^{-1}\)), which is in contrast to fast-reacting solutes with higher surface affinity (i.e., nitrite, with k\(_{rxn}\) \(\sim\) 10\(^5\) M\(^{-1}\) s\(^{-1}\)) where surface reactions strongly impact observed decay kinetics.

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1. Introduction

Atmospheric aerosol properties have important implications for climate, air-quality and health.\textsuperscript{1-3} Multiphase aerosol chemical transformations govern the fate of particle phase species, including organic pollutants,\textsuperscript{4, 5} and both climate and health-relevant aerosol properties.\textsuperscript{6-8} The rates and mechanisms of these reactions are governed not only by the concentrations of atmospheric oxidants (e.g., O$_3$, OH radicals), but also by the variable composition of organic and inorganic aerosol components and the often significant fraction of liquid water.\textsuperscript{9-11} To understand these chemical transformations, we need to consider multiphase reaction dynamics in concentrated to dilute aqueous phases relevant to aqueous aerosol and cloud water, which may not reflect the purely organic aerosol systems that are often the focus of mechanistic laboratory studies.\textsuperscript{12-15}

In tropospheric multiphase reactions, O$_3$ is an important oxidant that enters the condensed phase through partitioning from the gas phase. This Henry’s Law partitioning into atmospheric aqueous phases is governed by two coupled adsorption-desorption and solvation-desolvation equilibria; connecting the gas, interface and bulk phases.\textsuperscript{16, 17} The position of these two coupled equilibria will respond dynamically to the consumption of O$_3$ by both interfacial and bulk reactions, such that O$_3$ transport and chemical reaction are inherently coupled.\textsuperscript{15} A large number of reaction rate coefficients from beaker-scale laboratory experiments are available for atmospherically relevant aqueous phase ozonolysis reactions.\textsuperscript{18} However, to use these bulk rate coefficients to predict reaction timescales in atmospheric aqueous phases we must be able to accurately represent how adsorption, desorption, solvation, desolvation and diffusion processes control multiphase reaction rates.\textsuperscript{19-21} Further, evidence from both molecular dynamics simulations and experimental studies suggests that, compared to gas and bulk phases, O$_3$ is enhanced at the air-water interface.\textsuperscript{22-25} Models of multiphase reactions must adequately capture the steady-state position of these coupled equilibria to predict characteristic reaction timescales.

Most models used to interpret and predict timescales for multiphase aerosol chemistry rely upon resistor model formulations for limiting cases of reactivity and diffusivity. In these resistor models, kinetic steps that hinder uptake and reaction are represented in analogy to resistances in electric circuits.\textsuperscript{16, 21, 26, 27} To arrive at analytical expressions for reaction timescales, resistor models apply simplifying assumptions related to steady-state conditions, mixing, and decoupled surface and bulk processes.\textsuperscript{21, 27} The resulting set of idealized limiting cases yields significant insight into heterogeneous and multiphase chemistry, and has allowed identification of potential rate-limiting processes over a range of experimental conditions.\textsuperscript{3, 19, 27-32} For multiphase ozonolysis reactions, commonly applied limiting cases include: (1)
bulk reaction limited by ozone diffusion (i.e., reaction occurs in a thin shell below the interface, quantified by the reacto-diffusive length \( L_{RD} = (D_{O3}\tau_{O3})^{\frac{1}{2}} \) where \( \tau_{O3} \) is the chemical lifetime of O3 in the condensed phase); (2) bulk reactions not limited by ozone diffusion (i.e., a dilute or “phase-mixed” limit\(^{16} \)); and (3) interface-dominated reactions.\(^{16, 21, 27, 31, 32} \) A resistor model limiting-case, or combination of limiting cases, is fit to experimental data to yield an uptake coefficient (i.e., \( \gamma \), the fraction of gas collisions that lead to reaction in, or on, the particle). Experimental data is then interpreted in the context of the limiting processes required to adequately account for observations.\(^{30} \) This resistor approach is not computationally cumbersome; however, limiting cases often cannot describe the full range of atmospherically relevant regimes in particle-phase reactant concentrations and diffusivity, and by necessity neglect the coupled nature of interfacial and bulk processes.\(^{21, 27} \)

Efforts to overcome some of these challenges can be characterized by three broad approaches. First, the resistor model limiting cases can be extended to incorporate additional resistances to particle phase uptake.\(^{21} \) For example, a resistor model conductance for diffusion of particle-phase reactants has been derived and improves the accuracy of resistor model fits for viscous particles where diffusion of both reactants becomes limiting.\(^{21, 30} \) Second, flux-based kinetic multilayer models have been coupled with inverse modelling to infer kinetic parameters by fitting the model to large sets of experimental data.\(^{28, 33-37} \) These depth-resolved models can address previous challenges in representing non-uniform mixing, and provide insight into the coupling between reaction and diffusion in viscous systems.\(^{38-40} \) However, without extensive and targeted experimental data sets,\(^{34} \) this approach can result in under-constrained models. Even for well-studied pure organic systems, such as oleic acid,\(^{15} \) challenges arise in reconciling inverse-modelled kinetic parameters with experimental values. A third approach is to build kinetic models with computational and experimental constraints on elementary reaction steps. This approach aims to provide predictive, albeit simple, models that can be tested against experiment without adjustable parameters.\(^{41, 42} \) While this approach is independent of the numerical modelling tools used, it has been coupled with stochastic kinetic simulations\(^{43} \) to represent aerosol multiphase and heterogeneous chemistry in both pure organic and aqueous aerosol systems oxidized by OH or O3.\(^{42, 44-48} \) For O3 oxidation of pure organic sub-micron aerosol (e.g., squalene,\(^{13} \) tricosene\(^{45} \)) such models have indicated that only near-surface O3 reactions can explain the observed particle-phase decay timescales, whereas bulk reactions driven by Henry’s Law O3 partitioning provide kinetics that are too slow to explain experimental results.\(^{13, 49} \) These particular model frameworks have not been challenged with aqueous aerosol systems and micron-sized
particles, where the coupled nature of O$_3$ partitioning kinetics, diffusion and reaction may become important.

Existing models of multiphase O$_3$ chemistry often do not account for coupling of interfacial partitioning kinetics with diffusion and reaction, which may be important for predicting the timescale of bimolecular reactions in atmospheric aqueous phases. In this work, we apply a physically-constrained stochastic kinetic model of multiphase O$_3$ chemistry to predict the timescales of reactions in levitated aqueous, micron-sized particles. We test our predictive model using three model systems with different reaction rate coefficients with O$_3$ and differing affinities for the interface (trans-aconitic acid (C$_6$H$_6$O$_6$), maleic acid (C$_4$H$_4$O$_4$) and sodium nitrite (NaNO$_2$)). Our predictive kinetic model illustrates how multiphase reactions are governed by coupled kinetic steps in the gas-phase, at the particle interface and in its bulk. Our aim is to provide a quantitative model framework for multiphase O$_3$ chemistry that can be extended to quantify rate-limiting processes over a wide range of reaction conditions where traditional resistor model limiting cases may not be applicable.

2. Experimental Design

Table 1: Experimental conditions for the ozonolysis of aqueous trans-Aconitic Acid (AA) droplets.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>RH (%)</th>
<th>O$_3$ (ppm)</th>
<th>$r_0$ (Microns)</th>
<th>[AA]$_0$ (molec. cm$^{-3}$)</th>
<th>[AA]$_0$ (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>87.9 ± 0.6</td>
<td>58.4</td>
<td>9.23</td>
<td>1.9 x 10$^{21}$</td>
<td>3.2</td>
</tr>
<tr>
<td>2</td>
<td>88.1 ± 1.3</td>
<td>65.2</td>
<td>9.06</td>
<td>1.9 x 10$^{21}$</td>
<td>3.2</td>
</tr>
<tr>
<td>3</td>
<td>90.9 ± 0.6</td>
<td>79.9</td>
<td>10.18</td>
<td>1.63 x 10$^{21}$</td>
<td>2.7</td>
</tr>
<tr>
<td>4</td>
<td>89.6 ± 2.2</td>
<td>78.1</td>
<td>10.76</td>
<td>1.76 x 10$^{21}$</td>
<td>2.9</td>
</tr>
<tr>
<td>5</td>
<td>89.6 ± 1.3</td>
<td>79.4</td>
<td>9.11</td>
<td>1.76 x 10$^{21}$</td>
<td>2.9</td>
</tr>
</tbody>
</table>

In our experiments, we monitor loss of particle-phase trans-aconitic acid (AA) via O$_3$ reaction in a monodisperse population of micron-sized aqueous particles (RH > 85%, Table 1) in a linear quadrupole electrodynamic trap (QET), coupled to single-droplet mass spectrometry and optical single-droplet sizing. Below we describe the QET, single-droplet mass spectrometry techniques, and the experimental sequence for studying multiphase reaction kinetics in the QET.

2.1 Quadrupole Electrodynamic Trap. The branched quadrupole electrodynamic trap (QET) confines charged droplets along the axis of the quadrupole trapping electrodes, and is described in Willis et al.$^{50}$ and Jacobs et al.$^{51}$ Aqueous micron-sized droplets are generated with a piezoelectric droplet
dispenser (Microfab, Inc., MJ-ABP-01, 30µm orifice), and are introduced into the QET branch and subjected to an induction voltage (± 100 – 500 V) to induce a net charge on the droplet. Charged droplets are confined in the electric field generated by four stainless steel trapping electrodes, with an AC amplitude of 100 – 500 V and frequency of 100 – 500 Hz. Droplets fall in a humidity-controlled gas flow approximately 12 cm to the lower portion of the QET, where they are held by a static DC voltage (up to ± 500 V) applied to a balancing electrode.

The linear QET traps multiple droplets simultaneously, which facilitates time-resolved experiments with a monodisperse droplet population (variability in diameter on the order of ± 2.5%) with consistent chemical composition. Two balancing electrodes are fixed approximately 6 cm apart along the lower portion of the QET providing multiple compartments for droplet trapping. A population of tens to hundreds of droplets (depending on size and charge) is dispensed through the QET branch at constant droplet dispenser voltage and pulse width, and trapped in the upper compartment. A single droplet is then moved from the upper to the lower compartment by setting the upper DC balancing voltage to zero for a duration of 1 – 50 ms. The single droplet trapped in the lower compartment is then sized, as described below, and ejected from the trap into the ionization region of an atmospheric pressure mass spectrometer with the aid of a humidity-controlled gas flow (Fig. S1).

2.2 QET environmental control. The QET is enclosed in an environmentally controlled chamber at ambient temperature (297.5 ± 0.5 K), where humidity is controlled by a zero air flow of 500 cm³ min⁻¹ (STP), split into a dry flow and a wet flow that passes through a water bubbler. The portion of wet and dry flows are controlled by mass flow controllers (MKS instruments), and their relative magnitude determines the relative humidity in the trap, which was monitored with an RH probe (Honeywell International Inc., HIH-4602C, ± 3.5% accuracy) at the QET inlet. Experiments were performed at high humidity (Table 1). Ozone was generated by passing a small flow of oxygen, 20 – 100 cm³ min⁻¹ (STP), through a corona discharge ozone generator, and diluting the resulting flow with 2 – 4 L min⁻¹ (STP) of nitrogen. The resulting flow (100 – 700 ppmv O₃) was sampled by an ozone monitor (2B Technologies, model 202M) and a small portion, 35 – 70 cm³ min⁻¹ (STP), was diverted through a rotameter and mixed with the gas flow entering the QET.

2.3 Droplet sizing. Trapped droplets are illuminated axially with a 532 nm laser (ThorLabs, CPS532), introduced from the top of the QET and focused toward the lower sizing compartment. Scattered light is collected on two CCD cameras (ThorLabs, DCC1645C) for droplet sizing and vertical droplet positioning in the lower QET compartment.⁵¹, ⁵² The scattering angle for droplet sizing (19.6°) was
measured using polystyrene latex spheres of known size (24.61 ± 0.22 µm diameter). Droplets are sized using interference fringes in the Mie scattering pattern collected at 90° to the incident light, with the method described by Davies. Briefly, angular peak positions (maxima in the angular scattering pattern) are iteratively compared with a library of expected peak positions, generated with Mie theory over a range of size and refractive index. The droplet refractive index is estimated from calculated droplet composition and water content (described below) and allowed to vary over a range (1.45 ± 0.03). The mean squared error between reference and recorded peak positions is minimized to extract the best fit droplet size. This method can provide radius measurements with an accuracy of up to ± 60 nm from micron-sized droplets.

2.4 Single Droplet Ambient Ionization Mass Spectrometry. All measurements used a Q Exactive Orbitrap Mass Spectrometer (ThermoFisher Scientific). The instrument was operated in negative ion mode, with a typical scan range of m/z 50 – 200, a resolution of 17500 and a maximum inject-time of 50 ms, resulting in a scan rate of 8 – 9 Hz. The QET was positioned above the mass spectrometer inlet and was coupled to a home-built ambient pressure ionization source by a grounded, stainless steel exit tube. Two complementary ionization sources are used in these experiments: paper spray ionization and thermal desorption coupled to helium glow discharge ionization. Development and use of these ion sources for detection of single micron-sized droplets is described in detail in Jacobs et al., Kohli & Davies and Willis et al. Their operation is summarized below.

Measurements of ozonolysis kinetics of trans-aconitic acid were made by thermally desorbing single particles and ionizing the resulting gas with helium glow discharge (GD) ionization near the inlet of the Q Exactive Orbitrap (Fig. S1). A home-built helium GD ionization source was coupled to a temperature-controlled vaporization platform for single droplet detection. The GD source is similar to that described by Upton et al., and was constructed from 1/16" tungsten electrodes housed in a glass flow cell with a 0.5 L min\(^{-1}\) (STP) helium flow. The needle electrode operated at 3 kV with a current of ~2.7 mA limited by a 1MΩ (10 W) resistor, and a discharge gap of 2.5 mm from the ground electrode. This configuration corresponds to the corona-to-glow discharge (DART-like) regime described by Shelley et al. Outflow from the GD source entered a heated stainless steel vaporizing block held at ground. The vaporizer temperature was controlled with a cartridge heater and a temperature controller (Omega Engineering, CN9300). Ejected droplets impact the heated substrate in the QET gas flow and the resulting gas phase molecules intersect with the GD outflow in the ionization region to form ions sampled by the MS. The total flow directed toward the MS inlet was 1.0 L min\(^{-1}\) (STP), with an absolute humidity a factor of two lower than that in the QET due to dilution by dry helium. Droplet size and composition, and
vaporization temperature, were manipulated such that no evidence for reagent ion depletion was observed during single droplet detection events.  

Paper spray (PS) ionization was used primarily for confirmation of product ions detected by GD ionization, and identification of additional fragile products not detectable by thermal desorption. Whatman grade SG81 silica-coated chromatography paper was cut into triangular substrates using a universal laser cutter to create triangular substrates with a base of 8 mm and height of 10 mm, leading to a spray tip angle of ~45 degrees. PS substrates were mounted in a stainless steel alligator clip to apply a negative voltage of 3 – 5 kV. Solvent (80:20 v/v HPLC grade CH₃OH:CHCl₃) was continuously supplied to the underside of the substrate with a PEEK delivery tube connected to a syringe pump operating at 20 µL min⁻¹. The PS substrate was positioned below the QET outlet such that sharp single droplet events were observed with duration ~1 – 4 seconds. Single droplets with polarity opposite to that of the PS ion source likely impacted near the tip of the PS substrate.  

2.5 Data collection and analysis. After trapping a droplet population, initial sizing and MS detection of unreacted single droplets, the dry component of the QET flow is replaced by an equal mass flow containing ozone, such that the relative humidity in the QET is maintained. Trapped droplets are exposed to ozone for a period of time, during which the outflow of the QET is sent to exhaust, and the size of a single droplet is monitored in the sizing compartment. After an exposure time has elapsed, ozone introduction into the QET is switched off and a series of single droplets (n > 8) are individually sized and ejected for MS detection, so that ozone is not present in the ionization region during droplet detection. This approach avoids unwanted gas-phase ozone (i.e., ion-molecule) chemistry in the ionization region. To improve the signal-to-noise ratio of product ions, multiple droplets (n = 3 – 5) can be ejected simultaneously from the lower QET compartment. By repeating the above process over the course of minutes to hours, we obtain kinetics of the reaction between droplet components and ozone (Fig. S1). Raw mass spectra were analyzed using the python based pymshelfreader (available at: github.com/frallain/pymshelfreader, using python 3.7.3), and Thermo Xcalibur. Time series of relevant exact masses, or background-subtracted mass spectra corresponding to single or multiple droplets, were extracted for further analysis. A single droplet detection event was defined as a signal with magnitude > 5 standard deviations above a running mean baseline. Detected droplet signals were integrated to provide the peak area corresponding to a single droplet at a particular exact mass-to-charge ratio, and these integrated signals are averaged over several (n > 8) single droplets at each ozone exposure. Data analysis code is available at github.com/willismd.
3. Model Formulation

Figure 1. Overview of modelling approach and framework. (Left) Schematic showing the rectangular prism simulation geometry, which corresponds to the dimensions of a spherical particles with radius = r. The prism consists of a surface volume that is 1 nm thick (thickness chosen to be consistent with the estimated free energy profile for trace gas adsorption, see Section 3.3), which represents the interface and is located on top of a bulk compartment that has height of r/3. (Right) Overall modeling scheme that includes three coupled equilibria comprised of sets of forward and reverse kinetics steps that govern O3 Henry’s Law partitioning (i.e., adsorption (ads), desorption (des), solvation (solv), desolvation (desolv)). These kinetic steps are coupled with reactions of adsorbed species at the interface, and diffusion (diff) of solvated species into the bulk where they become available for bulk reaction.

3.1 Overall kinetic scheme. We represent the multiphase reaction of ozone using three coupled equilibria comprised of sets of forward and reverse kinetic steps, as well as both interfacial and bulk reactions (Fig. 1). Our model does not assume equilibrium is reached, rather the kinetics of each forward and backward elementary step are represented explicitly. Organic molecules, both reactants and products, can diffuse and partition from the bulk to the interface. For example, the magnitude of surface partitioning of trans-Aconitic Acid (i.e., AA = X) at equilibrium (AA(ads) ↔ AA(bulk)) is described by rate coefficients for its solvation into the bulk and desolvation to the interface (ksolv and kdesolv). O3 appears in gas and bulk-phases and at the interface. The interfacial and bulk concentrations are controlled by two coupled equilibria, whose product is the overall gas-bulk Henry’s law coefficient, $H_{cc}^{gb}$. The adsorbed O3 concentration is governed by the gas phase ozone concentration [O3(g)] and its adsorption (kads) and desorption (kdes) rate coefficients, while the bulk concentration is controlled by the rate coefficients for solvation (ksolv) and desolvation (kdesolv) of adsorbed O3 and the diffusion coefficient (represented by the pseudo-first order rate coefficient for diffusion, kdiff, in Fig. 1). In Section 3.4 – 3.10, we describe the
elementary steps needed to represent the processes depicted in Fig. 1, and how we constrain the relevant rate coefficients from prior literature and Molecular Dynamics simulations.

3.2 Simulation Software. Kinetiscope©, an open access software package, is used to numerically simulate the multiphase reaction of O₃ with trans-Aconitic Acid (AA). Kinetiscope© uses a stochastic algorithm to propagate the chemical evolution of a system by randomly selecting among probability-weighted elementary reaction and diffusion steps, and is well-suited to numerically solving stiff systems. Models built with this software package have been used extensively to predict heterogeneous and multiphase transformations in submicron aerosols, as well as micron-sized emulsions that require quantitative descriptions of surface and bulk reactions, diffusion, and evaporation.
### Table 2: List of elementary reaction, partitioning and diffusion steps with rate coefficients for the surface and bulk compartments of the explicit kinetic simulations for *trans*-Acronic Acid

<table>
<thead>
<tr>
<th>No.</th>
<th>Surface Step</th>
<th>Rate Coefficient</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\text{O}_2(\text{g}) + \text{O}_2(\text{Site}) \leftrightarrow \text{O}_2(\text{ads})$</td>
<td>$(9.0 \times 10^{-1}) \cdot \sigma$ cm$^3$ site$^{-1}$ s$^{-1}$</td>
<td>a,b,c,d</td>
</tr>
<tr>
<td>2</td>
<td>$\text{O}_2(\text{ads}) \leftrightarrow \text{O}_3(\text{b}) + \text{O}_2(\text{Site})$</td>
<td>$4.6 \times 10^3$ s$^{-1}$</td>
<td>a,b,c,d</td>
</tr>
<tr>
<td>3</td>
<td>$\text{AA}(\text{ads}) + \text{O}_2(\text{ads}) \rightarrow \text{C}_4\text{Cl}(\text{ads}) + \text{Glyoxylic Acid}(\text{ads})$</td>
<td>$1.4 \times 10^{-3}$ cm$^3$ molec.$^{-1}$s$^{-1}$</td>
<td>e</td>
</tr>
<tr>
<td>4</td>
<td>$\text{C}_4\text{Cl}(\text{ads}) \rightarrow \text{C}_4\text{Product}(\text{ads})$</td>
<td>$7.9 \times 10^5$ s$^{-1}$</td>
<td>f</td>
</tr>
<tr>
<td>5</td>
<td>$\text{C}_4\text{Cl}(\text{ads}) + \text{Glyoxylic Acid}(\text{ads}) \rightarrow \text{C}_6\text{SOZ}(\text{ads})$</td>
<td>$1.3 \times 10^{-11}$ cm$^3$ molec.$^{-1}$s$^{-1}$</td>
<td>f</td>
</tr>
<tr>
<td>6</td>
<td>$\text{C}_4\text{Cl}(\text{ads}) + \text{O}_2(\text{ads}) \rightarrow \text{C}_4\text{Product}(\text{ads})$</td>
<td>$4.0 \times 10^{-11}$ cm$^3$ molec.$^{-1}$s$^{-1}$</td>
<td>f</td>
</tr>
<tr>
<td>7</td>
<td>$\text{AA}(\text{b}) + \text{Site} \leftrightarrow \text{AA}(\text{ads})$</td>
<td>$1.2 \times 10^{-11}$ cm$^3$ molec.$^{-1}$s$^{-1}$</td>
<td>g</td>
</tr>
<tr>
<td>8</td>
<td>$\text{C}_4\text{Cl}(\text{b}) + \text{Site} \leftrightarrow \text{C}_4\text{Cl}(\text{ads})$</td>
<td>$5.1 \times 10^{-11}$ cm$^3$ molec.$^{-1}$s$^{-1}$</td>
<td>g</td>
</tr>
<tr>
<td>9</td>
<td>Glyoxylic Acid(ads) + Site $\leftrightarrow$ Glyoxylic Acid(ads)</td>
<td>$2.7 \times 10^{-11}$ cm$^3$ molec.$^{-1}$s$^{-1}$</td>
<td>g</td>
</tr>
<tr>
<td>10</td>
<td>$\text{C}_4\text{Product}(\text{ads}) + \text{Site} \leftrightarrow \text{C}_4\text{Product}(\text{ads})$</td>
<td>$1.2 \times 10^{-11}$ cm$^3$ molec.$^{-1}$s$^{-1}$</td>
<td>g</td>
</tr>
<tr>
<td>11</td>
<td>$\text{C}_4\text{Product}(\text{b}) + \text{Site} \leftrightarrow \text{C}_4\text{Product}(\text{ads})$</td>
<td>$5.1 \times 10^{-11}$ cm$^3$ molec.$^{-1}$s$^{-1}$</td>
<td>g</td>
</tr>
<tr>
<td>12</td>
<td>$\text{C}_6\text{SOZ}(\text{ads}) + \text{Site} \leftrightarrow \text{C}_6\text{SOZ}(\text{ads})$</td>
<td>$1.2 \times 10^{-11}$ cm$^3$ molec.$^{-1}$s$^{-1}$</td>
<td>g</td>
</tr>
<tr>
<td>13</td>
<td>Glyoxylic Acid(ads) $\rightarrow$ Glyoxylic Acid($\text{ads}$) + Site</td>
<td>$1.0 \times 10^{-1}$ s$^{-1}$</td>
<td>h</td>
</tr>
</tbody>
</table>

### Diffusion Pathways

| D1   | AA(b) (Bulk) $\leftrightarrow$ AA(b) (Surface) | $8.4 \times 10^{-4}$ cm$^2$ s$^{-1}$ | i |
| D2   | C$_4$Cl(b) (Bulk) $\leftrightarrow$ C$_4$Cl(b) (Surface) | $8.3 \times 10^{-4}$ cm$^2$ s$^{-1}$ | i |
| D3   | Glyoxylic Acid(b) (Bulk) $\leftrightarrow$ Glyoxylic Acid(b) (Surface) | $1.2 \times 10^{-4}$ cm$^2$ s$^{-1}$ | i |
| D4   | C$_4$Product(b) (Bulk) $\leftrightarrow$ C$_4$Product(b) (Surface) | $1.1 \times 10^{-4}$ cm$^2$ s$^{-1}$ | i |
| D5   | C$_4$Product(b) (Bulk) $\leftrightarrow$ C$_4$Product(b) (Surface) | $8.9 \times 10^{-4}$ cm$^2$ s$^{-1}$ | i |
| D6   | C$_6$SOZ(b) (Bulk) $\leftrightarrow$ C$_6$SOZ(b) (Surface) | $7.2 \times 10^{-4}$ cm$^2$ s$^{-1}$ | i |
| D7   | O$_2$(b) (Bulk) $\leftrightarrow$ O$_2$(b) (Surface) | $1.76 \times 10^{-4}$ cm$^2$ s$^{-1}$ | j |

### Bulk

<table>
<thead>
<tr>
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<th>Rate Coefficient</th>
<th>Ref.</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>AA(b) + O$_2$(b) $\rightarrow$ C$_4$Cl(b) + Glyoxylic Acid(b)</td>
<td>$1.4 \times 10^{-11}$ cm$^3$ molec.$^{-1}$s$^{-1}$</td>
<td>e</td>
</tr>
<tr>
<td>2</td>
<td>C$_4$Cl(b) $\rightarrow$ C$_4$Product(b)</td>
<td>$7.9 \times 10^{-7}$ s$^{-1}$</td>
<td>f</td>
</tr>
<tr>
<td>3</td>
<td>C$_4$Cl(b) + Glyoxylic Acid(b) $\rightarrow$ C$_6$SOZ(b)</td>
<td>$1.3 \times 10^{-11}$ cm$^3$ molec.$^{-1}$s$^{-1}$</td>
<td>f</td>
</tr>
<tr>
<td>4</td>
<td>C$_4$Cl(b) + O$_2$(b) $\rightarrow$ C$_4$Product(b)</td>
<td>$4.0 \times 10^{-11}$ cm$^3$ molec.$^{-1}$s$^{-1}$</td>
<td>f</td>
</tr>
</tbody>
</table>

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a: Vacha et al.$^{22}$; b: Vieceli et al.$^{23}$; c: Sander$^{66}$; d: Utter et al.$^{67}$, Hu et al.$^{68}$, Magi et al.$^{59}$, Schütze et al.$^{70}$, Müller & Heal$^{71}$; e: Leitzke & von Sonntag; f: Vereecken et al.$^{72}$; g: Bleys and Joos$^{73}$; h: Wiegel et al.$^{42}$; i: Bidstrup and Geankoplis$^{74}$; j: Gottschalk et al.$^{75}$
Figure 2. Reaction scheme for ozonolysis of \textit{trans}-Aconitic Acid, showing reaction pathways and molecular structures of reactants and potential products. Products identified by single-droplet mass spectrometry are noted in red, with their measured exact masses and negative ion molecular formulas. A dominance of ≥C$_3$ products, and glyoxylic acid, (Fig. S3 & S4) in reacted particles suggests that the primary ozonide decomposes preferentially to form the C$_4$ Criegee Intermediate (B1). We note that the expected C$_4$ ketone product (B2) was observed at very low signal intensities in all experiments despite its structural similarity to other products detected with high relative signal intensity (e.g., Malonic acid, “C3 Product”), suggesting other possible important reaction pathways (B2). While fragmentation of both the highly oxygenated \textit{trans}-Aconitic Acid and its reaction products complicates spectral interpretation, we see no evidence that the fate of the C$_4$ Criegee intermediate impacts the loss rate of \textit{trans}-Aconitic Acid under these high humidity conditions.

\textbf{3.3 Simulation Geometry.} To model a spherical droplet with radius $= r$, Houle and coworkers$^{42, 47}$ showed that a rectangular prism simulation geometry, with a height of $r/3$, could be used (Fig. 1). Here, the prism is divided into two sub-volumes: a surface, and a bulk region below. Molecules move between these volumes by Fickian diffusion. This simulation geometry preserves the correct scaling between interface and bulk processes and is computationally more efficient than simulating an entire sphere. We assume that each sub-volume is instantaneously mixed. This assumption was tested with additional simulations where the single bulk volume, shown in Fig. 1, was divided up into smaller sub-volumes. For these test simulations the concentrations of reactants and products were uniform and we did not observe the formation of concentration gradients in [AA$_b$]. Concentration gradients do form in [O$_3$$_b$] since under aqueous aerosol conditions the reacto-diffusive length for ozone (on the order of 200 – 300 nm for AA
under our experimental conditions) is less than the particle radius for micron-sized aerosol. However, our model aims to represent kinetically distinct regions (i.e., interface, or surface volume, and bulk), and does not resolve bulk-phase gradients in $[O_3(b)]$.

The length and width of the prism are 1 X 1 nm (Fig. 1). The simulation results presented below are insensitive to these dimensions and were checked by using larger 100 nm x 100 nm x r/3 nm simulation volumes (Fig. S2). These expanded dimensions correspond to a 4 order of magnitude change in the total number of molecules in the simulation. An additional parameter is required to define the surface volume (i.e. the interface thickness, $\delta$). A thickness of 1 nm is used and is selected to be reasonably consistent with the width of the solvation free energy profile observed for trace gas adsorption in Molecular Dynamics simulations.$^{22-25}$ Surface thickness is used to convert surface concentrations (i.e., molecules cm$^{-2}$) to surface volume concentrations (i.e., molecules cm$^{-3}$).

3.4 Bulk Reaction Steps. We use a series of elementary reaction and diffusion steps in the explicit simulation (Table 2), with four elementary reaction steps in the bulk compartment (Fig. 2). Step B1 describes the reaction of dissolved $O_3(b)$ with AA. To our knowledge, the rate coefficient for the ozonolysis of AA has not been measured so instead we use a rate constant for a suitable proxy (i.e. fumaric acid, $C_4H_4O_4$) measured in the bulk aqueous phase by Leitzke and von Sonntag.$^{76}$ Fumaric acid and AA both have a $trans$ structure around the C=C moiety. We expect that the decomposition of the primary ozonide (Fig. 2) is very fast and therefore we do not include this unimolecular step explicitly. The products of step B1 are a Criegee intermediate (CI) and a carbonyl. From the carbon number distribution of the products (Fig. S3 & S4), as well as previous experiments,$^{13}$ we infer that the POZ decomposes asymmetrically to form mainly a $C_4$ –CI (Fig. 2) on a secondary carbon atom, and glyoxylic acid (see B1, Fig. 2). Once formed, the CI can react with water (B2) or the carbonyl co-product (B3), likely within the same solvent cage. In the aqueous phase, the rate coefficient for B2 is assumed to be $4.3 \times 10^{-15}$ cm$^3$ molec.$^{-1}$ s$^{-1}$; a value computed$^{77}$ for a gas phase CI with the water dimer ((H$_2$O)$_2$). Step B2 is expressed as a pseudo first order rate coefficient using the [H$_2$O] in the droplet (see below and Table 2). Mass spectra of reacted droplets (Fig. S3 & S4) using both glow-discharge and paper spray ionization show a predominance of $>C_2$ products, as well as glyoxylic acid, which we expect to efficiently evaporate from the particles during the reaction time. The apparent importance of $C_3$ product ions may be consistent with decarboxylation of the $C_4$ hydroxy hydroperoxide (shown in Fig. 2 and by Leitzke and von Sonntag$^{76}$); however, if this mechanism is a two-electron process, as suggested by Leitzke and von Sonntag$^{76}$, it would require a deprotonated acid group to proceed, which appears unlikely under our experimental conditions (see
Section 3.5). These C₃ product ions may also arise from decarboxylation during particle detection with either ionization method (Fig. S3), so we do not interpret the implications of our observed product ion distributions further. The rate coefficient for step B3, is taken from a prior heterogeneous ozonolysis study,¹³ in which this rate constant was constrained as part of a larger kinetic model. The rate constant for Cl + O₃ (B4) is from Vereecken et al.⁷⁷ and is based on coupled cluster calculations in combination with theoretical kinetic predictions. We do not include reaction of the CI with carboxylic acids in this aqueous system, because available experimental evidence suggests that this pathway is not observed in the presence of large water concentrations.⁷⁸, ⁷⁹ Thus, our assumptions about the fate of the CI do not alter the overall decay rate of AA, which is the main focus of this study.

We assume that these elementary steps (B1-B4) also occur at the interface (S3-S6) albeit with reactants in their adsorbed states (i.e. AA(ads) + O₃(ads)); consistent with a Langmuir Hinshelwood mechanism. In the absence of any knowledge about the magnitude of the interfacial rate coefficients for these reactions we assume that they proceed in the surface volume with the same rate coefficients as used in the bulk.

### 3.5 Bulk Concentrations and Density

The AA concentration and water content in the particles were estimated using the Aerosol Inorganic-Organic Mixtures Functional groups Activity Coefficients (AIOMFAC) model (aiomfac.lab.mcgill.ca)⁸⁰ and the experimental relative humidity (Table 1, Fig. S5). Aconitic acid is described in AIOMFAC using a functional group contribution method, which assumes that organic acid functionalities remain protonated. This assumption is reasonable for our experimental conditions as predictions of particle pH from the Extended AIM Aerosol Thermodynamics Model (E-AIM, aim.env.uea.ac.uk)⁸¹, ⁸² indicate a pH < 2, and the first pKa of trans-Aconitic Acid is 2.91, ⁸³ so we do not expect that the carboxylic acid groups are significantly deprotonated. For the organic systems studied here, we neglect ionic strength effects on the O₃ Henry’s Law constant (see Section 3.9) and on the ozone-organic reaction rate coefficients.

Densities for each of the species in the simulation are shown in Table S1. These molar volumes in addition to vapor pressures (described below) are required to accurately predict the change in droplet size during the reaction. We do not account for changes in hygroscopcity that might accompany the formation of the ozonolysis products, which would alter the water content and therefore the size of the droplet.

### 3.6 Diffusion Pathways

Reactants, products and intermediates are allowed to move between the surface and bulk compartments according to Fick’s Law. Once molecules diffuse into the surface compartment, they can either adsorb (S7-S12) or diffuse back into the bulk. Diffusion constants of all of
the organic species are estimated using the semi-empirical relationship developed by Bidstrup and Geankoplis\textsuperscript{74} for aqueous molecular diffusivities of carboxylic acids. The diffusion constant of O\textsubscript{3} in water is fixed to a literature value of $D = 1.76 \times 10^{-5}$ cm\textsuperscript{2} s\textsuperscript{-1}.\textsuperscript{75} For the experimental relative humidity range explored here (Table 1), the AIOMFAC model predicts particle viscosities of $1.12 \times 10^{-2} – 8.03 \times 10^{-3}$ Pa s, which is in the range where diffusion coefficients for ozone in aqueous organic particles approach that in pure water.\textsuperscript{39}

3.7 Interfacial Reaction Steps. In addition to the reaction steps S3-S6 listed in Table 2, we define a series of steps that describe the adsorption and desorption kinetics of molecules to/from the interface as shown conceptually in Fig. 1. Using a Langmuir\textsuperscript{84} framework, this is implemented in the simulation by defining the concentration of available adsorption sites (i.e., “Sites” in S7-S13) in the surface compartment.\textsuperscript{44} For the organic molecules in the simulation we assume that a site corresponds to a mean molecular area of 66 Å\textsuperscript{2}. This corresponds to a maximum interfacial concentration ($\Gamma_{\infty}$) of $1.5 \times 10^{14}$ molecules cm\textsuperscript{-2} and is consistent with a series of C\textsubscript{7} to C\textsubscript{9} di-carboxylic acids.\textsuperscript{73} Interfacial concentration is converted to a volumetric concentration using the interface thickness, $\delta$, which we set to 1 nm to be consistent with the width of the free energy profile for trace gas adsorption (Section 3.3). The depth of the interface in our simulations is significantly smaller than the reacto-diffusive length of O\textsubscript{3} (> 200 nm). During the simulation, adsorption sites are conserved, and we assume that all organic species compete for the same set of adsorption sites. For the adsorption and desorption of O\textsubscript{3}, a separate set of sites is defined (termed “O\textsubscript{3} _site” in S1 and S2), corresponding to the smaller molecular area of ozone of 18.5 Å\textsuperscript{2}, as computed by Vieceli et al.\textsuperscript{23} If the interface were to become saturated the volumetric concentration of O\textsubscript{3} in the surface compartment would be $5.4 \times 10^{21}$ molecules cm\textsuperscript{-3}.

We estimate adsorption and desorption rate constants using data reported by Bleys and Joos\textsuperscript{73} for a series of water soluble compounds (e.g. alcohols and di-carboxylic acids). The desorption rate coefficients vary little with molecular structure or functional group and therefore we use a median value of 90 s\textsuperscript{-1} for all species in the simulation.\textsuperscript{73} Adsorption rate coefficients strongly depend upon functional group (i.e. –OH vs. –COOH) and increase\textsuperscript{73} exponentially with increasing carbon number. Extrapolating an exponential fit to the linear dicarboxylic acid data (Fig. S6) reported in Bleys and Joos\textsuperscript{73} allows us to estimate the adsorption rate coefficient of the C\textsubscript{2}, C\textsubscript{3}, and C\textsubscript{4} product species in the simulation (S8-S11).

AA has three –COOH groups and thus we expect its adsorption rate coefficient is over-estimated relative to a dicarboxylic acid with the same carbon number. Instead, we estimate its adsorption rate coefficient based upon the surface tension data of citric acid; a structurally similar tri-acid. Citric acid is
moderately surface active and depresses surface tension, as a function of mole fraction, to a similar extent as malonic acid (C$_3$H$_4$O$_4$). Therefore, we use the C$_3$ adsorption rate coefficient as an estimate for AA and the C$_6$ SOZ, which also contains three –COOH groups. All of these organic species are highly water soluble and only moderately surface active, as can be shown using computed Langmuir isotherms with the adsorption/desorption rate coefficients shown in Table 2.

3.8 Evaporation. The C$_2$ carbonyl reaction product (glyoxylic acid) is the only product allowed to evaporate in the simulation. This is reasonable given the low volatility of the reactants (Fig. S7) and other major reaction products. The evaporation rate constant for glyoxylic acid in the simulation is computed, as described by Wiegel et al., using an estimated vapor pressure of 25 Pa from EPI Suite (US EPA Estimation Program Interface Suite, v 4.11).

3.9 Ozone Gas – Interface – Bulk Partitioning. Two equilibria govern the partitioning of ozone. First, the equilibria shown in step S1 (Table 2 and Fig. 1) describes the adsorption and desorption of gas phase ozone (O$_3$(g)) to and from the interface. Second, the equilibria shown in step S2, in turn, describes the kinetics of bulk solvation of adsorbed O$_3$ (O$_3$(ads)) and the reverse step of desolvation of bulk ozone (O$_3$(b)) to the interface. The product of the two corresponding equilibrium constants is the Henry’s law constant for O$_3$ in H$_2$O, which from prior literature is $H_{cp} = 1.11 \times 10^{-2}$ M atm$^{-1}$ ($H_{gb}^G = 0.27$, where $H_{cp}$ is the Henry’s Law constant defined by aqueous concentration and gas partial pressure, and $H_{cc}$ is the unitless Henry’s Law constant). $H_{cc} < 1$ indicates that O$_3$ is hydrophobic relative to other atmospheric oxidants (e.g., OH, HO$_2$) and that the difference in solvation free energy of O$_3$(b) relative to O$_3$(g) is positive (i.e., $\Delta G_{sol(gb)} = +0.76$ kcal mol$^{-1}$) computed from,

$$H_{gb}^G = \exp\left(\frac{-\Delta G_{sol(gb)}}{RT}\right)$$

Eq. (1)

Molecular Dynamics (MD) simulations indicate that the change in solvation free energy of O$_3$(ads) relative to O$_3$(g) ($\Delta G_{sol(gs)}$) is negative. Together with $\Delta G_{sol(gb)} > 0$, this indicates that ozone is enriched at the interface compared to both the gas and bulk phases. The range of interfacial solvation free energies from prior MD simulations are: -1.2 kcal mol$^{-1}$, -1.46 kcal mol$^{-1}$, -1.30 kcal mol$^{-1}$, and -1.5 kcal mol$^{-1}$. The variability in these energies is likely due to differences in computational methods; nevertheless, this range of free energies correspond to values of the gas-surface partitioning coefficient ($H_{cc}^{gs}$) of 7.6 - 12.5 (Eq. (1)). We constrain our model using the value reported by Vieceli et al. (-1.30 kcal mol$^{-1}$), which yields $H_{cc}^{gs} = 8.9$. Since the product of $H_{cc}^{gs}$ and $H_{cc}^{gb}$ must necessarily yield the correct $H_{cc}^{gb}$ (0.27) as determined by experiment, this implies that the change in solvation free energy for O$_3$(ads)
$\rightarrow$ O$_3$(b) is positive (+ 2.06 kcal mol$^{-1}$) with a value of $H_{cc}^{gb} = 0.03$. The resulting surface enrichment of ozone relative to gas and bulk phases is illustrated in Fig. S8 with a simulation showing the non-reactive uptake of ozone and its time dependent concentrations in the gas, interface and bulk phases.

$H_{cc}^{gs}$ corresponds to the equilibria in step S1 (Table 1), which consists of a forward adsorption ($ads$) and reverse desorption ($des$) step. At steady state, O$_3$ adsorption and desorption rates are equal so that,

$$k_{ads} \cdot [O_3(g)] \cdot [O_3\_site] = k_{des} \cdot [O_3(ads)]$$  \hspace{1cm} Eq. (2)

where $k_{ads}$ is proportional to the rate of O$_3$(g) entry into the surface compartment,

$$k_{ads} \cdot \sigma = \frac{1}{4} \cdot A \cdot \bar{c} \cdot \sigma = 9.0 \times 10^{-11} \cdot \sigma \ (cm^3 \ molec^{-1} \cdot s^{-1}) .$$  \hspace{1cm} Eq. (3)

$A$ is the area (1 x 1 nm$^2$) of the surface compartment, $\bar{c}$ is the mean speed of O$_3$ (360 m/s at 294K) and $\sigma$ is the sticking coefficient per O$_3$ site. The surface concentration ($\Gamma_\infty$) of O$_3$, as described above, corresponds to a volumetric concentration of adsorption sites at the interface such that,

$$[O_3\_site] = \frac{\Gamma_\infty}{\delta} = 5.42 \times 10^{21} \ sites \cdot cm^{-3}$$  \hspace{1cm} Eq. (4)

yielding the following expression for $H_{cc}^{gs}$,

$$H_{cc}^{gs} = \frac{[O_3(ads)]}{[O_3(g)]} = \frac{k_{ads} \cdot \bar{c} \cdot \sigma}{k_{des} \cdot \delta} = 8.9$$  \hspace{1cm} Eq. (5)

A similar expression can be written for the equilibrium shown in step S2 and its relationship to the surface to bulk partitioning coefficient, $H_{cc}^{gb}$, which relates $[O_3(ads)]$ and $[O_3(b)]$. At steady state,

$$k_{solv} \cdot [O_3(ads)] = k_{desolv}[O_3(b)] \cdot [O_3\_site]$$  \hspace{1cm} Eq. (6)

which yields the following expression,

$$H_{cc}^{gb} = \frac{[O_3(b)]}{[O_3(ads)]} = \frac{k_{solv}}{k_{desolv} \cdot \Gamma_\infty} = 0.03$$  \hspace{1cm} Eq. (7)

The relationships shown in Eqs. (5) and (7) constrain the ratios of $k_{solv}$ to $k_{desolv}$, $k_{ads}$ to $k_{des}$ and $k_{solv}$ to $k_{des}$, which is summarized in Eq. (8a) and (8b).

$$H_{cc}^{gb} = H_{cc}^{gs} \cdot H_{cc}^{sb} = \frac{[O_3(ads)]}{[O_3(g)]} \cdot \frac{[O_3(b)]}{[O_3(ads)]} = \frac{k_{ads} \cdot \bar{c} \cdot \sigma}{k_{des} \cdot \delta} \cdot \frac{k_{solv} \cdot \delta}{k_{desolv} \cdot \Gamma_\infty} = \frac{k_{ads} \cdot \sigma}{k_{des} \cdot k_{desolv}}$$  \hspace{1cm} Eq. (8a)

$$H_{cc}^{gb} = H_{cc}^{gs} \cdot H_{cc}^{sb} = 8.9 \times 0.03 = 0.27$$  \hspace{1cm} Eq. (8b)

Equation (8a) is analogous to previous formulations of the Henry’s Law constant in terms of adsorption, desorption, solvation and desolvation rate coefficients, as presented by Hanson 1997 (their Eq. 8b), Remorov and George, 2006 (their Eq. 18), Pöschl et al., 2007 (their Eq. 73) and Ammann et al., 2013 (their Eq. 21).
3.10 Determination of absolute values for $\sigma$, $k_{ads}$, $k_{des}$, $k_{sol}$ and $k_{desolv}$. The above relationships constrain only the ratio of rate constants. As discussed extensively by Shi et al., determining the absolute values of $k_{ads}$, $k_{des}$, $k_{sol}$ and $k_{desolv}$ can be difficult because they depend upon the model framework used to describe trace gas uptake. For instance, while both the critical cluster nucleation and Gibb’s surface excess models account for the experimental observations of ethanol uptake, the absolute values for $k_{des}$ and $k_{sol}$ differ by some 5 orders of magnitude. This difference arises because both models preserve only key ratios, for example $k_{sol}/k_{des}$, which are constrained by the experimentally determined mass accommodation coefficient ($\alpha$). Nevertheless, the relationships shown in Eqs. (2-8) do provide some additional constraints.

$k_{ads}$ and $k_{des}$ are not independent quantities since rearranging Eq. (5) yields,

$$k_{des} \left( s^{-1} \right) = \frac{k_{ads} \Gamma_\infty \sigma}{H_{cc}^{gs} \delta} \quad \text{Eq. (9)}$$

Eq. (9) shows that $k_{des}$ is inversely proportional to $H_{cc}^{gs}$, or the interfacial solvation free energy, which means that for a larger free energy change between gas and partial solvation at the interface, $k_{des}$ would necessarily become smaller. Using the values of $\Gamma_\infty$, $\delta$, $H_{cc}^{gs}$ and $k_{ads}$ derived above yields,

$$k_{des} = 5.48 \cdot 10^{10} \cdot \sigma \left( s^{-1} \right) \quad \text{Eq. (10)}$$

Equations (9) and (10) show that $k_{des}$ is directly proportional to $\sigma$, the assumed sticking probability. If all of the incoming gas phase O3 molecules collide with the interface and stick (i.e., $\sigma = 1$), $k_{des} = 5.48 \cdot 10^{10} \cdot 10^{-1}$, corresponding to a desorption lifetime ($\tau_{des} = k_{des}^{-1}$) of 18.2 ps. This is consistent with the simulated mean residence time of O3 on a water slab. Alternatively, if only a small fraction of the colliding molecules stick to the interface, and $\sigma = 10^{-4}$, then $\tau_{des} = 182$ ns. This change in $\tau_{des}$ with $\sigma$ is consistent with our intuition that the fraction of molecules that appear to “stick” on the liquid interface depends upon the observation time. If the observation window is short (~ps), then all of the molecules that have impinged upon the interface appear frozen, yielding a value of $\sigma = 1$. However, over much longer observation timescales the fraction of impinging molecules that remain at the interface decreases so that $\sigma < 1$. In MD simulations the fraction of O3 sticking trajectories drops precipitously with the duration of the simulation; from 87% at 3 ps to 0.8% at 90 ps, which is the maximum simulation time. Pairs of $\sigma$ and $\tau_{des}$ that both satisfy Eq. (10) and accurately describe a given experiment may be situational, to reflect the nature of the reaction mechanism. If the interfacial reaction proceeds via an Eley Rideal type mechanism, where a prompt reaction occurs upon a gas phase collision with a surface molecule, then the larger fraction of molecules with short surface residence times (~10’s of ps, on the order of a molecular vibration) might play a controlling role in the observed kinetics. Alternatively, the much smaller fraction of molecules with
comparably longer interfacial residence times (~100-200 ns) would be more important for a Langmuir
Hinshelwood mechanism that proceeds through long-lived adsorbed states. In reality, desorption times
and corresponding sticking coefficients are likely best represented by a distribution of values.

Here, we find that predicted reaction kinetics are invariant if three criteria are satisfied (Fig. S9):
\( \sigma \geq 10^{-4} \), Eq. (9) is satisfied, and the ratio \( \frac{k_{\text{solv}}}{k_{\text{des}}} \) is constrained (described below) to experimental
measurements of \( \alpha \). To optimize simulation time for the results shown below we use \( \sigma = 10^{-4} \) and \( k_{\text{des}} =
5.48 \times 10^6 \text{ s}^{-1} \) (i.e. \( \tau = 182 \text{ ns} \)). While not observed in the multiphase systems examined here, very fast
reactions may lead to important sensitivity of the reaction kinetics to \( \sigma \) and \( \tau_{\text{des}} \). In a forthcoming
publication using the framework developed here, kinetic simulations of the \( \Gamma + \text{O}_3 \) reaction in aqueous
droplets do exhibit a sensitivity to the absolute values of \( \sigma \) and \( \tau_{\text{des}} \).

We constrain the absolute values of \( k_{\text{solv}} \) and \( k_{\text{desolv}} \) from \( k_{\text{des}} \). The ratio of \( k_{\text{solv}} \) to \( k_{\text{des}} \) governs the
fraction of adsorbed molecules (\( \text{O}_3(\text{ads}) \)) that ultimately become solvated (\( \text{O}_3(\text{b}) \)) within the bulk liquid. This
ratio \( \left( \frac{k_{\text{solv}}}{k_{\text{des}}} \right) \) is traditionally interpreted as the mass accommodation coefficient (\( \alpha \)).
From prior
measurements, \( \alpha \) for \( \text{O}_3 \) in aqueous solutions ranges from \( 10^{-3} \) to 1 \(^{67-71} \) as summarized in Müller and
Heal. \(^{71} \) From MD simulations \(^{23} \) the ratio of absorption (solvation) to desorption probabilities for \( \text{O}_3 \) at an
aqueous surface is \( \sim 0.06 \), and is within the range of these prior measurements of \( \alpha \). In steps S1 and S2
(Table 2) we use \( \frac{k_{\text{solv}}}{k_{\text{des}}} = 0.085 \), which is in the mid-range of previous measurements and consistent with
estimates provided by MD simulations. Finally, a value of \( k_{\text{desolv}} \) is computed in order to provide the correct
\( H_{cc}^{ab} \) yielding an overall Henry’s law constant that is consistent with prior measurements (i.e., \( H_{cc}^{ab} \) as shown in Eq. (1)).

In summary, the rate coefficients and diffusion constants used in the kinetic simulation are directly
obtained either from prior literature or are computed using experimentally validated parameterizations.
The absolute values of \( \sigma, k_{\text{ads}}, k_{\text{des}}, k_{\text{solv}} \) and \( k_{\text{desolv}} \) used in the model are derived self-consistently to produce
the correct values \( H_{cc}^{ab}, H_{cc}^{as}, H_{cc}^{sb} \) and \( \alpha \), which are quantities constrained by prior experiments or molecular
simulations.
4. Results & Discussion

To evaluate the coupled kinetic processes that drive \( \text{O}_3 \) multiphase reaction timescales, we use both new and prior experimental observations of multiphase ozone reactions with aqueous organic inorganic particles. Our aim is to use a single kinetic framework to explain reaction timescales across three systems (\textit{trans}-aconitic acid, maleic acid and sodium nitrite). We emphasize that our simple kinetic model uses the minimum possible number of kinetic parameters to represent elementary steps, and does not include fitted parameters. We compare our predictive model to experimental particle-phase decay kinetics and use the model to identify processes that govern observed reaction timescales.
Figure 3. Decay of trans-Aconitic Acid (AA, left panels) and change in particle radius (right panels) vs. reaction time for experiments: #1 (A,B), #2 (C,D), #3 (E,F), #4 (G,H), #5 (I,J). Table 1 shows the experimental conditions for experiments #1 – 5. Experimental data are shown as red circles (error bars for mass spectral and size data represent the standard deviation in measurements across multiple (n >8) single particles), explicit simulation predictions that include both interfacial and bulk reactions are solid black lines, and resistor model predictions (Eq. 11 & 12) are shown in dashed blue lines.
4.1 Multiphase reaction of ozone with aqueous organic acids.

4.1.1 trans-Aconitic Acid (AA). Our simple two-compartment kinetic model, which represents kinetically distinct regions (interfacial volume and bulk), captures the particle size change and AA decay timescale across five sets of measurements (Fig. 3). Experimental model inputs are the measured [O$_3$(g)], initial droplet radius ($r_0$) and [AA]$_0$ (Table 1). Each data point ([AA]/[AA]$_0$) in Fig. 3 corresponds to the mean peak area derived from multiple individual droplets (n > 8), which are sequentially sampled from a population of monodisperse droplets trapped together and simultaneously exposed to the same ozone concentration. Our explicit simulation predictions are consistent with the experimental reaction timescales (Fig. 3), though we do observe some variability in the experiments. This variability arises from differences in vaporization location and temperature, and ionization efficiency, as individual particles are ejected from the QET for analysis.$^{50}$ Our model’s ability to predict experimental particle size validates our assumption that the major volatile product in this system is glyoxylic acid (see Sections 3.4 and 3.8), which is formed during the primary ozonide decomposition (Fig. 2) and is a co-product of the C$_4$ Criegee Intermediate.

Our simulations demonstrate that over the reaction time 92 – 88% of reactions between O$_3$ and AA occur in the particle bulk (Fig. S10). Despite the enriched concentration of adsorbed ozone at the interface, this occurs due to the relatively slow reaction of AA with O$_3$ and AA’s low surface affinity (e.g., for Expt #1 in Table 1, [AA$_{(b)}$] = 3.2 M and from a Langmuir framework [AA$_{(ads)}$] = 0.42 M). The shape of the predicted decay kinetics from our explicit model (Fig. 3) are linear, which suggests that the multiphase reaction is zeroth-order in AA and is therefore governed by a process other than the bulk O$_3$ + AA reaction. Zeroth-order kinetics are also somewhat evident in the experimental data, but the number of data points, and their variability, in each experiment makes this conclusion difficult to draw from the experiment alone. In the predicted decay, the kinetics become more exponential in shape as [AA$_{(b)}$] becomes more dilute near the end of the reaction time (Fig. 3). These observations provide evidence that O$_3$ transport into the particle bulk may limit the reaction rate in aqueous AA particles.

Since AA decay kinetics appear O$_3$ transport-limited, we might expect a resistor model that represents bulk reactions limited by O$_3$ diffusion$^{21}$ to accurately predict experimental reaction timescales. Previous studies support this expectation, as the reactive uptake coefficient ($\gamma$) in micron-sized aqueous droplets is frequently represented by this resistor limiting case.$^{27, 31, 71, 92, 93}$ AA is well-mixed within the particle on the timescale of reaction (i.e., assuming a Henry’s Law concentration for O$_3$, the reacto-diffusive length, L$_{RD,AA}$ = (D$_{AA}$/k$_{rrn}[O_3]_0$)$^{1/2}$, for AA is > 100 μm). However, in contrast to our simple two-compartment model, which represents the average [O$_3$(b)], we do expect that a gradient in O$_3$ concentration
forms within the particle bulk.\textsuperscript{27} Therefore, the majority of bulk reactions occur in a layer with thickness on the order of the reacto-diffusive length for O\textsubscript{3} ($L_{RD,O3} = (D_{O3}/k_{rxn}[AA]_0)^{1/2}$, Section 3.3). With molar AA concentrations (Table 1) the reacto-diffusive length for ozone is smaller than the particle radius, and the decay of AA may be described by (i.e., in the limit where $L_{RD,O3} < r_0/20$):\textsuperscript{21, 27}

\[
\frac{[AA]}{[AA]_0} = \left(1 - \frac{3[D_{O3}(g)]\gamma^c c_\infty}{8\sigma_0'[AA]_0} \cdot t\right)^2
\]

Eq. (11)

where,

\[
\frac{1}{\gamma} = \frac{1}{\sigma} + \frac{1}{\alpha} + \frac{c}{4H_{cp} RT \sqrt{Dk_{rxn}[AA]_0}}
\]

Eq. (12)

For example, for our Expt. #5 (Table 1) $L_{RD,O3} = 0.26$ $\mu$m, which is less than $r_0/20 = 0.46$ $\mu$m. For a meaningful comparison, we use the same values in Eq. (12) for $H_{cp}$ ($1.11 \times 10^{-2}$ M/atm), $D_{O3}$ ($1.76 \times 10^{-5}$ cm$^2$ s$^{-1}$), $\sigma$ ($10^{-4}$), $\alpha$ ($8.5 \times 10^{-2}$), and $k_{rxn}$ ($1.4 \times 10^{-17}$ cm$^3$ molec.$^{-1}$ s$^{-1}$) that were used in our explicit simulations. We note that Equations (11) and (12) neglect surface reactions, which appears a reasonable assumption in this system (Fig. S10). Using the experimental values for $[O_3(g)]$, $r_0$ and $[AA]_0$ in Eqs. (11) and (12), we compare predicted kinetics from this resistor model limiting case with experimental data and explicit simulations (Fig. 3).

The predicted decay of AA using the resistor model is faster than our experimental observations and explicit stochastic simulations (Fig. 3). For example, using the reaction conditions from Expt. #1 in Eq. (12) yields $\gamma = 1.7 \times 10^{-5}$. If we assume instead that $\sigma = 1$, the uptake coefficient is only marginally larger ($2.0 \times 10^{-5}$) and the decay kinetics of AA are even faster. We note that under our experimental conditions, corrections to $\gamma$ arising from gas phase diffusional resistance of O\textsubscript{3} are minor ($< 0.1\%$).\textsuperscript{19, 71} If instead, Eq. (11) is used to fit the data, by allowing $\gamma$ to vary to best replicate the measurements, we obtain a value of $\gamma_{fit} \sim 4 \times 10^{-6}$ for experiment #1. This indicates that the explicit simulations, and our experimental observations, are a factor $\sim 4 - 5$ slower than the estimates provided by this resistor model limiting case.
In addition, resistor model predictions do not predict zeroth-order kinetics, but rather predict a more exponential-like decay of AA. We discuss the kinetic and diffusive steps that set the multiphase reaction timescale further in Sections 4.3.

**4.1.2 Maleic Acid (MA).** We further test our explicit simulations using data for maleic acid ozonolysis reported by Dennis-Smither et al.\(^3\) This data set (Table 3) is composed of ozonolysis studies in single micron-sized aqueous particles. The normalized decay kinetics of MA particles, obtained using Raman spectroscopy, and radius vs. reaction time are reproduced\(^3\) in Fig. 4. We modified our explicit model of AA ozonolysis to account for differences in the rate coefficient for the O\(_3\) + MA reaction, which is 6x slower\(^7\) than for AA. Further, MA is more volatile than AA, and evaporates from the droplet over the course of the reaction (Fig. S7 & S11). In addition, the diffusion coefficients for MA and its reaction products were modified to account for differences in molecular size (Table S2). We compare our model results to a subset of data from Dennis-Smither et al.\(^3\) recorded at RH < 73% (i.e., 6 individual droplet experiments, Table 3). We neglect the 3 experiments at RH > 73%, because particles grew during ozonolysis, likely due to an increase in hygroscopicity, which is a process not currently included in our model.

**Table 3.** Maleic acid droplet ozonolysis experiments reported by Dennis-Smither et al. and shown in Fig. 5.

<table>
<thead>
<tr>
<th>Droplet</th>
<th>RH (%)</th>
<th>O(_3) (ppm)</th>
<th>R(_0) (microns)</th>
<th>[MA](_0) (molec. cm(^{-3}))</th>
<th>[MA](_0) (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>63</td>
<td>38 ± 8</td>
<td>4.59</td>
<td>4.46 x 10(^{21})</td>
<td>7.4</td>
</tr>
<tr>
<td>B</td>
<td>72</td>
<td>38 ± 8</td>
<td>3.85</td>
<td>3.73 x 10(^{21})</td>
<td>6.2</td>
</tr>
<tr>
<td>D</td>
<td>54</td>
<td>48 ± 10</td>
<td>4.58</td>
<td>4.94 x 10(^{21})</td>
<td>8.2</td>
</tr>
<tr>
<td>E</td>
<td>64</td>
<td>52 ± 10</td>
<td>4.03</td>
<td>4.40 x 10(^{21})</td>
<td>7.3</td>
</tr>
<tr>
<td>F</td>
<td>72</td>
<td>53 ± 10</td>
<td>4.72</td>
<td>3.85 x 10(^{21})</td>
<td>6.4</td>
</tr>
<tr>
<td>H</td>
<td>62</td>
<td>65 ± 13</td>
<td>4.27</td>
<td>4.46 x 10(^{21})</td>
<td>7.4</td>
</tr>
</tbody>
</table>
Figure 4. Maleic acid (MA) data reproduced from Dennis-Smither et al. Decay of MA (left panels) and change in radius (right panels) vs. reaction time for particles: A (A,B), B (C,D), D (E,F), E (G,H), F (I,J) and H (K, L). Table 3 shows the experimental conditions for particles A – H, reported by Dennis-Smither et al. Solid black lines show explicit simulation predictions with both surface and bulk reactions, and dashed blue lines show resistor model (Eq 11 & 12) predictions.

Our explicit simulations can reasonably reproduce the decay kinetics of maleic acid as well as the decrease in droplet size with reaction time (Fig. 4). As is the case with AA, the predicted decay kinetics
appear nearly linear with reaction time, demonstrating kinetics that are zeroth-order in MA until near the end of the reaction. This feature is consistent with the MA experimental measurements, which have a higher time resolution than our AA dataset. The predicted decrease in droplet size at reaction times $>5000$ seconds deviates from observations. The origin of this discrepancy could arise for two reasons. First, simulated changes in droplet size are sensitive to the assumed molecular density, in addition to volatility, of the reaction products relative to MA. Second, as noted above, the simulations do not account for any changes in hygroscopicity during the reaction, which was clearly evident in the Dennis-Smither et al\textsuperscript{31} data recorded at RH $>73\%$. So, it is plausible for the reaction conditions shown in Table 3 there is a competition between chemical erosion (driven by volatility of glyoxylic acid) and hygroscopic growth that would account for the differences between the simulated particle size and observations.\textsuperscript{93}

Similar to AA, our explicit simulations demonstrate that bulk reaction dominates the decay of MA. Over the reaction time, $\sim96\%$ of reactions occur in the bulk, which is higher than for AA due largely to the smaller rate coefficient for reaction of MA with O$_3$ (Fig. S10). Despite the apparent validity of the common resistor model assumption that maleic acid ozonolysis in micron-sized particles should occur primarily in the bulk, with limitations to the reaction rate from O$_3$ diffusion, Eq (11) & (12) predictions do not agree quantitatively with experimental observations or our explicit simulations (Fig. 4). The resistor model predicts faster kinetics than are observed or simulated (with predicted $\gamma \sim 1 \times 10^{-5}$), whereas fits using Eq. (11) by Dennis-Smither et al\textsuperscript{31} yielded values that are $\sim2x$ smaller ($\gamma = 4-6 \times 10^{-6}$). This difference persists across observations that range in water content and MA concentration from 54 – 72\% humidity (Table 3).

Both aqueous organic acid systems examined here are dominated by bulk-phase reactions with O$_3$, and show evidence in the shape of their observed and predicted decay kinetics for O$_3$ transport limitation. In Section 4.3, we explore how coupled adsorption, desorption, solvation, desolvation and diffusion processes control the overall rate of these bulk-dominated multiphase reactions.

4.2 Multiphase reaction of ozone with aqueous sodium nitrite. Next, we examine the multiphase oxidation of nitrite (NO$_2^-$) to nitrate (NO$_3^-$) by O$_3$, using our model framework of O$_3$ partitioning. Nitrite is both a faster-reacting and more surface-active species than the two organic acids discussed above, and thus provides an informative contrasting case. We use experimental results reported by Hunt et al.\textsuperscript{92} for the reaction of O$_3$ with an aqueous nitrite particle (Fig. 5), where the decay of nitrite in optically trapped single particles was monitored using Raman spectroscopy. In their analysis, Hunt et al.\textsuperscript{92} fit the NO$_2^-$
signal decay to the resistor model shown in Eq. (11). Using the diffusion coefficient and Henry’s law constant for O₃ they extracted a rate coefficient for NO₂⁻ + O₃ from the fit, which provided a value consistent with previous bulk laboratory kinetic measurements. This analysis implied that surface reactions, which are neglected in Eq. (11), were not required for describing the multiphase reaction rate of NO₂⁻ + O₃. Here, we use our predictive kinetic model to re-examine this result.

![Figure 5: Normalized (A) [NO₂⁻] and (B) surface reaction fraction as a function of reaction time. Experiments are conducted using [O₃] ~ 12 ppmv, an 11.5 μm diameter aqueous droplet with an initial [NO₂⁻] = 0.2 mol L⁻¹ as reported by Hunt et al. (see Table S4, Droplet 0). The experimental conditions are used as inputs to the explicit simulation (black lines) as well as for the resistor model prediction (blue line). See Table S3 for elementary steps and corresponding rate coefficients included in these simulations.](image)

To explore the kinetic processes governing reaction timescales for NO₂⁻ + O₃, we first apply a modified version of our explicit kinetic model that assumes no surface reactions occur (Fig. 5a). We use a bulk reaction rate coefficient (5.6 x 10⁻¹⁶ cm³ molecule⁻¹ s⁻¹) that is consistent with the measurements reported by Garland et al., and within the experimental uncertainty of the value reported by Hoigne et al. (Table S3 shows elementary reaction and diffusion steps). The impact of ionic strength on the magnitude of this rate coefficient (28 – 56 %, for the experimental particle concentrations reported by Hunt et al.) is smaller than the experimental uncertainty in previously reported bulk-phase rate
coefficients (i.e., a factor of 2). For the NaNO₂ concentrations reported by Hunt et al., the effect of ionic strength on the magnitude of the O₃ Henry’s Law constant is <5%.²⁶,⁷¹ We assume that nitrite and nitrate diffusion coefficients in water are similar, and are taken from Yeh et al.¹⁰⁰

Our simulations demonstrate that surface reactions contribute significantly to NO₂⁻ decay. Unlike the diffusion-limited bulk reaction resistor prediction using Eq. (11), our explicit model assuming only bulk processes predicts a nitrite decay that is 5-times slower than the observations, which suggests that the reaction timescales in this system are not driven entirely by bulk reaction. The difference between our bulk-only simulation and experimental observations is larger than the uncertainty in the bulk phase rate coefficients, suggesting that surface reactions are important to include under the experimental conditions reported by Hunt et al. To include elementary steps at the interface, we assume that the interfacial rate coefficient for oxidation of nitrite by ozone is the same as that in the bulk (step S3 Table S3), and estimate values for the nitrite and nitrate bulk-interface partitioning equilibrium constant.

Figure 6. Interfacial concentration of (top) NO₂⁻ and (bottom) NO₃⁻ vs bulk concentration derived from prior literature observations.¹⁰¹-¹⁰³
The interfacial partitioning of anions, in particular nitrate, has been somewhat controversial with experiments and simulations arriving at different conclusions.\textsuperscript{101, 102, 104-109} We briefly discuss available literature on this topic, in order to constrain the solvation and desolvation rate coefficients for nitrite and nitrate. Brown \textit{et al.}\textsuperscript{102} used X-ray photoemission to quantify the interfacial concentration of NO\textsubscript{2}^- and NO\textsubscript{3}^- in a liquid jet. At a bulk concentration of 3 M, the interfacial concentration, over the probing depth of the method, was 2 ± 0.4 M\textsuperscript{102} indicating that although both ions reside near the interface (ca. 1.2 to 1.5 nm), their adsorbed concentrations are depleted relative to the bulk solution (2 vs. 3 M, Fig. 6a). Otten \textit{et al.}\textsuperscript{103} used Second-Harmonic Generation (SHG) spectroscopy to measure an adsorption isotherm for nitrite and found evidence for substantial surface partitioning and saturation. The square root of the SHG signal vs. bulk [NO\textsubscript{2}^-] measured by Otten \textit{et al.}\textsuperscript{103} is shown in Fig. 6a. We scale the SHG signal to achieve the correct interfacial concentration observed by Brown \textit{et al.},\textsuperscript{102} and fit the scaled data the Langmuir equation,

\[ [\text{NO}_2^-]_{\text{ads}} = \frac{\Gamma_{\infty}^{\text{NO}_2^-}}{\delta} \cdot \frac{K_{eq}^{\text{NO}_2^-} [\text{NO}_2^-]_{\text{bulk}}}{1 + K_{eq}^{\text{NO}_2^-} [\text{NO}_2^-]_{\text{bulk}}} \]  

Eq. (13)

where,

\[ K_{eq}^{\text{NO}_2^-} = \frac{k_{\text{desolv}}}{k_{\text{solv}}} \]  

Eq. (14)

to obtain \( K_{eq}^{\text{NO}_2^-} = 3.01 \text{ L mol}^{-1} \) (5.0 x 10\textsuperscript{-21} cm\textsuperscript{3} molec.\textsuperscript{-1}) and a maximum interface concentration (\( \frac{\Gamma_{\infty}^{\text{NO}_2^-}}{\delta} \)) of 2.25 M (1.35 x 10\textsuperscript{21} molec. cm\textsuperscript{-3}). \( K_{eq}^{\text{NO}_2^-} \) constrains the ratio of the desolvation (forward) and solvation (backward) rate coefficients for NO\textsubscript{2}^- (Table S3, step S4). Our simulation results are insensitive to the absolute magnitude of these forward and backward rates over a broad range; for example the simulation results are the same when using values for the adsorption and desorption rate constants that are each a factor of 10\textsuperscript{3} smaller than those shown in Table S3.

Evidence to date suggests\textsuperscript{101, 109} that unlike nitrite, nitrate is only weakly adsorbed to the aqueous interface. To constrain this equilibrium, we use the nitrate adsorption isotherm measured by Wren and Donaldson\textsuperscript{101} using glancing incidence Raman spectroscopy. In Fig. 6b, we show these measurements and scale the Raman intensity to the interfacial concentration observed by Brown \textit{et al.}\textsuperscript{102} A fit of this scaled data to the Langmuir isotherm yields \( K_{eq}^{\text{NO}_3^-} = 0.19 \text{ L mol}^{-1} \) (3 x 10\textsuperscript{-22} cm\textsuperscript{3} molec.\textsuperscript{-1}) and \( \frac{\Gamma_{\infty}^{\text{NO}_3^-}}{\delta} = 5.3 \text{ M} \) (3.2 x 10\textsuperscript{21} molec. cm\textsuperscript{3}). \( K_{eq}^{\text{NO}_3^-} \) is the same as that reported by Wren and Donaldson\textsuperscript{101} using the same analysis.
and within the estimates reported by Otten et al.\textsuperscript{109} $K_{eq}^{NO_3^-}$ is used in the equilibrium in step S5 (Table S3). As for nitrite, our simulation results are insensitive to the absolute magnitude of these forward and backward rates; for example simulation results are the same when using values that are a factor of $10^3$ smaller from those shown in Table S3.

From the Langmuir fits for nitrite and nitrate, we see that NO$_2^-$ is an order of magnitude more strongly partitioned to the interface than NO$_3^-$, which is reasonably consistent with prior observations. This implies that NO$_3^-$ will not compete significantly with NO$_2^-$ for sites at the interface. The reason for the factor of 3 difference in $\Gamma_{\infty}$ for these two ions is unclear and may suggest ion pairing as described by Otten et al.\textsuperscript{103} While the mechanism of anion adsorption to aqueous interfaces is not fully understood, the analysis above attempts to provide an experimentally constrained set of parameters for quantitative modeling of NO$_2^-$ partitioning and reaction at the aqueous interface.

Our explicit simulation with both bulk and interfacial reactions predicts the NO$_2^-$ reaction timescales observed by Hunt et al\textsuperscript{92} (Fig. 5 & 7). Our explicit simulation is insensitive to the magnitude of the O$_3$ sticking coefficient (Fig. S11), so we use a conservative estimate of $\sigma = 10^{-4}$ in our simulation. Our explicit simulations demonstrate that although [NO$_2^-$] is depleted relative to the corresponding bulk concentration, under the experimental conditions used by Hunt et al. (Table S4),\textsuperscript{92} 83 % of O$_3$ + NO$_2^-$ reactions occur at the interface over at the beginning of the reaction (Fig. 5b). As the NO$_2^-$ concentration decreases, the fraction of surface reactions decreases toward 70%. Compared to AA and MA, the larger importance of interfacial reactions occurs due to a combination of a larger bimolecular rate coefficient for reaction with ozone, and the relatively larger adsorbed nitrite concentration. The dominance of surface reactions suggests that agreement between experimental kinetics and Eq (11) & (12) predictions (Fig. 5A, blue dashed line) arises for the wrong mechanistic reasons. Unlike the organic systems examined above, both predicted and observed decay kinetics appear more exponential in shape (Fig. 5 & 7). This suggests that O$_3$ transport is not limiting the multiphase reaction kinetics in this system, which is consistent with a surface-dominated reaction not limited by bulk O$_3$ diffusion.

Overall, this model-observation comparison demonstrates that our kinetic framework can represent the timescales of multiphase ozone reactions across multiple systems with differing physical and chemical properties. In the next section, we explore the coupled kinetic processes that control the multiphase reaction rate across these three systems.
Figure 7. Decay of aqueous nitrite via multiphase reaction with ozone in micron-sized particles. Normalized nitrite concentration vs. time is shown for experiments (points) compared with explicit model predictions (lines). The experimental conditions for each droplet are shown in Table S4. The simulations are initialized with the experimental [NO$_2$] and [O$_3$(g)] reported by Hunt et al.$^{92}$ The panels correspond to: (A) Droplet 1 (B) Droplet 2 (C) Droplet 3, (D) Droplet 4, (E) Droplet 5, (F) Droplet 6, (G) Droplet 7, (H) Droplet 8, and (I) Droplet 9.

4.3 The impact of reaction on coupled O$_3$ partitioning kinetics and diffusion. To better understand the processes that govern ozone multiphase reaction timescales, we use a set of simulations that resolve the bulk ([O$_3$(b)]) and adsorbed ([O$_3$(ads)]) ozone concentrations for the initial experimental reaction conditions shown in Fig. 8. Further, we vary initial solute concentrations over a range corresponding to sub-saturated to super-saturated initial conditions (Fig. 9), or early to late reaction times, to examine the effects of changing the chemical lifetime on the balance between O$_3$ transport and bimolecular reaction. Since AA and MA behave similarly (dominance of bulk reaction (Section 4.1)), we use AA as a representative case. The selection frequencies of O$_3$ adsorption, desorption, solvation, desolvation and diffusion steps from these simulations (Fig. 9 & S13) illustrate how the relative importance of pairs of forward and reverse kinetic steps vary with droplet solute concentration.
In all three multiphase systems, \([O_3(b)]\) is depleted from its Henry’s Law concentration, though to differing extents (Fig. 8 & 9). NO\(_2^–\) droplets are most strongly depleted relative to the Henry’s Law ozone concentration, with \([O_3(b)] < 1\%\) of \(H_{cc}^{gb} [O_3(g)]\). The organic acid droplets are depleted to lesser extents; \([O_3(b)]\) in the AA system is \(\sim1\%\) of \(H_{cc}^{gb} [O_3(g)]\), while in the MA system \(O_3\) is depleted to \(\sim11\%\) of its Henry’s Law concentration. Both the AA and NO\(_2^–\) droplets approach the corresponding Henry’s Law ozone concentration with decreasing initial solute concentration (Fig. 9), though the extent of bulk \(O_3\) depletion at high solute concentrations differs significantly.

**Figure 8:** Simulated reactive uptake of \(O_3\) to aqueous (A) *trans*-aconitic acid, (B) maleic acid, and (C) sodium nitrite droplets vs. time showing the partitioning of \(O_3(g)\) to the interface and the bulk. Simulations are conducted with a steady state concentration of \(O_3(g)\) and initial solute concentrations corresponding to experimental conditions (Fig. 3 (Experiment 1, \(r_0 = 9.2\) \(\mu m\)), 4 (Droplet A, \(r_0 = 4.6\) \(\mu m\)) and 5 (Droplet 0, \(r_0 = 5.8\) \(\mu m\))). Also shown in each panel are results from analogous simulations with no reactions.
The varying extents of bulk O₃ depletion are partially controlled by two factors that describe the balance between the timescales for O₃ diffusion and its reaction. First, the pseudo-first order rate coefficients for O₃ loss are a dominant driver of bulk O₃ depletion, such that the nitrite system is most strongly depleted and the maleic acid system is least depleted (i.e., $k_{\text{rxn}[\text{NO}_2^-]} > k_{\text{rxn}[\text{AA}]} > k_{\text{rxn}[\text{MA}]}$; Fig. 8). We emphasize that this trend is governed by both the magnitude of the second order rate coefficient and the solute concentration (determined by experimental relative humidity). Second, the droplet size differs across these three sets of experiments, such that the characteristic timescale for bulk ozone diffusion into these liquid particles differs. The diffusion timescale can be estimated as $\tau_{\text{diffusion}} = 1/k_{\text{diffusion}} = \frac{r^2}{2D_{\text{O₃}}}$, such that $k_{\text{diffusion,MA}} > k_{\text{diffusion,NO}_2^-} > k_{\text{diffusion,AA}}$. We emphasize that this trend is driven by the experimental relative humidity and particle size (Tables 1, 3 and S4). Comparing the magnitudes of the rate coefficients for ozone diffusion with the pseudo-first order rate coefficients for O₃ consumption in the particle qualitatively explains the trends in $[\text{O₃(b)}]$ depletion, where MA is least depleted, followed by AA and with NO₂⁻ the most depleted (Fig. 8).

![Figure 9: (Left axes) Simulated mean $[\text{O₃(b)}]$ for a wide range of simulated initial solution concentrations, for reactive uptake of O₃ to (A) trans-aconitic acid (AA, $r_0 = 9.1 \ \mu\text{m}$, solid circles) and (B) sodium nitrite (NO₂⁻, $r_0 =$](image-url)
For both AA and NO$_2^-$, [O$_3$(b)] approaches its Henry’s Law concentration (Fig. 9) only when the pseudo-first order rate coefficient for O$_3$ loss approaches the first-order rate coefficient for O$_3$ diffusion (i.e., $k_{\text{rxn[solute]}} = k_{\text{diffusion}}$, where [AA]$_0 = 44$ mM and [NO$_2^-$]$_0 = 2.8$ mM). However, the solute concentration where diffusion and reaction timescales are equal ($k_{\text{rxn[solute]}} = k_{\text{diffusion}}$) does not mark the onset of bulk O$_3$ depletion. Rather, this solute concentration lies within a regime where diffusion to and from the interface has already shifted significantly away from the non-reactive or dilute state, such that diffusion is occurring predominantly in one direction. In contrast, under dilute conditions O$_3$ rapidly equilibrates to both its bulk and interfacial Henry’s Law concentrations (Fig. 8), and both diffusion and interfacial kinetic steps occur with equal frequency in both directions (Fig. 9 & S13). When diffusion and reaction timescales are equal, interface to bulk diffusion accounts for ~90% of the total diffusion steps (Fig. 9). At experimental initial solute concentrations (i.e., < 100% relative humidity), diffusion proceeds only from the interface to the bulk, but this maximum rate of O$_3$ delivery is not sufficient to compensate for the rate of O$_3$ reactive loss. Consequently, [O$_3$(b)] becomes depleted from its Henry’s Law concentration.

In addition to diffusion timescales, the thermodynamic properties of O$_3$ that govern gas-interface partitioning are a key component of our explicit kinetic model. While O$_3$ diffusion sets the transport rate for solvated O$_3$ to enter the particle bulk and become available for bulk reaction, non-reactive interfacial kinetic steps set the amount of adsorbed O$_3$ that is available to both become solvated and react at the interface. With and without reaction, and at all initial droplet concentrations ranging from molar to micromolar, [O$_3$(ads)] is rapidly maintained (on a timescale of ~200 – 500 nanoseconds, Fig. 8 and Fig. S8) and remains constant given that [O$_3$(g)] is constant. As initial solute concentrations increase, reactive loss of O$_3$ drives not only a shift in the dominant direction of diffusion steps, but also an increased frequency of O$_3$ solvation into the bulk and adsorption to the interface. This shift in the selection frequency, particularly in (de)solvation steps, can also be seen in the overall rate of each step as a function of reaction time (Fig. S14). These adjustments in the coupled O$_3$ partitioning equilibria maintain [O$_3$(ads)], even though the rate of interface to bulk diffusion is unable to maintain [O$_3$(b)] at high reaction rates. [O$_3$(ads)] is
maintained at its interfacial Henry’s Law concentration even for nitrite, where surface reactions are ~80% of all reaction events (Fig. 5b). Therefore, O₃ equilibration to the interface is fast relative to reactive loss in both the organic and inorganic systems examined here (Fig. S14), though this may not remain the case for faster-reacting solutes.⁹¹

The overall response of the coupled O₃ partitioning and diffusion processes to reaction depends on the magnitude and location of the O₃ reactive loss. The dominant location of the O₃ reactive sink differs in the organic and inorganic systems (Sections 4.1 & 4.2), because solute interfacial affinity and reaction rates differ significantly. NO₂⁻ is the most surface active (i.e., \( k_{\text{desolv,NO}_2} / k_{\text{solv,NO}_2} > k_{\text{desolv,AA}} / k_{\text{solv,AA}} \)), has the largest bimolecular rate coefficient and exhibits the largest fraction of interfacial reactions. Consequently, the selection frequency of O₃ adsorption and desorption are impacted more strongly by a change in NO₂⁻ concentration than for a similar change in AA concentration (Fig. 9 and S13), though the magnitude of these changes are relatively small. Even though a majority of NO₂⁻ reactions occur at the interface, O₃ solvation and desolvation frequencies are forced to adjust in response to a change in \([\text{NO}_2^-]_0\) (Fig. 9 & S13) because O₃ diffusion from the interface to the bulk cannot compensate for the rate of reactive loss. However, the dominance of surface reactions combined with the rapidly maintained \([\text{O}_3(\text{ads})]\] avoids transport limitations and produces exponential-like kinetics for NO₂⁻ droplets (Fig. 5 & 7). For AA and MA, the majority of reactions occur in the bulk and the frequency of O₃ solvation and interface to bulk diffusion are impacted by an increase in droplet solute concentration, while the adsorption response is almost negligible (Fig. 9 & S13). Despite the ample available adsorbed O₃, transport-limited (zeroth-order) kinetics arise for AA and MA at millimolar concentrations and above, because the rate of diffusion away from the interface is too slow to compensate for reactive O₃ loss in the bulk.

The analysis above demonstrates that over the course of a multiphase reaction, coupled kinetic and diffusion steps dynamically respond and seek to maintain an equilibrium position that is achieved only at very low bimolecular reaction rates, or in the absence of reaction. In Section 4.1 and 4.2, we have compared our experimental observations and explicit model simulations to predictions from the diffusion-limited bulk reaction resistor model (Eq. (11) & (12)), which is often applied to interpret the kinetics of multiphase reactions in micron-sized aqueous aerosol. However, this formulation overpredicts reaction rates for systems dominated by bulk reactions (AA and MA). We hypothesize that Eq. (11) & (12) may effectively overpredict the bulk O₃ concentration over the course of the reaction by assuming that O₃ partitioning kinetics are not coupled to interfacial O₃ transport and diffusion away from the interface. For
surface reaction dominated systems (NO$_2^-$), Eq (11) & (12) are not mechanistically applicable even though the predicted reaction timescales agree with observations. In a subsequent publication building on this and previous work, we will derive closed-form expressions for the bulk O$_3$ concentration and time-dependence of solute concentration during reaction, and will further examine the particle size-dependence of reactive O$_3$ uptake implied by rate-limiting diffusion processes.

5. Conclusions

Using new and prior experimental measurements of reaction kinetics in micron-sized particles, we consider the multiphase reaction kinetics of ozone in three organic and inorganic systems (trans-aconitic acid, maleic acid and sodium nitrite) that have a range of interfacial affinities and bimolecular rate coefficients for reaction with ozone. We show that by representing ozone multiphase partitioning as a set of coupled kinetic and diffusion steps between gas, interface and bulk in a simple two-compartment model, we can accurately predict reaction timescales across all three systems. Our kinetic model is applicable within a range of solute concentrations where resistor model limiting cases are not applicable (i.e., $r_0/20 < R_{RD,O3} < r_0$), and in high solute concentration regimes relevant to aqueous aerosol (i.e., $R_{RD,O3} < r_0/20$) where bulk O$_3$ depletion arises through transport limitations. The model framework can capture interfacial and bulk kinetics across all three multiphase systems, but to do so it must explicitly account for the coupling of elementary partitioning steps across the interface with diffusion and reaction. These coupled kinetic processes rapidly maintain [O$_3$(ads)] at the expense of [O$_3$(b)] as a combination of solvated and adsorbed O$_3$ is lost to reaction. Despite important differences in solute interfacial concentrations across the three systems examined here, our kinetic model demonstrates that enhanced interfacial O$_3$ concentrations, compared to gas and bulk phases, are an important driver of the multiphase reaction timescale. This enhanced [O$_3$(ads)] arises because of the free energy minimum at the interface implied by the magnitude of $H_{cc}^{gs}$ (8.9), $H_{cc}^{s}$ (0.03) and associated free energies for O$_3$ adsorption and solvation.

We find that the relative importance of interfacial and bulk reactions depends on the surface affinity of both O$_3$ and the reacting solute, and the magnitude of the chemical lifetime. During the course of a multiphase reaction, the coupled kinetic system dynamically seeks to maintain an equilibrium position that occurs only at millimolar and lower solute concentrations. For micron-sized multiphase reaction systems dominated by either bulk or interfacial reactions, transport limitations arise mainly due to the timescale for diffusion of solvated O$_3$ away from the interface and into the bulk. This diffusion limitation results in depletion of [O$_3$(b)] from Henry’s Law, which governs reaction timescales for slower-reacting,
low surface activity species. For faster-reacting, more surface active species, the rapidly maintained \([\text{O}_3(\text{ads})]\) allows interfacial reactions to proceed without significant transport limitation. In summary, our results demonstrate the importance of coupled reaction, diffusion and partitioning kinetics for setting the timescales of multiphase \(\text{O}_3\) reactions.

**Supporting Information**

Figures S1-S14 and Tables S1-S4

**Acknowledgements**

This work was supported by the Condensed Phase and Interfacial Molecular Science Program in the Chemical Sciences, Geosciences, and Biosciences Division of the Office of Basic Energy Sciences of the U.S. Department of Energy under Contract No. DEAC02-05CH11231. M.D.W. acknowledges a Natural Sciences and Engineering Research Council of Canada (NSERC) postdoctoral fellowship, which supported collection of experimental data used in this work. We thank Dr. Grazia Rovelli (LBNL) and Alex Prophet (LBNL) for many helpful discussions, Dr. Lance Lee (Stanford Research Systems) for the original design of the quadrupole electrodynamic trap, and Bruce Rude (LBNL) for technical support. We thank Professors Jonathan Reid (University of Bristol) and Martin King (Royal Holloway University of London) for providing previously published experimental data used in this work.

**References**


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