Supporting Information
Theoretical study on the aqueous phase oxidation of glyoxal

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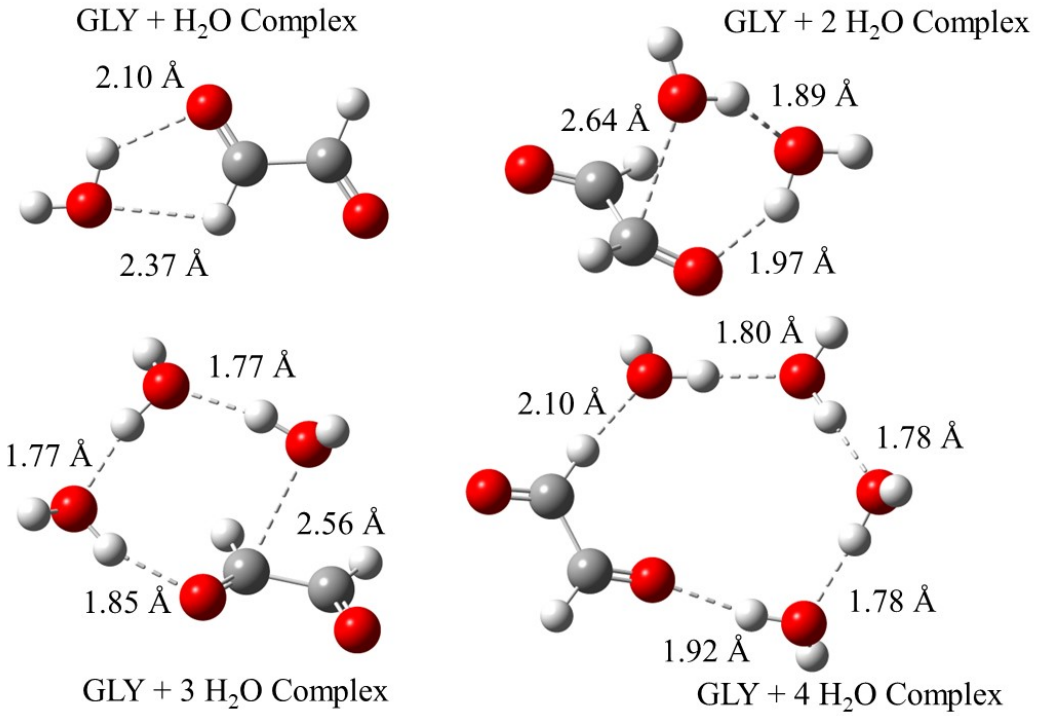


Fig S1-1 The Optimized geometries of GLY and water complex. (The oxygen atom is colored in red, the carbon atom is colored in grey and the hydrogen atom is colored in white.)

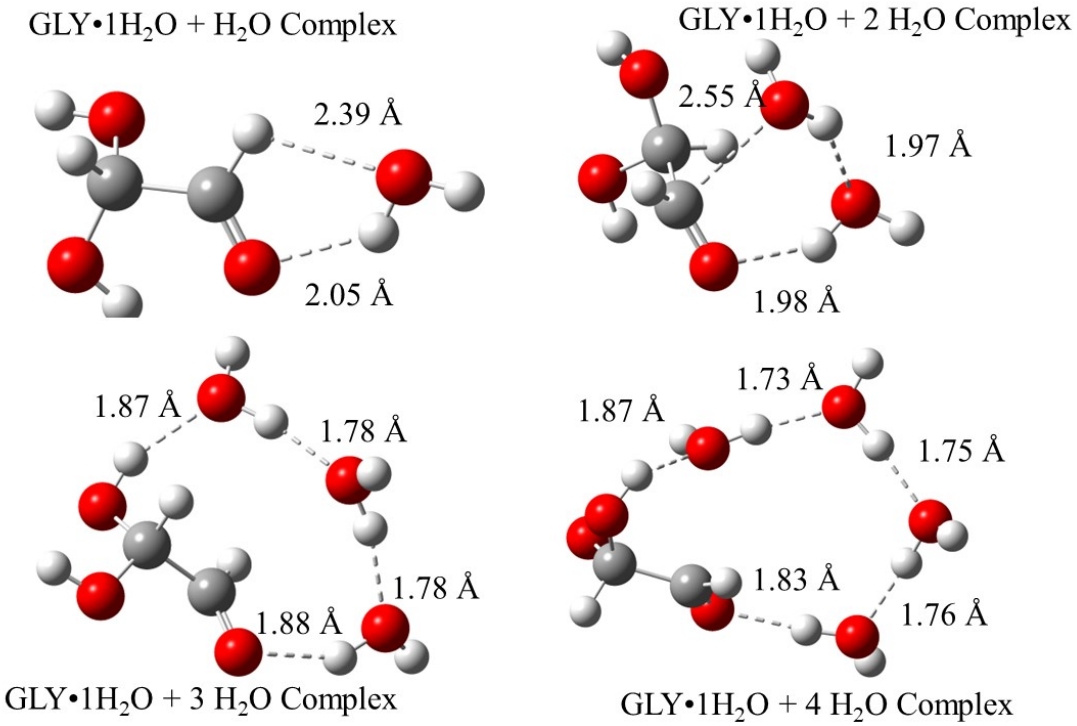


Fig S1-2 The Optimized geometries of GLY•1H_2O and water complex. (The oxygen atom is colored in red, the carbon atom is colored in grey and the hydrogen atom is colored in white.)

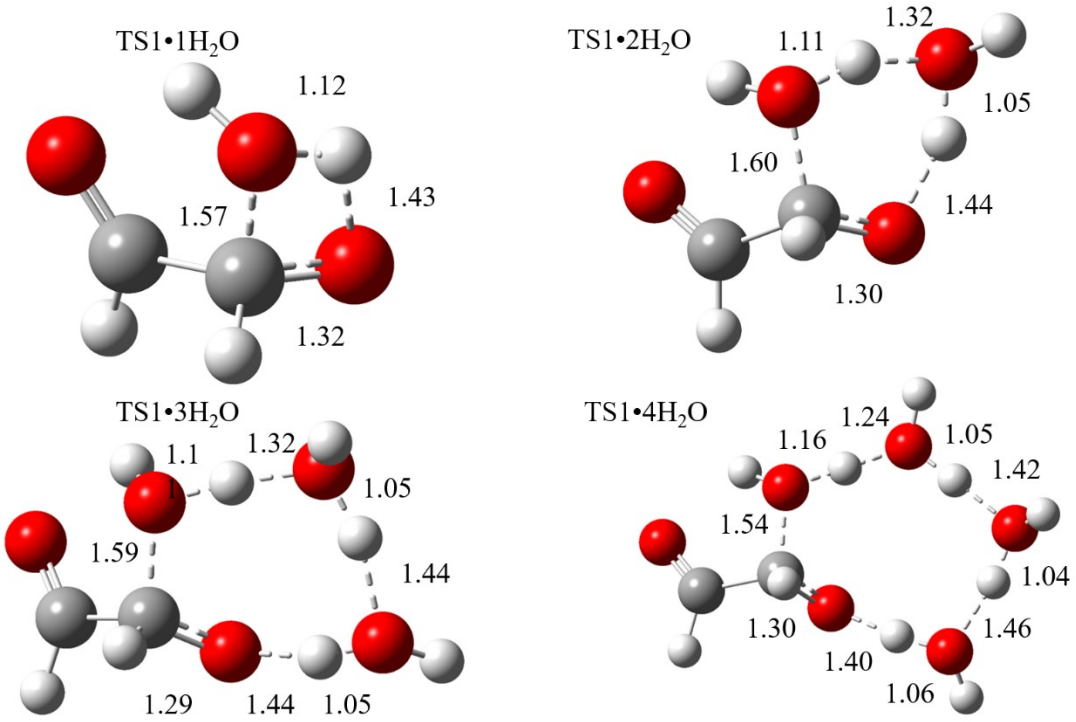


Fig S2 The Optimized geometries of transition states of GLY with water. (The oxygen atom is colored in red, the carbon atom is colored in grey and the hydrogen atom is colored in white.)

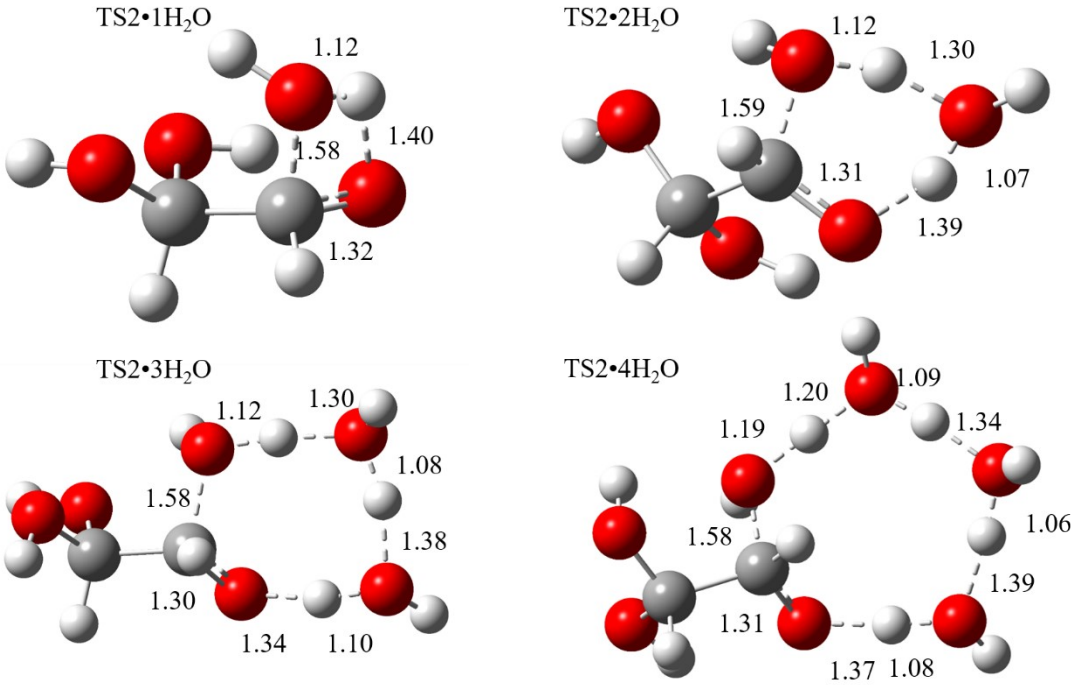


Fig S3 The Optimized geometries of transition states of GLY•1H_2O with water. (The oxygen atom is colored in red, the carbon atom is colored in grey and the hydrogen atom is colored in white.)

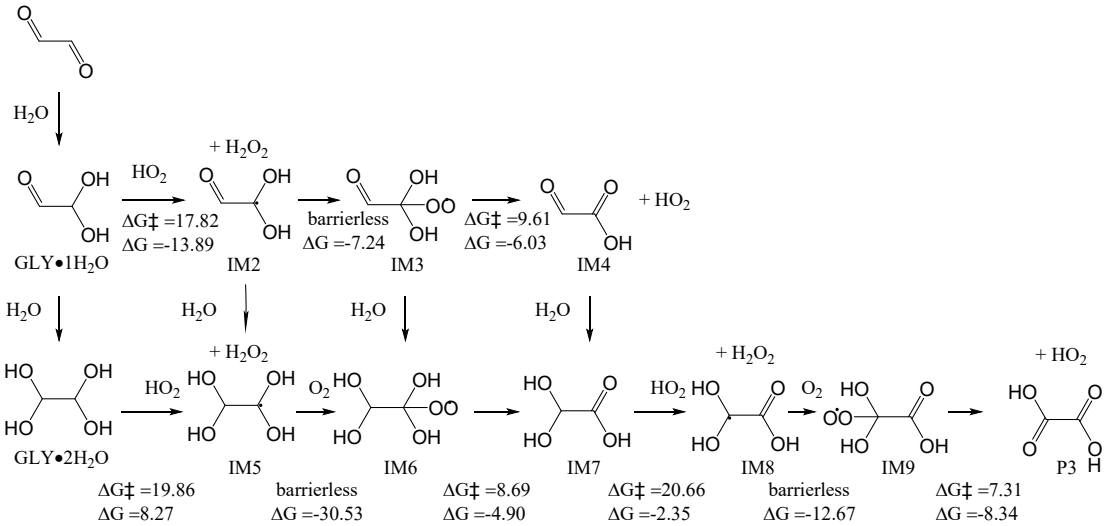


Figure S4 Mechanisms for the reactions of GLY with HO_2 and O_2 in the aqueous phase, with the energy barrier (ΔG‡) and reaction energy (ΔG) (kcal mol^{-1}).

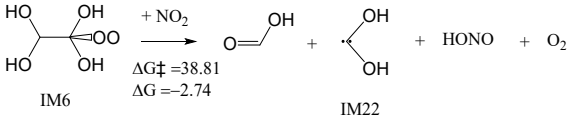


Figure S5 The pathway of IM6 with NO_2

Table S1 ΔG‡ (in kcal/mol) for Hydration Reactions

	TS1	TS2
1 H_2O	36.06	33.89
2 H_2O	19.01	17.90
3 H_2O	12.65	17.19
4 H_2O	11.64	14.57

The rate constants were calculated with transition-state theory (TST)

$$k^{TST}(T) = \sigma \frac{k_B T}{\mathrm{h}} \left(\frac{RT}{P^0}\right)^{\Delta n} e^{-\frac{\Delta ‡ G^0(T)}{k^B T}}$$

where σ is the reaction path degeneracy, k_B is Boltzmann's constant, T is temperature, h is Planck's constant, $\Delta^‡G^0(T)$ represents the standard Gibbs free energy of activation for the considered reaction (Δn=1 or 0 for gas-phase bimolecular or unimolecular reactions, respectively; RT/P^0 has the unit of the inverse of a concentration).

Table S2 The rate constants of the different reactions.

Reactions	Rate constants (s^{-1} M^{-1})
GLY⊂1H_2O + OH → IM2 + H_2O	1.52×10^{7}
IM3 → IM4 + HO_2	9.77×10^{5}
GLY⊂2H_2O + OH → IM5 + H_2O	6.75×10^{6}
IM6 → IM7 + HO_2	4.28×10^{6}
IM7 + OH → IM8 + H_2O	9.17×10^{6}
IM9 → P3 + HO_2	4.80×10^{7}
IM10 → IM11 + IM12 + IM13	7.86×10^{-14}
IM14 → P4 + HO_2	1.51×10^{6}
IM15 → IM16 + NHO_2	2.32×10^{-7}
IM16 → P4 + CO_2 + H_2O	6.26
IM17 → IM13 + CO + IM18	3.51×10^{-25}
IM18 → IM4 + H_2O	5.72×10^{-16}
IM19 → IM13 + NO_2 + CHO	7.46×10^{-26}
IM13 → CO_2 + H_2O	2.55×10^{-19}
IM23 → IM7 + HONO	3.64×10^{3}
IM7 + OH → IM8 + H_2O	2.77×10^{6}
IM24 → P3 + HONO	8.00×10^{3}
IM5 + NO_2 → P4 + IM22 + HONO	7.52×10^{9}
IM22 + H_2O → P4 + H_2O	12.95
GLY⊂1H_2O + O_3 → IM2 + OH + O_2	1.90×10^{-10}
GLY⊂2H_2O + O_3 → IM5 + OH + O_2	0.14
IM7 + O_3 → IM8 + OH + O_2	1.32×10^{-9}
GLY⊂1H_2O + HO_2 → IM2 + H_2O_2	52.84
GLY⊂2H_2O + HO_2 → IM5 + H_2O_2	1.35
IM7 + HO_2 → IM8 + H_2O_2	0.43
GLY + H_2O_2 → HHPE	1.52×10^{-5}
HHPE + OH → IM19 + H_2O	7.72×10^{9}
IM19 → P4 + CO + H_2O	8.05×10^{10}
GLY⊂1H_2O + H_2O_2 → HHPE⊂1H_2O	1.81×10^{-6}
HHPE⊂1H_2O + OH → IM20 + H_2O	1.21×10^{9}
IM20 → IM21 + OH	5.03×10^{6}
IM21 → P4 + IM22	3.95×10^{2}
IM4 + H_2O_2 → HPHA	6.74×10^{-2}
HPHA + OH → P3 + H_2O + OH	4.68×10^{6}

Table S3 The optimized structure of transition state for the GLY•1H_2O to IM2 reaction and its conformers.

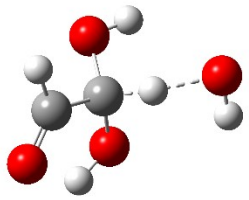
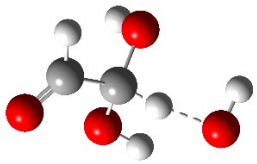
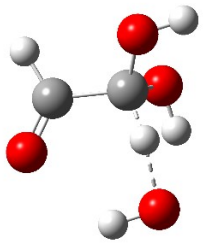
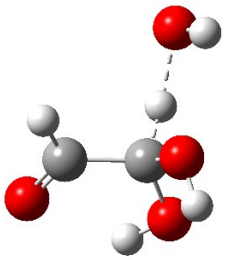
TS for GLY•1H_2O to IM2 reaction (a)	Conformer (b)
	
Conformer (c)	Conformer (d)
	

Table S4 The energy barriers (kcal/mol) for the transition state conformers (Table S3).

	Gas phase	Water
TS(a)	4.13	8.02
TS(b)	7.44	8.58
TS(c)	5.02	9.66
TS(d)	4.95	8.17

Table S5 The energy barrier of gas phase reaction GLY•2H_2O to IM5 calculated by M06-2X/6-311++G(3df,2p)//M06-2X/6−31+G(d,p) and CCSD(T)/aug-cc-pvTz //M06-2X/6−31+G(d,p).

	Energy Barrier
M06-2X/6-311++G(3df,2p)//M06-2X/6−31+G(d,p)	7.04 kcal/mol
CCSD(T)/aug-cc-pvTz //M06-2X/6−31+G(d,p)	7.77 kcal/mol