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# The effects of active chlorine on photooxidation of 2-methyl-2-butene

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ABSTRACT

Active chlorine comprising hypochlorite ($OCl^-$), hypochlorous acid (HOCl) and chlorine ($Cl_2$) is the active constituent in bleach formulations for a variety of industrial and consumer applications. However, the strong oxidative reactivity of active chlorine can cause adverse effects on both human health and the environment. In this study, aerosolized Oxone® [$2KHSO_5$, $KHSO_4$, $K_2SO_4$] with saline solution has been utilized to produce active chlorine (HOCl and $Cl_2$). To investigate the impact of active chlorine on volatile organic compound (VOC) oxidation, 2-methyl-2-butene (MB) was photoirradiated in the presence of active chlorine using a 2-$m^3$ Teflon film indoor chamber. The resulting carbonyl products produced from photooxidation of MB were derivatized with O-(2,3,4,5,6-pentafluorobenzyl) hydroxyamine hydrochloride (PFBHA) and analyzed using gas chromatograph–ion trap mass spectrometer (GC/ITMS). The photooxidation of MB in the presence of active chlorine was simulated with an explicit kinetic model using a chemical solver (Morpho) which included both Master Chemical Mechanism (MCM) and Cl radical reactions. The reaction rate constants of a Cl radical with MB and its oxidized products were estimated using a Structure–Reactivity Relationship method. Under dark conditions no effect of active chlorine on MB oxidation was apparent, whereas under simulated daylight conditions (UV irradiation) rapid MB oxidation was observed due to photo-dissociation of active chlorine. The model simulation agrees with chamber data showing rapid production of oxygenated products that are characterized using GC/ITMS. Ozone formation was enhanced when MB was oxidized in the presence of irradiated active chlorine and $NO_x$.

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## 1. Introduction

Active chlorine – hypochlorite ($OCl^-$), hypochlorous acid (HOCl) and chlorine gas ($Cl_2$) – has been commonly used for a variety of industrial and consumer applications such as household bleach [usually 3–6% NaOCl solution] (Odabasi, 2008), oxidizer in swimming pools, and a disinfectant in water purification or waste water treatment plants (Bellar et al., 1974). However, due to its strong reactivity, active chlorine directly affects human respiratory systems *via* inhalation (Winder, 2000) and indirectly affects health by producing secondary harmful pollutants that are recognized as carcinogens, toxicants, or irritants through reaction with ambient volatile organic compounds (VOCs) (Nazaroff and Weschler, 2004).

The active chlorine species (HOCl and $Cl_2$) produced in either aqueous solution or aerosolized particles can quickly evaporate into the air (Jang et al., 2010) and produce highly reactive radicals such as •OH and Cl• through direct photolysis.

$$HOCl + h\nu \rightarrow \bullet OH + Cl\bullet \quad (1)$$

$$Cl_2 + h\nu \rightarrow 2Cl\bullet \quad (2)$$

Such reactive radicals can react with atmospheric VOCs in the gas phase and produce a variety of oxygenated and chlorinated organic products. It has also been recognized that multifunctional oxygenated products such as α,β-unsaturated carbonyls and α-oxocarbonyls can cause health effects (Davidson et al., 2005; Pope and Dockery, 2006).

The impact of active chlorine on the atmospheric environment has been poorly understood, although the consumption of chlorine oxidants has enormously increased due to decontamination of unwanted chemicals and harmful biosystems such as bacteria and virus. Only a few studies have shown the impact of chlorine oxidants on indoor air quality. For example, Odabasi (2008) reported the production of halogenated VOCs such as chloroform and carbon

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tetrachloride from the application of chlorine bleach in house cleaning due to its reaction with organic matter on contaminated surfaces.

In this study, the impact of active chlorine species on the atmospheric environment was evaluated using a 2-m$^3$ indoor Teflon-film chamber. A solution containing Oxone® [$2KHSO_5$, $KHSO_4$, $K_2SO_4$] and saline was aerosolized into the chamber to produce active chlorine (Jang et al., 2010). The measured particle concentration of saline–Oxone® aerosol enables the estimation of active chlorine concentration in the air. 2-Methyl-2-butene (MB) was chosen as a surrogate VOC since MB is a simple five-carbon alkene that produces mostly gas-phase oxygenated products without secondary organic aerosol (SOA) formation (Cao and Jang, 2007). MB also yields high OH radical production when MB reacts with ozone. Among branched alkenes originating from automobile combustion of gasoline, MB is the most abundant (Schauer et al., 2002). The resulting oxygenated products were also analyzed using gas chromatograph–ion trap mass spectrometer (GC–ITMS). The observed MB decay, ozone production, and analyzed oxygenated products were simulated using the explicit chemical mechanisms.

## 2. Experimental section

### 2.1. Indoor Teflon-film chamber experiments

The photochemical reaction of MB in the presence of active chlorine was conducted using a 2-m$^3$ indoor Teflon-film chamber. The chamber was surrounded by 16 fluorescent lamps (Solarc Systems Inc., FS40T12/UVB, UVA340, UVA351, and TL40W/03RS) that were controlled by switching "on/off" (Fig. 1). Prior to experiments, the chamber was flushed with clean air from two clean air generators (Aadco Model 737, Rockville, MD; and Whatman Model 75-52, Haverhill, MA) in parallel.

Saline–Oxone® aerosol was used as the source of active chlorine because the concentrations of active chlorine in the gas phase were easily manipulated and estimated from SMPS particle concentration data. The chemical compositions of aqueous oxidant solutions used to produce saline–Oxone® aerosol are shown in Table 1. The amount of gas-phase active chlorine was estimated from SMPS data, oxidant aerosol density, and the water mass fraction of oxidant aerosol with the assumption that active chlorine originated from the oxidant aerosol was predominantly present in the gas phase (Jang et al., 2010) (see "Section 3.2 Active chlorine formation in saline–Oxone® aerosol").

The chamber experiment begins with injection of about 400 ppb of MB into the chamber using a *T*-shaped stainless tube under a clean air stream. Approximately 3 ppm of carbon tetrachloride ($CCl_4$) was added to the chamber as a non-reactive tracer (Demore et al., 1997; Huybrechts et al., 1996) to account for dilution. Both MB and $CCl_4$ concentrations were monitored using an HP-5890 GC-FID with a DB5 fused silica capillary column (15 m, 0.53 mm i.d., 1.5 μm thickness, J & W Scientific Inc., Cat# 1255012). The GC oven temperature was fixed at 50 °C. The carrier gas (nitrogen) flow rate was 10.0 mL/min. After the MB concentration was stabilized, UV–Visible lamps were turned on for photoirradiation. Then, an aqueous solution with 1% saline (sea salt, Sigma-Aldrich) and 2% Oxone® (potassium monopersulfate triple salt, ≥47% $KHSO_5$ basis, Sigma-Aldrich) was atomized into the chamber using a medical nebulizer (LC STAR, Pari Respiratory Equipment, Inc., Midlothian, VA) (Table 1). The particle concentration was monitored with a SMPS (TSI, Model 3080) integrated with a condensation nuclei counter (TSI, Model 3025A and Model 3022). The SMPS sampling and sheath flow rates were 0.3 L/min and 2 L/min, respectively. $NO_x$ and ozone concentrations were monitored with a chemiluminescence NO/$NO_2$ analyzer (Teledyne, Model 200E) and a photometric ozone analyzer (Teledyne, Model 400E), respectively. Temperature and relative humidity (RH) were measured with an electronic thermohygrometer (Dwyer Series 485).

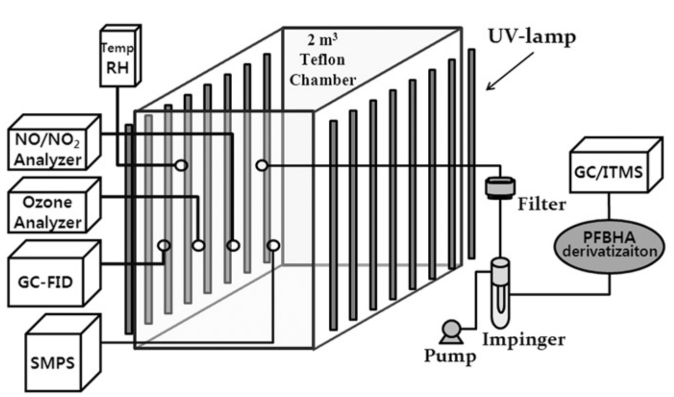

**Fig. 1.** The 2 m$^3$ Teflon film photoirradiation indoor chamber and instruments used for studies of the effect of the active chlorine on the MB oxidation.

To characterize the products from MB oxidation, the chamber air was sampled every 25 min (20 min sampling, 5 min preparing) for 2.5 h (total of six samples) with a flow rate of 1.0 L/min using an impinger containing 12 mL of acetonitrile (Aldrich). To collect gas-phase products without oxidant particles, the Teflon-coated borosilicate filter (PALL Membrane, 47 mm) was installed upstream of the impinger. Prior to each photoirradiation experiment, the chamber background air was analyzed for potential contamination.

### 2.2. MB oxidation product analysis

The carbonyl products of impinger samples were derivatized by O-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride (PFBHA) (Jang and Kamens, 2001; Le Lacheur et al., 1993; Yu et al., 1995). For each 10 mL of impinger sample, 10 μL of bornyl acetate (2.5 mg/mL in methylene chloride) as an internal standard was added. Then, 6 μL of PFBHA reagent (60 mg/mL in water) was added to the sample, mixed with a vortex mixer, and sonicated for 30 min. The resulting solution was held at 60 °C for 12 h to complete the derivatization reaction. Then, three drops of sulfuric acid (98%) were added to the solution to eliminate any unreacted PFBHA reagent in the reaction solution. After addition of 7 mL of water, the reaction solution was extracted with 1 mL of hexane three times. Extracts were dried using anhydrous magnesium sulfate ($MgSO_4$) powder and concentrated to 0.5 mL using a gentle stream of clean air.

PFBHA-carbonyl derivatives were analyzed using a GC/ITMS (VARIAN, CP-3800 GC, Saturn 2200) in the on-column mode associated with an auto injector (Varian 7800). GC analysis was performed on a 30 m × 0.25 mm i.d. HP-5MS capillary column (0.25 μm film thickness). The temperature program for the GC column was 60 °C for 0.5 min, 60–100 °C at 8 °C/min, and held for 2.5 min, 100 to 280 °C at 10 °C/min, and held for 8 min. Helium flow at 1.9 mL/min was used as GC carrier gas. Mass spectrometry employed both the chemical ionization (CI) mode with acetonitrile and the electron impact (EI) mode, over the mass range of m/z 50–650. The sample injector for GC–ITMS was operated in the on-column mode with temperature program (60 °C for 0.1 min, 60–250 °C at 150 °C/min, and held for 10 min).

For the product quantification, four levels of external standard solutions containing seven different carbonyl compounds (citral, hexanal, octanal, *trans*-2-hexenal, acrolein, methacrolein and *trans*-2-methyl-2-butenal) in acetonitrile were used. Calibration standard solutions were also derivatized using the PFBHA derivatization method and analyzed in the same way as the sample analytes described above. The area of the m/z 181 fragment peak of product derivatives, which is a characteristic fragment peak of PFBHA derivatives, was normalized by the area of the m/z 95 fragment peak associated with an internal standard (bornyl acetate) in electron impact (EI) mode. Using the normalized m/z 181 peak area, calibration curves were obtained ($R^2 \geq 0.995$).