

SUPPLEMENT

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

Erinn M. O'Neill, Alae Z. Kawam, Daryl Van Ry, and Ryan Z. Hinrichs*

Department of Chemistry, Drew University, Madison, NJ 07940 (rhinrich@drew.edu)

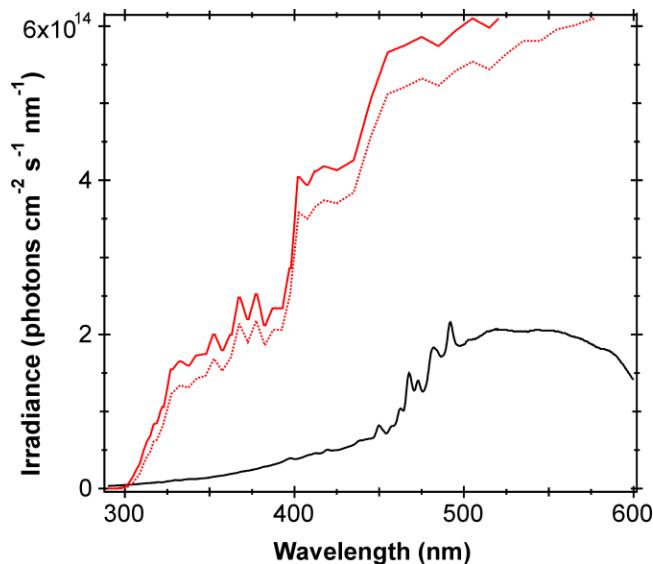


Figure S1. Spectral irradiance of xenon lamp solar simulator (black) used in eugenol photoenhanced ozonolysis study. For comparison, red lines show actinic flux at Earth's surface at 0° (solid) and 40° (dashed) zenith angles using best estimate surface albedo (Finlayson-Pitts and Pitts, 2000, and references 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.

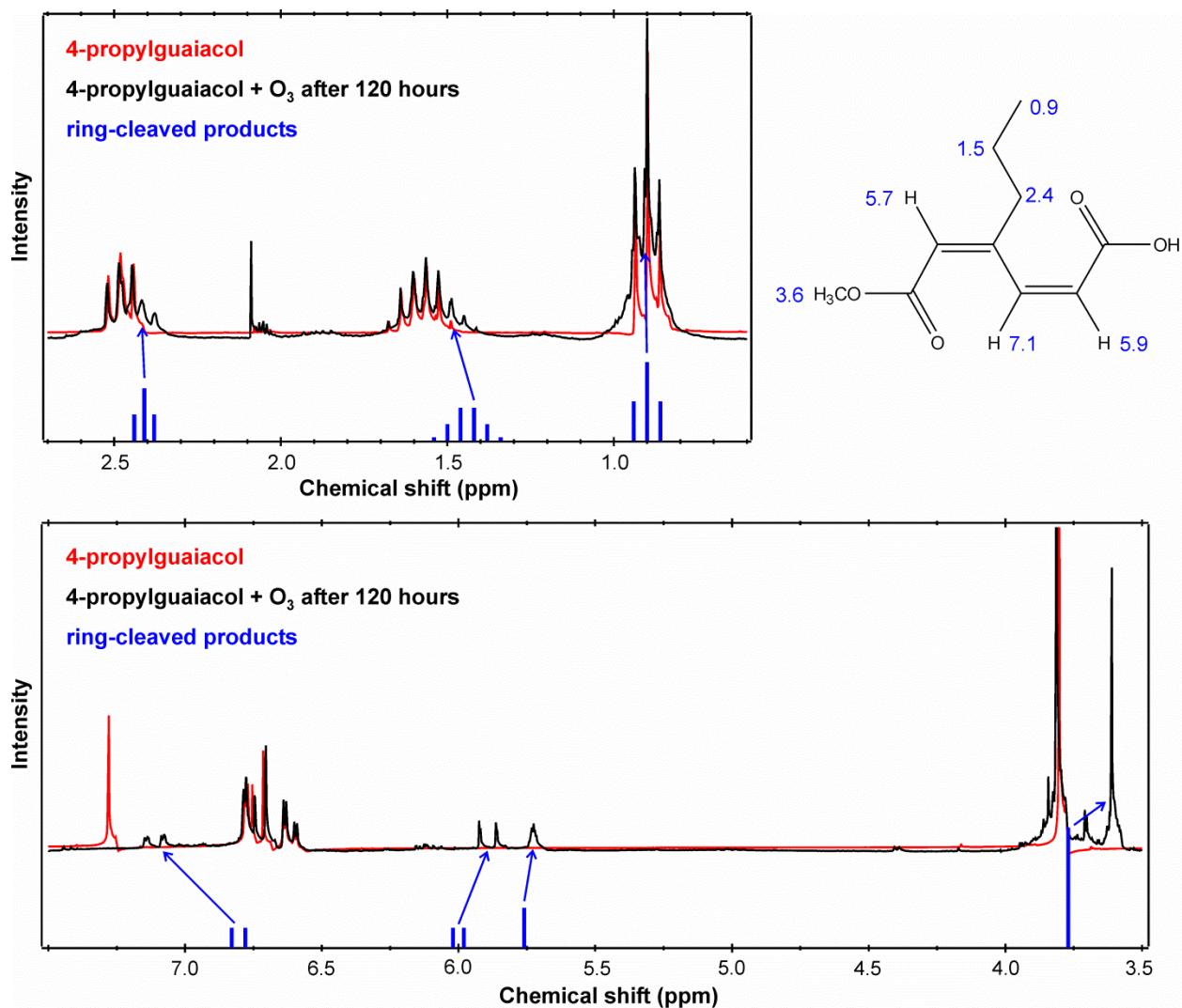


Figure S2. ¹H-NMR (200 MHz, *d*₆-acetone, Me₄Si) of 4-propylguaiacol (red), extracted reaction products for NaCl-adsorbed 4-propylguaiacol exposed to 1 ppm O₃ for 120 hours (black), and predicted spectrum for ring-cleaved product (blue) generated using ChemBioDraw Ultra, Version 11.0, 2007. Many unreacted 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_H 11.0, confidence “rough”).

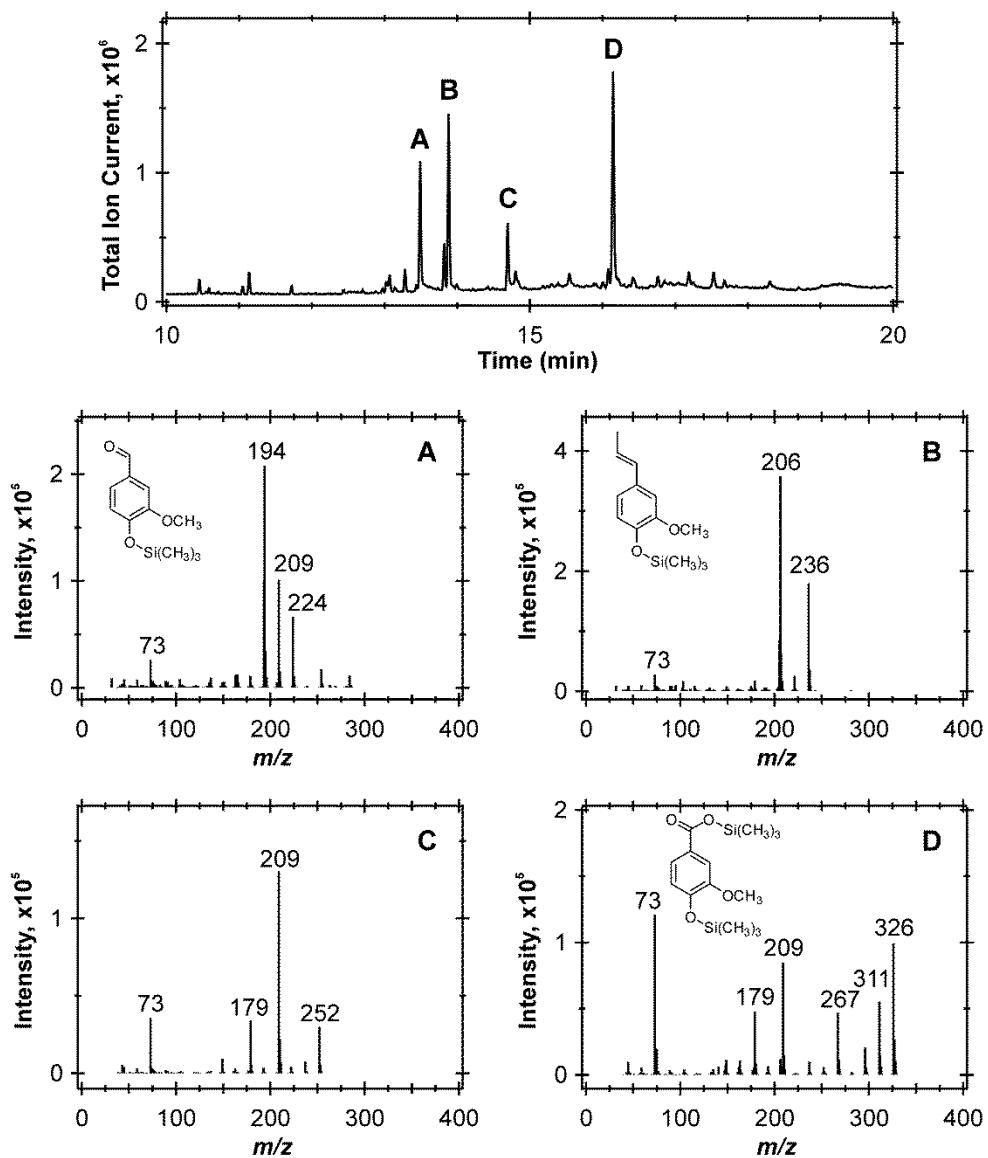


Figure S3. GC-MS analysis of isoeugenol ozonolysis products. Top: Total ion current chromatogram of extracted organics. Mass spectra of labeled peaks shown below. Peak A corresponds to vanillin; B to unreacted isoeugenol; C not conclusively identified, although contains a silylated methoxyphenol; and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

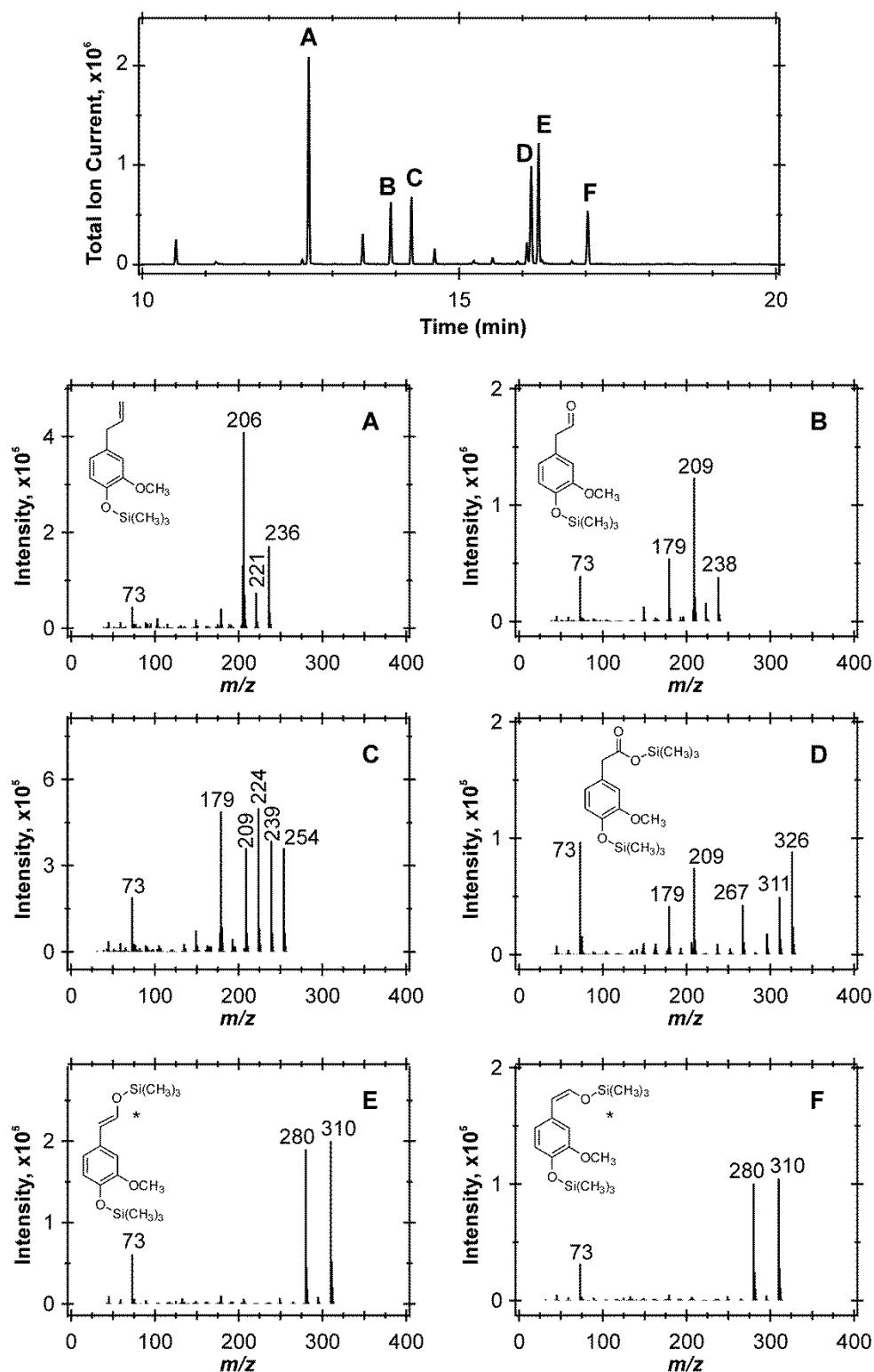


Figure S4. GC-MS analysis of eugenol ozonolysis products. Top: Total ion current chromatograph. Bottom: Mass spectra of major peaks. Peak A, unreacted eugenol; B, homovanillin; C, not conclusively identified, although contains a silylated methoxyphenol; D, homovanillic acid; E and F, proposed identification, *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 SiMe_3 fragment, while $m/z = 179$ and 209 are consistent with (4-hydroxy-3-methoxyphenyl)methylium 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 SiMe_3 . We propose that this product is a byproduct of BSTFA derivatization following a keto-enol isomerization of homovanillin.

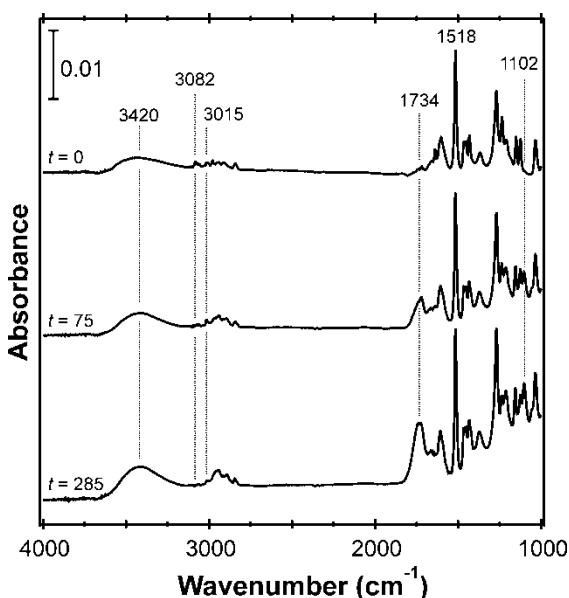
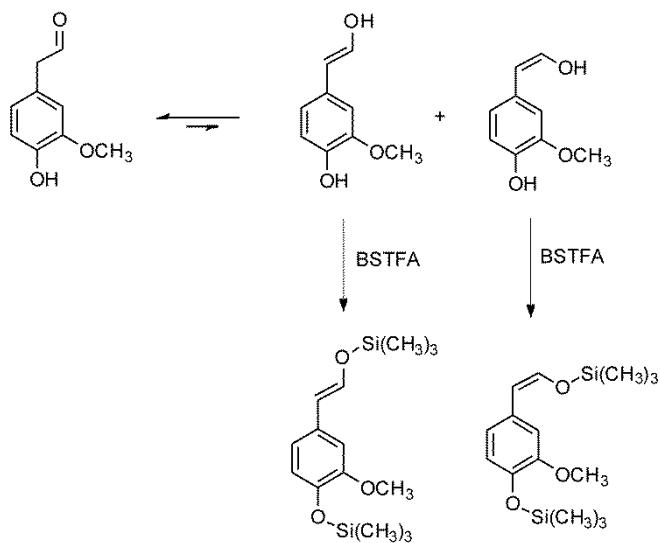


Figure S5. ATR-FTIR reaction spectra for $\alpha\text{-Al}_2\text{O}_3$ -adsorbed eugenol exposed to 208 ppb O_3 recorded at times 0, 75, and 285 minutes.

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 α -Al₂O₃/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⁻¹, increased OH stretching vibrations at 3420 cm⁻¹ attributed to carboxylic acid groups, and a few distinct peaks in the fingerprint region (e.g., 1102 cm⁻¹). The CH stretching region showed complete loss of the alkene peak at 3082 cm⁻¹ but only slight loss of the aromatic peak at 3015 cm⁻¹. The alkene C=C stretch peak at 1639 cm⁻¹ decayed at a rate similar to loss of the 3082 cm⁻¹ peak, while retention of the strong aromatic ring vibration at 1518 cm⁻¹ and phenol bend at 1373 cm⁻¹ was consistent with the minimal loss of the aromatic CH stretching peak. ATR reaction kinetics were consistent with DRIFTS reaction kinetics.