

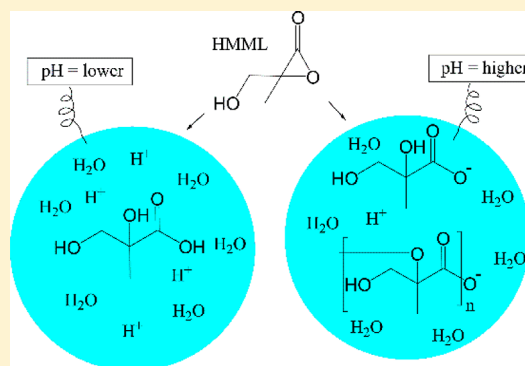
Assessing the Potential for Oligomer Formation from the Reactions of Lactones in Secondary Organic Aerosols

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Supporting Information

ABSTRACT: Laboratory and field measurements have demonstrated that 2-methyl glyceric acid (2-MG) is the base component of a wide range of chemical species found in methacrolein-derived secondary organic aerosol (SOA). In order to explore the recently proposed hypothesis that a lactone oxidation intermediate is the origin of 2-MG and its derivatives in SOA, nuclear magnetic resonance techniques were used to study kinetics and reaction products of the aqueous phase reactions of a model lactone, β -propiolactone (BPL). BPL was found to react with a lifetime of 4–10 h (depending on solution conditions) via a general acid catalyzed mechanism, which suggests that lactones similar to BPL are reactive on an atmospherically relevant time scale. BPL was also shown to form a variety of nucleophilic addition products (organosulfates and nitrates and oligomers) similar to the 2-MG-based species observed in previous experiments involving the photooxidation and SOA processing of methacrolein. While many of the BPL reaction products could be rationalized via an epoxide-like nucleophilic addition mechanism, evidence for ester-like nucleophilic addition was suggested through the observation of inorganic ion-catalyzed oligomer formation. The formation of oligomers was found to depend strongly on the proportion of organic acid nucleophile present in its deprotonated form. Therefore, due to the nature of the general acid catalysis and importance of deprotonated acids for efficient BPL oligomerization, it is suggested that oligomerization from lactone intermediates will be more efficient at higher SOA pH values. This result may help explain why overall isoprene-derived SOA formation has been observed to be largely pH-independent. Overall, the results strongly support the previous conclusion that a lactone intermediate is responsible for the formation of 2-MG-related species found in methacrolein-derived SOA.



INTRODUCTION

Isoprene is emitted into the atmosphere in very large quantities, with an annual emission budget of more than 500 Tg/yr.¹ Isoprene undergoes reactions with oxidants that can ultimately perturb the NO_x and HO_x radical cycles that govern the formation of tropospheric ozone, a key atmospheric pollutant, as well as produces oxidation products (such as methacrolein) that themselves are photochemically active.² Isoprene oxidation can also lead to secondary organic aerosol (SOA) formation—along with tropospheric ozone, SOA is a key component in air pollution situations and can also act as a climate change forcing agent.³

The role of an isoprene-derived epoxydiol (IEPOX)⁴ oxidation intermediate in the formation of SOA has been extensively studied in both laboratory situations^{5–11} and in field observations of SOA.^{6,12–16} The chemical structures of the various IEPOX-derived SOA constituents are characterized by the retention of the five-carbon backbone of isoprene in all identified species.

A second set of isoprene-derived SOA constituents has been identified via the observation of a set of species that involves the retention of a four-carbon backbone that is derived from the isoprene oxidation product methacrolein. In particular, it is

proposed that, under high NO_x conditions, methacrolein is further oxidized to the intermediate methacryloylperoxynitrate (MPAN),^{6,17} which then reacts with OH radical to form an intermediate that ultimately produces SOA constituents based upon a 2-methylglyceric acid (2-MG) backbone. 2-MG has been observed in several laboratory and ambient observation settings.^{18–23} Other 2-MG-related compounds have been observed in environmental chamber SOA experiments, such as oligomers containing as many as eight 2-MG subunits, nitric acid esters, and sulfuric acid esters.^{21–28} A dimer containing two 2-MG subunits connected via an ester linkage in ambient aerosol has also been reported.¹⁹ The formation of these species serves to lead to SOA growth because of the decreased volatility of these constituents due to increased molecular weights (for oligomers) and/or the presence of highly polar hydroxy, nitrate, and sulfate groups as compared to methacrolein itself.

There have been several proposals for the identity of the MPAN-derived intermediate that leads to the formation of 2-MG and related compounds. In particular, the evidence indicates that

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this intermediate must not only lead to 2-MG itself, but must also be the direct precursor of the other 2-MG-derived species. This is so because previous studies have shown that 2-MG reacts much too slowly with itself and other SOA components to account for the extent of oligomer formation observed in atmospheric chamber experiments.²⁹ Analogously to the role of IEPOX in the production of SOA constituents, it has been proposed that another epoxide species, methacrylic acid epoxide (MAE), may be the key MPAN oxidation intermediate³⁰ that can explain all 2-MG-derived components. However, MAE was subsequently shown to be a relatively minor gas phase product of methacrolein oxidation,¹⁷ and its SOA phase reactivity was also determined to be quite slow.³¹ Instead, these results were interpreted with the aid of a computational study³² which suggested that another MPAN oxidation intermediate, hydroxymethyl-methyl- α -lactone (HMML), may serve as the precursor to the 2-MG-derived SOA components (both the gas phase formation route for HMML and its predicted SOA phase products are given in Figure 1). The HMML precursor has never been observed in any

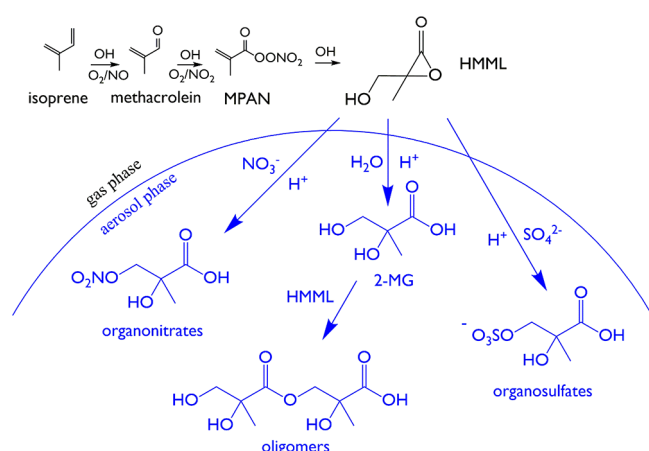


Figure 1. Proposed gas phase formation and SOA phase reactions of HMML.

experimental study; however, its extremely high reactivity could explain both its lack of detection as well as its ability to readily form the 2-MG-related SOA components. Indeed, the literature seems to indicate that only a single three-membered ring lactone similar to HMML, bis(trifluoromethyl)acetolactone, has ever been isolated.³³

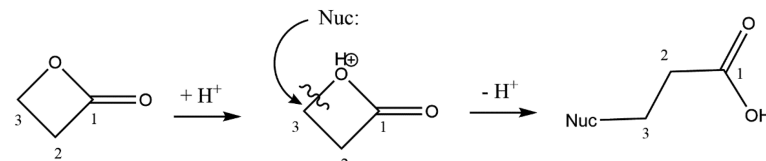
Because no known synthetic procedure has been published for HMML, we choose to study β -propiolactone (BPL) as a proxy system for the reactivity of HMML. A lactone is a cyclic ester which possesses a ring oxygen atom like epoxides. Therefore, they may possess both ester-like and epoxide-like reactive properties. Figure 2 illustrates how BPL may undergo nucleophilic addition at the 3-position carbon atom (like an epoxide would) or nucleophilic addition at the 1-position carbon (like an ester would). In their HMML hypothesis, Nguyen et al. postulated that all 2-MG-related constituents could be rationalized via the epoxide-like mechanism.¹⁷ In this paper, we investigate the reaction mechanism of BPL in order to evaluate the viability of the HMML hypothesis for the formation of 2-MG-related species in SOA. Specifically, we report measurements of the kinetics and products of the aqueous-phase reactions of BPL in the presence of a number of atmospherically relevant nucleophiles using nuclear magnetic resonance (NMR) as the analytic technique.

EXPERIMENTAL SECTION

Bulk Aqueous Solution Preparation. All experiments were carried out in deuterated solvents, which were necessary for NMR locking purposes. Most of the experiments involved the aqueous phase reaction of BPL with varying conditions of (1) added nucleophile reactants, (2) added acid to explore potential Bronsted acid catalysis, and (3) added base to explore the effects of deprotonation of potential organic acid nucleophiles. These solutions are listed in Table 1. In order to explore reaction mechanism aspects, a solution consisting of 0.80 M acetyl chloride in an equivolume solution of water and ethanol and a solution consisting of 0.80 M BPL and 1.68 M 2-chloropropionic acid was also studied. These solutions were prepared using commercially available β -propiolactone (Sigma-Aldrich, > 97% purity as established by ^1H NMR), 98% acetyl chloride (Sigma-Aldrich), 68 wt % DClO_4 (Sigma-Aldrich), 40 wt % NaOD (Sigma-Aldrich), 99.9% D_2O (Cambridge Isotope Laboratories, Inc.), Na_2SO_4 (Sigma-Aldrich), NaNO_3 (Sigma-Aldrich), NaCl (Sigma-Aldrich), 30 wt % 3-hydroxypropionic acid (TCI America), 98% 2-chloropropionic acid (TCI America). The commercial 3-hydroxypropionic acid (3-HP) source contained a significant amount ($\sim 10\%$ of the total 3-HP-derived content) of the asymmetric ester-linked dimer of 3-HP.

NMR Product Identification and Quantitation Methods. All NMR spectra were collected on a Varian 400 MHz instrument. The ^1H chemical shifts were calibrated to the solvent

Epoxide-like Nucleophilic Addition



Ester-like Nucleophilic Addition

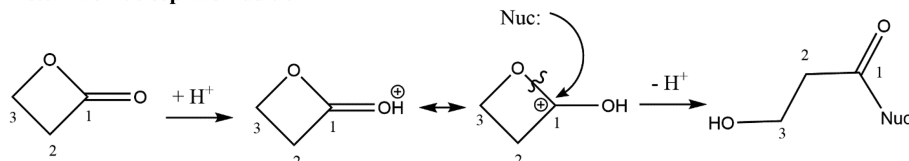


Figure 2. Potential nucleophilic addition pathways for BPL.

Table 1. Solution Compositions and Associated BPL Loss Rate Constants

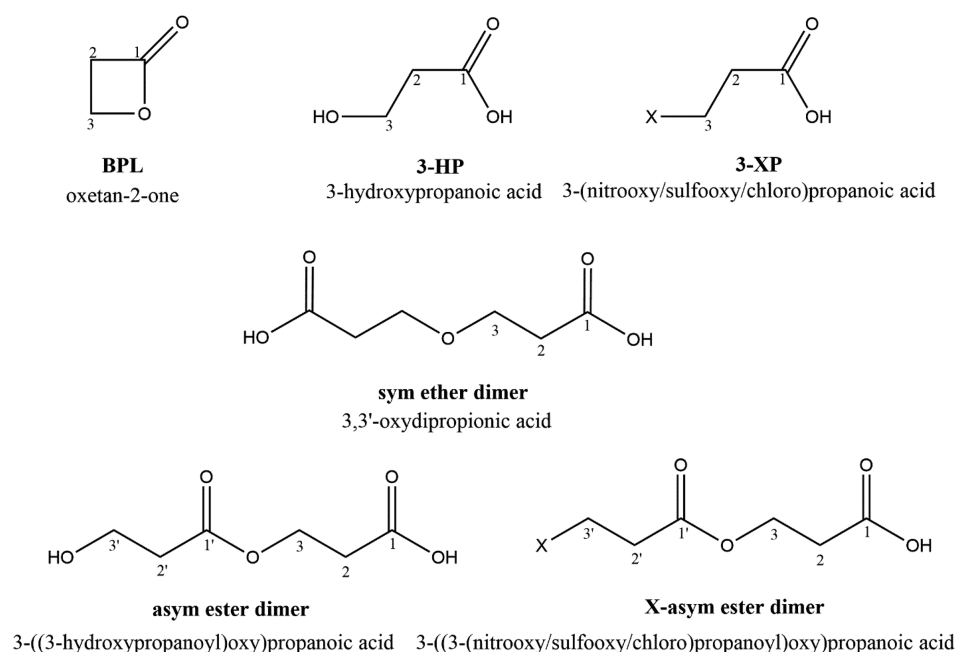
solution	BPL (M)	initial D ⁺ (M)	initial OD [−] (M)	added reactant	added reactant (M)	BPL k'' (10^{-5} s^{-1})
1	0.16	0	0	none	0	6.65
2	0.16	1.0	0	none	0	5.83
3	0.16	2.0	0	none	0	7.89
4	0.16	4.0	0	none	0	42.0
5	4.0	0	0	none	0	3.61
6	4.0	0.020	0	none	0	3.30
7	0.80	0.020	0	none	0	5.00
8	0.80	0.020	0	NaClO ₄	0.25	4.77
9	0.80	0.020	0	NaClO ₄	0.50	4.66
10	0.80	0.020	0	NaClO ₄	1.0	4.64
11	0.80	0.020	0	Na ₂ SO ₄	0.25	7.22
12	0.80	0.020	0	Na ₂ SO ₄	0.50	8.84
13	0.80	0.020	0	Na ₂ SO ₄	1.0	13.4
14	0.80	0.020	0	NaNO ₃	0.50	5.60
15	0.80	0.020	0	NaNO ₃	1.0	5.83
16	0.80	0.020	0	NaCl	0.50	11.6
17	0.80	0.020	0	NaCl	1.0	16.7
18	0.80	0	0	3-HP	1.68	2.93
19	0.80	0	0.060	3-HP	1.68	4.35
20	0.80	0	0.19	3-HP	1.68	7.11
21	0.80	0	0.76	3-HP	1.68	16.5
22	0.80	0	1.5	3-HP	1.68	34.5

at 4.79 ppm, and the ^{13}C chemical shifts were calibrated to 3-HP (which was present in nearly all of the solutions as a reaction product) at 178.6 ppm. The relative amounts of reaction products were calculated by peak integration of unique nuclei for each species. For the case of ^{13}C quantitation (which was critical for the oligomeric species), structurally similar nuclei (such as carbonyl carbon atoms) were used for peak integration in order to ensure that relaxation time effects did not affect the results.

In addition to standard one-dimensional ^1H and ^{13}C NMR spectroscopy methods, the following correlation NMR spectroscopy methods were also used: ^1H – ^1H correlation spectroscopy (COSY), ^{13}C distortionless enhancement by polarization transfer (DEPT), ^1H – ^{13}C heteronuclear single-quantum correlation (HSQC), and ^1H – ^{13}C heteronuclear multiple bond correlation (HMBC) techniques.³⁴ This suite of NMR experiments provided information about single- and multiple-bond couplings necessary to determine bond connectivity in product molecules and resolve overlapping peaks in one-dimensional NMR spectra, which was particularly important for the detected oligomeric species where the resonances often overlapped with the dominant monomer, 3-HP.

Kinetics Method. Kinetics measurements of the aqueous phase reactions of BPL were made by collecting sequential ^1H and ^{13}C NMR spectra over the course of the experiment. Each measurement was performed in similar manner: BPL was added to the specific aqueous solution, and the solution was stirred in a 20 mL vial to ensure solution homogeneity. After approximately 1 min, the entire reaction mixture was loaded into an NMR tube, and spectral collection was started. A first order decay rate law was found to fit the BPL concentration vs time data, and the first order rate constants were determined for each solution.

Product Relative Yield Calculations. In most cases, the relative yields of products were calculated by straightforward consideration of the individual product and total product integration ratios (and using the appropriate nuclei ratios for the individual products in order to ensure that correct molar ratios were calculated). In the case of solutions using added 3-HP, the presence of the asymmetric ester-linked dimer of 3-HP as an impurity creates complications in the calculation of product yields. While it was possible to calculate the net product yield of this species by simply subtracting the initial amount from the final amount, the fact that this impurity could be involved in higher order oligomer formation through its reaction with BPL meant that its presence affected the observed yields of the higher

**Figure 3.** Structures and nomenclature (shorthand and IUPAC) for BPL-related species.

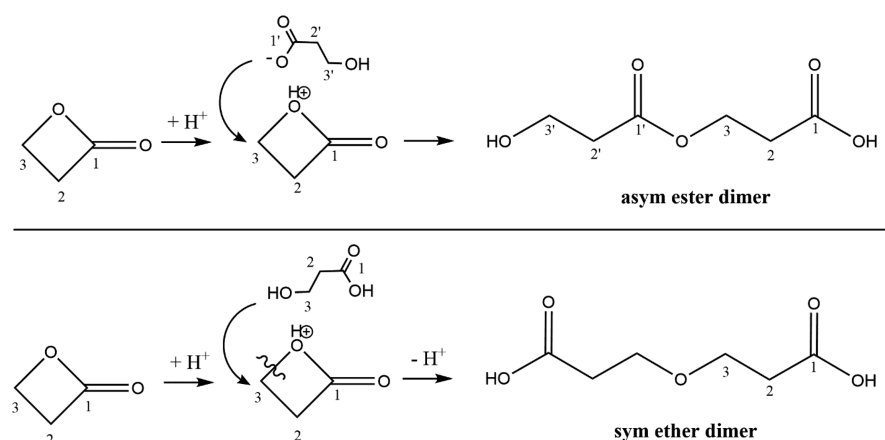


Figure 4. Nucleophilic attack of 3-HP⁻ and 3-HP on BPL to produce the asym ester dimer and the sym ether dimer, respectively.

order oligomers. Therefore, we choose to report the actual final postreaction relative amounts of all species.

RESULTS AND DISCUSSION

Product Identification. In order to aid in the discussion of the various products formed by reaction with BPL, the structures and nomenclature (shorthand and IUPAC) for the different classes of compounds are given in Figure 3. As discussed in the introduction, epoxide mechanism-like nucleophilic attack at the #3 carbon on BPL will lead to 3-HP in the case of water as the nucleophile, or more generally, 3-XP in the case of a generic nucleophile X. These 3-XP species were observed in every experiment in which known nucleophiles were added (i.e., sulfate, nitrate, and chloride, but not for the non-nucleophilic perchlorate case). The NMR assignments were aided by previously reported relative ¹H chemical shift trends for reaction of the epoxide butadiene monoxide with sulfate, nitrate, and chloride nucleophiles.³⁵ 3-XP itself can act as a nucleophile, with both the X moiety and carboxyl groups as potential nucleophilic sites in its reaction with BPL. In the case of 3-HP using its OH moiety as the nucleophile, BPL reaction is expected to lead a symmetric ether-linked dimer (labeled sym ether dimer in Figure 4), which was observed in some experiments. Although 3-XP species other than 3-HP itself could potentially lead to the formation of other symmetric dimers, no other symmetric dimers were observed. In the case of 3-HP using its carboxyl group as the nucleophile, BPL reaction is expected to lead to an asymmetric ester-linked dimer (labeled asym ester dimer in Figure 4). Except for dilute BPL reaction systems, this species was observed in every other reaction system. A similar reaction involving 3-XP species with BPL was observed to lead to related asymmetric ester linked dimers (X-asym ester dimer). For reaction systems in which the acid ionization equilibrium for 3-HP was intentionally shifted (via the addition of base) to favor the more nucleophilic deprotonated form of 3-HP (3-HP⁻), higher order asymmetric ester-linked oligomers were also observed. The NMR assignments of the oligomers were aided by the previously reported NMR assignments of similar symmetric and asymmetric dimers formed from the reaction of MAE with 2-MG.³¹ The Supporting Information contains ¹H and ¹³C assignments for all detected species, as well as sample spectra illustrating the use of correlation methods to identify the specific bond connectivities. While BPL and 3-HP have previously been extensively studied using NMR techniques in other previously reported work, to the

best of our knowledge, NMR data for all other detected species have not been previously reported in the literature.

BPL Loss Kinetics Analysis. Table 1 lists the first order BPL loss rate constants for each of the 22 solutions. Each of these first order rate constants was determined to a precision of about 1% at the one standard deviation level. The entry for solution 1 indicates that BPL undergoes relatively rapid reaction in neutral aqueous solution, with a lifetime of 4.2 h. Entries 2–4 indicate that very high Bronsted acid concentrations are required to significantly increase the BPL reaction rate constant above the neutral solution value. This Bronsted acid dependent kinetic behavior was also observed in a previous study of the aqueous reaction of BPL,³⁶ and the rate constants determined in that work are in good agreement with the present results. The fact that BPL is quite reactive in a pH-independent fashion from pH = 7 to below pH = 0 indicates that the mechanism likely involves solvent water acting as a general acid catalyst. In the general acid catalyzed hydrolysis process, one water molecule acts as the general acid by using one of its acidic hydrogen atoms to form a bond with the ring oxygen atom (as opposed to an H⁺ unit acting in this role in traditional acid catalysis). A second water molecule then acts as the attacking nucleophile on this intermediate species. Ultimately, the original catalytic water molecule is released to the aqueous solution as the final hydrolysis product is formed. This is a common mechanism for epoxide reaction,³⁷ and has been specifically identified as the reaction mechanism for some potentially atmospherically relevant epoxides.^{38–40} It is possible that the use of deuterated solutions in the present study could lead to the observation of different rates of reaction than would be observed for the normal isotope. For example, the *k*_{D₂O}/*k*_{H₂O} ratio was found to vary between 1.9 and 1.0 in a kinetics study of the hydrolysis of several hydroxyepoxides.⁴¹

The BPL loss rate constants are also clearly impacted by the presence of other species. For experiments involving high concentrations of largely non-nucleophilic components (such as neutral 3-HP and ClO₄⁻ for solutions 5–6, 8–10, and 18), the BPL loss rate constant is reduced by as much as a factor of 2 from its dilute aqueous value of 6.65 × 10⁻⁵ s⁻¹. This observation suggests that both neutral and ionic components serve to modify the solution properties in such a way to slow down the BPL hydrolysis reaction. For experiments involving the addition of nucleophilic components (such as SO₄²⁻, NO₃⁻, Cl⁻, and deprotonated 3-HP for solutions 11–22), the BPL loss rate constants are observed to increase from the dilute aqueous value. This result suggests that nucleophiles are active in the rate-

limiting step of the mechanism. Therefore, this result, in combination with the knowledge that water is acting as a general acid catalyst, indicates that the appropriate rate law for BPL loss is a termolecular one:

$$-\frac{d[\text{BPL}]}{dt} = k[\text{BPL}][\text{nucleophile}][\text{water}] \quad (1)$$

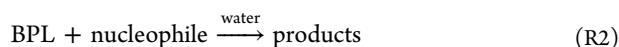
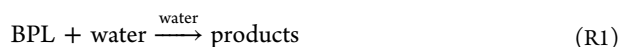
where k is the true termolecular rate constant. Since solvent water is, to a good approximation, constant in all of the experiments, the effective rate law becomes a bimolecular one:

$$-\frac{d[\text{BPL}]}{dt} = k'[\text{BPL}][\text{nucleophile}] \quad (2)$$

where $k' = k[\text{water}]$, or $k' = 55.5 \text{ M } k$. For experiments in which the BPL concentration is much less than the nucleophilic strength-weighted total nucleophile concentration, the rate law reduces to the observed pseudo first order case

$$-\frac{d[\text{BPL}]}{dt} = k''[\text{BPL}] \quad (3)$$

where $k'' = k'[\text{nucleophile}]$. For practical purposes, it is useful to derive a more specific rate law for the case of both water and a second nucleophile reacting with BPL.



Again using the simplification in the rate law for the general acid catalyst water that results due to its unchanging concentration, the explicit rate law for the R1-R2 mechanism is

$$-\frac{d[\text{BPL}]}{dt} = [\text{BPL}](k_{\text{water}}'[\text{water}] + k_{\text{nucleophile}}'[\text{nucleophile}]) \quad (4)$$

where $k_{\text{water}}' = k_{\text{water}}[\text{water}]$ and $k_{\text{nucleophile}}' = k_{\text{nucleophile}}[\text{water}]$. Again, because the concentration of the nucleophile water is also unchanging, eq 4 can be simplified for the nucleophile water similarly

$$-\frac{d[\text{BPL}]}{dt} = [\text{BPL}](k_{\text{water}}'' + k_{\text{nucleophile}}'[\text{nucleophile}]) \quad (5)$$

where $k_{\text{water}}'' = k_{\text{water}}'[\text{water}] = k_{\text{water}}[\text{water}]^2$. As was the case for the simplification of eq 2 to eq 3, eq 5 can be simplified to the pseudo first order eq 6 similarly

$$-\frac{d[\text{BPL}]}{dt} = [\text{BPL}](k_{\text{water}}'' + k_{\text{nucleophile}}'') = k''[\text{BPL}] \quad (6)$$

where $k_{\text{nucleophile}}'' = k_{\text{nucleophile}}'[\text{nucleophile}] = k_{\text{nucleophile}}[\text{water}]$ and $k'' = k_{\text{water}}'' + k_{\text{nucleophile}}''$. Therefore, a plot of k'' values determined from a set of pseudo first order kinetics experiments with different nucleophile concentrations versus the actual nucleophile concentrations will yield a slope equal to $k_{\text{nucleophile}}'$ and an intercept equal to k_{water}'' (which depends somewhat on the solvent properties, as discussed above). The concentrations for NO_3^- and Cl^- were assumed to be the same as the molar concentration of NaNO_3 and NaCl in the prepared solutions. The concentrations of 3-HP $^-$ were assumed to be equal to the added concentration of strong base. The concentrations of SO_4^{2-} were calculated using the Extended

AIM Aerosol Thermodynamics Model.⁴² In practice, relatively high BPL concentrations were used in some cases (to make ^{13}C data collection less time-consuming), and for the solutions with low nucleophile concentrations and/or high nucleophilic strength, the nucleophile concentrations significantly decreased throughout the course of the reaction. In order to minimize this effect, the pseudo first order kinetics analysis was performed on data collected early in the reaction when the nucleophile concentrations were near their initial levels. Some high $[\text{nucleophile}]/[\text{BPL}]$ ratio experiments were performed (where ^1H NMR sufficed to detect all species) to confirm the validity of this approach. Figure 5 shows the BPL loss kinetics

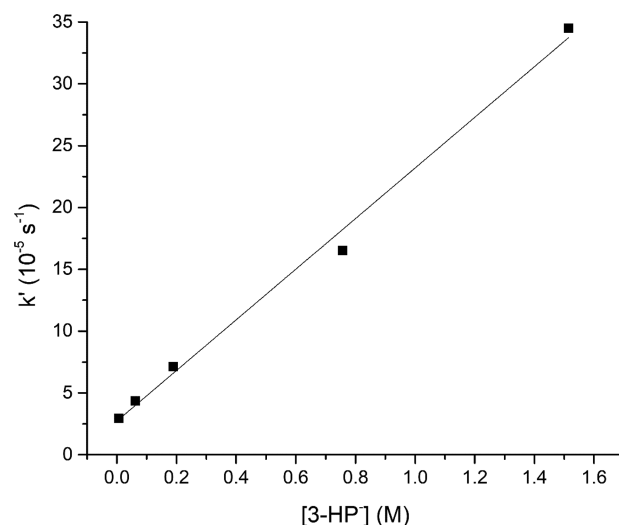


Figure 5. Pseudo second order rate constant determination of 3-HP $^-$ nucleophilic addition to BPL.

Table 2. Rate Constants and Relative Nucleophilic Strengths

nucleophile	$k_{\text{nucleophile}}'$ ($10^{-6} \text{ M}^{-1} \text{ s}^{-1}$)	k_{water}'' (10^{-5} s^{-1})	nucleophilic strength relative to water
NO_3^-	8.3 ± 2.0	5.06 ± 0.14	9.1
SO_4^{2-}	83.3 ± 3.3	5.03 ± 0.19	91.8
Cl^-	117.4 ± 8.4	5.25 ± 0.55	124
3-HP $^-$	204.8 ± 8.9	2.72 ± 0.68	418

analysis for BPL reaction with 3-HP $^-$. Table 2 contains the rate constants recovered from this analysis for all nucleophiles, as well as the nucleophilic strength of each nucleophile relative to water, which is simply calculated from the ratio $k_{\text{nucleophile}}'/k_{\text{water}}''$. Again, as discussed earlier, the high concentrations of some solution components can cause k_{water}'' to vary from solution to solution. These values are approximate due to the assumption that there are only two competing BPL fates, reactions R1 and R2. As will be discussed in the next section, the observed products for some solutions indicate that other BPL reactions can occur. The relative nucleophilicities for the inorganic ions follow the same trend ($\text{NO}_3^- < \text{SO}_4^{2-} < \text{Cl}^-$) as was observed in the reaction with the epoxide butadiene monoxide.³⁵ The relative nucleophilicity value for BPL reaction with NO_3^- is also very similar to those determined for epoxides related to isoprene⁷ and 2-methyl-3-buten-2-ol.⁴³ However, the relative nucleophilicity value for SO_4^{2-} is larger for BPL than for any of these previously investigated epoxides. Deprotonated 3-HP (3-HP $^-$) was found

Table 3. Final Species Relative Amounts for Selected Solutions

solution	major non-H ₂ O nucleophile(s)	3-HP (%)	3-XP (%)	sym ether dimer (%)	asym ester dimer (%)	X-asym ester dimer (%)	asym ester trimer (%)	asym ester tetramer (%)
1	none	100	—	0	0	—	0	0
5	3-HP, 3-HP [−]	93.80	—	2.64	3.56	—	0	0
7	3-HP, 3-HP [−]	97.30	—	0.45	2.25	—	0	0
13	SO ₄ ^{2−}	55.07	31.31	0	5.84	7.78	0	0
15	NO ₃ [−]	83.47	9.51	0	5.43	1.60	0	0
17	Cl [−]	28.31	53.98	0	5.07	12.63	0	0
18	3-HP	90.99	—	1.53	6.53 ^a	—	0.94 ^a	0
21	3-HP [−]	64.89	—	0.55	24.01 ^b	—	8.07 ^b	2.49

^aNo asym ester dimer or trimer product was formed from BPL reaction for this solution; therefore, these values represent the amount of asym ester oligomers present due to impurities in the commercial 3-HP source. ^bThe net asym ester dimer product yield for this solution is 24.01% − 6.53% = 17.48% and the net asym ester trimer product yield for this solution is 8.07% − 0.94% = 7.13%.

to be the strongest nucleophile of all those investigated. As will be discussed in a subsequent section, this property is crucial in rationalizing the facile formation of oligomers from 3-HP[−].

Product Analysis. Table 3 lists the final species relative amounts for a number of the BPL reaction systems listed in Table 1. In all cases, after all BPL reactant had been consumed, the final species concentrations were found to be stable for a period of weeks or more. Therefore, all of the various products listed in Table 3 appear to be quite stable in aqueous solution. For solution 1, the reaction of low concentration BPL with water, only the hydrolysis product, 3-HP, was detected. However, when higher BPL concentrations were used in aqueous solutions (solutions 5 and 7), additional nucleophilic addition products were observed. Figure 6 shows the time profile of the formation

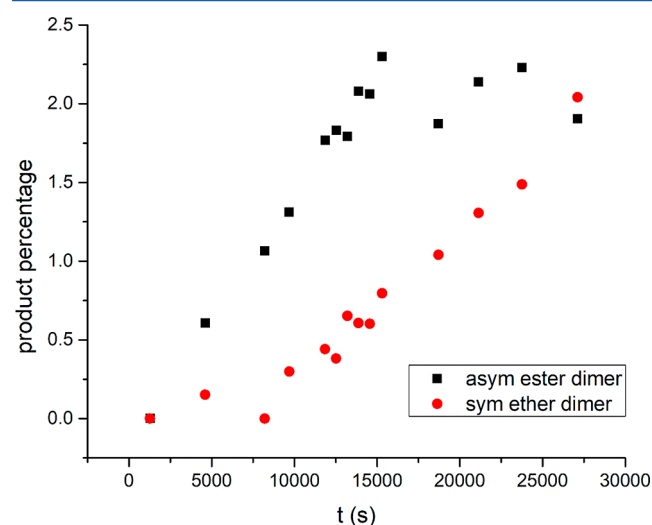


Figure 6. Product formation kinetics for solution 5.

of two of these products for solution 5. This kinetics data clearly shows different product formation behavior for the asym ester and sym ether dimers. Figure 4 illustrates the nucleophilic attack mechanisms for 3-HP[−] and 3-HP that rationalizes the formation of two observed dimers (note that in all mechanism schemes given in the manuscript “H⁺” represents all acid catalysts, including general acid catalysts such as water). Early in the reaction, the hydrolysis of BPL leads to relatively low concentrations of 3-HP. Because the concentration of 3-HP[−] (produced by the acid ionization of the weak acid, 3-HP) depends quadratically on the neutral 3-HP concentration, the [3-HP[−]]/[3-HP] ratio decreases nonlinearly as the amount of 3-HP

increases from BPL hydrolysis. Therefore, at very early times, the reaction of 3-HP[−] with BPL to produce the asym ester dimer is relatively more efficient than the reaction of 3-HP with BPL to produce the sym ether dimer. More specifically, at the early times of reaction shown in Figure 6, the relatively low concentration of 3-HP[−] and high nucleophilicity of the carboxyl group on 3-HP[−] leads to approximately equal reactivity as for the relatively high concentration of 3-HP and low nucleophilicity of the hydroxy group on 3-HP. At later times, as the amount of 3-HP rises, the acid ionization equilibrium shifts to produce relatively smaller amounts of 3-HP[−], and the sym ether dimer-producing reaction becomes dominant. The final species relative amounts listed in Table 3 for solution 7, which is intermediate in BPL (and ultimately 3-HP) concentration between solutions 1 and 5 further supports this interpretation. Since the 3-HP concentrations are lower for solution 7 than for solution 5, the asym ester dimer is formed in relatively higher amounts than was observed for solution 5. When high concentrations of 3-HP are initially present during BPL reaction (solution 18), no asym ester oligomer formation is observed (although the commercial 3-HP source does contain some asym ester oligomers as impurities, which accounts for the nonzero final species amount for 3-HP in the solution 18 entry in Table 3). The relatively small amount of sym ether dimer formed under the conditions of solution 18 suggests that the nucleophilicity of neutral 3-HP (which uses its hydroxy group as the nucleophilic attack moiety), is similar to that of water.

In order to further confirm the interpretation of the two product formation channels as arising from varying amounts of two different nucleophiles, an additional experiment was performed. Electron withdrawing substituent groups are known to reduce the pK_a of weak acids.⁴⁴ Since lower pK_a values lead to higher fractions of the deprotonated acid, 2-chloropropionic acid, was used as the nucleophile instead of 3-HP under experimental conditions similar to solution 18. The lowering of the pK_a from 3-HP's value of 4.5 to 2-chloropropionic acid's value of 2.8⁴⁵ for nucleophile concentration under solution 18 conditions is calculated to lead to a 8-fold higher concentration of the deprotonated form of 2-chloropropionic acid. Indeed, the asym ester dimer formed from the reaction of BPL with deprotonated 2-chloropropionic acid was observed under otherwise identical conditions to those of solution 18. By contrast, solution 18 did not have high enough 3-HP[−] concentrations to allow a detectable amount of the asym ester dimer to be formed. Therefore, both the BPL loss kinetics and product formation data strongly suggest that the 3-HP[−] is a very strong nucleophile. However, because 3-HP is a weak acid

(with a very similar pK_a to that of 2-MG itself), very small $[3\text{-HP}^-]/[3\text{-HP}]$ ratios typically exist in aqueous solution, which can allow for other nucleophiles (such as water) to compete effectively in the reactions with BPL.

Oligomerization Reaction Analysis. Through the addition of strong base, which directly modifies the $[3\text{-HP}^-]/[3\text{-HP}]$ ratio, the 3-HP $^-$ reaction with BPL can be made dominant. Solution 21 was prepared to have roughly equal concentrations of 3-HP $^-$ and 3-HP, whereas the $[3\text{-HP}^-]/[3\text{-HP}]$ ratio for solution 18 was about 0.004. It is important to note that solution 21 was a *partially* neutralized solution that remained acidic (with a pH of about 4.4). The carbonyl region of the ^{13}C NMR spectrum of solution 21 (shown in Figure 7) clearly shows the

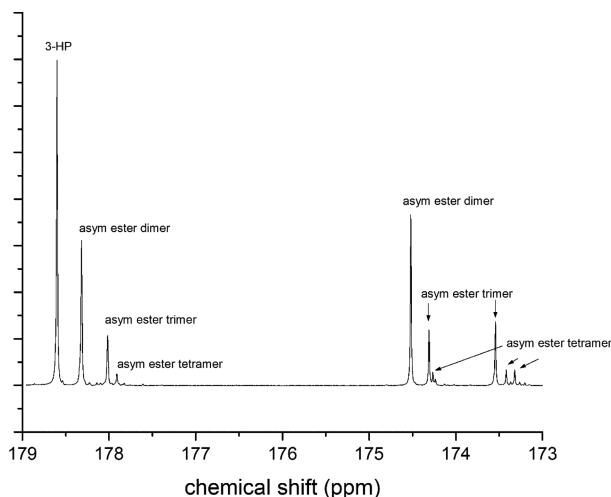


Figure 7. Carbonyl region ^{13}C NMR spectrum for solution 22.

effect of 3-HP $^-$ nucleophilic dominance in the reaction with BPL. The highly symmetric pattern of resonances in Figure 7 is characteristic of the presence of oligomers, as was previously reported for previous NMR studies of lactic acid⁴⁶ and 2-MG^{29,31} oligomerization. Figure 8 shows the time dependence of the various key species in solution 21. Indeed, although the concentration of 3-HP $^-$ for solution 21 was only about 0.8 M, its high nucleophilic strength more than compensated for water

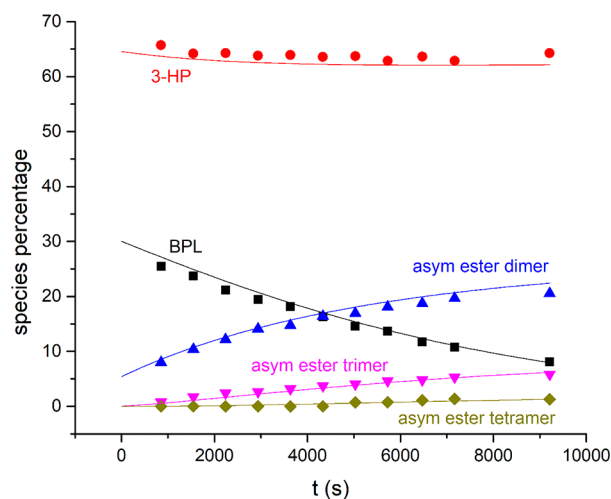
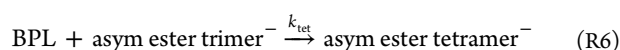
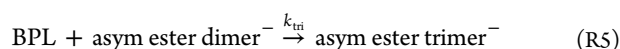
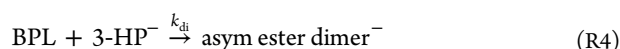


Figure 8. Experimental (points) and modeling (solid line) kinetics results for solution 21.

nucleophile's higher concentration, and Figure 8 directly reveals that oligomerization reactions dominated over hydrolysis. Previous chamber studies have found that the extent of oligomerization is inversely proportional to relative humidity (RH).^{22,28} This result is entirely consistent with the nucleophilic competition discussed above—enhanced aerosol liquid water content (LWC) at higher RH would tend to favor hydrolysis reactions over oligomerization reactions. However, the present results do indicate that oligomerization reactions can remain important at quite high LWC levels.

In an effort to extract kinetic parameters for the oligomer formation evident in Figure 8, a simple kinetic model was constructed. All weak acids (3-HP and its related oligomers) were assumed to have 3-HP's pK_a of 4.5, and the kinetic model enforced instantaneous acid ionization equilibrium on all species. The following reaction mechanism was used:



The k_h and k_{di} values were fixed at the $k_{\text{nucleophile}}$ ' and k_{water} ' water values determined from Table 2. It was found that accurate modeling of the experimental kinetics results was obtained with $k_{tri} = k_{tet} = 1.5 k_{di}$ values. Figure 8 shows that this very simple model is capable of reproducing the experimental kinetics data. It is important to note that because BPL reaction is not catalyzed by Bronsted acids above pH = 0 (unlike many epoxides, including IEPOX and MAE), the oligomerization reactions are actually faster at the higher pH values which support a higher $[3\text{-HP}^-]/[3\text{-HP}]$ ratio. These mechanistic features are similar to those revealed in a previous study of the reactions of epoxides with amines. In that case, the reactions were also found to be general acid catalyzed, and pH was found to play a critical role in controlling the amount of the relevant nucleophiles available for reaction (strongly nucleophilic neutral amines vs weakly nucleophilic protonated amines).⁴⁷

Inorganic Ion Catalyzed Oligomerization Observation.

As discussed in the Introduction, 2-MG-related species with sulfate and nitrate substituent groups have been detected in previous experiments. Therefore, it was of interest to explore the effect of inorganic ions on the products of reactions with BPL. The solution 13, 15, and 17 entries in Table 3 list the final species relative amounts for experiments involving the presence of sulfate, nitrate, and chloride ions, respectively.

As expected from the relatively high nucleophilic strengths for the inorganic ions revealed in the BPL loss kinetics analysis, 3-XP-type products were detected in all three cases, with the yield of these products paralleling the relative nucleophilic strengths ($\text{NO}_3^- < \text{SO}_4^{2-} < \text{Cl}^-$). Since the 3-XP species all have stronger electron withdrawing groups than 3-HP itself, it is expected that the pK_a values for the 3-XP species are lower than that for 3-HP. As discussed above, lower pK_a values lead to higher fractions of the deprotonated acid in aqueous solution. Indeed, the production of X-asym ester dimers from the reaction of BPL with 3-XP containing solutions (13, 15, and 17) was found to be more efficient than the production of asym ester dimers from the reaction of BPL with the similar 3-HP containing solution 7.

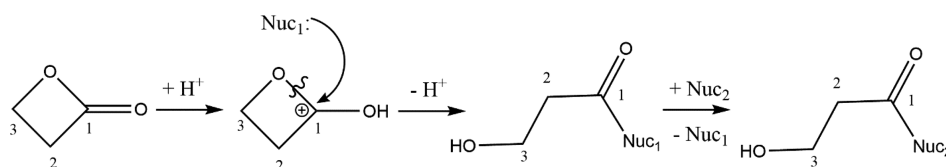


Figure 9. Proposed ester-like acyl intermediate formation followed by nucleophilic substitution mechanism to rationalize inorganic ion-catalyzed asym ester dimer formation.

However, the more efficient production of asym ester dimers for solutions 13, 15, and 17 (5–6%) than for solution 7 (2.25%) is somewhat more difficult to rationalize. Because of the presence of the inorganic nucleophiles in solutions 13, 15, and 17, there is actually less 3-HP produced for these solutions than for solution 7, as the 3-HP column in Table 3 indicates. Nevertheless, if there were some other solution chemistry that served to shift the 3-HP acid ionization toward a higher $[3\text{-HP}^-]/[3\text{-HP}]$ ratio, it is possible that lower concentration 3-HP solutions could still produce relatively high amounts of the asym ester dimer product from BPL reaction. However, these inorganic nucleophiles are weak bases (due to the strength of their conjugate acids), and their presence should not affect the extent of 3-HP ionization. It was also found that the addition of non-nucleophilic ClO_4^- did not lead to the more efficient production of asym ester dimers that followed from the addition of nucleophilic inorganic ions. As discussed in the Introduction, because the molecular structure of lactones resembles both epoxides and esters, it is possible that reactivity of lactones is simultaneously similar to epoxides and esters. While all of that BPL kinetics and product analysis results discussed thus far can be rationalized by the “epoxide-like nucleophilic addition” mechanism given at the top of Figure 1, it is important to consider the possibility manifestations of the “ester-like nucleophile addition” mechanism given at the bottom of Figure 1. The only clear indication of nucleophilic addition at the carbonyl carbon in the literature for BPL is the identification of esters formed from the reaction with methanol under base-catalyzed conditions.⁴⁸ In addition, the only three-membered ring lactone to be isolated and studied, bis(trifluoromethyl)-acetolactone, was shown to react in this fashion.³³ While no inorganic acyl species that are expected to result from the ester-like mechanism for BPL reaction were directly observed in any reaction system, it is possible that such species are reactive intermediates that can affect the final product distribution. In order to explore this possibility, commercially available acetyl chloride was reacted with an equimolar water/ethanol mixture. The reaction was found to proceed to completion more quickly than the time scale of the NMR experiment, and gave roughly equimolar amounts of the products acetic acid (from nucleophilic substitution of water for chloride) and ethyl acetate (from nucleophilic substitution of ethanol for chloride). Therefore, this experiment supports the hypothesis that inorganic acyl intermediates could react fast enough to escape NMR detection and produce ester products. This overall mechanism is depicted in Figure 9, with Nuc_1 representing the inorganic nucleophiles and Nuc_2 representing 3-HP (or its deprotonated form). In the language of organic reaction mechanisms, the last process in Figure 9 is a nucleophilic substitution reaction, with Nuc_1 possessing better “leaving group” properties than Nuc_2 . While no information concerning the aqueous phase reactivity of acyl nitrates and sulfates could be found in the literature, it is well-known that acyl chlorides are quite reactive due to the fact that chloride is an excellent leaving group, stronger than either water or the hydroxy group

nucleophiles of interest in the present mechanism.⁴⁴ In essence, the inorganic nucleophile (Nuc_1) is acting as a catalyst in this overall mechanism to produce esters. It is also worth noting the attack of water nucleophile on BPL via the ester-like mechanism would lead to the same product, 3-HP as does the epoxide-like mechanism. Therefore, a potential role for ester-like reaction for BPL can only be surmised from nonwater nucleophile systems.

Atmospheric Implications. As noted in the Introduction, Nguyen et al. proposed that the lactone HMML could rationalize the various 2-MG-related species observed in isoprene-derived SOA.¹⁷ BPL differs from HMML in that the latter has a more strained 3-membered lactone ring, and has two methyl substituents (one of which is alcohol functionalized) at the noncarbonyl carbon position. The less strained 5-membered lactone, γ -butyrolactone, is known to react only via a Bronsted acid catalyzed process,⁴⁹ thus indicating significantly lower reactivity than for 4-membered BPL. Therefore, it is likely that increased ring strain in HMML would lead to faster rate constants than were observed in the present study of BPL. It is also the case that more alkyl substituted epoxides generally undergo faster reaction than unsubstituted epoxides,³⁷ which suggests even faster HMML reaction as compared to BPL. Thus, since BPL was found to have a general acid-catalyzed, mostly pH-independent lifetime in aqueous solution of about 4 h, the lifetime of HMML is probably significantly shorter. Further, it is quite likely that HMML is a much more reactive intermediate than MAE (which has Bronsted acid catalyzed lifetime of 6.2 days at pH = 1.5),³¹ which would be more consistent with the efficient oligomer formation observed in methacrolein SOA experiments. In the top section of Figure 10, the BPL reaction mechanism determined in the present work is displayed in a similar format to the HMML reaction mechanism proposed by Nguyen et al. in their Figure 10.¹⁷ All species types proposed by Nguyen et al. (hydroxy acids, X-acids, asym ester oligomers, and X-asym ester oligomers) as HMML-derived products were observed as BPL-derived products. In the bottom section of Figure 10, reaction types not suggested by Nguyen et al. are presented. While the sym ether forming product channel shown in the lower right of Figure 10 is a minor pathway, this species, via deprotonation of one or both of its carboxylic acid group, could participate in further major ester-forming oligomerization reactions. Therefore, while the present work showed that the overall oligomerization of BPL was dominated by homogeneous asym ester oligomers, there is the possibility that HMML reaction could lead to some heterogeneous oligomers with both ester and ether linkages. The more important reaction type not suggested by Nguyen et al. is the one depicted in the lower left of Figure 10. As discussed above, it appears that inorganic ions can catalyze the formation of oligomers from BPL. Therefore, this possible oligomerization route should also be considered as possible for HMML.

Since the intrinsic rate of BPL reactions was found to be pH-independent (from pH = 7 to pH = 0), which is inclusive of the atmospherically relevant range,^{50,51} and the oligomerization

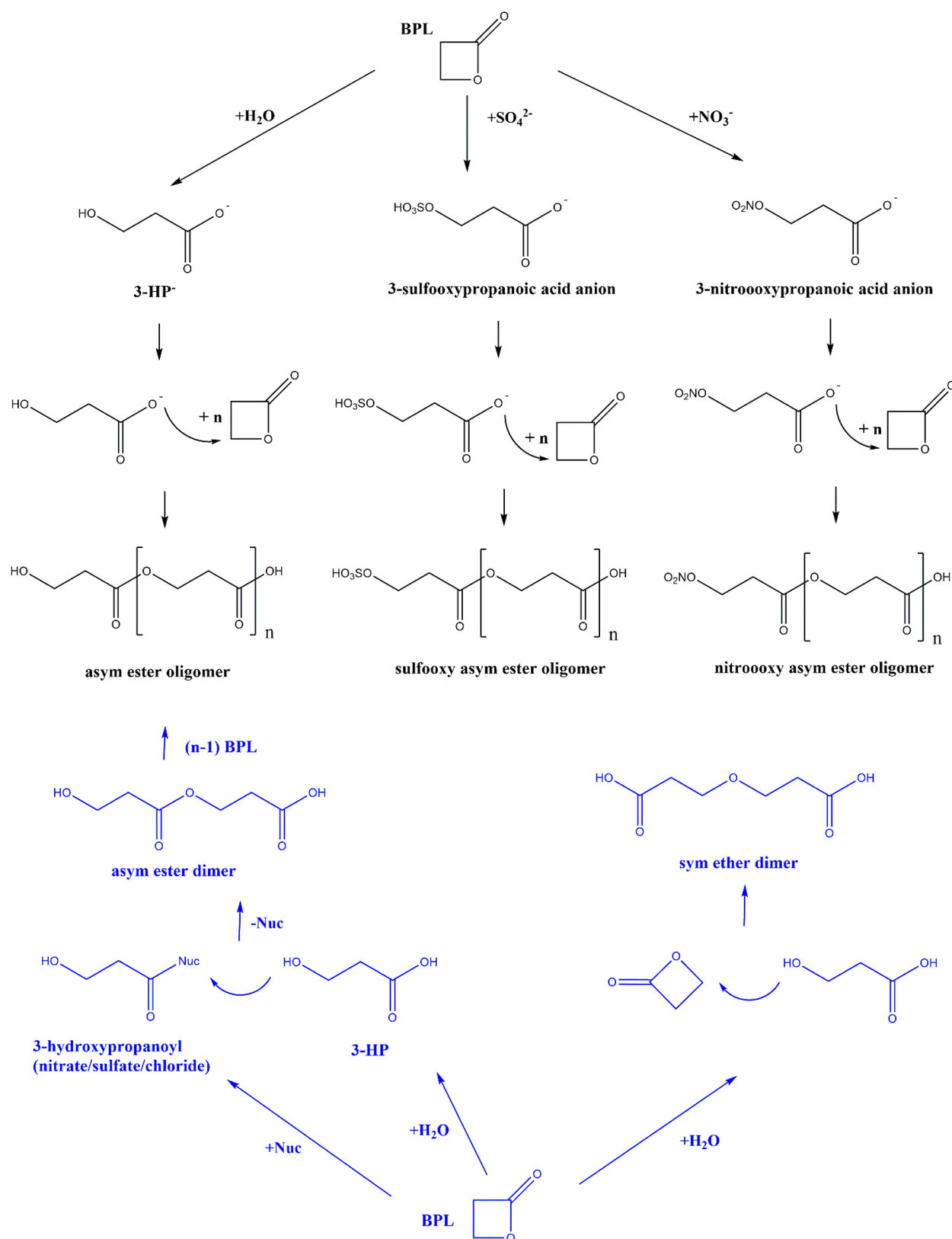


Figure 10. BPL reaction mechanism (steps similar to HMML hypothesis of Nguyen et al. in black, with additional steps uncovered in present work in blue).

reactions were found to be first order in the concentration of the deprotonated acid (which increases with pH), HMML-based oligomerization might actually be more efficient at higher SOA pH values. Specifically, the oligomerization would be expected to

accelerate as pH increases until pH reaches the value where the acid nucleophile nearly completely deprotonated. For example, 3-HP is more than 90% deprotonated at a pH value of 5.5, which is 1.0 units larger than its pK_a value of 4.5. Many field studies have

found that isoprene-derived SOA has only a weak correlation or no correlation at all with SOA acidity.^{16,52,53} The present study is consistent with this observation in that the fraction of isoprene-derived SOA that depends on the HMML precursor is not predicted to be enhanced by increased SOA acidity. Most field studies have shown a convincing correlation between sulfate and isoprene-derived SOA,^{16,52,53} while these studies are less conclusive on the correlation of nitrate with isoprene-derived SOA.^{16,53} In any case, the present study suggests that HMML precursors will interact with inorganic ions to produce products that incorporate the inorganic ion moiety (such as the X-acids and X-asym ester oligomers), and that the inorganic ions may also act as catalysts to more quickly produce SOA constituents.

CONCLUSION

To the extent that BPL is an appropriate proxy for the reactivity of HMML, the present work strongly supports the hypothesis of Nguyen et al., who concluded that the various methacrolein-derived constituents found in SOA who could be rationalized via a series of HMML reactions.¹⁷ In particular, BPL is found to react quickly via a general acid catalyzed mechanism (which is pH-independent over the atmospherically relevant range) and can readily form the whole series of compounds observed in laboratory and field observations for methacrolein-derived SOA. Because of its pH-independent reactivity and the importance of deprotonated acids for efficient oligomerization reactions, it is suggested that oligomerization from lactone intermediates will be more efficient at higher SOA pH values. This result, in combination with the knowledge that IEPOX-based SOA reactions are more efficient at lower pH, may help explain why field observations of overall isoprene-derived SOA formation has been observed to be largely pH-independent.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.7b10411.

¹H and ¹³C NMR assignments for the various species identified in the work and sample ¹H, ¹³C, GHMQC, and GHMBC NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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