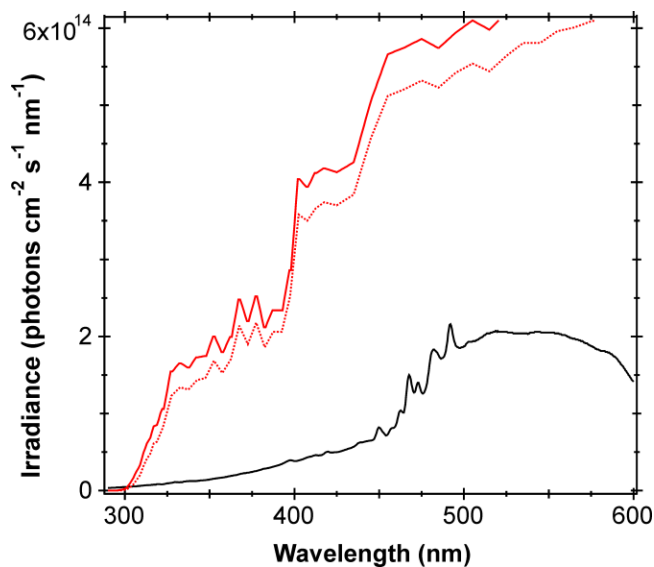


## SUPPLEMENT

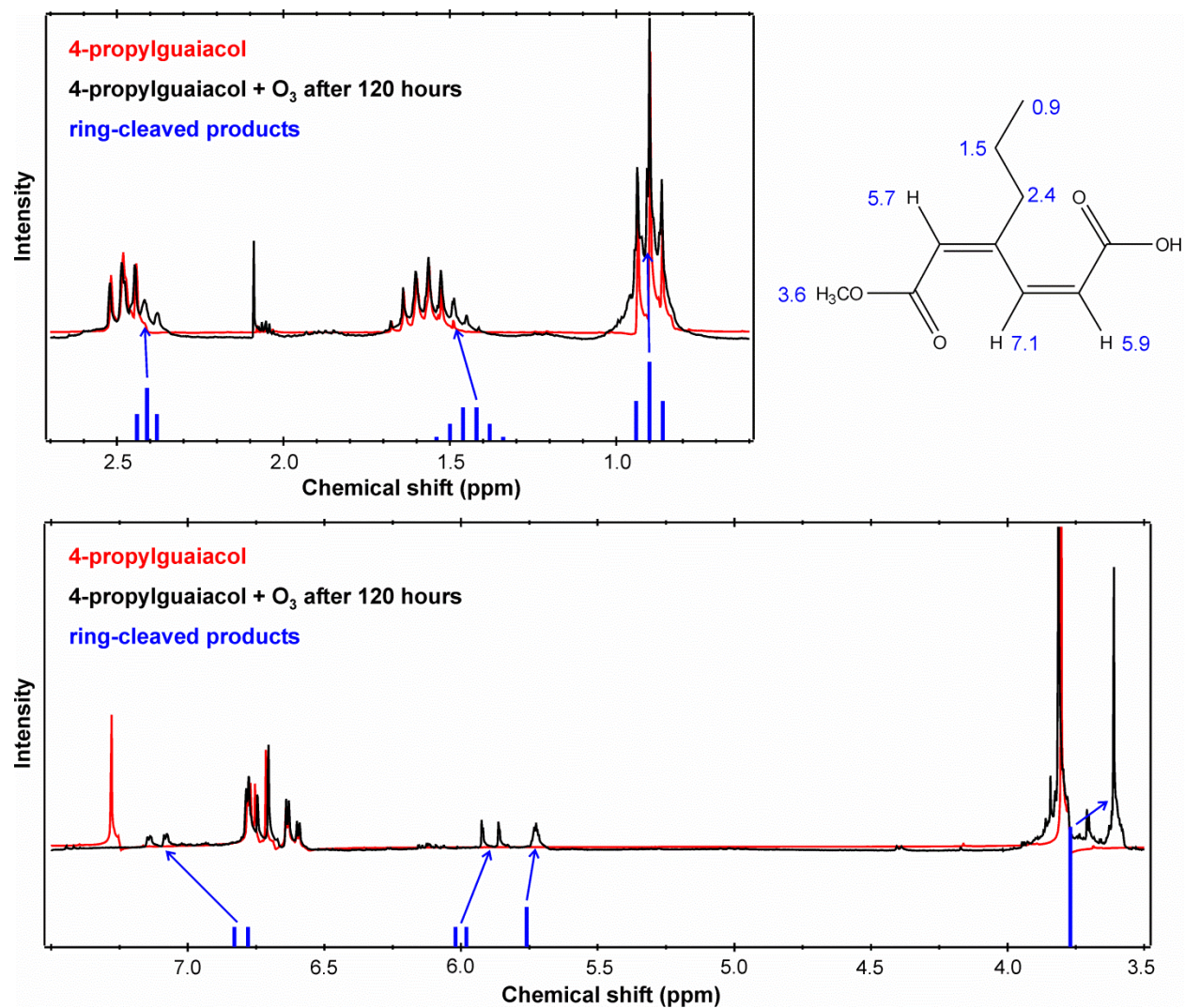
# Ozonolysis of surface adsorbed methoxyphenols: Kinetics of aromatic ring cleavage versus alkene side-chain oxidation.

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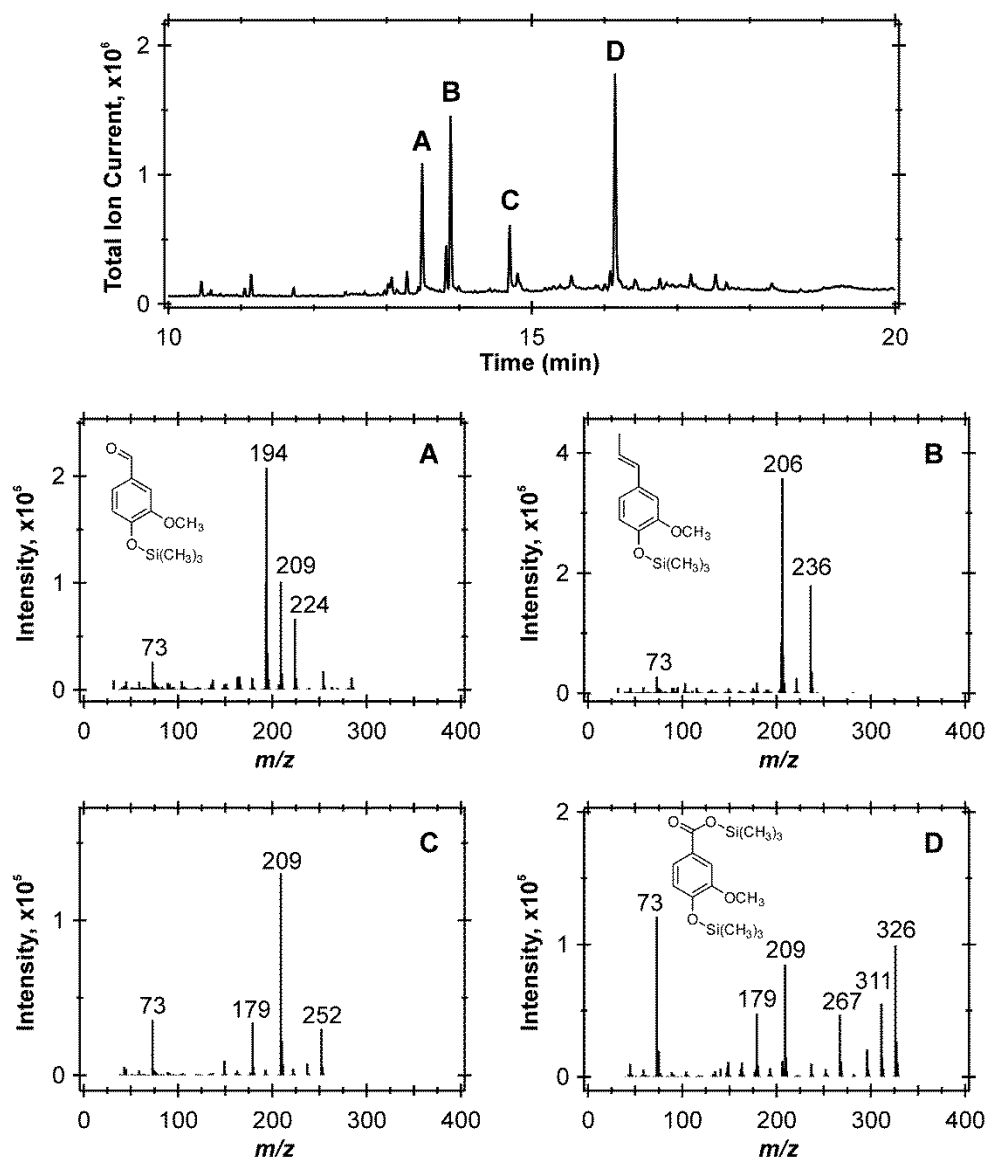


**Figure S1.** Spectral irradiance of xenon lamp solar simulator (black) used in eugenol photoenhanced ozonolysis study. For comparison, red lines show actinic flux at Earth's surface at 0° (solid) and 40° (dashed) zenith angles using best estimate surface albedo (Finlayson-Pitts and Pitts, 2000, and references therein). Spectral irradiance was determined by correlating the total integrated power ( $\lambda < 800$  nm), measured using a Newport Oriel power meter, and the relative intensity as a function of wavelength, which was measured using an Ocean Optics CCD spectrometer (HR2000).

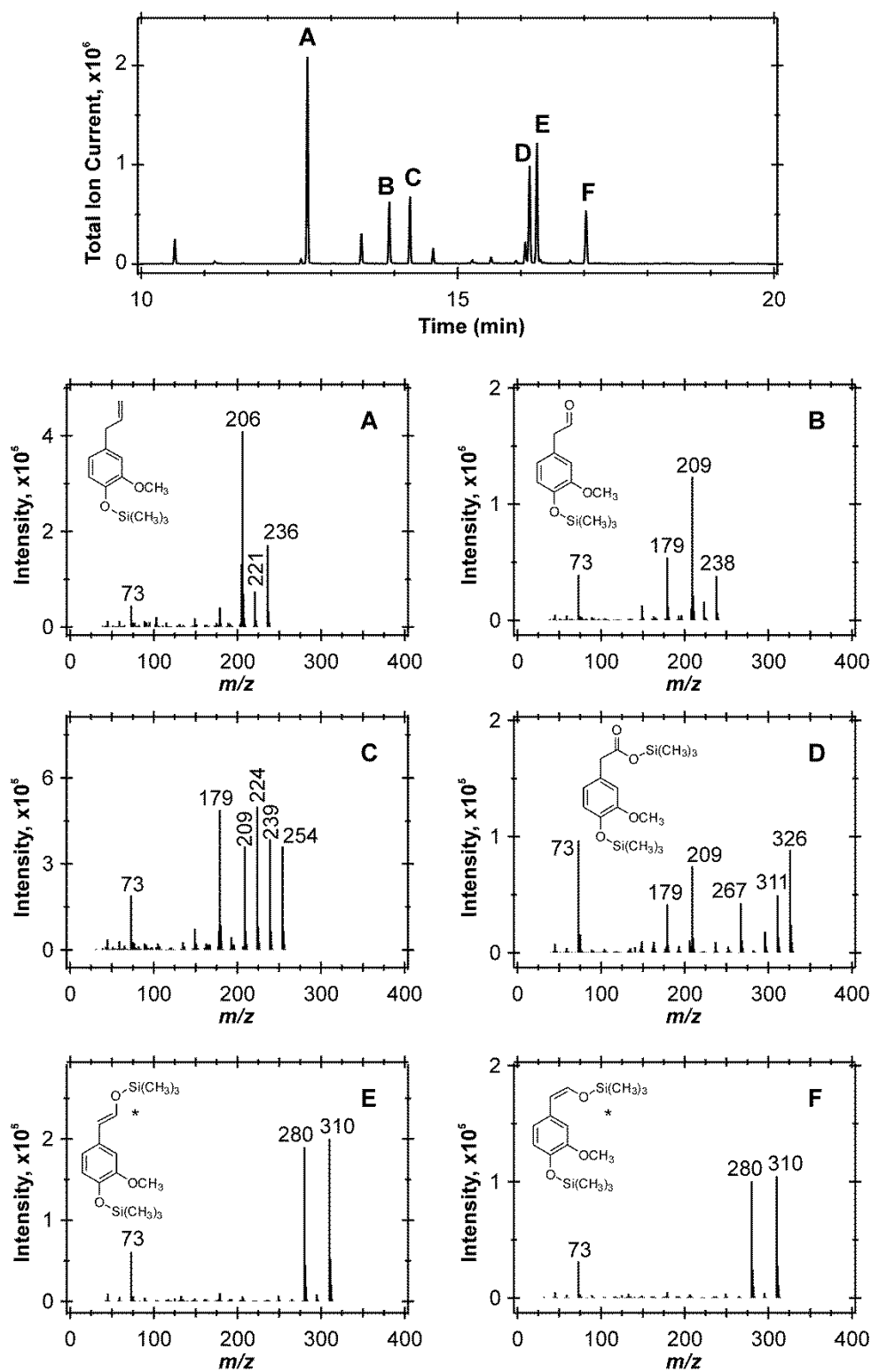
Finlayson-Pitts, B. J., and Pitts, N.: Chemistry of the upper and lower atmosphere: Theory, experiments, and applications, Academic Press, San Diego, 2000.



**Figure S2.** <sup>1</sup>H-NMR (200 MHz, *d*<sub>6</sub>-acetone, Me<sub>4</sub>Si) of 4-propylguaiacol (red), extracted reaction products for NaCl-adsorbed 4-propylguaiacol exposed to 1 ppm O<sub>3</sub> for 120 hours (black), and predicted spectrum for ring-cleaved product (blue) generated using ChemBioDraw Ultra, Version 11.0, 2007. Many unreacted 4-propylguaiacol features appear in black reacted spectrum, while the additional features are in good agreement with predicted spectrum. Observed chemical shifts for ring-cleaved product are denoted in blue on structure shown at top right. Ring-cleaved product carboxylic acid peak not identified (predicted δ<sub>H</sub> 11.0, confidence “rough”).

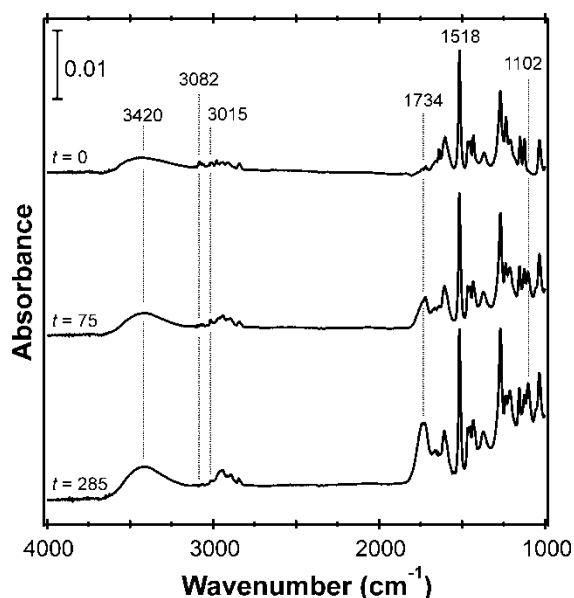
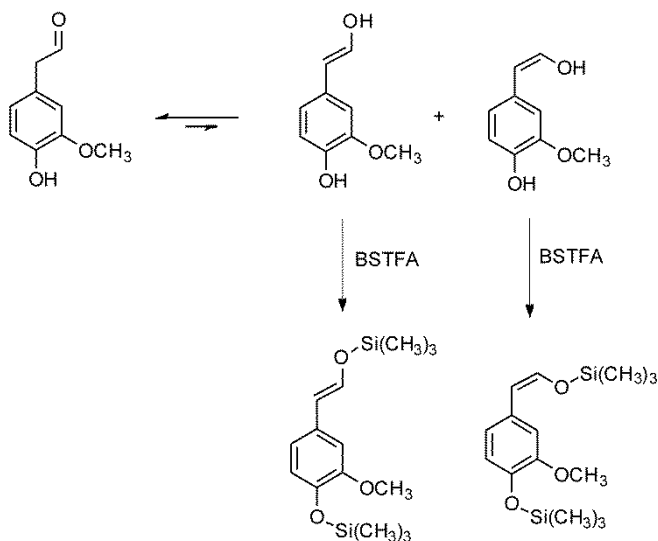


**Figure S3.** GC-MS analysis of isoeugenol ozonolysis products. Top: Total ion current chromatogram of extracted organics. Mass spectra of labeled peaks shown below. Peak A corresponds to vanillin; B to unreacted isoeugenol; C not conclusively identified, although contains a silylated methoxyphenol; and D, the dominant reaction product, identified as vanillic acid.



**Figure S4.** GC-MS analysis of eugenol ozonolysis products. Top: Total ion current chromatograph. Bottom: Mass spectra of major peaks. Peak A, unreacted eugenol; B, homovanillin; C, not conclusively identified, although contains a silylated methoxyphenol; D, homovanillic acid; E and F, proposed identification, \*see discussion below.

As noted in Fig. S4, three major TIC peaks following ozonolysis of eugenol were not conclusively identified by their mass spectra. For peak C, a comparison to library spectra suggests silylated methyl 4-hydroxy-3-methoxybenzoate, although the probability of this match was only 39%. Based on the mass spectrum, the MW of this compound is likely 254. Analysis of the fragmentation ions reveals many similarities to peaks B and D:  $m/z = 73$  indicates a  $\text{SiMe}_3$  fragment, while  $m/z = 179$  and  $209$  are consistent with (4-hydroxy-3-methoxyphenyl)methyl cation fragments. Product peaks E and F have identical mass spectra, suggesting *cis*- and *trans*- isomers with a MW of 310. Fragmentation patterns ( $m/z = 73$  and MW-30) indicate the presence of  $\text{SiMe}_3$ . We propose that this product is a byproduct of BSTFA derivatization following a keto-enol isomerization of homovanillin.



**Figure S5.** ATR-FTIR reaction spectra for  $\alpha\text{-Al}_2\text{O}_3$ -adsorbed eugenol exposed to 208 ppb  $\text{O}_3$  recorded at times 0, 75, and 285 minutes.

ATR-FTIR spectral features at  $t = 0$  minutes suggest physisorption of eugenol rather than monodentate binding as observed using DRIFTS. We attribute these differences to sample preparation. For ATR-FTIR, the ZnSe crystal was coated with an  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>/methanol slurry, which was subsequently dried in an oven at 100 °C and transferred in the ambient atmosphere to the FTIR flow cell. It seems possible that such a process may alter surface hydroxyl groups in such a way as to preclude monodentate binding. Eugenol ozonolysis product features were similar to those observed using DRIFTS and include carbonyl formation at 1734 cm<sup>-1</sup>, increased OH stretching vibrations at 3420 cm<sup>-1</sup> attributed to carboxylic acid groups, and a few distinct peaks in the fingerprint region (e.g., 1102 cm<sup>-1</sup>). The CH stretching region showed complete loss of the alkene peak at 3082 cm<sup>-1</sup> but only slight loss of the aromatic peak at 3015 cm<sup>-1</sup>. The alkene C=C stretch peak at 1639 cm<sup>-1</sup> decayed at a rate similar to loss of the 3082 cm<sup>-1</sup> peak, while retention of the strong aromatic ring vibration at 1518 cm<sup>-1</sup> and phenol bend at 1373 cm<sup>-1</sup> was consistent with the minimal loss of the aromatic CH stretching peak. ATR reaction kinetics were consistent with DRIFTS reaction kinetics.