

# Supplementary Material for “Photodegradation of secondary organic aerosol particles as a source of small, oxygenated volatile organic compounds”

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4 Pages, 1 Figure, 3 Tables

## PTR-ToF-MS Calibration

The PTR-ToF-MS was calibrated for the four OVOCs analyzed for this study (acetaldehyde, acetone, acetic acid, and formic acid) by evaporating a known amount of a given OVOC into the cleaned 5 m<sup>3</sup> chamber and monitoring the [M+1] peak, corresponding to the protonated OVOC. The OVOC was added to the chamber in small increments, and the corresponding PTR-ToF-MS signal was measured after each successive addition. The inlet line through which the OVOC was injected into the chamber was heated throughout the experiment to 60 °C, and the PTR-ToF-MS inlet line was also heated to the same temperature to prevent losses of OVOC on the steel surfaces of the inlets. We created a calibration plot for each OVOC comparing the actual amount of OVOC in the chamber with that reported by the PTR-ToF-MS instrument (Figure 1). The resulting calibration factors, representing the ratio of the measured to the actual OVOC concentrations, ranged from 1.1 to 4.9. Confidence intervals were calculated at the 95% level based on the uncertainty in the injection, the PTR-ToF-MS traces, and the resulting linear regression. These values are reported in Table S1.

We should point out that the calibration was done several months after the SOA photodegradation experiments, following a suggestion from the paper reviewers. To make the calibration as relevant as possible, the PTR-ToF-MS instrumental parameters were kept the same as when the photodegradation experiments were carried out. Nevertheless, because of the large time span between the experiments and the calibration, the conclusions reported in this paper should be viewed as qualitative.

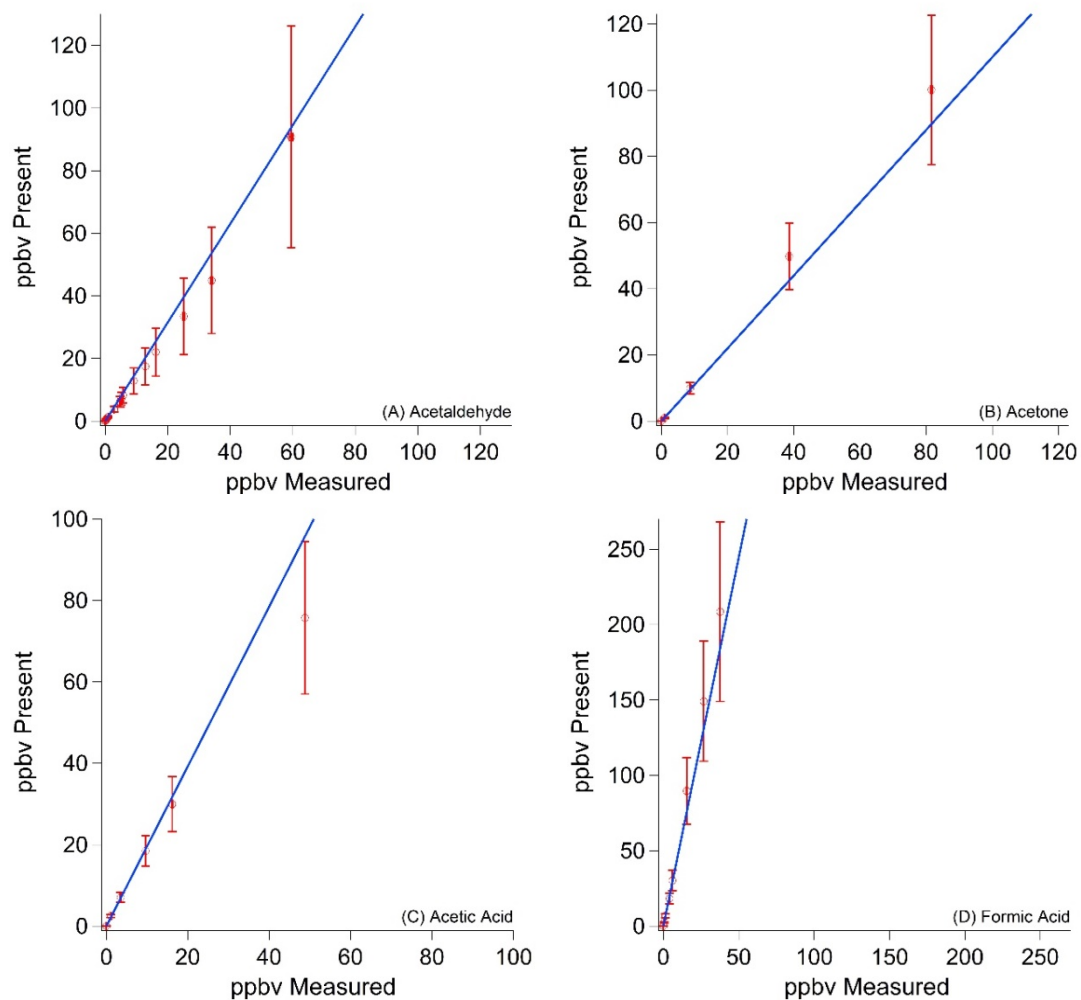


Figure S1: The PTR-ToF-MS calibration plots for (A) acetaldehyde, (B) acetone, (C) acetic acid, and (D) formic acid. The horizontal axis is the PTR-ToF-MS measured mixing ratio and the vertical axis is the known amount that was injected into the chamber. Each data point has vertical and horizontal error bars corresponding to 95% confidence intervals of the amount of OVOC present and measured, respectively. The vertical error bars increase with the OVOC amount because of the accumulation of errors in the successive injections of the OVOC in the chamber.

Table S1: The resulting calibration factors for each OVOC. For the SOA photodegradation experiments, we multiplied the mixing ratios measured by PTR-ToF-MS by this factor for each OVOC in the main text analysis.

OVOC	Calibration Factor	95% Confidence Interval
Acetaldehyde	1.5 <sub>8</sub>	0.2 <sub>3</sub>
Acetone	1.1 <sub>0</sub>	0.4 <sub>2</sub>
Acetic Acid	1.9 <sub>6</sub>	0.5 <sub>3</sub>
Formic Acid	4.8 <sub>9</sub>	0.9 <sub>7</sub>

## PTR-ToF-MS Peaks that Increased the Most during SOA Photodegradation

We investigated which peaks increased the most in the PTR-ToF-MS spectra during irradiation of a given SOA sample. This was performed by analyzing the time traces of the spectra, subtracting the baseline spectrum count, and analyzing the peaks that grew the most in intensity during irradiation. The 10 peaks that appeared to increase the most were examined to ensure they were indeed increasing in response to the UV radiation and not just drifting in intensity. Table S2 lists all the SOA systems analyzed for this paper and the top 10 increasing nominal  $m/z$  values below  $m/z$  100.

**Table S2: The top 10 increasing peaks (labeled by their nominal  $m/z$  values) during irradiation for each SOA system analyzed. The peaks are listed in descending order of the relative intensity change, with the peaks that increased the most appearing at the top. The precursors correspond to: "APIN" =  $\alpha$ -pinene, "ISO" = Isoprene, "TET" = Tetradecane, "TMB" = 1,3,5-Trimethylbenzene. The oxidants correspond to "O<sub>3</sub>" = Ozone, "OH, High NO<sub>x</sub>" = High NO<sub>x</sub> conditions, "OH, Low NO<sub>x</sub>" = Low NO<sub>x</sub> conditions. The peaks corresponding to acetaldehyde ( $m/z$  45, yellow), acetone ( $m/z$  59, green), acetic acid ( $m/z$  61, red), and formic acid ( $m/z$  47, blue), which could be assigned with more certainty and for which the PTR-ToF-MS calibration was done, are color coded.**

APIN/High NO <sub>x</sub>	APIN/Low NO <sub>x</sub>	APIN/O <sub>3</sub>	ISO/O <sub>3</sub>	ISO/High NO <sub>x</sub>	ISO/Low NO <sub>x</sub>	TET/High NO <sub>x</sub>	TET/Low NO <sub>x</sub>	TMB/High NO <sub>x</sub>	TMB/Low NO <sub>x</sub>
59	59	59	47	47	47	45	45	47	47
47	47	47	61	61	75	55	55	45	61
45	45	61	43	45	61	59	59	61	45
61	61	45	45	43	43	41	41	43	43
43	43	43	75	73	45	69	69	59	75
71	71	71	71	59	73	47	47	73	73
75	57	73	59	75	59	73	73	87	89
73	75	99	57	57	57	61	61	55	59
57	99	41	73	71	71	57	87	89	87
87	73	57	87	87	89	83	83	75	99

### APIN/O<sub>3</sub> SOA System Peak Assignments

The PTR-ToF-MS spectrum of OVOC emitted by the irradiated APIN/O<sub>3</sub> SOA system was further analyzed to assign peaks to the top increasing nominal  $m/z$  values. This system was chosen because it was quite efficient at producing OVOCs under irradiation. Table S3 lists the measured  $m/z$  values, the theoretically predicted  $m/z$  values, the potential chemical formula assignments, and possible assignments of the OVOCs. Because of the inability of PTR-ToF-MS to distinguish structural isomers the assignments cannot be made with certainty, especially at higher  $m/z$  values. However, chemical considerations help limit the assignments for the first four peaks to acetone, formic acid, acetic acid, and acetaldehyde.

**Table S3: The list of the high resolution  $m/z$  values for the PTR-ToF-MS peaks for the APIN/O<sub>3</sub> SOA system. The peaks are listed are in descending order for the overall intensity increase during irradiation.**

Measured $m/z$	Theoretical $m/z$ of the ion	Formula Assignment	Examples of OVOC that could match this formula
59.049	59.04914	C <sub>3</sub> H <sub>6</sub> OH <sup>+</sup>	<b>Acetone</b> , propanal, allyl alcohol
47.013	47.01276	CH <sub>2</sub> O <sub>2</sub> H <sup>+</sup>	<b>Formic acid</b>
61.027	61.02841	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> H <sup>+</sup>	<b>Acetic acid</b> , glycoaldehyde, methyl formate
45.033	45.03349	C <sub>2</sub> H <sub>4</sub> OH <sup>+</sup>	<b>Acetaldehyde</b>
43.018	43.01784	C <sub>2</sub> H <sub>2</sub> OH <sup>+</sup>	Ketene, ethynol, oxirene
71.049	71.04914	C <sub>4</sub> H <sub>6</sub> OH <sup>+</sup>	Cyclobutanone, crotonaldehyde, methyl vinyl ketone, dihydrofuran, many other possibilities
73.028	73.02841	C <sub>3</sub> H <sub>4</sub> O <sub>2</sub> H <sup>+</sup>	Methylglyoxal, acrylic acid, oxetanone, malondialdehyde, many other possibilities
99.080	99.08044	C <sub>6</sub> H <sub>10</sub> OH <sup>+</sup>	Cyclohexanone, cyclopentylformaldehyde, mesityl oxide, many other possibilities
41.039	41.03858	C <sub>3</sub> H <sub>5</sub> <sup>+</sup>	Propyne, allene, cyclopropene
57.033	57.03349	C <sub>3</sub> H <sub>4</sub> OH <sup>+</sup>	Acrolein, cyclopropanone, methylketene, other possibilities