Competitive Adsorption and Reaction at the Air-Water Interface studied by Iodide Ozonolysis in Microdroplets

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Abstract

The ozonolysis of iodide in seawater and sea-salt aerosol is a primary sink for ozone in the marine boundary layer and a major source of atmospheric iodine. While the chemical composition of the air/water interface has been shown to influence the overall chemistry in this system, it remains unclear to what extent the reaction occurs at the interface and how non-reactive solutes (\textit{i.e.}, surfactants and other salts) might alter the multiphase reaction mechanism of O\textsubscript{3} with I\textsuperscript{-}. Using a quadrupole electrodynamic trap (QET) and single-droplet paper-spray mass spectrometry, we examine the competition between solute adsorption and reaction at the air-water interface by measuring the ozonolysis kinetics of I\textsuperscript{-} in aqueous microdroplets in the presence of surface-active chlorate ions (ClO\textsubscript{3}\textsuperscript{-}). Iodide consumption kinetics depend upon both pH and the gas phase ozone concentration [O\textsubscript{3}], with a transition from zero to first-order kinetics (in [I\textsuperscript{-}]) with increasing [O\textsubscript{3}]. To explain these observations, a kinetic model is constructed that accounts for reaction and mass-transport of both I\textsuperscript{-} and O\textsubscript{3} and the competitive adsorption of iodide and chlorate at the microdroplet surface. Under our experimental conditions the reaction occurs at the air-water interface, where significant depletion of both ozone and iodide produces the observed shift from zero to first order kinetics with increasing [O\textsubscript{3}]. Analytical expressions for surface concentrations are derived to accurately predict the reactive uptake coefficients obtained from experiments ($\gamma = 2\times10^{-4}$). These predictions are extended over a range of [O\textsubscript{3}] and [I\textsuperscript{-}] to assess the impact of competitive adsorption on the multiphase reaction mechanism under more dilute reaction conditions.

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I. Introduction

Laboratory and field studies have shown that iodide ozonolysis occurring on the sea-surface and in atmospheric aerosol can impact a variety of chemical and physical processes occurring in the marine boundary layer (MBL).\textsuperscript{1,2} For example, this reaction accounts for the majority of ozone deposition from the MBL to the ocean surface,\textsuperscript{3–5} generating molecular iodine and iodine-containing species that contribute to the further destruction of atmospheric ozone and mediate the concentrations of atmospheric oxidants HO\textsubscript{x} and NO\textsubscript{x}.\textsuperscript{6–8} Volatile iodine products released in the MBL engage in reactive halogen-recycling in both the gas and condensed-phase, whereas less-volatile, highly oxidized products lead to secondary particle formation.\textsuperscript{9–13} Despite the clear importance of this chemistry in the marine atmosphere, uncertainty remains in the microscopic reaction mechanism of ozone with iodide at aqueous interfaces.

Multiphase ozonolysis kinetics of iodide have been studied in the laboratory using a variety of experimental approaches under a range of conditions.\textsuperscript{3,14–24} However, key microscopic aspects of the multiphase mechanism remain uncertain, including the role of the air-water interface, the relative contributions of surface and bulk reactions, and the influence of surfactants and spectator ions on the chemical mechanism and reaction rate. For instance, bulk reaction kinetics, inferred from resistor models,\textsuperscript{25–27} have been reported for both the ozonolysis of concentrated iodide aerosol\textsuperscript{15} and dilute solutions of iodide\textsuperscript{16,21} where the overall kinetics appear limited by O\textsubscript{3} solvation and diffusion into the bulk solution. Ozone-limited kinetics are also observed in simulated seawater by Schneider \textit{et al.}\textsuperscript{18} with the aid of kinetic multilayer modeling.\textsuperscript{28} In that study, gas to liquid mass transfer steps are coupled with reaction, leading to the general conclusion that the reaction occurs in the bulk aqueous solution under MBL conditions. Alternatively, a number of studies\textsuperscript{17,20,22} find evidence that under certain conditions, the reaction occurs primarily at the air-water interface and can be described by a Langmuir-Hinshelwood (LM) reaction mechanism. Kinetic and resistor-based models constructed by Moreno and coworkers\textsuperscript{23,29,30} include both LM and bulk reaction mechanisms to yield predictions for O\textsubscript{3} uptake across a wide range of reactant concentrations.

In addition, specific attention has been given to how the iodide-ozone reaction proceeds in complex mixtures, where organic and inorganic species may perturb the chemistry. Carpenter \textit{et al.}\textsuperscript{21} observed the suppression of I\textsubscript{2} emissions from both simulated and collected seawater relative to a buffered iodide solution. Rouvière and Ammann\textsuperscript{31} measured the uptake of ozone by aqueous potassium iodide aerosol, finding that reactive uptake is suppressed by ~50x with the addition of long-chained organic surfactants.
Reeser and Donaldson\textsuperscript{17} and Hayase \textit{et al.}\textsuperscript{20} observed a similar reduction of the ozonolysis rate by the addition of organic species to solution. Conversely, for the analogous (but much slower) bromide ozonolysis reaction, catalytic acceleration by chloride at the air-water interface has been proposed by Moreno and Romero\textsuperscript{30} to explain changes in bulk solution pH measured by Disselkamp \textit{et al.}\textsuperscript{32}

Here we measure the ozonolysis kinetics of iodide in microdroplets levitated in a quadrupole electrodynamic trap using single droplet mass spectrometry. We focus on elucidating the role of the surface and explore how unreactive species (i.e., chlorate ions, $\text{ClO}_3^-$) at the interface alter the observed multiphase ozonolysis rate of iodide. To do this, we measure how reactivity depends upon pH and the gas phase ozone concentration. Using a detailed kinetic model, based on the framework introduced in Willis and Wilson\textsuperscript{33} and Wilson \textit{et al.}\textsuperscript{34} we find evidence that the multiphase reaction rate is governed by strong coupling between reaction and transport at the air/water interface. Reaction-transport coupling from both the gas and liquid sides of the interface arises from the exceptionally fast reaction rate of iodide with ozone and the surface propensity of $\Gamma$, $\text{ClO}_3^-$, and $\text{O}_3$. It is only by describing the elementary steps of adsorption, reaction, and solvation at the air-water interface that the observed kinetics can be correctly predicted by the kinetic model. Informed by the model results, a set of analytical expressions for steady-state surface concentrations are derived and used to compute reactive uptake coefficients over a range of $[\text{O}_3]$ and $[\Gamma]$. This work is intended to provide insight into the key factors that might ultimately control the multiphase ozonolysis rate of iodide in more complex aqueous solutions such as seawater and marine aerosols.

The paper is organized as follows. In Section II an overview of the experimental approach is provided including a description of the quadrupole electrodynamic trap (QET) used for confining and reacting microdroplets, as well as the paper-spray ionization (PS) single droplet mass spectrometry detection scheme. Kinetic measurements for a series of solution pH and ozone concentrations are presented in Section III. To interpret these experimental results a kinetic model is developed (Section IV) and benchmarked against the experimental observations in Section V. This is followed by Section VI where a deeper analysis and discussion of the simulation results is presented in order to develop a comprehensive picture of the multiphase mechanism for the $\Gamma + \text{O}_3$ reaction and the effect of competitive ion adsorption to the interface.

\section*{II. Experimental Description}

\subsection*{A. Quadrupole electrodynamic trap (QET)}
The quadrupole electrodynamic trap (QET) charges and suspends aqueous microdroplets in an environmentally controlled chamber, as described in Jacobs *et al.*, Willis *et al.*, and recently by Willis and Wilson. Since a description of the QET has been recently reported, a full overview will not be presented; instead, we describe only those details relevant for the present experiments. The droplet-trapping regions of the QET are enclosed in a quartz tube, allowing for the humidity and gas phase composition to be controlled. For all experiments, a gas flow of 600 cm$^3$ min$^{-1}$ is maintained by a set of mass-flow controllers (MKS instruments) to regulate the relative amounts of dry and wet zero air, and a nitrogen flow containing ozone generated by a small flow of oxygen through a glow discharge ozone generator. Final ozone concentrations in the QET are measured with an ozone monitor (2B Technologies, model 202M), with a typical uncertainty of ± 100 ppb. The measured relative humidity is near 100% at the QET inlet and ~96.5% at the outlet. The difference between inlet and outlet RH is likely due to water sticking to the inner surfaces of the QET. In the following, we assume all experiments are done under 96.5% humidity. Microdroplets generated by a piezoelectric droplet dispenser (Microfab, Inc., MJ-ABP-01, 30 μm orifice) are charged by an induction electrode and trapped in the QET, where they are held for reaction. After reaction, droplets are individually sized using a 532 nm laser aligned axially to the quadrupole. Light scattered by a microdroplet is collected at 90° and the Mie scattering pattern subsequently analyzed as described by Davies where peak positions in the interference pattern are used to obtain droplet radius. A typical uncertainty in droplet radius for the present experimental configuration is ± 1 μm. All experiments reported used droplets with radius 22 ± 1 μm unless otherwise stated.

**B. Paper-Spray Ionization Mass Spectrometry**

Detection of single microdroplets is performed using paper-spray ionization (PS) coupled with a mass spectrometer (MS, Q Exactive Orbitrap, Thermo Fischer Scientific, Inc.) as previously described. The ionization source consists of a triangular-cut paper substrate (Whatman 3MM) attached to an alligator clip held at high voltage (± 3-5 kV) located approximately 5 cm below the QET outlet and approximately 3 cm from the MS inlet. A solvent mixture of 7:3 methanol to chloroform is continuously supplied to the underside of the paper using PEEK tubing connected to a syringe pump operating at 10-15 μL min$^{-1}$.

PS-MS detection of microdroplets with $[I^{-}]$ between 50 mM and 1 M yields typical S/N ratios of 100-1000 (see example spectrum in Fig. 1(A)). The experiments are conducted using a sodium iodide droplet concentration of 250 mM, which yields suitably long and intense droplet events. While droplet events are reproducible using PS-MS (Fig. 1(C)), reproducibility is diminished when comparing droplet...
events detected using different papers as the PS ionization source. The raw signal of a particular molecular ion can vary by ~50% or more between individual papers used. Furthermore, total ion intensity and ratios of intensities can change depending on the voltage applied to the paper and the relative distances between the QET outlet, ionization paper, and MS inlet. For these reasons, individual kinetic experiments are performed using a single paper as the PS ionization source, which is only exchanged between individual experiments while keeping the spray-voltage constant and the position fixed relative to the QET and the MS.

C. Droplet Composition and Internal Standard

Inherent variability observed in single-droplet responses in PS-MS results from differences in droplet-landing position on the ionization paper.\textsuperscript{38} This requires an internal-standard to perform quantitative kinetic experiments. The chlorate anion (ClO\textsubscript{3}\textsuperscript{−}), in addition to competing with the surface adsorption of iodide in the present experiments (see model description below), is used as an internal standard since it is easily detected by PS-MS, inert to ozone, and is hygroscopic. ClO\textsubscript{3}\textsuperscript{−} is also used to maintain a constant droplet water activity over the course of the experiment. Since the QET is held at a relative humidity of 96.5%, a droplet water activity of $a_w = 0.965$ is required to achieve stable sizes. The

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.jpg}
\caption{Mass spectra of unreacted (A) and reacted microdroplets (B) detected by PS-MS with the internal standard, reactant, product, and adducts identified. Time series of unreacted droplet events shown in (C) with iodide and the two major isotopes of the chlorate standard labeled. The mass spectrum in (B) shows droplet detection after 4 minutes of exposure to a flow containing $[O_3] = 40$ ppm.}
\end{figure}
[NaClO₃] needed to achieve $a_w = 0.965$ is determined by extrapolating a linear fit to previous measurements as a function of chlorate concentration. The calculated [NaClO₃] used in the following experiments is 875 mM, where the water activity is assumed to be unchanged by the addition of up to [NaI] = 250 mM and to remain constant throughout the reaction. This was verified by measuring droplet radius during ozonolysis, which remained unchanged within the measurement error of ± 1 μm. Kinetic measurements are performed by monitoring the peak area ratio $[I^-]/[ClO_3^-]$ as a function of ozone exposure time (see supplementary information, section SI-2, Fig. (S1)).

All experiments were performed using >99.9% purity HPLC grade water (Sigma-Aldrich), >99% sodium iodide (Fisher Scientific), and >99% sodium chlorate (Fisher Scientific). Solution pH was adjusted dropwise using 2M NaOH for basic experiments, and 1M H₂SO₄ for acidic experiments. Buffered experiments were performed using a 300 mM citric acid/citrate buffer at pH 4 and 200 mM TRIS buffer for pH 8. We note that the experiments performed at high pH avoid the known chlorate-iodide chemistry that occurs under acidic conditions. The chlorate ion signal is observed to remain relatively stable during the droplet ozonolysis experiment performed at pH 4. This was confirmed by comparing the relative signal of chlorate to citric acid buffer as a function of reaction time (see SI-3, Fig. (S2)). Thus, if there is any reaction between chlorate and iodide under these conditions it is significantly slower than the ozonolysis reaction. Unwanted gas-phase reactions with ozone in the ionization region are also avoided in the analysis by introducing 600 cm³/min of ozone-free air into the QET for 5 minutes prior to analyzing microdroplets.

**D. Droplet Kinetics and Mass Spectra with an Internal Standard**

The mass spectra in Fig. 1 show unreacted (A) and reacted (B) droplets along with a droplet time-series (C) for iodide (I⁻, m/z = 126.9) and the two major isotopes of the chlorate standard (Cl³⁵O₃⁻, m/z = 82.95 and Cl³⁷O₃⁻, m/z = 84.95). The spectra show single particle events for droplets containing 250 mM NaI and 875 mM NaClO₃ before and after being exposed to 40 ppm O₃ for 4 minutes. Comparing the unreacted and reacted spectra in Figs. 1(A) and (B) shows the appearance of iodate (IO₃⁻) at m/z = 174.8 and the relative decay of the iodide peak. In both spectra, small sodium-adduct peaks are observed. These peaks correspond to ((ClO₃)₂•Na)⁻ at m/z = 188.9, (ClO₃•I•Na)⁻ at m/z = 232.8, and (I₂•Na)⁻ at m/z = 276.8. The I⁻ adduct peaks exhibit the same decay kinetics as iodide suggesting that the adduct forms in the ionization region and not by reaction occurring in the droplet. The time-series in Fig. 1 (C) shows the reproducibility of single droplet events using a single paper-spray source. Shown in Fig. S1 is an example
time series of the iodide-to-chlorate and iodate-to-chlorate peak areas as a function of reaction time ([O₃] = 40 ppm). As expected over the course of the reaction, the reactant-to-standard ratio decays, while the product-to-standard ratio grows. Since the product (IO₃⁻) is observed to have a significantly lower ionization efficiency than iodide, only the decay of iodide is used to quantify reaction kinetics (see section SI-2).

III. Experimental Results

A. Reaction Kinetics as a Function of pH

The effect of pH (for pH = 4, 8, and 12) on the ozonolysis rate of iodide is shown in Fig. 2. For these experiments: [I⁻(b)] = 250 mM, [ClO₃⁻(b)] = 875 mM, and [O₃(g)] = 2 ppm where subscripts (b) and (g) denote the bulk-aqueous phase and gas phase. Experiments at pH 4 and 8 (Fig. 2 (A)) are conducted using two different buffers (sodium citrate and TRIS buffer, respectively). As shown in Fig. 2 (A) the iodide decay accelerates with decreasing pH, which is consistent with the presence of secondary consumption pathways of iodide by HOI and I₂, which are activated by H⁺. Figure 2 (B) shows the change in kinetics for buffered vs. unbuffered droplet solutions. When the initial solution is pH 4 and unbuffered, the iodide decay closely resembles the slower kinetics at pH 12, which can be explained by a rapid increase in pH as H⁺ is consumed during the production of HOI. These observations are consistent with previous reports, where 5 mM solutions of potassium iodide at an initial pH 7 are measured to be pH 11 after ozonolysis.
A series of kinetic measurements vs. ozone concentration were conducted at pH 12. While conducting experiments at high pH does not directly replicate atmospheric or environmental conditions, avoiding additional droplet chemistry produced by H⁺ enables us to more clearly address the specifics of the reaction occurring at the droplet surface as will be discussed in Section VI. Iodide decay kinetics are shown in Fig. 3 (A) and (B) with [O₃(g)] ranging from 500 ppb to 65 ppm. Model results are included and will be further discussed following the model description below. Figure 3 (A) shows the decay of iodide at pH = 12 becomes relatively insensitive for [O₃(g)] > 20 ppm, where the decay kinetics of iodide appear first-order in [I⁻(b)], exhibiting an exponential functional form with reaction time. Alternatively, for [O₃(g)] < 20 ppm, the decay rate of iodide depends upon [O₃(g)] and is accompanied by decay kinetics that appear zero-order in [I⁻(b)] (i.e., exhibit a linear-decrease of [I⁻(b)] with time).

Fig. 4 summarizes how the observed decay kinetics of [I⁻(b)] vary with [O₃(g)] (at constant [ClO₃⁻(b)]). Since the decay kinetics shown in Fig. 3 change from first to zero-order (i.e., exponential to linear
in their approximate functional form), a simple comparison is made using reciprocal half-lives ($\tau^{-1}$) vs. [O$_3$(g)]. Experimental half-lives are computed by fitting the decay kinetics with either an exponential (for [O$_3$(g)] > 20 ppm conditions) or linear (for [O$_3$(g)] < 20 ppm conditions) function. As observed in Fig. 4 there are two distinct kinetic regions. Below 20 ppm ozone, $\tau^{-1}$ increases linearly with [O$_3$(g)], which is accompanied by zero-order kinetics in [I$^-$(b)]. At [O$_3$(g)] > 20 ppm, $\tau^{-1}$ plateaus (or “saturates”) at a value just below 1 min$^{-1}$ where the decay kinetics are first-order in [I$^-$(b)]. Similar plateau or saturation behavior in reaction rate with increasing [O$_3$(g)] has been previously attributed to O$_3$ saturating the surface.$^{17,22}$ As will be discussed below, this is unlikely under the present experimental conditions and we suggest that previous observations be revisited in light of our analysis.

The datasets shown in Figs. 2-4 are used to benchmark a kinetic model with the aim of understanding the influence of competitive adsorption of I$^-$ and ClO$_3^-$ at the air-water interface, the changes in reaction pathways due to pH, and the scaling of reaction rate with [O$_3$(g)]. Furthermore, we seek to evaluate the relative contributions of the surface and bulk regions of the droplet to the overall reactivity.

![Figure 3: Iodide decay kinetics for a series of ozone concentrations (500 ppb – 65 ppm). Panel (A) shows kinetics for [O$_3$(g)] ranging from 6-65 ppm, while panel (B) shows [O$_3$] ranging from 500 ppb to 6 ppm. Individual datapoints represent at least 4 single-droplet detection events, with error bars extending one standard deviation about the mean. All droplet experiments performed using initial [I$^-$(b)] = 250 mM, [ClO$_3^-$(b)] = 875 mM, pH = 12, and droplet radius $r = 22\ \mu$m.](image)
By developing a kinetic model constrained by literature rate and diffusion coefficients, we intend for the model to be predictive and useful for understanding iodide reactivity and competitive surface processes over a broad range of conditions beyond those encountered in the experiments described above.

**Figure 4**: Reciprocal half-lives ($\tau^{-1}$) vs. $[O_3(g)]$ for experiments with droplet pH = 12. The overall rate of reaction, represented here by $\tau^{-1}$, scales linearly for $[O_3(g)] < 20$ ppm and becomes limited by an upper-bound for $[O_3(g)] > 20$ ppm. Limiting cases (presented in section VI.A) are compared to experiment and simulation, with the iodide-transport limit shown as a horizontal dashed line and the ozone-transport limit shown as a dotted line. Error bars on the experimental points are computed from standard error in time from a linear regression. The vertical dashed line indicates the ozone concentration at which the pseudo-first order loss of I$^-$ at the surface exceeds the solvation rate of adsorbed ClO$_3^-$ from the surface as discussed in section VI.B.

**IV. Model Description**

**A. Model/Simulation Overview**

Simulations are performed using Kinetiscope©, an open access software package, which numerically simulates the chemical evolution of a system using a stochastic algorithm. A number of
models implemented in this software platform have been used to understand chemical transformations in
submicron and micron-sized particles, ranging from multiphase reaction kinetics in the atmosphere to the
acceleration of reactions confined in emulsions.\textsuperscript{46–48} In Kinetiscope\textcopyright,\textsuperscript{45} space is divided up into
compartments, which are connected by diffusion pathways, to simulate for example, different regions of
a droplet with radius = \(r\). We use the rectangular prism simulation geometry (1 \text{nm} \times 1 \text{nm} \times r/3) described
in previous work,\textsuperscript{49,50} which includes two kinetically distinct regions or compartments: surface and bulk.
The bulk compartment height is \(r/3\) to correctly account for the surface-to-volume ratio of a sphere. The
surface compartment has a finite thickness (\(\delta\)) and is used to compute volumetric surface concentrations.
The approximate width of solvation free energy profiles obtained in Molecular Dynamics (MD)
simulations is used to define a surface thickness of 1 \text{nm}.\textsuperscript{51} Both surface and bulk compartments in the
simulation geometry are well-mixed and the formation of concentration gradients in the bulk phases are
not explicitly included in this scheme. For additional insight into reactant gradients, additional
compartments can be added, providing a finer degree of spatial resolution to the simulations.

The general kinetic scheme used in the simulation is based upon the framework developed by
Willis and Wilson\textsuperscript{33} and shown in Fig. 5. In each compartment there are a set of elementary steps that
describe reactions between individual chemical species. Species move between the bulk and surface
compartments by Fickian diffusion. Diffusion coefficients for species used in the model are based upon
prior literature and shown in steps D1-9 in Table S1.\textsuperscript{52–55} In the surface compartment, there are also a set
of non-reactive steps that include adsorption/desorption, and solvation/desolvation. These steps describe
the partitioning of species (e.g., O\textsubscript{3}, I\textsuperscript{-}, and ClO\textsubscript{3}\textsuperscript{-}) between phases. Once adsorbed to the surface, species
can either react, desorb back into the original phase, or desorb into the opposing phase based upon
volatility and/or solubility. A complete description of the model framework, simulation geometry and
approach used here has been recently given by Willis and Wilson\textsuperscript{33} and further generalized by Wilson \textit{et al.}\textsuperscript{34} Below we detail the specific elementary steps used in the simulation.
We use the ozone partitioning scheme developed by Willis and Wilson\textsuperscript{33} where the overall Henry’s law coefficient $H_{cc}^{gb}$ is decomposed into gas/surface ($H_{cc}^{gs}$) and surface/bulk ($H_{cc}^{sb}$) contributions. The total Henry’s law coefficient $H_{cc}^{gb}$ is a product of these individual terms, $H_{cc}^{gb} = H_{cc}^{gs} \cdot H_{cc}^{cb}$. $H_{cc}^{gs}$ and $H_{cc}^{sb}$ are computed\textsuperscript{34} using solvation energies obtained from MD simulations\textsuperscript{51,56} yielding $H_{cc}^{gs} = 8.9$, $H_{cc}^{sb} = 0.03$, and $H_{cc}^{gb} = 0.27$. $H_{cc}^{gb}$ is consistent with the prior measurements.\textsuperscript{57} $H_{cc}^{gs}$ and $H_{cc}^{sb}$ can also be expressed in Eqs. (1) and (2) as the ratio of rate coefficients for the forward and backward elementary kinetic steps shown in Fig. 5.

$$H_{cc}^{gs} = \frac{[O_3(ads)]}{[O_3(g)]} = \frac{k_{ads}^{\infty} v_{O_3}^{a} \cdot \delta}{k_{des}^{\infty} \cdot \sigma} \quad \text{Eq. (1)}$$

$$H_{cc}^{sb} = \frac{[O_3(b)]}{[O_3(ads)]} = \frac{k_{solv}^{\infty} \cdot \delta}{k_{desolv}^{\infty} \cdot \sigma} \quad \text{Eq. (2)}$$

$k_{ads}, k_{des}$ and $k_{solv}, k_{desolv}$ relate to the kinetic steps S1 and S2 in Table S1 and describe the kinetics of gas-to-bulk transport of $O_3$ in Fig. 5. The values for these rate constants are from Willis and Wilson.\textsuperscript{33}
this description, O₃ from either the gas or bulk phase enters the interfacial region and is adsorbed (O₃(ads)) onto a vacant site (step S1 in Table S1), analogous to gas-adsorption onto a surface site described by a Langmuir framework.⁵⁸ The maximum number of surface sites per area, Γₖ, is obtained from the surface excess of ozone computed by Vieceli et al.,⁵⁶ and is expressed in volumetric units as Γₖ/δ. The concentration of vacant sites throughout the simulation is: \[ \text{[site}_{O₃}] = \Gammaₖ / \delta - \{O₃(ads)\} \].

Eq. (1) includes \( \sigma \), the sticking coefficient of O₃(g) per surface site. In this framework, \( \sigma \) is different from the mass accommodation coefficient \( \alpha \), which is equal to the ratio of rate constants for solvation and desorption of ozone.²⁶ In the present work \( \alpha = k_{solv}/k_{des} = 0.085 \) and is consistent with MD simulations.⁵⁶ Previous simulations of other multiphase ozonolysis reactions were insensitive to the absolute value of \( \sigma \) for values > 10⁻⁴.³³ In the present modeling scheme, we assume \( \sigma = 10⁻⁴ \). The simulation results are observed to be very sensitive to this value as will be discussed below and in SI-5.

C. Solute Liquid-Surface Partitioning

Iodide Partitioning

The surface-adsorbed iodide concentration \([I-(ads)]\) is governed by the solvation and desolvation steps shown in Fig. 5 (step S3 in Table S1). Surface partitioning of I⁻ in pure water is described using the Langmuir isotherm in Eq. (3) where a site-description is used, similar to that described above for ozone. The Langmuir equation relates the bulk and adsorbed concentrations of I⁻,

\[
[I₋(ads)] = \frac{Γ₋/δ}{1 + K₋_{eq} [I₋(0)]} \quad \text{Eq. (3)}
\]

where

\[
K₋_{eq} = \frac{k₋_{desolv}}{k₋_{solv}}. \quad \text{Eq. (4)}
\]

The surface sites for I⁻ and O₃ are assumed to be independent, i.e., I⁻ and O₃ do not compete for the same set of surface sites. The maximum site concentration for I⁻ is constrained by the surface-sensitive measurements by Piatkowski et al.⁵⁹ and is \( Γ₋/δ = 6.38 \times 10^{14} \) molecules/cm². This corresponds to a volumetric concentration of \( Γ₋/δ = 6.38 \times 10^{21} \) molecules/cm³. The ratio of desolvation-to-solvation rate coefficients for iodide is the Langmuir adsorption equilibrium coefficient, \( K₋_{eq} = k₋_{desolv}/k₋_{solv} \). Previous determinations of \( K₋_{eq} \) and the associated Gibbs free energy of adsorption (\( ΔG₋_{ads} \)) have been measured.
through surface sensitive techniques such as photoemission\textsuperscript{60,61} and second-harmonic generation,\textsuperscript{62} as well as by kinetic measurements by Donaldson and coworkers.\textsuperscript{17,63} Additionally, estimates of $\Delta G_{ads}^{\Gamma^-}$ were obtained by MD simulations observing ion stabilization at the interface.\textsuperscript{64,65} However, previous reported values of $K_{eq}^{\Gamma^-}$ from experiment and simulation range between 2 and 500 L mol\textsuperscript{-1}, suggesting surface-adsorption behavior of iodide may be highly sensitive to the specific conditions and the composition of the interface. In the present approach, we use an intermediate value of $K_{eq}^{\Gamma^-}=70$ L mol\textsuperscript{-1} measured by Wren and Donaldson.\textsuperscript{63} The absolute values of the rate coefficients describing solvation and desolvation are, to the best of our knowledge, unknown. Furthermore, we find that model results are not sensitive to the absolute values $k_{desolv}^{I^-}$ and $k_{solv}^{I^-}$. The coefficients are therefore constrained by their relation to the desolvation of ClO$_3^-$, discussed in more detail in the following section. Since the surface partitioning of the intermediates in this system also remain largely unknown, it is assumed that they have the same rate coefficients as $\Gamma^-$, as shown in steps S4-S5 and S7-S9 of Table S1. In this partitioning description, iodide, reaction intermediates, volatile products, and chlorate ($\Gamma^-$, IO\textsuperscript{-}, IO\textsubscript{2}\textsuperscript{-}, I\textsuperscript{3}-, I\textsubscript{2}, HOI, ClO\textsubscript{3}-) all compete for the same set of surface sites. Surface partitioning of the final product iodate, IO\textsubscript{3}\textsuperscript{-}, is assumed to be different from other species in solution, as discussed in the following section.

\textit{Chlorate and Iodate Partitioning – Multicomponent Langmuir Description}

The chlorate anion, ClO$_3^-$, in addition to its utility as an internal standard and controlling the microdroplet hygroscopicity, competes with $\Gamma^-$ for occupancy at the air-water interface and provides a prototypical system for studying suppression of surface chemistry due to competition between multi-ion adsorption and reaction at the interface. ClO$_3^-$ is known to partition strongly to the air-water interface, with a surface propensity similar to $\Gamma^-$ as evidenced by its location in the Hofmeister series ($F^- < IO_3^- < Cl^- < BrO_3^- < Br^- < ClO_3^- < I^-$).\textsuperscript{66,67} The Hofmeister series, originally constructed to order ions by their effect on protein solubility,\textsuperscript{68} is also understood to reflect an ion’s relative surface propensity and its energetic effect on the hydrogen-bonding network.\textsuperscript{69} The surface propensity of ClO$_3^-$ has been observed in both surface tension measurements\textsuperscript{67} and through the hydrogen bonding structure of water at the air-water interface using vibrational sum-frequency generation.\textsuperscript{66} To our knowledge, direct measurements of the adsorption equilibrium coefficient $K_{eq}^{ClO_3^-}$ do not exist, with the only previous estimate made from fitting surface tension measurements to a modified Langmuir adsorption model.\textsuperscript{70} Here, we estimate $K_{eq}^{ClO_3^-}$ using previous measurements\textsuperscript{71} of the relative surface equilibrium coefficient of ClO$_3^-$ to $\Gamma^-$ obtained using a flotation technique in which competitive adsorption between anions to a charged surfactant at the air-
water interface is measured.\textsuperscript{72} The resulting relative equilibrium coefficients (termed “selective adsorption coefficients”), in conjunction with $K_{eq}^{I^-}$, suggests a value of $K_{eq}^{ClO_3^-} = 30 \text{ M}^{-1}$. This is consistent with the location of chlorate between Br$^-$ and I$^-$ in the Hofmeister series (Br$^-$ < ClO$_3^-$ < I$^-$) and previous measurements\textsuperscript{63,73} of $K_{eq}^{Br^-} \sim 3 \text{ M}^{-1}$ and $K_{eq}^{I^-} \sim 70 \text{ M}^{-1}$.

The desolvation and solvation steps of ClO$_3^-$ are treated in the same way as I$^-$ (step S6 in Table S1), where the ratio of $k_{desolv}^{ClO_3^-}$ to $k_{solv}^{ClO_3^-}$ is constrained by $K_{eq}^{ClO_3^-}$. To constrain the absolute rate coefficients $k_{desolv}^{ClO_3^-}$ and $k_{solv}^{ClO_3^-}$, we first assume $k_{desolv}^{I^-} = k_{desolv}^{ClO_3^-}$ and treat $k_{solv}^{ClO_3^-}$ as an adjustable parameter. As discussed below in section VI.A and in the supplementary information (section SI-5), a single value of $k_{solv}^{ClO_3^-} = 7 \text{ s}^{-1}$ is required in order for the simulation results to agree with the experimental kinetics. By constraining $k_{solv}^{ClO_3^-}$ to experiment in this way, $k_{desolv}^{ClO_3^-}$, $k_{desolv}^{I^-}$, and $k_{solv}^{I^-}$ are also constrained.

The equilibrium surface partitioning of I$^-$ and ClO$_3^-$ is described by a multi-component Langmuir equation,

$$
[I_{(ads)}^-] = \frac{I_{l}^{\infty}}{\delta} \cdot \frac{k_{eq}^{I^-}[I_{(b)}^-]}{1 + k_{eq}^{I^-}[I_{(b)}^-] + k_{eq}^{ClO_3^-}[ClO_3^-_{(b)}]} \quad \text{Eq. (5)}
$$

$$
[ClO_3^-_{(ads)}] = \frac{ClO_3^-_{l}^{\infty}}{\delta} \cdot \frac{k_{eq}^{ClO_3^-}[ClO_3^-_{(b)}]}{1 + k_{eq}^{I^-}[I_{(b)}^-] + k_{eq}^{ClO_3^-}[ClO_3^-_{(b)}]} \quad \text{Eq. (6)}
$$

Eqs. (5) and (6) provide useful benchmarks for examining how the chemical composition of the interface diverges from a non-reactive equilibrium description during reaction as iodide is consumed on a timescale faster than can be replenished by the bulk.

IO$_3^-$ is treated differently from I$^-$ and ClO$_3^-$ given its low propensity for the air-water interface (see its location above in Hofmeister series). The IO$_3^-$ hydration structure and its effect on the water hydrogen-bonding network has been studied\textsuperscript{74,75} and iodate is observed to be depleted from the air-water interface relative to the bulk.\textsuperscript{76} Given iodate’s apparent low surface-propensity, we assume that all IO$_3^-$ that is generated at the surface is rapidly solvated into the bulk solution. As such, reaction step S12 in Table S1 shows the production of IO$_3^-(b)$ as purely a bulk quantity, where IO$_3^-$ neither occupies nor competes for surface adsorption sites.

D. Reaction Steps
For the ozonolysis of iodide to iodate we use the gas phase sequential mechanism reported by Bhujel et al.\textsuperscript{77}:

\[
\begin{align*}
I^- + O_3 & \rightarrow IO^- + O_2 \quad \text{(R1)} \\
IO^- + O_3 & \rightarrow IO_2^- + O_2 \quad \text{(R2)} \\
IO_2^- + O_3 & \rightarrow IO_3^- + O_2. \quad \text{(R3)}
\end{align*}
\]

Rate coefficients R1-R3 (steps S10-S12 and steps B1-B3 in Table S1) are taken from Bhujel et al.,\textsuperscript{77} and are treated as irreversible given the slow reverse rate of reaction. This stepwise mechanism is included in the model at both the air-water interface and within the bulk liquid. The bulk-rate coefficients are assumed to be equal to those at the surface, although there are previous reports that the kinetics of R2 and R3 are significantly slower in the bulk.\textsuperscript{44,78}

Further reactions of iodide and iodine-oxides are sources of gaseous products I$_2$ and HOI, and aqueous I$_3^-$. From previous literature the most significant secondary loss channels for iodide in solution are,\textsuperscript{16,22,23}

\[
\begin{align*}
I^- + \text{HOI} + H^+ & \xrightleftharpoons[k_b]{k_f} I_2 + H_2O \quad \text{(R4)} \\
I^- + I_2 & \xrightleftharpoons[k_b]{k_f} I_3^- \quad \text{(R5)}
\end{align*}
\]

Reactions R4 and R5 depend on the production of HOI via,

\[
\begin{align*}
IO^- + H^+ & \xrightleftharpoons[k_b]{k_f} \text{HOI} \quad \text{(R6)}
\end{align*}
\]

Reactions R4-R6 require H$^+$ so are negligible under strongly basic conditions, where the major product is IO$_3^-$ (R3). Under neutral and acidic conditions, however, the production of HOI, I$_2$, and I$_3^-$ is significant as previously observed.\textsuperscript{16,22} The rate coefficients for R4-6 are taken from prior studies\textsuperscript{42–44,79} and shown in Table S1 (steps S13-S15 and B4-B6). Evaporation of volatile products (steps S16 and S17, Table S1) is also included in the model, a description of which is found in the supplemental information (see section SI-4).

V. Model Results
Shown in Figs. 2-4 are simulation results compared to experimental measurements. Experimental quantities such as [O₃(g)], pH, and droplet size are simulation inputs. As shown in Fig. 2 the simulations predict the pH dependence of the reaction kinetics for the buffered and unbuffered cases. Figure 2 (A) shows the consumption of iodide is accelerated with decreasing initial pH in both simulation and experiment. This acceleration results from the rapid formation of HOI and I₂ at lower pH, which is consistent with previous results reporting higher formation rates of iodine gas at low pH.²² Fig. 2 (B) shows droplet ozonolysis experiments in which the decay of an unbuffered solution with initial pH 4 resembles that of a solution with an initial pH of 12. Simulations confirm that the droplet solution becomes rapidly alkaline during ozonolysis due to the consumption of protons in the pathways leading to HOI and I₂, thus rendering an initial microdroplet pH of 4 virtually indistinguishable from basic conditions.

The simulations also replicate the ozone dependent reaction kinetics observed at pH 12, reproducing the shift observed in Fig. 3 from zero order to first order decay kinetics with increasing [O₃(g)]. The dependence of $\tau^{-1}$ on [O₃(g)], shown in Fig. 4, is also reproduced by the simulation and is consistent with observations within experimental uncertainty. We find that the simulation predictions are sensitive to $\sigma$, the ozone sticking coefficient (see step S1, Table S1) as well as the solvation rate constant of ClO₃⁻ $(k_{solv}^{ClO_3^-})$ in step S6, Table S1). This sensitivity is illustrated in Fig. S3, where $\tau^{-1}$ is shown as a function of $\sigma$ and $k_{solv}^{ClO_3^-}$. The present experiments constrain $\sigma$ to $10^{-4}$ and $k_{solv}^{ClO_3^-}$ to 7 s⁻¹ in the model. This level of sensitivity to $\sigma$ was not observed in simulations of previous ozonolysis reactions,³⁴ and likely results from the exceptionally fast reaction rate between iodide and ozone at the air-water interface. While we reserve a more thorough discussion of this observation for a future publication, it appears that the $I^- + O_3$ reaction serves as a kind of “chemical clock” for the non-reactive adsorption/desorption steps of O₃ and solvation/desolvation steps of $I^-$ at the interface.

The close correspondence between the simulation predictions and experimental observations (Fig. 2, 3, and 4) confirm that the essential mechanistic steps are correctly represented in the model framework discussed above. This then allows a closer examination of the simulation results to better understand the underlying steps at the surface and in the bulk liquid that are responsible for the pH and O₃ dependent kinetics observed in the experiment, which is ultimately needed to formulate a comprehensive multiphase mechanism for this reaction.

VI. Analysis and Discussion
In the following sections, we use the simulation results to develop kinetic expressions to more fully elucidate the $\Gamma^+ + O_3$ reaction mechanism in the presence of the surface-active ClO₃⁻ ions. First, we consider limiting kinetic cases to explain the differences in reactions conducted under high and low ozone concentrations, followed by an analysis of the depletion of $[O_3(ads)]$ and $[\Gamma(ads)]$ at the interface. Understanding these aspects of the reaction is required to translate the insight gained under these relatively narrow set of laboratory conditions to a broader range of conditions in order to make realistic predictions of aggregate reactive quantities such as the uptake coefficient of $O_3$.

A. Limiting Kinetic Cases at High and Low $[O_3]$ 

The iodide ozonolysis kinetics shown in Fig. 3 exhibit two prominent features. First, at low $[O_3(g)]$, $\tau^1$ increases linearly with increasing ozone concentration. In this region the iodide decay kinetics largely obey zero-order kinetics, and the rate of decay for a given set of conditions is fixed as shown in Fig. 3 (B). Second, at higher $[O_3(g)]$, $\tau^1$ reaches a plateau beyond which it remains constant. The iodide decay kinetics in this plateau region are first-order resulting in an exponential decay of $[I^-(b)]$ with time as seen from the data in Fig. 3 (A). Here we examine the simulation output to understand the origin of the kinetic behavior in these two cases. Event analysis in the simulation reveals that, under our experimental conditions, >99% of the reactive events occur in the surface compartment, indicating that the kinetic behavior observed in Figs. 3 and 4 is controlled by the interface and thus requires a deeper understanding of factors that control $[\Gamma(ads)]$ and $[O_3(ads)]$.

Figure 6 shows simulated surface concentrations ($[I^-(ads)]$, $[ClO_3^-(ads)]$, and $[O_3(ads)]$) for $[O_3(g)] = 2$ ppm and $[O_3(g)] = 40$ ppm with initial $[I^-(b)] = 250$ mM and $[ClO_3^-(b)] = 875$ mM. Fig. 6 (A) and (C) show $[I^-(ads)]$ and $[ClO_3^-(ads)]$ while (B) and (D) show $[O_3(ads)]$. Also shown for comparison in Fig. 6 (A) and (C) are the equilibrium surface concentrations (without reaction) computed from Eqs. (5) and (6). In the low-ozone regime, both $[\Gamma(ads)]$ and $[ClO_3^-(ads)]$ remain close to their non-reactive equilibrium concentration, whereas $[\Gamma(ads)]$ is depleted and $[ClO_3^-(ads)]$ is enriched under high-ozone conditions. The $[\Gamma(ads)]$ depletion in the high-ozone regime, along with the observation that the ozone concentration in the bulk is nearly zero, suggests that the reaction becomes limited by iodide transport to the interface under high ozone concentrations. We estimate the concentration above which this behavior dominates the kinetics is $[O_3(g)] \sim 20$ ppm. Figure 6 (C) and (D) also shows that $[O_3(ads)]$ is depleted by many orders of magnitude relative to the value predicted by $H_{cc}^{gs} \cdot [O_3(g)]$ when $[O_3(g)] = 2$ ppm, but is only ~3 times less than $H_{cc}^{gs} \cdot [O_3(g)]$ when $[O_3(g)] = 40$ ppm.
Using the simulation results shown in Fig. 6, simple expressions are derived to represent the iodide decay kinetics under the low and high [O₃(g)]. While the simulations allow us to examine the interface and bulk regions of the droplet separately, the experimental measurements do not, since the entire droplet is sampled by the mass spectrometer. However, the simulations indicate that the vast majority of the I⁻ + O₃ reactions occur at the droplet interface, suggesting that experimentally measured changes in [I⁻(b)] depend explicitly on [I⁻(ads)] and [O₃(ads)]. Thus, to link the simulation results with experimental observations, the kinetic expressions, shown below, are derived in terms of the decay of [I⁻(b)].
We first consider the case where \([\text{O}_3(\text{g})] < 20 \text{ ppm}\) and \([\text{I}^-(\text{ads})]\) is not substantially depleted relative to its Langmuir isotherm. We begin with the rate equations for \([\text{I}^-(\text{b})]\) and \([\text{I}^-(\text{ads})]\) to derive a simple expression for the overall consumption of bulk iodide \([\text{I}^-(\text{b})]\). As suggested by the simulation results in Fig. 6 (B), \([\text{O}_3(\text{ads})]\) is rapidly depleted and reaches steady state. A steady-state assumption for \([\text{O}_3(\text{ads})]\) is then used to illustrate that the decay of iodide can be described by the following differential equation (see derivation of Eq. S8 in supplementary section SI-6)

\[
\frac{d[\text{I}^-(\text{b})]}{dt} = -\frac{V_S}{V_B + V_S} \cdot \frac{1}{3} \cdot k_{\text{ads}} \cdot \sigma \cdot [\text{site}_{\text{O}_3}] \cdot [\text{O}_3(\text{g})]
\]

Eq. (7)

where \(V_S\) and \(V_B\) are the surface and bulk compartment volumes and \(k_{\text{ads}}\) is the rate coefficient for \(\text{O}_3\) adsorption and \(\sigma\) is the sticking coefficient for \(\text{O}_3\) (from step S1 in Table S1). In this case, the decay of iodide follows zero-order kinetics, and is therefore linear in time with the slope given in Eq. (7). To compare this limit with the experiments, half-lives are calculated as a function of \([\text{O}_3(\text{g})]\), providing the upper bound shown in Fig. 4 (labeled ozone-transport limit). Inspection of Eq. (7) suggests that, in this case, iodide ozonolysis at the surface is limited by the adsorption rate of \(\text{O}_3\) from the gas phase. This is consistent with the extreme depletion of ozone observed at the interface under all conditions used in the present experiments (Fig. 6 (B) and (D)).

The case where \([\text{O}_3(\text{g})] > 20 \text{ ppm}\) and \([\text{I}^-(\text{ads})]\) is depleted is also considered in section SI-6. The depletion of \([\text{I}^-(\text{ads})]\) relative to its Langmuir value shown in Fig. 6 (C) indicates that the decay of \([\text{I}^-(\text{b})]\) is limited by its mass-transfer to the surface. Simulation results suggest that this mass-transfer limit originates from the kinetics of desolvation of iodide from the solution rather than the diffusion of iodide to the interface. This is apparent in the scarcity of surface-sites available for desolvation of iodide resulting from it’s competition with chlorate. Under these conditions, the net consumption rate of \([\text{I}^-(\text{b})]\) is described by the following (Eq. S13 in SI-6)

\[
\frac{d[\text{I}^-(\text{b})]}{dt} = -\frac{V_S}{V_B + V_S} \cdot \frac{k_{\text{desolv}}}{K_{\text{ClO}_3}^{\text{eq}}} \cdot \theta_I \cdot [\text{I}^-(\text{b})]
\]

Eq. (8)

\[
\theta_I = \frac{[\text{ClO}_3^-_{\text{ads}}]}{[\text{ClO}_3^-_{\text{b}}]} = \left[ \frac{t_i}{\delta} \cdot \frac{K_{\text{ClO}_3}^{\text{eq}}}{1 + K_{\text{ClO}_3}^{\text{eq}} \cdot [\text{ClO}_3^-_{\text{b}}]} \right]
\]

Eq. (8a)

where \(k_{\text{desolv}}\) is the desolvation rate coefficient of \([\text{I}^-(\text{b})]\) (step S3 in Table S1), \(K_{\text{ClO}_3}^{\text{eq}}\) is the Langmuir adsorption equilibrium constant for \(\text{ClO}_3^-\), and the \(\theta_I\) is equal to the surface-to-bulk ratio of \(\text{ClO}_3^-\).
concentration, determined by the single-component Langmuir adsorption equation. The form of Eq. (8) predicts first-order kinetics for \([\Gamma(b)]\) in this regime, with a solution that is exponential in time with decay constant \(k_{\text{limit}} = \frac{v_s}{v_B+v_S} \frac{k_{\text{desolv}}^\Gamma}{k_{\text{eq}}^{\text{ClO}_3^-}} \cdot \theta_i\). Assuming, as discussed above, that \(k_{\text{desolv}}^\Gamma = k_{\text{desolv}}^{\text{ClO}_3^-}\), the decay constant is \(k_{\text{limit}} = \frac{v_s}{v_B+v_S} \cdot k_{\text{solv}}^{\text{ClO}_3^-} \cdot \theta_i = 0.668\ \text{min}^{-1}\). \(k_{\text{limit}}\) is used to compute \(\tau^{-1} = 0.97\ \text{min}^{-1}\) shown in Fig. 4 as a horizontal line, providing an upper-bound that agrees with experiments. Further inspection of \(k_{\text{limit}}\) suggests the solvation rate of ClO\(_3^-\), \(k_{\text{solv}}^{\text{ClO}_3^-}\), and the surface-to-bulk fraction of ClO\(_3^-\), \(\theta_i\), ultimately governs the reaction kinetics in this limiting case. The transfer of I\(^-\) from the bulk solution is limited by the availability of empty surface sites, which are produced at the solvation rate of ClO\(_3^-\) (\(k_{\text{solv}}^{\text{ClO}_3^-}\)). This explanation is consistent with simulation results that show high concentrations of ClO\(_3^-\) at the interface, which occupy a substantial fraction of surface sites and prevent iodide from accessing the interface and reacting with O\(_3\) (Fig. 6(C)).

The limiting cases presented above (and derived in section SI-6) are used to interpret features of the multiphase kinetics that occur in a narrow range of experimental conditions (i.e. \([\text{O}_3(\text{g})], [\Gamma(b)]\)). This analysis reveals that surface concentrations of O\(_3\), I\(^-\), and ClO\(_3^-\) are dynamic and coupled quantities. Below we expand this analysis to encompass a broader range of concentrations beyond the experimental conditions shown in Figs. 2, 3, and 4. This is required to formulate a general expression in Sect. VI.C for the overall reactive uptake coefficient of ozone by aqueous iodide over a range of concentrations.

### B. Mutual Reactant Depletion at the Gas-liquid Interface

A series of simulations and kinetic approximations are now used to quantitatively understand the factors that control \([\text{O}_3(\text{ads})]\) and \([\Gamma(\text{ads})]\) at the droplet interface. Shown as points in Fig. 7 are the simulated \([\text{O}_3(\text{ads})]\) as a function of initial bulk iodide concentration (\([\Gamma(b)]_0 = 100\ \text{nM to 1 M}\) at \([\text{O}_3(\text{g})] = 2\ \text{ppm}\)). Simulated values of \([\text{O}_3(\text{ads})]\) at each \([\Gamma(b)]\) are obtained using a pair of simulation runs. Two separate simulations are required since \([\text{O}_3(\text{ads})]\) and \([\Gamma(\text{ads})]\) are coupled quantities. First an ozonolysis simulation is used to find the steady-state values for \([\Gamma(\text{ads})], [\text{IO}^- (\text{ads})], [\text{IO}_2^- (\text{ads})],\) and \([\text{ClO}_3^- (\text{ads})]\). To do this, simulations are run for \(~1\ \text{s}\) or when the surface species reach steady-state (see example \([\Gamma(\text{ads})]\) in Fig. S4 (B)). For this simulation, the assumption is made that bulk quantities are not perturbed by the surface, i.e., the simulated bulk concentrations are at their initial conditions (\([\Gamma(b)] = [\Gamma(b)]_0, [\text{ClO}_3^- (b)] = [\text{ClO}_3^- (b)]_0, [\text{IO}^- (b)] = [\text{IO}_2^- (b)] = 0\)). The steady-state concentrations for \([\Gamma(\text{ads})], [\text{IO}^- (\text{ads})], [\text{IO}_2^- (\text{ads})],\) and \([\text{ClO}_3^- (\text{ads})]\) are then
used to initialize a second simulation to obtain \([O_3(ads)]\), which typically reaches steady-state within ~100 ps for a gas-phase concentration of \([O_3(g)] = 2 \text{ ppm}\) (see example \([O_3(ads)]\) in Fig S4 (A)). During this short reaction window, very little of the iodide and the intermediates are consumed by the reaction and their concentrations remain nearly equal to the initial concentrations at the start of this simulation.

**Figure 7:** \([O_3(ads)]\) vs. \([I^-(b)]\) showing depletion of \([O_3(ads)]\) using results from simulation and the analytic kinetic expressions. All results assume a gas phase \([O_3(g)] = 2 \text{ ppm}\) and aqueous \([\text{ClO}_3^-(b)] = 875 \text{ mM}\). Simulation results are shown as points and the analytical expression as a dashed red line. Simulated results are obtained by first finding steady-state concentrations of ions at the interface, which are then used to simulate a steady-state \([O_3(ads)]\). Results are compared to \([O_3(ads)]\) predicted by \(H_{ec}^{GS}[O_3(g)]\) which is denoted as a dashed horizontal line. Red vertical line denotes the two kinetic regimes dominated by mass transport or reaction of ozone as defined in the rate analysis in the text.

Fig. 7 show the results of this simulation procedure. At small \([I^-(b)], [O_3(ads)]\) is at its Henry’s Law value in the absence of a reaction (i.e., \([O_3(ads)] = H_{ec}^{GS}[O_3(g)]\)). Moving to higher iodide concentrations the simulated steady-state \([O_3(ads)]\) exhibits a sigmoidal shape, exhibiting a dramatic depletion relative to its Henry’s law value for \([I^-(b)] > 15 \text{ mM}\) (vertical red line in Fig. 7). This threshold where \([O_3(ads)]\) becomes significantly depleted reflects competing surface processes. Depletion of ozone at the interface occurs when the pseudo-first order reactive loss of \(O_3(ads) (k'_{rxn})\) exceeds the rate that it can be re-supplied from the gas phase. The pseudo-first order reaction rate of ozone includes all reactions at the surface \(k'_{rxn} =\)
The adsorption and desorption rates of ozone at the surface together control the characteristic equilibration time for ozone at the droplet interface as discussed in Wilson et al.\textsuperscript{34} Since the rate constant for desorption is much larger than adsorption in this case, the rate of desorption dominates this equilibration timescale. Comparing $k_{\text{des}}$ and $k'_{\text{rxn}}$ for ozone then shows that when $k'_{\text{rxn}} > k_{\text{des}}$, $O_3(\text{ads})$ will react on a timescale that is faster than that gas phase can replenish it at the surface, leading to strong depletion of $[O_3(\text{ads})]$. Conversely, when $k'_{\text{rxn}} < k_{\text{des}}$, $[O_3(\text{ads})]$ equilibrates at the interface on timescales that are faster than its reactive consumption, so that $[O_3(\text{ads})]$ can equilibrate to its Henry’s Law value of $H^g_{cc} \cdot [O_3(g)]$. This demonstrates that reactant concentrations are tightly coupled at the surface and mutually dependent.

In addition to simulations, Fig. 7 shows results from an analytical expression for $[O_3(\text{ads})]$ obtained using a set of 6 coupled kinetic equations for the concentrations of all surface species considered in the simulation (i.e., $[\Gamma(\text{ads})]$, $[\text{IO}^-(\text{ads})]$, $[\text{IO}_2^-(\text{ads})]$, $[\text{ClO}_3^-(\text{ads})]$, $[\text{site}]$, and $[O_3(\text{ads})]$). These equations include the production and consumption rates of each adsorbed species when the surface has reached a quasi-steady state,

$$\frac{d[O_3(\text{ads})]}{dt} = 0 = -k_{\text{r,zn}}^\Gamma \cdot [O_3(\text{ads})] \cdot [\Gamma(\text{ads})] - k_{\text{r,zn}}^{10^-} \cdot [O_3(\text{ads})] \cdot [\text{IO}^-(\text{ads})] - k_{\text{r,zn}}^{10^+} \cdot [O_3(\text{ads})] \cdot [\text{IO}_2^-(\text{ads})] + k_{\text{ads}} \cdot \sigma \cdot [O_3(g)] \cdot [\text{site}] - k_{\text{des}} \cdot [O_3(\text{ads})]$$

Eq. (9)

$$\frac{d[\Gamma(\text{ads})]}{dt} = 0 = -k_{\text{r,zn}}^\Gamma \cdot [O_3(\text{ads})] \cdot [\Gamma(\text{ads})] + k_{\text{desolv}}^\Gamma \cdot [\Gamma_0^\text{b}] \cdot [\text{site}] - k_{\text{solv}}^{\Gamma} \cdot [\Gamma(\text{ads})]$$

Eq. (10)

$$\frac{d[\text{IO}^-(\text{ads})]}{dt} = 0 = k_{\text{r,zn}}^\text{IO}^- \cdot [O_3(\text{ads})] \cdot [\Gamma(\text{ads})] - k_{\text{r,zn}}^{10^-} \cdot [O_3(\text{ads})] \cdot [\text{IO}^-(\text{ads})] - k_{\text{solv}}^{\text{IO}^-} \cdot [\text{IO}^-(\text{ads})]$$

Eq. (11)

$$\frac{d[\text{IO}_2^-(\text{ads})]}{dt} = 0 = k_{\text{r,zn}}^{10^+} \cdot [O_3(\text{ads})] \cdot [\text{IO}^-(\text{ads})] - k_{\text{r,zn}}^\text{IO}_2^- \cdot [O_3(\text{ads})] \cdot [\text{IO}_2^-(\text{ads})]$$

Eq. (12)

$$\frac{d[\text{ClO}_3^-(\text{ads})]}{dt} = 0 = k_{\text{desolv}}^{\text{ClO}_3^-} \cdot [\text{ClO}_3^-(\text{b})] \cdot [\text{site}] - k_{\text{solv}}^{\text{ClO}_3^-} \cdot [\text{ClO}_3^-(\text{ads})]$$

Eq. (13)

$$[\text{site}] = \frac{r^{\text{site}}}{\delta} - [\Gamma(\text{ads})] - [\text{IO}^-(\text{ads})] - [\text{IO}_2^-(\text{ads})] - [\text{ClO}_3^-(\text{ads})]$$

Eq. (14)

In Eqs. (9)-(14), $k_{\text{r,zn}}^\Gamma, k_{\text{r,zn}}^{10^-}, k_{\text{r,zn}}^{10^+}$ are the ozonolysis rate coefficients for $\Gamma$, $\text{IO}^-$, $\text{IO}_2^-$, respectively (see steps S10-S12 in Table S1). $k_{\text{ads}}, k_{\text{des}}, \sigma$ describe the partitioning of gaseous ozone (step S1 in Table S1) to the interface and $k_{\text{solv}}$ and $k_{\text{desolv}}$ describe the respective solvation and desolvation steps of each solute (steps S3-S6 in table S1). The 6 equations (9-14) are solved for the 6 unknowns (i.e., $[\Gamma(\text{ads})], [\text{IO}^-(\text{ads})]$,
[IO$_2^{\text{ads}}$, [ClO$_3^{-}\text{ads}$], [site] and [O$_3\text{ads}$]) using Mathematica\textsuperscript{80} (description of approach and code included in supplementary section SI-8). As shown in Fig. 7, the expression obtained for [O$_3\text{ads}$] fully agrees with the explicit simulations, verifying the kinetic description is accurate. The analytical results replicate the behavior observed in the simulation where the coupling of iodide and ozone depletion is captured using the complete equation set. As discussed above, the sigmoidal shape of the analytic expression reflects the competitive timescales of surface-reaction and surface-transport of ozone.

To further illustrate reagent depletion the occurs during the coupled adsorption and reaction at the interface, Fig. 8 shows the evolution of $[\Gamma_{\text{ads}}]$ vs. $[\Gamma_{\text{b}}]$ for a typical droplet simulation containing $[\Gamma_{\text{b}}] = 250$ mM, $[\text{ClO}_3^{-}\text{b}] = 875$ mM, and $[\text{O}_3\text{g}] = 10$ ppm. Points in Fig. 8 show the direct simulation output, where $[\Gamma_{\text{ads}}]$ decreases as $[\Gamma_{\text{b}}]$ is consumed by the reaction (although a time-axis is not shown, reaction time here corresponds to decreasing $[\Gamma_{\text{b}}]$ over the course of ozonolysis). Figure 8 also shows $[\Gamma_{\text{ads}}]$ computed as a function of $[\Gamma_{\text{b}}]$ (dashed blue line) using the solution $[\Gamma_{\text{ads}}]$ for Eqs.(9)-(14). The analytical expression agrees with the explicit simulations and demonstrates that under the present conditions, the decay of iodide differs significantly from the equilibrium multi-component Langmuir behavior (without reaction).
Using the discussion and equations described above, the origin of the two kinetic regimes observed in the experiments and shown in Fig. 4 can be further understood. The pseudo-first order loss rate of iodide at the interface is 

\[ k'_I = k_{\text{rxn}} \cdot [O_3(ads)] \]

Using the full analytical expression derived for \([O_3(ads)]\), \(k'_I\) is computed over the range of \([O_3(g)]\) used in the experiments. Comparing \(k'_I\) to the solvation rate of chlorate \(k_{\text{solv}}^{\text{ClO}_3^-}\) (the limiting step in iodide desolvation to the surface) reveals that the chemical loss of \([I-(ads)]\) from the reaction with ozone exceeds the solvation rate of \(\text{ClO}_3^-\) into the bulk liquid (i.e. \(k'_I > k_{\text{solv}}^{\text{ClO}_3^-}\)) when \([O_3(g)] > 20\) ppm (vertical line, Fig 4). Conversely, when \([O_3(g)] < 20\) ppm and \(k'_I < k_{\text{solv}}^{\text{ClO}_3^-}\), I- is replenished to the surface faster than can be consumed by reaction, whereby \([I(ads)]\) approaches its Langmuir equilibrium value and \([O_3(ads)]\) becomes depleted instead. Having constructed a kinetic understanding of the effect of the derived surface concentrations on this reaction system, the expressions for \([I(ads)]\) and \([O_3(ads)]\) are used in the next section to predict the reactive uptake coefficients of O3 over a range of

**Figure 8:** \([I(ads)]\) vs. \([I(b)]\) for a droplet simulation \((r = 22\) μm) with \([O_3(g)] = 10\) ppm, initial \([I(b)] = 250\) mM and \([\text{ClO}_3^-(b)] = 875\) mM. Simulation results are shown as points, where a simulated droplet was ozonized to completion (time axis not shown). The Langmuir equation gives the expected non-reactive equilibrium concentration of iodide at the interface as a function of bulk concentration. The steady-state expression, computed from Eq.(9)-(14), demonstrates the effect of competitive adsorption between I- and ClO3- on the overall reactive consumption of \([I(ads)]\).
concentrations. These will be compared with uptake coefficients determined from experiment and simulation to draw conclusions about this reaction from a broader perspective.

**C. Reactive Uptake Coefficient vs. \([I-(b)]\) and \([O3(g)]\)**

Wilson *et al.* presented a new set of equations for computing the total reactive uptake coefficient \((\gamma_{total} = \gamma_s + \gamma_b)\) in droplets that includes contributions from both surface \((\gamma_s)\) and bulk \((\gamma_b)\) reactions\(^{34}\)

\[
\gamma_s = \frac{4 \cdot r \cdot k_{rxn} [O_3(ads)] [I_-(ads)]}{3 \cdot c \cdot [O_3(g)]} \cdot \frac{(r^3 - (r - \delta)^3)}{r^3} \quad \text{Eq. (15)}
\]

\[
\gamma_b = \frac{4 \cdot r \cdot k_{rxn} [I_-(b)]}{3 \cdot c} \cdot \frac{k_{transport} \cdot H_{cc}^{gs} [O_3(g)]}{k_{rxn} [I_-(b)] + k_{transport}} \quad \text{Eq. (16)}
\]

In Eqs. (15) and (16), \(c\) is the mean molecular speed of ozone in the gas phase and \(r\) is the droplet radius. \(k_{transport}\) is a rate coefficient that describes the transport of ozone to and from the interface, which includes both diffusive and kinetic contributions as described in Wilson *et al.*\(^{34}\) In previous studies, \([O_3(ads)]\) was determined by \(H_{cc}^{gs} [O_3(g)]\), which is correct only for much slower ozonolysis reactions where \([O_3(ads)]\) and the \([\text{solute}(ads)]\) are not depleted relative to their equilibrium values in the absence of a reaction.\(^{33}\) For those cases, both the \([\text{solute}(ads)]\) and \([O_3(ads)]\) reside at their Langmuir equilibrium and Henry’s law \((H_{cc}^{gs} [O_3(g)])\) values, respectively. For the \(I^- + O_3\) reaction, as shown above, neither \([O_3(ads)]\) nor \([I_-(ads)]\) are at these equilibrium values due to reactive depletion during the reaction. Thus, to compute \(\gamma_s\), the expressions for \([O_3(ads)]\) and \([I_-(ads)]\) obtained by solving Eqs. (9)-(14) are used in Eq. (15).

\(\gamma_s\) and \(\gamma_b\) computed using Eqs. (15) and (16) are shown in Fig. 9 (A) and (B) for a droplet with \(r = 22 \mu m\). Fig. 9 (A) shows uptake coefficients as a function of \([I_-(b)]\) for \([O_3(g)] = 1 \text{ ppm}\), while Fig. 9 (B) shows uptake as a function of \([O_3(g)]\) for \([I_-(b)] = 250 \text{ mM}\). Also included in Fig. 9 are the reactive uptake coefficients obtained from simulation and experiment. Uptake coefficients from the simulation are simply the fraction of ozone-surface collisions that consume \(I^-\). Reactive uptake coefficients from the experiments, conducted at pH 12, are computed from the decay kinetics shown in Fig. 3 using,\(^{81}\)

\[
\gamma_{exp} = \frac{4 \cdot r \cdot k_{exp} [I_-(b)]_0}{3 \cdot [O_3(g)] \cdot c} \quad \text{Eq. (17)}
\]

where \([I_-(b)]_0 = 250 \text{ mM}\), droplet radius \(r = 22 \mu m\), and mean molecular speed of ozone \(c = 360 \text{ m/s}\) at 294 K. \(k_{exp}\) is obtained for each experiment by fitting the iodide decay with an exponential (for \([O_3(g)] > 20\)
pm) or linear function (for \([O_3(g)] < 20 \text{ ppm}\)). As shown in Fig. 9 there is reasonable agreement between
the experimental, simulated, and analytically computed uptake coefficients, where it is clear that under
our experimental conditions surface reactions dominate.

Results in Fig. 9 show how bulk-phase reactant concentrations influence the reactive uptake coefficient of \(O_3\). Results for uptake in this system are compared to limiting resistor-model cases for pure
iodide-ozone chemistry, specifically, the “uptake controlled by fast reaction” case given by Wornsop et
al.\(^{26}\) or “diffusion-limited” case given by Smith et al.\(^{25}\)

\[
\gamma_{\text{diff}} = \frac{4 \cdot H_{cc}^{gb} \cdot D_{O_3(b)} \cdot k_{r,xn} \cdot [O_3(b)]}{c} \quad \text{Eq. (18)}
\]

and the dilute-limit of “phase-mixed” case described by Schwartz\(^{82}\) and previously analyzed by Wilson
et al.\(^{34}\):

\[
\gamma_{\text{dilute}} = \frac{4 \cdot r \cdot H_{cc}^{gb} \cdot k_{r,xn} \cdot [I_{(b)}^\text{-}]}{3 \cdot c} \quad \text{Eq. (19)}
\]

The diffusion-limited resistor case has been widely used in context of this reaction for interpreting
experimental results of reactive ozone uptake, and for predicting both ozone consumption and emission
of volatile products under a large range of bulk concentrations and surface-to-volume ratios.\(^{14-16,21,24}\) This
case assumes uptake of ozone is driven by the bulk reaction and limited by \(O_3\) diffusion into the solution.
The dilute-limit case similarly assumes the reaction takes place in the bulk solution, but instead assumes
that \(O_3\) within the droplets resides at its Henry’s law concentration.

Fig. 9 (A) shows how the reactive uptake coefficient depends on \([I_{(b)}]\) for \([O_3(g)] = 1 \text{ ppm}\) and
\([\text{ClO}_3(b)] = 875 \text{ mM}\). For very low \([I_{(b)}] (< 10^{-6} \text{ M})\) uptake is dominated by reaction in the bulk. For \([I_{(b)}]
\sim \text{nM and below, } [O_3(b)] = H_{cc}^{gb} \cdot [O_3(g)] \text{ and the uptake coefficient is consistent with the dilute-limit, given
in Eq. (19). As } [I_{(b)}] \text{ approaches } \mu\text{M concentrations, the reactive uptake is still dominated by } \gamma_b \text{ but
becomes limited by the transport of } O_3 \text{ into the bulk liquid (i.e., } [O_3(b)] < H_{cc}^{gb} \cdot [O_3(g)] \text{).\(^{34}\) For } [I_{(b)}] > 1 \mu\text{M,}
\gamma \text{ shifts to a surface reaction. A plateau in } \gamma \text{ is reached with increasing concentration ((} [I_{(b)}] > 1 \text{ mM}) \text{ as
}[O_3(ads)] becomes strongly depleted due to reaction at the surface. This latter condition is characteristic of
the current experiments conducted using } [I_{(b)}] = 250 \text{ mM}. \text{ One of the present experiments, containing
initial } [I_{(b)}] = 250 \text{ mM and } [O_3(g)] = 2 \text{ ppm, is shown in Fig. 9 (A) for comparison. Also shown in Fig. 9}
(A) are predictions from the diffusion limited resistor case (i.e., Eq. (18)), which does not account for our experimental results and differs significantly from the predictions of Eq. (15) and (16).

**Figure 9:** Reactive uptake coefficients of ozone due to reaction with iodide. (A) Uptake coefficients vs. $[\Gamma_{(b)}]$ for $[O_3(g)] = 1$ ppm. (B) Uptake coefficients vs. $[O_3(g)]$ for $[\Gamma_{(b)}] = 250$ mM. Dotted and dashed black lines show $\gamma_s$ and $\gamma_b$, respectively, calculated from Eqs.(15) and (16). Black points show reactive uptake calculated directly from simulation output. Red points show experimental results, obtained using Eq. (17) (error bars represent standard error in fitting time constant $k_{exp}$). In (A), only one experimental point is given for conditions $[\Gamma_{(b)}] = 250$ mM, $[O_3(g)] = 2$ ppm. In (B), a series of experimental values are given with conditions $[\Gamma_{(b)}] = 250$ mM, $[O_3(g)] = 500$ ppb – 65 ppm. For all experiments, simulations, and expressions given, a droplet radius of 22 $\mu$m and a bulk $[\text{ClO}_3^{-}(b)] = 875$ mM is used.
The \([O_3(g)]\) dependence of the reactive uptake is shown in Fig. 9 (B). Here, the bulk iodide concentration is \([I^-(b)] = 250 \text{ mM}\), while \([O_3(g)]\) is varied from 1 ppb to 10^5 ppm. For ppb concentrations of \([O_3(g)]\) we find the uptake of \(O_3\) is \(\sim 5 \times 10^{-4}\) with the main product being \(IO^-\) (at pH 12). However, in the transition from 1 ppb to 1 ppm, the reactive uptake of ozone due to iodide decreases from \(5 \times 10^{-4}\) to \(2 \times 10^{-4}\) due to the changing composition of the surface. With increasing \([O_3(g)]\), the major reaction product becomes \(IO_3^-\) rather than \(IO^-\) due to the increasing availability of \(O_3\). The slight decrease in reactive uptake occurs due to competing reaction of \(O_3\) with intermediates \(IO^-\) and \(IO_2^-\). The experiments, measuring reactive uptake of ozone due to iodide, agree well with the simulated and analytical results for the range of 1-100 ppm, where the uptake is relatively constant for \([O_3(g)] < 20 \text{ ppm}\) and begins decreasing when \([O_3(g)] > 20 \text{ ppm}\). As in Fig. 9 (A), we include the diffusion-limited resistor case for comparison. The diffusion limited resistor case overestimates the uptake coefficient by an order of magnitude and cannot explain our experimental observations.

The sharp decrease in uptake for \([O_3(g)] > 20 \text{ ppm}\) results from competition for surface-sites among ions at the interface. As discussed in Section VI.A, we observe this effect in simulations (and analytical expressions) as resulting from site competition between \(I^-\) and \(ClO_3^-\) at the air-water interface. While we reserve a general discussion of how non-reactive ions at the interface effect uptake coefficients for a future publication, we note that the relation between surface composition and the sticking probability of \(O_3\) (\(\sigma\)) is largely unknown, with the present experiments being one example of possible coupling between these quantities. Reactive uptake continues to decrease from \([O_3(g)] = 100\) to 10^4 ppm as the reaction at the surface becomes limited by the availability of surface-sites for the iodide ion. For very large \([O_3(g)] > 10^4 \text{ ppm}\), the bulk reaction becomes the most significant contribution to the reactive uptake coefficient, as \([I^-_{(ads)}]\) becomes severely depleted by reaction. The expression for \(\gamma_b\) overestimates the uptake at high \([O_3(g)]\) by \(\sim 3\) since it neglects \(O_3\) reactions with reaction intermediates \(IO^-\) and \(IO_2^-\) in solution. While a similar treatment of the reactive intermediates could be included in the bulk as has been performed for the surface reaction, such a treatment is beyond the scope of the current work.

**D. Discussion and Comparison to Literature**

The present experiments were conducted at high \([I^-_{(b)}]\) and the analysis limited to pH 12, so a direct comparison to sea-spray aerosol, where \([I^-_{(b)}] \sim 100 \text{ nM}\) and pH \(\sim 8\) or lower is not possible. Nevertheless, many of the kinetic features identified in the present experiments are likely general, and warrant a deeper understanding into how reactant depletion, reactant partitioning, and competitive solute
adsorption at the air-water interface control observed reactive uptake of ozone in this system. The series of experiments by Rouvière et al.\textsuperscript{15} and Rouvière and Ammann\textsuperscript{31} offer the closest analogy to the present experiments, where submicron aerosols of concentrated iodide are exposed to a gas flow containing \([\text{O}_3]\) = 1-10 ppb. By monitoring the decay in the ozone at the apparatus outlet, Rouvière et al.\textsuperscript{15} measure ozone uptake coefficients of \(\sim 10^{-2}\) onto pure deliquesced sodium iodide. Their results, interpreted using a diffusion-limited resistor model (Eq. (18)), are consistent with previous studies indicating an upper bound for reactive uptake in this system on the order of \(10^{-2}\).\textsuperscript{14,24} In the presence of organic surfactants, however, Rouvière and Ammann\textsuperscript{31} observe that the uptake of ozone is reduced by \(\sim 50x\), which is consistent with our experimental results and model predictions, where an upper bound to reactive uptake is computed to be \(\sim 5 \times 10^{-4}\). Although the uptake coefficients are similar, Rouvière and Ammann\textsuperscript{31} suggests that the reduction in uptake by the presence of organic acids is due to the attenuation of \(\text{O}_3\) transport into the bulk liquid where the \(\text{I}^- + \text{O}_3\) reaction is presumed to occur. Specifically, they argue that the presence of surfactants enhances ozone desorption (\(\text{O}_3(\text{ads}) \rightarrow \text{O}_3(\text{g})\)) from the interface, relative to bulk solvation (\(\text{O}_3(\text{ads}) \rightarrow \text{O}_3(b)\)). In contrast, we find that it is the competition between \(\text{ClO}_3^-\) and iodide for adsorption sites at the air-water interface that suppresses the surface reaction and leads to a smaller observed uptake coefficient. This difference suggests that further work is needed to develop a general mechanism(s) to explain how non-reactive species residing at liquid interfaces of complex mixtures (such as seawater) alter multiphase reaction rates.

The ozone partitioning scheme used in our framework differs substantially from previous LM descriptions of ozone adsorption to the air-water interface. In past studies, Langmuir equilibrium coefficients (\(K \sim 1 \times 10^{-13}\) cm\(^3\)/molecule) are obtained indirectly from fitting experimental data,\textsuperscript{85,86} and appear inconsistent with the interfacial solvation energy and surface excess of ozone determined in MD simulations.\textsuperscript{51,56} For example, \(K \sim 1 \times 10^{-13}\) cm\(^3\)/molecule would imply an unreasonably high interface concentration of \([\text{O}_3(\text{ads})]\) in excess of 1 M at \([\text{O}_3(\text{g})]\) = 10 ppm. Alternatively, our analysis suggests that it is depletion of \(\text{O}_3\) at the surface, not its saturation, that shapes much of kinetic behavior in this system. While an in-depth discussion on the nature of previous experimental determinations of \(K\) will not be given here, we suggest that the effects of coupled reactant-depletion could be directly responsible for the kinetic trends previously ascribed to a Langmuir-Hinshelwood reaction mechanism.

\textbf{VII. Conclusions}
Kinetic measurements were performed on the ozonolysis of aqueous sodium iodide microdroplets containing a chlorate standard using single-droplet PS-MS for a series of ozone concentrations and as a function of pH. To interpret the experimental results a novel multiphase kinetic model is used, where we identify features in the observed kinetics that originate from depletion of reactants at the air-water interface due in part to the surface activity of ClO$_3^-$. In the case of surface-iodide depletion, first order kinetics in [I$_{(b)}$] are observed where increasing gas-phase [O$_3(g)$] produces a kinetic plateau resembling behavior previously interpreted as LM kinetics. However, unlike LM kinetics, this limiting behavior is not due to surface saturation of I$^-$ or O$_3$, but rather the depletion of iodide at the surface when the overall rate of the surface reaction exceeds that of desolvation to the interface. An ozone surface-transport limit is also identified and characterized by zero-order kinetics in [I$_{(b)}$], where both anions I$^-$ and ClO$_3^-$ coexist at the interface. Here, the exceptionally fast reaction between iodide and ozone is found to be a useful tool for quantifying the elementary steps of solute desolvation to the interface. Additionally, because of the model sensitivity to coupled timescales at the interface, we find the sticking coefficient of ozone (which is inversely proportional to the desorption lifetime of O$_3$ at the gas-liquid interface) must be constrained to a value of $\sigma = 10^{-4}$. This further emphasizes the importance of understanding trace gas accommodation in multiphase reactions at the level of elementary kinetic processes, which is one of the fundamental yet uncertain steps that governs reactive uptake.$^{87}$

A set of kinetic equations are solved to obtain concentrations for all surface-adsorbed species using a quasi-steady state description of the interface, demonstrating excellent agreement with results from both experiments and numerical simulations. The analytical expressions, although complex and containing many terms, are based upon relatively simple descriptions of surface chemistry, which can be used to predict uptake coefficients over a wide range of conditions. We aim to characterize the surface-activity of a series of ions and organics in future work and investigate any relation to ozone sticking in this system by modulating the mass fraction of the spectator ions to alter surface concentrations of non-reactive species.

Agreement between experiment, simulation, and the analytical expressions provides further evidence that the framework introduced by Willis and Wilson$^{33}$ and further generalized by Wilson et al.$^{34}$ provides a physically realistic approach for describing complex multiphase reactions. Moreover, the unique property of this system to highlight competing timescales of surface chemistry and transport leads us to conclude that future work with this system will allow for a further analysis of physical and chemical
lifetimes of reactants and spectators at the surface, with the potential to investigate competing reaction rates at the air-water interface. Ultimately, this work in conjunction with recent model constructions\textsuperscript{33,34} aids in a deeper understanding of the physical principles important not only in atmospheric and environmental chemistry, where complex mixtures and surfaces play a key role in reactivity, but also in the fields of surface science, catalysis, and heterogenous chemistry more generally through the quantification of surface dynamics that are typically obscured by bulk reactions and the separation of timescales at interfaces.

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**References**


