Coupling of Lipid Peroxidation and Criegee Intermediate Mediated Autoxidation in the Heterogeneous Oxidation of Linoleic Acid Aerosols

Meirong Zeng^{a*} and Kevin R. Wilson^{b*}

^a College of Smart Energy, Shanghai Jiao Tong University, Shanghai 200240, PR China ^b Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States.

Corresponding Authors*:

Meirong Zeng (email: meirongzeng@sjtu.edu.cn) and Kevin R. Wilson (email: krwilson@lbl.gov)

ABSTRACT

Lipid peroxidation (autoxidation) is an established mechanism for the degradation of organic molecules in the atmosphere and the environment. Autoxidation proceeds via radical chain reactions involving hydroxyl (•OH), peroxy (RO₂•), and alkoxy radicals, which are also prominent

oxidants in the atmosphere. Recent reports have provided evidence for an alternative autoxidation mechanism driven instead by β -hydroxy peroxy $(\beta$ -OH-RO₂•) radicals and Criegee intermediates (CI). This work evaluates the contributions of these two mechanisms in the •OH initiated heterogeneous



oxidation of linoleic acid (LA) aerosols. Reaction kinetics and product distributions are monitored using a vacuum ultraviolet photoionization aerosol time-of-flight mass spectrometer. To explain the observed kinetics, a kinetic model is developed that incorporates both the conventional peroxidation and alternative CI-mediated autoxidation mechanisms. We observe that the CI-mediated autoxidation pathways enhance the heterogeneous autoxidation rate, while the peroxidation reactions, although present, contributes less to the overall oxidation rate. α -acyloxyalkyl hydroperoxides (AAHPs) are identified as key indicators for bimolecular reactions of CI with LA, highlighting the role of LA as a CI scavenger. Moreover, the measured functionalized LA products with hydroxyl or carbonyl group(s), serve as markers for the peroxidation reactions. In summary, this work presents a quantitative framework to understand the coupled reaction network of "OH, RO₂", β -OH-RO₂" radicals, and CI in driving heterogeneous autoxidation, which is crucial for understanding degradation mechanisms of organic molecules in the environment and atmosphere.

KEYWORDS: Lipid peroxidation, Criegee intermediate, β -Hydroxy peroxy radical, α -acyloxyalkyl hydroperoxide, Heterogeneous autoxidation

SYNOPSIS: The traditional lipid peroxidation mechanism and the alternative Criegee intermediate mediated autoxidation mechanism are quantitatively coupled and evaluated in the hydroxyl radical initiated heterogeneous oxidation of linoleic acid.

1. INTRODUCTION

Autoxidation is a major pathway that is responsible for the oxidative degradation of molecules in the environment. In cells autoxidation causes damage when reactive oxygen species (ROS), such as the hydroxyl radical (•OH), hydroperoxyl radical (HO₂•), and hydrogen peroxide (H₂O₂), disrupt the cellular balance between ROS production and antioxidant defenses.¹⁻⁴ In the early 1980s, Porter and others^{5, 6} developed a lipid peroxidation (LP) mechanism centered on the Habstraction reaction from RH to produce an alkyl radical (R[•]), acting as a chain initiation step, which after oxygen addition forms a peroxy radical (RO₂•). This RO₂• radical propagates a radical chain reaction by extracting H-atoms from a second RH, yielding a hydroperoxide (R-OOH) and another alkyl radical (R[•]). The bimolecular reaction of RO₂[•] radicals, leading to the production of alcohols and ketones, terminates the chain reaction. Decomposition of the R-OOH product into •OH and an alkoxy radical (RO•), a chain branching step,⁷ continues the cycle of H-abstraction from RH, further accelerating autoxidation. Autoxidation mediated by •OH, RO₂•, RO•, and R-OOH is thought to be the key reactive steps in lipid peroxidation. This sequence is repeated many times leading to the slow decomposition of lipids, the onset of rancidity in foods and the widespread degradation of organic molecules in the environment. The design of antioxidants is generally based upon this LP mechanism and are aimed at quenching these free radical chain reactions.⁸⁻¹¹ In the atmosphere, RO₂[•] radicals and R-OOH have been shown to be key reactive species in multiphase autoxidation with significant environmental and health impacts.^{7, 12-14}

In recent studies, however, an alternative autoxidation mechanism has been reported and centers on Criegee Intermediates (CI) formed during reactions of *OH radicals with unsaturated lipids or alkenes.¹⁵⁻¹⁷ Here we refer to this mechanism as CI-mediated autoxidation (CIMA). The radical chain is initiated by the addition of *OH to the C=C bond of an alkene, generating a β -hydroxy alkyl radical, followed by the addition of O₂ to form a β -hydroxy peroxy radical (β -OH-RO₂*). Based on experimental evidence for the existence of CI reactions with water (or alcohols), which form unique hydroperoxide products, Beauchamp and coworkers first proposed that the CI could form via the dissociation of β -OH-RO₂*.^{15, 16} Wilson and coworkers developed CIMA further and proposed that CI-mediated *OH regeneration, i.e., CI \rightarrow *OH + vinoxy radical,¹⁸ acts as a propagation step, which significantly enhances the apparent heterogeneous reaction rate of *OH with squalene, linoleic acid, oleic acid, and arachidonic acid.¹⁷ This conclusion was based, in part, upon the detection of secondary ozonides (SOZs) and functionalized R-OOHs that serve as fingerprint for chain termination products in the presence of CI reactions.¹⁷

In this work we focus on the oxidation of linoleic acid (LA, C₁₈H₃₂O₂) by •OH. LA is a polyunsaturated fatty acid and a common lipid component containing two C=C bonds.¹⁹⁻²¹ The LA oxidation products as well as their formation pathways remain somewhat controversial.^{17, 22-24} The main oxidation products are commonly identified as functionalized LA species that are primarily formed through bimolecular reactions involving two peroxy radicals.²²⁻²⁴ For instance, Nah *et al.*^{22, 23} measured a series of these products that had one or more hydroxyl and/or carbonyl functional groups on the LA backbone. These products are denoted LAO, LAO₂, LAO₃, etc. In contrast, our recent work suggests the formation of a new class of products: α-acyloxyalkyl hydroperoxides (AAHPs) produced from bimolecular reactions of CI with LA.¹⁷

Our objective is to further elucidate the heterogeneous autoxidation mechanism of LA and [•]OH. The heterogeneous oxidation of LA by [•]OH is measured in a continuous flow stirred tank reactor. A vacuum ultraviolet aerosol mass spectrometer (VUV-AMS) is used to identify products and to measure the reaction kinetics as a function of [[•]OH] and reaction time. To interpret the data, a kinetic model is developed that includes both the lipid peroxidation (LP) and alternative CImediated autoxidation (CIMA) mechanisms. Lastly, an in-depth reaction pathway and sensitivity analysis is performed to quantitatively evaluate the relative importance of the two mechanisms (*i.e.*, LP vs. CIMA) in explaining LA decomposition, [•]OH regeneration, CI consumption, and product formation.

2. MATERIALS AND METHODS

2.1. Experimental Details

Heterogeneous autoxidation kinetics of LA are measured as a function of [*OH]. The heterogeneous reaction is conducted in a continuous flow stirred tank reactor (CFSTR).^{17, 25} The reaction kinetics are monitored using the VUV-AMS.²⁶⁻²⁸ The experimental setup has been thoroughly described in prior studies,²⁹⁻³¹ thus only an overview is provided here. Polydisperse LA aerosols are created via homogeneous nucleation by passing nitrogen (0.3 standard liter per minute, SLM) through a heated Pyrex tube filled with liquid LA. Stable particle generation is achieved at an oven temperature of 117 °C. LA aerosols, with an average particle diameter of approximately 160 nm, are then passed through an annular activated charcoal denuder to remove residual gas-phase species produced during nucleation. These particles are then mixed with hydrogen peroxide (H₂O₂) vapor, N₂, O₂, and a gas-phase tracer, to achieve a total flow of 1.1 SLM. The H₂O₂ vapor is produced by passing N₂ (0.1 SLM) through a heated bubbler (60 °C) containing a 1:1 mixture of solid urea-hydroperoxide (CO(NH₂)₂·H₂O₂, Sigma-Aldrich, 97% pure) and sand (SiO₂, 50-70

mesh particle size, Sigma-Aldrich). A flow containing the gas-phase tracer (2-methyl-2-butene, ~200 ppb in the CFSTR) is introduced to determine the [•OH] using a mixed-phase relative rate technique described in previous studies.²⁵

Before each experiment, the CFSTR is thoroughly purged with dry N₂ for several hours to eliminate residual particles and gas-phase components from previous experiments. Subsequently, the reactor is filled with reagents (LA particles, H₂O₂, tracer, N₂, and O₂) in the absence of light (*i.e.*, no reactions). Upon turning on the UV lamps (blacklights, $\lambda \sim 356$ nm), gas-phase H₂O₂ is photolyzed to produce *OH radicals, initiating the reaction. The chemical evolution of the reaction mixture is monitored as a function of time using the following instruments. The concentration of the tracer, namely 2-methyl-2-butene, is quantified using a gas chromatograph equipped with a flame ionization detector (GC-FID, SRI Instruments 8610C). This allows the average [*OH] in the CFSTR to be determined. A scanning mobility particle sizer (SMPS, TSI, 3080L DMA, and 3025A CPC) measures the particle size distribution. The chemical composition of the aerosol is analyzed using the VUV-AMS at the Chemical Dynamic Beamline 9.0.2, located at the Advanced Light Source, Lawrence Berkeley National Laboratory in Berkeley, California, USA.

To measure LA autoxidation under indoor [$^{\circ}$ OH],¹⁴ the reactions of LA particles were investigated across six [$^{\circ}$ OH] ranging from 3.0 × 10⁶ to 1.7 × 10⁷ molecules·cm⁻³. A series of mass spectra were recorded, tracking lipid autoxidation as a function of reaction time. Difference mass spectra, which reveal reaction products, are obtained by subtracting the unreacted spectrum from the reacted one. Figure 1A displays a representative difference mass spectrum at [$^{\circ}$ OH] = 1.4 × 10⁷ molecules·cm⁻³. From the mass spectra we can identify four distinct classes of reaction products. First, smaller aldehydes and acids (shown in purple in Fig. 1A) with mass-to-charge ratios (*m/z*) of 140, 172, and 212 are identified and arise from decomposition reactions of β -OH-RO₂• radicals. Second, four acids (or diacids) with *m/z* of 116, 156, 188, and 228 are identified and serve as fingerprint products arising from isomerization reactions of CI (shown in blue in Fig. 1A). Third, peaks at *m/z* = 262, 378, 418, 450, and 490 are identified to be fragments arising from dissociative photoionization of α -acyloxyalkyl hydroperoxides (AAHPs, shown in Red in Fig. 1A). Finally, functionalized LA products with hydroxyl or carbonyl group(s), denoted as LAO and LAO₂ with *m/z* 294, 296, 308, 310, and 312, are observed and shown in green in Fig. 1A. Detailed product assignments are provided in the Section 3.



Figure 1. (A) Difference mass spectra (reacted LA – unreacted LA) recorded at the $[^{\bullet}OH] = 1.4 \times 10^{-7}$ molecules·cm⁻³. (B) The CI-mediated autoxidation (CIMA) mechanism of LA driven by the reactions of Criegee intermediate (CI). (C) The lipid peroxidation (LP) mechanism controlled by reactions of peroxy radicals (RO₂[•]) and hydroperoxides (R-OOH).

2.2. Simulation Methods

Kinetiscope[®] has been used to develop chemical kinetic models simulating the heterogeneous reactions of particles upon the exposure of gas-phase oxidants.³²⁻³⁶ This method, which is thoroughly described in prior studies,³²⁻³⁶ is briefly summarized here. The LA particles are modelled as a single instantaneously mixed compartment with dimensions $1 \text{ nm} \times 1 \text{ nm} \times (R/3)$ nm, where R is the measured radius of the particles to properly represent the surface-to-volume scaling in spherical particles. The heterogenous process proceeds in three stages: the adsorption of gas-phase •OH radicals onto the particles, leading to the formation of adsorbed •OH radicals; the condensed-phase reactions of LA initiated by adsorbed •OH radicals; and the evaporation of volatile components. The adsorption and evaporation steps are examined in our previous work.³⁰ Here, we focus on the formulating a realistic autoxidation mechanism in the condensed-phase, which is shown in detail in Table S1.

Figures 1B and 1C show two distinct autoxidation pathways: one driven by β-OH-RO₂• and CI reactions (CIMA) and the other lipid peroxidation mechanism (LP) by RO₂• and R-OOH. These reaction pathways are used to examine the experimental observations in two respects. First, to explain the formation of distinctive products, such as AAHPs and acids (or diacids) depicted in Figure 1A, which underscores the need to include CI reaction pathways. Notably, AAHPs (colored red in Figs. 1A and 1B) are widely proposed to originate from reactions of CI with acids.^{37, 38} Zeng and Wilson observed evidence for the formation of CI during the heterogeneous reactions of squalene and •OH radicals,³⁹ which serves as the basis for proposing the CI-mediated autoxidation mechanism in current model. Second, functionalized LA products (denoted LAO and LAO₂) with additional hydroxyl or carbonyl group(s) (colored green in Fig. 1A), have been experimentally measured. Historically, similar products were attributed to bimolecular reactions of two RO₂•

radicals, which lead to the formation of alcohol and ketone products.^{40, 41} For instance, Zhang et al. recently explored RO_2^{\bullet} reactions and their significance in regulating the autoxidation process,¹² so these reactions in Figure 1C were proposed based on this prior work.¹²

The CIMA mechanism is initiated by an 'OH addition reaction to carbon-carbon double bond(s) of LA, yielding a β -OH-R[•] radical (R1, Table S1), which then undergoes an O₂ addition reaction to form a β -OH-RO₂[•] radical (R6, Table S1). As originally proposed by the Beauchamp group,^{15, 16} the unimolecular dissociation of the β -OH-RO₂[•] radical generates a CI and an α hydroxy alkyl radical (α -OH-R[•], R8, Table S1), whose bimolecular reaction with O₂ explains the formation of smaller oxygenated products (shown as R-CO, R17, Table S1). More recently, alternative bimolecular reactions of β -OH-RO₂• radicals were proposed to generate CI,^{39, 42, 43} but it was found that these pathways cannot explain the heterogeneous kinetics of squalene with 'OH radicals.³⁹ Thus, CI formation from the unimolecular dissociation pathway of β -OH-RO₂• radical is assumed in the present model. Additionally, bimolecular reactions of β -OH-RO₂• radical were considered, such as its reactions with β -OH-RO₂[•] radical to generate RO[•] radicals (R9, Table S1), or to form a β -hydroxy alcohol and ketone (R11, Table S1). Once a CI is formed, it primarily undergoes unimolecular dissociation to produce 'OH radical (R13, Table S1), isomerization to form acid or diacid (R14, Table S1), and bimolecular reactions with LA or acid products to generate AAHPs (R5 or R15, Table S1).

In contrast, Figure 1C highlights the steps in the LP mechanism that are incorporated in the present model. The radical chain starts with the H-abstraction at an allylic site on LA by ${}^{\circ}OH$, resulting in the formation of R ${}^{\circ}$ radical (R2, Table S1). Subsequently, the addition of O₂ to R ${}^{\circ}$ radical yields a RO_{2 ${}^{\circ}$} radical (R7, Table S1). Unlike the CIMA mechanism, RO_{2 ${}^{\circ}$} is consumed in

bimolecular reactions without the formation of CI. Bimolecular reactions of $RO_2^{\bullet} + RO_2^{\bullet}$, can produce two RO[•] radicals (R10, Table S1) or the formation of functionalized LA products (LAO, R12, Table S1). The bimolecular H abstraction reaction of RO_2^{\bullet} with LA (R4, Table S1) results in the generation of a hydroperoxide (R-OOH) and R[•], which is the propagation step in the LP mechanism. Additionally, the unimolecular dissociation (by light or heat) of R-OOH yields [•]OH and RO[•] radicals (R18, Table S1), serving to amplify the chain reaction. The RO[•] radical then consumes LA through H-abstraction (R3, Table S1), further perpetuating the radical recycling.

3. RESULTS AND DISCUSSION

Figure 2 provides an overview of the evolution of LA and its reaction products vs. time at $[^{\bullet}OH] = 8.3 \times 10^{6}$ molecules·cm⁻³. Figures S1 to S5 show the kinetics under five additional $[^{\bullet}OH]$ ranging from 3.0×10^{6} to 1.7×10^{7} molecules·cm⁻³. The four products classes, based on their formation reactions, are assigned a distinct color matching the labeled products in the difference mass spectra shown in Figure 1A and the mechanisms depicted in Figs. 1B and 1C. These include smaller aldehydes and acids (Figures 2E to 2G), acids or diacids (Figures 2I to 2L), AAHPs (Figures 2D and 2H), and functionalized LA products (Figures 2B and 2C). These profiles serve as a quantitative data for evaluating the coupled mechanism, which is organized into three sections. The decay kinetics of LA as a function of reaction time and [°OH] serves as a quantitative benchmark for assessing the overall heterogeneous autoxidation rate discussed in Section 3.1. Second, smaller oxygenated products and AAHPs that report on CI reactions are examined in Section 3.2. Lastly, the functionalized LA products (LAO and LAO₂) produced by reactions of RO₂[•] and β-OH-RO₂[•] radicals are examined in Section 3.3.



Figure 2. Experimental (symbols) and simulated (lines) concentrations of linoleic acid (LA), functionalized LA products (LAO and LAO₂), α -acyloxyalkyl hydroperoxides (AAHPs), 3-nonenal (C₉H₁₆O₂), 9-oxononanoic acid (C₉H₁₆O₃), 12-oxo-9-dodecenoic acid (C₁₂H₂₀O₃), hexanoic acid (C₆H₁₂O₂), 3-nonenoic acid (C₉H₁₆O₂), azelaic acid (C₉H₁₆O₄), and 3-dodecenedioic acid (C₁₂H₂₀O₄) as a function of reaction time at [•OH] = 8.3×10^6 molecules·cm⁻³.

3.1. Effective Reaction Probabilities and Heterogeneous Autoxidation Rates

Figure 3A shows the computed effective reaction probability (γ_{eff}) of LA as a function of [•OH] (3.0×10^6 to 1.70×10^7 molecules·cm⁻³). Each γ_{eff} is computed from the decay kinetics of LA as a function of reaction time, as shown in Figure 3B. γ_{eff} increases as the •OH concentration decreases. This trend is a distinctive signature for autoxidation, though the underlying autoxidation mechanism remains under unclear. For instance, Zeng *et al.*^{17, 39} observed a similar trend in

squalene, where decreasing [•OH] led to an increased γ_{eff} , which was explained by a CI-mediated autoxidation mechanism. Zhang *et al.*¹² also reported an analogous trend in γ_{eff} for saturated acid particles, including adipic acid, succinic acid, citric acid, and 3-methylgluaric acid. Zhang *et al.* explained these observations using the LP mechanism and by reactions of RO₂•, RO•, and R-OOH. While the former study centers on squalene, an alkene with six carbon-carbon double bonds, the later study explored saturated acids, without carbon-carbon double bonds.



Figure 3. (A) Experimental (symbols) and simulated (lines) γ_{eff} of LA as a function of [•OH] (molecules·cm⁻³). (B) Experimental (symbols) and simulated (lines) decay of LA as a function of reaction time under various [•OH]. (C) The contributions of LA consumption reactions (labeled as R1 to R5) at the reaction time of 3300 s and [•OH] = 8.3×10^6 molecules·cm⁻³. (D) Experimental (symbols) and simulated (lines) decay kinetics of LA as a function of reaction time at [•OH] = 8.3×10^6 molecules·cm⁻³, using different models.

As illustrated in Figures 1B and 1C, the radical chain initiation steps in these two autoxidation mechanisms differ significantly, with one involving 'OH addition to LA and the other a H-abstraction reaction of LA. To gain a better understanding, an analysis of LA consumption reactions is conducted by monitoring its competitive reactions. In the current model, five distinct categories of LA consumption reactions (*i.e.*, reactive sinks) are considered, as depicted in Figure 3C. These include 'OH addition to LA (R1, Table S1), H-abstraction reactions of LA by 'OH (R2, Table S1), RO' (R3, Table S1), and RO₂[•] (R4, Table S1). Bimolecular reactions between LA and CI (R5, Table S1), leading to the formation of AAHPs, are also included in this analysis.

This reaction pathway analysis reveals that LA is mainly consumed (~52% of the total reactions) through *OH addition reactions (R1, Table S1), with H-abstraction reactions (R2, Table S1) accounting for a smaller fraction (~22%). This breakdown in reactivity follows closely from the respective rate constants. For example, the rate constant for *OH addition to each carbon-carbon double bond to produce β -OH-RO₂* radical is 6.6×10^{-11} cm³·molecule⁻¹·s⁻¹.⁴⁴ Therefore, the total rate constant for two C=C bonds of LA is ~1.32 × 10⁻¹⁰ cm³·molecule⁻¹·s⁻¹. For comparison, H-abstraction reactions of LA by *OH, incorporate contributions from various sites, including the biallylic site (2 H atoms),⁴⁵ allylic sites (4 H atoms),⁴⁶ alkyl -CH₂ sites (18 H atoms),⁴⁷ and -CH₃ site (3 H atoms),⁴⁷ with an estimated total rate constant of ~4.5 × 10⁻¹¹ cm³·molecule⁻¹·s⁻¹. The ratio between these rate constants for *OH addition and H-abstraction explains their relative importance, as shown in Figure 3C. Additionally, approximately 25% of LA undergoes bimolecular reactions with CI, thereby highlighting the significance of LA itself as a CI scavenger.

From the reaction pathway analysis above, it becomes evident that the H-abstraction reactions have a smaller impact on the overall consumption rate of LA. To further quantify the significance of lipid peroxidation reactions under the present conditions, a test model (designated as Test model 1) is constructed. This test model excludes lipid peroxidation reactions from the base model, which includes the H-abstraction reactions of LA by the attack of °OH (R2, Table S1), RO° (R3, Table S1), and RO₂° radicals (R4, Table S1), as well as subsequent reactions involving RO₂° radicals (R7, R10, and R12, Table S1) and R-OOH (R18, Table S1). As depicted in Figure 3D, simulations using this test model closely match both the experimental data and the base model simulations at [°OH] of 8.3×10^6 molecules cm⁻³. This suggests that eliminating these lipid peroxidation reactions have a negligible effect on the predicted LA decay kinetics. In other words, the lipid peroxidation mechanism makes a smaller contribution to the autoxidation process of LA than does CIMA. Further simulations of the LA decay using Test model 1 as a function of [°OH] is shown in Figure S6.

A second test model, designated as Test model 2, is formulated to assess the importance of the CIMA mechanism. This test model excludes the **°**OH addition reactions to LA that lead to the formation of β -OH-R**°** radicals (R1, Table S1), along with relevant reactions involving β -OH-R**°** (R6, Table S1), β -OH-RO₂**°** (R8, R9, and R11, Table S1), β -OH-RO[•] (R16, Table S1), CI (R5, R13-R15, Table S1), and AAHP (R19, Table S1). As illustrated in Figures 3D and S7, simulations using Test model 2 predict a significantly slower LA decay than is observed in the experiment or the base model simulations. This difference further highlights the central role that the autoxidation mechanism initiated by **°**OH addition plays in capturing the autoxidation rate of LA. To gain insights into the role of CI reactions in the autoxidation process, an additional test model 3 is constructed by specifically excluding CI reactions (R5, R13-R15, Table S1) from the base model.

Notably, this Test model 3 underestimates the decay rate of LA as shown in Figures 3D and S8, indicating that CI reactions promote the heterogeneous autoxidation reactivity of LA.

Recognizing the importance of 'OH radicals in chain cycling, a reaction pathway analysis for •OH regeneration is conducted, as illustrated in Figure S10. The current model encompasses three distinct pathways for 'OH formation: the unimolecular dissociation reactions of CI (R13, Table S1), AAHP (R19, Table S1), and R-OOH (R18, Table S1). Notably, AAHPs are generated from bimolecular reactions between CI and acids, including LA itself. Furthermore, CI can be traced to the β -OH-RO₂ radical, which originates from the OH addition-initiated autoxidation process. Regarding R-OOH, it is produced from bimolecular reaction of RO₂[•] radicals and LA (R4, Table S1), where RO_2^{\bullet} radicals participate in the lipid peroxidation reaction network, initiated by Habstraction of LA. As evident from Figure S10, the primary regeneration source of •OH is the direct unimolecular dissociation of CI. In contrast, the dissociation of AAHPs contribute less (~ 10%), while the contribution from R-OOH reaction is minimal (< 1%) at a reaction time of 3300 seconds under $[^{\bullet}OH] = 8.3 \times 10^{6}$ molecules cm⁻³. Therefore, we conclude that $^{\bullet}OH$ radicals are predominantly produced either directly through the unimolecular dissociation of CI or indirectly through AAHPs (i.e., $CI \rightarrow AAHP \rightarrow OH$). In other words, CI reactions amplify the autoxidation process by regenerating 'OH radicals, which subsequently consume LA molecules.

3.2. Fingerprint Products Consistent with the CIMA Mechanism

This section examines CI reactions and their characteristic fingerprint products. As illustrated in Figure 4A, four distinct β -OH-RO₂• radicals are formed in LA autoxidation. This is because LA has two carbon-carbon double bonds, enabling •OH addition at four specific locations, labeled 6, 7, 9, and 10 in Fig. 4A, thereby generating four distinct β -OH-R• radicals. Upon O₂ addition, these β-OH-R• radicals become four β-OH-RO₂• radicals, whose chemical structures are shown in Figure 4A. The bond dissociation reactions of the β-OH-RO₂• radicals yield four α-hydroxy alkyl radicals (α-OH-R•) and four distinct CIs. Following this, the bimolecular reactions of α-OH-R• radicals with O₂ lead to the formation of *n*-hexanal (C₆H₁₂O, *m/z* =100), 3-nonenal (C₉H₁₆O, *m/z* = 140), 9-oxononanoic acid (C₉H₁₆O₃, *m/z* = 172), and 12-oxo-9-dodecenoic acid (C₁₂H₂₀O₃, *m/z* = 212). The kinetics of these four products are experimentally monitored as a function of reaction time and [•OH]. For instance, the proposed reactions in the current model replicate the observed evolution of C₁₂H₂₀O₃, as illustrated in Figure 4B.



Figure 4. (A) Reaction pathways of β -OH-RO₂[•] radicals to produce α -OH-R[•] radicals and CIs, subsequently yielding aldehydes, acids, and diacids. (B and C) Experimental (symbols) and

simulated (lines) results of 12-oxo-9-dodecenoic acid ($C_{12}H_{20}O_3$) and 3-dodecenedioic acid ($C_{12}H_{20}O_4$) as a function of reaction time and [•OH].

Once formed the CI can undergo unimolecular isomerization reaction to generate an acid,^{48,} 49 which is a well-established maker of CI chemistry during the heterogeneous reactions of LA + O₃. For instance, Müller et al.⁴⁹ identified peaks at m/z 115, 155, 187, and 227 (in their deprotonated forms) and assigned them to acids arising from the isomerization reactions of CIs. In that study, these CIs originate from the unimolecular dissociation of primary ozonides (POZs), generated by the addition of O₃ to the carbon-carbon double bonds of LA. However, in the context of heterogeneous reactions of LA with •OH radicals, similar acid products are rarely reported.¹⁷ In this work, a series of peaks at m/z of 116, 156, 188, and 228 are identified to be C₆H₁₂O₂, C₉H₁₆O₂, C₉H₁₆O₄, and C₁₂H₂₀O₄, respectively. Further reaction analysis reveals that these products are acids or diacids (denoted as R-COOH), specifically hexanoic acid, 3-nonenoic acid, azelaic acid, and 3dodecenedioic acid, as illustrated in Figure 4A. This work suggests an alternative pathway for acid formation in the absence of O₃: LA + ${}^{\bullet}OH \rightarrow \beta$ -OH-RO₂ ${}^{\bullet} \rightarrow CI \rightarrow R$ -COOH, distinct from the more conventional ozonolysis pathway of LA + $O_3 \rightarrow POZ \rightarrow CI \rightarrow R$ -COOH.^{48, 49} The kinetic evolution of these acids provides valuable insights into the submechanism of CI within the present model. For example, the kinetic model reasonably explains the formation trends of acids or diacids, such as 3-dodecenedioic acid ($C_{12}H_{20}O_4$) illustrated in Figure 4C.

Apart from CI unimolecular dissociation reaction (R13, Table S1) and CI unimolecular isomerization reaction of (R14, Table S1), the CI can be consumed in bimolecular reactions with carboxylic acids to yield α -acyloxyalkyl hydroperoxides (AAHPs). LA is present in the aerosol in large quantities and thus promotes this bimolecular reaction evidenced by a series of product peaks at m/z of 262, 378, 418, 450, and 490 that are assigned to AAHPs. Figure 5A illustrates the

bimolecular reactions of LA with four distinct CIs, resulting in the generation of four AAHPs with chemical compositions of $C_{24}H_{44}O_4$, $C_{27}H_{48}O_4$, $C_{27}H_{48}O_6$, and $C_{30}H_{52}O_6$. Although peaks corresponding to these exact masses are not observed in the spectra, these products are instead detected after water elimination as fragments at m/z 378 ($C_{24}H_{42}O_3$), 418 ($C_{27}H_{46}O_3$), 450 ($C_{27}H_{46}O_5$), and 490 ($C_{30}H_{50}O_5$), which is consistent with previous observations.¹⁷ Additionally, the peak at m/z 262 ($C_{18}H_{30}O$) was identified as another fragment of AAHPs produced by dissociative photoionization as illustrated in Figure 5A. This dissociative photoionization pathway is proposed based on an analogous observations by Welz *et al.*⁵⁰ In their work, the reaction between a CI (CH₂OO) and formic acid (HCOOH) was expected to yield hydroperoxyalkyl carboxylate (HPMF, $C_2H_4O_4$), but this was not experimentally observed.⁵⁰ Instead, a peak at m/z 64 was attributed to dissociative photoionization fragment of HPMF. Figure S9 offers a more direct comparison of these photoionization fragmentation pathways.



Figure 5. (A) Reactions of linoleic acid with four Criegee intermediates (CIs) generating α -acyloxyalkyl hydroperoxides (AAHPs). The dissociative VUV photoionization fragment peaks of AAHPs are labeled. (B) Normalized experimental signals of five distinct AAHP fragments detected at *m*/*z* 262, 378, 418, 450, and 490. (C) Experimental (symbols) and simulated (lines) concentrations of a C₃₀ AAHP (C₃₀H₅₂O₆), using *m*/*z* 262 as a representative AAHP fragment.

Figure 5B shows the kinetic evolution and characterization of AAHP fragments. Notably, the evolution of these AAHP fragments as a function of reaction time exhibits remarkable consistency, thereby validating the photoionization fragment pathways for their generation from AAHPs discussed above, particularly for m/z 262. This fragment peak, with its pronounced intensity above all other AAHP fragments, serves as the representative benchmark for comparison with simulated results, further constraining the submechanism of AAHPs in the current kinetic model. The submechanism of AAHPs includes the sole formation pathway from the bimolecular reactions of

CIs with LA or acid products (R5 or R15, Table S1). Conversely, AAHP consumption occurs via multiple pathways, including bimolecular reactions with 'OH radicals, via addition or Habstraction, and unimolecular 'OH elimination reactions (R19, Table S1). R19 is a secondary means of regenerating 'OH radicals in this system, as demonstrated in Figure S10. In other words, an alternative propagation pathway is: LA + 'OH $\rightarrow \beta$ -OH-RO₂' \rightarrow CI \rightarrow AAHP \rightarrow 'OH, emphasizing the role of CI reactions in driving heterogeneous oxidation. As shown in Figure 5C, the present model can reasonably explain the observed kinetics of AAHPs as a function of reaction time and ['OH].

After carefully examining the submechanism of CI in relation to product formation, a subsequent analysis of CI reaction pathways was conducted. Figure S11 clearly illustrates the relative contributions of three distinct CI consumption pathways: unimolecular 'OH elimination (R13, Table S1), unimolecular isomerization (R14, Table S1), and bimolecular reactions with R-COOH forming AAHPs (R5 and R15, Table S1). Vereecken et al.¹⁸ developed theory-based structure-activity relationships (SARs) for unimolecular reactions of CI with diverse substituents, emphasizing over half of CI loss is attributed to the unimolecular decay. The rate constants for these unimolecular reactions of CI (R13 and R14, Table S1) in the present model were derived from Vereecken *et al.*¹⁸ Reynolds *et al.*³⁸ reported that the CI + R-COOH reaction acts as a CI scavenger, outcompeting the unimolecular decay of CI under acid-rich experimental conditions. In their work, CIs were formed from reactions of alkene with O₃, while a saturated acid (2hexyldecanoic acid) served as an additive. In contrast, this work utilizes reactions between LA and •OH to generate CIs, with LA itself acting as a CI scavenger within the particles. As shown in Figure S11, the ratio of unimolecular decay (R13 and R14, Table S1) and bimolecular reaction (R5 and R15, Table S1) is approximately 1:1. This is consistent with Reynolds et al.³⁸ and further underscores the facile competition between unimolecular and bimolecular reactions of CI in organic aerosols.

3.3. Products Consistent with the LP Mechanism

Figure 6 illustrates the experimental and simulated kinetic profiles of the functionalized LA products: LAO and LAO₂. For LAO, two distinct peaks at m/z 294 and 296 are observed, corresponding to C₁₈H₃₀O₃ and C₁₈H₃₂O₃. The peak at m/z 294 represents LAO with an additional carbonyl group (denoted as R-CO), whereas the one at m/z 296 is LAO with an additional hydroxyl group (denoted as R-CO), comparing to LA (C₁₈H₃₂O₂). For LAO₂, three peaks are observed at m/z 308, 310, and 312 corresponding to C₁₈H₂₈O₄, C₁₈H₃₀O₄, and C₁₈H₃₂O₄. These LAO₂ are hypothesized to be oxygenated LA products with one or more hydroxyl, carbonyl, or hydroperoxide groups. For instance, C₁₈H₂₈O₄ could be an oxidized LA, containing two additional carbonyl groups, compared to the reactant LA. Figure 6B further elucidates the temporal evolution of LAO and LAO₂ at [°OH] = 8.3×10^6 molecules·cm⁻³. The normalized intensities of LAO peaks (m/z 294 and 296) exhibit similar trends, indicating they are formed nearly simultaneously. Similarly, the LAO₂ peaks display a high degree of similarity in their normalized intensities.



Figure 6. (A) The H-abstraction initiated peroxidation reactions to produce functionalized LA products (LAO and LAO₂). (B) The normalized signals of LAO peaks at m/z 294 and 296, as well as LAO₂ peaks at m/z 308, 310, and 312. (C and D) Experimental (symbols) and simulated (lines) results of representative LAO (m/z 294) and LAO₂ (m/z 312).

According to the traditional LP mechanism outlined in Porter *et al.*,¹ bimolecular reactions involving RO₂• radicals, resulting from H-abstraction reactions of fatty acids, produce the oxygenated products. For example, Nah *et al.*^{22, 23} observed a series of functionalized LA products and attributed their formation to bimolecular reactions of β -OH-RO₂• radicals, which were

initiated by •OH addition reactions of LA. Zhang *et al.*⁵¹ further explored the hydroxyl radical oxidation of oleic acid (OA), a fatty acid structurally analogous to LA but having only a single carbon-carbon double bond. A series of peaks were observed corresponding to functionalized OA products, consistent with both β -OH-RO₂• radicals and RO₂• radicals contributing significantly to the formation of functionalized OA products.

To investigate the relative contributions to the formation of functionalized LA products, the present model incorporates reactions involving both β -OH-RO₂• radicals and RO₂• radicals. Figure 1 offers a skeletal overview, while Figures 6A and S13 show a more detailed mechanism for the formation of these species. Specifically, Figure 6A outlines the representative pathways leading to the formation of LAO (*m/z* 294 and 296). These involve a H-abstraction reaction at the bi-allylic site of LA, generating a conjugated R• radical that subsequently contributes to the production of a RO₂• radical. Following the pathways proposed by Benneett,⁴¹ Summers⁴¹ and Russell,⁴⁰ bimolecular reactions of this RO₂• radical form products with either an additional carbonyl (C₁₈H₃₀O₃, *m/z* 294) or a hydroxyl (C₁₈H₃₂O₃, *m/z* 296) group. In other words, the LAO peaks observed in this work are attributed to reactions involving RO₂• radicals. As illustrated in Figure 6B, this sub mechanism for LAO production in the kinetic model reasonably captures the observed trends in C₁₈H₃₀O₃.

The subsequent oxidation of LAO produces LAO₂, i.e., $C_{18}H_{28}O_4$, $C_{18}H_{30}O_4$, and $C_{18}H_{32}O_4$, as shown mechanistically in Figure 6A. For example, the kinetics of $C_{18}H_{32}O_4$ (*m/z* 312) is shown in Figures 6D and S12. The simulated profiles of three $C_{18}H_{32}O_4$ isomers are summarized and compared with experiment values. These isomers include molecules with a hydroperoxide group (denoted as R-OOH), or two hydroxyl groups (R-OH), or combination of a hydroxyl group and a carbonyl group (β -OH-RCO). The reaction pathways for these isomers are compared in Figure

S13. First, the bimolecular reaction of a RO₂• radical with RH (e.g., LA) forms R-OOH and R• radical, as illustrated in Figure S13A. Second, R-OH is derived from LAO via the H-abstraction reaction, as illustrated in Figures 6A and S13B. Lastly, β -OH-RCO is proposed to be produced from the bimolecular reaction of two β -OH-RO₂• radicals, initiated by •OH addition to LA, as illustrated in Figure S13C. As depicted in Figure S12, R-OOH forms earlier than β -OH-RCO, which is faster than R-OH. The agreement between simulated and experimental kinetics of C₁₈H₃₂O₄ validates the submechanism for the formation of LAO₂ isomers.

4. Atmospheric Implications

In this work, we present direct evidence for the heterogeneous autoxidation of LA, a model organic acid, initiated by 'OH radicals. The substantial increase in γ_{eff} observed under lower ['OH] signifies an increase in the autoxidation rate. Distinct fingerprint products, including acids, diacids, aldehydes, and α -acyloxyalkyl hydroperoxides, confirm the presence of CI chemistry (in the absence of O₃), while functionalized LA products are consistent with reactions of RO₂ and β -OH-RO₂ radicals. To explain these observations, a kinetic model is developed that combines both the peroxidation (dominated by RO₂ and R-OOH reactions) and a CI-mediated autoxidation mechanisms. Reaction pathway and sensitivity analysis shows that CI reactions that regenerate 'OH radicals play a dominant role in the autoxidation process. Conversely, RO₂ radical mediated peroxidation (LP) reactions are found to also contribute be are found to be less significant. The CI pathways form unique products (*i.e.*, smaller acids, diacids, and aldehydes), whereas peroxidation reactions produce functionalized LA products. Importantly, CI reactions with LA explain the formation of AAHP isomers, consistent with the role of LA itself as an effective CI scavenger.

In the atmosphere and environment, in all likelihood, there is an facile interplay of the LP and CIMA mechanisms, which both contribute to the accelerated oxidative aging of organic aerosols. The model shows how reactive radicals ($^{\circ}OH$, RO₂ $^{\circ}$, and β -OH-RO₂ $^{\circ}$), and other species (R-OOH, AAHP, and CI) contribute to the overall autoxidation kinetics. Moreover, the chemical structure of LA subtly determines its multiphase chemistry, influencing the relative contributions of two competitive radical chain initiation steps, *i.e.*, $^{\circ}OH$ addition vs. H-abstraction. In summary, the fully coupled autoxidation mechanism developed here, that includes contributions of the LP and the CIMA mechanisms, further elucidates the environmental and atmospheric degradation pathways and resulting products that could be formed during autoxidation.

ASSOCIATED CONTENT

Supporting Information.

Additional details regarding the experimental results and coupled autoxidation mechanisms are provided. Table S1 lists the reactions and their rate constants used in the present model. Figures S1-S5 showcase additional experimental and simulated profiles under various [•OH]. Meanwhile, Figures S6-S13 present further analyses into species identification and reaction pathways.

AUTHOR INFORMATION

Corresponding Author

Meirong Zeng – College of Smart Energy, Shanghai Jiao Tong University, Shanghai 200240, PR China; orcid.org/0000-0003-3902-7430; Email: meirongzeng@sjtu.edu.cn

Kevin R. Wilson – Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States; orcid.org/0000-0003-0264-0872; Email: kwilson@lbl.gov

Notes

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