

1 **Supplemental information for**
2 **Kinetics of the nitrate-mediated photooxidation of monocarboxylic acids in the aqueous**
3 **phase**

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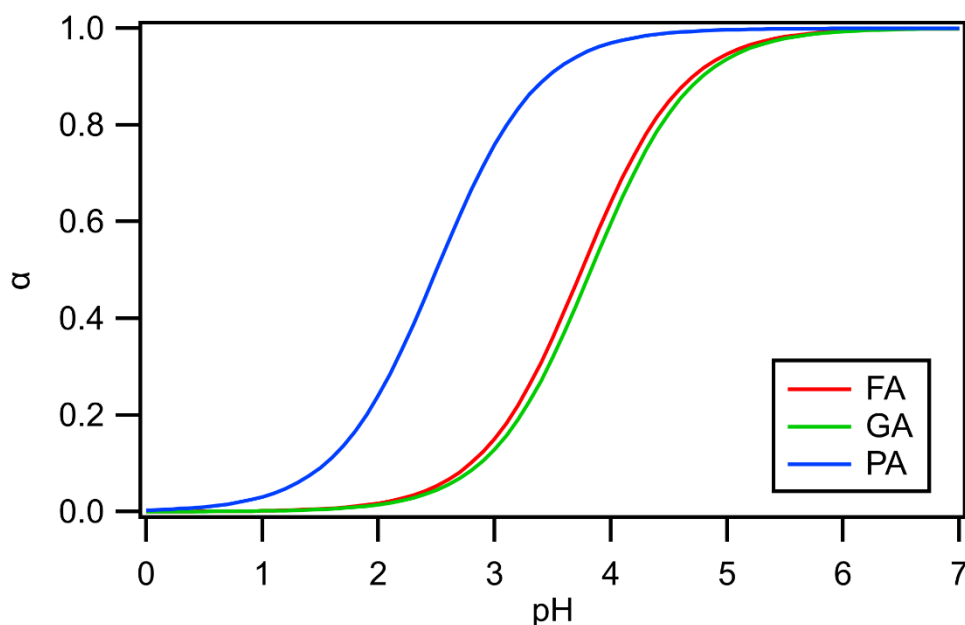
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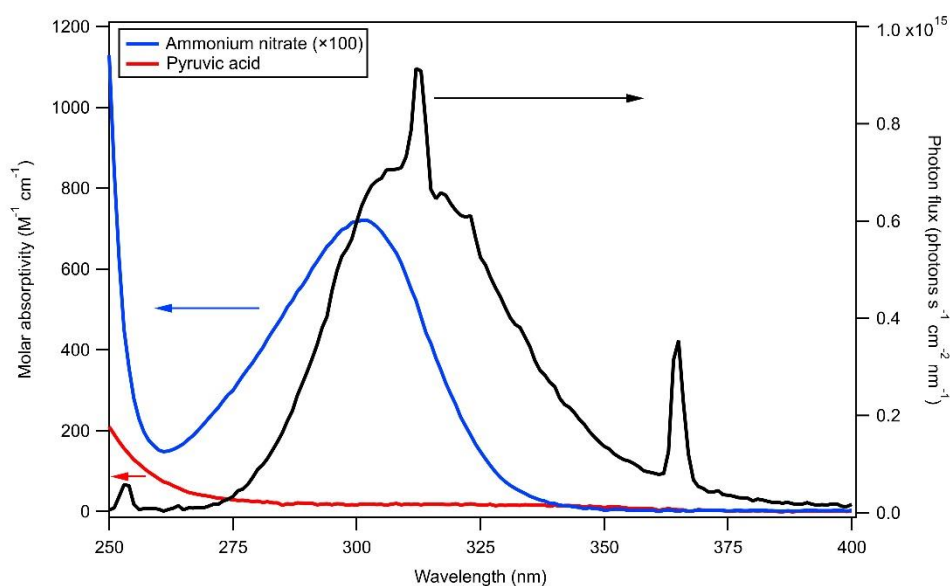
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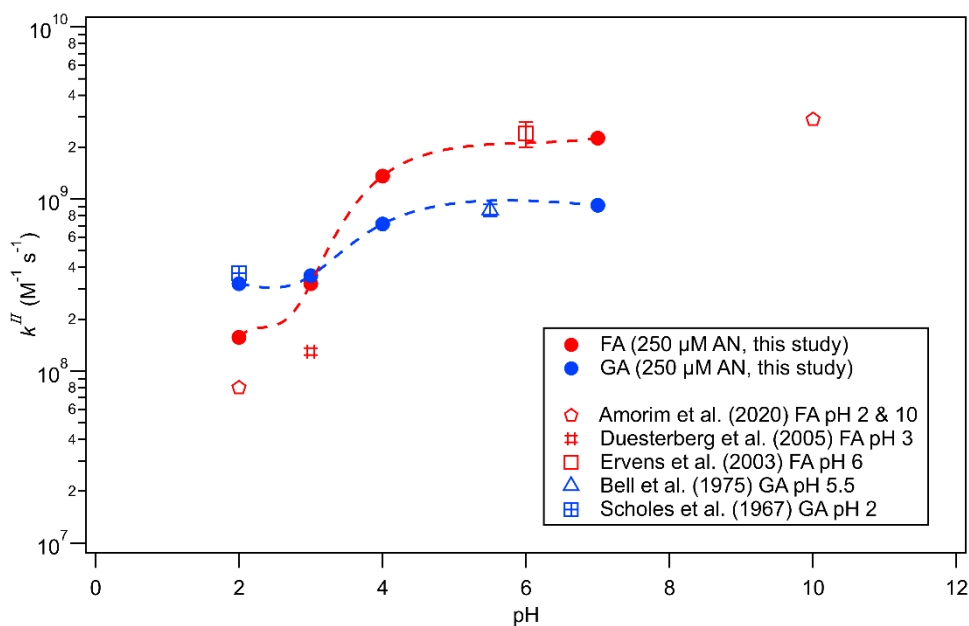
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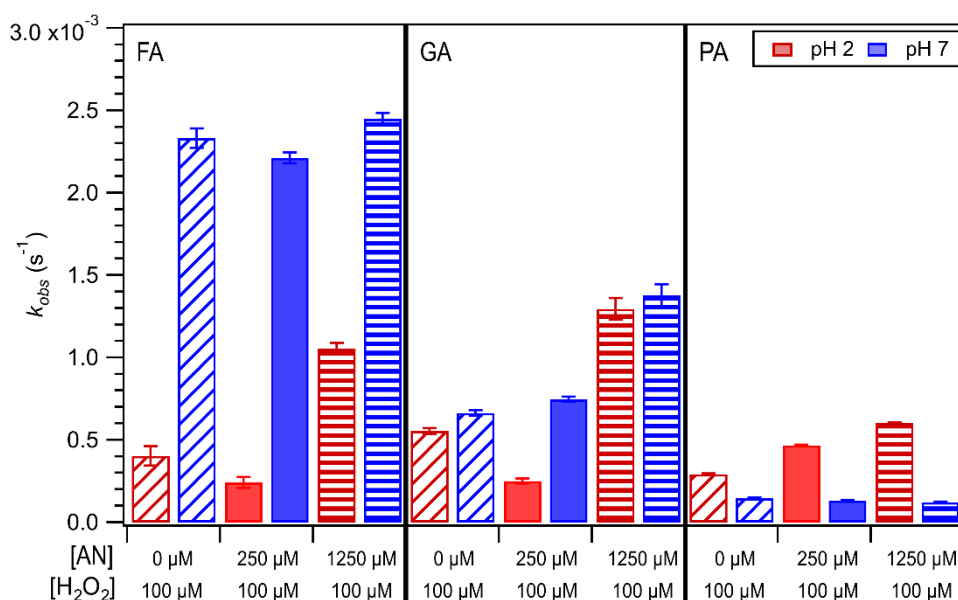
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 36 **Figure S1.** Dissociation curves of FA, GA, and PA. The pK_a values used for the calculation of
 37 FA, GA, and PA were 3.75¹, 3.82², and 2.50³, respectively.



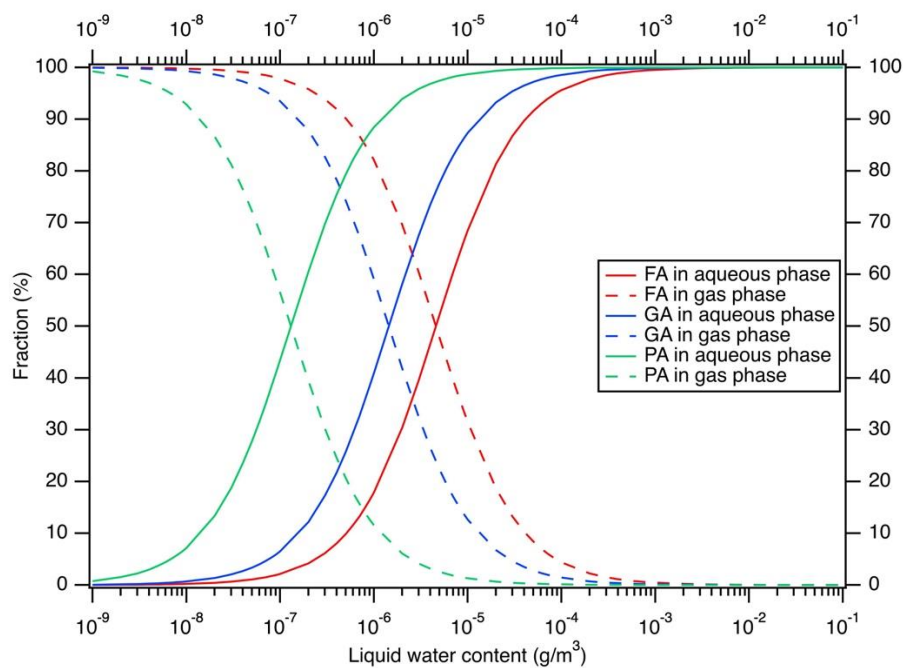
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 39 **Figure S2.** The photon flux in the photoreactor and the molar absorptivity ammonium nitrate
 40 and pyruvic acid. Note that the molar absorptivity values of ammonium nitrate shown here
 41 have been multiplied by 100 for easier comparison. The molar absorptivities of ammonium
 42 nitrate and pyruvic acid were obtained using 104 mM and 1 mM solutions, respectively, since
 43 the absorption signals for 250/1250 μ M ammonium nitrate and 10 μ M pyruvic acid were very
 44 low. The photon flux in the photoreactor was determined using the method detailed by Li et al.
 45 (2022).⁴



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 47 **Figure S3.** Calculated second-order rate constants (k^II) vs. pH using actual k_{obs} and estimated
 48 $[OH]_{ss}$ values from this study (filled blue and red symbols). Dotted lines are used to guide the
 49 eyes. We assumed that k_{obs} was the product of k^II and $[\cdot OH]_{ss}$. Also included are the k^II
 50 values for FA and GA from previous studies.^{1,5-8} Note that the y axis is presented in a logarithm
 51 scale to accommodate the drastically different k^II of FA at pH 2 and pH 10 reported by
 52 Amorim et al. (2020) and Ervens et al. (2003).



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 54 **Figure S4.** k_{obs} of FA, GA, and PA at pH 2 and 7. The carboxylic acid concentrations were
 55 fixed at 10 μM , the H_2O_2 concentration was fixed at 100 μM , while either 0 μM or 250 μM or
 56 1250 μM AN were used in these experiments. Error bars indicate standard deviation of multiple
 57 experiments.



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59 **Figure S5.** Calculated carboxylic acids partitioning between gas phase and aqueous phase as a
 60 function of liquid water content (LWC). The Henry's law solubility coefficients used for
 61 calculation are listed in Table S5.

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73 **Table S1.** Concentrations of NH₄OH or H₂SO₄ in the solutions and the resulting ionic strengths
 74 (*I*) of the solutions.

Solution pH	NH ₄ NO ₃	NH ₄ OH	H ₂ SO ₄	<i>I</i>
2	250 μM	0	0.00535 M	0.01095 M
2	1250 μM	0	0.00535 M	0.01195 M
3	250 μM	0	0.00107 M	0.00239 M
3	1250 μM	0	0.00107 M	0.00309 M
4	250 μM	0	0	0.00025 M
4	1250 μM	0	0	0.00125 M
7	250 μM	0.000039 M	0	0.0002695 M
7	1250 μM	0.000039 M	0	0.0012695 M

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76 **Table S2.** List of reactions pathways initiated by the aqueous photolysis of inorganic nitrate.⁹⁻

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No.	Reactions	Quantum yield (Φ)/ Acid dissociation constant (pK _a)
1	NO ₃ ⁻ + hv → [•NO ₂ + O• ⁻] _{cage}	Φ = 0.01
2	[•NO ₂ + O• ⁻] _{cage} → •NO ₂ + O• ⁻	—
3	O• ⁻ + H ₂ O ⇌ •OH + OH ⁻	pK _a (•OH) = 11.9
4	[•NO ₂ + O• ⁻] _{cage} → OONO ⁻	—
5	OONO ⁻ + H ⁺ ⇌ HOONO	pK _a = 7
6	HOONO → •OH + •NO ₂	—
7	2 •NO ₂ ⇌ N ₂ O ₄	—
8	N ₂ O ₄ + H ₂ O → HNO ₂ + NO ₃ ⁻ + H ⁺	—
9	HNO ₂ ⇌ H ⁺ + NO ₂ ⁻	pK _a = 3 ~ 3.5
10	NO ₂ ⁻ + hv → •NO + O• ⁻	Φ = 0.025–0.065
11	NO ₂ ⁻ + hv → •NO ₂ + e ⁻	Φ = ~ 0.001
12	NO ₂ ⁻ + •OH → •NO ₂ + OH ⁻	—
13	•NO + •NO ₂ ⇌ N ₂ O ₃	—
14	N ₂ O ₃ + H ₂ O → 2 NO ₂ ⁻ + 2 H ⁺	—

15	$\text{HNO}_2 + \text{h}\nu \rightarrow \cdot\text{NO} + \cdot\text{OH}$	$\Phi = 0.35$
16	$\text{HNO}_2 + \cdot\text{OH} \rightarrow \cdot\text{NO}_2 + \text{H}_2\text{O}$	—
17	$2 \text{HNO}_2 \rightarrow \cdot\text{NO} + \cdot\text{NO}_2 + \text{H}_2\text{O}$	—

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79 **Table S3.** Dissociation fractions for FA and GA used to calculate k_{OH} .

	FA		GA	
	HA	A ⁻	HA	A ⁻
pH 2	98.3%	1.7%	98.5%	1.5%
pH 3	84.9%	15.1%	87.1%	12.9%
pH 4	18.3%	81.7%	21.2%	78.8%
pH 7	0.01%	99.9%	0.01%	99.9%

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81 **Table S4.** Second-order rate constants (k_{rxn}^{HA+OH} and $k_{rxn}^{A^-+OH}$) for the HA and A⁻ forms of FA
82 and GA

FA				GA			
HA (M ⁻¹ s ⁻¹)	Ref.	A ⁻ (M ⁻¹ s ⁻¹)	Ref.	HA (M ⁻¹ s ⁻¹)	Ref.	A ⁻ (M ⁻¹ s ⁻¹)	Ref.
1.0×10^8	1	2.4×10^9	1	3.8×10^8	7	$(8.6 \pm 0.7) \times 10^8$	6
0.8×10^8	5	2.9×10^9	5				

83 Note: The average of two rate constants were used to calculate the simulated k_{obs} of FA.84 **Table S5.** Parameters used to calculate the first-order rate constants of FA, GA, and PA in
85 Figure 7.

		FA	Ref.	GA	Ref.	PA	Ref.
Property	pK _a	3.75	1	3.82	2	2.5	3
	K_H	88 mol cm ⁻³ Pa ⁻¹	14	280 mol cm ⁻³ Pa ⁻¹	14	3100 mol cm ⁻³ Pa ⁻¹	14
Gas	$k_{rxn,g}^{OH}$	6.24×10^{-7} cm ³ molec. ⁻¹ s ⁻¹	15	3.11×10^{-6} cm ³ molec. ⁻¹ s ⁻¹	16	$*4.60 \times 10^{-4}$ s ⁻¹	17
Aerosols (pH 3)	$k_{rxn,aq}^{OH}$	3.22×10^8 M ⁻¹ s ⁻¹	This study	3.58×10^8 M ⁻¹ s ⁻¹	This study	$*1.91 \times 10^{-4}$ s ⁻¹	This study
Clouds (pH 4)	$k_{rxn,aq}^{OH}$	1.36×10^9 M ⁻¹ s ⁻¹	This study	7.16×10^8 M ⁻¹ s ⁻¹	This study	$*7.73 \times 10^{-5}$ s ⁻¹	This study

86 * Direct photolysis rates were used instead of much slower rate constants with ·OH.

87 **Section S1. SPE protocol and UPLC-MS measurements of BA and PHBA**

88 SPE was performed to desalt the samples using SPE cartridges (Oasis MAX, 60 mg, 3
89 cc, 60 μm , Waters). First, the sorbent was conditioned and equilibrated using 3 mL methanol
90 (LC-MS grade) followed by 3 mL Milli-Q water. Next, the cartridge was loaded with 3 mL of
91 1 \times diluted sample solutions and then purged with 6 mL Milli-Q water. A vacuum pump was
92 used to dry out the sorbent before elution using 3 mL 2% formic acid (LC-MS grade) in
93 methanol (LC-MS grade). All the desalted samples were filtered using 0.2 μm nylon syringe
94 membrane to remove any particulates prior to UPLC-MS analysis.

95 UPLC-MS analyses were performed using a reverse phase Kinetex Polar C18 column
96 (2.6 μm , 150 \times 2.1 mm) equipped with a Polar C18 guard column. For the mobile phase, eluent
97 A was 10 mM ammonia acetate (LC-MS grade) in Milli-Q water buffered with 0.03% acetic
98 acid (LC-MS grade), and eluent B was pure methanol (LC-MS grade). A gradient elution
99 program was used, and it was delivered at a flow rate of 0.3 mL min⁻¹. The following mobile
100 phase gradient was used for the detection of BA and its product PHBA: 0 to 3 min 1% B, 3 to
101 5 min linear rise to 80% B and hold to 6 min, 6 to 6.5 min linear drop to 1 % B and then hold
102 to 10 min for equilibrium. The sample injection volume was set to 10 μL . The following tandem
103 MS conditions were used: -4500 V ESI ion spray voltage, 80 V declustering potential, -20 V
104 collision energy, 50 psi ion source gas, 25 psi curtain gas, and 450 $^{\circ}\text{C}$ source temperature.

105 **Section S2. Calculations of the first-order rate constants of FA, GA, and PA**

106 We used a similar methodology as the one used by Yang et al. (2021) to calculate the
107 first-order rate constants of FA, GA, and PA.¹⁸ Briefly, to represent the realistic conditions of
108 atmospheric aqueous phase, we used the liquid water content (LWC) and pH of aqueous
109 aerosols and clouds compiled by Herrmann et al. (2015).¹⁹ We used pH 3 and 4 as the pH
110 conditions of aqueous aerosols and cloud water, respectively, which are close to their global
111 average pH values reported by previous studies.^{20, 21} The LWC values used for the first-order
112 decays of carboxylic acids in aerosols and clouds were set to 3 $\times 10^{-5}$ g m⁻³ and 1 g m⁻³,
113 respectively. The fraction of the three carboxylic acids present in the gas and aqueous phases
114 as a function of LWC is shown in Figure S5. The fractions were calculated using the Henry's
115 law solubility coefficient, K_H , and the method described by Witkowski et al. (2019).²² The
116 concentrations of $\cdot\text{OH}$ ($[\cdot\text{OH}]$) in the gas phase, aerosols, and clouds were set to 1 $\times 10^6$
117 molecules cm⁻³, 5 $\times 10^{-13}$ M, and 5 $\times 10^{-14}$ M, respectively. The first-order rate constants of FA

118 and GA in the gas phase (k_g^I , s⁻¹) and aqueous aerosols/clouds ($k_{aerosols/clouds}^I$, s⁻¹) were
119 subsequently calculated using following equations:

$$120 \quad k_g^I = \frac{k_{Heff} \times LWC}{1 + k_{Heff} \times LWC} \times k_{rxn,g}^{OH\cdot} \times [\cdot OH]_{gas} \quad (S1)$$

$$121 \quad k_{aerosols/clouds}^I = \frac{1}{1 + k_{Heff} \times LWC} \times k_{rxn,g}^{OH\cdot} \times [\cdot OH]_{aq} \quad (S2)$$

122 where k_{Heff} is the effective Henry's law constants and is expressed as:

$$123 \quad k_{Heff} = k_H \times \left(1 + \frac{[H^+]}{K_a}\right) \quad (S3)$$

124 It should be noted that photolysis is the dominant sink of PA in both the atmospheric gas phase
125 and aqueous phase. The PA photolysis rate is nearly two orders of magnitude faster than the
126 rate of its reaction with $\cdot OH$.^{17, 23} Therefore, we used the direct photolysis rates from the
127 literature (gas phase) and from this study (aqueous phase) to simulate the decay and lifetime of
128 PA in atmosphere. The parameters used to calculate the first-order rate constants of FA, GA,
129 and PA are summarized in Table S5.

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