

Materials and Methods

Chemicals

Sodium hypochlorite (11-15% active chlorine) and sodium phosphate monobasic, monohydrate (99.5%, NaH_2PO_4) were purchased from Thermo Fisher Scientific. Cl_2 compressed gas cylinder (951 ppm Cl_2 , nitrogen balance) and a certified gas standard mixture (17 compounds, ISO 17025 compliant) were purchased from Linde Inc. North America (Alpha, NJ). Limonene (R, +, 99%) was purchased from Sigma Aldrich (St. Louis, MO). *N,O*-Bis(trimethylsilyl)trifluoroacetamide (BSTFA, with 1% TMCS) was purchased from Cerilliant Corporation (Round Rock, TX). The endocyclic limonene chlorohydrin products were independently prepared following literature procedures³⁹ to assist in identification of gas-phase products.

HOCl and Cl_2 production

Gaseous HOCl and Cl_2 were produced using procedures adapted from previous studies.^{32, 36} To a solution of NaH_2PO_4 (348 mM, pH 4.2), NaOCl (11-15% active chlorine) was added for a final concentration of 367 mM and pH of 6.8, which is below the pK_a of HOCl at 7.5. Ultra-high purity nitrogen gas was bubbled at 50 ml/min through this solution. The volatilized HOCl and Cl_2 flowed through Teflon-lined tubing attached to a custom 10 cm UV gas cell (Firefly Sci, Inc., Northport, NY) within a Cary 60 UV/Vis spectrophotometer (Agilent, Santa Clara, CA). Following blank correction with nitrogen, the UV absorbance at 242 and 330 nm were monitored for HOCl and Cl_2 , respectively. For each experiment, flow was maintained and absorbance data collected until a steady state concentration was attained, and following this, absorbances were converted to concentrations using Beer's law and corresponding absorption cross sections of $2.03 \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$ for HOCl and $2.55 \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$ for Cl_2 .⁴⁰

Chamber Experiments

Gas-phase reactions were performed in collapsible 100 L Teflon chambers filled with clean air that was prepared by passing compressed house air through anhydrous calcium sulfate (Drierite, Xenia, OH) and 4 Å molecular sieves (Sigma Aldrich, St. Louis, MO) to eliminate moisture and contaminants. The clean air was then humidified using a bubbler to a desired relative humidity (RH) of $5 \pm 3\%$ or $50 \pm 3\%$, depending on the experiment. RH was confirmed with a hygrometer (HMI38, Vaisala, Vantaa, Finland). A separate Teflon chamber containing concentrated, gas-phase limonene (20 ppm) was prepared by passing the cleaned, humidified air through a heated 6.4 mm Swagelok® stainless-steel tee into which 10.7 μL limonene (99%) had been injected. The introduction of the conditioned air was controlled by a mass flow controller (GGFC37, Aalborg Instruments & Controls, Inc., Orangeburg, NY) to a flow rate of 5 L/min and a total volume of 80 L. Chambers containing 100 ppb of limonene were created by transferring aliquots from the concentrated 20 ppm limonene chamber to the prepared reaction chamber via 100-mL gas tight syringe (Hamilton, Franklin, MA). To prevent photolysis, all experiments were performed in the dark.

HOCl was added to the reaction chamber at the specific mixing ratio of 500 ppb HOCl to 100 ppb limonene. Using the concentration of HOCl determined by spectrophotometry (described above), the specific volume of gas needed was determined, which was introduced by timed infusion through the bubbler. Cl_2 is inherently produced using this method^{32, 36} and, thus, was simultaneously introduced with

HOCl during infusion. Cl_2 concentrations averaged 515 ± 45 ppb when HOCl was held constant at 500 ppb.

Experiments to evaluate the effect of Cl_2 in the absence of HOCl were performed using a certified standard of compressed Cl_2 . The concentration of Cl_2 within the cylinder was $951 \text{ ppm} \pm 2\%$, and the balance of the cylinder volume was nitrogen. **Caution!** *Chlorine is classified as a GHS Oxidizing Gas, Category 1; Acute Toxicity (inhalation), Category 2; Skin Corrosion, Category 1; Serious Eye Damage, Category 1; and Aquatic Hazard, Category 1. Working with chlorine gas at high concentrations carries the risk of significant injury or death. For these experiments, chlorine gas was handled within a chemical fume hood while wearing gas tight goggles, corrosive-resistant gloves, and half-mask respirators with approved gas/vapor cartridges. Additionally, personal chlorine gas monitors were worn by laboratorians while carrying out these experiments.* Within a chemical fume hood, the Cl_2 was flowed from the compressed cylinder into a small, intermediary Teflon chamber. From there, a gas-tight syringe was used to transfer the Cl_2 from the intermediate chamber to the 80 L Teflon reaction chambers, producing a final concentration of 500 to 1000 ppb, depending on the experiment.

For experiments incorporating ozone, a mercury pen lamp (Double Bore[®] lamp, Jelight, Irvine, CA) was used to photolyze molecular oxygen. The ozone concentration was measured using an 49i UV photometric ozone monitor (Thermo Fisher, Pittsburgh, PA) and was stored in a small Teflon chamber until use. Immediately at the start of HOCl/ Cl_2 infusion, a 100-mL gas tight syringe was used to transfer concentrated ozone to the 80 L limonene reaction chambers, yielding a final ozone concentration of 30 ppb.

BSTFA derivatization of impinger-collected gas-phase products

Reactions between limonene (5 ppm) and HOCl/ Cl_2 (approximately 5 ppm each) were prepared in Teflon chambers (80 L) followed by collection of products via impingers into 20 mL of acetonitrile at 3 L/min. Higher mixing ratios of reactants were chosen to ensure sufficient hydroxylated product concentrations for derivatization by BSTFA using previously published conditions.⁴¹ Solvent was removed under a stream of nitrogen, and the collected products were reconstituted in pyridine and heptane, and derivatized using BSTFA at 75°C for 70 minutes with agitation. After cooling, samples were analyzed by Orbitrap GC-MS (Trace 1310 gas chromatograph and Exactive Orbitrap MS, Thermo Scientific) and Agilent GC-MS (7890 GC and 240 EI/CI ion trap MS, Santa Clara, CA).

Gas-phase sampling and GC HRMS

In order to monitor the gas- phase products from the reaction between limonene + HOCl/ Cl_2 , immediately after introduction of the bleach oxidants, Teflon chambers were connected to a 7200 CTS cryogen-free gas preconcentrator (Entech, Simi Valley, CA) coupled to an Orbitrap GC-MS, and 50 mL of the atmosphere within was collected. From the preconcentrator, the sample was introduced onto the analytical GC column (DB-1, 60 m x 0.25 mm i.d., 1 μm film thickness, Agilent, Santa Clara, CA) using splitless mode and a sample loading flow program wherein helium began at 0.3 mL/min from 0 to 0.9 min, followed by 1.2 mL/min flow rate through the remainder of the temperature gradient. The temperature gradient consisted of the following: 35°C held isothermally for 3 min, 10°C/min ramp rate to a final temperature of 250°C, followed by an isothermal hold for 0.5 min. The Exactive mass spectrometer data were collected using a scan range of 30 to 500 Da, a resolution of 60,000, and electron ionization (EI) in positive ion mode. For more definitive molecular ion confirmation, positive

chemical ionization (PCI) mode, scanning from 50 to 500 Da, was utilized. The ion source temperature was set to 250°C for EI and 200°C for PCI, and the transfer line temperature was 280°C and 250°C for EI and PCI, respectively. Methane was used as the PCI reagent gas at a flow rate of 1.5 ml/min.

Calibration of chlorinated limonene species

Calibration of gas-phase limonene was performed using an evacuated 6L Silonite®-coated canister that was filled with a known volume with an ISO 17025-compliant, certified VOC standard mixture (Linde Inc., North America, Alpha, NJ) and humidified UHP nitrogen using an Entech 4700 static diluter (Entech, Simi Valley, CA). For calibration, the standardized canister was attached to the Entech 7200 preconcentrator, and varying volumes of gas were sampled to create the concentration range. The TIC peaks areas of limonene were integrated (Thermo Xcalibur, version 4.4.16.14) to generate a calibration curve to which TIC peak areas of chlorinated limonene species were calibrated. Yield values were calculated as the concentration of chlorinated product divided by the concentration of the consumed limonene, multiplied by 100.⁴²

Data processing and analysis

Mass spectral peak annotation was achieved through high-resolution accurate mass analysis, which allowed the elemental composition of monoisotopic and fragment ions to be determined. Calculation of elemental composition from m/z values was performed in Qual Browser (Thermo Xcalibur, version 4.4.16.14), which were compared to molecular formulas of suspected chlorinated limonene species. Ranges used for elemental composition were as follows: ¹²C, 0-30; ¹⁶O, 0-15; ¹H, 0-60; ³⁵Cl, 0-10; ³⁷Cl, 0-10, and a 5-ppm mass tolerance was used. Mass spectral peak identification was further supported by isotope pattern matching performed in Qual Browser and matching of experimental fragment ions to in silico fragmentation spectra generated in Mass Frontier (Thermo Fisher Scientific, version 8.0.577.177). Chromatographic peak areas for chlorinated limonene species were normalized by the limonene peak area measured at time zero for each experiment.