Electronic Supplementary Material (ESI) for Environmental Science: Atmospheres.

# Electronic Supplementary Information

# Photo-oxidation of pinic acid in the aqueous phase: a mechanistic investigation under acidic and basic pH conditions

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## *Quantification of Initial PA*

The initial concentration of PA was quantified using proton nuclear magnetic resonance ($^1$H NMR) spectroscopy. The PA stock solution (in $H_2O$) was diluted by a factor of ten into $D_2O$, with dimethyl sulfoxide (DMSO, 1.0 mM) added as an internal standard. By relating the peak integration of PA to that of DMSO, the concentration of PA can be determined. The accuracy of quantitative $^1$H NMR can be within a few percent. A similar approach to the current method has been utilized by a previous study to quantify reaction products of carbonyl compounds.[1] Dilution in $D_2O$ was necessary to minimize the impact of the $H_2O$ peak appearing at approximately 4.8 ppm.

The $^1$H NMR data were acquired on a 700 MHz system equipped with a cold probe and an Agilent 7620 Sample Handling Robot. Simple presat was used for water suppression. Two seconds of saturation were allowed during the relaxation delay before issuing the pulse command, with 20 s relaxation delay and 2 s acquisition (total relaxation time of 22 s). Data were processed with 0.25 Hz of line broadening added to the FID to enhance signal to noise and a digital filter to further remove the residual water peak prior to Fourier transform. The relaxation delay and water suppression were both optimized prior to data acquisition. The spectrum is referenced to DMSO, set to 2.71 ppm. The recorded $^1$H NMR spectrum is shown in Fig. S1.

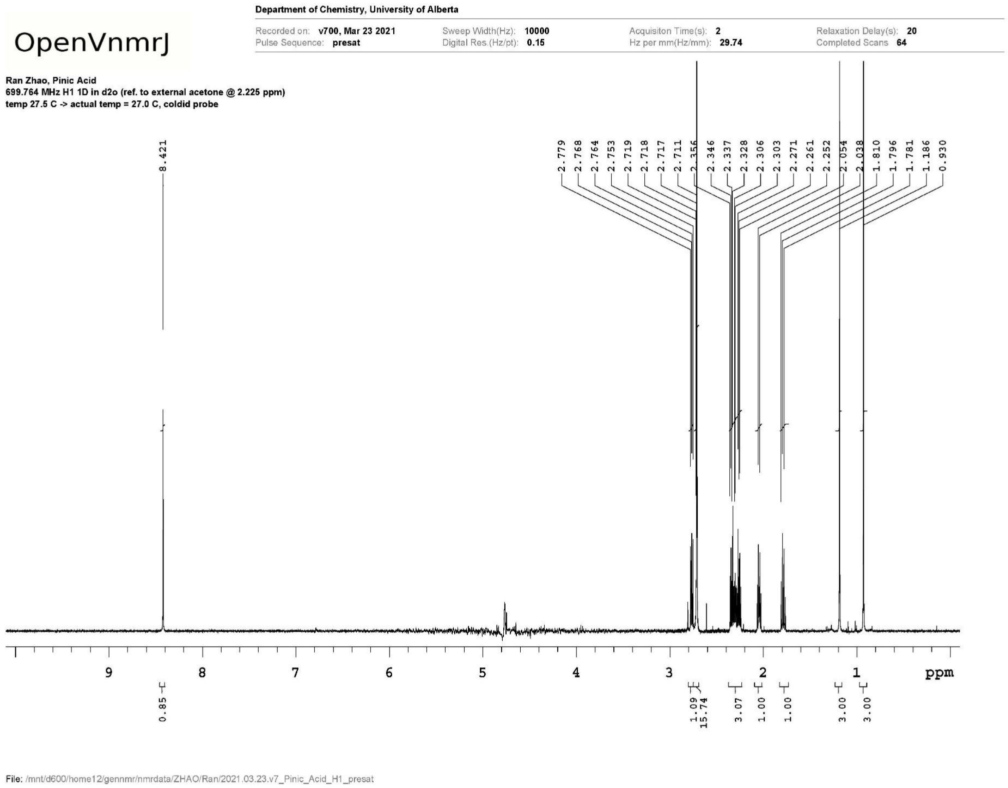

**Fig. S1.** $^1$H NMR spectrum of the PA stock solution diluted in $D_2O$. DMSO was added as an internal standard. The chemical shifts are shown on the top of the peaks, while the peak integrations are indicated below the x-axis.

DMSO appears as a singlet peak with an integration of 15.74. While numerous PA peaks are detected, we focus on the singlet peak at 1.2 ppm, which is attributed to one of the two (-$CH_3$) groups on PA. The integration of this peak is 3.00. The concentration of PA can be calculated by Eq. S1:

$$[PA] = [DMSO]\ x \frac{I_{PA} / n_{H,\,PA}}{I_{DMSO} / n_{H,\,DMSO}} \qquad Eq.S1$$

[DMSO] is the concentration of DMSO added to the solution ( 1.0 mM). $I_{\mathrm{PA}}$ and $I_{\mathrm{DMSO}}$ are the integration of peaks for PA and DMSO, respectively. $n_{\mathrm{H,PA}}$ and $n_{\mathrm{H,DMSO}}$ are numbers of protons responsible for the peaks of interest. In this case, $n_{\mathrm{H,PA}}$ = 3 (-$CH_3$ group), and $n_{\mathrm{H,DMSO}}$ = 6. Note that all the six protons on DMSO are responsible for its singlet peak. Using Eqn S1, the concentration of PA in the solution was calculated to be 0.38 mM, which is translated into 3.8 mM in the PA stock solution. This concentration is used throughout this work for yield determination. The 1H NMR also indicates the absence of other impurities in the stock solution, except for a peak attributed to formic acid (8.421 ppm). The concentration of formic acid impurities is estimated to be 0.32 mM and is likely present in the $D_2O$ we used to dilute the sample.

### *Offline (-)ESI–LC–MS for Elemental Analysis of CPA Oxidation Products*

**Table S1.** List of Major CPA OH-oxidation Peaks Detected by (-)ESI–LC–MS.[2]

| MW (g/mol) | $[M–H]^-$ | Elemental Composition |
|---|---|---|
| 188 | 187 | $C_8H_{12}O_5$ |
| 198 | 197 | $C_{10}H_{14}O_4$ |
| 200 | 199 | $C_{10}H_{16}O_4$ |
| 204 | 203 | $C_8H_{12}O_6$ |
| 214 | 213 | $C_{10}H_{14}O_5$ |
| 216 | 215 | $C_{10}H_{16}O_5$ |
| 232 | 231 | $C_{10}H_{16}O_6$ |
| 234 | 233 | $C_{10}H_{18}O_6$ |

### *Online PILS–MS Analysis of PA*

**Table S2.** Online PILS–MS Instrument's Parameters for the Analysis of PA OH-Oxidation.

| | | | |
|---|---|---|---|
| **Injection flow rate** | ~18 µL/min | **ESI- Capillary voltage** | –40 V |
| **Nebulizer gas (air) pressure** | 20 psi | **ESI- Detector Voltage** | 1270 V |
| **Drying gas ($N_2$) pressure** | 20 psi | **ESI+ Shield voltage** | +600 V |
| **Drying gas temperature** | 200℃ | **ESI+ Capillary voltage** | 100 V |
| **API housing temperature** | 50℃ | **ESI+ Detector voltage** | 1270 V |
| **Manifold temperature** | 40℃ | **ESI- Needle voltage** | –3700 V |
| **CID gas** | Ar | **ESI- Shield voltage** | –600 V |
| **CID gas pressure** | 1.50 mTorr | **ESI+ Needle voltage** | +4000 V |

## *MS/MS for Structural Confirmation of PA Oxidation Products*

The fragmentation spectra of the oxidation products of *m/z* 155, *m/z* 187, and *m/z* 215 are shown in Fig. S2. The product detected as *m/z* 155 produced an intense fragmentation ion at *m/z* 111 due to $CO_2$ elimination (–44 au), which indicates the presence of a carboxylic group. The *m/z* 187 fragmentation spectrum produced ions of *m/z* 169 (neutral loss of $H_2O$) and *m/z* 143 ($CO_2$ elimination), and *m/z* 125 (–62 au, neutral loss of $CO_2$ and $H_2O$). By changing the fragmentor voltage from 10 to 20 eV, a fragment ion of *m/z* 99 (–88 au) was observed, representing the loss of two carboxylic acid functional groups. The *m/z* 215 fragmentation spectrum produced ions of *m/z* 197*, m/z* 173, and *m/z* 127*,* representing the loss of $H_2O$, $CO_2$ and the presence of up to two carboxylic groups, respectively.

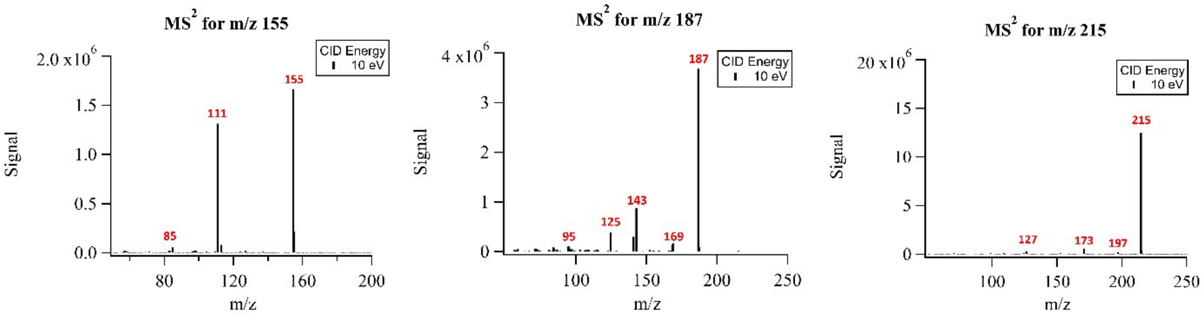

**Fig. S2.** MS/MS fragmentation spectra of PA oxidation products under uncontrolled pH conditions.

## *Structures of Surrogates Used for NPA and MBTCA*

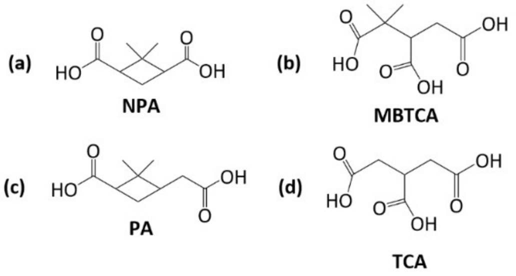

**Fig. S3.** Structure of PA oxidation products (a) NPA, and (b) MBTCA, and their respective surrogate compounds (c) PA, and (d) TCA.

## *References*

(1) Zhao, R.; Lee, A. K. Y.; Soong, R.; Simpson, A. J.; Abbatt, J. P. D. Formation of Aqueous-Phase α-Hydroxyhydroperoxides (α-HHP): Potential Atmospheric Impacts. *Atmospheric Chem. Phys.* **2013**, *13* (12), 5857–5872.

(2) Witkowski, B.; Gierczak, T. Cis-Pinonic Acid Oxidation by Hydroxyl Radicals in the Aqueous Phase under Acidic and Basic Conditions: Kinetics and Mechanism. *Environ. Sci. Technol.* **2017**, *51* (17), 9765–9773.