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1 Aerosol Fragmentation Driven by Coupling of Acid-Base and Free Radical 2 Chemistry in the Heterogeneous Oxidation of Aqueous Citric Acid by OH 3 Radicals

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11

12 Abstract

13 A key uncertainty in the heterogeneous oxidation of carboxylic acids by hydroxyl radicals (OH)
14 in aqueous phase aerosol is how the free radical reaction pathways might be altered by acid-base
15 chemistry. In particular, if acid-base reactions occur concurrently with acyloxy radical formation
16 and unimolecular decomposition of alkoxy radicals, there is a possibility that differences in
17 reaction pathways impact the partitioning of organic carbon between the gas and aqueous phases.
18 To examine these questions, a kinetic model is developed for the OH initiated oxidation of citric
19 acid aerosol at high relative humidity. The reaction scheme, containing both free radical and
20 acid-base elementary reaction steps with physically validated rate coefficients, accurately
21 predicts the experimentally observed molecular composition, particle size, and average elemental
22 composition of the aerosol upon oxidation. The difference between the two reaction channels
23 centers on the reactivity of carboxylic acid groups. Free radical reactions mainly add functional
24 groups to the carbon skeleton of neutral citric acid, because carboxylic acid moieties deactivate
25 the unimolecular fragmentation of alkoxy radicals. In contrast, the conjugate carboxylate groups
26 originating from acid-base equilibria activate both acyloxy radical formation and carbon-carbon
27 bond scission of alkoxy radicals, leading to the formation of low molecular weight, highly
28 oxidized products such as oxalic and mesoxalic acid. Subsequent hydration of carbonyl groups in
29 the oxidized products increases the aerosol hygroscopicity and accelerates the substantial water
30 uptake and volume growth that accompany oxidation. These results frame the oxidative lifecycle
31 of atmospheric aerosol: it is governed by feedbacks between reactions that first increase the
32 particle oxidation state, then eventually promote water uptake and acid-base chemistry. When
33 coupled to free radical reactions, acid-base channels lead to formation of low molecular weight
34 gas phase reaction products and decreasing particle size.

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40 I. Introduction

41Sub-micron-sized atmospheric organic aerosols profoundly influence Earth's climate by
42interacting with incoming solar radiation and serving as cloud condensation nuclei, altering
43cloud formation and albedo.¹ The extent to which these processes occur is determined by the
44size, chemical composition, shape, and lifetime of the aerosol, making their characterization
45crucial for the predictive accuracy of air quality and climate models. However, describing the
46oxidative evolution (aging) of organic aerosol is difficult due to the extensive and complex
47chemical reactions that occur. The oxidation of organic aerosol is thought to have a major
48influence on particle composition and size, leading to numerous studies of the heterogeneous
49oxidation of organic particles by gas-phase hydroxyl radicals (OH). Laboratory investigations of
50model atmospheric aerosols² provide insight into how the formation of new oxygenated
51functional groups (i.e. functionalization) and C-C bond scission (i.e. fragmentation) reactions
52together alter particle composition and size.³⁻⁷ These experimental studies are particularly
53valuable when coupled with detailed kinetics models since the resulting predictive description
54connects key elementary reaction steps to changes in the physical properties of the aerosol.

55

56When an organic aerosol becomes very heavily oxidized, significant concentrations of carboxylic
57acid groups build up on the particle surface.⁸ As a result, initially hydrophobic aerosol develops
58hydrophilic character. Under humid conditions, water will accumulate on a hydrophilic surface
59over time, transforming the reaction environment from a purely organic matrix into an aqueous
60solution. This is a very late phase of chemical ageing of a chemical reduced aerosol, and gaining
61an understanding of the factors that control reactivity in this regime and what role may be played
62by carboxylic acid moieties are the primary goals of this work.

63

64 There have been a number of important studies of the aqueous phase chemistry of oxidized
65 aerosol constituents that examine reaction rates and mechanisms⁹⁻¹⁵ as well as the relationship
66 between aerosol phase state, heterogeneous reaction rate and ultimately cloud nucleation
67 activity.¹⁶⁻²⁵ In general these systems exhibit substantial C-C bond fragmentation and
68 volatilization, in contrast to what is generally observed in the heterogeneous oxidation of reduced
69 organics.^{20, 26} For example, levoglucosan, an anhydrosugar, has been widely studied as a model
70 for aqueous biomass derived aerosol, undergoes significant fragmentation.^{21-22, 27-29} The same
71 behavior is reported for the heterogeneous oxidation of aqueous erythritol, another highly
72 oxygenated model system.^{20, 30} In this case, Kessler et. al.²⁰ found evidence that hydrogen
73 abstraction by OH from a hydroxyl group leads to α -hydroxy alkoxy radical formation and
74 subsequent decomposition by C-C bond scission.

75

76 The differences in reactivity between heavily and lightly oxidized systems originate from the
77 presence of oxygen-containing functional groups located on or adjacent to peroxy and alkoxy
78 radical intermediates, whose chemistry in turn controls the extent of fragmentation and
79 subsequent volatilization.^{20, 31} For example, for a series of structurally related model dicarboxylic
80 acid aerosol with a common C₄ backbone, the distribution of primary, secondary and tertiary
81 peroxy and alkoxy radicals, formed after the initial OH radical reaction, was observed to play a
82 large role in ultimately governing the quantity and identity of smaller molecular weight C-C
83 bond scission products.¹⁶⁻¹⁸ In most of these previous studies experimental observations were
84 rationalized solely by free radical reaction pathways initiated by OH. However, we expect that
85 for the vast majority of highly oxidized ambient organic aerosol (e.g. secondary organic aerosol),
86 which are hydrophilic in nature, the presence of an aqueous phase will lead to carboxylic acids

87being in equilibrium with their conjugate base. Thus, OH will react with both neutral and ionic
88forms. Acid-base chemistry should occur simultaneously with free radical oxidation, and
89constitute an important aging mechanism for particles in the troposphere.

90

91To our knowledge there have been only a few detailed experimental investigations³²⁻³⁶ of
92heterogeneous OH reactions in systems where free radical and acid-base chemistry can occur
93simultaneously. In this work, we investigate the heterogeneous OH oxidation of aqueous citric
94acid (CA) aerosol by OH. CA is a reasonable model for highly oxidized organic aerosol
95($C_6H_8O_7$), containing three carboxylic acid functional groups and a single alcohol moiety. CA
96should exhibit many of the OH-driven aging pathways that occur in secondary organic aerosol.
97Because of its low pKa, CA is expected to react with OH in both neutral and acid-base forms.
98We develop a molecular level kinetic description of the chemistry for this system using the
99generalized oxidation mechanism for triacontane as a foundation.⁸ The model predictions are
100compared to an extensive experimental dataset obtained previously by Davies and Wilson,³⁷
101which includes the CA decay kinetics, product mass spectra, elemental ratios, and aerosol size;
102all of which evolve with OH exposure. We focus on the dataset obtained at a relative humidity
103(RH) of 64.5%, where the aerosol is liquid and well-mixed on the timescale of the OH reaction
104frequency. Since the aerosol is an aqueous solution of CA in equilibrium with its conjugate base,
105we have included reactions of OH with ionic species as well as with neutrals. We have performed
106simulations for three scenarios to elucidate how key reaction steps control reactivity and physical
107properties of the aerosol in aqueous vs. non-aqueous aerosol systems. We find that only those
108simulations that include both acid-base and free radical pathways yield model predictions
109consistent with the global experimental dataset.

110

111II. Model Framework

112Complex sets of chemical reactions are traditionally analyzed using sets of coupled ordinary
113differential equations in which continuous variables evolve deterministically. Although this
114reasonably describes test-tube sized or larger systems,³⁸ as system size decreases to the size of an
115aerosol, discreteness and stochasticity can have much greater impacts on system behavior. Under
116such conditions, molecular populations are better viewed as integer variables evolving
117stochastically. Kinetiscope³⁹, the software used here, is based on a stochastic algorithm that
118propagates a simulation by randomly selecting among probability-weighted elementary reaction
119steps (events).⁴⁰⁻⁴¹ The rate law for each of elementary step is used to calculate the probabilities,
120and establish an absolute time base for direct comparison of simulations to experiment. The
121method has been shown to be a rigorous solution to the master equation for Markov processes. It
122has been extended to simulate kinetics in systems with variable volume⁴² and is well suited to
123cases such as aqueous citric acid aerosol oxidation. Additional information is available on the
124software's website and in prior work on aerosol oxidation.^{31, 43} Reaction mechanisms are
125constructed inductively, that is, by starting from the simplest description and adding new reaction
126steps when the simulation results fail to agree with experiment. Rate coefficients for each step
127are taken directly from literature, calculated from experimental data or quantum theory, or
128estimated using quantitative structure-activity relationship models. Initial concentrations are used
129to replicate experimental conditions. Further discussion of the methodology is presented in the
130Supplementary Information (SI), section S1.

131

The current model includes a number of elements previously developed^{8, 31, 43} to describe the multiphase chemistry of organic aerosols. These elements (outlined briefly in Sec. IIa), include the simulation geometry, kinetic descriptions of OH sticking and reaction, evaporation of products as well as the central pathways for peroxy and alkoxy reactions. Several new elements, outlined in detail in Sec. IIb-d, have been added to simulate the heterogeneous reaction of CA aerosol by OH. They include acid-base reactions and equilibria, and accurately capture the changes in aerosol size during oxidation due to dynamic uptake and release of ambient water.

139

140a. OH uptake and reaction, evaporation, and radical reaction pathways

OH uptake. As described in previous studies, the reaction rate of OH at the surface of the aerosol is controlled by two separate elementary steps.^{8, 31, 43} First the OH absorbs to a surface site from the gas phase, then it reacts with CA or its products. The absorption step is described by a pseudo first order rate coefficient (k_{ad} in Table 1). k_{ad} depends on three factors: the OH concentration in the gas phase, the gas-surface collision frequency, and the OH sticking probability. While two of these are known quantities, the sticking probability is usually not known and for this system is expected to be rather complex since the aerosol surface has substantial water coverage in addition to organic reactants and products.³⁷ Accordingly, a value of 0.052 s^{-1} is determined for k_{ad} by adjusting it until the calculated citric acid concentration vs time curve is in quantitative agreement with experiment.^{8, 43} The collision frequency of OH, k_{coll} , at a density of $7.5 \times 10^{10} \text{ molec/cm}^3$ with the 10^{-14} cm^2 surface area of the reaction compartment (Section II d) is calculated to be 12.4 s^{-1} . Since $k_{ads} = \alpha k_{coll}$, this gives a value of 4.2×10^{-3} for α , the sticking coefficient. This is in the range estimated for α in simulations of OH reacting with squalane (10^{-4})⁴³ and triacontane (5×10^{-5} , calculated from the reported rate coefficient).⁸ Since

the sticking coefficient for water to water surfaces is 1,⁴⁴ and OH to water is in the same range,⁴⁵ the low value suggests that the outer surface of the aerosol has a strongly organic character despite the significant amount of water present. All other coefficients in the mechanism are derived from experiment and theory.

159

Evaporation. The simulated aerosol volume dynamically evolves both by the formation of higher density reaction products that bind water formed by OH reactions or accrete waters of solvation from the ambient, and by the evaporation of high volatility small molecule products and eventually their water shells. Loss of water is assumed to be instantaneous following desorption of products from the aerosol surface. Products containing 2 carbons, such as oxalic acid, have much higher vapor pressure than those with 3 carbons and greater,⁴⁶ and are assumed to be the only ones that undergo significant evaporation. Their vapor pressures are set to be 1×10^{-4} Pa, a value typical for small dicarboxylic acids at room temperature.⁴⁶ The evaporation rate coefficient computed from this vapor pressure and the simulation geometry, as described in Wiegel et al,^{8, 31} is 0.35 s^{-1} .

170

Radical reaction pathways. Because the possible reactions are relatively few, the elementary steps used to describe the heterogeneous reaction of CA with OH are written explicitly (i.e. involving individual molecules) rather than using the lumped reaction scheme based on functional group chemistry introduced previously to model the multi-generational oxidation of alkanes.^{8, 31} As shown in Table S1 in the SI, the full range of possible reaction products is considered and includes C₆ functionalization products as well as C₂-C₅ species formed via C-C

177bond scission reactions. These product species are formed via the generic elementary reaction
178steps, shown in Figure 1, that have been used in previous studies.^{4-5, 8, 31, 43, 47-48}

179

180Briefly, OH can abstract a hydrogen atom from a $-CH_2$ or $-OH$ moiety located on CA or its
181reaction products (generically represented as RH in Figure 1). The rate coefficient for H-
182abstraction from these sites are taken from the literature and shown in Table 1. The resulting H-
183abstraction reaction at the $-CH_2$ group produces an alkyl radical (R), which is rapidly converted
184(in the presence of O_2) into a peroxy radical (RO_2). RO_2 is the central intermediate that controls
185much of the oxidative transformation of CA and its subsequent products. For instance, $RO_2 +$
186 RO_2 reactions produce either stable products with new alcohol and carbonyl functionalities or
187alkoxy radicals (RO). Previous work³¹ has shown that the aerosol oxidation chemistry is
188consistent with 90% of the secondary $RO_2 + RO_2$ reactions yielding stable products (i.e. carbonyl
189and alcohol), and the remaining 10% forming alkoxy radicals and O_2 . H abstraction from the $-$
190OH group directly forms an alkoxy (RO) radical or, in the case of an -OH group on a carboxylic
191acid, an acyloxy radical. Unimolecular decomposition of alkoxy and acyloxy radicals as well as
192intermolecular H-abstraction by RO are included in the model. As shown in Figure 1,
193hydroperoxide ($ROOH$) products are formed by the $RO_2 + HO_2$ reaction.

194

195In following sections, we describe extensions to the oxidation mechanism. They include the
196implementation of the new acid-base reaction steps, the calculation of their rate constants, and a
197description of how these acid-base equilibria are coupled to the free radical reaction scheme
198described above. This is followed by a description of how water is included in the simulation to
199order to properly account for the hygroscopic growth of the aerosol during oxidation.

200

201**b. Acid-Base chemistry**

202The aqueous environment requires the inclusion of acid-base chemistry in modeling the
203oxidative evolution of the aerosol. While free radical chemistry in hydrophobic organic aerosol is
204well-constrained by known reaction pathways and rate coefficients, little work has explicitly
205focused on how free radical chemistry is modified in aqueous organic aerosol where acid-base
206chemistry occurs simultaneously. CA has a pK_{a1} of 3.13, and dissociates in water to produce
207hydronium and citrate, the conjugate base of CA. This relatively acidic environment leads to
208further deprotonation of the numerous triacid and diacid products (see Table S1) formed from
209CA oxidation. Thus, we expect the formation of radical anions as the system is oxidized, and are
210interested in how the reactivity of these radical anions differs from their neutral counterparts (e.g.
211citrate vs citric acid). In particular, we focus on the unimolecular fragmentation rates of anionic
212alkoxy radicals compared to their neutral analogs. Because several key rate coefficients have not
213been measured, we used *ab initio* calculations of the reaction barriers to estimate them.

214

215Using Gaussian09,⁴⁹ the ground state energy of the radical is obtained by optimization of all its
216conformers using the SMD/IEF-PCM solvent model for water and the M06-2x functional and the
2176-31G(d,p) basis set. The solvent model was shown by Marenich et. al.⁵⁰ to reduce mean
218unsigned errors in the solvation energies of both neutral and charged species while the functional
219was shown by Walker et. al.⁵¹ to be a superior choice compared to B3LYP in systems with
220dispersion and ionic hydrogen-bonding interactions. Vibrational frequencies of the ground state
221are computed at the same level of theory to ensure the optimized structure corresponds to a local
222minimum. For the transition state calculation, the Berny option with a calculation of force
223constants is used. The length of the fragmenting C-C bond is set to the value obtained by a

relaxed potential energy surface scan for a local maximum in total molecular energy. The barrier height for dissociation, E_b , is taken as the difference between the ground and transition state energies. Rate coefficients for β C-C bond scission of substituted alkoxy radicals are estimated using the following structure-activity relationship model developed by Vereecken and Peeters,⁵²

$$k_{diss}(T) = L \times A_{TST}(298\text{ K}) \times \left(\frac{T}{298\text{ K}} \right)^{\frac{E_b}{RT}} \quad (\text{Eq. 1})$$

where L is the number of identical bond scissions and $A_{TST}(298\text{ K})$ is the pre-exponential factor at 298 K based on Transition State Theory. Further details are presented in section S5 of the SI.

As observed in previous work^{31, 52-53} and further confirmed by this set of calculations, the barrier height for β -scission of an alkoxy radical is found to be lowered when a ketone or hydroxyl functional group is located on an adjacent carbon atom as shown in Scheme 1. The reduction in barrier height is significant, such that unimolecular decomposition of activated RO is the primary sink for alkoxy radicals rather than, for example, hydrogen abstraction (i.e. RO + RH).

As shown in Scheme 1c, the barrier height for the already-activated alkoxy radical is reduced even further when the adjacent carboxyl group is deprotonated. Indeed, $\cdot\text{COOH}$ is reported

to be a fleeting radical while the $\cdot\text{COO}^-$ radical anion has been observed to form in aqueous

242solutions due to stabilization by the solvent.⁵⁴⁻⁵⁷ However, activation of the carboxylate group is

243not limited to those pathways that form $\cdot\text{COO}^{\cdot}$. As shown in Scheme 2, formation of a larger
244radical anion is still more favorable than its neutral form. The difference in fragmentation rate
245coefficients calculated using these barriers confirms the necessity of including acid-base
246chemistry in the model to capture the low energy reaction pathways.

247

248c. *Inclusion of rapidly maintained equilibria.*

249Explicit simulations of rapidly maintained acid-base equilibria using stochastic methods are
250exceedingly slow.^{39, 58-59} This is because reaction steps at equilibrium have a high probability of
251being selected relative to the other reaction steps, and the simulation's timescale barely advances.
252Thus, explicit inclusion of equilibrium steps for the deprotonation and protonation of carboxyl
253groups in CA is impractical, and they are included implicitly, as described below. Extensive
254checks were made to verify that this approximation does not change the simulation results; they
255are presented in section S3 of the SI.

256

257The deprotonation of CA to form citrate and its subsequent reaction with OH can be described by
258the following steps, where R1 and R2 are added together, and explicit treatment of water and
259hydronium formation becomes implicit:

260

261

262

263

264 The forward rate of reaction (R3)

, where

. This yields the rate constant

265

. In explicit model runs performed to test this approximation,

266a nearly constant ratio (section S3 in the SI). This justifies the assumption that a strict
267equilibrium between water and hydronium is maintained, i.e. pH is constant. By using the

268 average value of $\frac{H}{3O} \frac{[H_2O]}{[H_2O]}$ from the explicit model, k_3 is easily computed and is shown in

269 Table 1. Thus, CA^{-} is no longer explicitly included in the mechanism, since its concentration
 270 is embedded in the rate constant k_3 which is proportional to the CA acid-base, K_{eq} . We extend
 271 this method of modeling protonation and deprotonation to all other acid products in the system
 272 by using their respective K_a values (Table S1 in the SI), making simulation runtimes much more
 273 practical.

274

275 Some reaction products observed in the experiment contain new carbonyl functionalities. As a
 276 result, hydration reactions of these species ($R=O \leftrightarrow R(OH)_2$) are included in the simulations. The
 277 equilibrium constants K_h for these products, described below, are computed using structure
 278 activity relationships in Ref ⁶⁰ and listed in Table S1 in the SI. In the simulation, hydration is
 279 assumed to be instantaneous for species with $K_h > 100$. Otherwise, using the treatment for acid-
 280 base chemistry described above, K_h is combined with the OH abstraction reaction coefficient for
 281 the alcohol form (Table 1) to generate an effective rate coefficient.

282

283d. *Treatment of water and aerosol volume.*

284 As will be discussed further below, the experimentally observed CA aerosol volume increases by
 285 ~50% during the initial stages of the reaction. In the simulations, the volume is calculated

286dynamically using the instantaneous amounts and densities of all species present (Table S1 in the
287SI). This allows concentrations and reaction rates to be continuously corrected as the volume
288changes.

289

290The substantial volume increase is much larger than can be rationalized solely by the formation
291of oxidation products. Previous studies report a variety of approaches to estimate the
292hygroscopicity of oxidized aerosol, the simplest of which uses O/C as the primary predictor.⁶¹⁻⁶²
293Suda et. al.⁶³ examined the influence of the location and number of functional groups on organic
294aerosol hygroscopicity, and concluded that hydroxylation is a key pathway by which aerosols
295become more hygroscopic. In view of the literature, the likeliest explanation for the initial
296increase in volume is uptake of ambient water, promoted by formation of new hygroscopic
297species during oxidation. After the initial period of growth, the subsequent volume loss
298originates from the desorption of volatile organic compounds and their waters of solvation when
299fragmentation becomes kinetically significant.

300

301In the model described here, the rates of adsorption, absorption and desorption of water
302molecules are assumed to be very fast relative to the chemical reaction rate, and therefore are not
303treated explicitly. Instead, each species in the simulation is assumed always to have a number of
304water molecules solvating it, contributing to its effective density. Because few data are available
305for the size of stable water solvation shells for species involved in the oxidation reactions,
306estimates are made based on the literature value of 6-7 waters per CA molecule, computed for
307neutral species from room temperature solubility data.⁶⁴ The average number of waters, 6.5, are
308apportioned among the functionalities as 2 waters per -COOH moiety, and 0.5 waters per alcohol

309or carbonyl moiety. If a species can deprotonate to form hydronium, the hydronium is modeled
310as having 3 additional water molecules.⁶⁵ We assume that the formation of two adjacent alcohol
311groups via the hydration of carbonyls results in the addition of 0.5 waters to the solvation shell.
312Because the model does not explicitly contain ionic species their waters are included indirectly.
313The percent CA dissociation obtained from explicit model simulations is used as a weighting
314factor to calculate the average number of water molecules associated with each acidic species.
315The total number of waters estimated using these criteria for each species is shown in Table S1 in
316the SI. The partial volume of water is added to the molar volume of the organic to estimate the
317density of each organic+water group. These values are also listed in Table S1.

318

319In addition to changes of volume and concentrations in the particle, and thus reaction rates,
320changes in the surface to volume ratio of the aerosol impact the relative importance of surface
321and bulk chemical reactions. Because the aqueous aerosol has low viscosity, it is represented
322using a single instantaneously mixed compartment rather than multiple diffusion-coupled
323compartments, which has been shown to be valid for reactions in well-mixed aerosol.^{31, 43} This is
324computationally efficient but poses challenges for proper weighting of surface to volume kinetics
325when there are large volume changes. Bulk reactions occur throughout the volume, but OH
326adsorption only takes place at the surface. To ensure that this balance is correctly represented in
327the simulations, the single compartment is treated as a slim 1 nm x 1 nm x $R/3$ nm cuboid in the
328aerosol, where the outer surface of the aerosol is represented as a fixed 1 nm² square and R is the
329instantaneous radius of the spherical aerosol that is being simulated. This is implemented by
330assuming that the number of surface sites (1 site per initial surface CA molecule within 1 nm of
331the surface, calculated from the density of CA in solution), available for adsorption and
332desorption as the reaction proceeds, is constant. Consequently, the dimension of $R/3$ is equal to

the ratio of the instantaneous volume to the fixed surface area. This representation maintains the correct scaling between compartment volume and area of the spherical aerosol modeled in the experiment, and thus the correct weighting of surface and bulk chemical processes.

336

337e. *Photolysis of hydroperoxides*

There are reaction pathways in the model that produce hydroperoxides (ROOH). As such we consider that possibility that if these species are formed that they could be photolyzed by the 254 nm light source used in the experiment to generate OH. We assume that the photon flux incident on particle phase ROOH is the same as that for ozone in the flow tube reactor (value in Table 1). The photolysis of ozone can be described as:

where we determine value of k_p that best replicates the experimental [OH]. A value of

$k_p = 0.5 s^{-1}$ produces an average [OH] which matches experiment. From this value, we can

estimate the rate coefficient for ROOH photolysis by scaling k_p by ratio of ROOH and O_3 cross sections (σ) at 254 nm and 293.15K,

$$ROOH \xrightarrow{h\nu} RO\cdot + \cdot OH, k_{photolysis} = \frac{k_p * \sigma_{ROOH}}{\sigma_{ozone}} \quad (R5)$$

σ_{ROOH} is estimated by averaging values for small hydroperoxides CH_3OOH and

$HOCH_2OO$ (see Table 1).⁶⁶

351

352 **III. Results**

353 The simulation results are compared with previous measurements reported in Davies and
354 Wilson.³⁷ As detailed below, the experimental measurements include: (a) the reactive decay of
355 CA, (b) average aerosol elemental composition, product mass spectra and formation kinetics, (c)
356 particle volume as a function of OH exposure. A successful model will generate predictions that
357 are within the experimental errors for this entire suite of measurements. Three model scenarios
358 are considered and compared with experiment in order to explore separately the effects of free
359 radical and acid-base chemistry, and to assess the importance of fragment evaporation on the
360 physiochemical evolution of the aerosol. As summarized in Table 2, Scenario 1 includes free
361 radical chemistry only without evaporation; Scenario 2 includes free radical and acid base
362 chemistry without evaporation and Scenario 3, the most complete simulation, includes free
363 radical + acid base chemistry and evaporation of C₂ reaction products.

364

365 **a. Citric Acid Decay as a Function of OH Exposure**

366 The normalized decay of CA as a function of OH exposure is plotted for the experiment and the
367 three model scenarios in Figure 2. All three scenarios accurately predict, within experimental
368 error, most of the exponential decay of CA observed in the experiment. The first few
369 experimental points at low exposure are the exception: they deviate from a purely exponential
370 function. The reason for this is unclear, and is not predicted by any of the model scenarios.
371 Phenomenological CA disappearance rate constants (k_{obs}) are extracted from exponential fits to
372 the experiment and simulations. As shown in Table 3 the range is relatively small, but Scenario 3
373 is in closest agreement with observations.

374

375 ***b. Average Aerosol Elemental Composition and Product Mass Spectra***

376 The average aerosol elemental composition observed during the reaction is shown in Figure 3.
377 This representation, known as a van Krevelen diagram, shows the relationship between the
378 hydrogen-to-carbon (H/C) and oxygen-to-carbon (O/C) ratios. Before reaction the elemental
379 composition of CA is H/C = 1.33 and O/C = 1.16. Both the H/C and O/C change substantially
380 during the experiment yielding a final average elemental composition of H/C = 1.1 and O/C =
381 1.4 at $[\text{OH}]t = 4.4 \times 10^{12} \text{ molec. cm}^{-3} \text{ s}$. All three scenarios predict similar van Krevelen trends
382 and all are within the overall experimental error of the experiment.

383

384 Despite similarities in average aerosol composition, significant differences among the scenario
385 predictions appear when they are compared to the experimentally observed population of major
386 reaction products detected via aerosol mass spectrometry.³⁷ The ionization source used in the
387 experiments is Direct Analysis in Real Time (DART), which produces negatively charged M-H⁻
388 ions. For example, neutral CA ($\text{C}_6\text{H}_8\text{O}_7$) molecules appear in the negative ion mass spectrum at
389 $m/z = 191.02$ ($\text{C}_6\text{H}_7\text{O}_7^-$). The experimental data are not corrected for ionization cross section
390 differences. Data are shown in Figures 4 and 5.

391

392 It is clear from Figure 4 that only Scenario 3 predicts all 5 major products observed aerosol mass
393 spectra. There is also good agreement between Scenario 3 and the experimental mass spectrum
394 recorded at lower OH exposures (OH exposure = $2.2 \times 10^{12} \text{ molec. cm}^{-3} \text{ s}$) as shown in Figure S5
395 in the SI, indicating that this scenario replicates all of the major reaction products observed over
396 the course of the reaction. Scenarios 1 and 2 fail to capture the dominant product peak observed
397 at $m/z = 116.98$, which is assigned to mesoxalic acid. Furthermore, Scenario 2 predicts little if

398any $m/z = 207.01$, assigned to the $C_6H_8O_8$ functionalization product (i.e. CA + an alcohol group).
399Scenario 1 produces only small quantities of the product at $m/z = 133.01$, assigned to the C_4
400fragmentation product malic acid ($C_4H_6O_5$).

401

402The experimental mesoxalic acid ($m/z = 116.98$) formation kinetics are compared to predictions
403by the model scenarios in Figure 6. It is clear that while all the scenarios produce some
404mesoxalic acid, since there are multiple pathways for its formation, Scenarios 1 and 2 produce
405mesoxalic acid either too quickly or slowly relative to the experiment. Only Scenario 3 correctly
406predicts the experimentally observed mesoxalic acid formation as a function of OH exposure.

407

408c. *Aerosol volume*

409The measured change in aerosol volume vs. OH exposure is shown in Figure 7. At the start of
410oxidation the aerosol grows by ~50% from the initial unreacted aerosol. As noted above, the
411magnitude of this volume increase cannot be explained solely from a change in density as CA is
412consumed and the reaction products observed in the experimental mass spectrum form (Figure
4134). Rather it is more likely that much of the observed growth is due to an increase in the aerosol
414hygroscopicity (water uptake). The measured aerosol volume reaches a maximum around an OH
415exposure of $\sim 2 \times 10^{12}$ molec. cm^{-3} s after which it decreases towards the end of the reaction, with
416a final volume ~25% larger than the unreacted CA aerosol. It is clear from the experiment that
417there is a complex interplay between the formation and evaporation of reaction products and
418water uptake.

419

Figure 7 compares experiment with predictions from Scenario 1 (radical only chemistry, no evaporation) and Scenario 2 (radical + acid-base chemistry, no evaporation) and Scenario 3 (radical + acid-base chemistry, with evaporation). Scenario 1 under-predicts the magnitude of the change in aerosol volume with OH exposure, while Scenario 2 greatly overestimates the change in aerosol volume. Neither Scenario 1 or 2 includes product evaporation, and thus as expected cannot capture the decrease in volume at larger OH exposures. In contrast, Scenario 3 produces the correct shape, within experimental uncertainty, as well as the absolute magnitude of the aerosol volume over the entire range of OH exposures used in the experiment.

428

429IV. Discussion

It is clear from Figures 2, 3, 4, 6, and 7 that the Scenario 3 predictions, involving simultaneous free radical and acid-base OH oxidation channels with fragmentation and volatilization, correctly describe the observed trends in volume, composition and reactivity as a function of OH exposure. Comparison of the Scenario predictions reveals that OH-abstraction initiates free radical reactions that functionalize the carbon skeleton, while OH reactions with carboxylate groups arising from acid-base chemistry activate carbon-carbon bond scission in alkoxy radicals, leading to the formation of low molecular weight, highly oxidized products such as malic and mesoxalic acid. The extensive fragmentation predicted by Scenarios 2 and 3 is consistent with the results of previous studies of oxidation of highly oxidized aerosol as discussed in the Introduction, suggesting that carboxylate formation is a key species that drives aerosol volatilization. As more highly oxidized products are formed, they accrete water, which causes the substantial initial volume growth observed to accompany oxidation. The decrease in volume, at larger OH exposures, originates from the formation and subsequent evaporation of volatile C_2 reaction products along with their waters of solvation into the gas phase, which is held at 62.5%

444RH. These results highlight the significant role of water in controlling not only changes in
445physical properties but also the mechanisms of oxidation and fragmentation of aerosol
446components in the atmosphere.

447

448The importance of including coupled acid-base/free radical reaction pathways is primarily
449revealed by predictions of aerosol composition, since there are no clear features in the CA decay
450kinetics or the average O/C and H/C to indicate that more than free radical chemistry is occurring
451(i.e. all scenario predictions compare favorably with experiment within the error). Rather, a
452primary signature of acid-base chemistry is found in the formation of a specific product:
453mesoxalic acid ($m/z = 116.98$), which is the most abundant product in CA oxidation. The specific
454reaction channel controlling the formation of this C_3 diacid is the rate at which acyloxy radicals
455form from carboxyl groups. This can occur *via* two distinct pathways: (1) the H atom abstraction
456from a carboxylic acid group by OH and (2) the OH charge transfer reaction at a carboxylate
457group. Figure 8 compares the rate coefficients for these channels,⁶⁷⁻⁶⁸ showing that k for the
458charge transfer pathway is 80 times larger. This explains the simulation predictions using
459Scenario 1, which lacks acid/base chemistry. In Scenario 1, the acyloxy radical formation
460channel, and hence fragmentation, is less important because it is slower than other competing
461hydrogen abstraction reactions (e.g. H atom abstraction from a $-CH_2$ group). The lack of
462carboxylate species in Scenario 1 eliminates the additional carboxylic acid formation pathways
463shown in Figure 9. These pathways, which involve fragmentation and decrease carboxylic acid
464carbons numbers by 1, account for over 90% of the total malonic acid ($C_3H_4O_4$) production in the
465model. As shown in Figure 10, malonic acid is a critical precursor for mesoxalic acid. OH
466radical abstraction from malonic acid followed by O_2 addition forms a peroxy radical which can

467then react with RO_2 or HO_2 to yield mesoxalic acid. The simulations suggest that the RO_2 and
468 HO_2 pathways to form mesoxalic acid are equally important.

469

470The decarboxylation pathway (Figure 9), is operative only in those Scenarios that include acid
471-base chemistry (Scenarios 2 and 3) and is the major source of C_3 products generated by CO_2
472elimination from C_4 species. This is clearly seen in the carbon number plot in Figure 11, where
473Scenario 1 produces mainly C_4 products and only very small quantities of C_3 reaction products,
474unlike Scenarios 2 and 3 (which include carboxylate pathways) and the experimental
475observations.

476

477As seen in Figure 11, another notable difference between Scenario 1 and Scenarios 2 and 3 is the
478production rate of C_5 products, which are observed in the experiments. This result can be
479explained by the relative barrier heights for alkoxy radical decomposition. As shown in Figure
48012, H atom abstraction by OH from the alcohol group of CA forms an alkoxy radical adjacent to
481a carboxyl functionality. The subsequent unimolecular fragmentation rate of the alkoxy radical
482anion in aqueous solution is many orders of magnitude faster than that of its neutral form,
483particularly if a carboxylate forms during the C-C bond rupture. Accordingly, the resulting C_5
484product, β -ketoglutaric acid ($\text{C}_5\text{H}_6\text{O}_5$), which is observed experimentally is only produced in
485Scenarios 2 and 3 (Figure 11) via reaction pathways involving the conjugate base of CA. When
486acid-base chemistry is absent (i.e. Scenario 1) this particular fragmentation pathway is of minor
487importance because it is slow relative to other possible alkoxy radical reactions. Interestingly, the
488differences in product distributions due to the presence or absence of acid-base chemistry have a
489negligible impact on the predicted van Krevelen diagrams. This suggests that average aerosol

490elemental composition, not surprisingly, is a blunt probe of the underlying elementary reaction
491pathways.

492

493The acyloxy reaction pathway shown in Figure 9 is the direct route to transform mesoxalic acid
494into oxalic acid. Oxalic acid, the most abundant atmospheric particulate organic diacid, has
495temporally varying concentrations (seasonal and diurnal) that suggest its abundance is controlled
496by secondary processes.⁶⁹⁻⁷² Indeed, field measurements of oxalic acid support an in-cloud
497formation mechanism.⁷³⁻⁷⁴ In model scenarios 2 and 3, oxalic acid is the most abundant acid in
498the system by the end of the simulation runs. Thus, the activation of the carboxylate group
499towards acyloxy radical formation and its subsequent reactions as shown in Figures 8 and 9
500provide a possible mechanism for oxalic acid formation in the atmosphere.

501

502The aerosol volumes (Figure 7) predicted in Scenarios 1 and 2 continuously increase over time,
503in contrast to Scenario 3 (and the experiment), which exhibit a maximum. This is not surprising
504since only Scenario 3 allows for the production of reaction products that partition to the gas
505phase resulting in a net decrease of material in the aerosol. In particular, we find that C₂ product
506evaporation is the most important contributor to the observed decrease in aerosol volume. The
507large increase in aerosol volume at early OH exposures can be explained by an increase of
508aerosol hygroscopicity due to the increase in the total quantity of soluble molecules (i.e.
509fragmentation products) originating from the extensive C-C bond scission chemistry discussed
510above. This initial increase is much steeper for Scenario 2 than 1 and can be explained by the
511larger population of C₃ and C₅ fragmentation products (Figure 11) produced in Scenario 2 via the
512carboxylate reactions discussed above.

513

514 Finally, in all three scenarios, ROOH photolysis is found to be a negligible reaction pathway. In
515 the simulations, photolysis occurs on average once for every 20,000 β -scission reactions. Rather,
516 the main sink for ROOH is C-H attack by OH, as shown in Figure 13, which functionalizes the
517 carbon skeleton with a ketone group. Subsequent hydration, hydrogen abstraction from the
518 hydroxyl group, and fragmentation yields oxaloacetic acid ($C_4H_4O_5$), the key C_4 product
519 undergoing the carboxyl-forming pathway in Figure 9. Thus, ketone production from ROOH
520 reaction with OH is a major contributor to eventual C_3 product formation. This is only possible
521 when acid-base chemistry activates acyloxy radical formation.

522

523 V. Conclusion

524 A detailed, physically based kinetics model is formulated for the heterogeneous oxidation of
525 aqueous citric acid aerosol by OH. Citric acid is a reasonable proxy for understanding the
526 fundamental chemical pathways that might be important for prediction of secondary organic
527 aerosol and late-stage aging of primary aerosol in the troposphere. We find that substantial
528 coupling of acid-base and free radical chemistry is needed to explain the heterogeneous
529 oxidation of CA by OH, and that carboxylate groups are central to trends in aerosol composition
530 and size observed as a function of OH exposure. When present in carboxylic acid form only,
531 reactions with OH lead mainly to functionalization of CA. When neutral CA is equilibrated with
532 its conjugate base, extensive fragmentation occurs following H abstraction. Larger carbon
533 numbered diacids are transformed into smaller diacids through the interplay of acid-base and free
534 radical chemistry, activating acyloxy formation and driving subsequent decarboxylation and
535 carboxyl-group formation. In addition, the carboxylate group significantly lowers the barrier

height to C-C bond scission in alkoxy radicals. Together, these two effects of acid-base chemistry are essential to simultaneously predict the kinetic decay of citric acid, changes in aerosol volume, and the product distribution within the aerosol. The presence of mesoxalic acid as a product is a key signature of acid-base chemistry in this system; reaction rates and elemental compositions alone do not provide evidence that this reaction channel is occurring. The simulation results also provide insight to how elementary reaction steps controls the evolution of aerosol size during oxidation. The detailed trend is controlled by a subtle balance of chemical erosion and hygroscopic growth.

544

How does this fit in with what is known about aerosol ageing processes? As shown by Lambe et al.,⁷⁵ the quantity of secondary aerosol formed by the reaction of OH with alkanes evolves dynamically by functionalization and fragmentation.³ Functionalization dominates early stage oxidation and leads to substantial aerosol yield. At higher oxidation levels, the aerosol yield reaches a maximum, and further reaction reduces the quantity of aerosol by the production of gas phase products (i.e. fragmentation). Carboxylic acids are expected to be key particle phase products that contribute substantially to lowering aerosol volatility (i.e. enhancing the quantity of aerosol) while raising its oxidation state and hygroscopicity. Our results suggest a new connection between aerosol pH and water that may govern the balance of functionalization and fragmentation in aqueous secondary organic aerosol. As the oxidation state of the aerosol increases by the formation of acids, water uptake naturally follows, opening acid-base reaction channels. This indicates that carboxylic acids could play a dual role. At early stages, these highly oxidized species mainly contribute to increase in aerosol mass and water uptake. When the

character of the aerosol becomes aqueous, acid-base equilibria lead to an increase in carboxylate-mediated chemistry which largely consists of C-C bond scission reactions (i.e. chemical erosion).

Here we have considered only a single relative humidity (RH = 64.5%) where the aerosol is a well-mixed aqueous solution on the timescale of the OH reaction frequency. We expect more complex behavior to appear as the RH is lowered and the aerosol and its subsequent transformations are governed increasingly by nanoscale interfacial gradients produced by slow diffusional timescales in the particle.^{8, 37} For these cases we might expect much more complex feedbacks to emerge between aerosol viscosity and hygroscopicity and the underlying elementary free radical and acid-base reaction pathways.

Supporting Information

Model construction; Structures, pKa, Kh and densities of organic acid species used in simulations; Validation of implicit acid-base modeling (explicit acid-base model results); Comparison of scenario 3 mass spectrum with experiment; Sample Gaussian09 results for alkoxy radical anion ground state and transition state; Evaluation of sensitivity of the simulation results for Scenario 3 with faster peroxy-peroxy kinetics

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844**Table 1: Key Model Parameters and Rate Coefficients**

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Parameter	Value	Description and References
<i>RH</i>	64.5%	Relative Humidity
<i>d_p</i>	97 nm	Diameter of particle
<i>k_{ad}</i>	0.052 s ⁻¹	Pseudo-first order adsorption rate coefficient of OH
[OH]	7.5 × 10 ¹⁰ molec. cm ⁻³	Average experimental [OH] ³⁷
<i>k_{RO2+O2}</i>	2.0 × 10 ⁵ s ⁻¹	Pseudo-first order reaction rate coefficient of RO ₂ + O ₂ ^a
<i>k_{photolysis}</i>	1.3 × 10 ⁻⁴ s ⁻¹	Rate coefficient of ROOH photolysis (see text for details)
<i>k_{CA(CH2)+OH}</i>	5.1 × 10 ⁻¹⁴ cm ³ molecules ⁻¹ s ⁻¹	Rate coefficient of H abstraction from -CH ₂ group in CA ^b
<i>k_{CA(OH)+OH}</i>	9.7 × 10 ⁻¹⁴ cm ³ molecules ⁻¹ s ⁻¹	Rate coefficient of H abstraction from -OH group in CA ^b
<i>k_{RO2+HO2}</i>	3.8 × 10 ⁻¹⁵ cm ³ molecules ⁻¹ s ⁻¹	Rate coefficient of RO ₂ + HO ₂ ^c
<i>k_{ROOH+OH}</i>	3.7 × 10 ⁻¹² cm ³ molecules ⁻¹ s ⁻¹	Rate coefficient of ROOH + OH ^d
<i>k_{RO2+RO2}</i>	1.6 × 10 ⁻¹⁵ cm ³ molecules ⁻¹ s ⁻¹	Rate coefficient of RO ₂ + RO ₂ ⁷⁶
<i>k_{RCOOH+OH}</i>	2.3 × 10 ⁻¹⁵ cm ³ molecules ⁻¹ s ⁻¹	Rate coefficient of RCOOH + OH ^{e, 67}
<i>k_{RCOO-+OH}</i>	2.0 × 10 ⁻¹³ cm ³ molecules ⁻¹ s ⁻¹	Rate coefficient of RCOO ⁻ + OH ⁶⁸
<i>k_{HO2+OH}</i>	1.7 × 10 ⁻¹¹ cm ³ molecules ⁻¹ s ⁻¹	Rate coefficient of HO ₂ + OH ⁶⁶
<i>k_{HO2+HO2}</i>	1.7 × 10 ⁻¹⁵ cm ³ molecules ⁻¹ s ⁻¹	Rate coefficient of HO ₂ + HO ₂ ⁶⁶
<i>K_{hydration}</i>	Structure activity relationships	Equilibrium Constant for R=O ↔ R(OH) ₂ ^f

846^a Pseudo first order rate coefficient was computed using the Henry's Law constant⁷⁷ of 0.0138 and a rate
847coefficient⁷⁶ for RO₂ + O₂ of 2.5 × 10⁻¹² cm³ molec⁻¹ s⁻¹

848^b Computed via structure activity relationships described in Refs. ⁷⁸⁻⁷⁹ Values for all the other species in the
849reaction (Table S1 in the SI) are similarly calculated and fall in the range of 10⁻¹⁴ – 10⁻¹³ cm³ molecules⁻¹ s⁻¹
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851^c The RO₂ + HO₂ rate coefficient in the aqueous phase is estimated using the 2-3 times difference in the
852rate coefficient⁸⁰ from HO₂ + HO₂ observed in the gas phase.⁸¹⁻⁸² Peroxy-peroxy rate coefficients in
853solution can span a large range, and the values used here are at the lower end of the range. The sensitivity
854of the results to values set to the high end of the range is discussed in the SI (See section S6, Scenario 4).

855^d Rate coefficient used is consistent with values (~ 10⁻¹² cm³ molec⁻¹ s⁻¹) reported in Refs. ^{80, 83}

856^e This rate coefficient is that for abstraction of H from the carboxylic acid group in oxalic acid.

857^f The equilibrium constants for hydration reactions were calculated from the structure activity
858relationships and are listed in Table S1 in the SI. (see Ref. ⁶⁰) As described for acid-base chemistry, this
859equilibrium constant was folded into an effective rate constant.

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866**Table 2: Model Scenarios**

867	Scenario	Free Radical	Acid-Base	Evaporation of C ₂
868				Fragments
	1	✓	✗	✗
	2	✓	✓	✗
	3	✓	✓	✓

869**Table 3: Decay Constant Comparison:** Experimental and simulated reaction rate constant of
 870CA. Coefficient of determination values (R^2) are calculated for the model scenarios to validate
 871the exponential fit. Note that only scenario 3 has a reaction rate constant value within
 872experimental error.

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<i>Model Scenario</i>	$k_{obs} \text{ cm}^3 \text{ s}^{-1} \text{ molec}^{-1}$	R^2
<i>Experiment</i>	$(5.27 \pm 0.28) \times 10^{-13}$	
1	4.68×10^{-13}	.99
2	6.08×10^{-13}	.99
3	5.38×10^{-13}	.99

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877**Figure 1:** Reaction pathways of RO_2 to yield functionalized and/or fragmented products. A
 878diagram of the free radical, pathways of RO_2 and subsequent acid-base and hydration reactions
 879used to model the heterogeneous oxidation of aqueous citric acid aerosol by OH radicals. The
 880left and right branches of the RO_2 reactions generate functionalized organic products. The top and
 881bottom branches not only promote free radical cycling, but lead to bond cleaving reactions that
 882produce lower weight, more functionalized reaction products. The RO fragmentation channel is
 883significantly activated by an adjacent functional group and/or the deprotonation of a carboxyl
 884group in the radical, as suggested by *ab initio* calculations (see text for details).

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Scheme 1

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Scheme 2

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904**Figure 2.** Experimental and simulated reactive decay of CA as a function of OH exposure. The
 905experimental and simulation results were normalized to unreacted $[CA]_0$ prior to heterogeneous
 906reaction. See Table 1 for simulations parameters and Table 2 for scenario descriptions.

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Figure 3. Experimental and simulated Van Krevelen plots (H/C vs. O/C) of average aerosol elemental composition. Simulation results fall within experimental error regardless of the model scenario. Note unreactive CA has H/C = 1.33 and O/C = 1.16. As the reaction progress the average H/C of the aerosol decreases and the O/C increases.

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935**Figure 4.** Experimental and simulated negative ion mass spectra of the major oxidation products
 936of CA produced at an OH exposure of 4.4×10^{12} molecules s cm^{-3} . See Figure 5 for structures of
 937these reaction products.

m/z	-ve ion	Structure	pKa	O/C	H/C
73.03	C ₂ HO ₃		3.32	1.50	1.00
116.98	C ₃ HO ₅	Mesoxalic acid	1.15	1.67	0.67
119.00	C ₃ H ₃ O ₅		1.98	1.67	1.33
133.01	C ₄ H ₅ O ₅	Malic Acid	3.40	1.25	1.50
191.02	C ₆ H ₇ O ₇	Citric Acid	3.13	1.17	1.33
205.00	C ₆ H ₅ O ₈		2.23	1.33	1.00
207.01	C ₆ H ₇ O ₈		2.90	1.33	1.33

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939 **Figure 5:** Molecular structures, negative ion m/z, H/C, O/C and pK_a of the major reaction
940 products observed experimentally by Davies and Wilson.³⁷

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Figure 6: Experimental and simulated concentration of mesoxalic acid ($m/z = 116.98$) as function of OH exposure. For comparison the experimental and simulated concentration was normalized to the maximum value. Scenario 3 predictions are within experimental error.

Figure 7: Experimental and simulated normalized aerosol volume as a function of OH exposure. The volume is normalized to the unreacted CA aerosol. The rapid growth observed in Scenario 2 is due to lack of evaporation in this scenario. Scenario 1 fails to capture the initial increase in volume and similar to scenario 1, does not predict the decrease in volume due to a lack of evaporation. Scenario 3 is the only model to predict within experimental error the complex growth and decay in aerosol volume observed over the course of the reaction.

Figure 8: A comparison in acyloxy radical formation rate between an α -keto acid and its conjugate base. The charge transfer reaction of the base (bottom) has a rate coefficient that is approximately 2 orders of magnitude larger than the hydrogen abstraction reaction on the acid (top). The inclusion of acid-base chemistry substantially increases acyloxy radical formation rates.

Figure 9: Carboxyl group formation accompanied by one-carbon loss via acyloxy radical formation. After decarboxylation of the acyloxy radical, addition of oxygen to the resulting α -di-hydroxyalkyl radical and subsequent decomposition yields an acid that differs only by 1 carbon atom from the original reactant. Hydration is an essential part of this pathway, making it unique to the aqueous-phase.

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1023**Figure 10:** The two reaction pathways that produce mesoxalic acid (m/z = 116.98). In the right
 1024branch, RO_2 may also react to yield 2-hydroxymalonic acid (i.e. $\text{C}_3\text{H}_4\text{O}_5$, tartronic acid). The
 1025 $\text{ROOH} + \text{OH}$ reaction in the left branch regenerates OH further propagating the reaction.

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Figure 11: Simulated product carbon number (N_c) distributions (at OH exposure = 2.2×10^{12} molec. cm^{-3} s) for Scenarios 1, 2 and 3. The experimental data are also shown at OH exposure = 2.1×10^{12} molec. cm^{-3} s, for qualitative comparison to the calculations. Each carbon number is computed by dividing the sum of all species corresponding to a carbon number by the initial concentration of CA. Scenario 1 lacks C_5 products, which are only produced when acid-base chemistry is included in the reaction scheme (i.e. Scenario 2 and 3).

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Figure 12: Computed rate coefficients for the unimolecular decomposition of alkoxy radicals (see text for details). Fragmentation of the radical anion (bottom) is many orders of magnitude faster than the neutral case (top).

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1110 **Figure 13:** A significant reaction pathway that converts a ROOH group into a carbonyl with H₂O
1111 and OH as coproducts.

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1120 TOC Graphic

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