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

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Figure SI-1. $^1$H-NMR (200 MHz, $d_6$-acetone, Me$_4$Si) of 4-propylguaiacol (red), extracted reaction products for NaCl-adsorbed 4-propylguaiacol exposed to 1 ppm O$_3$ 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 $\delta_H$ 11.0, confidence “rough”).
Figure SI-2. 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 silated methoxyphenol; and D, the dominant reaction product, identified as vanillic acid.
Figure SI-3. 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 silated methoxyphenol; D, homovanillic acid; E and F, proposed identification, *see discussion below.
As noted in Fig. SI-3, 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 silated 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 SiMe₃ 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 SiMe₃. We propose that this product is a byproduct of BSTFA derivatization following a keto-enol isomerization of homovanillin.

![Diagram of chemical structures and reagents](image)

**Figure SI-4.** ATR-FTIR reaction spectra for α-Al₂O₃-adsorbed eugenol exposed to 208 ppb O₃ 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 \( \alpha\text{-Al}_2\text{O}_3\)/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.

![Figure SI-5](image.png)

**Figure SI-5.** 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).