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Atmospheric oxidation of selected chlorinated alkenes by O_3, OH, NO_3 and Cl

Qun Zhang [a, b], Yi Chen [c], Shengrui Tong [c], Maofa Ge [c], Justin Shenolikar [d], Matthew S. Johnson [d], Yifeng Wang [e], Narcisse T. Tsona [a], Abdelwahid Mellouki [f], Lin Du [b, a, *]

[a] Environment Research Institute, Shandong University, 250100 Shandong, China
[b] Shenzhen Research Institute, Shandong University, 518057 Shenzhen, China
[c] Beijing National Laboratory for Molecular Sciences (BNLMS), State Key Laboratory for Structural Chemistry of Unstable and Stable Species, Institute of Chemistry, Chinese Academy of Sciences, 100190 Beijing, China
[d] Department of Chemistry, University of Copenhagen, DK-2100 Copenhagen, Denmark
[e] Key Lab for Colloid and Interface Science of Ministry of Education, School of Chemistry and Chemical Engineering, Shandong University, 250100 Shandong, China
[f] Institut de Combustion, Aérothermique, Réactivité et Environnement (ICARE), CNRS/OSUC, 45071 Orléans Cedex 02, France

HIGHLIGHTS

- Rate constants of CMP, DCP and DCB reactions with atmospheric oxidants are determined.
- Possible CMP reaction mechanisms are proposed.
- The atmospheric lifetime of CMP, DCP and DCB are determined.
- The atmospheric implications of the CMP reactions are discussed.

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ABSTRACT

An experimental study on the 3-chloro-2-methyl-1-propene (CMP), 2,3-dichloropropene (DCP) and 3,4-dichlorobutene (DCB) reactions with atmospheric oxidants at (298 ± 1) K and atmospheric pressure is reported. Rate constants for the gas phase reactions of the three chlorinated alkenes with O_3, OH and NO_3 radicals and Cl atom were determined in a 100 L Teflon reactor by gas chromatography with flame ionization detector (GC-FID). The obtained rate constants are $(3.03 \pm 0.15) \times 10^{-18}$, $(3.83 \pm 1.30) \times 10^{-11}$, $(1.99 \pm 0.19) \times 10^{-14}$, and $(2.40 \pm 0.41) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} for CMP reactions with O_3, OH, NO_3, and Cl, respectively, $(4.62 \pm 1.41) \times 10^{-20}$, $(1.37 \pm 1.02) \times 10^{-11}$, $(1.45 \pm 0.15) \times 10^{-15}$ and $(1.30 \pm 0.99) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} for DCP reactions and $(2.09 \pm 0.24) \times 10^{-19}$, $(1.45 \pm 0.59) \times 10^{-11}$, $(3.00 \pm 0.82) \times 10^{-16}$ and $(1.91 \pm 0.19) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} for DCB reactions. The CMP reaction products were detected and possible reaction mechanisms of their formation were proposed. Chloroacetone was found to be the major product in all four oxidation reactions. The loss process of CMP in the atmosphere is mostly controlled by its reaction with the OH radical during daytime and with NO_3 during nighttime, with lifetimes of 3.6 h and 27.9 h respectively. Atmospheric implications of both these reactions and their potential products are discussed.

1. Introduction

Large amounts of anthropogenic organic compounds are emitted into the troposphere, leading to serious concerns about the increasing risks to human health (Finlayson-Pitts and Pitts, 2000). Among these anthropogenic compounds, the chlorinated volatile

* Corresponding author. Environment Research Institute, Shandong University, 250100 Shandong, China.
E-mail address: lindu@sdu.edu.cn (L. Du).

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organic compounds are produced in large quantities and they are widely used as solvents, pesticides and building blocks in synthesis. These compounds are ubiquitous contaminants in the environment and have received significant attention from researchers (Oki et al., 1990; Nishikawa et al., 1993; Huang et al., 2014; Narayanan et al., 1995). 3-Chloro-2-methyl-1-propene (CMP, CH_2=C(CH_3)CH_2Cl), 2,3-dichloropropene (DCP, CH_2=$CClCH_2Cl$), and 3,4-dichlorobutene (DCB, CH_2=$CHCHClCH_2Cl$) are selected examples of chlorinated alkenes used in industry for synthetic processes and known to be hazardous to human health. Due to the toxic and non-biodegradable properties of these compounds, their use has been restricted or even banned for some. The fate of these anthropogenic chlorinated alkenes mainly depends on their physicochemical properties and degradation in different environmental media and different environmental conditions (Bidleman, 1988; Mackay et al., 1996).

To a great extent, the degradation of chlorinated alkenes differs between various environmental media, but air is the most reactive medium (Gouin et al., 2000). After their emission into the atmosphere, chlorinated alkenes could be removed by wet and dry deposition, and photochemical reactions. Once in the troposphere, these compounds may react with the tropospheric oxidants, O_3, OH and NO_3 radicals, etc., and may lead to the formation of more stable chlorinated products which can be transported into the stratosphere, providing additional chlorine with implications for the ozone layer (Mu and Mellouki, 2001). In addition to reactions with the above mentioned tropospheric oxidants, in the marine troposphere where there is a high concentration of chlorine, reactions with Cl atoms are believed to be of potential relevance (Finlayson-Pitts, 1993; Keene et al., 1996).

While CMP reactions with the main atmospheric oxidants have been extensively studied, reactions of DCP and DCB with the same oxidants remain poorly investigated. Using the relative rate method with different reference compounds, the rate constants of CMP reactions with O_3, OH, and Cl were determined at room temperature and atmospheric pressure to be $k_{O3} = (3.71 \pm 0.49) \times 10^{-18}$, $k_{OH} = (3.23 \pm 0.35) \times 10^{-11}$ and $k_{Cl} = (2.1 \pm 0.8) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} (Johnson et al., 2000; Rivela et al., 2015), while the structure activity relationship (SAR) estimation method gave rate constants of 1.02×10^{-17} and 3.96×10^{-11} cm^3 $molecule^{-1}$ s^{-1} for reactions with O_3 and OH, respectively (Kwok and Atkinson, 1995; USEPA, 2012; Rivela et al., 2015). The rate constant for the CMP reaction with NO_3 was measured using the discharge-flow technique coupled to optical-absorption detection and found to be $(2.5 \pm 0.4) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} (Aird et al., 1992). Using the SAR estimation method, rate constants of 2.25×10^{-19}, 8.56×10^{-12}, 1.20×10^{-17}, 2.04×10^{-11} cm^3 $molecule^{-1}$ s^{-1} were determined for DCP reactions with O_3 and OH, and for DCB reactions with O_3 and OH, respectively. However, mechanisms and products of these reactions, including the kinetics of reactions with other oxidants, remain poorly explored.

In the present study, we determine the rate constants for the reactions of CMP, DCP and DCB with O_3, OH, NO_3 and Cl, using the absolute rate method and the relative rate method. Reactions mechanisms and potential products of the CMP reactions are examined. The atmospheric lifetimes of CMP, DCP and DCB based on the rate constants of the different oxidation reactions are determined in order to further assess their chemical fate. The atmospheric implications of the CMP, DCP, and DCB oxidation reactions and reaction products are considered.

2. Experimental

All experiments were performed in a light-tight smog chamber with a 100 L Teflon film bag as the reactor at (298 ± 1) K and atmospheric pressure. More details about the smog chamber have been described in some previous studies (Gai et al., 2009a; Wang et al., 2010). A zero-air generator (Thermo 111-D3R) was used to provide purified dry air to dilute reactants and as bath gas in the reactor. The total volume of the gas in the bag was recorded through a flow accumulator (D08-8C/ZM, Beijing Sevenstar Electron Corporation).

2.1. O_3 reaction

The rate constants for reactions of CMP, DCP and DCB with O_3 were determined using the absolute rate method, similar to previous work (Gai et al., 2009b; Wang et al., 2015). The decay process of O_3 during these reactions was in agreement with the kinetics of pseudo-first-order reactions, in which the initial concentration of the chlorinated alkenes remains in large excess over that of O_3. The decay of O_3 is mainly caused by wall loss and reaction with chlorinated alkenes (here denoted as VOC), as shown below.

$$O_3 + wall \rightarrow products \quad (R1)$$

$$O_3 + VOC \rightarrow products \quad (R2)$$

As the concentrations of chlorinated alkenes could be treated as constants during the experiments, the following equation can be obtained for all experiments:

$$\frac{-d\ln[O_3]}{dt} = k_0 + k_r[VOC]_0 \quad (1)$$

where k_0 and k_r are rate constants of reactions (R1) and (R2), respectively. The consumption of O_3 was monitored to obtain -$d$ln $[O_3]/dt$. In the background experiment with no chlorinated alkenes in the reactor, the wall decay of O_3 (k_0) was determined, and k_r could be obtained using Equation (1).

To minimize the effect of wall loss, the Teflon bags were deactivated with ppm mixing ratios of O_3 for about 24 h before being used as a reactor. It has been found that the gas phase ozonolysis of chlorinated alkenes could produce OH radicals that could result in uncertainties in measuring the rate constants of reactions with O_3. Hence, during our experiments, an excess of cyclohexane was added as an OH radical scavenger since cyclohexane hardly reacts with O_3 and does not interfere with the kinetic experiment. The concentrations of cyclohexane were 3.35×10^{15} molecule cm^{-3} in the reaction with CMP, and 8.37×10^{15} molecule cm^{-3} in both reactions with DCP and DCB. The reactants were mixed for about an hour after being introduced into the reactor, and then a small amount of O_3 was injected to start the reactions. O_3 was generated via electrical discharge by flowing oxygen gas through an ozone generator (BGF-YQ, Beijing Ozone, China). The accurate concentration of ozone was measured with an ozone analyzer (Model 49i, Thermo Electron Corporation). The initial concentrations of CMP, DCP and DCB were in the ranges of $(1.92–6.25) \times 10^{14}$, $(2.29–13.1) \times 10^{14}$ and $(7.64–18.3) \times 10^{14}$ molecule cm^{-3}, respectively and the initial concentrations of O_3 were in the range of $(2.10–5.01) \times 10^{12}$ molecule cm^{-3}.

Based on the O_3 wall loss reaction, the O_3 decay in the absence of chlorinated alkenes in the reactor was a first order reaction and monitored during the nine-hour reaction time. The measured rate constant of O_3 decay was $(3.80 \pm 0.27) \times 10^{-6}$ s^{-1}, which was in good agreement with a previous work (Gai et al., 2009b). As the O_3 decay caused by the wall loss was about two to three orders of magnitude lower than the rate constant of the pseudo-first-order reactions with CMP, it could be neglected compared to the pseudo-first-order reactions in our work. However, the wall loss could not be neglected in DCP and DCB experiments as the rate