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Theoretical study on the aqueous phase oxidation of glyoxal†

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Glyoxal (GLY) is an important precursor of aqueous secondary organic aerosol (aqSOA). Knowledge of the reaction mechanisms of GLY in the aqueous phase is not complete, and the oxidation mechanisms of GLY in the presence of different oxidants are under debate. Our recent experimental studies of GLY oxidation mediated by nitrate photolysis yielded formic acid instead of oxalic acid which was commonly found in bulk GLY oxidation experiments. In this work, we investigated the hydration and oligomer formation mechanism of GLY in the aqueous phase theoretically. Furthermore, we calculated the energetics for the mechanisms of GLY oxidation by OH radicals in the presence of O₂ and NO₂. Results showed that the hydration reaction plays a significant role in GLY uptake into the aqueous phase, and oligomers are likely to form at intermediate RH. The formation of formic acid in the presence of OH and NO₂ is more favorable, while oxalic acid is the main product in the presence of OH and O₂. The present study provides a theoretical insight into the aqueous-phase chemistry of GLY, and the results may be helpful for understanding the atmospheric evolution of GLY.

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Environmental significance

Glyoxal (GLY) is an important precursor of aqueous secondary organic aerosol (aqSOA). We have previously reported formic acid/formate production as the main oxidation product from the photooxidation of glyoxal during particulate sodium nitrate photolysis (*Environ. Sci. Technol.*, 2021, 55, 9, 5711–5720). To better understand these reactions, we calculated the energetics for the mechanisms of glyoxal oxidation by OH radicals in the presence of O₂ and NO₂. Results showed that the formation of formic acid in the presence of OH and NO₂ is more favorable, while oxalic acid is the main product in the presence of OH and O₂. Furthermore, the hydration reaction plays a significant role in glyoxal uptake into bulk solutions or cloud droplets, and oligomers are likely to form at intermediate relative humidity. Our study provides a theoretical insight into the aqueous-phase chemistry of glyoxal, and the results may be helpful for understanding the atmospheric evolution of glyoxal under different oxidative environments.

1. Introduction

Glyoxal (GLY) is the simplest α -dicarbonyl intermediate product from the atmospheric oxidation of biogenic VOCs such as isoprene^{1–3} and anthropogenic precursors such as isoprene and aromatics,^{4,5} primarily emitted from biomass burning and vehicle emission, respectively.^{5,6} Glyoxal can exist in the gas

phase, the air–water interface, and the aqueous phase. The major removal processes of glyoxal have been reported to be gas-phase photolysis,^{7,8} with a lifetime $\tau_{\text{photo}} \approx 2$ to 3 h. Due to its atmospheric abundance and high effective Henry's law constant, aqueous chemistry of glyoxal has been shown as an important source of SOA *via* cloud processing.^{9–13} In addition, Zhang *et al.*¹⁴ reported that glyoxal interfacial photochemistry may elevate its uptake onto the aqueous surface, contributing to aqSOA formation, surface activity, and aerosol nucleation as a result of multiphase chemistry.

GLY in cloud/fog droplets and aerosol particles undergoes a series of atmospheric processes such as photolysis, photochemical oxidation, acid/ammonium-catalyzed reactions, and oligomerization to form carboxylic acid, oligomers, organosulfate, and nitrogen-containing organics as SOA.^{10,15} Several experimental and theoretical studies have examined the photooxidation of GLY.^{16–19} Aqueous-phase OH oxidation of GLY can generate low volatile products contributing to the formation of SOA in the atmosphere.^{20,21} Furthermore, brown carbon (BrC), a significant factor in assessing aerosol radiative climate

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effects,²² can be formed when GLY reacts with ammonia in ammonium containing solutions.^{23,24}

Knowledge of the reaction mechanisms of GLY in the aqueous phase is not complete, and the oxidation mechanisms of GLY in the presence of different oxidants are under debate. Using H₂O₂ photolysis as the source of OH radicals, low-volatility compounds such as glyoxylic acid and oxalic acid^{10,20,25} have generally been reported while formic acid, a volatile species, was found in some studies.^{21,25} Recently, we reported that formic acid/formate was the main oxidation product of glyoxal during particulate sodium nitrate photolysis.²⁶ Nitrate photolysis can produce a series of reactive species, including OH radicals, NO₂, and N(III) (NO₂[−]/HONO).^{27,28} Whether the presence of reactive nitrogen species (*e.g.*, NO₂) modifies the mechanism of GLY oxidation and promotes the formation of formic acid/formate deserves further investigation.

In this study, we first investigated the hydration and oligomer formation mechanism of GLY in aqueous phase theoretically. We calculated the energetics for the mechanisms of GLY oxidation by OH radicals in the presence of O₂ and NO₂. The oxidation mechanisms of GLY under other oxidative environments (O₃, HO₂ and H₂O₂) were also determined. We found that the hydration reaction plays a significant role in GLY uptake into diluted bulk solutions and cloud/fog droplets, and oligomers are likely to form at intermediate relative humidity. Furthermore, the formation of formic acid in the presence of OH and NO₂ is more favorable, while oxalic acid is the main product in the presence of OH and O₂. Overall, in the aqueous phase, reaction with OH radicals is the primary initial loss process for glyoxal, compared to reactions with O₃, HO₂, and H₂O₂. Our study provides a theoretical insight into the aqueous-phase chemistry of GLY, and the results may be helpful for understanding the atmospheric evolution of GLY.

2. Computational methods

All of the electronic structure calculations were conducted using the Gaussian 16 program²⁹ employing the M06-2X³⁰ method with the 6-31+G(d,p) basis set. The M06-2X functional has been shown to be reliable to predict the geometries and frequencies of the stationary points^{31,32} and thermodynamic data for main-group elements.^{33,34} We also calculated the energy barrier of gas phase reaction GLY · 2H₂O to IM5 by using CCSD(T) with the aug-cc-pvTz basis set at the optimized geometry to verify the reliability of results. As shown in Table S5,[†] the energy barrier calculated by M06-2X/6-311++G(3df,2p)//M06-2X/6-31+G(d,p) was 7.04 kcal mol^{−1}, while the energy barrier calculated by CCSD(T)/aug-cc-pvTz//M06-2X/6-31+G(d,p) was 7.77 kcal mol^{−1}. Considering the computational cost and accuracy, the methods used in this work are reliable. The vibrational frequencies at the same level were used to verify all stationary points as either the transition state (TS, only one imaginary frequency) or the minima (zero imaginary frequency). The reaction pathways were confirmed by intrinsic reaction coordinate (IRC) analysis. The single point energies of the optimized structures were further calculated with the 6-311++G(3df,2p) basis set, and the

thermal corrections and the basis set superposition error (BSSE) corrections were also included in the potential energies. The continuum solvation model 'SMD' was used to determine the solvent effect of water.³⁵ The reaction kinetics was calculated with transition-state theory (TST) based on the KiSThelP³⁶ program. Because of the interaction between GLY, GLY · 1H₂O, and water molecules, the geometries of GLY and GLY · 1H₂O with water complex were also determined. Such interaction was also considered for the energy barriers calculation of hydration processes. The complexes of GLY with oxidants were not investigated in the oxidation pathways, due to the minor impact of molecular interaction.

The trans form of glyoxal was used in this study, because it is more easily solvated in the bulk.³⁷ We optimized the conformers of transition state for the GLY · 1H₂O to IM2 reaction (Fig. 2). The structures of the conformers are shown in Table S3.[†] We calculated the energy barriers for the conformers in the gas phase and aqueous phase. As shown in Table S4,[†] the solvation effects cause a significant change in the energy barriers of the transition state conformers. The solvent changes the order of these relative energy values, from $a < d < c < b$ in the gas phase to $a < d < b < c$ in the aqueous phase. Further studies are needed to confirm the solvation effect on the relative energies of conformers. However, regardless of these solvation effects, the trend of the reactivity of different oxidants toward GLY remains valid, because the difference between the relative energies of the transition state conformers in any of the oxidation reaction is less than 2 kcal mol^{−1}.

The atmospheric lifetime can be estimated as:

$$\tau = \frac{1}{k[\text{oxidant}]}$$

where k represents the rate constant of the reactant with the oxidant and $[\text{oxidant}]$ represents the atmospheric concentration of the oxidant.

3. Results and discussion

3.1 Glyoxal hydration and oligomer mechanism

Before we present the results of oxidation of GLY, it is useful to discuss its hydration characteristics. The hydration of GLY to produce glyoxal-diol (GLY · 1H₂O) is an important initiation reaction for GLY in the aqueous formation of SOA and BrC in the atmosphere.^{38,39} Once formed, the glyoxal-diol (GLY · 1H₂O) can undergo further hydrolysis to form the glyoxal dihydrate (GLY · 2H₂O) (Fig. 1). Furthermore, two glyoxal-diols can combine to form the open dimer IM1. Intramolecular nucleophilic attack on the sp² carbon of IM1 can yield two possible ring structures: the five-membered dioxolane ring dimer P1 and the six-membered dioxane ring dimer P2. Formation of both rings from IM1 is thermodynamically favorable but the ring closure to form P1 has a relatively lower barrier ($\Delta G^\ddagger = 14.34$ kcal mol^{−1}) than P2 ($\Delta G^\ddagger = 18.36$ kcal mol^{−1}). The formation of P1 is also thermodynamically more favorable ($\Delta G = -12.36$ kcal mol^{−1}) than P2 ($\Delta G = -5.89$ kcal mol^{−1}). Hence, P1 is more likely to be formed, in agreement with experimental results.^{40–42}



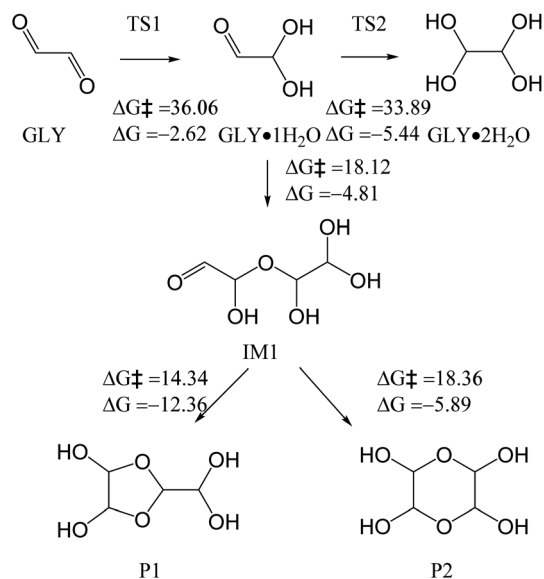


Fig. 1 The hydration and polymerization mechanism of glyoxal.

The formation of $\text{GLY} \cdot 2\text{H}_2\text{O}$ is a two-step hydrolysis reaction. The energy barriers for the above hydrolysis reactions (*via* TS1 and TS2) with the addition of one water molecule are high, at 36.06 and 33.89 kcal mol^{-1} , respectively. We investigated the hydrolysis reactions by introducing extra water molecules to participate in the hydrolysis reactions in the implicit solvent model. The geometries of GLY and $\text{GLY} \cdot 1\text{H}_2\text{O}$ with water complex were determined, as depicted in Fig. S1-1 and S1-2.† The structures of TS1 and TS2 with extra water molecules are summarized in Fig. S2 and S3.† The hydrogen atom from water molecules can attach to the aldehyde group of GLY, while the hydroxyl group ($-\text{OH}$) can attach to the carbon atom of GLY. When the extra water molecules are involved, they act as a bridge to the aldehyde, thus making the hydration reaction more likely to occur. As illustrated in Table S1,† when there are four water molecules in the reactions, the barriers decrease to 11.64 and 14.57 kcal mol^{-1} for TS1 and TS2, respectively. Water molecules have a catalytic effect in lowering the energy barriers

for the hydrolysis reaction. Hence when the humidity increases, it is possible for more water molecules to participate and facilitate the hydration reactions and GLY is likely in the $\text{GLY} \cdot 2\text{H}_2\text{O}$ form. In addition, Rypkema *et al.*⁴³ and Long *et al.*³¹ reported that carboxylic acids and sulfuric acid can act effectively as catalysts in the hydration of aldehydes. Hence, the uptake of glyoxal can be facilitated in complex atmospheric aqueous aerosol.^{19,44} In cloud droplets, with the concentrations in the range of μM , GLY predominantly exists in $\text{GLY} \cdot 2\text{H}_2\text{O}$ form.⁴⁵ In aerosol droplets, $\text{GLY} \cdot 1\text{H}_2\text{O}$ may also be important.

3.2 Aqueous oxidation pathways of GLY to form low volatility organic acids

Previous studies focused on the aqueous oxidation of GLY by OH radicals generated from the H_2O_2 photolysis.^{10,21,25} In such situations, the OH radicals and H_2O_2 are the main oxidants, and they promote the formation of low-volatility organic acids (*e.g.*, oxalic acid and glyoxylic acid). These first-generation oxidants can also undergo further radical chain reactions to form second-/third-generation oxidants (*e.g.*, O_3 and HO_2). Hence, we investigated the reaction mechanisms of GLY and these oxidants using quantum chemistry calculation.

3.2.1 The oxidation of GLY by OH radical. As mentioned above, GLY predominantly (98%) exists in $\text{GLY} \cdot 2\text{H}_2\text{O}$ form in bulk solutions and cloud/fog droplets.^{19,46} As shown in Fig. 2, $\text{GLY} \cdot 2\text{H}_2\text{O}$ can react with OH radicals to generate IM5 that transforms to IM7 *via* subsequent molecular oxygen addition and HO_2 radical elimination. IM7 can react with OH radical to form the glyoxylic acid alkyl radical IM8, which undergoes oxygen addition reaction and HO_2 elimination to finally yield oxalic acid P3. The energy barriers through this pathway are generally low, 7.31–8.69 kcal mol^{-1} , which means that oxalic acid is likely to form in the presence of oxygen. The mechanism is consistent with the radical reactions proposed in previous studies.^{19,25} We also investigated the mechanism of $\text{GLY} \cdot 1\text{H}_2\text{O}$. OH radical reacts with $\text{GLY} \cdot 1\text{H}_2\text{O}$ *via* H atom abstraction to form the glyoxal radical IM2, which can further react with molecular oxygen to form the glyoxal peroxy radical IM3, which forms glyoxylic acid IM4 after an HO_2 radical elimination. This

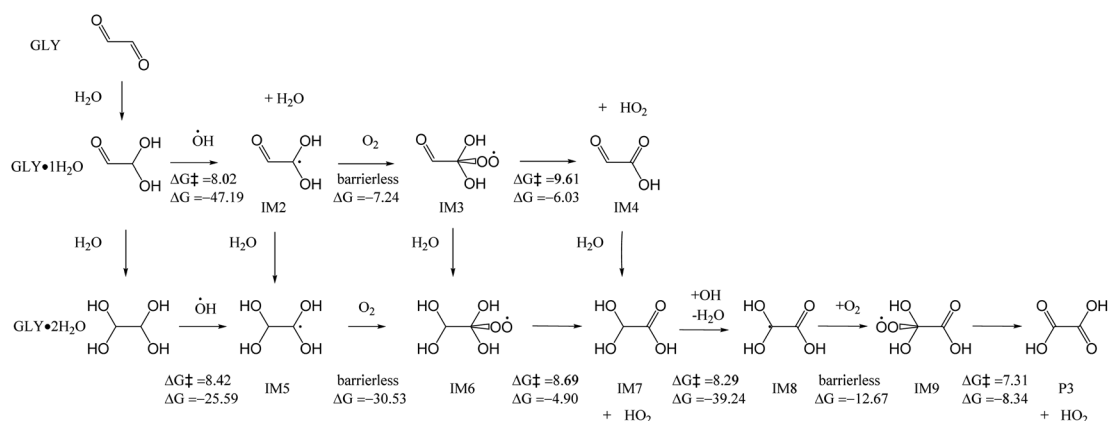


Fig. 2 Mechanisms for the reactions of GLY with OH radicals and O_2 in the aqueous phase, with the energy barrier (ΔG^\ddagger) and reaction energy (ΔG) (kcal mol^{-1}).

mechanism can explain experimental observations of glyoxylic acid and oxalic acid in aqueous reactions of GLY in H_2O_2 photolysis.^{10,21,25}

Furthermore, two IM6 molecules can yield IM10 by $\text{RO}_2\text{-RO}_2$ reaction^{10,47} (Fig. 3a). IM10 undergoes subsequent decomposition to yield IM11, IM12, and IM13. IM12 can also react with O_2 to form the peroxy radical IM14, which undergoes a HO_2 elimination to generate formic acid P4. However, due to the high energy barrier between IM10 and IM12 ($35.55 \text{ kcal mol}^{-1}$), this reaction is not expected to occur easily. Fig. 3b shows that IM6 can also react with NO to form intermediate IM15, followed by the NHO_2 elimination to form IM16. IM16 finally decomposes to formic acid, CO_2 and H_2O . However, the energy barrier between IM15 and IM16 is $26.68 \text{ kcal mol}^{-1}$, which is quite high and hinders the reaction. The above two pathways of IM6 can end up in formic acid, however, they both have a step with a relative high energy barrier. Hence, they may not be the main pathway to form formic acid.

Alternatively, the formed glyoxal peroxy radical IM3 (Fig. 2), an RO_2 , can also undergo a $\text{RO}_2\text{-RO}_2$ reaction to form IM17 (Fig. 3c). IM17 decomposes to carbon monoxide, IM13, and IM18, with the energy barrier of $51.25 \text{ kcal mol}^{-1}$. IM13 transforms into water and carbon dioxide, while IM18 transforms into water and IM4. IM4 likely undergoes hydration reaction to form IM7 (Fig. 2) and oxalic acid P3 eventually. Because of the high energy barrier ($51.25 \text{ kcal mol}^{-1}$), the above $\text{RO}_2\text{-RO}_2$ pathway is not feasible energetically. IM3 can also react with NO, followed by the NHO_2 elimination, finally decomposes to formic acid and CO_2 , which is also not likely to occur, due to the high energy barrier ($40.90 \text{ kcal mol}^{-1}$) (Fig. 3d). Overall, OH reactions with GLY can form glyoxylic acid and oxalic acid, but not likely formic acid.

3.2.2 The oxidation of GLY by H_2O_2 . Recent studies have reported hydroxyhydroperoxide (HHP) formation from reactions between H_2O_2 and GLY.^{48–50} HHP is formed *via* the nucleophilic attack of an O atom from H_2O_2 to the carbonyl

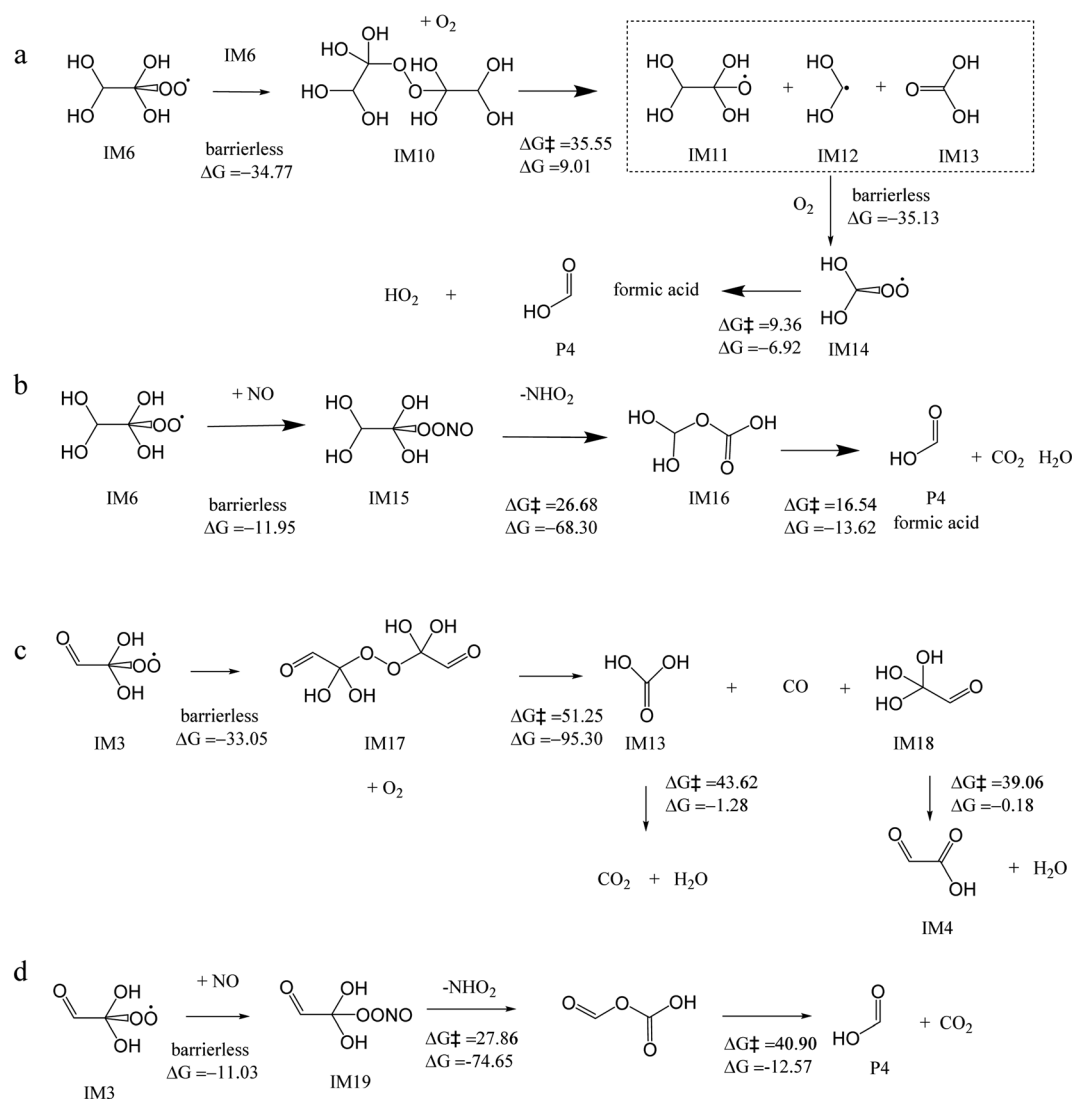


Fig. 3 Mechanisms for the subsequent reactions of IM3 and IM6 in the aqueous phase, with the energy barrier (ΔG^\ddagger) and reaction energy (ΔG) (kcal mol^{-1}), to produce formic acid.



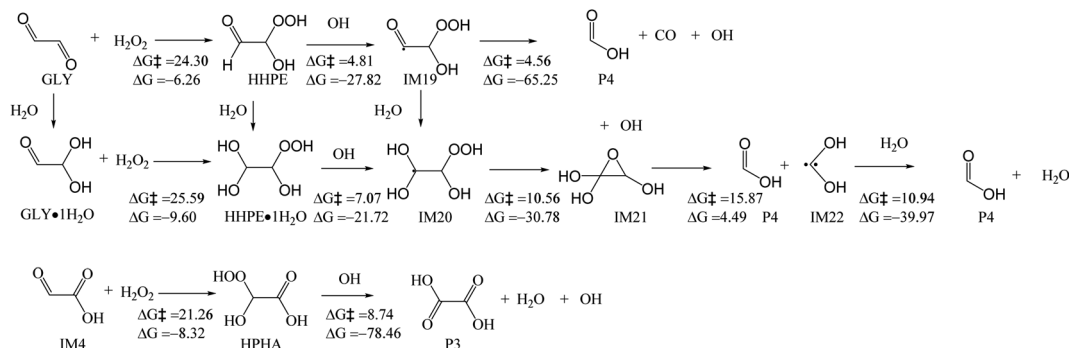


Fig. 4 Mechanisms for the reactions of GLY with H_2O_2 and OH in the aqueous phase, with the energy barrier (ΔG^\ddagger) and reaction energy (ΔG) (kcal mol^{-1}).

group, followed by the migration of one of the H atoms of H_2O_2 to the oxygen of the carbonyl group.^{51,52} We also calculated the energy barrier of the reaction of GLY and H_2O_2 in the presence of a H_2O molecule. Fig. 4 shows that H_2O_2 reacts with GLY and $\text{GLY}\cdot\text{H}_2\text{O}$ to form 2-hydroxy-2-hydroperoxyethanal (HHPE) and its hydrated counterpart (HHPE· H_2O), with the energy barriers of 24.30 and 25.59 kcal mol^{-1} , respectively. HHPE can react with OH radical to form acyl radical IM19 by H abstraction, and then IM19 decomposes to formic acid (P4), CO, and OH radical. HHPE· H_2O can also react with OH to form IM20, and with the elimination of an OH radical to form epoxy intermediate IM21. Through a decomposition reaction, IM21 can transform into formic acid (P4) and IM22. In the presence of water, IM22 can transform to formic acid (P4) by H shift reaction, with the energy barrier of 10.94 kcal mol^{-1} . The glyoxylic acid IM4 can also react with H_2O_2 to form 2-hydroperoxy-2-hydroxyacetic acid (HPHA), with the energy barrier of 21.26 kcal mol^{-1} . Similarly, an OH radical abstracts a H atom from HPHA to form oxalic acid P3, OH and H_2O . The rate constants of reaction GLY and $\text{GLY}\cdot\text{H}_2\text{O}$ towards H_2O_2 are 2.11×10^{-2} and $1.39 \text{ s}^{-1} \text{ M}^{-1}$, respectively (Table S2†). The rate constant of reaction IM4 towards H_2O_2 is $6.74 \times 10^{-2} \text{ s}^{-1} \text{ M}^{-1}$.

These rate constants are much lower than those of $\text{GLY}\cdot\text{H}_2\text{O}$ and $\text{GLY}\cdot 2\text{H}_2\text{O}$ reacting with OH (1.52×10^7 and $6.75 \times 10^6 \text{ s}^{-1} \text{ M}^{-1}$). In our recent study of nitrate photolysis that produces OH radicals in the particles,²⁶ the model predicted steady-state concentration of H_2O_2 and OH were $\sim 10^{-4} \text{ M}$ and $\sim 10^{-15} \text{ M}$, respectively. Using these concentrations as references, the atmospheric aqueous-phase lifetimes (τ) for the initial reaction of GLY and $\text{GLY}\cdot\text{H}_2\text{O}$ with H_2O_2 were 5.49 days and 0.08 days. The atmospheric aqueous-phase lifetimes (τ) for the initial reaction of $\text{GLY}\cdot\text{H}_2\text{O}$ and $\text{GLY}\cdot 2\text{H}_2\text{O}$ with OH radicals were 761.45 days and 1714.68 days. Although the reactions with H_2O_2 can be competitive to that with OH radicals, the reactions with H_2O_2 are also not dominant pathways to form formic acid, since GLY predominantly exists in $\text{GLY}\cdot 2\text{H}_2\text{O}$.

3.2.3 The oxidation of GLY by O_3 and HO_2 . Ozone abstracts the most weakly bound H atom of $\text{GLY}\cdot\text{H}_2\text{O}$ to form OH radical, molecular oxygen, and alkyl radical IM2⁵³ (Fig. 5). It has a high energy barrier of 33.03 kcal mol^{-1} . Subsequent reaction with O_2 forms peroxy radical IM3 which quickly decomposes to form IM4 and HO_2 radical. Similar to $\text{GLY}\cdot\text{H}_2\text{O}$, $\text{GLY}\cdot 2\text{H}_2\text{O}$ can also react with O_3 , with the loss of OH and O_2 , to form IM5. IM5 transforms to IM6, with the addition of molecular oxygen,

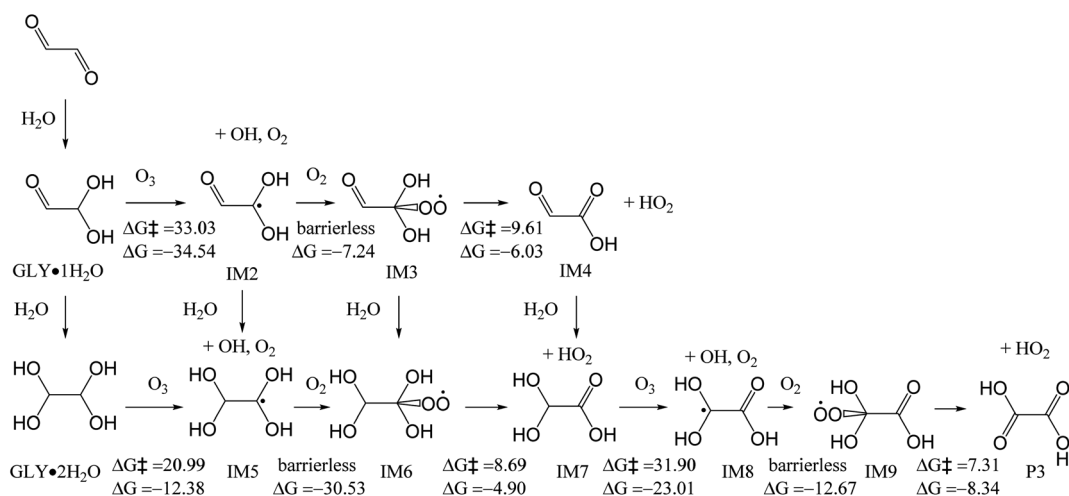


Fig. 5 Mechanisms for the reactions of GLY with ozone and O_2 in the aqueous phase, with the energy barrier (ΔG^\ddagger) and reaction energy (ΔG) (kcal mol^{-1}).



In the presence of NO₂, IM5 formed from GLY·2H₂O (Fig. 2) can undergo further reactions in the aqueous phase. One pathway is the NO₂ addition to the carbon position and forms a nitro-product IM23 (Fig. 6). IM7 is formed after a HONO elimination reaction from IM23. IM7 can react with OH radical, followed by NO₂ addition and HONO elimination, to form oxalic acid P3. IM7 could also decompose into two formic acid (P4) molecules, but the energy barrier is 67.97 kcal mol⁻¹, too high for the reaction to occur. NO₂ can also abstract a H atom of IM5, resulting in the cleavage of C–C bond to form formic acid P4,



HONO and IM22. This reaction is relatively fast because the energy barrier is only 6.45 kcal mol⁻¹. IM22 can also produce formic acid P4 through H transfer reaction involving water molecules, with the energy barrier of 16.72 kcal mol⁻¹. We also added the pathway of IM6 with NO₂ as a possibility (Fig. S5†). However, its energy barrier is 38.81 kcal mol⁻¹, higher than the pathway of IM5 with NO₂. Hence, it is not likely to occur.

In conclusion, formic acid can be formed *via* IM5 and IM22 (Fig. 6) in the presence of OH and NO₂. As depicted in Fig. 3a and b, it can also be formed in the presence of OH and O₂. The formation of glyoxylic acid and oxalic acid is also feasible in the presence of OH and O₂, as shown in Fig. 2 and 3c. On the basis of the rate constants of the related reactions (Table S1†), the reaction of IM5 with NO₂ to form formic acid is very fast, with the rate constants of $7.52 \times 10^9 \text{ s}^{-1} \text{ M}^{-1}$, which is in the same order of the reported overall rate constant of OH + GLY ($4.5 \times 10^{10} \text{ s}^{-1} \text{ M}^{-1}$) in our earlier work.²⁶ The rate constants of reaction IM10 to IM11, IM15 to IM16, and IM17 to IM13 is $7.86 \times 10^{-14} \text{ s}^{-1} \text{ M}^{-1}$, $2.32 \times 10^{-7} \text{ s}^{-1} \text{ M}^{-1}$, and $3.51 \times 10^{-25} \text{ s}^{-1} \text{ M}^{-1}$, respectively; thus these pathways Fig. 3a–c are not feasible. The rate constants of the dominant reactions (in thick arrows) to form formic acid in Fig. 6 are between 10^5 and $10^7 \text{ s}^{-1} \text{ M}^{-1}$. Hence, the formation of formic acid with the presence of NO₂ is the most favorable among all the pathways discussed. The mechanism above may explain why formic acid/formate is the predominant product in our earlier study of GLY oxidation under nitrate photolysis.²⁶

3.4 Atmospheric implication

This work provides theoretical insights into the hydration, polymerization and oxidation mechanisms of GLY in the aqueous phase. Several previous studies^{46,62,63} have reported that GLY exist in the form of hydrates and oligomers in SOA particulate phase, and GLY has been found to easily transfer from the gas phase to the aerosol phase at RH > 26%.⁴⁶ Our computational results showed that four or more water molecules are required to make the hydrolysis energetically favorable compared with the polymerization reaction. Hence hydrolysis is favored at high RH, whereas GLY polymerization is active at relatively low humidity levels. In addition, if other aldehyde molecules can be incorporated into glyoxal copolymers, as suggested by Kalberer *et al.*,^{46,64} this process may partially explain the underprediction of the aerosol uptake of atmospheric aldehydes.

Recent studies found that glyoxal can be oxidized to produce formic acid, glyoxylic acid and oxalic acid in the aqueous phase under photochemical conditions.^{20,25,65} The common dominant product in GLY oxidation were glyoxylic and oxalic acid, but we²⁶ reported earlier that formic acid was the main product in GLY oxidation under nitrate photolysis. This study showed that the formation of formic acid was more favorable in the presence of OH and NO₂. In the presence of OH and O₂, oxalic acid is the main product. The oxidation mechanisms of GLY towards HO₂, O₃ and H₂O₂ were also determined. Compared with OH radicals, the reactions of GLY with O₃ and HO₂ are quite slow and are of minor importance in the atmospheric liquid phase.

Carlton *et al.*²⁵ expanded the mechanism of direct formic acid production from GLY through reactions with H₂O₂. Our theoretical results showed that although the H₂O₂ induced reactions can be competitive to that with OH radicals, the reactions with H₂O₂ are also not dominant pathways to form formic acid. NO₂ can be either from the gas-particle partitioning or generated from in-particle source, such as nitrate photolysis. Its presence might modify the oxidation processes initiated by OH radicals and change the product distribution. Since OH radicals and NO₂ both exist in the atmosphere, they should both be included in GLY oxidation mechanisms and have important implications for the role of GLY in SOA formation.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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