Factors affecting chlorinated product formation from sodium hypochlorite bleach and limonene reactions in the gas phase

Introduction

The application of sodium hypochlorite bleach to surfaces causes the release of chlorine (Cl_2) and hypochlorous acid (HOCl) into the gas phase where reactions with organic compounds can occur. The purpose of the current study was to investigate the reaction products generated from gas-phase bleach oxidants and limonene, a fragrance compound commonly found in indoor air due to personal care products and cleaning products. Gas-phase reactions were prepared in Teflon chambers housing HOCl, Cl_2, and limonene. The resulting chemical products were collected and analyzed using gas-phase preconcentration following by gas chromatography and high-resolution mass spectrometry. Several chlorinated products were detected including a limonene chlorohydrin and limonene species containing one, two, and three chlorines. Product concentration and yields were estimated for the most abundant products, and greater than 80% of the transformed limonene was represented in the detected products. Temporal sampling of the reactions allowed time courses to be plotted for limonene transformation and chlorinated limonene product generation under different conditions including the treatments of HOCl/Cl_2, Cl_2 only, high vs. low relative humidity, and +/- ozone. These experiments provide additional insight into the chemical transformations initiated by sodium hypochlorite bleach oxidants in the gas phase which may be of interest to human health.

Methods Collection

HOCl and Cl_2 production

- To a solution of NaH_2PO_4 (348 mM, pH 4.2), NaOCl (11-15% active chlorine) was added to a final concentration of 367 mM and pH of 6.8.
- Ultra-high purity nitrogen gas was bubbled at 50 ml/min through the above 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.

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).
- The clean air was humidified using a bubbler to a desired relative humidity of 5 ± 3 % or 50 ± 3%, depending on the experiment.
- 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 and a flow rate of 5 L/min was used to fill to 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.
- Experiments to evaluate the effect of Cl_2 in the absence of HOCl were performed using a certified standard of compressed Cl_2. 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.

Gas-phase sampling and gas chromatography – high resolution mass spectrometry

- 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.

Citations – publications based on the dataset

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